

Reaction Kinetics of Meisenheimer -Complex
Formation between 2,4,6-Trinitrophenyl
Chloride and Hydroxide Ion in Cationic
Micellar Solution

著者 (英)	Rie MATSUI, Yoshiyuki IKEDA, Muneo SASAKI
journal or publication title	Memoirs of Konan University. Science and engineering series
volume	55
number	1
page range	39-51
year	2008-07-31
URL	http://doi.org/10.14990/00000154

Reaction Kinetics of Meisenheimer σ -Complex Formation between 2,4,6-Trinitrophenyl Chloride and Hydroxide Ion in Cationic Micellar Solution

Rie MATSUI, Yoshiyuki IKEDA and Muneo SASAKI

Department of Chemistry, Faculty of Science and Engineering, Konan University,
Higashinada-ku, Kobe 658-8501, Japan

(Received April 25, 2008)

Abstract

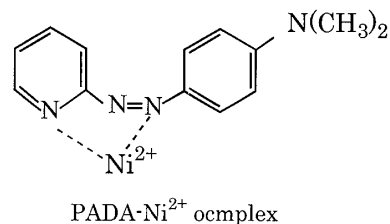
Kinetic study was carried out by using stopped-flow method for the Meisenheimer σ -complex formation reaction between 2,4,6-trinitrophenyl chloride (picryl chloride: Pic-Cl) and hydroxide in aqueous cationic micellar solutions of dodecyltrimethylammonium bromide (DTAB), myristyltrimethylammonium bromide (MyTAB) and cetyltrimethylammonium bromide (CTAB) dissolved in aqueous solution, for the purpose of elucidating the influence of the microscopic heterogeneity of reaction field on activation parameters. The reaction rate analysis based on a pseudo-phase ion exchange model led us to a conclusion that on the activation process the enthalpy-entropy compensation relationships worked over the wide range of surfactant concentration, and that, for the reaction occurring at the micellar surface, a reactant molecule effective to the reaction had to move into some restricted direction.

Introduction

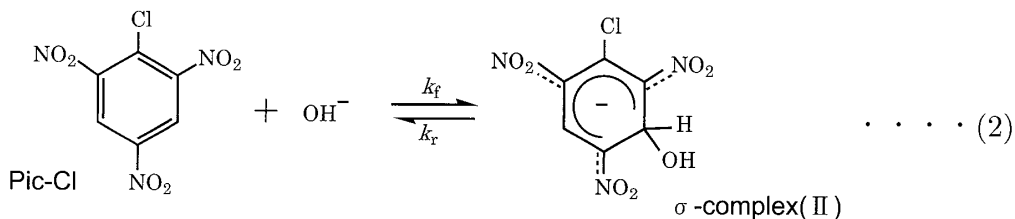
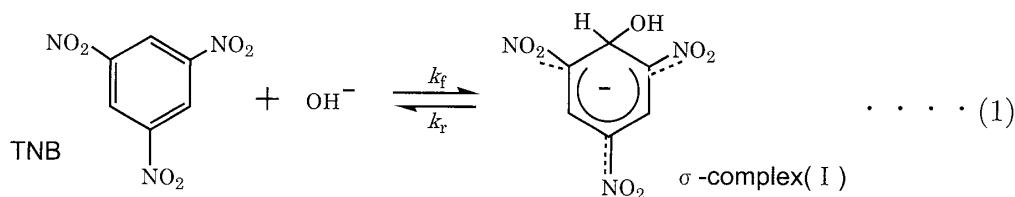
Since chemical reactivity in solution is much affected by solvent structure around the reactive site, chemical reactions in micellar solution have attracted much attention^{1,2)} from the viewpoints of microscopic heterogeneity of reaction field involved in solution. That influence often appears as a "micellar catalysis", which is mainly caused by either environmental effect of the reaction field or increasing reactant concentration in a micellar particle. The former effect works essentially in analogy with the solvent effect or solvation effect mainly associated with electrostatic properties of micellar phase. The latter effect works remarkably in reactions of highly polar molecules in ionic micellar solutions.³⁾

On the catalytic micellar effect, the PADA-Ni²⁺ complex formation reaction

between Ni^{2+} and pyridine-2-azo-*p*-dimethylaniline (PADA) in cationic(CTAB), nonionic(hexaethylene glycol monododecylether, C_{12}E_6) and anionic (sodium decylsulfate, SDeS) micellar solutions was studied in detail^{4,5}. It was revealed that in the anionic micellar solution, the reactant cation was almost completely concentrated on the micellar surface, and rate constant reached a maximum at cmc(critical micelle concentration) and decreased slowly with increasing surfactant concentration. That behavior was adequately explained on the basis of the cell model⁶.



In the previous paper⁷), effect of cationic micellar solutions has been examined on a Meisenheimer σ -complex formation reaction⁸) between 1,3,5-trinitrobenzene (TNB) and hydroxide ion as represented by reaction (1). And it was revealed that ion exchange between hydroxide ion and bromide ion existing as counter ions of cationic micellar surface was importantly participated in the reaction rate. In the present paper, we have examined a similar reaction as represented by reaction (2) between 2,4,6-trinitrophenyl chloride(picryl chloride: Pic-Cl) and hydroxide ion for the purposes of not only analyzing the apparent reaction rate on the basis of mixed reaction fields, but considering the activation parameters intrinsic to the respective reaction field. The cationic surfactants used in this study were the same as those in the previous study, dodecyltrimethylammonium bromide(DTAB, $\text{CH}_3(\text{CH}_2)_{11}\text{N}(\text{CH}_3)_3\text{Br}$), myristyltrimethylammonium bromide(MyTAB, $\text{CH}_3(\text{CH}_2)_{13}\text{N}(\text{CH}_3)_3\text{Br}$), and cetyltrimethylammonium bromide(CTAB, $\text{CH}_3(\text{CH}_2)_{15}\text{N}(\text{CH}_3)_3\text{Br}$) dissolved in aqueous solution.



Experiment

Materials: 2,4,6-Trinitrophenyl chloride(picryl chloride: Pic-Cl) obtained commercially(Tokyo Kasei Co. Ltd.) was recrystallized twice from ethanol. Aqueous sodium hydroxide solution prepared commercially for volumetric analysis was used as a source of hydroxide ion. DTAB(AVOCADO Co. Ltd.), MyTAB (Wako Pure Chemical Industries, Ltd.) and CTAB(Nacalai Tesque, Inc.) were used as obtained commercially. Distilled water was used throughout this work.

UV Spectra and Kinetic Measurements: UV spectrum was recorded by a Hitachi U-2000 spectrophotometer. Kinetic measurement was carried out with a RA-2000 stopped-flow spectrophotometer (Otsuka Electronics Co., Ltd.) in which each reaction solution was driven directly by nitrogen gaseous pressure into a mixing chamber. The temperature range was 293-313 K, which was regulated within ± 0.1 K by circulating thermostated water around the optical observation cell.

All kinetic runs were performed with hydroxide ion concentration in large excess over substrates. The concentration of Pic-Cl was around 40 μ M, and hydroxide ion was in the range 1.0 mM \sim 10 mM. The ionic strength was controlled, when necessary, by adding potassium bromide. The concentrations of surfactants varied 1.0 mM \sim 10 mM for DTAB, 1.0 mM \sim 10 mM for MyTAB, and 2.0 mM \sim 10 mM for CTAB, respectively. The pseudo-first order rate constants were determined by fitting to a single exponential function.

Results and Discussions

The electronic absorption spectra of Pic-Cl in aqueous micellar solution showed the peaks around 350, 420 and 500 nm after addition of OH^- ion, as shown in Fig. 1, and the absorption at 520 nm decreasing and 350 and 420 nm peaks increasing slowly. Finally absorption spectra showed the double peaks at 350 and 420 nm which completely agreed with the spectrum of 2,4,6-trinitrophenol(picric acid). The product formed rapidly after mixing showed double peaks at 420 and 520 nm, which is one of spectroscopic characteristics of Meisenheimer σ -complexes formed from aromatic nitro compounds^{9,10}. So, the absorbance at 500 nm increased within several seconds, and then decreased slowly. In the present reaction system two kinds of Meisenheimer complexes, σ -complex(II) and σ -complex(III) are possible to be formed as shown in the reaction scheme written below. Considering that final product is picric acid, the σ -complex(III) should exist on the route to the final product. Comparison of stability between σ -complex(II) and σ -complex(III) suggested that the electronic absorption immediately after beginning of reaction represents σ -complex(II), since the reaction from σ -complex(III) to picric acid proceeds too fast for σ -complex(III) to be observed spectroscopically. Similar features were observed in the reaction of Pic-Cl with sulfite ion¹¹.

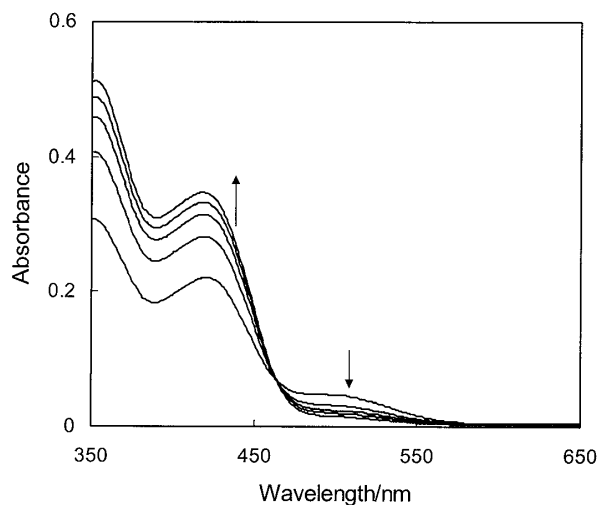
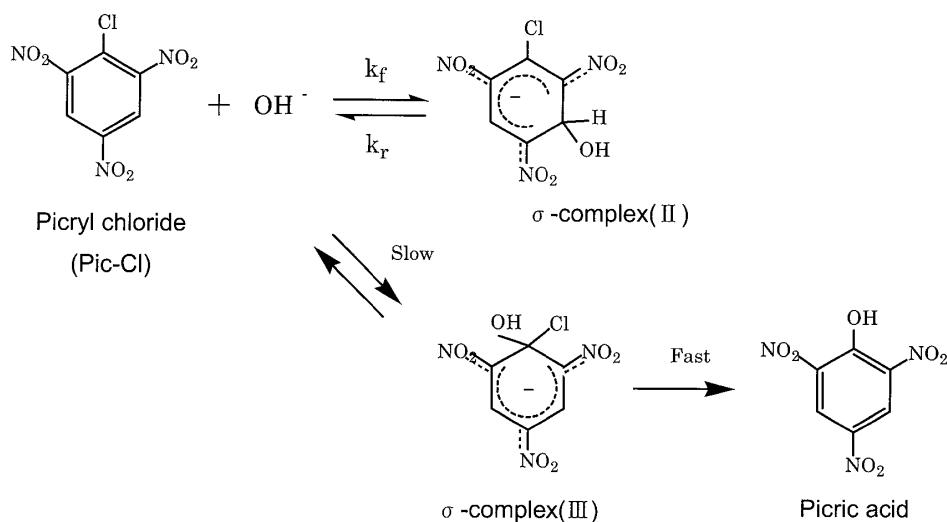


Fig. 1 Change of absorption spectra with reaction time for the aqueous reaction mixture of 40 μM Pic-Cl and 1.0 mM OH^- . Ionic strength $\mu=0.1$ with KBr. Toward the arrows, reaction time is 20 s, 170 s, 320 s, 470 s, and 770 s, respectively.



When $[\text{OH}^-]$ existed in large excess over $[\text{Pic-Cl}]$, a spectrophotometric stopped-flow kinetic trace as shown in Fig. 2 obeyed a first order kinetics within several seconds, after which the kinetic curves began to deviate from a first order kinetics because the succeeding slow reaction producing the picric acid became remarkable. The pseudo-first order rate constants determined for the initial fast process, k_{obsd} , can be represented by eq. (3).

$$k_{\text{obsd}} = k_f[\text{OH}^-]_0 + k_r \cdot \cdot \cdot \cdot (3)$$

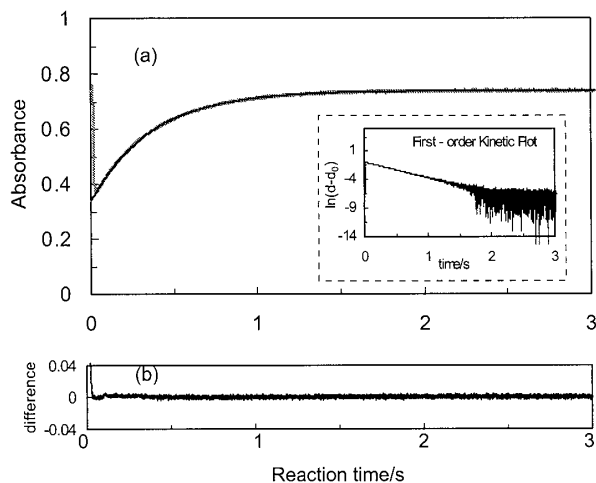


Fig. 2 Stopped-flow kinetic trace(a) at 500 nm for Pic-Cl-OH⁻ reaction in 1.0 mM MyTAB micellar solution at 298 K, and absorbance difference between experimental absorbance and calculated one fitted to a first-order kinetic law(b). The insert in (a) shows the first-order kinetic plot. $[\text{Pic-Cl}]_0 = 40 \mu\text{M}$, $[\text{OH}^-]_0 = 10 \text{mM}$.

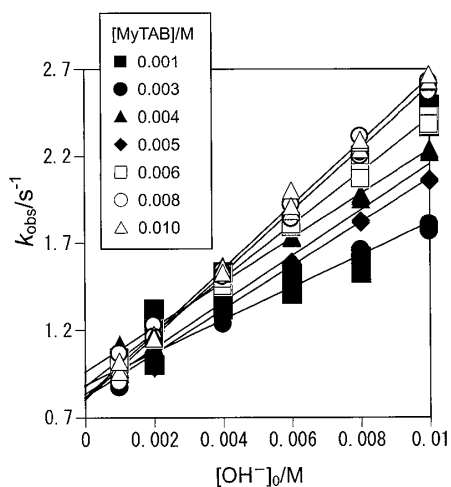


Fig. 3 Pseudo-first order plots for Pic-Cl-OH⁻ reaction at 298 K in MyTAB micellar solution. Ionic Strength $\mu=0.1$.

Fig. 3 shows the dependence of k_{obsd} on initial hydroxide ion concentration $[\text{OH}^-]_0$ in MyTAB micellar solution, which is well represented by eq. (3) based on reaction (2). Since the forward rate constant k_f and reverse one k_r determined by eq. (3) are responsible for reaction steps occurring in both micelle and bulk water phases, these are composite terms of rate constants in the respective phase. Table 1 lists the k_f values in various surfactant concentrations for both $\mu=0$ and

Table 1 Forward rate constant $k_f/M^{-1}s^{-1}$ in various micellar solutions at ionic strength $\mu=0^a$ and $\mu=0.1$, determined from the plot according to eq. (3).

surfactant		CTAB		MyTAB		DTAB	
T/K	[S]/mM ^{b)}	$\mu=0.1$	$\mu=0$	$\mu=0.1$	$\mu=0$	$\mu=0.1$	$\mu=0$
293	1.0	—	—	—	—	69.8	—
	2.0	—	—	—	—	113	252
	3.0	—	—	57.5	—	—	—
	4.0	—	—	71.9	315	148	499
	5.0	—	—	86.2	637	156	491
	6.0	—	—	97.4	845	162	474
	8.0	—	—	111	1160	166	447
	10	—	—	162	1260	165	404
298	1.0	—	—	—	—	103	—
	2.0	103	2150	—	—	181	376
	3.0	—	—	93.0	—	—	—
	4.0	145	3310	128	419	254	705
	5.0	—	—	125	866	245	706
	6.0	181	3850	154	1200	246	689
	8.0	202	3490	180	1670	264	677
	10	232	3860	183	1820	261	626
303	1.0	—	—	—	—	141	—
	2.0	132	2930	—	—	256	512
	3.0	—	—	123	—	—	—
	4.0	240	4690	140	536	328	1090
	5.0	—	—	174	1070	336	1030
	6.0	279	5370	212	1520	370	1964
	8.0	267	4730	228	2000	389	923
	10	340	6100	252	2600	372	870
308	1.0	—	—	—	—	194	—
	2.0	200	3550	—	—	366	642
	3.0	—	—	153	—	—	—
	4.0	264	5670	214	680	472	1560
	5.0	—	—	231	1400	538	1350
	6.0	336	6070	230	1890	514	1310
	8.0	408	6270	303	2830	525	1260
	10	449	6670	385	3460	546	1160
313	2.0	278	4020	—	—	—	—
	4.0	356	7170	—	—	—	—
	6.0	530	7770	—	—	—	—
	8.0	557	8410	—	—	—	—
	10	603	8040	—	—	—	—

^{a)} The ionic strength “ $\mu=0$ ” means that no potassium bromide is added to the solution for controlling ionic strength.

^{b)} Surfactant concentration.

$\mu=0.1$. Hereafter the ionic strength “ $\mu=0$ ” means that no potassium bromide is added to the solution for controlling ionic strength. Fig. 3 shows that k_f thus determined by eq. (3) increases with surfactant concentration, however, reverse rate constant k_r doesn't show any systematic dependency on surfactant concentration.

Rate Analysis in Cationic Micellar Solution: The feature as shown in Figs. 3 results from the existence of multi reaction fields in a micellar solution, and the distribution of reactants between micelle phase and water one. Quite similar feature was observed previously in TNB–OH[−] reaction system, and well understood on the basis of a pseudo-phase ion exchange model⁷⁾ that the partition of reactant molecules between the micelle and water phase, and ion exchange between hydroxide ion and bromide ion existing as counter ions of cationic micellar surface were importantly participated in reaction rate process. That reaction scheme is different from the cell-model⁶⁾ in which the reactants may become initially concentrated with increasing micellar concentration, and then with further increase of surfactant concentration the quantity of each reactant molecule contained or solubilized per micelle decreases.

The characteristics of a pseudo-phase ion exchange model is the ionic exchange between micelle and water phases^{12,13)}.



In reaction (4), subscript m denotes the species in micelle phase, and w denotes the water phase.

The condensation of both reactant molecules Pic-Cl and OH[−] in or around a micelle due to partition equilibrium will, in general, lead to enhancement of reaction rate compared to the case of the absence of a micelle, and in contrast the ion exchange on a micelle surface as expressed by reaction (4) will lead to the decrease of reaction rate with increasing ionic strength. The ionic exchange equilibrium constants, K_X , K_{OH} , and K_X^{OH} are defined by eqs. (5) and (6), as explained in the previous paper⁷⁾, where K_X^{OH} corresponds to the ionic exchange of reaction (4). In these equations [S] denotes the surfactant concentration.

$$K_X = \frac{[\text{Br}^-]_m}{[\text{Br}^-]_w \times [\text{S}]} = \frac{\beta}{[\text{Br}^-]_w} \quad K_{\text{OH}} = \frac{[\text{OH}^-]_m}{[\text{OH}^-]_w \times [\text{S}]} \quad \cdot \cdot \cdot \cdot \quad (5)$$

$$K_X^{\text{OH}} = \left[\frac{[\text{OH}^-]_w}{[\text{OH}^-]_m} \right] \left[\frac{[\text{Br}^-]_m}{[\text{Br}^-]_w} \right] = \frac{K_X}{K_{\text{OH}}} = \text{constant} \quad \cdot \cdot \cdot \cdot \quad (6)$$

So, similarly to the previous TNB–OH[−] reaction system⁷⁾, the reaction scheme of pseudo-phase model with the ion exchange as reaction (4) can be applied to

analyze the kinetic data. In this model k_{wf} and k_{mf} are forward rate constants in water phase and micelle one, respectively.

Then the apparent forward rate constant k_f is represented by eq. (7), and the reverse one k_r by eq. (8), where K_s and K_s' are partition constants between the two phases for Pic-Cl and σ -complex(II), respectively.

$$k_f = \frac{k_{\text{wf}} + k_{\text{mf}}K_s(K_{\text{OH}})^{-1}K_X([S] - \text{cmc})}{1 + K_{\text{OH}}([S] - \text{cmc})} \cdot \cdot \cdot (7)$$

$$k_r = k_{\text{mr}} + k_{\text{wr}}/K_s'([S] - \text{cmc}) \cdot \cdot \cdot (8)$$

The observed dependence of k_f on surfactant concentration as shown in Table 1 and Fig. 3 was fitted to eq. (7), and numerical values of k_{wf} and k_{mf} were determined as listed on Table 2. In the course of above calculation, since the partition constant K_s had to be known in advance, we used the literature value⁷⁾ of $K_s = \sim 10^2 \text{M}^{-1}$. The values of β , K_{OH} and K_X^{OH} were also assumed to be 0.72,

Table 2 Forward rate constants for the Meisenheimer σ -complex(II) formation for Pic-Cl-OH⁻ reaction in the water and the micelle phases, calculated on the basis of pseudo-phase ion exchange model.

ionic strength		$\mu=0.1$		$\mu=0$	
surfactant	T/K	$k_{\text{wf}}^{\text{a)}/\text{M}^{-1}\text{s}^{-1}}$	$k_{\text{mf}}^{\text{b)}/\text{M}^{-1}\text{s}^{-1}}$	$k_{\text{wf}}^{\text{a)}/\text{M}^{-1}\text{s}^{-1}}$	$k_{\text{mf}}^{\text{b)}/\text{M}^{-1}\text{s}^{-1}}$
CTAB	298	53.9	0.32	919-	4.30
	303	99.4	0.56	1390	6.67
	308	142	1.02	1900	8.84
	313	203	1.19	2450	10.5
MyTAB	293	57.0	0.19	1.87	64.9
	298	94.5	0.27	2.87	113
	303	117	0.39	4.76	192
	308	141	0.53	7.95	295
DTAB	293	69.1	0.19	—	—
	298	102	0.29	—	—
	303	141	0.42	—	—
	308	192	0.60	—	—

a) Forward rate constant in the water phase.

b) Forward rate constant in the micelle phase. On calculating k_{mf} from fitting parameters to eq. (7), the partition constant K_s between water and micelle phase was assumed to be $1.0 \times 10^2 \text{M}^{-1}$ and to be independent of temperature.

10 ~ 30 and 0.4 ~ 0.5, respectively as assumed previously.⁷⁾

The adequacy of the ion exchange model can be shown by the dependency of k_f on ionic strength. That reaction model should lead to reduction of apparent rate constant k_f with increasing ionic strength⁷⁾, as really found in Table 1 for any surfactant used in the present study.

Isokinetic Condition: The “apparent” activation parameters, ΔH_f^\ddagger , ΔS_f^\ddagger and ΔG_f^\ddagger ¹⁴⁾, which were derived from Arrhenius activation energy(E_{af}) and A -factor for k_f , are listed in Table 3 for CTAB micellar solution.

In Fig. 4 is given the plot of the compensation effect¹⁵⁾ between ΔH_f^\ddagger and ΔS_f^\ddagger , whose slopes give the isokinetic temperatures (T_{iso}) at which the reaction rate is kept constant^{15,16)}, even if the reaction field is varied by changing surfactant composition. Table 4 lists T_{iso} for the surfactant solutions examined in the present study. Because the enthalpy-entropy compensation relationships work over the wide range of surfactant concentration, the reaction mechanism is unchanged even if the reaction field changes so as to affect thermodynamic quantities of the transition state. Fig. 5 shows the plot of ΔG_{iso}^\ddagger corresponding to isokinetic rate constant against T_{iso} , for Pic-Cl-OH⁻ and TNB-OH⁻ reactions⁷⁾, where the shadowed area is the experimental temperature range. And so, it can be said that TNB-OH⁻ in CTAB is of enthalpy-control, and that the others, except Pic-Cl-OH⁻ in MyTAB and in CTAB which are not clearly distinguished, are mostly of entropy-control^{7,15)}.

Activation Parameters Intrinsic to Micelle Phase : The “intrinsic” activation parameters, assigned to purely micelle phase, were determined by use of k_{mf} in Table 2. As seen in Table 5 the activation enthalpy thus obtained is reduced by transferring from water to CTAB micelle phase, $\Delta H_{mf}^\ddagger < \Delta H_{wf}^\ddagger$. That trend, which is similar to the case of TNB-OH⁻, reflects mainly the difference of the

Table 3 Activation parameters for the Meisenheimer σ -complex(II) formation reaction of Pic-Cl-OH⁻ in the CTAB micellar solution at 298K and ionic strength $\mu=0.1$.

[CTAB]/mM	E_{af}/kJmol^{-1}	$\Delta H_f^\ddagger/\text{kJmol}^{-1}$	$\Delta S_f^\ddagger/\text{JK}^{-1}\text{mol}^{-1}$	$\Delta G_f^\ddagger/\text{kJmol}^{-1}$
3.0	48.1	45.6	-54.8	62.0
4.0	50.4	47.9	-44.9	61.3
5.0	49.4	46.9	-47.4	61.0
6.0	43.8	41.3	-65.0	60.7
8.0	48.8	46.3	-46.9	60.3
10	43.6	41.1	-62.8	59.8

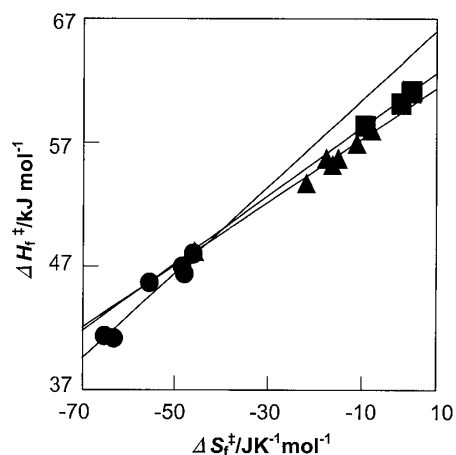


Fig. 4 $\Delta H_f^\ddagger - \Delta S_f^\ddagger$ compensation relationships for σ -complex(II) formation reaction of Pic-Cl-OH⁻ in CTAB(■), MyTAB(●) and DTAB(▲) micellar solutions.

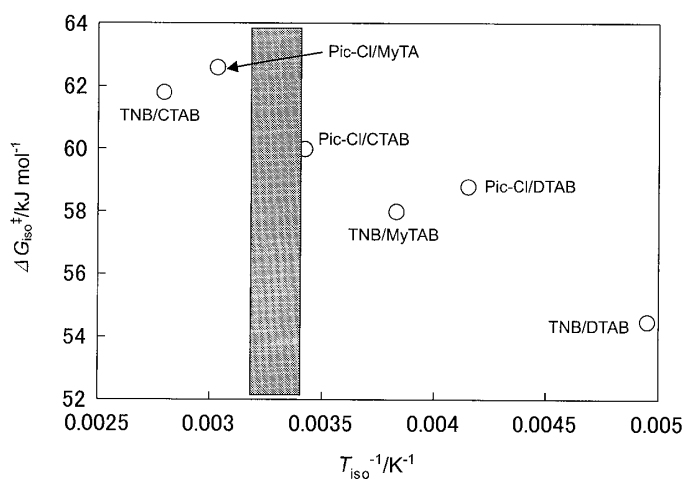


Fig. 5 Plot of isokinetic activation Gibbs free energy, ΔG_{iso}^\ddagger , against T_{iso} for Meisenheimer σ -complex formation of Pic-Cl-OH⁻ and TNB-OH⁻ reactions in some cationic micellar solutions at ionic strength $\mu=0.1$.

dehydration enthalpy of an OH⁻ on the activation between water and micelle^{4,5,7}). Since the degree of hydration of OH⁻ at the initial state in the micelle phase is weaker than that in the water phase because of the difference of dielectric constant, the dehydration energy required for the activation is less in micelle phase.

The activation entropy is also less in the micelle phase than the water phase,

Table 4 Isokinetic temperatures, T_{iso} , and $\Delta G_{\text{iso}}^\ddagger$ at T_{iso} for the Meisenheimer σ -complex(II) formation reaction of Pic-Cl-OH⁻ in the cationic micellar solutions at 298 K.

surfactant	$k_{\text{mf}}/\text{M}^{-1}\text{s}^{-1}$				k_r/s^{-1}	
	$\mu=0.1$		$\mu=0$		$\mu=0.1$	
	$\frac{T_{\text{iso}}}{\text{K}}$	$\frac{\Delta G_{\text{iso}}^\ddagger}{\text{kJ mol}^{-1}}$	$\frac{T_{\text{iso}}}{\text{K}}$	$\frac{\Delta G_{\text{iso}}^\ddagger}{\text{kJ mol}^{-1}}$	$\frac{T_{\text{iso}}}{\text{K}}$	$\frac{\Delta G_{\text{iso}}^\ddagger}{\text{kJ mol}^{-1}}$
CTAB	292	60.0	283	51.9	—	—
MyTAB	330	62.6	232	52.4	306	73.5
DTAB	241	58.8	—	—	291	73.1

a) $\Delta G_{\text{iso}}^\ddagger$ is related to the rate constant at T_{iso} and invariable even with different micellar concentration.

 Table 5 Activation parameters for the intrinsic phases^{a)} of the Meisenheimer σ -complex^{b)} formation reaction of Pic-Cl-OH⁻ and TNB-OH⁻ in the cationic micellar solutions at 298 K and ionic strength $\mu=0.1$.

reaction system	surfactant	$\frac{\Delta H_{\text{mf}}^\ddagger}{\text{kJ mol}^{-1}}$	$\frac{\Delta S_{\text{mf}}^\ddagger}{\text{J K}^{-1}\text{mol}^{-1}}$	$\frac{\Delta H_{\text{wf}}^\ddagger}{\text{kJ mol}^{-1}}$	$\frac{\Delta S_{\text{wf}}^\ddagger}{\text{J K}^{-1}\text{mol}^{-1}}$
Pic-Cl-OH ⁻	CTAB	68.2	-25.1	74.8	39.5
	MyTAB	49.9	-88.4	41.8	-67.8
	DTAB	56.4	-66.2	48.9	-42.7
TNB-OH ⁻	CTAB	86.6	48.9	90.2	50.7
	MyTAB	76.2	15.2	85.6	35.1
	DTAB	49.4	-77.4	53.5	-60.2

a) Subscripts m and w denote micelle phase and water one, respectively, and subscript f the forward process of the Meisenheimer σ -complex formation reaction.

b) σ -complex(II) for Pic-Cl-OH⁻ and σ -complex(I) for TNB-OH⁻.

$\Delta S_{\text{mf}}^\ddagger < \Delta S_{\text{wf}}^\ddagger$. The activation entropy difference between the two phases could be understood also on the basis of the difference of dehydration of OH⁻ ion. The large decrease in micelle has been found very often in various reactions^{3,7)}. However, if the dehydration were mostly decisive factor, activation entropy might be expected to be less negative, contrary to the experimental results. So the largely negative activation entropy $\Delta S_{\text{mf}}^\ddagger$ found in Pic-Cl-OH⁻ may reflect the other factors. The following consideration may be possible. If the reaction takes

place just at the surface of the micelle, one reactant(Pic-Cl) is inside the boundary, and the other(OH⁻) outside. So a reactant molecule effective to the reaction has to move into some restricted direction: for example, OH⁻ having net moving velocity directed toward the micelle-core will be only effective to react. And OH⁻ ions moving toward the water phase are inactive for the reaction. The same thing can be said for Pic-Cl molecules. Such restriction of moving direction of reactant molecules results in large decrease of entropy. That considerations expressed in the previous researches^{5,7)} have been supported more strongly by the present study.

Conclusion

The kinetics on the Meisenheimer σ -complex formation between 2,4,6-trinitrophenyl chloride(Pic-Cl) and hydroxide ion in several cationic surfactant solutions obeyed well the pseudo-phase ion exchange model, which could reasonably explain that the increase of micellar concentration resulted in the enhancement of reaction rate.

The largely negative activation entropy ΔS_{mf}^\ddagger , intrinsic to micelle phase, found in Pic-Cl-OH⁻ may reflect that for the reaction occurring at the micellar surface a reactant molecule effective to the reaction has to move into some restricted direction.

For the activation process, the enthalpy-entropy compensation relationships worked over the wide concentration range of surfactants. The reaction of TNB-OH⁻ in CTAB is of enthalpy-control, and the others, except Pic-Cl-OH⁻ in MyTAB and in CTAB which are not clearly distinguished, are mostly of entropy-control.

References

- 1) K. S. Birdi, "*Handbook of Surface and Colloid Chemistry*", CRC Press, New York, 1997
- 2) P. C. Hiemenz and R. Rajagopalan, "*Principles of Colloid and Surface Chemistry*", Marcel Dekker, Inc, New York, Basel, Hong Kong, 1997
- 3) M. Sasaki, A. Tanaka, N. Sugimoto and T. Sugano, *Chemistry Express*, **5**, 41 (1990)
- 4) T. Akazawa, Y. Ikeda and M. Sasaki, *Mem. Konan Univ., Sci. and Eng. Ser.*, **48**, 33 (2001)
- 5) T. Akazawa, Y. Ikeda and M. Sasaki, *Mem. Konan Univ., Sci. and Eng. Ser.*, **49**, 97 (2002)
- 6) S. Diekman and J. Frahm, *J. Chem. Soc. Faraday Trans.1*, **75**, 2199 (1979)

- 7) R. Matsui, Y. Ikeda and M. Sasaki, *Mem. Konan Univ., Sci. and Eng. Ser.*, **54**, 61 (2007)
- 8) J. Meisenheimer, *Ann.* **323**, 205, (1902)
- 9) F. Terrier, “*Nucleophilic Aromatic Displacement: the Influence of the Nitro Group*”, VCH Publishers Inc, New York, Weinheim, Cambridge, 1991
- 10) C. F. Bernasconi, *J. Am. Chem. Soc.*, **92**, 4682, (1970)
- 11) M. Sasaki, *Rev. Phys. Chem. Jpn.*, **45**, 45 (1975)
- 12) H. Chaimovich, J. B. S. Boniha, M. J. Politi and F. H. Quina, *J. Phys. Chem.*, **83**, 1851, (1979)
- 13) E. Abuin and E. Lissi, *J. Colloid Interface Sci.*, **143**, 97, (1991)
- 14) E. F. Caldin, “*The Mechanisms of Fast Reactions in Solution*”, IOS Press, Amsterdam, Berlin, Oxford, Washington, DC, 2001
- 15) J. E. Leffler and E. Grunwald, “*Rate and Equilibrium in Organic Chemistry*”, John Wiley & Sons Inc, (1963)
- 16) E. A. Gonzalez, M. A. Nazareno and C. D. Borsarelli, *J. Chem. Soc., Perkin Trans. 2*, 2052, (2002)