Dissertation zur Erlangung des Doktorgrades

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Nucleophilicities of Amines, Amino Acids and Pyridines

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aus

Tiraspol

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Erklärung

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Ehrenwörtliche Versicherung

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München, am 30.05.2008

Frank Brotzel

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Für Erika, Markus
und Alida

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Konfuzius (ca. 500 v. Chr.): “Was du mir sagst, das vergesse ich.
Was du mir zeigst, daran erinnere ich mich.
Was du mich tun lässt, das verstehe ich.”

Die einzelnen Abschnitte dieser Dissertation sind publiziert in:

Nucleophilicities and Carbon Basicities of Pyridines.
F. Brotzel, B. Kempf, T. Singer, H. Zipse, H. Mayr, *Chem. Eur. J.* **2007**, *13*, 336-345.

Nucleophilicities of Primary and Secondary Amines in Water.
F. Brotzel, Y. C. Chu, H. Mayr, *J. Org. Chem.* **2007**, *72*, 3679-3688.

DABCO or DMAP – What Makes Their Difference in Organocatalysis?
M. Baidya, S. Kobayashi, F. Brotzel, U. Schmidhammer, E. Riedle, H. Mayr, *Angew. Chem.* **2007**, *119*, 6288-6292; *Angew. Chem. Int. Ed.* **2007**, *46*, 6176-6179.

Nucleophilicities of Amino Acids and Peptides.
F. Brotzel, H. Mayr, *Org. Biomol. Chem.* **2007**, 5, 3814-3820.

Table of contents

0. Summary

0.1. General

In line with earlier work of the Mayr group, diarylcarbenium ions (benzhydryl cations) Ar_2CH^+ have been employed as reference electrophiles for the construction of nucleophilicity scales for amines, amino acids, some di- and tripeptides, and pyridines using the relationship eq. (0.1).

$$\log k_{20^\circ C} = s(N + E) \qquad (0.1)$$

k = second-order rate constant in $M^{-1}\ s^{-1}$

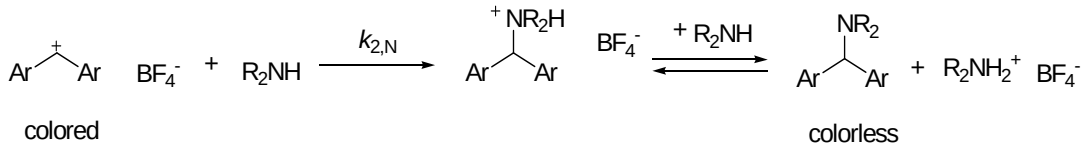
s = nucleophile specific slope parameter

N = nucleophilicity parameter

E = electrophilicity parameter

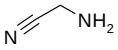
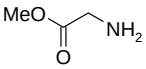
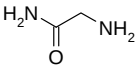
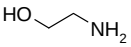
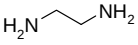
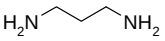
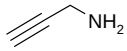
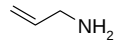
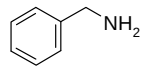
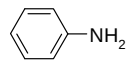
0.2. Primary and Secondary Amines

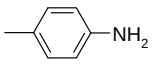
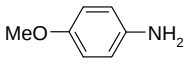
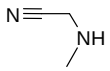
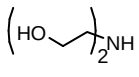
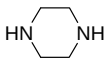
The kinetics of the reactions of 26 primary and secondary amines with benzhydrylium ions in water were investigated photometrically. Because the parallel reactions of the benzhydrylium ions with hydroxide and water are much slower, the second-order rate constants for the reactions of amines with benzhydrylium ions could be determined reliably (Scheme 0.1). Reactivities of anilines were also studied in acetonitrile solution. Plots of log $k_{2,N}$ for these reactions versus the electrophilicity parameters E of the benzhydrylium ions were linear, which allowed us to derive the nucleophilicity parameters N and s for amines as defined by eq. (0.1). Because the slope parameters for the different amines are closely similar, the relative nucleophilicities are almost independent of the electrophiles and can be expressed by the nucleophilicity parameters N (Table 0.1).



Scheme 0.1. Reaction of amines with benzhydryl salts.

Table 0.1: Nucleophilicity parameters (*N*, *s*) for primary and secondary amines in water (other solvents marked).

Amine	*N*	*s*
NH_3	9.48	0.59
$MeNH_2$	13.85	0.53
$EtNH_2$	12.87	0.58
i$PrNH_2$	12.00	0.56
t$BuNH_2$	10.48	0.65
	10.80	0.61
	12.08	0.60
	12.29	0.58
	12.61	0.58
	13.28	0.58
	14.02	0.54
	12.29	0.59
	13.21	0.54
	13.44	0.55
Solvent: CH_3CN	12.92	0.60
		
Solvent: H_2O	12.99	0.73
Solvent: CH_3CN	12.64	0.68

Amine	*N*	*s*
		
Solvent: H_2O	13.00	0.79
Solvent: CH_3CN	13.19	0.69
		
Solvent: H_2O	16.53	0.50
Solvent: CH_3CN	13.42	0.73
Me_2NH	17.12	0.50
Et_2NH	14.68	0.53
	13.50	0.59
	13.00	0.61
	17.21	0.49
	18.13	0.44
	18.29	0.46
	15.62	0.54
	17.22	0.50

The correlation between nucleophilicity *N* and pK_{aH} values is poor (Figure 0.1), and it is found that secondary alkyl amines and anilines are considerably more nucleophilic, while ammonia is much less nucleophilic than expected on the basis of their pK_{aH} values.

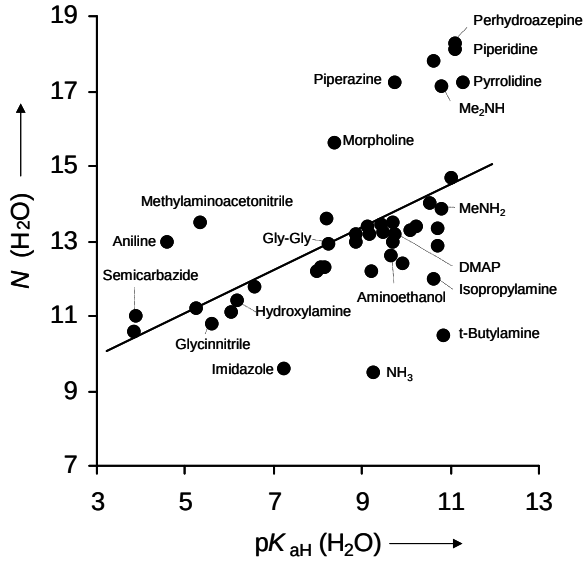


Figure 0.1. Plot of the nucleophilicity parameters *N* of amines versus pK_{aH} in water.

It has been demonstrated that *N* parameters can be used for the prediction of second-order rate constants for the reactions of amines with other electrophiles like 1-methyl-4-vinylpyridinium, methyl 4-nitrobenzenesulfonate, iron π-complexes or an *o*-quinone methide. Moreover, *N* parameters can be used for a direct comparison of reactivity of different nucleophiles as shown in Figure 0.2. Therefore it becomes possible to predict the active species in equilibrium mixtures of various nucleophiles (amines, carbanions, phenolates) in aqueous solution.

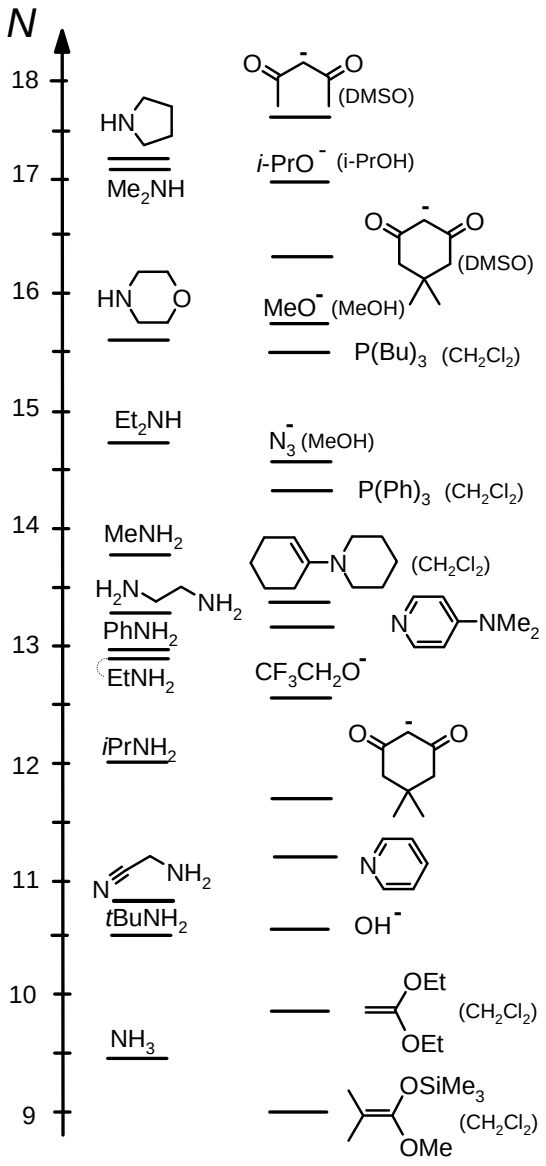
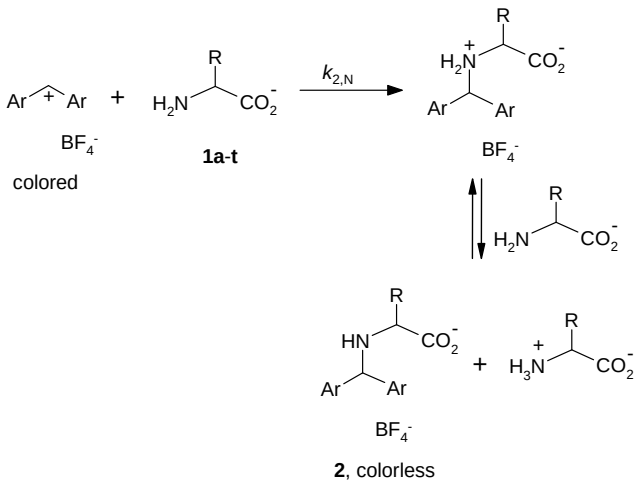


Figure 0.2. Comparison of the nucleophilic reactivities of amines with other types of nucleophiles in water. Other solvents are given in parentheses.

0.3. Amino acids and Peptides

The kinetics of the reactions of amino acids with stabilized diarylcarbenium ions (Ar_2CH^+) have been studied photometrically in aqueous solution at variable pH (Scheme 0.2). In the range of 10.5 < pH < 12, the amino acids react much faster than the competing nucleophiles hydroxide and water (Figure 0.3).



Scheme 0.2.

Though the pK_{aH} values of the amino acids vary by almost four units, the nucleophilic reactivities of all primary amino groups differ by less than a factor of 4. The secondary amino group of proline is 10^2 times more reactive, and the thiolate site in cysteine exceeds the reactivities of the primary amino groups by a factor of 10^4.

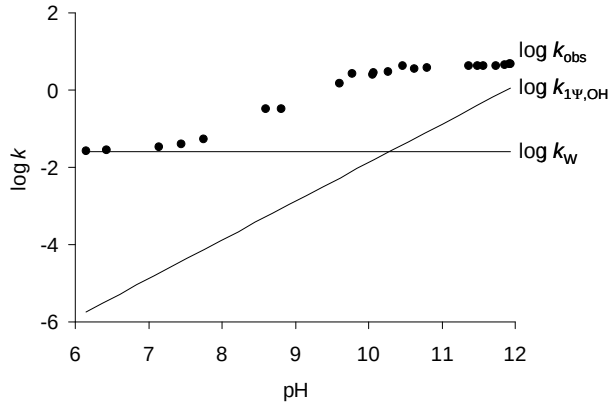


Figure 0.3. Plot of the measured rate constants log k_{obs} for the reactions of glycine (c_0 = 9.05 × 10^{-4} M) with $(dma)_2CH^+$ (c_0 = 3.36 × 10^{-5} M) at 20 °C in aqueous phosphate buffer vs pH compared with log k_W for the reaction with water and log $k_{1\Psi,OH}$ for the reaction with OH^-.

Nucleophilicity parameters *N* as defined by eq. (0.1) have been determined for the amino acids in order to provide a direct comparison with other n-, π-, and σ-nucleophiles. The *N* parameters have been used for the prediction of second-order rate constants of nucleophilic aromatic (picryl chloride) and aliphatic substitutions (methyl 4-nitrobenzenesulfonate) with amino acids and in reactions of amino acids with Michael acceptors (1-methyl-4-vinylpyridinium).

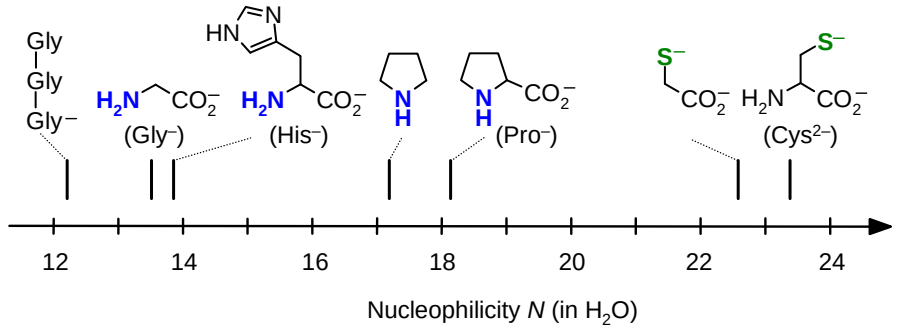
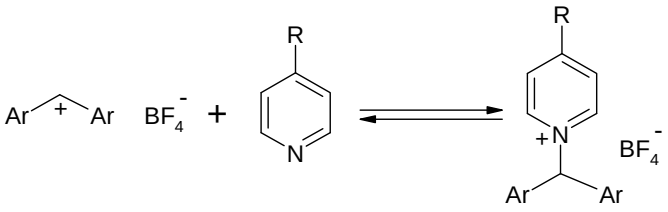


Figure 0.4. Comparison of the nucleophilicities of amino acids and peptides in water.

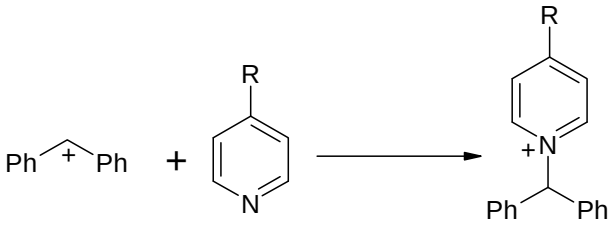
0.4. Pyridines

Rate and equilibrium constants for the reactions of pyridines with donor-substituted benzhydrylium ions have been determined photometrically (Scheme 0.3). The correlation equation (0.1) has been used to determine the nucleophilicity parameters of various pyridines in CH_2Cl_2 and aqueous solution and to compare them with *N* of other nucleophiles (Figure 0.6). Pyridines are found to be generally two to three orders of magnitude more nucleophilic in dichloromethane than in water. It is demonstrated that the reactivity of pyridine decreases slightly with the solvent polarity parameters E_T.



Scheme 0.3. Addition of para-substituted pyridine derivatives to benzhydryl salts.

Ab initio MO calculations have been used to obtain energies for the reactions of the parent benzhydrylium ion with pyridines in the gas phase (Scheme 0.4). The reaction energies ΔG_{298} become more negative as the basicity of the pyridines increases. Nucleophilicity parameters *N* determined in CH_2Cl_2 and the reaction free energies ΔG_{298} have been correlated.



Scheme 0.4.

It is shown that there is a good correlation between reactivity *N* and the calculated reaction energies within the pyridines as nucleophile class (Figure 0.5).

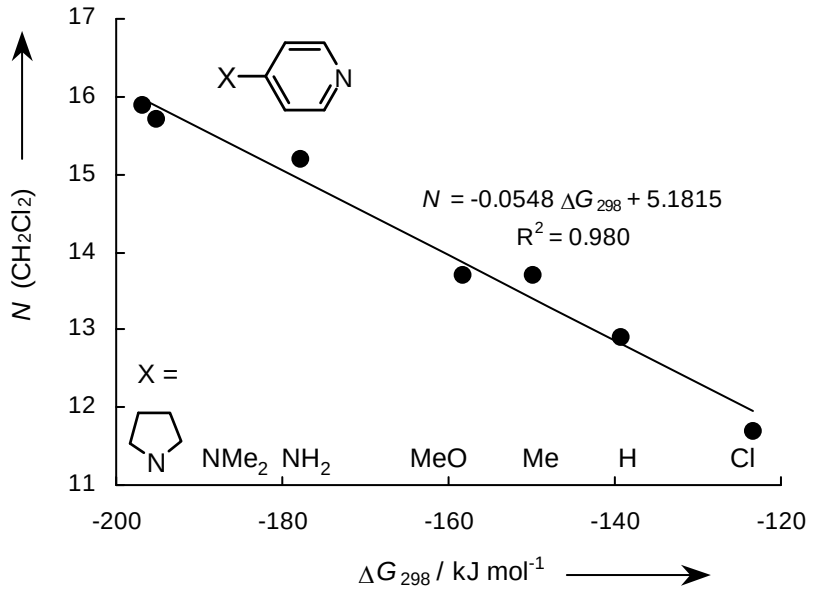


Figure 0.5. Plot of nucleophilicity parameters *N* of pyridines in CH_2Cl_2 versus ΔG_{298} for the reaction with the unsubstituted benzhydrylium cation calculated at the MP2(fc)/6-31G(d)// MP2(fc)/6-31G(d) level.

Figure 0.6 shows that the nucleophilic organocatalyst 4-(*N*,*N*-dimethylamino)pyridine and tertiary phosphanes have comparable nucleophilicities. They also have comparable carbon basicities despite widely differing Brønsted basicities. For that reason, the nucleophilicity parameters *N* are suggested as guidelines for the development of novel organocatalysts. The intrinsic barriers of these reactions, as defined by the Marcus equation are derived from the corresponding rate and equilibrium constants.

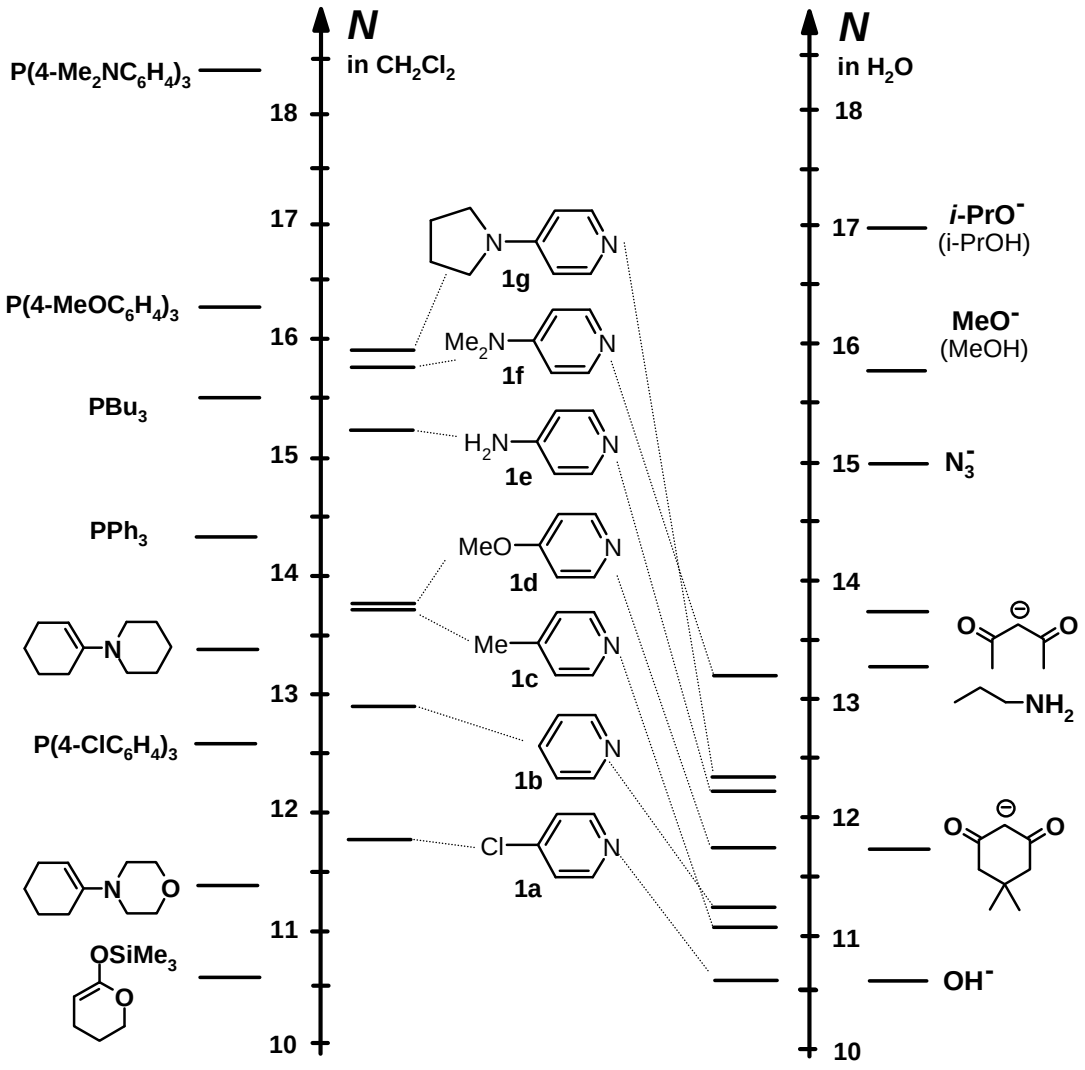


Figure 0.6. Comparison of the nucleophilic reactivities of pyridines with other types of nucleophiles in CH_2Cl_2 and water. Other solvents are given in parenthesis.

0.5. Organocatalysts

Rate and equilibrium constants for the reactions of 1,4-diazabicyclo[2.2.2]octane (DABCO), quinuclidine, and 4-(dimethylamino)pyridine (DMAP, Steglich's base) with stabilized diarylcarbenium ions (Ar_2CH^+) have been determined in acetonitrile. It is demonstrated that the bicyclic amines are 10^3 times more nucleophilic than DMAP, but at the same time significantly better nucleofuges (10^6 and 10^5, respectively) due to different intrinsic barriers of these reactions. DMAP which shows higher reorganization energy than the bicyclic amines is supposed to be a better organocatalyst in reactions, where the overall rate is determined by the concentration of the intermediate ammonium ions produced by the reactions of the amines with the electrophiles. If reactivity is controlled by the rate of nucleophilic attack of the organocatalyst or by the release of the amine component in the final stage of the reaction, DABCO and quinuclidine should be superior catalysts.

1. Introduction

The chemistry of amines is largely determined by their basicity and nucleophilicity (Scheme 1.1). Whereas there exist a large body of data about the basicities of amines in different solvents (pK_{aH}) much less is known about their nucleophilicities.[1] For long time it was believed that the relative nucleophilicities of amines can be derived from their basicities.

basicity: $R_3\bar{N} + H^+ \overset{pK_B}{\rightleftharpoons} R_3\overset{+}{N}H$

nucleophilicity: $R_3\bar{N} + R'—X \xrightarrow{k_{Nu}} R_3\overset{+}{N}—R' + X^-$

Scheme 1.1.

The first systematic attempt to quantify nucleophilicity was reported by Swain and Scott, who studied the rates of reactions of amines with CH_3Br and CH_3I in several solvents and characterized their reactivities by the parameter *n*, which is defined by eq. (1.1). A scale of *n* values is based on the rate coefficients for the reactions of methyl bromide with nucleophiles in water at 25 °C, the substrate dependent constant *s* being defined as 1.00 for these reactions and *n* being defined as 0.00 for the hydrolysis of methylbromide.[2]

$$\log (k/k_0) = sn \qquad (1.1)$$

Ritchie determined the rates of the reactions of amines with stabilized carbocations and identified their nucleophilicities by N_+, which is defined by eq. (1.2), where *k* is the rate constant for reaction of a given cation with a given nucleophile in a given solvent. k_0 is the rate constant for the same cation with water in water and N_+ is a parameter which is characteristic of the nucleophilic system and independent of the cation.[3]

$$\log (k/k_0) = N_+ \qquad (1.2)$$

The parameters N_+ have later been reported also to be applicable for the reactions of amines with cationic transition metal π-complexes.[4] The most comprehensive study of amine reactivity so far was published by Heo and Bunting,[5] and the goal of this work was to include

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[1] in water: Albert, A.; Serjeant, E. P. *The Determination of Ionization Constants: A Laboratory Manual*, *3rd edition*, Chapman and Hall, London, **1984**, p. 136-149.

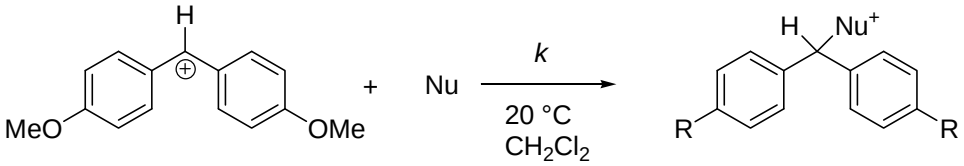
[2] Swain, C. G.; Scott, C. B. *J. Am. Chem. Soc.* **1953**, *75*, 141-147.

[3] (a) Ritchie, C. D. *Acc. Chem. Res.* **1972**, *5*, 348-354. (b) Ritchie, C. D.; Virtanen, P. O. I. *J. Am. Chem. Soc.* **1972**, *94*, 4966-4971.

[4] Kane-Maguire, L. A. P.; Honig, E. D.; Sweigart, D. A. *Chem. Rev.* **1984**, *84*, 525-543.

[5] (a) Heo, C. K. M.; Bunting, J. W. *J. Chem. Soc. Perkin Trans. 2* **1994**, 2279-2290. (b) Bunting, J. W.; Mason, J. M.; Heo, C. K. M. *J. Chem. Soc. Perkin Trans. 2* **1994**, 2291-2300.

amine reactivities into the most comprehensive nucleophilicity scales presently available, which have been derived by the benzhydrylium method:[6]



Scheme 1.2. General equation for the determination of reactivity of a nucleophile Nu towards the red bis-*p*-methoxybenzhydrylium cation in dichloromethane at 20 °C.

The bis-*p*-methoxybenzhydrylium cation was selected as a reference electrophile, together with a reference solvent (CH_2Cl_2), and a reference temperature (20 °C). From the second-order rate constants for the reactions of this electrophile with various nucleophiles like alkenes,[7] electron-rich heteroarenes,[8] enol ethers,[9] or water[10] it became possible to compare the relative reactivities of these classes of nucleophiles.
Nevertheless the majority of nucleophiles could not be characterized in this way. While electron poor arenes or alkenes are too weak nucleophiles and do not react at all with the bis-*p*-methoxybenzhydryl cation with measurable rates at 20 °C, amines or carbanions on the other hand are too reactive and all of them react with similar rates (diffusion control). The consequence is obvious: A single electrophile only allows one to compare a rather limited group of compounds, which differ by less than 14 orders of magnitude in reactivity and, whichever electrophile is selected, most nucleophiles will be outside of this window. (Figure 1.1)

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[6] (a) H. Mayr, M. Patz, *Angew. Chem.* **1994**, *106*, 990–1010; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 938–957. (b) H. Mayr, T. Bug, M. F. Gotta, N. Hering, B. Irrgang, B. Janker, B. Kempf, R. Loos, A. R. Ofial, G. Remennikov, H. Schimmel, *J. Am. Chem. Soc.* **2001**, *123*, 9500–9512. (c) H. Mayr, B. Kempf, A. R. Ofial, *Acc. Chem. Res.* **2003**, *36*, 66–77. (d) H. Mayr, A. R. Ofial in *Carbocation Chemistry* (Eds.: G. A. Olah, G. K. S. Prakash), Wiley, Hoboken, NJ, **2004**, Chapt. 13, pp. 331–358. (e) H. Mayr, A. R. Ofial, *Pure Appl. Chem.* **2005**, *77*, 1807–1821.

[7] (a) H. Mayr, R. Schneider, U. Grabis, *J. Am. Chem. Soc.* **1990**, *112*, 4460-4467. (b) H. Mayr, J. Bartl, G. Hagen, *Angew. Chem.* **1992**, *104*, 1689-1691; *Angew. Chem. Int. Ed.* **1992**, *31*, 1613-1615.

[8] M. F. Gotta, H. Mayr, *J. Org. Chem.* **1998**, *63*, 9769-9775.

[9] J. Burfeindt, M. Patz, M. Müller, H. Mayr, *J. Am. Chem. Soc.* **1998**, *120*, 3629-3634.0

[10] S, Minegishi, S. Kobayashi, H. Mayr, *J. Am. Chem. Soc.* **2004**, *126*, 5174-5181.

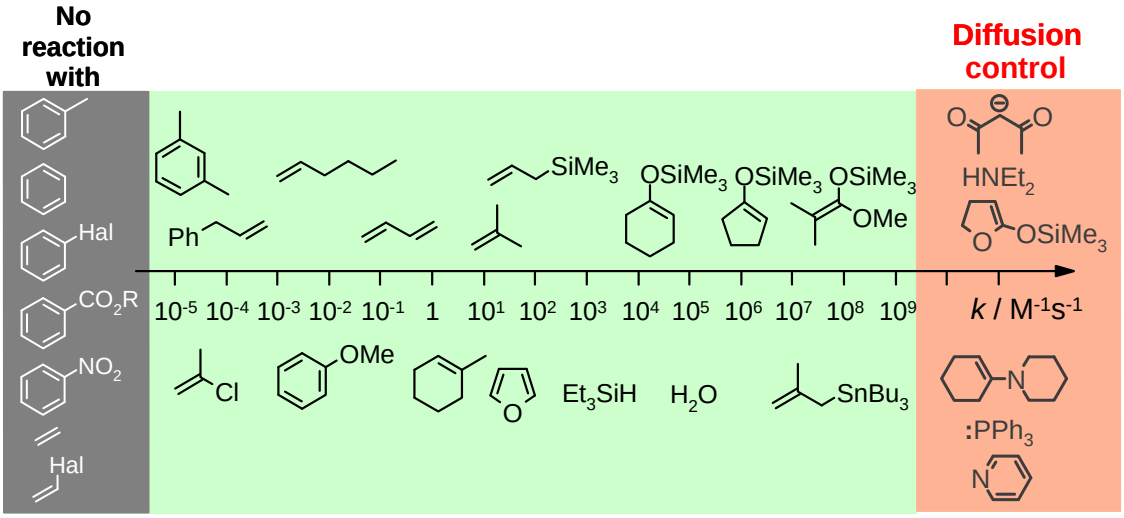


Figure 1.1. Construction of a nucleophilicity scale with respect to the bis-p-methoxybenzhydrylium ion (CH_2Cl_2, 20 °C).[6e]

For that reason, more than 30 structurally related electrophiles were selected as reference electrophiles which possess all the same steric surroundings at the reaction center and whose reactivities can be modified by the substituents. Subsequently, the kinetics of their reactions with a variety of carbon nucleophiles were studied by photometric monitoring of the consumption of the electrophiles.

The vertical lines in Figure 1.2 correspond to 29 nucleophilicity scales, each one with respect to another electrophile. Least-squares analysis of the rate constants for these reactions gave the correlation lines shown in Figure 1.2, which can be described by the correlation equation (1.3). Rate constants greater than 10^7 to 10^8 M^{-1} s^{-1} deviate from the linear correlations, because the diffusion limit is approached, and are not considered for the construction of the correlation lines.

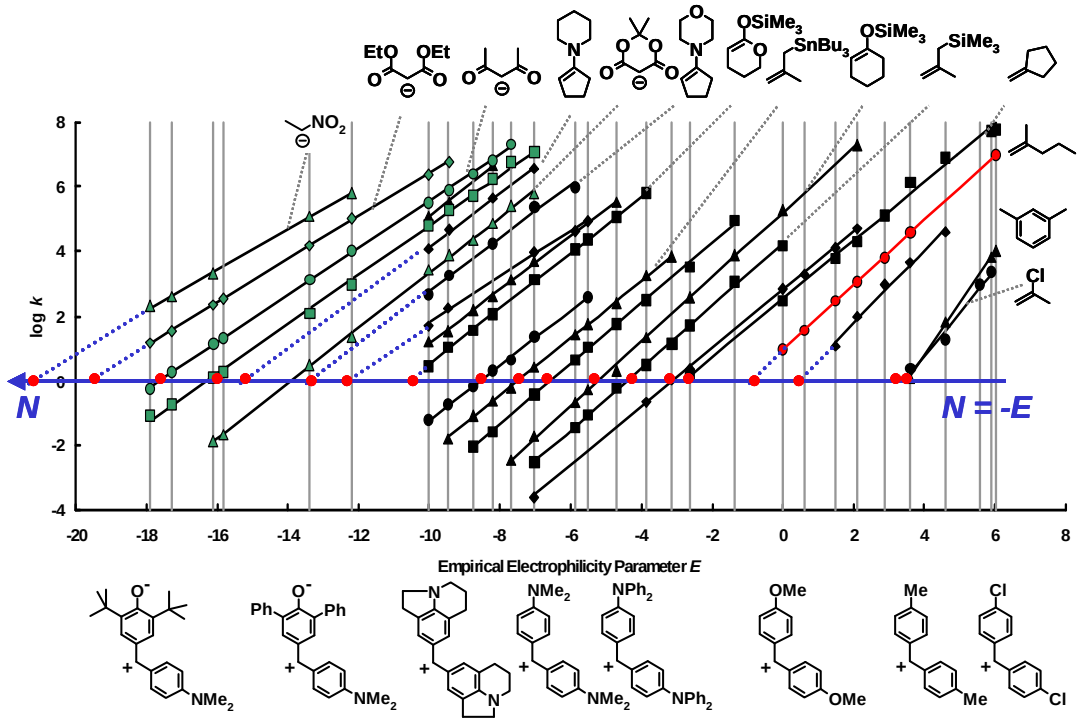


Figure 1.2. Fit of second-order rate constants for electrophile-nucleophile combinations (20 °C) to eq.(1.3).

$$\log k\ (20\ ^\circ\mathrm{C}) = s(N + E) \qquad (1.3)$$

Each of the electrophiles is thus characterized by an electrophilicity parameter E [E(p-$MeOC_6H_4)_2CH^+$ = 0] and each of the nucleophiles is characterized by the nucleophilicity parameter N (= negative intercept on the abscissa) and the slope parameter s (s = 1.0 for 2-methyl-1-pentene).

Similarly the second-order rate constants k for the reactions of different amines with benzhydrylium cations can be used for the construction of a nucleophilicity scale for amines. Since benzhydrylium ions have previously been used for the construction of nucleophilicity scales for other classes of compounds, it should become possible to directly compare the reactivities of amines with other types of *n*-nucleophiles (alcohols, phosphanes), π-nucleophiles (alkenes, arenes, organometallics), and σ-nucleophiles (hydride donors).

Since the major parts of this thesis have been published in a series of papers, individual introductions will be given at the beginning of each chapter. In order to identify my contributions to the multiauthor publications the Experimental Sections report exclusively the experiments in which I have been involved.

2. Nucleophilicities of Primary and Secondary Amines in Water

2.1. Introduction

Relationships between structure and nucleophilic reactivities of amines have been derived from kinetic investigations of nucleophilic additions[1] as well as nucleophilic substitutions[2] including nucleophilic vinylic substitutions[3] and nucleophilic aromatic substitutions.[4] Swain and Scott studied the rates of reactions of amines with CH_3Br and CH_3I in several solvents and characterized their reactivities by the parameter n, which is defined by eq 2.1.[5]

$$\log (k/k_0) = s\,n \qquad (2.1)$$

Ritchie determined the rates of the reactions of primary and secondary amines with stabilized carbocations and identified their nucleophilicities by the electrophile independent parameter N_+, which is defined by eq 2.2[6]

$$\log (k/k_0) = N_+ \qquad (2.2)$$

The parameters N_+ have later been reported also to be applicable for the reactions of amines with cationic transition metal π-complexes.[7] The most comprehensive investigation of amine reactivities has so far been performed by Bunting, who reported second-order rate constants for the reactions of 72 primary and secondary amines with the 1-methyl-4-vinylpyridinium cation in aqueous solution[8] and investigated their relationship with the corresponding reactivities toward methyl 4-nitrobenzenesulfonate.[9]

In earlier work we have reported that benzhydrylium ions can be used as reference electrophiles[10] for characterizing a large variety of π-nucleophiles (alkenes,[11] arenes,[11] enol ethers,[11] ketene acetals,[11,12] enamines,[11,13] allyl element compounds,[11, 14] transition metal π-complexes,[15] diazoalkanes,[16] delocalized carbanions[17]), n-nucleophiles (amines,[18] alcohols,[19] alkoxides,[20] phosphanes,[21] inorganic anions,[22] pyridines[23]), and σ-nucleophiles (hydrides[10,24]). The rate constants have been correlated on the basis of eq 2.3.

$$\log k_{20^\circ C} = s(N + E) \qquad (2.3)$$

k = second-order rate constant in $M^{-1}\ s^{-1}$

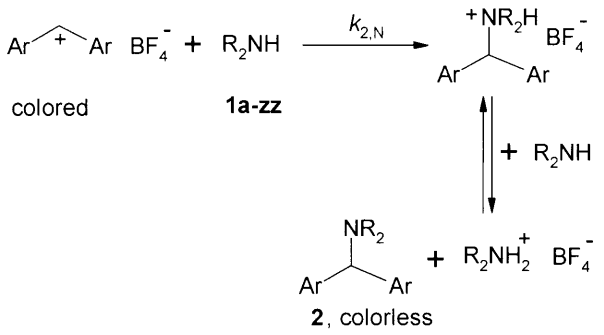
s = nucleophile specific slope parameter

N = nucleophilicity parameter

E = electrophilicity parameter

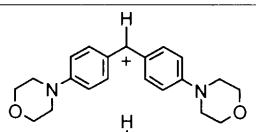
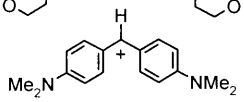
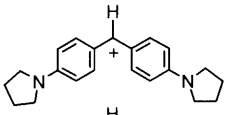
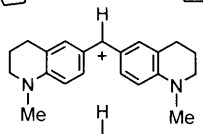
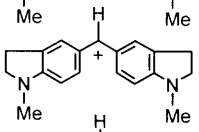
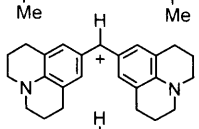
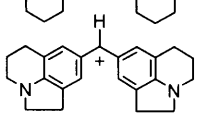
Only few amines have so far been characterized by eq 2.3.[18] Because the nucleophilicity parameters N have recently been reported to hold also for S_N2 type reactions,[25] and the systematic design of organocatalytic reactions requires the comparison of the nucleophilicities of amines with those of other nucleophiles, we set out to extend our nucleophilicity scales by

determining *N* parameters for various types of amines. We now report on the kinetics of the reactions of amines with the reference electrophiles listed in Table 1, and use these data to determine *N* and *s* of these nitrogen nucleophiles (Scheme 1).



Scheme 1.

Table 2.1. Benzhydrylium ions Ar_2CH^+ employed in this work.

Electrophile	Ar_2CH^+	E[a]
$(mor)_2CH^+$		-5.53
$(dma)_2CH^+$		-7.02
$(pyr)_2CH^+$		-7.69
$(thq)_2CH^+$		-8.22
$(ind)_2CH^+$		-8.76
$(jul)_2CH^+$		-9.45
$(lil)_2CH^+$		-10.04

[a] Electrophilicity parameters *E* from ref 10.

2.2. Results

Because the reactions were carried out in water, three parallel reactions may account for the consumption of the benzhydrylium ions, and the observed first-order rate constants k_{obs} reflect

the sum of the reactions of the electrophile with the amine **1** ($k_{1\Psi,N}$), with OH^- ($k_{1\Psi,OH^-}$) and with water (k_W).

$$k_{obs} = k_{1\Psi,N} + k_{1\Psi,OH^-} + k_W \quad (4)$$
$$= k_{2,N}[\mathbf{1}] + k_{2,OH^-}[OH^-] + k_W$$

Rearrangement of eq 2.4 yields eq 2.5, which defines $k_{1\Psi}$ as the overall rate constant minus the contribution by hydroxide.

$$k_{1\Psi} = k_{obs} - k_{2,OH^-}[OH^-] = k_{2,N}[\mathbf{1}] + k_W \quad (5)$$

The actual concentrations of the amines [**1**] and of hydroxide [OH^-] are calculated from $[\mathbf{1}]_0$ and pK_{aH} as described in the experimental part. With the previously published values[18] for k_{2,OH^-} and the calculated concentrations of hydroxide [OH^-], the partial pseudo-first-order rate constants $k_{1\Psi,OH^-}$ can be derived. The slopes of the plots of $k_{1\Psi}$ (= k_{obs} - $k_{1\Psi,OH^-}$) versus [**1**] correspond to the second-order rate constants $k_{2,N}$, as shown in Figure 2.1 and in the experimental part. The intercepts, which correspond to the reactions of the benzhydrylium ions with water (eq 2.5), are generally negligible in agreement with previous work,[18] showing that water (N = 5.11) reacts more than 4.5 orders of magnitude slower with benzhydrylium ions than the amines investigated in this work.

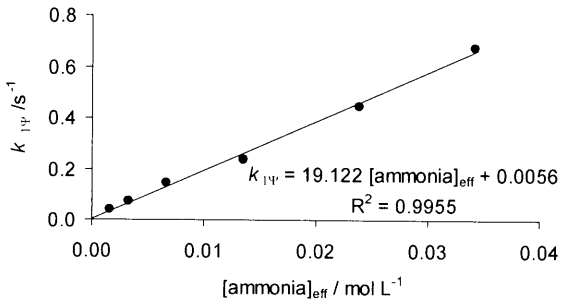


Figure 2.1. Determination of the second-order rate constant ($k_{2,N}$ = 19.1 M^{-1} s^{-1}) for the reaction of $(dma)_2CH^+$ with ammonia (**1a**) in water at 20 °C.

The linear dependence of $k_{1\Psi}$ on the concentration of amine, as depicted in Figure 2.1, indicates either that the attack of the amines at the benzhydrylium ions is rate-determining (Scheme 2.1) or that amines act as general base catalysts for the attack of water on Ar_2CH^+. The latter explanation has been excluded by Bunton[26] by demonstrating amine formation in the reaction of the tris-(p-methoxy)tritylium ions with ammonia and with several amines. In accordance with rate determining attack of the amines at the benzhydrylium ions, identical rate constants were found within experimental error when the reaction of $(dma)_2CH^+$ and aniline (**1p**) was studied at different pH (phosphate buffer) and without buffer (Figure 2.2).

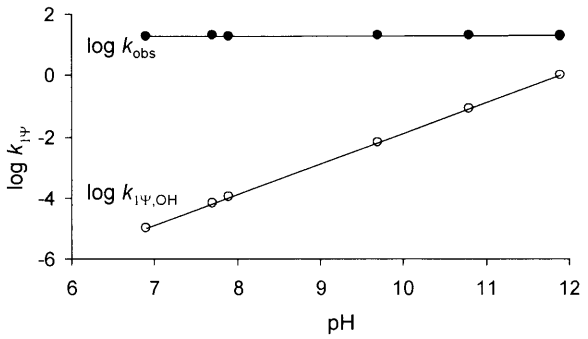
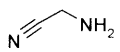
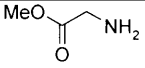
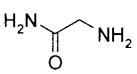
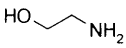
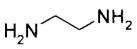
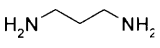
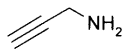


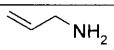
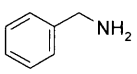
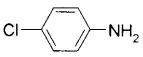
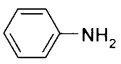
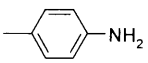
Figure 2.2. Plot of the measured rate constants log k_{obs} (•) and the calculated rate constants log $k_{1\Psi,OH^-}$ (○) versus pH for the reactions of aniline (c_0 = 9.27 × 10^{-4} M) with $(dma)_2CH^+$ (c_0 = 3.47 × 10^{-5} M) at 20 °C in aqueous phosphate buffer (cosolvent: 9 vol-% CH_3CN; $k_{1\Psi,OH^-}$ = k_{2,OH^-}[OH^-] was calculated from the measured pH and k_{2,OH^-} from ref 18).

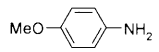
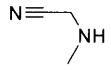
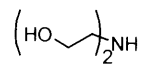
In the reactions of anilines with less electrophilic benzhydrylium ions, reversibility of the initial attack was indicated by a deviation of the disappearance of [Ar_2CH^+] from the single-exponential decay. In such cases, first-order decay of [Ar_2CH^+] was achieved by using high concentrations of the anilines or by working in buffered solutions (HPO_4^{2-} /PO_4^{3-}) at pH 11.
Table 2.2 collects all second-order rate constants determined in this investigation.

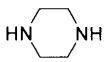
Table 2.2. Second-order rate constants for the reactions of benzhydrylium tetrafluoroborates with primary amines **1** in water (20 °C).

	Amine	*N*	*s*	Ar_2CH^+	$k_{2,N}$ / $M^{-1}s^{-1}$
1a	NH_3	9.48	0.59	$(mor)_2CH^+$	2.51×10^2 [a]
				$(dma)_2CH^+$	1.91×10^1
				$(pyr)_2CH^+$	1.43×10^1
				$(thq)_2CH^+$	5.39
				$(ind)_2CH^+$	2.39
				$(jul)_2CH^+$	1.41
				$(lil)_2CH^+$	4.07×10^{-1}
1b	$MeNH_2$	13.85	0.53	$(dma)_2CH^+$	4.25×10^3
				$(pyr)_2CH^+$	1.72×10^3
				$(thq)_2CH^+$	9.21×10^2
				$(ind)_2CH^+$	4.24×10^2
				$(jul)_2CH^+$	2.03×10^2
				$(lil)_2CH^+$	1.11×10^2
1c	$EtNH_2$	12.87	0.58	$(dma)_2CH^+$	2.39×10^3
				$(pyr)_2CH^+$	9.70×10^2
				$(ind)_2CH^+$	2.36×10^2
1d	$iPrNH_2$	12.00	0.56	$(dma)_2CH^+$	6.70×10^2
				$(pyr)_2CH^+$	2.52×10^2
				$(thq)_2CH^+$	1.34×10^2
				$(jul)_2CH^+$	2.79×10^1
1e	$tBuNH_2$	10.48	0.65	$(mor)_2CH^+$	2.14×10^3 [a]
				$(dma)_2CH^+$	1.60×10^2
				$(pyr)_2CH^+$	6.01×10^1
				$(thq)_2CH^+$	2.97×10^1
				$(ind)_2CH^+$	9.90
				$(lil)_2CH^+$	2.61
	Amine	*N*	*s*	Ar_2CH^+	
1f		10.80	0.61	$(dma)_2CH^+$	2.19×10^2
				$(pyr)_2CH^+$	7.74×10^1
				$(thq)_2CH^+$	3.91×10^1
				$(ind)_2CH^+$	1.79×10^1
				$(jul)_2CH^+$	6.08
				$(lil)_2CH^+$	3.20

	Amine	*N*	*s*	Ar_2CH^+	$k_{2,N}$ / $M^{-1}s^{-1}$
1g		12.08	0.60	$(dma)_2CH^+$	1.21×10^3
				$(pyr)_2CH^+$	4.09×10^2
				$(thq)_2CH^+$	2.04×10^2
				$(jul)_2CH^+$	4.02×10^1
1h		12.29	0.58	$(mor)_2CH^+$	1.03×10^4 [a]
				$(dma)_2CH^+$	1.05×10^3
				$(pyr)_2CH^+$	4.19×10^2
				$(thq)_2CH^+$	2.38×10^2
				$(ind)_2CH^+$	9.22×10^1
				$(jul)_2CH^+$	4.77×10^1
				$(lil)_2CH^+$	2.45×10^1
1i		12.61	0.58	$(mor)_2CH^+$	1.40×10^4 [a]
				$(dma)_2CH^+$	1.64×10^3
				$(pyr)_2CH^+$	6.38×10^2
				$(thq)_2CH^+$	3.23×10^2
				$(jul)_2CH^+$	6.49×10^1
				$(lil)_2CH^+$	3.50×10^1
1j		13.28	0.58	$(mor)_2CH^+$	3.78×10^4 [a]
				$(dma)_2CH^+$	4.19×10^3
				$(pyr)_2CH^+$	1.69×10^3
				$(thq)_2CH^+$	8.67×10^2
				$(ind)_2CH^+$	3.78×10^2
				$(jul)_2CH^+$	1.74×10^2
				$(lil)_2CH^+$	9.03×10^1
1k		14.02	0.54	$(dma)_2CH^+$	5.80×10^3
				$(pyr)_2CH^+$	2.28×10^3
				$(thq)_2CH^+$	1.30×10^3
				$(jul)_2CH^+$	2.73×10^2
				$(lil)_2CH^+$	1.38×10^2
1l		12.29	0.59	$(mor)_2CH^+$	1.17×10^4 [a]
				$(dma)_2CH^+$	1.20×10^3
				$(pyr)_2CH^+$	4.47×10^2
				$(thq)_2CH^+$	2.42×10^2
				$(ind)_2CH^+$	1.09×10^2
				$(jul)_2CH^+$	4.81×10^1
				$(lil)_2CH^+$	2.57×10^1

	Amine	*N*	*s*	Ar_2CH^+	$k_{2,N}$ / $M^{-1}s^{-1}$
1m		13.21	0.54	$(dma)_2CH^+$	2.35×10^3
				$(pyr)_2CH^+$	9.55×10^2
				$(thq)_2CH^+$	4.98×10^2
				$(jul)_2CH^+$	1.03×10^2
				$(lil)_2CH^+$	5.53×10^1
1n		13.44	0.55	$(mor)_2CH^+$	3.13×10^4 [a]
				$(dma)_2CH^+$	3.04×10^3
				$(pyr)_2CH^+$	1.29×10^3
				$(thq)_2CH^+$	7.82×10^2
				$(ind)_2CH^+$	3.06×10^2
				$(jul)_2CH^+$	1.82×10^2
				$(lil)_2CH^+$	9.46×10^1
1o					
	Solvent: CH_3CN	12.92	0.60	$(mor)_2CH^+$	3.29×10^4
				$(dma)_2CH^+$	2.63×10^3
				$(pyr)_2CH^+$	1.85×10^3
1p					
	Solvent: H_2O	12.99	0.73	$(mor)_2CH^+$	4.06×10^5 [a]
				$(dma)_2CH^+$	1.70×10^4
				$(pyr)_2CH^+$	4.98×10^3
				$(thq)_2CH^+$	3.26×10^3
				$(thq)_2CH^+$	3.38×10^3 [b]
				$(ind)_2CH^+$	1.27×10^3
				$(jul)_2CH^+$	5.17×10^2 [b]
	Solvent: CH_3CN	12.64	0.68	$(mor)_2CH^+$	7.02×10^4
				$(dma)_2CH^+$	7.16×10^3
				$(pyr)_2CH^+$	3.14×10^3
				$(thq)_2CH^+$	8.71×10^2
1q					
	Solvent: H_2O	13.00	0.79	$(mor)_2CH^+$	1.06×10^6 [a]
				$(dma)_2CH^+$	3.99×10^4
				$(pyr)_2CH^+$	1.07×10^4
				$(thq)_2CH^+$	7.34×10^3
				$(ind)_2CH^+$	2.88×10^3
	Solvent: CH_3CN	13.19	0.69	$(mor)_2CH^+$	2.07×10^5
				$(dma)_2CH^+$	1.98×10^4
				$(pyr)_2CH^+$	6.21×10^3
				$(thq)_2CH^+$	2.90×10^3

	Amine	*N*	*s*	Ar_2CH^+	$k_{2,N}$ / $M^{-1}s^{-1}$
1r					
	Solvent: H_2O	16.53	0.50	$(dma)_2CH^+$	6.68×10^4
				$(thq)_2CH^+$	1.31×10^4
				$(lil)_2CH^+$	1.96×10^3
	Solvent: CH_3CN	13.42	0.73	$(mor)_2CH^+$	6.23×10^5
				$(dma)_2CH^+$	4.72×10^4
				$(pyr)_2CH^+$	1.65×10^4
1s	Me_2NH	17.12	0.50	$(mor)_2CH^+$	6.10×10^5 [a]
				$(dma)_2CH^+$	1.05×10^5
				$(pyr)_2CH^+$	4.89×10^4
				$(thq)_2CH^+$	2.87×10^4
				$(ind)_2CH^+$	1.20×10^4
				$(jul)_2CH^+$	7.06×10^3
				$(lil)_2CH^+$	3.52×10^3
1t	Et_2NH	14.68	0.53	$(mor)_2CH^+$	7.92×10^4 [a]
				$(dma)_2CH^+$	1.12×10^4
				$(pyr)_2CH^+$	4.88×10^3
				$(thq)_2CH^+$	2.84×10^3
				$(ind)_2CH^+$	1.16×10^3
				$(jul)_2CH^+$	6.46×10^2
				$(lil)_2CH^+$	3.16×10^2
1u		13.50	0.59	$(dma)_2CH^+$	6.47×10^3
				$(pyr)_2CH^+$	2.37×10^3
				$(thq)_2CH^+$	1.29×10^3
1v		13.00	0.61	$(dma)_2CH^+$	4.88×10^3
				$(pyr)_2CH^+$	1.70×10^3
				$(thq)_2CH^+$	9.01×10^2
1w		17.21	0.49	$(dma)_2CH^+$	1.06×10^5
				$(pyr)_2CH^+$	5.08×10^4
				$(thq)_2CH^+$	2.62×10^4
				$(ind)_2CH^+$	1.22×10^4
				$(jul)_2CH^+$	7.33×10^3
				$(lil)_2CH^+$	3.41×10^3
1x		18.13	0.44	$(dma)_2CH^+$	6.09×10^4
				$(pyr)_2CH^+$	3.68×10^4
				$(thq)_2CH^+$	2.64×10^4
				$(ind)_2CH^+$	9.01×10^3
				$(jul)_2CH^+$	6.99×10^3
				$(lil)_2CH^+$	3.05×10^3

Amine		N	s	Ar_2CH^+	$k_{2,N}$ / $M^{-1}s^{-1}$
1y		18.29	0.46	$(dma)_2CH^+$	1.60×10^5
				$(pyr)_2CH^+$	7.29×10^4
				$(thq)_2CH^+$	4.40×10^4
				$(ind)_2CH^+$	2.13×10^4
				$(jul)_2CH^+$	1.23×10^4
				$(lil)_2CH^+$	6.37×10^3
1z		15.62	0.54	$(mor)_2CH^+$	3.16×10^5 [a]
				$(dma)_2CH^+$	4.61×10^4
				$(pyr)_2CH^+$	1.89×10^4
				$(thq)_2CH^+$	1.08×10^4
				$(ind)_2CH^+$	4.51×10^3
				$(jul)_2CH^+$	2.36×10^3
				$(lil)_2CH^+$	1.14×10^3
1zz		17.22	0.50	$(mor)_2CH^+$	6.10×10^5 [a]
				$(dma)_2CH^+$	1.27×10^5
				$(pyr)_2CH^+$	5.34×10^4
				$(thq)_2CH^+$	3.04×10^4
				$(ind)_2CH^+$	1.36×10^4
				$(jul)_2CH^+$	7.50×10^3
				$(lil)_2CH^+$	3.74×10^3

[a] Cosolvent: 9 vol-% CH_3CN. [b] At pH = 11.

2.3. Structure Nucleophilicity Relationships

As previously reported for analogous reactions of numerous other nucleophiles, linear correlations are obtained (Figure 2.3), when log $k_{2,N}$ for the reactions of the amines **1a** – **zz** with benzhydrylium ions are plotted against their electrophilicity parameters *E*, indicating that these reactions follow eq 2.3. The intercepts on the abscissa correspond to the negative values of the nucleophilicity parameters *N*, and the slopes of these correlations yield the parameters *s* (= s_N, if they are used for S_N2 reactions[25]).

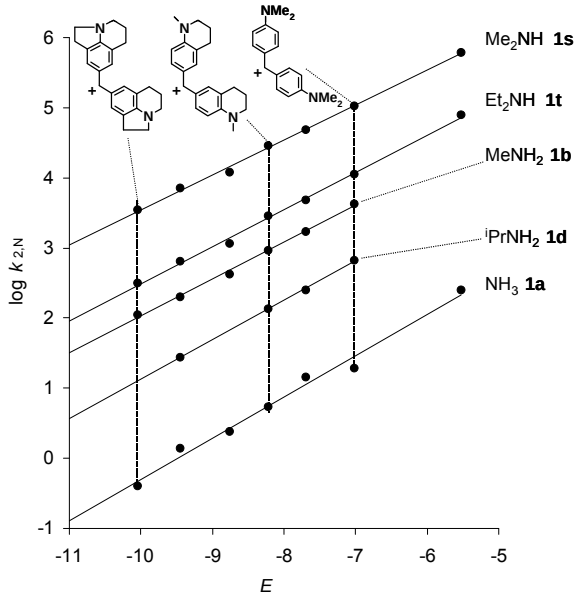


Figure 2.3. Plots of the rate constants log $k_{2,N}$ for the reactions of amines with benzhydrylium cations (from Table 2.2) versus the electrophilicity parameters *E* of Ar_2CH^+ (from Table 2.1).

The second-order rate constants $k_{2,N}$ for the reactions of the amines **1b-zz** with $(dma)_2CH^+$ are between 1.6×10^2 M^{-1} s^{-1} (**1e**) and 1.6×10^5 M^{-1} s^{-1} (**1y**), and only ammonia ($k_{2,N}$ = 19 M^{-1} s^{-1}) reacts more slowly. Because all reactivities are thus within four orders of magnitude, structure reactivity relationships might be based on reactivities toward a single electrophile, e.g., toward $(dma)_2CH^+$. However, the small differences in slopes *s* imply that the relative nucleophilicities of the amines depend only slightly on the electrophilicity of the reaction partners (as in Ritchie-type correlations),[27] which allows us to base the discussion on the nucleophilicity parameters *N*, which reflect the negative intercepts of the correlation lines of Figure 2.3 on the abscissa.

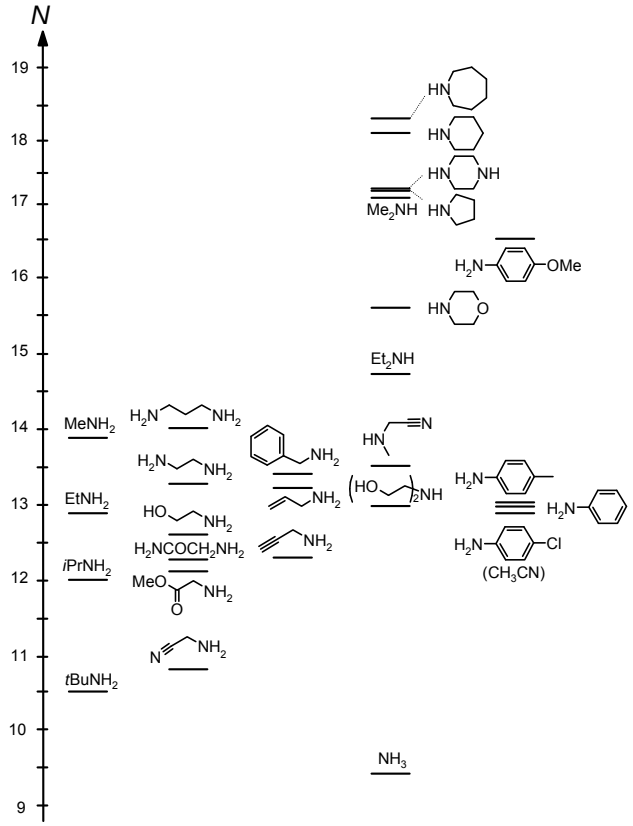


Figure 2.4. Comparison of the nucleophilic reactivities of amines in water. Other solvents are given in parentheses.

Figure 2.4 illustrates that the nucleophilicities of primary alkyl amines decrease significantly with increasing branching from $MeNH_2$ (N = 13.85) to *tert*-butylamine (N = 10.48). The second column of Figure 2.4 reveals that the decrease of nucleophilicity caused by an α-cyano group is significantly stronger than the effect of an α-ester, α-amido, or β-hydroxy group. Because the N parameters refer to molecules and do not contain statistical corrections, the increase of N from aminoethane (**1c**) to 1,2-diaminoethane (**1j**) and 1,3-diaminopropane (**1k**) does not indicate increased nucleophilicities of the individual amino groups. The approximate doubling of the rate constants for the reactions of $(dma)_2CH^+$ with 1,2-diaminoethane (**1j**) (4190 $M^{-1}s^{-1}$) and 1,3-diaminopropane (**1k**, 5800 $M^{-1}s^{-1}$) relative to aminoethane (**1c**, 2390 $M^{-1}s^{-1}$) shows that there is only little interaction between the amino groups in 1,2-diaminoethane (**1j**) and 1,3-diaminopropane (**1k**), and the individual amino groups have approximately the same reactivity in all three compounds. Closely similar reactivities of aminoethane (**1c**), benzylamine (**1n**), allyl amine (**1m**) and propargyl amine (**1l**) show (Column 3, Figure 2.4) that replacement of the methyl group in aminoethane (**1c**) by unsaturated hydrocarbon groups also has only little influence on the reactivity of the amino group.

Tremendous effects are observed, however, when the hydrogens of ammonia (N = 9.48) are successively replaced by one ($MeNH_2$, N = 13.85) and two methyl groups (Me_2NH, N = 17.12). While the pK_{aH} values in water show only a moderate increase in basicity from NH_3 (pK_{aH} = 9.25) to $MeNH_2$ (pK_{aH} = 10.66) and Me_2NH (pK_{aH} = 10.73), nucleophilicity grows

steadily in this series and can be explained by the decrease of hydration energy as the hydrogen atoms of ammonia are successively replaced by methyl groups.[26] As shown by the comparison of dimethylamine (**1s**, N = 17.12) and diethylamine (**1t**, N = 14.68) steric factors play a considerably greater role for secondary amines than for primary amines ($MeNH_2$: N = 13.85, $EtNH_2$: N = 12.87).

Most remarkable in view of nucleophilicity/basicity correlations is the fact that aniline, which is less basic than ammonia by 4.7 pK_{aH} units, is a considerably stronger nucleophile than ammonia. The direct comparison of the rate constants shows that $(dma)_2CH^+$ reacts even 7 times faster with aniline (**1p**) than with ethylamine (**1c**), and it is because of the different slope parameters that aniline (**1p**) and ethylamine (**1c**) have comparable values of N. Due to the much smaller value of s for p-methoxyaniline (**1r**) in water in comparison with the other anilines, its N parameter turns out to be particularly high, and good Hammett correlations N/σ do not result. When the rate constants for the reactions of **1o**-**r** with $(dma)_2CH^+$ are plotted versus σ (Figure 2.5) linear correlations are obtained, from which ρ values of –2.1 (in H_2O) and –2.5 (in CH_3CN) result.

The cyclic amines **1w**-**1y** show similar reactivities toward $(dma)_2CH^+$ comparable to dimethylamine, and the small differences in N are due to differences in s. The noticeably smaller N value for morpholine (**1z**, N = 15.62) compared to piperidine (**1x**, N = 18.13) is also a consequence of the different slopes (0.54 vs. 0.44): While $(dma)_2CH^+$ reacts only 1.3 times faster with **1x** than with **1z**, this ratio increases to 3 for the less reactive $(jul)_2CH^+$ and is expected to grow even more as the electrophilicity of the reaction partner decreases further.

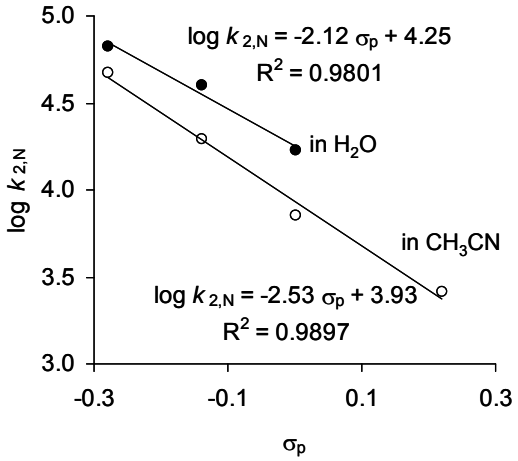


Figure 2.5. Correlation of the rate constants log $k_{2,N}$ versus σ_p for the reactions of anilines with $(dma)_2CH^+$ in H_2O and CH_3CN at 20 °C.

2.4. **Solvent effects**

Figure 2.5 shows that anilines react approximately two times faster in water than in acetonitrile. Obviously, hydrogen-bond stabilization of anilines in water plays a minor role because of their low basicity. On the other hand, pyridines which have similar pK_{aH} values in water as anilines react 90 times faster with benzhydrylium ions in acetonitrile than in water.[23]

For a variety of alkyl amines reactivities toward benzhydrylium ions have also been determined in methanol.[25] While the *N* parameters are of comparable magnitude as in water, the rate constants for the reactions with $(dma)_2CH^+$ are generally three to six times greater in methanol than in water.

In previous work we have found, that the rates of the reactions of carbocations with neutral σ- and π-nucleophiles are only slightly affected by solvent polarity, because charges are neither created nor destroyed in the rate-determining step.[28] Figure 2.6 shows that the situation is different for amines: the rate constants decrease with increasing E_T^N-values[29,30] of the solvents; the reaction of morpholine (**1z**) with $(ind)_2CH^+$ is 72 times slower in water than in DMSO. A similar behavior was found for the reaction of 4-(dimethylamino)pyridine with $(dma)_2CH^+$ in different solvents (log $k_{2,N}$ = -3.35 E_T^N + 6.75).[23]

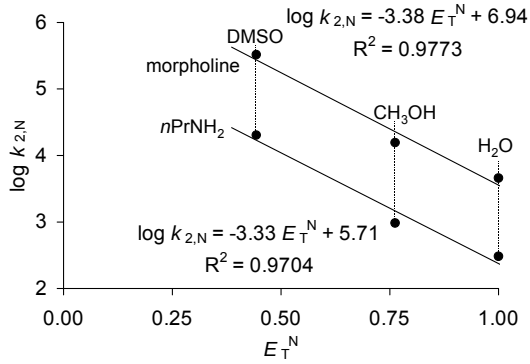
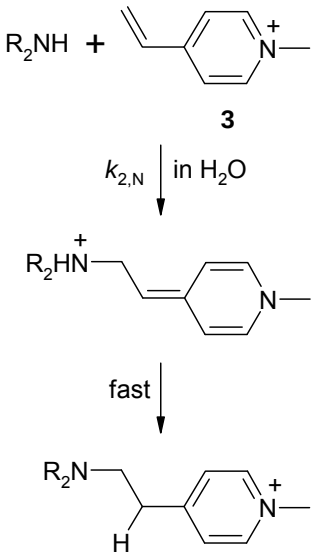


Figure 2.6. Plot of the rate constants log $k_{2,N}$ versus E_T^N for the reactions of morpholine (**1z**) and nPrNH$_2$ with $(ind)_2CH^+$ in different solvents at 20 °C (rate constants from Table 2, ref 28 and ref 25; E_T^N from refs 29 and 30; MeOH containing 9 vol-% MeCN as a cosolvent)

2.5. **Reactions of Amines with other Electrophiles**

The most comprehensive work on amine nucleophilicities in water was previously published by Heo and Bunting[8] who investigated the reactivities of 91 amines towards the 1-methyl-4-vinylpyridinum cation **3** (Scheme 2.2).



Scheme 2.2.

It was reported[8] that the correlation between nucleophilicity and basicity of amines was rather poor (Figure 2.7). Although the subclasses of primary, secondary and tertiary amines cluster together in the same regions of Fig 2.7, the individual treatments of these subclasses still show poor rate equilibrium relationships.

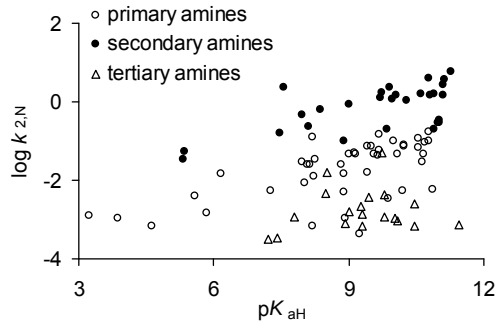


Figure 2.7. Plot of the rate constants log $k_{2,N}$ versus pK_{aH} for the reactions of amines with 1-methyl-4-vinylpyridinium **3** in water at 25 °C (rate constants from ref 8).

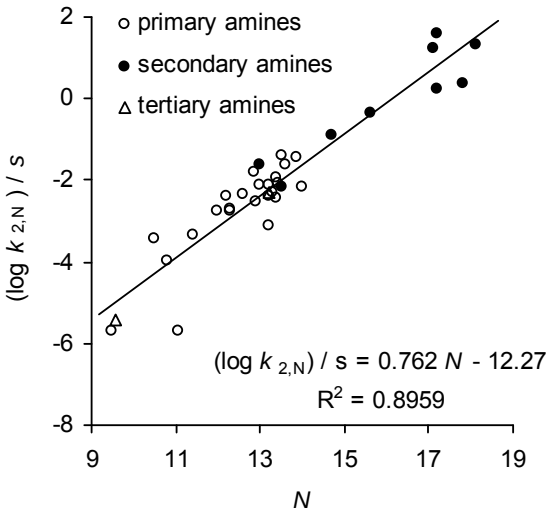


Figure 2.8. Relationship between the rate constants for the reactions of amines with 1-methyl-4-vinylpyridinium **3** in water at 25 °C with the *N* and *s* parameters of amines given in Table 2.2 (rate constants $k_{2,N}$ from ref 8; data for imidazole, amino acids and peptides, which will be reported separately, have also been included).

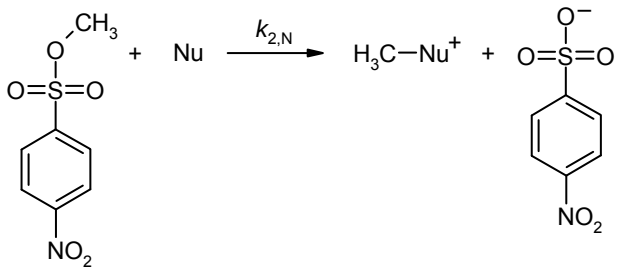
Figure 2.8 shows a linear correlation of moderate quality between (log $k_{2,N}$)/*s* and *N*, where $k_{2,N}$ refers to the reactions of amines with the vinylpyridinium ion **3**, and *N* and *s* are derived from the reactions of amines with benzhydrylium ions (Table 2.2 and ref 23). Because the slope of this correlation line (0.765) deviates from 1, the rate constants for the nucleophilic additions of amines to **3** are not properly reproduced by eq 2.3, and it has to be examined whether the consideration of an additional, electrophile-specific slope parameter, as previously described for S_N2 reactions,[25] is sufficient to reproduce also the rate constants for the reactions of **3** with other types of nucleophiles. Irrespective of the outcome of this analysis, the correlation given in Figure 2.8 can be used to estimate *N* parameters for further amines from their reactivities toward **3** which have been reported by Heo and Bunting. In order to calculate the estimated *N* parameters given in Table 2.3, the *s* parameters were assumed to be the same as for structurally analogous amines.

Table 2.3. Estimates of *N* parameters for amines from reactivities toward the 1-methyl-4-vinylpyridinium ion **3** from the correlation given in Figure 2.8.

Nucleophile	$k_{2,N}$ / M^{-1} s^{-1} [a]	Model for *s*	*s*	$N_{estimated}$
$HO(CH_2)_3NH_2$	7.30×10^{-2}	$H_2N(CH_2)_3NH_2$	0.54	13.3
$C_6H_5(CH_2)_2NH_2$	9.86×10^{-2}	$C_6H_5CH_2NH_2$	0.55	13.7
$CH_3O(CH_2)_2NH_2$	4.60×10^{-2}	$HO(CH_2)_2NH_2$	0.58	13.1
$H_3N^+(CH_2)_3NH_2$	1.50×10^{-2}	$H_2N(CH_2)_3NH_2$	0.54	11.7
$H_3N^+(CH_2)_2NH_2$	5.57×10^{-3}	$H_2N(CH_2)_2NH_2$	0.58	11.0
$CF_3CH_2NH_2$	1.52×10^{-3}	$EtNH_2$	0.58	9.7
Cyclohexylamine	4.80×10^{-2}	$(CH_3)_2CHNH_2$	0.56	13.0
$HOCH_2CH(CH_3)NH_2$	1.62×10^{-2}	$(CH_3)_2CHNH_2$	0.56	11.9
$HOCH_2C(CH_3)_2NH_2$	3.40×10^{-3}	$HO(CH_2)_2NH_2$	0.58	10.5
$(HOCH_2)_2C(CH_3)NH_2$	1.05×10^{-3}	$HO(CH_2)_2NH_2$	0.58	9.4
$(HOCH_2)_3CNH_2$	6.57×10^{-4}	$HO(CH_2)_2NH_2$	0.58	8.9
$H_2NCOCH(CH_3)NH_2$	8.60×10^{-3}	$(CH_3)_2CHNH_2$	0.56	11.3
CH_3ONH_2	6.70×10^{-4}	$HONH_2$	0.55	8.5
$CH_3CONHNH_2$	1.24×10^{-3}	$H_2NCONHNH_2$	0.52	8.8
$CH_3(CH_2)_3NHCH_3$	1.63	$(CH_3)_2NH$	0.50	16.7
$CH_3NH(CH_2)_3NHCH_3$	1.52	$(CH_3)_2NH$	0.50	16.6
$CH_3NH(CH_2)_2NHCH_3$	1.08	$(CH_3)_2NH$	0.50	16.2
$HO(CH_2)_2NHCH_3$	1.17	$(CH_3)_2NH$	0.50	16.3
$NC(CH_2)_2NHCH_3$	2.30×10^{-1}	$(CH_3)_2NH$	0.50	14.4
$CH_3NH_2(CH_2)_2NHCH_3$	1.55×10^{-1}	$(CH_3)_2NH$	0.50	14.0
$(CH_3)_2CHNHCH_3$	2.02×10^{-1}	$(CH_3)_2NH$	0.50	14.3
$C_6H_5CH_2NHCH_3$	1.77	$(CH_3)_2NH$	0.50	16.8
$CH_3NHNHCH_3$	2.30	$(CH_3)_2NH$	0.50	17.1
$(CH_3CH_2CH_2)_2NH$	3.00×10^{-1}	$(CH_3CH_2)_2NH$	0.53	14.8
$HO(CH_2)_2NHCH_2CH_3$	2.00×10^{-1}	$(CH_3CH_2)_2NH$	0.53	14.4
Perhydroazocine	1.42	Perhydroazepine	0.46	16.5
Thiamorpholine	8.64×10^{-1}	Morpholine	0.54	15.9
4-Formylpiperidine	4.67×10^{-1}	Piperidine	0.44	15.1
2-Methylpiperidine	2.92×10^{-1}	Piperidine	0.44	14.5
2-Hydroxylmethylpiperidine	2.31	Piperidine	0.44	17.2
Piperazinium cation	3.54×10^{-2}	Piperazine	0.50	12.3

[a] Rate constants for reaction of the amines with **3** in H_2O at 25 °C (data from ref 8)

Bunting and Heo have previously reported that the rate constants for the reactions of amines with methyl 4-nitrobenzenesulfonate (Scheme 2.3) correlate linearly with their reactivities toward **3**.[9]



Scheme 2.3.

In line with this report, Figure 2.9 shows that the *N* and *s* parameters of amines (Table 2.2) can also be used to describe the S_N2 reactions of amines with methyl 4-nitrobenzenesulfonate. The slope of 0.31 shows that variation of the amines affects the reactivities toward the methyl 4-nitrobenzenesulfonate by only 31% of the amount that is observed in reactions with benzhydrylium ions (slope = 1.00). Accordingly, we have previously shown that (log $k_{2,N}$)/*s* versus *N* plots have electrophile-specific slopes <1 in the case of S_N2 reactions, which had prompted us to extend eq 2.3 by an electrophile-specific slope parameter s_E.[25]

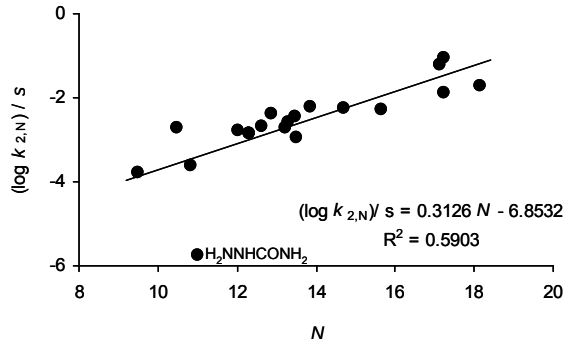
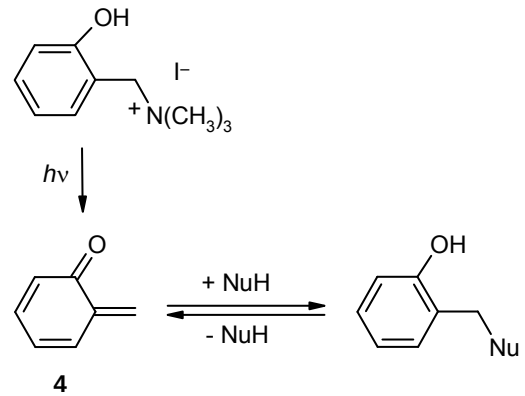


Figure 2.9. Relationship between the rate constants for the reactions of amines with methyl 4-nitrobenzenesulfonate in water at 25 °C with the *N* and *s* parameters of amines given in Table 2.2 (rate constants $k_{2,N}$ from ref 9; *N* and *s* parameter for semicarbazide taken from ref 28).



Scheme 2.4.

Freccero et al. determined the rate constants for the Michael additions of nucleophiles towards the *o*-quinone methide **4** (Scheme 2.4).[31] Figure 2.10 shows a good correlation between the reactivities of nucleophiles toward **4** and the nucleophilicity parameters *N* and *s*. The slope close to 1 derived from reactions with widely differing rate constants shows that the reactions of **4** with nucleophiles may be described by eq 2.3. If a slope of 1 is enforced, as required by eq 2.3 one can calculate an electrophilicity parameter *E*(**4**) = -2.79. This value can be used for estimating *N* parameters for further nucleophiles from their reported rate constants toward **4**.

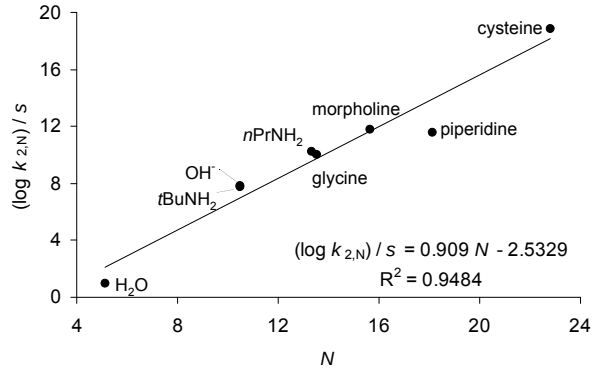


Figure 2.10. Relationship between the rate constants for the reactions of nucleophiles with *o*-quinone methide **4** in water (rate constants $k_{2,N}$ from ref 31; for H_2O determined at ionic strength I = 0.0; for *t*$BuNH_2$, *n*$PrNH_2$, glycine, morpholine, piperidine at pH = 12.0; for cysteine at pH = 12.2) with the *N* and *s* parameters of amines given in Table 2.2 (For this correlation, data from ref 28 and data from amino acids, which will be reported later, have also been included).

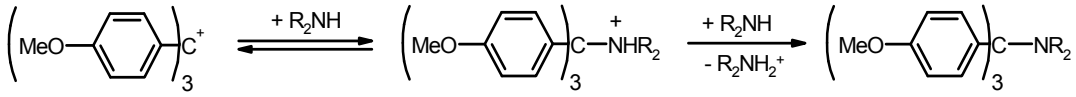
Kane-Maguire reported on the reactions of anilines with iron π-complexes in acetonitrile.[7,32] Because electrophilicity parameters for the iron π-complexes have previously been derived from the rates of their reactivities with π-nucleophiles,[11] it is now possible to analyze the reliability of eq 2.3 for reproducing Kane-Maguire's rate constants with the *N* and *s* parameters determined in this work (Table 2.4).

Table 2.4. Comparison of calculated and observed second-order rate constants (20 °C, CH_3CN) for the reactions of tricarbonyl iron dienylium ions $[Fe(CO)_3R]^+$ with anilines **1p**-**q**.

$XC_6H_4NH_2$	R =	C_6H_7	2-$MeOC_6H_6$	C_7H_9
	E[a]	-7.76	-8.94	-9.21
X = H	k_{calc} / M^{-1} s^{-1} [b]	2.33×10^3	3.57×10^2	
	k_{exp} / M^{-1} s^{-1} [c]	3.09×10^3	6.99×10^2	
X = CH_3	k_{calc} / M^{-1} s^{-1} [b]	5.58×10^3	8.56×10^2	5.57×10^2
	k_{exp} / M^{-1} s^{-1} [c]	1.43×10^4	3.93×10^3	9.06×10^2

[a] From ref 11. [b] Calculated by eq 2.3, using the E parameters of ref 11 and N and s for the anilines in acetonitrile from Table 2.2. [c] Rate constants in acetonitrile calculated for 20 °C from the Eyring activation parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$ given in ref 32.

Bunton investigated the reactivities of primary and secondary amines towards the tris-(*p*-anisyl)methyl cation **5** (Scheme 2.5) in water.[26]



5

Scheme 2.5.

Figure 2.11 shows that the reactivities of amines toward the tritylium ion **5** correlate only modestly with the benzhydrylium-derived nucleophilicity parameters N, in agreement with our previous warning to apply eq 2.3 for reactions with tritylium ions.[11] Because tritylium reactivities are significantly controlled by steric effects, it appears likely that the small slope of the correlation in Figure 2.11 is due to the steric retardation of the reactions of the more nucleophilic secondary amines with the tritylium ion **5**.[11, 18] The bulky tBuNH$_2$ (**1e**), which reacts 190 times more slowly with the tritylium ion **5** than predicted by eq 2.3, can also be explained by a steric effect.

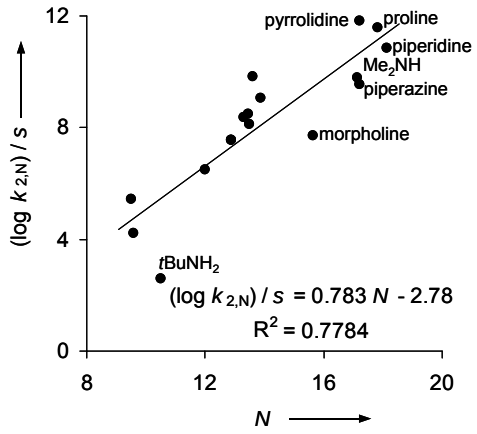
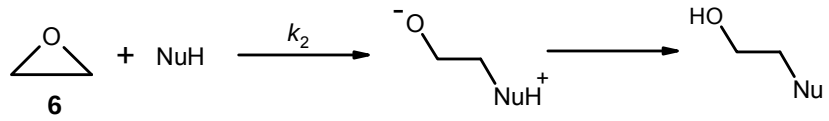


Figure 2.11. Relationship between the rate constants for the reactions of primary and secondary amines with tris-(*p*-anisyl)methyl cation **5** in water (rate constants $k_{2,N}$ at 25 °C from ref 26) with the N and s parameters of amines given in Table 2.2.

Because of the narrow reactivity ranges investigated, meaningful correlations between the reactivities of amines with ethyleneoxide, benzoylacetylene, 5-nitrosopenicillamine, and *N*-nitrososulfonamides could not be obtained as shown in Figures 2.12-2.15.

Virtanen and Korhonen studied the kinetics of the reaction of ethylene oxide with a series of nucleophiles in aqueous solution at 25 °C (Scheme 2.6). Figure 2.12 shows a correlation between the reactivities of nucleophiles toward ethylene oxide **6** and the reactivities of the nucleophiles determined toward benzhydrylium ions.



6

Scheme 2.6

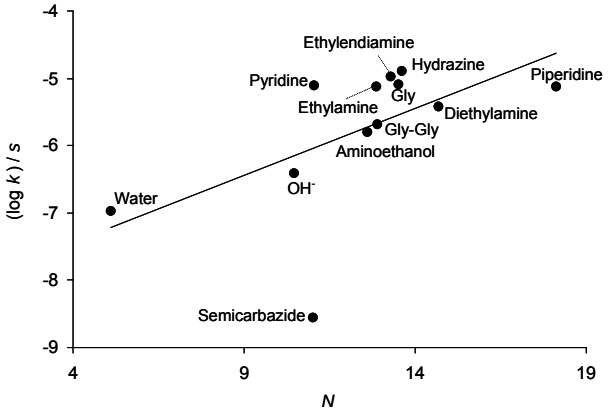
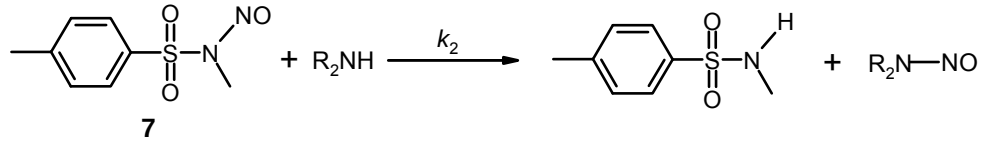


Figure 2.12. Relationship between the rate constants for the reactions of various nucleophiles with ethylene oxide **6** in water at 25°C (rate constants *k* from ref 33; the rate constant for water is first-order, all others are second-order) with the *N* and s parameters (determined at 20 °C in this work and in refs 18, 19, 20; correlation line shown includes all data (log *k*) / *s* = 0.199 *N* – 8.23 ; R^2 = 0.3147; without semicarbazide (log *k*) / *s* = 0.160 *N* – 7.52 ; R^2 = 0.5821).

Leis investigated the kinetics of the reaction of *N*-methyl-*N*-nitrosotoluene-*p*-sulfonamide **7** with several primary, secondary and tertiary amines in aqueous solution at 25 °C (Scheme 2.7).[34] Figure 2.13 shows a moderate correlation between reactivities of amines toward the nitrogen electrophile **7** and toward benzhydrylium ions.



7

Scheme 2.7

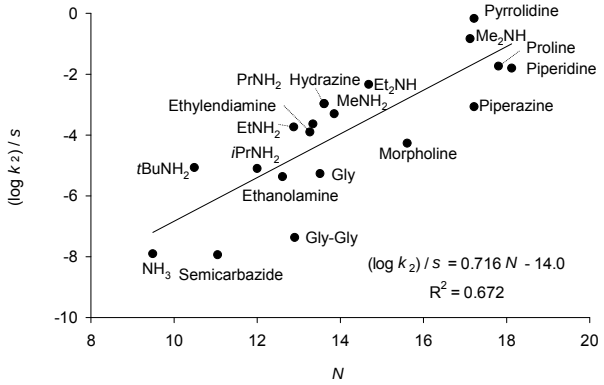
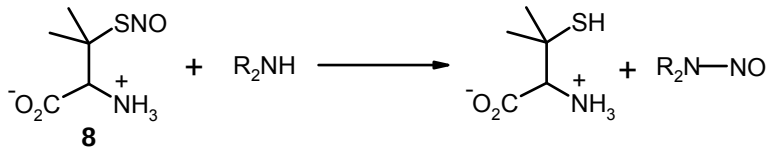


Figure 2.13. Relationship between the rate constants for the reactions of various amines with *N*-nitrososulfonamide **7** in water at 25°C (second-order rate constants k_2 from ref 34) with the *N* and s parameters (determined at 20 °C in this work and in refs 18, 35).

Williams reported on the kinetics of the reaction of *S*-nitrosopenicillamine **8** with various amines in aqueous solution at 25 °C (Scheme 2.8).[36] Figure 14 shows no correlation between the reactivities of amines determined toward **8** and the reactivities of amines determined toward benzhydrylium ions.



Scheme 2.8

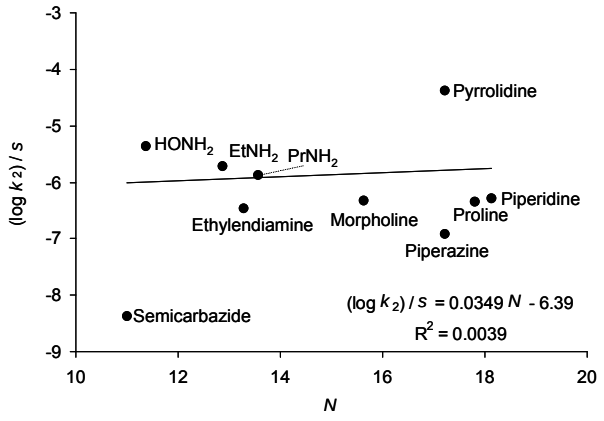
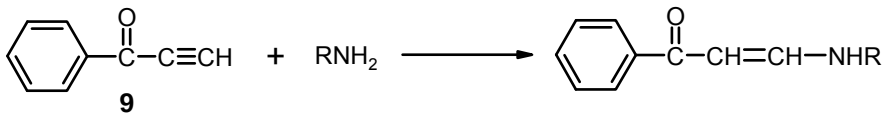


Figure 2.14. Relationship between the rate constants for the reactions of various amines with *S*-nitrosopenicillamine **8** in water at 25 °C (second-order rate constants k_2 from ref 36) with the *N* and s parameters (determined at 20 °C in this work and in refs 18, 35).

Um investigated the kinetics of the reactions of 1-phenyl-2-propyn-1-one **9** with primary amines in aqueous solution at 25 °C (Scheme 2.9).[37] Figure 2.15 shows a poor correlation

between the two data sets. Because of the narrow reactivity range investigated, the slope of this correlation cannot be interpreted.



9

Scheme 2.9

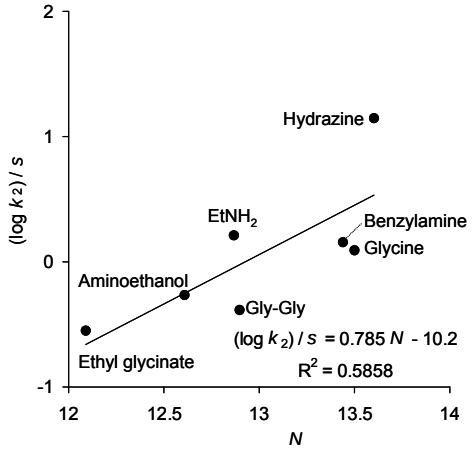


Figure 2.15. Relationship between the rate constants for the reactions of primary amines with 1-phenyl-2-propyn-1-one **9** in water at 25 °C (second-order rate constants k_2 from ref 37) with the *N* and *s* parameters (determined at 20 °C in this work and ref 35; the *N* parameter for ethyl glycinate was assumed to be the same as for methyl glycinate).

2.6. **Correlations between nucleophilicity and basicity**

The qualitative discussion in the section “Structure Nucleophilicity Relationships” has already shown that the nucleophilicities of some amines deviate dramatically from those expected from their basicities. Figure 2.16 shows, that the correlation between *N* and pK_{aH} is indeed very poor, in line with Bunting’s conclusion derived from the correlation of the reactivities of amines toward the 1-methyl-4-vinylpyridinium ion with their pK_{aH} values (Figure 2.7).[8]

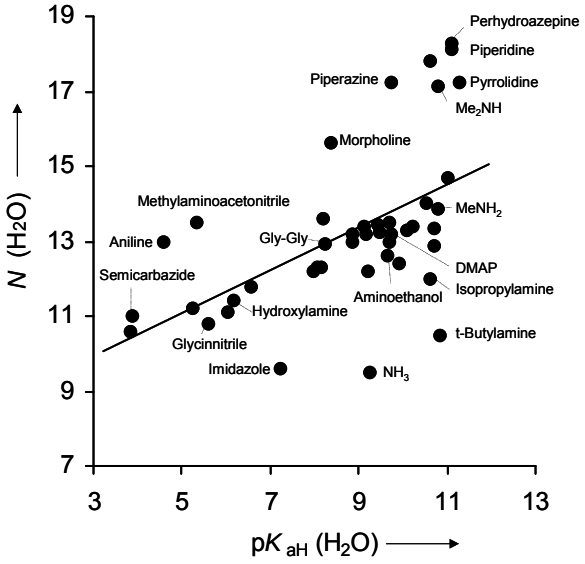


Figure 2.16. Plot of the nucleophilicity parameters *N* of amines versus pK_{aH} in water.

Figure 2.16 shows that not only cyclic amines such as piperidine, piperazine and pyrrolidine, but also acyclic secondary amines are more nucleophilic than expected from their basicities. Particularly striking is the large difference in nucleophilicity between Me_2NH (*N* = 17.12) and $MeNH_2$ (*N* = 13.85) despite comparable Brønsted basicities (pK_{aH} = 10.66 vs. 10.73). The unexpectedly high nucleophilicity of aniline, which was already mentioned above, is visualized in Figure 2.16: Despite its considerably lower basicity, aniline shows a nucleophilicity comparable to that of primary alkyl amines. The smaller energy of hydration, which may account for the reactivity increase from ammonia to alkyl amines is unlikely to be the only reason for the high nucleophilicity of aniline. Aniline, as well as secondary alkyl amines have lower oxidation potentials than primary alkyl amines.[38] For that reason, one can assume that in these reactions, the intrinsic barrier will be lower because of a larger contribution by inner-sphere electron transfer (favorable HOMO-LUMO interactions).[39] While this explanation has to be considered tentative, it is obvious from Figure 2.16 that more factors, in addition to basicity, have to be considered when explaining nucleophilicity.

2.7. Conclusions

The reactions of amines with benzhydrylium ions follow the correlation eq 2.3, which allows us to include amines into our comprehensive nucleophilicity scales[40] and compare amine nucleophilicities with those of other nucleophiles (Figure 2.17). In this way it becomes possible to predict the active species in equilibrium mixtures of various nucleophiles (amines, carbanions, phenolates) in aqueous solution. For the nucleophilicity series NH_3 < $PhNH_2$ ≈ $EtNH_2$ ≈ $MeNH_2$ < Me_2NH it was shown that predictions of nucleophilicities on the basis of basicities are misleading. Thus, ordinary secondary amines are considerably more nucleophilic than primary amines, and ammonia is much less reactive than primary alkyl amines, aniline, and pyridine. Because of the poor correlation between nucleophilic reactivities and pK_{aH} values of amines on one side and the demonstrated ability of the *N* and

s parameters to properly predict nucleophilic reactivities with a variety of structurally diverse electrophiles, we recommend to replace pK_{aH} as a tool for forecasting nucleophilic reactivity by *N* and *s*.

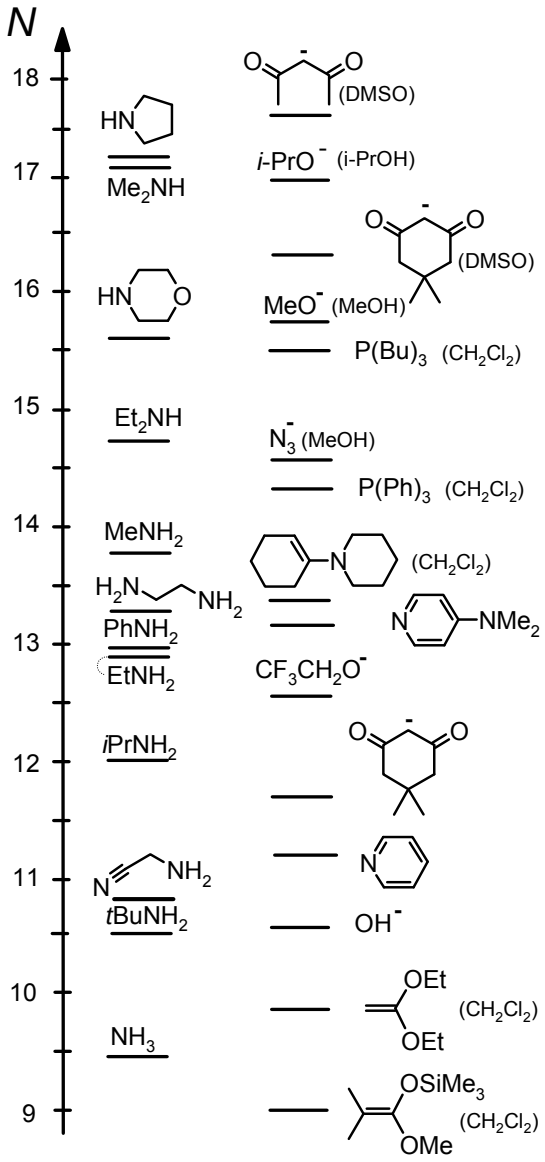


Figure 2.17. Comparison of the nucleophilic reactivities of amines with other types of nucleophiles in water.[40] Other solvents are given in parentheses.

2.8. Experimental

Kinetics

The reaction of benzhydrylium ions with amines were studied in aqueous solution. All amines were used as free bases.

As the reactions of the colored benzhydrylium ions with amines gave rise to colorless products, the reactions could be followed by employing UV-vis spectroscopy. The rates of slow reactions ($\tau_{1/2}$ > 10 s) were determined by using a J&M TIDAS diode array spectrophotometer, which was controlled by Labcontrol Spectacle software and connected to

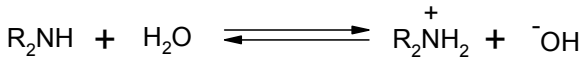
a Hellma 661.502-QX quartz Suprasil immersion probe (5 mm light path) via fiber optic cables and standard SMA connectors. The temperature of solutions during all kinetic studies was kept constant (usually 20.0 ± 0.2 °C) by using a circulating bath thermostat and monitored with a thermocouple probe that was inserted into the reaction mixture.
Hi-Tech SF-61DX2 stopped-flow spectrophotometer systems (controlled by Hi-Tech KinetAsyst2 software) were used for the investigation of rapid reactions of benzhydrylium ions with nucleophiles ($\tau_{1/2}$ < 10 s at 20 °C). The kinetic runs were initiated by mixing solutions of the nucleophile and the benzhydrylium salt in a 1:1 or 10:1 ratio. Amine concentrations at least 10 times higher than the benzhydrylium ions concentrations were usually employed, resulting in pseudo-first-order kinetics with an exponential decay of the Ar_2CH^+ concentration. First-order rate constants k_{obs} (s^{-1}) were obtained by least-squares fitting of the absorbance data (averaged from at least five kinetic runs at each nucleophile concentration) to the single-exponential $A_t = A_0 \exp(-k_{obs}\, t) + C$. The most electrophilic benzhydrylium ion used in this work, $(mor)_2CH^+$ cannot be stored in aqueous solution (k_W = 0.331 s^{-1} at 20 °C). For that reason, solutions of $(mor)_2CH^+$ BF_4^- were prepared in dry CH_3CN and combined with the ten-fold volume of aqueous solutions of nucleophiles in the stopped-flow instrument.

Materials

The benzhydrylium ions used in this work were synthesized according to literature procedures.[41] Potassium hydroxide was purchased as an aqueous standard solution. All amines **1a**-**1zz** were from commercial sources. They were purified, as appropriate, by recrystallization or distillation prior to use. The amines **1a**, **b**, **f**, **h**, **l** ,**u** were purchased as hydrochloride salts, and the free base was liberated with potassium hydroxide. Water was distilled and passed through a Milli-Q water purification system. Acetonitrile was distilled over diphenylketene.

2.8.1. Determination of rate constants in water

When an amine is dissolved in water, the concentration of hydroxide increases by protolysis. For that reason we have to calculate the concentration of the free amines $[Nu]_{eff}$ and of hydroxide $[OH^-]$ with the pK_B of the amines. The pK_B values of the amines are taken from ref [42] unless otherwise stated.



$$K_B = \frac{[\text{ammonium}]\,[OH^-]}{[\text{amine}]_{eff}} \qquad (1)$$

(2) in (1)

$[\text{amine}]_0 = [\text{amine}]_{\text{eff}} + [\text{ammonium}] = [\text{amine}]_{\text{eff}} + [\text{OH}^-]$ (2)

$$K_B = \frac{[\text{OH}^-]^2}{[\text{amine}]_0 - [\text{OH}^-]} \quad (3)$$

Solving of the quadratic equation (3) leads to one logic solution for $[\text{OH}^-]$ (The one with the "+" in the numerator).

$$[\text{OH}^-] = -\frac{K_B}{2} + \sqrt{\left(\frac{K_B}{2}\right)^2 + K_B[\text{amine}]_0} \quad (4)$$

The rates of the combination reactions were determined by mixing the colored aqueous solutions of the benzhydrylium salts with aqueous solutions of the amines (usually >10 equivalents). Because the products are colorless, the rates of the reactions were determined by UV-Vis spectroscopic monitoring of the absorbances with time.

$$-\frac{d[\text{R}^+]}{dt} = k_{\text{obs}}[\text{R}^+] \quad (5)$$

The consumption of the benzhydrylium cations may be due to the reaction with the amines, hydroxide ions and the solvent water.

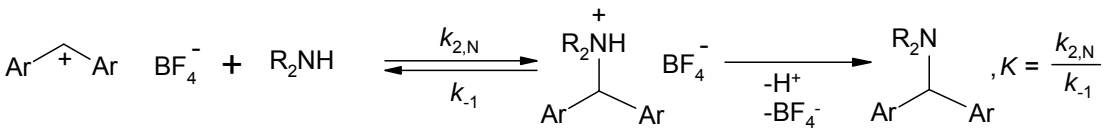
$k_{\text{obs}} = k_{2,\text{N}}\,[\text{amine}]_{\text{eff}} + k_{2,\text{OH-}}\,[\text{OH}^-] + k_{\text{W}} + k_{-1}$ (6)

$= k_{1\Psi} + k_{2,\text{OH-}}\,[\text{OH}^-]$, with $k_{1\Psi} = k_{2,\text{N}}\,[\text{amine}]_{\text{eff}} + k_{\text{W}} + k_{-1}$, and $[\text{OH}^-]$ from eq. (4)

The amines are usually used in more than 10-fold excess over the benzhydrylium cations in order to arrive at pseudo first-order conditions. The concentrations of the amines as well as that of hydroxide therefore remains constant during the reactions. With the already published second-order rate constants $k_{2,\text{OH-}}$ for the reactions of hydroxide with benzhydrylium ions and the first-order rate constants k_{W} for the reactions of water with benzhydrylium ions,[43] we get the second-order rate constants for the reactions of the amines with the benzhydrylium ions $k_{2,\text{N}}$ from a plot of $k_{1\Psi}$ versus $[\text{amine}]_{\text{eff}}$.

2.8.2. Determination of the equilibrium constants in water

Scheme 1



colored **1a-zz** colorless

We were not able to measure the equilibrium constants K (Scheme 1) in water directly. When an aqueous solution of the benzhydrylium salt was combined with the amines **1f**, **1p**, **1q** or **1r**, the UV/Vis spectrum for the benzhydrylium ion did not show a constant end

absorption because of the slow reactions of the benzhydrylium ions with hydroxide and water in the presence of amine. Equilibrium constants were, therefore calculated from the ratio of the second order rate constants $k_{2,N}$ for the forward reaction and the first order rate constant k_{-1} for the backward reaction. The thus obtained equilibrium constants are less accurate than the directly measured ones and are, therefore, written in parentheses.

2.8.3. Ammonia (1a)

Rate constants in water

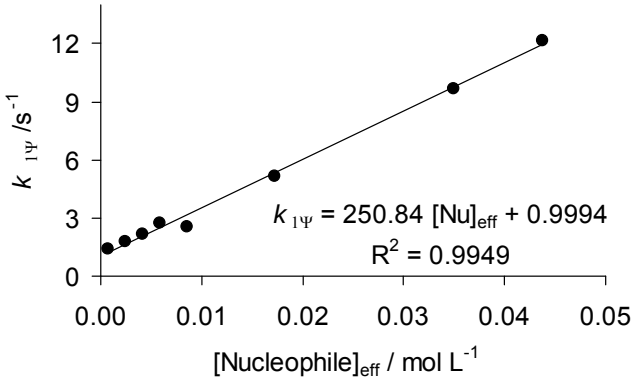
Reaction of Ammonia (**1a**) with $(mor)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 9 vol-% CH_3CN, stopped-flow, detection at 607 nm)

No.	$[(mor)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fb33.2	1.41×10^{-5}	4.46×10^{-2}	4.37×10^{-2}	8.72×10^{-4}	3101	13.1	0.924	12.2
fb33.3	1.41×10^{-5}	3.57×10^{-2}	3.49×10^{-2}	7.79×10^{-4}	2477	10.5	0.826	9.67
fb33.4	1.41×10^{-5}	1.78×10^{-2}	1.73×10^{-2}	5.48×10^{-4}	1224	5.72	0.580	5.14
fb33.5	1.41×10^{-5}	8.92×10^{-3}	8.53×10^{-3}	3.85×10^{-4}	605	2.94	0.408	2.53
fb33.6	1.41×10^{-5}	6.24×10^{-3}	5.92×10^{-3}	3.21×10^{-4}	420	3.07	0.340	2.73
fb33.7	1.41×10^{-5}	4.46×10^{-3}	4.19×10^{-3}	2.70×10^{-4}	297	2.42	0.286	2.13
fb33.8	1.41×10^{-5}	2.68×10^{-3}	2.47×10^{-3}	2.07×10^{-4}	175	1.97	0.220	1.75
fb33.9	1.41×10^{-5}	8.92×10^{-4}	7.76×10^{-4}	1.16×10^{-4}	55	1.53	0.123	1.41

$k_{2,N} = 2.51 \times 10^2\ M^{-1}s^{-1}$

$k_{2,OH^-} = 1060\ M^{-1}s^{-1}$

$pK_B = 4.76$



Reaction of Ammonia (**1a**) with $(dma)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.4 vol-% CH_3CN, stopped-flow, detection at 613 nm)

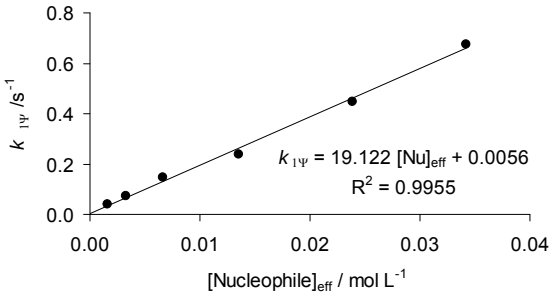
No.	$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fb37.2	7.12×10^{-5}	3.50×10^{-2}	3.42×10^{-2}	7.71×10^{-4}	481	0.778	0.101	0.677
fb37.3	7.12×10^{-5}	2.45×10^{-2}	2.39×10^{-2}	6.44×10^{-4}	335	0.531	8.43×10^{-2}	0.447
fb37.4	7.12×10^{-5}	1.40×10^{-2}	1.35×10^{-2}	4.85×10^{-4}	190	0.303	6.35×10^{-2}	0.240
fb37.5	7.12×10^{-5}	7.00×10^{-3}	6.66×10^{-3}	3.40×10^{-4}	94	0.192	4.46×10^{-2}	0.147
fb37.6	7.12×10^{-5}	3.50×10^{-3}	3.26×10^{-3}	2.38×10^{-4}	46	0.105	3.12×10^{-2}	7.38×10^{-2}
fb37.7	7.12×10^{-5}	1.75×10^{-3}	1.58×10^{-3}	1.66×10^{-4}	22	6.04×10^{-2}	2.17×10^{-2}	3.87×10^{-2}

$k_{2,N}$ = 19.1 M^{-1}s^{-1}

k_W = 2.6×10^{-2} s^{-1}

k_{2,OH^-} = 131 M^{-1}s^{-1}

pK_B = 4.76



Reaction of Ammonia (**1a**) with $(pyr)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 0.4 vol-% CH_3CN, J&M, detection at 611 nm)

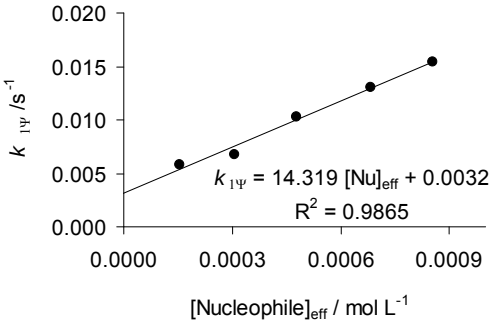
No.	$[(pyr)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fb71.1	1.24×10^{-5}	9.76×10^{-4}	8.54×10^{-4}	1.22×10^{-4}	69	2.13×10^{-2}	5.91×10^{-3}	1.54×10^{-2}
fb71.2	1.26×10^{-5}	7.93×10^{-4}	6.84×10^{-4}	1.09×10^{-4}	54	1.83×10^{-2}	5.29×10^{-3}	1.30×10^{-2}
fb71.3	1.20×10^{-5}	5.69×10^{-4}	4.78×10^{-4}	9.11×10^{-5}	40	1.47×10^{-2}	4.42×10^{-3}	1.03×10^{-2}
fb71.4	1.20×10^{-5}	3.79×10^{-4}	3.06×10^{-4}	7.29×10^{-5}	26	1.03×10^{-2}	3.54×10^{-3}	6.76×10^{-3}
fb71.5	1.30×10^{-5}	2.05×10^{-4}	1.53×10^{-4}	5.16×10^{-5}	12	8.31×10^{-3}	2.50×10^{-3}	5.81×10^{-3}

$k_{2,N}$ = 14.3 M^{-1}s^{-1}

k_W = 5.57×10^{-3} s^{-1}

k_{2,OH^-} = 48.5 M^{-1}s^{-1}

pK_B = 4.76



Reaction of Ammonia (**1a**) with $(thq)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 0.4 vol-% CH_3CN, J&M, detection at 618 nm)

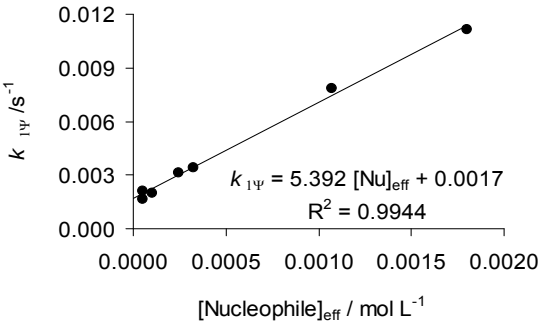
No.	$[(thq)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi, OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fb69.4	1.62×10^{-6}	1.98×10^{-3}	1.80×10^{-3}	1.77×10^{-4}	1113	1.53×10^{-2}	4.18×10^{-3}	1.11×10^{-2}
fb69.5	1.57×10^{-6}	1.21×10^{-3}	1.07×10^{-3}	1.37×10^{-4}	684	1.11×10^{-2}	3.22×10^{-3}	7.88×10^{-3}
fb69.6	1.63×10^{-6}	3.99×10^{-4}	3.24×10^{-4}	7.50×10^{-5}	199	5.21×10^{-3}	1.77×10^{-3}	3.44×10^{-3}
fb69.7	1.64×10^{-6}	8.01×10^{-5}	5.05×10^{-5}	2.96×10^{-5}	31	2.35×10^{-3}	6.99×10^{-4}	1.65×10^{-3}
fb69.8	4.14×10^{-6}	1.48×10^{-4}	1.05×10^{-4}	4.28×10^{-5}	25	3.01×10^{-3}	1.01×10^{-3}	2.00×10^{-3}
fb69.9	4.18×10^{-6}	8.19×10^{-5}	5.19×10^{-5}	3.00×10^{-5}	12	2.81×10^{-3}	7.09×10^{-4}	2.10×10^{-3}
fb69.10	3.92×10^{-6}	3.08×10^{-4}	2.43×10^{-4}	6.50×10^{-5}	62	4.68×10^{-3}	1.53×10^{-3}	3.15×10^{-3}

$k_{2,N}$ = 5.39 $M^{-1}s^{-1}$

k_W = 2.20×10^{-3} s^{-1}

k_{2,OH^-} = 23.6 $M^{-1}s^{-1}$

pK_B = 4.76



Reaction of Ammonia (**1a**) with $(ind)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 0.4 vol-% CH_3CN, J&M, detection at 614 nm)

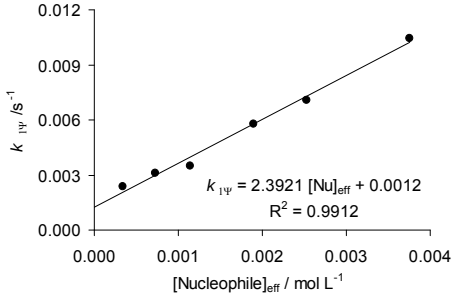
No.	$[(ind)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi, OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fb68.1	1.49×10^{-5}	4.01×10^{-3}	3.75×10^{-3}	2.55×10^{-4}	252	1.32×10^{-2}	2.76×10^{-3}	1.04×10^{-2}
fb68.2	1.45×10^{-5}	2.74×10^{-3}	2.53×10^{-3}	2.10×10^{-4}	175	9.34×10^{-3}	2.26×10^{-3}	7.08×10^{-3}
fb68.3	1.54×10^{-5}	2.08×10^{-3}	1.90×10^{-3}	1.82×10^{-4}	123	7.74×10^{-3}	1.96×10^{-3}	5.78×10^{-3}
fb68.4	1.58×10^{-5}	1.28×10^{-3}	1.14×10^{-3}	1.41×10^{-4}	72	5.03×10^{-3}	1.52×10^{-3}	3.51×10^{-3}
fb68.5	1.56×10^{-5}	8.42×10^{-4}	7.29×10^{-4}	1.13×10^{-4}	47	4.31×10^{-3}	1.22×10^{-3}	3.09×10^{-3}
fb68.6	1.53×10^{-5}	4.13×10^{-4}	3.37×10^{-4}	7.65×10^{-5}	22	3.18×10^{-3}	8.26×10^{-4}	2.35×10^{-3}

$k_{2,N}$ = 2.39 $M^{-1}s^{-1}$

k_W = 5.64×10^{-4} s^{-1} [calculated from *N* and *s*]

k_{2,OH^-} = 10.8 $M^{-1}s^{-1}$

pK_B = 4.76



Reaction of Ammonia (**1a**) with $(jul)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 0.4 vol-% CH_3CN, stopped-flow, detection at 634 nm)

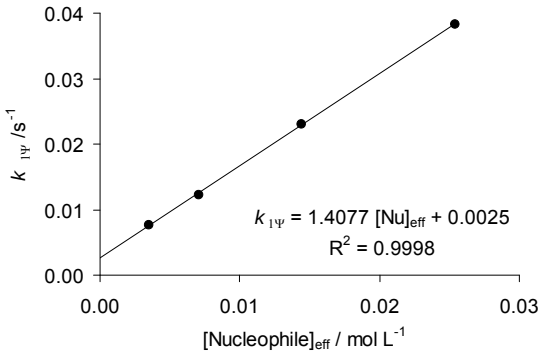
No.	$[(jul)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fb44.3	1.27×10^{-5}	2.61×10^{-2}	2.54×10^{-2}	6.57×10^{-4}	2003	4.06×10^{-2}	2.26×10^{-3}	3.83×10^{-2}
fb44.4	1.27×10^{-5}	1.49×10^{-2}	1.44×10^{-2}	4.95×10^{-4}	1134	2.47×10^{-2}	1.70×10^{-3}	2.30×10^{-2}
fb44.5	1.27×10^{-5}	7.45×10^{-3}	7.10×10^{-3}	3.47×10^{-4}	559	1.35×10^{-2}	1.19×10^{-3}	1.23×10^{-2}
fb44.6	1.27×10^{-5}	3.72×10^{-3}	3.48×10^{-3}	2.43×10^{-4}	274	8.41×10^{-3}	8.36×10^{-4}	7.57×10^{-3}

$k_{2,N} = 1.41\ M^{-1}s^{-1}$

$k_W = 1.37 \times 10^{-4}\ s^{-1}$ [calculated from *N* and *s*]

$k_{2,OH^-} = 3.44\ M^{-1}s^{-1}$

$pK_B = 4.76$



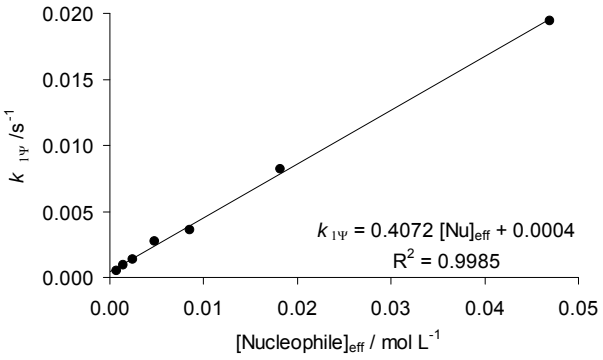
Reaction of Ammonia (**1a**) with $(lil)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 0.4 vol-% CH_3CN, J&M, detection at 630 nm)

No.	$[(lil)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fb39.2	1.55×10^{-5}	4.79×10^{-2}	4.70×10^{-2}	9.04×10^{-4}	3032	2.14×10^{-2}	1.95×10^{-3}	1.94×10^{-2}
fb39.3	1.21×10^{-5}	1.88×10^{-2}	1.82×10^{-2}	5.63×10^{-4}	1507	9.45×10^{-3}	1.22×10^{-3}	8.23×10^{-3}
fb39.4	1.45×10^{-5}	8.94×10^{-3}	8.55×10^{-3}	3.86×10^{-4}	590	4.45×10^{-3}	8.33×10^{-4}	3.62×10^{-3}
fb39.5	1.63×10^{-5}	5.04×10^{-3}	4.75×10^{-3}	2.87×10^{-4}	292	3.34×10^{-3}	6.21×10^{-4}	2.72×10^{-3}
fb39.6	1.20×10^{-5}	2.61×10^{-3}	2.41×10^{-3}	2.04×10^{-4}	200	1.84×10^{-3}	4.42×10^{-4}	1.40×10^{-3}
fb39.7	1.31×10^{-5}	1.63×10^{-3}	1.47×10^{-3}	1.60×10^{-4}	112	1.29×10^{-3}	3.45×10^{-4}	9.45×10^{-4}
fb39.8	1.32×10^{-5}	8.16×10^{-4}	7.05×10^{-4}	1.11×10^{-4}	53	7.48×10^{-4}	2.39×10^{-4}	5.09×10^{-4}

$k_{2,N} = 4.07 \times 10^{-1}\ M^{-1}s^{-1}$

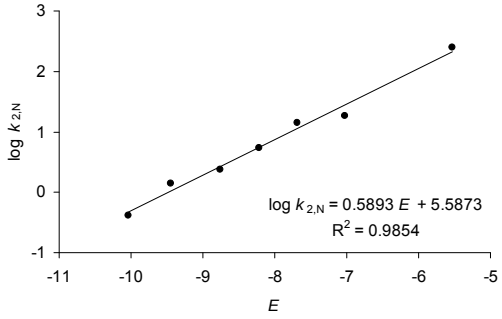
$k_{2,OH^-} = 2.16\ M^{-1}s^{-1}$

$pK_B = 4.76$



Reactivity parameters in water: N = 9.48; s = 0.59

Reference electrophile	E parameter	$k_{2,N}$(20°C) / M^{-1} s^{-1}
$(mor)_2CH^+$	-5.53	2.51×10^2
$(dma)_2CH^+$	-7.02	18.5
$(pyr)_2CH^+$	-7.69	14.3
$(thq)_2CH^+$	-8.22	5.39
$(ind)_2CH^+$	-8.76	2.39
$(jul)_2CH^+$	-9.45	1.41
$(lil)_2CH^+$	-10.04	0.407



2.8.4. Methylamine (1b)

Rate constants in water

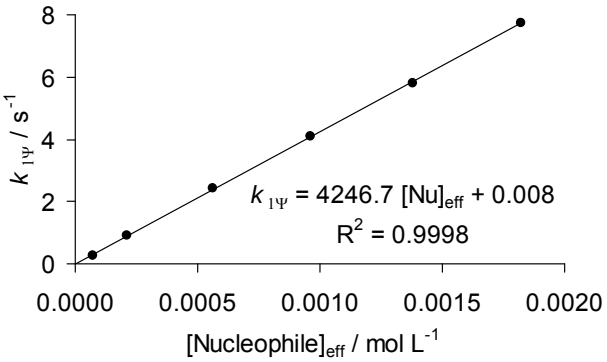
Reaction of methylamine (**1b**) with $(dma)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 1.5 vol-% CH_3CN, stopped-flow, detection at 605 nm)

No.	$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy33.1	1.26×10^{-5}	2.88×10^{-3}	1.82×10^{-3}	1.06×10^{-3}	144	7.89	0.139	7.75
ccy33.2	1.26×10^{-5}	2.30×10^{-3}	1.38×10^{-3}	9.22×10^{-4}	109	5.93	0.121	5.81
ccy33.3	1.26×10^{-5}	1.73×10^{-3}	9.60×10^{-4}	7.70×10^{-4}	76	4.21	0.101	4.11
ccy33.4	1.26×10^{-5}	1.15×10^{-3}	5.62×10^{-4}	5.88×10^{-4}	45	2.52	7.71×10^{-2}	2.44
ccy33.5	1.26×10^{-5}	5.76×10^{-4}	2.13×10^{-4}	3.63×10^{-4}	17	0.972	4.75×10^{-2}	0.924
ccy33.6	1.26×10^{-5}	2.88×10^{-4}	7.42×10^{-5}	2.14×10^{-4}	6	0.307	2.80×10^{-2}	0.279

$k_{2,N} = 4.25 \times 10^3$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 131$ $M^{-1}s^{-1}$

$pK_B = 3.21$



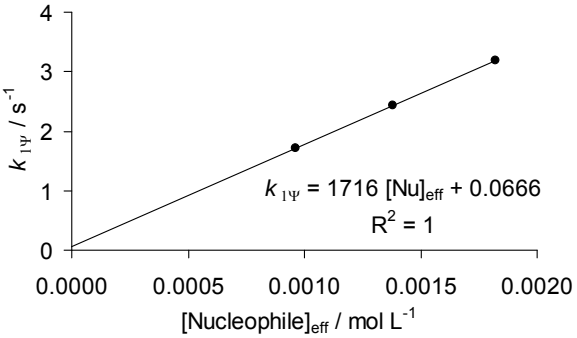
Reaction of methylamine (**1b**) with $(pyr)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 605 nm)

No.	$[(pyr)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy34.1	1.33×10^{-5}	2.88×10^{-3}	1.82×10^{-3}	1.06×10^{-3}	137	3.24	5.14×10^{-2}	3.19
ccy34.2	1.33×10^{-5}	2.30×10^{-3}	1.38×10^{-3}	9.22×10^{-4}	104	2.48	4.47×10^{-2}	2.44
ccy34.3	1.33×10^{-5}	1.73×10^{-3}	9.60×10^{-4}	7.70×10^{-4}	72	1.75	3.73×10^{-2}	1.71

$k_{2,N} = 1.72 \times 10^3\ M^{-1}s^{-1}$

$k_{2,OH^-} = 48.5\ M^{-1}s^{-1}$

$pK_B = 3.21$



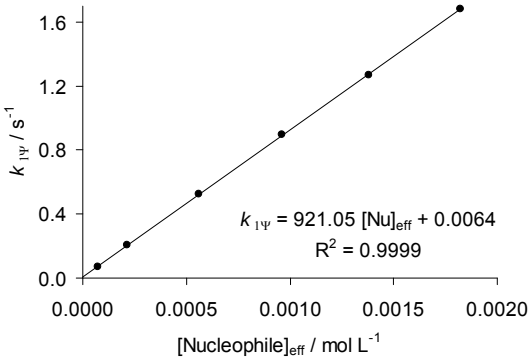
Reaction of methylamine (**1b**) with $(thq)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 615 nm)

No.	$[(thq)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy35.1	1.63×10^{-5}	2.88×10^{-3}	1.82×10^{-3}	1.06×10^{-3}	112	1.71	2.50×10^{-2}	1.68
ccy35.2	1.63×10^{-5}	2.30×10^{-3}	1.38×10^{-3}	9.22×10^{-4}	85	1.29	2.18×10^{-2}	1.27
ccy35.3	1.63×10^{-5}	1.73×10^{-3}	9.60×10^{-4}	7.70×10^{-4}	59	0.916	1.82×10^{-2}	0.898
ccy35.4	1.63×10^{-5}	1.15×10^{-3}	5.62×10^{-4}	5.88×10^{-4}	34	0.538	1.39×10^{-2}	0.524
ccy35.5	1.63×10^{-5}	5.76×10^{-4}	2.13×10^{-4}	3.63×10^{-4}	13	0.214	8.56×10^{-3}	0.205
ccy35.6	1.63×10^{-5}	2.88×10^{-4}	7.42×10^{-5}	2.14×10^{-4}	5	7.56×10^{-2}	5.05×10^{-3}	7.06×10^{-2}

$k_{2,N} = 9.21 \times 10^2\ M^{-1}s^{-1}$

$k_{2,OH^-} = 23.6\ M^{-1}s^{-1}$

$pK_B = 3.21$



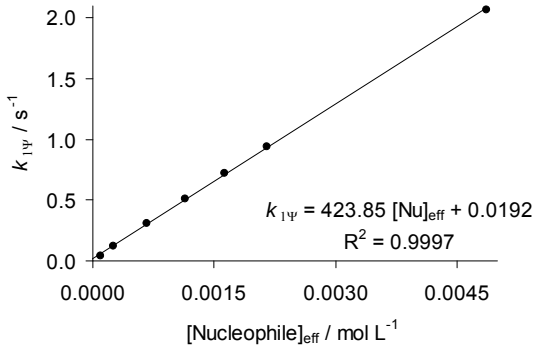
Reaction of methylamine (**1b**) with $(ind)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 614 nm)

No.	$[(ind)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy36.1	1.48×10^{-5}	6.60×10^{-3}	4.87×10^{-3}	1.73×10^{-3}	329	2.09	1.87×10^{-2}	2.07
ccy36.2	1.48×10^{-5}	3.30×10^{-3}	2.15×10^{-3}	1.15×10^{-3}	145	0.956	1.24×10^{-2}	0.944
ccy36.3	1.48×10^{-5}	2.64×10^{-3}	1.64×10^{-3}	1.00×10^{-3}	111	0.735	1.08×10^{-2}	0.724
ccy36.4	1.48×10^{-5}	1.98×10^{-3}	1.14×10^{-3}	8.39×10^{-4}	77	0.518	9.06×10^{-3}	0.509
ccy36.5	1.48×10^{-5}	1.32×10^{-3}	6.75×10^{-4}	6.45×10^{-4}	46	0.315	6.97×10^{-3}	0.308
ccy36.6	1.48×10^{-5}	6.60×10^{-4}	2.60×10^{-4}	4.00×10^{-4}	18	0.124	4.32×10^{-3}	0.120
ccy36.7	1.48×10^{-5}	3.30×10^{-4}	9.19×10^{-5}	2.38×10^{-4}	6	4.71×10^{-2}	2.57×10^{-3}	4.45×10^{-2}

$k_{2,N} = 4.24 \times 10^2\ M^{-1}s^{-1}$

$k_{2,OH^-} = 10.8\ M^{-1}s^{-1}$

$pK_B = 3.21$



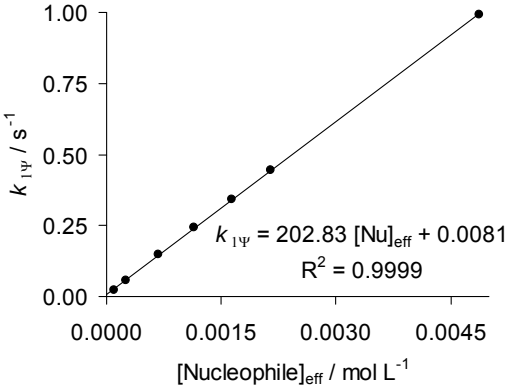
Reaction of methylamine (**1b**) with $(jul)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 614 nm)

No.	$[(jul)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy37.1	1.26×10^{-5}	6.60×10^{-3}	4.87×10^{-3}	1.73×10^{-3}	386	0.999	5.96×10^{-3}	0.993
ccy37.2	1.26×10^{-5}	3.30×10^{-3}	2.15×10^{-3}	1.15×10^{-3}	171	0.449	3.96×10^{-3}	0.445
ccy37.3	1.26×10^{-5}	2.64×10^{-3}	1.64×10^{-3}	1.00×10^{-3}	130	0.347	3.45×10^{-3}	0.344
ccy37.4	1.26×10^{-5}	1.98×10^{-3}	1.14×10^{-3}	8.39×10^{-4}	91	0.245	2.89×10^{-3}	0.242
ccy37.5	1.26×10^{-5}	1.32×10^{-3}	6.75×10^{-4}	6.45×10^{-4}	54	0.149	2.22×10^{-3}	0.147
ccy37.6	1.26×10^{-5}	6.60×10^{-4}	2.60×10^{-4}	4.00×10^{-4}	21	5.89×10^{-2}	1.38×10^{-3}	5.75×10^{-2}
ccy37.7	1.26×10^{-5}	3.30×10^{-4}	9.19×10^{-5}	2.38×10^{-4}	7	2.40×10^{-2}	8.19×10^{-4}	2.32×10^{-2}

$k_{2,N} = 2.03 \times 10^2\ M^{-1}s^{-1}$

$k_{2,OH^-} = 3.44\ M^{-1}s^{-1}$

$pK_B = 3.21$



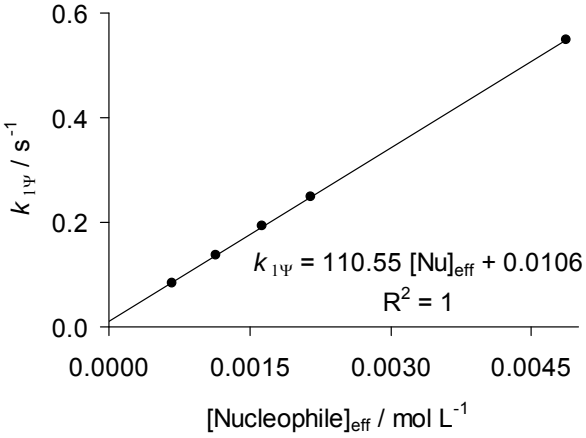
Reaction of methylamine (**1b**) with $(lil)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 614 nm)

No.	$[(lil)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy38.1	1.32×10^{-5}	6.60×10^{-3}	4.87×10^{-3}	1.73×10^{-3}	369	0.552	3.74×10^{-3}	0.548
ccy38.2	1.32×10^{-5}	3.30×10^{-3}	2.15×10^{-3}	1.15×10^{-3}	163	0.251	2.49×10^{-3}	0.249
ccy38.3	1.32×10^{-5}	2.64×10^{-3}	1.64×10^{-3}	1.00×10^{-3}	124	0.195	2.17×10^{-3}	0.193
ccy38.4	1.32×10^{-5}	1.98×10^{-3}	1.14×10^{-3}	8.39×10^{-4}	86	0.138	1.81×10^{-3}	0.136
ccy38.5	1.32×10^{-5}	1.32×10^{-3}	6.75×10^{-4}	6.45×10^{-4}	51	8.57×10^{-2}	1.39×10^{-3}	8.43×10^{-2}

$k_{2,N} = 1.11 \times 10^2\ M^{-1}s^{-1}$

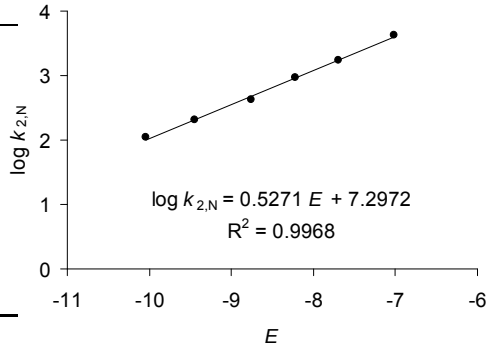
$k_{2,OH^-} = 2.16\ M^{-1}s^{-1}$

$pK_B = 3.21$



Reactivity parameters in water: *N* = 13.85; *s* = 0.53

Reference electrophile	*E* parameter	$k_{2,N}$(20°C) / M^{-1} s^{-1}
$(dma)_2CH^+$	-7.02	4.25×10^3
$(pyr)_2CH^+$	-7.69	1.72×10^3
$(thq)_2CH^+$	-8.22	9.21×10^2
$(ind)_2CH^+$	-8.76	4.24×10^2
$(jul)_2CH^+$	-9.45	2.03×10^2
$(lil)_2CH^+$	-10.04	1.11×10^2



2.8.5. Ethylamine (1c)

Rate constants in water

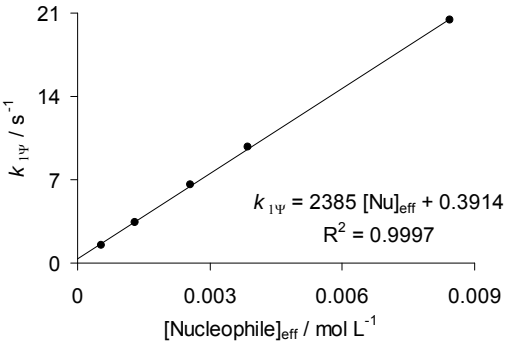
Reaction of ethylamine (**1c**) with $(dma)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 2.0 vol-% CH_3CN, stopped-flow, detection at 615 nm)

No.	$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
jo39.1	6.70×10^{-5}	1.05×10^{-2}	8.44×10^{-3}	2.06×10^{-3}	126	20.7	0.269	20.4
jo39.2	6.70×10^{-5}	5.25×10^{-3}	3.86×10^{-3}	1.39×10^{-3}	58	9.95	0.182	9.77
jo39.3	6.70×10^{-5}	3.68×10^{-3}	2.55×10^{-3}	1.13×10^{-3}	38	6.73	0.148	6.58
jo39.4	6.70×10^{-5}	2.10×10^{-3}	1.29×10^{-3}	8.05×10^{-4}	19	3.55	0.106	3.44
jo39.5	6.70×10^{-5}	1.05×10^{-3}	5.33×10^{-4}	5.17×10^{-4}	8	1.58	6.77×10^{-2}	1.51

$k_{2,N} = 2.39 \times 10^3\ M^{-1}s^{-1}$

$k_{2,OH^-} = 131\ M^{-1}s^{-1}$

$pK_B = 3.30$



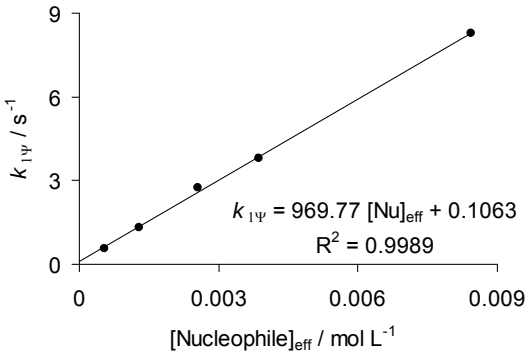
Reaction of ethylamine (**1c**) with $(pyr)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 0.5 vol-% CH_3CN, stopped-flow, detection at 605 nm)

No.	$[(pyr)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
jo40.1	7.65×10^{-6}	1.05×10^{-2}	8.44×10^{-3}	2.06×10^{-3}	1104	8.37	9.98×10^{-2}	8.27
jo40.2	7.65×10^{-6}	5.25×10^{-3}	3.86×10^{-3}	1.39×10^{-3}	504	3.88	6.75×10^{-2}	3.81
jo40.3	7.65×10^{-6}	3.68×10^{-3}	2.55×10^{-3}	1.13×10^{-3}	333	2.81	5.48×10^{-2}	2.76
jo40.4	7.65×10^{-6}	2.10×10^{-3}	1.29×10^{-3}	8.05×10^{-4}	169	1.34	3.91×10^{-2}	1.30
jo40.5	7.65×10^{-6}	1.05×10^{-3}	5.33×10^{-4}	5.17×10^{-4}	70	0.593	2.51×10^{-2}	0.568

$k_{2,N} = 9.70 \times 10^2\ M^{-1}s^{-1}$

$k_{2,OH^-} = 48.5\ M^{-1}s^{-1}$

$pK_B = 3.30$



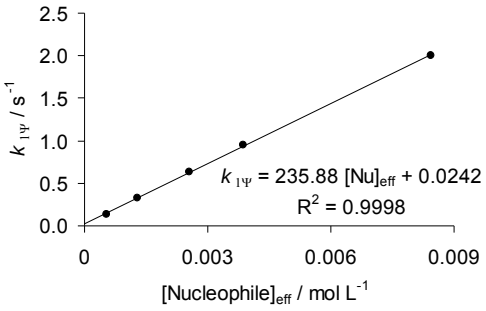
Reaction of ethylamine (**1c**) with $(ind)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 614 nm)

No.	$[(ind)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi, OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
jo41.1	1.48×10^{-5}	1.05×10^{-2}	8.44×10^{-3}	2.06×10^{-3}	570	2.03	2.22×10^{-2}	2.01
jo41.2	1.48×10^{-5}	5.25×10^{-3}	3.86×10^{-3}	1.39×10^{-3}	261	0.965	1.50×10^{-2}	0.950
jo41.3	1.48×10^{-5}	3.68×10^{-3}	2.55×10^{-3}	1.13×10^{-3}	172	0.645	1.22×10^{-2}	0.633
jo41.4	1.48×10^{-5}	2.10×10^{-3}	1.29×10^{-3}	8.05×10^{-4}	87	0.334	8.70×10^{-3}	0.325
jo41.5	1.48×10^{-5}	1.05×10^{-3}	5.33×10^{-4}	5.17×10^{-4}	36	0.145	5.58×10^{-3}	0.139

$k_{2,N} = 2.36 \times 10^2$ $M^{-1}s^{-1}$

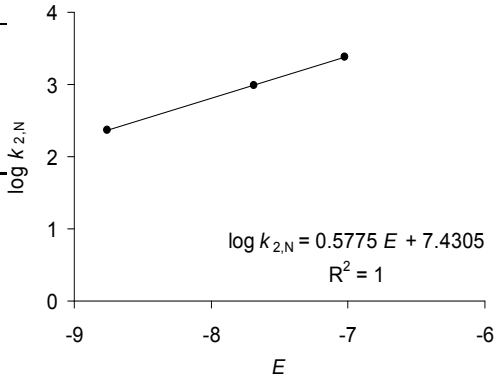
$k_{2,OH^-} = 10.8$ $M^{-1}s^{-1}$

$pK_B = 3.30$



Reactivity parameters in water: $N = 12.87$; $s = 0.58$

Reference electrophile	E parameter	$k_{2,N}$(20°C) / M^{-1} s^{-1}
$(dma)_2CH^+$	-7.02	2.39×10^3
$(pyr)_2CH^+$	-7.69	9.70×10^2
$(ind)_2CH^+$	-8.76	2.36×10^2



2.8.6. Isopropylamine (1d)

Rate constants in water

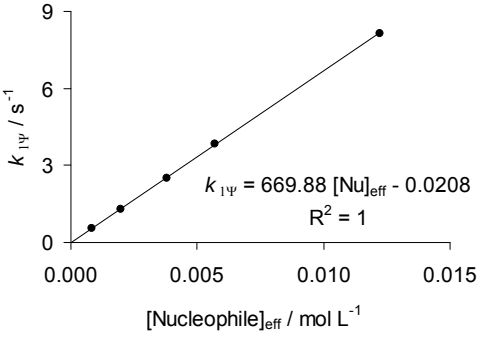
Reaction of Isopropylamine (**1d**) with $(dma)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 0.5 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy196.1	5.95×10^{-5}	1.45×10^{-2}	1.22×10^{-2}	2.28×10^{-3}	205	8.45	0.299	8.15
ccy196.2	5.95×10^{-5}	7.25×10^{-3}	5.69×10^{-3}	1.56×10^{-3}	96	4.03	0.204	3.83
ccy196.3	5.95×10^{-5}	5.08×10^{-3}	3.81×10^{-3}	1.27×10^{-3}	64	2.69	0.167	2.52
ccy196.4	5.95×10^{-5}	2.90×10^{-3}	1.98×10^{-3}	9.19×10^{-4}	33	1.42	0.120	1.30
ccy196.5	5.95×10^{-5}	1.45×10^{-3}	8.48×10^{-4}	6.02×10^{-4}	14	0.617	7.88×10^{-2}	0.538

$k_{2,N} = 6.70 \times 10^2\ M^{-1}s^{-1}$

$k_{2,OH^-} = 131\ M^{-1}s^{-1}$

$pK_B = 3.37$



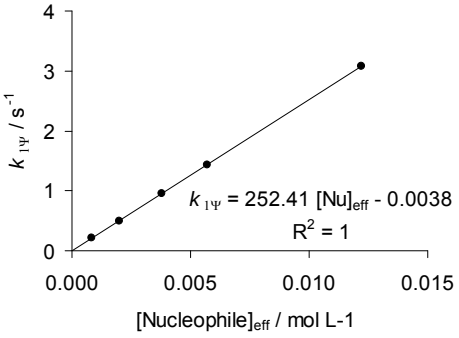
Reaction of Isopropylamine (**1d**) with $(pyr)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 0.1 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(pyr)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy197.1	1.12×10^{-5}	1.45×10^{-2}	1.22×10^{-2}	2.28×10^{-3}	1091	3.19	0.111	3.08
ccy197.2	1.12×10^{-5}	7.25×10^{-3}	5.69×10^{-3}	1.56×10^{-3}	508	1.51	7.56×10^{-2}	1.43
ccy197.3	1.12×10^{-5}	5.08×10^{-3}	3.81×10^{-3}	1.27×10^{-3}	340	1.02	6.18×10^{-2}	0.958
ccy197.4	1.12×10^{-5}	2.90×10^{-3}	1.98×10^{-3}	9.19×10^{-4}	177	0.537	4.46×10^{-2}	0.492
ccy197.5	1.12×10^{-5}	1.45×10^{-3}	8.48×10^{-4}	6.02×10^{-4}	76	0.241	2.92×10^{-2}	0.212

$k_{2,N} = 2.52 \times 10^2\ M^{-1}s^{-1}$

$k_{2,OH^-} = 48.5\ M^{-1}s^{-1}$

$pK_B = 3.37$



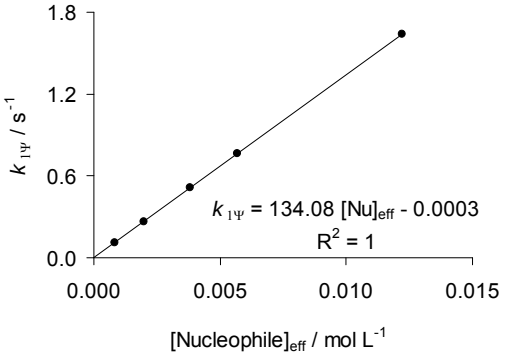
Reaction of Isopropylamine (**1d**) with $(thq)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(thq)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy198.1	1.91×10^{-5}	1.45×10^{-2}	1.22×10^{-2}	2.28×10^{-3}	640	1.69	5.39×10^{-2}	1.64
ccy198.2	1.91×10^{-5}	7.25×10^{-3}	5.69×10^{-3}	1.56×10^{-3}	298	0.803	3.68×10^{-2}	0.766
ccy198.3	1.91×10^{-5}	5.08×10^{-3}	3.81×10^{-3}	1.27×10^{-3}	199	0.542	3.01×10^{-2}	0.512
ccy198.4	1.91×10^{-5}	2.90×10^{-3}	1.98×10^{-3}	9.19×10^{-4}	104	0.284	2.17×10^{-2}	0.262
ccy198.5	1.91×10^{-5}	1.45×10^{-3}	8.48×10^{-4}	6.02×10^{-4}	44	0.127	1.42×10^{-2}	0.113

$k_{2,N} = 1.34 \times 10^2\ M^{-1}s^{-1}$

$k_{2,OH^-} = 23.6\ M^{-1}s^{-1}$

$pK_B = 3.37$



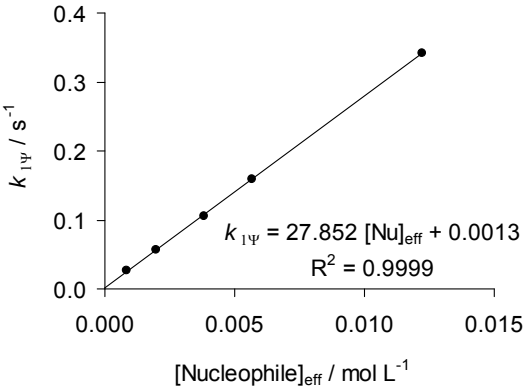
Reaction of Isopropylamine (**1d**) with $(jul)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 634 nm)

No.	$[(jul)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy199.1	8.55×10^{-6}	1.45×10^{-2}	1.22×10^{-2}	2.28×10^{-3}	1429	0.350	7.85×10^{-3}	0.342
ccy199.2	8.55×10^{-6}	7.25×10^{-3}	5.69×10^{-3}	1.56×10^{-3}	666	0.165	5.36×10^{-3}	0.160
ccy199.3	8.55×10^{-6}	5.08×10^{-3}	3.81×10^{-3}	1.27×10^{-3}	445	0.110	4.38×10^{-3}	0.106
ccy199.4	8.55×10^{-6}	2.90×10^{-3}	1.98×10^{-3}	9.19×10^{-4}	232	5.97×10^{-2}	3.16×10^{-3}	5.65×10^{-2}
ccy199.5	8.55×10^{-6}	1.45×10^{-3}	8.48×10^{-4}	6.02×10^{-4}	99	2.84×10^{-2}	2.07×10^{-3}	2.63×10^{-2}

$k_{2,N} = 27.9\ M^{-1}s^{-1}$

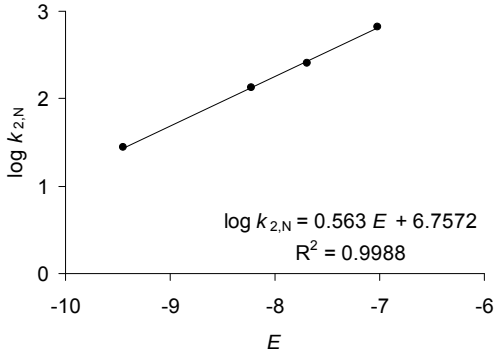
$k_{2,OH^-} = 3.44\ M^{-1}s^{-1}$

$pK_B = 3.37$



Reactivity parameters in water: N = 12.00; s = 0.56

Reference electrophile	E parameter	$k_{2,N}$(20°C) / M^{-1} s^{-1}
$(dma)_2CH^+$	-7.02	6.70×10^2
$(pyr)_2CH^+$	-7.69	2.52×10^2
$(thq)_2CH^+$	-8.22	1.34×10^2
$(jul)_2CH^+$	-9.45	27.9



2.8.7. tert-Butylamine (1e)

Rate constants in water

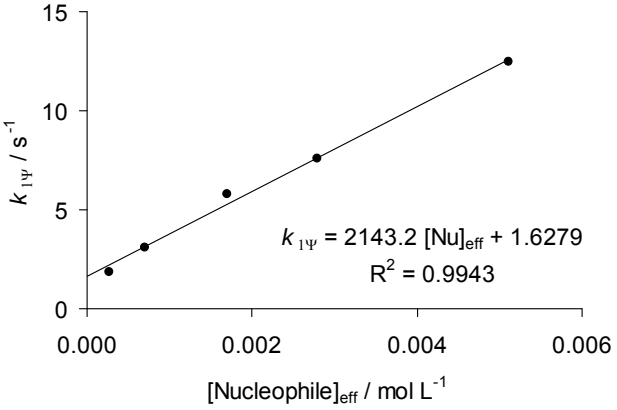
Reaction of tert-Butylamine (**1e**) with $(mor)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 9 vol-% CH_3CN, stopped-flow, detection at 607 nm)

No.	$[(mor)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fb201.1	1.72×10^{-5}	7.04×10^{-3}	5.12×10^{-3}	1.92×10^{-3}	297	14.5	2.04	12.5
fb201.2	1.72×10^{-5}	4.22×10^{-3}	2.80×10^{-3}	1.42×10^{-3}	163	9.09	1.51	7.58
fb201.3	1.72×10^{-5}	2.81×10^{-3}	1.70×10^{-3}	1.11×10^{-3}	99	6.97	1.18	5.79
fb201.4	1.72×10^{-5}	1.41×10^{-3}	6.99×10^{-4}	7.11×10^{-4}	41	3.85	0.754	3.10
fb201.5	1.72×10^{-5}	7.04×10^{-4}	2.65×10^{-4}	4.39×10^{-4}	15	2.34	0.465	1.88

$k_{2,N} = 2.14 \times 10^3$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 1060$ $M^{-1}s^{-1}$

pK_B = 3.14



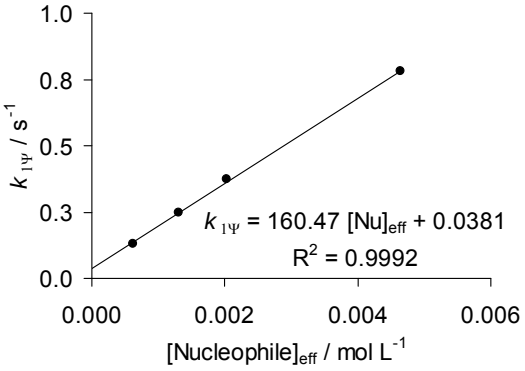
Reaction of tert-Butylamine (**1e**) with $(dma)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 0.5 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi, OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy111.1	1.08×10^{-4}	6.48×10^{-3}	4.65×10^{-3}	1.83×10^{-3}	43	1.02	0.240	0.780
ccy111.2	1.08×10^{-4}	3.24×10^{-3}	2.03×10^{-3}	1.21×10^{-3}	19	0.534	0.159	0.375
ccy111.3	1.08×10^{-4}	2.27×10^{-3}	1.30×10^{-3}	9.70×10^{-4}	12	0.373	0.127	0.246
ccy111.4	1.08×10^{-4}	1.30×10^{-3}	6.26×10^{-4}	6.74×10^{-4}	6	0.220	8.82×10^{-2}	0.132

$k_{2,N} = 1.60 \times 10^2$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 131$ $M^{-1}s^{-1}$

$pK_B = 3.14$



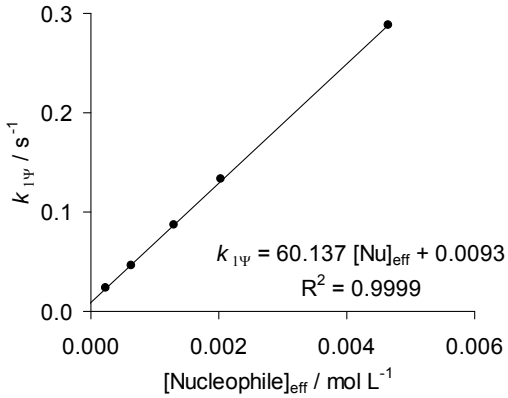
Reaction of tert-Butylamine (**1e**) with $(pyr)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(pyr)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi, OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy112.1	2.12×10^{-5}	6.48×10^{-3}	4.65×10^{-3}	1.83×10^{-3}	219	0.377	8.90×10^{-2}	0.288
ccy112.2	2.12×10^{-5}	3.24×10^{-3}	2.03×10^{-3}	1.21×10^{-3}	96	0.192	5.88×10^{-2}	0.133
ccy112.3	2.12×10^{-5}	2.27×10^{-3}	1.30×10^{-3}	9.70×10^{-4}	61	0.134	4.71×10^{-2}	8.69×10^{-2}
ccy112.4	2.12×10^{-5}	1.30×10^{-3}	6.26×10^{-4}	6.74×10^{-4}	30	7.85×10^{-2}	3.27×10^{-2}	4.58×10^{-2}
ccy112.5	2.12×10^{-5}	6.48×10^{-4}	2.35×10^{-4}	4.13×10^{-4}	11	4.36×10^{-2}	2.00×10^{-2}	2.36×10^{-2}

$k_{2,N} = 60.1$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 48.5$ $M^{-1}s^{-1}$

$pK_B = 3.14$



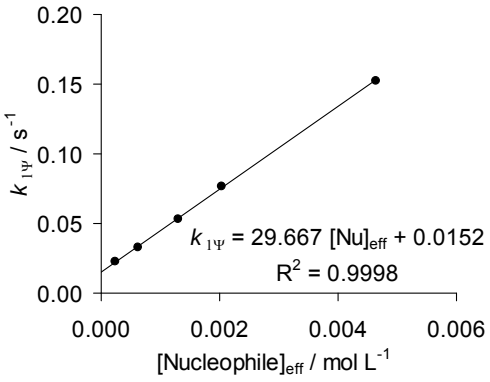
Reaction of tert-Butylamine (**1e**) with $(thq)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(thq)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy113.1	1.57×10^{-5}	6.48×10^{-3}	4.65×10^{-3}	1.83×10^{-3}	296	0.196	4.33×10^{-2}	0.153
ccy113.2	1.57×10^{-5}	3.24×10^{-3}	2.03×10^{-3}	1.21×10^{-3}	129	0.105	2.86×10^{-2}	7.64×10^{-2}
ccy113.3	1.57×10^{-5}	2.27×10^{-3}	1.30×10^{-3}	9.70×10^{-4}	83	7.63×10^{-2}	2.29×10^{-2}	5.34×10^{-2}
ccy113.4	1.57×10^{-5}	1.30×10^{-3}	6.26×10^{-4}	6.74×10^{-4}	40	4.89×10^{-2}	1.59×10^{-2}	3.30×10^{-2}
ccy113.5	1.57×10^{-5}	6.48×10^{-4}	2.35×10^{-4}	4.13×10^{-4}	15	3.22×10^{-2}	9.74×10^{-3}	2.25×10^{-2}

$k_{2,N}$ = 29.7 $M^{-1}s^{-1}$

k_{2,OH^-} = 23.6 $M^{-1}s^{-1}$

pK_B = 3.14



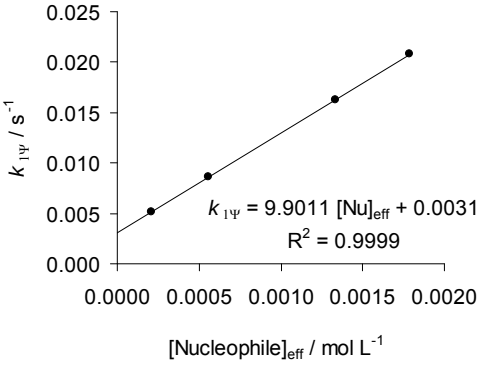
Reaction of tert-Butylamine (**1e**) with $(ind)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, J&M, detection at 614 nm)

No.	$[(ind)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fb200.1	2.20×10^{-5}	2.92×10^{-3}	1.78×10^{-3}	1.14×10^{-3}	81	3.31×10^{-2}	1.23×10^{-2}	2.08×10^{-2}
fb200.2	2.20×10^{-5}	2.32×10^{-3}	1.34×10^{-3}	9.84×10^{-4}	61	2.69×10^{-2}	1.06×10^{-2}	1.63×10^{-2}
fb200.3	2.24×10^{-5}	1.19×10^{-3}	5.56×10^{-4}	6.34×10^{-4}	25	1.55×10^{-2}	6.85×10^{-3}	8.65×10^{-3}
fb200.4	2.26×10^{-5}	5.98×10^{-4}	2.09×10^{-4}	3.89×10^{-4}	9	9.39×10^{-3}	4.20×10^{-3}	5.19×10^{-3}

$k_{2,N}$ = 9.90 $M^{-1}s^{-1}$

k_{2,OH^-} = 10.8 $M^{-1}s^{-1}$

pK_B = 3.14



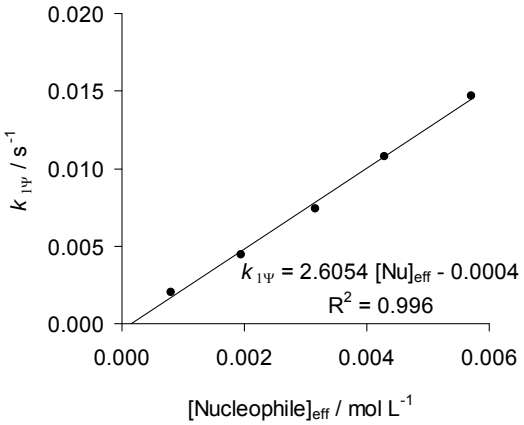
Reaction of tert-Butylamine (**1e**) with $(lil)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, J&M, detection at 614 nm)

No.	$[(lil)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy201.1	3.59×10^{-5}	7.74×10^{-3}	5.71×10^{-3}	2.03×10^{-3}	159	1.91×10^{-2}	4.39×10^{-3}	1.47×10^{-2}
ccy201.2	3.51×10^{-5}	6.05×10^{-3}	4.29×10^{-3}	1.76×10^{-3}	122	1.46×10^{-2}	3.81×10^{-3}	1.08×10^{-2}
ccy201.3	3.62×10^{-5}	4.68×10^{-3}	3.17×10^{-3}	1.51×10^{-3}	87	1.07×10^{-2}	3.27×10^{-3}	7.43×10^{-3}
ccy201.4	3.63×10^{-5}	3.13×10^{-3}	1.94×10^{-3}	1.19×10^{-3}	54	7.04×10^{-3}	2.56×10^{-3}	4.48×10^{-3}
ccy201.5	3.62×10^{-5}	1.56×10^{-3}	7.99×10^{-4}	7.61×10^{-4}	22	3.69×10^{-3}	1.64×10^{-3}	2.05×10^{-3}

$k_{2,N} = 2.61\ M^{-1}s^{-1}$

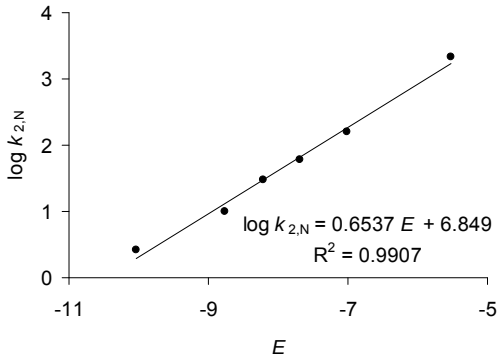
$k_{2,OH^-} = 2.16\ M^{-1}s^{-1}$

$pK_B = 3.14$



Reactivity parameters in water: *N* = 10.48; *s* = 0.65

Reference electrophile	*E* parameter	$k_{2,N}$(20°C) / M^{-1} s^{-1}
$(mor)_2CH^+$	-5.53	2.14×10^3
$(dma)_2CH^+$	-7.02	1.60×10^2
$(pyr)_2CH^+$	-7.69	60.1
$(thq)_2CH^+$	-8.22	29.7
$(ind)_2CH^+$	-8.76	9.90
$(lil)_2CH^+$	-10.04	2.61

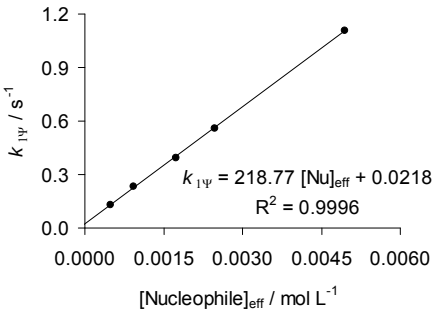


2.8.8. Glycinenitrile (1f)

Rate constants and equilibrium constants in water

Reaction of glycinenitrile (**1f**) with $(dma)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 1.5 vol-% CH_3CN, stopped-flow, detection at 610 nm, $[Nu]_{eff} = [Nu]_0$, $k_{obs} = k_{1\Psi}$)

No.	$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	$k_{1\Psi}$ / s^{-1}
ccy39.1	9.50×10^{-5}	4.96×10^{-3}	52	1.11
ccy39.2	9.50×10^{-5}	2.48×10^{-3}	26	0.560
ccy39.3	9.50×10^{-5}	1.74×10^{-3}	18	0.393
ccy39.4	9.50×10^{-5}	9.22×10^{-4}	10	0.234
ccy39.5	9.50×10^{-5}	4.95×10^{-4}	5	0.130



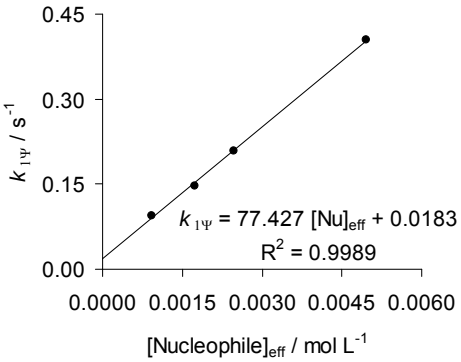
$k_{2,N} = 2.19 \times 10^2$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 131$ $M^{-1}s^{-1}$

$pK_B = 8.41$

Reaction of glycinenitrile (**1f**) with $(pyr)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 610 nm; $[Nu]_{eff} = [Nu]_0$, $k_{obs} = k_{1\Psi}$)

No.	$[(pyr)_2CH^+]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	$k_{1\Psi}$ / s^{-1}
ccy40.1	2.66×10^{-5}	4.96×10^{-3}	186	0.404
ccy40.2	2.66×10^{-5}	2.48×10^{-3}	93	0.208
ccy40.3	2.66×10^{-5}	1.74×10^{-3}	65	0.148
ccy40.4	2.66×10^{-5}	9.22×10^{-4}	35	9.49×10^{-2}



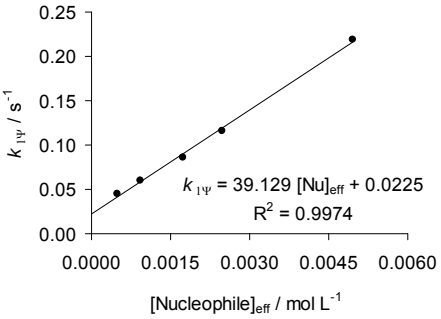
$k_{2,N} = 77.4$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 48.5$ $M^{-1}s^{-1}$

$pK_B = 8.41$

Reaction of glycinenitrile (**1f**) with $(thq)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 610 nm, $[Nu]_{eff} = [Nu]_0$, $k_{obs} = k_{1\Psi}$)

No.	$[(thq)_2CH^+]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	$k_{1\Psi}$ / s^{-1}
ccy41.1	1.63×10^{-5}	4.96×10^{-3}	304	0.219
ccy41.2	1.63×10^{-5}	2.48×10^{-3}	152	0.116
ccy41.3	1.63×10^{-5}	1.74×10^{-3}	107	8.64×10^{-2}
ccy41.4	1.63×10^{-5}	9.22×10^{-4}	57	6.00×10^{-2}
ccy41.5	1.63×10^{-5}	4.95×10^{-4}	30	4.54×10^{-2}



$k_{2,N} = 39.1\ M^{-1}s^{-1}$; $k_{-1} = 2.3 \times 10^{-2}\ s^{-1}$

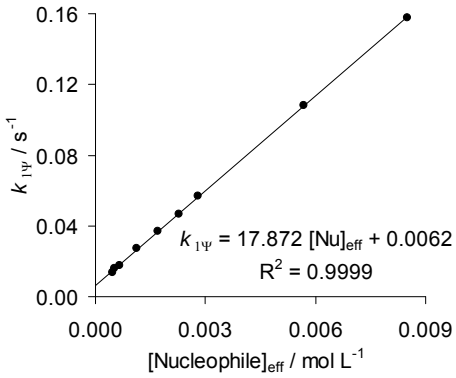
$K = k_{2,N} / k_{-1} = 1.7 \times 10^3\ M^{-1}$

$k_{2,OH^-} = 23.6\ M^{-1}s^{-1}$

$pK_B = 8.41$

Reaction of glycinenitrile (**1f**) with $(ind)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow and J&M, detection at 614 nm, $[Nu]_{eff} = [Nu]_0$, $k_{obs} = k_{1\Psi}$)

No.	$[(ind)_2CH^+]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	$k_{1\Psi}$ / s^{-1}
ccy55.1[a]	1.48×10^{-5}	8.51×10^{-3}	575	0.158
ccy55.2[a]	1.48×10^{-5}	5.68×10^{-3}	383	0.108
ccy55.3[a]	1.48×10^{-5}	2.80×10^{-3}	189	5.67×10^{-2}
ccy55.4[a]	1.48×10^{-5}	2.27×10^{-3}	153	4.70×10^{-2}
ccy55.5[a]	1.48×10^{-5}	1.70×10^{-3}	115	3.70×10^{-2}
ccy55.6[a]	1.48×10^{-5}	1.14×10^{-3}	77	2.71×10^{-2}
ccy55.8[b]	1.89×10^{-5}	6.48×10^{-4}	34	1.74×10^{-2}
ccy55.9[b]	1.90×10^{-5}	5.23×10^{-4}	28	1.57×10^{-2}
ccy55.7[b]	1.90×10^{-5}	4.78×10^{-4}	25	1.37×10^{-2}



[a] Method: Stopped-flow

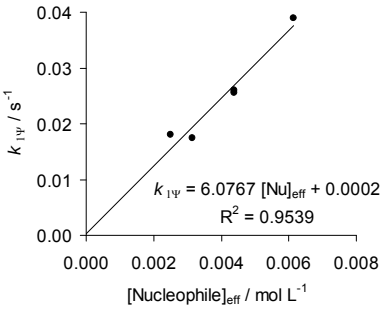
[b] Method: J&M

$k_{2,N} = 17.9\ M^{-1}s^{-1}$; $k_{-1} = 6.2 \times 10^{-3}\ s^{-1}$; $K = k_{2,N} / k_{-1} = 2.9 \times 10^3\ M^{-1}$

$k_{2,OH^-} = 10.8\ M^{-1}s^{-1}$; $pK_B = 8.41$

Reaction of glycinenitrile (**1f**) with $(jul)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 0.1 vol-% CH_3CN, J&M, detection at 634 nm, $[Nu]_{eff} = [Nu]_0$, $k_{obs} = k_{1\Psi}$)

No.	$[(jul)_2CH^+]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	$k_{1\Psi}$ / s^{-1}
ccy66.1	2.56×10^{-5}	6.15×10^{-3}	240	3.90×10^{-2}
ccy66.2	2.62×10^{-5}	4.39×10^{-3}	167	2.61×10^{-2}
ccy66.5	2.62×10^{-5}	4.39×10^{-3}	167	2.56×10^{-2}
ccy66.6	2.62×10^{-5}	3.14×10^{-3}	120	1.75×10^{-2}
ccy66.3	2.62×10^{-5}	2.51×10^{-3}	96	1.80×10^{-2}



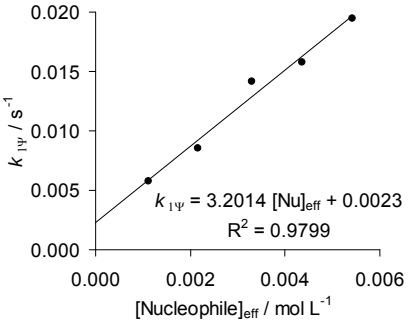
$k_{2,N} = 6.08\ M^{-1}s^{-1}$

$k_{2,OH^-} = 3.44\ M^{-1}s^{-1}$

$pK_B = 8.41$

Reaction of glycinenitrile (**1f**) with $(lil)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, J&M, detection at 630 nm, $[Nu]_{eff} = [Nu]_0$, $k_{obs} = k_{1\Psi}$)

No.	$[(lil)_2CH^+]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	$k_{1\Psi}$ / s^{-1}
ccy204.1	2.16×10^{-5}	5.43×10^{-3}	251	1.95×10^{-2}
ccy204.2	2.17×10^{-5}	4.37×10^{-3}	201	1.58×10^{-2}
ccy204.3	2.19×10^{-5}	3.30×10^{-3}	151	1.42×10^{-2}
ccy204.4	2.14×10^{-5}	2.16×10^{-3}	101	8.57×10^{-3}
ccy204.5	2.23×10^{-5}	1.12×10^{-3}	50	5.80×10^{-3}



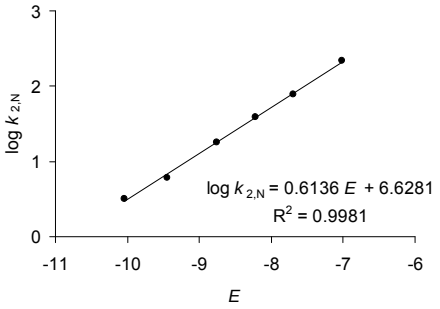
$k_{2,N} = 3.20\ M^{-1}s^{-1}$; $k_{-1} = 2.3 \times 10^{-3}\ s^{-1}$; $K = k_{2,N} / k_{-1} = 1.4 \times 10^3\ M^{-1}$

$k_{2,OH^-} = 2.16\ M^{-1}s^{-1}$

$pK_B = 8.41$

Reactivity parameters in water: *N* = 10.80; *s* = 0.61

Reference electrophile	*E* parameter	$k_{2,N}$(20°C) / M^{-1} s^{-1}
$(dma)_2CH^+$	-7.02	2.19×10^2
$(pyr)_2CH^+$	-7.69	77.4
$(thq)_2CH^+$	-8.22	39.1
$(ind)_2CH^+$	-8.76	17.9
$(jul)_2CH^+$	-9.45	6.08
$(lil)_2CH^+$	-10.04	3.20



2.8.9. Methyl glycinate (1g)

Rate constants in water

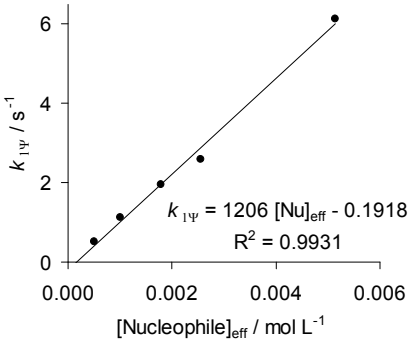
Reaction of methyl glycinate (**1g**) with $(dma)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 0.5 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi, OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy172.1	5.95×10^{-5}	5.20×10^{-3}	5.14×10^{-3}	5.70×10^{-5}	86	6.15	7.46×10^{-3}	6.14
ccy172.2	5.95×10^{-5}	2.60×10^{-3}	2.56×10^{-3}	4.02×10^{-5}	43	2.59	5.26×10^{-3}	2.58
ccy172.3	5.95×10^{-5}	1.82×10^{-3}	1.79×10^{-3}	3.36×10^{-5}	30	1.95	4.40×10^{-3}	1.95
ccy172.4	5.95×10^{-5}	1.04×10^{-3}	1.01×10^{-3}	2.53×10^{-5}	17	1.13	3.31×10^{-3}	1.13
ccy172.5	5.95×10^{-5}	5.20×10^{-4}	5.02×10^{-4}	1.78×10^{-5}	8	0.517	2.33×10^{-3}	0.515

$k_{2,N} = 1.21 \times 10^3$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 131$ $M^{-1}s^{-1}$

$pK_B = 6.20$[44]



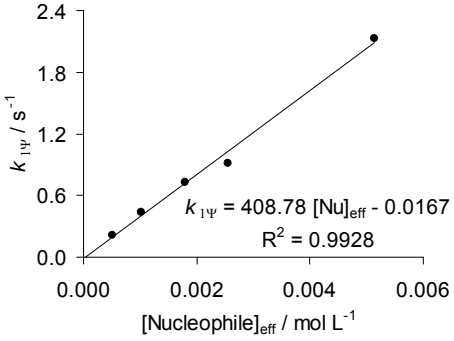
Reaction of methyl glycinate (**1g**) with $(pyr)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 0.1 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(pyr)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi, OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy173.1	1.12×10^{-5}	5.20×10^{-3}	5.14×10^{-3}	5.70×10^{-5}	459	2.13	2.76×10^{-3}	2.13
ccy173.2	1.12×10^{-5}	2.60×10^{-3}	2.56×10^{-3}	4.02×10^{-5}	229	0.920	1.95×10^{-3}	0.918
ccy173.3	1.12×10^{-5}	1.82×10^{-3}	1.79×10^{-3}	3.36×10^{-5}	160	0.730	1.63×10^{-3}	0.728
ccy173.4	1.12×10^{-5}	1.04×10^{-3}	1.01×10^{-3}	2.53×10^{-5}	91	0.434	1.23×10^{-3}	0.433
ccy173.5	1.12×10^{-5}	5.20×10^{-4}	5.02×10^{-4}	1.78×10^{-5}	45	0.210	8.63×10^{-4}	0.209

$k_{2,N} = 4.09 \times 10^2$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 48.5$ $M^{-1}s^{-1}$

$pK_B = 6.20$[44]



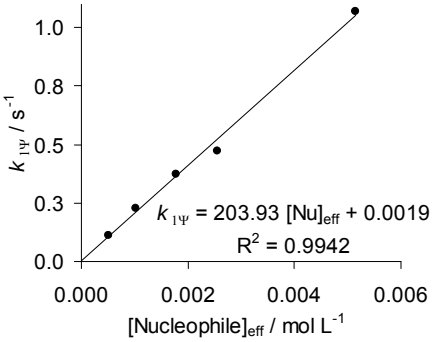
Reaction of methyl glycinate (**1g**) with $(thq)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 0.8 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(thq)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy174.1	6.28×10^{-5}	5.20×10^{-3}	5.14×10^{-3}	5.70×10^{-5}	82	1.07	1.34×10^{-3}	1.07
ccy174.2	6.28×10^{-5}	2.60×10^{-3}	2.56×10^{-3}	4.02×10^{-5}	41	0.475	9.48×10^{-4}	0.474
ccy174.3	6.28×10^{-5}	1.82×10^{-3}	1.79×10^{-3}	3.36×10^{-5}	28	0.375	7.92×10^{-4}	0.374
ccy174.4	6.28×10^{-5}	1.04×10^{-3}	1.01×10^{-3}	2.53×10^{-5}	16	0.227	5.97×10^{-4}	0.226
ccy174.5	6.28×10^{-5}	5.20×10^{-4}	5.02×10^{-4}	1.78×10^{-5}	8	0.111	4.20×10^{-4}	0.111

$k_{2,N} = 2.04 \times 10^2$ M^{-1}s^{-1}

$k_{2,OH^-} = 23.6$ M^{-1}s^{-1}

p$K_B = 6.20$[44]



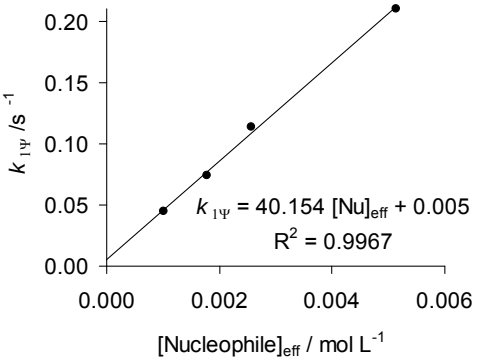
Reaction of methyl glycinate (**1g**) with $(jul)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 634 nm)

No.	$[(jul)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy175.1	6.28×10^{-5}	5.20×10^{-3}	5.14×10^{-3}	5.70×10^{-5}	82	0.210	1.96×10^{-4}	0.210
ccy175.2	6.28×10^{-5}	2.60×10^{-3}	2.56×10^{-3}	4.02×10^{-5}	41	0.114	1.38×10^{-4}	0.114
ccy175.3	6.28×10^{-5}	1.82×10^{-3}	1.79×10^{-3}	3.36×10^{-5}	28	7.38×10^{-2}	1.15×10^{-4}	7.37×10^{-2}
ccy175.4	6.28×10^{-5}	1.04×10^{-3}	1.01×10^{-3}	2.53×10^{-5}	16	4.45×10^{-2}	8.70×10^{-5}	4.44×10^{-2}

$k_{2,N} = 40.2$ M^{-1}s^{-1}

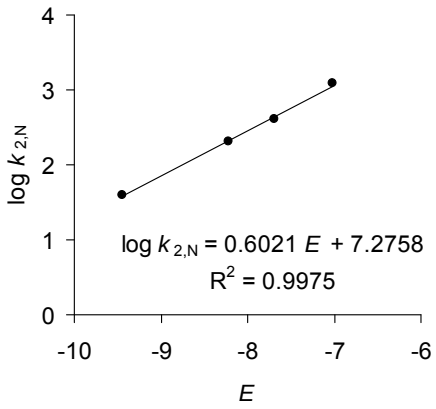
$k_{2,OH^-} = 3.44$ M^{-1}s^{-1}

p$K_B = 6.20$[44]



Reactivity parameters in water: N = 12.08; s = 0.60

Reference electrophile	E parameter	$k_{2,N}$(20°C) / M^{-1} s^{-1}
$(dma)_2CH^+$	-7.02	1.21×10^3
$(pyr)_2CH^+$	-7.69	4.09×10^2
$(thq)_2CH^+$	-8.22	2.04×10^2
$(jul)_2CH^+$	-9.45	40.2



2.8.10. Glycinamide (1h)

Rate constants in water

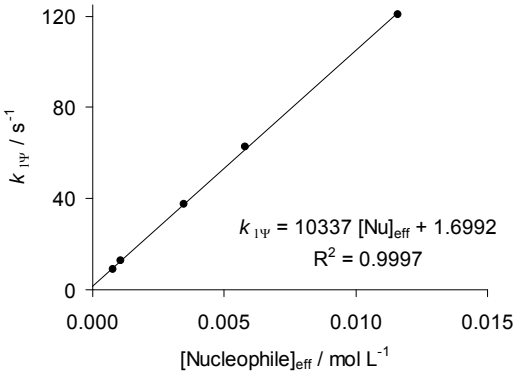
Reaction of glycinamide (**1h**) with $(mor)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 9 vol-% CH_3CN, stopped-flow, detection at 607 nm)

No.	$[(mor)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fb34.1	1.41×10^{-5}	1.17×10^{-2}	1.16×10^{-2}	1.17×10^{-4}	822	1.21×10^2	0.124	1.21×10^2
fb34.2	1.41×10^{-5}	5.87×10^{-3}	5.79×10^{-3}	8.25×10^{-5}	410	62.7	8.74×10^{-2}	62.6
fb34.3	1.41×10^{-5}	3.52×10^{-3}	3.46×10^{-3}	6.37×10^{-5}	245	37.7	6.75×10^{-2}	37.6
fb34.4	1.41×10^{-5}	1.12×10^{-3}	1.08×10^{-3}	3.56×10^{-5}	77	13.0	3.78×10^{-2}	13.0
fb34.5	1.41×10^{-5}	8.22×10^{-4}	7.92×10^{-4}	3.05×10^{-5}	56	9.09	3.23×10^{-2}	9.06

$k_{2,N} = 1.03 \times 10^4$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 1060$ $M^{-1}s^{-1}$

$pK_B = 5.93$



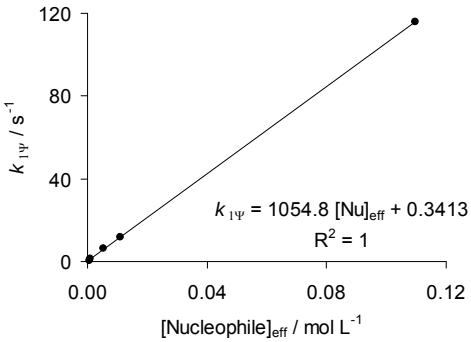
Reaction of glycinamide (**1h**) with $(dma)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 0.4 vol-% CH_3CN, stopped-flow, detection at 604 nm)

No.	$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fb17.1	2.21×10^{-5}	0.110	0.110	3.59×10^{-4}	4961	1.16×10^{2}	4.70×10^{-2}	1.16×10^{2}
fb17.2	2.21×10^{-5}	1.10×10^{-2}	1.09×10^{-2}	1.13×10^{-4}	493	12.0	1.48×10^{-2}	12.0
fb17.3	2.21×10^{-5}	5.52×10^{-3}	5.44×10^{-3}	7.99×10^{-5}	246	6.50	1.05×10^{-2}	6.49
fb17.4	2.21×10^{-5}	1.10×10^{-3}	1.06×10^{-3}	3.54×10^{-5}	48	1.24	4.63×10^{-3}	1.24
fb17.5	2.21×10^{-5}	5.52×10^{-4}	5.27×10^{-4}	2.49×10^{-5}	24	0.591	3.26×10^{-3}	0.588

$k_{2,N} = 1.05 \times 10^3\ M^{-1}s^{-1}$

$k_{2,OH^-} = 131\ M^{-1}s^{-1}$

$pK_B = 5.93$



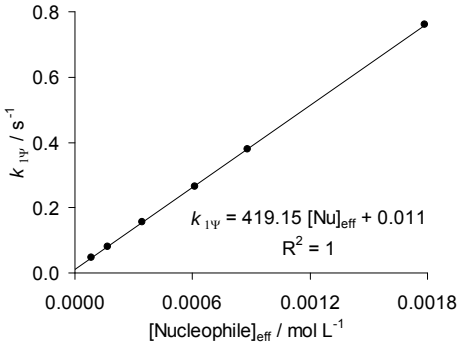
Reaction of glycinamide (**1h**) with $(pyr)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 0.1 vol-% CH_3CN, stopped-flow, detection at 615 nm)

No.	$[(pyr)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy24.1	1.26×10^{-5}	1.83×10^{-3}	1.78×10^{-3}	4.58×10^{-5}	142	0.762	2.22×10^{-3}	0.760
ccy24.2	1.26×10^{-5}	9.12×10^{-4}	8.80×10^{-4}	3.22×10^{-5}	70	0.381	1.56×10^{-3}	0.379
ccy24.3	1.26×10^{-5}	6.38×10^{-4}	6.11×10^{-4}	2.68×10^{-5}	49	0.266	1.30×10^{-3}	0.265
ccy24.4	1.26×10^{-5}	3.65×10^{-4}	3.45×10^{-4}	2.01×10^{-5}	27	0.156	9.76×10^{-4}	0.155
ccy24.5	1.26×10^{-5}	1.82×10^{-4}	1.68×10^{-4}	1.40×10^{-5}	13	8.25×10^{-2}	6.81×10^{-4}	8.18×10^{-2}
ccy24.6	1.26×10^{-5}	9.12×10^{-5}	8.14×10^{-5}	9.78×10^{-6}	6	4.74×10^{-2}	4.74×10^{-4}	4.69×10^{-2}

$k_{2,N} = 4.19 \times 10^2\ M^{-1}s^{-1}$

$k_{2,OH^-} = 48.5\ M^{-1}s^{-1}$

$pK_B = 5.93$



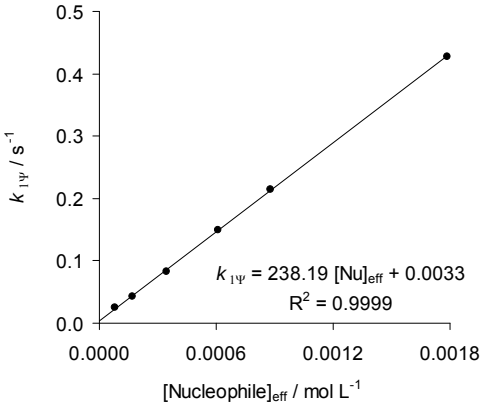
Reaction of glycinamide (**1h**) with $(thq)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 615 nm)

No.	$[(thq)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy25.1	1.58×10^{-5}	1.83×10^{-3}	1.78×10^{-3}	4.58×10^{-5}	113	0.429	1.08×10^{-3}	0.428
ccy25.2	1.58×10^{-5}	9.12×10^{-4}	8.80×10^{-4}	3.22×10^{-5}	56	0.215	7.59×10^{-4}	0.214
ccy25.3	1.58×10^{-5}	6.38×10^{-4}	6.11×10^{-4}	2.68×10^{-5}	39	0.150	6.32×10^{-4}	0.149
ccy25.4	1.58×10^{-5}	3.65×10^{-4}	3.45×10^{-4}	2.01×10^{-5}	22	8.40×10^{-2}	4.75×10^{-4}	8.35×10^{-2}
ccy25.5	1.58×10^{-5}	1.82×10^{-4}	1.68×10^{-4}	1.40×10^{-5}	11	4.25×10^{-2}	3.32×10^{-4}	4.22×10^{-2}
ccy25.6	1.58×10^{-5}	9.12×10^{-5}	8.14×10^{-5}	9.78×10^{-6}	5	2.47×10^{-2}	2.31×10^{-4}	2.45×10^{-2}

$k_{2,N} = 2.38 \times 10^2\ M^{-1}s^{-1}$

$k_{2,OH^-} = 23.6\ M^{-1}s^{-1}$

$pK_B = 5.93$



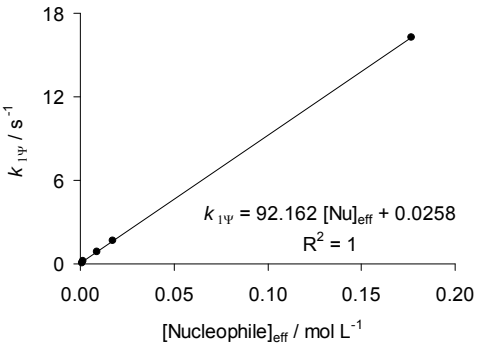
Reaction of glycinamide (**1h**) with $(ind)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 0.4 vol-% CH_3CN, stopped-flow, detection at 614 nm)

No.	$[(ind)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fb14.1	1.39×10^{-5}	0.177	0.177	4.55×10^{-4}	12700	16.3	4.92×10^{-3}	16.3
fb14.2	1.39×10^{-5}	1.77×10^{-2}	1.76×10^{-2}	1.44×10^{-4}	1260	1.65	1.55×10^{-3}	1.65
fb14.3	1.39×10^{-5}	8.83×10^{-3}	8.73×10^{-3}	1.01×10^{-4}	628	0.852	1.09×10^{-3}	0.851
fb14.4	1.39×10^{-5}	1.77×10^{-3}	1.72×10^{-3}	4.50×10^{-5}	124	0.176	4.86×10^{-4}	0.176
fb14.5	1.39×10^{-5}	8.83×10^{-4}	8.51×10^{-4}	3.16×10^{-5}	61	8.98×10^{-2}	3.42×10^{-4}	8.95×10^{-2}

$k_{2,N} = 92.2\ M^{-1}s^{-1}$

$k_{2,OH^-} = 10.8\ M^{-1}s^{-1}$

$pK_B = 5.93$



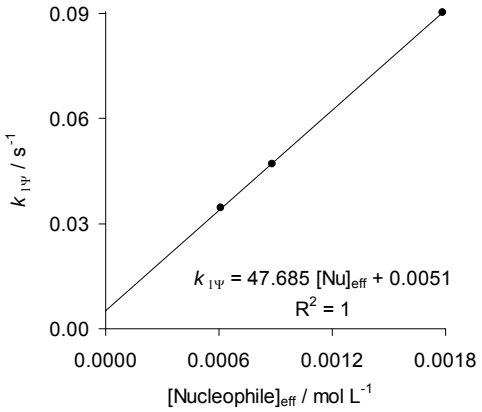
Reaction of glycinamide (**1h**) with $(jul)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 634 nm)

No.	$[(jul)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy26.1	1.26×10^{-5}	1.83×10^{-3}	1.78×10^{-3}	4.58×10^{-5}	142	9.04×10^{-2}	1.58×10^{-4}	9.02×10^{-2}
ccy26.2	1.26×10^{-5}	9.12×10^{-4}	8.80×10^{-4}	3.22×10^{-5}	70	4.70×10^{-2}	1.11×10^{-4}	4.69×10^{-2}
ccy26.3	1.26×10^{-5}	6.38×10^{-4}	6.11×10^{-4}	2.68×10^{-5}	49	3.45×10^{-2}	9.22×10^{-5}	3.44×10^{-2}

$k_{2,N}$ = 47.7 M^{-1}s^{-1}

k_{2,OH^-} = 3.44 M^{-1}s^{-1}

pK_B = 5.93



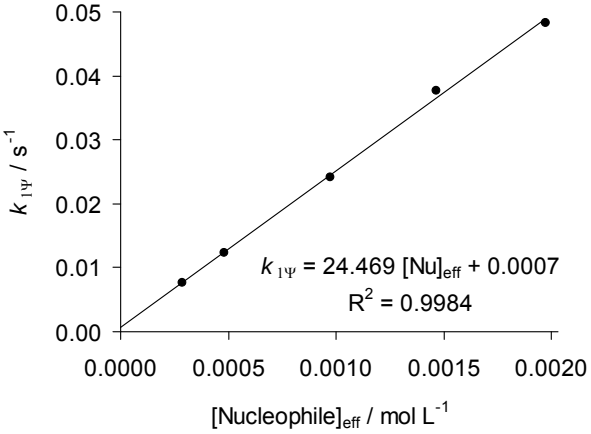
Reaction of glycinamide (**1h**) with $(lil)_2CH^+BF_4^-$: (at 20 °C, coslvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 630 nm)

No.	$[(lil)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fb22.2	8.84×10^{-6}	2.02×10^{-3}	1.97×10^{-3}	4.81×10^{-5}	223	4.84×10^{-2}	1.04×10^{-4}	4.83×10^{-2}
fb22.3	8.84×10^{-6}	1.51×10^{-3}	1.47×10^{-3}	4.15×10^{-5}	166	3.78×10^{-2}	8.97×10^{-5}	3.77×10^{-2}
fb22.4	8.84×10^{-6}	1.01×10^{-3}	9.76×10^{-4}	3.39×10^{-5}	110	2.42×10^{-2}	7.31×10^{-5}	2.41×10^{-2}
fb22.5	8.84×10^{-6}	5.04×10^{-4}	4.80×10^{-4}	2.38×10^{-5}	54	1.23×10^{-2}	5.13×10^{-5}	1.22×10^{-2}
fb22.6	8.84×10^{-6}	3.03×10^{-4}	2.85×10^{-4}	1.83×10^{-5}	32	7.70×10^{-3}	3.95×10^{-5}	7.66×10^{-3}

$k_{2,N}$ = 24.5 M^{-1}s^{-1}

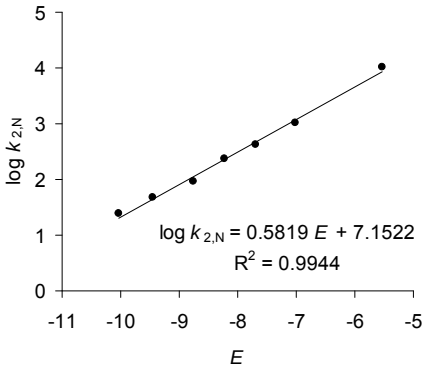
k_{2,OH^-} = 2.16 M^{-1}s^{-1}

pK_B = 5.93



Reactivity parameters in water: *N* = 12.29; *s* = 0.58

Reference electrophile	*E* parameter	$k_{2,N}$(20°C) / M^{-1} s^{-1}
$(mor)_2CH^+$	-5.53	1.03×10^4
$(dma)_2CH^+$	-7.02	1.05×10^3
$(pyr)_2CH^+$	-7.69	4.19×10^2
$(thq)_2CH^+$	-8.22	2.38×10^2
$(ind)_2CH^+$	-8.76	92.2
$(jul)_2CH^+$	-9.45	47.7
$(lil)_2CH^+$	-10.04	24.5



2.8.11. 2-Aminoethanol (1i)

Rate constants in water

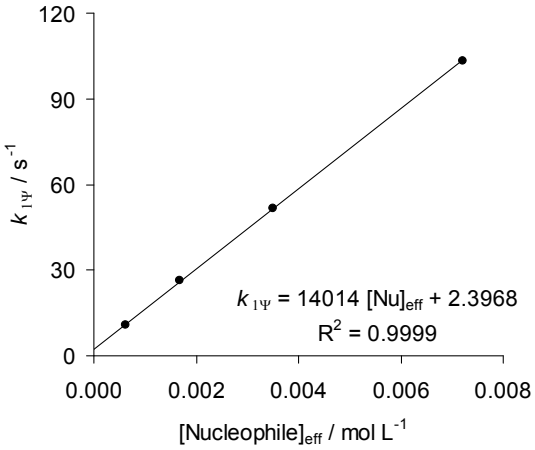
Reaction of 2-Aminoethanol (**1i**) with $(mor)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 9 vol-% CH_3CN, stopped-flow, detection at 607 nm)

No.	$[(mor)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fb176.3	2.57×10^{-5}	7.78×10^{-3}	7.22×10^{-3}	5.61×10^{-4}	281	1.04×10^2	0.595	1.03×10^2
fb176.4	2.57×10^{-5}	3.89×10^{-3}	3.50×10^{-3}	3.91×10^{-4}	136	52.1	0.414	51.7
fb176.5	2.57×10^{-5}	1.95×10^{-3}	1.68×10^{-3}	2.71×10^{-4}	65	26.5	0.287	26.2
fb176.6	2.57×10^{-5}	7.78×10^{-4}	6.14×10^{-4}	1.64×10^{-4}	24	10.8	0.174	10.6

$k_{2,N} = 1.40 \times 10^4$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 1060$ $M^{-1}s^{-1}$

$pK_B = 4.36$



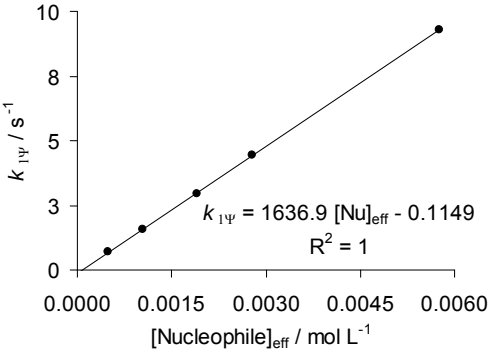
Reaction of 2-Aminoethanol (**1i**) with $(dma)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 0.5 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy130.1	5.95×10^{-5}	6.25×10^{-3}	5.75×10^{-3}	5.01×10^{-4}	97	9.37	6.56×10^{-2}	9.30
ccy130.2	5.95×10^{-5}	3.13×10^{-3}	2.78×10^{-3}	3.48×10^{-4}	47	4.48	4.56×10^{-2}	4.43
ccy130.3	5.95×10^{-5}	2.19×10^{-3}	1.90×10^{-3}	2.88×10^{-4}	32	3.01	3.77×10^{-2}	2.97
ccy130.4	5.95×10^{-5}	1.25×10^{-3}	1.04×10^{-3}	2.13×10^{-4}	17	1.61	2.79×10^{-2}	1.58
ccy130.5	5.95×10^{-5}	6.25×10^{-4}	4.80×10^{-4}	1.45×10^{-4}	8	0.712	1.90×10^{-2}	0.693

$k_{2,N} = 1.64 \times 10^3\ M^{-1}s^{-1}$

$k_{2,OH^-} = 131\ M^{-1}s^{-1}$

$pK_B = 4.36$



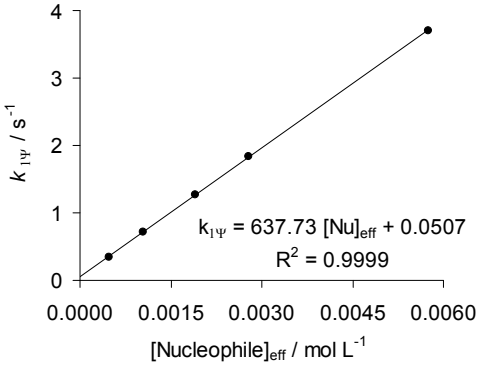
Reaction of 2-Aminoethanol (**1i**) with $(pyr)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(pyr)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy131.1	2.12×10^{-5}	6.25×10^{-3}	5.75×10^{-3}	5.01×10^{-4}	271	3.73	2.43×10^{-2}	3.71
ccy131.2	2.12×10^{-5}	3.13×10^{-3}	2.78×10^{-3}	3.48×10^{-4}	131	1.86	1.69×10^{-2}	1.84
ccy131.3	2.12×10^{-5}	2.19×10^{-3}	1.90×10^{-3}	2.88×10^{-4}	90	1.29	1.40×10^{-2}	1.28
ccy131.4	2.12×10^{-5}	1.25×10^{-3}	1.04×10^{-3}	2.13×10^{-4}	49	0.722	1.03×10^{-2}	0.712
ccy131.5	2.12×10^{-5}	6.25×10^{-4}	4.80×10^{-4}	1.45×10^{-4}	23	0.345	7.02×10^{-3}	0.338

$k_{2,N} = 6.38 \times 10^2\ M^{-1}s^{-1}$

$k_{2,OH^-} = 48.5\ M^{-1}s^{-1}$

$pK_B = 4.36$



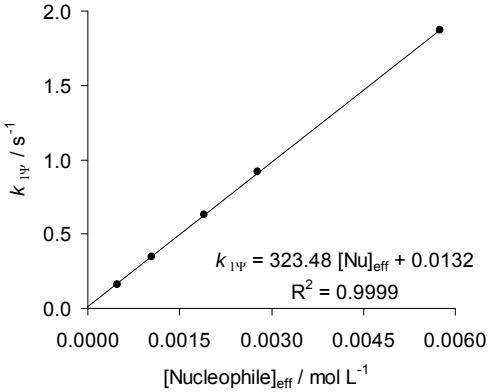
Reaction of 2-Aminoethanol (**1i**) with $(thq)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 0.4 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(thq)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy132.1	3.14×10^{-5}	6.25×10^{-3}	5.75×10^{-3}	5.01×10^{-4}	183	1.88	1.18×10^{-2}	1.87
ccy132.2	3.14×10^{-5}	3.13×10^{-3}	2.78×10^{-3}	3.48×10^{-4}	89	0.930	8.22×10^{-3}	0.922
ccy132.3	3.14×10^{-5}	2.19×10^{-3}	1.90×10^{-3}	2.88×10^{-4}	61	0.639	6.80×10^{-3}	0.632
ccy132.4	3.14×10^{-5}	1.25×10^{-3}	1.04×10^{-3}	2.13×10^{-4}	33	0.353	5.02×10^{-3}	0.348
ccy132.5	3.14×10^{-5}	6.25×10^{-4}	4.80×10^{-4}	1.45×10^{-4}	15	0.165	3.42×10^{-3}	0.162

$k_{2,N} = 3.23 \times 10^2$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 23.6$ $M^{-1}s^{-1}$

$pK_B = 4.36$



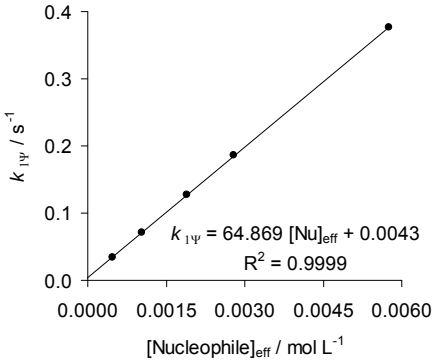
Reaction of 2-Aminoethanol (**1i**) with $(jul)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 634 nm)

No.	$[(jul)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy137.1	8.55×10^{-6}	6.25×10^{-3}	5.75×10^{-3}	5.01×10^{-4}	672	0.378	1.72×10^{-3}	0.376
ccy137.2	8.55×10^{-6}	3.13×10^{-3}	2.78×10^{-3}	3.48×10^{-4}	325	0.188	1.20×10^{-3}	0.187
ccy137.3	8.55×10^{-6}	2.19×10^{-3}	1.90×10^{-3}	2.88×10^{-4}	222	0.129	9.91×10^{-4}	0.128
ccy137.4	8.55×10^{-6}	1.25×10^{-3}	1.04×10^{-3}	2.13×10^{-4}	121	7.19×10^{-2}	7.32×10^{-4}	7.12×10^{-2}
ccy137.5	8.55×10^{-6}	6.25×10^{-4}	4.80×10^{-4}	1.45×10^{-4}	56	3.49×10^{-2}	4.98×10^{-4}	3.44×10^{-2}

$k_{2,N} = 64.9$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 3.44$ $M^{-1}s^{-1}$

$pK_B = 4.36$



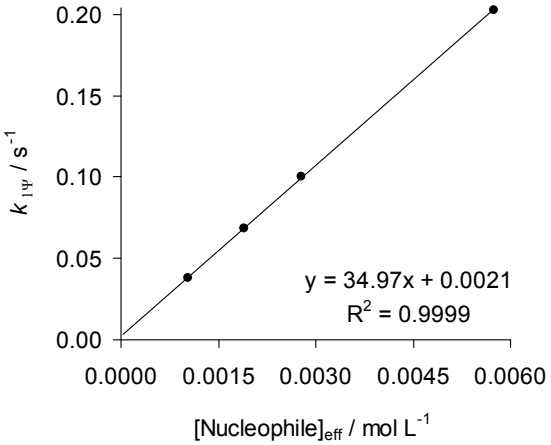
Reaction of 2-Aminoethanol (**1i**) with $(lil)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 634 nm)

No.	$[(lil)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy138.1	1.02×10^{-5}	6.25×10^{-3}	5.75×10^{-3}	5.01×10^{-4}	564	0.204	1.08×10^{-3}	0.203
ccy138.2	1.02×10^{-5}	3.13×10^{-3}	2.78×10^{-3}	3.48×10^{-4}	273	0.101	7.53×10^{-4}	0.100
ccy138.3	1.02×10^{-5}	2.19×10^{-3}	1.90×10^{-3}	2.88×10^{-4}	186	6.91×10^{-2}	6.22×10^{-4}	6.85×10^{-2}
ccy138.4	1.02×10^{-5}	1.25×10^{-3}	1.04×10^{-3}	2.13×10^{-4}	102	3.85×10^{-2}	4.60×10^{-4}	3.80×10^{-2}

$k_{2,N}$ = 35.0 $M^{-1}s^{-1}$

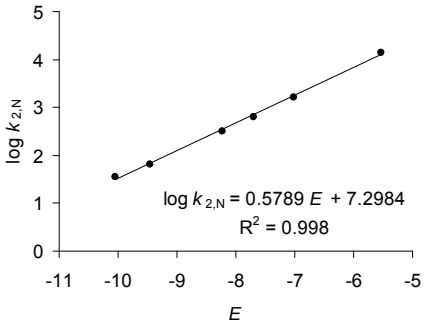
k_{2,OH^-} = 2.16 $M^{-1}s^{-1}$

pK_B = 4.36



Reactivity parameters in water: *N* = 12.61; *s* = 0.58

Reference electrophile	*E* parameter	$k_{2,N}$(20°C) / M^{-1} s^{-1}
$(mor)_2CH^+$	-5.53	1.40×10^4
$(dma)_2CH^+$	-7.02	1.64×10^3
$(pyr)_2CH^+$	-7.69	6.38×10^2
$(thq)_2CH^+$	-8.22	3.23×10^2
$(jul)_2CH^+$	-9.45	64.9
$(lil)_2CH^+$	-10.04	35.0



2.8.12. 1,2-Ethanediamine (1j)

Rate constants in water

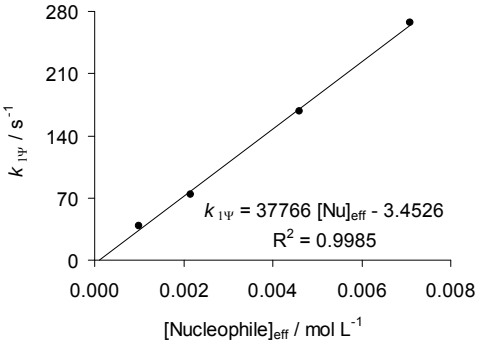
Reaction of 1,2-Ethanediamine (**1j**) with $(mor)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 9 vol-% CH_3CN, stopped-flow, detection at 618 nm)

No.	$[(mor)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fb192.2	1.72×10^{-5}	8.02×10^{-3}	7.10×10^{-3}	9.24×10^{-4}	413	2.68×10^{2}	0.979	2.67×10^{2}
fb192.3	1.72×10^{-5}	5.34×10^{-3}	4.60×10^{-3}	7.43×10^{-4}	267	1.68×10^{2}	0.788	1.67×10^{2}
fb192.4	1.72×10^{-5}	2.67×10^{-3}	2.16×10^{-3}	5.10×10^{-4}	126	74.8	0.540	74.3
fb192.5	1.72×10^{-5}	1.34×10^{-3}	9.94×10^{-4}	3.46×10^{-4}	58	38.8	0.366	38.4

$k_{2,N} = 3.78 \times 10^4\ M^{-1}s^{-1}$

$k_{2,OH^-} = 1060\ M^{-1}s^{-1}$

$pK_B = 3.92$



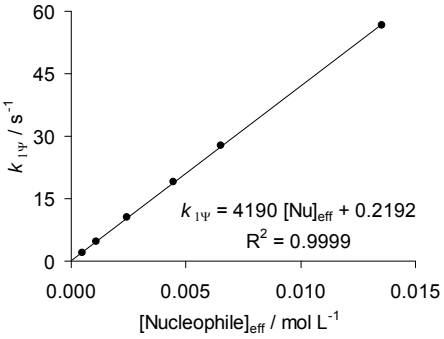
Reaction of 1,2-Ethanediamine (**1j**) with $(dma)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 0.5 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy133.1	5.95×10^{-5}	1.48×10^{-2}	1.35×10^{-2}	1.28×10^{-3}	227	56.9	0.167	56.7
ccy133.2	5.95×10^{-5}	7.40×10^{-3}	6.51×10^{-3}	8.85×10^{-4}	109	27.8	0.116	27.7
ccy133.3	5.95×10^{-5}	5.18×10^{-3}	4.45×10^{-3}	7.31×10^{-4}	75	19.2	9.58×10^{-2}	19.1
ccy133.4	5.95×10^{-5}	2.96×10^{-3}	2.42×10^{-3}	5.39×10^{-4}	41	10.5	7.07×10^{-2}	10.4
ccy133.5	5.95×10^{-5}	1.48×10^{-3}	1.11×10^{-3}	3.66×10^{-4}	19	4.82	4.79×10^{-2}	4.77
ccy133.6	5.95×10^{-5}	7.40×10^{-4}	4.96×10^{-4}	2.44×10^{-4}	8	2.12	3.20×10^{-2}	2.09

$k_{2,N} = 4.19 \times 10^3\ M^{-1}s^{-1}$

$k_{2,OH^-} = 131\ M^{-1}s^{-1}$

$pK_B = 3.92$



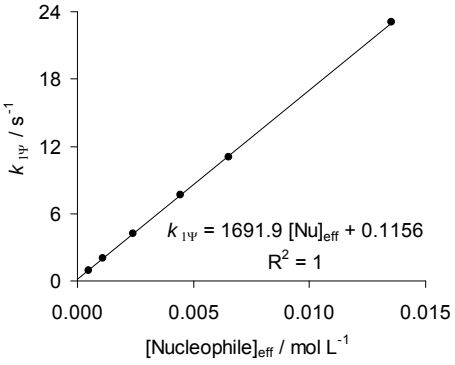
Reaction of 1,2-Ethanediamine (**1j**) with $(pyr)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(pyr)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy134.1	2.12×10^{-5}	1.48×10^{-2}	1.35×10^{-2}	1.28×10^{-3}	638	23.1	6.18×10^{-2}	23.0
ccy134.2	2.12×10^{-5}	7.40×10^{-3}	6.51×10^{-3}	8.85×10^{-4}	307	11.1	4.29×10^{-2}	11.1
ccy134.3	2.12×10^{-5}	5.18×10^{-3}	4.45×10^{-3}	7.31×10^{-4}	210	7.66	3.55×10^{-2}	7.62
ccy134.4	2.12×10^{-5}	2.96×10^{-3}	2.42×10^{-3}	5.39×10^{-4}	114	4.25	2.62×10^{-2}	4.22
ccy134.5	2.12×10^{-5}	1.48×10^{-3}	1.11×10^{-3}	3.66×10^{-4}	53	2.06	1.77×10^{-2}	2.04
ccy134.6	2.12×10^{-5}	7.40×10^{-4}	4.96×10^{-4}	2.44×10^{-4}	23	0.972	1.18×10^{-2}	0.960

$k_{2,N} = 1.69 \times 10^3$ M^{-1}s^{-1}

$k_{2,OH^-} = 48.5$ M^{-1}s^{-1}

p$K_B = 3.92$



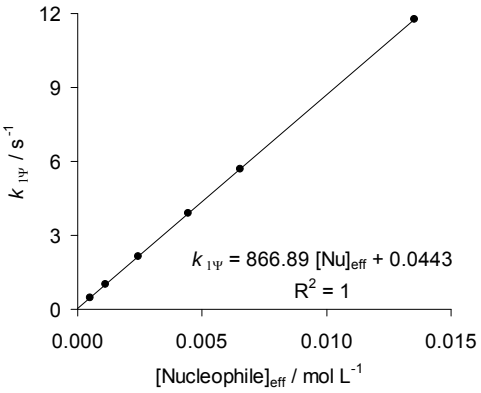
Reaction of 1,2-Ethanediamine (**1j**) with $(thq)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 0.4 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(thq)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy135.1	3.14×10^{-5}	1.48×10^{-2}	1.35×10^{-2}	1.28×10^{-3}	431	11.8	3.01×10^{-2}	11.8
ccy135.2	3.14×10^{-5}	7.40×10^{-3}	6.51×10^{-3}	8.85×10^{-4}	207	5.71	2.09×10^{-2}	5.69
ccy135.3	3.14×10^{-5}	5.18×10^{-3}	4.45×10^{-3}	7.31×10^{-4}	142	3.92	1.73×10^{-2}	3.90
ccy135.4	3.14×10^{-5}	2.96×10^{-3}	2.42×10^{-3}	5.39×10^{-4}	77	2.15	1.27×10^{-2}	2.14
ccy135.5	3.14×10^{-5}	1.48×10^{-3}	1.11×10^{-3}	3.66×10^{-4}	35	1.03	8.64×10^{-3}	1.02
ccy135.6	3.14×10^{-5}	7.40×10^{-4}	4.96×10^{-4}	2.44×10^{-4}	16	0.474	5.76×10^{-3}	0.468

$k_{2,N} = 8.67 \times 10^2$ M^{-1}s^{-1}

$k_{2,OH^-} = 23.6$ M^{-1}s^{-1}

p$K_B = 3.92$



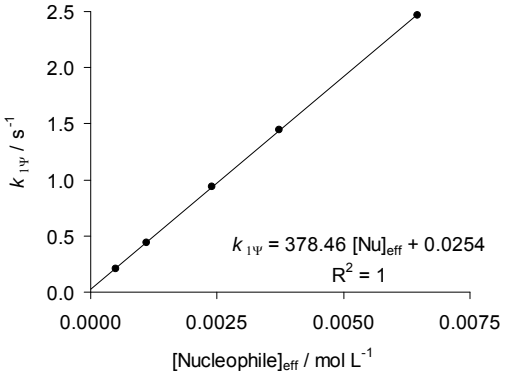
Reaction of 1,2-Ethanediamine (**1j**) with $(ind)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 0.4 vol-% CH_3CN, stopped-flow, detection at 614 nm)

No.	$[(ind)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi, OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fb191.1	2.34×10^{-5}	7.35×10^{-3}	6.47×10^{-3}	8.82×10^{-4}	276	2.48	9.52×10^{-3}	2.47
fb191.2	2.34×10^{-5}	4.41×10^{-3}	3.74×10^{-3}	6.71×10^{-4}	160	1.45	7.24×10^{-3}	1.44
fb191.3	2.34×10^{-5}	2.94×10^{-3}	2.40×10^{-3}	5.37×10^{-4}	103	0.946	5.80×10^{-3}	0.940
fb191.4	2.34×10^{-5}	1.47×10^{-3}	1.11×10^{-3}	3.65×10^{-4}	47	0.447	3.94×10^{-3}	0.443
fb191.5	2.34×10^{-5}	7.35×10^{-4}	4.92×10^{-4}	2.43×10^{-4}	21	0.210	2.63×10^{-3}	0.207

$k_{2,N} = 3.78 \times 10^2$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 10.8$ $M^{-1}s^{-1}$

$pK_B = 3.92$



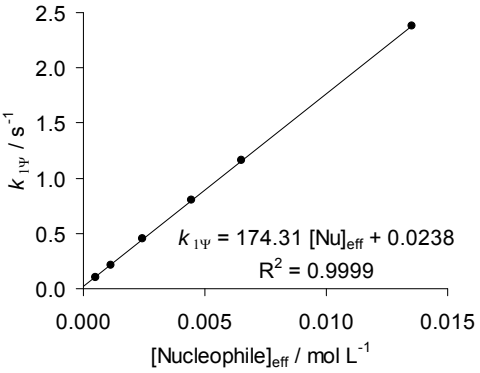
Reaction of 1,2-Ethanediamine (**1j**) with $(jul)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 634 nm)

No.	$[(jul)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi, OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy136.1	8.55×10^{-6}	1.48×10^{-2}	1.35×10^{-2}	1.28×10^{-3}	1582	2.38	4.39×10^{-3}	2.38
ccy136.2	8.55×10^{-6}	7.40×10^{-3}	6.51×10^{-3}	8.85×10^{-4}	762	1.17	3.04×10^{-3}	1.17
ccy136.3	8.55×10^{-6}	5.18×10^{-3}	4.45×10^{-3}	7.31×10^{-4}	520	0.807	2.52×10^{-3}	0.804
ccy136.4	8.55×10^{-6}	2.96×10^{-3}	2.42×10^{-3}	5.39×10^{-4}	283	0.453	1.86×10^{-3}	0.451
ccy136.5	8.55×10^{-6}	1.48×10^{-3}	1.11×10^{-3}	3.66×10^{-4}	130	0.217	1.26×10^{-3}	0.216
ccy136.6	8.55×10^{-6}	7.40×10^{-4}	4.96×10^{-4}	2.44×10^{-4}	58	0.101	8.40×10^{-4}	0.100

$k_{2,N} = 1.74 \times 10^2$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 3.44$ $M^{-1}s^{-1}$

$pK_B = 3.92$



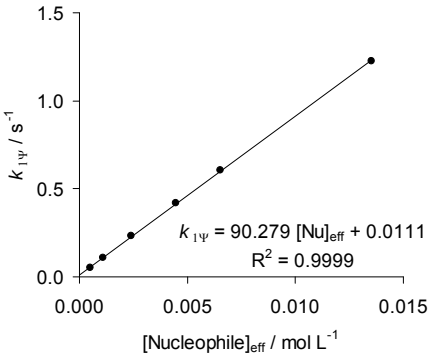
Reaction of 1,2-Ethanediamine (**1j**) with $(lil)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 634 nm)

No.	$[(lil)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy139.1	1.02×10^{-5}	1.48×10^{-2}	1.35×10^{-2}	1.28×10^{-3}	1326	1.23	2.75×10^{-3}	1.23
ccy139.2	1.02×10^{-5}	7.40×10^{-3}	6.51×10^{-3}	8.85×10^{-4}	639	0.609	1.91×10^{-3}	0.607
ccy139.3	1.02×10^{-5}	5.18×10^{-3}	4.45×10^{-3}	7.31×10^{-4}	436	0.418	1.58×10^{-3}	0.416
ccy139.4	1.02×10^{-5}	2.96×10^{-3}	2.42×10^{-3}	5.39×10^{-4}	237	0.232	1.17×10^{-3}	0.231
ccy139.5	1.02×10^{-5}	1.48×10^{-3}	1.11×10^{-3}	3.66×10^{-4}	109	0.110	7.90×10^{-4}	0.109
ccy139.6	1.02×10^{-5}	7.40×10^{-4}	4.96×10^{-4}	2.44×10^{-4}	49	5.08×10^{-2}	5.27×10^{-4}	5.03×10^{-2}

$k_{2,N} = 90.3\ M^{-1}s^{-1}$

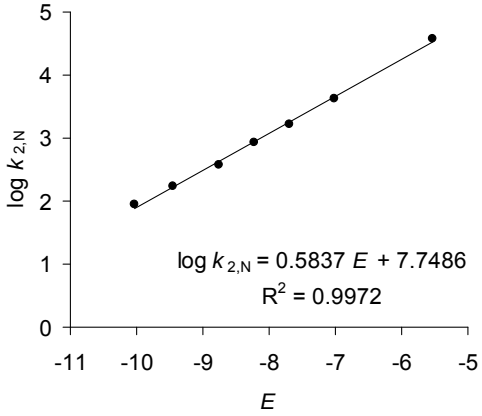
$k_{2,OH^-} = 2.16\ M^{-1}s^{-1}$

$pK_B = 3.92$



Reactivity parameters in water: *N* = 13.28; *s* = 0.58

Reference electrophile	*E* parameter	$k_{2,N}$(20°C) / M^{-1} s^{-1}
$(mor)_2CH^+$	-5.53	3.78×10^4
$(dma)_2CH^+$	-7.02	4.19×10^3
$(pyr)_2CH^+$	-7.69	1.69×10^3
$(thq)_2CH^+$	-8.22	8.67×10^2
$(ind)_2CH^+$	-8.76	3.78×10^2
$(jul)_2CH^+$	-9.45	1.74×10^2
$(lil)_2CH^+$	-10.04	90.3



2.8.13. 1,3-Propanediamine (1k)

Rate constants in water

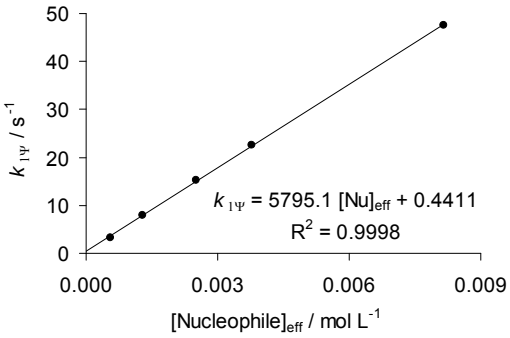
Reaction of 1,3-Propanediamine (**1k**) with $(dma)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 0.5 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi, OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy154.1	5.95×10^{-5}	9.85×10^{-3}	8.15×10^{-3}	1.70×10^{-3}	137	47.7	0.223	47.5
ccy154.2	5.95×10^{-5}	4.93×10^{-3}	3.77×10^{-3}	1.16×10^{-3}	63	22.8	0.152	22.6
ccy154.3	5.95×10^{-5}	3.45×10^{-3}	2.51×10^{-3}	9.43×10^{-4}	42	15.3	0.124	15.2
ccy154.4	5.95×10^{-5}	1.97×10^{-3}	1.29×10^{-3}	6.77×10^{-4}	22	7.94	8.87×10^{-2}	7.85
ccy154.5	5.95×10^{-5}	9.85×10^{-4}	5.45×10^{-4}	4.40×10^{-4}	9	3.38	5.76×10^{-2}	3.32

$k_{2,N} = 5.80 \times 10^3$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 131$ $M^{-1}s^{-1}$

$pK_B = 3.45$



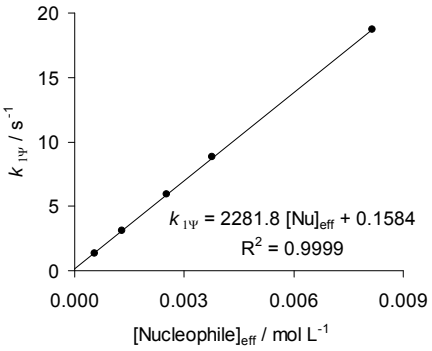
Reaction of 1,3-Propanediamine (**1k**) with $(pyr)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 0.1 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(pyr)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi, OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy155.1	1.13×10^{-5}	9.85×10^{-3}	8.15×10^{-3}	1.70×10^{-3}	721	18.8	8.25×10^{-2}	18.7
ccy155.2	1.13×10^{-5}	4.93×10^{-3}	3.77×10^{-3}	1.16×10^{-3}	334	8.90	5.61×10^{-2}	8.84
ccy155.3	1.13×10^{-5}	3.45×10^{-3}	2.51×10^{-3}	9.43×10^{-4}	222	5.95	4.57×10^{-2}	5.90
ccy155.4	1.13×10^{-5}	1.97×10^{-3}	1.29×10^{-3}	6.77×10^{-4}	114	3.12	3.28×10^{-2}	3.09
ccy155.5	1.13×10^{-5}	9.85×10^{-4}	5.45×10^{-4}	4.40×10^{-4}	48	1.38	2.13×10^{-2}	1.36

$k_{2,N} = 2.28 \times 10^3$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 48.5$ $M^{-1}s^{-1}$

$pK_B = 3.45$



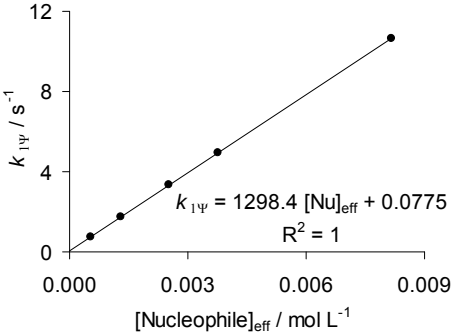
Reaction of 1,3-Propanediamine (**1k**) with $(thq)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 0.4 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(thq)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy156.1	3.14×10^{-5}	9.85×10^{-3}	8.15×10^{-3}	1.70×10^{-3}	260	10.7	4.01×10^{-2}	10.7
ccy156.2	3.14×10^{-5}	4.93×10^{-3}	3.77×10^{-3}	1.16×10^{-3}	120	4.99	2.73×10^{-2}	4.96
ccy156.3	3.14×10^{-5}	3.45×10^{-3}	2.51×10^{-3}	9.43×10^{-4}	80	3.37	2.23×10^{-2}	3.35
ccy156.4	3.14×10^{-5}	1.97×10^{-3}	1.29×10^{-3}	6.77×10^{-4}	41	1.78	1.60×10^{-2}	1.76
ccy156.5	3.14×10^{-5}	9.85×10^{-4}	5.45×10^{-4}	4.40×10^{-4}	17	0.785	1.04×10^{-2}	0.775

$k_{2,N} = 1.30 \times 10^3\ M^{-1}s^{-1}$

$k_{2,OH^-} = 23.6\ M^{-1}s^{-1}$

$pK_B = 3.45$



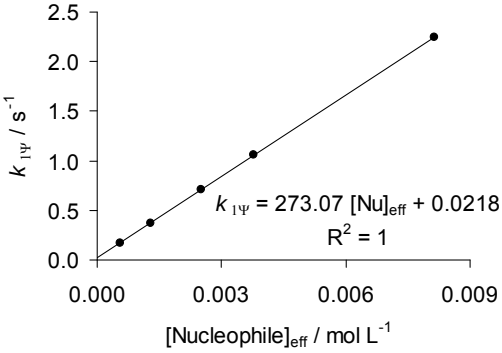
Reaction of 1,3-Propanediamine (**1k**) with $(jul)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 0.1 vol-% CH_3CN, stopped-flow, detection at 634 nm)

No.	$[(jul)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy157.1	8.55×10^{-6}	9.85×10^{-3}	8.15×10^{-3}	1.70×10^{-3}	953	2.25	5.85×10^{-3}	2.24
ccy157.2	8.55×10^{-6}	4.93×10^{-3}	3.77×10^{-3}	1.16×10^{-3}	441	1.06	3.98×10^{-3}	1.06
ccy157.3	8.55×10^{-6}	3.45×10^{-3}	2.51×10^{-3}	9.43×10^{-4}	293	0.715	3.24×10^{-3}	0.712
ccy157.4	8.55×10^{-6}	1.97×10^{-3}	1.29×10^{-3}	6.77×10^{-4}	151	0.377	2.33×10^{-3}	0.375
ccy157.5	8.55×10^{-6}	9.85×10^{-4}	5.45×10^{-4}	4.40×10^{-4}	64	0.166	1.51×10^{-3}	0.164

$k_{2,N} = 2.73 \times 10^2\ M^{-1}s^{-1}$

$k_{2,OH^-} = 3.44\ M^{-1}s^{-1}$

$pK_B = 3.45$



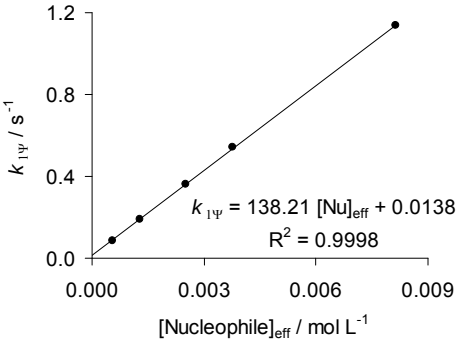
Reaction of 1,3-Propanediamine (**1k**) with $(lil)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 634 nm)

No.	$[(lil)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy158.1	1.02×10^{-5}	9.85×10^{-3}	8.15×10^{-3}	1.70×10^{-3}	799	1.14	3.67×10^{-3}	1.14
ccy158.2	1.02×10^{-5}	4.93×10^{-3}	3.77×10^{-3}	1.16×10^{-3}	370	0.545	2.50×10^{-3}	0.543
ccy158.3	1.02×10^{-5}	3.45×10^{-3}	2.51×10^{-3}	9.43×10^{-4}	246	0.366	2.04×10^{-3}	0.364
ccy158.4	1.02×10^{-5}	1.97×10^{-3}	1.29×10^{-3}	6.77×10^{-4}	127	0.192	1.46×10^{-3}	0.191
ccy158.5	1.02×10^{-5}	9.85×10^{-4}	5.45×10^{-4}	4.40×10^{-4}	53	8.49×10^{-2}	9.50×10^{-4}	8.39×10^{-2}

$k_{2,N} = 1.38 \times 10^2\ M^{-1}s^{-1}$

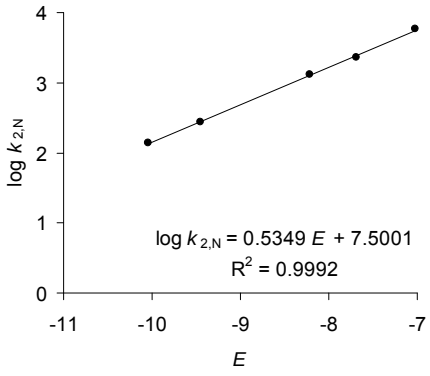
$k_{2,OH^-} = 2.16\ M^{-1}s^{-1}$

$pK_B = 3.45$



Reactivity parameters in water: *N* = 14.02; *s* = 0.54

Reference electrophile	*E* parameter	$k_{2,N}$(20°C) / M^{-1} s^{-1}
$(dma)_2CH^+$	-7.02	5.80×10^3
$(pyr)_2CH^+$	-7.69	2.28×10^3
$(thq)_2CH^+$	-8.22	1.30×10^3
$(jul)_2CH^+$	-9.45	2.73×10^2
$(lil)_2CH^+$	-10.04	1.38×10^2



2.8.14. Propargylamine (1l)

Rate constants in water

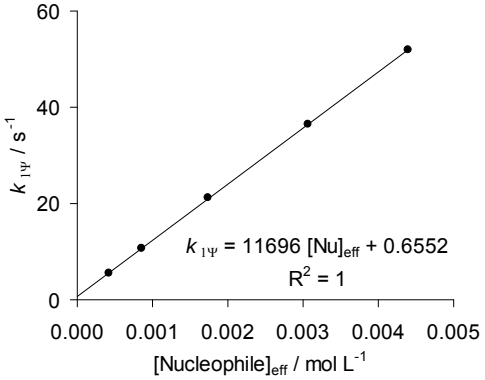
Reaction of Propargylamine (**1l**) with $(mor)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 9 vol-% CH_3CN, stopped-flow, detection at 614 nm)

No.	$[(mor)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fb193.1	2.35×10^{-5}	4.47×10^{-3}	4.39×10^{-3}	7.88×10^{-5}	187	52.1	8.35×10^{-2}	52.0
fb193.2	2.35×10^{-5}	3.13×10^{-3}	3.06×10^{-3}	6.58×10^{-5}	130	36.5	6.97×10^{-2}	36.4
fb193.3	2.35×10^{-5}	1.79×10^{-3}	1.74×10^{-3}	4.96×10^{-5}	74	21.2	5.26×10^{-2}	21.1
fb193.4	2.35×10^{-5}	8.94×10^{-4}	8.59×10^{-4}	3.48×10^{-5}	37	10.7	3.69×10^{-2}	10.7
fb193.5	2.35×10^{-5}	4.47×10^{-4}	4.23×10^{-4}	2.44×10^{-5}	18	5.59	2.59×10^{-2}	5.56

$k_{2,N} = 1.17 \times 10^4$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 1060$ $M^{-1}s^{-1}$

$pK_B = 5.85$



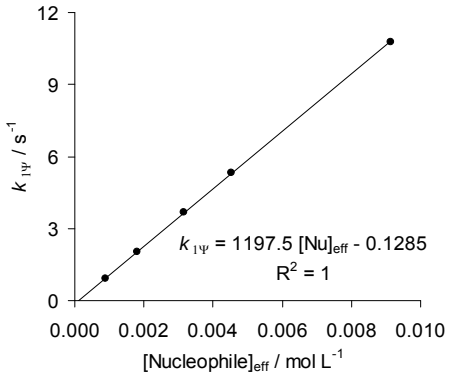
Reaction of Propargylamine (**1l**) with $(dma)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.5 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy100.1	1.08×10^{-4}	9.24×10^{-3}	9.13×10^{-3}	1.14×10^{-4}	85	10.8	1.49×10^{-2}	10.8
ccy100.2	1.08×10^{-4}	4.62×10^{-3}	4.54×10^{-3}	8.01×10^{-5}	42	5.35	1.05×10^{-2}	5.34
ccy100.3	1.08×10^{-4}	3.23×10^{-3}	3.16×10^{-3}	6.68×10^{-5}	29	3.68	8.76×10^{-3}	3.67
ccy100.4	1.08×10^{-4}	1.85×10^{-3}	1.80×10^{-3}	5.04×10^{-5}	17	2.02	6.60×10^{-3}	2.01
ccy100.5	1.08×10^{-4}	9.24×10^{-4}	8.89×10^{-4}	3.54×10^{-5}	8	0.926	4.64×10^{-3}	0.921

$k_{2,N} = 1.20 \times 10^3$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 131$ $M^{-1}s^{-1}$

$pK_B = 5.85$



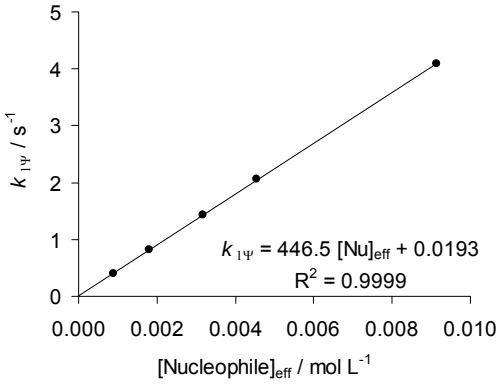
Reaction of Propargylamine (**1l**) with $(pyr)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(pyr)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy101.1	1.71×10^{-5}	9.24×10^{-3}	9.13×10^{-3}	1.14×10^{-4}	534	4.09	5.51×10^{-3}	4.08
ccy101.2	1.71×10^{-5}	4.62×10^{-3}	4.54×10^{-3}	8.01×10^{-5}	265	2.07	3.88×10^{-3}	2.07
ccy101.3	1.71×10^{-5}	3.23×10^{-3}	3.16×10^{-3}	6.68×10^{-5}	185	1.44	3.24×10^{-3}	1.44
ccy101.4	1.71×10^{-5}	1.85×10^{-3}	1.80×10^{-3}	5.04×10^{-5}	105	0.822	2.45×10^{-3}	0.820
ccy101.5	1.71×10^{-5}	9.24×10^{-4}	8.89×10^{-4}	3.54×10^{-5}	52	0.406	1.72×10^{-3}	0.404

$k_{2,N} = 4.47 \times 10^2\ M^{-1}s^{-1}$

$k_{2,OH^-} = 48.5\ M^{-1}s^{-1}$

$pK_B = 5.85$



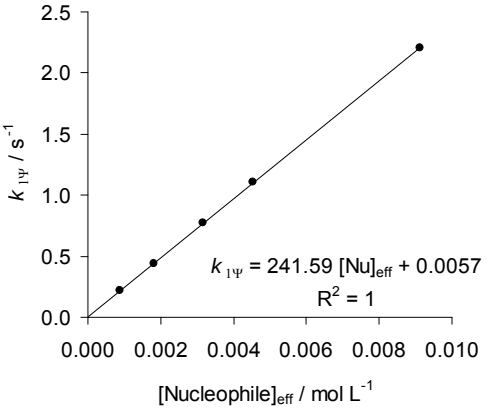
Reaction of Propargylamine (**1l**) with $(thq)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(thq)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy102.1	1.57×10^{-5}	9.24×10^{-3}	9.13×10^{-3}	1.14×10^{-4}	581	2.21	2.68×10^{-3}	2.21
ccy102.2	1.57×10^{-5}	4.62×10^{-3}	4.54×10^{-3}	8.01×10^{-5}	289	1.11	1.89×10^{-3}	1.11
ccy102.3	1.57×10^{-5}	3.23×10^{-3}	3.16×10^{-3}	6.68×10^{-5}	201	0.775	1.58×10^{-3}	0.773
ccy102.4	1.57×10^{-5}	1.85×10^{-3}	1.80×10^{-3}	5.04×10^{-5}	115	0.440	1.19×10^{-3}	0.439
ccy102.5	1.57×10^{-5}	9.24×10^{-4}	8.89×10^{-4}	3.54×10^{-5}	57	0.217	8.36×10^{-4}	0.216

$k_{2,N} = 2.42 \times 10^2\ M^{-1}s^{-1}$

$k_{2,OH^-} = 23.6\ M^{-1}s^{-1}$

$pK_B = 5.85$



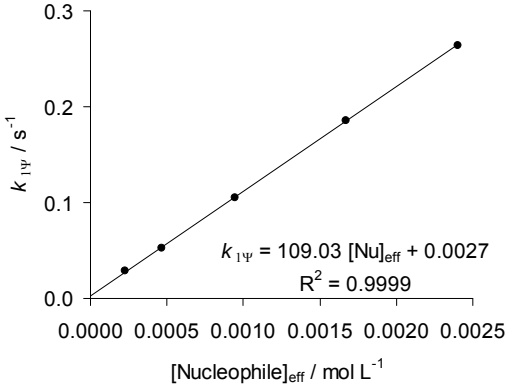
Reaction of Propargylamine (**1l**) with $(ind)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 614 nm)

No.	$[(ind)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fb186.1	2.34×10^{-5}	2.46×10^{-3}	2.40×10^{-3}	5.82×10^{-5}	103	0.265	6.29×10^{-4}	0.264
fb186.2	2.34×10^{-5}	1.72×10^{-3}	1.67×10^{-3}	4.86×10^{-5}	71	0.186	5.25×10^{-4}	0.185
fb186.3	2.34×10^{-5}	9.84×10^{-4}	9.47×10^{-4}	3.66×10^{-5}	40	0.106	3.95×10^{-4}	0.106
fb186.4	2.34×10^{-5}	4.92×10^{-4}	4.66×10^{-4}	2.57×10^{-5}	20	5.26×10^{-2}	2.77×10^{-4}	5.23×10^{-2}
fb186.5	2.34×10^{-5}	2.46×10^{-4}	2.28×10^{-4}	1.79×10^{-5}	10	2.88×10^{-2}	1.94×10^{-4}	2.86×10^{-2}

$k_{2,N} = 1.09 \times 10^2\ M^{-1}s^{-1}$

$k_{2,OH^-} = 10.8\ M^{-1}s^{-1}$

$pK_B = 5.85$



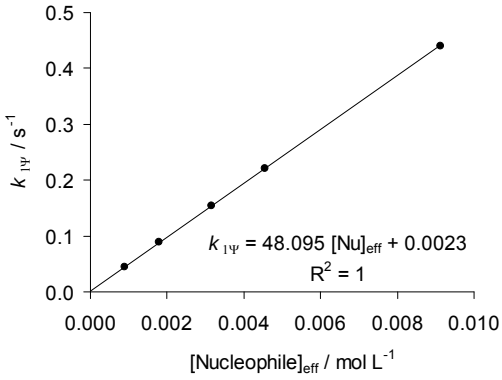
Reaction of Propargylamine (**1l**) with $(jul)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 635 nm)

No.	$[(jul)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy103.1	8.55×10^{-6}	9.24×10^{-3}	9.13×10^{-3}	1.14×10^{-4}	1067	0.441	3.91×10^{-4}	0.441
ccy103.2	8.55×10^{-6}	4.62×10^{-3}	4.54×10^{-3}	8.01×10^{-5}	531	0.222	2.75×10^{-4}	0.222
ccy103.3	8.55×10^{-6}	3.23×10^{-3}	3.16×10^{-3}	6.68×10^{-5}	370	0.155	2.30×10^{-4}	0.155
ccy103.4	8.55×10^{-6}	1.85×10^{-3}	1.80×10^{-3}	5.04×10^{-5}	210	8.89×10^{-2}	1.73×10^{-4}	8.87×10^{-2}
ccy103.5	8.55×10^{-6}	9.24×10^{-4}	8.89×10^{-4}	3.54×10^{-5}	104	4.43×10^{-2}	1.22×10^{-4}	4.42×10^{-2}

$k_{2,N} = 48.1\ M^{-1}s^{-1}$

$k_{2,OH^-} = 3.44\ M^{-1}s^{-1}$

$pK_B = 5.85$



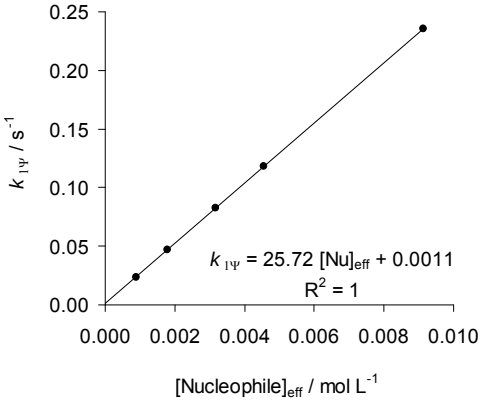
Reaction of Propargylamine (**1l**) with $(lil)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 635 nm)

No.	$[(lil)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy104.1	1.02×10^{-5}	9.24×10^{-3}	9.13×10^{-3}	1.14×10^{-4}	895	0.236	2.45×10^{-4}	0.236
ccy104.2	1.02×10^{-5}	4.62×10^{-3}	4.54×10^{-3}	8.01×10^{-5}	445	0.118	1.73×10^{-4}	0.118
ccy104.3	1.02×10^{-5}	3.23×10^{-3}	3.16×10^{-3}	6.68×10^{-5}	310	8.28×10^{-2}	1.44×10^{-4}	8.27×10^{-2}
ccy104.4	1.02×10^{-5}	1.85×10^{-3}	1.80×10^{-3}	5.04×10^{-5}	176	4.74×10^{-2}	1.09×10^{-4}	4.73×10^{-2}
ccy104.5	1.02×10^{-5}	9.24×10^{-4}	8.89×10^{-4}	3.54×10^{-5}	87	2.39×10^{-2}	7.65×10^{-5}	2.38×10^{-2}

$k_{2,N} = 25.7\ M^{-1}s^{-1}$

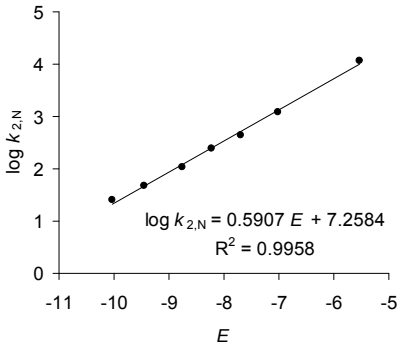
$k_{2,OH^-} = 2.16\ M^{-1}s^{-1}$

$pK_B = 5.85$



Reactivity parameters in water: *N* = 12.29; *s* = 0.59

Reference electrophile	*E* parameter	$k_{2,N}$(20°C) / M^{-1} s^{-1}
$(mor)_2CH^+$	-5.53	1.17×10^4
$(dma)_2CH^+$	-7.02	1.20×10^3
$(pyr)_2CH^+$	-7.69	4.47×10^2
$(thq)_2CH^+$	-8.22	2.42×10^2
$(ind)_2CH^+$	-8.76	1.09×10^2
$(jul)_2CH^+$	-9.45	48.1
$(lil)_2CH^+$	-10.04	25.7



2.8.15. Allylamine (1m)

Rate constants in water

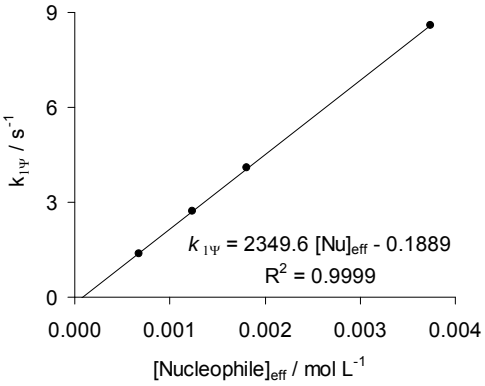
Reaction of Allylamine (**1m**) with $(dma)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.5 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy106.1	1.08×10^{-4}	4.08×10^{-3}	3.74×10^{-3}	3.40×10^{-4}	35	8.63	4.45×10^{-2}	8.59
ccy106.2	1.08×10^{-4}	2.04×10^{-3}	1.80×10^{-3}	2.36×10^{-4}	17	4.11	3.09×10^{-2}	4.08
ccy106.3	1.08×10^{-4}	1.43×10^{-3}	1.23×10^{-3}	1.95×10^{-4}	11	2.75	2.56×10^{-2}	2.72
ccy106.4	1.08×10^{-4}	8.16×10^{-4}	6.72×10^{-4}	1.44×10^{-4}	6	1.38	1.89×10^{-2}	1.36

$k_{2,N} = 2.35 \times 10^3\ M^{-1}s^{-1}$

$k_{2,OH^-} = 131\ M^{-1}s^{-1}$

$pK_B = 4.51$



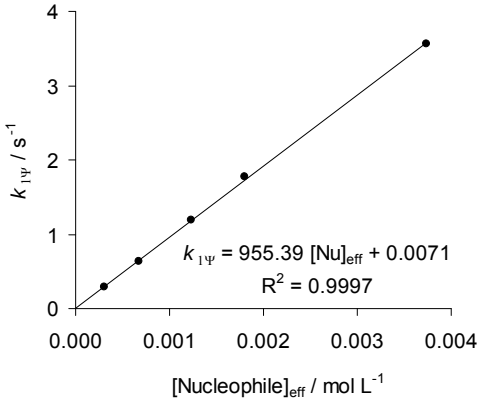
Reaction of Allylamine (**1m**) with $(pyr)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(pyr)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy107.1	1.71×10^{-5}	4.08×10^{-3}	3.74×10^{-3}	3.40×10^{-4}	219	3.58	1.65×10^{-2}	3.56
ccy107.2	1.71×10^{-5}	2.04×10^{-3}	1.80×10^{-3}	2.36×10^{-4}	105	1.78	1.15×10^{-2}	1.77
ccy107.3	1.71×10^{-5}	1.43×10^{-3}	1.23×10^{-3}	1.95×10^{-4}	72	1.20	9.47×10^{-3}	1.19
ccy107.4	1.71×10^{-5}	8.16×10^{-4}	6.72×10^{-4}	1.44×10^{-4}	39	0.648	6.99×10^{-3}	0.641
ccy107.5	1.71×10^{-5}	4.08×10^{-4}	3.10×10^{-4}	9.79×10^{-5}	18	0.291	4.75×10^{-3}	0.286

$k_{2,N} = 9.55 \times 10^2\ M^{-1}s^{-1}$

$k_{2,OH^-} = 48.5\ M^{-1}s^{-1}$

$pK_B = 4.51$



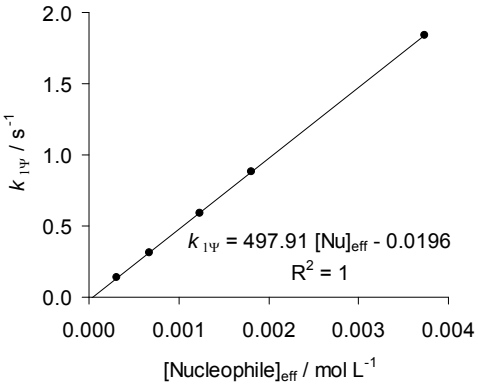
Reaction of Allylamine (**1m**) with $(thq)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(thq)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy108.1	1.57×10^{-5}	4.08×10^{-3}	3.74×10^{-3}	3.40×10^{-4}	238	1.85	8.02×10^{-3}	1.84
ccy108.2	1.57×10^{-5}	2.04×10^{-3}	1.80×10^{-3}	2.36×10^{-4}	115	0.887	5.57×10^{-3}	0.881
ccy108.3	1.57×10^{-5}	1.43×10^{-3}	1.23×10^{-3}	1.95×10^{-4}	79	0.598	4.61×10^{-3}	0.593
ccy108.4	1.57×10^{-5}	8.16×10^{-4}	6.72×10^{-4}	1.44×10^{-4}	43	0.317	3.40×10^{-3}	0.314
ccy108.5	1.57×10^{-5}	4.08×10^{-4}	3.10×10^{-4}	9.79×10^{-5}	20	0.138	2.31×10^{-3}	0.136

$k_{2,N} = 4.98 \times 10^2\ M^{-1}s^{-1}$

$k_{2,OH^-} = 23.6\ M^{-1}s^{-1}$

$pK_B = 4.51$



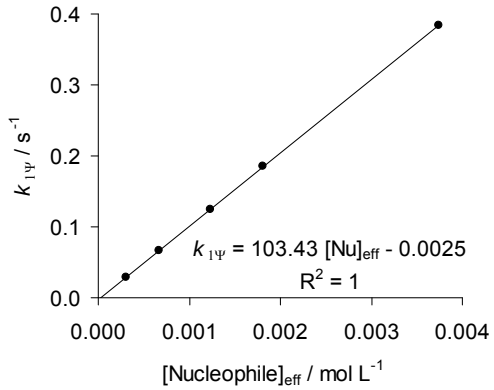
Reaction of Allylamine (**1m**) with $(jul)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 634 nm)

No.	$[(jul)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy109.1	8.55×10^{-6}	4.08×10^{-3}	3.74×10^{-3}	3.40×10^{-4}	437	0.385	1.17×10^{-3}	0.384
ccy109.2	8.55×10^{-6}	2.04×10^{-3}	1.80×10^{-3}	2.36×10^{-4}	211	0.186	8.12×10^{-4}	0.185
ccy109.3	8.55×10^{-6}	1.43×10^{-3}	1.23×10^{-3}	1.95×10^{-4}	144	0.126	6.72×10^{-4}	0.125
ccy109.4	8.55×10^{-6}	8.16×10^{-4}	6.72×10^{-4}	1.44×10^{-4}	79	6.72×10^{-2}	4.96×10^{-4}	6.67×10^{-2}
ccy109.5	8.55×10^{-6}	4.08×10^{-4}	3.10×10^{-4}	9.79×10^{-5}	36	2.94×10^{-2}	3.37×10^{-4}	2.91×10^{-2}

$k_{2,N} = 1.03 \times 10^2\ M^{-1}s^{-1}$

$k_{2,OH^-} = 3.44\ M^{-1}s^{-1}$

$pK_B = 4.51$



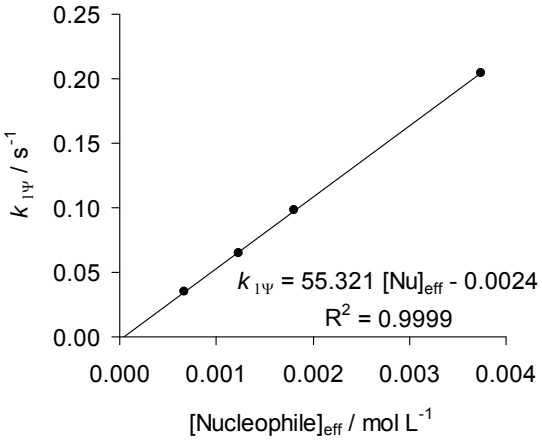
Reaction of Allylamine (**1m**) with $(lil)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 634 nm)

No.	$[(lil)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy110.1	1.02×10^{-5}	4.08×10^{-3}	3.74×10^{-3}	3.40×10^{-4}	367	0.205	7.34×10^{-4}	0.204
ccy110.2	1.02×10^{-5}	2.04×10^{-3}	1.80×10^{-3}	2.36×10^{-4}	177	9.88×10^{-2}	5.10×10^{-4}	9.83×10^{-2}
ccy110.3	1.02×10^{-5}	1.43×10^{-3}	1.23×10^{-3}	1.95×10^{-4}	121	6.55×10^{-2}	4.22×10^{-4}	6.51×10^{-2}
ccy110.4	1.02×10^{-5}	8.16×10^{-4}	6.72×10^{-4}	1.44×10^{-4}	66	3.51×10^{-2}	3.11×10^{-4}	3.48×10^{-2}

$k_{2,N}$ = 55.3 $M^{-1}s^{-1}$

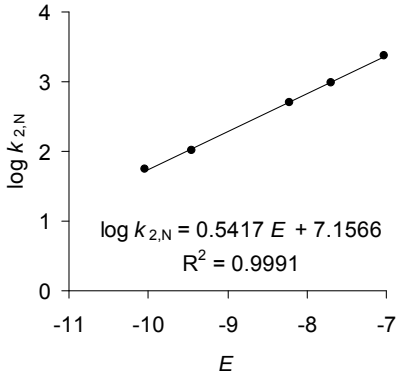
k_{2,OH^-} = 2.16 $M^{-1}s^{-1}$

pK_B = 4.51



Reactivity parameters in water: *N* = 13.21; *s* = 0.54

Reference electrophile	*E* parameter	$k_{2,N}$(20°C) / M^{-1} s^{-1}
$(dma)_2CH^+$	-7.02	2.35×10^3
$(pyr)_2CH^+$	-7.69	9.55×10^2
$(thq)_2CH^+$	-8.22	4.98×10^2
$(jul)_2CH^+$	-9.45	1.03×10^2
$(lil)_2CH^+$	-10.04	55.3



2.8.16. Benzylamine (1n)

Rate constants in water

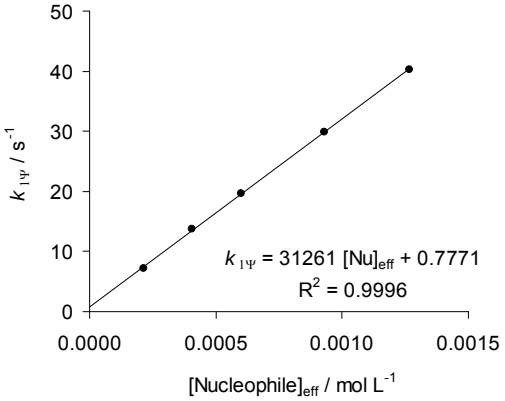
Reaction of Benzylamine (**1n**) with $(mor)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 9 vol-% CH_3CN, stopped-flow, detection at 607 nm)

No.	$[(mor)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fb91.2	2.29×10^{-5}	1.45×10^{-3}	1.27×10^{-3}	1.85×10^{-4}	55	40.4	0.196	40.2
fb91.3	2.29×10^{-5}	1.09×10^{-3}	9.32×10^{-4}	1.58×10^{-4}	41	30.1	0.168	29.9
fb91.1	2.29×10^{-5}	7.26×10^{-4}	5.99×10^{-4}	1.27×10^{-4}	26	19.8	0.135	19.7
fb91.4	2.29×10^{-5}	5.08×10^{-4}	4.04×10^{-4}	1.04×10^{-4}	18	13.8	0.111	13.7
fb91.5	2.29×10^{-5}	2.90×10^{-4}	2.14×10^{-4}	7.59×10^{-5}	9	7.20	8.05×10^{-2}	7.12

$k_{2,N} = 3.13 \times 10^4\ M^{-1}s^{-1}$

$k_{2,OH^-} = 1060\ M^{-1}s^{-1}$

$pK_B = 4.57$[45]



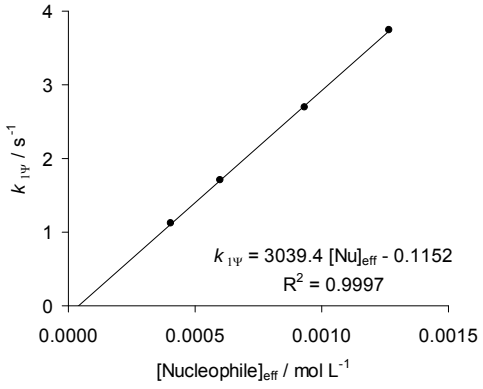
Reaction of Benzylamine (**1n**) with $(dma)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.4 vol-% CH_3CN, stopped-flow, detection at 607 nm)

No.	$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fb92.2	7.62×10^{-5}	1.45×10^{-3}	1.27×10^{-3}	1.85×10^{-4}	17	3.77	2.42×10^{-2}	3.75
fb92.3	7.62×10^{-5}	1.09×10^{-3}	9.32×10^{-4}	1.58×10^{-4}	12	2.71	2.07×10^{-2}	2.69
fb92.1	7.62×10^{-5}	7.26×10^{-4}	5.99×10^{-4}	1.27×10^{-4}	8	1.73	1.66×10^{-2}	1.71
fb92.4	7.62×10^{-5}	5.08×10^{-4}	4.04×10^{-4}	1.04×10^{-4}	5	1.13	1.37×10^{-2}	1.12

$k_{2,N} = 3.04 \times 10^3\ M^{-1}s^{-1}$

$k_{2,OH^-} = 131\ M^{-1}s^{-1}$

$pK_B = 4.57$[45]



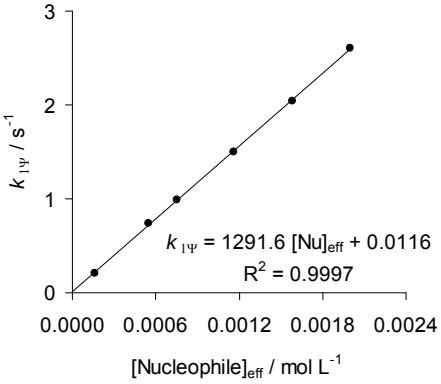
Reaction of Benzylamine (**1n**) with $(pyr)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 607 nm)

No.	$[(pyr)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy30.1	1.33×10^{-5}	2.23×10^{-3}	2.00×10^{-3}	2.32×10^{-4}	150	2.62	1.12×10^{-2}	2.61
ccy30.2	1.33×10^{-5}	1.79×10^{-3}	1.58×10^{-3}	2.06×10^{-4}	119	2.05	1.00×10^{-2}	2.04
ccy30.3	1.33×10^{-5}	1.34×10^{-3}	1.16×10^{-3}	1.77×10^{-4}	87	1.51	8.58×10^{-3}	1.50
ccy30.4	1.33×10^{-5}	8.96×10^{-4}	7.54×10^{-4}	1.42×10^{-4}	57	0.992	6.91×10^{-3}	0.985
ccy30.5	1.33×10^{-5}	6.72×10^{-4}	5.50×10^{-4}	1.22×10^{-4}	41	0.745	5.90×10^{-3}	0.739
ccy30.6	1.33×10^{-5}	2.24×10^{-4}	1.59×10^{-4}	6.53×10^{-5}	12	0.216	3.17×10^{-3}	0.213

$k_{2,N} = 1.29 \times 10^3\ M^{-1}s^{-1}$

$k_{2,OH^-} = 48.5\ M^{-1}s^{-1}$

$pK_B = 4.57$[45]



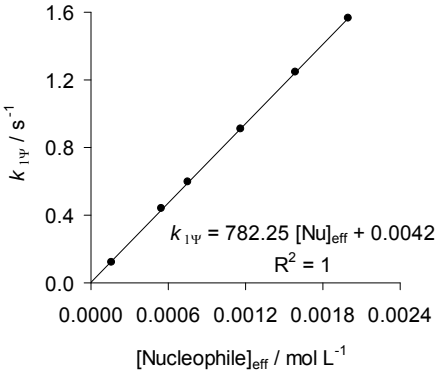
Reaction of Benzylamine (**1n**) with $(thq)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 607 nm)

No.	$[(thq)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy31.1	1.58×10^{-5}	2.23×10^{-3}	2.00×10^{-3}	2.32×10^{-4}	126	1.57	5.47×10^{-3}	1.56
ccy31.2	1.58×10^{-5}	1.79×10^{-3}	1.58×10^{-3}	2.06×10^{-4}	100	1.25	4.87×10^{-3}	1.25
ccy31.3	1.58×10^{-5}	1.34×10^{-3}	1.16×10^{-3}	1.77×10^{-4}	74	0.917	4.18×10^{-3}	0.913
ccy31.4	1.58×10^{-5}	8.96×10^{-4}	7.54×10^{-4}	1.42×10^{-4}	48	0.599	3.36×10^{-3}	0.596
ccy31.5	1.58×10^{-5}	6.72×10^{-4}	5.50×10^{-4}	1.22×10^{-4}	35	0.442	2.87×10^{-3}	0.439
ccy31.6	1.58×10^{-5}	2.24×10^{-4}	1.59×10^{-4}	6.53×10^{-5}	10	0.125	1.54×10^{-3}	0.123

$k_{2,N} = 7.82 \times 10^2\ M^{-1}s^{-1}$

$k_{2,OH^-} = 23.6\ M^{-1}s^{-1}$

$pK_B = 4.57$[45]



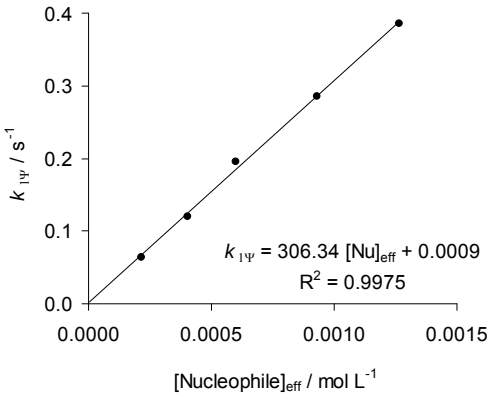
Reaction of Benzylamine (**1n**) with $(ind)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 607 nm)

No.	$[(ind)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi, OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fb93.2	1.76×10^{-5}	1.45×10^{-3}	1.27×10^{-3}	1.85×10^{-4}	72	0.388	1.99×10^{-3}	0.386
fb93.3	1.76×10^{-5}	1.09×10^{-3}	9.32×10^{-4}	1.58×10^{-4}	53	0.287	1.71×10^{-3}	0.285
fb93.1	1.76×10^{-5}	7.26×10^{-4}	5.99×10^{-4}	1.27×10^{-4}	34	0.197	1.37×10^{-3}	0.196
fb93.4	1.76×10^{-5}	5.08×10^{-4}	4.04×10^{-4}	1.04×10^{-4}	23	0.121	1.13×10^{-3}	0.120
fb93.5	1.76×10^{-5}	2.90×10^{-4}	2.14×10^{-4}	7.59×10^{-5}	12	6.44×10^{-2}	8.20×10^{-4}	6.36×10^{-2}

$k_{2,N} = 3.06 \times 10^2$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 10.8$ $M^{-1}s^{-1}$

$pK_B = 4.57$[45]



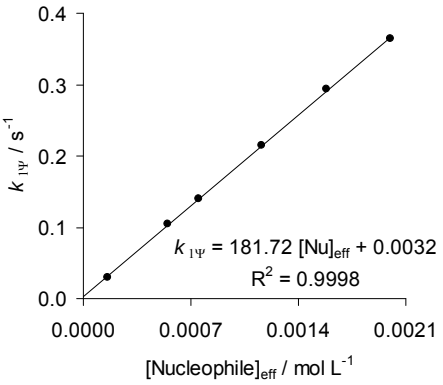
Reaction of Benzylamine (**1n**) with $(jul)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 630 nm)

No.	$[(jul)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi, OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy32.1	1.26×10^{-5}	2.23×10^{-3}	2.00×10^{-3}	2.32×10^{-4}	159	0.365	7.98×10^{-4}	0.364
ccy32.2	1.26×10^{-5}	1.79×10^{-3}	1.58×10^{-3}	2.06×10^{-4}	126	0.294	7.10×10^{-4}	0.293
ccy32.3	1.26×10^{-5}	1.34×10^{-3}	1.16×10^{-3}	1.77×10^{-4}	92	0.215	6.09×10^{-4}	0.214
ccy32.4	1.26×10^{-5}	8.96×10^{-4}	7.54×10^{-4}	1.42×10^{-4}	60	0.141	4.90×10^{-4}	0.141
ccy32.5	1.26×10^{-5}	6.72×10^{-4}	5.50×10^{-4}	1.22×10^{-4}	44	0.105	4.19×10^{-4}	0.105
ccy32.6	1.26×10^{-5}	2.24×10^{-4}	1.59×10^{-4}	6.53×10^{-5}	13	3.05×10^{-2}	2.25×10^{-4}	3.03×10^{-2}

$k_{2,N} = 1.82 \times 10^2$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 3.44$ $M^{-1}s^{-1}$

$pK_B = 4.57$[45]



Reaction of Benzylamine (**1n**) with $(lil)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, Stopped-flow and J&M, detection at 634 nm)

No.	$[(lil)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi, OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fb95.1[a]	2.66×10^{-5}	4.49×10^{-3}	4.16×10^{-3}	3.34×10^{-4}	156	0.392	7.22 10^{-4}	0.391
fb95.2[a]	2.66×10^{-5}	3.14×10^{-3}	2.86×10^{-3}	2.78×10^{-4}	108	0.276	6.00 10^{-4}	0.275
fb95.3[a]	2.66×10^{-5}	2.24×10^{-3}	2.01×10^{-3}	2.32×10^{-4}	75	0.195	5.02 10^{-4}	0.194
fb95.4[a]	2.66×10^{-5}	1.35×10^{-3}	1.17×10^{-3}	1.78×10^{-4}	44	0.115	3.84 10^{-4}	0.115
fb94.1[b]	1.07×10^{-5}	5.56×10^{-4}	4.46×10^{-4}	1.10×10^{-4}	42	4.40×10^{-2}	2.37×10^{-4}	4.38×10^{-2}
fb94.4[b]	1.07×10^{-5}	4.45×10^{-4}	3.48×10^{-4}	9.68×10^{-5}	33	3.46×10^{-2}	2.09×10^{-4}	3.44×10^{-2}
fb94.3[b]	1.06×10^{-5}	2.21×10^{-4}	1.56×10^{-4}	6.48×10^{-5}	15	1.46×10^{-2}	1.40×10^{-4}	1.45×10^{-2}
fb95.5[a]	2.66×10^{-5}	4.49×10^{-4}	3.52×10^{-4}	9.73×10^{-5}	13	3.79×10^{-2}	2.10×10^{-4}	3.77×10^{-2}
fb94.2[b]	1.10×10^{-5}	1.15×10^{-4}	7.12×10^{-5}	4.38×10^{-5}	6	5.62×10^{-3}	9.46×10^{-5}	5.53×10^{-3}

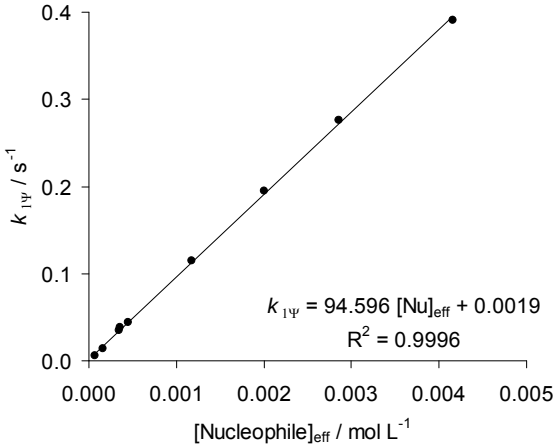
[a] Method: Stopped-flow

[b] Method: J&M

$k_{2,N}$ = 94.6 $M^{-1}s^{-1}$

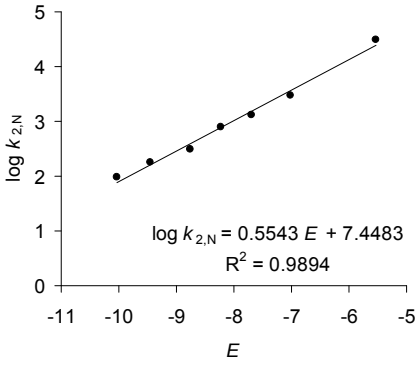
k_{2,OH^-} = 2.16 $M^{-1}s^{-1}$

pK_B = 4.57[45]



Reactivity parameters in water: *N* = 13.44; *s* = 0.55

Reference electrophile	*E* parameter	$k_{2,N}$(20°C) / M^{-1} s^{-1}
$(mor)_2CH^+$	-5.53	3.13×10^4
$(dma)_2CH^+$	-7.02	3.04×10^3
$(pyr)_2CH^+$	-7.69	1.29×10^3
$(thq)_2CH^+$	-8.22	7.82×10^2
$(ind)_2CH^+$	-8.76	3.06×10^2
$(jul)_2CH^+$	-9.45	1.82×10^2
$(lil)_2CH^+$	-10.04	94.6



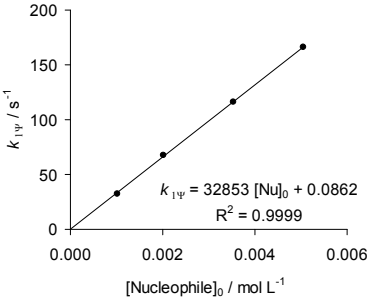
2.8.17. 4-Chloroaniline (1o)

Rate constants in Acetonitrile

Reaction of 4-Chloroaniline (**1o**) with $(mor)_2CH^+BF_4^-$ (at 20 °C, stopped-flow, detection at 620 nm)

No.	$[(mor)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_0/[El]_0$	$k_{1\Psi}$ / s^{-1}
fb344.2	3.54×10^{-5}	5.05×10^{-3}	143	1.66×10^{2}
fb344.3	3.54×10^{-5}	3.54×10^{-3}	100	1.16×10^{2}
fb344.4	3.54×10^{-5}	2.02×10^{-3}	57	67.4
fb344.5	3.54×10^{-5}	1.01×10^{-3}	29	32.7

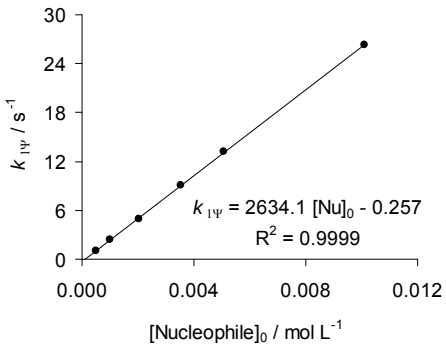
$k_{2,N} = 3.29 \times 10^4$ M^{-1}s^{-1}



Reaction of 4-Chloroaniline (**1o**) with $(dma)_2CH^+BF_4^-$ (at 20 °C, stopped-flow, detection at 620 nm)

No.	$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_0/[El]_0$	$k_{1\Psi}$ / s^{-1}
jo18.1	3.35×10^{-5}	1.01×10^{-2}	301	26.3
jo18.2	3.35×10^{-5}	5.05×10^{-3}	151	13.2
jo18.3	3.35×10^{-5}	3.54×10^{-3}	106	9.05
jo18.4	3.35×10^{-5}	2.02×10^{-3}	60	4.91
jo18.5	3.35×10^{-5}	1.01×10^{-3}	30	2.47
jo18.6	3.35×10^{-5}	5.05×10^{-4}	15	1.07

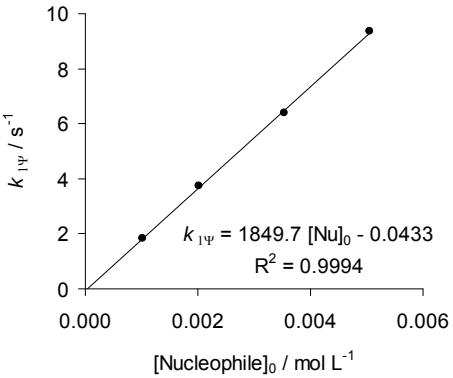
$k_{2,N} = 2.63 \times 10^3$ M^{-1}s^{-1}



Reaction of 4-Chloroaniline (**1o**) with $(pyr)_2CH^+BF_4^-$ (at 20 °C, stopped-flow, detection at 620 nm)

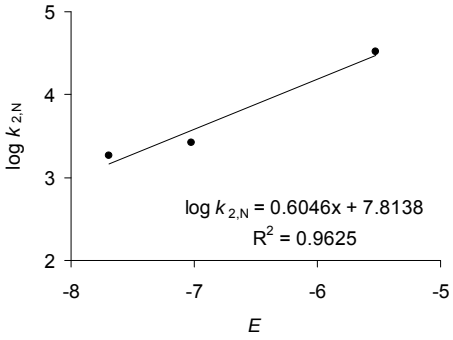
No.	$[(pyr)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_0/[El]_0$	$k_{1\Psi}$ / s^{-1}
fb345.2	3.57×10^{-5}	5.05×10^{-3}	141	9.36
fb345.3	3.57×10^{-5}	3.54×10^{-3}	99	6.39
fb345.4	3.57×10^{-5}	2.02×10^{-3}	57	3.73
fb345.5	3.57×10^{-5}	1.01×10^{-3}	28	1.84

$k_{2,N} = 1.85 \times 10^3$ M^{-1}s^{-1}



Reactivity parameters in Acetonitrile: *N* = 12.92; *s* = 0.60

Reference electrophile	*E* parameter	$k_{2,N}$(20°C) / M^{-1} s^{-1}
$(mor)_2CH^+$	-5.53	3.29×10^4
$(dma)_2CH^+$	-7.02	2.63×10^3
$(pyr)_2CH^+$	-7.69	1.85×10^3

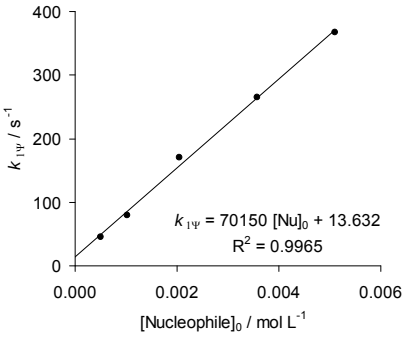


2.8.18. Aniline (1p)

Rate constants in Acetonitrile

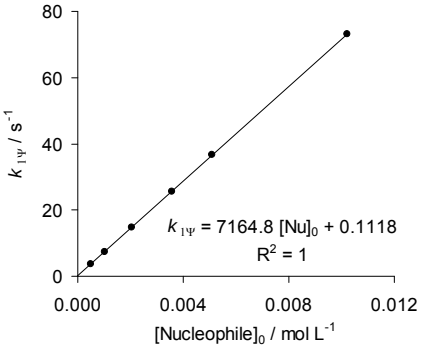
Reaction of Aniline (**1p**) with $(mor)_2CH^+BF_4^-$ (at 20 °C, stopped-flow, detection at 620 nm)
$k_{2,N} = 7.02 \times 10^4$ $M^{-1}s^{-1}$

No.	$[(mor)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_0/[El]_0$	$k_{1\Psi}$ / s^{-1}
jo16.1	5.30×10^{-5}	5.10×10^{-3}	96	3.67×10^2
jo16.2	5.30×10^{-5}	3.57×10^{-3}	67	2.65×10^2
jo16.3	5.30×10^{-5}	2.04×10^{-3}	38	1.70×10^2
jo16.4	5.30×10^{-5}	1.02×10^{-3}	19	79.4
jo16.5	5.30×10^{-5}	5.10×10^{-4}	10	45.4



Reaction of Aniline (**1p**) with $(dma)_2CH^+BF_4^-$ (at 20 °C, stopped-flow, detection at 610 nm)

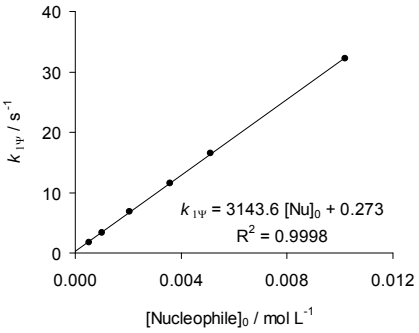
No.	$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_0/[El]_0$	$k_{1\Psi}$ / s^{-1}
fb341.1	2.87×10^{-5}	1.02×10^{-2}	355	73.1
fb341.2	2.87×10^{-5}	5.10×10^{-3}	178	36.8
fb341.3	2.87×10^{-5}	3.57×10^{-3}	124	25.7
fb341.4	2.87×10^{-5}	2.04×10^{-3}	71	14.9
fb341.5	2.87×10^{-5}	1.02×10^{-3}	36	7.29
fb341.6	2.87×10^{-5}	5.10×10^{-4}	18	3.66



$k_{2,N} = 7.16 \times 10^3$ $M^{-1}s^{-1}$

Reaction of Aniline (**1p**) with $(pyr)_2CH^+BF_4^-$ (at 20 °C, stopped-flow, detection at 610 nm)

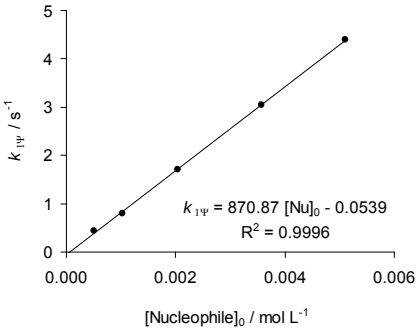
No.	$[(pyr)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_0/[El]_0$	$k_{1\Psi}$ / s^{-1}
fb343.1	3.57×10^{-5}	1.02×10^{-2}	286	32.2
fb343.2	3.57×10^{-5}	5.10×10^{-3}	143	16.5
fb343.3	3.57 × 10-5	3.57×10^{-3}	100	11.6
fb343.4	3.57×10^{-5}	2.04×10^{-3}	57	6.82
fb343.5	3.57×10^{-5}	1.02×10^{-3}	29	3.31
fb343.6	3.57×10^{-5}	5.10×10^{-4}	14	1.75



$k_{2,N} = 3.14 \times 10^3$ $M^{-1}s^{-1}$

Reaction of Aniline (**1p**) with $(thq)_2CH^+BF_4^-$ (at 20 °C, stopped-flow, detection at 620 nm)

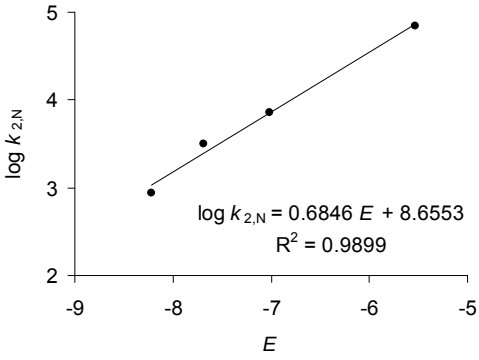
No.	$[(thq)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_0/[El]_0$	$k_{1\Psi}$ / s^{-1}
jo15.1	7.39×10^{-5}	5.10×10^{-3}	69	4.40
jo15.2	7.39×10^{-5}	3.57×10^{-3}	48	3.05
jo15.3	7.39×10^{-5}	2.04×10^{-3}	28	1.71
jo15.4	7.39×10^{-5}	1.02×10^{-3}	14	0.791
jo15.5	7.39×10^{-5}	5.10×10^{-4}	7	0.439



$k_{2,N} = 8.71 \times 10^2$ $M^{-1}s^{-1}$

Reactivity parameters in Acetonitrile: *N* = 12.64; *s* = 0.68

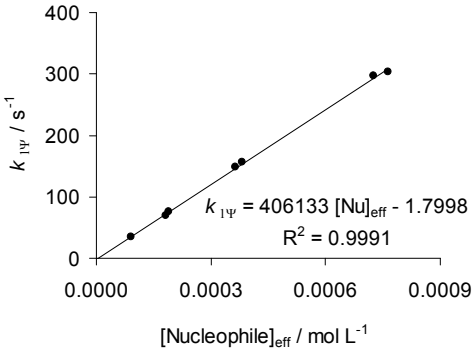
Reference electrophile	*E* parameter	$k_{2,N}$(20°C) / M^{-1} s^{-1}
$(mor)_2CH^+$	-5.53	7.02×10^4
$(dma)_2CH^+$	-7.02	7.16×10^3
$(pyr)_2CH^+$	-7.69	3.14×10^3
$(thq)_2CH^+$	-8.22	8.71×10^2



Rate constants and equilibrium constants in water

Reaction of Aniline (**1p**) with $(mor)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 9 vol-% CH_3CN, stopped-flow, detection at 614 nm, $[Nu]_{eff} = [Nu]_0$, $k_{obs} = k_{1\Psi}$)

No.	$[(mor)_2CH^+]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	$k_{1\Psi}$ / s^{-1}
fb130.3	1.81×10^{-5}	7.26×10^{-4}	40	2.97×10^2
fb147.5	2.57×10^{-5}	7.63×10^{-4}	30	3.03×10^2
fb130.4	1.81×10^{-5}	3.64×10^{-4}	20	1.48×10^2
fb147.6	2.57×10^{-5}	3.82×10^{-4}	15	1.56×10^2
fb130.5	1.81×10^{-5}	1.82×10^{-4}	10	68.8
fb147.7	2.57×10^{-5}	1.91×10^{-4}	7	76.2
fb130.6	1.81×10^{-5}	9.07×10^{-5}	5	34.3



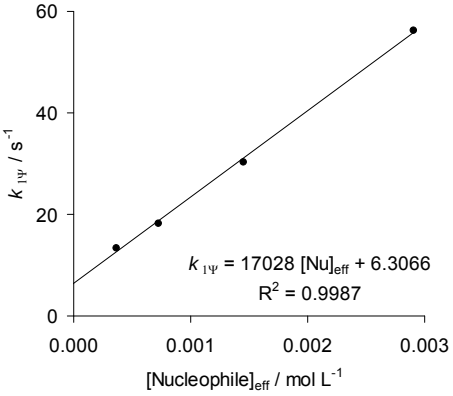
$k_{2,N} = 4.06 \times 10^5\ M^{-1}s^{-1}$

$k_{2,OH^-} = 1060\ M^{-1}s^{-1}$

$pK_B = 9.42$[46]

Reaction of Aniline (**1p**) with $(dma)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.1 vol-% CH_3CN, stopped-flow, detection at 614 nm, $[Nu]_{eff} = [Nu]_0$, $k_{obs} = k_{1\Psi}$)

No.	$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	$k_{1\Psi}$ / s^{-1}
fb131.1	3.43×10^{-5}	2.91×10^{-3}	85	56.2
fb131.2	3.43×10^{-5}	1.45×10^{-3}	42	30.3
fb131.3	3.43×10^{-5}	7.26×10^{-4}	21	18.2
fb131.4	3.43×10^{-5}	3.64×10^{-4}	11	13.3



$k_{2,N} = 1.70 \times 10^4\ M^{-1}s^{-1}$; $k_{-1} = 6.3\ s^{-1}$

$K = k_{2,N} / k_{-1} = 2.7 \times 10^3\ M^{-1}$

$k_{2,OH^-} = 131\ M^{-1}s^{-1}$

$pK_B = 9.42$[46]

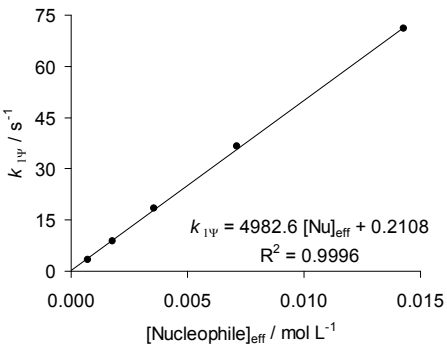
Reaction of Aniline (**1p**) with $(pyr)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.1 vol-% CH_3CN, stopped-flow, detection at 612 nm, $[Nu]_{eff} = [Nu]_0$, $k_{obs} = k_{1\Psi}$)

No.	$[(pyr)_2CH^+]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	$k_{1\Psi}$ / s^{-1}
fb132.1	1.90×10^{-5}	1.43×10^{-2}	753	71.0
fb132.2	1.90×10^{-5}	7.13×10^{-3}	375	36.6
fb132.3	1.90×10^{-5}	3.57×10^{-3}	188	18.3
fb132.4	1.90×10^{-5}	1.78×10^{-3}	94	8.76
fb132.5	1.90×10^{-5}	7.12×10^{-4}	37	3.35

$k_{2,N} = 4.98 \times 10^3$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 48.5$ $M^{-1}s^{-1}$

$pK_B = 9.42$[46]



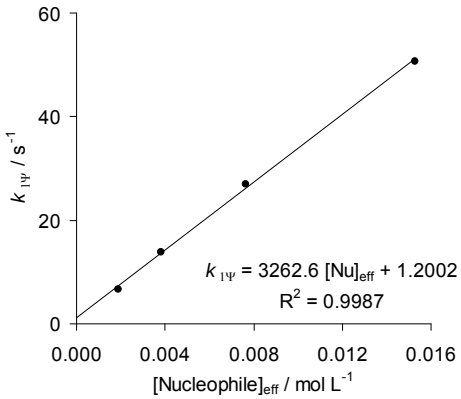
Reaction of Aniline (**1p**) with $(thq)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.4 vol-% CH_3CN, stopped-flow, detection at 611 nm, $[Nu]_{eff} = [Nu]_0$, $k_{obs} = k_{1\Psi}$)

No.	$[(thq)_2CH^+]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	$k_{1\Psi}$ / s^{-1}
fb144.1	1.63×10^{-5}	1.53×10^{-2}	939	50.7
fb144.2	1.63×10^{-5}	7.64×10^{-3}	469	27.0
fb144.3	1.63×10^{-5}	3.82×10^{-3}	234	13.9
fb144.4	1.63×10^{-5}	1.91×10^{-3}	117	6.72

$k_{2,N} = 3.26 \times 10^3$ $M^{-1}s^{-1}$

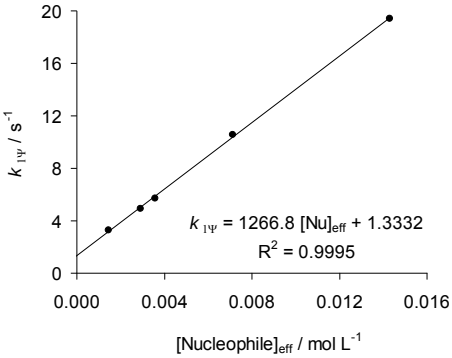
$k_{2,OH^-} = 23.6$ $M^{-1}s^{-1}$

$pK_B = 9.42$[46]



Reaction of Aniline (**1p**) with $(ind)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.4 vol-% CH_3CN, stopped-flow, detection at 612 nm, $[Nu]_{eff} = [Nu]_0$, $k_{obs} = k_{1\Psi}$)

No.	$[(ind)_2CH^+]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	$k_{1\Psi}$ / s^{-1}
fb133.1	1.81×10^{-5}	1.43×10^{-2}	790	19.4
fb133.2	1.81×10^{-5}	7.13×10^{-3}	394	10.6
fb133.3	1.81×10^{-5}	3.57×10^{-3}	197	5.71
fb129.1	1.81×10^{-5}	2.91×10^{-3}	161	4.90
fb129.2	1.81×10^{-5}	1.45×10^{-3}	80	3.29



$k_{2,N} = 1.27 \times 10^3$ $M^{-1}s^{-1}$; $k_{-1} = 1.3$ s^{-1}

$K = k_{2,N} / k_{-1} = 9.5 \times 10^2$ M^{-1}

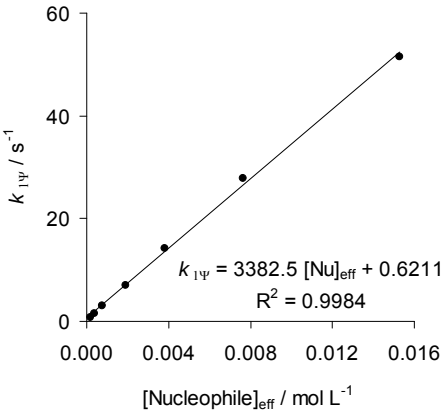
$k_{2,OH^-} = 10.8$ $M^{-1}s^{-1}$

$pK_B = 9.42$[46]

Rate constants in water at pH = 11

Reaction of Aniline (**1p**) with $(thq)_2CH^+BF_4^-$ (pH = 11, at 20 °C, cosolvent: 0.4 vol-% CH_3CN, stopped-flow, detection at 611 nm, $[Nu]_{eff} = [Nu]_0$, $k_{obs} = k_{1\Psi}$)

No.	$[(thq)_2CH^+]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi}$ / s^{-1}
fb145.1	1.63×10^{-5}	1.53×10^{-2}	939	51.6	51.6
fb145.2	1.63×10^{-5}	7.64×10^{-3}	469	27.8	27.8
fb145.3	1.63×10^{-5}	3.82×10^{-3}	234	14.2	14.2
fb145.4	1.63×10^{-5}	1.91×10^{-3}	117	7.09	7.07
fb145.5	1.63×10^{-5}	7.63×10^{-4}	47	2.99	2.97
fb145.6	1.63×10^{-5}	3.82×10^{-4}	23	1.52	1.50
fb145.7	1.63×10^{-5}	1.91×10^{-4}	12	0.785	0.761



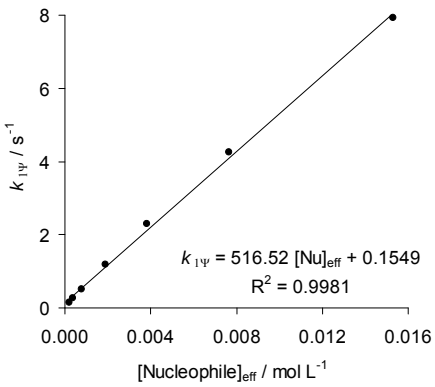
$k_{2,N} = 3.38 \times 10^3$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 23.6$ $M^{-1}s^{-1}$

$pK_B = 9.42$[46]

Reaction of Aniline (**1p**) with $(jul)_2CH^+BF_4^-$ (pH = 11, at 20 °C, cosolvent: 0.4 vol-% CH_3CN, stopped-flow, detection at 625 nm, $[Nu]_{eff} = [Nu]_0$, $k_{obs} = k_{1\Psi}$)

No.	$[(jul)_2CH^+]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi}$ / s^{-1}
fb146.1	1.30×10^{-5}	1.53×10^{-2}	1177	7.94	7.94
fb146.2	1.30×10^{-5}	7.64×10^{-3}	588	4.26	4.26
fb146.3	1.30×10^{-5}	3.82×10^{-3}	294	2.30	2.30
fb146.4	1.30×10^{-5}	1.91×10^{-3}	147	1.19	1.19
fb146.5	1.30×10^{-5}	7.63×10^{-4}	59	0.503	0.500
fb146.6	1.30×10^{-5}	3.82×10^{-4}	29	0.271	0.268
fb146.7	1.30×10^{-5}	1.91×10^{-4}	15	0.140	0.137



$k_{2,N} = 5.17 \times 10^2$ $M^{-1}s^{-1}$

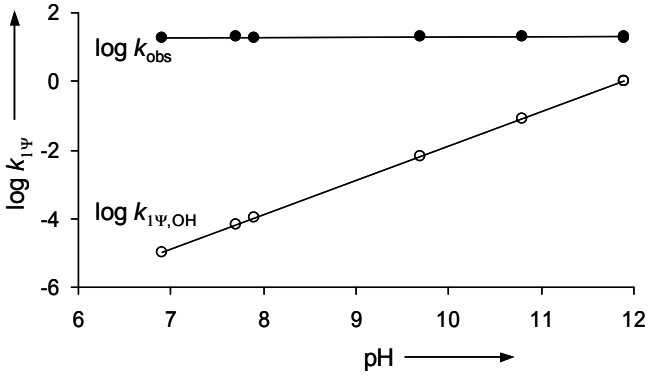
$k_{2,OH^-} = 3.44$ $M^{-1}s^{-1}$

$pK_B = 9.42$[46]

pH dependance of rate constants for the reaction of Aniline (**1p**) with $(dma)_2CH^+BF_4^-$ (phosphate buffer, at 20 °C, cosolvent: 9 vol-% CH_3CN, stopped-flow, detection at 614 nm, pH measured, $[Nu]_{eff} = [Nu]_0$, $k_{obs} = k_{1\Psi}$, $k_{1\Psi,OH^-} = k_{2,OH^-}$ $[OH^-]$ calculated)

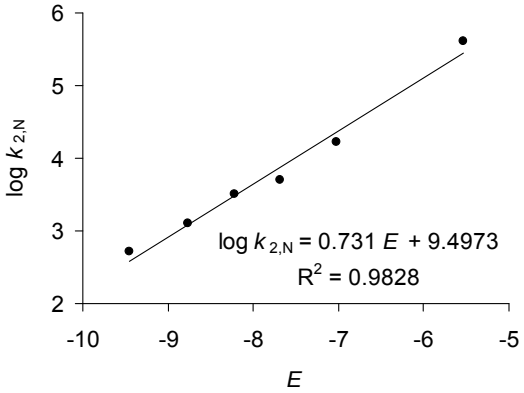
No.	$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[PO_4^{3-}]_0$ / mol L^{-1}	$[HPO_4^{2-}]_0$ / mol L^{-1}	$[H_2PO^{4-}]_0$ / mol L^{-1}	pH	$k_{1\Psi}$ / s^{-1}
jo14.1	3.47×10^{-5}	9.27×10^{-4}	4.52×10^{-3}	4.64×10^{-4}		11.9	1.90×10^{1}
jo14.5	3.47×10^{-5}	9.27×10^{-4}	4.52×10^{-3}	4.64×10^{-3}		11.9	1.80×10^{1}
jo14.2	3.47×10^{-5}	9.27×10^{-4}	4.52×10^{-4}	4.64×10^{-3}		10.8	1.96×10^{1}
jo14.6	3.47×10^{-5}	9.27×10^{-4}	9.04×10^{-5}	9.27×10^{-4}		9.7	1.95×10^{1}
jo14.3	3.47×10^{-5}	9.27×10^{-4}		4.64×10^{-3}	4.73×10^{-4}	7.9	1.93×10^{1}
jo14.7	3.47×10^{-5}	9.26×10^{-4}		9.27×10^{-3}	9.45×10^{-5}	7.7	1.95×10^{1}
jo14.8	3.47×10^{-5}	9.23×10^{-4}		4.64×10^{-3}	4.73×10^{-3}	6.9	1.90×10^{1}

$k_{2,OH^-} = 131$ $M^{-1}s^{-1}$



Reactivity parameters in water: N = 12.99; s = 0.73

Reference electrophile	E parameter	$k_{2,N}$(20°C) / M^{-1} s^{-1}
$(mor)_2CH^+$	-5.53	4.06×10^5
$(dma)_2CH^+$	-7.02	1.70×10^4
$(pyr)_2CH^+$	-7.69	4.98×10^3
$(thq)_2CH^+$	-8.22	3.26×10^3
$(ind)_2CH^+$	-8.76	1.27×10^3
$(jul)_2CH^+$	-9.45	5.17×10^2



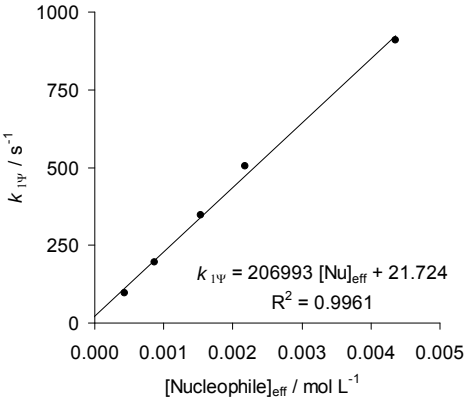
2.8.19. p-Toluidine (1q)

Rate constants in Acetonitrile

Reaction of p-Toluidine (**1q**) with $(mor)_2CH^+BF_4^-$ (at 20 °C, stopped-flow, detection at 620 nm)

No.	$[(mor)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_0/[El]_0$	$k_{1\Psi}$ / s^{-1}
fb347.1	5.31×10^{-5}	4.36×10^{-3}	82	9.09×10^2
fb347.2	5.31×10^{-5}	2.18×10^{-3}	41	5.04×10^2
fb347.3	5.31×10^{-5}	1.53×10^{-3}	29	3.46×10^2
fb347.4	5.31×10^{-5}	8.72×10^{-4}	16	1.96×10^2
fb347.5	5.31×10^{-5}	4.36×10^{-4}	8	94.8

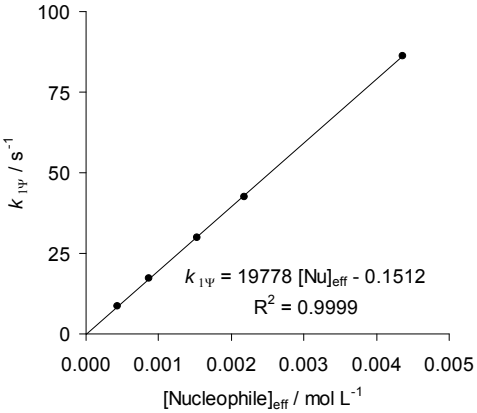
$k_{2,N} = 2.07 \times 10^5$ $M^{-1}s^{-1}$



Reaction of p-Toluidine (**1q**) with (dma)2CH+BF4- (at 20 °C, stopped-flow, detection at 620 nm)

No.	$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_0/[El]_0$	$k_{1\Psi}$ / s^{-1}
fb348.1	1.68×10^{-5}	4.36×10^{-3}	260	86.4
fb348.2	1.68×10^{-5}	2.18×10^{-3}	130	42.5
fb348.3	1.68×10^{-5}	1.53×10^{-3}	91	30.0
fb348.4	1.68×10^{-5}	8.72×10^{-4}	52	17.3
fb348.5	1.68×10^{-5}	4.36×10^{-4}	26	8.66

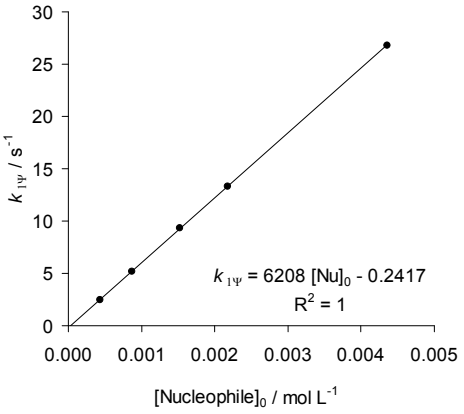
$k_{2,N} = 1.98 \times 10^4$ $M^{-1}s^{-1}$



Reaction of p-Toluidine (**1q**) with $(pyr)_2CH^+BF_4^-$ (at 20 °C, stopped-flow, detection at 620 nm)

No.	$[(pyr)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_0/[El]_0$	$k_{1\Psi}$ / s^{-1}
jo21.1	1.79×10^{-5}	4.36×10^{-3}	244	26.8
jo21.2	1.79×10^{-5}	2.18×10^{-3}	122	13.3
jo21.3	1.79×10^{-5}	1.53×10^{-3}	85	9.35
jo21.4	1.79×10^{-5}	8.72×10^{-4}	49	5.13
jo21.5	1.79×10^{-5}	4.36×10^{-4}	24	2.43

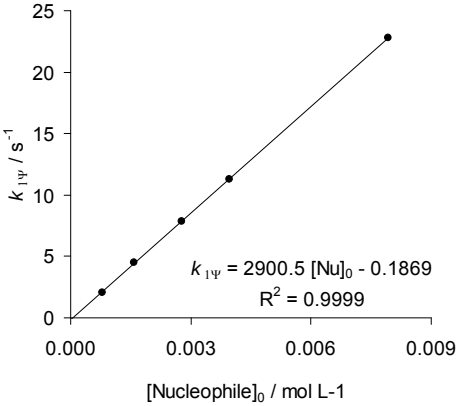
$k_{2,N} = 6.21 \times 10^3$ M^{-1}s^{-1}



Reaction of p-Toluidine (**1q**) with $(thq)_2CH^+BF_4^-$ (at 20 °C, stopped-flow, detection at 620 nm)

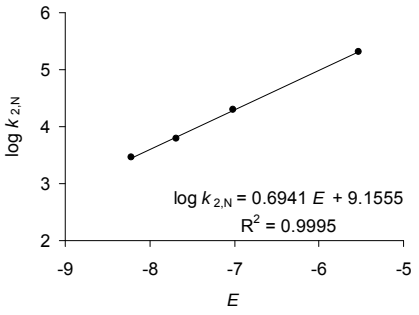
No.	$[(thq)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_0/[El]_0$	$k_{1\Psi}$ / s^{-1}
jo20.1	1.35×10^{-5}	7.93×10^{-3}	587	22.8
jo20.2	1.35×10^{-5}	3.96×10^{-3}	293	11.3
jo20.3	1.35×10^{-5}	2.77×10^{-3}	205	7.86
jo20.4	1.35×10^{-5}	1.58×10^{-3}	117	4.49
jo20.5	1.35×10^{-5}	7.93×10^{-4}	59	2.02

$k_{2,N} = 2.90 \times 10^3$ M^{-1}s^{-1}



Reactivity parameters in Acetonitrile: *N* = 13.19; *s* = 0.69

Reference electrophile	*E* parameter	$k_{2,N}$(20°C) / M^{-1} s^{-1}
$(mor)_2CH^+$	-5.53	2.07×10^5
$(dma)_2CH^+$	-7.02	1.98×10^4
$(pyr)_2CH^+$	-7.69	6.21×10^3
$(thq)_2CH^+$	-8.22	2.90×10^3



Rate constants in water

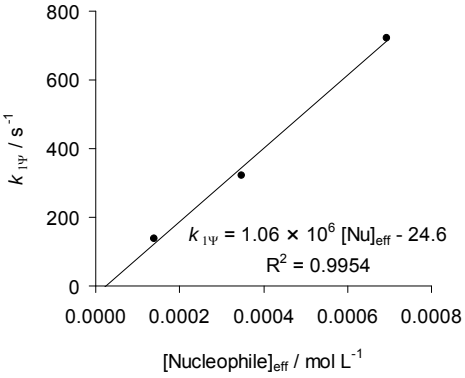
Reaction of p-Toluidine (**1q**) with $(mor)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 9 vol-% CH_3CN, stopped-flow, detection at 611 nm, $[Nu]_{eff} = [Nu]_0$, $k_{obs} = k_{1\Psi}$)

No.	$[(mor)_2CH^+]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	$k_{1\Psi}$ / s^{-1}
fb137.5	2.57×10^{-5}	6.94×10^{-4}	27	7.21×10^{2}
fb137.6	2.57×10^{-5}	3.47×10^{-4}	14	3.21×10^{2}
fb137.7	2.57×10^{-5}	1.39×10^{-4}	5	1.37×10^{2}

$k_{2,N} = 1.06 \times 10^6\ M^{-1}s^{-1}$

$k_{2,OH^-} = 1060\ M^{-1}s^{-1}$

$pK_B = 8.93$



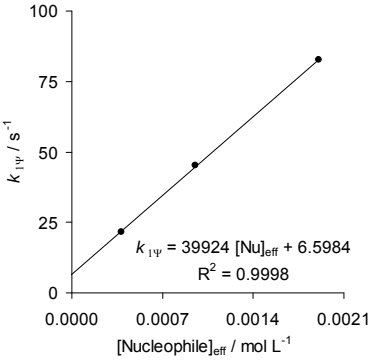
Reaction of p-Toluidine (**1q**) with $(dma)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 1 vol-% CH_3CN, stopped-flow, detection at 604 nm, $[Nu]_{eff} = [Nu]_0$, $k_{obs} = k_{1\Psi}$)

No.	$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	$k_{1\Psi}$ / s^{-1}
fb142.3	3.79×10^{-5}	1.91×10^{-3}	50	82.6
fb142.4	3.79×10^{-5}	9.54×10^{-4}	25	45.2
fb142.5	3.79×10^{-5}	3.81×10^{-4}	10	21.5

$k_{2,N} = 3.99 \times 10^4\ M^{-1}s^{-1}$

$k_{2,OH^-} = 131\ M^{-1}s^{-1}$

$pK_B = 8.93$



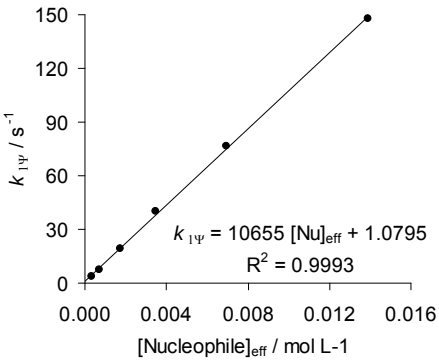
Reaction of p-Toluidine (**1q**) with $(pyr)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.3 vol-% CH_3CN, stopped-flow, detection at 611 nm, $[Nu]_{eff} = [Nu]_0$, $k_{obs} = k_{1\Psi}$)

No.	$[(pyr)_2CH^+]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	$k_{1\Psi}$ / s^{-1}
fb138.1	1.90×10^{-5}	1.39×10^{-2}	731	1.48×10^{2}
fb138.2	1.90×10^{-5}	6.95×10^{-3}	366	76.5
fb138.3	1.90×10^{-5}	3.48×10^{-3}	183	40.4
fb138.4	1.90×10^{-5}	1.74×10^{-3}	92	19.3
fb138.5	1.90×10^{-5}	6.94×10^{-4}	37	7.24
fb138.6	1.90×10^{-5}	3.47×10^{-4}	18	3.80

$k_{2,N} = 1.07 \times 10^4\ M^{-1}s^{-1}$

$k_{2,OH^-} = 48.5\ M^{-1}s^{-1}$

$pK_B = 8.93$

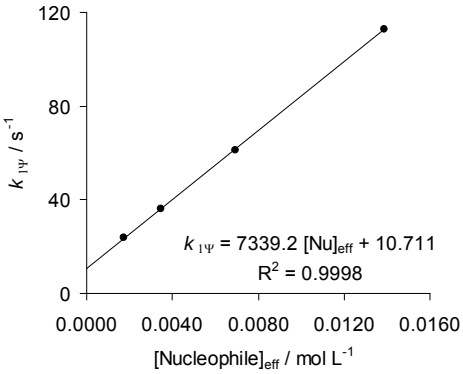


Reaction of p-Toluidine (**1q**) with $(thq)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.4 vol-% CH_3CN, stopped-flow, detection at 611 nm, $[Nu]_{eff} = [Nu]_0$, $k_{obs} = k_{1\Psi}$)

No.	$[(thq)_2CH^+]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	$k_{1\Psi}$ / s^{-1}
fb140.1	1.63×10^{-5}	1.39×10^{-2}	853	1.13×10^{2}
fb140.2	1.63×10^{-5}	6.95×10^{-3}	426	61.0
fb140.3	1.63×10^{-5}	3.48×10^{-3}	213	36.2
fb140.4	1.63×10^{-5}	1.74×10^{-3}	107	23.9

$k_{2,N} = 7.34 \times 10^3\ M^{-1}s^{-1}$; $k_{-1} = 10.7\ s^{-1}$

$K = k_{2,N} / k_{-1} = 6.9 \times 10^2\ M^{-1}$



$k_{2,OH^-} = 23.6\ M^{-1}s^{-1}$

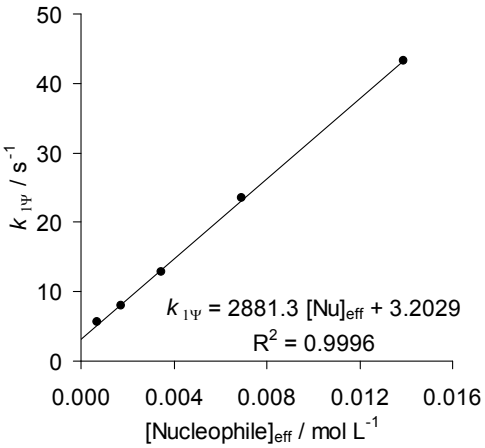
$pK_B = 8.93$

Reaction of p-Toluidine (**1q**) with $(ind)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.4 vol-% CH_3CN, stopped-flow, detection at 611 nm, $[Nu]_{eff} = [Nu]_0$, $k_{obs} = k_{1\Psi}$)

No.	$[(ind)_2CH^+]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	$k_{1\Psi}$ / s^{-1}
fb139.1	1.90×10^{-5}	1.39×10^{-2}	732	43.2
fb139.2	1.90×10^{-5}	6.95×10^{-3}	366	23.5
fb139.3	1.90×10^{-5}	3.48×10^{-3}	183	12.9
fb139.4	1.90×10^{-5}	1.74×10^{-3}	92	7.92
fb139.5	1.90×10^{-5}	6.94×10^{-4}	37	5.58

$k_{2,N} = 2.88 \times 10^3\ M^{-1}s^{-1}$; $k_{-1} = 3.20\ s^{-1}$

$K = k_{2,N} / k_{-1} = 9.0 \times 10^2\ M^{-1}$

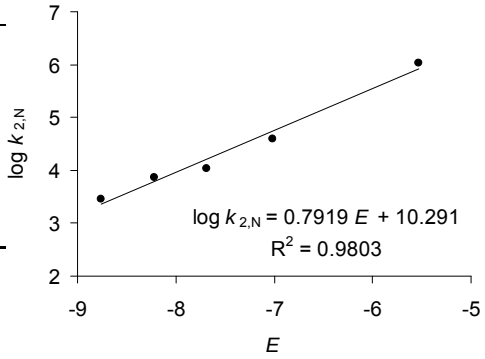


$k_{2,OH^-} = 10.8\ M^{-1}s^{-1}$

$pK_B = 8.93$

Reactivity parameters in water: N = 13.00; s = 0.79

Reference electrophile	E parameter	$k_{2,N}$(20°C) / M^{-1} s^{-1}
$(mor)_2CH^+$	-5.53	1.06×10^6
$(dma)_2CH^+$	-7.02	3.99×10^4
$(pyr)_2CH^+$	-7.69	1.07×10^4
$(thq)_2CH^+$	-8.22	7.34×10^3
$(ind)_2CH^+$	-8.76	2.88×10^3



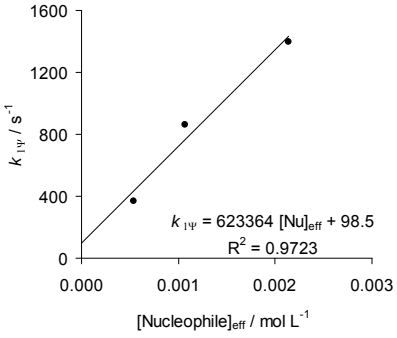
2.8.20. p-Anisidine (1r)

Rate constants in Acetonitrile

Reaction of p-Anisidine (**1r**) with $(mor)_2CH^+BF_4^-$ (at 20 °C, stopped-flow, detection at 620 nm)

No.	$[(mor)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_0/[El]_0$	$k_{1\Psi}$ / s^{-1}
jo24.4	3.42×10^{-5}	2.14×10^{-3}	63	1.40×10^3
jo24.5	3.42×10^{-5}	1.07×10^{-3}	31	8.63×10^2
jo24.6	3.42×10^{-5}	5.35×10^{-4}	16	3.67×10^2

$k_{2,N} = 6.23 \times 10^5$ $M^{-1}s^{-1}$

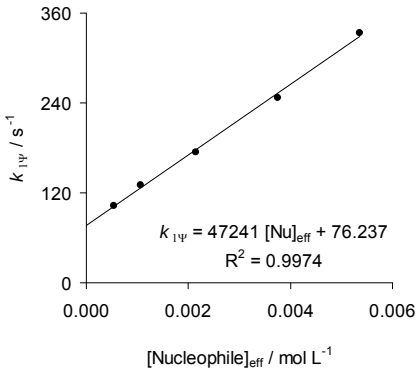


Reaction of p-Anisidine (**1r**) with $(dma)_2CH^+BF_4^-$ (at 20 °C, stopped-flow, detection at 620 nm)

No.	$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_0/[El]_0$	$k_{1\Psi}$ / s^{-1}
jo25.2	1.68×10^{-5}	5.35×10^{-3}	318	3.34×10^2
jo25.3	1.68×10^{-5}	3.75×10^{-3}	223	2.47×10^2
jo25.4	1.68×10^{-5}	2.14×10^{-3}	127	1.74×10^2
jo25.5	1.68×10^{-5}	1.07×10^{-3}	64	1.30×10^2
jo25.6	1.68×10^{-5}	5.35×10^{-4}	32	1.03×10^2

$k_{2,N} = 4.72 \times 10^4$ $M^{-1}s^{-1}$; $k_{-1} = 76.2$ s^{-1}

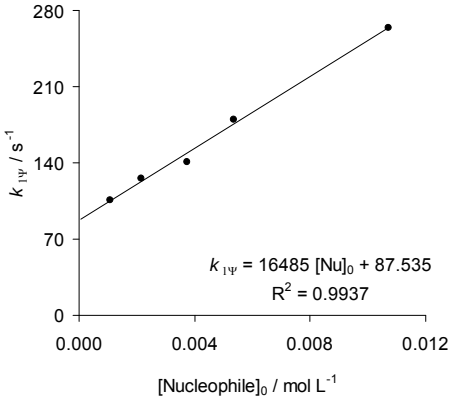
$K = k_{2,N} / k_{-1} = 6.2 \times 10^2$ M^{-1}



Reaction of p-Anisidine (**1r**) with $(pyr)_2CH^+BF_4^-$ (at 20 °C, stopped-flow, detection at 620 nm)

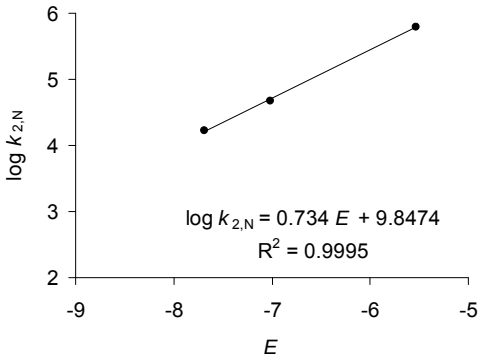
No.	$[(pyr)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_0/[El]_0$	$k_{1\Psi}$ / s^{-1}
jo26.1	2.17×10^{-5}	1.07×10^{-2}	493	2.64×10^{2}
jo26.2	2.17×10^{-5}	5.35×10^{-3}	247	1.80×10^{2}
jo26.3	2.17×10^{-5}	3.75×10^{-3}	173	1.41×10^{2}
jo26.4	2.17×10^{-5}	2.14×10^{-3}	99	1.26×10^{2}
jo26.5	2.17×10^{-5}	1.07×10^{-3}	49	1.06×10^{2}

$k_{2,N} = 1.65 \times 10^4$ M^{-1}s^{-1}



Reactivity parameters in Acetonitrile: N = 13.42; s = 0.73

Reference electrophile	*E* parameter	$k_{2,N}$(20°C) / M^{-1} s^{-1}
$(mor)_2CH^+$	-5.53	6.23×10^5
$(dma)_2CH^+$	-7.02	4.72×10^4
$(pyr)_2CH^+$	-7.69	1.65×10^4



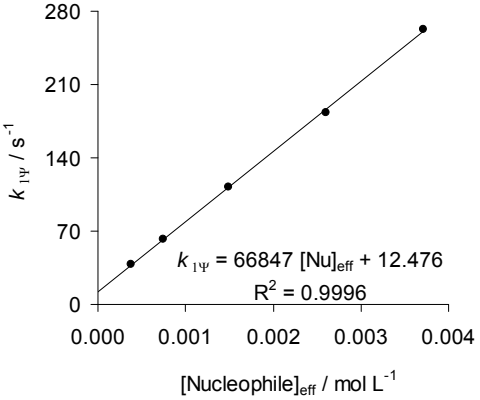
Rate constants in water

Reaction of p-Anisidine (**1r**) with $(dma)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 9 vol-% CH_3CN, stopped-flow, detection at 610 nm, $[Nu]_{eff} = [Nu]_0$, $k_{obs} = k_{1\Psi}$)

No.	$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	$k_{1\Psi}$ / s^{-1}
fb353.2	1.22×10^{-5}	3.72×10^{-3}	305	2.63×10^{2}
fb353.3	1.22×10^{-5}	2.60×10^{-3}	213	1.83×10^{2}
fb353.4	1.22×10^{-5}	1.49×10^{-3}	122	1.12×10^{2}
fb353.5	1.22×10^{-5}	7.43×10^{-4}	61	62.4
fb353.6	1.22×10^{-5}	3.76×10^{-4}	31	38.4

$k_{2,N} = 6.68 \times 10^4$ M^{-1}s^{-1}; $k_{-1} = 12.5$ s^{-1}

$K = k_{2,N} / k_{-1} = 5.4 \times 10^3$ M^{-1}

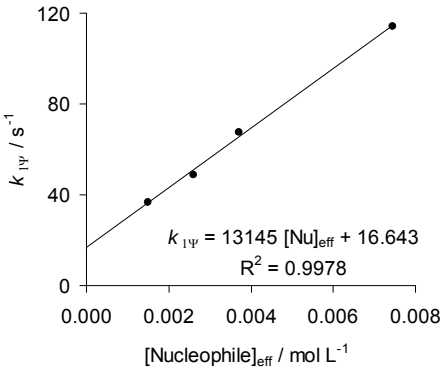


$k_{2,OH^-} = 131$ M^{-1}s^{-1}

pK_B = 8.70

Reaction of p-Anisidine (**1r**) with $(thq)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.4 vol-% CH_3CN, stopped-flow, detection at 620 nm, $[Nu]_{eff} = [Nu]_0$, $k_{obs} = k_{1\Psi}$)

No.	$[(thq)_2CH^+]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	$k_{1\Psi}$ / s^{-1}
fb356.1	8.90×10^{-6}	7.44×10^{-3}	836	1.14×10^2
fb356.2	8.90×10^{-6}	3.72×10^{-3}	418	67.5
fb356.3	8.90×10^{-6}	2.60×10^{-3}	292	48.9
fb356.4	8.90×10^{-6}	1.49×10^{-3}	167	36.5



$k_{2,N} = 1.31 \times 10^4$ $M^{-1}s^{-1}$; $k_{-1} = 16.6$ s^{-1}

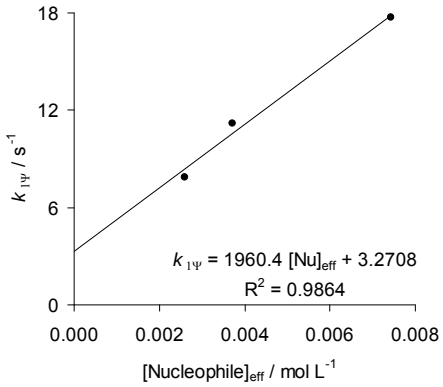
$K = k_{2,N} / k_{-1} = 7.9 \times 10^2$ M^{-1}

$k_{2,OH^-} = 23.6$ $M^{-1}s^{-1}$

$pK_B = 8.70$

Reaction of p-Anisidine (**1r**) with $(lil)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 634 nm, $[Nu]_{eff} = [Nu]_0$, $k_{obs} = k_{1\Psi}$)

No.	$[(lil)_2CH^+]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	$k_{1\Psi}$ / s^{-1}
fb354.1	9.82×10^{-6}	7.44×10^{-3}	757	17.7
fb354.2	9.82×10^{-6}	3.72×10^{-3}	379	11.2
fb354.3	9.82×10^{-6}	2.60×10^{-3}	265	7.87



$k_{2,N} = 1.96 \times 10^3$ $M^{-1}s^{-1}$; $k_{-1} = 3.27$ s^{-1}

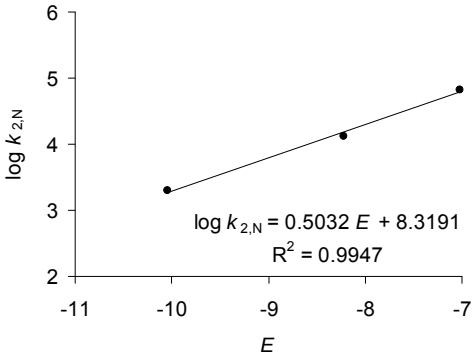
$K = k_{2,N} / k_{-1} = 6.0 \times 10^2$ M^{-1}

$k_{2,OH^-} = 2.16$ $M^{-1}s^{-1}$

$pK_B = 8.70$

Reactivity parameters in water: $N = 16.53$; $s = 0.50$

Reference electrophile	E parameter	$k_{2,N}$(20°C) / M^{-1} s^{-1}
$(dma)_2CH^+$	-7.02	6.68×10^4
$(thq)_2CH^+$	-8.22	1.31×10^4
$(lil)_2CH^+$	-10.04	1.96×10^3



2.8.21. Dimethylamine (1s)

Rate constants in water

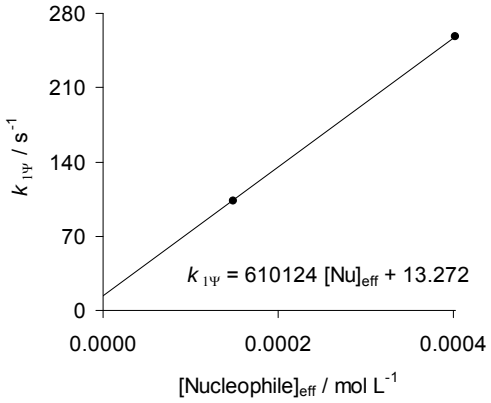
Reaction of Dimethylamine (**1s**) with $(mor)_2CH^+BF_4^-$ (at 20 °C, cosolvent 9 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(mor)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fb198.4	1.50×10^{-5}	8.94×10^{-4}	4.02×10^{-4}	4.92×10^{-4}	27	2.59×10^{2}	0.522	2.58×10^{2}
fb198.5	1.50×10^{-5}	4.47×10^{-4}	1.48×10^{-4}	2.99×10^{-4}	10	1.04×10^{2}	0.317	1.04×10^{2}

$k_{2,N} = 6.10 \times 10^5\ M^{-1}s^{-1}$

$k_{2,OH^-} = 1060\ M^{-1}s^{-1}$

$pK_B = 3.22$



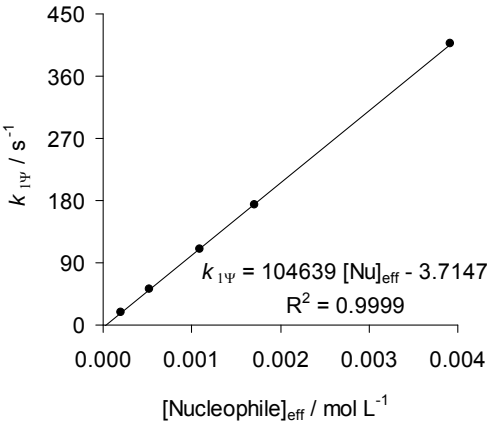
Reaction of Dimethylamine (**1s**) with $(dma)_2CH^+BF_4^-$ (at 20 °C, cosolvent 0.5 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy124.1	5.95×10^{-5}	5.45×10^{-3}	3.91×10^{-3}	1.54×10^{-3}	66	407	0.201	407
ccy124.2	5.95×10^{-5}	2.73×10^{-3}	1.71×10^{-3}	1.02×10^{-3}	29	174	0.133	174
ccy124.3	5.95×10^{-5}	1.91×10^{-3}	1.10×10^{-3}	8.13×10^{-4}	18	110	0.107	110
ccy124.4	5.95×10^{-5}	1.09×10^{-3}	5.27×10^{-4}	5.63×10^{-4}	9	52.2	7.38×10^{-2}	52.1
ccy124.5	5.95×10^{-5}	5.45×10^{-4}	1.99×10^{-4}	3.46×10^{-4}	3	18.4	4.53×10^{-2}	18.4

$k_{2,N} = 1.05 \times 10^5\ M^{-1}s^{-1}$

$k_{2,OH^-} = 131\ M^{-1}s^{-1}$

$pK_B = 3.22$



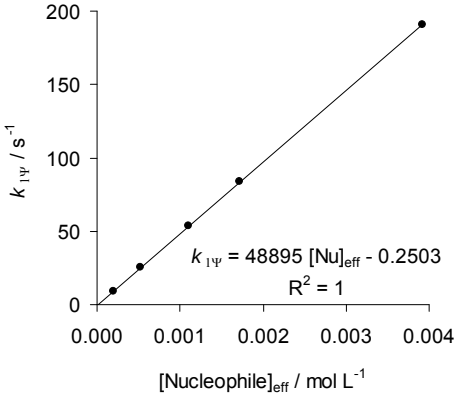
Reaction of Dimethylamine (**1s**) with $(pyr)_2CH^+BF_4^-$ (at 20 °C, cosolvent 0.2 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(pyr)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy120.1	2.12×10^{-5}	5.45×10^{-3}	3.91×10^{-3}	1.54×10^{-3}	185	191	7.45×10^{-2}	191
ccy120.2	2.12×10^{-5}	2.73×10^{-3}	1.71×10^{-3}	1.02×10^{-3}	81	84.0	4.93×10^{-2}	84.0
ccy120.3	2.12×10^{-5}	1.91×10^{-3}	1.10×10^{-3}	8.13×10^{-4}	52	53.7	3.94×10^{-2}	53.7
ccy120.4	2.12×10^{-5}	1.09×10^{-3}	5.27×10^{-4}	5.63×10^{-4}	25	25.3	2.73×10^{-2}	25.3
ccy120.5	2.12×10^{-5}	5.45×10^{-4}	1.99×10^{-4}	3.46×10^{-4}	9	9.25	1.68×10^{-2}	9.23

$k_{2,N} = 4.89 \times 10^4\ M^{-1}s^{-1}$

$k_{2,OH^-} = 48.5\ M^{-1}s^{-1}$

$pK_B = 3.22$



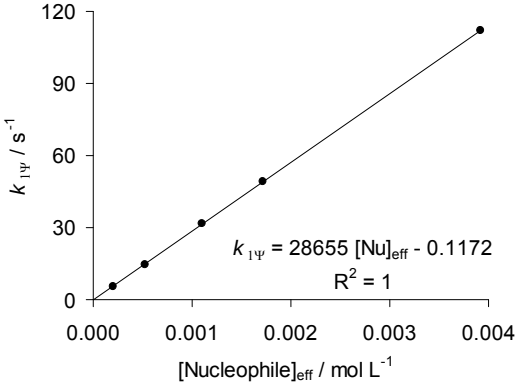
Reaction of Dimethylamine (**1s**) with $(thq)_2CH^+BF_4^-$ (at 20 °C, cosolvent 0.2 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(thq)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy121.1	1.57×10^{-5}	5.45×10^{-3}	3.91×10^{-3}	1.54×10^{-3}	249	112	3.62×10^{-2}	112
ccy121.2	1.57×10^{-5}	2.73×10^{-3}	1.71×10^{-3}	1.02×10^{-3}	109	49.1	2.40×10^{-2}	49.1
ccy121.3	1.57×10^{-5}	1.91×10^{-3}	1.10×10^{-3}	8.13×10^{-4}	70	31.6	1.92×10^{-2}	31.6
ccy121.4	1.57×10^{-5}	1.09×10^{-3}	5.27×10^{-4}	5.63×10^{-4}	34	14.8	1.33×10^{-2}	14.8
ccy121.5	1.57×10^{-5}	5.45×10^{-4}	1.99×10^{-4}	3.46×10^{-4}	13	5.51	8.17×10^{-3}	5.50

$k_{2,N} = 2.87 \times 10^4\ M^{-1}s^{-1}$

$k_{2,OH^-} = 23.6\ M^{-1}s^{-1}$

$pK_B = 3.22$



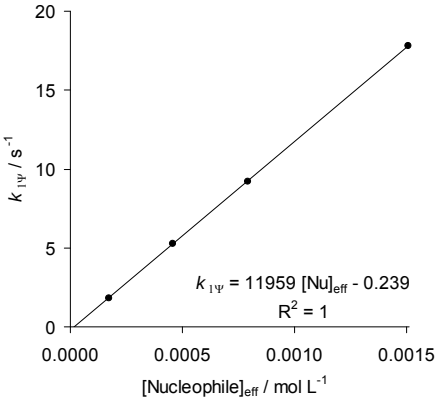
Reaction of Dimethylamine (**1s**) with $(ind)_2CH^+BF_4^-$ (at 20 °C, cosolvent 0.3 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(ind)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi, OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fb199.1	2.93×10^{-5}	2.46×10^{-3}	1.51×10^{-3}	9.53×10^{-4}	51	17.8	1.03×10^{-2}	17.8
fb199.2	2.93×10^{-5}	1.48×10^{-3}	7.90×10^{-4}	6.90×10^{-4}	27	9.20	7.45×10^{-3}	9.19
fb199.3	2.93×10^{-5}	9.84×10^{-4}	4.58×10^{-4}	5.26×10^{-4}	16	5.26	5.68×10^{-3}	5.25
fb199.4	2.93×10^{-5}	4.92×10^{-4}	1.71×10^{-4}	3.21×10^{-4}	6	1.81	3.47×10^{-3}	1.81

$k_{2,N} = 1.20 \times 10^4$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 10.8$ $M^{-1}s^{-1}$

$pK_B = 3.22$



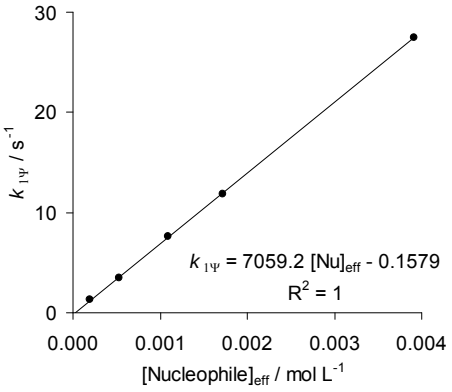
Reaction of Dimethylamine (**1s**) with $(jul)_2CH^+BF_4^-$ (at 20 °C, cosolvent 0.2 vol-% CH_3CN, stopped-flow, detection at 634 nm)

No.	$[(jul)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi, OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy122.1	8.55×10^{-6}	5.45×10^{-3}	3.91×10^{-3}	1.54×10^{-3}	458	27.5	5.28×10^{-3}	27.5
ccy122.2	8.55×10^{-6}	2.73×10^{-3}	1.71×10^{-3}	1.02×10^{-3}	200	11.9	3.50×10^{-3}	11.9
ccy122.3	8.55×10^{-6}	1.91×10^{-3}	1.10×10^{-3}	8.13×10^{-4}	128	7.59	2.80×10^{-3}	7.59
ccy122.4	8.55×10^{-6}	1.09×10^{-3}	5.27×10^{-4}	5.63×10^{-4}	62	3.52	1.94×10^{-3}	3.52
ccy122.5	8.55×10^{-6}	5.45×10^{-4}	1.99×10^{-4}	3.46×10^{-4}	23	1.31	1.19×10^{-3}	1.31

$k_{2,N} = 7.06 \times 10^3$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 3.44$ $M^{-1}s^{-1}$

$pK_B = 3.22$



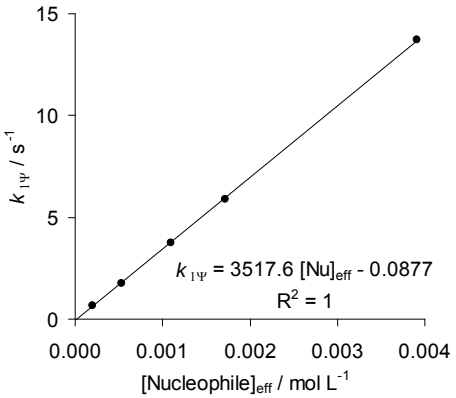
Reaction of Dimethylamine (**1s**) with $(lil)_2CH^+BF_4^-$ (at 20 °C, cosolvent 0.2 vol-% CH_3CN, stopped-flow, detection at 634 nm)

No.	$[(lil)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi, OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy123.1	8.55×10^{-6}	5.45×10^{-3}	3.91×10^{-3}	1.54×10^{-3}	458	13.7	3.32×10^{-3}	13.7
ccy123.2	8.55×10^{-6}	2.73×10^{-3}	1.71×10^{-3}	1.02×10^{-3}	200	5.91	2.19×10^{-3}	5.91
ccy123.3	8.55×10^{-6}	1.91×10^{-3}	1.10×10^{-3}	8.13×10^{-4}	128	3.77	1.76×10^{-3}	3.77
ccy123.4	8.55×10^{-6}	1.09×10^{-3}	5.27×10^{-4}	5.63×10^{-4}	62	1.75	1.22×10^{-3}	1.75
ccy123.5	8.55×10^{-6}	5.45×10^{-4}	1.99×10^{-4}	3.46×10^{-4}	23	0.649	7.48×10^{-4}	0.648

$k_{2,N} = 3.52 \times 10^3$ $M^{-1}s^{-1}$

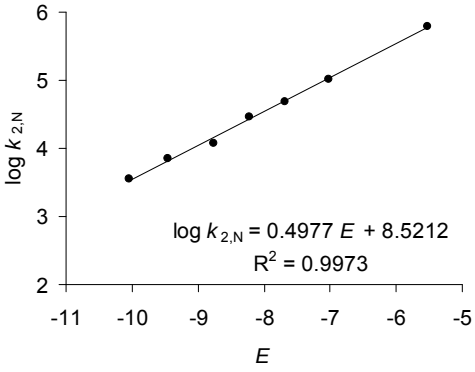
$k_{2,OH^-} = 2.16$ $M^{-1}s^{-1}$

$pK_B = 3.22$



Reactivity parameters in water: $N = 17.12$; $s = 0.50$

Reference electrophile	E parameter	$k_{2,N}$(20°C) / M^{-1} s^{-1}
$(mor)_2CH^+$	-5.53	6.10×10^5
$(dma)_2CH^+$	-7.02	1.05×10^5
$(pyr)_2CH^+$	-7.69	4.89×10^4
$(thq)_2CH^+$	-8.22	2.87×10^4
$(ind)_2CH^+$	-8.76	1.20×10^4
$(jul)_2CH^+$	-9.45	7.06×10^3
$(lil)_2CH^+$	-10.04	3.52×10^3



2.8.22. Diethylamine (1t)

Rate constants in water

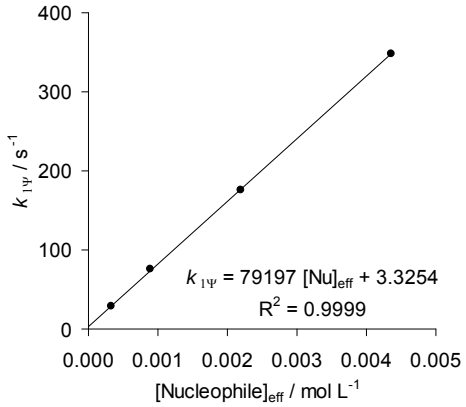
Reaction of Diethylamine (1t) with $(mor)_2CH^+BF_4^-$ (at 20 °C, cosolvent 9 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(mor)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi, OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fb190.2	1.72×10^{-5}	6.49×10^{-3}	4.35×10^{-3}	2.14×10^{-3}	253	3.51×10^{2}	2.26	3.49×10^{2}
fb190.3	1.72×10^{-5}	3.71×10^{-3}	2.19×10^{-3}	1.52×10^{-3}	128	1.77×10^{2}	1.61	1.75×10^{2}
fb190.4	1.72×10^{-5}	1.85×10^{-3}	8.87×10^{-4}	9.63×10^{-4}	52	76.4	1.02	75.4
fb190.5	1.72×10^{-5}	9.27×10^{-4}	3.35×10^{-4}	5.92×10^{-4}	19	29.8	0.628	29.2

$k_{2,N} = 7.92 \times 10^4$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 1060$ $M^{-1}s^{-1}$

$pK_B = 2.98$



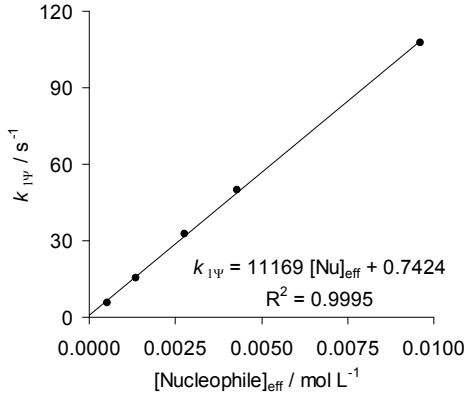
Reaction of Diethylamine (**1t**) with $(dma)_2CH^+BF_4^-$ (at 20 °C, cosolvent 0.5 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi, OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy145.1	5.95×10^{-5}	1.28×10^{-2}	9.63×10^{-3}	3.17×10^{-3}	162	108	0.416	108
ccy145.2	5.95×10^{-5}	6.40×10^{-3}	4.28×10^{-3}	2.12×10^{-3}	72	50.1	0.277	49.8
ccy145.3	5.95×10^{-5}	4.48×10^{-3}	2.78×10^{-3}	1.70×10^{-3}	47	32.7	0.223	32.5
ccy145.4	5.95×10^{-5}	2.56×10^{-3}	1.36×10^{-3}	1.20×10^{-3}	23	15.7	0.157	15.5
ccy145.5	5.95×10^{-5}	1.28×10^{-3}	5.33×10^{-4}	7.47×10^{-4}	9	5.90	9.79×10^{-2}	5.80

$k_{2,N} = 1.12 \times 10^4$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 131$ $M^{-1}s^{-1}$

$pK_B = 2.98$



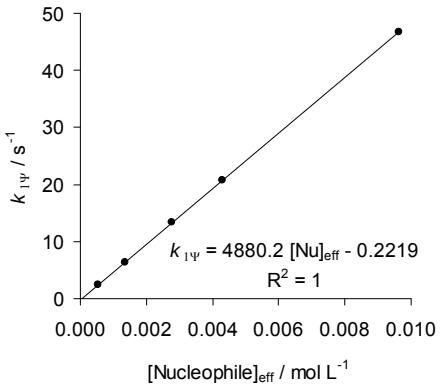
Reaction of Diethylamine (**1t**) with $(pyr)_2CH^+BF_4^-$ (at 20 °C, cosolvent 0.1 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(pyr)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy146.1	1.14×10^{-5}	1.28×10^{-2}	9.63×10^{-3}	3.17×10^{-3}	844	46.9	0.154	46.7
ccy146.2	1.14×10^{-5}	6.40×10^{-3}	4.28×10^{-3}	2.12×10^{-3}	376	20.8	0.103	20.7
ccy146.3	1.14×10^{-5}	4.48×10^{-3}	2.78×10^{-3}	1.70×10^{-3}	243	13.4	8.27×10^{-2}	13.3
ccy146.4	1.14×10^{-5}	2.56×10^{-3}	1.36×10^{-3}	1.20×10^{-3}	120	6.47	5.80×10^{-2}	6.41
ccy146.5	1.14×10^{-5}	1.28×10^{-3}	5.33×10^{-4}	7.47×10^{-4}	47	2.43	3.62×10^{-2}	2.39

$k_{2,N} = 4.88 \times 10^3\ M^{-1}s^{-1}$

$k_{2,OH^-} = 48.5\ M^{-1}s^{-1}$

$pK_B = 2.98$



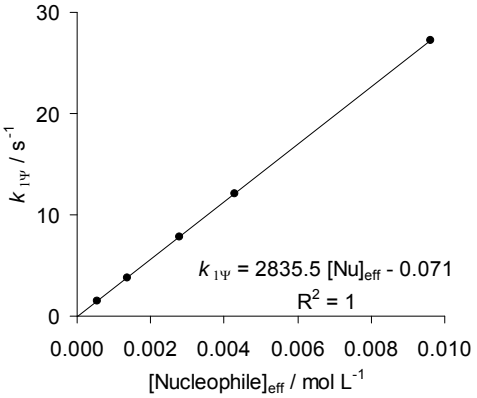
Reaction of Diethylamine (**1t**) with $(thq)_2CH^+BF_4^-$ (at 20 °C, cosolvent 0.4 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(thq)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy147.1	3.14×10^{-5}	1.28×10^{-2}	9.63×10^{-3}	3.17×10^{-3}	307	27.3	7.49×10^{-2}	27.2
ccy147.2	3.14×10^{-5}	6.40×10^{-3}	4.28×10^{-3}	2.12×10^{-3}	136	12.1	5.00×10^{-2}	12.1
ccy147.3	3.14×10^{-5}	4.48×10^{-3}	2.78×10^{-3}	1.70×10^{-3}	88	7.86	4.02×10^{-2}	7.82
ccy147.4	3.14×10^{-5}	2.56×10^{-3}	1.36×10^{-3}	1.20×10^{-3}	43	3.82	2.82×10^{-2}	3.79
ccy147.5	3.14×10^{-5}	1.28×10^{-3}	5.33×10^{-4}	7.47×10^{-4}	17	1.46	1.76×10^{-2}	1.44

$k_{2,N} = 2.84 \times 10^3\ M^{-1}s^{-1}$

$k_{2,OH^-} = 23.6\ M^{-1}s^{-1}$

$pK_B = 2.98$



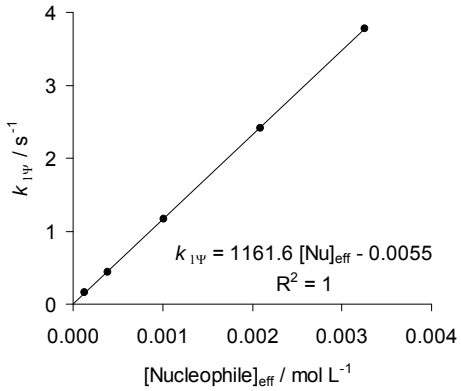
Reaction of Diethylamine (**1t**) with $(ind)_2CH^+BF_4^-$ (at 20 °C, cosolvent 0.2 vol-% CH_3CN, stopped-flow, detection at 613 nm)

No.	$[(ind)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi, OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fb188.1	2.34×10^{-5}	5.10×10^{-3}	3.25×10^{-3}	1.85×10^{-3}	139	3.80	1.99×10^{-2}	3.78
fb188.2	2.34×10^{-5}	3.57×10^{-3}	2.09×10^{-3}	1.48×10^{-3}	89	2.43	1.60×10^{-2}	2.41
fb188.3	2.34×10^{-5}	2.04×10^{-3}	1.01×10^{-3}	1.03×10^{-3}	43	1.18	1.11×10^{-2}	1.17
fb188.4	2.34×10^{-5}	1.02×10^{-3}	3.85×10^{-4}	6.35×10^{-4}	16	0.449	6.86×10^{-3}	0.442
fb188.5	2.34×10^{-5}	5.10×10^{-4}	1.35×10^{-4}	3.75×10^{-4}	6	0.158	4.05×10^{-3}	0.154

$k_{2,N} = 1.16 \times 10^3$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 10.8$ $M^{-1}s^{-1}$

$pK_B = 2.98$



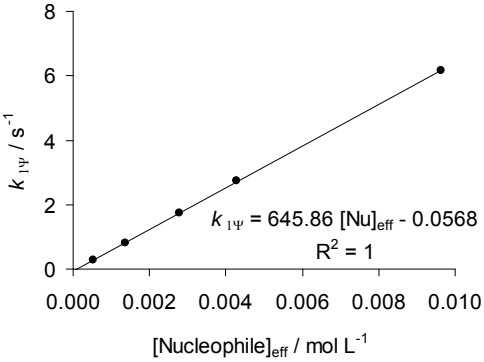
Reaction of Diethylamine (**1t**) with $(jul)_2CH^+BF_4^-$ (at 20 °C, cosolvent 0.2 vol-% CH_3CN, stopped-flow, detection at 634 nm)

No.	$[(jul)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi, OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy148.1	8.56×10^{-6}	1.28×10^{-2}	9.63×10^{-3}	3.17×10^{-3}	1124	6.16	1.09×10^{-2}	6.15
ccy148.2	8.56×10^{-6}	6.40×10^{-3}	4.28×10^{-3}	2.12×10^{-3}	500	2.74	7.28×10^{-3}	2.73
ccy148.3	8.56×10^{-6}	4.48×10^{-3}	2.78×10^{-3}	1.70×10^{-3}	324	1.75	5.86×10^{-3}	1.74
ccy148.4	8.56×10^{-6}	2.56×10^{-3}	1.36×10^{-3}	1.20×10^{-3}	159	0.815	4.11×10^{-3}	0.811
ccy148.5	8.56×10^{-6}	1.28×10^{-3}	5.33×10^{-4}	7.47×10^{-4}	62	0.282	2.57×10^{-3}	0.279

$k_{2,N} = 6.46 \times 10^2$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 3.44$ $M^{-1}s^{-1}$

$pK_B = 2.98$



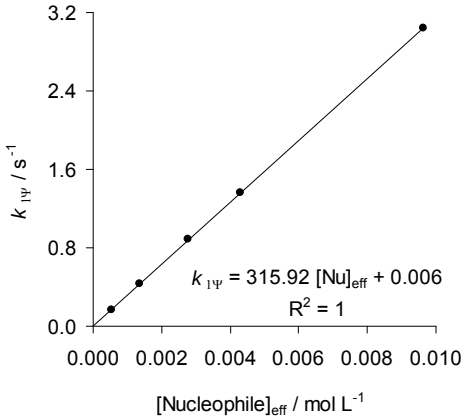
Reaction of Diethylamine (**1t**) with $(lil)_2CH^+BF_4^-$ (at 20 °C, cosolvent 0.2 vol-% CH_3CN, stopped-flow, detection at 634 nm)

No.	$[(lil)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy149.1	1.02×10^{-5}	1.28×10^{-2}	9.63×10^{-3}	3.17×10^{-3}	944	3.05	6.86×10^{-3}	3.04
ccy149.2	1.02×10^{-5}	6.40×10^{-3}	4.28×10^{-3}	2.12×10^{-3}	420	1.37	4.57×10^{-3}	1.37
ccy149.3	1.02×10^{-5}	4.48×10^{-3}	2.78×10^{-3}	1.70×10^{-3}	272	0.891	3.68×10^{-3}	0.887
ccy149.4	1.02×10^{-5}	2.56×10^{-3}	1.36×10^{-3}	1.20×10^{-3}	134	0.437	2.58×10^{-3}	0.434
ccy149.5	1.02×10^{-5}	1.28×10^{-3}	5.33×10^{-4}	7.47×10^{-4}	52	0.171	1.61×10^{-3}	0.169

$k_{2,N} = 3.16 \times 10^2\ M^{-1}s^{-1}$

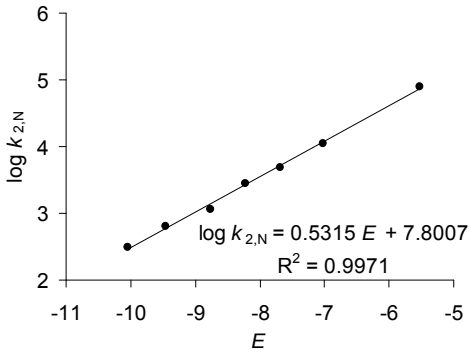
$k_{2,OH^-} = 2.16\ M^{-1}s^{-1}$

$pK_B = 2.98$



Reactivity parameters in water: *N* = 14.68; *s* = 0.53

Reference electrophile	*E* parameter	$k_{2,N}$(20°C) / M^{-1} s^{-1}
$(mor)_2CH^+$	-5.53	7.92×10^4
$(dma)_2CH^+$	-7.02	1.12×10^4
$(pyr)_2CH^+$	-7.69	4.88×10^3
$(thq)_2CH^+$	-8.22	2.84×10^3
$(ind)_2CH^+$	-8.76	1.16×10^3
$(jul)_2CH^+$	-9.45	6.46×10^2
$(lil)_2CH^+$	-10.04	3.16×10^2



2.8.23. Methylaminoacetonitrile (1u)

Rate constants in water

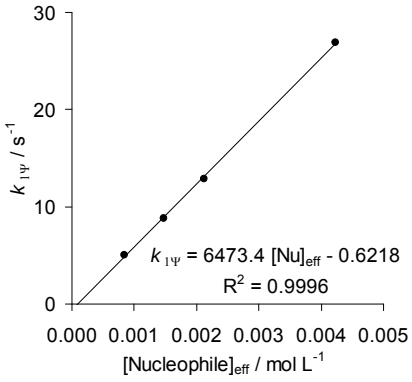
Reaction of Methylaminoacetonitrile (**1u**) with $(dma)_2CH^+BF_4^-$ (at 20 °C, cosolvent 0.5 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi, OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy140.1	5.95×10^{-5}	4.24×10^{-3}	4.24×10^{-3}	3.08×10^{-6}	71	26.9	4.03×10^{-4}	26.9
ccy140.2	5.95×10^{-5}	2.12×10^{-3}	2.12×10^{-3}	2.18×10^{-6}	36	12.9	2.85×10^{-4}	12.9
ccy140.3	5.95×10^{-5}	1.48×10^{-3}	1.48×10^{-3}	1.82×10^{-6}	25	8.82	2.38×10^{-4}	8.82
ccy140.4	5.95×10^{-5}	8.48×10^{-4}	8.47×10^{-4}	1.38×10^{-6}	14	5.08	1.80×10^{-4}	5.08

$k_{2,N} = 6.47 \times 10^3$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 131$ $M^{-1}s^{-1}$

$pK_B = 8.65$



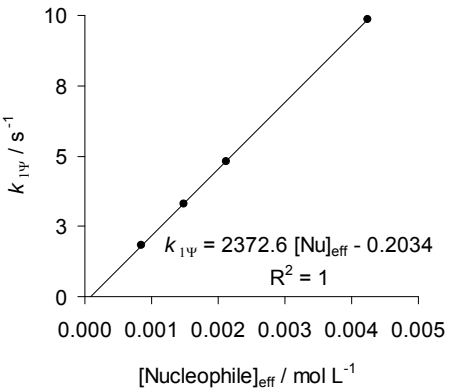
Reaction of Methylaminoacetonitrile (**1u**) with $(pyr)_2CH^+BF_4^-$ (at 20 °C, cosolvent 0.1 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(pyr)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]$	k_{obs} / s^{-1}	$k_{1\Psi, OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy142.1	2.12×10^{-5}	4.24×10^{-3}	4.24×10^{-3}	3.08×10^{-6}	200	9.86	1.49×10^{-4}	9.86
ccy142.2	2.12×10^{-5}	2.12×10^{-3}	2.12×10^{-3}	2.18×10^{-6}	100	4.79	1.06×10^{-4}	4.79
ccy142.3	2.12×10^{-5}	1.48×10^{-3}	1.48×10^{-3}	1.82×10^{-6}	70	3.31	8.82×10^{-5}	3.31
ccy142.4	2.12×10^{-5}	8.48×10^{-4}	8.47×10^{-4}	1.38×10^{-6}	40	1.82	6.68×10^{-5}	1.82

$k_{2,N} = 2.37 \times 10^3$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 48.5$ $M^{-1}s^{-1}$

$pK_B = 8.65$



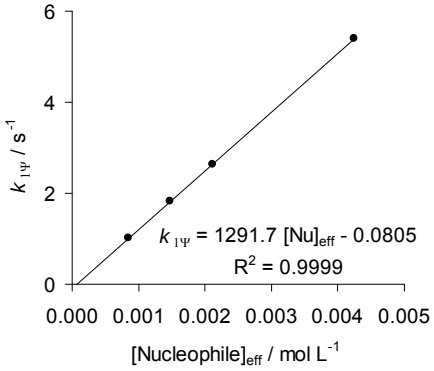
Reaction of Methylaminoacetonitrile (**1u**) with $(thq)_2CH^+BF_4^-$ (at 20 °C, cosolvent 0.4 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(thq)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy141.1	3.14×10^{-5}	4.24×10^{-3}	4.24×10^{-3}	3.08×10^{-6}	135	5.40	7.27×10^{-5}	5.40
ccy141.2	3.14×10^{-5}	2.12×10^{-3}	2.12×10^{-3}	2.18×10^{-6}	67	2.64	5.14×10^{-5}	2.64
ccy141.3	3.14×10^{-5}	1.48×10^{-3}	1.48×10^{-3}	1.82×10^{-6}	47	1.82	4.29×10^{-5}	1.82
ccy141.4	3.14×10^{-5}	8.48×10^{-4}	8.47×10^{-4}	1.38×10^{-6}	27	1.03	3.25×10^{-5}	1.03

$k_{2,N} = 1.29 \times 10^3$ $M^{-1}s^{-1}$

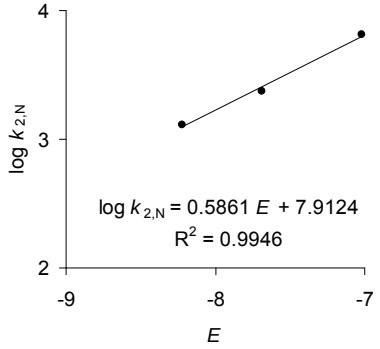
$k_{2,OH^-} = 23.6$ $M^{-1}s^{-1}$

$pK_B = 8.65$



Reactivity parameters in water: N = 13.5; s = 0.59

Reference electrophile	E parameter	$k_{2,N}$(20°C) / M^{-1} s^{-1}
$(dma)_2CH^+$	-7.02	6.47×10^3
$(pyr)_2CH^+$	-7.69	2.37×10^3
$(thq)_2CH^+$	-8.22	1.29×10^3



2.8.24. 2,2'-Iminodiethanol (1v)

Rate constants in water

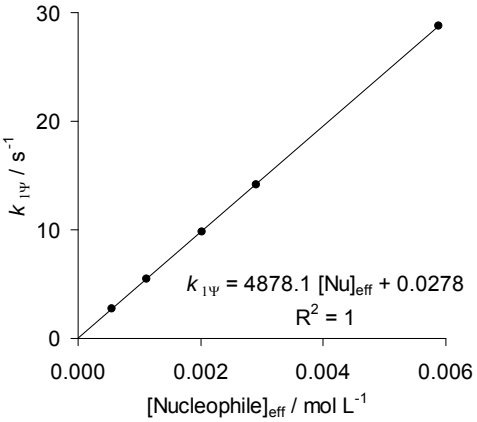
Reaction of 2,2'-Iminodiethanol (**1v**) with $(dma)_2CH^+BF_4^-$ (at 20 °C, cosolvent 0.5 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy193.1	5.95×10^{-5}	6.10×10^{-3}	5.89×10^{-3}	2.11×10^{-4}	99	28.8	2.77×10^{-2}	28.8
ccy193.2	5.95×10^{-5}	3.05×10^{-3}	2.90×10^{-3}	1.48×10^{-4}	49	14.2	1.94×10^{-2}	14.2
ccy193.3	5.95×10^{-5}	2.14×10^{-3}	2.02×10^{-3}	1.24×10^{-4}	34	9.82	1.62×10^{-2}	9.80
ccy193.4	5.95×10^{-5}	1.22×10^{-3}	1.13×10^{-3}	9.25×10^{-5}	19	5.52	1.21×10^{-2}	5.51
ccy193.5	5.95×10^{-5}	6.10×10^{-4}	5.46×10^{-4}	6.43×10^{-5}	9	2.76	8.43×10^{-3}	2.75

$k_{2,N} = 4.88 \times 10^3$ M^{-1}s^{-1}

$k_{2,OH^-} = 131$ M^{-1}s^{-1}

p$K_B = 5.12$



Reaction of 2,2'-Iminodiethanol (**1v**) with $(pyr)_2CH^+BF_4^-$ (at 20 °C, cosolvent 0.1 vol-% CH_3CN, stopped-flow, detection at 610 nm)

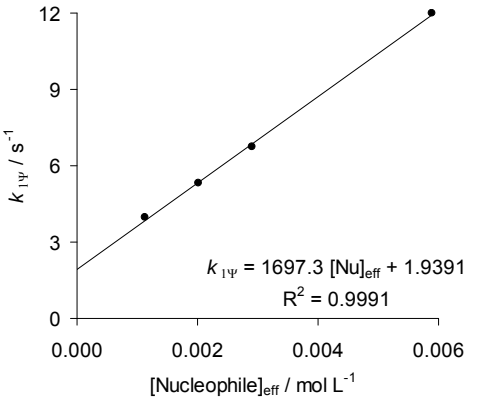
No.	$[(pyr)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy194.1	1.12×10^{-5}	6.10×10^{-3}	5.89×10^{-3}	2.11×10^{-4}	526	12.0	1.03×10^{-2}	12.0
ccy194.2	1.12×10^{-5}	3.05×10^{-3}	2.90×10^{-3}	1.48×10^{-4}	259	6.74	7.20×10^{-3}	6.73
ccy194.3	1.12×10^{-5}	2.14×10^{-3}	2.02×10^{-3}	1.24×10^{-4}	180	5.33	6.00×10^{-3}	5.32
ccy194.4	1.12×10^{-5}	1.22×10^{-3}	1.13×10^{-3}	9.25×10^{-5}	101	3.97	4.49×10^{-3}	3.97

$k_{2,N} = 1.70 \times 10^3$ M^{-1}s^{-1}; $k_{-1} = 1.94$ s^{-1}

$K = k_{2,N} / k_{-1} = 8.8 \times 10^2$ M^{-1}

$k_{2,OH^-} = 48.5$ M^{-1}s^{-1}

p$K_B = 5.12$



Reaction of 2,2'-Iminodiethanol (**1v**) with $(thq)_2CH^+BF_4^-$ (at 20 °C, cosolvent 0.2 vol-% CH_3CN, stopped-flow, detection at 610 nm)

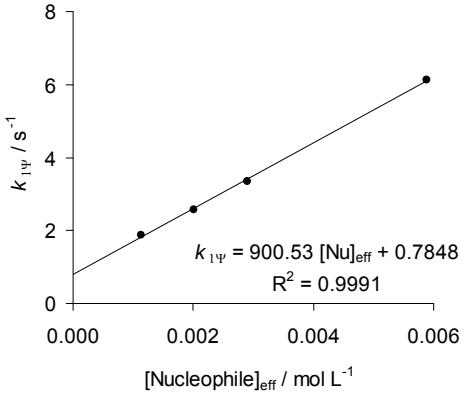
No.	$[(thq)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy195.1	1.91×10^{-5}	6.10×10^{-3}	5.89×10^{-3}	2.11×10^{-4}	308	6.12	4.99×10^{-3}	6.12
ccy195.2	1.91×10^{-5}	3.05×10^{-3}	2.90×10^{-3}	1.48×10^{-4}	152	3.35	3.50×10^{-3}	3.35
ccy195.3	1.91×10^{-5}	2.14×10^{-3}	2.02×10^{-3}	1.24×10^{-4}	106	2.56	2.92×10^{-3}	2.56
ccy195.4	1.91×10^{-5}	1.22×10^{-3}	1.13×10^{-3}	9.25×10^{-5}	59	1.87	2.18×10^{-3}	1.87

$k_{2,N} = 9.01 \times 10^2$ $M^{-1}s^{-1}$; $k_{-1} = 0.785$ s^{-1}

$K = k_{2,N} / k_{-1} = 1.1 \times 10^3$ M^{-1}

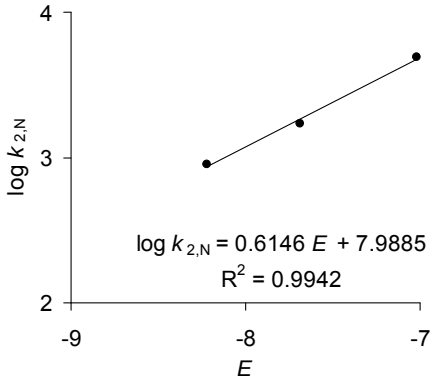
$k_{2,OH^-} = 23.6$ $M^{-1}s^{-1}$

$pK_B = 5.12$



Reactivity parameters in water: $N = 13.00$; $s = 0.61$

Reference electrophile	E parameter	$k_{2,N}$(20°C) / M^{-1} s^{-1}
$(dma)_2CH^+$	-7.02	4.88×10^3
$(pyr)_2CH^+$	-7.69	1.70×10^3
$(thq)_2CH^+$	-8.22	9.01×10^2



2.8.25. Pyrrolidine (1w)

Rate constants in water

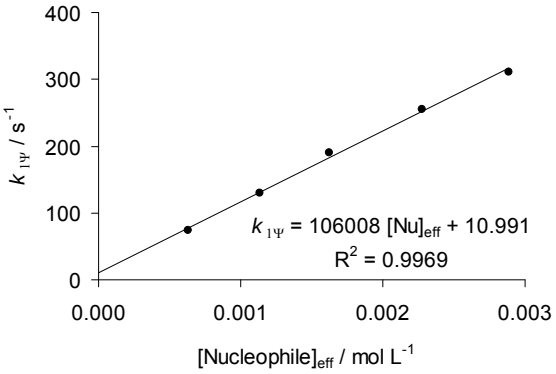
Reaction of Pyrrolidine (**1w**) with $(dma)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.4 vol-% CH_3CN, stopped-flow, detection at 604 nm)

No.	$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fb64.1	8.32×10^{-5}	5.31×10^{-3}	2.88×10^{-3}	2.43×10^{-3}	35	3.12×10^{2}	0.318	3.12×10^{2}
fb64.2	8.32×10^{-5}	4.43×10^{-3}	2.27×10^{-3}	2.16×10^{-3}	27	2.55×10^{2}	0.282	2.55×10^{2}
fb64.3	8.32×10^{-5}	3.44×10^{-3}	1.62×10^{-3}	1.82×10^{-3}	19	1.91×10^{2}	0.238	1.91×10^{2}
fb64.4	8.32×10^{-5}	2.66×10^{-3}	1.14×10^{-3}	1.52×10^{-3}	14	1.30×10^{2}	0.200	1.30×10^{2}
fb64.5	8.32×10^{-5}	1.77×10^{-3}	6.33×10^{-4}	1.14×10^{-3}	8	74.4	0.149	74.3

$k_{2,N} = 1.06 \times 10^5\ M^{-1}s^{-1}$

$k_{2,OH^-} = 131\ M^{-1}s^{-1}$

$pK_B = 2.69$[47]



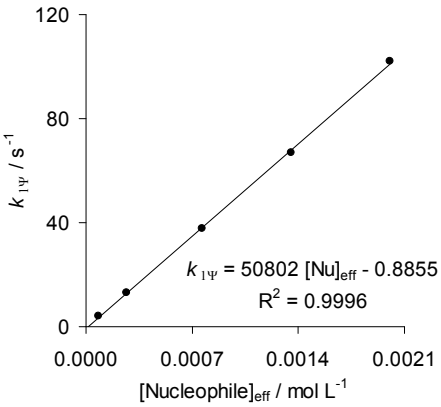
Reaction of Pyrrolidine (**1w**) with $(pyr)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 611 nm)

No.	$[(pyr)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy28.2	1.33×10^{-5}	4.03×10^{-3}	2.01×10^{-3}	2.35×10^{-3}	151	102	9.82×10^{-2}	102
ccy28.3	1.33×10^{-5}	3.02×10^{-3}	1.36×10^{-3}	2.02×10^{-3}	102	67.0	8.07×10^{-2}	66.9
ccy28.4	1.33×10^{-5}	2.02×10^{-3}	7.68×10^{-4}	1.66×10^{-3}	58	37.7	6.07×10^{-2}	37.6
ccy28.5	1.33×10^{-5}	1.01×10^{-3}	2.69×10^{-4}	1.25×10^{-3}	20	13.0	3.59×10^{-2}	13.0
ccy28.6	1.33×10^{-5}	5.04×10^{-4}	8.57×10^{-5}	7.41×10^{-4}	6	4.00	2.03×10^{-2}	3.98

$k_{2,N} = 5.08 \times 10^4\ M^{-1}s^{-1}$

$k_{2,OH^-} = 48.5\ M^{-1}s^{-1}$

$pK_B = 2.69$[47]



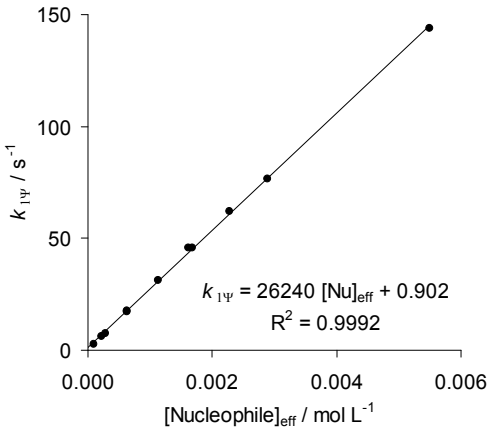
Reaction of Pyrrolidine (**1w**) with $(thq)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.4 vol-% CH_3CN, stopped-flow, detection at 618 nm)

No.	$[(thq)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi, OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fb60.1	1.86×10^{-5}	8.85×10^{-3}	5.50×10^{-3}	3.35×10^{-3}	296	1.44×10^{2}	7.91×10^{-2}	1.44×10^{2}
fb60.2	1.86×10^{-5}	5.31×10^{-3}	2.88×10^{-3}	2.43×10^{-3}	155	76.4	5.73×10^{-2}	76.3
fb60.3	1.86×10^{-5}	4.43×10^{-3}	2.27×10^{-3}	2.16×10^{-3}	122	62.2	5.09×10^{-2}	62.1
fb59.1	1.86×10^{-5}	3.54×10^{-3}	1.69×10^{-3}	1.85×10^{-3}	91	45.6	4.38×10^{-2}	45.6
fb60.4	1.86×10^{-5}	3.44×10^{-3}	1.62×10^{-3}	1.82×10^{-3}	87	45.9	4.29×10^{-2}	45.9
fb60.5	1.86×10^{-5}	2.66×10^{-3}	1.14×10^{-3}	1.52×10^{-3}	61	31.1	3.60×10^{-2}	31.1
fb60.6	1.86×10^{-5}	1.77×10^{-3}	6.33×10^{-4}	1.14×10^{-3}	34	17.5	2.68×10^{-2}	17.5
fb59.2	1.86×10^{-5}	1.77×10^{-3}	6.33×10^{-4}	1.14×10^{-3}	34	17.0	2.68×10^{-2}	17.0
fb59.3	1.86×10^{-5}	1.06×10^{-3}	2.90×10^{-4}	7.70×10^{-4}	16	7.42	1.82×10^{-2}	7.40
fb60.7	1.86×10^{-5}	8.85×10^{-4}	2.18×10^{-4}	6.67×10^{-4}	12	6.00	1.57×10^{-2}	5.98
fb60.8	1.86×10^{-5}	5.31×10^{-4}	9.37×10^{-5}	4.37×10^{-4}	5	2.45	1.03×10^{-2}	2.44

$k_{2,N} = 2.62 \times 10^4$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 23.6$ $M^{-1}s^{-1}$

$pK_B = 2.69$[47]



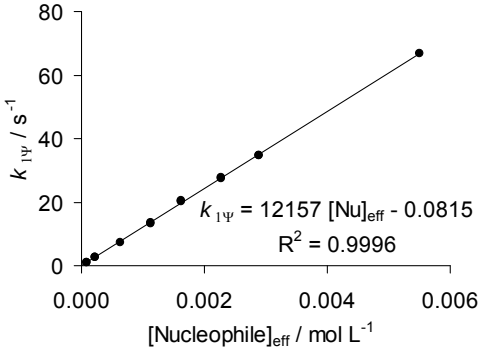
Reaction of Pyrrolidine (**1w**) with $(ind)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 614 nm)

No.	$[(ind)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fb61.1	1.65×10^{-5}	8.85×10^{-3}	5.50×10^{-3}	3.35×10^{-3}	333	66.8	3.62×10^{-2}	66.8
fb61.2	1.65×10^{-5}	5.31×10^{-3}	2.88×10^{-3}	2.43×10^{-3}	175	34.7	2.62×10^{-2}	34.7
fb65.1	1.65×10^{-5}	5.31×10^{-3}	2.88×10^{-3}	2.43×10^{-3}	175	34.6	2.62×10^{-2}	34.6
fb65.2	1.65×10^{-5}	4.43×10^{-3}	2.27×10^{-3}	2.16×10^{-3}	138	27.5	2.33×10^{-2}	27.5
fb61.3	1.65×10^{-5}	4.43×10^{-3}	2.27×10^{-3}	2.16×10^{-3}	138	27.9	2.33×10^{-2}	27.9
fb61.4	1.65×10^{-5}	3.44×10^{-3}	1.62×10^{-3}	1.82×10^{-3}	98	20.3	1.96×10^{-2}	20.3
fb65.3	1.65×10^{-5}	3.44×10^{-3}	1.62×10^{-3}	1.82×10^{-3}	98	20.4	1.96×10^{-2}	20.4
fb65.4	1.65×10^{-5}	2.66×10^{-3}	1.14×10^{-3}	1.52×10^{-3}	69	13.4	1.65×10^{-2}	13.4
fb61.5	1.65×10^{-5}	2.66×10^{-3}	1.14×10^{-3}	1.52×10^{-3}	69	13.7	1.65×10^{-2}	13.7
fb65.5	1.65×10^{-5}	1.77×10^{-3}	6.33×10^{-4}	1.14×10^{-3}	38	7.25	1.23×10^{-2}	7.24
fb65.6	1.65×10^{-5}	8.85×10^{-4}	2.18×10^{-4}	6.67×10^{-4}	13	2.51	7.20×10^{-3}	2.50
fb61.7	1.65×10^{-5}	8.85×10^{-4}	2.18×10^{-4}	6.67×10^{-4}	13	2.57	7.20×10^{-3}	2.57
fb61.8	1.65×10^{-5}	5.31×10^{-4}	9.37×10^{-5}	4.37×10^{-4}	6	1.03	4.72×10^{-3}	1.03
fb65.7	1.65×10^{-5}	5.31×10^{-4}	9.37×10^{-5}	4.37×10^{-4}	6	1.02	4.72×10^{-3}	1.02

$k_{2,N} = 1.22 \times 10^4\ M^{-1}s^{-1}$

$k_{2,OH^-} = 10.8\ M^{-1}s^{-1}$

$pK_B = 2.69$[47]



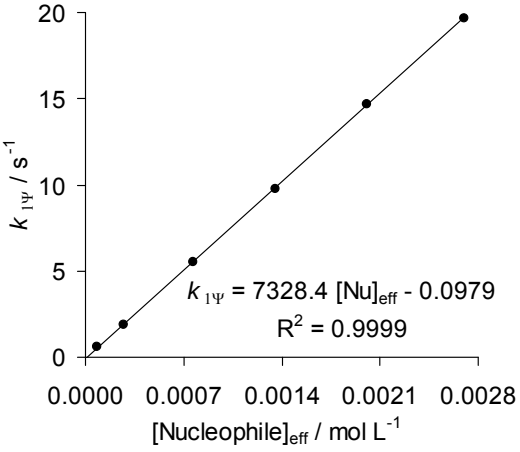
Reaction of Pyrrolidine (**1w**) with $(jul)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 634 nm)

No.	$[(jul)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy27.1	1.26×10^{-5}	5.05×10^{-3}	2.70×10^{-3}	2.35×10^{-3}	214	19.7	8.08×10^{-3}	19.7
ccy27.2	1.26×10^{-5}	4.03×10^{-3}	2.01×10^{-3}	2.02×10^{-3}	159	14.7	6.96×10^{-3}	14.7
ccy27.3	1.26×10^{-5}	3.02×10^{-3}	1.36×10^{-3}	1.66×10^{-3}	108	9.74	5.72×10^{-3}	9.73
ccy27.4	1.26×10^{-5}	2.02×10^{-3}	7.68×10^{-4}	1.25×10^{-3}	61	5.51	4.31×10^{-3}	5.51
ccy27.5	1.26×10^{-5}	1.01×10^{-3}	2.69×10^{-4}	7.41×10^{-4}	21	1.87	2.55×10^{-3}	1.87
ccy27.6	1.26×10^{-5}	5.04×10^{-4}	8.57×10^{-5}	4.18×10^{-4}	7	0.585	1.44×10^{-3}	0.584

$k_{2,N} = 7.33 \times 10^3$ M^{-1}s^{-1}

$k_{2,OH^-} = 3.44$ M^{-1}s^{-1}

p$K_B = 2.69$[47]



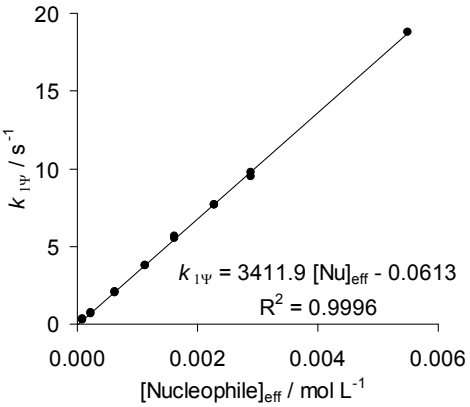
Reaction of Pyrrolidine (**1w**) with $(lil)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.4 vol-% CH_3CN, stopped-flow, detection at 634 nm)

No.	$[(lil)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fb62.1	1.81×10^{-5}	8.85×10^{-3}	5.50×10^{-3}	3.35×10^{-3}	304	18.8	7.24×10^{-3}	18.8
fb62.2	1.81×10^{-5}	5.31×10^{-3}	2.88×10^{-3}	2.43×10^{-3}	159	9.52	5.24×10^{-3}	9.51
fb63.1	1.81×10^{-5}	5.31×10^{-3}	2.88×10^{-3}	2.43×10^{-3}	159	9.80	5.24×10^{-3}	9.79
fb63.2	1.81×10^{-5}	4.43×10^{-3}	2.27×10^{-3}	2.16×10^{-3}	126	7.71	4.66×10^{-3}	7.71
fb62.3	1.81×10^{-5}	4.43×10^{-3}	2.27×10^{-3}	2.16×10^{-3}	126	7.68	4.66×10^{-3}	7.68
fb62.4	1.81×10^{-5}	3.44×10^{-3}	1.62×10^{-3}	1.82×10^{-3}	90	5.51	3.93×10^{-3}	5.51
fb63.3	1.81×10^{-5}	3.44×10^{-3}	1.62×10^{-3}	1.82×10^{-3}	90	5.68	3.93×10^{-3}	5.68
fb63.4	1.81×10^{-5}	2.66×10^{-3}	1.14×10^{-3}	1.52×10^{-3}	63	3.78	3.29×10^{-3}	3.78
fb62.5	1.81×10^{-5}	2.66×10^{-3}	1.14×10^{-3}	1.52×10^{-3}	63	3.76	3.29×10^{-3}	3.76
fb62.6	1.81×10^{-5}	1.77×10^{-3}	6.33×10^{-4}	1.14×10^{-3}	35	2.05	2.46×10^{-3}	2.05
fb63.5	1.81×10^{-5}	1.77×10^{-3}	6.33×10^{-4}	1.14×10^{-3}	35	2.07	2.46×10^{-3}	2.07
fb63.6	1.81×10^{-5}	8.85×10^{-4}	2.18×10^{-4}	6.67×10^{-4}	12	0.721	1.44×10^{-3}	0.720
fb62.7	1.81×10^{-5}	8.85×10^{-4}	2.18×10^{-4}	6.67×10^{-4}	12	0.701	1.44×10^{-3}	0.700
fb62.8	1.81×10^{-5}	5.31×10^{-4}	9.37×10^{-5}	4.37×10^{-4}	5	0.269	9.45×10^{-4}	0.268
fb63.7	1.81×10^{-5}	5.31×10^{-4}	9.37×10^{-5}	4.37×10^{-4}	5	0.306	9.45×10^{-4}	0.305

$k_{2,N}$ = 3.41 × 10^3 $M^{-1}s^{-1}$

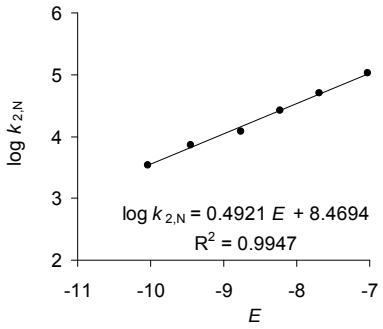
k_{2,OH^-} = 2.16 $M^{-1}s^{-1}$

pK_B = 2.69[47]



Reactivity parameters in water: *N* = 17.21; *s* = 0.49

Reference electrophile	*E* parameter	$k_{2,N}$(20°C) / M^{-1} s^{-1}
$(dma)_2CH^+$	-7.02	1.06 × 10^5
$(pyr)_2CH^+$	-7.69	5.08 × 10^4
$(thq)_2CH^+$	-8.22	2.62 × 10^4
$(ind)_2CH^+$	-8.76	1.22 × 10^4
$(jul)_2CH^+$	-9.45	7.33 × 10^3
$(lil)_2CH^+$	-10.04	3.41 × 10^3



2.8.26. Piperidine (1x)

Rate constants in water

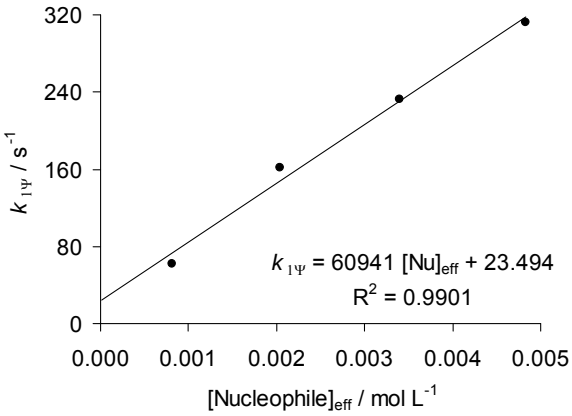
Reaction of Piperidine (**1x**) with $(dma)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.4 vol-% CH_3CN, stopped-flow, detection at 604 nm)

No.	$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fb75.2	8.32 × 10^{-5}	7.36 × 10^{-3}	4.84 × 10^{-3}	2.52 × 10^{-3}	58	3.13 × 10^2	0.331	3.13 × 10^2
fb75.3	8.32 × 10^{-5}	5.52 × 10^{-3}	3.40 × 10^{-3}	2.12 × 10^{-3}	41	2.33 × 10^2	0.277	2.33 × 10^2
fb75.4	8.32 × 10^{-5}	3.68 × 10^{-3}	2.04 × 10^{-3}	1.64 × 10^{-3}	25	1.62 × 10^2	0.215	1.62 × 10^2
fb75.5	8.32 × 10^{-5}	1.84 × 10^{-3}	8.08 × 10^{-4}	1.03 × 10^{-3}	10	62.5	0.135	62.4

$k_{2,N}$ = 6.09 × 10^4 $M^{-1}s^{-1}$

k_{2,OH^-} = 131 $M^{-1}s^{-1}$

pK_B = 2.88



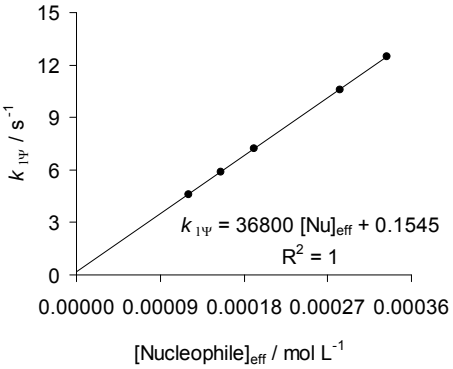
Reaction of Piperidine (**1x**) with $(pyr)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 611 nm)

No.	$[(pyr)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy10.7	1.25×10^{-5}	9.98×10^{-4}	3.34×10^{-4}	6.64×10^{-4}	27	12.5	3.22×10^{-2}	12.5
ccy10.8	1.25×10^{-5}	8.95×10^{-4}	2.84×10^{-4}	6.11×10^{-4}	23	10.6	2.97×10^{-2}	10.6
ccy10.4	1.25×10^{-5}	6.94×10^{-4}	1.92×10^{-4}	5.02×10^{-4}	15	7.22	2.44×10^{-2}	7.20
ccy10.5	1.25×10^{-5}	6.08×10^{-4}	1.55×10^{-4}	4.53×10^{-4}	12	5.92	2.20×10^{-2}	5.90
ccy10.6	1.25×10^{-5}	5.20×10^{-4}	1.21×10^{-4}	3.99×10^{-4}	10	4.61	1.94×10^{-2}	4.59

$k_{2,N} = 3.68 \times 10^4\ M^{-1}s^{-1}$

$k_{2,OH^-} = 48.5\ M^{-1}s^{-1}$

$pK_B = 2.88$



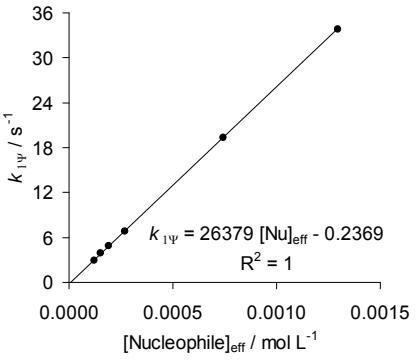
Reaction of Piperidine (**1x**) with $(thq)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 618 nm)

No.	$[(thq)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy8.1	1.58×10^{-5}	2.60×10^{-3}	1.29×10^{-3}	1.31×10^{-3}	82	33.9	3.08×10^{-2}	33.9
ccy8.2	1.58×10^{-5}	1.73×10^{-3}	7.41×10^{-4}	9.89×10^{-4}	47	19.4	2.33×10^{-2}	19.4
ccy8.3	1.58×10^{-5}	8.65×10^{-4}	2.69×10^{-4}	5.96×10^{-4}	17	6.85	1.41×10^{-2}	6.84
ccy8.4	1.58×10^{-5}	6.95×10^{-4}	1.92×10^{-4}	5.03×10^{-4}	12	4.83	1.19×10^{-2}	4.82
ccy8.5	1.58×10^{-5}	6.05×10^{-4}	1.54×10^{-4}	4.51×10^{-4}	10	3.89	1.06×10^{-2}	3.88
ccy8.6	1.58×10^{-5}	5.20×10^{-4}	1.21×10^{-4}	3.99×10^{-4}	8	2.92	9.42×10^{-3}	2.91

$k_{2,N} = 2.64 \times 10^4\ M^{-1}s^{-1}$

$k_{2,OH^-} = 23.6\ M^{-1}s^{-1}$

$pK_B = 2.88$



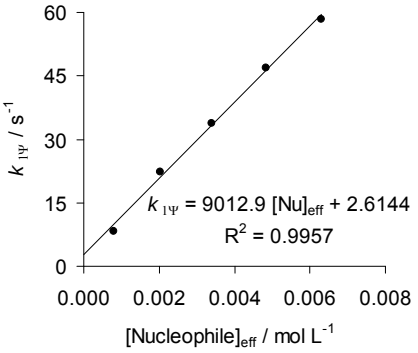
Reaction of Piperidine (**1x**) with $(ind)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.4 vol-% CH_3CN, stopped-flow, detection at 614 nm)

No.	$[(ind)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fb76.1	1.65×10^{-5}	9.20×10^{-3}	6.31×10^{-3}	2.89×10^{-3}	383	58.4	3.12×10^{-2}	58.4
fb76.2	1.65×10^{-5}	7.36×10^{-3}	4.84×10^{-3}	2.52×10^{-3}	293	47.0	2.73×10^{-2}	47.0
fb76.3	1.65×10^{-5}	5.52×10^{-3}	3.40×10^{-3}	2.12×10^{-3}	206	33.9	2.29×10^{-2}	33.9
fb76.4	1.65×10^{-5}	3.68×10^{-3}	2.04×10^{-3}	1.64×10^{-3}	124	22.4	1.77×10^{-2}	22.4
fb76.5	1.65×10^{-5}	1.84×10^{-3}	8.08×10^{-4}	1.03×10^{-3}	49	8.31	1.11×10^{-2}	83.0

$k_{2,N} = 9.01 \times 10^3$ M^{-1}s^{-1}

$k_{2,OH^-} = 10.8$ M^{-1}s^{-1}

p$K_B = 2.88$



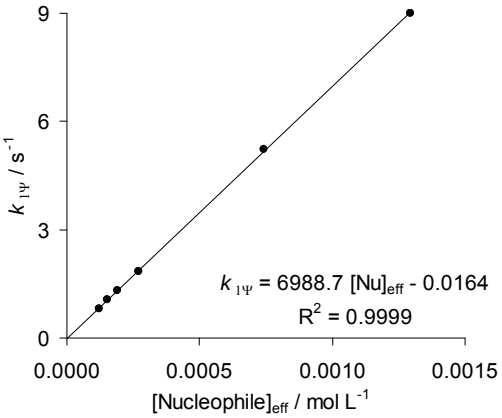
Reaction of Piperidine (**1x**) with $(jul)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 634 nm)

No.	$[(jul)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy7.1	1.26×10^{-5}	2.60×10^{-3}	1.29×10^{-3}	1.31×10^{-3}	103	9.00	4.49×10^{-3}	9.00
ccy7.2	1.26×10^{-5}	1.73×10^{-3}	7.41×10^{-4}	9.89×10^{-4}	59	5.23	3.40×10^{-3}	5.23
ccy7.3	1.26×10^{-5}	8.65×10^{-4}	2.69×10^{-4}	5.96×10^{-4}	21	1.86	2.05×10^{-3}	1.86
ccy7.4	1.26×10^{-5}	6.95×10^{-4}	1.92×10^{-4}	5.03×10^{-4}	15	1.32	1.73×10^{-3}	1.32
ccy7.5	1.26×10^{-5}	6.05×10^{-4}	1.54×10^{-4}	4.51×10^{-4}	12	1.06	1.55×10^{-3}	1.06
ccy7.6	1.26×10^{-5}	5.20×10^{-4}	1.21×10^{-4}	3.99×10^{-4}	10	0.816	1.37×10^{-3}	0.815

$k_{2,N} = 6.99 \times 10^3$ M^{-1}s^{-1}

$k_{2,OH^-} = 3.44$ M^{-1}s^{-1}

p$K_B = 2.88$



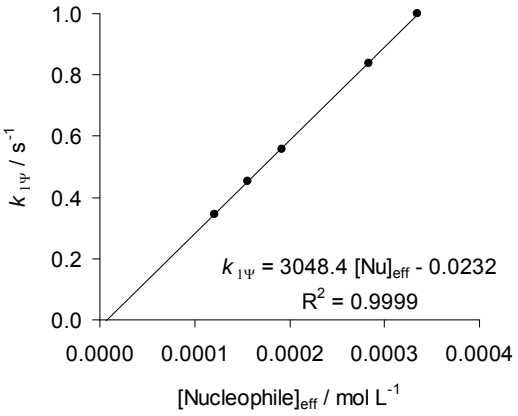
Reaction of Piperidine (**1x**) with $(lil)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.4 vol-% CH_3CN, stopped-flow, detection at 625 nm)

No.	$[(lil)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy9.7	1.32×10^{-5}	9.98×10^{-4}	3.34×10^{-4}	6.64×10^{-4}	25	1.00	1.43×10^{-3}	0.999
ccy9.8	1.32×10^{-5}	8.95×10^{-4}	2.84×10^{-4}	6.11×10^{-4}	21	0.839	1.32×10^{-3}	0.838
ccy9.4	1.32×10^{-5}	6.94×10^{-4}	1.92×10^{-4}	5.02×10^{-4}	15	0.560	1.09×10^{-3}	0.559
ccy9.5	1.32×10^{-5}	6.08×10^{-4}	1.55×10^{-4}	4.53×10^{-4}	12	0.454	9.78×10^{-4}	0.453
ccy9.6	1.32×10^{-5}	5.20×10^{-4}	1.21×10^{-4}	3.99×10^{-4}	9	0.346	8.62×10^{-4}	0.345

$k_{2,N} = 3.05 \times 10^3\ M^{-1}s^{-1}$

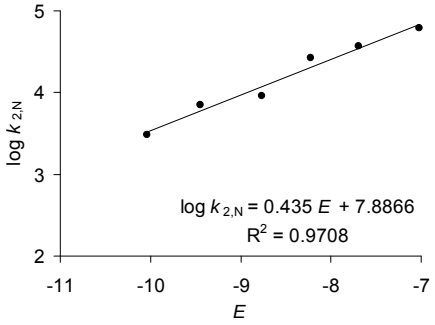
$k_{2,OH^-} = 2.16\ M^{-1}s^{-1}$

$pK_B = 2.88$



Reactivity parameters in water: $N = 18.13$; $s = 0.44$

Reference electrophile	E parameter	$k_{2,N}$(20°C) / M^{-1} s^{-1}
$(dma)_2CH^+$	-7.02	6.09×10^4
$(pyr)_2CH^+$	-7.69	3.68×10^4
$(thq)_2CH^+$	-8.22	2.64×10^4
$(ind)_2CH^+$	-8.76	9.01×10^3
$(jul)_2CH^+$	-9.45	6.99×10^3
$(lil)_2CH^+$	-10.04	3.05×10^3



2.8.27. Perhydroazepine (1y)

Rate constants in water

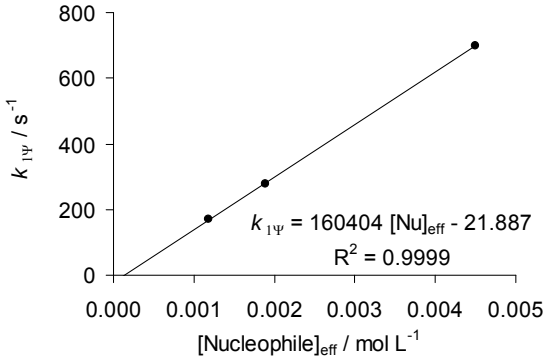
Reaction of Perhydroazepine (**1y**) with $(dma)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.5 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy94.1	1.08×10^{-4}	6.90×10^{-3}	4.49×10^{-3}	2.41×10^{-3}	42	7.00×10^{2}	0.315	7.00×10^{2}
ccy94.2	1.08×10^{-4}	3.45×10^{-3}	1.89×10^{-3}	1.56×10^{-3}	17	2.78×10^{2}	0.204	2.78×10^{2}
ccy94.3	1.08×10^{-4}	2.42×10^{-3}	1.18×10^{-3}	1.24×10^{-3}	11	1.71×10^{2}	0.162	1.71×10^{2}

$k_{2,N} = 1.60 \times 10^5\ M^{-1}s^{-1}$

$k_{2,OH^-} = 131\ M^{-1}s^{-1}$

$pK_B = 2.89$



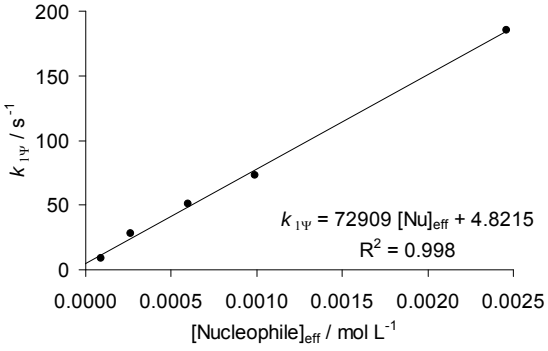
Reaction of Perhydroazepine (**1y**) with $(pyr)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 615 nm)

No.	$[(pyr)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy82.1	1.56×10^{-5}	4.24×10^{-3}	2.46×10^{-3}	1.78×10^{-3}	158	1.85×10^{2}	8.63×10^{-2}	1.85×10^{2}
ccy82.2	1.56×10^{-5}	2.12×10^{-3}	9.90×10^{-4}	1.13×10^{-3}	63	73.3	5.48×10^{-2}	73.2
ccy82.3	1.56×10^{-5}	1.48×10^{-3}	6.00×10^{-4}	8.80×10^{-4}	38	50.6	4.27×10^{-2}	50.6
ccy82.4	1.56×10^{-5}	8.48×10^{-4}	2.64×10^{-4}	5.84×10^{-4}	17	27.8	2.83×10^{-2}	27.8
ccy82.5	1.56×10^{-5}	4.24×10^{-4}	8.78×10^{-5}	3.36×10^{-4}	6	8.65	1.63×10^{-2}	8.63

$k_{2,N} = 7.29 \times 10^4\ M^{-1}s^{-1}$

$k_{2,OH^-} = 48.5\ M^{-1}s^{-1}$

$pK_B = 2.89$



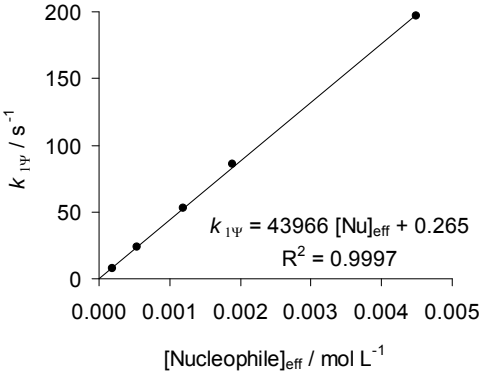
Reaction of Perhydroazepine (**1y**) with $(thq)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(thq)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy96.1	1.57×10^{-5}	6.90×10^{-3}	4.49×10^{-3}	2.41×10^{-3}	286	1.97×10^{2}	5.68×10^{-2}	1.97×10^{2}
ccy96.2	1.57×10^{-5}	3.45×10^{-3}	1.89×10^{-3}	1.56×10^{-3}	120	85.7	3.68×10^{-2}	85.7
ccy96.3	1.57×10^{-5}	2.42×10^{-3}	1.18×10^{-3}	1.24×10^{-3}	75	52.6	2.92×10^{-2}	52.6
ccy96.4	1.57×10^{-5}	1.38×10^{-3}	5.43×10^{-4}	8.37×10^{-4}	35	23.4	1.97×10^{-2}	23.4
ccy96.5	1.57×10^{-5}	6.90×10^{-4}	1.92×10^{-4}	4.98×10^{-4}	12	7.87	1.17×10^{-2}	7.86

$k_{2,N} = 4.40 \times 10^4\ M^{-1}s^{-1}$

$k_{2,OH^-} = 23.6\ M^{-1}s^{-1}$

$pK_B = 2.89$



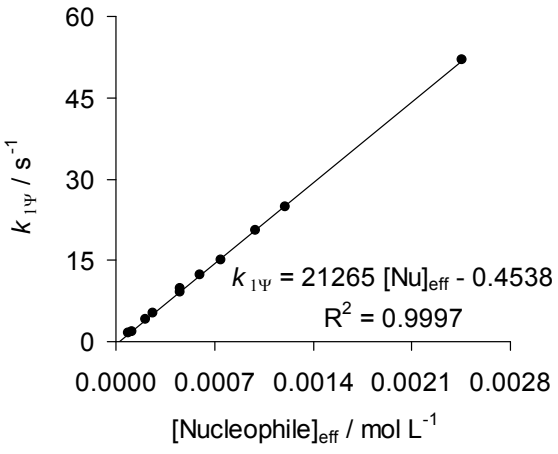
Reaction of Perhydroazepine (**1y**) with $(ind)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 615 nm)

No.	$[(ind)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy83.1	1.32×10^{-5}	4.24×10^{-3}	2.46×10^{-3}	1.78×10^{-3}	186	52.1	1.92×10^{-2}	52.1
ccy83.2	1.32×10^{-5}	2.12×10^{-3}	9.90×10^{-4}	1.13×10^{-3}	75	20.5	1.22×10^{-2}	20.5
fb203.1	2.34×10^{-5}	2.45×10^{-3}	1.20×10^{-3}	1.25×10^{-3}	51	24.9	1.35×10^{-2}	24.9
ccy83.3	1.32×10^{-5}	1.48×10^{-3}	6.00×10^{-4}	8.80×10^{-4}	45	12.3	9.50×10^{-3}	12.3
fb203.2	2.34×10^{-5}	1.72×10^{-3}	7.42×10^{-4}	9.78×10^{-4}	32	15.0	1.06×10^{-2}	15.0
fb203.3	2.34×10^{-5}	1.23×10^{-3}	4.60×10^{-4}	7.70×10^{-4}	20	9.91	8.31×10^{-3}	9.90
fb203.3b	2.34×10^{-5}	1.23×10^{-3}	4.60×10^{-4}	7.70×10^{-4}	20	9.04	8.31×10^{-3}	9.03
ccy83.4	1.32×10^{-5}	8.48×10^{-4}	2.64×10^{-4}	5.84×10^{-4}	20	5.27	6.30×10^{-3}	5.26
fb203.4b	2.34×10^{-5}	7.35×10^{-4}	2.12×10^{-4}	5.23×10^{-4}	9	4.01	5.65×10^{-3}	4.00
ccy83.5	1.32×10^{-5}	4.24×10^{-4}	8.78×10^{-5}	3.36×10^{-4}	7	1.63	3.63×10^{-3}	1.63
fb203.5	2.34×10^{-5}	4.90×10^{-4}	1.11×10^{-4}	3.79×10^{-4}	5	1.92	4.09×10^{-3}	1.92

$k_{2,N}$ = 2.13 × 10^4 $M^{-1}s^{-1}$

k_{2,OH^-} = 10.8 $M^{-1}s^{-1}$

pK_B = 2.89



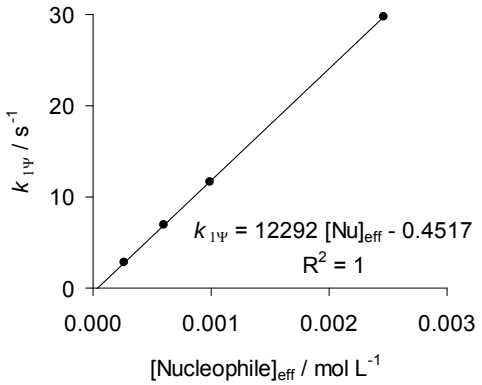
Reaction of Perhydroazepine (**1y**) with $(jul)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 630 nm)

No.	$[(jul)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy85.1	8.56 × 10^{-6}	4.24 × 10^{-3}	2.46 × 10^{-3}	1.78 × 10^{-3}	287	29.8	6.12 × 10^{-3}	29.8
ccy85.2	8.56 × 10^{-6}	2.12 × 10^{-3}	9.90 × 10^{-4}	1.13 × 10^{-3}	116	11.7	3.89 × 10^{-3}	11.7
ccy85.3	8.56 × 10^{-6}	1.48 × 10^{-3}	6.00 × 10^{-4}	8.80 × 10^{-4}	70	6.93	3.03 × 10^{-3}	6.93
ccy85.4	8.56 × 10^{-6}	8.48 × 10^{-4}	2.64 × 10^{-4}	5.84 × 10^{-4}	31	2.82	2.01 × 10^{-3}	2.82

$k_{2,N}$ = 1.23 × 10^4 $M^{-1}s^{-1}$

k_{2,OH^-} = 3.44 $M^{-1}s^{-1}$

pK_B = 2.89



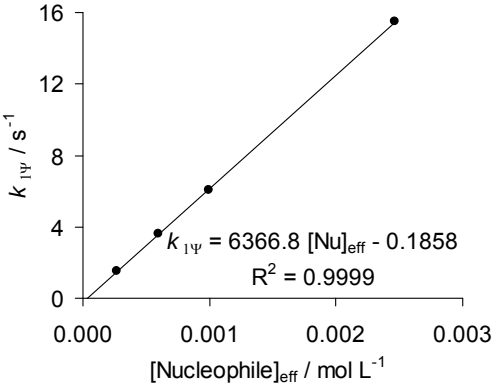
Reaction of Perhydroazepine (**1y**) with $(lil)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.4 vol-% CH_3CN, stopped-flow, detection at 630 nm)

No.	$[(lil)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy84.1	2.04×10^{-5}	4.24×10^{-3}	2.46×10^{-3}	1.78×10^{-3}	121	15.5	3.85×10^{-3}	15.5
ccy84.2	2.04×10^{-5}	2.12×10^{-3}	9.90×10^{-4}	1.13×10^{-3}	49	6.06	2.44×10^{-3}	6.06
ccy84.3	2.04×10^{-5}	1.48×10^{-3}	6.00×10^{-4}	8.80×10^{-4}	29	3.64	1.90×10^{-3}	3.64
ccy84.4	2.04×10^{-5}	8.48×10^{-4}	2.64×10^{-4}	5.84×10^{-4}	13	1.54	1.26×10^{-3}	1.54

$k_{2,N} = 6.37 \times 10^3\ M^{-1}s^{-1}$

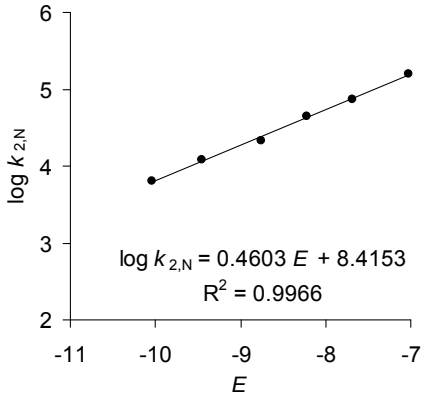
$k_{2,OH^-} = 2.16\ M^{-1}s^{-1}$

$pK_B = 2.89$



Reactivity parameters in water: N = 18.29; s = 0.46

Reference electrophile	E parameter	$k_{2,N}$(20°C) / M^{-1} s^{-1}
$(dma)_2CH^+$	-7.02	1.60×10^5
$(pyr)_2CH^+$	-7.69	7.29×10^4
$(thq)_2CH^+$	-8.22	4.40×10^4
$(ind)_2CH^+$	-8.76	2.13×10^4
$(jul)_2CH^+$	-9.45	1.23×10^4
$(lil)_2CH^+$	-10.04	6.37×10^3



2.8.28. Morpholine (1z)

Rate constants in water

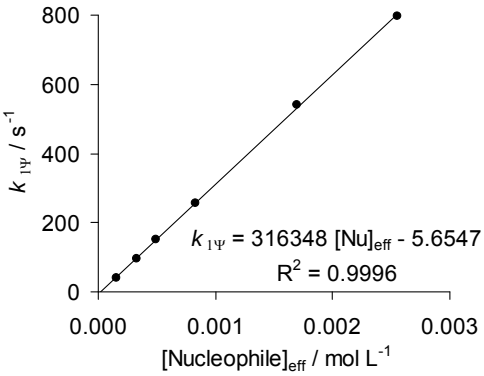
Reaction of Morpholine (**1z**) with $(mor)_2CH^+BF_4^-$ (at 20 °C, cosolvent 9 vol-% CH_3CN, stopped-flow, detection at 605 nm)

No.	$[(mor)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy14.1	7.28×10^{-6}	2.63×10^{-3}	2.55×10^{-3}	7.65×10^{-5}	351	7.96×10^{2}	8.11×10^{-2}	7.96×10^{2}
ccy14.2	7.28×10^{-6}	1.76×10^{-3}	1.70×10^{-3}	6.24×10^{-5}	233	5.42×10^{2}	6.61×10^{-2}	5.42×10^{2}
ccy14.3	7.28×10^{-6}	8.78×10^{-4}	8.34×10^{-4}	4.37×10^{-5}	115	2.56×10^{2}	4.63×10^{-2}	2.56×10^{2}
ccy14.4	7.28×10^{-6}	5.27×10^{-4}	4.93×10^{-4}	3.36×10^{-5}	68	1.51×10^{2}	3.56×10^{-2}	1.51×10^{2}
ccy14.5	7.28×10^{-6}	3.51×10^{-4}	3.24×10^{-4}	2.72×10^{-5}	44	97.2	2.89×10^{-2}	97.2
ccy14.6	7.28×10^{-6}	1.76×10^{-4}	1.57×10^{-4}	1.90×10^{-5}	22	41.1	2.01×10^{-2}	41.1

$k_{2,N} = 3.16 \times 10^5\ M^{-1}s^{-1}$

$k_{2,OH^-} = 1060\ M^{-1}s^{-1}$

$pK_B = 5.64$



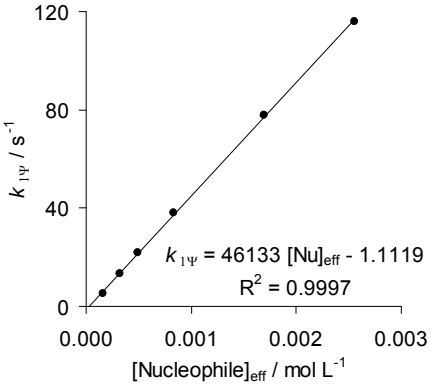
Reaction of Morpholine (**1z**) with $(dma)_2CH^+BF_4^-$ (at 20 °C, cosolvent 0.5 vol-% CH_3CN, stopped-flow, detection at 605 nm)

No.	$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy13.1	3.16×10^{-5}	2.63×10^{-3}	2.55×10^{-3}	7.65×10^{-5}	81	116	1.00×10^{-2}	116
ccy13.2	3.16×10^{-5}	1.76×10^{-3}	1.70×10^{-3}	6.24×10^{-5}	54	77.9	8.17×10^{-3}	77.9
ccy13.3	3.16×10^{-5}	8.78×10^{-4}	8.34×10^{-4}	4.37×10^{-5}	26	38.3	5.73×10^{-3}	38.3
ccy13.4	3.16×10^{-5}	5.27×10^{-4}	4.93×10^{-4}	3.36×10^{-5}	16	21.8	4.40×10^{-3}	21.8
ccy13.5	3.16×10^{-5}	3.51×10^{-4}	3.24×10^{-4}	2.72×10^{-5}	10	13.5	3.57×10^{-3}	13.5
ccy13.6	3.16×10^{-5}	1.76×10^{-4}	1.57×10^{-4}	1.90×10^{-5}	5	5.41	2.48×10^{-3}	5.41

$k_{2,N} = 4.61 \times 10^4\ M^{-1}s^{-1}$

$k_{2,OH^-} = 131\ M^{-1}s^{-1}$

$pK_B = 5.64$



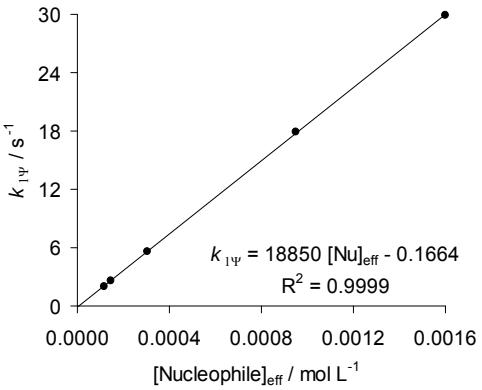
Reaction of Morpholine (**1z**) with $(pyr)_2CH^+BF_4^-$ (at 20 °C, cosolvent 9 vol-% CH_3CN, stopped-flow, detection at 614 nm)

No.	$[(pyr)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fb51.1	9.73×10^{-6}	1.66×10^{-3}	1.60×10^{-3}	6.05×10^{-5}	164	29.9	2.94×10^{-3}	29.9
fb51.2	9.73×10^{-6}	9.97×10^{-4}	9.50×10^{-4}	4.67×10^{-5}	98	17.9	2.26×10^{-3}	17.9
fb51.3	9.73×10^{-6}	3.32×10^{-4}	3.06×10^{-4}	2.65×10^{-5}	31	5.61	1.28×10^{-3}	5.61
fb51.4	9.73×10^{-6}	1.66×10^{-4}	1.48×10^{-4}	1.84×10^{-5}	15	2.59	8.92×10^{-4}	2.59
fb51.5	9.73×10^{-6}	1.33×10^{-4}	1.17×10^{-4}	1.63×10^{-5}	12	1.98	7.93×10^{-4}	1.98

$k_{2,N} = 1.89 \times 10^4$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 48.5$ $M^{-1}s^{-1}$

$pK_B = 5.64$



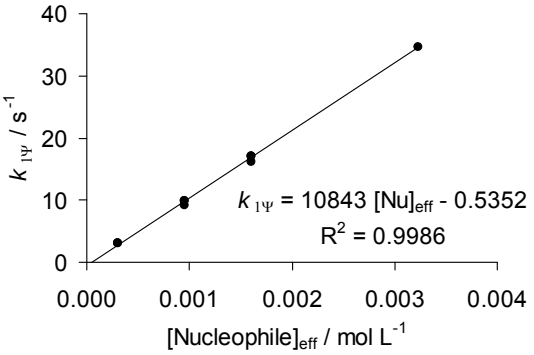
Reaction of Morpholine (**1z**) with $(thq)_2CH^+BF_4^-$ (at 20 °C, cosolvent 0.4 vol-% CH_3CN, stopped-flow, detection at 618 nm)

No.	$[(thq)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fb57.1	1.86×10^{-5}	3.32×10^{-3}	3.23×10^{-3}	8.61×10^{-5}	174	34.7	2.03×10^{-3}	34.7
fb58.2	1.86×10^{-5}	1.66×10^{-3}	1.60×10^{-3}	6.05×10^{-5}	86	17.1	1.43×10^{-3}	17.1
fb57.2	1.86×10^{-5}	1.66×10^{-3}	1.60×10^{-3}	6.05×10^{-5}	86	17.0	1.43×10^{-3}	17.0
fb58.3	1.86×10^{-5}	9.97×10^{-4}	9.50×10^{-4}	4.67×10^{-5}	51	9.88	1.10×10^{-3}	9.88
fb57.3	1.86×10^{-5}	9.97×10^{-4}	9.50×10^{-4}	4.67×10^{-5}	51	9.78	1.10×10^{-3}	9.78
fb53.1	5.36×10^{-5}	1.66×10^{-3}	1.60×10^{-3}	6.05×10^{-5}	30	16.2	1.43×10^{-3}	16.2
fb53.2	5.36×10^{-5}	9.97×10^{-4}	9.50×10^{-4}	4.67×10^{-5}	18	9.15	1.10×10^{-3}	9.15
fb58.4	1.86×10^{-5}	3.32×10^{-4}	3.06×10^{-4}	2.65×10^{-5}	16	2.97	6.24×10^{-4}	2.97
fb57.4	1.86×10^{-5}	3.32×10^{-4}	3.06×10^{-4}	2.65×10^{-5}	16	3.05	6.24×10^{-4}	3.05

$k_{2,N} = 1.08 \times 10^4$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 23.6$ $M^{-1}s^{-1}$

$pK_B = 5.64$



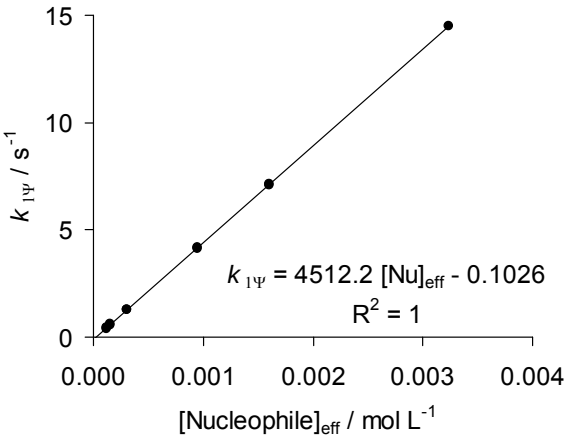
Reaction of Morpholine (**1z**) with $(ind)_2CH^+BF_4^-$ (at 20 °C, cosolvent 0.4 vol-% CH_3CN, stopped-flow, detection at 614 nm)

No.	$[(ind)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fb55.0	1.65×10^{-5}	3.32×10^{-3}	3.23×10^{-3}	8.61×10^{-5}	196	14.5	9.30×10^{-4}	14.5
fb52.1	1.36×10^{-5}	1.66×10^{-3}	1.60×10^{-3}	6.05×10^{-5}	118	7.10	6.54×10^{-4}	7.10
fb55.1	1.65×10^{-5}	1.66×10^{-3}	1.60×10^{-3}	6.05×10^{-5}	97	7.14	6.54×10^{-4}	7.14
fb52.2	1.36×10^{-5}	9.97×10^{-4}	9.50×10^{-4}	4.67×10^{-5}	70	4.13	5.04×10^{-4}	4.13
fb55.2	1.65×10^{-5}	9.97×10^{-4}	9.50×10^{-4}	4.67×10^{-5}	58	4.19	5.04×10^{-4}	4.19
fb52.3	1.36×10^{-5}	3.32×10^{-4}	3.06×10^{-4}	2.65×10^{-5}	22	1.28	2.86×10^{-4}	1.28
fb55.3	1.65×10^{-5}	3.32×10^{-4}	3.06×10^{-4}	2.65×10^{-5}	19	1.26	2.86×10^{-4}	1.26
fb52.4	1.36×10^{-5}	1.66×10^{-4}	1.48×10^{-4}	1.84×10^{-5}	11	0.572	1.99×10^{-4}	0.572
fb55.4	1.65×10^{-5}	1.66×10^{-4}	1.48×10^{-4}	1.84×10^{-5}	9	0.628	1.99×10^{-4}	0.628
fb52.5	1.36×10^{-5}	1.33×10^{-4}	1.17×10^{-4}	1.63×10^{-5}	9	0.421	1.77×10^{-4}	0.421
fb55.5	1.65×10^{-5}	1.33×10^{-4}	1.17×10^{-4}	1.63×10^{-5}	7	0.400	1.77×10^{-4}	0.400

$k_{2,N} = 4.51 \times 10^3\ M^{-1}s^{-1}$

$k_{2,OH^-} = 10.8\ M^{-1}s^{-1}$

$pK_B = 5.64$



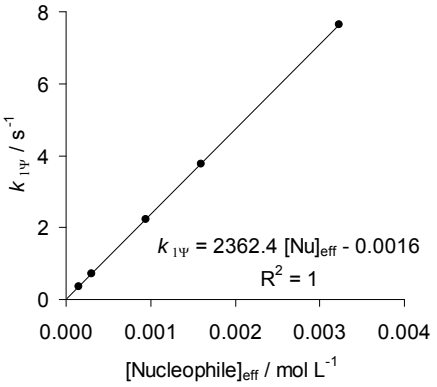
Reaction of Morpholine (**1z**) with $(jul)_2CH^+BF_4^-$ (at 20 °C, cosolvent 0.4 vol-% CH_3CN, stopped-flow, detection at 634 nm)

No.	$[(jul)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fb54.0	1.35×10^{-5}	3.32×10^{-3}	3.23×10^{-3}	8.61×10^{-5}	240	7.65	2.96×10^{-4}	7.65
fb54.1	1.35×10^{-5}	1.66×10^{-3}	1.60×10^{-3}	6.05×10^{-5}	118	3.76	2.08×10^{-4}	3.76
fb54.2	1.35×10^{-5}	9.97×10^{-4}	9.50×10^{-4}	4.67×10^{-5}	70	2.23	1.61×10^{-4}	2.23
fb54.3	1.35×10^{-5}	3.32×10^{-4}	3.06×10^{-4}	2.65×10^{-5}	23	0.724	9.10×10^{-5}	0.724
fb54.4	1.35×10^{-5}	1.66×10^{-4}	1.48×10^{-4}	1.84×10^{-5}	11	0.363	6.33×10^{-5}	0.363

$k_{2,N} = 2.36 \times 10^3\ M^{-1}s^{-1}$

$k_{2,OH^-} = 3.44\ M^{-1}s^{-1}$

$pK_B = 5.64$



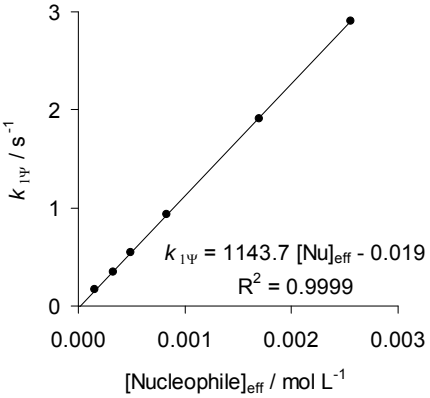
Reaction of Morpholine (**1z**) with $(lil)_2CH^+BF_4^-$ (at 20 °C, cosolvent 0.2 vol-% CH_3CN, stopped-flow, detection at 630 nm)

No.	$[(lil)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy12.1	1.58×10^{-5}	2.63×10^{-3}	2.55×10^{-3}	7.65×10^{-5}	162	2.91	1.65×10^{-4}	2.91
ccy12.2	1.58×10^{-5}	1.76×10^{-3}	1.70×10^{-3}	6.24×10^{-5}	107	1.91	1.35×10^{-4}	1.91
ccy12.3	1.58×10^{-5}	8.78×10^{-4}	8.34×10^{-4}	4.37×10^{-5}	53	0.936	9.44×10^{-5}	0.936
ccy12.4	1.58×10^{-5}	5.27×10^{-4}	4.93×10^{-4}	3.36×10^{-5}	31	0.543	7.26×10^{-5}	0.543
ccy12.5	1.58×10^{-5}	3.51×10^{-4}	3.24×10^{-4}	2.72×10^{-5}	20	0.350	5.88×10^{-5}	0.350
ccy12.6	1.58×10^{-5}	1.76×10^{-4}	1.57×10^{-4}	1.90×10^{-5}	10	0.168	4.10×10^{-5}	0.168

$k_{2,N} = 1.14 \times 10^3\ M^{-1}s^{-1}$

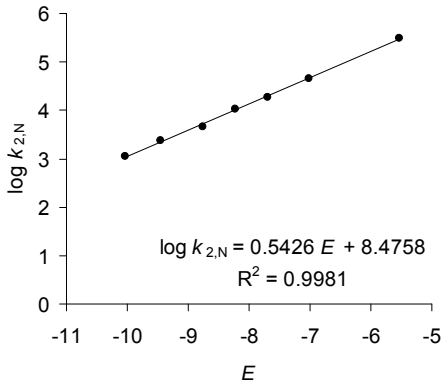
$k_{2,OH^-} = 2.16\ M^{-1}s^{-1}$

$pK_B = 5.64$



Reactivity parameters in water: *N* = 15.62; *s* = 0.54

Reference electrophile	*E* parameter	$k_{2,N}$(20°C) / M^{-1} s^{-1}
$(mor)_2CH^+$	-5.53	3.16×10^5
$(dma)_2CH^+$	-7.02	4.61×10^4
$(pyr)_2CH^+$	-7.69	1.89×10^4
$(thq)_2CH^+$	-8.22	1.08×10^4
$(ind)_2CH^+$	-8.76	4.51×10^3
$(jul)_2CH^+$	-9.45	2.36×10^3
$(lil)_2CH^+$	-10.04	1.14×10^3



2.8.29. Piperazine (1zz)

Rate constants in water

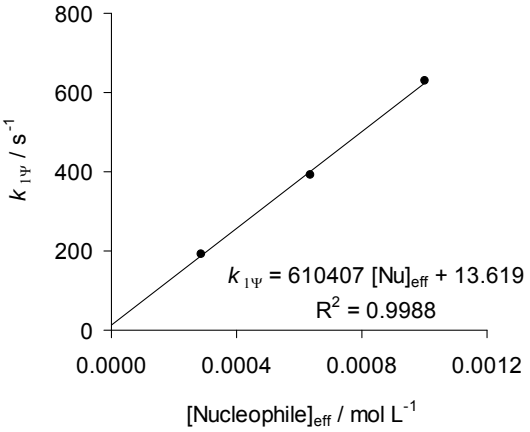
Reaction of Piperazine (**1zz**) with $(mor)_2CH^+BF_4^-$ (at 20 °C, cosolvent 9 vol-% CH_3CN, stopped-flow, detection at 607 nm)

No.	$[(mor)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fb23.3	4.41×10^{-5}	1.23×10^{-3}	1.00×10^{-3}	2.29×10^{-4}	23	6.29×10^2	0.243	6.29×10^2
fb23.4	4.41×10^{-5}	8.18×10^{-4}	6.35×10^{-4}	1.83×10^{-4}	14	3.93×10^2	0.194	3.93×10^2
fb23.5	4.41×10^{-5}	4.09×10^{-4}	2.86×10^{-4}	1.23×10^{-4}	6	1.93×10^2	0.130	1.93×10^2

$k_{2,N} = 6.10 \times 10^5$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 1060$ $M^{-1}s^{-1}$

pK_B = 4.28



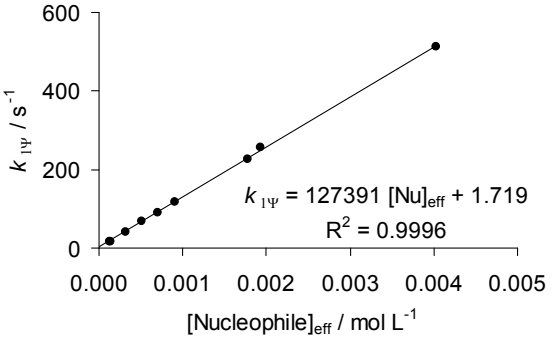
Reaction of Piperazine (**1zz**) with $(dma)_2CH^+BF_4^-$ (at 20 °C, cosolvent 0.4 vol-% CH_3CN, stopped-flow, detection at 604 nm)

No.	$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fb18.1	2.21×10^{-5}	4.49×10^{-3}	4.03×10^{-3}	4.60×10^{-4}	182	5.12×10^{2}	6.02×10^{-2}	5.12×10^{2}
fb18.2	2.21×10^{-5}	2.25×10^{-3}	1.93×10^{-3}	3.18×10^{-4}	87	2.56×10^{2}	4.17×10^{-2}	2.56×10^{2}
fb15.2	2.21×10^{-5}	2.08×10^{-3}	1.77×10^{-3}	3.05×10^{-4}	80	2.27×10^{2}	4.00×10^{-2}	2.27×10^{2}
fb18.3	2.21×10^{-5}	1.13×10^{-3}	9.11×10^{-4}	2.19×10^{-4}	41	1.17×10^{2}	2.86×10^{-2}	1.17×10^{2}
fb18.4	2.21×10^{-5}	9.00×10^{-4}	7.07×10^{-4}	1.93×10^{-4}	32	91.2	2.52×10^{-2}	91.2
fb18.5	2.21×10^{-5}	6.75×10^{-4}	5.11×10^{-4}	1.64×10^{-4}	23	67.8	2.15×10^{-2}	67.8
fb18.6	2.21×10^{-5}	4.50×10^{-4}	3.20×10^{-4}	1.30×10^{-4}	14	41.3	1.70×10^{-2}	41.3
fb18.7	2.21×10^{-5}	2.25×10^{-4}	1.39×10^{-4}	8.55×10^{-5}	6	17.7	1.12×10^{-2}	17.7
fb15.3	2.21×10^{-5}	2.08×10^{-4}	1.27×10^{-4}	8.15×10^{-5}	6	17.3	1.07×10^{-2}	17.3

$k_{2,N} = 1.27 \times 10^5\ M^{-1}s^{-1}$

$k_{2,OH^-} = 131\ M^{-1}s^{-1}$

$pK_B = 4.28$



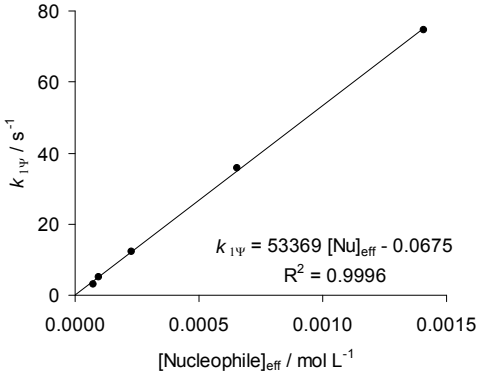
Reaction of Piperazine (**1zz**) with $(pyr)_2CH^+BF_4^-$ (at 20 °C, cosolvent 0.9 vol-% CH_3CN, stopped-flow, detection at 611 nm)

No.	$[(pyr)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fb50.3	9.73×10^{-6}	1.68×10^{-3}	1.41×10^{-3}	2.72×10^{-4}	145	74.7	1.32×10^{-2}	74.7
fb50.4	9.73×10^{-6}	8.40×10^{-4}	6.55×10^{-4}	1.85×10^{-4}	67	35.7	8.99×10^{-3}	35.7
fb50.5	9.73×10^{-6}	3.36×10^{-4}	2.27×10^{-4}	1.09×10^{-4}	23	12.4	5.29×10^{-3}	12.4
fb50.6	9.73×10^{-6}	1.68×10^{-4}	9.67×10^{-5}	7.13×10^{-5}	10	5.03	3.46×10^{-3}	5.03
fb50.7	9.73×10^{-6}	1.34×10^{-4}	7.24×10^{-5}	6.16×10^{-5}	7	3.09	2.99×10^{-3}	3.09

$k_{2,N} = 5.34 \times 10^4\ M^{-1}s^{-1}$

$k_{2,OH^-} = 48.5\ M^{-1}s^{-1}$

$pK_B = 4.28$



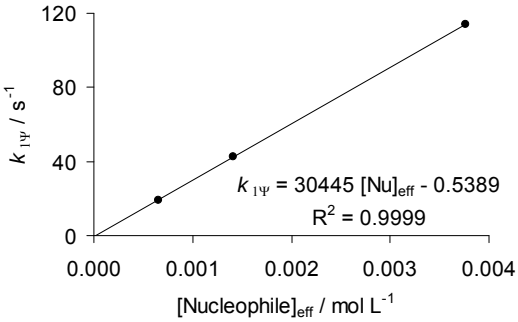
Reaction of Piperazine (**1zz**) with $(thq)_2CH^+BF_4^-$ (at 20 °C, cosolvent 0.4 vol-% CH_3CN, stopped-flow, detection at 618 nm)

No.	$[(thq)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fb47.2	5.36×10^{-5}	4.21×10^{-3}	3.77×10^{-3}	4.45×10^{-4}	70	1.14×10^{2}	1.05×10^{-2}	1.14×10^{2}
fb47.3	5.36×10^{-5}	1.68×10^{-3}	1.41×10^{-3}	2.72×10^{-4}	26	42.8	6.42×10^{-3}	42.8
fb47.4	5.36×10^{-5}	8.42×10^{-4}	6.56×10^{-4}	1.86×10^{-4}	12	19.1	4.38×10^{-3}	19.1

$k_{2,N} = 3.04 \times 10^4\ M^{-1}s^{-1}$

$k_{2,OH^-} = 23.6\ M^{-1}s^{-1}$

$pK_B = 4.28$



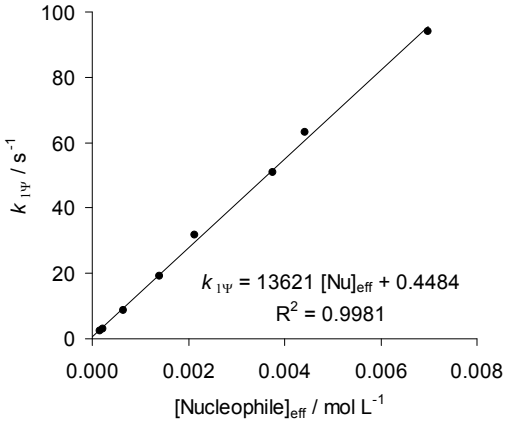
Reaction of Piperazine (**1zz**) with $(ind)_2CH^+BF_4^-$ (at 20 °C, cosolvent 0.4 vol-% CH_3CN, stopped-flow, detection at 618 nm)

No.	$[(ind)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fb48.1	1.36×10^{-5}	7.58×10^{-3}	6.97×10^{-3}	6.05×10^{-4}	513	94.0	6.53×10^{-3}	94.0
fb12.2	1.39×10^{-5}	4.91×10^{-3}	4.43×10^{-3}	4.82×10^{-4}	319	63.1	5.21×10^{-3}	63.1
fb48.2	1.36×10^{-5}	4.21×10^{-3}	3.77×10^{-3}	4.45×10^{-4}	277	50.8	4.80×10^{-3}	50.8
fb12.3	1.39×10^{-5}	2.46×10^{-3}	2.13×10^{-3}	3.34×10^{-4}	153	31.7	3.61×10^{-3}	31.7
fb48.3	1.36×10^{-5}	1.68×10^{-3}	1.41×10^{-3}	2.72×10^{-4}	104	19.2	2.94×10^{-3}	19.2
fb48.4	1.36×10^{-5}	8.42×10^{-4}	6.56×10^{-4}	1.86×10^{-4}	48	8.71	2.00×10^{-3}	8.71
fb48.5	1.36×10^{-5}	3.37×10^{-4}	2.28×10^{-4}	1.09×10^{-4}	17	2.85	1.18×10^{-3}	2.85
fb12.4	1.39×10^{-5}	2.46×10^{-4}	1.56×10^{-4}	9.04×10^{-5}	11	2.26	9.76×10^{-4}	2.26

$k_{2,N} = 1.36 \times 10^4\ M^{-1}s^{-1}$

$k_{2,OH^-} = 10.8\ M^{-1}s^{-1}$

$pK_B = 4.28$



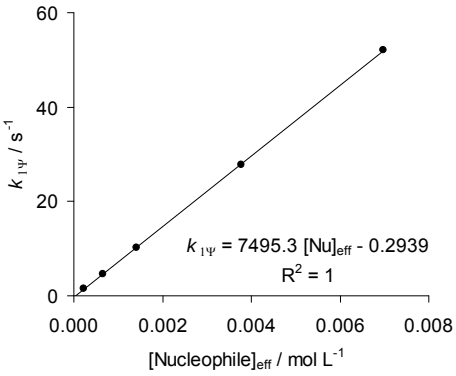
Reaction of Piperazine (**1zz**) with $(jul)_2CH^+BF_4^-$ (at 20 °C, cosolvent 0.4 vol-% CH_3CN, stopped-flow, detection at 634 nm)

No.	$[(jul)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi, OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fb49.1	1.27×10^{-5}	7.58×10^{-3}	6.97×10^{-3}	6.05×10^{-4}	549	52.1	2.08×10^{-3}	52.1
fb49.2	1.27×10^{-5}	4.21×10^{-3}	3.77×10^{-3}	4.45×10^{-4}	296	27.7	1.53×10^{-3}	27.7
fb49.3	1.27×10^{-5}	1.68×10^{-3}	1.41×10^{-3}	2.72×10^{-4}	111	10.3	9.35×10^{-4}	10.3
fb49.4	1.27×10^{-5}	8.42×10^{-4}	6.56×10^{-4}	1.86×10^{-4}	52	4.66	6.38×10^{-4}	4.66
fb49.5	1.27×10^{-5}	3.37×10^{-4}	2.28×10^{-4}	1.09×10^{-4}	18	1.46	3.76×10^{-4}	1.46

$k_{2,N} = 7.50 \times 10^3$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 3.44$ $M^{-1}s^{-1}$

$pK_B = 4.28$



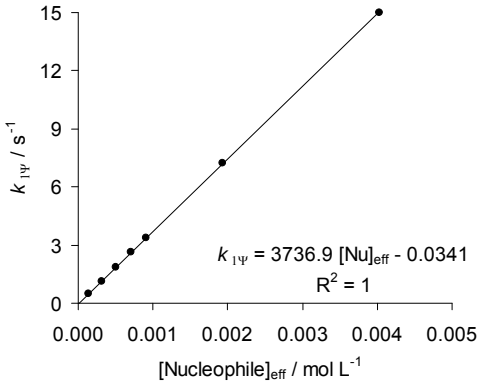
Reaction of Piperazine (**1zz**) with $(lil)_2CH^+BF_4^-$ (at 20 °C, cosolvent 0.4 vol-% CH_3CN, stopped-flow, detection at 604 nm)

No.	$[(lil)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi, OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fb20.1	8.84×10^{-6}	4.49×10^{-3}	4.03×10^{-3}	4.60×10^{-4}	456	15.0	9.93×10^{-4}	15.0
fb20.2	8.84×10^{-6}	2.25×10^{-3}	1.93×10^{-3}	3.18×10^{-4}	219	7.24	6.88×10^{-4}	7.24
fb20.3	8.84×10^{-6}	1.13×10^{-3}	9.11×10^{-4}	2.19×10^{-4}	103	3.37	4.72×10^{-4}	3.37
fb20.4	8.84×10^{-6}	9.00×10^{-4}	7.07×10^{-4}	1.93×10^{-4}	80	2.63	4.16×10^{-4}	2.63
fb20.5	8.84×10^{-6}	6.75×10^{-4}	5.11×10^{-4}	1.64×10^{-4}	58	1.88	3.54×10^{-4}	1.88
fb20.6	8.84×10^{-6}	4.50×10^{-4}	3.20×10^{-4}	1.30×10^{-4}	36	1.13	2.80×10^{-4}	1.13
fb20.7	8.84×10^{-6}	2.25×10^{-4}	1.39×10^{-4}	8.55×10^{-5}	16	0.470	1.85×10^{-4}	0.470

$k_{2,N} = 3.74 \times 10^3$ $M^{-1}s^{-1}$

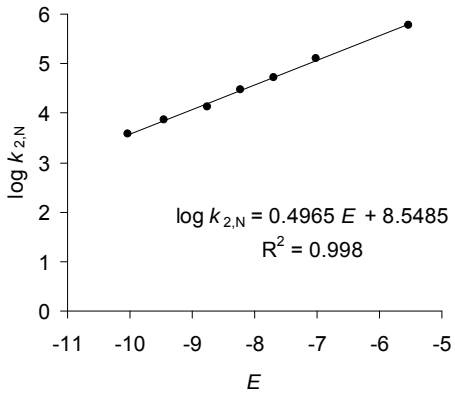
$k_{2,OH^-} = 2.16$ $M^{-1}s^{-1}$

$pK_B = 4.28$



Reactivity parameters in water: N = 17.22; s = 0.50

Reference electrophile	E parameter	$k_{2,N}$(20°C) / M^{-1} s^{-1}
$(mor)_2CH^+$	-5.53	6.10×10^5
$(dma)_2CH^+$	-7.02	1.27×10^5
$(pyr)_2CH^+$	-7.69	5.34×10^4
$(thq)_2CH^+$	-8.22	3.04×10^4
$(ind)_2CH^+$	-8.76	1.36×10^4
$(jul)_2CH^+$	-9.45	7.48×10^3
$(lil)_2CH^+$	-10.04	3.74×10^3



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3. Nucleophilicities of Amino Acids and Peptides

3.1. Introduction

Nucleophilic reactivities of amino acids and their derivatives have been the topic of numerous kinetic investigations, including nucleophilic aromatic [1-3] and aliphatic substitutions,[4] additions to carbonyl groups [5] and Michael acceptors [6-9] as well as reactions with heteroelectrophiles, e.g. nitrosonium ions.[10] Amino acid esters form adducts with cationic transition metal-π-complexes,[11] and the kinetics of these reactions have been used by Sweigart and Kane-Maguire to develop a nucleophilicity scale for amino acid derivatives.[12] While the latter study includes also numerous other nucleophiles,[12] most previous kinetic investigations provide a good comparison of nucleophilic reactivities within the group of amino acids and small peptides, but do not allocate these compounds in a general scheme of nucleophilicity.

The most comprehensive nucleophilicity scale presently available is based on reactions with benzhydrylium ions of different reactivity, and it has become possible to directly compare *n*-nucleophiles (amines, alcohols, phosphanes), π-nucleophiles (alkenes, arenes, organometallics), and σ-nucleophiles (hydride donors) with each other.[13-17] The rate constants have been correlated on the basis of eqn (3.1), where nucleophilicity *N* is defined as the negative value of the intercepts on the *E*-axis of log *k* vs *E* correlations.

$$\log k_{20^\circ C} = s(N + E) \qquad (3.1)$$

k = second-order rate constant in M^{-1} s^{-1}

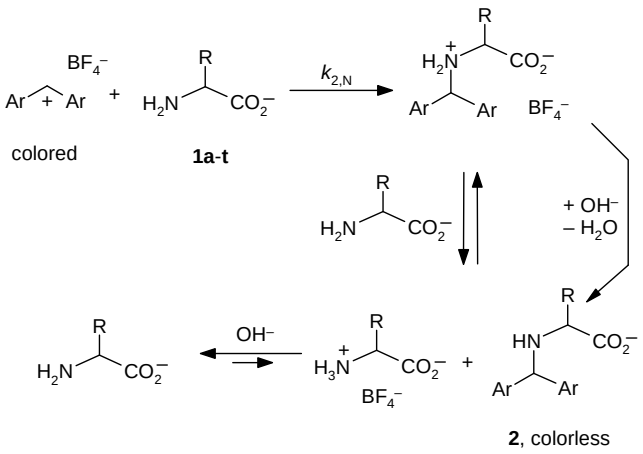
s = nucleophile-specific slope parameter

N = nucleophilicity parameter

E = electrophilicity parameter

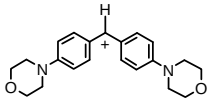
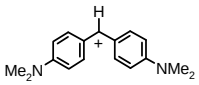
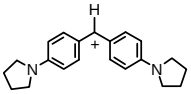
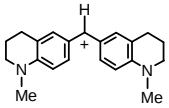
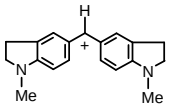
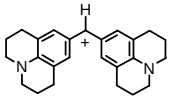
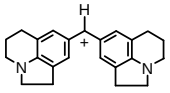
We have demonstrated that the nucleophilicity scales derived from reactions with benzhydrylium ions also hold for reactions with ordinary Michael systems[18,19] as well as for S_N2 reactions, though in the latter case eqn (3.1) has to be extended by an additional, electrophile-specific slope parameter.[20]

We have now started a program to investigate the nucleophilic and electrophilic reactivities of biomolecules, which is not only intended as a guide for their use in synthesis but also for predicting rates of individual steps in biotransformations in the absence of an enzyme. Because such rate constants are often too small for direct measurements the comparison of calculated rate constants with the rates of the enzymatic processes shall be used to predict the absolute magnitudes of enzyme activities. In this part, we will report on the determination of the reactivity parameters *N* and *s* (eqn 3.1) for a variety of amino acids and their derivatives, and we will include these compounds in our comprehensive nucleophilicity scale which puts the nucleophilic reactivities of amino acids in relation to numerous other nucleophiles of different structures. For that purpose we have investigated the kinetics of the reactions of amino acids and peptides with the reference electrophiles listed in Table 3.1 (Scheme 3.1).



Scheme 3.1

Table 3.1. Benzhydrylium ions $(Aryl)_2CH^+$ employed in this work.

Electrophile		E^a
$(mor)_2CH^+$		–5.53
$(dma)_2CH^+$		–7.02
$(pyr)_2CH^+$		–7.69
$(thq)_2CH^+$		–8.22
$(ind)_2CH^+$		–8.76
$(jul)_2CH^+$		–9.45
$(lil)_2CH^+$		–10.04

[a] Electrophilicity parameters E from ref. 14

Experimental Procedures

3.2. Kinetics

The reactions of benzhydrylium ions with the anions of the amino acids were studied in aqueous solution at a pH where the α-amino group was deprotonated.

As the reactions of the colored benzhydrylium ions with amino acid anions gave rise to colorless products, the reactions could be followed by UV-vis spectroscopy. The rates of slow reactions

($\tau_{1/2}$ > 10 s) were determined by using a J&M TIDAS diode array spectrophotometer, which was controlled by Labcontrol Spectacle software and connected to a Hellma 661.502-QX quartz Suprasil immersion probe (5 mm light path) via fiber optic cables and standard SMA connectors. The temperature of the solutions was kept constant (usually 20 ± 0.2 °C) during all kinetic studies by using a circulating bath thermostat and monitored with a thermocouple probe that was inserted into the reaction mixture.

Hi-Tech SF-61DX2 stopped-flow spectrophotometer systems (controlled by Hi-Tech KinetAsyst2 software) were used for the investigation of rapid reactions of benzhydrylium ions with the anions of the amino acids ($\tau_{1/2}$ < 10 s at 20 °C).

3.3. Results

The rates of the reactions of the colored benzhydrylium tetrafluoroborates with amino acids were followed photometrically under pseudo-first-order conditions by using usually more than ten equivalents of the amino acid anions. Under such conditions, the concentrations of the amino acid anions **1a**–**t** were almost constant throughout the reactions and resulted in an exponential decay of the benzhydrylium absorbances, from which the pseudo-first-order rate constants k_{obs} were derived. As shown in Fig. 3.1 for the reaction of glycine with $(dma)_2CH^+$, k_{obs} depends on the pH value. At pH < 7, the observed rate constant k_{obs} corresponds to the previously reported rate constant k_W for the reaction of this carbocation with water.[21] As the pH value is increased by changing the phosphate buffer solution, the rate constant increases by a factor of 2×10^2 when a 0.905 mM glycine solution is used. Control experiments with the corresponding buffer solutions in the absence of the amino acid indicate a reaction rate which is similar to that previously reported for the reaction of $(dma)_2CH^+$ with OH^-.[22] Fig. 3.1 shows that at pH 10 to 11.5, the contribution of the reaction with water (k_W) and with hydroxide ($k_{1\Psi,OH}$) is negligible, and the slight increase of k_{obs} in this range is caused by the change of the zwitterion/anion ratio of the amino acid. The pH-rate-profiles for the reactions of **1b**, **1i**, **1j**, **1l**, **1m**, **1q** with $(dma)_2CH^+$ and for the reaction of **1o** with $(ind)_2CH^+$ and $(lil)_2CH^+$ are similar and are given in the experimental part.

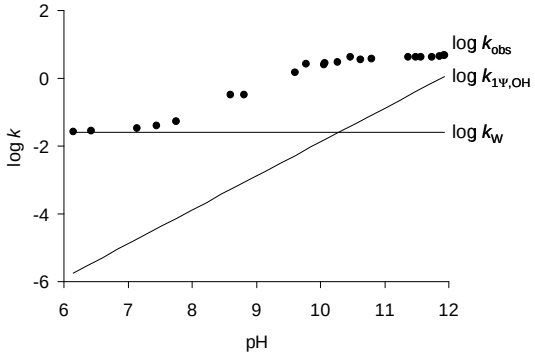


Figure 3.1. Plot of the measured rate constants log k_{obs} for the reactions of glycine ($c_0 = 9.05 \times 10^{-4}$ M) with $(dma)_2CH^+$ ($c_0 = 3.36 \times 10^{-5}$ M) at 20 °C in aqueous phosphate buffer vs pH compared with log k_W for the reaction with water and log $k_{1\Psi,OH}$ for the reaction with OH^- ($k_{1\Psi,OH} = k_{2,OH}[OH^-]$ was calculated from the measured pH and $k_{2,OH}$ from ref. 22; k_W from ref. 21).

When the benzhydrylium ions are combined with amino acids in water, competing reactions of the carbocations with hydroxide and water have to be considered. The observed pseudo-first-order rate constants k_{obs} reflect the sum of the reactions of the electrophile with the amino acid **1** ($k_{1\Psi,N}$), with OH^-($k_{1\Psi,OH}$), and with water (k_W).

$$k_{obs} = k_{1\Psi,N} + k_{1\Psi,OH} + k_W \qquad (3.2)$$
$$= k_{2,N}\,[\mathbf{1}] + k_{2,OH}\,[OH^-] + k_W$$

Rearrangement of eqn (3.2) yields eqn (3.3), which defines $k_{1\Psi}$ as the overall rate constant minus the contribution of hydroxide.

$$k_{1\Psi} = k_{obs} - k_{2,OH}\,[OH^-] = k_{2,N}[\mathbf{1}] + k_W \qquad (3.3)$$

The concentrations of the amino acids [**1**] and of hydroxide [OH^-] are calculated from pK_{aH} as described in the experimental part. With the already published values for $k_{2,OH}$ and the calculated concentrations of hydroxide [OH^-],[22] the partial pseudo-first-order rate constants $k_{1\Psi,OH}$ can be calculated. Control experiments showed that the consumption of the benzhydrylium ions in the phosphate buffers agreed with those calculated for the reactions with OH^- at the corresponding pH value within experimental error. The slopes of the plots of $k_{1\Psi}$ (= $k_{obs} - k_{1\Psi,OH}$) versus [**1**] correspond to the second-order rate constants $k_{2,N}$, as shown in Fig. 3.2. The intercepts, which correspond to the reactions of the benzhydrylium ions with water (eqn 3.3), are generally negligible in agreement with the previously reported rate constants k_W for the reactions of benzhydrylium ions with water.[21]

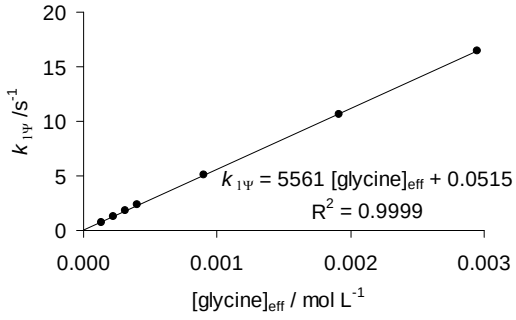


Figure 3.2. Determination of the second-order rate constant $k_{2,N} = 5.56 \times 10^3$ L mol^{-1} s^{-1} for the reaction of $(dma)_2CH^+$ with glycine(**1a**) in water at 20 °C (k_W = 0.0206 s^{-1}).

The linear dependence of $k_{1\Psi}$ on the concentration of amino acid anion, as depicted in Fig. 3.2, indicates rate-determining attack of the amino acid anion at the benzhydrylium ion (Scheme 3.1), because in the case of rate-determining proton transfer (second step in Scheme 3.1) a concave shape of this plot should result. The independence of $k_{1\Psi}$ of the pH value and the buffer concentration is also in accord with rate-determining attack of the amino acid anions at the benzhydrylium ions.

Table 3.2 collects all second-order rate constants determined in this investigation.

3.4. Structure Nucleophilicity Relationships

When log $k_{2,N}$ for the reactions of the amino acid anions and peptide anions **1a**–**t** with benzhydrylium ions are plotted against their electrophilicity parameters *E*, linear correlations are obtained (Fig. 3.3) indicating that these reactions follow eqn (3.1). The slopes of these correlations yield the parameters *s* [= s_N, if they are used for S_N2 reactions],[20] and the intercepts on the abscissa correspond to the negative values of the nucleophilicity parameters *N*.

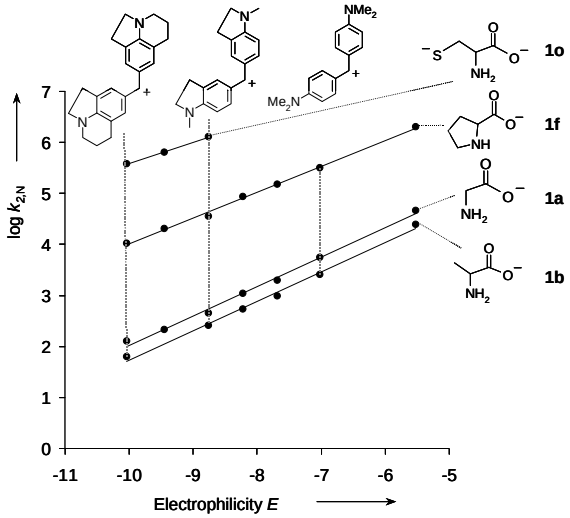
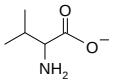
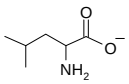
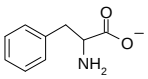
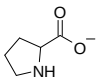
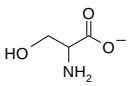
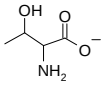
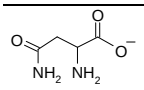
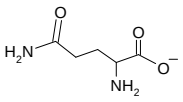
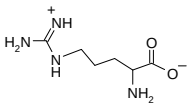
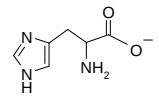
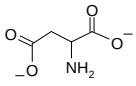
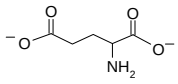
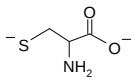
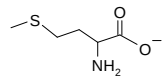
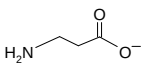
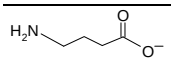


Figure 3.3. Plots of the rate constants log $k_{2,N}$ (in H_2O, 20 °C) for the reactions of amino acid anions with benzhydrylium ions (from Table 3.2) towards the electrophilicity parameters *E* of Ar_2CH^+ (from Table 3.1).

Table 3.2. Second-order rate constants for the reactions of benzhydrylium tetrafluoroborates **2** with amino acid anions and peptide anions **1** in water (20 °C).

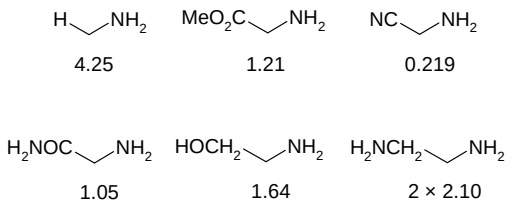
amino acid		*N*	*s*	Ar_2CH^+	$k_{2,N}/M^{-1}s^{-1}$
	**1a**	13.51	0.58	$(mor)_2CH^+$	4.62×10^4
				$(dma)_2CH^+$	5.56×10^3
				$(pyr)_2CH^+$	1.96×10^3
				$(thq)_2CH^+$	1.11×10^3
				$(ind)_2CH^+$	4.55×10^2
				$(jul)_2CH^+$	2.19×10^2
				$(lil)_2CH^+$	1.26×10^2
	**1b**	13.01	0.58	$(mor)_2CH^+$	2.46×10^4
				$(dma)_2CH^+$	2.57×10^3
				$(pyr)_2CH^+$	1.00×10^3
				$(thq)_2CH^+$	5.53×10^2
				$(ind)_2CH^+$	2.56×10^2
				$(lil)_2CH^+$	6.27×10^1
	**1c**	13.65	0.57	$(dma)_2CH^+$	5.79×10^3
				$(pyr)_2CH^+$	2.20×10^3
				$(thq)_2CH^+$	1.21×10^3
				$(jul)_2CH^+$	2.38×10^2
	**1d**	14.01	0.52	$(dma)_2CH^+$	4.40×10^3
				$(pyr)_2CH^+$	1.66×10^3
				$(thq)_2CH^+$	1.05×10^3
				$(jul)_2CH^+$	2.31×10^2
	**1e**	14.12	0.53	$(dma)_2CH^+$	6.14×10^3
				$(pyr)_2CH^+$	2.64×10^3
				$(jul)_2CH^+$	3.10×10^2
	**1f**	18.08	0.50	$(dma)_2CH^+$	3.22×10^5
				$(pyr)_2CH^+$	1.50×10^5
				$(thq)_2CH^+$	8.80×10^4
				$(ind)_2CH^+$	3.64×10^4
				$(jul)_2CH^+$	2.02×10^4
				$(lil)_2CH^+$	1.05×10^4
	**1g**	13.16	0.55	$(dma)_2CH^+$	2.49×10^3
				$(pyr)_2CH^+$	9.07×10^2
				$(thq)_2CH^+$	5.05×10^2
				$(jul)_2CH^+$	9.53×10^1
				$(lil)_2CH^+$	5.68×10^1
	**1h**	12.69	0.60	$(dma)_2CH^+$	2.29×10^3
				$(pyr)_2CH^+$	9.73×10^2
				$(ind)_2CH^+$	2.45×10^2
				$(jul)_2CH^+$	7.86×10^1

amino acid		*N*	*s*	Ar_2CH^+	$k_{2,N}/M^{-1}s^{-1}$
	**1i**	13.03	0.53	$(dma)_2CH^+$	1.82×10^3
				$(pyr)_2CH^+$	6.47×10^2
				$(thq)_2CH^+$	3.81×10^2
				$(jul)_2CH^+$	7.36×10^1
				$(lil)_2CH^+$	4.47×10^1
	**1j**	13.45	0.54	$(dma)_2CH^+$	3.06×10^3
				$(pyr)_2CH^+$	1.13×10^3
				$(thq)_2CH^+$	6.50×10^2
				$(jul)_2CH^+$	1.30×10^2
				$(lil)_2CH^+$	7.31×10^1
	**1k**	12.96	0.57	$(dma)_2CH^+$	2.61×10^3
				$(pyr)_2CH^+$	9.85×10^2
				$(thq)_2CH^+$	5.53×10^2
				$(jul)_2CH^+$	1.09×10^2
				$(lil)_2CH^+$	4.55×10^1
	**1l**	13.83	0.54	$(dma)_2CH^+$	4.31×10^3
				$(pyr)_2CH^+$	2.32×10^3
				$(thq)_2CH^+$	1.28×10^3
				$(jul)_2CH^+$	2.16×10^2
	**1m**	13.81	0.53	$(dma)_2CH^+$	3.77×10^3
				$(pyr)_2CH^+$	1.69×10^3
				$(thq)_2CH^+$	8.96×10^2
				$(ind)_2CH^+$	4.54×10^2
	**1n**	13.96	0.54	$(dma)_2CH^+$	5.77×10^3
				$(pyr)_2CH^+$	2.09×10^3
				$(thq)_2CH^+$	1.17×10^3
				$(jul)_2CH^+$	2.37×10^2
				$(lil)_2CH^+$	1.40×10^2
	**1o**	23.43	0.42	$(ind)_2CH^+$	1.29×10^6
				$(jul)_2CH^+$	6.41×10^5
				$(lil)_2CH^+$	3.79×10^5
	**1p**	13.16	0.58	$(mor)_2CH^+$	3.45×10^4
				$(dma)_2CH^+$	3.11×10^3
				$(pyr)_2CH^+$	1.33×10^3
				$(thq)_2CH^+$	7.85×10^2
				$(ind)_2CH^+$	2.76×10^2
				$(jul)_2CH^+$	1.51×10^2
				$(lil)_2CH^+$	8.22×10^1
	**1q**	13.26	0.58	$(mor)_2CH^+$	3.62×10^4
				$(dma)_2CH^+$	3.62×10^3
				$(pyr)_2CH^+$	1.45×10^3
				$(thq)_2CH^+$	6.40×10^2
				$(lil)_2CH^+$	9.10×10^1

amino acid		*N*	*s*	Ar_2CH^+	$k_{2,N}/M^{-1}s^{-1}$
	**1r**	13.55	0.56	$(dma)_2CH^+$	4.64×10^3
				$(pyr)_2CH^+$	1.97×10^3
				$(thq)_2CH^+$	1.03×10^3
				$(ind)_2CH^+$	4.81×10^2
gly-gly$^-$	**1s**	12.91	0.59	$(mor)_2CH^+$	2.55×10^4
				$(dma)_2CH^+$	2.72×10^3
				$(pyr)_2CH^+$	9.44×10^2
				$(ind)_2CH^+$	1.88×10^2
				$(lil)_2CH^+$	6.72×10^1
gly-gly-gly$^-$	**1t**	12.26	0.63	$(mor)_2CH^+$	1.76×10^4
				$(dma)_2CH^+$	1.90×10^3
				$(pyr)_2CH^+$	7.33×10^2
				$(ind)_2CH^+$	1.64×10^2

An important message comes from the reactivity data in Table 3.2: All *N*-parameters for the primary amino groups in α-amino acids are closely similar (12.7 < *N* < 14.1). The same information can also directly be derived from the rates of the reactions of these amino acid anions with the bis(dimethylamino) substituted benzhydrylium ion $(dma)_2CH^+$ which vary by less than a factor of 4 (1820 < $k_{2,N}$ < 6140 M^{-1} s^{-1}). A significantly higher nucleophilic reactivity is found for proline, the only proteinogenic amino acid with a secondary amine structure (*N* = 18.1) which reacts approximately 100 times faster with benzhydrylium ions than all the primary amino groups of the amino acids investigated in this work.

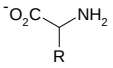
In previous work we have shown that the introduction of neutral electron acceptor groups in amines causes a reduction of nucleophilic reactivity by factors of 2 to 8 (Scheme 3.2).



Scheme 3.2. Second-order rate constants $k_{2,N}/10^3$ M^{-1} s^{-1} for the reactions of amines with $(dma)_2CH^+$ (H_2O, 20 °C, data from ref. 24).

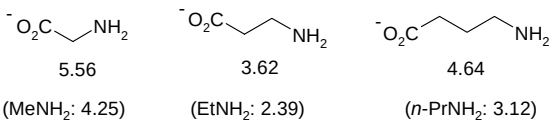
In contrast, a CO_2^- group causes a slight increase of nucleophilic reactivity. As shown in Table 3.3, the anions of glycine, alanine, serine, aspartate (dianion) and glutamate (dianion) are 1.05 to 1.5 times more nucleophilic than the corresponding amines. This finding, though surprising that the Coulombic attraction between the negatively charged amino acid anions and the positively charged benzhydrylium ions does not cause a more significant rate enhancement, is in line with Hammett's substituent constants for CO_2^- (σ_p = 0.0 and σ_m = -0.1, ref. 23).

Table 3.3. Rate constants $k_{2,N}/10^3$ M^{-1} s^{-1} for the reactions of amines and amino acid anions with $(dma)_2CH^+$ (H_2O, 20 °C).

R		
H	4.25 [a]	5.56 (Gly^-)
CH_3	2.39 [a]	2.57 (Ala^-)
CH_2OH	1.64 [a]	2.49 (Ser^-)
$CH_2CO_2^-$	3.62	3.77 (Asp^{2-})
$CH_2CH_2CO_2^-$	4.64	5.77 (Glu^{2-})

[a] From ref. 24.

Pyrrolidine and proline are 10^2 times more reactive than the analogous compounds in Table 3.3, but the reactivity ratio $k_{proline}/k_{pyrrolidine}$ = 3 again indicates that the CO_2^- substituent causes only a slight increase of nucleophilicity.



Scheme 3.3. Second-order rate constants $k_{2,N}/10^3$ $M^{-1}s^{-1}$ for the reactions of amino acid anions and amines with $(dma)_2CH^+$ (H_2O, 20 °C, data from Table 3.2 and refs 22, 24).

Comparison of the anions of glycine, β-alanine, and γ-aminobutyric acid with the corresponding amines shows that the introduction of CO_2^- groups in positions more remote from the amino group has a comparable small accelerating effect. (Scheme 3.3)

According to its *N* parameter, the dianion of cysteine (**1o**) is by far the most nucleophilic amino acid investigated, indicating the much higher reactivity of sulphur. Because **1o** could only be investigated with three benzhydrylium ions which do not differ very much in electrophilicity, the separation of log $k_{2,N}$ into *N* and *s* is associated with some uncertainty. However, from the rate constants towards $(lil)_2CH^+$ one can derive that the sulphur of **1o** is approximately 6000 times more reactive than the corresponding amino group (from ratio **1o**/**1b**). This finding is in line with previous work of Thompson,[7] who showed that in reactions of amino acids with quinone methides the primary site of alkylation is sulphur for cysteine and the α-amino groups for glycine (**1a**), serine (**1g**) and histidine (**1l**).

Figure 3.4 shows that all amino acid anions except that of proline have reactivities of the α-amino group within one order of magnitude, despite basicities which vary by almost four orders of magnitude. This finding is in line with our previous report about the poor correlation between reactivities of amines in water and their corresponding basicities.[24]

3.5. Reactions of Amino Acids with Other Electrophiles

In previous work, we have shown that the *N* and *s* parameters for amines which are derived from reactions with benzhydrylium ions can also be used to derive reactivities toward the 1-methyl-4-

vinylpyridinium ion.[24] It has also been demonstrated that the rates of the reactions of amines with methyl 4-nitrobenzenesulfonate, typical S_N2 reactions, can be expressed by eqn (3.4).[24]

$$\log k = s(0.313\ N - 6.85) \qquad (3.4)$$

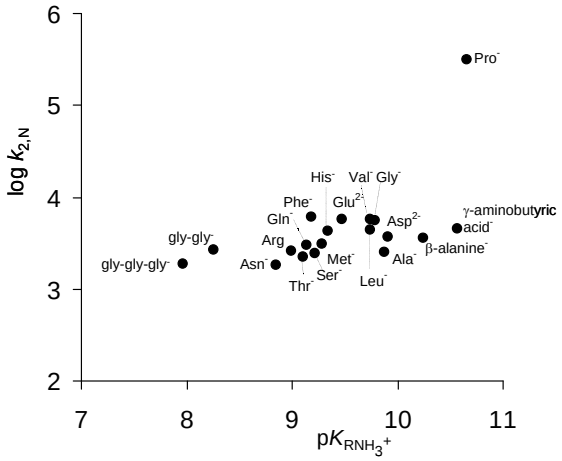
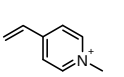
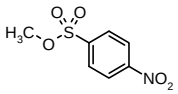


Figure 3.4. Plots of the rate constants log $k_{2,N}$ (from Table 3.2) for the reactions of amino acid anions with $(dma)_2CH^+$ BF_4^- vs pK_{aH}.

Substitution of the *N* and *s* values of the amino acids given in Table 3.2 into eqn (3.4) yields rate constants, which agree within a standard deviation of factor 2.9 with Bunting´s experimental data (Table 3.4). The applicability of the reactivity parameters *N* and *s* given in Table 3.2 for S_N2 type reactions has thus been demonstrated.

Table 3.4. Comparison of calculated (20 °C) and observed second-order rate constants for the reactions of amino acid anions with 1-methyl-4-vinylpyridinium ion and methyl 4-nitrobenzenesulfonate in H_2O.

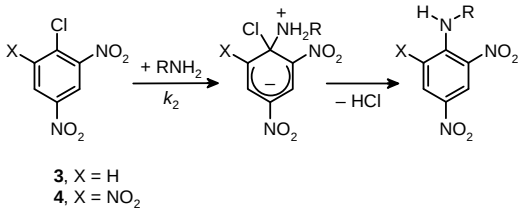




	k_{calc}/$M^{-1}s^{-1}$ [a]	k_{exp}/$M^{-1}s^{-1}$ [b]	k_{calc}/$M^{-1}s^{-1}$ [a]	k_{exp}/$M^{-1}s^{-1}$ [b]
1a	7.15×10^{-2}	1.51×10^{-1}	2.98×10^{-2}	5.38×10^{-2}
1b	4.30×10^{-2}	6.00×10^{-2}	2.42×10^{-2}	2.06×10^{-2}
1f	5.67	1.58	—	—
1g	5.85×10^{-2}	4.76×10^{-2}	3.11×10^{-2}	1.99×10^{-2}
1i	5.74×10^{-2}	2.44×10^{-2}	3.36×10^{-2}	1.72×10^{-2}
1j	4.32×10^{-2}	4.9×10^{-2}	2.53×10^{-2}	2.09×10^{-2}
1q	5.54×10^{-2}	8.1×10^{-2}	2.69×10^{-2}	4.05×10^{-2}
1r	8.14×10^{-2}	1.14×10^{-1}	3.42×10^{-2}	4.78×10^{-2}
1s	3.67×10^{-2}	3.37×10^{-2}	2.18×10^{-2}	1.74×10^{-2}
1t	1.43×10^{-2}	2.88×10^{-2}	1.25×10^{-2}	1.42×10^{-2}

[a] Calculated by correlation log $k_{2,N} = s(0.762N - 12.27)$ from ref. 24 and *N* and *s* for the amino acid anions from Table 3.2. [b] I = 0.1 mol L^{-1}, at 25 °C, refs 4, 9. [c] Calculated by eqn (3.4) from ref. 24 and *N* and *s* for the amino acid anions from Table 3.2.

Gandler investigated the reactivity of different O-, S- and N-nucleophiles towards 2,4-dinitrochlorobenzene **3** and picryl chloride **4** (Scheme 3.4).[2]



3, X = H
4, X = NO_2

Scheme 3.4.

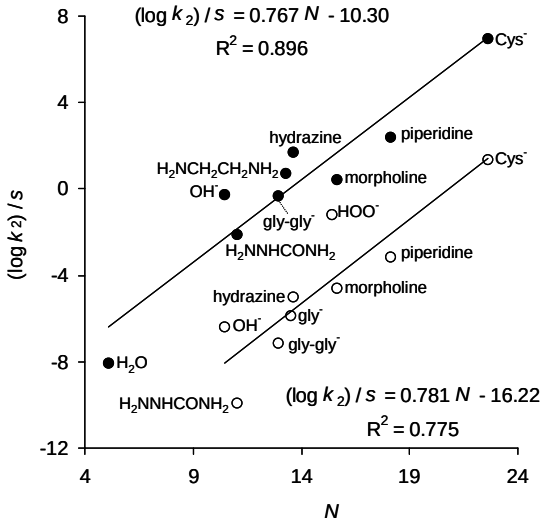
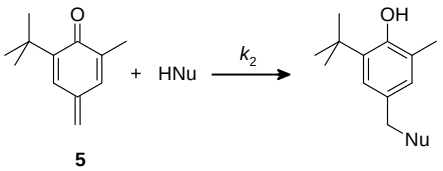


Figure 3.5. Correlation between the rate constants k_2 for the reactions of O-, S- and N-nucleophiles with the chloronitrobenzenes **3** (open circles) and **4** (filled circles) in water at 25 °C (k_2 from ref. 2) with the *N* and *s* parameters given in Table 2 and in refs 22, 24. Data for hydrazine, which will be reported later, have also been included.

Figure 3.5 shows a linear correlation between (log k_2)/*s* and *N*, where k_2 refers to the reactions of the nucleophiles with **3** (open circles) and with **4** (filled circles), and *N* and *s* are derived from the reactions of these nucleophiles with benzhydrylium ions (Table 3.2 and refs 22, 24). Because the slopes of these correlation lines (0.767 and 0.781) are deviating from unity, the rate constants for the nucleophilic additions to **3** and **4** are not properly reproduced by eqn (3.1), and it has to be examined whether the consideration of an additional, electrophile-specific slope parameter, as previously described for S_N2 reactions,[20] should generally be employed for nucleophilic aromatic substitutions of **3** and **4**.

Bolton and Thatcher determined the rate constants for the nucleophilic additions of amino acids and other nucleophiles towards the quinone methide **5** (Scheme 3.5).[6] Fig. 3.6 shows a good correlation between reactivities of nucleophiles toward **5** and the nucleophilicity parameters *N* and *s*.



5

Scheme 3.5

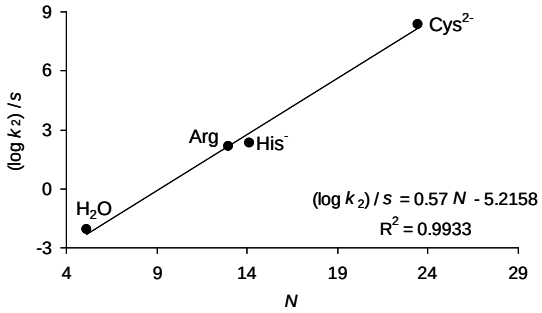


Figure 3.6. Relationship between the rate constants for the reactions of nucleophiles with quinone methide **5** in water with the *N* and *s* parameters for amino acids given in Table 3.2 (*N* and *s* parameters for water taken from ref. 22).

3.6. Conclusions

Primary amino groups in amino acids and small peptides have closely similar nucleophilicities in water, significantly higher than that of hydroxide. While the pK_{aH} value of proline is comparable to that of β-alanine and γ-aminobutyric acid, its nucleophilic reactivity exceeds that of all other amino acids by orders of magnitude. Only cysteine, where thiolate is the reactive site is even more nucleophilic. Because the *N* parameters derived from the reactions with benzhydrylium ions are known also to hold for reactions with ordinary Michael acceptors and alkyl esters, it has become possible to predict absolute rate constants for the reactions of amino acids with a large variety of electrophiles.

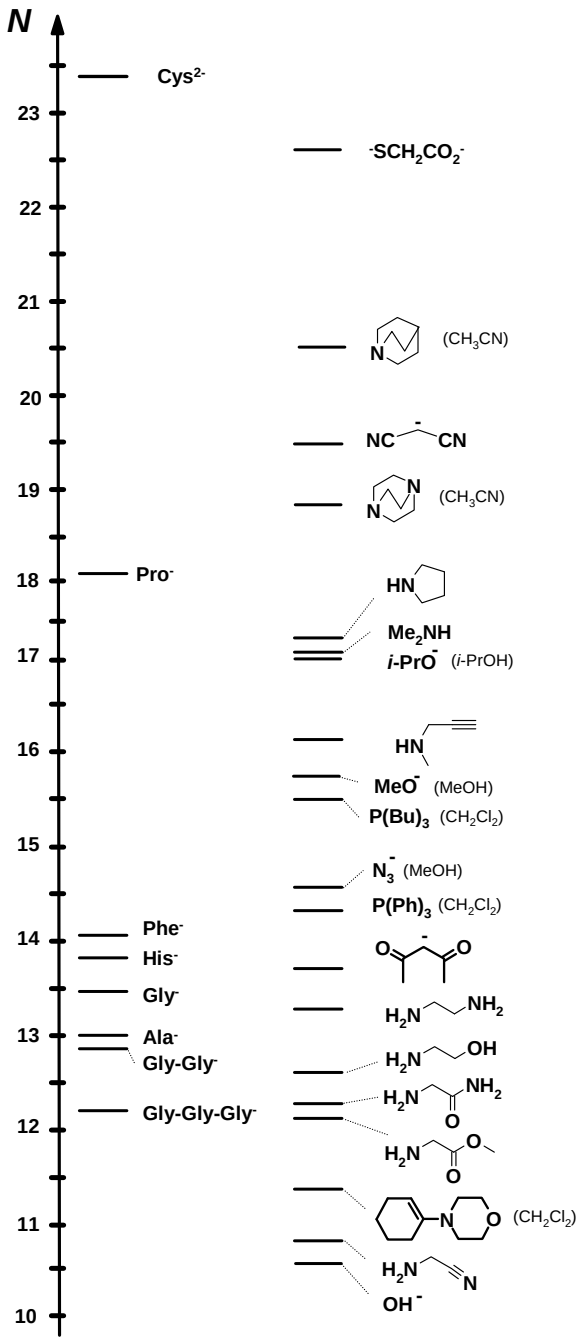


Fig. 3.7 Comparison of nucleophilicities of amino acid anions with other C-, N-, P- and O-nucleophiles in water (data referring to other solvents are marked)

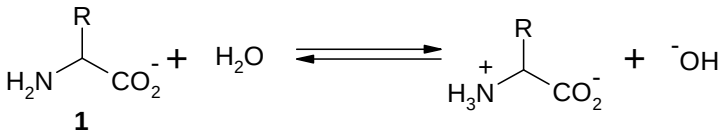
3.7. Experimental

Materials

Glycine (Acros, > 99 %), DL-alanine (Acros, 99 %), L-valine (Fluka, 99 %), L-leucine (Acros, 99%), L-phenylalanine (Sigma-Aldrich, 98%), L-proline (Fluka, 99 %), L-serine (Acros, 99 %), L-threonine (Acros, 98 %), DL-asparagine monohydrate (Acros, 98 %), L-glutamine (Aldrich, 98 %), L-arginine monohydrochloride (Fluka, 99 %), L-histidine (Acros, 98 %), L-aspartic acid (Aldrich, 98 %), L-glutamic acid (AppliChem, 99 %), L-cysteine (Fluka, 99 %), L-methionine (Acros, 98 %), β-alanine (Fluka, 99 %), γ-aminobutyric acid (Acros, 99 %), gly-gly (Acros, 99 %), gly-gly-gly (Acros, 98 %)

3.7.1. Determination of rate constants in water

The amino acid anions **1** were used as aqueous stock solutions. When the sodium salt of an amino acid **1** is dissolved in water, the concentration of hydroxide increases by protolysis. For that reason we have to calculate the concentration of the free amino acid anions $[Nu]_{eff}$ and of hydroxide $[OH^-]$ from the pK_B of the amino acids. The pK_B values of the amino acids are taken from ref 25 and refer to the α-NH_2 group unless otherwise stated.



1 (1)

Scheme 1

(3) in (2)

$$K_B = \frac{[\text{zwitterion}]\,[OH^-]}{[\text{amino acid anion}]_{eff}} \qquad (2)$$

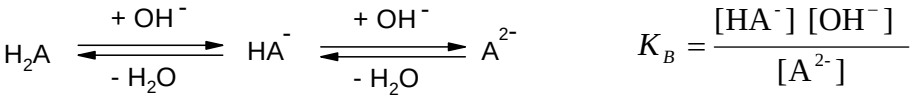
$$[\text{amino acid anion}]_0 = [\text{amino acid anion}]_{eff} + [\text{zwitterion}] = [\text{amino acid anion}]_{eff} + [OH^-] \qquad (3)$$

$$K_B = \frac{[OH^-]^2}{[\text{amino acid anion}]_0 - [OH^-]} \qquad (4)$$

Solving the quadratic equation (4) leads to one logic solution for $[OH^-]$ (The one with the "+" in the numerator).

$$[OH^-] = -\frac{K_B}{2} + \sqrt{\left(\frac{K_B}{2}\right)^2 + K_B[\text{amino acid anion}]_0} \qquad (5)$$

In cases where OH^- was used in exess over the amino acids H_2A (Scheme 2), the equilibrium concentration of the deprotonated amino acid A^{2-} (= $[Nu]_{eff}$) was calculated by equation (9) and the concentration of OH^- by equation (7). In these cases (**1m**, **1n**, **1o**) the starting concentrations of OH^- are given in the tables in an additional column.



$$K_B = \frac{[HA^-]\,[OH^-]}{[A^{2-}]}$$

Scheme 2

$[H_2A]_0 = [HA^-] + [A^{2-}]$; $[OH^-]_0 = [OH^-] + [HA^-] + 2\,[A^{2-}]$ (6)

Rearrangement of (6) gives

$[OH]^- = [OH^-]_0 - [H_2A]_0 - [A^{2-}]$ (7)

The concentration of the deprotonated amino acids A^{2-} was calculated by solving the quadratic equation (8), which gives one logic solution (9).

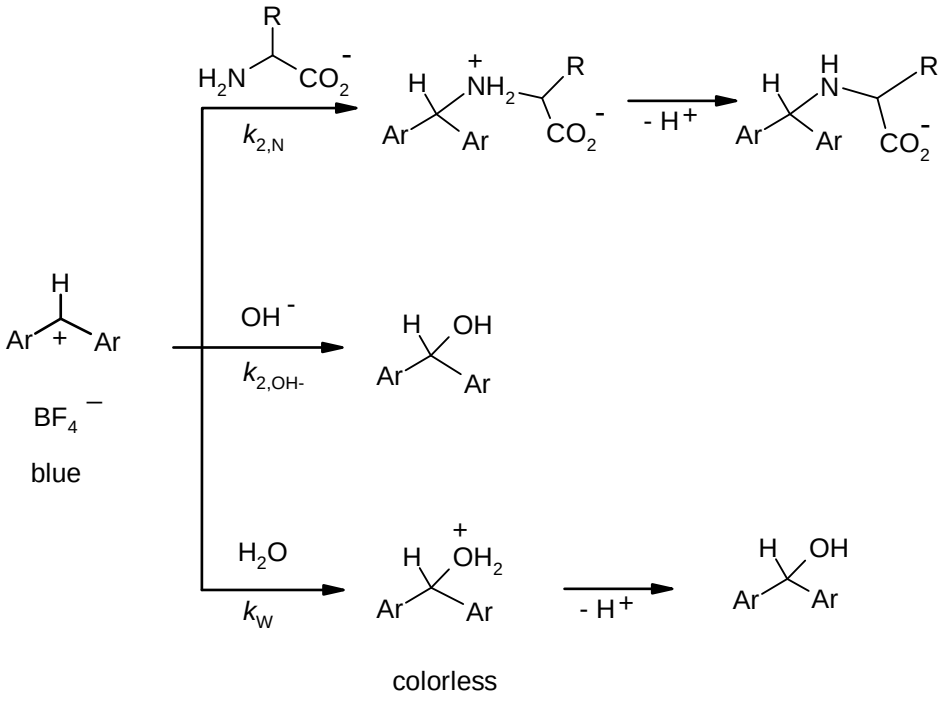
$$K_B = \frac{([H_2A]_0 - [A^{2-}])([OH^-]_0 - [H_2A]_0 - [A^{2-}])}{[A^{2-}]} \quad (8)$$

$$[A^{2-}] = \frac{[OH^-]_0 + K_B}{2} - \sqrt{\left(\frac{[OH^-]_0 + K_B}{2}\right)^2 - [H_2A]_0[OH^-]_0 + [H_2A]_0^2} \quad (9)$$

The rates of the combination reactions were determined by mixing the colored aqueous solutions of the benzhydrylium salts with aqueous solutions of the amino acid anions (usually >10 equivalents). Because the products are colorless, the rates of the reactions were determined by UV-Vis spectroscopic monitoring of the absorbances with time.

$$-\frac{d[R^+]}{dt} = k_{obs}[R^+] \quad (10)$$

The consumption of the benzhydrylium ions may be due to the reaction with the amino acids, hydroxide ions and the solvent water (Scheme 3).



Scheme 3

$k_{obs} = k_{2,N}$ [amino acid anion]$_{eff} + k_{2,OH^-}$ [OH^-] + k_W (11)

$= k_{1\Psi} + k_{2,OH^-}$ [OH^-] , with $k_{1\Psi} = k_{2,N}$ [amino acid anion]$_{eff} + k_W$ and [OH^-] from eq. (5) or eq.(7)

The amino acid anions are usually used in more than 10-fold excess over the benzhydrylium cations in order to arrive at pseudo first-order conditions. It can therefore, be assumed that the concentrations of the amino acid anions as well as that of hydroxide remain constant during the reactions. With the already published second-order rate constants k_{2,OH^-} for the reactions of hydroxide with benzhydrylium ions and the first-order rate constants k_W for the reactions of water with benzhydrylium ions,[22] we get the second-order rate constants for the reactions of the amino acid anions with the benzhydrylium ions $k_{2,N}$ from a plot of $k_{1\Psi}$ versus [amino acid anion]$_{eff}$.

3.7.2. Glycine (1a)

Rate constants in water

Typical procedure:

Glycine (42.2 mg, 0.562 mmol) was dissolved in 1.117 mL of aqueous KOH (0.5033 mol L^{-1}), then the solution was filled up to 25 mL with water ($c_{glycine}$ = 0.0225 mol L^{-1}). 3 mL of this solution was diluted with water to 10 mL. Ten parts of this solution were combined with one part of a solution of $[(mor)_2CH^+]$ in CH_3CN (4.85×10^{-4} mol L^{-1}) in the stopped-flow instrument to give the final concentrations listed in the table.

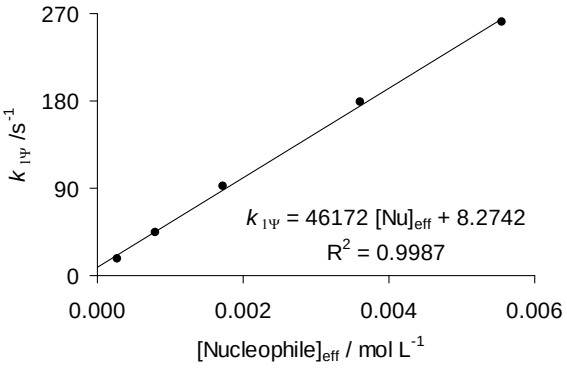
Reaction of glycine (**1a**) with $(mor)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 9 vol-% CH_3CN, stopped-flow, detection at 607 nm)

No.	$[(mor)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi, OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fb24.1	4.41×10^{-5}	6.13×10^{-3}	5.55×10^{-3}	5.78×10^{-4}	126	2.62×10^{2}	0.613	2.61×10^{2}
fb24.2	4.41×10^{-5}	4.08×10^{-3}	3.61×10^{-3}	4.67×10^{-4}	82	1.79×10^{2}	0.495	1.79×10^{2}
fb24.3	4.41×10^{-5}	2.04×10^{-3}	1.72×10^{-3}	3.22×10^{-4}	39	92.1	0.341	91.8
fb24.4	4.41×10^{-5}	1.02×10^{-3}	8.00×10^{-4}	2.20×10^{-4}	18	44.8	0.233	44.6
fb24.5	4.41×10^{-5}	4.08×10^{-4}	2.78×10^{-4}	1.30×10^{-4}	6	17.6	0.137	17.5

$k_{2,N} = 4.62 \times 10^4$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 1060$ $M^{-1}s^{-1}$

$pK_B = 4.22$



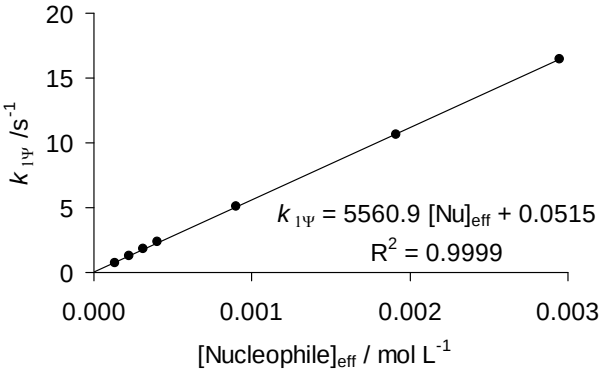
Reaction of glycine (**1a**) with $(dma)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.4 vol-% CH_3CN, stopped-flow, detection at 604 nm)

No.	$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fb19.1	2.21×10^{-5}	3.37×10^{-3}	2.95×10^{-3}	4.22×10^{-4}	133	16.5	5.52×10^{-2}	16.4
fb19.2	2.21×10^{-5}	2.25×10^{-3}	1.91×10^{-3}	3.39×10^{-4}	86	10.7	4.44×10^{-2}	10.7
fb19.3	2.21×10^{-5}	1.13×10^{-3}	8.97×10^{-4}	2.33×10^{-4}	41	5.11	3.05×10^{-2}	5.08
fb19.4	2.21×10^{-5}	5.60×10^{-4}	4.04×10^{-4}	1.56×10^{-4}	18	2.37	2.04×10^{-2}	2.35
fb19.5	2.21×10^{-5}	4.50×10^{-4}	3.13×10^{-4}	1.37×10^{-4}	14	1.85	1.80×10^{-2}	1.83
fb19.6	2.21×10^{-5}	3.37×10^{-4}	2.21×10^{-4}	1.16×10^{-4}	10	1.25	1.51×10^{-2}	1.23
fb19.7	2.21×10^{-5}	2.25×10^{-4}	1.35×10^{-4}	9.01×10^{-5}	6	7.55×10^{-1}	1.18×10^{-2}	7.43×10^{-1}

$k_{2,N} = 5.56 \times 10^3\ M^{-1}s^{-1}$

$k_{2,OH^-} = 131\ M^{-1}s^{-1}$

$pK_B = 4.22$



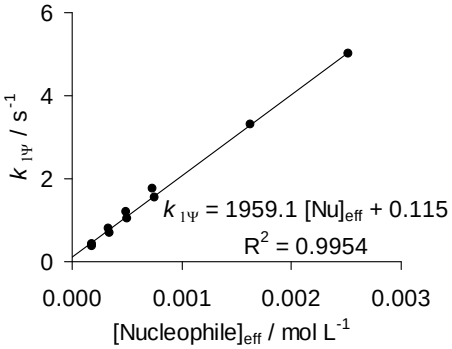
Reaction of glycine (**1a**) with $(pyr)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 611 nm)

No.	$[(pyr)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy16.1	2.53×10^{-5}	2.91×10^{-3}	2.52×10^{-3}	3.90×10^{-4}	100	5.03	1.89×10^{-2}	5.01
ccy16.2	2.53×10^{-5}	1.94×10^{-3}	1.63×10^{-3}	3.13×10^{-4}	64	3.31	1.52×10^{-2}	3.29
ccy15.3	1.25×10^{-5}	9.46×10^{-4}	7.35×10^{-4}	2.11×10^{-4}	59	1.78	1.02×10^{-2}	1.77
ccy15.4	1.25×10^{-5}	6.62×10^{-4}	4.90×10^{-4}	1.72×10^{-4}	39	1.20	8.33×10^{-3}	1.19
ccy16.3	2.53×10^{-5}	9.70×10^{-4}	7.56×10^{-4}	2.14×10^{-4}	30	1.57	1.04×10^{-2}	1.56
ccy15.5	1.25×10^{-5}	4.73×10^{-4}	3.32×10^{-4}	1.41×10^{-4}	27	8.15×10^{-1}	6.86×10^{-3}	8.08×10^{-1}
ccy16.4	2.53×10^{-5}	6.79×10^{-4}	5.05×10^{-4}	1.74×10^{-4}	20	1.06	8.46×10^{-3}	1.05
ccy15.6	1.25×10^{-5}	2.84×10^{-4}	1.80×10^{-4}	1.04×10^{-4}	14	4.37×10^{-1}	5.05×10^{-3}	4.32×10^{-1}
ccy16.5	2.53×10^{-5}	4.85×10^{-4}	3.42×10^{-4}	1.43×10^{-4}	13	7.05×10^{-1}	6.96×10^{-3}	6.98×10^{-1}
ccy16.6	2.53×10^{-5}	2.91×10^{-4}	1.85×10^{-4}	1.06×10^{-4}	7	3.71×10^{-1}	5.13×10^{-3}	3.66×10^{-1}

$k_{2,N} = 1.96 \times 10^3$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 48.5$ $M^{-1}s^{-1}$

$pK_B = 4.22$



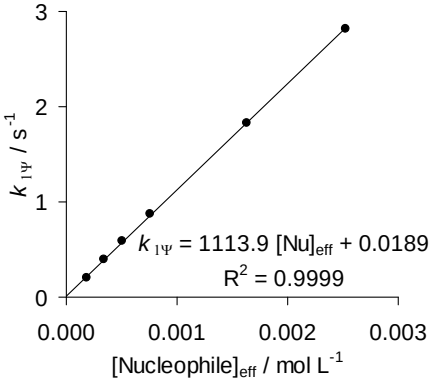
Reaction of glycine (**1a**) with $(thq)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 615 nm)

No.	$[(thq)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy17.1	1.58×10^{-5}	2.91×10^{-3}	2.52×10^{-3}	3.90×10^{-4}	160	2.83	9.20×10^{-3}	2.82
ccy17.2	1.58×10^{-5}	1.94×10^{-3}	1.63×10^{-3}	3.13×10^{-4}	103	1.84	7.39×10^{-3}	1.83
ccy17.3	1.58×10^{-5}	9.70×10^{-4}	7.56×10^{-4}	2.14×10^{-4}	48	0.881	5.04×10^{-3}	0.876
ccy17.4	1.58×10^{-5}	6.79×10^{-4}	5.05×10^{-4}	1.74×10^{-4}	32	0.592	4.12×10^{-3}	0.588
ccy17.5	1.58×10^{-5}	4.85×10^{-4}	3.42×10^{-4}	1.43×10^{-4}	22	0.402	3.39×10^{-3}	0.399
ccy17.6	1.58×10^{-5}	2.91×10^{-4}	1.85×10^{-4}	1.06×10^{-4}	12	0.211	2.49×10^{-3}	0.209

$k_{2,N} = 1.11 \times 10^3$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 23.6$ $M^{-1}s^{-1}$

$pK_B = 4.22$



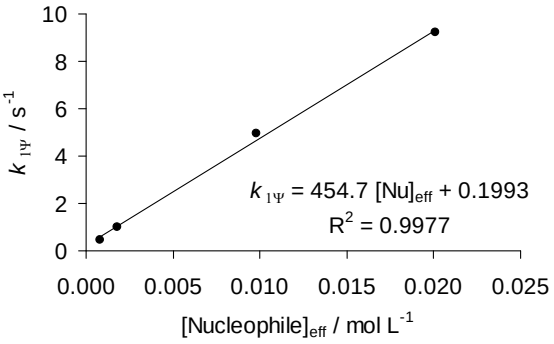
Reaction of glycine (**1a**) with $(ind)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.4 vol-% CH_3CN, stopped-flow, detection at 614 nm)

No.	$[(ind)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fb13.2	1.39×10^{-5}	2.12×10^{-2}	2.01×10^{-2}	1.10×10^{-3}	1446	9.22	1.19×10^{-2}	9.21
fb13.3	1.39×10^{-5}	1.06×10^{-2}	9.83×10^{-3}	7.70×10^{-4}	707	4.96	8.31×10^{-3}	4.95
fb13.4	1.39×10^{-5}	2.12×10^{-3}	1.79×10^{-3}	3.29×10^{-4}	129	9.88×10^{-1}	3.55×10^{-3}	9.84×10^{-1}
fb13.5	1.39×10^{-5}	1.06×10^{-3}	8.36×10^{-4}	2.24×10^{-4}	60	4.59×10^{-1}	2.42×10^{-3}	4.57×10^{-1}

$k_{2,N} = 4.55 \times 10^2$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 10.8$ $M^{-1}s^{-1}$

$pK_B = 4.22$



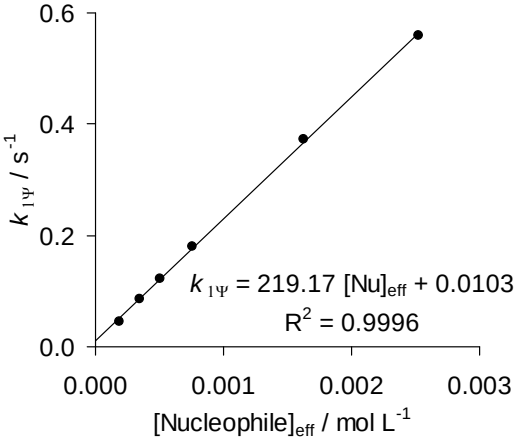
Reaction of glycine (**1a**) with $(jul)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 630 nm)

No.	$[(jul)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy18.1	1.26×10^{-5}	2.91×10^{-3}	2.52×10^{-3}	3.90×10^{-4}	200	0.560	1.34×10^{-3}	0.559
ccy18.2	1.26×10^{-5}	1.94×10^{-3}	1.63×10^{-3}	3.13×10^{-4}	129	0.373	1.08×10^{-3}	0.372
ccy18.3	1.26×10^{-5}	9.70×10^{-4}	7.56×10^{-4}	2.14×10^{-4}	60	0.180	7.34×10^{-4}	0.179
ccy18.4	1.26×10^{-5}	6.79×10^{-4}	5.05×10^{-4}	1.74×10^{-4}	40	0.123	6.00×10^{-4}	0.122
ccy18.5	1.26×10^{-5}	4.85×10^{-4}	3.42×10^{-4}	1.43×10^{-4}	27	8.52×10^{-2}	4.93×10^{-4}	8.47×10^{-2}
ccy18.6	1.26×10^{-5}	2.91×10^{-4}	1.85×10^{-4}	1.06×10^{-4}	15	4.62×10^{-2}	3.64×10^{-4}	4.58×10^{-2}

$k_{2,N} = 2.19 \times 10^2$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 3.44$ $M^{-1}s^{-1}$

$pK_B = 4.22$



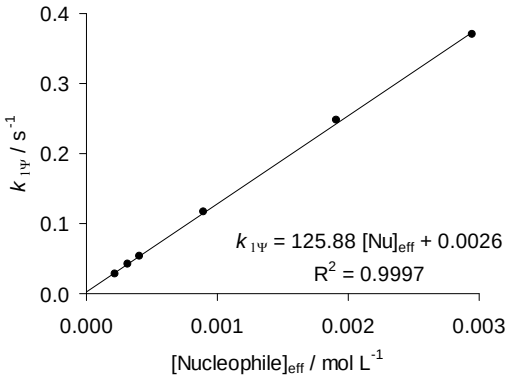
Reaction of glycine (**1a**) with $(lil)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.4 vol-% CH_3CN, stopped-flow, detection at 630 nm)

No.	$[(lil)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fb21.1	8.84×10^{-6}	3.37×10^{-3}	2.95×10^{-3}	4.22×10^{-4}	334	3.72×10^{-1}	9.10×10^{-4}	3.71×10^{-1}
fb21.2	8.84×10^{-6}	2.25×10^{-3}	1.91×10^{-3}	3.39×10^{-4}	216	2.48×10^{-1}	7.33×10^{-4}	2.47×10^{-1}
fb21.3	8.84×10^{-6}	1.13×10^{-3}	8.97×10^{-4}	2.33×10^{-4}	102	1.17×10^{-1}	5.02×10^{-4}	1.16×10^{-1}
fb21.4	8.84×10^{-6}	5.60×10^{-4}	4.04×10^{-4}	1.56×10^{-4}	46	5.35×10^{-2}	3.37×10^{-4}	5.32×10^{-2}
fb21.5	8.84×10^{-6}	4.50×10^{-4}	3.13×10^{-4}	1.37×10^{-4}	35	4.24×10^{-2}	2.97×10^{-4}	4.21×10^{-2}
fb21.6	8.84×10^{-6}	3.37×10^{-4}	2.21×10^{-4}	1.16×10^{-4}	25	2.88×10^{-2}	2.50×10^{-4}	2.86×10^{-2}

$k_{2,N} = 1.26 \times 10^2\ M^{-1}s^{-1}$

$k_{2,OH^-} = 2.16\ M^{-1}s^{-1}$

$pK_B = 4.22$

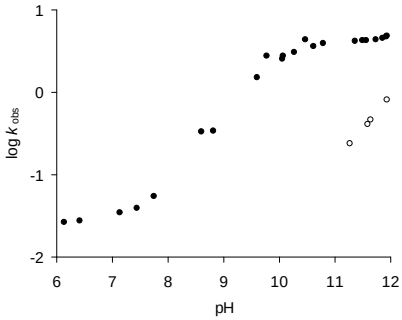


pH Dependance of rate constants for the reaction of glycine (**1a**) with $(dma)_2CH^+BF_4^-$ (phosphate buffer, at 20 °C, cosolvent: 0.5 vol % CH_3CN, stopped-flow, detection at 610 nm, pH measured, No. fn289 and fn298)

$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[PO_4^{3-}]$ / mol L^{-1}	$[HPO_4^{2-}]$ / mol L^{-1}	$[H_2PO_4^-]$ / mol L^{-1}	pH	k_{obs} / s^{-1}
3.36×10^{-5}		9.18×10^{-3}			11.93	8.18×10^{-1}
3.36×10^{-5}		4.59×10^{-3}	2.30×10^{-3}		11.64	4.64×10^{-1}
3.36×10^{-5}		4.59×10^{-3}	4.59×10^{-3}		11.58	4.09×10^{-1}
3.36×10^{-5}		2.30×10^{-3}	4.59×10^{-3}		11.27	2.40×10^{-1}
3.36×10^{-5}	9.05×10^{-4}	9.18×10^{-3}			11.93	4.80
3.36×10^{-5}	9.05×10^{-4}	9.18×10^{-3}	9.18×10^{-4}		11.92	4.78
3.36×10^{-5}	9.05×10^{-4}	9.18×10^{-3}	4.59×10^{-3}		11.85	4.56
3.36×10^{-5}	9.05×10^{-4}	9.18×10^{-3}	9.18×10^{-3}		11.73	4.33
4.09×10^{-5}	9.06×10^{-4}	4.55×10^{-3}	9.07×10^{-3}		11.56	4.24
3.36×10^{-5}	9.05×10^{-4}	4.59×10^{-3}	9.18×10^{-3}		11.49	4.27
4.09×10^{-5}	9.06×10^{-4}	2.73×10^{-3}	9.07×10^{-3}		11.36	4.18
3.36×10^{-5}	9.05×10^{-4}	9.18×10^{-4}	9.18×10^{-3}		10.79	3.92
4.09×10^{-5}	9.06×10^{-4}	4.55×10^{-4}	9.07×10^{-3}		10.62	3.62
4.09×10^{-5}	9.06×10^{-4}	9.09×10^{-4}	9.07×10^{-3}		10.46	4.39
4.09×10^{-5}	9.06×10^{-4}	9.09×10^{-5}	9.07×10^{-3}		10.26	3.07
4.09×10^{-5}	9.06×10^{-4}		9.07×10^{-3}		10.06	2.79
4.09×10^{-5}	9.06×10^{-4}		9.07×10^{-3}	$9.18\ 10^{-5}$	10.05	2.54
3.36×10^{-5}	9.05×10^{-4}		9.18×10^{-3}		9.78	2.77
4.09×10^{-5}	9.06×10^{-4}		9.07×10^{-3}	$4.59\ 10^{-4}$	9.60	1.50
4.09×10^{-5}	9.06×10^{-4}		9.07×10^{-3}	$9.18\ 10^{-4}$	8.81	3.39×10^{-1}
3.36×10^{-5}	9.05×10^{-4}		9.18×10^{-3}	$9.18\ 10^{-4}$	8.60	3.30×10^{-1}
4.09×10^{-5}	9.06×10^{-4}		9.07×10^{-3}	$2.75\ 10^{-3}$	7.75	5.45×10^{-2}
4.09×10^{-5}	9.06×10^{-4}		9.07×10^{-3}	$4.59\ 10^{-3}$	7.44	3.97×10^{-2}
3.36×10^{-5}	9.05×10^{-4}		9.18×10^{-3}	$9.18\ 10^{-3}$	7.14	3.44×10^{-2}
3.36×10^{-5}	9.05×10^{-4}		9.18×10^{-4}	$9.18\ 10^{-3}$	6.42	2.79×10^{-2}
3.36×10^{-5}	9.05×10^{-4}			$9.18\ 10^{-3}$	6.14	2.64×10^{-2}

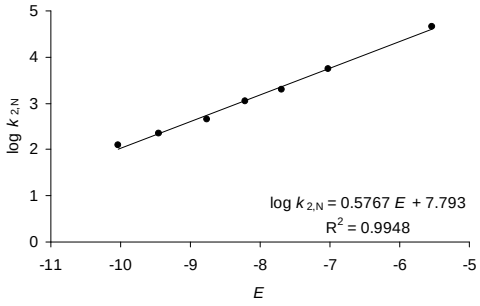
dots: with glycine

circles: without glycine



Reactivity parameters for glycine (1a) in water: *N* = 13.51; *s* = 0.58

Reference electrophile	*E* parameter	$k_{2,N}$(20°C) / M^{-1} s^{-1}
$(mor)_2CH^+$	-5.53	4.62×10^4
$(dma)_2CH^+$	-7.02	5.56×10^3
$(pyr)_2CH^+$	-7.69	1.96×10^3
$(thq)_2CH^+$	-8.22	1.11×10^3
$(ind)_2CH^+$	-8.76	4.55×10^2
$(jul)_2CH^+$	-9.45	2.19×10^2
$(lil)_2CH^+$	-10.04	1.26×10^2



3.7.3. Alanine (1b)

Rate constants in water

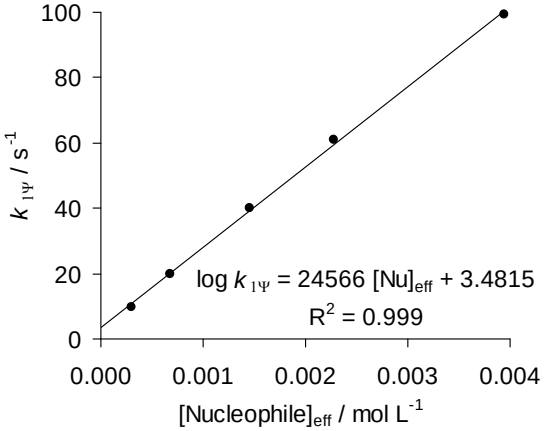
Reaction of alanine (**1b**) with $(mor)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 9 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(mor)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fb196.1	1.50×10^{-5}	4.49×10^{-3}	3.95×10^{-3}	5.41×10^{-4}	263	1.00×10^2	5.74×10^{-1}	99.4
fb196.2	1.50×10^{-5}	2.69×10^{-3}	2.28×10^{-3}	4.11×10^{-4}	152	61.5	4.36×10^{-1}	61.1
fb196.3	1.50×10^{-5}	1.79×10^{-3}	1.46×10^{-3}	3.29×10^{-4}	97	40.4	3.49×10^{-1}	40.1
fb196.4	1.50×10^{-5}	8.97×10^{-4}	6.74×10^{-4}	2.23×10^{-4}	45	20.1	2.37×10^{-1}	19.9
fb196.5	1.50×10^{-5}	4.49×10^{-4}	3.00×10^{-4}	1.49×10^{-4}	20	9.96	1.58×10^{-1}	9.80

$k_{2,N} = 2.46 \times 10^4$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 1060$ $M^{-1}s^{-1}$

$pK_B = 4.13$



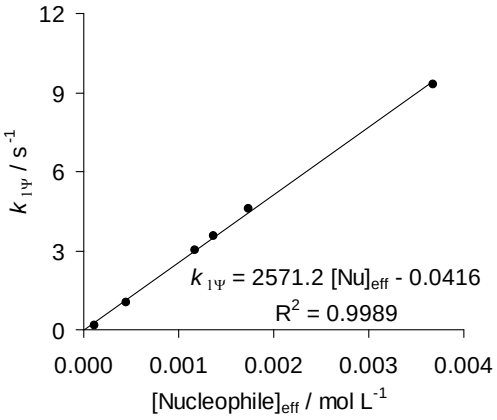
Reaction of alanine (**1b**) with $(dma)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.5 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy88.1	1.56×10^{-5}	4.20×10^{-3}	3.68×10^{-3}	5.22×10^{-4}	236	9.38	6.84×10^{-2}	9.31
ccy88.2	1.56×10^{-5}	2.10×10^{-3}	1.74×10^{-3}	3.59×10^{-4}	112	4.62	4.71×10^{-2}	4.57
ccy88.3	1.56×10^{-5}	1.68×10^{-3}	1.36×10^{-3}	3.18×10^{-4}	87	3.59	4.16×10^{-2}	3.55
ccy88.4	1.56×10^{-5}	1.47×10^{-3}	1.17×10^{-3}	2.95×10^{-4}	75	3.07	3.87×10^{-2}	3.03
ccy88.5	1.56×10^{-5}	6.30×10^{-4}	4.48×10^{-4}	1.82×10^{-4}	29	1.07	2.39×10^{-2}	1.05
ccy88.6	1.56×10^{-5}	2.10×10^{-4}	1.17×10^{-4}	9.31×10^{-5}	7	0.160	1.22×10^{-2}	0.148

$k_{2,N} = 2.57 \times 10^3\ M^{-1}s^{-1}$

$k_{2,OH^-} = 131\ M^{-1}s^{-1}$

$pK_B = 4.13$



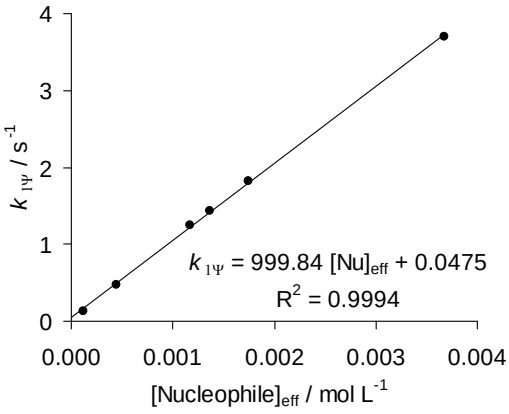
Reaction of alanine (**1b**) with $(pyr)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(pyr)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy86.1	1.56×10^{-5}	4.20×10^{-3}	3.68×10^{-3}	5.22×10^{-4}	236	3.72	2.53×10^{-2}	3.69
ccy86.2	1.56×10^{-5}	2.10×10^{-3}	1.74×10^{-3}	3.59×10^{-4}	112	1.84	1.74×10^{-2}	1.82
ccy86.3	1.56×10^{-5}	1.68×10^{-3}	1.36×10^{-3}	3.18×10^{-4}	87	1.45	1.54×10^{-2}	1.43
ccy86.4	1.56×10^{-5}	1.47×10^{-3}	1.17×10^{-3}	2.95×10^{-4}	75	1.26	1.43×10^{-2}	1.25
ccy86.5	1.56×10^{-5}	6.30×10^{-4}	4.48×10^{-4}	1.82×10^{-4}	29	0.489	8.84×10^{-3}	0.480
ccy86.6	1.56×10^{-5}	2.10×10^{-4}	1.17×10^{-4}	9.31×10^{-5}	7	0.131	4.52×10^{-3}	0.126

$k_{2,N} = 1.00 \times 10^3\ M^{-1}s^{-1}$

$k_{2,OH^-} = 48.5\ M^{-1}s^{-1}$

$pK_B = 4.13$



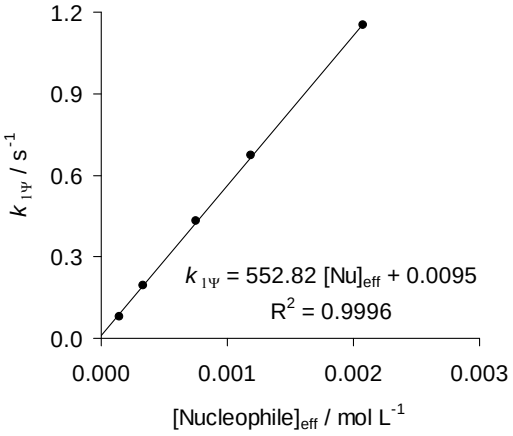
Reaction of alanine (**1b**) with $(thq)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.5 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(thq)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fb197.1	1.15×10^{-5}	2.47×10^{-3}	2.08×10^{-3}	3.92×10^{-4}	181	1.16	9.26×10^{-3}	1.15
fb197.2	1.15×10^{-5}	1.48×10^{-3}	1.18×10^{-3}	2.96×10^{-4}	103	6.80×10^{-1}	6.99×10^{-3}	6.73×10^{-1}
fb197.3	1.15×10^{-5}	9.87×10^{-4}	7.51×10^{-4}	2.36×10^{-4}	65	4.38×10^{-1}	5.57×10^{-3}	4.32×10^{-1}
fb197.4	1.15×10^{-5}	4.94×10^{-4}	3.36×10^{-4}	1.58×10^{-4}	29	1.99×10^{-1}	3.73×10^{-3}	1.95×10^{-1}
fb197.5	1.15×10^{-5}	2.47×10^{-4}	1.44×10^{-4}	1.03×10^{-4}	13	8.20×10^{-2}	2.44×10^{-3}	7.96×10^{-2}

$k_{2,N} = 5.53 \times 10^2$ M^{-1}s^{-1}

$k_{2,OH^-} = 23.6$ M^{-1}s^{-1}

p$K_B = 4.13$



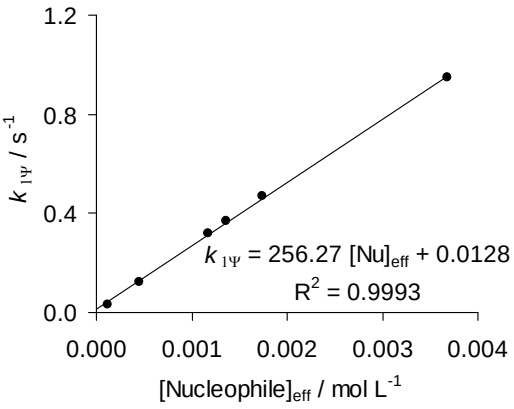
Reaction of alanine (**1b**) with $(ind)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(ind)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy87.1	1.56×10^{-5}	4.20×10^{-3}	3.68×10^{-3}	5.22×10^{-4}	236	0.953	5.64×10^{-3}	0.947
ccy87.2	1.56×10^{-5}	2.10×10^{-3}	1.74×10^{-3}	3.59×10^{-4}	112	0.473	3.88×10^{-3}	0.469
ccy87.3	1.56×10^{-5}	1.68×10^{-3}	1.36×10^{-3}	3.18×10^{-4}	87	0.371	3.43×10^{-3}	0.368
ccy87.4	1.56×10^{-5}	1.47×10^{-3}	1.17×10^{-3}	2.95×10^{-4}	75	0.323	3.19×10^{-3}	0.320
ccy87.5	1.56×10^{-5}	6.30×10^{-4}	4.48×10^{-4}	1.82×10^{-4}	29	0.125	1.97×10^{-3}	0.123
ccy87.6	1.56×10^{-5}	2.10×10^{-4}	1.17×10^{-4}	9.31×10^{-5}	7	3.45×10^{-2}	1.01×10^{-3}	3.35×10^{-2}

$k_{2,N} = 2.56 \times 10^2$ M^{-1}s^{-1}

$k_{2,OH^-} = 10.8$ M^{-1}s^{-1}

p$K_B = 4.13$



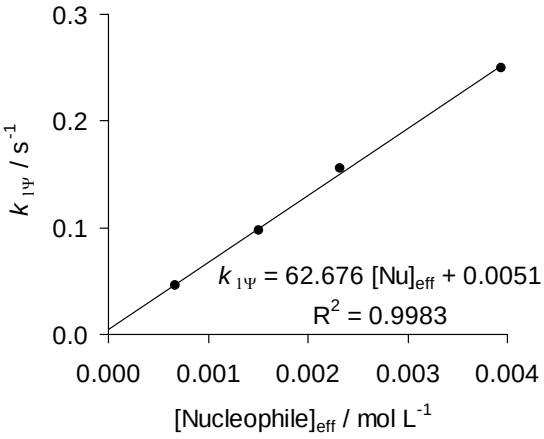
Reaction of alanine (**1b**) with $(lil)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, J&M, detection at 630 nm)

No.	$[(lil)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fb174.5	1.97×10^{-5}	4.48×10^{-3}	3.94×10^{-3}	5.40×10^{-4}	200	2.51×10^{-1}	1.17×10^{-3}	2.50×10^{-1}
fb174.4	2.01×10^{-5}	2.74×10^{-3}	2.32×10^{-3}	4.15×10^{-4}	116	1.57×10^{-1}	8.97×10^{-4}	1.56×10^{-1}
fb174.3	2.02×10^{-5}	1.84×10^{-3}	1.51×10^{-3}	3.34×10^{-4}	75	9.81×10^{-2}	7.22×10^{-4}	9.74×10^{-2}
fb174.2	1.97×10^{-5}	8.99×10^{-4}	6.75×10^{-4}	2.24×10^{-4}	34	4.68×10^{-2}	4.83×10^{-4}	4.63×10^{-2}

$k_{2,N} = 62.7\ M^{-1}s^{-1}$

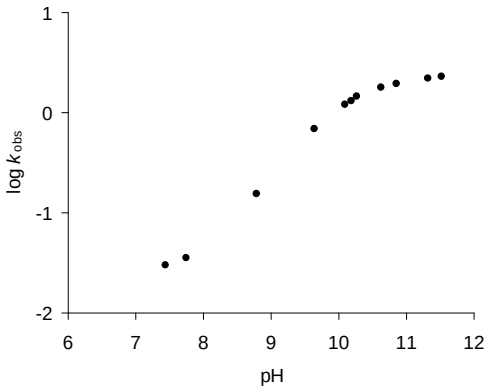
$k_{2,OH^-} = 2.16\ M^{-1}s^{-1}$

$pK_B = 4.13$



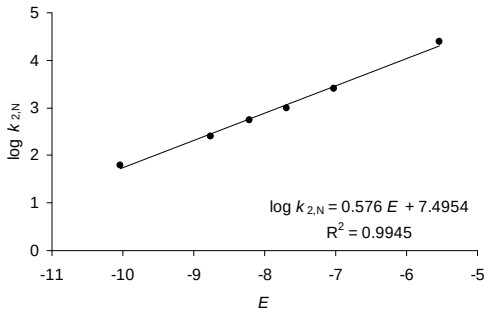
pH Dependance of rate constants for the reaction of alanine (**1b**) with $(dma)_2CH^+BF_4^-$ (phosphate buffer, at 20 °C, cosolvent: 0.5 vol % CH_3CN, stopped-flow, detection at 610 nm, pH measured, No. fn299)

$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[PO_4^{3-}]$ / mol L^{-1}	$[HPO_4^{2-}]$ / mol L^{-1}	$[H_2PO_4^-]$ / mol L^{-1}	pH	k_{obs} / s^{-1}
4.09×10^{-5}	9.09×10^{-4}	4.55×10^{-3}	9.98×10^{-3}		11.52	2.28
4.09×10^{-5}	9.09×10^{-4}	2.73×10^{-3}	9.98×10^{-3}		11.32	2.22
4.09×10^{-5}	9.09×10^{-4}	9.09×10^{-4}	9.98×10^{-3}		10.86	1.96
4.09×10^{-5}	9.09×10^{-4}	4.55×10^{-4}	9.98×10^{-3}		10.63	1.78
4.09×10^{-5}	9.09×10^{-4}	9.09×10^{-5}	9.98×10^{-3}		10.27	1.45
4.09×10^{-5}	9.09×10^{-4}		9.98×10^{-3}		10.18	1.32
4.09×10^{-5}	9.09×10^{-4}		9.98×10^{-3}	1.01×10^{-4}	10.09	1.21
4.09×10^{-5}	9.09×10^{-4}		9.98×10^{-3}	5.05×10^{-4}	9.64	6.86×10^{-1}
4.09×10^{-5}	9.09×10^{-4}		9.98×10^{-3}	1.01×10^{-3}	8.79	1.53×10^{-1}
4.09×10^{-5}	9.09×10^{-4}		9.98×10^{-3}	3.03×10^{-3}	7.74	3.58×10^{-2}
4.09×10^{-5}	9.09×10^{-4}		9.98×10^{-3}	5.05×10^{-3}	7.44	2.99×10^{-2}



Reactivity parameters for alanine (1b) in water: *N* = 13.01; *s* = 0.58

Reference electrophile	*E* parameter	$k_{2,N}$(20°C) / M^{-1} s^{-1}
$(mor)_2CH^+$	-5.53	2.46×10^4
$(dma)_2CH^+$	-7.02	2.57×10^3
$(pyr)_2CH^+$	-7.69	1.00×10^3
$(thq)_2CH^+$	-8.22	5.53×10^2
$(ind)_2CH^+$	-8.76	2.56×10^2
$(lil)_2CH^+$	-10.04	62.7



3.7.4. Valine (1c)

Rate constants in water

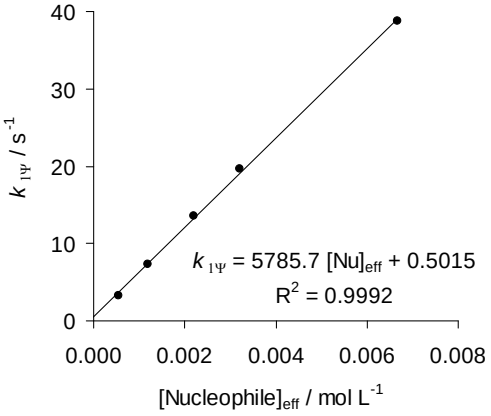
Reaction of valine (**1c**) with $(dma)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.5 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy163.1	5.95×10^{-5}	7.28×10^{-3}	6.67×10^{-3}	6.06×10^{-4}	112	38.9	7.93×10^{-2}	38.8
ccy163.2	5.95×10^{-5}	3.64×10^{-3}	3.22×10^{-3}	4.21×10^{-4}	54	19.7	5.51×10^{-2}	19.6
ccy163.3	5.95×10^{-5}	2.55×10^{-3}	2.20×10^{-3}	3.48×10^{-4}	37	13.6	4.56×10^{-2}	13.6
ccy163.4	5.95×10^{-5}	1.46×10^{-3}	1.20×10^{-3}	2.57×10^{-4}	20	7.38	3.37×10^{-2}	7.35
ccy163.5	5.95×10^{-5}	7.28×10^{-4}	5.54×10^{-4}	1.74×10^{-4}	9	3.31	2.28×10^{-2}	3.29

$k_{2,N} = 5.79 \times 10^3$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 131$ $M^{-1}s^{-1}$

$pK_B = 4.26$



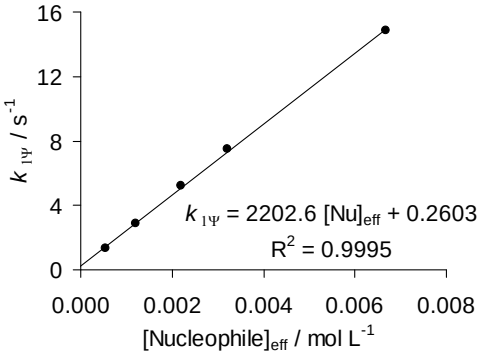
Reaction of valine (**1c**) with $(pyr)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.1 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(pyr)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy164.1	1.13×10^{-5}	7.28×10^{-3}	6.67×10^{-3}	6.06×10^{-4}	591	14.9	2.94×10^{-2}	14.9
ccy164.2	1.13×10^{-5}	3.64×10^{-3}	3.22×10^{-3}	4.21×10^{-4}	285	7.53	2.04×10^{-2}	7.51
ccy164.3	1.13×10^{-5}	2.55×10^{-3}	2.20×10^{-3}	3.48×10^{-4}	195	5.22	1.69×10^{-2}	5.20
ccy164.4	1.13×10^{-5}	1.46×10^{-3}	1.20×10^{-3}	2.57×10^{-4}	106	2.89	1.25×10^{-2}	2.88
ccy164.5	1.13×10^{-5}	7.28×10^{-4}	5.54×10^{-4}	1.74×10^{-4}	49	1.36	8.46×10^{-3}	1.35

$k_{2,N} = 2.20 \times 10^3\ M^{-1}s^{-1}$

$k_{2,OH^-} = 48.5\ M^{-1}s^{-1}$

$pK_B = 4.26$



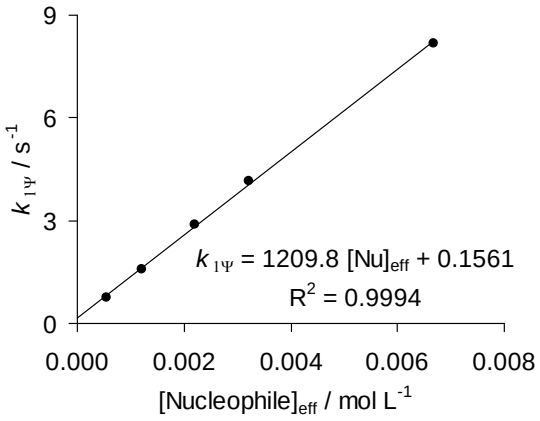
Reaction of valine (**1c**) with $(thq)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.4 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(thq)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy165.1	3.14×10^{-5}	7.28×10^{-3}	6.67×10^{-3}	6.06×10^{-4}	213	8.19	1.43×10^{-2}	8.18
ccy165.2	3.14×10^{-5}	3.64×10^{-3}	3.22×10^{-3}	4.21×10^{-4}	103	4.16	9.93×10^{-3}	4.15
ccy165.3	3.14×10^{-5}	2.55×10^{-3}	2.20×10^{-3}	3.48×10^{-4}	70	2.88	8.21×10^{-3}	2.87
ccy165.4	3.14×10^{-5}	1.46×10^{-3}	1.20×10^{-3}	2.57×10^{-4}	38	1.60	6.07×10^{-3}	1.59
ccy165.5	3.14×10^{-5}	7.28×10^{-4}	5.54×10^{-4}	1.74×10^{-4}	18	0.752	4.12×10^{-3}	0.748

$k_{2,N} = 1.21 \times 10^3\ M^{-1}s^{-1}$

$k_{2,OH^-} = 23.6\ M^{-1}s^{-1}$

$pK_B = 4.26$



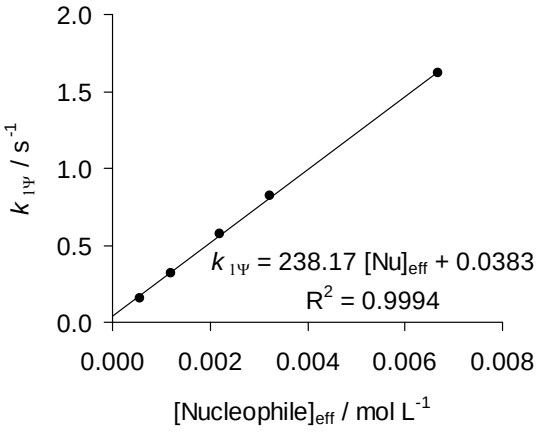
Reaction of valine (**1c**) with $(jul)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 634 nm)

No.	$[(jul)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy166.1	3.14×10^{-5}	7.28×10^{-3}	6.67×10^{-3}	6.06×10^{-4}	213	1.62	2.08×10^{-3}	1.62
ccy166.2	3.14×10^{-5}	3.64×10^{-3}	3.22×10^{-3}	4.21×10^{-4}	103	0.823	1.45×10^{-3}	0.822
ccy166.3	3.14×10^{-5}	2.55×10^{-3}	2.20×10^{-3}	3.48×10^{-4}	70	0.576	1.20×10^{-3}	0.575
ccy166.4	3.14×10^{-5}	1.46×10^{-3}	1.20×10^{-3}	2.57×10^{-4}	38	0.322	8.84×10^{-4}	0.321
ccy166.5	3.14×10^{-5}	7.28×10^{-4}	5.54×10^{-4}	1.74×10^{-4}	18	0.156	6.00×10^{-4}	0.155

$k_{2,N} = 2.38 \times 10^2\ M^{-1}s^{-1}$

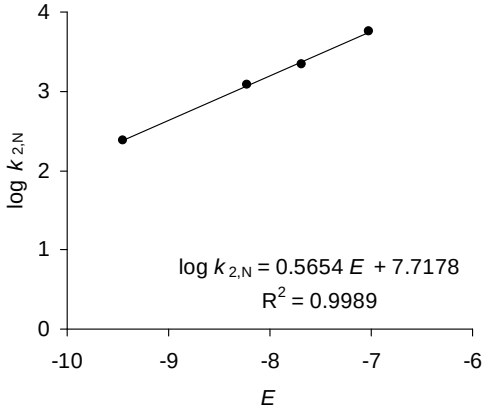
$k_{2,OH^-} = 3.44\ M^{-1}s^{-1}$

$pK_B = 4.26$



Reactivity parameters for valine (1c) in water: *N* = 13.65; *s* = 0.57

Reference electrophile	*E* parameter	$k_{2,N}$(20°C) / M^{-1} s^{-1}
$(dma)_2CH^+$	-7.02	5.79×10^3
$(pyr)_2CH^+$	-7.69	2.20×10^3
$(thq)_2CH^+$	-8.22	1.21×10^3
$(jul)_2CH^+$	-9.45	2.38×10^2



3.7.5. Leucine (1d)

Rate constants in water

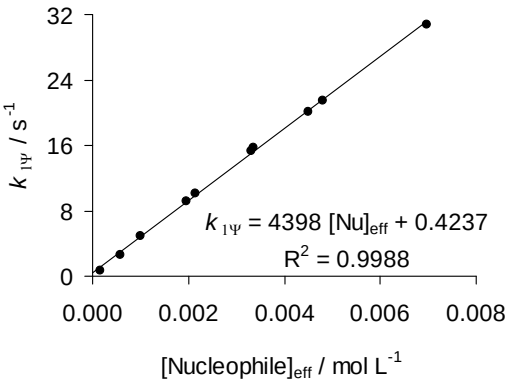
Reaction of leucine (**1d**) with $(dma)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.5 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fb378.1	2.32×10^{-5}	5.00×10^{-3}	4.50×10^{-3}	4.97×10^{-4}	194	20.2	6.52×10^{-2}	20.1
fb378.2	2.32×10^{-5}	3.75×10^{-3}	3.32×10^{-3}	4.27×10^{-4}	143	15.4	5.60×10^{-2}	15.3
ccy171.1	5.95×10^{-5}	7.60×10^{-3}	6.98×10^{-3}	6.19×10^{-4}	117	30.8	8.11×10^{-2}	30.7
fb378.3	2.32×10^{-5}	2.50×10^{-3}	2.16×10^{-3}	3.44×10^{-4}	93	10.2	4.51×10^{-2}	10.2
ccy171.2	5.95×10^{-5}	5.32×10^{-3}	4.81×10^{-3}	5.14×10^{-4}	81	21.6	6.73×10^{-2}	21.5
ccy171.3	5.95×10^{-5}	3.80×10^{-3}	3.37×10^{-3}	4.30×10^{-4}	57	15.8	5.64×10^{-2}	15.7
fb378.4	2.32×10^{-5}	1.25×10^{-3}	1.01×10^{-3}	2.36×10^{-4}	44	4.98	3.09×10^{-2}	4.95
ccy171.4	5.95×10^{-5}	2.28×10^{-3}	1.95×10^{-3}	3.28×10^{-4}	33	9.23	4.29×10^{-2}	9.19
ccy171.5	5.95×10^{-5}	7.60×10^{-4}	5.81×10^{-4}	1.79×10^{-4}	10	2.63	2.34×10^{-2}	2.61
fb378.5	2.32×10^{-5}	2.50×10^{-4}	1.57×10^{-4}	9.29×10^{-5}	7	7.25 10^{-1}	1.22×10^{-2}	7.13×10^{-1}

$k_{2,N} = 4.40 \times 10^3$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 131$ $M^{-1}s^{-1}$

$pK_B = 4.26$



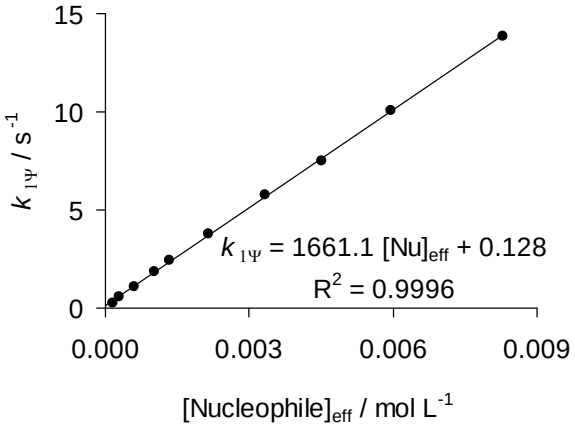
Reaction of leucine (**1d**) with $(pyr)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.3 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(pyr)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy168.1	1.13×10^{-5}	8.98×10^{-3}	8.30×10^{-3}	6.76×10^{-4}	735	13.9	3.28×10^{-2}	13.9
ccy168.2	1.13×10^{-5}	6.53×10^{-3}	5.96×10^{-3}	5.72×10^{-4}	527	10.1	2.78×10^{-2}	10.1
fb379.1	1.56×10^{-5}	5.00×10^{-3}	4.50×10^{-3}	4.97×10^{-4}	289	7.53	2.41×10^{-2}	7.51
fb379.2	1.56×10^{-5}	3.75×10^{-3}	3.32×10^{-3}	4.27×10^{-4}	213	5.77	2.07×10^{-2}	5.75
fb379.3	1.56×10^{-5}	2.50×10^{-3}	2.16×10^{-3}	3.44×10^{-4}	138	3.79	1.67×10^{-2}	3.77
ccy168.3	1.13×10^{-5}	1.60×10^{-3}	1.33×10^{-3}	2.70×10^{-4}	118	2.48	1.31×10^{-2}	2.47
fb379.4	1.56×10^{-5}	1.25×10^{-3}	1.01×10^{-3}	2.36×10^{-4}	65	1.85	1.14×10^{-2}	1.84
ccy168.4	1.13×10^{-5}	7.93×10^{-4}	6.10×10^{-4}	1.83×10^{-4}	54	1.13	8.88×10^{-3}	1.12
ccy168.5	1.13×10^{-5}	4.12×10^{-4}	2.87×10^{-4}	1.25×10^{-4}	25	5.54×10^{-1}	6.09×10^{-3}	5.48×10^{-1}
fb379.5	1.56×10^{-5}	2.50×10^{-4}	1.57×10^{-4}	9.29×10^{-5}	10	2.55×10^{-1}	4.51×10^{-3}	2.50×10^{-1}

$k_{2,N} = 1.66 \times 10^3\ M^{-1}s^{-1}$

$k_{2,OH^-} = 48.5\ M^{-1}s^{-1}$

$pK_B = 4.26$



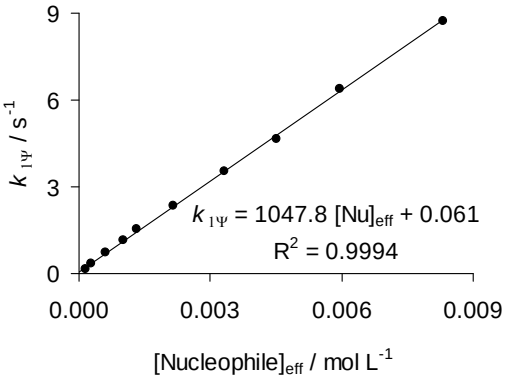
Reaction of leucine (**1d**) with $(thq)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.4 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(thq)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi, OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy169.1	3.14×10^{-5}	8.98×10^{-3}	8.30×10^{-3}	6.76×10^{-4}	264	8.76	1.59×10^{-2}	8.74
ccy169.2	3.14×10^{-5}	6.53×10^{-3}	5.96×10^{-3}	5.72×10^{-4}	190	6.41	1.35×10^{-2}	6.40
fb380.1	3.70×10^{-5}	5.00×10^{-3}	4.50×10^{-3}	4.97×10^{-4}	122	4.66	1.17×10^{-2}	4.65
fb380.2	3.70×10^{-5}	3.75×10^{-3}	3.32×10^{-3}	4.27×10^{-4}	90	3.56	1.01×10^{-2}	3.55
fb380.3	3.70×10^{-5}	2.50×10^{-3}	2.16×10^{-3}	3.44×10^{-4}	58	2.34	8.12×10^{-3}	2.33
ccy169.3	3.14×10^{-5}	1.60×10^{-3}	1.33×10^{-3}	2.70×10^{-4}	42	1.56	6.38×10^{-3}	1.55
fb380.4	3.70×10^{-5}	1.25×10^{-3}	1.01×10^{-3}	2.36×10^{-4}	27	1.15	5.57×10^{-3}	1.14
ccy169.4	3.14×10^{-5}	7.93×10^{-4}	6.10×10^{-4}	1.83×10^{-4}	19	7.16×10^{-1}	4.32×10^{-3}	7.12×10^{-1}
ccy169.5	3.14×10^{-5}	4.12×10^{-4}	2.87×10^{-4}	1.25×10^{-4}	9	3.46×10^{-1}	2.96×10^{-3}	3.43×10^{-1}
fb380.5	3.70×10^{-5}	2.50×10^{-4}	1.57×10^{-4}	9.29×10^{-5}	4	1.52×10^{-1}	2.19×10^{-3}	1.50×10^{-1}

$k_{2,N} = 1.05 \times 10^3$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 23.6$ $M^{-1}s^{-1}$

$pK_B = 4.26$



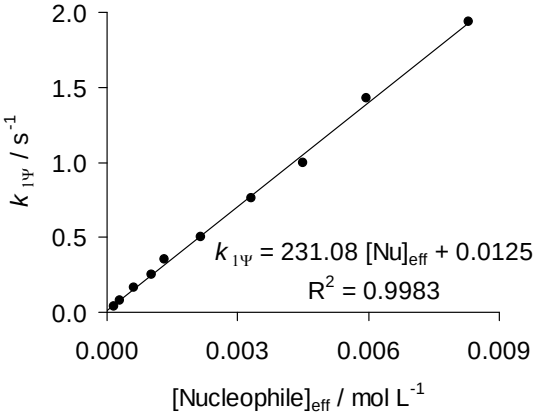
Reaction of leucine (**1d**) with $(jul)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 1.0 vol-% CH_3CN, stopped-flow, detection at 630 nm)

No.	$[(jul)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi, OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy170.1	8.55×10^{-6}	8.98×10^{-3}	8.30×10^{-3}	6.76×10^{-4}	971	1.94	2.32×10^{-3}	1.94
ccy170.2	8.55×10^{-6}	$6.53\ 10^{-3}$	5.96×10^{-3}	5.72×10^{-4}	697	1.43	1.97×10^{-3}	1.43
fb381.1	1.69×10^{-5}	5.00×10^{-3}	4.50×10^{-3}	4.97×10^{-4}	266	1.00	1.71×10^{-3}	9.98×10^{-1}
fb381.2	1.69×10^{-5}	3.75×10^{-3}	3.32×10^{-3}	4.27×10^{-4}	197	7.60×10^{-1}	1.47×10^{-3}	7.59×10^{-1}
ccy170.3	8.55×10^{-6}	1.60×10^{-3}	1.33×10^{-3}	2.70×10^{-4}	156	3.51×10^{-1}	9.30×10^{-4}	3.50×10^{-1}
fb381.3	1.69×10^{-5}	2.50×10^{-3}	2.16×10^{-3}	3.44×10^{-4}	128	5.06×10^{-1}	1.18×10^{-3}	5.05×10^{-1}
ccy170.4	8.55×10^{-6}	7.93×10^{-4}	6.10×10^{-4}	1.83×10^{-4}	71	1.63×10^{-1}	6.30×10^{-4}	1.62×10^{-1}
fb381.4	1.69×10^{-5}	1.25×10^{-3}	1.01×10^{-3}	2.36×10^{-4}	60	2.51×10^{-1}	8.12×10^{-4}	2.50×10^{-1}
ccy170.5	8.55×10^{-6}	4.12×10^{-4}	2.87×10^{-4}	1.25×10^{-4}	34	8.25×10^{-2}	4.32×10^{-4}	8.21×10^{-2}
fb381.5	1.69×10^{-5}	2.50×10^{-4}	1.57×10^{-4}	9.29×10^{-5}	9	4.06×10^{-2}	3.20×10^{-4}	4.03×10^{-2}

$k_{2,N} = 2.31 \times 10^2\ M^{-1}s^{-1}$

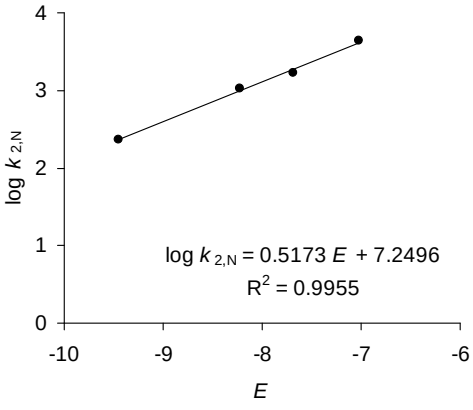
$k_{2,OH^-} = 3.44\ M^{-1}s^{-1}$

$pK_B = 4.26$



Reactivity parameters for leucine (1d) in water: *N* = 14.01; *s* = 0.52

Reference electrophile	*E* parameter	$k_{2,N}$(20°C) / M^{-1} s^{-1}
$(dma)_2CH^+$	-7.02	4.40×10^3
$(pyr)_2CH^+$	-7.69	1.66×10^3
$(thq)_2CH^+$	-8.22	1.05×10^3
$(jul)_2CH^+$	-9.45	2.31×10^2



3.7.6. Phenylalanine (1e)

Rate constants in water

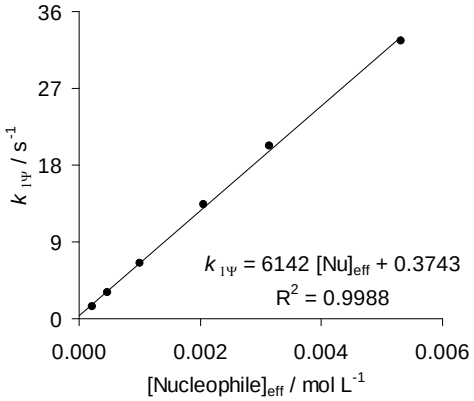
Reaction of phenylalanine (**1e**) with $(dma)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fn272.1	1.12×10^{-5}	5.60×10^{-3}	5.32×10^{-3}	2.84×10^{-4}	475	32.6	3.72×10^{-2}	32.6
fn272.2	1.12×10^{-5}	3.36×10^{-3}	3.14×10^{-3}	2.18×10^{-4}	281	20.3	2.86×10^{-2}	20.3
fn272.3	1.12×10^{-5}	2.24×10^{-3}	2.06×10^{-3}	1.77×10^{-4}	184	13.4	2.31×10^{-2}	13.4
fn272.4	1.12×10^{-5}	1.12×10^{-3}	9.97×10^{-4}	1.23×10^{-4}	89	6.58	1.61×10^{-2}	6.56
fn272.5	1.12×10^{-5}	5.60×10^{-4}	4.75×10^{-4}	8.48×10^{-5}	42	3.14	1.11×10^{-2}	3.13
fn272.6	1.12×10^{-5}	2.80×10^{-4}	2.22×10^{-4}	5.80×10^{-5}	20	1.38	7.59×10^{-3}	1.37

$k_{2,N} = 6.14 \times 10^3\ M^{-1}s^{-1}$

$k_{2,OH^-} = 131\ M^{-1}s^{-1}$

$pK_B = 4.82$



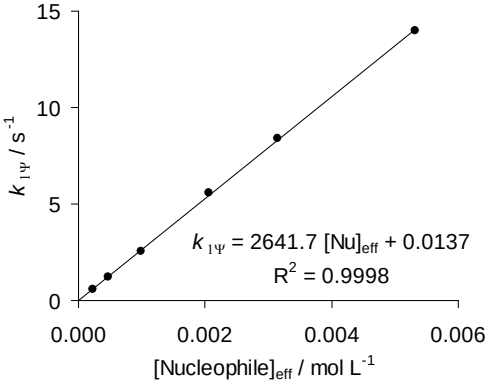
Reaction of phenylalanine (**1e**) with $(pyr)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(pyr)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fn271.1	6.02×10^{-6}	5.60×10^{-3}	5.32×10^{-3}	2.84×10^{-4}	883	13.7	1.38×10^{-2}	13.7
fn271.2	6.02×10^{-6}	3.36×10^{-3}	3.14×10^{-3}	2.18×10^{-4}	522	8.40	1.06×10^{-2}	8.39
fn271.3	6.02×10^{-6}	2.24×10^{-3}	2.06×10^{-3}	1.77×10^{-4}	343	5.59	8.57×10^{-3}	5.58
fn271.4	6.02×10^{-6}	1.12×10^{-3}	9.97×10^{-4}	1.23×10^{-4}	166	2.57	5.96×10^{-3}	2.56
fn271.5	6.02×10^{-6}	5.60×10^{-4}	4.75×10^{-4}	8.48×10^{-5}	79	1.25	4.11×10^{-3}	1.25
fn271.6	6.02×10^{-6}	2.80×10^{-4}	2.22×10^{-4}	5.80×10^{-5}	37	5.89×10^{-1}	2.81×10^{-3}	5.86×10^{-1}

$k_{2,N} = 2.64 \times 10^3\ M^{-1}s^{-1}$

$k_{2,OH^-} = 48.5\ M^{-1}s^{-1}$

$pK_B = 4.82$



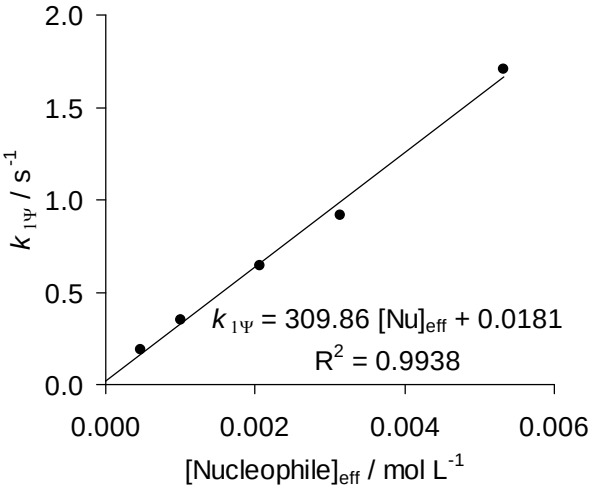
Reaction of phenylalanine (**1e**) with $(jul)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.4 vol-% CH_3CN, stopped-flow, detection at 634 nm)

No.	$[(jul)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fn273.1	2.37×10^{-5}	5.60×10^{-3}	5.32×10^{-3}	2.84×10^{-4}	224	1.71	9.76×10^{-4}	1.71
fn273.2	2.37×10^{-5}	3.36×10^{-3}	3.14×10^{-3}	2.18×10^{-4}	133	9.16×10^{-1}	7.50×10^{-4}	9.15×10^{-1}
fn273.3	2.37×10^{-5}	2.24×10^{-3}	2.06×10^{-3}	1.77×10^{-4}	87	6.47×10^{-1}	6.08×10^{-4}	6.46×10^{-1}
fn273.4	2.37×10^{-5}	1.12×10^{-3}	9.97×10^{-4}	1.23×10^{-4}	42	3.47×10^{-1}	4.23×10^{-4}	3.47×10^{-1}
fn273.5	2.37×10^{-5}	5.60×10^{-4}	4.75×10^{-4}	8.48×10^{-5}	20	1.90×10^{-1}	2.92×10^{-4}	1.90×10^{-1}

$k_{2,N} = 3.10 \times 10^2\ M^{-1}s^{-1}$

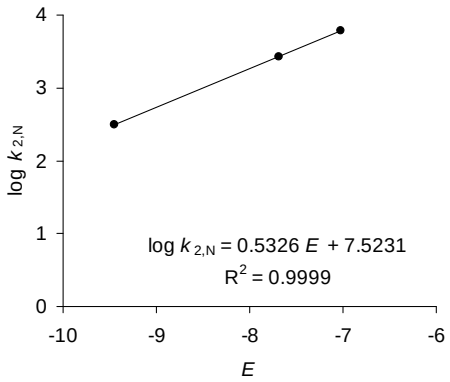
$k_{2,OH^-} = 3.44\ M^{-1}s^{-1}$

$pK_B = 4.82$



Reactivity parameters for phenylalanine (1e) in water: *N* = 14.12; *s* = 0.53

Reference electrophile	*E* parameter	$k_{2,N}$(20°C) / M^{-1} s^{-1}
$(dma)_2CH^+$	-7.02	6.14×10^3
$(pyr)_2CH^+$	-7.69	2.64×10^3
$(jul)_2CH^+$	-9.45	3.10×10^2



3.7.7. Proline (1f)

Rate constants in water

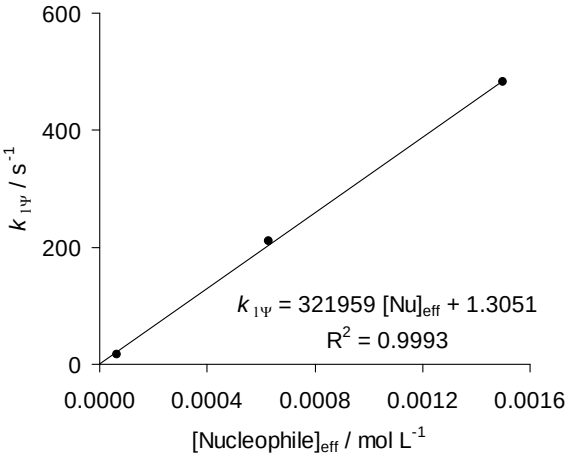
Reaction of proline (**1f**) with $(dma)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.3 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fb382.3	1.16×10^{-5}	2.32×10^{-3}	1.50×10^{-3}	8.19×10^{-4}	129	4.82×10^{2}	1.07×10^{-1}	4.82×10^{2}
fb382.4	1.16×10^{-5}	1.16×10^{-3}	6.30×10^{-4}	5.30×10^{-4}	54	2.11×10^{2}	6.95×10^{-2}	2.11×10^{2}
fb382.5	1.16×10^{-5}	2.32×10^{-4}	6.35×10^{-5}	1.68×10^{-4}	5	17.6	2.21×10^{-2}	17.6

$k_{2,N} = 3.22 \times 10^5\ M^{-1}s^{-1}$

$k_{2,OH^-} = 131\ M^{-1}s^{-1}$

$pK_B = 3.35$



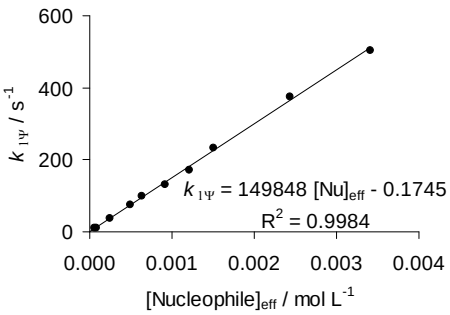
Reaction of proline (**1f**) with $(pyr)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.3 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(pyr)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fb383.1	1.57×10^{-5}	4.64×10^{-3}	3.41×10^{-3}	1.23×10^{-3}	217	5.03×10^{2}	5.98×10^{-2}	5.03×10^{2}
fb383.2	1.57×10^{-5}	3.48×10^{-3}	2.44×10^{-3}	1.04×10^{-3}	155	3.76×10^{2}	5.06×10^{-2}	3.76×10^{2}
fb383.3	1.57×10^{-5}	2.32×10^{-3}	1.50×10^{-3}	8.19×10^{-4}	96	2.33×10^{2}	3.97×10^{-2}	2.33×10^{2}
ccy4.1	1.25×10^{-5}	1.94×10^{-3}	1.21×10^{-3}	7.34×10^{-4}	96	1.71×10^{2}	3.56×10^{-2}	1.71×10^{2}
ccy4.2	1.25×10^{-5}	1.55×10^{-3}	9.12×10^{-4}	6.38×10^{-4}	73	1.31×10^{2}	3.10×10^{-2}	1.31×10^{2}
fb383.4	1.57×10^{-5}	1.16×10^{-3}	6.30×10^{-4}	5.30×10^{-4}	40	99.2	2.57×10^{-2}	99.2
ccy4.3	1.25×10^{-5}	9.71×10^{-4}	4.99×10^{-4}	4.72×10^{-4}	40	73.7	2.29×10^{-2}	73.7
ccy4.4	1.25×10^{-5}	5.83×10^{-4}	2.49×10^{-4}	3.34×10^{-4}	20	36.4	1.62×10^{-2}	36.4
ccy4.5	1.25×10^{-5}	2.72×10^{-4}	8.14×10^{-5}	1.91×10^{-4}	7	11.4	9.25×10^{-3}	11.4
fb383.5	1.57×10^{-5}	2.32×10^{-4}	6.35×10^{-5}	1.68×10^{-4}	4	9.92	8.17×10^{-3}	9.91

$k_{2,N} = 1.50 \times 10^5$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 48.5$ $M^{-1}s^{-1}$

$pK_B = 3.35$



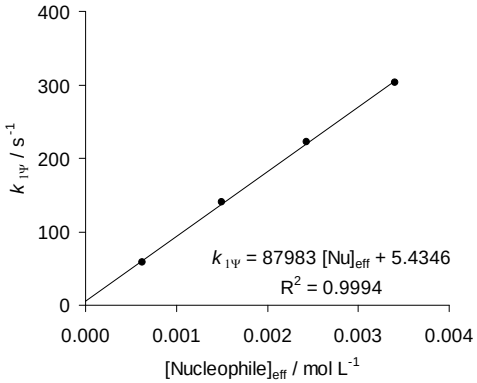
Reaction of proline (**1f**) with $(thq)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.5 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(thq)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi, OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fb384.1	3.70×10^{-5}	4.64×10^{-3}	3.41×10^{-3}	1.23×10^{-3}	92	3.03×10^{2}	2.91×10^{-2}	3.03×10^{2}
fb384.2	3.70×10^{-5}	3.48×10^{-3}	2.44×10^{-3}	1.04×10^{-3}	66	2.22×10^{2}	2.46×10^{-2}	2.22×10^{2}
fb384.3	3.70×10^{-5}	2.32×10^{-3}	1.50×10^{-3}	8.19×10^{-4}	41	1.40×10^{2}	1.93×10^{-2}	1.40×10^{2}
fb384.4	3.70×10^{-5}	1.16×10^{-3}	6.30×10^{-4}	5.30×10^{-4}	17	58.4	1.25×10^{-2}	58.4

$k_{2,N} = 8.80 \times 10^4$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 23.6$ $M^{-1}s^{-1}$

$pK_B = 3.35$



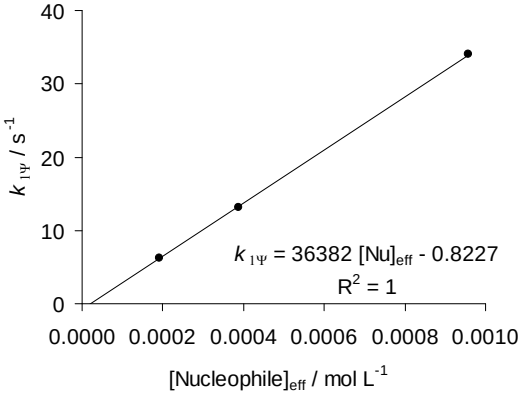
Reaction of proline (**1f**) with $(ind)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.4 vol-% CH_3CN, stopped-flow, detection at 608 nm)

No.	$[(ind)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi, OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fb104.2	1.76×10^{-5}	1.61×10^{-3}	9.56×10^{-4}	6.54×10^{-4}	54	34.0	7.06×10^{-3}	34.0
fb104.3	1.76×10^{-5}	8.04×10^{-4}	3.88×10^{-4}	4.16×10^{-4}	22	13.2	4.49×10^{-3}	13.2
fb104.4	1.76×10^{-5}	4.82×10^{-4}	1.90×10^{-4}	2.92×10^{-4}	11	6.17	3.15×10^{-3}	6.17

$k_{2,N} = 3.64 \times 10^4$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 10.8$ $M^{-1}s^{-1}$

$pK_B = 3.35$



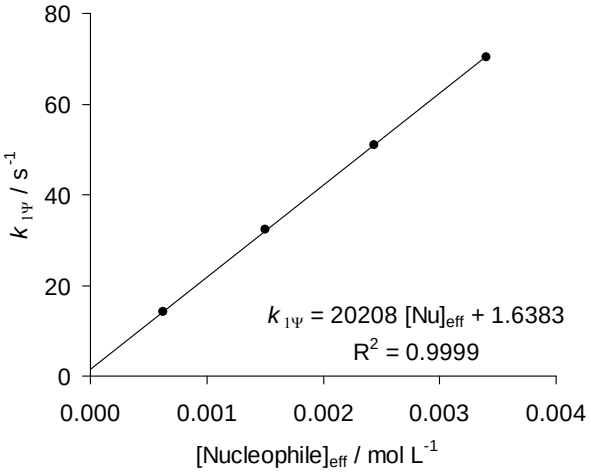
Reaction of proline (**1f**) with $(jul)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 1.0 vol-% CH_3CN, stopped-flow, detection at 630 nm)

No.	$[(jul)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi, OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fb385.1	1.69×10^{-5}	4.64×10^{-3}	3.41×10^{-3}	1.23×10^{-3}	202	70.3	4.24×10^{-3}	70.3
fb385.2	1.69×10^{-5}	3.48×10^{-3}	2.44×10^{-3}	1.04×10^{-3}	144	51.0	3.59×10^{-3}	51.0
fb385.3	1.69×10^{-5}	2.32×10^{-3}	1.50×10^{-3}	8.19×10^{-4}	89	32.3	2.82×10^{-3}	32.3
fb385.4	1.69×10^{-5}	1.16×10^{-3}	6.30×10^{-4}	5.30×10^{-4}	37	14.1	1.82×10^{-3}	14.1

$k_{2,N} = 2.02 \times 10^4$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 3.44$ $M^{-1}s^{-1}$

$pK_B = 3.35$



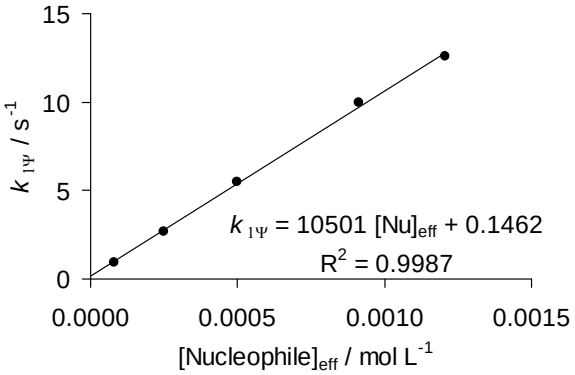
Reaction of proline (**1f**) with $(lil)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 620 nm)

No.	$[(lil)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi, OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy3.1	1.32×10^{-5}	1.94×10^{-3}	1.21×10^{-3}	7.34×10^{-4}	91	12.6	1.59×10^{-3}	12.6
ccy3.2	1.32×10^{-5}	1.55×10^{-3}	9.12×10^{-4}	6.38×10^{-4}	69	9.98	1.38×10^{-3}	9.98
ccy3.3	1.32×10^{-5}	9.71×10^{-4}	4.99×10^{-4}	4.72×10^{-4}	38	5.47	1.02×10^{-3}	5.47
ccy3.4	1.32×10^{-5}	5.83×10^{-4}	2.49×10^{-4}	3.34×10^{-4}	19	2.71	7.21×10^{-4}	2.71
ccy3.5	1.32×10^{-5}	2.72×10^{-4}	8.14×10^{-5}	1.91×10^{-4}	6	9.28×10^{-1}	4.12×10^{-4}	9.28×10^{-1}

$k_{2,N} = 1.05 \times 10^4$ $M^{-1}s^{-1}$

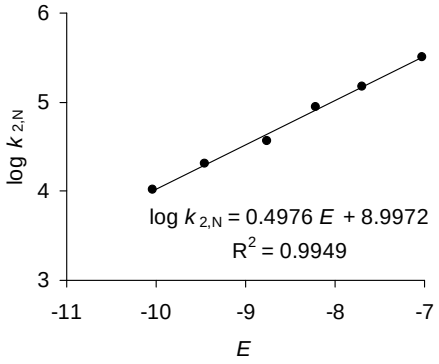
$k_{2,OH^-} = 2.16$ $M^{-1}s^{-1}$

$pK_B = 3.35$



Reactivity parameters for proline (1f) in water: *N* = 18.08; *s* = 0.50

Reference electrophile	*E* parameter	$k_{2,N}$(20°C) / M^{-1} s^{-1}
$(dma)_2CH^+$	-7.02	3.22×10^5
$(pyr)_2CH^+$	-7.69	1.50×10^5
$(thq)_2CH^+$	-8.22	8.80×10^4
$(ind)_2CH^+$	-8.76	3.64×10^4
$(jul)_2CH^+$	-9.45	2.02×10^4
$(lil)_2CH^+$	-10.04	1.05×10^4



3.7.8. Serine (1g)

Rate constants in water

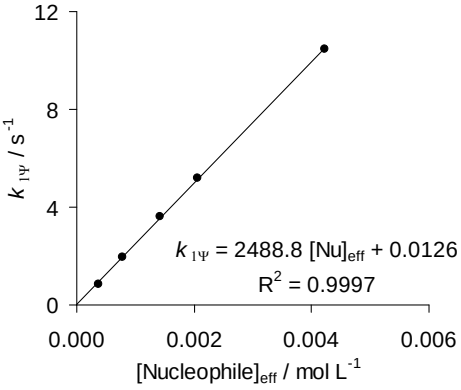
Reaction of serine (**1g**) with $(dma)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.5 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy125.1	5.95×10^{-5}	4.48×10^{-3}	4.22×10^{-3}	2.62×10^{-4}	71	10.5	3.43×10^{-2}	10.5
ccy125.2	5.95×10^{-5}	2.24×10^{-3}	2.06×10^{-3}	1.83×10^{-4}	35	5.23	2.39×10^{-2}	5.21
ccy125.3	5.95×10^{-5}	1.57×10^{-3}	1.42×10^{-3}	1.52×10^{-4}	24	3.62	1.99×10^{-2}	3.60
ccy125.4	5.95×10^{-5}	8.96×10^{-4}	7.83×10^{-4}	1.13×10^{-4}	13	1.96	1.48×10^{-2}	1.95
ccy125.5	5.95×10^{-5}	4.48×10^{-4}	3.70×10^{-4}	7.75×10^{-5}	6	0.877	1.02×10^{-2}	0.867

$k_{2,N} = 2.49 \times 10^3$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 131$ $M^{-1}s^{-1}$

$pK_B = 4.79$



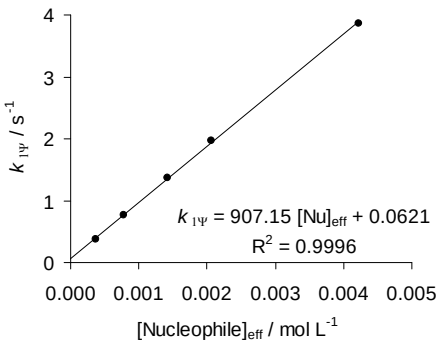
Reaction of serine (**1g**) with $(pyr)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(pyr)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy126.1	2.12×10^{-5}	4.48×10^{-3}	4.22×10^{-3}	2.62×10^{-4}	199	3.88	1.27×10^{-2}	3.87
ccy126.2	2.12×10^{-5}	2.24×10^{-3}	2.06×10^{-3}	1.83×10^{-4}	97	1.98	8.86×10^{-3}	1.97
ccy126.3	2.12×10^{-5}	1.57×10^{-3}	1.42×10^{-3}	1.52×10^{-4}	67	1.37	7.36×10^{-3}	1.36
ccy126.4	2.12×10^{-5}	8.96×10^{-4}	7.83×10^{-4}	1.13×10^{-4}	37	0.769	5.47×10^{-3}	0.764
ccy126.5	2.12×10^{-5}	4.48×10^{-4}	3.70×10^{-4}	7.75×10^{-5}	17	0.376	3.76×10^{-3}	0.372

$k_{2,N} = 9.07 \times 10^2$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 48.5$ $M^{-1}s^{-1}$

$pK_B = 4.79$



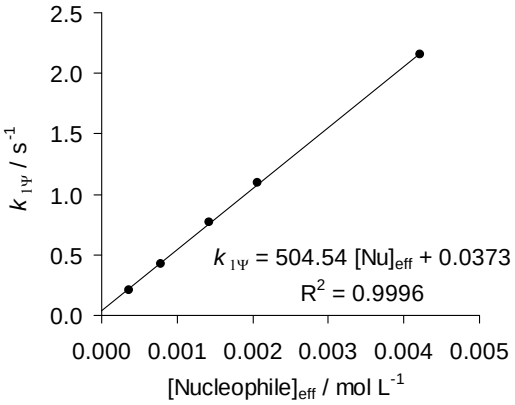
Reaction of serine (**1g**) with $(thq)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(thq)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy127.1	1.57×10^{-5}	4.48×10^{-3}	4.22×10^{-3}	2.62×10^{-4}	269	2.16	6.17×10^{-3}	2.15
ccy127.2	1.57×10^{-5}	2.24×10^{-3}	2.06×10^{-3}	1.83×10^{-4}	131	1.10	4.31×10^{-3}	1.10
ccy127.3	1.57×10^{-5}	1.57×10^{-3}	1.42×10^{-3}	1.52×10^{-4}	90	0.769	3.58×10^{-3}	0.765
ccy127.4	1.57×10^{-5}	8.96×10^{-4}	7.83×10^{-4}	1.13×10^{-4}	50	0.430	2.66×10^{-3}	0.427
ccy127.5	1.57×10^{-5}	4.48×10^{-4}	3.70×10^{-4}	7.75×10^{-5}	24	0.210	1.83×10^{-3}	0.208

$k_{2,N} = 5.05 \times 10^2$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 23.6$ $M^{-1}s^{-1}$

$pK_B = 4.79$



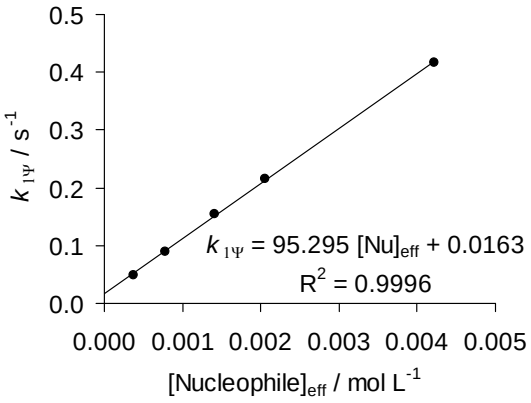
Reaction of serine (**1g**) with $(jul)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 634 nm)

No.	$[(jul)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy128.1	8.55×10^{-6}	4.48×10^{-3}	4.22×10^{-3}	2.62×10^{-4}	493	0.417	9.00×10^{-4}	0.416
ccy128.2	8.55×10^{-6}	2.24×10^{-3}	2.06×10^{-3}	1.83×10^{-4}	241	0.217	6.28×10^{-4}	0.216
ccy128.3	8.55×10^{-6}	1.57×10^{-3}	1.42×10^{-3}	1.52×10^{-4}	166	0.154	5.22×10^{-4}	0.153
ccy128.4	8.55×10^{-6}	8.96×10^{-4}	7.83×10^{-4}	1.13×10^{-4}	92	8.97×10^{-2}	3.88×10^{-4}	8.93×10^{-2}
ccy128.5	8.55×10^{-6}	4.48×10^{-4}	3.70×10^{-4}	7.75×10^{-5}	43	4.95×10^{-2}	2.67×10^{-4}	4.92×10^{-2}

$k_{2,N}$ = 95.3 $M^{-1}s^{-1}$

k_{2,OH^-} = 3.44 $M^{-1}s^{-1}$

pK_B = 4.79



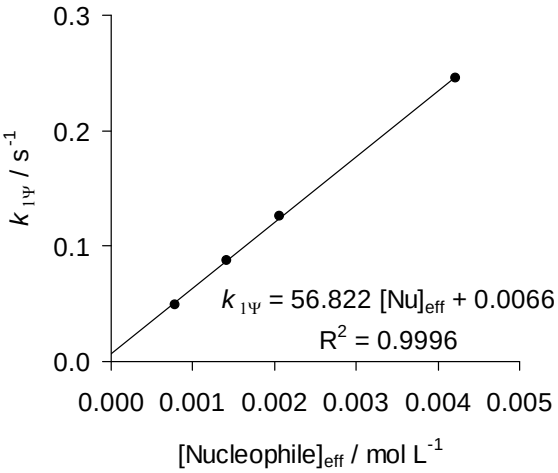
Reaction of serine (**1g**) with $(lil)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 634 nm)

No.	$[(lil)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy129.1	1.02×10^{-5}	4.48×10^{-3}	4.22×10^{-3}	2.62×10^{-4}	414	0.246	5.65×10^{-4}	0.245
ccy129.2	1.02×10^{-5}	2.24×10^{-3}	2.06×10^{-3}	1.83×10^{-4}	202	0.126	3.95×10^{-4}	0.126
ccy129.3	1.02×10^{-5}	1.57×10^{-3}	1.42×10^{-3}	1.52×10^{-4}	139	8.77×10^{-2}	3.28×10^{-4}	8.74×10^{-2}
ccy129.4	1.02×10^{-5}	8.96×10^{-4}	7.83×10^{-4}	1.13×10^{-4}	77	4.98×10^{-2}	2.43×10^{-4}	4.96×10^{-2}

$k_{2,N}$ = 56.8 $M^{-1}s^{-1}$

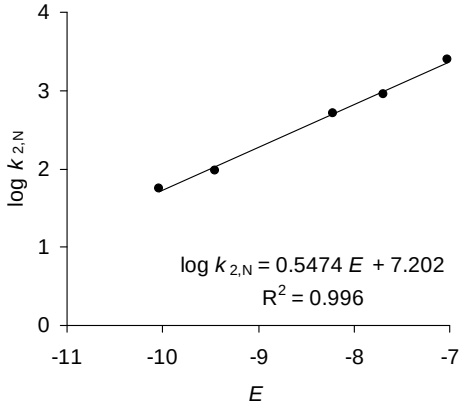
k_{2,OH^-} = 2.16 $M^{-1}s^{-1}$

pK_B = 4.79



Reactivity parameters of serine (1g) in water: *N* = 13.16; *s* = 0.55

Reference electrophile	*E* parameter	$k_{2,N}$(20°C) / M^{-1} s^{-1}
$(dma)_2CH^+$	-7.02	2.49×10^3
$(pyr)_2CH^+$	-7.69	9.07×10^2
$(thq)_2CH^+$	-8.22	5.05×10^2
$(jul)_2CH^+$	-9.45	95.3
$(lil)_2CH^+$	-10.04	56.8



3.7.9. Threonine (1h)

Rate constants in water

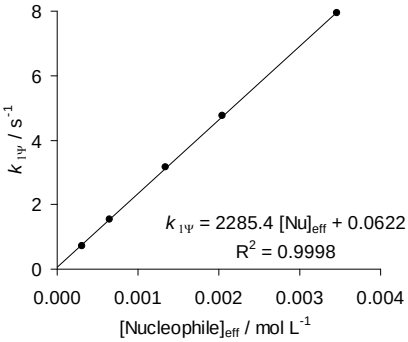
Reaction of threonine (**1h**) with $(dma)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 9 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fn267.2	3.47×10^{-5}	3.67×10^{-3}	3.46×10^{-3}	2.09×10^{-4}	100	7.97	2.73×10^{-2}	7.94
fn267.3	3.47×10^{-5}	2.20×10^{-3}	2.04×10^{-3}	1.60×10^{-4}	59	4.77	2.10×10^{-2}	4.75
fn267.4	3.47×10^{-5}	1.47×10^{-3}	1.34×10^{-3}	1.30×10^{-4}	39	3.19	1.70×10^{-2}	3.17
fn267.5	3.47×10^{-5}	7.34×10^{-4}	6.44×10^{-4}	9.00×10^{-5}	19	1.55	1.18×10^{-2}	1.54
fn267.6	3.47×10^{-5}	3.67×10^{-4}	3.05×10^{-4}	6.20×10^{-5}	9	7.20×10^{-1}	8.12×10^{-3}	7.12×10^{-1}

$k_{2,N} = 2.29 \times 10^3\ M^{-1}s^{-1}$

$k_{2,OH^-} = 131\ M^{-1}s^{-1}$

$pK_B = 4.90$



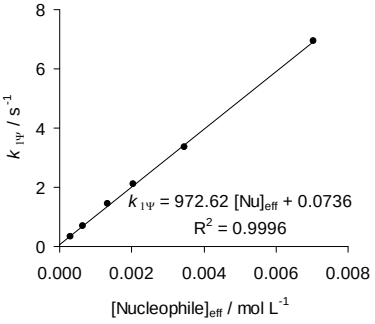
Reaction of threonine (**1h**) with $(pyr)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.8 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(pyr)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fn268.1	2.47×10^{-5}	7.34×10^{-3}	7.04×10^{-3}	2.98×10^{-4}	285	6.95	1.44×10^{-2}	6.94
fn268.2	2.47×10^{-5}	3.67×10^{-3}	3.46×10^{-3}	2.09×10^{-4}	140	3.38	1.01×10^{-2}	3.37
fn268.3	2.47×10^{-5}	2.20×10^{-3}	2.04×10^{-3}	1.60×10^{-4}	83	2.11	7.77×10^{-3}	2.10
fn268.4	2.47×10^{-5}	1.47×10^{-3}	1.34×10^{-3}	1.30×10^{-4}	54	1.44	6.30×10^{-3}	1.43
fn268.5	2.47×10^{-5}	7.34×10^{-4}	6.44×10^{-4}	9.00×10^{-5}	26	7.08×10^{-1}	4.37×10^{-3}	7.04×10^{-1}
fn268.6	2.47×10^{-5}	3.67×10^{-4}	3.05×10^{-4}	6.20×10^{-5}	12	3.26×10^{-1}	3.01×10^{-3}	3.23×10^{-1}

$k_{2,N} = 9.73 \times 10^2\ M^{-1}s^{-1}$

$k_{2,OH^-} = 48.5\ M^{-1}s^{-1}$

$pK_B = 4.90$



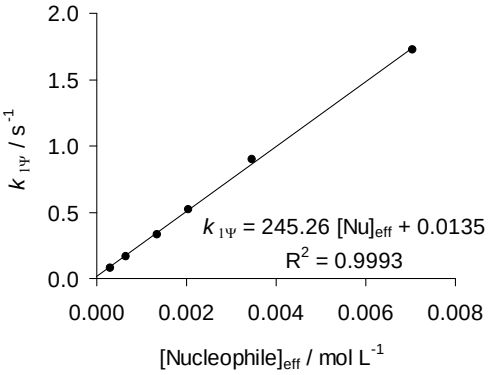
Reaction of threonine (**1h**) with $(ind)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.4 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(ind)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fn269.1	1.05×10^{-5}	7.34×10^{-3}	7.04×10^{-3}	2.98×10^{-4}	671	1.73	3.22×10^{-3}	1.73
fn269.2	1.05×10^{-5}	3.67×10^{-3}	3.46×10^{-3}	2.09×10^{-4}	330	8.96×10^{-1}	2.25×10^{-3}	8.94×10^{-1}
fn269.3	1.05×10^{-5}	2.20×10^{-3}	2.04×10^{-3}	1.60×10^{-4}	194	5.19×10^{-1}	1.73×10^{-3}	5.17×10^{-1}
fn269.4	1.05×10^{-5}	1.47×10^{-3}	1.34×10^{-3}	1.30×10^{-4}	128	3.34×10^{-1}	1.40×10^{-3}	3.33×10^{-1}
fn269.5	1.05×10^{-5}	7.34×10^{-4}	6.44×10^{-4}	9.00×10^{-5}	61	1.68×10^{-1}	9.72×10^{-4}	1.67×10^{-1}
fn269.6	1.05×10^{-5}	3.67×10^{-4}	3.05×10^{-4}	6.20×10^{-5}	29	8.20×10^{-2}	6.69×10^{-4}	8.13×10^{-2}

$k_{2,N} = 2.45 \times 10^2\ M^{-1}s^{-1}$

$k_{2,OH^-} = 10.8\ M^{-1}s^{-1}$

$pK_B = 4.90$



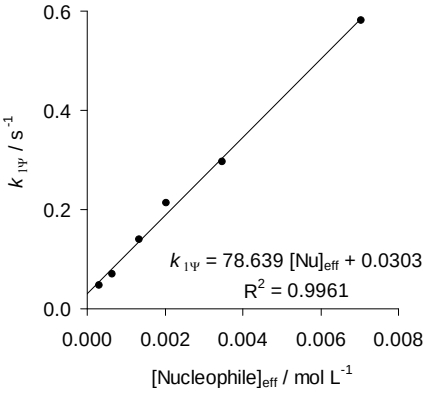
Reaction of threonine (**1h**) with $(jul)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.4 vol-% CH_3CN, stopped-flow, detection at 620 nm)

No.	$[(jul)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fn270.1	2.37×10^{-5}	7.34×10^{-3}	7.04×10^{-3}	2.98×10^{-4}	297	5.82×10^{-1}	1.02×10^{-3}	5.81×10^{-1}
fn270.2	2.37×10^{-5}	3.67×10^{-3}	3.46×10^{-3}	2.09×10^{-4}	146	2.97×10^{-1}	7.18×10^{-4}	2.96×10^{-1}
fn270.3	2.37×10^{-5}	2.20×10^{-3}	2.04×10^{-3}	1.60×10^{-4}	86	2.14×10^{-1}	5.51×10^{-4}	2.13×10^{-1}
fn270.4	2.37×10^{-5}	1.47×10^{-3}	1.34×10^{-3}	1.30×10^{-4}	57	1.41×10^{-1}	4.47×10^{-4}	1.41×10^{-1}
fn270.5	2.37×10^{-5}	7.34×10^{-4}	6.44×10^{-4}	9.00×10^{-5}	27	7.00×10^{-2}	3.10×10^{-4}	6.97×10^{-2}
fn270.6	2.37×10^{-5}	3.67×10^{-4}	3.05×10^{-4}	6.20×10^{-5}	13	4.75×10^{-2}	2.13×10^{-4}	4.73×10^{-2}

$k_{2,N} = 78.6\ M^{-1}s^{-1}$

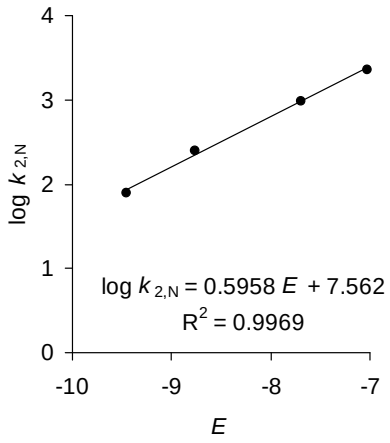
$k_{2,OH^-} = 3.44\ M^{-1}s^{-1}$

$pK_B = 4.90$



Reactivity parameters of threonine (1h) in water: *N* = 12.69; *s* = 0.60

Reference electrophile	*E* parameter	$k_{2,N}$(20°C) / M^{-1} s^{-1}
$(dma)_2CH^+$	-7.02	2.29×10^3
$(pyr)_2CH^+$	-7.69	9.73×10^2
$(ind)_2CH^+$	-8.76	2.45×10^2
$(jul)_2CH^+$	-9.45	78.6



3.7.10. Asparagine (1i)

Rate constants in water

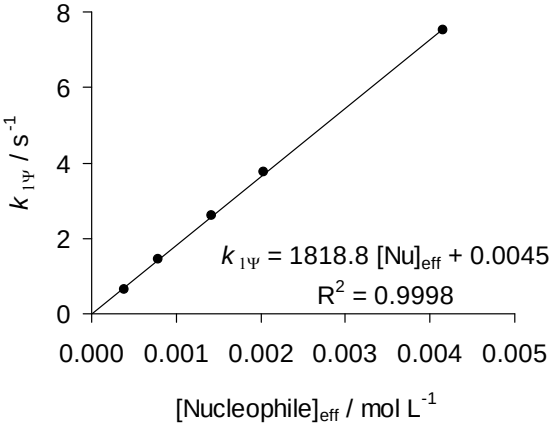
Reaction of asparagine (**1i**) with $(dma)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.5 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy150.1	5.95×10^{-5}	4.32×10^{-3}	4.15×10^{-3}	1.69×10^{-4}	70	7.55	2.22×10^{-2}	7.53
ccy150.2	5.95×10^{-5}	2.16×10^{-3}	2.04×10^{-3}	1.19×10^{-4}	34	3.78	1.56×10^{-2}	3.76
ccy150.3	5.95×10^{-5}	1.52×10^{-3}	1.42×10^{-3}	9.91×10^{-5}	24	2.62	1.30×10^{-2}	2.61
ccy150.4	5.95×10^{-5}	8.64×10^{-4}	7.90×10^{-4}	7.39×10^{-5}	13	1.45	9.69×10^{-3}	1.44
ccy150.5	5.95×10^{-5}	4.32×10^{-4}	3.81×10^{-4}	5.13×10^{-5}	6	0.665	6.72×10^{-3}	0.658

$k_{2,N} = 1.82 \times 10^3$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 131$ $M^{-1}s^{-1}$

$pK_B = 5.16$



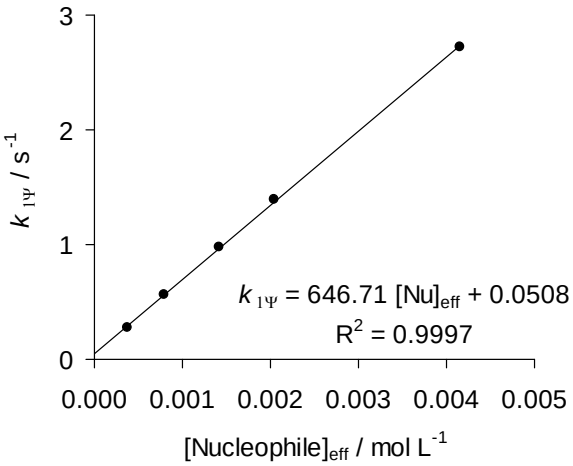
Reaction of asparagine (**1i**) with $(pyr)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.1 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(pyr)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy151.1	1.14×10^{-5}	4.32×10^{-3}	4.15×10^{-3}	1.69×10^{-4}	364	2.73	8.22×10^{-3}	2.72
ccy151.2	1.14×10^{-5}	2.16×10^{-3}	2.04×10^{-3}	1.19×10^{-4}	179	1.40	5.76×10^{-3}	1.39
ccy151.3	1.14×10^{-5}	1.52×10^{-3}	1.42×10^{-3}	9.91×10^{-5}	125	0.985	4.81×10^{-3}	0.980
ccy151.4	1.14×10^{-5}	8.64×10^{-4}	7.90×10^{-4}	7.39×10^{-5}	69	0.565	3.59×10^{-3}	0.561
ccy151.5	1.14×10^{-5}	4.32×10^{-4}	3.81×10^{-4}	5.13×10^{-5}	33	0.279	2.49×10^{-3}	0.277

$k_{2,N} = 6.47 \times 10^2\ M^{-1}s^{-1}$

$k_{2,OH^-} = 48.5\ M^{-1}s^{-1}$

$pK_B = 5.16$



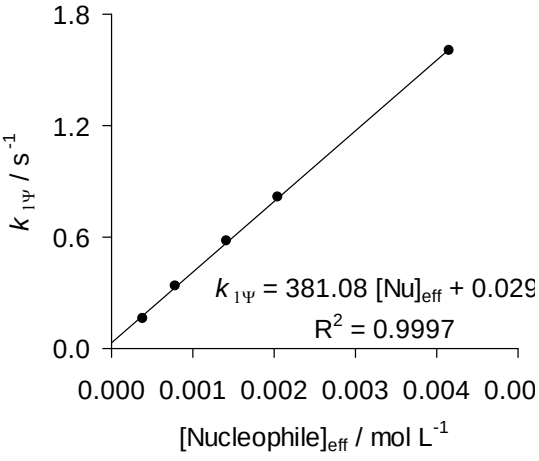
Reaction of asparagine (**1i**) with $(thq)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.4 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(thq)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy152.1	3.14×10^{-5}	4.32×10^{-3}	4.15×10^{-3}	1.69×10^{-4}	132	1.61	4.00×10^{-3}	1.61
ccy152.2	3.14×10^{-5}	2.16×10^{-3}	2.04×10^{-3}	1.19×10^{-4}	65	0.817	2.80×10^{-3}	0.814
ccy152.3	3.14×10^{-5}	1.52×10^{-3}	1.42×10^{-3}	9.91×10^{-5}	45	0.581	2.34×10^{-3}	0.579
ccy152.4	3.14×10^{-5}	8.64×10^{-4}	7.90×10^{-4}	7.39×10^{-5}	25	0.337	1.74×10^{-3}	0.335
ccy152.5	3.14×10^{-5}	4.32×10^{-4}	3.81×10^{-4}	5.13×10^{-5}	12	0.163	1.21×10^{-3}	0.162

$k_{2,N} = 3.81 \times 10^2\ M^{-1}s^{-1}$

$k_{2,OH^-} = 23.6\ M^{-1}s^{-1}$

$pK_B = 5.16$



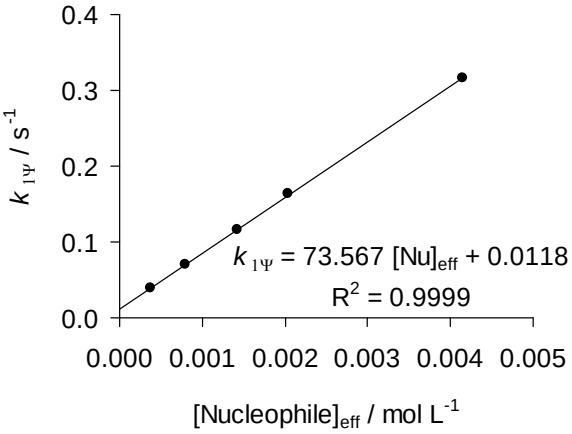
Reaction of asparagine (**1i**) with $(jul)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 634 nm)

No.	$[(jul)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy153.1	8.56×10^{-6}	4.32×10^{-3}	4.15×10^{-3}	1.69×10^{-4}	485	0.317	5.83×10^{-4}	0.316
ccy153.2	8.56×10^{-6}	2.16×10^{-3}	2.04×10^{-3}	1.19×10^{-4}	238	0.164	4.09×10^{-4}	0.164
ccy153.3	8.56×10^{-6}	1.52×10^{-3}	1.42×10^{-3}	9.91×10^{-5}	166	0.117	3.41×10^{-4}	0.117
ccy153.4	8.56×10^{-6}	8.64×10^{-4}	7.90×10^{-4}	7.39×10^{-5}	92	7.00×10^{-2}	2.54×10^{-4}	6.97×10^{-2}
ccy153.5	8.56×10^{-6}	4.32×10^{-4}	3.81×10^{-4}	5.13×10^{-5}	44	3.91×10^{-2}	1.77×10^{-4}	3.89×10^{-2}

$k_{2,N}$ = 73.6 $M^{-1}s^{-1}$

k_{2,OH^-} = 3.44 $M^{-1}s^{-1}$

pK_B = 5.16



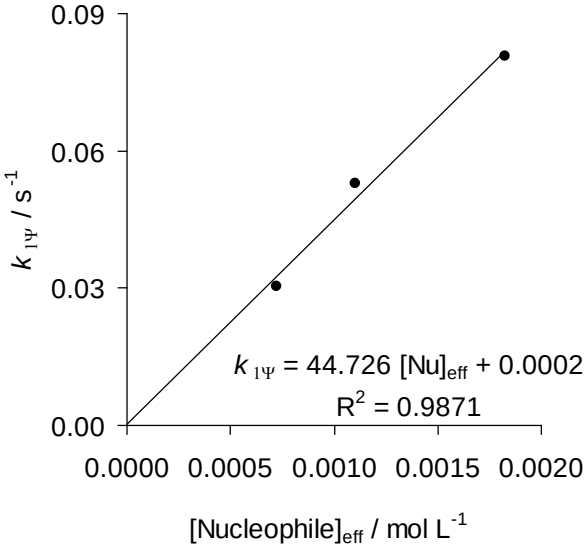
Reaction of asparagine (**1i**) with $(lil)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.4 vol-% CH_3CN, J&M, detection at 630 nm)

No.	$[(lil)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fn265.2	1.34×10^{-5}	1.94×10^{-3}	1.83×10^{-3}	1.12×10^{-4}	136	8.11×10^{-2}	2.43×10^{-4}	8.09×10^{-2}
fn265.3	1.38×10^{-5}	1.19×10^{-3}	1.10×10^{-3}	8.73×10^{-5}	80	5.30×10^{-2}	1.89×10^{-4}	5.28×10^{-2}
fn265.4	1.38×10^{-5}	7.94×10^{-4}	7.23×10^{-4}	7.07×10^{-5}	52	3.06×10^{-2}	1.53×10^{-4}	3.04×10^{-2}

$k_{2,N}$ = 44.7 $M^{-1}s^{-1}$

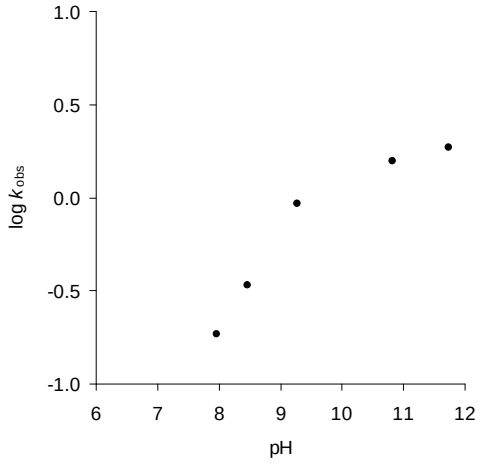
k_{2,OH^-} = 2.16 $M^{-1}s^{-1}$

pK_B = 5.16



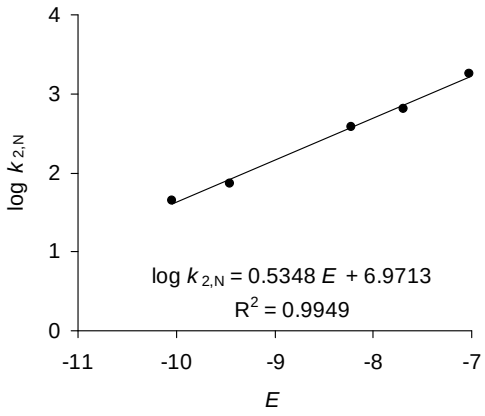
pH Dependance of rate constants for the reaction of asparagine (**1i**) with $(dma)_2CH^+BF_4^-$ (phosphate buffer, at 20 °C, cosolvent: 0.4 vol % CH_3CN, stopped-flow, detection at 610 nm, pH measured, No. fn321)

$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[PO_4^{3-}]$ / mol L^{-1}	$[HPO_4^{2-}]$ / mol L^{-1}	$[H_2PO_4^-]$ / mol L^{-1}	pH	k_{obs} / s^{-1}
4.27×10^{-5}	9.09×10^{-4}	9.09×10^{-3}	9.09×10^{-3}		11.73	1.87
4.27×10^{-5}	9.09×10^{-4}	9.09×10^{-4}	9.09×10^{-3}		10.82	1.58
4.27×10^{-5}	9.09×10^{-4}		9.09×10^{-3}	1.82×10^{-4}	9.27	9.25×10^{-1}
4.27×10^{-5}	9.09×10^{-4}		9.09×10^{-3}	9.09×10^{-4}	8.46	3.40×10^{-1}
4.27×10^{-5}	9.09×10^{-4}		9.09×10^{-3}	1.82×10^{-3}	7.96	1.85×10^{-1}



Reactivity parameters of asparagine (1i) in water: *N* = 13.03; *s* = 0.53

Reference electrophile	*E* parameter	$k_{2,N}$(20°C) / M^{-1} s^{-1}
$(dma)_2CH^+$	-7.02	1.82×10^3
$(pyr)_2CH^+$	-7.69	6.47×10^2
$(thq)_2CH^+$	-8.22	3.81×10^2
$(jul)_2CH^+$	-9.45	73.6
$(lil)_2CH^+$	-10.04	44.7



3.7.11. Glutamine (1j)

Rate constants in water

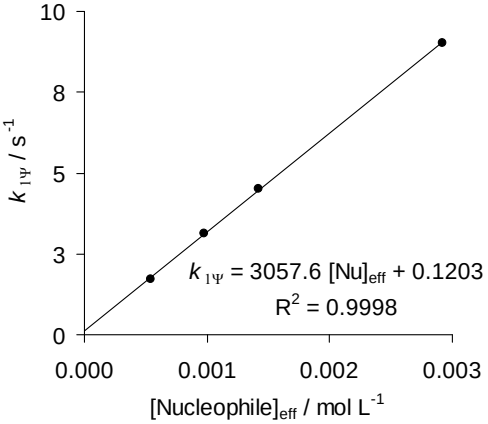
Reaction of glutamine (**1j**) with $(dma)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.5 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy115.1	1.08×10^{-4}	3.12×10^{-3}	2.92×10^{-3}	1.99×10^{-4}	27	9.06	2.60×10^{-2}	9.03
ccy115.2	1.08×10^{-4}	1.56×10^{-3}	1.42×10^{-3}	1.38×10^{-4}	13	4.52	1.81×10^{-2}	4.50
ccy115.3	1.08×10^{-4}	1.09×10^{-3}	9.75×10^{-4}	1.15×10^{-4}	9	3.15	1.50×10^{-2}	3.13
ccy115.4	1.08×10^{-4}	6.24×10^{-4}	5.39×10^{-4}	8.52×10^{-5}	5	1.73	1.12×10^{-2}	1.72

$k_{2,N} = 3.06 \times 10^3\ M^{-1}s^{-1}$

$k_{2,OH^-} = 131\ M^{-1}s^{-1}$

$pK_B = 4.87$



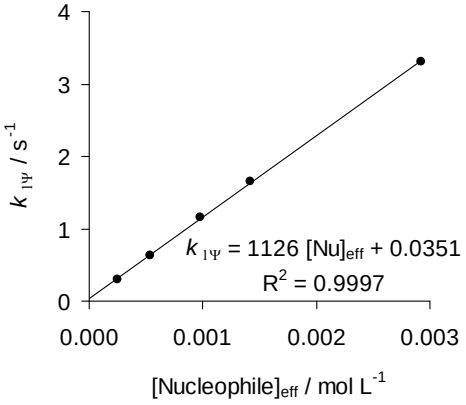
Reaction of glutamine (**1j**) with $(pyr)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(pyr)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy116.1	2.16×10^{-5}	3.12×10^{-3}	2.92×10^{-3}	1.99×10^{-4}	135	3.32	9.63×10^{-3}	3.31
ccy116.2	2.16×10^{-5}	1.56×10^{-3}	1.42×10^{-3}	1.38×10^{-4}	66	1.66	6.72×10^{-3}	1.65
ccy116.3	2.16×10^{-5}	1.09×10^{-3}	9.75×10^{-4}	1.15×10^{-4}	45	1.16	5.56×10^{-3}	1.15
ccy116.4	2.16×10^{-5}	6.24×10^{-4}	5.39×10^{-4}	8.52×10^{-5}	25	0.643	4.13×10^{-3}	0.639
ccy116.5	2.16×10^{-5}	3.12×10^{-4}	2.54×10^{-4}	5.85×10^{-5}	12	0.300	2.84×10^{-3}	0.297

$k_{2,N} = 1.13 \times 10^3\ M^{-1}s^{-1}$

$k_{2,OH^-} = 48.5\ M^{-1}s^{-1}$

$pK_B = 4.87$



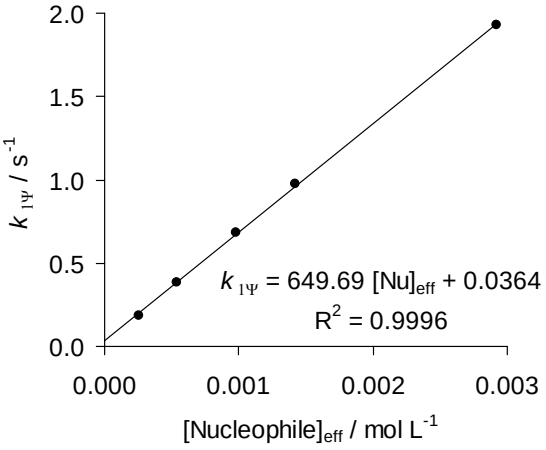
Reaction of glutamine (**1j**) with $(thq)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(thq)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi, OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy117.1	1.57×10^{-5}	3.12×10^{-3}	2.92×10^{-3}	1.99×10^{-4}	186	1.93	4.69×10^{-3}	1.93
ccy117.2	1.57×10^{-5}	1.56×10^{-3}	1.42×10^{-3}	1.38×10^{-4}	91	0.975	3.27×10^{-3}	0.972
ccy117.3	1.57×10^{-5}	1.09×10^{-3}	9.75×10^{-4}	1.15×10^{-4}	62	0.688	2.71×10^{-3}	0.685
ccy117.4	1.57×10^{-5}	6.24×10^{-4}	5.39×10^{-4}	8.52×10^{-5}	34	0.387	2.01×10^{-3}	0.385
ccy117.5	1.57×10^{-5}	3.12×10^{-4}	2.54×10^{-4}	5.85×10^{-5}	16	0.186	1.38×10^{-3}	0.185

$k_{2,N} = 6.50 \times 10^2\ M^{-1}s^{-1}$

$k_{2,OH^-} = 23.6\ M^{-1}s^{-1}$

$pK_B = 4.87$



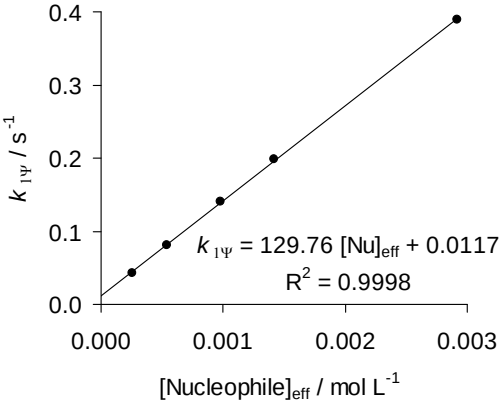
Reaction of glutamine (**1j**) with $(jul)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 634 nm)

No.	$[(jul)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi, OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy118.1	8.55×10^{-6}	3.12×10^{-3}	2.92×10^{-3}	1.99×10^{-4}	342	0.390	6.83×10^{-4}	0.389
ccy118.2	8.55×10^{-6}	1.56×10^{-3}	1.42×10^{-3}	1.38×10^{-4}	166	0.199	4.76×10^{-4}	0.199
ccy118.3	8.55×10^{-6}	1.09×10^{-3}	9.75×10^{-4}	1.15×10^{-4}	114	0.141	3.95×10^{-4}	0.141
ccy118.4	8.55×10^{-6}	6.24×10^{-4}	5.39×10^{-4}	8.52×10^{-5}	63	8.09×10^{-2}	2.93×10^{-4}	8.06×10^{-2}
ccy118.5	8.55×10^{-6}	3.12×10^{-4}	2.54×10^{-4}	5.85×10^{-5}	30	4.28×10^{-2}	2.01×10^{-4}	4.26×10^{-2}

$k_{2,N} = 1.30 \times 10^2\ M^{-1}s^{-1}$

$k_{2,OH^-} = 3.44\ M^{-1}s^{-1}$

$pK_B = 4.87$



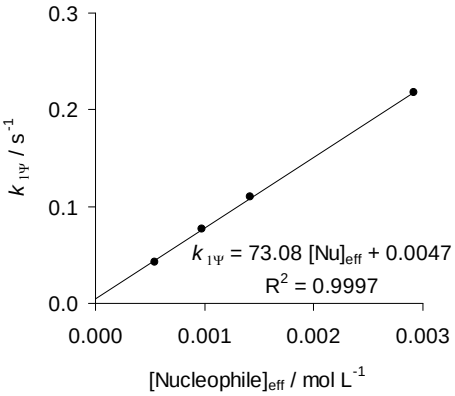
Reaction of glutamine (**1j**) with $(lil)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 634 nm)

No.	$[(lil)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy119.1	1.02×10^{-5}	3.12×10^{-3}	2.92×10^{-3}	1.99×10^{-4}	286	0.218	4.29×10^{-4}	0.218
ccy119.2	1.02×10^{-5}	1.56×10^{-3}	1.42×10^{-3}	1.38×10^{-4}	139	0.110	2.99×10^{-4}	0.110
ccy119.3	1.02×10^{-5}	1.09×10^{-3}	9.75×10^{-4}	1.15×10^{-4}	96	7.70×10^{-2}	2.48×10^{-4}	7.68×10^{-2}
ccy119.4	1.02×10^{-5}	6.24×10^{-4}	5.39×10^{-4}	8.52×10^{-5}	53	4.28×10^{-2}	1.84×10^{-4}	4.26×10^{-2}

$k_{2,N}$ = 73.1 $M^{-1}s^{-1}$

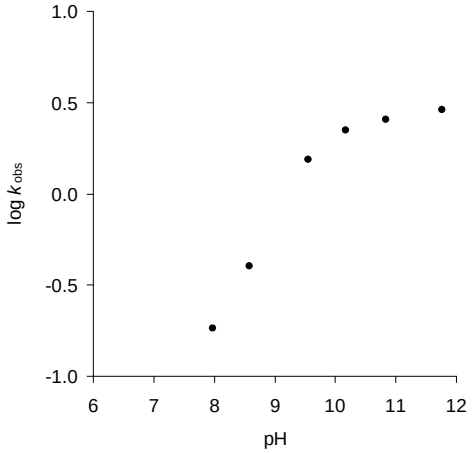
k_{2,OH^-} = 2.16 $M^{-1}s^{-1}$

pK_B = 4.87



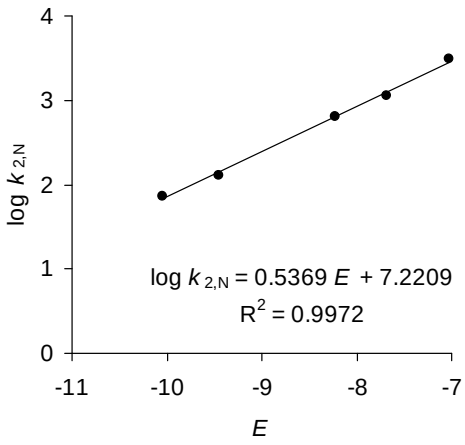
pH Dependance of rate constants for the reaction of glutamine (**1j**) with $(dma)_2CH^+BF_4^-$ (phosphate buffer, at 20 °C, cosolvent: 0.4 vol % CH_3CN, stopped-flow, detection at 610 nm, pH measured, No. fn320)

$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[PO_4^{3-}]$ / mol L^{-1}	$[HPO_4^{2-}]$ / mol L^{-1}	$[H_2PO_4^-]$ / mol L^{-1}	pH	k_{obs} / s^{-1}
4.27×10^{-5}	9.09×10^{-4}	9.09×10^{-3}	9.09×10^{-3}		11.77	2.87
4.27×10^{-5}	9.09×10^{-4}	9.09×10^{-4}	9.09×10^{-3}		10.83	2.54
4.27×10^{-5}	9.09×10^{-4}	1.82×10^{-4}	9.09×10^{-3}		10.17	2.22
4.27×10^{-5}	9.09×10^{-4}		9.09×10^{-3}	1.82×10^{-4}	9.56	1.54
4.27×10^{-5}	9.09×10^{-4}		9.09×10^{-3}	9.09×10^{-4}	8.58	4.03×10^{-1}
4.27×10^{-5}	9.09×10^{-4}		9.09×10^{-3}	1.82×10^{-3}	7.97	1.84×10^{-1}



Reactivity parameters of glutamine (1j) in water: *N* = 13.45; *s* = 0.54

Reference electrophile	*E* parameter	$k_{2,N}$(20°C) / M^{-1} s^{-1}
$(dma)_2CH^+$	-7.02	3.06×10^3
$(pyr)_2CH^+$	-7.69	1.13×10^3
$(thq)_2CH^+$	-8.22	6.50×10^2
$(jul)_2CH^+$	-9.45	1.30×10^2
$(lil)_2CH^+$	-10.04	73.1



3.7.12. Arginine (1k)

Rate constants in water

Typical procedure:

L-Arginine monohydrochloride (318.1 mg, 1.510 mmol) was dissolved in 3 mL of aqueous KOH (0.5033 mol L^{-1}), then the solution was filled up to 10 mL with water ($c_{arginine}$ = 0.151 mol L^{-1}). 2 mL of this solution was combined with 600 µL of aqueous KOH (0.5033 mol L^{-1}) and diluted with water to 25 mL. Equal volumes of this solution were combined with a solution of [$(dma)_2CH^+$] (1.19×10^{-4} mol L^{-1}) in the stopped-flow instrument to give the final concentrations listed in the table.

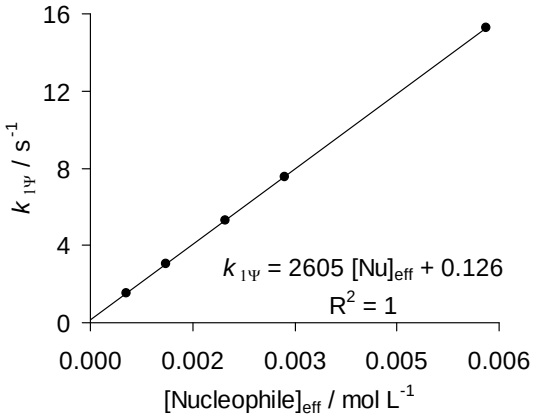
Reaction of arginine (**1k**) with $(dma)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.5 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi, OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy159.1	5.95×10^{-5}	6.05×10^{-3}	5.81×10^{-3}	2.38×10^{-4}	98	15.3	3.12×10^{-2}	15.3
ccy159.2	5.95×10^{-5}	3.03×10^{-3}	2.86×10^{-3}	1.67×10^{-4}	48	7.57	2.19×10^{-2}	7.55
ccy159.3	5.95×10^{-5}	2.12×10^{-3}	1.98×10^{-3}	1.39×10^{-4}	33	5.34	1.82×10^{-2}	5.32
ccy159.4	5.95×10^{-5}	1.21×10^{-3}	1.11×10^{-3}	1.04×10^{-4}	19	3.04	1.36×10^{-2}	3.03
ccy159.5	5.95×10^{-5}	6.05×10^{-4}	5.33×10^{-4}	7.22×10^{-5}	9	1.50	9.45×10^{-3}	1.49

$k_{2,N} = 2.61 \times 10^3$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 131$ $M^{-1}s^{-1}$

$pK_B = 5.01$



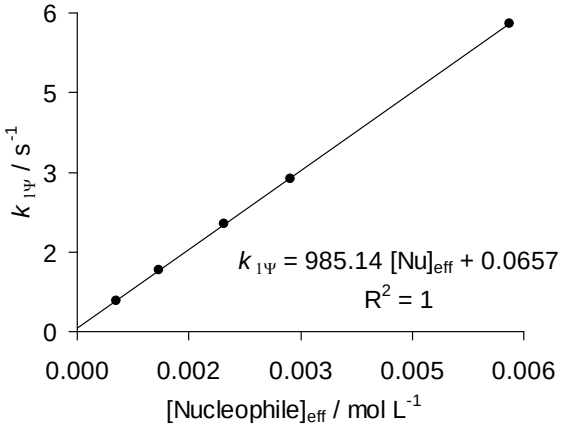
Reaction of arginine (**1k**) with $(pyr)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.1 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(pyr)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi, OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy160.1	1.13×10^{-5}	6.05×10^{-3}	5.81×10^{-3}	2.38×10^{-4}	514	5.80	1.16×10^{-2}	5.79
ccy160.2	1.13×10^{-5}	3.03×10^{-3}	2.86×10^{-3}	1.67×10^{-4}	253	2.89	8.11×10^{-3}	2.88
ccy160.3	1.13×10^{-5}	2.12×10^{-3}	1.98×10^{-3}	1.39×10^{-4}	175	2.04	6.75×10^{-3}	2.03
ccy160.4	1.13×10^{-5}	1.21×10^{-3}	1.11×10^{-3}	1.04×10^{-4}	98	1.16	5.04×10^{-3}	1.15
ccy160.5	1.13×10^{-5}	6.05×10^{-4}	5.33×10^{-4}	7.22×10^{-5}	47	0.585	3.50×10^{-3}	0.582

$k_{2,N} = 9.85 \times 10^2$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 48.5$ $M^{-1}s^{-1}$

$pK_B = 5.01$



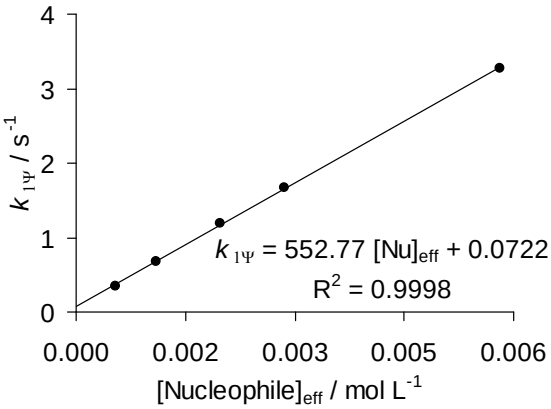
Reaction of arginine (**1k**) with $(thq)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.4 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(thq)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy161.1	3.14×10^{-5}	6.05×10^{-3}	5.81×10^{-3}	2.38×10^{-4}	185	3.28	5.62×10^{-3}	3.28
ccy161.2	3.14×10^{-5}	3.03×10^{-3}	2.86×10^{-3}	1.67×10^{-4}	91	1.67	3.95×10^{-3}	1.67
ccy161.3	3.14×10^{-5}	2.12×10^{-3}	1.98×10^{-3}	1.39×10^{-4}	63	1.19	3.28×10^{-3}	1.19
ccy161.4	3.14×10^{-5}	1.21×10^{-3}	1.11×10^{-3}	1.04×10^{-4}	35	0.686	2.45×10^{-3}	0.686
ccy161.5	3.14×10^{-5}	6.05×10^{-4}	5.33×10^{-4}	7.22×10^{-5}	17	0.348	1.70×10^{-3}	0.348

$k_{2,N} = 5.53 \times 10^2\ M^{-1}s^{-1}$

$k_{2,OH^-} = 23.6\ M^{-1}s^{-1}$

$pK_B = 5.01$



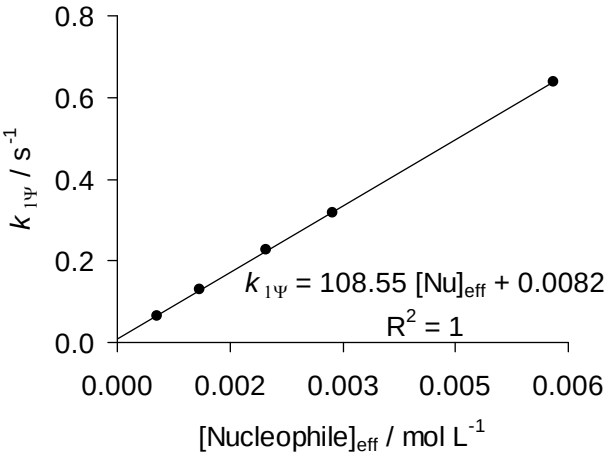
Reaction of arginine (**1k**) with $(jul)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 634 nm)

No.	$[(jul)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
ccy162.1	8.55×10^{-6}	6.05×10^{-3}	5.81×10^{-3}	2.38×10^{-4}	680	0.640	8.20×10^{-4}	0.639
ccy162.2	8.55×10^{-6}	3.03×10^{-3}	2.86×10^{-3}	1.67×10^{-4}	335	0.318	5.75×10^{-4}	0.317
ccy162.3	8.55×10^{-6}	2.12×10^{-3}	1.98×10^{-3}	1.39×10^{-4}	232	0.226	4.79×10^{-4}	0.226
ccy162.4	8.55×10^{-6}	1.21×10^{-3}	1.11×10^{-3}	1.04×10^{-4}	129	0.129	3.58×10^{-4}	0.129
ccy162.5	8.55×10^{-6}	6.05×10^{-4}	5.33×10^{-4}	7.22×10^{-5}	62	6.53×10^{-2}	2.48×10^{-4}	6.51×10^{-2}

$k_{2,N} = 1.09 \times 10^2\ M^{-1}s^{-1}$

$k_{2,OH^-} = 3.44\ M^{-1}s^{-1}$

$pK_B = 5.01$



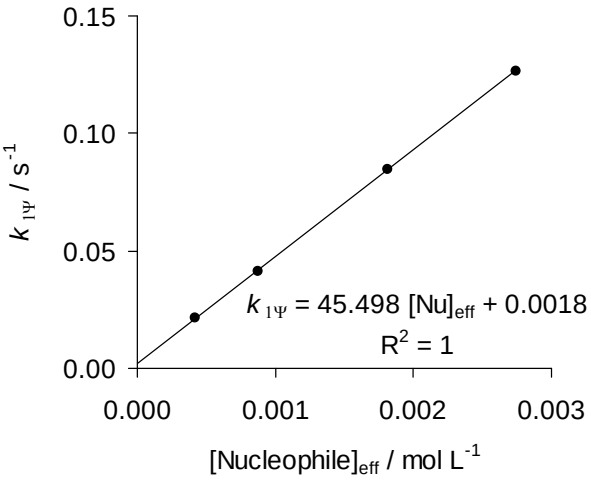
Reaction of arginine (**1k**) with $(lil)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.4 vol-% CH_3CN, J&M, detection at 630 nm)

No.	$[(lil)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fn264.2	1.37×10^{-5}	2.91×10^{-3}	2.75×10^{-3}	1.64×10^{-4}	200	1.27×10^{-1}	3.54×10^{-4}	1.27×10^{-1}
fn264.3	1.38×10^{-5}	1.95×10^{-3}	1.82×10^{-3}	1.33×10^{-4}	132	8.49×10^{-2}	2.88×10^{-4}	8.46×10^{-2}
fn264.4	1.37×10^{-5}	9.69×10^{-4}	8.76×10^{-4}	9.25×10^{-5}	64	4.16×10^{-2}	2.00×10^{-4}	4.14×10^{-2}
fn264.5	1.38×10^{-5}	4.88×10^{-4}	4.24×10^{-4}	6.43×10^{-5}	31	2.13×10^{-2}	1.39×10^{-4}	2.12×10^{-2}

$k_{2,N} = 45.5\ M^{-1}s^{-1}$

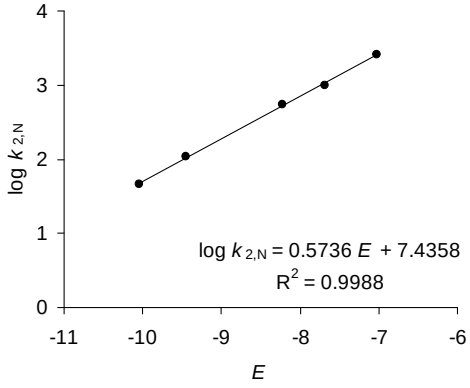
$k_{2,OH^-} = 2.16\ M^{-1}s^{-1}$

$pK_B = 5.01$



Reactivity parameters of arginine (1k) in water: *N* = 12.96; *s* = 0.57

Reference electrophile	*E* parameter	$k_{2,N}$(20°C) / M^{-1} s^{-1}
$(dma)_2CH^+$	-7.02	2.61×10^3
$(pyr)_2CH^+$	-7.69	9.85×10^2
$(thq)_2CH^+$	-8.22	5.53×10^2
$(jul)_2CH^+$	-9.45	1.09×10^2
$(lil)_2CH^+$	-10.04	45.5



3.7.13. Histidine (1l)

Rate constants in water

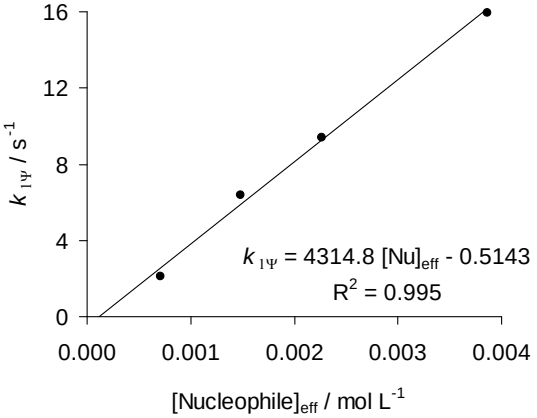
Reaction of histidine (**1l**) with $(dma)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.5 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fn281.1	3.36×10^{-5}	4.15×10^{-3}	3.86×10^{-3}	2.87×10^{-4}	115	16.0	3.76×10^{-2}	16.0
fn281.2	3.36×10^{-5}	2.49×10^{-3}	2.27×10^{-3}	2.20×10^{-4}	68	9.44	2.89×10^{-2}	9.41
fn281.3	3.36×10^{-5}	1.66×10^{-3}	1.48×10^{-3}	1.78×10^{-4}	44	6.41	2.33×10^{-2}	6.39
fn281.4	3.36×10^{-5}	8.29×10^{-4}	7.06×10^{-4}	1.23×10^{-4}	21	2.10	1.61×10^{-2}	2.08

$k_{2,N} = 4.31 \times 10^3\ M^{-1}s^{-1}$

$k_{2,OH^-} = 131\ M^{-1}s^{-1}$

$pK_B = 4.67$



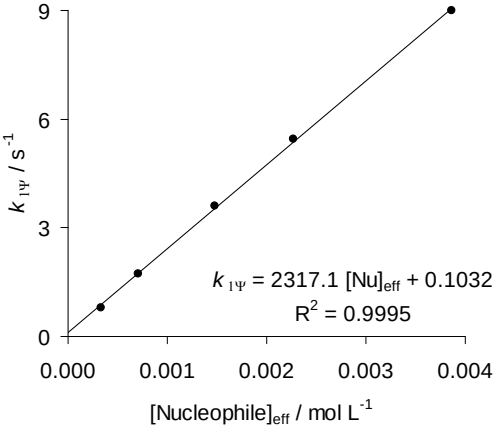
Reaction of histidine (**1l**) with $(pyr)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.4 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(pyr)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fn282.1	1.20×10^{-5}	4.15×10^{-3}	3.86×10^{-3}	2.87×10^{-4}	322	9.00	1.39×10^{-2}	8.99
fn282.2	1.20×10^{-5}	2.49×10^{-3}	2.27×10^{-3}	2.20×10^{-4}	189	5.46	1.07×10^{-2}	5.45
fn282.3	1.20×10^{-5}	1.66×10^{-3}	1.48×10^{-3}	1.78×10^{-4}	123	3.61	8.63×10^{-3}	3.60
fn282.4	1.20×10^{-5}	8.29×10^{-4}	7.06×10^{-4}	1.23×10^{-4}	59	1.73	5.96×10^{-3}	1.72
fn282.5	1.20×10^{-5}	4.15×10^{-4}	3.31×10^{-4}	8.41×10^{-5}	28	8.05×10^{-1}	4.08×10^{-3}	8.01×10^{-1}

$k_{2,N} = 2.32 \times 10^3\ M^{-1}s^{-1}$

$k_{2,OH^-} = 48.5\ M^{-1}s^{-1}$

$pK_B = 4.67$



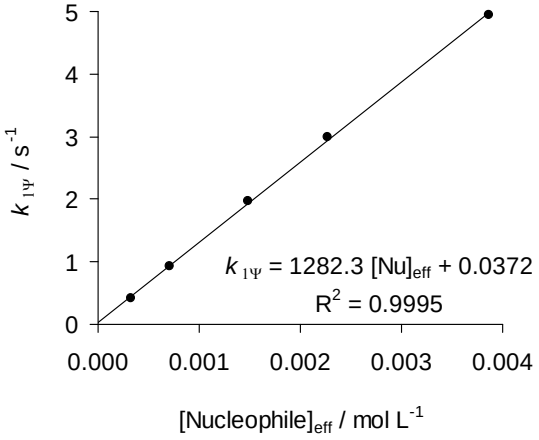
Reaction of histidine (**1l**) with $(thq)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.7 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(thq)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fn283.1	2.41×10^{-5}	4.15×10^{-3}	3.86×10^{-3}	2.87×10^{-4}	160	4.96	6.78×10^{-3}	4.95
fn283.2	2.41×10^{-5}	2.49×10^{-3}	2.27×10^{-3}	2.20×10^{-4}	94	3.00	5.20×10^{-3}	2.99
fn283.3	2.41×10^{-5}	1.66×10^{-3}	1.48×10^{-3}	1.78×10^{-4}	61	1.98	4.20×10^{-3}	1.98
fn283.4	2.41×10^{-5}	8.29×10^{-4}	7.06×10^{-4}	1.23×10^{-4}	29	9.35×10^{-1}	2.90×10^{-3}	9.32×10^{-1}
fn283.5	2.41×10^{-5}	4.15×10^{-4}	3.31×10^{-4}	8.41×10^{-5}	14	4.26×10^{-1}	1.98×10^{-3}	4.24×10^{-1}

$k_{2,N} = 1.28 \times 10^3\ M^{-1}s^{-1}$

$k_{2,OH^-} = 23.6\ M^{-1}s^{-1}$

$pK_B = 4.67$



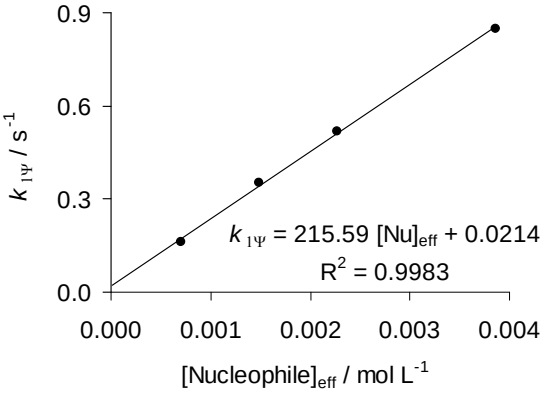
Reaction of histidine (**1l**) with $(jul)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.4 vol-% CH_3CN, stopped-flow, detection at 634 nm)

No.	$[(jul)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fn284.1	1.19×10^{-5}	4.15×10^{-3}	3.86×10^{-3}	2.87×10^{-4}	325	8.49×10^{-1}	9.89×10^{-4}	8.48×10^{-1}
fn284.2	1.19×10^{-5}	2.49×10^{-3}	2.27×10^{-3}	2.20×10^{-4}	191	5.17×10^{-1}	7.58×10^{-4}	5.16×10^{-1}
fn284.3	1.19×10^{-5}	1.66×10^{-3}	1.48×10^{-3}	1.78×10^{-4}	125	3.55×10^{-1}	6.12×10^{-4}	3.54×10^{-1}
fn284.4	1.19×10^{-5}	8.29×10^{-4}	7.06×10^{-4}	1.23×10^{-4}	59	1.61×10^{-1}	4.23×10^{-4}	1.61×10^{-1}

$k_{2,N} = 2.16 \times 10^2\ M^{-1}s^{-1}$

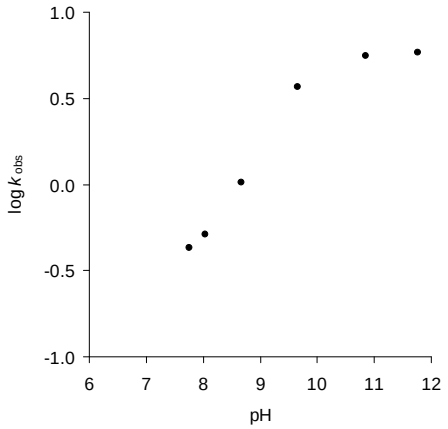
$k_{2,OH^-} = 3.44\ M^{-1}s^{-1}$

$pK_B = 4.67$



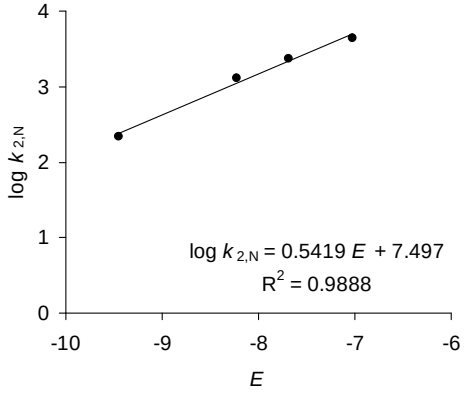
pH Dependance of rate constants for the reaction of histidine (**1l**) with $(dma)_2CH^+BF_4^-$ (phosphate buffer, at 20 °C, cosolvent: 0.4 vol % CH_3CN, stopped-flow, detection at 610 nm, pH measured, No. fn312)

$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[PO_4^{3-}]$ / mol L^{-1}	$[HPO_4^{2-}]$ / mol L^{-1}	$[H_2PO_4^-]$ / mol L^{-1}	pH	k_{obs} / s^{-1}
4.27×10^{-5}	9.08×10^{-4}	9.09×10^{-3}	9.09×10^{-3}		11.76	5.87
4.27×10^{-5}	9.08×10^{-4}	9.09×10^{-4}	9.09×10^{-3}		10.85	5.60
4.27×10^{-5}	9.08×10^{-4}		9.09×10^{-3}	1.82×10^{-4}	9.65	3.69
4.27×10^{-5}	9.08×10^{-4}		9.09×10^{-3}	9.09×10^{-4}	8.67	1.03
4.27×10^{-5}	9.08×10^{-4}		9.09×10^{-3}	1.82×10^{-3}	8.04	5.11×10^{-1}
4.27×10^{-5}	9.08×10^{-4}		9.09×10^{-3}	2.73×10^{-3}	7.75	4.30×10^{-1}



Reactivity parameters of histidine (1l) in water: *N* = 13.83; *s* = 0.54

Reference electrophile	*E* parameter	$k_{2,N}$(20°C) / M^{-1} s^{-1}
$(dma)_2CH^+$	-7.02	4.31×10^3
$(pyr)_2CH^+$	-7.69	2.32×10^3
$(thq)_2CH^+$	-8.22	1.28×10^3
$(jul)_2CH^+$	-9.45	2.16×10^2



3.7.14. Aspartate (1m)

Rate constants in water

Typical procedure:

L-Aspartic acid (232.7 mg, 1.75 mmol) was dissolved in 4.760 mL of aqueous KOH (0.5033 mol L^{-1}), then the solution was filled up to 11 mL with water (c_{Nu} = 0.159 mol L^{-1}, $c_{0,OH}$ = 0.218 mol L^{-1}). 1 mL of this solution was combined with 1 mL of aqueous KOH (0.5033 mol L^{-1}) and diluted with water to 25 mL. Equal volumes of this solution were combined with a solution of $[(dma)_2CH^+]$ (2.16×10^{-4} mol L^{-1}) in the stopped-flow instrument to give the final concentrations listed in the table.

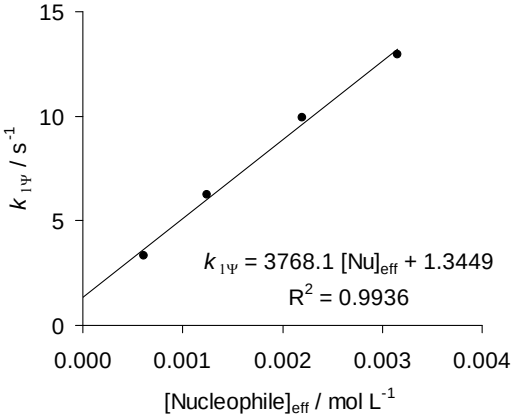
Reaction of aspartate (**1m**) with $(dma)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.5 vol-% CH_3CN, stopped-flow, detection at 610 nm, No. ccy77)

$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]_0$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
1.08×10^{-4}	3.18×10^{-3}	3.15×10^{-3}	1.44×10^{-2}	8.10×10^{-3}	29	14.0	1.06	12.9
1.08×10^{-4}	2.23×10^{-3}	2.20×10^{-3}	1.01×10^{-2}	5.68×10^{-3}	20	10.7	7.44×10^{-1}	9.96
1.08×10^{-4}	1.27×10^{-3}	1.24×10^{-3}	5.77×10^{-3}	3.26×10^{-3}	11	6.69	4.27×10^{-1}	6.26
1.08×10^{-4}	6.36×10^{-4}	6.07×10^{-4}	2.89×10^{-3}	1.65×10^{-3}	6	3.54	2.16×10^{-1}	3.32

$k_{2,N} = 3.77 \times 10^3\ M^{-1}s^{-1}$

$k_{2,OH^-} = 131\ M^{-1}s^{-1}$

$pK_B = 4.10$



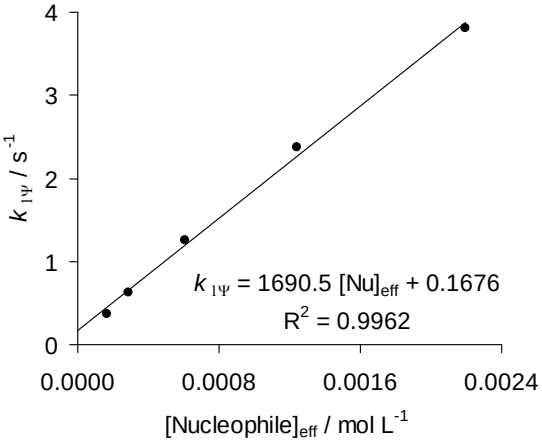
Reaction of aspartate (**1m**) with $(pyr)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 610 nm, No. ccy75)

$[(pyr)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]_0$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
1.56×10^{-5}	2.23×10^{-3}	2.20×10^{-3}	1.01×10^{-2}	5.68×10^{-3}	141	4.08	2.75×10^{-1}	3.80
1.56×10^{-5}	1.27×10^{-3}	1.24×10^{-3}	5.77×10^{-3}	3.26×10^{-3}	80	2.54	1.58×10^{-1}	2.38
1.56×10^{-5}	6.36×10^{-4}	6.07×10^{-4}	2.89×10^{-3}	1.64×10^{-3}	39	1.34	7.97×10^{-2}	1.26
1.56×10^{-5}	3.18×10^{-4}	2.90×10^{-4}	1.44×10^{-3}	8.34×10^{-4}	19	6.73×10^{-1}	4.05×10^{-2}	6.33×10^{-1}
1.56×10^{-5}	1.91×10^{-4}	1.65×10^{-4}	8.66×10^{-4}	5.10×10^{-4}	11	3.89×10^{-1}	2.47×10^{-2}	3.64×10^{-1}

$k_{2,N} = 1.69 \times 10^3\ M^{-1}s^{-1}$

$k_{2,OH^-} = 48.5\ M^{-1}s^{-1}$

$pK_B = 4.10$



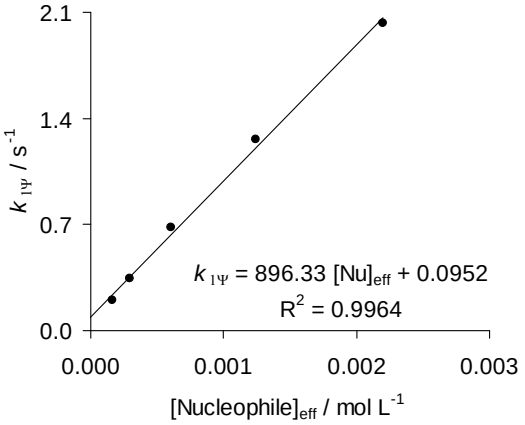
Reaction of aspartate (**1m**) with $(thq)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 610 nm, No. ccy74)

$[(thq)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]_0$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
1.61×10^{-5}	2.23×10^{-3}	2.20×10^{-3}	1.01×10^{-2}	5.68×10^{-3}	136	2.16	1.34×10^{-1}	2.03
1.61×10^{-5}	1.27×10^{-3}	1.24×10^{-3}	5.77×10^{-3}	3.26×10^{-3}	77	1.34	7.69×10^{-2}	1.26
1.61×10^{-5}	6.36×10^{-4}	6.07×10^{-4}	2.89×10^{-3}	1.64×10^{-3}	38	7.17×10^{-1}	3.88×10^{-2}	6.78×10^{-1}
1.61×10^{-5}	3.18×10^{-4}	2.90×10^{-4}	1.44×10^{-3}	8.34×10^{-4}	18	3.62×10^{-1}	1.97×10^{-2}	3.42×10^{-1}
1.61×10^{-5}	1.91×10^{-4}	1.65×10^{-4}	8.66×10^{-4}	5.10×10^{-4}	10	2.11×10^{-1}	1.20×10^{-2}	1.99×10^{-1}

$k_{2,N} = 8.96 \times 10^2\ M^{-1}s^{-1}$

$k_{2,OH^-} = 23.6\ M^{-1}s^{-1}$

$pK_B = 4.10$



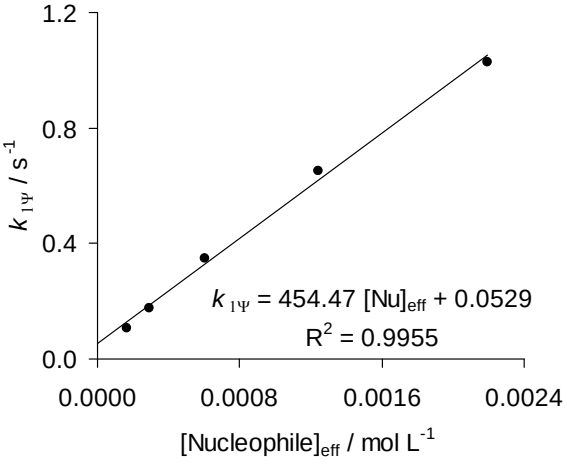
Reaction of aspartate (**1m**) with $(ind)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 610 nm, No. ccy76)

$[(ind)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]_0$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
1.32×10^{-5}	2.23×10^{-3}	2.20×10^{-3}	1.01×10^{-2}	5.68×10^{-3}	166	1.09	6.13×10^{-2}	1.03
1.32×10^{-5}	1.27×10^{-3}	1.24×10^{-3}	5.77×10^{-3}	3.26×10^{-3}	94	6.87×10^{-1}	3.52×10^{-2}	6.52×10^{-1}
1.32×10^{-5}	6.36×10^{-4}	6.07×10^{-4}	2.89×10^{-3}	1.64×10^{-3}	46	3.65×10^{-1}	1.77×10^{-2}	3.47×10^{-1}
1.32×10^{-5}	3.18×10^{-4}	2.90×10^{-4}	1.44×10^{-3}	8.34×10^{-4}	22	1.86×10^{-1}	9.01×10^{-3}	1.77×10^{-1}
1.32×10^{-5}	1.91×10^{-4}	1.65×10^{-4}	8.66×10^{-4}	5.10×10^{-4}	13	1.10×10^{-1}	5.50×10^{-3}	1.04×10^{-1}

$k_{2,N} = 4.54 \times 10^2\ M^{-1}s^{-1}$

$k_{2,OH^-} = 10.8\ M^{-1}s^{-1}$

$pK_B = 4.10$

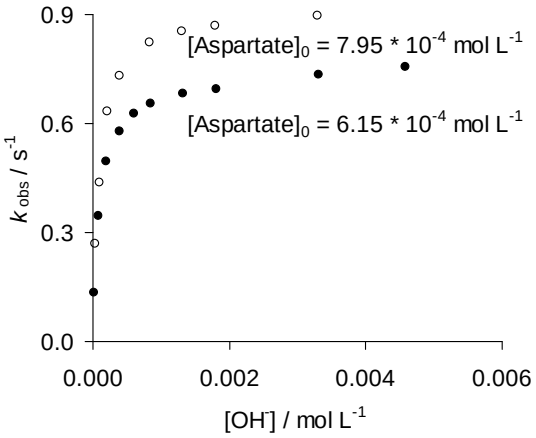


pH Dependance of rate constants for the reaction of aspartate (**1m**) with $(thq)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 610 nm, No. ccy73 and ccy78)

$[(thq)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]_0$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
1.61×10^{-5}	6.15×10^{-4}	3.13×10^{-4}	1.01×10^{-3}	8.22×10^{-5}	19	3.46×10^{-1}	1.94×10^{-3}	3.44×10^{-1}
1.61×10^{-5}	6.15×10^{-4}	4.42×10^{-4}	1.26×10^{-3}	2.03×10^{-4}	27	4.97×10^{-1}	4.79×10^{-3}	4.92×10^{-1}
1.61×10^{-5}	6.15×10^{-4}	5.10×10^{-4}	1.51×10^{-3}	3.85×10^{-4}	32	5.79×10^{-1}	9.09×10^{-3}	5.70×10^{-1}
1.61×10^{-5}	6.15×10^{-4}	5.43×10^{-4}	1.76×10^{-3}	6.02×10^{-4}	34	6.27×10^{-1}	1.42×10^{-2}	6.13×10^{-1}
1.61×10^{-5}	6.15×10^{-4}	5.62×10^{-4}	2.02×10^{-3}	8.43×10^{-4}	35	6.55×10^{-1}	1.99×10^{-2}	6.35×10^{-1}
1.61×10^{-5}	6.15×10^{-4}	5.80×10^{-4}	2.52×10^{-3}	1.32×10^{-3}	36	6.82×10^{-1}	3.13×10^{-2}	6.51×10^{-1}
1.61×10^{-5}	6.15×10^{-4}	5.89×10^{-4}	3.02×10^{-3}	1.82×10^{-3}	37	6.96×10^{-1}	4.29×10^{-2}	6.53×10^{-1}
1.61×10^{-5}	6.15×10^{-4}	6.01×10^{-4}	4.53×10^{-3}	3.31×10^{-3}	37	7.36×10^{-1}	7.82×10^{-2}	6.58×10^{-1}
1.61×10^{-5}	6.15×10^{-4}	6.05×10^{-4}	5.80×10^{-3}	4.58×10^{-3}	38	7.56×10^{-1}	1.08×10^{-1}	6.48×10^{-1}
1.61×10^{-5}	6.15×10^{-4}	1.21×10^{-4}	7.55×10^{-4}	1.94×10^{-5}	7	1.34×10^{-1}	4.57×10^{-4}	1.34×10^{-1}
1.61×10^{-5}	7.95×10^{-4}	2.57×10^{-4}	1.09×10^{-3}	3.80×10^{-5}	16	2.70×10^{-1}	8.96×10^{-4}	2.69×10^{-1}
1.61×10^{-5}	7.95×10^{-4}	4.45×10^{-4}	1.34×10^{-3}	1.01×10^{-4}	28	4.38×10^{-1}	2.39×10^{-3}	4.36×10^{-1}
1.61×10^{-5}	7.95×10^{-4}	5.82×10^{-4}	1.59×10^{-3}	2.17×10^{-4}	36	6.35×10^{-1}	5.11×10^{-3}	6.30×10^{-1}
1.61×10^{-5}	7.95×10^{-4}	6.60×10^{-4}	1.84×10^{-3}	3.90×10^{-4}	41	7.31×10^{-1}	9.19×10^{-3}	7.22×10^{-1}
1.61×10^{-5}	7.95×10^{-4}	7.25×10^{-4}	2.35×10^{-3}	8.28×10^{-4}	45	8.25×10^{-1}	1.95×10^{-2}	8.05×10^{-1}
1.61×10^{-5}	7.95×10^{-4}	7.49×10^{-4}	2.85×10^{-3}	1.31×10^{-3}	47	8.54×10^{-1}	3.08×10^{-2}	8.23×10^{-1}
1.61×10^{-5}	7.95×10^{-4}	7.61×10^{-4}	3.35×10^{-3}	1.80×10^{-3}	47	8.69×10^{-1}	4.24×10^{-2}	8.27×10^{-1}
1.61×10^{-5}	7.95×10^{-4}	7.76×10^{-4}	4.86×10^{-3}	3.29×10^{-3}	48	8.96×10^{-1}	7.77×10^{-2}	8.18×10^{-1}

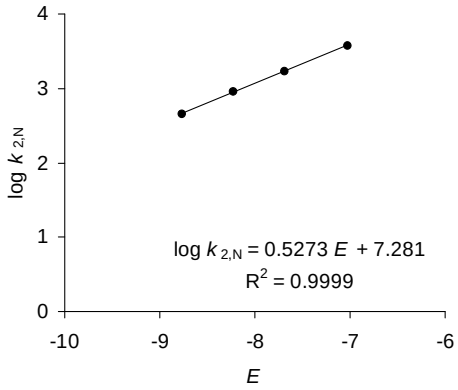
$k_{2,OH^-} = 23.6\ M^{-1}s^{-1}$

$pK_B = 4.10$



Reactivity parameters of aspartate (1m) in water: *N* = 13.81; *s* = 0.53

Reference electrophile	*E* parameter	$k_{2,N}$(20°C) / M^{-1} s^{-1}
$(dma)_2CH^+$	-7.02	3.77×10^3
$(pyr)_2CH^+$	-7.69	1.69×10^3
$(thq)_2CH^+$	-8.22	8.96×10^2
$(ind)_2CH^+$	-8.76	4.54×10^2



3.7.15. Glutamate (1n)

Rate constants in water

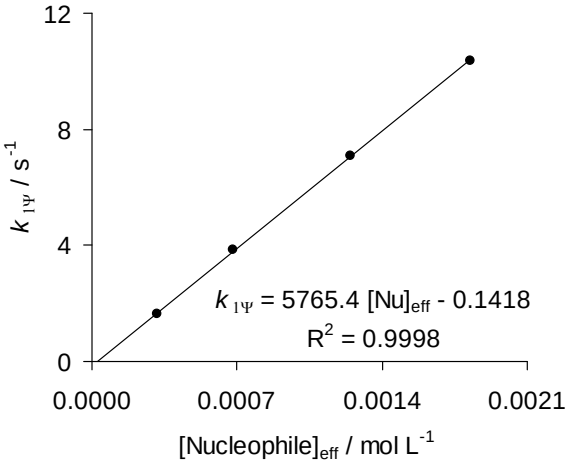
Reaction of glutamate (**1n**) with $(dma)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.5 vol-% CH_3CN, stopped-flow, detection at 610 nm, No. ccy182)

$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]_0$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}$/ $[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
5.95×10^{-5}	2.06×10^{-3}	1.83×10^{-3}	4.12×10^{-3}	2.32×10^{-4}	31	10.4	3.04×10^{-2}	10.4
5.95×10^{-5}	1.44×10^{-3}	1.25×10^{-3}	2.88×10^{-3}	1.92×10^{-4}	21	7.10	2.51×10^{-2}	7.07
5.95×10^{-5}	8.24×10^{-4}	6.83×10^{-4}	1.65×10^{-3}	1.43×10^{-4}	11	3.87	1.87×10^{-2}	3.85
5.95×10^{-5}	4.12×10^{-4}	3.16×10^{-4}	8.24×10^{-4}	9.65×10^{-5}	5	1.64	1.26×10^{-2}	1.63

$k_{2,N} = 5.77 \times 10^3\ M^{-1}s^{-1}$

$k_{2,OH^-} = 131\ M^{-1}s^{-1}$

$pK_B = 4.53$



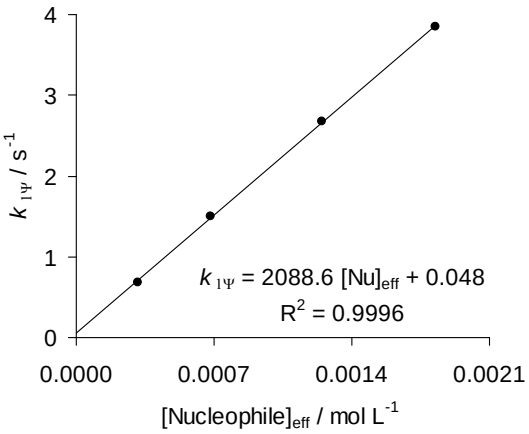
Reaction of glutamate (**1n**) with $(pyr)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.1 vol-% CH_3CN, stopped-flow, detection at 610 nm, No. ccy183)

$[(pyr)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]_0$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}$/ $[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
1.12×10^{-5}	2.06×10^{-3}	1.83×10^{-3}	4.12×10^{-3}	2.32×10^{-4}	163	3.86	1.13×10^{-2}	3.85
1.12×10^{-5}	1.44×10^{-3}	1.25×10^{-3}	2.88×10^{-3}	1.92×10^{-4}	111	2.68	9.31×10^{-3}	2.67
1.12×10^{-5}	8.24×10^{-4}	6.83×10^{-4}	1.65×10^{-3}	1.43×10^{-4}	61	1.51	6.93×10^{-3}	1.50
1.12×10^{-5}	4.12×10^{-4}	3.16×10^{-4}	8.24×10^{-4}	9.65×10^{-5}	28	6.84×10^{-1}	4.68×10^{-3}	6.79×10^{-1}

$k_{2,N} = 2.09 \times 10^3$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 48.5$ $M^{-1}s^{-1}$

$pK_B = 4.53$



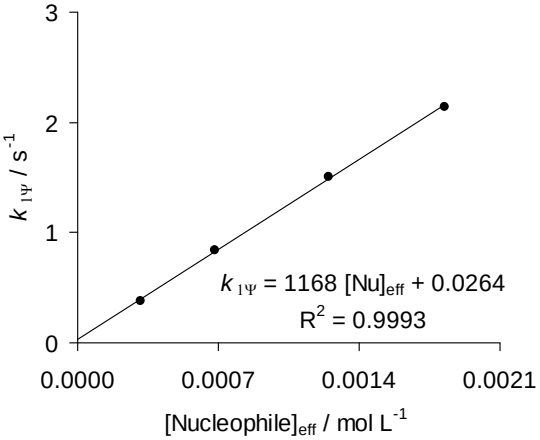
Reaction of glutamate (**1n**) with $(thq)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 610 nm, No. ccy184)

$[(thq)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]_0$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
1.91×10^{-5}	2.06×10^{-3}	1.83×10^{-3}	4.12×10^{-3}	2.32×10^{-4}	96	2.15	5.48×10^{-3}	2.14
1.91×10^{-5}	1.44×10^{-3}	1.25×10^{-3}	2.88×10^{-3}	1.92×10^{-4}	65	1.51	4.53×10^{-3}	1.51
1.91×10^{-5}	8.24×10^{-4}	6.83×10^{-4}	1.65×10^{-3}	1.43×10^{-4}	36	8.42×10^{-1}	3.37×10^{-3}	8.39×10^{-1}
1.91×10^{-5}	4.12×10^{-4}	3.16×10^{-4}	8.24×10^{-4}	9.65×10^{-5}	17	3.78×10^{-1}	2.28×10^{-3}	3.76×10^{-1}

$k_{2,N} = 1.17 \times 10^3$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 23.6$ $M^{-1}s^{-1}$

$pK_B = 4.53$



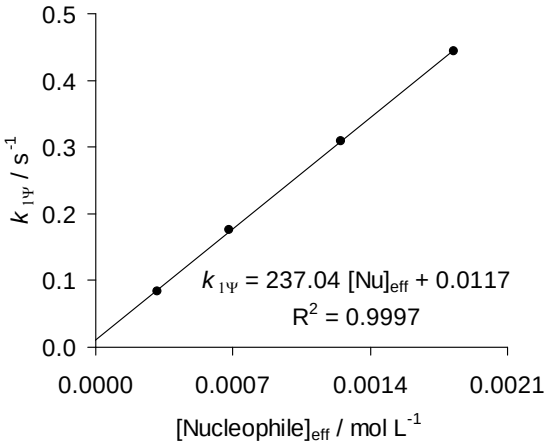
Reaction of glutamate (**1n**) with $(jul)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 634 nm, No. ccy185)

$[(jul)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]_0$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
8.55×10^{-6}	2.06×10^{-3}	1.83×10^{-3}	4.12×10^{-3}	2.32×10^{-4}	214	4.44×10^{-1}	7.99×10^{-4}	4.43×10^{-1}
8.55×10^{-6}	1.44×10^{-3}	1.25×10^{-3}	2.88×10^{-3}	1.92×10^{-4}	146	3.10×10^{-1}	6.60×10^{-4}	3.09×10^{-1}
8.55×10^{-6}	8.24×10^{-4}	6.83×10^{-4}	1.65×10^{-3}	1.43×10^{-4}	80	1.77×10^{-1}	4.92×10^{-4}	1.77×10^{-1}
8.55×10^{-6}	4.12×10^{-4}	3.16×10^{-4}	8.24×10^{-4}	9.65×10^{-5}	37	8.40×10^{-2}	3.32×10^{-4}	8.37×10^{-2}

$k_{2,N} = 2.37 \times 10^2$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 3.44$ $M^{-1}s^{-1}$

$pK_B = 4.53$



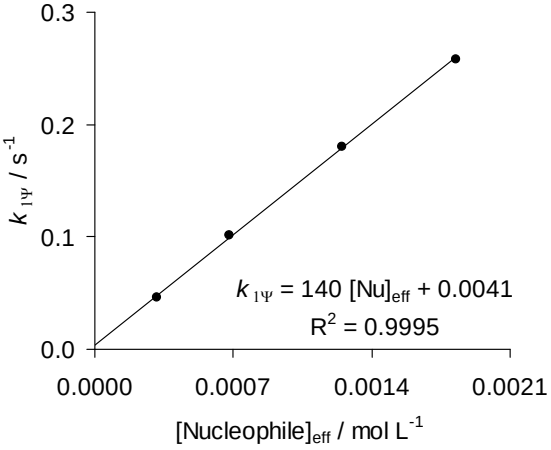
Reaction of glutamate (**1n**) with $(lil)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.1 vol-% CH_3CN, stopped-flow, detection at 634 nm, No. ccy186)

$[(lil)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]_0$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
9.35×10^{-6}	2.06×10^{-3}	1.83×10^{-3}	4.12×10^{-3}	2.32×10^{-4}	195	2.59×10^{-1}	5.02×10^{-4}	2.58×10^{-1}
9.35×10^{-6}	1.44×10^{-3}	1.25×10^{-3}	2.88×10^{-3}	1.92×10^{-4}	133	1.81×10^{-1}	4.15×10^{-4}	1.81×10^{-1}
9.35×10^{-6}	8.24×10^{-4}	6.83×10^{-4}	1.65×10^{-3}	1.43×10^{-4}	73	1.02×10^{-1}	3.09×10^{-4}	1.02×10^{-1}
9.35×10^{-6}	4.12×10^{-4}	3.16×10^{-4}	8.24×10^{-4}	9.65×10^{-5}	34	4.64×10^{-2}	2.08×10^{-4}	4.62×10^{-2}

$k_{2,N} = 1.40 \times 10^2$ $M^{-1}s^{-1}$

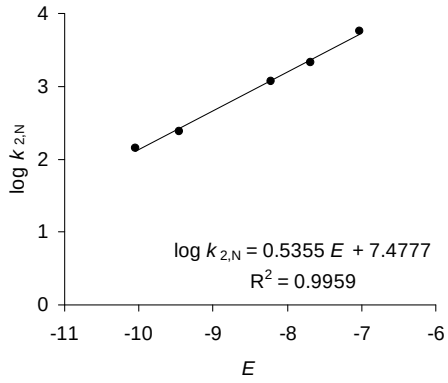
$k_{2,OH^-} = 2.16$ $M^{-1}s^{-1}$

$pK_B = 4.53$



Reactivity parameters of glutamate (1n) in water: *N* = 13.96; *s* = 0.54

Reference electrophile	*E* parameter	$k_{2,N}$(20°C) / M^{-1} s^{-1}
$(dma)_2CH^+$	-7.02	5.77×10^3
$(pyr)_2CH^+$	-7.69	2.09×10^3
$(thq)_2CH^+$	-8.22	1.17×10^3
$(jul)_2CH^+$	-9.45	2.37×10^2
$(lil)_2CH^+$	-10.04	1.40×10^2



3.7.16. Cysteine (1o)

Rate constants in water

Typical procedure:

L-Cysteine (131.6 mg, 1.086 mmol) was dissolved in 2.170 mL of aqueous KOH (0.5033 mol L^{-1}), then the solution was filled up to 10 mL with water (c_{Nu} = 0.109 mol L^{-1}, $c_{0,OH}$ = 0.109 mol L^{-1}). 200 µL of this solution was combined with 400 µL of aqueous KOH (0.5033 mol L^{-1}) and diluted with water to 25 mL. Equal volumes of this solution were combined with a solution of [$(ind)_2CH^+$] (3.95×10^{-5} mol L^{-1}) in the stopped-flow instrument to give the final concentrations listed in the table.

Reaction of cysteine (**1o**) with $(ind)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 610 nm, No. fb170)

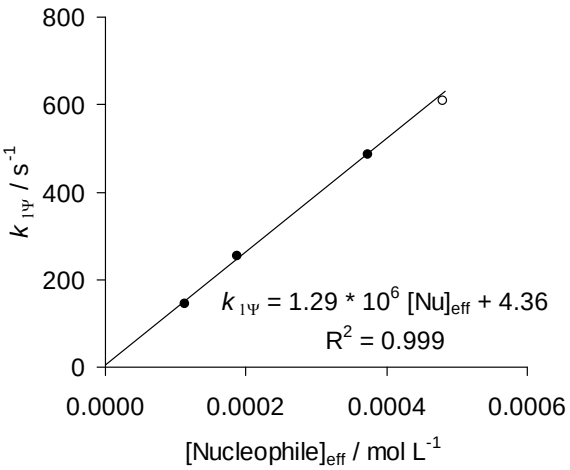
$[(ind)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]_0$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
1.98×10^{-5}	5.43×10^{-4}	4.80×10^{-4}	5.60×10^{-3}	4.58×10^{-3}	24	6.09×10^{2}	4.94×10^{-2}	6.09×10^{2}
1.98×10^{-5}	4.36×10^{-4}	3.74×10^{-4}	4.46×10^{-3}	3.65×10^{-3}	19	4.86×10^{2}	3.94×10^{-2}	4.86×10^{2}
1.98×10^{-5}	2.18×10^{-4}	1.88×10^{-4}	4.24×10^{-3}	3.83×10^{-3}	10	2.55×10^{2}	4.14×10^{-2}	2.55×10^{2}
1.98×10^{-5}	1.31×10^{-4}	1.13×10^{-4}	4.15×10^{-3}	3.91×10^{-3}	6	1.46×10^{2}	4.22×10^{-2}	1.46×10^{2}

$k_{2,N} = 1.29 \times 10^6$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 10.8$ $M^{-1}s^{-1}$

$pK_B = 3.22$

One data point from an independent measurement of the cysteine reactivity at different pH (No. fb169.10, first row in the table) is included in the figure on the right. This data has not been used for the derivation of the correlation equation shown in the figure



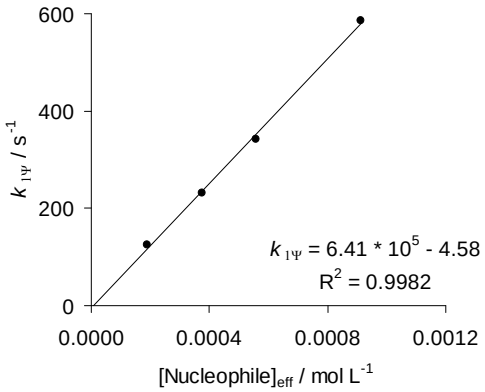
Reaction of cysteine (**1o**) with $(jul)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.4 vol-% CH_3CN, stopped-flow, detection at 634 nm, No. fb171)

$[(jul)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]_0$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
2.70×10^{-5}	1.09×10^{-3}	9.12×10^{-4}	5.10×10^{-3}	3.10×10^{-3}	34	5.86×10^{2}	1.07×10^{-2}	5.86×10^{2}
2.70×10^{-5}	6.55×10^{-4}	5.58×10^{-4}	4.68×10^{-3}	3.47×10^{-3}	21	3.43×10^{2}	1.19×10^{-2}	3.43×10^{2}
2.70×10^{-5}	4.36×10^{-4}	3.74×10^{-4}	4.46×10^{-3}	3.65×10^{-3}	14	2.31×10^{2}	1.26×10^{-2}	2.31×10^{2}
2.70×10^{-5}	2.18×10^{-4}	1.88×10^{-4}	4.24×10^{-3}	3.83×10^{-3}	7	1.24×10^{2}	1.32×10^{-2}	1.24×10^{2}

$k_{2,N} = 6.41 \times 10^5\ M^{-1}s^{-1}$

$k_{2,OH^-} = 3.44\ M^{-1}s^{-1}$

$pK_B = 3.22$



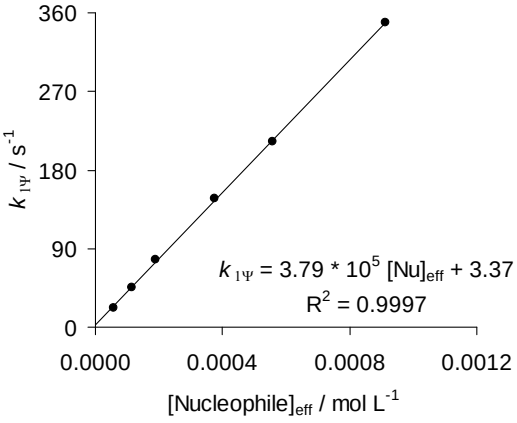
Reaction of cysteine (**1o**) with $(lil)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.4 vol-% CH_3CN, stopped-flow, detection at 634 nm, No. fb172)

$[(lil)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]_0$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
1.20×10^{-5}	1.09×10^{-3}	9.12×10^{-4}	5.10×10^{-3}	3.10×10^{-3}	76	3.49×10^{2}	6.69×10^{-3}	3.49×10^{2}
1.20×10^{-5}	6.55×10^{-4}	5.58×10^{-4}	4.68×10^{-3}	3.47×10^{-3}	47	2.13×10^{2}	7.49×10^{-3}	2.13×10^{2}
1.20×10^{-5}	4.36×10^{-4}	3.74×10^{-4}	4.46×10^{-3}	3.65×10^{-3}	31	1.47×10^{2}	7.88×10^{-3}	1.47×10^{2}
1.20×10^{-5}	2.18×10^{-4}	1.88×10^{-4}	4.24×10^{-3}	3.83×10^{-3}	16	7.75×10^{1}	8.28×10^{-3}	7.75×10^{1}
1.20×10^{-5}	1.31×10^{-4}	1.13×10^{-4}	4.15×10^{-3}	3.91×10^{-3}	9	4.59×10^{1}	8.44×10^{-3}	4.59×10^{1}
1.20×10^{-5}	6.55×10^{-5}	5.69×10^{-5}	4.09×10^{-3}	3.97×10^{-3}	5	2.26×10^{1}	8.57×10^{-3}	2.26×10^{1}

$k_{2,N} = 3.79 \times 10^5\ M^{-1}s^{-1}$

$k_{2,OH^-} = 2.16\ M^{-1}s^{-1}$

$pK_B = 3.22$

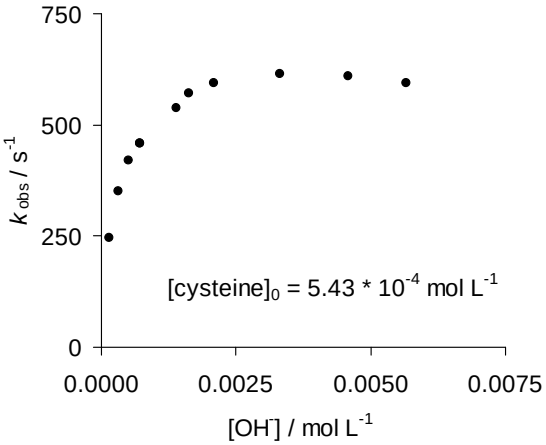


pH Dependance of rate constants for the reaction of cysteine (**1o**) with $(ind)_2CH^+BF_4^-$: (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 610 nm, No. fb169)

$[(ind)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]_0$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
1.98×10^{-5}	5.43×10^{-4}	1.06×10^{-4}	7.95×10^{-4}	1.46×10^{-4}	5	2.47×10^{2}	1.58×10^{-3}	2.47×10^{2}
1.98×10^{-5}	5.43×10^{-4}	1.88×10^{-4}	1.05×10^{-3}	3.19×10^{-4}	9	3.50×10^{2}	3.45×10^{-3}	3.50×10^{2}
1.98×10^{-5}	5.43×10^{-4}	2.49×10^{-4}	1.30×10^{-3}	5.08×10^{-4}	13	4.21×10^{2}	5.49×10^{-3}	4.21×10^{2}
1.98×10^{-5}	5.43×10^{-4}	2.94×10^{-4}	1.55×10^{-3}	7.13×10^{-4}	15	4.58×10^{2}	7.70×10^{-3}	4.58×10^{2}
1.98×10^{-5}	5.43×10^{-4}	2.94×10^{-4}	1.55×10^{-3}	7.13×10^{-4}	15	4.58×10^{2}	7.70×10^{-3}	4.58×10^{2}
1.98×10^{-5}	5.43×10^{-4}	3.79×10^{-4}	2.31×10^{-3}	1.39×10^{-3}	19	5.37×10^{2}	1.50×10^{-2}	5.37×10^{2}
1.98×10^{-5}	5.43×10^{-4}	3.96×10^{-4}	2.56×10^{-3}	1.62×10^{-3}	20	5.70×10^{2}	1.75×10^{-2}	5.70×10^{2}
1.98×10^{-5}	5.43×10^{-4}	4.22×10^{-4}	3.06×10^{-3}	2.10×10^{-3}	21	5.95×10^{2}	2.26×10^{-2}	5.95×10^{2}
1.98×10^{-5}	5.43×10^{-4}	4.60×10^{-4}	4.32×10^{-3}	3.32×10^{-3}	23	6.14×10^{2}	3.58×10^{-2}	6.14×10^{2}
1.98×10^{-5}	5.43×10^{-4}	4.80×10^{-4}	5.60×10^{-3}	4.58×10^{-3}	24	6.09×10^{2}	4.94×10^{-2}	6.09×10^{2}
1.98×10^{-5}	5.43×10^{-4}	4.91×10^{-4}	6.70×10^{-3}	5.67×10^{-3}	25	5.95×10^{2}	6.12×10^{-2}	5.95×10^{2}

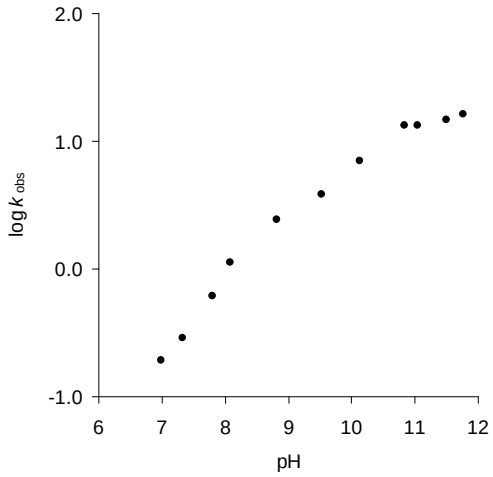
$k_{2,OH^-} = 10.8\ M^{-1}s^{-1}$

$pK_B = 3.22$



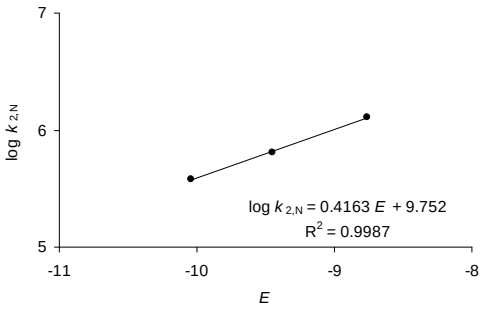
pH Dependance of rate constants for the reaction of cysteine (**1o**) with $(lil)_2CH^+BF_4^-$: (phosphate buffer, at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 630 nm, pH measured, No. fn310)

$[(lil)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[PO_4^{3-}]$ / mol L^{-1}	$[HPO_4^{2-}]$ / mol L^{-1}	$[H_2PO_4^-]$ / mol L^{-1}	pH	k_{obs} / s^{-1}
7.43×10^{-6}	7.32×10^{-5}	9.09×10^{-3}	9.09×10^{-3}		11.76	1.63×10^{1}
7.43×10^{-6}	7.32×10^{-5}	4.55×10^{-3}	9.09×10^{-3}		11.50	1.48×10^{1}
7.43×10^{-6}	7.32×10^{-5}	1.36×10^{-3}	9.09×10^{-3}	1.82×10^{-3}	11.04	1.33×10^{1}
7.43×10^{-6}	7.32×10^{-5}	9.09×10^{-4}	9.09×10^{-3}		10.84	1.34×10^{1}
7.43×10^{-6}	7.32×10^{-5}	1.82×10^{-4}	9.09×10^{-3}		10.13	7.04
7.43×10^{-6}	7.32×10^{-5}		9.09×10^{-3}		9.52	3.84
7.43×10^{-6}	7.32×10^{-5}		9.09×10^{-3}	1.82×10^{-4}	8.81	2.43
7.43×10^{-6}	7.32×10^{-5}		9.09×10^{-3}	9.09×10^{-4}	8.08	1.12
7.43×10^{-6}	7.32×10^{-5}		9.09×10^{-3}	9.09×10^{-3}	7.80	6.19×10^{-1}
7.43×10^{-6}	7.32×10^{-5}		9.09×10^{-3}	4.55×10^{-3}	7.32	2.88×10^{-1}
7.43×10^{-6}	7.32×10^{-5}		9.09×10^{-3}	9.09×10^{-3}	6.99	1.94×10^{-1}



Reactivity parameters of cysteine (1o) in water: N = 23.43; s = 0.42

Reference electrophile	E parameter	$k_{2,N}$(20°C) / M^{-1} s^{-1}
$(ind)_2CH^+$	-8.76	1.29×10^6
$(jul)_2CH^+$	-9.45	6.41×10^5
$(lil)_2CH^+$	-10.04	3.79×10^5



3.7.17. Methionine (1p)

Rate constants in water

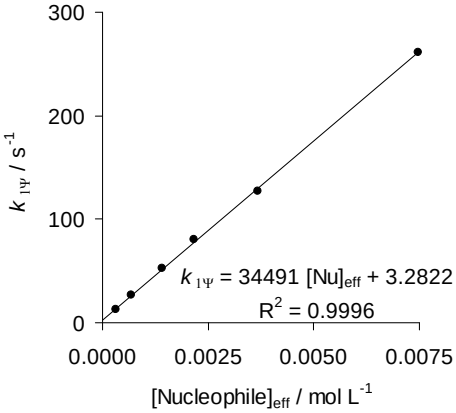
Reaction of methionine (**1p**) with $(mor)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 9 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(mor)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}$/ $[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi, OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fn276.1	1.73×10^{-5}	7.85×10^{-3}	7.47×10^{-3}	3.77×10^{-4}	432	2.62×10^{2}	4.00×10^{-1}	2.62×10^{2}
fn276.2	1.73×10^{-5}	3.93×10^{-3}	3.67×10^{-3}	2.64×10^{-4}	212	1.27×10^{2}	2.80×10^{-1}	1.27×10^{2}
fn276.3	1.73×10^{-5}	2.36×10^{-3}	2.16×10^{-3}	2.03×10^{-4}	125	8.05×10^{1}	2.15×10^{-1}	8.03×10^{1}
fn276.4	1.73×10^{-5}	1.57×10^{-3}	1.41×10^{-3}	1.64×10^{-4}	81	5.30×10^{1}	1.74×10^{-1}	5.28×10^{1}
fn276.5	1.73×10^{-5}	7.85×10^{-4}	6.72×10^{-4}	1.13×10^{-4}	39	2.65×10^{1}	1.20×10^{-1}	2.64×10^{1}
fn276.6	1.73×10^{-5}	3.93×10^{-4}	3.15×10^{-4}	7.75×10^{-5}	18	1.31×10^{1}	8.22×10^{-2}	1.30×10^{1}

$k_{2,N} = 3.45 \times 10^4$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 1060$ $M^{-1}s^{-1}$

$pK_B = 4.72$



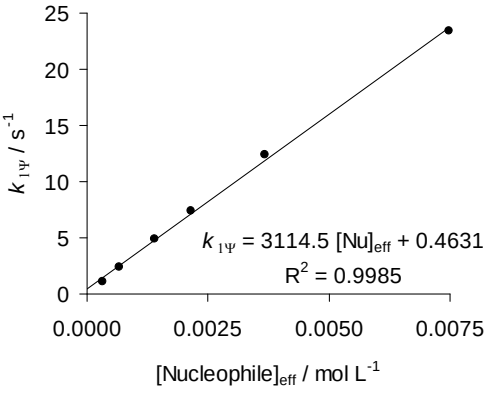
Reaction of methionine (**1p**) with $(dma)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 9 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}$/ $[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi, OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fn277.1	3.37×10^{-5}	7.85×10^{-3}	7.47×10^{-3}	3.77×10^{-4}	222	2.35×10^{1}	4.94×10^{-2}	2.35×10^{1}
fn277.2	3.37×10^{-5}	3.93×10^{-3}	3.67×10^{-3}	2.64×10^{-4}	109	1.24×10^{1}	3.46×10^{-2}	1.24×10^{1}
fn277.3	3.37×10^{-5}	2.36×10^{-3}	2.16×10^{-3}	2.03×10^{-4}	64	7.43	2.66×10^{-2}	7.40
fn277.4	3.37×10^{-5}	1.57×10^{-3}	1.41×10^{-3}	1.64×10^{-4}	42	4.92	2.14×10^{-2}	4.90
fn277.5	3.37×10^{-5}	7.85×10^{-4}	6.72×10^{-4}	1.13×10^{-4}	20	2.44	1.48×10^{-2}	2.43
fn277.6	3.37×10^{-5}	3.93×10^{-4}	3.15×10^{-4}	7.75×10^{-5}	9	1.11	1.02×10^{-2}	1.10

$k_{2,N} = 3.11 \times 10^3$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 131$ $M^{-1}s^{-1}$

$pK_B = 4.72$



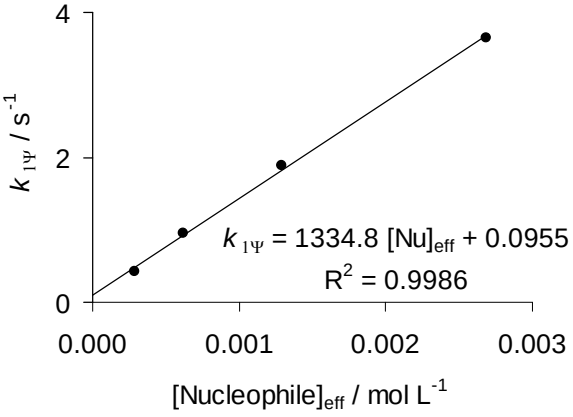
Reaction of methionine (**1p**) with $(pyr)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.4 vol-% CH_3CN, stopped-flow, detection at 611 nm)

No.	$[(pyr)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi, OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fn274.3	1.20×10^{-5}	2.91×10^{-3}	2.68×10^{-3}	2.26×10^{-4}	224	3.66	1.10×10^{-2}	3.65
fn274.4	1.20×10^{-5}	1.45×10^{-3}	1.29×10^{-3}	1.57×10^{-4}	108	1.89	7.61×10^{-3}	1.88
fn274.5	1.20×10^{-5}	7.27×10^{-4}	6.18×10^{-4}	1.09×10^{-4}	52	9.51×10^{-1}	5.26×10^{-3}	9.46×10^{-1}
fn274.6	1.20×10^{-5}	3.64×10^{-4}	2.90×10^{-4}	7.43×10^{-5}	24	4.29×10^{-1}	3.60×10^{-3}	4.25×10^{-1}

$k_{2,N} = 1.33 \times 10^3$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 48.5$ $M^{-1}s^{-1}$

$pK_B = 4.72$



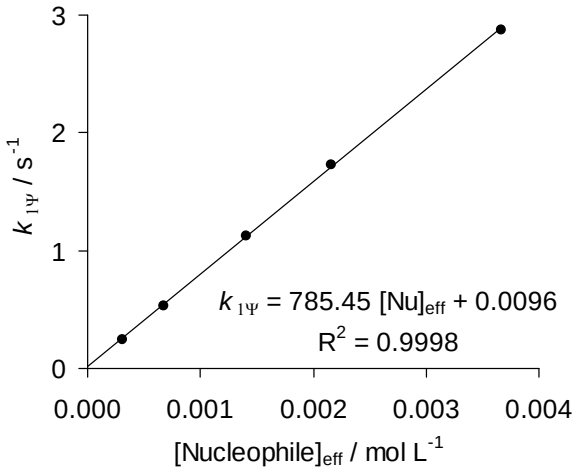
Reaction of methionine (**1p**) with $(thq)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.8 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(thq)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi, OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fn278.2	2.41×10^{-5}	3.93×10^{-3}	3.67×10^{-3}	2.64×10^{-4}	152	2.88	6.24×10^{-3}	2.87
fn278.3	2.41×10^{-5}	2.36×10^{-3}	2.16×10^{-3}	2.03×10^{-4}	90	1.73	4.78×10^{-3}	1.73
fn278.4	2.41×10^{-5}	1.57×10^{-3}	1.41×10^{-3}	1.64×10^{-4}	58	1.13	3.86×10^{-3}	1.13
fn278.5	2.41×10^{-5}	7.85×10^{-4}	6.72×10^{-4}	1.13×10^{-4}	28	5.35×10^{-1}	2.67×10^{-3}	5.32×10^{-1}
fn278.6	2.41×10^{-5}	3.93×10^{-4}	3.15×10^{-4}	7.75×10^{-5}	13	2.46×10^{-1}	1.83×10^{-3}	2.44×10^{-1}

$k_{2,N} = 7.85 \times 10^2$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 23.6$ $M^{-1}s^{-1}$

$pK_B = 4.72$



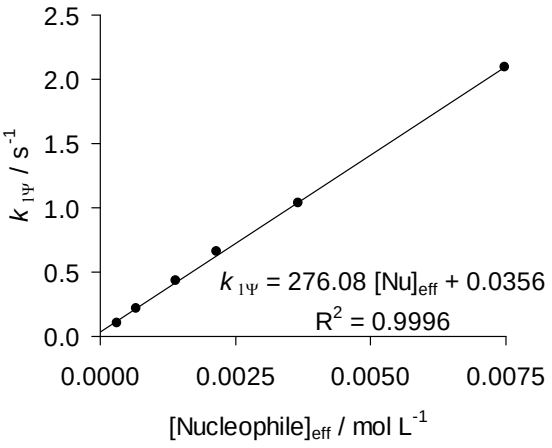
Reaction of methionine (**1p**) with $(ind)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.8 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(ind)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi, OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fn279.1	1.95×10^{-5}	7.85×10^{-3}	7.47×10^{-3}	3.77×10^{-4}	383	2.10	4.08×10^{-3}	2.10
fn279.2	1.95×10^{-5}	3.93×10^{-3}	3.67×10^{-3}	2.64×10^{-4}	188	1.04	2.85×10^{-3}	1.04
fn279.3	1.95×10^{-5}	2.36×10^{-3}	2.16×10^{-3}	2.03×10^{-4}	111	6.58×10^{-1}	2.19×10^{-3}	6.56×10^{-1}
fn279.4	1.95×10^{-5}	1.57×10^{-3}	1.41×10^{-3}	1.64×10^{-4}	72	4.36×10^{-1}	1.77×10^{-3}	4.34×10^{-1}
fn279.5	1.95×10^{-5}	7.85×10^{-4}	6.72×10^{-4}	1.13×10^{-4}	34	2.16×10^{-1}	1.22×10^{-3}	2.15×10^{-1}
fn279.6	1.95×10^{-5}	3.93×10^{-4}	3.15×10^{-4}	7.75×10^{-5}	16	1.08×10^{-1}	8.37×10^{-4}	1.07×10^{-1}

$k_{2,N} = 2.76 \times 10^2\ M^{-1}s^{-1}$

$k_{2,OH^-} = 10.8\ M^{-1}s^{-1}$

$pK_B = 4.72$



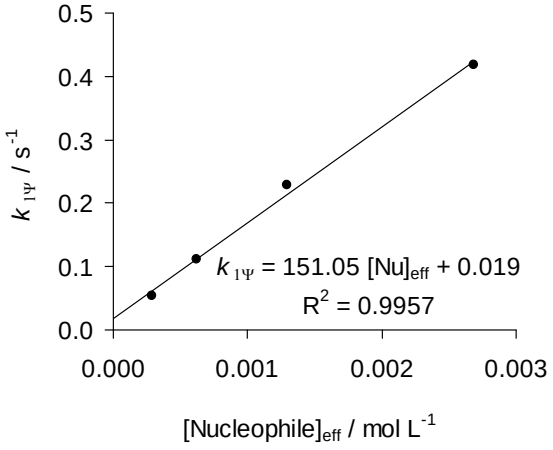
Reaction of methionine (**1p**) with $(jul)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.4 vol-% CH_3CN, stopped-flow, detection at 634 nm)

No.	$[(jul)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi, OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fn275.3	2.37×10^{-5}	2.91×10^{-3}	2.68×10^{-3}	2.26×10^{-4}	113	4.19×10^{-1}	7.78×10^{-4}	4.18×10^{-1}
fn275.4	2.37×10^{-5}	1.45×10^{-3}	1.29×10^{-3}	1.57×10^{-4}	55	2.30×10^{-1}	5.40×10^{-4}	2.29×10^{-1}
fn275.5	2.37×10^{-5}	7.27×10^{-4}	6.18×10^{-4}	1.09×10^{-4}	26	1.12×10^{-1}	3.73×10^{-4}	1.12×10^{-1}
fn275.6	2.37×10^{-5}	3.64×10^{-4}	2.90×10^{-4}	7.43×10^{-5}	12	5.50×10^{-2}	2.56×10^{-4}	5.47×10^{-2}

$k_{2,N} = 1.51 \times 10^2\ M^{-1}s^{-1}$

$k_{2,OH^-} = 3.44\ M^{-1}s^{-1}$

$pK_B = 4.72$



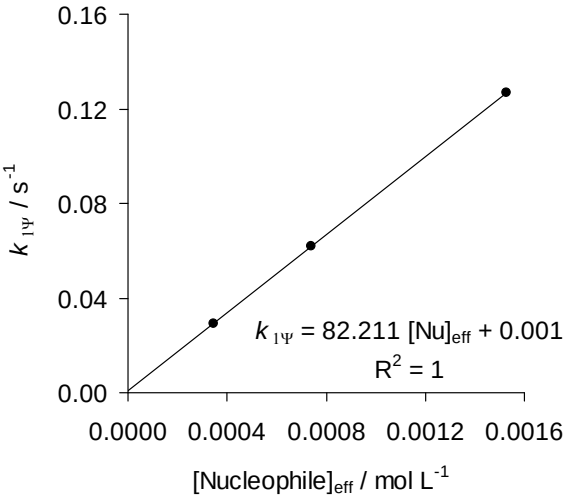
Reaction of methionine (**1p**) with $(lil)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.4 vol-% CH_3CN, J&M, detection at 630 nm)

No.	$[(lil)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fn280.3	1.51×10^{-5}	1.70×10^{-3}	1.53×10^{-3}	1.71×10^{-4}	101	1.27×10^{-1}	3.69×10^{-4}	1.27×10^{-1}
fn280.2	1.52×10^{-5}	8.57×10^{-4}	7.38×10^{-4}	1.19×10^{-4}	49	6.21×10^{-2}	2.56×10^{-4}	6.18×10^{-2}
fn280.6	1.52×10^{-5}	4.29×10^{-4}	3.48×10^{-4}	8.14×10^{-5}	23	2.96×10^{-2}	1.76×10^{-4}	2.94×10^{-2}

$k_{2,N}$ = 82.2 $M^{-1}s^{-1}$

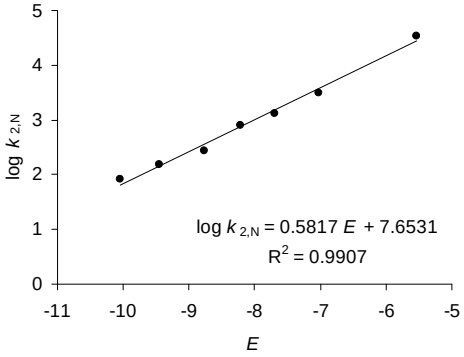
k_{2,OH^-} = 2.16 $M^{-1}s^{-1}$

pK_B = 4.72



Reactivity parameters of methionine (1p) in water: *N* = 13.16; *s* = 0.58

Reference electrophile	*E* parameter	$k_{2,N}$(20°C) / M^{-1} s^{-1}
$(mor)_2CH^+$	-5.53	3.45×10^4
$(dma)_2CH^+$	-7.02	3.11×10^3
$(pyr)_2CH^+$	-7.69	1.33×10^3
$(thq)_2CH^+$	-8.22	7.85×10^2
$(ind)_2CH^+$	-8.76	2.76×10^2
$(jul)_2CH^+$	-9.45	1.51×10^2
$(lil)_2CH^+$	-10.04	8.22×10^1



3.7.18. β-Alanine (1q)

Rate constants in water

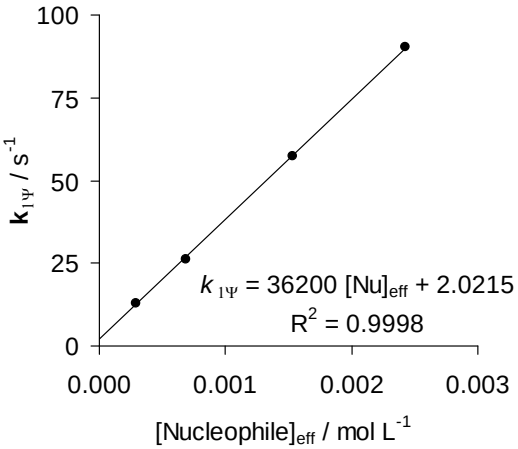
Reaction of β-alanine (**1q**) with $(mor)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 9 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(mor)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fn224.3	1.93×10^{-5}	3.08×10^{-3}	2.43×10^{-3}	6.50×10^{-4}	126	9.09×10^{1}	6.89×10^{-1}	9.02×10^{1}
fn224.4	1.93×10^{-5}	2.05×10^{-3}	1.53×10^{-3}	5.16×10^{-4}	79	5.79×10^{1}	5.47×10^{-1}	5.74×10^{1}
fn224.5	1.93×10^{-5}	1.03×10^{-3}	6.85×10^{-4}	3.45×10^{-4}	35	2.66×10^{1}	3.66×10^{-1}	2.62×10^{1}
fn224.6	1.93×10^{-5}	5.14×10^{-4}	2.90×10^{-4}	2.24×10^{-4}	15	1.33×10^{1}	2.38×10^{-1}	1.31×10^{1}

$k_{2,N} = 3.62 \times 10^4\ M^{-1}s^{-1}$

$k_{2,OH^-} = 1060\ M^{-1}s^{-1}$

$pK_B = 3.76$ (ref 4)



Reaction of β-alanine (**1q**) with $(dma)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 9 vol-% CH_3CN, stopped-flow, detection at 610 nm)

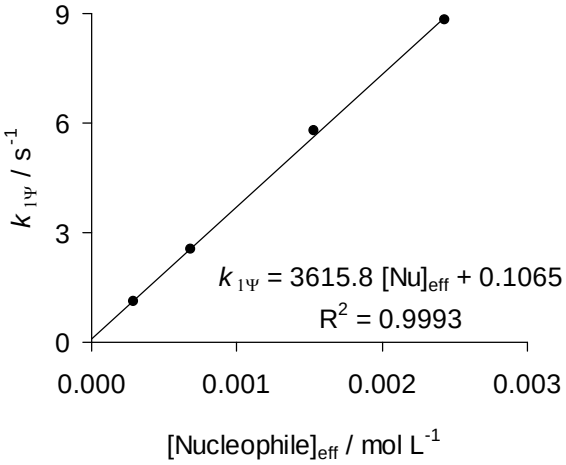
No.	$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fn225.3	2.18×10^{-5}	3.08×10^{-3}	2.43×10^{-3}	6.50×10^{-4}	111	8.91	8.51×10^{-2}	8.82
fn225.4	2.18×10^{-5}	2.05×10^{-3}	1.53×10^{-3}	5.16×10^{-4}	70	5.85	6.76×10^{-2}	5.78
fn225.5	2.18×10^{-5}	1.03×10^{-3}	6.85×10^{-4}	3.45×10^{-4}	31	2.59	4.52×10^{-2}	2.54
fn225.6	2.18×10^{-5}	5.14×10^{-4}	2.90×10^{-4}	2.24×10^{-4}	13	1.16	2.94×10^{-2}	1.13

$k_{2,N} = 3.62 \times 10^3\ M^{-1}s^{-1}$

$k_{2,O}$

$_{H^-} = 131\ M^{-1}s^{-1}$

$pK_B = 3.76$ (ref 4)



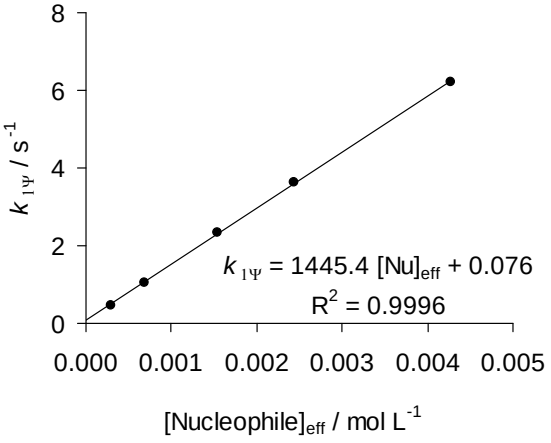
Reaction of β-alanine (**1q**) with $(pyr)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(pyr)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi, OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fn226.2	2.14×10^{-5}	5.14×10^{-3}	4.28×10^{-3}	8.62×10^{-4}	200	6.26	4.18×10^{-2}	6.22
fn226.3	2.14×10^{-5}	3.08×10^{-3}	2.43×10^{-3}	6.50×10^{-4}	114	3.67	3.15×10^{-2}	3.64
fn226.4	2.14×10^{-5}	2.05×10^{-3}	1.53×10^{-3}	5.16×10^{-4}	72	2.37	2.50×10^{-2}	2.34
fn226.5	2.14×10^{-5}	1.03×10^{-3}	6.85×10^{-4}	3.45×10^{-4}	32	1.06	1.67×10^{-2}	1.04
fn226.6	2.14×10^{-5}	5.14×10^{-4}	2.90×10^{-4}	2.24×10^{-4}	14	4.67×10^{-1}	1.09×10^{-2}	4.56×10^{-1}

$k_{2,N} = 1.45 \times 10^3$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 48.5$ $M^{-1}s^{-1}$

$pK_B = 3.76$ (ref 4)



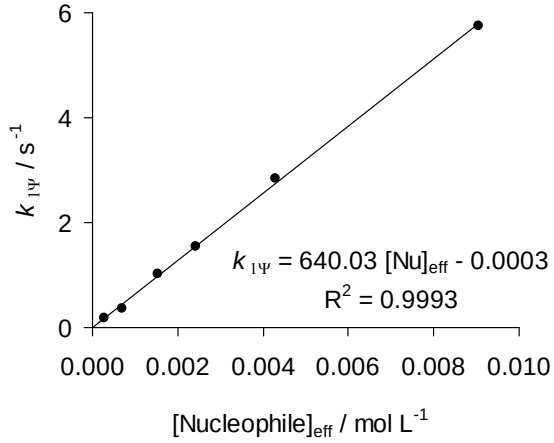
Reaction of β-alanine (**1q**) with $(thq)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 9 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(thq)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi, OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fn227.1	1.85×10^{-5}	1.03×10^{-2}	9.05×10^{-3}	1.25×10^{-3}	489	5.78	2.96×10^{-2}	5.75
fn227.2	1.85×10^{-5}	5.14×10^{-3}	4.28×10^{-3}	8.62×10^{-4}	231	2.85	2.03×10^{-2}	2.83
fn227.3	1.85×10^{-5}	3.08×10^{-3}	2.43×10^{-3}	6.50×10^{-4}	131	1.55	1.53×10^{-2}	1.53
fn227.4	1.85×10^{-5}	2.05×10^{-3}	1.53×10^{-3}	5.16×10^{-4}	83	1.03	1.22×10^{-2}	1.02
fn227.5	1.85×10^{-5}	1.03×10^{-3}	6.85×10^{-4}	3.45×10^{-4}	37	3.83×10^{-1}	8.14×10^{-3}	3.75×10^{-1}
fn227.6	1.85×10^{-5}	5.14×10^{-4}	2.90×10^{-4}	2.24×10^{-4}	16	1.85×10^{-1}	5.29×10^{-3}	1.80×10^{-1}

$k_{2,N} = 6.40 \times 10^2$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 23.6$ $M^{-1}s^{-1}$

$pK_B = 3.76$ (ref 4)



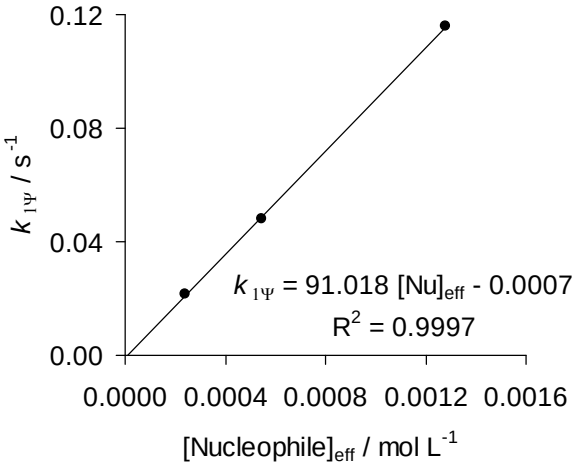
Reaction of β-alanine (**1q**) with $(lil)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.8 vol-% CH_3CN, J&M, detection at 630 nm)

No.	$[(lil)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fn228.4	1.11×10^{-5}	1.75×10^{-3}	1.28×10^{-3}	4.71×10^{-4}	115	1.17×10^{-1}	1.02×10^{-3}	1.16×10^{-1}
fn228.5	1.08×10^{-5}	8.55×10^{-4}	5.47×10^{-4}	3.08×10^{-4}	51	4.88×10^{-2}	6.66×10^{-4}	4.81×10^{-2}
fn228.6	1.12×10^{-5}	4.43×10^{-4}	2.39×10^{-4}	2.04×10^{-4}	21	2.22×10^{-2}	4.40×10^{-4}	2.18×10^{-2}

$k_{2,N} = 9.10 \times 10^1\ M^{-1}s^{-1}$

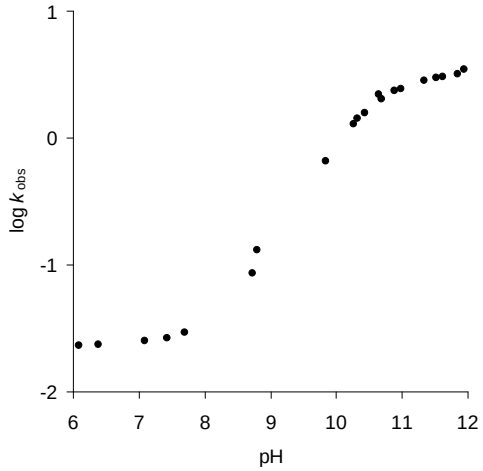
$k_{2,OH^-} = 2.16\ M^{-1}s^{-1}$

$pK_B = 3.76$ (ref 4)



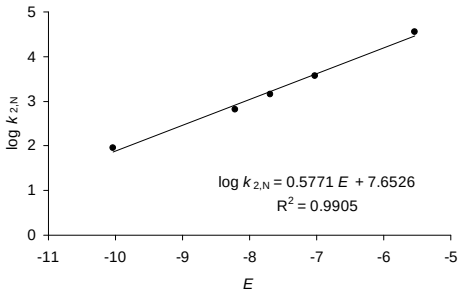
pH Dependance of rate constants for the reaction of β-alanine (**1q**) with $(dma)_2CH^+BF_4^-$ (phosphate buffer, at 20 °C, cosolvent: 0.5 vol % CH_3CN, stopped-flow, detection at 610 nm, pH measured, No. fn295 and fn300)

$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[PO_4^{3-}]$ / mol L^{-1}	$[HPO_4^{2-}]$ / mol L^{-1}	$[H_2PO_4^-]$ / mol L^{-1}	pH	k_{obs} / s^{-1}
2.24×10^{-5}	9.09×10^{-4}	9.09×10^{-3}			12.03	3.63
2.24×10^{-5}	9.09×10^{-4}	9.09×10^{-3}	9.18×10^{-4}		12.01	3.56
2.24×10^{-5}	9.09×10^{-4}	9.09×10^{-3}	4.59×10^{-3}		11.95	3.44
2.24×10^{-5}	9.09×10^{-4}	9.09×10^{-3}	9.18×10^{-3}		11.85	3.19
2.24×10^{-5}	9.09×10^{-4}	4.55×10^{-3}	9.18×10^{-3}		11.62	3.02
4.09×10^{-5}	9.09×10^{-4}	4.55×10^{-3}	9.07×10^{-3}		11.52	2.96
4.09×10^{-5}	9.09×10^{-4}	2.73×10^{-3}	9.07×10^{-3}		11.34	2.82
2.24×10^{-5}	9.09×10^{-4}	9.09×10^{-4}	9.18×10^{-3}		10.99	2.42
4.09×10^{-5}	9.09×10^{-4}	9.09×10^{-4}	9.07×10^{-3}		10.88	2.35
4.09×10^{-5}	9.09×10^{-4}	4.55×10^{-4}	9.07×10^{-3}		10.69	2.03
2.24×10^{-5}	9.09×10^{-4}				10.64	2.22
4.09×10^{-5}	9.09×10^{-4}	9.09×10^{-5}	9.07×10^{-3}		10.44	1.58
4.09×10^{-5}	9.09×10^{-4}		9.07×10^{-3}		10.32	1.42
4.09×10^{-5}	9.09×10^{-4}		9.07×10^{-3}	9.18×10^{-5}	10.26	1.28
4.09×10^{-5}	9.09×10^{-4}		9.07×10^{-3}	4.59×10^{-4}	9.84	6.52×10^{-1}
2.24×10^{-5}	9.09×10^{-4}		9.18×10^{-3}	9.18×10^{-4}	8.80	1.30×10^{-1}
4.09×10^{-5}	9.09×10^{-4}		9.07×10^{-3}	9.18×10^{-4}	8.73	8.59×10^{-2}
4.09×10^{-5}	9.09×10^{-4}		9.07×10^{-3}	2.75×10^{-3}	7.70	2.95×10^{-2}
4.09×10^{-5}	9.09×10^{-4}		9.07×10^{-3}	4.59×10^{-3}	7.42	2.64×10^{-2}
2.24×10^{-5}	9.09×10^{-4}		9.18×10^{-3}	9.18×10^{-3}	7.09	2.54×10^{-2}
2.24×10^{-5}	9.09×10^{-4}		9.18×10^{-4}	9.18×10^{-3}	6.38	2.37×10^{-2}
2.24×10^{-5}	9.09×10^{-4}		9.18×10^{-4}	9.18×10^{-3}	6.08	2.33×10^{-2}



Reactivity parameters of β-alanine (1q) in water: *N* = 13.26; *s* = 0.58

Reference electrophile	*E* parameter	$k_{2,N}$(20°C) / M^{-1} s^{-1}
$(mor)_2CH^+$	-5.53	3.62×10^4
$(dma)_2CH^+$	-7.02	3.62×10^3
$(pyr)_2CH^+$	-7.69	1.45×10^3
$(thq)_2CH^+$	-8.22	6.40×10^2
$(lil)_2CH^+$	-10.04	9.10×10^1



3.7.19. γ-Aminobutyric acid (1r)

Rate constants in water

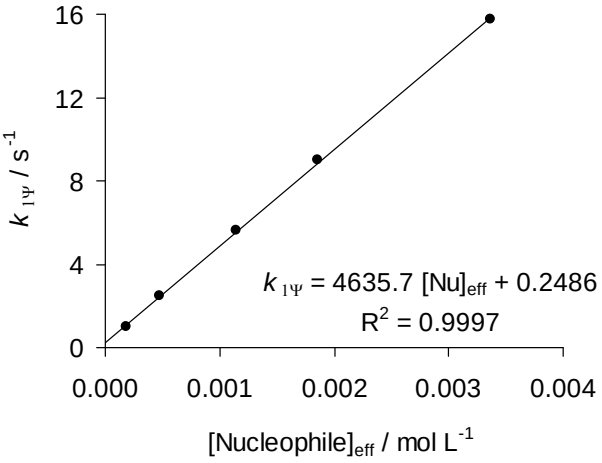
Reaction of γ-aminobutyric acid (**1r**) with $(dma)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 9 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fn242.2	9.64×10^{-6}	4.47×10^{-3}	3.36×10^{-3}	1.11×10^{-3}	349	1.59×10^1	1.45×10^{-1}	1.58×10^1
fn242.3	9.64×10^{-6}	2.68×10^{-3}	1.86×10^{-3}	8.21×10^{-4}	193	9.10	1.08×10^{-1}	8.99
fn242.4	9.64×10^{-6}	1.79×10^{-3}	1.15×10^{-3}	6.45×10^{-4}	119	5.72	8.45×10^{-2}	5.64
fn242.5	9.64×10^{-6}	8.94×10^{-4}	4.78×10^{-4}	4.16×10^{-4}	50	2.52	5.46×10^{-2}	2.47
fn242.6	9.64×10^{-6}	4.47×10^{-4}	1.87×10^{-4}	2.60×10^{-4}	19	1.03	3.41×10^{-2}	9.96×10^{-1}

$k_{2,N} = 4.64 \times 10^3$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 131$ $M^{-1}s^{-1}$

pK_B = 3.44 (ref 4)



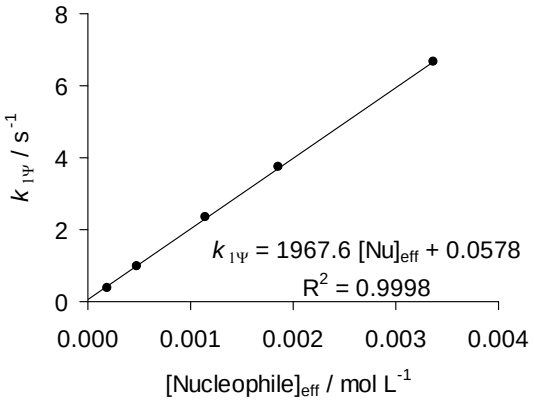
Reaction of γ-aminobutyric acid (**1r**) with $(pyr)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.7 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(pyr)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fn243.2	1.48×10^{-5}	4.47×10^{-3}	3.36×10^{-3}	1.11×10^{-3}	227	6.71	5.36×10^{-2}	6.66
fn243.3	1.48×10^{-5}	2.68×10^{-3}	1.86×10^{-3}	8.21×10^{-4}	126	3.77	3.98×10^{-2}	3.73
fn243.4	1.48×10^{-5}	1.79×10^{-3}	1.15×10^{-3}	6.45×10^{-4}	77	2.39	3.13×10^{-2}	2.36
fn243.5	1.48×10^{-5}	8.94×10^{-4}	4.78×10^{-4}	4.16×10^{-4}	32	1.01	2.02×10^{-2}	9.90×10^{-1}
fn243.6	1.48×10^{-5}	4.47×10^{-4}	1.87×10^{-4}	2.60×10^{-4}	13	4.04×10^{-1}	1.26×10^{-2}	3.91×10^{-1}

$k_{2,N} = 1.97 \times 10^3\ M^{-1}s^{-1}$

$k_{2,OH^-} = 48.5\ M^{-1}s^{-1}$

pK_B = 3.44 (ref 4)



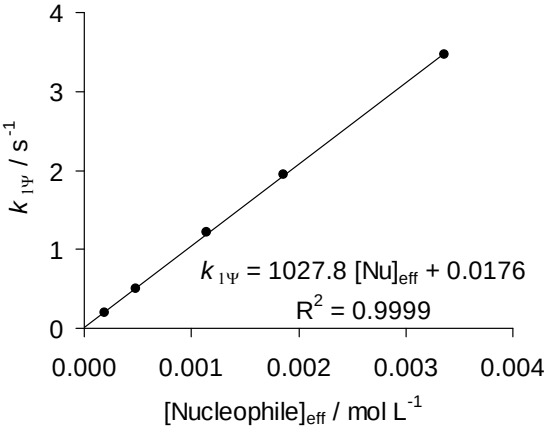
Reaction of γ-aminobutyric acid (**1r**) with $(thq)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.9 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(thq)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fn244.2	1.74×10^{-5}	4.47×10^{-3}	3.36×10^{-3}	1.11×10^{-3}	193	3.49	2.61×10^{-2}	3.46
fn244.3	1.74×10^{-5}	2.68×10^{-3}	1.86×10^{-3}	8.21×10^{-4}	107	1.96	1.94×10^{-2}	1.94
fn244.4	1.74×10^{-5}	1.79×10^{-3}	1.15×10^{-3}	6.45×10^{-4}	66	1.23	1.52×10^{-2}	1.21
fn244.5	1.74×10^{-5}	8.94×10^{-4}	4.78×10^{-4}	4.16×10^{-4}	27	5.10×10^{-1}	9.83×10^{-3}	5.00×10^{-1}
fn244.6	1.74×10^{-5}	4.47×10^{-4}	1.87×10^{-4}	2.60×10^{-4}	11	2.03×10^{-1}	6.14×10^{-3}	1.97×10^{-1}

$k_{2,N} = 1.03 \times 10^3\ M^{-1}s^{-1}$

$k_{2,OH^-} = 23.6\ M^{-1}s^{-1}$

pK_B = 3.44 (ref 4)



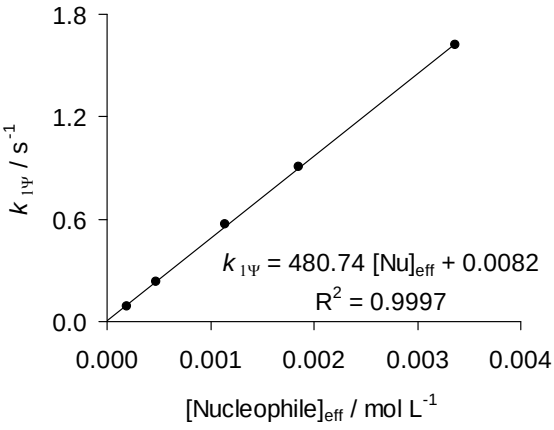
Reaction of γ-aminobutyric acid (**1r**) with $(ind)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(ind)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fn245.2	5.24×10^{-6}	4.47×10^{-3}	3.36×10^{-3}	1.11×10^{-3}	642	1.63	1.19×10^{-2}	1.62
fn245.3	5.24×10^{-6}	2.68×10^{-3}	1.86×10^{-3}	8.21×10^{-4}	355	9.18×10^{-1}	8.87×10^{-3}	9.09×10^{-1}
fn245.4	5.24×10^{-6}	1.79×10^{-3}	1.15×10^{-3}	6.45×10^{-4}	219	5.79×10^{-1}	6.96×10^{-3}	5.72×10^{-1}
fn245.5	5.24×10^{-6}	8.94×10^{-4}	4.78×10^{-4}	4.16×10^{-4}	91	2.39×10^{-1}	4.50×10^{-3}	2.35×10^{-1}
fn245.6	5.24×10^{-6}	4.47×10^{-4}	1.87×10^{-4}	2.60×10^{-4}	36	9.08×10^{-2}	2.81×10^{-3}	8.80×10^{-2}

$k_{2,N} = 4.81 \times 10^2$ $M^{-1}s^{-1}$

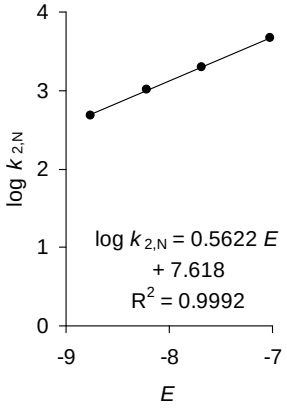
$k_{2,OH^-} = 10.8$ $M^{-1}s^{-1}$

pK_B = 3.44 (ref 4)



Reactivity parameters of γ-aminobutyric acid (1r) in water: *N* = 13.55; *s* = 0.56

Reference electrophile	*E* parameter	$k_{2,N}$(20°C) / M^{-1} s^{-1}
$(dma)_2CH^+$	-7.02	4.64×10^3
$(pyr)_2CH^+$	-7.69	1.97×10^3
$(thq)_2CH^+$	-8.22	1.03×10^3
$(ind)_2CH^+$	-8.76	4.81×10^2



3.7.20. Gly-Gly (1s)

Rate constants in water

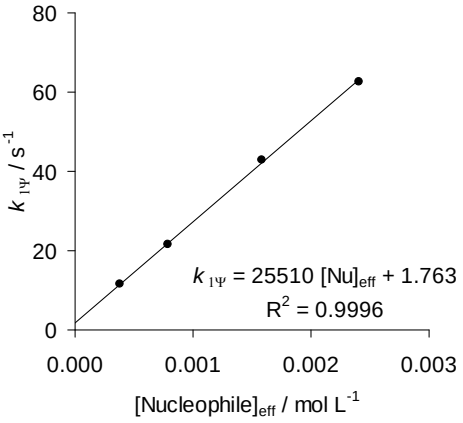
Reaction of Gly-Gly (**1s**) with $(mor)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 9 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(mor)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fn234.2	1.93×10^{-5}	2.47×10^{-3}	2.40×10^{-3}	6.54×10^{-5}	125	6.28×10^{1}	6.93×10^{-2}	6.27×10^{1}
fn234.3	1.93×10^{-5}	1.64×10^{-3}	1.59×10^{-3}	5.31×10^{-5}	82	4.30×10^{1}	5.63×10^{-2}	4.29×10^{1}
fn234.4	1.93×10^{-5}	8.22 × 10-4	7.85×10^{-4}	3.74×10^{-5}	41	2.16×10^{1}	3.96×10^{-2}	2.16×10^{1}
fn234.5	1.93×10^{-5}	4.11×10^{-4}	3.85×10^{-4}	2.62×10^{-5}	20	1.15×10^{1}	2.77×10^{-2}	1.15×10^{1}

$k_{2,N} = 2.55 \times 10^4\ M^{-1}s^{-1}$

$k_{2,OH^-} = 1060\ M^{-1}s^{-1}$

$pK_B = 5.75$ (ref 4)



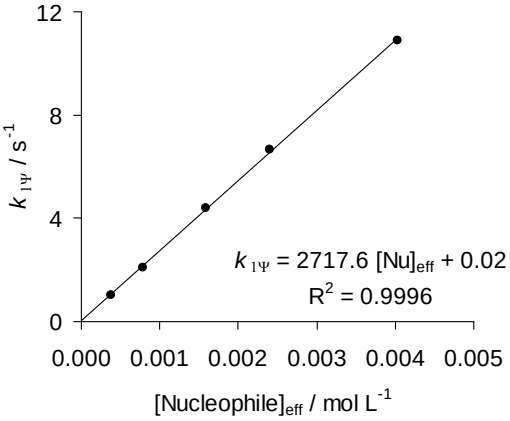
Reaction of Gly-Gly (**1s**) with $(dma)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.5 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fn235.1	2.14×10^{-5}	4.11×10^{-3}	4.03×10^{-3}	8.46×10^{-5}	188	1.09×10^{1}	1.11×10^{-2}	1.09×10^{1}
fn235.2	2.14×10^{-5}	2.47×10^{-3}	2.40×10^{-3}	6.54×10^{-5}	112	6.66	8.57×10^{-3}	6.65
fn235.3	2.14×10^{-5}	1.64×10^{-3}	1.59×10^{-3}	5.31×10^{-5}	74	4.41	6.96×10^{-3}	4.40
fn235.4	2.14×10^{-5}	8.22×10^{-4}	7.85×10^{-4}	3.74×10^{-5}	37	2.10	4.89×10^{-3}	2.10
fn235.5	2.14×10^{-5}	4.11×10^{-4}	3.85×10^{-4}	2.62×10^{-5}	18	1.03	3.43×10^{-3}	1.03

$k_{2,N} = 2.72 \times 10^3\ M^{-1}s^{-1}$

$k_{2,OH^-} = 131\ M^{-1}s^{-1}$

$pK_B = 5.75$ (ref 4)



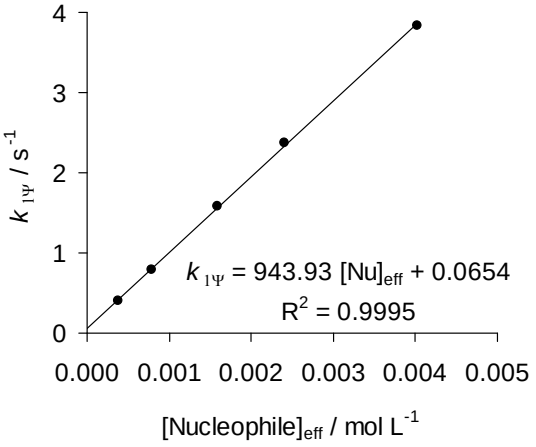
Reaction of Gly-Gly (**1s**) with $(pyr)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(pyr)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fn236.1	2.14×10^{-5}	4.11×10^{-3}	4.03×10^{-3}	8.46×10^{-5}	188	3.84	4.10×10^{-3}	3.84
fn236.2	2.14×10^{-5}	2.47×10^{-3}	2.40×10^{-3}	6.54×10^{-5}	112	2.38	3.17×10^{-3}	2.38
fn236.3	2.14×10^{-5}	1.64×10^{-3}	1.59×10^{-3}	5.31×10^{-5}	74	1.59	2.58×10^{-3}	1.59
fn236.4	2.14×10^{-5}	8.22×10^{-4}	7.85×10^{-4}	3.74×10^{-5}	37	7.90×10^{-1}	1.81×10^{-3}	7.88×10^{-1}
fn236.5	2.14×10^{-5}	4.11×10^{-4}	3.85×10^{-4}	2.62×10^{-5}	18	4.11×10^{-1}	1.27×10^{-3}	4.10×10^{-1}

$k_{2,N} = 9.44 \times 10^2\ M^{-1}s^{-1}$

$k_{2,OH^-} = 48.5\ M^{-1}s^{-1}$

$pK_B = 5.75$ (ref 4)



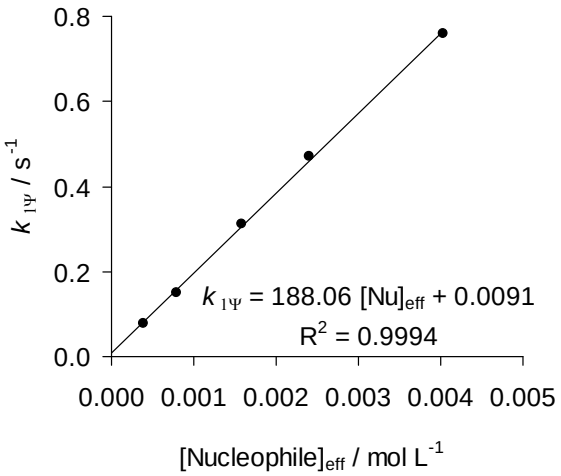
Reaction of Gly-Gly (**1s**) with $(ind)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.4 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(ind)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fn237.1	2.14×10^{-5}	4.11×10^{-3}	4.03×10^{-3}	8.46×10^{-5}	188	7.61×10^{-1}	9.14×10^{-4}	7.60×10^{-1}
fn237.2	2.14×10^{-5}	2.47×10^{-3}	2.40×10^{-3}	6.54×10^{-5}	112	4.71×10^{-1}	7.06×10^{-4}	4.70×10^{-1}
fn237.3	2.14×10^{-5}	1.64×10^{-3}	1.59×10^{-3}	5.31×10^{-5}	74	3.13×10^{-1}	5.74×10^{-4}	3.12×10^{-1}
fn237.4	2.14×10^{-5}	8.22×10^{-4}	7.85×10^{-4}	3.74×10^{-5}	37	1.52×10^{-1}	4.03×10^{-4}	1.52×10^{-1}
fn237.5	2.14×10^{-5}	4.11×10^{-4}	3.85×10^{-4}	2.62×10^{-5}	18	7.90×10^{-2}	2.83×10^{-4}	7.87×10^{-2}

$k_{2,N} = 1.88 \times 10^2\ M^{-1}s^{-1}$

$k_{2,OH^-} = 10.8\ M^{-1}s^{-1}$

$pK_B = 5.75$ (ref 4)



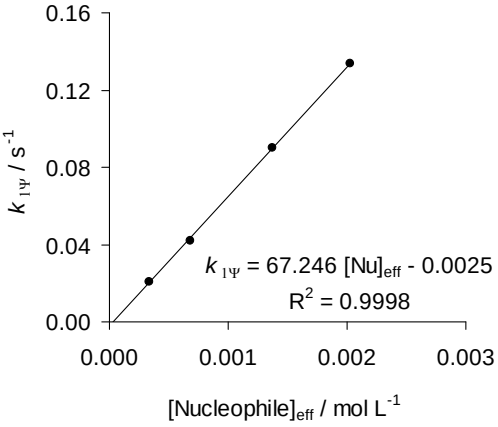
Reaction of Gly-Gly (**1s**) with $(lil)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.4 vol-% CH_3CN, J&M, detection at 630 nm)

No.	$[(lil)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fn229.2	1.09×10^{-5}	2.09×10^{-3}	2.03×10^{-3}	6.01×10^{-5}	186	1.34×10^{-1}	1.30×10^{-4}	1.34×10^{-1}
fn229.3	1.11×10^{-5}	1.42×10^{-3}	1.37×10^{-3}	4.94×10^{-5}	123	9.02×10^{-2}	1.07×10^{-4}	9.01×10^{-2}
fn229.4	1.12×10^{-5}	7.15×10^{-4}	6.80×10^{-4}	3.48×10^{-5}	61	4.23×10^{-2}	7.51×10^{-5}	4.22×10^{-2}
fn229.5	1.13×10^{-5}	3.59×10^{-4}	3.35×10^{-4}	2.44×10^{-5}	30	2.06×10^{-2}	5.27×10^{-5}	2.05×10^{-2}

$k_{2,N} = 6.72 \times 10^1\ M^{-1}s^{-1}$

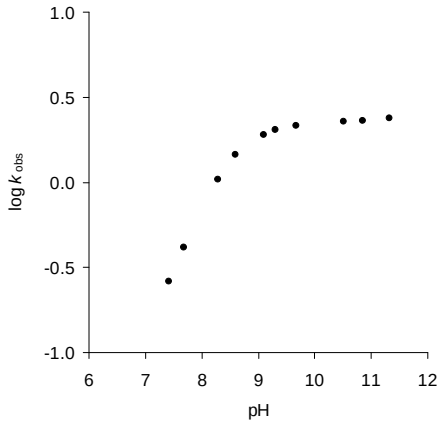
$k_{2,OH^-} = 2.16\ M^{-1}s^{-1}$

$pK_B = 5.75$ (ref 4)



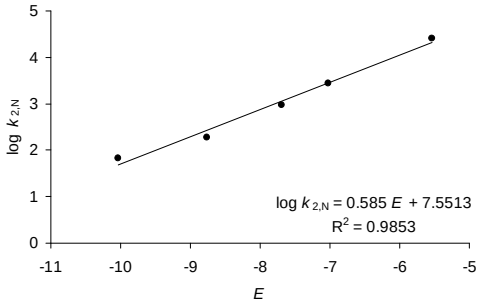
pH Dependance of rate constants for the reaction of Gly-Gly (**1s**) with $(dma)_2CH^+BF_4^-$ (phosphate buffer, at 20 °C, cosolvent: 0.5 vol % CH_3CN, stopped-flow, detection at 610 nm, pH measured, No. fn301)

$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[PO_4^{3-}]$ / mol L^{-1}	$[HPO_4^{2-}]$ / mol L^{-1}	$[H_2PO_4^-]$ / mol L^{-1}	pH	k_{obs} / s^{-1}
4.09×10^{-5}	9.05×10^{-4}	2.73×10^{-3}	9.07×10^{-3}		11.32	2.38
4.09×10^{-5}	9.05×10^{-4}	9.09×10^{-3}	9.07×10^{-3}		10.85	2.30
4.09×10^{-5}	9.05×10^{-4}	4.55×10^{-4}	9.07×10^{-3}		10.51	2.29
4.09×10^{-5}	9.05×10^{-4}	9.09×10^{-5}	9.07×10^{-3}		9.67	2.15
4.09×10^{-5}	9.05×10^{-4}		9.07×10^{-3}		9.30	2.04
4.09×10^{-5}	9.05×10^{-4}		9.07×10^{-3}	9.18×10^{-5}	9.09	1.91
4.09×10^{-5}	9.05×10^{-4}		9.07×10^{-3}	4.59×10^{-4}	8.60	1.46
4.09×10^{-5}	9.05×10^{-4}		9.07×10^{-3}	9.18×10^{-4}	8.29	1.04
4.09×10^{-5}	9.05×10^{-4}		9.07×10^{-3}	2.75×10^{-3}	7.68	4.14×10^{-1}
4.09×10^{-5}	9.05×10^{-4}		9.07×10^{-3}	4.59×10^{-3}	7.41	2.63×10^{-1}



Reactivity parameters of Gly-Gly (1s) in water: *N* = 12.91; *s* = 0.59

Reference electrophile	*E* parameter	$k_{2,N}$(20°C) / M^{-1} s^{-1}
$(mor)_2CH^+$	-5.53	2.55×10^4
$(dma)_2CH^+$	-7.02	2.72×10^3
$(pyr)_2CH^+$	-7.69	9.44×10^2
$(ind)_2CH^+$	-8.76	1.88×10^2
$(lil)_2CH^+$	-10.04	6.72×10^1



3.7.21. Gly-Gly-Gly (1t)

Rate constants in water

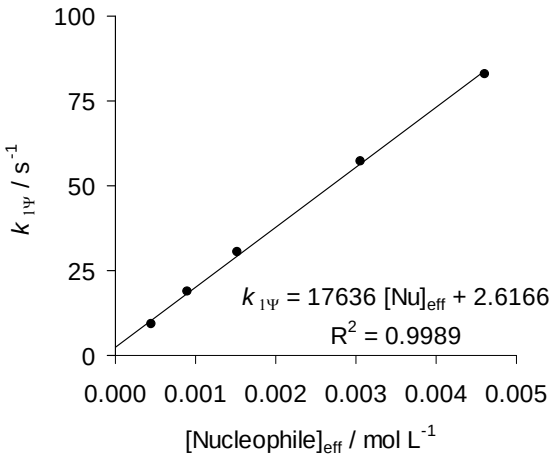
Reaction of Gly-Gly-Gly (**1t**) with $(mor)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 9 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(mor)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fn251.1	4.07×10^{-5}	4.67×10^{-3}	4.61×10^{-3}	6.48×10^{-5}	113	8.31×10^1	6.87×10^{-2}	8.30×10^1
fn251.2	4.07×10^{-5}	3.11×10^{-3}	3.06×10^{-3}	5.28×10^{-5}	75	5.74×10^1	5.60×10^{-2}	5.73×10^1
fn251.3	4.07×10^{-5}	1.56×10^{-3}	1.52×10^{-3}	3.73×10^{-5}	37	3.06×10^1	3.95×10^{-2}	3.06×10^1
fn251.4	4.07×10^{-5}	9.34×10^{-4}	9.05×10^{-4}	2.87×10^{-5}	22	1.87×10^1	3.05×10^{-2}	1.87×10^1
fn251.5	4.07×10^{-5}	4.67×10^{-4}	4.47×10^{-4}	2.02×10^{-5}	11	9.33	2.14×10^{-2}	9.31

$k_{2,N} = 1.76 \times 10^4$ $M^{-1}s^{-1}$

$k_{2,OH^-} = 1060$ $M^{-1}s^{-1}$

pK_B = 6.04 (ref 4)



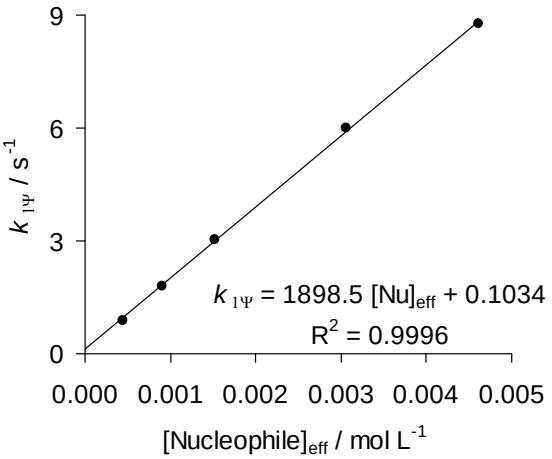
Reaction of Gly-Gly-Gly (**1t**) with $(dma)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fn252.1	9.64×10^{-6}	4.67×10^{-3}	4.61×10^{-3}	6.48×10^{-5}	478	8.79	8.49×10^{-3}	8.78
fn252.2	9.64×10^{-6}	3.11×10^{-3}	3.06×10^{-3}	5.28×10^{-5}	317	6.00	6.92×10^{-3}	5.99
fn252.3	9.64×10^{-6}	1.56×10^{-3}	1.52×10^{-3}	3.73×10^{-5}	158	3.05	4.88×10^{-3}	3.05
fn252.4	9.64×10^{-6}	9.34×10^{-4}	9.05×10^{-4}	2.87×10^{-5}	94	1.81	3.76×10^{-3}	1.81
fn252.5	9.64×10^{-6}	4.67×10^{-4}	4.47×10^{-4}	2.02×10^{-5}	46	8.99×10^{-1}	2.64×10^{-3}	8.96×10^{-1}

$k_{2,N} = 1.90 \times 10^3\ M^{-1}s^{-1}$

$k_{2,OH^-} = 131\ M^{-1}s^{-1}$

$pK_B = 6.04$ (ref 4)



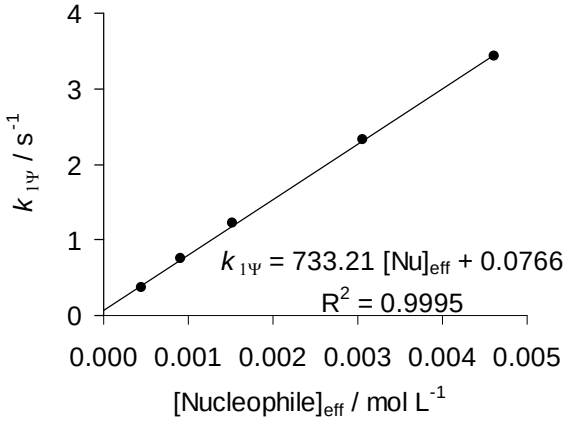
Reaction of Gly-Gly-Gly (**1t**) with $(pyr)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.9 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(pyr)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fn253.1	1.85×10^{-5}	4.67×10^{-3}	4.61×10^{-3}	6.48×10^{-5}	249	3.44	3.14×10^{-3}	3.44
fn253.2	1.85×10^{-5}	3.11×10^{-3}	3.06×10^{-3}	5.28×10^{-5}	165	2.33	2.56×10^{-3}	2.33
fn253.3	1.85×10^{-5}	1.56×10^{-3}	1.52×10^{-3}	3.73×10^{-5}	82	1.23	1.81×10^{-3}	1.23
fn253.4	1.85×10^{-5}	9.34×10^{-4}	9.05×10^{-4}	2.87×10^{-5}	49	7.55×10^{-1}	1.39×10^{-3}	7.54×10^{-1}
fn253.5	1.85×10^{-5}	4.67×10^{-4}	4.47×10^{-4}	2.02×10^{-5}	24	3.64×10^{-1}	9.79×10^{-4}	3.63×10^{-1}

$k_{2,N} = 7.33 \times 10^2\ M^{-1}s^{-1}$

$k_{2,OH^-} = 48.5\ M^{-1}s^{-1}$

$pK_B = 6.04$ (ref 4)



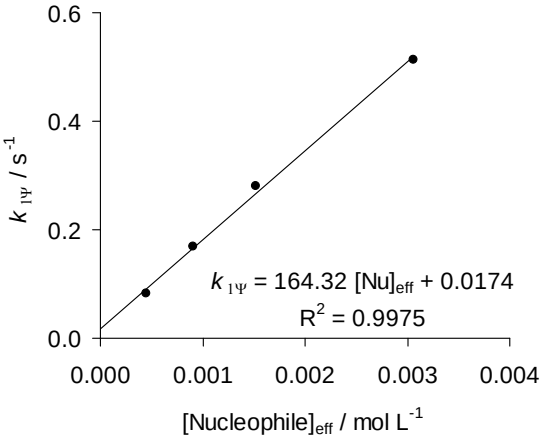
Reaction of Gly-Gly-Gly (**1t**) with $(ind)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.4 vol-% CH_3CN, stopped-flow, detection at 610 nm)

No.	$[(ind)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
fn254.2	5.24×10^{-6}	3.11×10^{-3}	3.06×10^{-3}	5.28×10^{-5}	583	5.15×10^{-1}	5.70×10^{-4}	5.14×10^{-1}
fn254.3	5.24×10^{-6}	1.56×10^{-3}	1.52×10^{-3}	3.73×10^{-5}	291	2.80×10^{-1}	4.02×10^{-4}	2.80×10^{-1}
fn254.4	5.24×10^{-6}	9.34×10^{-4}	9.05×10^{-4}	2.87×10^{-5}	173	1.69×10^{-1}	3.10×10^{-4}	1.69×10^{-1}
fn254.5	5.24×10^{-6}	4.67×10^{-4}	4.47×10^{-4}	2.02×10^{-5}	85	8.20×10^{-2}	2.18×10^{-4}	8.18×10^{-2}

$k_{2,N} = 1.64 \times 10^2$ $M^{-1}s^{-1}$

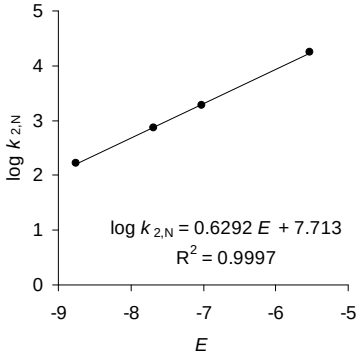
$k_{2,OH^-} = 10.8$ $M^{-1}s^{-1}$

$K_B = 6.04$ (ref 4)



Reactivity parameters of Gly-Gly-Gly (1t) in water: *N* = 12.26; *s* = 0.63

Reference electrophile	*E* parameter	$k_{2,N}$(20°C) / M^{-1} s^{-1}
$(mor)_2CH^+$	-5.53	1.76×10^4
$(dma)_2CH^+$	-7.02	1.90×10^3
$(pyr)_2CH^+$	-7.69	7.33×10^2
$(ind)_2CH^+$	-8.76	1.64×10^2



3.8. References

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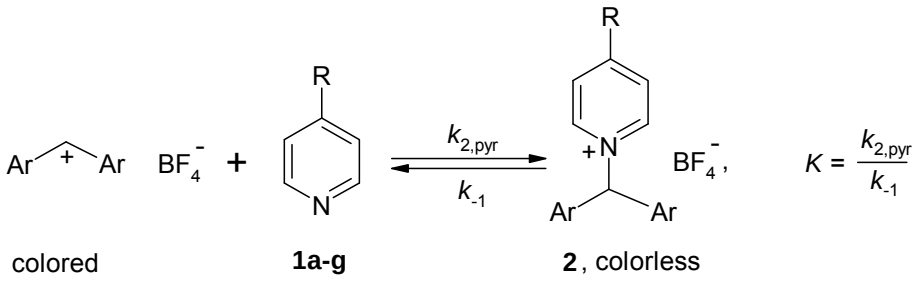
4. Nucleophilicities and Carbon Basicities of Pyridines

4.1. Introduction

Pyridines, in particular 4-dimethylaminopyridine (DMAP), are important catalysts for many reactions, primarily acylations.[1] Though the mechanisms of pyridine catalysis have previously been studied,[1,2] and correlations between the catalytic activities of pyridines and their pK_{Ha} values[1b] and calculated acyl cation affinities[3] have been discussed, systematic studies on the relationships between the nucleophilic reactivities of pyridines and their Lewis basicities towards carbon centers have not yet been performed.[4,5] Since such data are crucial for understanding the catalytic activities of pyridines in comparison with other organocatalysts, we set out to investigate these relationships employing benzhydrylium ions as reference substrates.



Scheme 4.1.

Previously, we have reported that benzhydrylium ions of different electrophilicity can be utilized for comparing the reactivities of nucleophiles of widely varying structure.[6] We will now report on the kinetics of the reactions of various benzhydrylium ions (Table 4.1) with several pyridines 1 in different solvents (Scheme 4.1). The data will then be used to determine the nucleophilicity parameters *N* and *s* of the pyridines **1a** – **1g** according to eq. (4.1), which has been used for characterizing a large variety of electrophiles and nucleophiles.

$$\log k_{20^\circ C} = s(N + E) \qquad (4.1)$$

k = second-order rate constant in M^{-1} s^{-1}

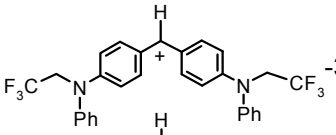
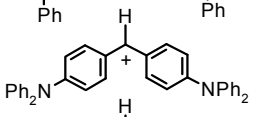
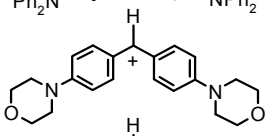
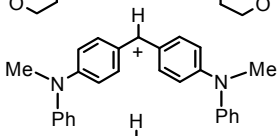
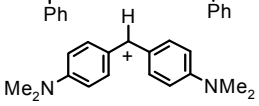
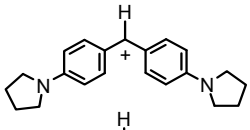
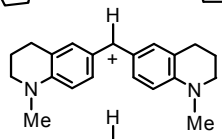
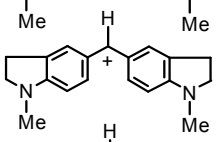
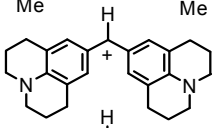
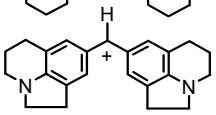
s = nucleophile specific slope parameter

N = nucleophilicity parameter

E = electrophilicity parameter

Several of these reactions do not proceed to completion, which allowed us to determine the equilibrium constants of the reactions in Scheme 4.1 and to compare the resulting carbon basicities of pyridines(*K* of Scheme 4.1) with the corresponding Brønsted basicities(pK_{Ha}).

Table 4.1. Benzhydrylium ions employed in this work.

Electrophile		E[a]
$(pfa)_2CH^+$		-3.14
$(dpa)_2CH^+$		-4.72
$(mor)_2CH^+$		-5.53
$(mpa)_2CH^+$		-5.89
$(dma)_2CH^+$		-7.02
$(pyr)_2CH^+$		-7.69
$(thq)_2CH^+$		-8.22
$(ind)_2CH^+$		-8.76
$(jul)_2CH^+$		-9.45
$(lil)_2CH^+$		-10.04

[a] Electrophilicity parameters E from ref. [6]

Results

4.2. Reaction Products

Products (**2a**-**c**)-BF_4^- of the reactions of $(dma)_2CH^+$ BF_4^-, $(jul)_2CH^+$ BF_4^- and $(lil)_2CH^+$ BF_4^- with 4-dimethylaminopyridine **1f** were obtained by treatment of the corresponding benzhydrylium tetrafluoroborates with equimolar amounts of **1f** in CH_2Cl_2 solution and were characterized by ^{1}H-NMR and ^{13}C-NMR spectroscopy. Combinations of highly stabilized benzhydryl cations with pyridine derivatives of low basicity were reversible, which prevented the isolation of the reaction products.

Table 4.2. Chemical shifts (CD_3CN) of pyridinium tetrafluoroborates **2** $-BF_4^-$ obtained from 4-dimethylaminopyridine and Ar_2CH^+ BF_4^- (Scheme 4.1).

		$(4\text{-}(CH_3)_2N\text{-}C_5H_4N\text{-}\underline{CH}Ar_2)^+$		$(4\text{-}(\underline{CH_3})_2N\text{-}C_5H_4N\text{-}CHAr_2)^+$	
Ar_2CH^+	Product	δ (^{1}H-NMR)	δ (^{13}C-NMR)	δ (^{1}H-NMR)	δ (^{13}C-NMR)
$(dma)_2CH^+$	**2a**	6.57[a]	73.9[a]	3.18[a]	40.0[a]
$(jul)_2CH^+$	**2b**	6.29	73.7	2.96-3.16[b]	39.3
$(lil)_2CH^+$	**2c**	6.46	74.3	3.15	39.3

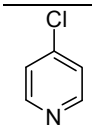
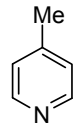
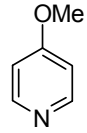
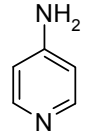
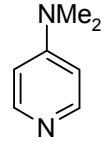
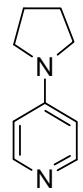
[a] Solvent: $CDCl_3$, [b] Signal is covered by signals of the benzhydryl substituents.

The ^{1}H-NMR and ^{13}C-NMR shifts in Table 4.2 do not correlate with the electrophilicities of the benzhydrylium ions.

4.3. Kinetic investigations

The rates of the reactions of the colored benzhydrylium tetrafluoroborates with pyridines were followed photometrically under pseudo-first-order conditions by using more than ten equivalents of the pyridines. Under such conditions, the concentrations of the pyridines **1a** – **1g** were almost constant throughout the reaction and resulted in an exponential decay of the benzhydrylium absorbances, from which the pseudo-first-order rate constants $k_{1\Psi}$ were derived. The slopes of the linear plots of $k_{1\Psi}$ vs. [**1**] gave the second order rate constants $k_{2,pyr}$ which are listed in Table 4.3. Instrumentation and kinetic method have been described previously [6].

Table 4.3. Second-order rate constants and equilibrium constants for the reactions of benzhydrylium tetrafluoroborates with pyridines **1** (20 °C).

Pyridine		Solvent	*N*	*s*	Ar_2CH^+	$k_{2,pyr}$ / $M^{-1}s^{-1}$	*K* / M^{-1} [c]
	**1a**	CH_2Cl_2	(11.7)	(0.67 [a])	$(pfa)_2CH^+$	5.17×10^5	(4.83×10^3)[d]
		H_2O	(10.6)	(0.72 [a])	$(mor)_2CH^+$	4.58×10^3	(3.73×10^3)[d]
	**1b**	CH_2Cl_2	(12.9)	(0.67 [a])	$(dpa)_2CH^+$	3.02×10^5	2.23×10^4
		H_2O	11.2	0.72	$(mor)_2CH^+$	1.08×10^4	
		H_2O			$(dma)_2CH^+$	8.82×10^2	(9.04×10^2)[d]
	**1c**	CH_2Cl_2	(13.7)	(0.67 [a])	$(dpa)_2CH^+$	8.90×10^5	5.07×10^5
		H_2O	11.1	0.75	$(mor)_2CH^+$	1.53×10^4	
		H_2O			$(dma)_2CH^+$	1.16×10^3	
	**1d**	CH_2Cl_2	(13.7)	(0.67 [a])	$(dpa)_2CH^+$	8.97×10^5	
		H_2O	11.4	0.68	$(mor)_2CH^+$	1.15×10^4	
		H_2O			$(dma)_2CH^+$	9.50×10^2	
		H_2O			$(pyr)_2CH^+$	3.98×10^2	(1.59×10^2)[d]
	**1e**	CH_2Cl_2	(15.2)	(0.67 [a])	$(dma)_2CH^+$	2.88×10^5	
		H_2O	12.2	0.66	$(mor)_2CH^+$	2.58×10^4	
		H_2O			$(dma)_2CH^+$	2.23×10^3	
		H_2O			$(pyr)_2CH^+$	8.04×10^2	
		H_2O			$(thq)_2CH^+$	4.81×10^2	
	**1f**	CH_2Cl_2	15.7	0.67	$(mpa)_2CH^+$	3.00×10^6	
		CH_2Cl_2			$(dma)_2CH^+$	6.43×10^5	
		CH_2Cl_2			$(thq)_2CH^+$	1.35×10^5	2.81×10^5
		CH_2Cl_2			$(ind)_2CH^+$	4.96×10^4	1.71×10^5
		CH_2Cl_2			$(jul)_2CH^+$	9.84×10^3	5.85×10^3
		CH_2Cl_2			$(lil)_2CH^+$	6.45×10^3 [b]	5.70×10^3
		CH_3CN	15.0	0.67	$(dma)_2CH^+$	2.31×10^5	
		CH_3CN			$(thq)_2CH^+$	3.32×10^4	
		CH_3CN			$(ind)_2CH^+$	1.29×10^4	
		CH_3CN			$(jul)_2CH^+$	5.30×10^3	
		CH_3CN			$(lil)_2CH^+$	2.11×10^3	
		H_2O	13.2	0.56	$(mor)_2CH^+$	2.39×10^4	
		H_2O			$(dma)_2CH^+$	2.66×10^3	
		H_2O			$(pyr)_2CH^+$	9.88×10^2	
		H_2O			$(thq)_2CH^+$	5.81×10^2	
		H_2O			$(ind)_2CH^+$	2.41×10^2	
		H_2O			$(jul)_2CH^+$	1.31×10^2	
		H_2O			$(lil)_2CH^+$	7.42×10^1	
		CH_3OH	(13.2)	(0.67 [a])	$(dma)_2CH^+$	1.46×10^4	
		DMSO	(14.8)	(0.67 [a])	$(dma)_2CH^+$	1.53×10^5	
		DMF	(14.9)	(0.67 [a])	$(dma)_2CH^+$	2.04×10^5	
	**1g**	CH_2Cl_2	(15.9)	(0.67 [a])	$(dma)_2CH^+$	8.76×10^5	
		H_2O	12.4	0.66	$(mor)_2CH^+$	3.49×10^4	
		H_2O			$(dma)_2CH^+$	3.60×10^3	
		H_2O			$(pyr)_2CH^+$	1.16×10^3	
		H_2O			$(thq)_2CH^+$	6.17×10^2	

[a] estimated value, see text, [b] Eyring activation parameters: $\Delta H^{\#}$ = 37.1 kJ mol^{-1}, $\Delta S^{\#}$ = - 45.3 J mol^{-1} K^{-1}, [c] The equilibrium constants *K* have been derived from the photometrically determined absorbances of the benzhydrylium ions and the initial concentrations of the reactants as described in the supporting information, [d] determined by $K = k_{2,pyr} / k_{-1}$.

At first glance, the choice of benzhydrylium ions, which were selected for characterizing the reactivities of the individual pyridines, looks rather arbitrary. Why have different electrophiles, sometimes only one of them, been employed for the kinetic studies? The problem of these experiments is that all reactions are reversible, and in many cases, we can only find one or two benzhydrylium ions where the equilibrium is on the product side (*N*-benzhydrylpyridinium ions **2**, Scheme 4.1) and which at the same time react slowly enough ($k_{2,pyr} < 10^6$ $M^{-1}s^{-1}$) that we can follow the kinetics with our stopped-flow apparatus. The unsubstituted pyridine **1b**, for example, has only been studied with $(dpa)_2CH^+$ in CH_2Cl_2. Benzhydrylium ions, which are more electrophilic than $(dpa)_2CH^+$, react so fast in CH_2Cl_2 that we can not follow the kinetics, and benzhydrylium ions, which are less electrophilic than $(dpa)_2CH^+$, give such low degree of conversion that we were again unable to determine the combination rates. It will be discussed below that it is due to the higher intrinsic barriers of the reactions with 4-dimethylaminopyridine **1f** that a series of rate constants could be measured with this amine. When CH_2Cl_2, CH_3CN, DMF or DMSO were used as solvents, reversibilities of the reactions were the only complications in the evaluation of the kinetics. When the benzhydrylium ions were not consumed completely, plots of $k_{1\Psi}$ vs. [**1**] gave straight lines with intercepts that corresponded to the rate constants k_{-1} of the reverse reactions.[7] Details of the evaluation are discussed below.

$$k_{obs} = k_{1\Psi} = k_{1\Psi,pyr} + k_{-1} \quad (4.2)$$
$$= k_{2,pyr}\,[\mathbf{1}] + k_{-1}$$

When the benzhydrylium ions were combined with pyridines in water, competing reactions of the carbocations with hydroxide and water have to be considered. The observed pseudo-first-order rate constants k_{obs} reflect the sum of the reactions of the electrophile with the pyridine **1**($k_{1\Psi,pyr}$), OH^-($k_{1\Psi,OH^-}$), water(k_W), and the reverse reaction(k_{-1}).

$$k_{obs} = k_{1\Psi,pyr} + k_{1\Psi,OH^-} + k_W + k_{-1} \quad (4.3)$$
$$= k_{2,pyr}\,[\mathbf{1}] + k_{2,OH^-}\,[OH^-] + k_W + k_{-1}$$

Rearrangement of eq. (4.3) yields eq. (4.4), which defines $k_{1\Psi}$ as the overall rate constant minus the contribution by hydroxide.

$$k_{1\Psi} = k_{obs} - k_{2,OH^-}\,[OH^-] = k_{2,pyr}\,[\mathbf{1}] + k_W + k_{-1} \quad (4.4)$$

The concentrations of the pyridines [**1**] and of hydroxide [OH^-] are calculated from pK_{Ha} as described on page 3 of the Supporting Information. With the already published values for k_{2,OH^-} [8c] and the calculated concentrations of hydroxide [OH^-], the partial pseudo-first-order rate constants $k_{1\Psi,OH^-}$ can be calculated. The slopes of the plots of $k_{1\Psi}$(= k_{obs} - $k_{1\Psi,OH^-}$) versus [**1**] correspond to the second-order rate constants $k_{2,pyr}$, as shown in Figure 4.1. The intercepts, which corresponds to the sum of the reverse reactions and the reactions of the

benzhydrylium ions with water[eq. (4.4)], are generally negligible when the equilibrium is far on the product side. This finding is in agreement with the previously reported rate constants for the reactions of benzhydrylium ions with water(k_W).[8c]

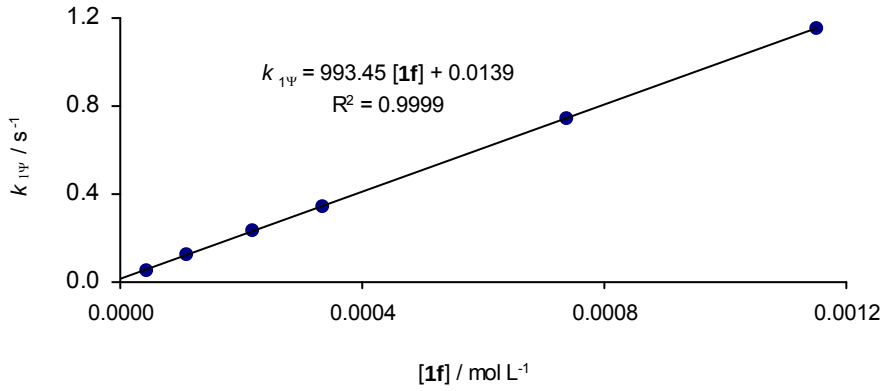


Figure 4.1. Determination of the second-order rate constant $k_{2,pyr}$ = 993 L mol^{-1} s^{-1} for the reaction of $(pyr)_2CH^+$ with 4-dimethylaminopyridine(**1f**) in water at 20 °C.

In the case of incomplete consumption of the benzhydrylium ions (Figure 4.2), the pseudo-first-order rate constants were obtained as the slopes of the linear plots of ln $[(A_0-A_\infty)/(A_t-A_\infty)]$ versus t, with A_0 = starting absorbance, A_∞ = end absorbance and A_t = absorbance at time t. According to ref. [7] the slope of the plot of $k_{1\Psi}$ versus [**1**] corresponds to the second-order rate constant for the forward reaction $k_{2,pyr}$, and the intercept corresponds to the first-order rate constant for the backward reaction k_{-1}[Eq. (4.2), if CH_2Cl_2 is used as the solvent] or the sum $k_W + k_{-1}$[Eq. (4.4), if water is the solvent].

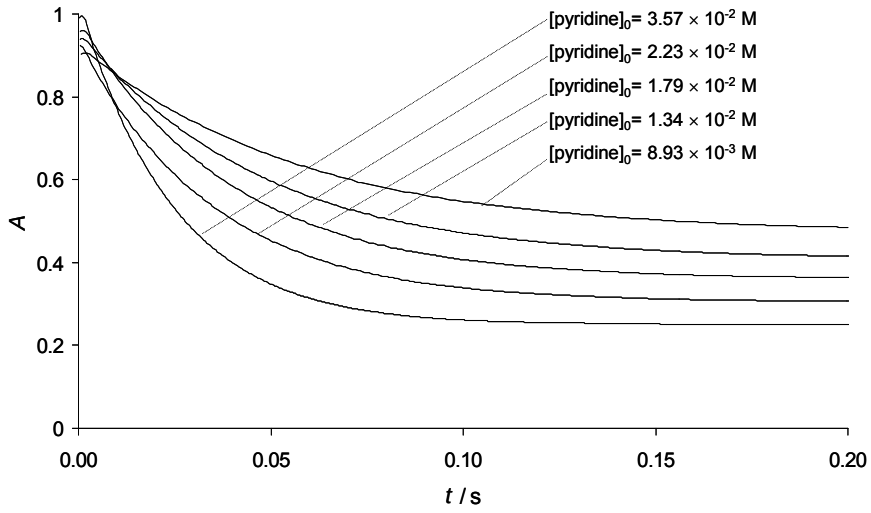


Figure 4.2. Plot of the absorbance (λ = 607 nm) versus *t* for the reactions of pyridine(**1b**) with $(dma)_2CH^+$ (c_0 = 7.62 × 10^{-5} M) at different concentrations of pyridine in water (20° C).

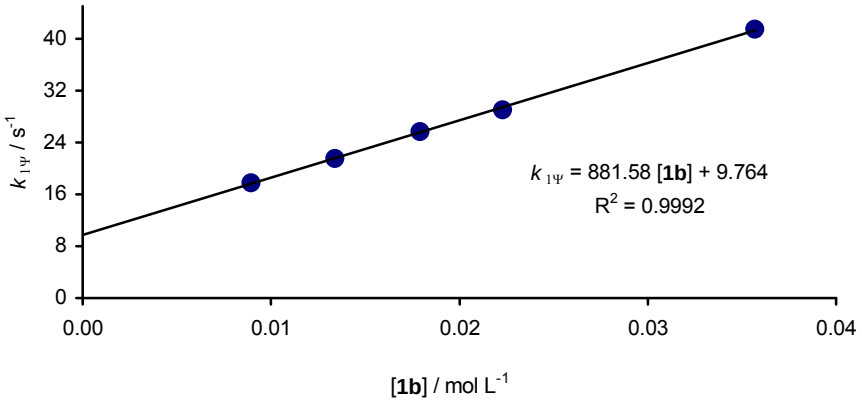


Figure 4.3. Determination of the forward ($k_{2,pyr}$ = 882 M^{-1} s^{-1}) and reverse rate constant (k_{-1} = 9.76 s^{-1}) for the reaction of $(dma)_2CH^+$ with pyridine(**1b**) in water at 20 °C (k_W = 0.0206 s^{-1}, ref.[8c], can be neglected).

As shown in Figure 4.3, the plot of $k_{1\Psi}$ vs. [**1b**] is linear. As we observed linear plots also for all other reaction series, we exclude the association of the pyridines in the concentration ranges investigated. Such association has been observed at higher pyridine concentrations from convex k_{obs} vs. [pyridine] plots in reactions of pyridines with phosphate derivatives.[9]

Discussion

4.4. Nucleophilic Reactivities of Pyridines

When log $k_{2,pyr}$ for the reactions of pyridines **1a** – **g** with benzhydrylium ions are plotted against their electrophilicity parameters *E*, linear correlations are obtained (Figure 4.4) indicating that these reactions follow eq. (4.1). The slopes of these correlations yield the parameters *s*, and the intercepts on the abscissa correspond to the negative values of the nucleophilicity parameters *N*.

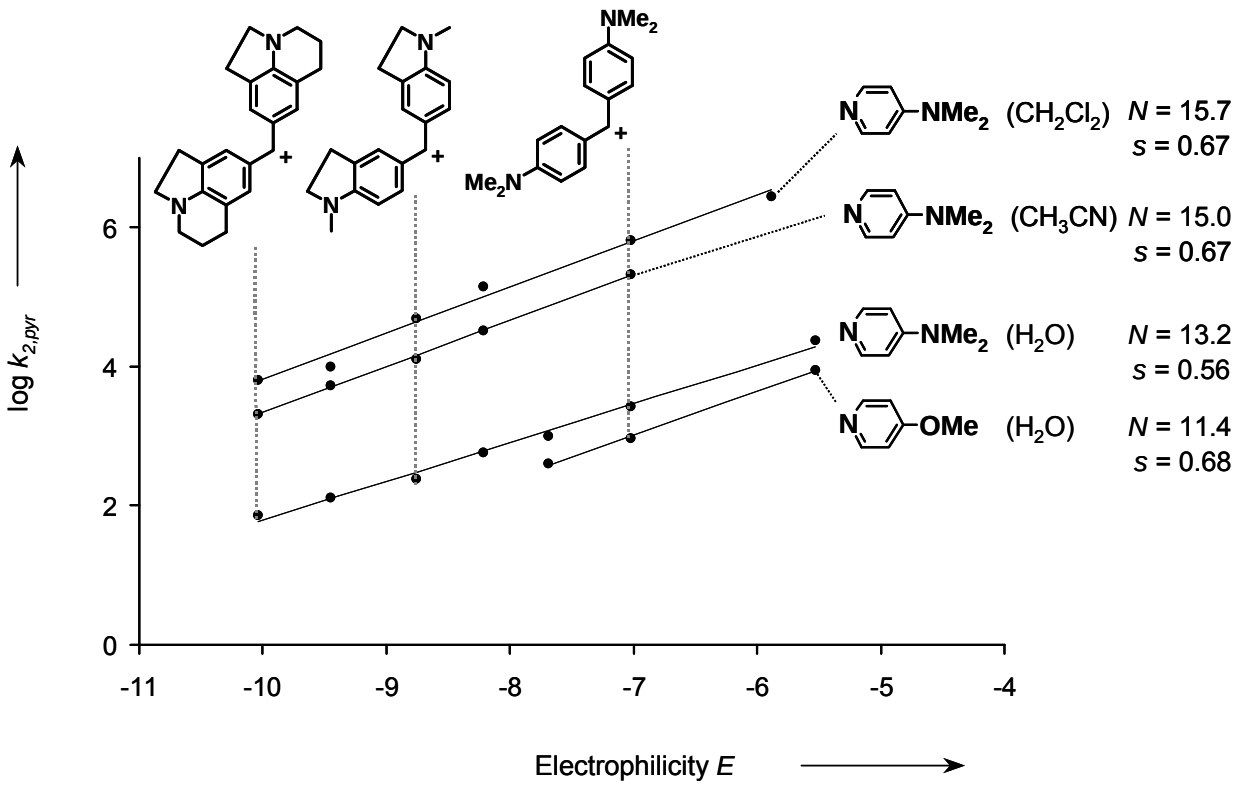


Figure 4.4. Plots of the rate constants log $k_{2,pyr}$ for the reactions of pyridines with benzhydrylium cations versus the electrophilicity parameters *E* (rate constants from Table 4.3).

In all cases, where rate constants with more than one electrophile have been determined, slope parameters of $s = 0.67 \pm 0.08$ were obtained (exception s(**1f** in H_20) = 0.56). Because there is no systematic dependence of *s* on the reactivity of the pyridine, the average value of $s = 0.67$ was adopted for calculating the nucleophilicity parameters *N* of such pyridines, which have only been studied with one electrophile in CH_2Cl_2, DMF, DMSO or CH_3OH (Table 4.3). For p-chloropyridine(**1a**) in water, the same *s*-value was assumed as for the unsubstituted pyridine in water. Figure 4.4, which depicts correlations with slopes from $s = 0.56$ to 0.67, illustrates that because of the small differences in *s* the relative nucleophilic reactivities of pyridines are almost independent of the nature of the benzhydrylium ions. Therefore, the following structure-reactivity discussions can be based on the nucleophilicity parameters *N*.

Figure 4.5 illustrates that pyridines are 2 to 3 orders of magnitude more nucleophilic in CH_2Cl_2 than in water. The larger spread of *N* in CH_2Cl_2 than in water can be explained by hydrogen bonding in water, which increases with increasing basicity of the pyridines. It is particularly noteworthy that p-methyl- and p-methoxypyridine have similar reactivities in dichloromethane, whereas p-methylpyridine and the parent compound have similar nucleophilicities in water. Comparison with other classes of nucleophiles in Figure 4.5 shows that the reactivity of pyridines in dichloromethane is comparable to that of phosphanes, an observation which is relevant for organocatalysis. [10] In aqueous solution, pyridines are more

nucleophilic than hydroxide. This fact, in combination with the higher acidity of pyridinium ions compared to water, explains why in aqueous solutions of pyridines, generally pyridines and not hydroxide are the active nucleophiles.

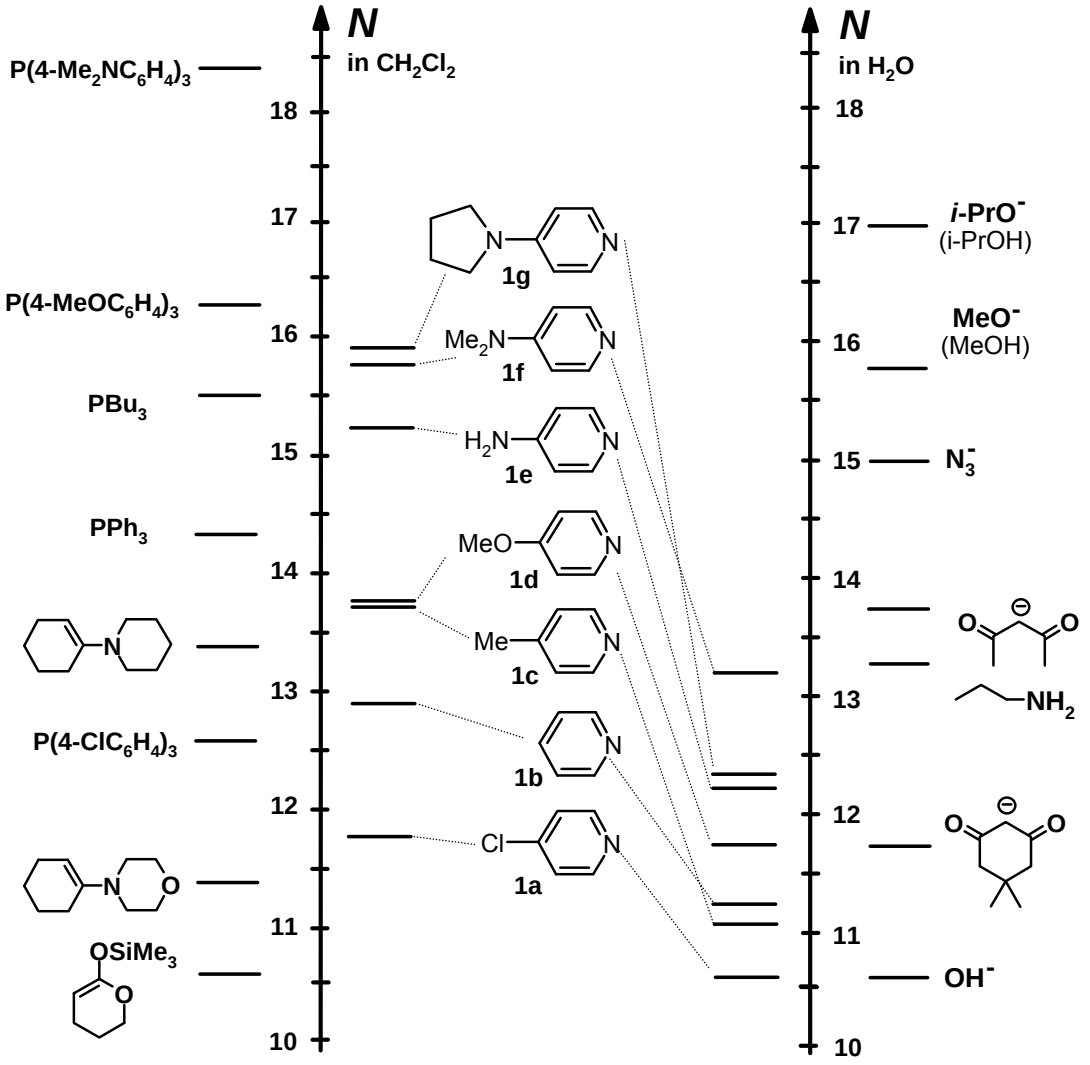


Figure 4.5. Comparison of the nucleophilic reactivities of pyridines with other types of nucleophiles[8] in CH_2Cl_2 and water. Other solvents are given in parenthesis.

Figure 4.6 shows a moderate correlation of *N* with Hammett's σ_p constants. The large scatter around the correlation lines can be explained by the fact that the nucleophilic site of the pyridines is the lone-pair at nitrogen, which is perpendicular to the π system. For that reason, the substituent constant which describes a combination of mesomeric and inductive effects fails to give a good correlation with *N*. The smaller slope of the correlation line in water, which reflects the smaller reactivity range in water (Figure 4.5), can again be explained by the fact that the more basic, donor substituted pyridines experience a higher stabilization by hydrogen bonding in water.

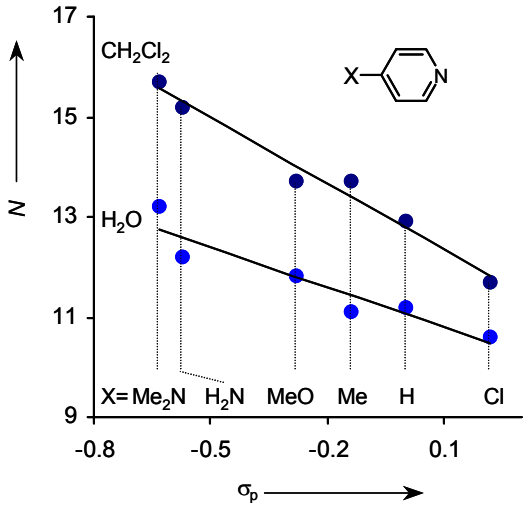


Figure 4.6. Correlation of *N* with σ_p[11,12] for 4-substituted pyridine derivatives in CH_2Cl_2 (*N* = - 4.42 σ_p + 12.8) and water (*N* = - 2.66 σ_p + 11.1).

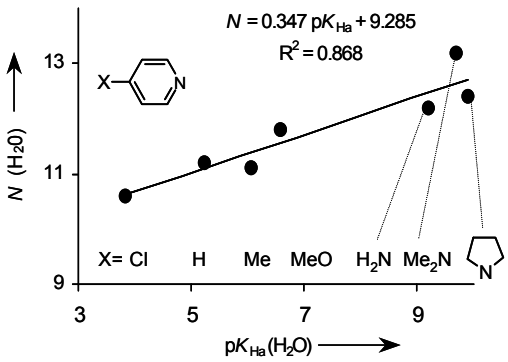


Figure 4.7a. Correlation of *N* (H_2O) with pK_{Ha} (H_2O)[13] for 4-substituted pyridine derivatives.

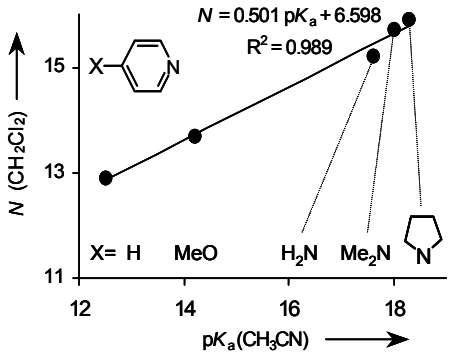


Figure 4.7b. Correlation of *N* (CH_2Cl_2) with pK_{Ha} (CH_3CN)[14] for 4-substituted pyridine derivatives.

While the correlation between pyridine nucleophilicities *N* in water and pK_{Ha} (H_2O) is only of moderate quality (R^2 = 0.868, Fig. 4.7a), a fairly good correlation is observed between the *N* parameters for pyridines in CH_2Cl_2 and their pK_{Ha} parameters for acetonitrile (R^2 = 0.989, Fig. 4.7b), which can be assumed to mimic the situation in CH_2Cl_2 better than the pK_{Ha} values for water.

In previous work we have found that the rates of the reactions of carbocations with uncharged nucleophiles are only slightly affected by solvent polarity since charges are neither created nor destroyed in reactions of benzhydrylium ions with neutral nucleophiles.[15] Figure 4.8 illustrates a different situation for the reactions with pyridines. While the correlation between the rate constants for the reactions of $(dma)_2CH^+$ with DMAP(**1f**) and

Gutmann's donor numbers *DN* [16,17] is rather poor(not depicted), Figure 4.8 shows that the rate constants decrease slightly with increasing E_T^N-values [16,18] of the solvents; the reaction of DMAP(**1f**) with $(dma)_2CH^+$ is 240 times slower in water than in dichloromethane.

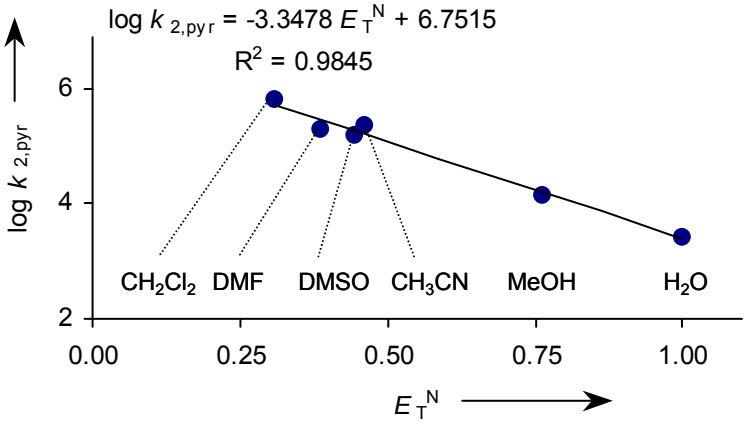
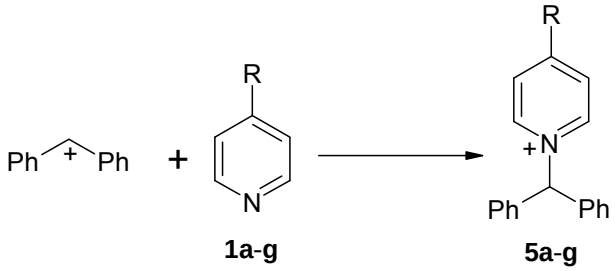


Figure 4.8. Plot of the rate constants log $k_{2,pyr}$ versus E_T^N for the reactions of DMAP(**1f**) with $(dma)_2CH^+$ in different solvents at 20 °C (rate constants from Table 4.3, E_T^N from ref. [16]; MeOH corresponds to a mixture of 91 % MeOH and 9 % acetonitrile(v/v)).

Energies for the reactions of the parent benzhydrylium ion with the pyridines **1a**-**g** in the gas phase (Scheme 4.2) have been obtained by ab initio MO calculations at the MP2(fc)/6-31G(d) level of theory (Table 4).[19] As expected from the results shown in Figure 4.7, the reaction energies become more negative as the basicity of the pyridines increases. The range of the reaction energies amounts to 80 ± 1 kJ mol^{-1} when using E_{tot}, E_0 or H_{298} molecular energies. Essentially the same results are obtained when using MP2(fc)/6-311++G(d,p)//MP2(fc)/6-31G(d) energies (see supporting information for details). The inclusion of entropy narrows the range to 73 kJ mol^{-1} in G_{298}.



Scheme 4.2.

Table 4.4. Reaction energies for the additions of the parent benzhydrylium cation to 4-substituted pyridines (**1a**-**g**, Scheme 4.2), charge parameters and structural characteristics of the corresponding adducts **5a**-**g** as calculated at the MP2(fc)/6-31G(d) level of theory.

Pyridine	ΔE_{tot}/ kJ mol^{-1}	ΔE_0/ kJ mol^{-1}	ΔH_{298}/ kJ mol^{-1}	ΔG_{298}/ kJ mol^{-1}	q(Py) [a] / e	r (C-N) / pm
1a	-182.2	-172.2	-172.8	-123.2	0.645	152.5
1b	-198.7	-187.8	-188.8	-139.2	0.648	152.6
1c	-210.5	-200.1	-200.8	-149.9	0.654	152.2
1d	-219.4	-209.1	-209.2	-158.2	0.661	151.7
1e	-236.4	-227.3	-227.3	-177.8	0.671	151.2
1f	-253.7	-244.0	-243.7	-195.1	0.679	150.8
1g	-263.2	-251.7	-252.6	-196.9	0.682	150.6

[a] overall charges in the pyridine fragments of the adducts 5 as calculated at the MP2(fc)/6-31G(d) level of theory using the NPA scheme.

As shown in Figure 4.9 there is a good linear correlation (R^2 = 0.980) between the nucleophilicity parameter *N* determined in CH_2Cl_2 and the reaction free energies ΔG_{298}. The small negative slope of –0.0548 of this correlation indicates that only a small amount of the reaction energy differences enters into the lowering of the reaction barrier. Because multiplication of ΔN(ordinate of Figure 4.9) with s = 0.67 yields relative rate constants (Δlog $k_{2,pyr}$) and division of ΔG_{298} by 5.71(= 2.303 *RT*) yields Δlog *K*, one can calculate a slope of 0.21 for the log $k_{2,pyr}$ /log *K* correlation corresponding to the plot of Figure 4.9.

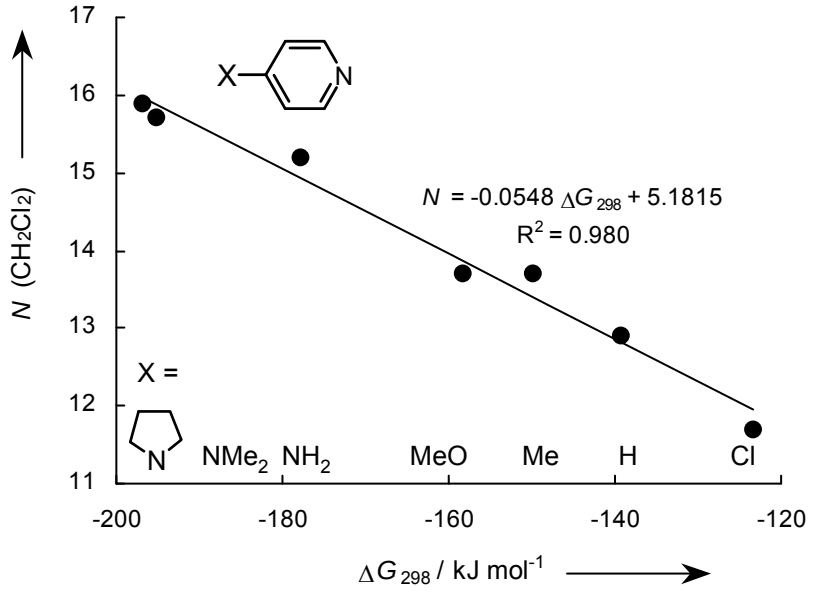


Figure 4.9. Plot of nucleophilicity parameters *N* of pyridines in CH_2Cl_2 versus ΔG_{298} (Scheme 4.2) at the MP2(fc)/6-31G(d)// MP2(fc)/6-31G(d) level.

As exemplified for the reaction of DMAP(**1f**) with the parent benzhydrylium ion in Figure 4.10, the reaction is accompanied by substantial changes in structural and electronic characteristics of the reactants. Formation of the new C-N bond transforms the formerly fully planar cationic center of the benzhydrylium ion (with d_{def}= 0.0 °) into an adduct of almost ideal tetrahedral structure (with d_{def}= 58.2 °).[20] Despite these structural changes, only 68 % of the positive charge are transferred from the benzhydrylium cation to the pyridine moiety in the course of the reaction, leaving the former with a charge of + 0.32 in the adduct **5f**. Despite the fact that the calculated degree of charge transfer depends somewhat on the particular quantum mechanical level and charge derivation scheme [21], it remains without doubt that the Lewis structure shown in Scheme 4.2 does not fully reflect the charge distribution in the reaction products **5**. The overall positive charge of the pyridine moiety also depends on the substituent present in 4-position, but as shown in Table 4.4 the range covered from the least to the most reactive pyridine is rather small (+0.645 to +0.682). The most pronounced stabilization is achieved through dialkylamino substituents, whose electron donation to the pyridine ring is accompanied by substantial shortening of the C-NMe_2 bond from 138.9 pm in DMAP(**1f**) to 134.5 pm in the adduct **5f**.

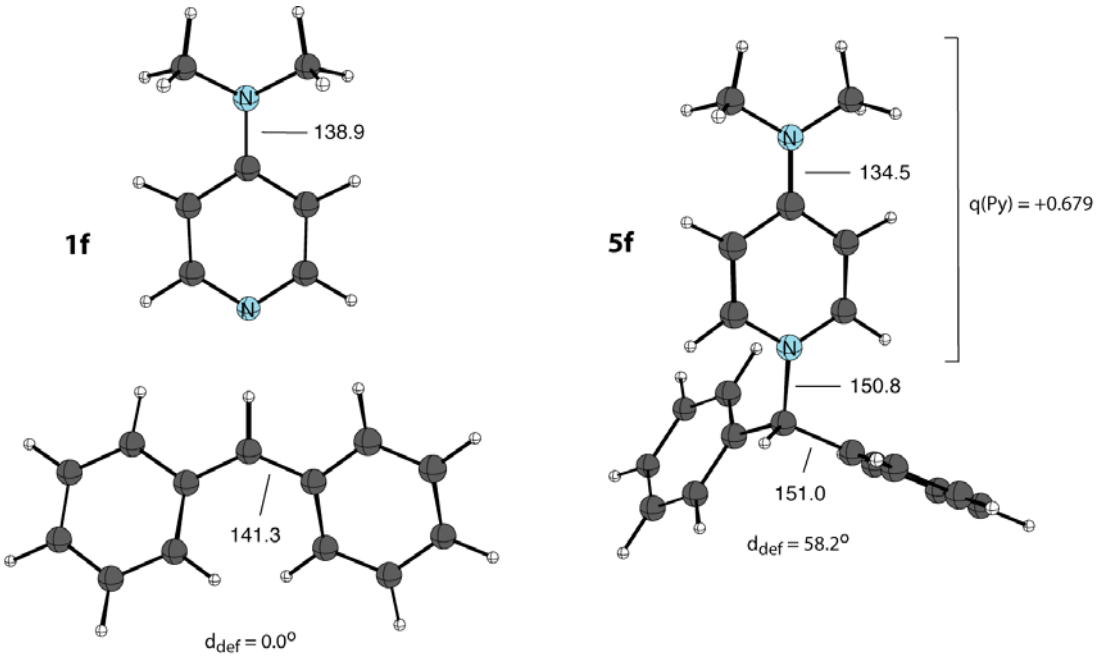


Figure 4.10. Structures of DMAP(**1f**), benzhydrylium cation, and the corresponding reaction product **5f** according to Scheme 4.2 as calculated at the MP2(fc)/6-31G(d) level of theory. All distances are in pm and all angles in degrees.

4.5. Reactions of pyridines with other electrophiles

Numerous kinetic studies on the nucleophilicities of pyridines have been published,[22] supplemented by a recent theoretical work by Campodónico et al.[23] However only in few

cases the overlap with the systems studied in this work was sufficient to perform meaningful correlations, which will be discussed later.

The potential of eq. (4.1) to predict absolute rate constants is convincingly demonstrated by Table 4.5. When the nucleophilicity parameters *N* and *s* for pyridine determined in this work(Table 4.3) are combined with previously published electrophilicity parameters for tricarbonyliron dienyl complexes, eq. (4.1) yields rate constants which closely resemble those measured by Kane-Maguire (Table 4.5).

Table 4.5. Comparison of calculated and observed rate constants for the reactions of tricarbonylirondienylium ions with the unsubstituted pyridine.

	$Fe(CO)_3(C_6H_7)^+$	$Fe(CO)_3(2\text{-}MeOC_6H_6)^+$	$Fe(CO)_3(C_7H_9)^+$	
E	-7.76	-8.94	-9.21	ref. [8a]
$k_{20\,°C}(CH_2Cl_2)$	2.78×10^3	4.49×10^2	2.97×10^2	[a]
$k_{25\,°C}(CH_3CN)$	2.20×10^3	4.25×10^2	1.40×10^2	ref. [5]

[a] Calculated by eq. (4.1), using the *E* parameters of this Table and *N* and *s* from Table 4.3.

Johnson determined the rates of the ethylations of various 3- and 4-substituted pyridine derivatives with ethyl iodide in various solvents.[4h] In numerous solvents(CH_3OH, CH_2Cl_2, CH_3CN, $PhNO_2$) donor substituted pyridines reacted considerably faster than acceptor substituted derivatives, and approximately one third of the differences in $pK_{Ha}(H_2O)$ were found in the rate constants of the nucleophilic substitutions(log k_2). Figure 4.11 shows that the rate constants for the reactions of pyridines with iodoethane in CH_2Cl_2 (log k_2/s) correlate linearly with the nucleophilicity parameters *N*, but as previously reported for other S_N2 type reactions,[4n] the slope is smaller than 1, and the previously proposed equation (4.5) can be used to calculate s_E = 0.75 and an electrophilicity parameter *E* = -22.1 for ethyl iodide in CH_2Cl_2.

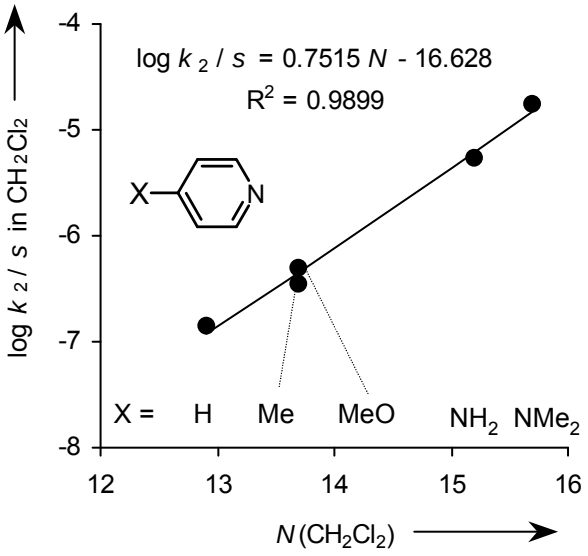


Figure 4.11. Correlation of (log k_2) / s for the reactions of ethyl iodide with para-substituted pyridines at 25 °C versus their N parameters in CH_2Cl_2. Rate constants taken from ref. [4h].

$$\log k_{20^\circ C} = s_E s_N(E + N) \qquad (4.5)$$

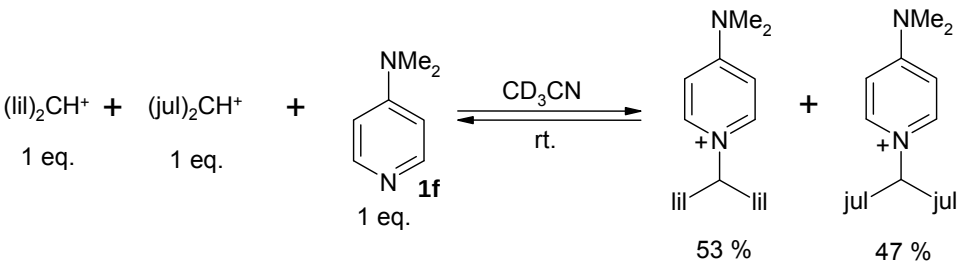
k, N, E as in eq. 4.1

s_N = nucleophile-specific slope(= s of eq. 4.1)

s_E = electrophile-specific slope

4.6. Equilibrium Constants and Intrinsic Barriers

Because of the reversibility of these reactions, for some of them rate and equilibrium constants are available as listed in Table 4.3. It is remarkable that the equilibrium constant for the reaction of $(lil)_2CH^+$ with **1f** in CH_2Cl_2 was found to be slightly larger than for the corresponding reaction of $(jul)_2CH^+$, though in dozens of reactions $(jul)_2CH^+$ has generally been found to react approximately four times faster than $(lil)_2CH^+$. Though a breakdown of rate-equilibrium relationships had already been observed for the reactions of these two carbocations with phosphanes[8e] and the azide ion[8h], we wanted to exclude an error in the relative Lewis acidities of these two carbocations indicated by the equilibrium constants of Table 4.3. We therefore mixed equimolar amounts of $(lil)_2CH^+$, $(jul)_2CH^+$, and DMAP(**1f**) in CD_3CN in an NMR tube. Comparison of the integral heights of the methine signals indicated a 53:47 ratio of the two adducts(Scheme 4.3) in agreement with the relative reaction free energies $\Delta_r G°$ derived from K (Table 4.3) and listed in Table 4.5.



Scheme 4.3.

Table 4.5. Activation free energies $\Delta G^{\neq}$, reaction free energies $\Delta_r G°$, and intrinsic barriers $\Delta G_0^{\neq}$ for the reactions of benzhydrylium tetrafluoroborates with pyridines **1** in dichloromethane (20 °C).

X =		Ar_2CH^+	$\Delta G^{\neq}$ / kJ mol^{-1}	$\Delta_r G°$ / kJ mol^{-1}	$\Delta G_0^{\neq}$ / kJ mol^{-1}
H	**1b**	$(dpa)_2CH^+$	41.0	- 24.4	52.5
Me	**1c**	$(dpa)_2CH^+$	38.4	- 32.0	53.2
NMe_2	**1f**	$(lil)_2CH^+$	50.3	- 21.1	60.4
		$(jul)_2CH^+$	49.3	-21.1	59.9
		$(ind)_2CH^+$	45.4	- 29.4	59.2
		$(thq)_2CH^+$	42.8	- 30.6	57.1

As a consequence, a rather poor correlation was found between the rate and equilibrium constants of the reactions of DMAP(**1f**) with benzhydrylium ions. These deviations are reminiscent of previously reported reactions of triphenylphosphane[8e] and the azide ion[8h] with benzhydrylium ions, where $(jul)_2CH^+$ and $(thq)_2CH^+$, the benzhydrylium ions with annelated six-membered rings also react faster than expected from log $k_{2,pyr}$ versus log K correlations.

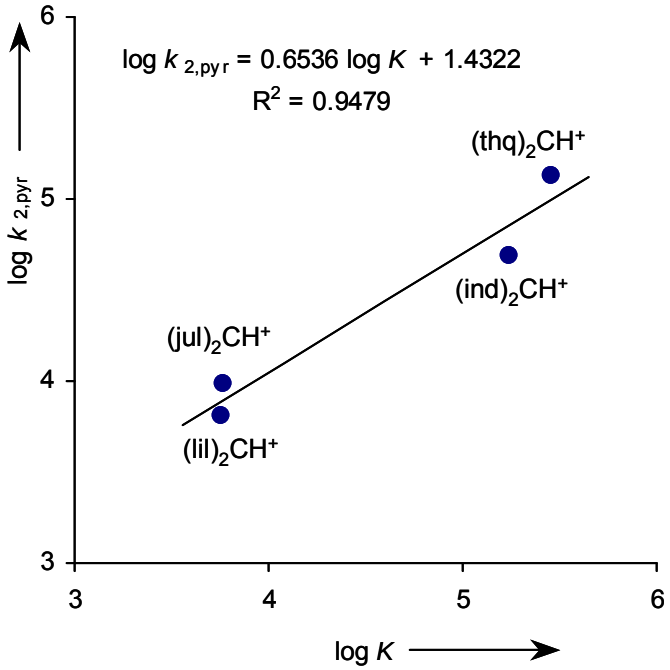
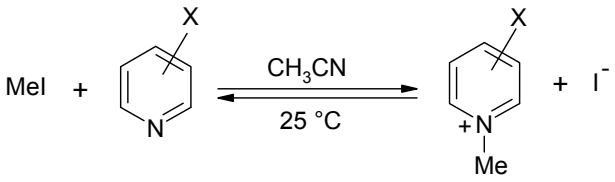


Figure 4.12. Plot of log $k_{2,pyr}$ versus log K for the reactions of DMAP with Ar_2CH^+ in CH_2Cl_2 at 20 °C.

Deviations from rate equilibrium relationships reveal variable intrinsic barriers $\Delta G_0^{\neq}$, which can be calculated by substituting $\Delta_r G°$ and $\Delta G^{\neq}$ from the equilibrium and rate constants given in Table 4.3 into the Marcus equation [eq. (4.6)], where the work term has been omitted.

$$\Delta G^{\neq} = \Delta G_0^{\neq} + 0.5\ \Delta_r G° + [(\Delta_r G°)^2 / 16\Delta G_0^{\neq}] \qquad (4.6)$$

The last four entries of Table 4.5 show the origin of the deviations from the correlation line in Figure 4.12. For unknown reasons the reactions of $(jul)_2CH^+$ and $(thq)_2CH^+$ with nucleophiles proceed with less reorganization energy λ(= 4 $\Delta G_0^{\neq}$) than the reactions of the corresponding benzhydrylium ions with annelated five-membered rings [$(lil)_2CH^+$ and $(ind)_2CH^+$].
Though the intrinsic barriers are thus not independent of the nature of the carbocation, Table 4.5 shows that the dependence of $\Delta G_0^{\neq}$ on the nature of the benzhydrylium ion is not very strong. For that reason it is concluded that the significantly lower intrinsic barriers observed for the reactions of **1b** and **1c** with $(dpa)_2CH^+$ are predominantly due to variation of the pyridine.
Arnett had previously reported rate and equilibrium constants for the reactions of differently substituted pyridines with iodomethane[4g].



Scheme 4.4.

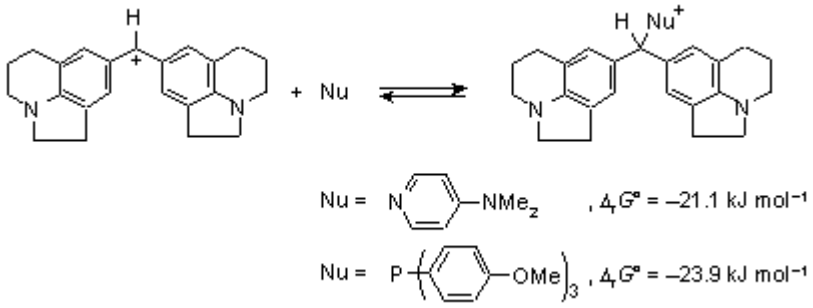
Table 4.6. Activation free energies $\Delta G^{\neq}$, reaction free energies $\Delta_r G°$, and intrinsic barriers $\Delta G_0^{\neq}$ for the reactions of iodomethane with pyridines in acetonitrile (25 °C). Data from ref. [4g].

X =	$\Delta G^{\neq}$ / kJ mol^{-1}	$\Delta_r G°$ / kJ mol^{-1}	$\Delta G_0^{\neq}$ / kJ mol^{-1}
4-H	92.6	-49.9	117.6
3-Br	97.8	-26.1	110.8
3-Cl	98.0	-24.7	110.3
4-CN	100.5	-21.3	111.2
3,5-diCl	103.3	-11.4	108.9
2-Cl	103.7	-11.4	109.4

It is obvious that the S_N2 reactions of pyridines (Scheme 4.4) which have comparable reaction free energies $\Delta_r G°$ (Table 4.6) as the reactions of pyridines with carbocations (Table 4.5) have considerably higher activation free energies $\Delta G^{\neq}$. The differences are caused by the higher intrinsic barriers of the reactions with iodomethane, where the breaking of the C-I bond requires additional reorganization energy. Like in the reactions of pyridines with carbocations, also in S_N2 reactions of pyridines, the intrinsic barriers $\Delta G_0^{\neq}$ decrease with decreasing basicities of the pyridines(Table 4.6).

4.7. Conclusion

Organocatalytic activities of amines have often been correlated with their pK_{Ha} values. While such correlations hold within a narrow class of compounds, they cannot be used for the comparison of different classes of compounds. With pK_{Ha} values of 7.61 (Ph_3P) and 9.96 ($MePh_2P$) tertiary phosphanes are considerably weaker Brønsted bases in acetonitrile than pyridine (pK_{Ha} = 12.53) and DMAP (pK_{Ha} =17.95) [14]. These pK_{Ha} values do not rationalize the observation that DMAP and phosphanes, but not the unsubstituted pyridine are efficient catalysts for Baylis-Hillman and related reactions. Our finding that the well known organocatalyst DMAP(**1f**) and triarylphosphanes or trialkylphosphanes have comparable nucleophilicity parameters N , and even more important, comparable carbon basicities[24] (Scheme 4.5) suggests to employ these quantities for the systematic analysis of nucleophilic organocatalysts.

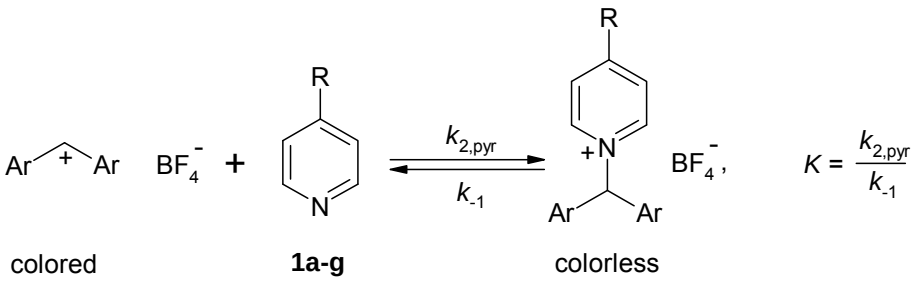


Scheme 4.5.

4.8. Experimental

4.8.1. Kinetic measurements in dichloromethane

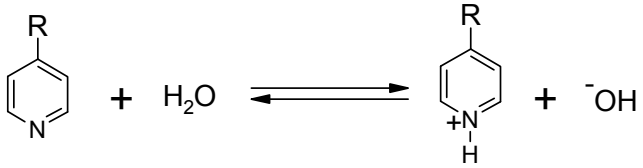
The rates of slow reactions ($\tau_{1/2}$ > 10 s) were determined by using a J&M TIDAS diode array spectrophotometer, which was controlled by Labcontrol Spectacle software and connected to a Hellma 661.502-QX quartz Suprasil immersion probe (5 mm light path) via fiber optic cables and standard SMA connectors. A tungsten lamp (10 W) was used as light source. The temperature of solutions during all kinetic studies was kept constant (usually 20.0 $\pm$ 0.2 °C) by using a circulating bath thermostat and monitored with a thermocouple probe. For the evaluation of rate constants, absorption-time curves at the absorption maxima of the diarylcarbenium ions Ar_2CH^+ were fitted to a single exponential $A = A_0 \exp(-k_{obs}t) + C$.
UV-Vis kinetic measurements of rapid reactions ($\tau_{1/2}$ < 10 s) were performed on a Hi-Tech SF-61DX2 stopped flow spectrophotometer system. The kinetic experiments were initiated by rapidly mixing equal volumes of the nucleophile and the diarylcarbenium salt solution, using syringes with pneumatically driven pistons. The pseudo-first-order rate constants k_{obs} for the reactions were obtained from at least five runs at each nucleophile concentration.



Scheme 1a.

4.8.2. Kinetic measurements in water

If pyridine is dissolved in water, the concentration of hydroxide increases by protolysis. For that reason we have to calculate the concentration of the free pyridines $[Nu]_{eff}$ and of hydroxide $[OH^-]$ with the pK_B of the pyridines.



$$K_B = \frac{[\text{pyridinium}]\ [OH^-]}{[\text{pyridine}]_{eff}} \tag{1}$$

$$[\text{pyridine}]_0 = [\text{pyridine}]_{eff} + [\text{pyridinium}] = [\text{pyridine}]_{eff} + [OH^-] \tag{2}$$

(2) in (1)

$$K_B = \frac{[OH^-]^2}{[\text{pyridine}]_0 - [OH^-]} \tag{3}$$

Solving of the quadratic equation (3) leads to one logic solution for $[OH^-]$ (The one with the "+" in the numerator).

$$[OH^-] = -\frac{K_B}{2} + \sqrt{\left(\frac{K_B}{2}\right)^2 + K_B[\text{pyridine}]_0} \tag{4}$$

The rates of the combination reactions were determined by mixing a colored aqueous solution of a benzhydrylium salt with an aqueous solution of a pyridine (>10 equivalents). As the products are colorless, we studied the reactions by UV-Vis spectroscopic monitoring of the decay of absorption with time.

$$-\frac{d[R^+]}{dt} = k_{obs}[R^+] \tag{5}$$

The consumption of the benzhydrylium cations may be due to the reaction with the pyridines,hydroxide ions and the solvent water.

$k_{obs} = k_{2,pyr}\,[pyridine]_{eff} + k_{2,OH^-}\,[OH^-] + k_W + k_{-1}$ (6)

$= k_{1\Psi} + k_{2,OH^-}\,[OH^-]$, with $k_{1\Psi} = k_{2,pyr}\,[pyridine]_{eff} + k_W + k_{-1}$ and $[OH^-]$ from eq. (4)

The pyridines are usually used in more than 10-fold excess over the benzhydrylium cations in order to run the reactions under pseudo first-order conditions. The concentrations of the pyridines as well as that of hydroxide therefore remains constant during the reactions. With the already published second-order rate constants k_{2,OH^-} for the reactions of hydroxide with benzhydrylium ions and the first-order rate constants k_W for the reactions of water with benzhydrylium ions,[8c] we get the second-order rate constants for the reactions of the pyridines with the benzhydrylium ions $k_{2,pyr}$ from a plot of $k_{1\Psi}$ versus $[pyridine]_{eff}$.

4.8.3. Determination of the equilibrium constants in water

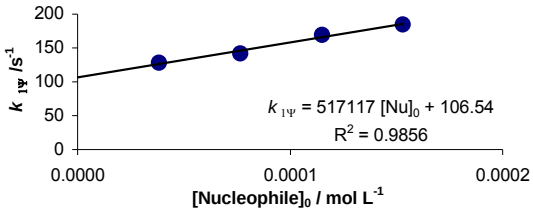
We were not able to measure the equilibrium constants *K* (Scheme 1) in water directly. When an aqueous solution of the benzhydrylium salt was combined with the pyridine, the UV/Vis spectrum for the benzhydrylium ion did not show a constant end absorption, because of the slow reactions of the benzhydrylium ions with hydroxide and water in the presence of pyridine. Hower, the ratio of the second order rate constants $k_{2,pyr}$ for the forward reaction and the first order rate constant k_{-1} for the backward reaction, gave equilibrium constants, which are less accurate than the directly measured ones and are written in parentheses.

4.8.4. 4-Chloropyridine (1a)

Rate constants and equilibrium constants in Dichloromethane

Reaction of 4-Chloropyridine (**1a**) with $(pfa)_2CH^+BF_4^-$:
(at 20 °C, in CH_2Cl_2, J&M, detection at 601 nm)

$[(pfa)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_0/[El]_0$	$k_{1\Psi}$ / s^{-1}
4.80×10^{-6}	3.82×10^{-5}	8	1.28×10^{2}
4.80×10^{-6}	7.64×10^{-5}	16	1.42×10^{2}
4.80×10^{-6}	1.15×10^{-4}	24	1.69×10^{2}
4.80×10^{-6}	1.53×10^{-4}	32	1.85×10^{2}



$k_{2,pyr}$ = 5.17×10^{5} $M^{-1}s^{-1}$

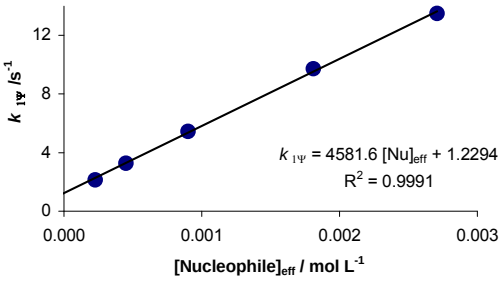
k_{-1} = 1.07×10^{2} s^{-1}

K = 4.83×10^{3} M^{-1}

Rate constants and equilibrium constants in water

Reaction of 4-Chloropyridine (**1a**) with $(mor)_2CH^+BF_4^-$:
(at 20 °C, in 91 Vol% H_2O / 9 Vol% CH_3CN, Stopped-flow, detection at 610 nm)

$[(mor)_2CH^+]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	$k_{1\Psi}$ / s^{-1}
2.57×10^{-5}	2.71×10^{-3}	105	13.5
2.57×10^{-5}	1.81×10^{-3}	70	9.71
2.57×10^{-5}	9.03×10^{-4}	35	5.46
2.57×10^{-5}	4.51×10^{-4}	18	3.27
2.57×10^{-5}	2.26×10^{-4}	9	2.15



$k_{2,pyr}$ = 4.58×10^{3} $M^{-1}s^{-1}$

k_{-1} = 1.23 s^{-1}

K = 3.73×10^{3} M^{-1}

k_{2,OH^-} = 1.06×10^{3} $M^{-1}s^{-1}$

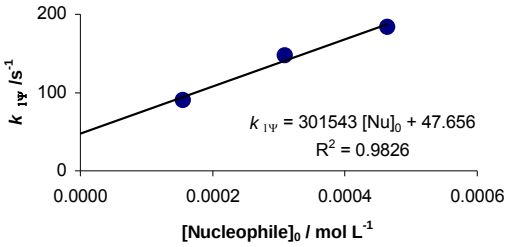
pK_B = 10.17

4.8.5. Pyridine (1b)

Rate constants in Dichloromethane

Reaction of Pyridine (**1b**) with $(dpa)_2CH^+BF_4^-$:
(at 20 °C, in CH_2Cl_2, Stopped-flow, detection at 674 nm)

$[(dpa)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_0/[El]_0$	$k_{1\Psi}$ / s^{-1}
7.51×10^{-6}	4.64×10^{-4}	62	1.84×10^2
7.51×10^{-6}	3.09×10^{-4}	41	1.48×10^2
7.51×10^{-6}	1.55×10^{-4}	21	90.8



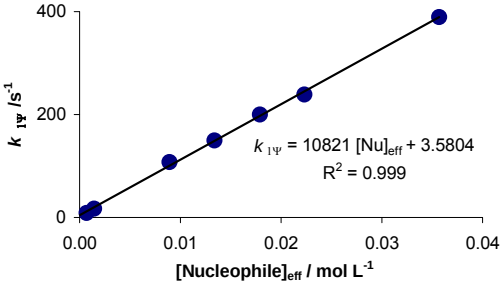
$k_{2,pyr}$ = 3.02×10^5 $M^{-1}s^{-1}$

k_{-1} = 47.7 s^{-1}

Rate constants and equilibrium constants in water

Reaction of Pyridine (**1b**) with $(mor)_2CH^+BF_4^-$:
(at 20 °C, in 91 Vol% H_2O / 9 Vol% CH_3CN, Stopped-flow, detection at 607 nm)

$[(mor)_2CH^+]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	$k_{1\Psi}$ / s^{-1}
2.29×10^{-5}	3.57×10^{-2}	1560	3.90×10^2
2.29×10^{-5}	2.23×10^{-2}	974	2.39×10^2
2.29×10^{-5}	1.79×10^{-2}	781	2.00×10^2
2.29×10^{-5}	1.34×10^{-2}	585	1.50×10^2
2.29×10^{-5}	8.93×10^{-3}	390	1.07×10^2
2.29×10^{-5}	1.43×10^{-3}	62	16.4
2.29×10^{-5}	7.13×10^{-4}	31	8.57



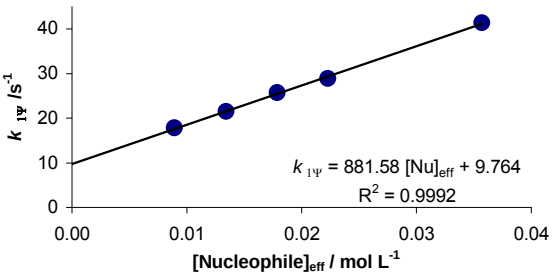
$k_{2,pyr}$ = 1.08×10^4 $M^{-1}s^{-1}$

k_{2,OH^-} = 1.06×10^3 $M^{-1}s^{-1}$

pK_B = 8.77

Reaction of Pyridine (**1b**) with $(dma)_2CH^+BF_4^-$:
(at 20 °C, in 99.6 Vol% H_2O / 0.4 Vol% CH_3CN, Stopped-flow, detection at 607 nm)

$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	$k_{1\Psi}$ / s^{-1}
7.62×10^{-5}	3.57×10^{-2}	468	41.4
7.62×10^{-5}	2.23×10^{-2}	293	29.0
7.62×10^{-5}	1.79×10^{-2}	235	25.7
7.62×10^{-5}	1.34×10^{-2}	176	21.5
7.62×10^{-5}	8.93×10^{-3}	117	17.8



$k_{2,pyr}$ = 8.82×10^2 $M^{-1}s^{-1}$

k_{-1} = 9.76 s^{-1}

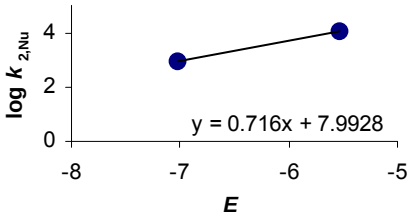
K = 9.04×10^2 M^{-1}

k_{2,OH^-} = 1.31×10^2 $M^{-1}s^{-1}$

pK_B = 8.77

Reactivity parameters in water: N = 11.2; s = 0.72

Reference electrophile	E parameter	$k_{2,pyr}$(20°C) / M^{-1} s^{-1}
$(mor)_2CH^+$	-5.53	1.08×10^4
$(dma)_2CH^+$	-7.02	9.26×10^2

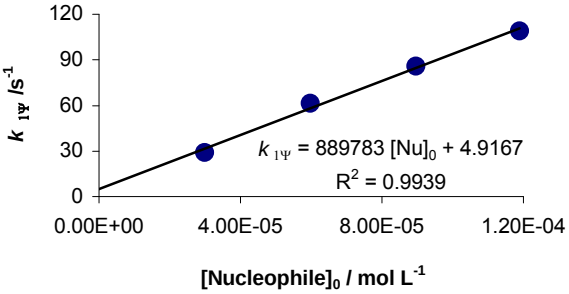


4.8.6. 4-Methylpyridine (1c)

Rate constants in Dichloromethane

Reaction of 4-Methylpyridine (**1c**) with $(dpa)_2CH^+BF_4^-$:
(at 20 °C, in CH_2Cl_2, Stopped-flow, detection at 674 nm)

$[(dpa)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_0/[El]_0$	$k_{1\Psi}$ / s^{-1}
4.30×10^{-6}	1.19×10^{-4}	28	1.09×10^2
4.30×10^{-6}	8.96×10^{-5}	21	85.7
4.30×10^{-6}	5.97×10^{-5}	14	61.3
4.30×10^{-6}	2.99×10^{-5}	7	29.0



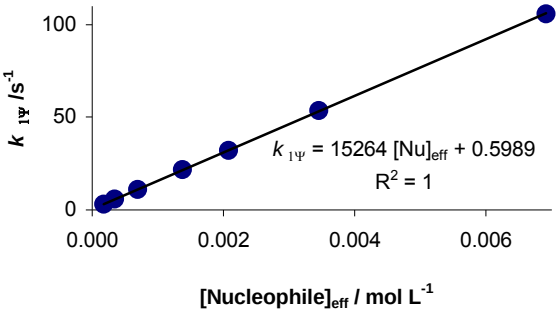
$k_{2,pyr}$ = 8.90×10^5 $M^{-1}s^{-1}$

k_{-1} = 4.92 s^{-1}

Rate constants and equilibrium constants in water

Reaction of 4-Methylpyridine (**1c**) with $(mor)_2CH^+BF_4^-$:
(at 20 °C, in 91 Vol% H_2O / 9 Vol% CH_3CN, Stopped-flow, detection at 610 nm)

$[(mor)_2CH^+]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	$k_{1\Psi}$ / s^{-1}
1.72×10^{-5}	6.91×10^{-3}	402	1.06×10^2
1.72×10^{-5}	3.45×10^{-3}	201	53.5
1.72×10^{-5}	2.08×10^{-3}	121	32.3
1.72×10^{-5}	1.38×10^{-3}	80	21.8
1.72×10^{-5}	6.89×10^{-4}	40	10.9
1.72×10^{-5}	3.44×10^{-4}	20	5.95
1.72×10^{-5}	1.72×10^{-4}	10	3.08



$k_{2,pyr}$ = 1.53×10^4 $M^{-1}s^{-1}$

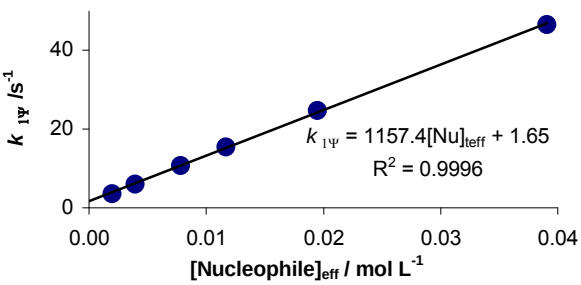
k_W = 0.673 s^{-1} [8c]

k_{2,OH^-} = 1.06×10^3 $M^{-1}s^{-1}$

pK_B = 7.94

Reaction of 4-Methylpyridine (**1c**) with $(dma)_2CH^+BF_4^-$:
(at 20 °C, in 99.5 Vol% H_2O / 0.5 Vol% CH_3CN, Stopped-flow, detection at 610 nm)

$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	$k_{1\Psi}$ / s^{-1}
4.61×10^{-5}	3.91×10^{-2}	848	46.6
4.61×10^{-5}	1.95×10^{-2}	423	24.7
4.61×10^{-5}	1.17×10^{-2}	254	15.4
4.61×10^{-5}	7.81×10^{-3}	169	10.7
4.61×10^{-5}	3.90×10^{-3}	85	5.97
4.61×10^{-5}	1.95×10^{-3}	42	3.66



$k_{2,pyr}$ = 1.16×10^3 $M^{-1}s^{-1}$

k_{-1} = 1.65 s^{-1}

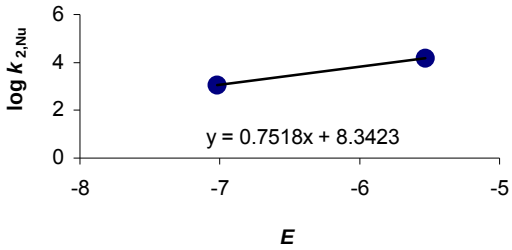
K = 7.03×10^2 M^{-1}

k_{2,OH^-} = 1.31×10^2 $M^{-1}s^{-1}$

pK_B = 7.94

Reactivity parameters in water: *N* = 11.1; *s* = 0.75

Reference electrophile	*E* parameter	$k_{2,pyr}$(20°C) / M^{-1} s^{-1}
$(mor)_2CH^+$	-5.53	1.53×10^4
$(dma)_2CH^+$	-7.02	1.16×10^3

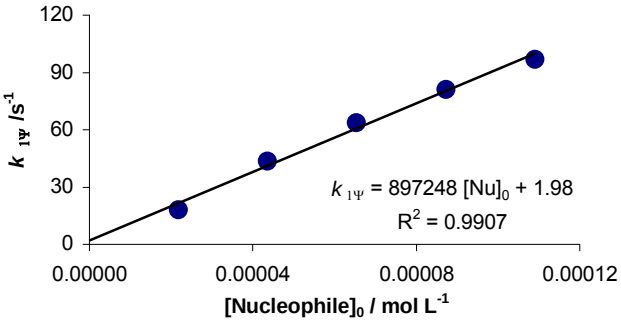


4.8.7. 4-Methoxypyridine (1d)

Rate constants and equilibrium constants in Dichloromethane

Reaction of 4-Methoxypyridine (**1d**) with $(dpa)_2CH^+BF_4^-$:
(at 20 °C, in CH_2Cl_2, Stopped-flow, detection at 674 nm)

$[(dpa)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_0/[El]_0$	$k_{1\Psi}$ / s^{-1}
4.30×10^{-6}	1.09×10^{-4}	25	97.0
4.30×10^{-6}	8.72×10^{-5}	20	81.1
4.30×10^{-6}	6.54×10^{-5}	15	63.7
4.30×10^{-6}	4.36×10^{-5}	10	43.5
4.30×10^{-6}	2.18×10^{-5}	5	18.0



$k_{2,pyr}$ = 8.97×10^5 $M^{-1}s^{-1}$

k_{-1} = 1.98 s^{-1}

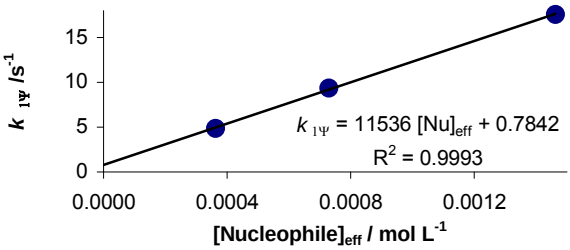
(K = 4.53×10^5 M^{-1})

Rate constants and equilibrium constants in water

Reaction of 4-Methoxypyridine (**1d**) with $(mor)_2CH^+BF_4^-$:
(at 20 °C, in 91 Vol% H_2O / 9 Vol% CH_3CN, Stopped-flow, detection at 610 nm)

$[(mor)_2CH^+]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	$k_{1\Psi}$ / s^{-1}
1.72×10^{-5}	1.46×10^{-3}	85	17.6
1.72×10^{-5}	7.29×10^{-4}	42	9.39
1.72×10^{-5}	3.63×10^{-4}	21	4.85

$k_{2,pyr} = 1.15 \times 10^4$ $M^{-1}s^{-1}$



$k_W = 0.673$ s^{-1} [8c]

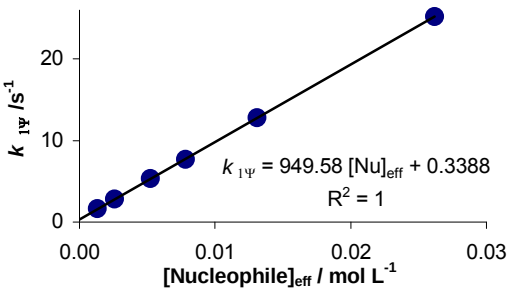
$k_{2,OH^-} = 1.06 \times 10^3$ $M^{-1}s^{-1}$

$pK_B = 7.42$

Reaction of 4-Methoxypyridine (**1d**) with $(dma)_2CH^+BF_4^-$:
(at 20 °C, in 99.5 Vol% H_2O / 0.5 Vol% CH_3CN, Stopped-flow, detection at 610 nm)

$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	$k_{1\Psi}$ / s^{-1}
4.61×10^{-5}	2.62×10^{-2}	568	25.2
4.61×10^{-5}	1.31×10^{-2}	284	12.8
4.61×10^{-5}	7.83×10^{-3}	170	7.67
4.61×10^{-5}	5.23×10^{-3}	113	5.31
4.61×10^{-5}	2.60×10^{-3}	56	2.82
4.61×10^{-5}	1.30×10^{-3}	28	1.62

$k_{2,pyr} = 9.50 \times 10^2$ $M^{-1}s^{-1}$



$k_W = 0.0206$ s^{-1} [8cFehler! Textmarke nicht definiert.]

$k_{2,OH^-} = 1.31 \times 10^2$ $M^{-1}s^{-1}$

$pK_B = 7.42$

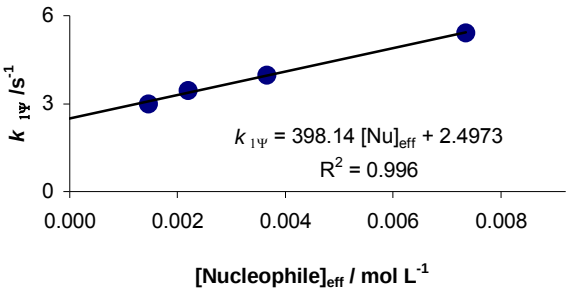
Reaction of 4-Methoxypyridine (**1d**) with $(pyr)_2CH^+BF_4^-$:
(at 20 °C, in 99.5 Vol% H_2O / 0.5 Vol% CH_3CN, Stopped-flow, detection at 610 nm)

$[(pyr)_2CH^+]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	$k_{1\Psi}$ / s^{-1}
2.54×10^{-5}	7.35×10^{-3}	289	5.41
2.54×10^{-5}	3.66×10^{-3}	144	3.97
2.54×10^{-5}	2.19×10^{-3}	86	3.45
2.54×10^{-5}	1.46×10^{-3}	58	3.01

$k_{2,pyr} = 3.98 \times 10^2$ $M^{-1}s^{-1}$

$k_{-1} = 2.50$ s^{-1}

$K = 1.59 \times 10^2$ M^{-1}

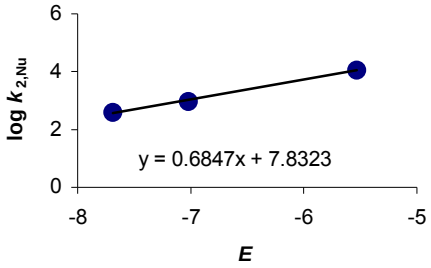


$k_{2,OH^-} = 48.5$ $M^{-1}s^{-1}$

$pK_B = 7.42$

Reactivity parameters in water: *N* = 11.4; *s* = 0.68

Reference electrophile	*E* parameter	$k_{2,pyr}$(20°C) / M^{-1} s^{-1}
$(mor)_2CH^+$	-5.53	1.15×10^4
$(dma)_2CH^+$	-7.02	9.50×10^2
$(pyr)_2CH^+$	-7.69	3.98×10^2

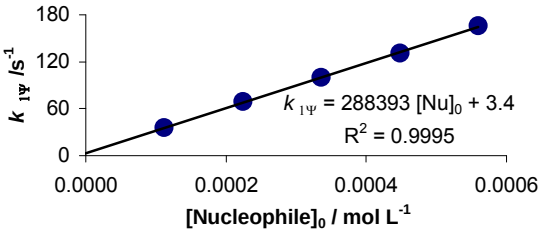


4.8.8. 4-Aminopyridine (1e)

Rate constants and equilibrium constants in Dichloromethane

Reaction of 4-Aminopyridine (**1e**) with $(dma)_2CH^+BF_4^-$:
(at 20 °C, in CH_2Cl_2, Stopped-flow, detection at 612 nm)

$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_0/[El]_0$	$k_{1\Psi}$ / s^{-1}
7.80×10^{-6}	5.60×10^{-4}	72	1.66×10^2
7.80×10^{-6}	4.48×10^{-4}	57	1.31×10^2
7.80×10^{-6}	3.36×10^{-4}	43	1.00×10^2
7.80×10^{-6}	2.24×10^{-4}	29	69.0
7.80×10^{-6}	1.12×10^{-4}	14	35.5



$k_{2,pyr}$ = 2.88×10^5 $M^{-1}s^{-1}$

k_{-1} = 3.40 s^{-1}

K = 8.48×10^4 M^{-1}

Rate constants and equilibrium constants in water

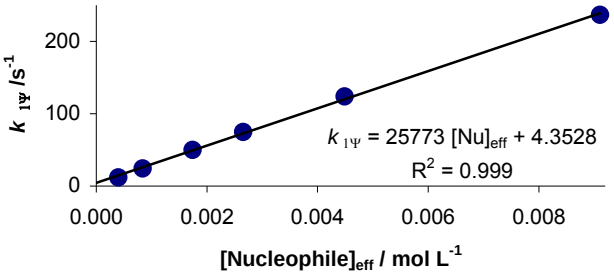
Reaction of 4-Aminopyridine (**1e**) with $(mor)_2CH^+BF_4^-$:
(at 20 °C, in 91 Vol% H_2O / 9 Vol% CH_3CN, Stopped-flow, detection at 610 nm)

$[(mor)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,\ OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
3.65×10^{-5}	9.45×10^{-3}	9.10×10^{-3}	3.46×10^{-4}	249	2.37×10^2	3.67×10^{-1}	2.37×10^2
3.65×10^{-5}	4.73×10^{-3}	4.49×10^{-3}	2.43×10^{-4}	123	1.24×10^2	2.58×10^{-1}	1.24×10^2
3.65×10^{-5}	2.84×10^{-3}	2.65×10^{-3}	1.87×10^{-4}	73	74.9	1.98×10^{-1}	74.7
3.65×10^{-5}	1.89×10^{-3}	1.74×10^{-3}	1.51×10^{-4}	48	50.3	1.60×10^{-1}	50.1
3.65×10^{-5}	9.45×10^{-4}	8.40×10^{-4}	1.05×10^{-4}	23	24.6	1.12×10^{-1}	24.5
3.65×10^{-5}	4.73×10^{-4}	4.00×10^{-4}	7.26×10^{-5}	11	11.9	7.70×10^{-2}	11.8

$k_{2,pyr}$ = 2.58 × 10^4 $M^{-1}s^{-1}$

k_{2,OH^-} = 1.06 × 10^3 $M^{-1}s^{-1}$

pK_B = 4.88



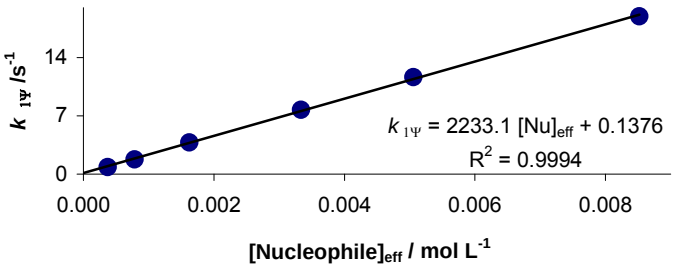
Reaction of 4-Aminopyridine (**1e**) with $(dma)_2CH^+BF_4^-$:
(at 20 °C, in 99.7 Vol% H_2O / 0.3 Vol% CH_3CN, Stopped-flow, detection at 610 nm)

$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi, OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
5.95 × 10^{-5}	8.85 × 10^{-3}	8.51 × 10^{-3}	3.35 × 10^{-4}	143	19.0	4.39 × 10^{-2}	19.0
5.95 × 10^{-5}	5.31 × 10^{-3}	5.05 × 10^{-3}	2.58 × 10^{-4}	85	11.7	3.38 × 10^{-2}	11.7
5.95 × 10^{-5}	3.54 × 10^{-3}	3.33 × 10^{-3}	2.10 × 10^{-4}	56	7.75	2.74 × 10^{-2}	7.72
5.95 × 10^{-5}	1.77 × 10^{-3}	1.62 × 10^{-3}	1.46 × 10^{-4}	27	3.82	1.92 × 10^{-2}	3.80
5.95 × 10^{-5}	8.85 × 10^{-4}	7.83 × 10^{-4}	1.02 × 10^{-4}	13	1.80	1.33 × 10^{-2}	1.79
5.95 × 10^{-5}	4.43 × 10^{-4}	3.73 × 10^{-4}	7.01 × 10^{-5}	6	8.44 × 10^{-1}	9.18 × 10^{-3}	8.35 × 10^{-1}

$k_{2,pyr}$ = 2.23 × 10^3 $M^{-1}s^{-1}$

k_{2,OH^-} = 1.31 × 10^2 $M^{-1}s^{-1}$

pK_B = 4.88



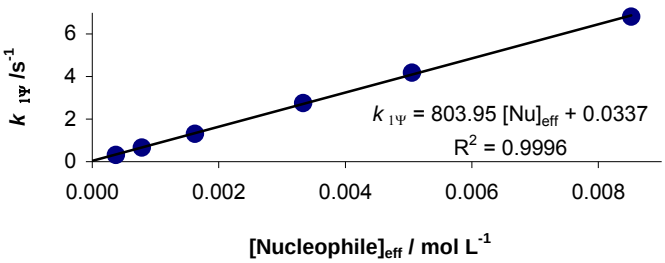
Reaction of 4-Aminopyridine (**1e**) with $(pyr)_2CH^+BF_4^-$:
(at 20 °C, in 99.8 Vol% H_2O / 0.2 Vol% CH_3CN, Stopped-flow, detection at 608 nm)

$[(pyr)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi, OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
1.05 × 10^{-5}	8.85 × 10^{-3}	8.51 × 10^{-3}	3.35 × 10^{-4}	811	6.84	1.62 × 10^{-2}	6.82
1.05 × 10^{-5}	5.31 × 10^{-3}	5.05 × 10^{-3}	2.58 × 10^{-4}	481	4.19	1.25 × 10^{-2}	4.18
1.05 × 10^{-5}	3.54 × 10^{-3}	3.33 × 10^{-3}	2.10 × 10^{-4}	317	2.76	1.02 × 10^{-2}	2.75
1.05 × 10^{-5}	1.77 × 10^{-3}	1.62 × 10^{-3}	1.46 × 10^{-4}	155	1.31	7.10 × 10^{-3}	1.30
1.05 × 10^{-5}	8.85 × 10^{-4}	7.83 × 10^{-4}	1.02 × 10^{-4}	75	6.63 × 10^{-1}	4.93 × 10^{-3}	6.58 × 10^{-1}
1.05 × 10^{-5}	4.43 × 10^{-4}	3.73 × 10^{-4}	7.01 × 10^{-5}	36	3.13 × 10^{-1}	3.40 × 10^{-3}	3.10 × 10^{-1}

$k_{2,pyr}$ = 8.04 × 10^2 $M^{-1}s^{-1}$

k_{2,OH^-} = 48.5 $M^{-1}s^{-1}$

pK_B = 4.88



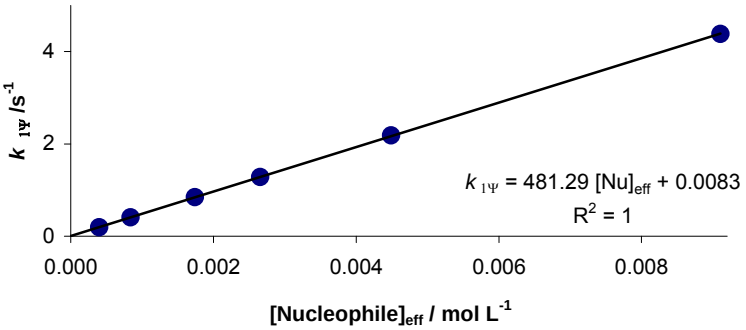
Reaction of 4-Aminopyridine (**1e**) with $(thq)_2CH^+BF_4^-$:
(at 20 °C, in 99.1 Vol% H_2O / 0.9 Vol% CH_3CN, Stopped-flow, detection at 610 nm)

$[(thq)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi, OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
3.01 × 10^{-5}	9.45 × 10^{-3}	9.10 × 10^{-3}	3.46 × 10^{-4}	302	4.39	8.18 × 10^{-3}	4.38
3.01 × 10^{-5}	4.73 × 10^{-3}	4.49 × 10^{-3}	2.43 × 10^{-4}	149	2.19	5.74 × 10^{-3}	2.18
3.01 × 10^{-5}	2.84 × 10^{-3}	2.65 × 10^{-3}	1.87 × 10^{-4}	88	1.29	4.41 × 10^{-3}	1.29
3.01 × 10^{-5}	1.89 × 10^{-3}	1.74 × 10^{-3}	1.51 × 10^{-4}	58	8.50 × 10^{-1}	3.57 × 10^{-3}	8.46 × 10^{-1}
3.01 × 10^{-5}	9.45 × 10^{-4}	8.40 × 10^{-4}	1.05 × 10^{-4}	28	4.10 × 10^{-1}	2.48 × 10^{-3}	4.08 × 10^{-1}
3.01 × 10^{-5}	4.73 × 10^{-4}	4.00 × 10^{-4}	7.26 × 10^{-5}	13	1.97 × 10^{-1}	1.71 × 10^{-3}	1.95 × 10^{-1}

$k_{2,pyr}$ = 4.81 × 10^2 $M^{-1}s^{-1}$

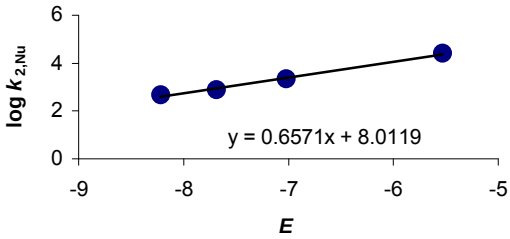
k_{2,OH^-} = 23.6 $M^{-1}s^{-1}$ [calculated]

pK_B = 4.88



Reactivity parameters in water: *N* = 12.2; *s* = 0.66

Reference electrophile	*E* parameter	$k_{2,pyr}$(20°C) / M^{-1} s^{-1}
$(mor)_2CH^+$	-5.53	2.58 × 10^4
$(dma)_2CH^+$	-7.02	2.23 × 10^3
$(pyr)_2CH^+$	-7.69	8.04 × 10^2
$(thq)_2CH^+$	-8.22	4.81 × 10^2



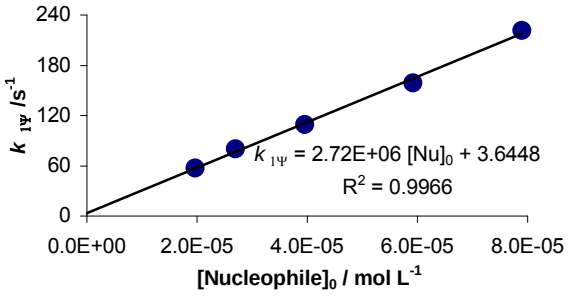
4.8.9. 4-(*N*,*N*-Dimethylamino)pyridine (1f)

Rate constants in Dichloromethane

Reaction of 4-(*N*,*N*-Dimethylamino)pyridine (**1f**) with $(mpa)_2CH^+BF_4^-$:
(at 20 °C, in CH_2Cl_2, Stopped-flow, detection at 622 nm)

$[(mpa)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_0/[El]_0$	$k_{1\Psi}$ / s^{-1}
2.76×10^{-6}	7.89×10^{-5}	29	2.22×10^{2}
2.76×10^{-6}	5.92×10^{-5}	21	1.59×10^{2}
2.76×10^{-6}	3.95×10^{-5}	14	1.09×10^{2}
2.76×10^{-6}	2.70×10^{-5}	10	80.0
2.76×10^{-6}	1.97×10^{-5}	7	57.7

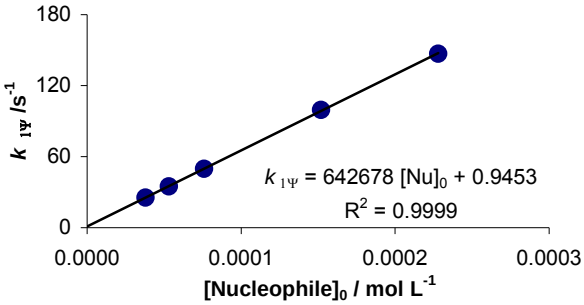
$k_{2,pyr}$ = 3.00×10^{6} M^{-1}s^{-1}



Reaction of 4-(*N*,*N*-Dimethylamino)pyridine (**1f**) with $(dma)_2CH^+BF_4^-$:
(at 20 °C, in CH_2Cl_2, Stopped-flow, detection at 613 nm)

$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_0/[El]_0$	$k_{1\Psi}$ / s^{-1}
7.20×10^{-6}	2.28×10^{-4}	32	1.47×10^{2}
7.20×10^{-6}	1.52×10^{-4}	21	99.5
7.20×10^{-6}	7.60×10^{-5}	11	49.7
7.20×10^{-6}	5.32×10^{-5}	7	34.8
7.20×10^{-6}	3.80×10^{-5}	5	25.4

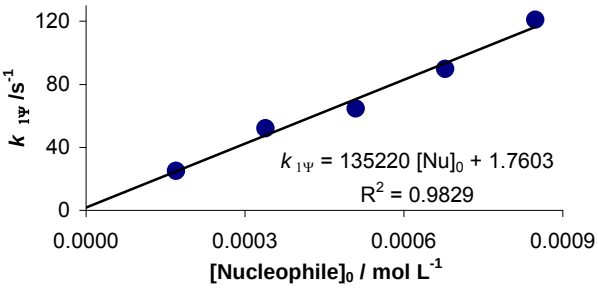
$k_{2,pyr}$ = 6.43×10^{5} M^{-1}s^{-1}



Reaction of 4-(*N*,*N*-Dimethylamino)pyridine (**1f**) with $(thq)_2CH^+BF_4^-$:
(at 20 °C, in CH_2Cl_2, Stopped-flow, detection at 628 nm)

$[(thq)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_0/[El]_0$	$k_{1\Psi}$ / s^{-1}
7.59×10^{-6}	8.48×10^{-4}	112	1.21×10^{2}
7.59×10^{-6}	6.78×10^{-4}	89	89.8
7.59×10^{-6}	5.09×10^{-4}	67	64.6
7.59×10^{-6}	3.39×10^{-4}	45	52.2
7.59×10^{-6}	1.70×10^{-4}	22	25.2

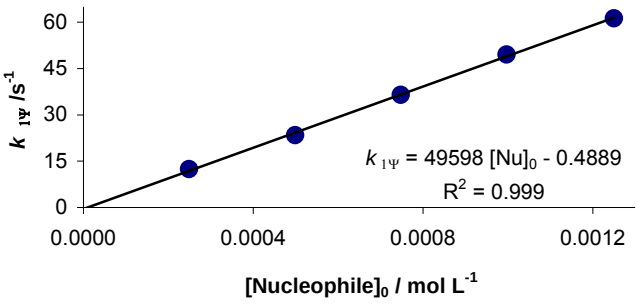
$k_{2,pyr}$ = 1.35×10^{5} M^{-1}s^{-1}



Reaction of 4-(*N*,*N*-Dimethylamino)pyridine (**1f**) with $(ind)_2CH^+BF_4^-$:
(at 20 °C, in CH_2Cl_2, Stopped-flow, detection at 625 nm)

$[(ind)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_0/[El]_0$	$k_{1\Psi}$ / s^{-1}
7.48×10^{-6}	1.25×10^{-3}	167	61.3
7.48×10^{-6}	9.97×10^{-4}	133	49.6
7.48×10^{-6}	7.48×10^{-4}	100	36.5
7.48×10^{-6}	4.99×10^{-4}	67	23.4
7.48×10^{-6}	2.49×10^{-4}	33	12.4

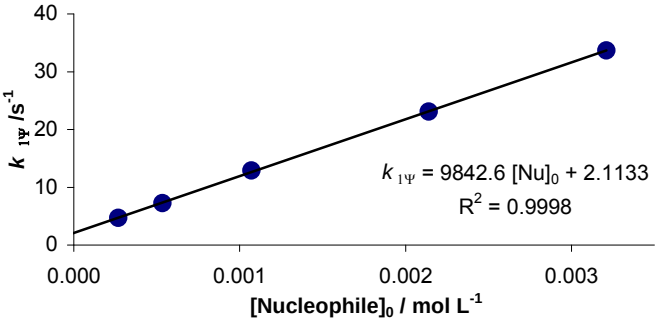
$k_{2,pyr} = 4.96 \times 10^4$ M^{-1}s^{-1}



Reaction of 4-(*N*,*N*-Dimethylamino)pyridine (**1f**) with $(jul)_2CH^+BF_4^-$:
(at 20 °C, in CH_2Cl_2, Stopped-flow, detection at 642 nm)

$[(jul)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_0/[El]_0$	$k_{1\Psi}$ / s^{-1}
7.65×10^{-6}	3.21×10^{-3}	420	33.7
7.65×10^{-6}	2.14×10^{-3}	280	23.1
7.65×10^{-6}	1.07×10^{-3}	140	12.9
7.65×10^{-6}	5.35×10^{-4}	70	7.24
7.65×10^{-6}	2.68×10^{-4}	35	4.72

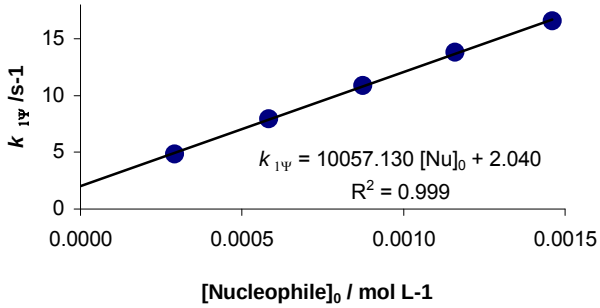
$k_{2,pyr} = 9.84 \times 10^3$ M^{-1}s^{-1}



Reaction of 4-(*N*,*N*-Dimethylamino)pyridine (**1f**) with $(jul)_2CH^+PF_6^-$:
(at 20 °C, in CH_2Cl_2, Stopped-flow, detection at 642 nm)

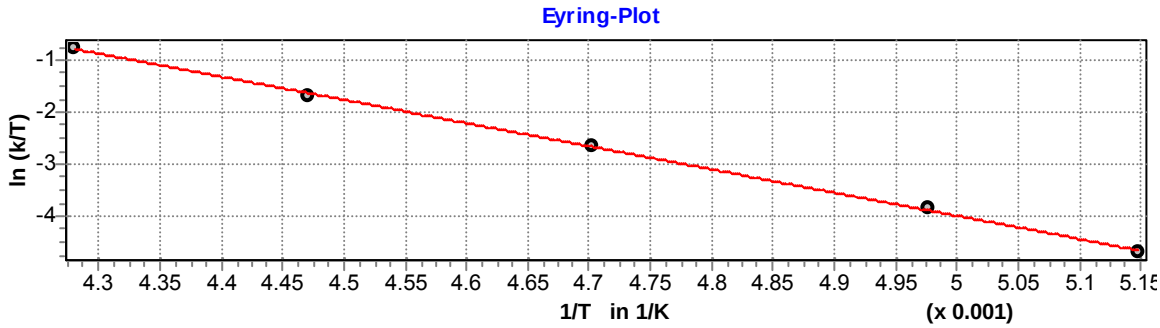
$[(jul)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_0/[El]_0$	$k_{1\Psi}$ / s^{-1}
8.40×10^{-6}	1.46×10^{-3}	174	16.6
8.40×10^{-6}	1.16×10^{-3}	138	13.8
8.40×10^{-6}	8.73×10^{-4}	104	10.9
8.40×10^{-6}	5.82×10^{-4}	69	7.95
8.40×10^{-6}	2.91×10^{-4}	38	4.86

$k_{2,pyr} = 1.01 \times 10^4$ M^{-1}s^{-1}



Reaction of 4-(*N*,*N*-Dimethylamino)pyridine (**1f**) with $(lil)_2CH^+BF_4^-$:
(in CH_2Cl_2, Schölly, detection at 640 nm)

$[(lil)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_0/[El]_0$	Conv. / %	T / °C	$k_{2,pyr}$ / L mol^{-1} s^{-1}
3.00×10^{-5}	3.27×10^{-3}	109	84	-78.9	1.77
3.61×10^{-5}	3.04×10^{-3}	84	87	-72.2	4.27
2.69×10^{-5}	2.35×10^{-3}	87	76	-60.5	1.50×10^1
3.13×10^{-5}	1.71×10^{-3}	55	73	-49.5	4.13×10^1
2.40×10^{-5}	1.05×10^{-3}	44	90	-39.5	1.09×10^2



Eyring parameters:

$\Delta H^{\neq}$ = 37.1 ± 0.52 kJ mol^{-1}

$\Delta S^{\neq}$ = -45.3 ± 2.5 J mol^{-1} K^{-1}

r^2 = 0.9994

$k_{2,pyr}$ (20 °C) = (6.45 ± 0.53) × 10^3 L mol^{-1} s^{-1}

Arrhenius parameters:

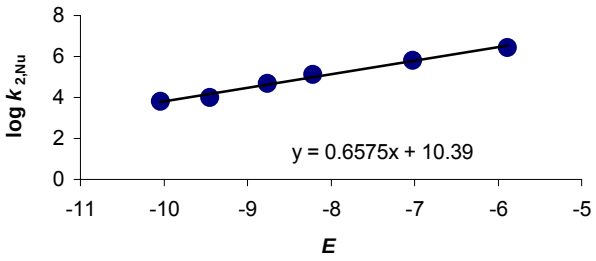
E_a = 38.9 ± 0.52 kJ mol^{-1}

ln A = 24.7 ± 0.30

r^2 = 0.9995

Reactivity parameters in Dichloromethane: *N* = 15.80; *s* = 0.66

Reference electrophile	*E* parameter	$k_{2,pyr}$(20°C) / M^{-1} s^{-1}
$(mpa)_2CH^+$	-5.89	2.72 × 10^6
$(dma)_2CH^+$	-7.02	6.43 × 10^5
$(thq)_2CH^+$	-8.22	1.35 × 10^5
$(ind)_2CH^+$	-8.76	4.96 × 10^4
$(jul)_2CH^+$	-9.45	9.84 × 10^3
$(lil)_2CH^+$	-10.04	6.45 × 10^3

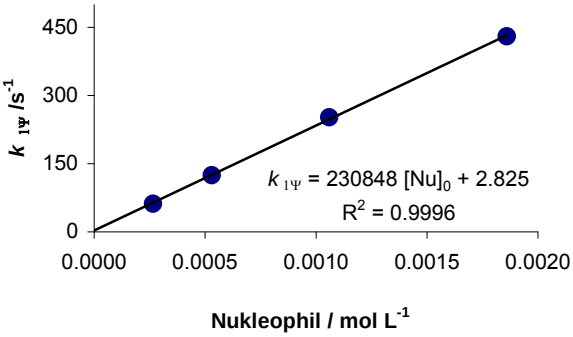


Rate constants in Acetonitrile

Reaction of 4-(*N*,*N*-Dimethylamino)pyridine (**1f**) with $(dma)_2CH^+BF_4^-$:
(at 20 °C, in CH_3CN, Stopped-flow, detection at 610 nm)

$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_0/[El]_0$	$k_{1\Psi}$ / s^{-1}
1.14 × 10^{-5}	1.86 × 10^{-3}	163	4.30 × 10^2
1.14 × 10^{-5}	1.06 × 10^{-3}	93	2.52 × 10^2
1.14 × 10^{-5}	5.30 × 10^{-4}	46	1.25 × 10^2
1.14 × 10^{-5}	2.65 × 10^{-4}	23	61.9

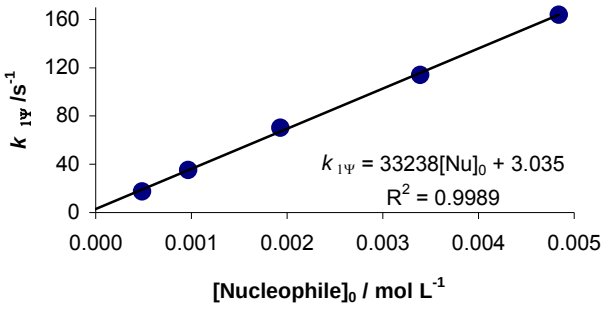
$k_{2,pyr}$ = 2.31 × 10^5 M^{-1}s^{-1}



Reaction of 4-(*N*,*N*-Dimethylamino)pyridine (**1f**) with $(thq)_2CH^+BF_4^-$:
(at 20 °C, in CH_3CN, Stopped-flow, detection at 622 nm)

$[(thq)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_0/[El]_0$	$k_{1\Psi}$ / s^{-1}
9.64×10^{-6}	4.84×10^{-3}	502	1.64×10^{2}
9.64×10^{-6}	3.39×10^{-3}	352	1.14×10^{2}
9.64×10^{-6}	1.93×10^{-3}	200	70.3
9.64×10^{-6}	9.67×10^{-4}	100	35.3
9.64×10^{-6}	4.84×10^{-4}	50	17.5

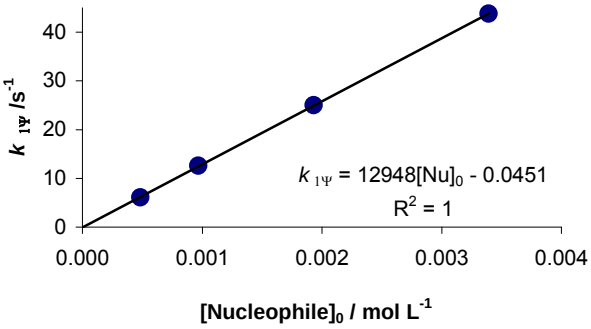
$k_{2,pyr}$ = 3.32×10^{4} $M^{-1}s^{-1}$



Reaction of 4-(*N*,*N*-Dimethylamino)pyridine (**1f**) with $(ind)_2CH^+BF_4^-$:
(at 20 °C, in CH_3CN, Stopped-flow, detection at 630 nm)

$[(ind)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_0/[El]_0$	$k_{1\Psi}$ / s^{-1}
7.74×10^{-6}	3.39×10^{-3}	438	43.8
7.74×10^{-6}	1.93×10^{-3}	249	25.0
7.74×10^{-6}	9.67×10^{-4}	125	12.6
7.74×10^{-6}	4.84×10^{-4}	63	6.09

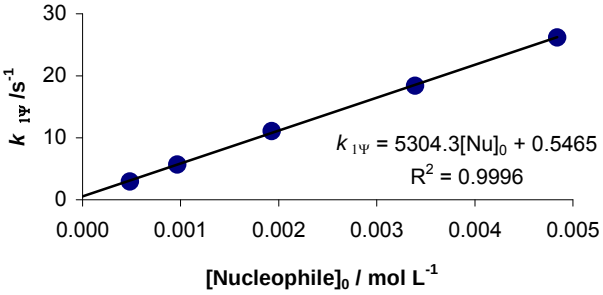
$k_{2,pyr}$ = 1.29×10^{4} $M^{-1}s^{-1}$



Reaction of 4-(*N*,*N*-Dimethylamino)pyridine (**1f**) with $(jul)_2CH^+BF_4^-$:
(at 20 °C, in CH_3CN, Stopped-flow, detection at 630 nm)

$[(jul)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_0/[El]_0$	$k_{1\Psi}$ / s^{-1}
2.86×10^{-6}	4.84×10^{-3}	1692	26.2
2.86×10^{-6}	3.39×10^{-3}	1185	18.4
2.86×10^{-6}	1.93×10^{-3}	675	11.1
2.86×10^{-6}	9.67×10^{-4}	338	5.67
2.86×10^{-6}	4.84×10^{-4}	169	2.95

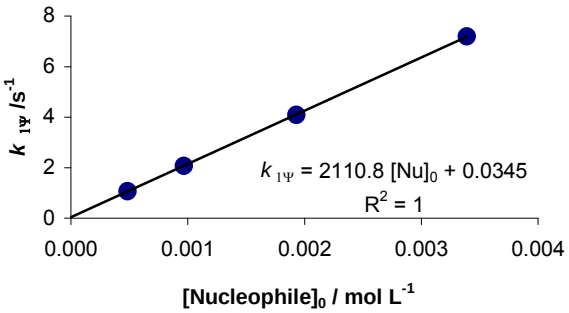
$k_{2,pyr}$ = 5.30×10^{3} $M^{-1}s^{-1}$



Reaction of 4-(*N*,*N*-Dimethylamino)pyridine (**1f**) with $(lil)_2CH^+BF_4^-$:
(at 20 °C, in CH_3CN, Stopped-flow, detection at 630 nm)

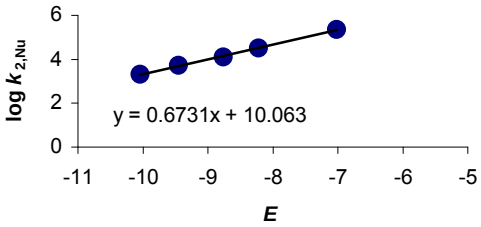
$[(lil)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_0/[El]_0$	$k_{1\Psi}$ / s^{-1}
9.18×10^{-6}	3.39×10^{-3}	369	7.20
9.18×10^{-6}	1.93×10^{-3}	210	4.09
9.18×10^{-6}	9.67×10^{-4}	105	2.07
9.18×10^{-6}	4.84×10^{-4}	53	1.07

$k_{2,pyr}$ = 2.11×10^3 $M^{-1}s^{-1}$



Reactivity parameters in Acetonitrile: *N* = 15.0; *s* = 0.67

Reference electrophile	*E* parameter	$k_{2,pyr}$(20°C) / M^{-1} s^{-1}
$(dma)_2CH^+$	-7.02	2.31×10^5
$(thq)_2CH^+$	-8.22	3.32×10^4
$(ind)_2CH^+$	-8.76	1.29×10^4
$(jul)_2CH^+$	-9.45	5.30×10^3
$(lil)_2CH^+$	-10.04	2.11×10^3



Rate constants and equilibrium constants in water

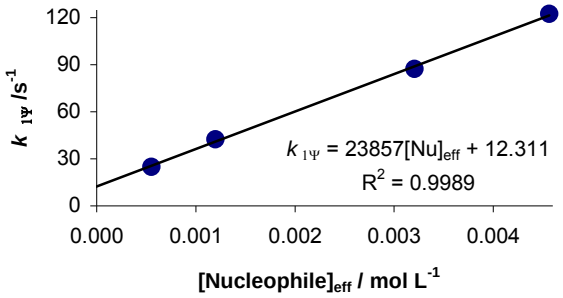
Reaction of 4-(*N*,*N*-Dimethylamino)pyridine (**1f**) with $(mor)_2CH^+BF_4^-$:
(at 20 °C, in 91 Vol% H_2O / 9 Vol% CH_3CN, Stopped-flow, detection at 607 nm)

$[(mor)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi, OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
8.35×10^{-5}	5.06×10^{-3}	4.58×10^{-3}	4.79×10^{-4}	55	1.23×10^2	5.08×10^{-1}	1.22×10^2
8.35×10^{-5}	3.62×10^{-3}	3.22×10^{-3}	4.02×10^{-4}	39	87.8	4.26×10^{-1}	87.4
8.35×10^{-5}	1.45×10^{-3}	1.20×10^{-3}	2.46×10^{-4}	14	42.8	2.60×10^{-1}	42.5
8.35×10^{-5}	7.24×10^{-4}	5.52×10^{-4}	1.67×10^{-4}	7	25.1	1.77×10^{-1}	24.9

$k_{2,pyr}$ = 2.39×10^4 $M^{-1}s^{-1}$

k_{2,OH^-} = 1.06×10^3 $M^{-1}s^{-1}$

pK_B = 4.30



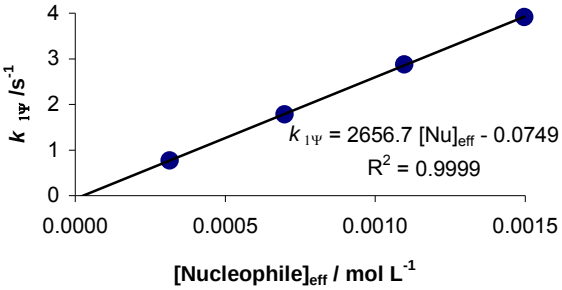
Reaction of 4-(*N*,*N*-Dimethylamino)pyridine (**1f**) with $(dma)_2CH^+BF_4^-$:
(at 20 °C, in 99.6 Vol% H_2O / 0.4 Vol% CH_3CN, Stopped-flow, detection at 604 nm)

$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi, OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
8.32×10^{-5}	1.78×10^{-3}	1.51×10^{-3}	2.75×10^{-4}	18	3.95	3.60×10^{-2}	3.91
8.32×10^{-5}	1.34×10^{-3}	1.10×10^{-3}	2.35×10^{-4}	13	2.91	3.08×10^{-2}	2.88
8.32×10^{-5}	8.91×10^{-4}	7.03×10^{-4}	1.88×10^{-4}	8	1.81	2.46×10^{-2}	1.79
8.32×10^{-5}	4.45×10^{-4}	3.19×10^{-4}	1.26×10^{-4}	4	$7.87\ 10^{-1}$	1.66×10^{-2}	7.70×10^{-1}

$k_{2,pyr} = 2.66 \times 10^3\ M^{-1}s^{-1}$

$k_{2,OH^-} = 1.31 \times 10^2\ M^{-1}s^{-1}$

$pK_B = 4.30$

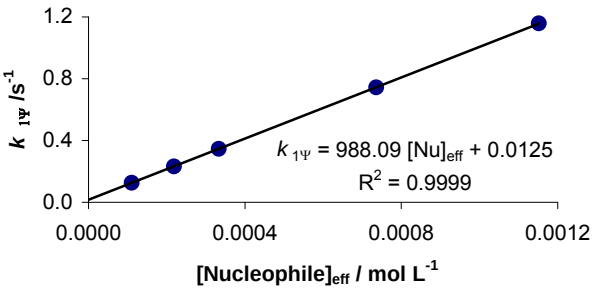


Reaction of 4-(*N*,*N*-Dimethylamino)pyridine (**1f**) with $(pyr)_2CH^+BF_4^-$:
(at 20 °C, in 99.8 Vol% H_2O / 0.2 Vol% CH_3CN, Stopped-flow, detection at 611 nm)

$[(pyr)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi, OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
1.26×10^{-5}	1.40×10^{-3}	1.16×10^{-3}	2.41×10^{-4}	92	1.17	1.17×10^{-2}	1.16
1.26×10^{-5}	9.35×10^{-4}	7.42×10^{-4}	1.93×10^{-4}	59	7.53×10^{-1}	9.35×10^{-3}	7.44×10^{-1}
1.26×10^{-5}	4.67×10^{-4}	3.37×10^{-4}	1.30×10^{-4}	27	3.53×10^{-1}	6.30×10^{-3}	3.47×10^{-1}
1.26×10^{-5}	3.27×10^{-4}	2.22×10^{-4}	1.05×10^{-4}	18	2.38×10^{-1}	5.11×10^{-3}	2.33×10^{-1}
1.26×10^{-5}	1.87×10^{-4}	1.12×10^{-4}	7.49×10^{-5}	9	1.31×10^{-1}	3.63×10^{-3}	1.27×10^{-1}

$k_{2,pyr} = 9.88 \times 10^2\ M^{-1}s^{-1}$ $k_{2,OH^-} =$ 48.5 $M^{-1}s^{-1}$

$pK_B = 4.30$



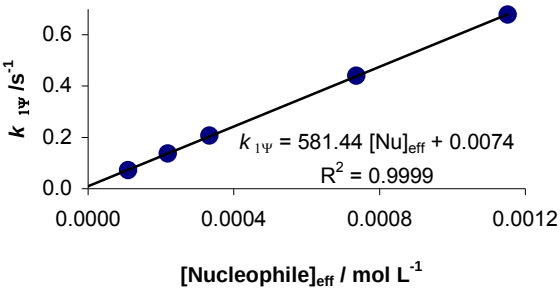
Reaction of 4-(*N*,*N*-Dimethylamino)pyridine (**1f**) with $(thq)_2CH^+BF_4^-$:
(at 20 °C, in 99.8 Vol% H_2O / 0.2 Vol% CH_3CN, Stopped-flow, detection at 611 nm)

$[(thq)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi, OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
1.58×10^{-5}	1.40×10^{-3}	1.16×10^{-3}	2.41×10^{-4}	73	6.85×10^{-1}	5.69×10^{-3}	6.79×10^{-1}
1.58×10^{-5}	9.35×10^{-4}	7.42×10^{-4}	1.93×10^{-4}	47	4.45×10^{-1}	4.55×10^{-3}	4.40×10^{-1}
1.58×10^{-5}	4.67×10^{-4}	3.37×10^{-4}	1.30×10^{-4}	21	2.10×10^{-1}	3.07×10^{-3}	2.07×10^{-1}
1.58×10^{-5}	3.27×10^{-4}	2.22×10^{-4}	1.05×10^{-4}	14	1.40×10^{-1}	2.49×10^{-3}	1.38×10^{-1}
1.58×10^{-5}	1.87×10^{-4}	1.12×10^{-4}	7.49×10^{-5}	7	7.40×10^{-2}	1.77×10^{-3}	7.22×10^{-2}

$k_{2,pyr}$ = 5.81 × 10^2 $M^{-1}s^{-1}$

k_{2,OH^-} = 23.6 $M^{-1}s^{-1}$ [calculated]

pK_B = 4.30



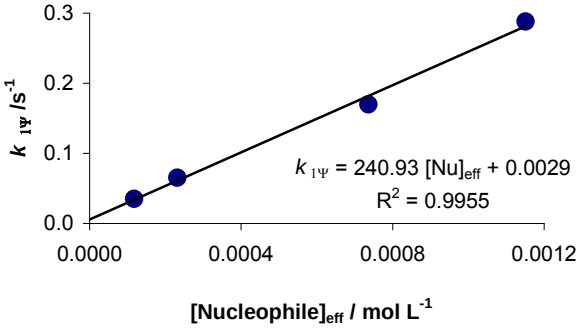
Reaction of 4-(*N*,*N*-Dimethylamino)pyridine (**1f**) with $(ind)_2CH^+BF_4^-$:
(at 20 °C, in 99.6 Vol% H_2O / 0.4 Vol% CH_3CN, Stopped-flow and J&M, detection at 614 nm)

$[(ind)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi, OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
1.48 × 10^{-5}	1.40 × 10^{-3}	1.16 × 10^{-3}	2.41 × 10^{-4}	78	2.91 × 10^{-1}	2.60 × 10^{-3}	2.88 × 10^{-1}
1.48 × 10^{-5}	9.35 × 10^{-4}	7.42 × 10^{-4}	1.93 × 10^{-4}	50	1.72 × 10^{-1}	2.08 × 10^{-3}	1.70 × 10^{-1}
1.47 × 10^{-5}	3.43 × 10^{-4}	2.35 × 10^{-4}	1.08 × 10^{-4}	16	6.63 × 10^{-2}	1.17 × 10^{-3}	6.51 × 10^{-2}
1.48 × 10^{-5}	1.97 × 10^{-4}	1.20 × 10^{-4}	7.74 × 10^{-5}	8	3.60 × 10^{-2}	8.36 × 10^{-4}	3.52 × 10^{-2}

$k_{2,pyr}$ = 2.41 × 10^2 $M^{-1}s^{-1}$

k_{2,OH^-} = 10.8 $M^{-1}s^{-1}$

pK_B = 4.30



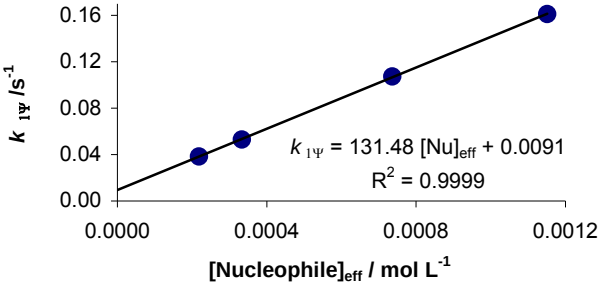
Reaction of 4-(*N*,*N*-Dimethylamino)pyridine (**1f**) with $(jul)_2CH^+BF_4^-$:
(at 20 °C, in 99.8 Vol% H_2O / 0.2 Vol% CH_3CN, Stopped-flow, detection at 630 nm)

$[(jul)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi, OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
1.26 × 10^{-5}	1.40 × 10^{-3}	1.16 × 10^{-3}	2.41 × 10^{-4}	92	1.62 × 10^{-1}	8.29 × 10^{-4}	1.61 × 10^{-1}
1.26 × 10^{-5}	9.35 × 10^{-4}	7.42 × 10^{-4}	1.93 × 10^{-4}	59	1.08 × 10^{-1}	6.63 × 10^{-4}	1.07 × 10^{-1}
1.26 × 10^{-5}	4.67 × 10^{-4}	3.37 × 10^{-4}	1.30 × 10^{-4}	27	5.34 × 10^{-2}	4.47 × 10^{-4}	5.30 × 10^{-2}
1.26 × 10^{-5}	3.27 × 10^{-4}	2.22 × 10^{-4}	1.05 × 10^{-4}	18	3.87 × 10^{-2}	3.63 × 10^{-4}	3.83 × 10^{-2}

$k_{2,pyr}$ = 1.31 × 10^2 $M^{-1}s^{-1}$

k_{2,OH^-} = 3.44 $M^{-1}s^{-1}$

pK_B = 4.30



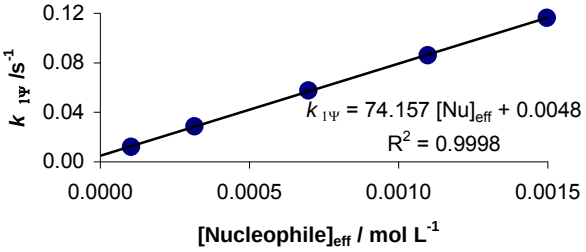
Reaction of 4-(*N*,*N*-Dimethylamino)pyridine (**1f**) with $(lil)_2CH^+BF_4^-$:
(at 20 °C, in 99.6 Vol% H_2O / 0.4 Vol% CH_3CN, Stopped-flow, detection at 630 nm)

$[(lil)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi, OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
1.81 × 10^{-5}	1.78 × 10^{-3}	1.51 × 10^{-3}	2.75 × 10^{-4}	83	1.17 × 10^{-1}	5.93 × 10^{-4}	1.16 × 10^{-1}
1.81 × 10^{-5}	1.34 × 10^{-3}	1.10 × 10^{-3}	2.35 × 10^{-4}	61	8.66 × 10^{-2}	5.08 × 10^{-4}	8.61 × 10^{-2}
1.81 × 10^{-5}	8.91 × 10^{-4}	7.03 × 10^{-4}	1.88 × 10^{-4}	39	5.82 × 10^{-2}	4.06 × 10^{-4}	5.78 × 10^{-2}
1.81 × 10^{-5}	4.45 × 10^{-4}	3.19 × 10^{-4}	1.26 × 10^{-4}	18	2.89 × 10^{-2}	2.73 × 10^{-4}	2.86 × 10^{-2}
1.81 × 10^{-5}	1.78 × 10^{-4}	1.05 × 10^{-4}	7.27 × 10^{-5}	6	1.22 × 10^{-2}	1.57 × 10^{-4}	1.20 × 10^{-2}

$k_{2,pyr}$ = 74.2 $M^{-1}s^{-1}$

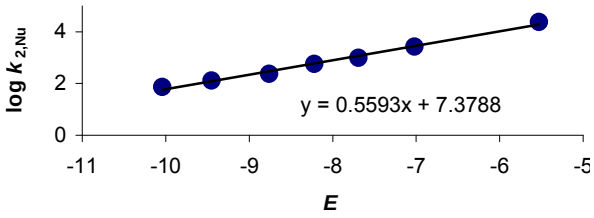
k_{2,OH^-} = 2.16 $M^{-1}s^{-1}$

pK_B = 4.30



Reactivity parameters in Water: *N* = 13.2; *s* = 0.56

Reference electrophile	*E* parameter	$k_{2,pyr}$(20°C) / M^{-1} s^{-1}
$(mor)_2CH^+$	-5.53	2.39 × 10^4
$(dma)_2CH^+$	-7.02	2.66 × 10^3
$(pyr)_2CH^+$	-7.69	9.88 × 10^2
$(thq)_2CH^+$	-8.22	5.81 × 10^2
$(ind)_2CH^+$	-8.76	2.41 × 10^2
$(jul)_2CH^+$	-9.45	1.31 × 10^2
$(lil)_2CH^+$	-10.04	74.2



Rate constants in Methanol

In the reaction of the $(dma)_2CH^+$ BF_4^- with **1f** in Methanol, competing reaction of the carbocation with the solvent Methanol have to be considered. The observed pseudo-first-order rate constants k_{obs} reflect the sum of the reactions of the electrophile with **1f**($k_{1\Psi,pyr}$), Methanol ($k_{1\Psi,MeOH}$) and the reverse reaction(k_{-1}).

$$k_{obs} = k_{1\Psi,pyr} + k_{1\Psi,MeOH} + k_{-1} \quad (7)$$

$$k_{1\Psi} = k_{obs} = k_{2,pyr}\,[\mathbf{1f}] + k_{1\Psi,MeOH} + k_{-1}$$

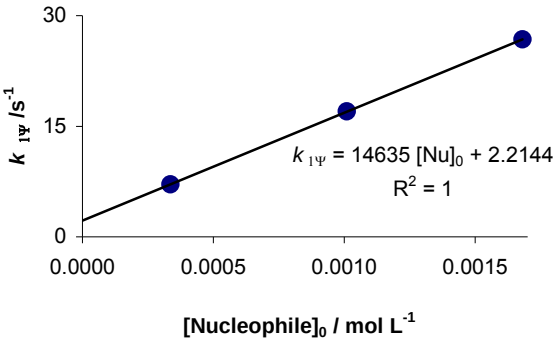
The slopes of the plots $k_{1\Psi}$ versus [**1f**] corresponds to the second-order rate constant $k_{2,pyr}$. The intercept, which correspond to the reverse reactions and the reactions of $(dma)_2CH^+$ BF_4^- with Methanol is negligible. For technical reasons the experiment was performed in a solvent mixture containing 91 Vol% CH_3OH and 9 Vol% CH_3CN.

Reaction of 4-(*N*,*N*-Dimethylamino)pyridine (**1f**) with $(dma)_2CH^+BF_4^-$:
(at 20 °C, in 91 Vol% CH_3OH / 9 Vol% CH_3CN, Stopped-flow, detection at 610 nm)

$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_0/[El]_0$	$k_{1\Psi}$ / s^{-1}
2.02×10^{-5}	1.68×10^{-3}	83	26.8
2.02×10^{-5}	1.01×10^{-3}	50	11.7
2.02×10^{-5}	3.36×10^{-4}	17	7.13

$k_{2,pyr}$ = 1.46×10^4 $M^{-1}s^{-1}$

$k_{1\Psi,MeOH}$(91 Vol% CH_3OH / 9 Vol% CH_3CN)= 2.31 s^{-1} [13g]

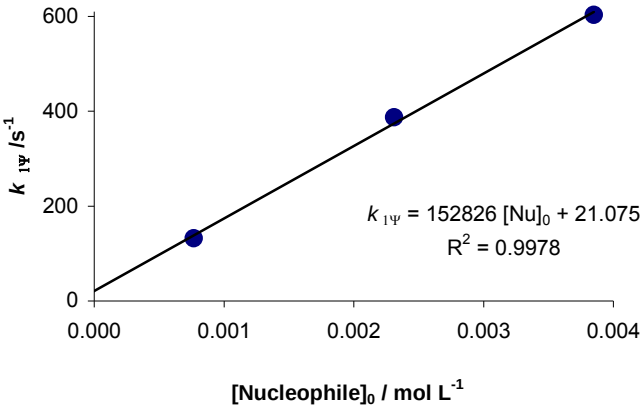


Rate constants in DMSO

Reaction of 4-(*N*,*N*-Dimethylamino)pyridine (**1f**) with $(dma)_2CH^+BF_4^-$:
(at 20 °C, in DMSO, Stopped-flow, detection at 616 nm)

$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_0/[El]_0$	$k_{1\Psi}$ / s^{-1}
9.27×10^{-6}	3.85×10^{-3}	415	6.03×10^{2}
9.27×10^{-6}	2.31×10^{-3}	249	3.87×10^{2}
9.27×10^{-6}	7.68×10^{-4}	83	1.32×10^{2}

$k_{2,pyr} = 1.53 \times 10^5\ M^{-1}s^{-1}$

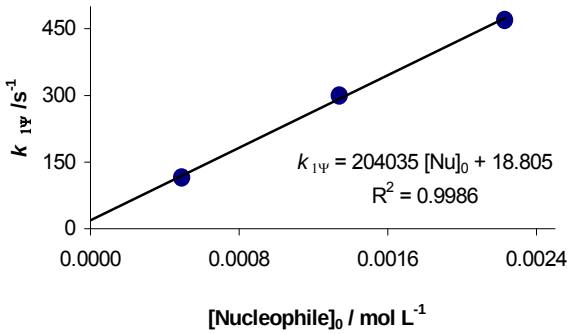


Rate constants in DMF

Reaction of 4-(*N*,*N*-Dimethylamino)pyridine (**1f**) with $(dma)_2CH^+BF_4^-$:
(at 20 °C, in DMF, Stopped-flow, detection at 616 nm)

$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_0/[El]_0$	$k_{1\Psi}$ / s^{-1}
9.27×10^{-6}	2.23×10^{-3}	241	4.70×10^{2}
9.27×10^{-6}	1.34×10^{-3}	145	3.00×10^{2}
9.27×10^{-6}	4.91×10^{-4}	53	1.15×10^{2}

$k_{2,pyr} = 2.04 \times 10^5\ M^{-1}s^{-1}$



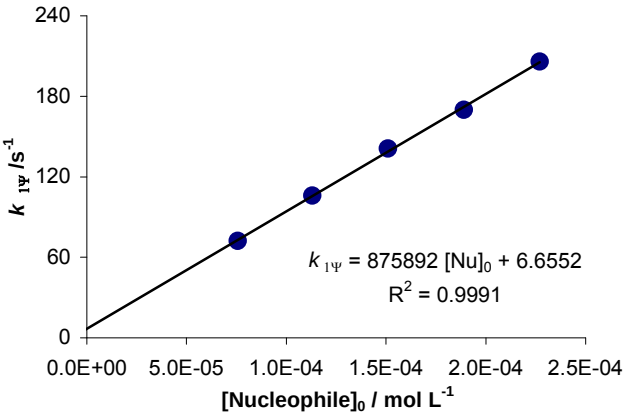
4.8.10. 4-(Pyrrolidino)pyridine (1g)

Rate constants in Dichloromethane

Reaction of 4-(Pyrrolidino)pyridine (**1g**) with $(dma)_2CH^+BF_4^-$:
(at 20 °C, in CH_2Cl_2, Stopped-flow, detection at 612 nm)

$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_0/[El]_0$	$k_{1\Psi}$ / s^{-1}
8.61×10^{-6}	2.27×10^{-4}	26	2.06×10^{2}
8.61×10^{-6}	1.89×10^{-4}	22	1.70×10^{2}
8.61×10^{-6}	1.51×10^{-4}	18	1.41×10^{2}
8.61×10^{-6}	1.13×10^{-4}	13	1.06×10^{2}
8.61×10^{-6}	7.56×10^{-5}	9	72.1

$k_{2,pyr}$ = 8.76×10^{5} $M^{-1}s^{-1}$



Rate constants in water

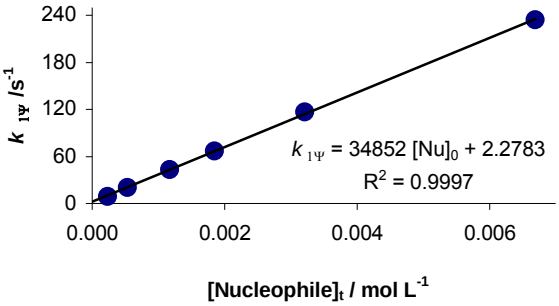
Reaction of 4-(Pyrrolidino)pyridine (**1g**) with $(mor)_2CH^+BF_4^-$:
(at 20 °C, in 91 Vol% H_2O / 9 Vol% CH_3CN, Stopped-flow, detection at 610 nm)

$[(mor)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi, OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
3.65×10^{-5}	7.42×10^{-3}	6.69×10^{-3}	7.29×10^{-4}	183	2.35×10^{2}	7.73×10^{-1}	2.34×10^{2}
3.65×10^{-5}	3.71×10^{-3}	3.21×10^{-3}	5.05×10^{-4}	88	1.17×10^{2}	5.35×10^{-1}	1.16×10^{2}
3.65×10^{-5}	2.23×10^{-3}	1.85×10^{-3}	3.83×10^{-4}	51	67.4	4.06×10^{-1}	67.0
3.65×10^{-5}	1.48×10^{-3}	1.17×10^{-3}	3.05×10^{-4}	32	43.9	3.24×10^{-1}	43.6
3.65×10^{-5}	7.42×10^{-4}	5.36×10^{-4}	2.06×10^{-4}	15	20.5	2.19×10^{-1}	20.3
3.65×10^{-5}	3.71×10^{-4}	2.35×10^{-4}	1.36×10^{-4}	6	9.33	1.45×10^{-1}	9.19

$k_{2,pyr}$ = 3.49×10^{4} $M^{-1}s^{-1}$

k_{2,OH^-} = 1.06×10^{3} $M^{-1}s^{-1}$

pK_B = 4.1



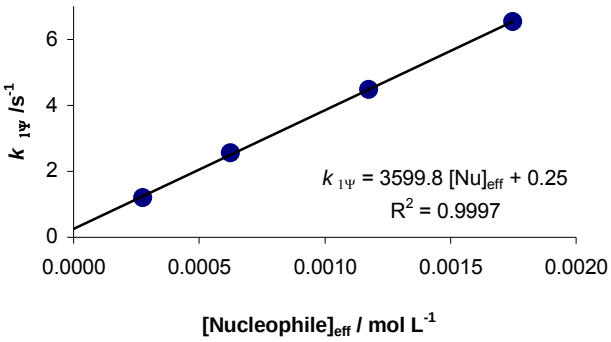
Reaction of 4-(Pyrrolidino)pyridine (**1g**) with $(dma)_2CH^+BF_4^-$:
(at 20 °C, in 99.6 Vol% H_2O / 0.4 Vol% CH_3CN, Stopped-flow, detection at 610 nm)

$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi, OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
1.22×10^{-5}	2.12×10^{-3}	1.75×10^{-3}	3.73×10^{-4}	143	6.58	4.88×10^{-2}	6.53
1.22×10^{-5}	1.48×10^{-3}	1.17×10^{-3}	3.05×10^{-4}	96	4.51	4.00×10^{-2}	4.47
1.22×10^{-5}	8.48×10^{-4}	6.25×10^{-4}	2.23×10^{-4}	51	2.59	2.92×10^{-2}	2.56
1.22×10^{-5}	4.24×10^{-4}	2.76×10^{-4}	1.48×10^{-4}	23	1.22	1.94×10^{-2}	1.20

$k_{2,pyr}$ = 3.60×10^3 $M^{-1}s^{-1}$

k_{2,OH^-} = 1.31×10^2 $M^{-1}s^{-1}$

pK_B = 4.1



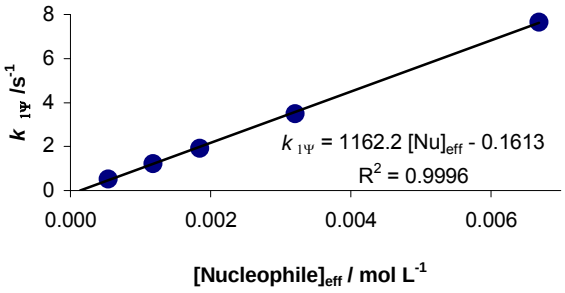
Reaction of 4-(Pyrrolidino)pyridine (**1g**) with $(pyr)_2CH^+BF_4^-$:
(at 20 °C, in 99.1 Vol% H_2O / 0.9 Vol% CH_3CN, Stopped-flow, detection at 610 nm)

$[(pyr)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi, OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
2.78×10^{-5}	7.42×10^{-3}	6.69×10^{-3}	7.29×10^{-4}	241	7.69	3.54×10^{-2}	7.65
2.78×10^{-5}	3.71×10^{-3}	3.21×10^{-3}	5.05×10^{-4}	115	3.52	2.45×10^{-2}	3.50
2.78×10^{-5}	2.23×10^{-3}	1.85×10^{-3}	3.83×10^{-4}	66	1.95	1.86×10^{-2}	1.93
2.78×10^{-5}	1.48×10^{-3}	1.17×10^{-3}	3.05×10^{-4}	42	1.23	1.48×10^{-2}	1.22
2.78×10^{-5}	7.42×10^{-4}	5.36×10^{-4}	2.06×10^{-4}	19	5.42×10^{-1}	1.00×10^{-2}	5.32×10^{-1}

$k_{2,pyr}$ = 1.16×10^3 $M^{-1}s^{-1}$

k_{2,OH^-} = 48.5 $M^{-1}s^{-1}$

pK_B = 4.1



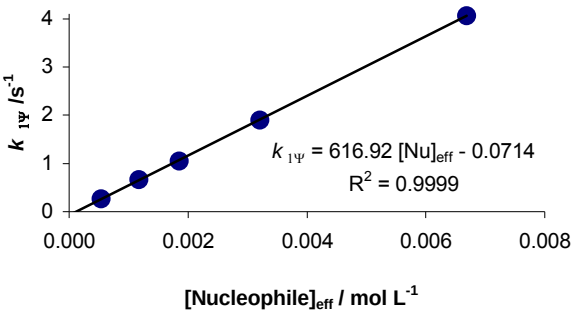
Reaction of 4-(Pyrrolidino)pyridine (**1g**) with $(thq)_2CH^+BF_4^-$:
(at 20 °C, in 99.1 Vol% H_2O / 0.9 Vol% CH_3CN, Stopped-flow, detection at 610 nm)

$[(thq)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi, OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
3.01×10^{-5}	7.42×10^{-3}	6.69×10^{-3}	7.29×10^{-4}	222	4.08	1.72×10^{-2}	4.06
3.01×10^{-5}	3.71×10^{-3}	3.21×10^{-3}	5.05×10^{-4}	106	1.91	1.19×10^{-2}	1.90
3.01×10^{-5}	2.23×10^{-3}	1.85×10^{-3}	3.83×10^{-4}	61	1.06	9.04×10^{-3}	1.05
3.01×10^{-5}	1.48×10^{-3}	1.17×10^{-3}	3.05×10^{-4}	39	6.67×10^{-1}	7.21×10^{-3}	6.60×10^{-1}
3.01×10^{-5}	7.42×10^{-4}	5.36×10^{-4}	2.06×10^{-4}	18	2.76×10^{-1}	4.87×10^{-3}	2.71×10^{-1}

$k_{2,pyr}$ = 6.17×10^2 $M^{-1}s^{-1}$

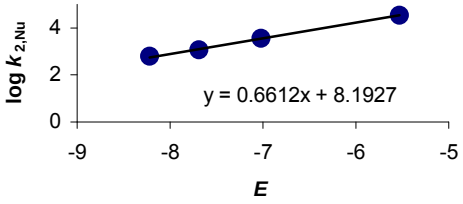
k_{2,OH^-} = 23.6 $M^{-1}s^{-1}$ [calculated]

pK_B = 4.1



Reactivity parameters in Water: *N* = 12.4; *s* = 0.66

Reference electrophile	*E* parameter	k_2(20°C) / M^{-1} s^{-1}
$(mor)_2CH^+$	-5.53	3.49×10^4
$(dma)_2CH^+$	-7.02	3.60×10^3
$(pyr)_2CH^+$	-7.69	1.16×10^3
$(thq)_2CH^+$	-8.22	6.17×10^2



4.9. References

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[20] The out-of-plane deformation angle d_{def} is defined here as the deviation of the C-H bond connected to the benzylic reaction center from the plane defined by the two C-C bonds attached to this same center.

[21] The following overall charges of the DMAP moiety in benzhydryl cation adduct **5f** have been calculated: RHF/6-31G(d)//MP2(fc)/6-31G(d): +0.568 (Mulliken), +0.663 (NPA); MP2(fc)/6-31G(d)//MP2(fc)/6-31G(d): +0.621 (Mulliken), +0.679 (NPA); MP2(fc)/6-31+G(d)//MP2(fc)/6-31G(d): +1.159 (Mulliken), +0.676 (NPA); MP2(fc)/6-31G(d,p)//MP2(fc)/6-31G(d): +0.616 (Mulliken), +0.679 (NPA).

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5. DABCO or DMAP – What Makes Their Difference in Organocatalysis?

5.1. Introduction

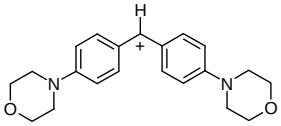
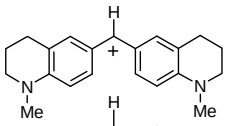
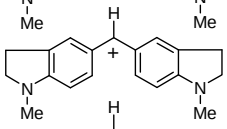
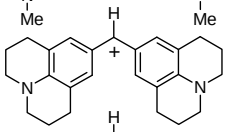
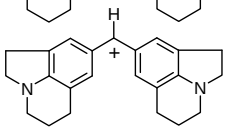
1,4-Diazabicyclo[2.2.2]octane (DABCO, **1**), quinuclidine (**2**), and 4-(dimethylamino)pyridine (DMAP, Steglich's base, **3**) are important catalysts for a large variety of organic reactions.[1] Attempts have been made to correlate the efficiency of organocatalysts with their Brønsted basicities.[2]

DABCO (**1**) Quinuclidine (**2**) DMAP (**3**)

Because the relative reactivities of different nucleophiles towards electrophiles correlate only poorly with the corresponding pK_{Ha} values,[3] we have recently employed the benzhydrylium ion method[4] for comparing nucleophilicities and carbon basicities of pyridines[5a] and tertiary phosphanes.[5b] By studying rates and equilibria of the reactions of these nucleophiles with a series of benzhydrylium ions **4** we showed that despite widely differing Brønsted basicities, triarylphosphanes and donor-substituted pyridines show similar basicities (*K*) and nucleophilicities (*k*) toward carbon electrophiles. Our attempts to use the same spectrophotometric method also for characterizing the nucleophilicities of trialkylamines, e. g., the well-known organocatalysts **1** or **2** turned out to be unsuccessful. When benzhydrylium ions **4** (Table 5.1) of high reactivity ($E > -9$) were combined with **1** or **2**, the reactions were too fast ($k > 10^6$ M^{-1} s^{-1} at 20 °C) to be followed by conventional stopped-flow methods. Less electrophilic benzhydrylium ions ($E < -9$), on the other hand, did not react with **1** or **2**. Only when high concentrations of **1** or **2** were added to solutions of $(jul)_2CH^+$ or $(lil)_2CH^+$, a small percentage of the carbocations were consumed. In these cases, the quaternary ammonium ions **5** are obviously thermodynamically less favorable than the corresponding reactants.

We now report on the use of laser flash techniques[6,7] for the determination of the nucleophilicities of the tertiary amines **1** and **2**. We will then compare the nucleophilicities[3c] and the corresponding carbon basicities[8] (derived from equilibrium constants) with those of other organocatalysts and discuss the consequences.

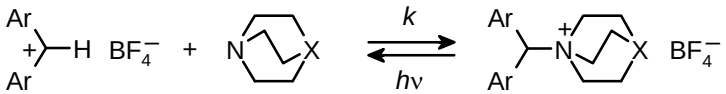
Table 5.1. Benzhydrylium ions Ar_2CH^+ (**4**) and their electrophilicity parameters *E* (from ref. [4b]).

Ar_2CH^+	X	Y	*E*
Ph_2CH^+	H	H	5.90
$(tol)_2CH^+$	CH_3	CH_3	3.63
$(ani)_2CH^+$	OCH_3	OCH_3	0.00
$(pfa)_2CH^+$	$N(Ph)CH_2CF_3$	$N(Ph)CH_2CF_3$	–3.14
$(mfa)_2CH^+$	$N(CH_3)CH_2CF_3$	$N(CH_3)CH_2CF_3$	–3.85
$(dpa)_2CH^+$	NPh_2	NPh_2	–4.72
$(mor)_2CH^+$			–5.53
$(mpa)_2CH^+$	$N(Ph)CH_3$	$N(Ph)CH_3$	–5.89
$(dma)_2CH^+$	$N(CH_3)_2$	$N(CH_3)_2$	–7.02
$(pyr)_2CH^+$	$N(CH_2)_4$	$N(CH_2)_4$	–7.69
$(thq)_2CH^+$			–8.22
$(ind)_2CH^+$			–8.76
$(jul)_2CH^+$			–9.45
$(lil)_2CH^+$			–10.04

Results and Discussion

5.2. Kinetic investigations

When the tertiary amines **1** or **2** (1 mM) were added to the colored solutions of **4**-BF_4 ($-3 > E > -9$, $c_0 \approx 10^{-5}$ M) in acetonitrile, immediate decolorization was observed, indicating the formation of the colorless ammonium salts **5**-BF_4 (Scheme 5.1).



4-BF_4 **1** (X = N) **5**-BF_4
2 (X = CH)

Scheme 5.1. Formation of ammonium salts **5**-BF_4 from benzhydrylium tetrafluoroborates **4**-BF_4 and bicyclic amines (**1** or **2**) and laser flash induced heterolytic cleavage of **5**-BF_4 to the starting materials.

Irradiation of the resulting solutions of **5** ($c \approx 10^{-5}$ M) with 7-ns laser pulses (266 nm, 40-60 mJ) gave rise to the heterolytic cleavage of **5** with regeneration of the benzhydrylium ions **4**, which were detected by their UV-vis spectra.[7] The benzhydrylium ions Ph_2CH^+ and $(tol)_2CH^+$ were obtained by irradiation of corresponding diarylchloromethanes, and $(ani)_2CH^+$ was generated by irradiation of $(p\text{-}MeOC_6H_4)_2CHOAc$.

Because of the high concentrations of the amines **1** and **2** relative to the benzhydrylium ions, the reactions followed first-order rate laws (exponential decay of the absorbances of **4**). Figure 5.1 shows that the first-order rate constants k_{obs} increased linearly with the concentration of amine, and the second-order rate constants derived from the slopes of such plots[9] are listed in Table 5.2.

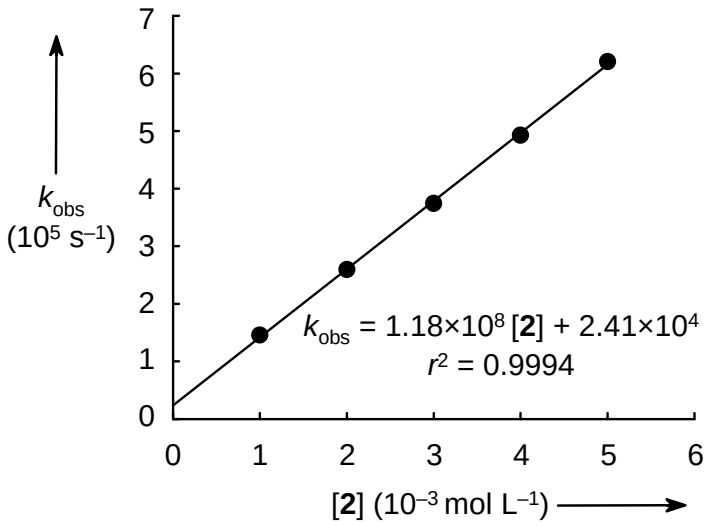


Figure 5.1. Plot of the first-order rate constants k_{obs} for the reaction of $(dma)_2CH^+$ with amine **2** versus the amine concentration.

Table 5.2. Second-order rate constants (k) for the reactions of benzhydrylium ions Ar_2CH^+ with the amines **1**, **2**, and **3** in acetonitrile at 20°C.

Ar_2CH^+	k (M^{-1} s^{-1})		
	DABCO (**1**)	Quinuclidine (**2**)	DMAP (**3**)[a]
$(lil)_2CH^+$	no rxn	no rxn	2.11×10^3
$(jul)_2CH^+$	no rxn	no rxn	5.30×10^3
$(ind)_2CH^+$	1.10×10^7	1.08×10^7	1.29×10^4
$(thq)_2CH^+$	2.79×10^7	2.41×10^7	3.32×10^4
$(pyr)_2CH^+$	6.95×10^7	5.22×10^7	
$(dma)_2CH^+$	1.82×10^8	1.18×10^8	2.31×10^5
$(mpa)_2CH^+$	5.77×10^8	2.97×10^8	
$(mor)_2CH^+$	6.16×10^8	3.34×10^8	
$(dpa)_2CH^+$	1.57×10^9	9.70×10^8	
$(mfa)_2CH^+$	1.82×10^9	9.97×10^8	
$(pfa)_2CH^+$	2.50×10^9	1.59×10^9	
$(ani)_2CH^+$	4.55×10^9	2.49×10^9	
$(tol)_2CH^+$	6.33×10^9	5.25×10^9	
Ph_2CH^+	6.71×10^9	5.44×10^9	

[a] Second-order rate constants for DMAP (**3**) from ref. [5a].

5.3. Nucleophilic reactivities of DABCO, Quinuclidine and DMAP

It can be seen that $(ind)_2CH^+$, the least electrophilic benzhydrylium ion which combines with **1** and **2** to give the ammonium ion **5**, reacts at almost equal rates with both amines. Considering the statistical factor, the reactivity per nitrogen is half as high for DABCO (**1**), which can be explained by the electron-withdrawing inductive effect of the second nitrogen. When reactions with more electrophilic benzhydrylium ions are considered and diffusion control[10,11] is approached, DABCO becomes slightly more reactive than quinuclidine (**2**).

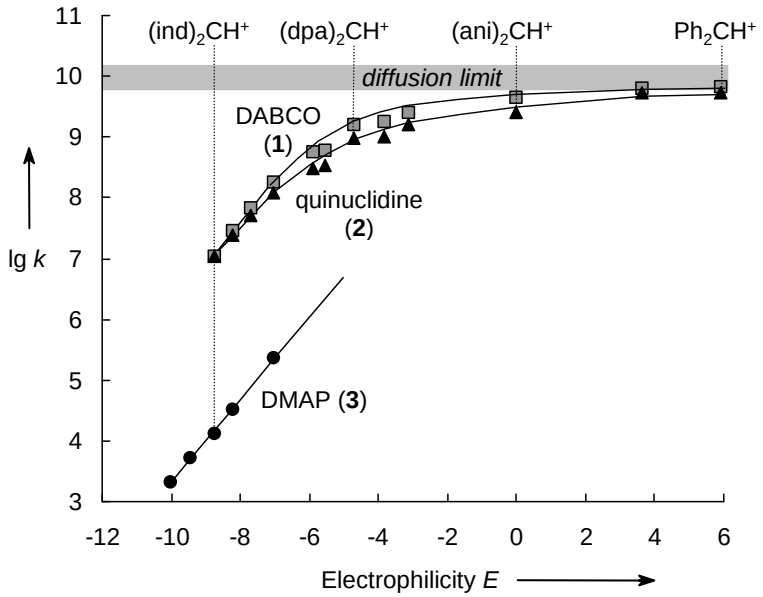


Figure 5.2. Plot of lg *k* vs the electrophilicity parameters *E* for the reactions of the bicyclic amines DABCO (**1**) and quinuclidine (**2**) and of DMAP (**3**) with benzhydrylium ions in acetonitrile at 20°C.

Because the linear sections of the lg *k* vs *E* correlations for DABCO (**1**) and quinuclidine (**2**) in Figure 5.2 are very short, the nucleophile-specific reactivity parameters for **1** (N = 18.80, s = 0.70), and **2** (N = 20.54, s = 0.60), as defined by the correlation equation (1)[4] are not very accurate.[12] Figure 5.2 shows clearly, however, that the bicyclic amines **1** and **2** are three orders of magnitude more nucleophilic than DMAP (**3**).

$$\log k_{20°C} = s(N + E) \qquad (5.1)$$

k: second-order rate constant (L mol^{-1} s^{-1})
N: nucleophilicity parameter
E: electrophilicity parameter
s: nucleophile-specific slope parameter

5.4. Equilibrium constants and intrinsic barriers

By contrast, the thermodynamic stabilities of the ammonium ions **5** obtained from **1** and **2** appeared to be much smaller than those of the corresponding DMAP-derived ammonium ions, because **1** and **2** do not react with $(lil)_2CH^+$ and $(jul)_2CH^+$ despite the expected high rates of reaction. In order to quantify the thermodynamic effects, the carbon basicities[8] of **1**, **2**, and **3** were determined by measuring the equilibrium constants for some of the reactions described in Scheme 1.

While the amines **1**–**3** react quantitatively with benzhydrylium ions of $E > -7$, their reactions with less reactive benzhydrylium ions proceed incompletely. As benzhydrylium ions are

colored and the resulting adducts **5** are colorless, the equilibrium constants (Table 5.3) can be determined by UV-vis spectroscopy.

Table 5.3. Equilibrium constants (K) for the reactions of amines with some benzhydrylium cations Ar_2CH^+ in acetonitrile at 20°C.[a]

Ar_2CH^+	K (M^{-1})		
	DABCO (**1**)	Quinuclidine (**2**)	DMAP (**3**)[a]
$(lil)_2CH^+$	(4×10^1)	(4×10^2)	2.44×10^4
$(jul)_2CH^+$	(4×10^1)	(4×10^2)	2.60×10^4
$(ind)_2CH^+$	(8.7×10^2)	(9.3×10^3)	5.60×10^5
$(thq)_2CH^+$	1.56×10^3	1.68×10^4	(1×10^6)
$(pyr)_2CH^+$	4.89×10^3	4.49×10^4	(3×10^6)

[a] For the determination of the equilibrium constants given in parentheses, see text.

Assuming a proportionality between absorbances and concentrations of the benzhydrylium ions, the equilibrium constant for eq. (5.2) can be expressed by the absorbances of the benzhydrylium ions before (A_0) and after (A) addition of the amine (eq. 5.3).

$$Ar_2CH^+ + NR_3 \underset{}{\overset{K}{\rightleftharpoons}} Ar_2CH\text{-}NR_3^+ \qquad (2)$$

$$K = \frac{[Ar_2CH\text{-}NR_3^+]}{[Ar_2CH^+]\ [NR_3]} = \frac{(A_0 - A)}{A\ [NR_3]} \qquad (3)$$

where $[NR_3] = [NR_3]_0 - [Ar_2CH\text{-}NR_3^+]$

Only the equilibrium constants given without parentheses in Table 5.3 could be determined directly by this procedure. High concentrations of **1** and **2** were needed to observe at least partial consumption of the least electrophilic benzhydrylium ions $(lil)_2CH^+$ and $(jul)_2CH^+$. However, the absorbances did not remain constant under such conditions, indicating a slow consecutive reaction which has not been identified so far. Also, in the reaction of $(ind)_2CH^+$ with **1** and **2**, the composition of the rapidly formed equilibrium mixture (eq. 5.2) was not constant, and $(ind)_2CH^+$ was consumed by a slow, unknown consecutive reaction. The direct determination of the equilibrium constants for the reactions of $(thq)_2CH^+$ and $(pyr)_2CH^+$ with DMAP (**3**) failed because of the high value of K.

For that reason, an indirect method was used for estimating the numbers of Table 5.3 which are given in parentheses. Equilibrium constants for the reactions of benzhydrylium ions with other pyridines which have been determined as described above (eqs. 5.2, 5.3) are given in Table 5.4.

Table 5.4. Comparison of equilibrium constants (*K*) for the reactions of benzhydrylium ions Ar_2CH^+ with differently substituted pyridines in acetonitrile at 20°C.

Ar_2CH^+	*K* (M^{-1})		
			
$(ind)_2CH^+$	7.02×10^1	4.68×10^1	
$(thq)_2CH^+$	1.31×10^2	8.04×10^1	3.02×10^1
$(pyr)_2CH^+$	3.70×10^2		9.52×10^1

A comparison of Tables 5.3 and 5.4 shows that the directly measured equilibrium constants for $(pyr)_2CH^+$ are (2.67 to 3.15) times higher than those for $(thq)_2CH^+$, almost independent of the nature of the amine. Because the first two lines of Table 5.4 show that the reactions of $(ind)_2CH^+$ with pyridines have *K* values which are 1.80 ± 0.08 times lower than the corresponding values for $(thq)_2CH^+$, this value was used for estimating the equilibrium constants for the combinations of $(ind)_2CH^+$ with **1** and **2** in Table 5.2. With the assumption that the same ratios also hold for DMAP (**3**), the missing equilibrium constants in Table 5.3 have been calculated.

The availability of rate and equilibrium constants now allows us to calculate the intrinsic barriers $\Delta G_0^{\ddagger}$ for these reactions, i. e., the barriers for $\Delta_r G^0 = 0$ by substituting $\Delta G^{\ddagger}$ and $\Delta_r G^0$ for these reactions into the Marcus equation (5.4)[13]

$$\Delta G^{\ddagger} = \Delta G_0^{\ddagger} + 0.5\Delta_r G^0 + [(\Delta_r G^0)^2/16\Delta G_0^{\ddagger}] \qquad (5.4)$$

where the work term has been omitted (Table 5.5). In order to avoid ambiguity, data which have been derived from estimated equilibrium constants are identified by the "≈" sign in Table 5.5.

Table 5.5 shows a significant difference in the intrinsic barriers for the reactions of DABCO (**1**) and quinuclidine (**2**) on one side and DMAP (**3**) on the other side. While $\Delta G_0^{\ddagger}$ for the bicyclic amines are around 40 kJ mol^{-1}, those for DMAP (**3**) are higher than 60 kJ mol^{-1}. Considerably more reorganization energy is obviously needed for the reactions with the pyridine **3** than for the reactions with **1** and **2**.

From the rate constants given in Table 5.2 and the equilibrium constants in Table 5.3 one can also calculate the rate constants of the reverse reactions which are listed in the last column of Table 5.5. As a consequence of similar nucleophilicities of **1** and **2**, but 10 times higher equilibrium constants for quinuclidine (**2**), the nucleofugality of DABCO (**1**) is derived to be about 10 times higher than that of quinuclidine (**2**).

Table 5.5. Activation energies $\Delta G^{\ddagger}$, reaction free energies $\Delta_r G^0$, and intrinsic barriers $\Delta G_0^{\ddagger}$ (in kJ mol^{-1}) for the reactions of benzhydrylium tetrafluoroborates $Ar_2CH^+ BF_4^-$ with amines **1**, **2**, and **3** as well as rate constants $k_{\leftarrow}$ for the back reactions (CH_3CN, 20°C).

amines	Ar_2CH^+	$\Delta G^{\ddagger}$	$\Delta_r G^0$	$\Delta G_0^{\ddagger}$	$k_{\leftarrow}$ (s^{-1})
1	$(ind)_2CH^+$	≈ 32.2	≈ –16.2	≈ 40.3	≈ 1×10^4
	$(thq)_2CH^+$	30.0	–17.9	38.9	1.79×10^4
	$(pyr)_2CH^+$	27.7	–20.7	38.1	1.42×10^4
2	$(ind)_2CH^+$	≈ 32.3	≈ –22.0	≈ 43.3	≈ 1×10^3
	$(thq)_2CH^+$	30.3	–23.9	42.2	1.43×10^3
	$(pyr)_2CH^+$	28.4	–26.1	41.5	1.16×10^3
3	$(lil)_2CH^+$	53.1	–24.6	65.4[a]	8.65×10^{-2}
	$(jul)_2CH^+$	50.8	–24.8	63.2[a]	2.04×10^{-1}
	$(ind)_2CH^+$	48.7	–32.2	64.8[a]	2.30×10^{-2}
	$(thq)_2CH^+$	≈ 46.4	≈ –33.7	≈ 63.2[a]	≈ 3×10^{-2}

[a] $\Delta G_0^{\ddagger}$ (in CH_2Cl_2) = 60.4, 59.9, 59.2, 57.1 kJ mol^{-1}, respectively; from ref. [5a].

A larger difference is found for DMAP (**3**), however: Its considerably lower nucleophilicity and higher carbon basicity (compared with **1** and **2**) implies that the leaving group ability of **3** is 10^5 to 10^6 times lower than that of the bicyclic amines **1** and **2**.

In summary, we can conclude that DABCO (**1**) and quinuclidine (**2**) are significantly better nucleophiles than DMAP (**3**) (by a factor of 10^3) but at the same time significantly better nucleofuges (by a factor of 10^6 and 10^5, respectively). What is the impact of these findings for organocatalysis? It has previously been shown that the relative reactivities of nucleophiles towards typical Michael acceptors closely resemble those toward benzhydrylium ions.[14] For that reason, the different properties of **1**–**3** described in Tables 5.2 and 5.3 can be expected to reflect their efficiency in Baylis-Hillman reactions. Because of the higher carbon basicity of DMAP (**3**) compared to **1** and **2**, DMAP (**3**) will generally be superior over DABCO (**1**) and quinuclidine (**2**), if reactivity is controlled by the concentration of the intermediate ammonium ions which are produced by the reactions of the amines with the electrophiles.[1,15,16] If, however, reactivity is controlled by the rate of nucleophilic attack of the organocatalyst or by the release of the amine component in the final stage of the reaction, DABCO (**1**) and quinuclidine (**2**) will be superior.[1,15,16]

The fact that Baylis-Hillman reactions with cycloalkenones and acrylates are better catalyzed by DMAP (**3**) than by the standard catalyst DABCO (**1**)[17] possibly reflects the need for higher concentrations of the zwitterionic intermediates in these cases. The relevance of the kinetic and thermodynamic data determined in this work for acylation reactions is presently not known.

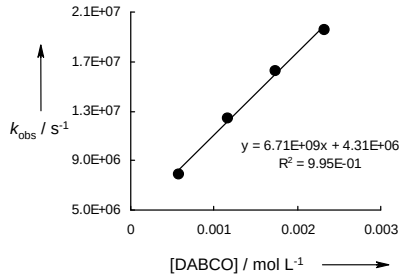
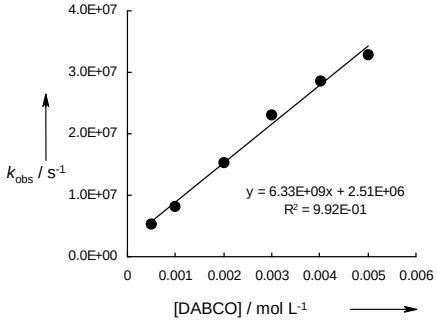
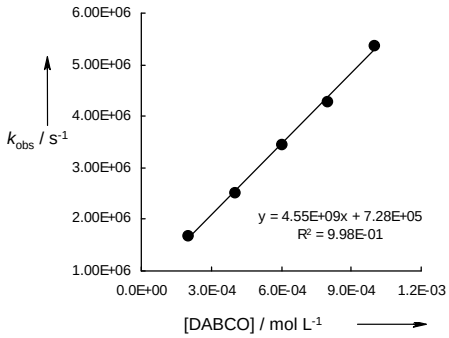
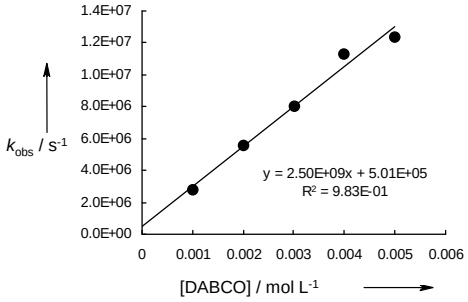
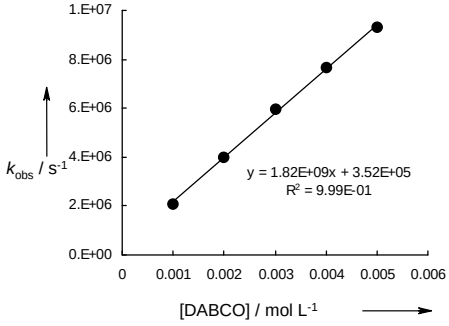
5.5. Experimental

5.5.1. Determination of the Rate Constants for the Reactions of DABCO with Benzhydrylium Ions

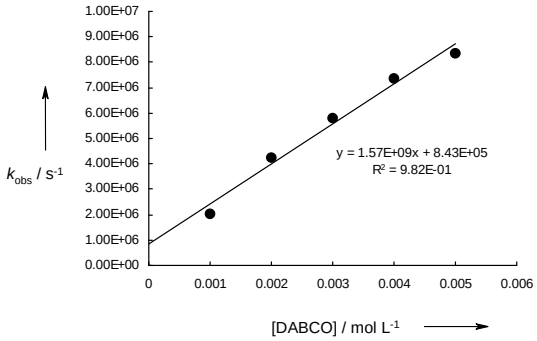
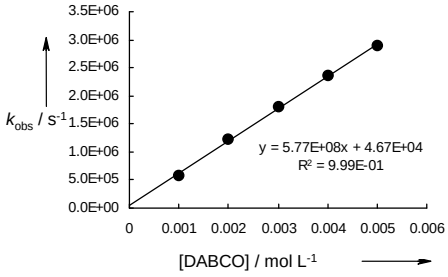
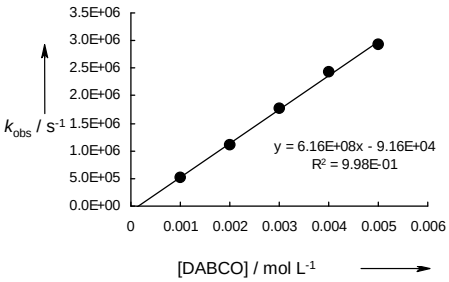
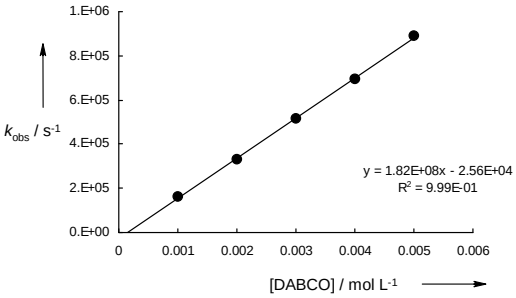
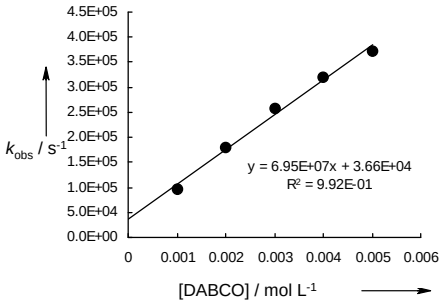
All rate constants were measured by the laser-flash photolysis technique. A solution of known concentration of benzhydrylium tetrafluoroborate in CH_3CN ($\approx 10^{-5}$ mol L^{-1}) was mixed with a known concentration of DABCO solution in CH_3CN ($\approx 10^{-3}$ mol L^{-1}) and the resulting colorless solution was then irradiated with 7-ns laser pulses (266 nm) to regenerate the benzhydrylium ions Ar_2CH^+. The decay of their absorbance was monitored by UV/Vis spectroscopy at their absorption maxima. The resulting pseudo-first-order rate constants k_{obs} were obtained from at least five runs (typically 8–9 runs) at each DABCO concentration. The temperature of the solutions was kept constant at 20 °C by using a circulating bath thermostat and monitored with a thermocouple probe. The absorbance-time curves were fitted to the single exponential function, $A = A_0 \exp(-k_{obs}t) + C$ to yield the rate constants k_{obs} (s^{-1}).

The less stabilized benhydrylium ions ($E \geq 0$) were generated from suitable precursors [Ph_2CH^+ from Ph_2CH-Cl, $(tol)_2CH^+$ from $(tol)_2CH$-Cl, and $(ani)_2CH^+$ from $(ani)_2CH$-OAc] by laser pulse. Initial concentrations of the cation precursors are given in the Tables. The actual carbocation concentrations are much lower than the initial precursor concentrations because each laser pulse converts only 1-4% of the precursor molecules into the corresponding carbocations.

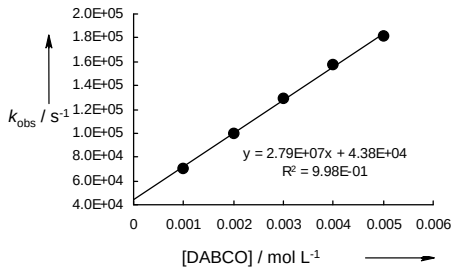
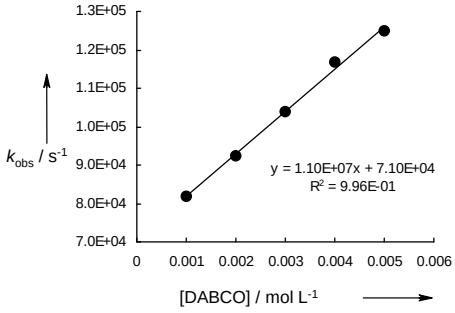
Kinetics of the Reactions of DABCO (1) with Ar_2CH^+ (20°C, MeCN)

Ar_2CH^+	[DABCO] (mol L^{-1})	k_{obs} (s^{-1})		k_2 (L mol^{-1} s^{-1})
$[(Ph_2CHCl)]_0 = 1.00 \times 10^{-3}$ mol L^{-1}				
Ph_2CH^+	0.0006	7.88×10^6		6.71×10^9
	0.0012	1.25×10^7		
	0.0017	1.62×10^7		
	0.0023	1.96×10^7		
$[(tol)_2CHCl]_0 = 1.00 \times 10^{-3}$ mol L^{-1}				
$(tol)_2CH^+$	0.0005	5.28×10^6		6.33×10^9
	0.0010	8.19×10^6		
	0.0020	1.56×10^7		
	0.0030	2.14×10^7		
	0.0040	2.28×10^7		
	0.0050	3.29×10^7		
$[(ani)_2CHOAc)]_0 = 1.00 \times 10^{-3}$ mol L^{-1}				
$(ani)_2CH^+$	0.0002	1.68×10^6		4.55×10^9
	0.0004	2.52×10^6		
	0.0006	3.46×10^6		
	0.0008	4.28×10^6		
	0.0010	5.36×10^6		
$[(pfa)_2CH^+BF_4^-]_0 = 2.00 \times 10^{-5}$ mol L^{-1}				
$(pfa)_2CH^+$	0.001	2.75×10^6		2.50×10^9
	0.002	5.57×10^6		
	0.003	8.02×10^6		
	0.004	1.13×10^7		
	0.005	1.24×10^7		
$[(mfa)_2CH^+BF_4^-]_0 = 2.00 \times 10^{-5}$ mol L^{-1}				
$(mfa)_2CH^+$	0.001	2.07×10^6		1.82×10^9
	0.002	4.01×10^6		
	0.003	5.94×10^6		
	0.004	7.66×10^6		
	0.005	9.32×10^6		

Kinetics of the Reactions of DABCO (1) with Ar_2CH^+ (20°C, MeCN) (continued).

Ar_2CH^+	[DABCO] (mol L^{-1})	k_{obs} (s^{-1})		k_2 (L mol^{-1} s^{-1})
$[(dpa)_2CH^+BF_4^-]_0 = 2.00 \times 10^{-5}$ mol L^{-1}				
$(dpa)_2CH^+$	0.001	2.04×10^6		1.57×10^9
	0.002	4.25×10^6		
	0.003	5.79×10^6		
	0.004	7.38×10^6		
	0.005	8.34×10^6		
$[(mor)_2CH^+BF_4^-]_0 = 2.00 \times 10^{-5}$ mol L^{-1}				
$(mor)_2CH^+$	0.001	5.19×10^5		5.77×10^8
	0.002	1.12×10^6		
	0.003	1.77×10^6		
	0.004	2.44×10^6		
	0.005	2.93×10^6		
$[(mpa)_2CH^+BF_4^-]_0 = 2.00 \times 10^{-5}$ mol L^{-1}				
$(mpa)_2CH^+$	0.001	5.86×10^5		6.16×10^8
	0.002	1.23×10^6		
	0.003	1.80×10^6		
	0.004	2.37×10^6		
	0.005	2.90×10^6		
$[(dma)_2CH^+BF_4^-]_0 = 8.00 \times 10^{-6}$ mol L^{-1}				
$(dma)_2CH^+$	0.001	1.65×10^5		1.82×10^8
	0.002	3.31×10^6		
	0.003	5.14×10^6		
	0.004	6.97×10^6		
	0.005	8.90×10^6		
$[(pyr)_2CH^+BF_4^-]_0 = 2.00 \times 10^{-5}$ mol L^{-1}				
$(pyr)_2CH^+$	0.001	9.61×10^4		6.95×10^7
	0.002	1.79×10^5		
	0.003	2.57×10^5		
	0.004	3.21×10^5		
	0.005	3.73×10^5		

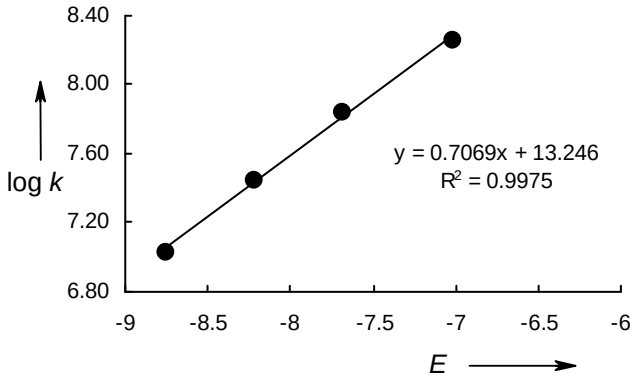
Kinetics of the Reactions of DABCO (1) with Ar_2CH^+ (20°C, MeCN) (continued).

Ar_2CH^+	[DABCO] (mol L^{-1})	k_{obs} (s^{-1})		k_2 (L mol^{-1} s^{-1})
$[(thq)_2CH^+BF_4^-]_0 = 5.00 \times 10^{-5}$ mol L^{-1}				
$(thq)_2CH^+$	0.001	7.00×10^4		2.79×10^7
	0.002	1.00×10^5		
	0.003	1.29×10^5		
	0.004	1.57×10^5		
	0.005	1.81×10^5		
$[(ind)_2CH^+BF_4^-]_0 = 5.00 \times 10^{-5}$ mol L^{-1}				
$(ind)_2CH^+$	0.001	8.20×10^4		1.10×10^7
	0.002	9.25×10^4		
	0.003	1.04×10^5		
	0.004	1.17×10^5		
	0.005	1.25×10^5		

Determination of the Nucleophilicity Parameters *N* and *s* for DABCO (**1**)

Reactions with rate constants $k_2 > 5 \times 10^8$ L $mol^{-1}s^{-1}$ have not been used for the determination of the reactivity parameters *N* and *s*.

Ar_2CH^+	E	log *k*
$(ind)_2CH^+$	–8.76	7.03
$(thq)_2CH^+$	–8.22	7.45
$(pyr)_2CH^+$	–7.69	7.84
$(dma)_2CH^+$	–7.02	8.26



Nucleophilicity parameters for **DABCO (in MeCN): *N* = 18.74, *s* = 0.70**[7]

5.6. References

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