

Kinetics of reaction of 2,4-dinitrophenyl acetate with 3- and 4-substituted pyridines and 4'-substituted 4-styrylpyridines

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Second order rate constants have been determined for the reaction of 2,4-dinitrophenyl acetate with 3- and 4-substituted pyridines and 4'-substituted 4-styrylpyridines in acetonitrile-water (50%, v/v) mixture at 25°, 30°, 35° and 40°C. Activation parameters have been evaluated. Electron-releasing substituents increase the rate while electron-withdrawing substituents retard it. In both the reaction series linear free energy relationship is found to exist between the logarithms of rate constants and σ constants with $\rho = -3.39 \pm 0.38$ ($r = 0.989$; $s = 0.163$; $n = 12$) for 3- and 4-substituted pyridines and $\rho = -0.390 \pm 0.080$ ($r = 0.984$; $s = 0.028$; $n = 8$) for 4'-substituted 4-styrylpyridines at 30°C. The ratio of effectiveness of transmission of substituent effect in styryl system relative to pyridine system in this reaction is 0.115. The Brönsted plot obtained is linear and β_N is found to be 0.692 ± 0.056 ($r = 0.990$; $s = 0.146$; $n = 16$) indicating the extensive bond formation between pyridine and the reaction centre in the transition state.

The kinetics of pyridinolysis of some phenolic esters such as phenyl acetate¹, *p*-nitrophenyl acetate², 2,4-dinitrophenyl acetate³⁻⁵ and 2,4-dinitrophenyl *p*-nitrobenzoate⁶ have been reported. The present work has been undertaken to extend the range of substituents, obtain a series of rate constants under a single set of experimental conditions and gain information about the transmission of substituent effects through the styryl group to the pyridine ring.

Materials and Methods

While 2,4-dinitrophenyl acetate (DNPA) was prepared⁴ in the laboratory, pyridine, 3-methylpyridine, 4-methylpyridine, 4-ethylpyridine and 3-acetylpyridine were commercial samples and were purified by distillation. Nicotinic acid and isonicotinic acid were recrystallised from water and 3-cyanopyridine and 4-cyanopyridine were recrystallised from light petroleum. Methyl isonicotinate, isonicotinamide and substituted 4-styrylpyridines were also prepared in the laboratory. Acetonitrile was purified before use.

Doubly distilled water was used for all kinetic runs. Stock solutions of pyridines were prepared in acetonitrile. Freshly prepared solutions were always used.

Rate measurement

The solvent used in all the kinetic runs was 1 : 1 (v/v) acetonitrile-water mixture. The kinetics were followed upto 60% completion or more spectro-

photometrically at 400 nm under pseudo-first order conditions with excess of [pyridine], [substrate] = 5×10^{-5} mol dm⁻³ and fixed ionic strength (0.2 mol dm⁻³, NaClO₄). The second order rate constants were calculated from the relation $k_2 = k_1/[pyridine]$. Solvolysis of the ester was negligible under the experimental conditions and the precision of k_2 values is given in terms of 95% confidence limit.

Product analysis

2,4-Dinitrophenolate ion was quantitatively obtained as one of the products of the reaction and fully characterised by comparing the UV spectrum with that of an authentic sample under identical conditions. The other possible product is N-acetylpyridinium ion which has not been isolated from the reaction mixture.

Results and Discussion

The pseudo-first order plot is linear, showing first order dependence in [DNPA]. The log-log plot of pseudo-first order rate constant versus [pyridine] is linear passing through the origin indicating that order in [pyridine] is also unity.

Since both the reactants are neutral molecules, the reaction should not exhibit primary salt effect. Addition of sodium perchlorate does not change the rate appreciably (Table 1). The rate of reaction increases with increase in the polarity of the solvent (Table 1) probably due to the greater solvation of the transition state as compared to that of the

Table 1—Effect of varying [DNPA], [Pyridine], [NaClO₄] and solvent composition on the second order rate constants at 30°C

[DNPA] × 10 ⁵ (mol dm ⁻³)	[Pyridine] × 10 ³ (mol dm ⁻³)	[NaClO ₄] (mol dm ⁻³)	Solvent composition % Acetonitrile	k ₂ × 10 ² (dm ³ mol ⁻¹ s ⁻¹)
5.0	3.0	0.20	50	27.9 ± 0.3
5.0	5.0	0.20	50	27.7 ± 0.6
5.0	7.0	0.20	50	25.6 ± 0.6
5.0	9.0	0.20	50	27.3 ± 0.6
3.0	5.0	0.20	50	30.7 ± 0.5
7.0	5.0	0.20	50	28.4 ± 0.4
9.0	5.0	0.20	50	27.1 ± 0.2
5.0	5.0	0.10	50	28.0 ± 0.3
5.0	5.0	0.15	50	31.1 ± 0.2
5.0	5.0	0.25	50	30.8 ± 0.5
5.0	5.0	0.20	20	106.5 ± 1.8
5.0	5.0	0.20	30	53.4 ± 0.4
5.0	5.0	0.20	40	36.7 ± 0.4
5.0	5.0	0.20	60	16.2 ± 0.2
5.0	5.0	0.20	70	15.6 ± 0.3

Table 2—Second order rate constants and activation parameters for the reaction of 2,4-dinitrophenyl acetate with 3- and 4-substituted pyridines and 4'-substituted 4-styrylpyridines at 400 nm in 50% acetonitrile-50% water (v/v) mixture.

[DNPA] = 5 × 10⁻⁵ mol dm⁻³; [Pyridine] = 2 × 10⁻² – 7 × 10⁻⁴ mol dm⁻³; [NaClO₄] = 0.2 mol dm⁻³

Substituent	k ₂ × 10 ² dm ³ mol ⁻¹ s ⁻¹				ΔH‡ kJ mol ⁻¹ (at 30°C)	-ΔS‡ JK ⁻¹ mol ⁻¹ (at 30°C)
	25°	30°	35°	40°C		
Pyridines						
4-Me	86.9 ± 0.8	109 ± 2	138 ± 3	176 ± 5	34.0 ± 1.8	132 ± 6
4-Et	81.2 ± 0.3	117 ± 1	152 ± 3	188 ± 2	40.0 ± 1.2	112 ± 4
3-Me	38.4 ± 0.5	50.5 ± 0.5	63.4 ± 0.5	89.8 ± 2.0	40.5 ± 1.4	117 ± 5
H	17.6 ± 0.2	27.9 ± 0.3	34.4 ± 0.7	46.7 ± 0.8	47.3 ± 1.5	99.7 ± 5.2
4-COOH	4.32 ± 0.02	9.33 ± 0.07	12.70 ± 0.10	18.4 ± 0.4	69.9 ± 1.2	34.1 ± 4.1
3-COOH	2.69 ± 0.01	3.61 ± 0.03	6.11 ± 0.27	8.20 ± 0.02	57.5 ± 2.0	82.9 ± 6.0
3-COMe	0.957 ± 0.006	1.44 ± 0.02	2.00 ± 0.01	2.67 ± 0.01	50.4 ± 0.8	114 ± 3
4-CONH ₂	0.732 ± 0.004	1.69 ± 0.01	2.46 ± 0.02	3.55 ± 0.04	77.1 ± 0.8	24.7 ± 2.7
4-COOMe	0.613 ± 0.006	0.920 ± 0.005	1.34 ± 0.02	1.93 ± 0.02	56.6 ± 1.1	97.5 ± 3.9
4-CN	0.111 ± 0.001	0.320 ± 0.002	0.491 ± 0.003	0.853 ± 0.006	75.1 ± 0.7	44.9 ± 2.5
3-CN	0.097 ± 0.001	0.119 ± 0.001	0.212 ± 0.007	0.342 ± 0.003	65.0 ± 1.6	85.3 ± 5.4
4-Styrylpyridines						
OMe	88.3 ± 1.6	123 ± 5	161 ± 3	197 ± 7	37.8 ± 2.8	119 ± 10
Me	71.1 ± 2.1	103 ± 1	129 ± 2	168 ± 2	40.9 ± 1.9	110 ± 7
H	52.8 ± 0.1	80.9 ± 0.3	112 ± 2	139 ± 2	47.6 ± 0.9	90.0 ± 3.0
F	51.3 ± 0.3	80.0 ± 0.6	108 ± 1	137 ± 1	48.0 ± 0.7	88.6 ± 2.4
Cl	47.2 ± 0.4	66.9 ± 0.5	103 ± 6	115 ± 2	45.6 ± 2.6	98.0 ± 8.8
Br	53.7 ± 0.4	72.6 ± 0.7	90.4 ± 1.3	110 ± 2	34.2 ± 1.4	135 ± 5
CN	32.4 ± 0.2	51.5 ± 0.2	69.1 ± 0.2	85.9 ± 2	47.6 ± 0.9	93.8 ± 2.9
NO ₂	26.9 ± 0.5	43.6 ± 0.6	63.3 ± 1.0	80.2 ± 2.8	54.2 ± 2.2	73.2 ± 7.4

Table 3--Linear correlations for the reaction of substituted pyridines and 4-styrylpyridines with DNPA

Parameter used in correlation			ρ/β	r	s	n
Pyridine and Styrylpyridine	vs	σ_p/σ_m (Katritzky)	-3.425 ± 0.276	0.991	0.144	16
Pyridines	vs	σ (Hammett)	-3.385 ± 0.375	0.989	0.163	12
Styrylpyridines	vs	σ (Hammett)	-0.390 ± 0.080	0.984	0.028	8
Pyridines and Styrylpyridines	vs	pK_a	0.692 ± 0.056	0.990	0.146	16

ground state. The second order rate constants obtained for the title reaction at 25°, 30°, 35° and 40°C and the activation parameters calculated are listed in Table 2. The reaction rate depends upon the electron density of nitrogen atom of pyridine nucleus. The data in Table 2 reveal that the reaction is accelerated by electron-releasing substituents and retarded by electron-withdrawing substituents present in the pyridine ring or in the phenyl ring of the styryl group.

The rate data were correlated with various substituent constants and Table 3 summarises the results of correlation analysis. Correlation of $\log k_2$ at 30°C with σ_m and σ_p substituent constants for pyridines and σ_p constant of Katritzky *et al.*⁷ for styrylpyridines is good ($r=0.991$) as has been observed in the earlier studies on styrylpyridines⁸⁻¹⁰.

The procedure of Katritzky *et al.*⁷ for obtaining σ_p values for the substituted styryl groups from the pK_a values of the substituted styrylpyridinium ions did not appear adequate as the effect of substituent on the pK_a values was very small. Therefore it was decided to correlate the rate data for 3- and 4-substituted pyridines and 4'-substituted 4-styrylpyridines separately with the Hammett σ constants¹¹. In both these cases the correlations are found to be good (Table 3).

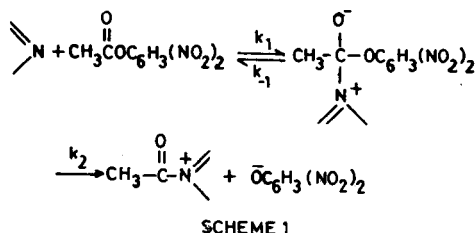
The observed ρ -value -3.39 ± 0.38 in the present study shows that the effect of substituents is less pronounced as compared to that of the protonated equilibrium of 3- and 4-substituted pyridines¹² and slightly more pronounced as compared to the reactions of methyl iodide¹³, phenacyl bromide¹⁰ and perbenzoic acid¹³ with 3- and 4-substituted pyridines and also to the charge transfer equilibrium between pyridines and iodine, iodine monochloride and iodine monobromide as acceptors¹⁴. The magnitude of ρ in comparison with the value -5.71 obtained for the ionisation of pyridinium ion in water¹², suggests that only 60% of the positive charge carried by the pyridinium ion is developed in the transition state of the reaction of substituted pyridines with DNPA.

The application of the Hammett equation using σ values of 4'-substituents in styrylpyridines is used to calculate the reaction constant ρ for the 4-styrylpyridines. The ρ -value so calculated reflects not only the sensitivity of the reaction to the substituents but also the degree of the transmission of the substituent effect through the styryl group to the reaction centre. From the basicities of 4-styrylpyridines the value of ρ was found to be -0.85 . The ratio of effectiveness of transmission of substituent effect in styryl system relative to phenyl system in the protonated equilibrium was calculated to be 0.15. In the charge transfer complex formation between iodine and pyridines the ratio was found to be 0.18. For the reaction between phenacyl bromide and pyridines¹⁰ the ratio was found to be 0.104. The ratio 0.115 (0.390/3.385) obtained in the present study compares satisfactorily with the above values.

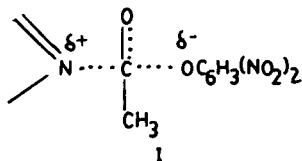
The Brönsted-type plot for this reaction obtained by plotting $\log k_2$ at 30°C versus the pK_a values of corresponding conjugate acids of substituted pyridines¹⁵⁻¹⁷ and styrylpyridines⁷ is linear with $\beta_N = 0.692 \pm 0.056$ ($r=0.990$; $s=0.146$; $n=16$) indicating that the reaction rate depends on the basicity of the nucleophiles. The present β_N value is lower than that found in the nucleophilic reaction of substituted pyridines with *p*-nitrophenyl acetate ($\beta_N = 0.93$)², 2,4-dinitrophenyl methyl carbonate ($\beta_N = 0.9$)¹⁸, 2,4-dinitrophenyl acetate ($\beta_N = 0.85$)⁴, 2,4-dinitrophenyl *p*-nitrobenzoate ($\beta_N = 0.9$)⁶ and acetic anhydride ($\beta_N = 1.0$)¹⁹. The aminolysis reactions of phenyl acetate¹, arylphenyl carbonates^{20,21}, acylpyridinium ions²² and phthalic and succinic anhydrides²³ also give Brönsted-type plots with higher slopes. The present value of β_N (0.692 ± 0.056) shows that the extent of bond formation in the transition state is less as compared to the above reactions. Relatively high value of ρ (-3.39) observed in the present reaction series also suggests that the bond breaking takes place more readily than bond making.

The Brönsted plot appeared curved⁴ in the case of nucleophilic attack of a series of 3- and

4-substituted pyridines on 2,4-dinitrophenyl acetate. This non-linearity was accounted in terms of a tetrahedral intermediate in the reaction path and a change in the rate determining step from the second to the first in Scheme 1 as the nucleophile becomes more basic.



The observed linearity in the Hammett and the Brönsted plots under the present experimental conditions could be explained by assuming a one-step reaction with the formation of intermediate (I).



A similar linear Brönsted plot has been observed in the reactions of pyridinolysis of 2,4-dinitrophenyl *p*-nitrobenzoate⁶ and of 2,4-dinitrophenyl *p*-chlorobenzoate²⁴.

The entropies of activations are all negative (Table 2) as expected for S_N2 reactions. Because of the development of charge in the transition state (formed from neutral molecules), the entropies of activation are more negative. There is a fair correlation between Δ*H*‡ and Δ*S*‡ (*r* = 0.931). The isokinetic temperature is found to be 397 K. Exner plot of log *k*₂ at 313 K versus log *k*₂ at 298 K for the reaction of DNPA with pyridines and 4-styrylpyridines is linear (*r* = 0.995) and the value of isokinetic temperature is found to be 216 K. The existence of good correlation implies that all the pyridines and styrylpyridines undergo nucleophilic substitution by an identical mechanism.

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