August, 1976] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49 (8), 2043—2046 (1976) 2043

Group Interactions in Polyelectrolytes. XII. Amination Kinetics of Chloromethylated Polystyrene in Binary Solvent Systems Composed of Dioxane and Dipolar Aprotic Solvents

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(Received August 28, 1975)

The activation parameters ($\Delta G^{\neq}$, $\Delta H^{\neq}$, $\Delta S^{\neq}$) in the amination reaction of chloromethylated polystyrene (CMPS) and benzyl chloride with *s*-butylamine in *N*,*N*-dimethylformamide (DMF)–dioxanes mixtures and with 2-amino-1-butanol in dimethyl sulfoxide (DMSO)-dioxane mixtures were investigated as a function of x_1, the mole fraction of DMF or DMSO in the binary mixed solvents. A similar dependence of the parameters on x_1 was found in both systems, and the observed values of the parameters were in fair agreement with those calculated on the basis of Kondo and Tokura's theory concerning reaction rates in binary mixed solvents, assuming that the activated complex is solvated selectively with DMF or DMSO to form an addition product. The solvation in the DMSO–dioxane system was stronger than that in the DMF–dioxane system. Although $\Delta G^{\neq}$ decreases relatively uniformly with the increase in x_1, $\Delta H^{\neq}$ decreases sharply and reaches nearly a constant value at $x_1 \approx 0.2$. It was suggested that the increase of $T\Delta S^{\neq}$ in the range of $x_1 > 0.2$, which is approximately proportional to that of x_1, may be due to the relative increase in the configurational entropy change of the reaction system on transfer from dioxane to the dipolar aprotic solvents.

It has previously been reported that the amination rates of chloromethylated polystyrene (CMPS) and benzyl chloride with alkylamines and amino alcohols increase markedly on transfer of solvent from dioxane to such dipolar aprotic solvents as *N*,*N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO).[1–3] This enhanced reactivity was ascribed to the solvation of the activated complex in the dipolar aprotic solvents. The dependence of the amination rate constants of CMPS and benzyl chloride with isobutylamine and *s*-butylamine on the composition of DMF–dioxane system was also investigated at a constant temperature;[4] the relation could be represented by curves calculated on the basis of Kondo and Tokura's theory concerning reaction rates in binary mixed solvents.[5]

In the present study, the amination with *s*-butylamine in the DMF–dioxane system has been surveyed at various temperatures in order to discuss the dependence of the activation parameters on the solvent composition. In the DMSO–dioxane system, since the polymer was precipitated in the initial stage of the amination with *s*-butylamine in pure DMSO, the amination kinetics has been investigated with 2-amino-1-butanol, the alkyl structure of which is the same as that of *s*-butylamine.

Experimental

Materials. The chloromethylated polystyrenes (CMPS-14, chlorine content: 20.30%, degree of chloromethylation: 0.829, mol wt: 1.17×10^5; CMPS-12, chlorine content: 21.83%, degree of chloromethylation: 0.914, mol wt: 1.04×10^5) were prepared and purified by the procedures described in previous papers.[6,7] The (*R*)-2-amino-1-butanol was also prepared as has been reported previously;[7] bp 92—93 °C/30 mmHg, n^{20} 1.457, $[\alpha]^{20}_{\mathrm{D}}$ −9.96. The other chemicals and solvents were of a 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 in previous papers.[1,6,7] The temperature of the reaction mixture was kept constant within ±0.1°. In the amination with *s*-butylamine in the DMF–dioxane system, the initial concentration of the amine (*a*) was about 0.400 M and that of the chloromethyl group (*b*) was about 0.040 M ($a/b = 10$). The polymer used was CMPS-14. In the amination with 2-amino-1-butanol in the DMSO-dioxane system, *a* was about 0.21—0.22 M and *b* was about 0.044 M ($a/b = 4.8$—5.0). The polymer used was CMPS-12.

Results and Discussion

Amination with s*-Butylamine in DMF–Dioxane Systems.* Chloromethylated polystyrene (CMPS) and benzyl chloride were aminated with *s*-butylamine in DMF–dioxane mixtures at 45, 60, and 75 °C. The rate constants in the mixed solvents, k_{M}, were computed on the basis of the second-order equation, as has been described previously.[4] The values of the activation energy, E_{a}, and the frequency factor, *A*, are listed in Table 1.

The plots of log k_{M} against x_1 are shown in Figs. 1 and 2, where the circles represent the observed values, while the solid and broken lines represent the

TABLE 1. ACTIVATION ENERGY AND FREQUENCY FACTOR IN THE AMINATION OF CMPS AND BENZYL CHLORIDE WITH *s*-BUTYLAMINE IN DMF–DIOXANE MIXTURE

x_1	Chloride	E_{a}, kcal/mol	log A[a)]
0.1	CMPS	12.5±0.2	5.94±0.14
	Benzyl	12.5±0.7	5.73±0.32
0.20	CMPS	12.3±0.3	5.94±0.01
	Benzyl	$12.4 \pm 0.0_2$	5.99±0.02
0.35	CMPS	12.2±0.3	6.12±0.18
	Benzyl	12.3±0.3	6.28±0.28
0.50	CMPS	12.2±0.4	6.28±0.24
	Benzyl	12.2±0.4	6.40±0.24
0.60	CMPS	12.2±0.3	6.42±0.18
	Benzyl	12.3±0.2	6.61±0.13
0.80	CMPS	12.1±0.1	6.51±0.09
	Benzyl	12.2±0.4	6.68±0.25

a) *A* is expressed by l/mol min.

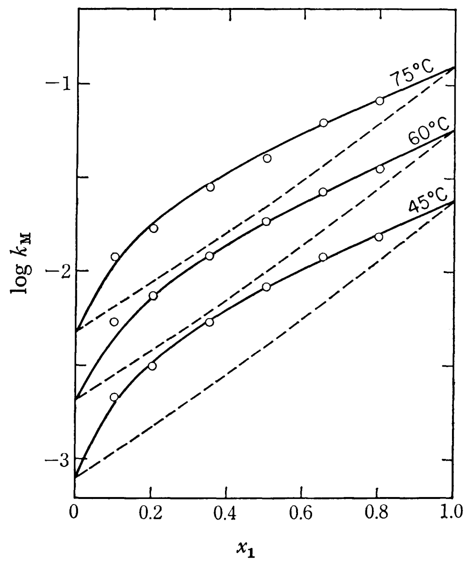

Fig. 1. Plot of log k_M *vs.* mole fraction of DMF, x_1, for the amination of CMPS with *s*-butylamine in DMF-dioxane mixture.
——: Calculated on the basis of Eq. 1.
----: Calculated on the basis of Eq. 2.

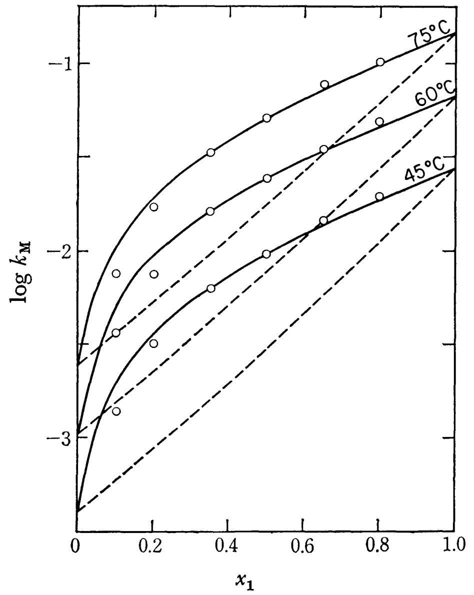

Fig. 2. Plot of log k_M *vs.* mole fraction of DMF, x_1, for the amination of benzyl chloride with *s*-butylamine in DMF-dioxane mixture.
——: Calculated on the basis of Eq. 1.
----: Calculated on the basis of Eq. 2.

values computed on the basis of Eq. 1 and of Eq. 2 respectively:

$$\log k_M = x_1 \log k_1 + x_4 \log k_4 - [x_1 \log (K+1) - \log (x_1K+1) + x_1x_4 \alpha_{14}/2.303] \qquad (1)$$

$$\log k_M = x_1 \log k_1 + x_4 \log k_4 - x_1x_4 \alpha_{14}/2.303 \qquad (2)$$

where x_1 and x_4 $(=1-x_1)$ are the mole fractions of DMF and dioxane respectively in a DMF–dioxane system, where k_1 and k_4 are the rate constants in pure DMF and dioxane respectively, where K is the equilibrium constant of the specific interaction between the activated complex and DMF, expressed by the mole fractions of the species, and where α_{14} is an empirical coefficient which is related to the interaction between DMF and dioxane. The α_{14} may be evaluated by means of this relation:[4,8]

$$\Delta G_M^E/RT = x_1x_4\,\alpha_{14} \qquad (3)$$

where ΔG_M^E represent the molar excess free energy of mixing in the binary system. The values of α_{14} and K were determined, by the procedures previously described,[4] to be:

α_{14}(at x_1=0.5)=0.408(45 °C), 0.390(60 °C), 0.374(75 °C)
K(for CMPS)=14.5(45 °C), 11.1(60 °C), 12.4(75 °C)
K(for benzyl chloride)=37.6(45 °C), 38.1(60 °C), 31.4(75 °C)

The fact that the observed values shown in Figs. 1 and 2 are well expressed by Eq. 1 suggests that the activated complex is solvated selectively with DMF to form an addition product, as has been discussed previously.[4]

By differentiating Eq. 1, Kondo and Tokura gave the following expression for the activation energy in the binary system, ΔE_M^{*}:[5]

$$\Delta E_M^{*} = x_1\Delta E_1^{*} + x_4\Delta E_4^{*} + \frac{x_1x_4(\Delta E_1^{*}-\Delta E_4^{*})}{x_1+(1/K)} \qquad (4)$$

where ΔE_1^{*} and ΔE_4^{*} represent the activation energies in the respective pure solvents.

The ΔE_M^{*} in the DMF–dioxane reaction system was computed on the basis of Eq. 4; the numerical values of E_a and log A in the pure solvents were given in

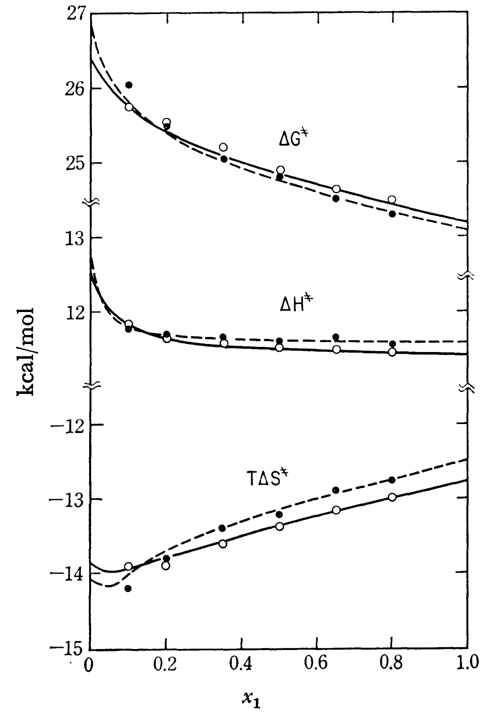

Fig. 3. Plot of the activation parameters *vs.* mole fraction of DMF, x_1, for the amination of CMPS (○) and benzyl chloride (●) with *s*-butylamine in DMF–dioxane mixture at 60 °C.
——: Calculated for CMPS.
----: Calculated for benzyl chloride.

Refs. 2 and 4. The activation parameters ($\Delta G_M^{\neq}$, $\Delta H_M^{\neq}$, and $\Delta S_M^{\neq}$) were calculated for 60 °C from the $\Delta E_M^{\neq}$ and log k_M values and plotted against x_1 in Fig. 3. The observed values of the activation parameters were obtained from the E_a and log A values listed in Table 1. The observed values expressed by the circles in Fig. 3 fall substantially on the calculated curves.

Amination with 2-Amino-1-butanol in the DMSO–Dioxane System. Although the amination of CMPS with *s*-butylamine in DMSO was heterogeneous because of the deposition of the polymer, the amination with 2-amino-1-butanol was throughly homogeneous in the overall range of the DMSO–dioxane system. Since the activated complex is also considered to be solvated with DMSO, the dependence of log k_M and $\Delta E_M^{\neq}$ on x_1, the mole fraction of DMSO, is expected to be similar to that in the DMF–dioxane system.

The amination of CMPS with 2-amino-1-butanol in pure dioxane was self-accelerated because of the neighboring group interaction;7) however, this self-acceleration diminished upon the addition of a small amount of DMSO; the amination of CMPS in the DMSO–dioxane system conformed to the second-order equation in the range of $x_1=0.16$—1.0. Table 2 shows the values of E_a and log A computed by the least squares method from the observed k_M values at various temperatures.

The plots of log k_M at 60 °C against x_1 are shown in Fig. 4. The α_{14} value used for the calculation was evaluated in accordance with Eq. 3 by using the data on the DMSO–dioxane system given by Quitzsch *et al*:9)

$$\alpha_{14}(\text{at } x_1=0.5) = 0.626(40\ ^\circ\text{C})$$

Table 2. Activation energy and frequency factor in the amination of CMPS and benzyl chloride with 2-amino-1-butanol in DMSO–dioxane mixture

x_1	Chloride	E_a, kcal/mol	log Aa)
0.16	CMPS	13.2±0.4	6.70±0.25
	Benzyl	12.7±0.1	6.34±0.09
0.32	CMPS	12.8±0.2	6.74±0.14
	Benzyl	12.3±0.3	6.49±0.21
0.50	CMPS	12.7±0.3	6.92±0.05
	Benzyl	12.8±0.4	7.16±0.25
0.66	CMPS	12.5±0.3	7.00±0.27
	Benzyl	12.5±0.6	7.15±0.41
0.82	CMPS	12.7±0.2	7.24±0.10
	Benzyl	12.4±0.1	7.32±0.09

a) A is expressed by l/mol min.

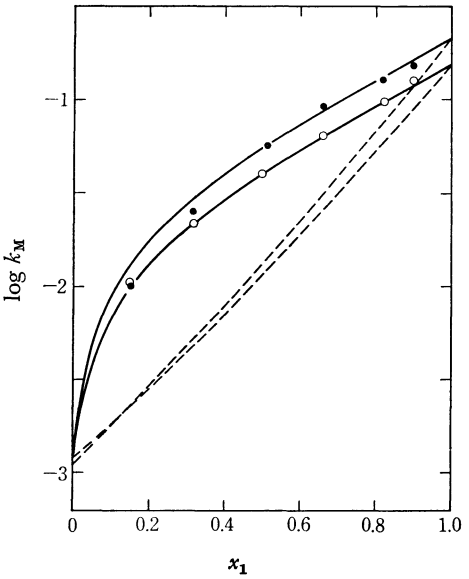

Fig. 4. Plot of log k_M *vs.* mole fraction of DMSO, x_1, for the amination of CMPS (○) and benzyl chloride (●) with 2-amino-1-butanol in DMSO–dioxane mixture at 60 °C.

——: Calculated on the basis of Eq. 1.

----: Calculated on the basis of Eq. 2.

The K values are shown in Table 3. The observed log k_M values fall substantially on the curves calculated on the basis of Eq. 1.

The $\Delta E_M^{\neq}$ values were calculated on the basis of Eq. 4. The observed values of the activation parameters for 60 °C are compared with the calculated values in Fig. 5. In the calculation of $\Delta E_M^{\neq}$, we used $\Delta E_1^{\neq}=12.5$ ckal/mol for both CMPS and benzyl chloride by considering the E_a values in pure DMSO1) and those given in Table 2. In the calculation of the solid lines in Fig. 5, we used $\Delta E_4^{\neq}=13.5$ kcal/mol for both CMPS and benzyl chloride in view of the E_a value in pure dioxane.7) Recently, however, it has been found that both the k_0 of CMPS, the rate constant independent of the neighboring groups, and the k of benzyl chloride are linear functions of the molar concentration of amine, a, for the amination with 2-amino-1-butanol in dioxane, unlike the amination in DMSO.10) The Arrhenius plot of the intrinsic rate constants, $k_{\text{int}}=\lim_{a\to 0}(k_0 \text{ and } k)$, gave $E_a=16.5$ kcal/mol. We used this value for $\Delta E_4^{\neq}$ in the caluclation of the broken lines in Fig. 5, which indicated that $T\Delta S^{\neq}$ decreases in a lower range of x_1; a similar decrease in $T\Delta S^{\neq}$ is also shown in Fig. 3 for the DMF–dioxane system.

Table 3. Equilibrium constant in the solvation of the activation complex and thermodynamic quantities in the amination with 2-amino-1-butanol at 60 °C

Solvent	Chloride	K	K_c l/mol	$\Delta G^{\neq\text{solv}}$ kcal/mol	$\Delta H^{\neq\text{solv}}$ kcal/mol	$T\Delta S^{\neq\text{solv}}$ kcal/mol	$T\delta\Delta S^{\neq\text{conf}}$ kcal/mol
DMSO	CMPS	44.6	3.83	−0.9	−4.0	−3.1	2.5
	Benzyl	63.3	5.44	−1.1	−4.0	−2.9	2.5
DMF	CMPS			−0.6	−3.4	−2.8	1.9
	Benzyl			−0.8	−3.1	−2.3	1.9

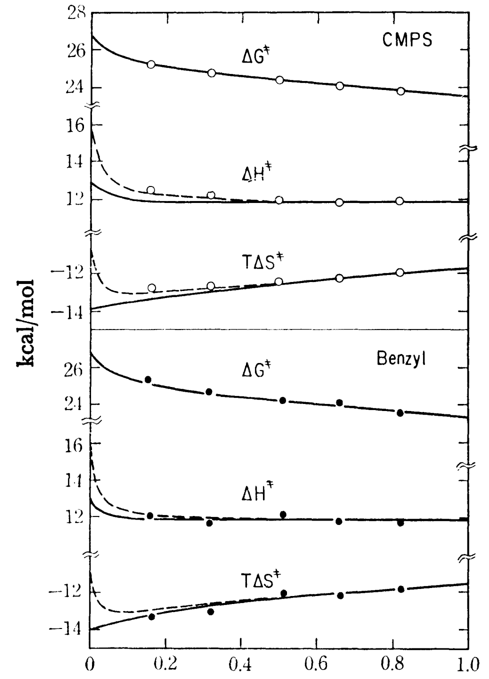

Fig. 5. Plot of the activation parameters *vs.* mole fraction of DMSO, x_1, for the amination of CMPS (○) and benzyl chloride (●) with 2-amino-1-butanol in DMSO-dioxane mixture at 60 °C.
——: Calculated by setting $E_4 = 13.5$ kcal/mol.
----: Calculated by setting $E_4 = 16.5$ kcal/mol.

Comparison between DMF–Dioxane System and DMSO–Dioxane System. The activation parameters of the amination change to various extents upon a change in solvent.[1–4] These changes are related to both the specific solvation of the activated complex in the dipolar aprotic solvents and the change in the configurational entropy of the reaction system from the initial state to the transition state, $\Delta S_1^{*\text{conf}}$.

On the basis of the present amination data with 2-amino-1-butanol in the DMSO–dioxane system, we calculated the equilibrium constant of the solvation, expressed on the basis of the molar concentration ($K_c = KV_{\text{sol}}$), the thermodynamic quantities of the solvation ($\Delta G^{*\text{solv}}$, $\Delta H^{*\text{solv}}$ and $T\Delta S^{*\text{solv}}$), and the difference between the configurational entropy change in DMSO and that in dioxane ($\delta\Delta S^{*\text{conf}} = \Delta S_1^{*\text{conf}} - \Delta S_4^{*\text{conf}}$), according to procedures described previously.[4] The value of $\Delta E_4^{*} = 16.5$ kcal/mol was employed for this calculation, because the value of $\Delta E_4^{*} = 13.5$ kcal/mol yielded $T\Delta S^{*\text{solv}} \approx 0$. The results listed in Table 3 suggest that the decrease in ΔG^{*} from dioxane to DMSO is caused not only by the negative $\Delta G^{*\text{solv}}$, but also by the positive $T\delta\Delta S^{*\text{conf}}$. The $T\delta\Delta S^{*\text{conf}}$ value is the same for CMPS and benzyl chloride. Similar findings are obtained for the DMF–dioxane–*s*-butylamine reaction system (or isobutylamine) (*cf.* Table 4 of Ref. 4). Table 3 also shows the parameters of the DMF–dioxane–2-amino-1-butanol reaction system, which were calculated from the previously reported kinetic data in pure DMF[1] on the assumption that the $\Delta G^{*\text{solv}}$ value of benzyl chloride in this system equals that in the DMF–dioxane–*s*-butylamine (or isobutylamine) system and that the difference in ΔG^{*} between CMPS and benzyl chloride is based on the difference in $\Delta G^{*\text{solv}}$. The $\delta\Delta S^{*\text{conf}}$ value in the former system thus obtained is almost the same as that in the latter system.

A comparison between the two systems in Table 3 indicates that the $\Delta G^{*\text{solv}}$ in the DMSO–dioxane system is lower than that in the DMF–dioxane system. It also indicates that the $T\delta\Delta S^{*\text{conf}}$ in the former system is higher than that in the latter system. These results may be ascribed to the fact that DMSO is more polar than DMF.

In view of Figs. 3 and 5, indicating a similar dependence of the activation parameters on x_1 for both DMF–dioxane and DMSO–dioxane systems, it seems that there is the same kind of solvation effect in both systems. Although ΔG^{*} decreases relatively uniformly with x_1, ΔH^{*} decreases sharply in the range of $x_1 < 0.2$ and then reaches an almost constant value. This may be ascribed to the selective solvation of the activated complex with the dipolar aprotic solvents; consequently, $T\Delta S^{*}$ may be expected to drop in this range. The relatively uniform increase in $T\Delta S^{*}$ in the range of $x_1 > 0.2$ may be ascribed to the relative increase in the $T\Delta S^{*\text{conf}}$ of the system, which is proportional to x_1.

The author wishes to express his thanks to Dr. Masaya Yanagita for his valuable discussions. He is also grateful to Mr. Yasunori Anami for his helpful assistance in carrying out the measurements.

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