

Influence of Cationic Polyelectrolytes in the Aromatic Nucleophilic Substitution Reaction of 3,5-Dinitro-4-chlorobenzoate*

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(Received December 3, 1973)

ABSTRACT: The aromatic nucleophilic substitution of 3,5-dinitro-4-chlorobenzoate with OH^- was studied in the presence and absence of cationic polyelectrolytes. The cationic polyelectrolytes enhanced the reaction much more appreciably than did the low-molecular-weight electrolytes. The more hydrophobic the polyelectrolyte, the larger the rate enhancement. The acceleration observed was due to a decrease in the enthalpy of activation, as has been found for a variety of reaction systems studied previously.

KEY WORDS Aromatic Nucleophilic Substitution / 3,5-Dinitro-4-chlorobenzoate / Polyelectrolyte Acceleration / Hydrophobic Interactions / Enthalpy of Activation / Dimethyldiallylammonium Chloride—Methylnaphthomethyldiallylammonium Chloride—Sulfur Oxide Terpolymer /

It is now well established that interionic reactions can be noticeably influenced by polyelectrolyte addition.¹ As a continuation of our study on polyelectrolyte influence in interionic reactions we report here the S_NAr reaction of 3,5-dinitro-4-chlorobenzoate with hydroxide ion. The effects of low-molecular-weight ammonium salts and cationic polyelectrolytes on the reaction rate were investigated.

EXPERIMENTAL

Materials

3,5-dinitro-4-chlorobenzoic acid (DNCBA) was twice recrystallized from benzene. Quaternary salts, such as tetramethylammonium chloride [TMACl], trimethylbenzylammonium chloride [TMBACl], tetrabutylammonium chloride [TBACl], and cetyltrimethylammonium bromide [CTABr], were of the GR grade and were used without further purification.

* Presented at SPSJ 20th Annual Meeting, Japan, Tokyo, 1972.

The polycations used were alternative copolymers of diallylamine derivatives and SO_2 ; namely, copolymers of dimethyldiallylammonium chloride and SO_2 (DM), methylbenzyldiallylammonium chloride and SO_2 (MBZ), and methyl-*p*-nitrobenzyldiallylammonium chloride and SO_2 (MNBZ). The syntheses of the copolymers were reported earlier.^{2,3}

In addition to the copolymers, a terpolymer of dimethyldiallylammonium chloride—methylnaphthomethyldiallylammonium chloride— SO_2 (DM-Nap) was synthesized as follows. First, naphthalene was chloromethylated according to the method of Cambron.⁴ A mixture of naphthalene, paraformaldehyde, glacial acetic acid, concentrated hydrochloric acid, and phosphoric acid was heated to 98–100°C with stirring for 5 hr. Then the mixture was thoroughly washed with water and distilled under a reduced pressure, bp 147–152°C/7 mmHg (lit. 145–160°C/6–8 mmHg),⁴ yield 52%. 1-Chloromethylnaphthalene (80 g) thus obtained, freshly distilled methyldiallylamine (50 g), and benzene (130 g)

were mixed and kept standing at room temperature for a week. Then the benzene and the unreacted reactants were distilled off under a reduced pressure. The residual glassy solid was methylnaphthomethylallylammonium chloride at a yield of 9.3%; this was washed with benzene several times and dried under vacuum. Into a mixture of dimethyldiallylammonium chloride (DM monomer) and methylnaphthomethylallylammonium chloride (Nap monomer), equimolar SO_2 (to both the quaternary ammonium salts) was slowly introduced; the gas was quickly absorbed into the monomers with generation of heat to form a viscous homogeneous mixture. The mixture was exposed to light from a fluorescent lamp (Toshiba FL-40BL) for 24 hr. The whole mixture solidified to 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 a reduced pressure. Three kinds of terpolymers with various monomer ratios were prepared (Table I).

The IR spectra of the polymers thus obtained (Figure 1) showed absorptions at 1305, 1130, and 515 cm^{-1} due to $\text{S}=\text{O}$ and 1595 and 1510 cm^{-1} due to the naphthalene residue. In the spectra, no strong absorption at 990 and 940 cm^{-1} due to $\delta_{=\text{CH}_2}$ was observable. In Table II, the results of elemental analyses of the terpolymers

Table I. Ternary photocopolymerization of dimethyldiallylammonium chloride, methylnaphthomethylallylammonium chloride, and sulfur dioxide

	DM/Nap		Yield, %	η_{inh}^b
	In feed	In co-polymer ^a		
DM-Nap (I)	0.75/0.25	0.77/0.23	66	0.13
" (II)	0.50/0.50	0.61/0.39	54	0.11
" (III)	0.25/0.75	0.32/0.68	42	

^a Composition of copolymer was calculated from the C value of the elemental analyses.

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

are given. The values of each element are intermediate between DM(calcd) and Nap(calcd). From this fact, the terpolymer is believed to have the following structure and is abbreviated as DM-Nap.

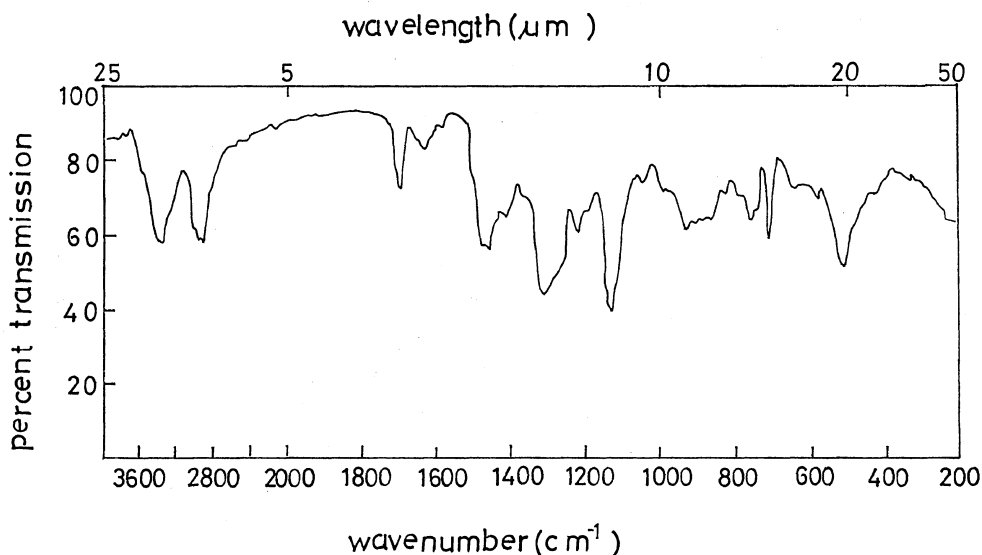
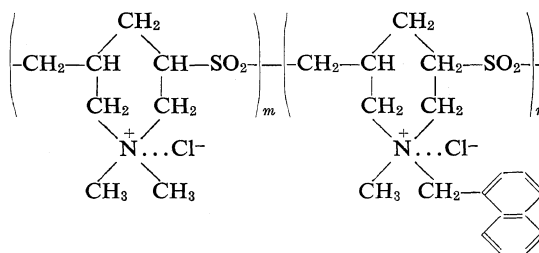


Figure 1. IR spectra of DM-Nap (KBr disk).

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Table II. Elemental analyses of DM-Nap

	C, %	H, %	N, %	S, %
DM-Nap (I)	46.90	7.01	5.65	13.01
" (II)	49.89	6.89	5.33	12.19
" (III)	55.33	6.59	4.68	10.66
DM (calcd) ^a	42.56	7.14	6.21	14.20
Nap (calcd) ^b	61.44	6.30	3.98	9.11

^a Calculated for an alternative copolymer of dimethylallylammonium chloride and SO₂.

^b Calculated for an alternative copolymer of methyl-naphthomethylallylammonium chloride and SO₂.

DM-Nap was water-soluble, but the solubility decreased with increasing Nap content in the terpolymer and the copolymer without DM component was hardly soluble in cold water.

Polyvinylpyrrolidone (PVP) was obtained from the Nakarai Chemical Co., Kyoto. The molecular weight was 24,500.

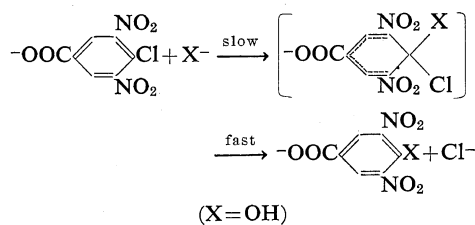
All polymers were subjected to dialysis for ten days against distilled water, using a cellophane membrane.

Kinetics

The reaction was carried out in aqueous media. Stock solutions of DNCBA, NaOH, and polycation were mixed in an Erlenmeyer flask and placed in a thermostat. At intervals, a portion of the solution was transferred to an optical cell and the appearance of 3,5-dinitro-4-hydroxybenzoic acid was followed by a UV spectrophotometer (Hitachi EPS-3T) at 425 nm. The second-order rate constant k_2 was calculated graphically. Rapid reactions were followed directly in the spectrophotometer with a water-jacketed cell compartment around which water from a thermostat was circulated.

RESULTS AND DISCUSSION

DNCBA reacts with nucleophilic reagents such as hydroxide ions, amines, thiols, *et al.* However, the reactions of DNCBA with those reagents have not been studied kinetically so far. Thus we first studied the reaction of DNCBA with hydroxide ions kinetically and determined the second-order rate constant at 30°C (Table III). It is believed that the S_NAr reaction proceeds as follows.

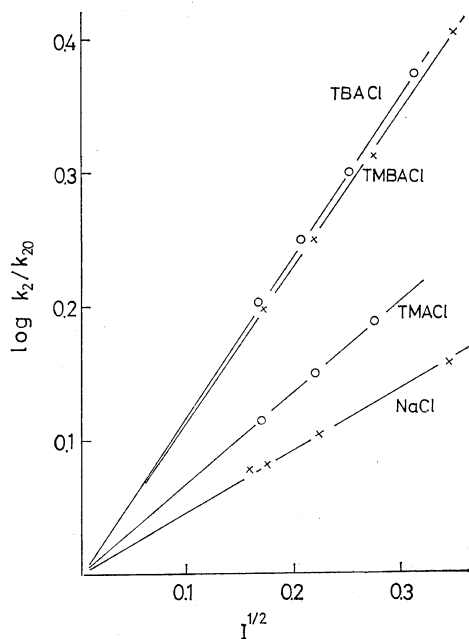

Table III. Second-order rate constant for the S_NAr reaction of DNCBA with OH⁻ at 30°C^a

NaCl, M	$k_2 \times 10^3$, 1/M sec
—	0.954
—	0.963 ^b
—	0.950 ^c
0.005	0.987
0.01	0.997
0.03	1.05
0.1	1.18
0.3	1.34

^a [NaOH], 1.98×10^{-2} N; [DNCBA], 10^{-4} M, unless otherwise stated.

^b [NaOH], 3.96×10^{-2} N.

^c [DNCBA], 10^{-4} M.


Figure 2. The effect of simple electrolytes on the reaction rate of the S_NAr reaction of DNCBA at 30°C: [DNCBA], 2×10^{-4} M; [NaOH], 1.98×10^{-2} N.

The reaction was enhanced by the addition of sodium chloride (as is shown in Figure 2). This is the primary salt effect for reactions between similarly charged ions.

Quaternary ammonium salts, such as TMACI, TMBACI, TBACI, and CTABr, showed a rate-enhancing influence. In Figure 2, $\log k_2/k_{20}^*$ is plotted as a function of the square root of ionic strength (I) (k_{20}^* denotes the rate constant at zero ionic strength). The plots gave, except for CTABr, straight lines at the ionic strengths studied (the behavior of CTABr will be discussed later). The rate constant increased in the order $TBACI \approx TMBACI > TMACI > NaCl$. The acceleration is mainly due to the cations, since the anionic components of these salts are identical. The more bulky or hydrophobic the cation, the more the reaction was accelerated.

Then, the effect of the cationic polyelectrolyte on the rate constant was examined; the results are summarized in Figures 3 and 4.

In these figures, the broken lines show the rate constant value without the electrolytes. It should be noted that the cationic polyelectrolytes have larger acceleration effects at lower concentrations than do the low-molecular-weight electrolytes, such as NaCl, and simple quaternary salts. The rate constant increased with increasing concentration of the polycations, and finally leveled off or decreased. The rate enhancement is 20–30 fold at the maxima. It is seen that the higher the Nap content in the terpolymer, the larger the rate-enhancing effect of DM-Nap. Also, MBZ and MNBZ containing phenyl residue

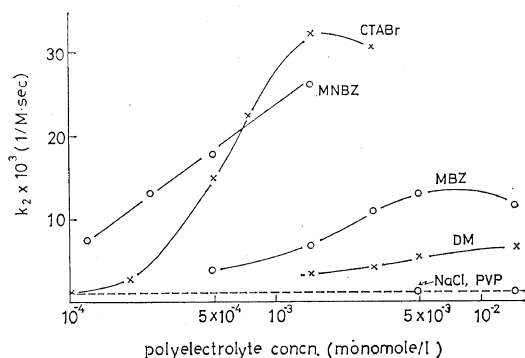


Figure 3. Polyelectrolyte influence on the S_NAr reaction of DNCBA at 30°C: [DNCBA], $2 \times 10^{-4} M$; [NaOH], $1.98 \times 10^{-2} N$.

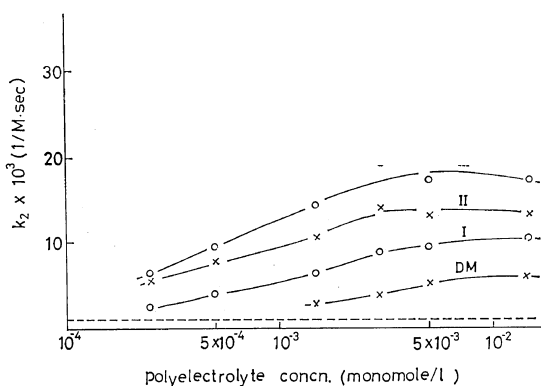


Figure 4. Influence of DM-Nap in the S_NAr reaction of DNCBA at 30°C: [DNCBA], $2 \times 10^{-4} M$; [NaOH], $1.98 \times 10^{-2} N$.

showed a larger rate-enhancing effect than did DM containing no phenyl residue (Figure 3). From these facts it may be concluded that the rate enhancement becomes larger with increasing hydrophobicity of the polycations. These results are consistent with those obtained for low-molecular-weight quaternary ammonium salts and suggest the importance of the hydrophobic interactions in the reaction.

The behavior of CTABr makes the point clearer. As shown in Figures 2 and 3, the rate enhancement by the low-molecular-weight quaternary salts (TMACI, TMBACI, TBACI), which do not form micelles, are much lower than those by the polycations. The effect of CTABr is small at low concentrations; however, above $3-5 \times 10^{-4} M$ (which corresponds to the critical micelle concentration of CTABr in aqueous NaOH),⁶ it increased sharply and became larger than that of the polycations. This behavior is attributed to the formation of hydrophobic micelles of CTABr. On the other hand, polyvinylpyrrolidone (PVP), which is a hydrophobic nonionic polymer, showed no rate enhancement at all, as is shown by the broken line in Figure 3.

From these results it became apparent that the effect of the polycations was due to both electrostatic and nonelectrostatic, particularly hydrophobic, interactions between the substrate ions and the polyelectrolytes of the two kinds of reactant ions, i.e., hydroxide ions and 3,5-dinitro-4-chlorobenzoate ions; the former interacts only electrostatically with the polycations and the

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 Table IV. Temperature dependence of the S_NAr reaction^a

Temp, °C	Electrolyte, monomol/l	$k_2 \times 10^{-3}$, l/M sec	k_2/k_{20}
25	—	0.623	1.0
	NaCl	3×10^{-1}	0.743
	DM	3×10^{-3}	2.69
	MBZ	"	7.72
	MNBZ	1.5×10^{-3}	18.7
30	—	0.954	1.0
	NaCl	3×10^{-1}	1.34
	DM	3×10^{-3}	3.98
	MBZ	"	10.8
	MNBZ	5×10^{-3}	26.0
35	—	1.60	1.0
	NaCl	3×10^{-1}	2.20
	DM	3×10^{-3}	6.68
	MBZ	"	17.4
	MNBZ	1.5×10^{-3}	37.4

^a [DNCBA], 2×10^{-4} M; [NaOH], 1.98×10^{-2} N.

latter both electrostatically and hydrophobically. These interactions lower the activity coefficients of the reactants (f_A and f_B) and even more appreciably that (f_X) of the divalent activated complex. According to the Brønsted equation, $k_2/k_{20}^* = f_A \cdot f_B / f_X$,⁵ these changes in the activity coefficients should cause rate enhancement.

The larger rate-enhancing effect of MNBZ compared with MBZ may be considered to be due to the stronger affinity of the former for 3,5-dinitro-4-chlorobenzoate through van der Waals interactions.

The temperature dependence of the reaction rate is illustrated in Table IV. From these data the thermodynamic parameters of the reaction at 30°C were calculated; these are shown in Table V. The addition of the polycations decreased the enthalpy (ΔH^\ddagger), entropy (ΔS^\ddagger), and free

 Table V. Thermodynamic quantities for the S_NAr reaction of DNCBA at 30°C

Electrolyte, monomol/l	ΔH^\ddagger , kcal/mol	ΔS^\ddagger , e.u.	ΔG^\ddagger , kcal/mol
—	18.1	-13	21.9
NaCl	3×10^{-1}	-7.6	21.8
DM	3×10^{-3}	-17	21.0
MBZ	3×10^{-3}	-22	20.5
MNBZ	1.5×10^{-3}	-26	20.0

energy (ΔG^\ddagger) of activation; the acceleration is due to the lowering of the enthalpy (or the activation energy), as was observed for a variety of reaction systems.¹ On the other hand, the addition of NaCl resulted in an increase of ΔH^\ddagger and ΔS^\ddagger ; the decrease of ΔG^\ddagger and the acceleration was due to the increase of the entropy.

Acknowledgment. We express our thanks to Mr. M. Haruta for his valuable discussions and to Mr. K. Takabayashi for carrying out the elemental analyses.

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