

Influence of Cationic Polyelectrolytes on the Reaction of Chloroacetate with Thiosulfate*

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(Received December 3, 1973)

ABSTRACT: A substitution reaction of chloroacetate with thiosulfate was studied in the presence and absence of cationic polyelectrolytes. The reaction was largely enhanced by the polyelectrolytes. The acceleration did not change when the hydrophobicity of the polyelectrolytes was varied. The rate enhancement was shown to be due to a decrease in the enthalpy of activation.

KEY WORDS Thiosulfate—Chloroacetate Reaction / Polyelectrolyte Acceleration / Diallylammonium Chloride—Sulfur Dioxide Copolymer / Enthalpy of Activation /

In reactions between similarly charged ions a significant acceleration effect due to the presence of polyelectrolytes was observed; this was attributed to electrostatic interaction between ionic species and polyelectrolytes.¹ Ise and Matsui² found that poly(ethylenimine hydrochloride) had a larger rate-enhancing action for the reaction between bromoacetate and thiosulfate than its low-molecular-weight homologs. They also reported that the rate enhancement by polyethylenimine was about the same as that by a copolymer of dimethyldiallylammonium chloride and sulfur dioxide.

In this report, a substitution reaction of chloroacetate and thiosulfate anions was studied in the presence of cationic polyelectrolytes of various degrees of hydrophobicity. The polyelectrolytes used were ammonium salts which were copolymers of diallylamine derivatives and sulfur dioxide.

EXPERIMENTAL

Materials

Sodium thiosulfate and cetyltrimethylammonium bromide were of the highest commercial

grade and were used without further purification. Sodium chloroacetate was purified by recrystallization from methanol.

The synthesis of the copolymer of dimethyldiallylammonium chloride and SO₂(DE) was reported earlier.^{3,4} The diallylamine derivative was shown to copolymerize alternatively with sulfur dioxide, irrespective of the composition in feed. Such a behavior may be understood in terms of the formation of an amine—SO₂ complex.

The terpolymerization of SO₂, dimethyldiallylammonium chloride, and methylbenzyl-diallylammonium chloride was attempted in the present paper. Into a mixture of dimethyldiallylammonium chloride and methylbenzyl-diallylammonium chloride, equimolar sulfur dioxide was gradually blown to form a homogeneous viscous mixture. Then the mixture was exposed for 24 hr to light from a fluorescent lamp (Toshiba FL-4OBL) having the wavelength distribution shown in Figure 1. The whole mixture solidified into a glass-like state. The solid was dissolved in water and poured into a large amount of acetone. The precipitated polymer was collected by filtration and dried at 50°C under reduced pressure (Table I).

The IR spectra of the polymers thus obtained

* Presented at SPSJ 21st Symposium on Macromolecules, Japan, Kyoto, October, 1972.

had strong adsorption bands at 510, 1130, and 1305 cm^{-1} due to the S=O group and at 700–1000, 1500, and 1585 cm^{-1} due to the phenyl group (Figure 2). In the spectra no strong absorption at 940 or 990 cm^{-1} due to $\delta_{=\text{CH}_2}$ was

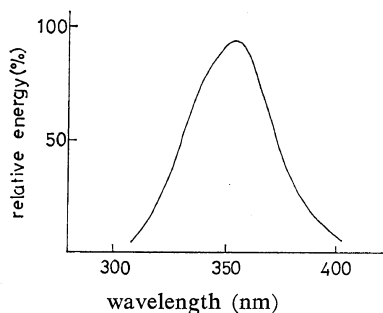


Figure 1. Wavelength distribution of the fluorescent lamp.

Table I. Ternary photocopolymerizations of dimethyldiallylammonium chloride, methylbenzyl-diallylammonium chloride, and SO_2

	DM/MBZ		Yield, %	η_{inh}^a
	In feed	In co-polymer		
DM-MBZ (I)	0.8/0.2	0.83/0.17	75	0.64
" (II)	0.6/0.4	0.66/0.34	66	0.40
" (III)	0.4/0.6	0.45/0.55	72	0.47

^a Inherent viscosity ($\ln \eta_{\text{rel}}/C$) for 0.5-g polymer/100 ml of 0.1-N NaCl aqueous solution at 30°C.

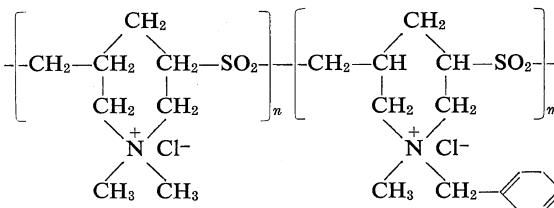
Table II. Elemental analyses of DM-MBZ

	C, %	H, %	N, %	S, %
DM-MBZ (I)	44.80	6.89	5.83	12.85
" (II)	46.98	6.74	5.61	11.33
" (III)	48.25	6.52	5.52	11.10
DM (calcd) ^a	42.56	7.14	6.21	14.20
MBZ (calcd) ^b	55.71	6.68	4.64	10.62

^a Calculated for an alternative copolymer of dimethyldiallylammonium chloride and SO_2 .

^b Calculated for an alternative copolymer of methylbenzyl-diallylammonium chloride and SO_2 .

observable. In Table II the results of elemental analyses of the polymer are given. The sulfur contents showed that sulfur dioxide copolymerized with the ammonium salt in an equimolar ratio. The terpolymer is considered to have the following structure and is abbreviated as DM-MBZ hereafter.



In Figure 3 are shown the UV spectra of an aqueous solution of DM-MBZ, together with those of DM and a copolymer of methylbenzyl-diallylammonium chloride and SO_2 (MBZ). The absorptions due to phenyl residue in the terpoly-

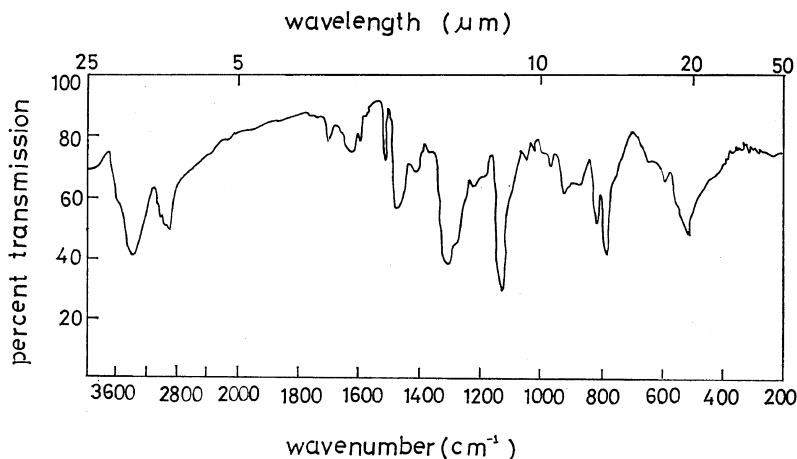


Figure 2. IR spectrum of DM-MBZ (KBr disk).

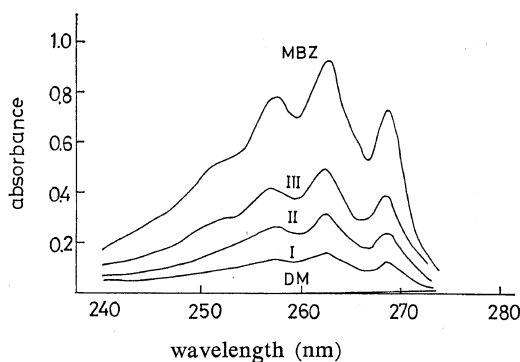


Figure 3. UV spectra of aqueous solution of DM-MBZ: [polyelectrolyte] = 2×10^{-3} monomol/l.

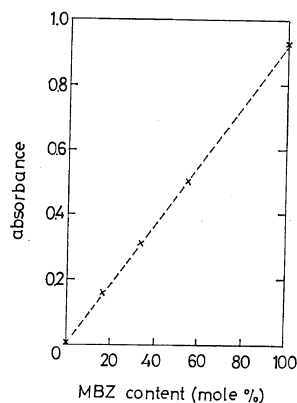


Figure 4. Determination of the composition of the DM-MBZ copolymer from the UV absorbance at 263 nm: [polyelectrolyte] = 2×10^{-3} monomol/l.

mer were observable at 257, 263, and 269 nm and they increased with increasing methylbenzylammonium chloride content. If the absorbance is assumed to be proportional to the concentration of phenyl residue, the constitution of the terpolymer can be determined from the absorbance (Figure 4). The composition given in Table I is the value thus determined.

All polymers were water-soluble; before use, they were subjected to dialysis against distilled water for ten days using a cellophane membrane.

Kinetics

The reaction was carried out in water. Stock solutions of sodium chloroacetate, sodium thiosulfate, and polyelectrolyte were mixed in an Erlenmeyer flask and placed in a thermostat (at 30°C, unless otherwise specified). At suitable intervals, aliquots of the mixture were withdrawn

and titrated with an iodine solution, using starch as an indicator; the rate constant k_2 was determined graphically using the second-order rate equation.

RESULTS AND DISCUSSION

The effect of DE on the rate constant of the reaction is shown in Figure 5. In all cases the rate constant increased with increasing amount of DE. Moreover, the acceleration by DE increased with decreasing concentration of the reactants. This is characteristic of the influence of polyelectrolytes on ionic reactions. At 0.005-M reactant concentration, k_2 was 9.68×10^{-5} 1/Msec without the polyelectrolyte, and 9.58×10^{-3} 1/Msec in the presence of 0.02 mol/l of DE; thus the rate enhancement was 100-fold.

Next, the effect of the structure of the polyelectrolytes on the rate-enhancing effect was examined; the results are summarized in Figure 6. Besides DE, DM, DM-MBZ (I), DM-MBZ (II), and DM-MBZ (III) were used. As seen from the figure, there is no difference in the rate-enhancing effect of DM and DE. The effect of DM-MBZ (I) or (II) is slightly smaller in comparison with that of DM, whereas that of DM-MBZ (III) is nearly equal.

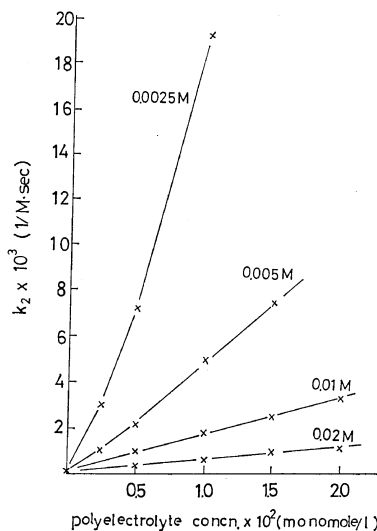


Figure 5. Rate-enhancing effects of DE on the reaction of chloroacetate with thiosulfate at 30°C. The reactant concentrations are indicated in the figure.

Rate-Enhancing Effect of Polyelectrolytes

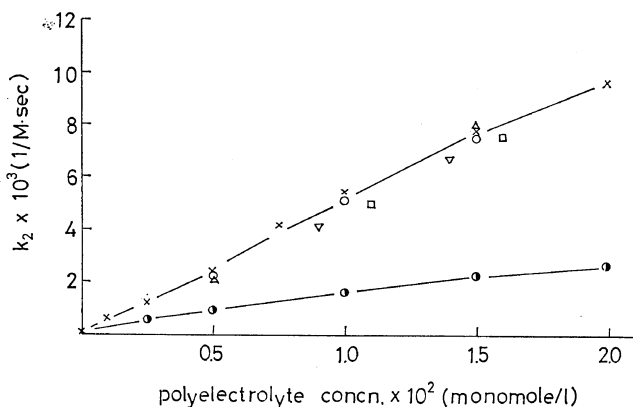


Figure 6. Rate-enhancing actions of some polycations on the reaction of chloroacetate with thiosulfate at 30°C: $[\text{Na}_2\text{S}_2\text{O}_3]=[\text{ClCH}_2\text{COONa}]=0.005\text{ M}$; \times , DM; \circ , DE; ∇ , DM-MBZ (I); \square , DM-MBZ (II); \triangle , DM-MBZ (III); \bullet , CTA.

DM-MBZ is thought to become more hydrophobic with increasing content of methylbenzylallylammonium chloride in the copolymer. The fact that no difference was found in the rate-enhancing effect of any of the three DM-MBZ copolymers, DM, or DE may suggest that the hydrophobicity of the polyelectrolytes has no influence on the reaction.

On the other hand, a significant difference was noted in the acceleration effect of DM and MBZ for other ionic reactions; for example, in the reaction of 3,5-dinitro-4-chlorobenzoate and OH^- , MBZ exhibits a larger rate-enhancing effect than DM.⁵ In that reaction, cetyltrimethylammonium bromide (CTA), a cationic surfactant, shows a much larger acceleration than MBZ. These results imply that the rate enhancement increased with the hydrophobicity of the polyelectrolyte. In the present reaction, the acceleration by CTA was smaller than that by DM or MBZ.

It should be noted that the electrostatic interactions between the polyelectrolytes and the reactant ions decrease the activity coefficients of the reactants (f_A and f_B) and even more strongly the activity coefficient of the critical complex (f_X). The Brønsted equation,⁶ $k_2/k_{20}^* = f_A \cdot f_B / f_X$, suggests that the k_2 value should be larger than the rate constant at zero ionic strength k_{20}^* ; in other words, acceleration would result, as already mentioned in the previous review.¹

Table III. Thermodynamic quantities for the reaction of chloroacetate with thiosulfate at 35°C^a

Polyelectrolyte ^b	ΔH^\ddagger , kcal/mol	ΔS^\ddagger , e.u.	ΔG^\ddagger , kcal/mol
—	17.2	-20	23.4
DM	12.8	-27	21.0
DE	12.9	-26	21.0
DM-MBZ (I)	13.0	-26	21.1
" (II)	13.0	-26	21.1
" (III)	13.2	-26	21.1

^a $[\text{Na}_2\text{S}_2\text{O}_3]=[\text{ClCH}_2\text{COONa}]=0.005\text{ M}$.

^b $[\text{polyelectrolyte}]=0.01\text{ monomol/l}$.

It is interesting to note the acceleration factors for the bromoacetate—thiosulfate reaction and the chloroacetate—thiosulfate reaction previously studied.² In spite of a large difference in the rate constant without polyelectrolytes (1.13×10^{-4} 1/Msec and 0.4 1/Msec for bromoacetate and chloroacetate, respectively), the acceleration factors were approximately equal for the two acetates: 16 for the chloroacetate at 30°C and 18 for the bromoacetate at 25°C at a polyelectrolyte concentration of 0.010 monomol/l. This indicates that the polyelectrolyte influence is determined by the valency of the reactant.

The thermodynamic quantities for the present reaction at 35°C are given in Table III. The addition of polyelectrolyte decreased the enthalpy (ΔH^\ddagger) and the entropy (ΔS^\ddagger) of activation, and

the acceleration is due to this lowering of enthalpy, as was pointed out for various reaction systems by Ise.¹

Acknowledgment. The authors wish to express their thanks to Miss M. Koyama for her assistance in the experimental work and Mr. K. Takabayashi for carrying out the elemental analyses.

REFERENCES

1. For a convenient review on this subject, see review articles presented by N. Ise at the Symposium on Polyelectrolytes, Pasadena, May 1973, and at the Advanced Studies Institute, Troy, New York, July 1973, to be published, in which earlier studies are referred to.
2. N. Ise and F. Matsui, *J. Amer. Chem. Soc.*, **90**, 4242 (1968).
3. S. Harada and K. Arai, *Makromol. Chem.*, **107**, 64 (1967).
4. S. Harada and K. Arai, *ibid.*, **107**, 78 (1967).
5. T. Ueda, S. Harada, and N. Ise, *Polymer J.*, **6**, 319 (1974).
6. J. N. Brønsted and R. Livingston, *J. Amer. Chem. Soc.*, **49**, 435 (1927).