Amination Kinetics of Chloromethylated Polystyrene Accompanied by Acceleration and Deceleration[1)]

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(Received August 30, 1980)

Procedures to evaluate rigorously the rate constants in the aminations of chloromethylated polystyrene which are accompanied by acceleration and deceleration have been developed. The calculated fractional conversions in the reaction of chloromethylated polystyrene with 2-amino-1-butanol in dioxane, accompanied by acceleration, and the reaction with triethylamine in dimethyl sulfoxide, accompanied by deceleration, are proved to be in good agreement with the observed ones. The activation parameters of these reactions, in addition to the kinetic data in *N,N*-dimethylformamide, support the conclusion that the acceleration and the deceleration are due to the formation of the hydrogen bond and to the electrostatic effect from the neighboring groups in the respective transition states.

The rate constants of the chemical reactions of ploymers with small molecules in homogeneous solutions sometimes increase or decrease during the reactions, as observed in the aminations of chloromethylated polystyrene (CMPS). Although the reaction of CMPS with 2-amino-1-butanol in *N,N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) follows the second-order kinetics, the rate constant increases during the reaction in dioxane.[2)] Such acceleration was also observed in the amination of CMPS with diethanolamine in dioxane and it was considered to be caused by the hydroxyl groups of the already-aminated neighbors in the macromolecule.[3)] Similar acceleration was reported by Drăgan *et al.*[4)] in the reaction of CMPS with 1-dimethylamino-3-propanol and 1-dimethylamino-2-propanol in dioxane and dimethylacetamide. Tsuchida and Irie[5)] observed the acceleration during the reaction of CMPS with γ-picolin in DMF.

On the other hand, the rate constant of the reaction of CMPS with butylamine decreases during the reaction in dioxane, though the reaction in DMF follows the second-order kinetics.[6,7)] Such deceleration was also observed in the reaction of CMPS with diethylamine in both dioxane and DMF and in the reaction with diethanolamine in both DMF and DMSO. The deceleration in these reactions was considered to due to the steric effect of the already-aminated neighboring groups.[3,8)]

The reaction kinetics in polymer solutions which deal with the deceleration was first proposed by Fouss *et al.*,[9)] who studied the quaternization of poly(4-vinylpyridine) with butyl bromide in sulfolane and propyrene carbonate. Since then, deceleration during the quaternization of poly(vinylpyridine) in sulfolane has been investigated kinetically by many investigators,[10—13)] who ascribed it to the steric hindrance or the electrostatic effect by the already-reacted groups in the polymer. But the quaternization of triethylamine with CMPS in DMF was reported to obey the ordinary second-order rate equation by Noda and Kagawa.[14)] Yet the deceleration in DMF was observed in the quaternization of poly(4-dimethylaminostyrene) with methyl iodide by Arcus and Hall[15)] and in the quaternization of poly(4-vinylpyridine) with benzyl chloride by Tsuchida and Irie;[5)] Kawabe and Yanagita[3)] observed also that the quaternization of poly[4-[bis(2-hydroxyethyl)aminomethyl]styrene] with methyl iodide decelerated in an aqueous DMF solution.

The aminations of CMPS accompanied by the deceleration were previously reported by Kawabe and Yanagita[3,6—8)] to conform to a modified second-order rate equation. Recently the present author has also found that the quaternization of triethylamine with CMPS in DMSO is accompanied by deceleration and that the reaction kinetics conforms to the modified rate equation. In the amination of CMPS with 2-amino-1-butanol, which is accompanied by acceleration, however, the conformity of the kinetic data to a similarly modified second-order rate equation was not so excellent, as reported previously.[2)] This reaction is re-examined and a procedure to evaluate the rate constants rigorously is described in this paper. The activation parameters of these reactions will be discussed in relation to their reaction mechanism.

Experimental

Materials. Chloromethylated polystyrenes (chlorine content: 21.4—22.8%, degree of chloromethylation: 0.89—0.97, mol wt: about 1×10^5) were prepared and purified by the procedures described in previous papers.[2,6)] (*R*)-2-Amino-1-butanol was prepared as reported previously.[2)] Triethylamine and solvents were of reagent grade and were distilled before use; they were proved to be pure by their refractive indices.

Kinetic Measurements. The procedures of the kinetic measurements in the amination of CMPS and benzyl chloride were the same as those described previously.[2,6)] The temperature of the reaction mixture was kept constant within ±0.1 K. The initial concentration of chloromethyl group was 0.04 mol dm^{-3}, that of 2-amino-1-butanol was 0.40—0.86 mol dm^{-3}, and that of triethylamine was 0.04 mol dm^{-3}.

Rate Equations

All the reactions of benzyl chloride with 2-amino-1-butanol and triethylamine conform to the second-order rate equation, Eq. 1. The reactions of CMPS with both amines in DMF also conform to Eq. 1:

$$kt = \frac{1}{a-b}\ln\frac{b(a-x)}{a(b-x)} = \frac{1}{a-b}\ln\frac{1-\alpha}{1-\beta} \equiv \overline{kt}, \qquad (1)$$

where a is the initial concentration of the amines; b, that of the chloromethyl groups; x, the concentra-

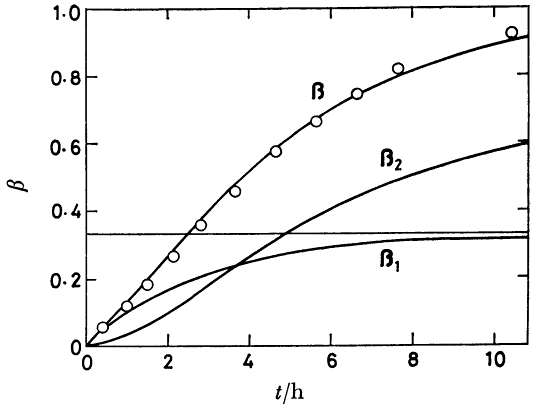

Fig. 1. Amination of CMPS with 2-amino-1-butanol in dioxane at 333.2 K.

tion of chloride ions at time t; and where $\alpha = x/a$ and $\beta = x/b$.

Amination of CMPS with 2-Amino-1-butanol in Dioxane. The second-order rate constant of the reaction of CMPS with 2-amino-1-butanol (k in Eq. 1) increases as the reaction proceeds, and k is a linear function of β:[2]

$$k = k_0(1+m\beta), \tag{2}$$

where k_0 and m are constants. On the basis of a model which represents the neighboring-group effect, β was expressed by Eq. 3 under the condition that a large excess of the amine is present ($a \gg b$):[2]

$$\beta = 1 - A'\exp(-3k_1at) - B'\exp(-k_2at), \tag{3}$$

$$k_1t = \frac{1}{D'a-b}\ln\frac{1-\alpha}{1-D'\beta} \equiv \overline{k_1t} \quad (\beta<1/3), \tag{4}$$

$$k_2t = \overline{kt} - C' \qquad (\beta>1/3), \tag{5}$$

where $A' = (k_1-k_2)/(3k_1-k_2)$, $B' = 2k_1/(3k_1-k_2)$, $D' = 3-2k_2/k_1$, and $C' = \ln[(1-\chi'/a)/(1-\chi'/b)]/(a-b)-k_2\tau'$; τ' and χ' are the values of t and x when $x_1 \simeq b/3$. The k_2 value was obtained from the plot of $\overline{kt}$ against t by virtue of Eq. 5 within the range $\beta>1/3$, while k_1 was obtained on the basis of Eq. 4 by the use of the k_2 value and an approximate value of k_1 which was determined by Eq. 1 in the range $\beta<1/3$.

The over-all course of the reaction was expressed on the basis of Eq. 3 by the use of the k_1 and k_2 values thus obtained; however, the agreement between the calculated and observed values was not so excellent.[2] To explain this discrepancy, the following points need clarification: (i) evaluation of k_1 and k_2, (ii) conditions of the reaction, (iii) the character of the group interaction, and (iv) the model from which the rate equations are derived.

Let us first re-examine the estimation of the rate constants. Taking a glance at Fig. 1, where β is divided into $\beta_1(=x_1/b)$ and $\beta_2(=x_2/b)$ by Eq. 6, we realize that the over-all reaction rate is still controlled by k_1 in a range far beyond the β value of 1/3; β_1 is given by

$$\beta_1 = x_1/b = [1-\exp(-3k_1at)]/3. \tag{6}$$

This may arise owing to the facts that $k_2>k_1$, where k_1 and k_2 are the rate constants of the elementary reactions which are independent of the neighboring group and under the influence of it respectively, and that the elementary reaction characterized by k_1 takes place in a range where β is still larger than 1/3. The k_2 value obtained simply by means of Eq. 5 will have to be corrected in this case, since it does not represent the genuine k_2.

From Eq. 3, we obtain

$$\left.\begin{aligned} k_2t &= -\ln X'/a \equiv \overline{k_2t}, \\ X' &\equiv [(1-\beta)-A'\exp(-3k_1at)]/B'. \end{aligned}\right\} \tag{7}$$

The k_1 value used in the computation is first obtained from a linear plot of $\overline{k_1t}$ against t in a range of $\beta<1/3$ on the basis of Eq. 4. After repeating the computation according to Eq. 7, one may obtain finally a linear plot of $\overline{k_2t}$ against t, which starts from the origin and covers data in a whole range of β; the corrected value of k_2 is thus obtained from the slope of this line. The value of k_1 may further be corrected, if necessary, on the basis of the following equations, which are derived also from Eq. 3:

$$\left.\begin{aligned} k_1t &= -\ln Y'/3a \equiv \overline{k_1t}, \\ Y' &= [(1-\beta)-B'\exp(-k_2at)]/A'. \end{aligned}\right\} \tag{8}$$

After repeating the computation, the final plot of $\overline{k_1t}$ against t will be represented by a straight line which starts from the origin and covers the whole range of β. When neccesary, one may repeat the computations by means of Eqs. 7 and 8 until fixed values of k_1 and k_2 are obtained. In the following section of this paper, it is shown that, in the amination of CMPS with 2-amino-1-butanol, Eq. 7 yields a somewhat greater k_2 value than that determined on the basis of Eq. 5, though Eqs. 4 and 8 yield the same k_1 value.

Quaternization of Triethylamine with CMPS in DMSO. The present author has found that the second-order rate constant (k in Eq. 1) of the reaction of CMPS with triethylamine decreases with the progression of the reaction and that the kinetic data fit Eq. 9; the equation was derived previously on the assumption that the reactivity of a group present between two already-reacted neighboring groups decreases owing to neighboring-group interaction:[3]

$$\beta = 1 - A\exp(-2k_1at) - B\exp(-k_2at), \tag{9}$$

$$k_1t = \frac{1}{Da-b}\ln\frac{1-\alpha}{1-D\beta} \equiv \overline{k_1t} \quad (\beta<1/2), \tag{10}$$

$$k_2t = kt - C \qquad (\beta>1/2), \tag{11}$$

where $A = (k_1-k_2)/(2k_1-k_2)$, $B = k_1(2k_1-k_2)$, $D = 2-k_2/k_1$, and $C = [(1-\chi/a)/(1-\chi/b)]/(a-b)-k_2\tau$; τ and χ are the values of t and x when $x_1 \simeq b/2$. Not only the present quaternization reaction but also many amination reactions of CMPS accompanied by deceleration fit Eq. 9 with k_1 and k_2 values estimated by Eqs. 10 and 11.[3,6,8] This may be understood by referring to Fig. 4 (also refer to Fig. 9 in Ref. 6), where β of the reaction at 303 K is divided into β_1 and β_2 by virtue of the equation;

$$\beta_1 = [1-\exp(-2k_1at)]/2. \tag{12}$$

Since $k_1>k_2$ in these cases, k_1 is no longer an important kinetic parameter in a range beyond $\beta>1/2$. In cases

Table 1. Kinetic parameters in the amination of CMPS with 2-amino-1-butanol in dioxane[a)]

Temp/K	Rate constants × 10^5/dm^3 mol^{-1} s^{-1} k_0 (Eq. 2)	k_1 (Eq. 8)	k_2 (Eq. 5)	k_2 (Eq. 7)
313.2	0.933	0.960	2.20	2.72
323.2	1.87	1.88	4.62	5.38
333.2	3.50	3.77	8.02	10.8
343.2	6.30	6.32	15.5	18.2
E_a/kJ mol^{-1}	56.8±0.3	56.8±1.1	57.3±1.2	57.3±1.1
log A[b)]	4.45±0.05	4.46±0.18	4.90±0.19	4.99±0.17

a) a=0.86 mol dm^{-3}, b=0.043 mol dm^{-3}. b) A is expressed by dm^3 mol^{-1} s^{-1}.

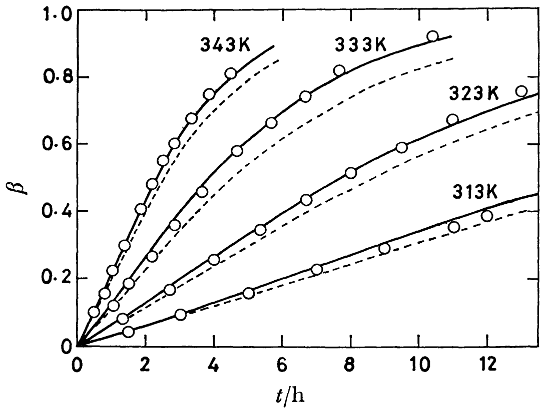

Fig. 2. Amination of CMPS with 2-amino-1-butanol in dioxane.

Table 2. Rate constants in the amination of benzyl chloride with 2-amino-1-butanol in dioxane[a)]

Temp/K	a/mol dm^{-3}	$k\times 10^5$/dm^3 mol^{-1} s^{-1}
333.2	0.396	2.53
	0.656	3.00
	1.055	4.10
348.2	0.400	6.23
	0.656	7.17
	0.860	8.00
363.2	0.400	14.5
	0.656	15.8
	0.860	16.8

a) b=0.041—0.044 mol dm^{-3}.

where k_1/k_2 is not large, however, the agreement between observed and calculated values may not be so excellent. Rigorous treatment of this kinetics then requires the correction of k_2 and also k_1, if necessary, on the basis of the following equations which are derived from Eq. 9:

$$\left.\begin{aligned} k_2t &= -\ln X/a \equiv \overline{k_2t}, \\ X &\equiv [(1-\beta)-A\exp(-2k_1at)]/B, \end{aligned}\right\} \tag{13}$$

$$\left.\begin{aligned} k_1t &= -\ln Y/2a \equiv \overline{k_1t}, \\ Y &\equiv [(1-\beta)-B\exp(-k_2at)]/A. \end{aligned}\right\} \tag{14}$$

Results and Discussion

Amination Kinetics of CMPS and Benzyl Chloride with 2-Amino-1-butanol in Dioxane. The previously reported kinetic data of the amination of CMPS with 2-amino-1-butanol in dioxane (a=0.86 and b=0.043 mol dm^{-3})[2)] have been re-examined by the procedures described in the preceding section. The rate constants k_1 and k_2, evaluated on the basis of Eqs. 7 and 8, are listed in Table 1. Although the numerical values of k_1 thus obtained are the same as those obtained by means of Eq. 4 and also the same as the k_0 values obtained by Eq. 2, the k_2 values are a little greater than those obtained by Eq. 5. The plots of β against t represented by the solid lines in Fig. 2 are calculated on the basis of Eq. 3; they are in good agreement with the observed values represented by the circles. In the figure, the dotted lines are the previously reported ones, which were computed by using the k_2 values determined by means of Eq. 5. It may therefore be concluded that the disagreement between the calculated and observed values shown in the previous paper[2)] originated in the fact that the evaluation of the rate constants, especially k_2, was not accurate. This correction of k_2, nevertheless, does not cause any change in activation energy, E_a, though the frequency factor, A, for k_2 (Eq. 7) is a little greater than that for k_2 (Eq. 5).

The second problem we concern ourselves with is the effect of the reaction conditions, such as the initial concentration of 2-amino-1-butanol and the reaction temperature. Although the amination kinetics of benzyl chloride fits Eq. 1, k has been found to be dependent on the initial concentration of 2-amino-1-butanol, a, as shown in Table 2. The kinetic data in the amination of CMPS in various conditions have been treated on the basis of Eqs. 2, 4, 5, 7, and 8; the results are summarized in Table 3. The table shows that the k_0 values, which are equal to the k_1 values obtained on the basis of both Eq. 4 and Eq. 8, are also dependent on a, and that the k_2 values obtained by Eq. 5, which are almost equal to the k values extrapolated to β=1 according to Eq. 3, are independent of a. The agreement between the calculated and observed β values is better when the k_2 values obtained on the basis of Eq. 7, instead of Eq. 5, are used.

Tables 2 and 3 indicate that k of benzyl chloride is equal to k_0 of CMPS at the same a and that they increase a little with a, while k_2 of CMPS is independent

TABLE 3. RATE CONSTANTS IN THE AMINATION OF CMPS WITH 2-AMINO-1-BUTANOL IN DIOXANE[a)]

Temp/K	a/mol dm^{-3}	m	Rate constants × 10^5/dm^3 mol^{-1} s^{-1} k_0 (Eq. 2)	k_2 (Eq. 5)	k_2 (Eq. 7)
333.2	0.400	1.77	2.68	7.52	10.8
	0.656	1.55	2.95	7.50	
	0.859	1.24	3.50	8.02	
348.2	0.400	1.89	6.42	18.8	25.1
	0.656	1.61	7.13	20.8	
	0.860	1.43	7.75	18.7	
363.2	0.400	1.83	14.5	41.0	56.7
	0.656	1.72	15.8	43.5	
	0.860	1.57	16.9	42.0	

a) $b = 0.040$ mol dm^{-3}.

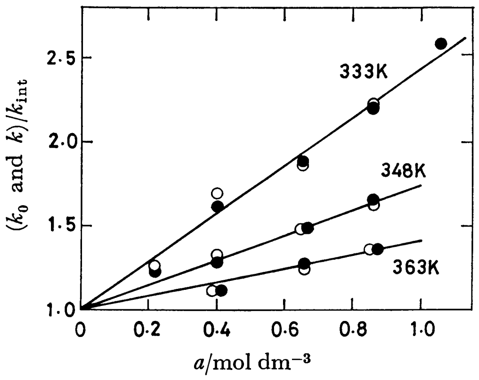

Fig. 3. Dependence of rate constants on a in the amination of CMPS (k_0, ○) and benzyl chloride (k, ●) with 2-amino-1-butanol in dioxane.

TABLE 4. INTRINSIC RATE CONSTANTS IN THE AMINATION OF BENZYL CHLORIDE AND CMPS WITH 2-AMINO-1-BUTANOL IN DIOXANE

Temp/K	$k_{\rm int}\times10^5$/dm^3 mol^{-1} s^{-1}	K/mol dm^{-3}	$k_2/k_{\rm int}$
333.2	1.58	1.41	6.80
348.2	4.83	0.74	5.17
363.2	12.4	0.42	4.56
E_a/kJ mol^{-1}	69.1±1.0		
log A[a)]	6.04±0.16		

a) A is expressed by dm^3 mol^{-1} s^{-1}.

TABLE 5. KINETIC PARAMETERS IN THE QUATERNIZATION OF TRIETHYLAMINE WITH CMPS AND BENZYL CHLORIDE IN DMF

Temp/K	$k\times10^5$/dm^3 mol^{-1} s^{-1} CMPS	Benzyl chloride
303.2	3.58	2.07
318.2	9.22	5.38
333.2	22.0	13.4
E_a/kJ mol^{-1}	50.8±0.1	52.3±0.5
log A[a)]	4.31±0.02	4.32±0.08

a) A is expressed by dm^3 mol^{-1} s^{-1}.

of a. Figure 3 shows that k and k_0 increase linearly with a according to the relation:

$$(k_0 \text{ and } k) = k_{\rm int}(1+Ka), \qquad (15)$$

where $k_{\rm int}$ and K are constants. The numerical values of $k_{\rm int}$ and K are listed in Table 4; E_a for $k_{\rm int}$ is greater than that for k_0 in Table 1. Consider that the hydroxyl group of 2-amino-1-butanol can form a hydrogen bond, in a non-polar solvent such as dioxane, with the chlorine of the chloromethyl group in the transition state to accelerate the reaction. Then an expression similar to Eq. 15 is easily derived according to the theory of transition states, on the assumption that two kinds of activation complexes coexist, the ordinary one and the hydrogen-bonded one. The physical meaning of the constants in Eq. 15 may thus be realized by considering that $k_{\rm int}$ corresponds to the intrinsic rate constant independent of the hydrogen bond and K is a measure of the force of the hydrogen bond.

The acceleration during the amination of CMPS may be explained by assuming that it is caused by the intramolecular hydrogen bond between the hydroxyl group of the already-aminated neignbor and the chlorine in the transition state. Provided that the intramolecular hydrogen bond is stronger than the intermolecular hydrogen bond, k_2 will be independent of a. The ratio, $k_2/k_{\rm int}$, is also interpreted as a measure of the intramolecular hydrogen bond. Table 4 indicates that both K and $k_2/k_{\rm int}$ decrease with the increase of temperature; this is not inconsistent with the assumption of the hydrogen bonds.

Quaternization Kinetics of Triethylamine with CMPS and Benzyl Chloride in DMF. In DMF, the quaternization of triethylamine with CMPS as well as with benzyl chloride fits to the ordinary second-order rate equation, Eq. 1. The results are shown in Table 5.

Quaternization Kinetics of Triethylamine with CMPS and Benzyl Chloride in DMSO. Although the quaternization of triethylamine with benzyl chloride fits Eq. 1, that with CMPS is accompanied by deceleration and its rate constants are computed on the basis of Eqs. 10, 11, and 13. The results are summarized in Table 6. Equation 13 gives slightly smaller values of k_2 than those obtained by Eq. 11. The plots of β against t calculated on the basis of Eq. 9, represented by the solid lines in Fig. 4, are in excellent agreement with the observed values represented by the circles.

TABLE 6. KINETIC PARAMETERS IN THE QUATERNIZATION OF TRIETHYLAMINE WITH CMPS AND BENZYL CHLORIDE IN DMSO

Temp	Rate constants × 10^4/dm^3 mol^{-1} s^{-1}			
K	k[a) (Eq. 1)	k_1 (Eq. 10)	k_2 (Eq. 11)	k_2 (Eq. 13)
303.2	1.01	1.83	1.05	0.853
318.2	2.60	4.47	2.35	2.21
333.2	5.87	9.87	5.95	5.18
E_a/kJ mol^{-1}	49.2±0.5	47.2±0.2	48.6±2.1	50.5±0.2
log A[b)	4.49±0.08	4.39±0.04	4.38±0.35	4.63±0.03

a) The rate constant of benzyl chloride. b) A is expressed by dm^3 mol^{-1} s^{-1}.

TABLE 7. ACTIVATION PARAMETERS AT 298.2 K[a)

Solvent	Amine	Chloride	ΔS^*/J K^{-1}	ΔH^*/kJ	ΔG^*/kJ
Dioxane	2-Amino-1-butanol	CMPS, k_1	−168±3	54.3	104.4
		k_2	−158±3	54.8	101.8
		k_{int}	−138±3	66.7	107.7
DMF	Triethylamine	BC[a)	−171±1	49.8	100.7
		CMPS	$-171\pm0._3$	48.4	99.3
DMSO	Triethylamine	BC[a)	−167±2	46.7	96.6
		CMPS, k_1	−169±1	44.7	95.1
		k_2	−165±1	48.0	97.1

a) BC: benzyl chloride.

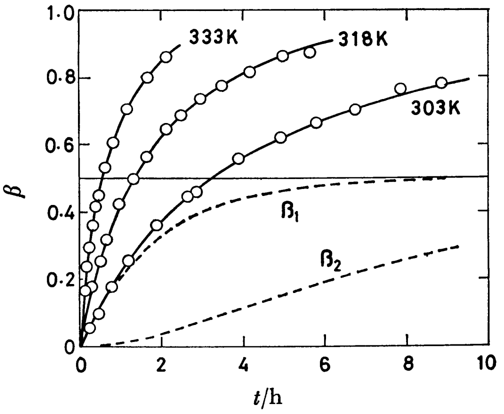

Fig. 4. Amination of CMPS with triethylamine in DMSO.

Activation Parameters. The activation parameters of the reactions are listed in Table 7. In dioxane the ΔG^* values for k_1 and k_2 are lower than that for k_{int} owing to their lower ΔH^* values; this fact supports the assumption that the hydroxyl group of 2-amino-1-butanol in the solution or the already-aminated neighbor in the polymer forms the inter- or intramolecular hydrogen bond with the chlorine of the chloromethyl group in the transition state. On the other hand, the lower ΔG^* value for k_2 than for k_1 is ascribed to the higher ΔS^* value; this suggests that the intramolecular hydrogen bond is formed in preference to the intermolecular one because the former is favorable with respect to entropy.

In the amination with 2-amino-1-butanol of a definite concentration, a, the ΔG^* values of both CMPS and benzyl chloride are the same, since k_0 (or k_1) of CMPS is equal to k of benzyl chloride, as shown in Fig. 3. In the quaternization of triethylamine in DMF, the ΔG^* of CMPS is lower than that of benzyl chloride owing to its lower ΔH^*; the same trend is noticed also in DMSO, when one compares the ΔG^* and ΔH^* values of benzyl chloride and CMPS (k_1).

The present work finds that the quaternization of triethylamine with CMPS in DMF conforms to the ordinary second-order rate equation, as was already reported by Noda and Kagawa,[14) whereas Arcus and Hall[15) found that the quaternization of poly(4-dimethylaminostyrene) with methyl iodide in DMF was accompanied by deceleration. They concluded that this deceleration was caused by the accumulation of positive charges on the polymer. Arcus and Hall[16) also noticed the reduction of rate during the quaternization of poly(4-vinylpyridine) with butyl bromide in sulfolane, as had been reported by Coleman and Fouss,[17) though they found that the reaction followed the second-order kinetics in DMF. It is interesting to note that the quaternization of poly(vinylpyridine) with butyl bromide and the quaternization of triethylamine with CMPS have the similar feature that they behave "normally" in DMF but "autodecelerate" in more polar solvents, such as DMSO and sulfolane.[18) In these cases, the deceleration may be explained by the electrostatic effect of the neighboring quaternary groups rather than by the steric obstruction by the neighbors. The more polar the solvent is, the more easy the ionization of quaternary ammonium chloride formed by the reaction on the polymer may become. As the reaction proceeds, the formation of a positive activation complex may become more difficult owing to the electrostatic effect of the positive charges of the neighboring quaternary ammonium groups. Table 7 indicates that, in the quaternization of triethylamine in DMSO, the ΔG^* for k_2 is higher than that for k_1, owing to the higher ΔH^*.

Table 7 indicates also that ΔG^* values of the quaternization in DMSO are lower than those in DMF owing to the lower ΔH^* values. The same fact was also found in the amination of CMPS and benzyl chloride with 2-amino-1-butanol and diethanolamine.[7,21] This may be explained, as discussed in a previous paper,[1] by assuming that the positive activation complex is stabilized by solvation in dipolar aprotic solvents and that the solvated complex is more stable in DMSO than in DMF.

The author wishes to express his thanks to Dr. Masaya Yanagita for his valuable discussions. He is also grateful to Mr. Masaaki Kodera and Mr. Yukio Uesugi for their generous assistance in carrying out the measurements.

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