Catalysis by Cationic Polyelectrolytes in Hydrolysis of Dinitrophenyl Phosphate Dianions

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ABSTRACT: The hydrolysis of dinitrophenyl phosphate dianions was studied in the presence of cationic polyelectrolytes. The polyelectrolytes used were dimethyldiallyl-ammonium chloride—SO_2 copolymer (DM), diethyldiallylammonium chloride—SO_2 copolymer (DE), methylbenzyldiallylammonium chloride—SO_2 copolymer (MBZ) and methyl-*p*-nitrobenzyldiallylammonium chloride—SO_2 copolymer (MNBZ). The hydrolysis was a first-order reaction both in the presence and in the absence of the polyelectrolytes and was largely accelerated thereby as a consequence of the electrostatic interactions, even more appreciably than by low molecular weight electrolytes. For both 2,4-dinitro- and 2,6-dinitrophenylphosphates, the acceleration factor was in the order MNBZ > MBZ > DE > DM, the largest factors being about 60 and 20 for 2,4- and 2,6-phosphates, respectively. The acceleration was found to be again due to the enthalpy decrease; the activation entropy was shown to decrease by polyelectrolyte addition.

KEY WORDS Polyelectrolyte Catalysis / Dinitrophenyl Phosphate / Diallylammonium Chloride—SO_2 Copolymers / Solubility / Entropy of Activation /

In a continuation of our work on polyelectrolyte catalysis in ionic reactions,[1-4] we report here the catalytic action of cationic polyelectrolytes in the hydrolysis of dinitrophenyl phosphate dianions. This reaction has been established to be of the first order,[5,6] unlike the reactions so far studied in this laboratory, which were of the second order. It has also been established[5,6] that the dianions undergo the spontaneous decomposition into a phenoxide ion and the metaphosphate ion. Bunton, *et al.*, have demonstrated

$$ArOPO_3{}^{2-} \rightarrow [ArO^- \cdots PO_3{}^-] \rightarrow ArO^- + PO_3{}^-$$
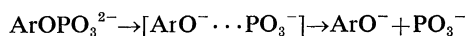
furthermore[6] that this reaction was largely accelerated by cetyltrimethylammonium bromide, a cationic surfactant, at concentrations above the CMC.

We prepared polyelectrolytes of a quaternized ammonium salt type such as dimethyldiallyl-ammonium chloride—SO_2 copolymer (DM), diethyld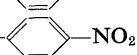iallylammonium chloride—SO_2 copolymer (DE), methylbenzyldiallylammonium chloride—SO_2 copolymer (MBZ), and methyl-*p*-nitrobenzyldiallylammonium chloride—SO_2 copolymer (MNBZ), and investigated polyelectrolyte catalyses in the hydrolysis of the phosphate dianions mentioned above. The syntheses of DM and DE were reported in detail earlier[7,8] and DM was used in the previous work[1] with an abbreviation of DACS. MBZ and MNBZ are novel.
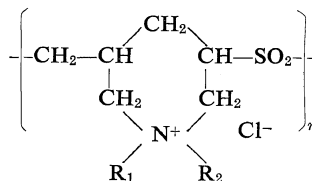
DM, $R_1 = R_2 = CH_3$
DE, $R_1 = R_2 = C_2H_5$
MBZ, $R_1 = CH_3$, $R_2 = CH_2-\langle\text{phenyl}\rangle$
MNBZ, $R_1 = CH_3$, $R_2 = CH_2-\langle\text{phenyl}\rangle-NO_2$

EXPERIMENTAL

Materials

Dinitrophenyl phosphate

2,4- and 2,6-dinitrophenyl phosphates (2,4-DNPP and 2,6-DNPP) were prepared according to the methods described by Bunton, et al.[5] Dinitrophenol and phosphorous oxychloride were heated under reflux, and dinitrophenyl phosphoryl dichloride was obtained. The dichloride was treated with silver oxide and then with cyclohexylamine hydrochloride. This treatment gave the monohydrate of dinitrophenyl phosphate monocyclohexylamine salt. The melting point was 145°C for 2,4-DNPP and 146°C for 2,6-DNPP. The literature values are 147 and 146°C, respectively.[5]

Polyelectrolytes

Monomer of MBZ. Distilled methyldiallylamine (111 g), benzyl chloride (127 g), and benzene (240 g) were mixed and kept standing at room temperature for one week. Then benzene and the unreacted reactants were distilled off under reduced pressure. The residual viscous fluid was methylbenzyldiallylammonium chloride at a yield of 70%, which was washed with benzene several times and dried under vacuum.

Monomer of MNBZ. Distilled methyldiallylamine (22 g), *p*-nitrobenzyl chloride (34 g) and acetone (60 g) were mixed. The quaternized product precipitated from the mixture as light yellow crystals at a yield of 85%, which were recrystallized from a mixture of ethanol and acetone (1 : 5 by volume).

Copolymerization with SO₂. A methanol solution of *tert*-butylhydroperoxide (10%) was added drop by drop with stirring into methanol solution of methylbenzyldiallylammonium chloride or methyl-*p*-nitrobenzyldiallylammonium chloride and SO_2. Copolymerization took place instantaneously. The reaction mixture was poured into aceton to separate MBZ, which was dissolved in methanol and precipitated with acetone. In the case of MNBZ, the raw product was washed with ethanol to remove unreacted monomer and initiator. In Table I, polymerization conditions are shown. Table II gives the results of the elemental analysis of MBZ and MNBZ. For these polymers, the observed results are in rough agreement with the theoretical values obtained with an assumption that the copolymer contains the chloride and SO_2 with a ratio of 1 : 1. The IR spectra (Figure 1) show adsorptions at 1125 cm^{-1} and 1305 cm^{-1}, which correspond to ν_s (S=O) and ν_a (S=O), In the spectra, no strong adsorption at 990 cm^{-1} due to out-of-plane deformation vibration of the C—H bond in the allyl double bond is observable. Thus, MBZ and MNBZ are believed to be alternating copolymers of the respective chloride and SO_2, as was described above.

Ternary copolymerization of methylbezyldiallylammonium chloride, *p*-nitrobenzyldiallylammonium chloride and SO_2 was also tried. The polymerization condition and the characterization of the copolymer will be described in a forthcoming paper. The copolymer obtained is denoted by MBZ—MNBZ.

All polymers prepared were water-soluble. Before use, the polymers were subjected to dialysis against distilled water for ten days.

Table I. Preparation of the cationic polyelectrolytes

	Monomers		Methanol,[a] ml	*t*-BHP,[b] g	Temp, °C	Yield, g	η_{inh}[c]
	Amine, g	SO₂, g					
MBZ	125	34	350	5.65	28—33	120	0.15
MNBZ	51	11	50	1.87	25—32	25	
DM	152	64	500	4.46	27—33	183	0.21
DE	165	65	530	4.59	26—32	192	0.43

[a] Solvent.

[b] *tert*-Butyl hydroperoxide.

[c] Inherent viscosity for 0.5 g of polymer/100 ml of 0.1-*N* NaCl aqueous solution at 30°C. MNBZ is insoluble to the solvent at 30°C.

Table II. Elemental Analyses of MBZ and MNBZ

	C, %	H, %	N, %	S, %
MBZ				
Obsd	53.89	6.86	4.18	10.42
Calcd	55.71	6.68	4.64	10.64
MNBZ				
Obsd	46.86	5.59	7.61	10.47
Calcd	48.48	5.52	8.08	9.24

Solubility of the Polyelectrolytes in Water and Aqueous Sodium Chloride Solution

DM and DE are highly soluble in water, but MBZ and MNBZ have limited solubilities. At room temperature the solubilities of the latter two are 16 g/100 cc and 0.6 g/100 cc, respectively.

DM and DE are soluble in aqueous sodium chloride solutions of concentrations higher than 1 M at room temperature. The incorporation of benzene ring and nitro group into polymer decreases sharply the solubility. In Figure 2, the phase separation temperature of MBZM—NBZ is given as a function of the content (in feed) of the nitrobenzyldiallylammonium chloride monomer. It is seen that the larger the content, the higher the phase separation temperature. The phase separation temperature is raised with increasing concentration of sodium chloride. In the case of 1 M solution of sodium chloride, the copolymer being discussed was not soluble.

The experimental results suggest that the solubility of the cationic polyelectrolytes decreases with the order DM, DE > MBZ > MNBZ. Evidently, the hydrophobicity of the benzene ring caused a lowering of solubility.

Kinetics

The hydrolysis was carried out in water, and the pH was maintained at 9 by using a borate

(a) MBZ
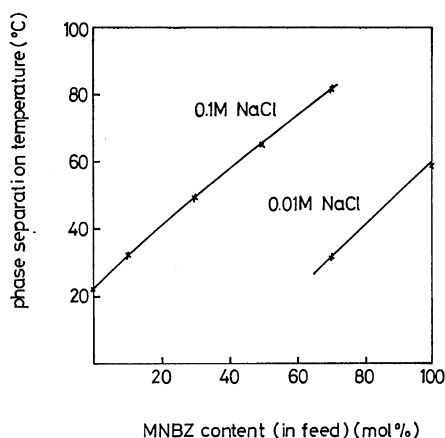

(b) MNBZ
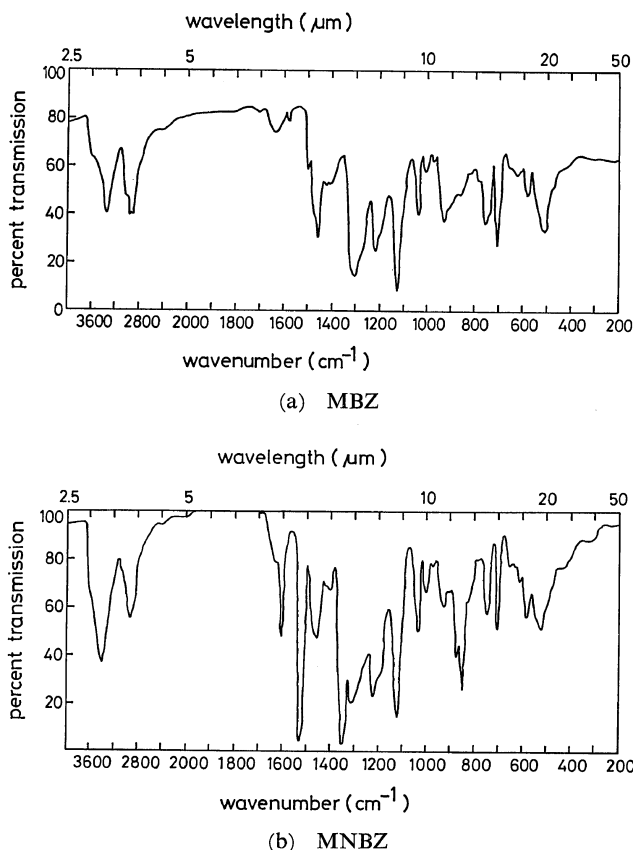
Figure 1. IR spectra of MBZ and MNBZ (KBr disk).

Figure 2. Phase separation temperature of the MBZ—MNBZ copolymer in aqueous solutions of sodium chloride: [copolymer], 0.5 g/100 ml.

RESULTS AND DISCUSSION

Addition of low molecular weight salts could accelerate the hydrolysis. Table III shows the results on 2,4-DNPP, which appears to indicate that the acceleration is mainly due to cations.

The rate constants of the hydrolysis of 2,4- and 2,6-DNPP in the presence and absence of polyelectrolytes are given in Figures 4 and 5, respectively. k and k_0 are the rate constants with and without the polyelectrolyte. When the polyelectrolyte concentration is as high as or higher than the substrate concentration, the hydrolysis was largely accelerated. For both 2,4- and 2,6-DNPP, the acceleration factor increased in the order DM < DE < MBZ < MNBZ. It is to be noted that, at the same concentration, low molecular weight salts such as NaCl and tetra-

Table III. Catalysis of low-molecular-weight salts in the hydrolysis of 2,4-DNPP[a]

Salt	Concn, equiv/l	$k \times 10^5$, 1/sec
—	—	3.7
NaCl	0.25	4.4
"	0.50	5.5
BaCl$_2$	0.25	17
"	0.50	28

[a] [2,4-DNPP], 6.78×10^{-5} M; [buffer], 1.5×10^{-2} M; 35°C.

buffer. At this pH, 2,4- and 2,6-DNPP are dissociated to the corresponding dianions. The appearance of dinitrophenoxide was followed by a UV spectophotometer (Hitachi EPS-3T) at 358 mμ and 431 mμ for 2,4- and 2,6-DNPP. As will be discussed later, the addition of MBZ and MNBZ caused a shift in the absorbance of the dinitrophenoxide, so that control experiments were carried out using dinitrophenoxide—polymer solutions of known compositions. The hydrolysis was found to be of the first order over a wide range of conversion, as shown in Figure 3.
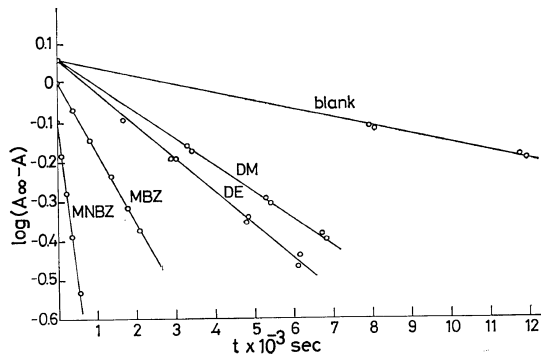

Figure 3. First-order plot of the hydrolysis of 2,4-DNPP: 35°C; pH, 9.2; [copolymer], 5×10^{-4} equiv/l. A and A_∞ represent absorbances of 2,4-dinitrophenoxide ion at time $= t$ and ∞.

Figure 4. Catalysis in the hydrolysis of 2,4-DNPP: 30°C; [2,4-DNPP], 7.7×10^{-5} M; [borate buffer], 3×10^{-3} M; pH, 9.
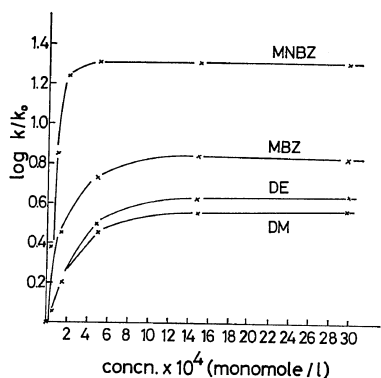
Figure 5. Polyelectrolyte catalysis in the hydrolysis of 2,6-DNPP: 25°C; [2,6-DNPP], 1.53×10^{-4} M; [borate buffer], $3 \times 10^{-3} M$; pH, 9.

Table IV. Thermodynamic quantities for the hydrolysis of 2,4-DNPP at 30°C[a]

Polyelec-trolytes	Concn, equiv/l	$\Delta H^{\neq}$, kcal/mol	$\Delta S^{\neq}$, e.u.	$\Delta G^{\neq}$ kcal/mol
—	—	25	2.2	24.3
DM	5×10^{-4}	24	1.8	23.6
DE	〃	23	−1.4	23.3
MBZ	〃	21	−6.2	22.8
MNBZ	〃	18	−12	21.9

[a] [2,4-DNPP], $7.7 \times 10^{-5} M$; [Buffer], $3 \times 10^{-3} M$.

methylammonium chloride (TMACl) showed negligibly small acceleration factors.

We further note the superiority of the polyelectrolytes over the cationic detergents. The latter could accelerate the hydrolysis[6] to the same extent as by the former, only when the concentration of the latter is ten times higher than the substrate concentration. No catalysis was found below the CMC.[6]

It is to be remarked that neutral polymers such as polyvinylpyrolidone (PVP) and polyethylene glycol (PEG) did not show any acceleration. This implies that the observed acceleration is, in the first place, due to electrostatic interactions. Factors other than this interaction are not negligible, however. Actually, the fact that the acceleration factors varied with the polycations suggests that non-electrostatic interactions are of the secondary importance, since all of the polyelectrolytes under consideration are strongly basic and can be regarded as completely dissociated at the hydrolysis condition (pH=9). It is interesting to note that the catalytic action is in parallel with the solubility of the polyelectrolyte. In other words, the more hydrophobic the polyelectrolyte, the larger the acceleration factor. Evidently, the hydrophobic interactions between the substrate and the polyelectrolyte are factors determining the catalytic action of the polyelectrolyte. Furthermore, the largest catalysis of MNBZ suggests the likewise important role of the van der Waals interaction between the nitro groups in the substrate and the polyelectrolyte.

Table IV shows thermodynamic parameters of the hydrolysis. The addition of the polyelectrolytes decreased the enthalpy ($\Delta H^{\neq}$), entropy ($\Delta S^{\neq}$) and free energy ($\Delta G^{\neq}$) of activation. In accord with the previous finding on polyelectrolyte catalysis in ionic reactions[1,2,4] and also with the previous observation for the micellar-catalyzed hydrolysis of the substrate under consideration,[6] the acceleration is due to lowering of the enthalpy (or the activation energy),[9] since the decrease in $\Delta S^{\neq}$ should act to decelerate the reaction. These observed changes of the thermodynamic quantities are consistent with the previous interpretation[6] that the phosphorous-oxygen bond angles were changed toward those of the metaphosphate ion by the electrostatic effect so that the reaction may be accelerated.

The large acceleration by the polyelectrolytes was diminished by addition of low molecular weight electrolytes. Table V shows the results for MNBZ. The diminution would be a consequence of competitive interaction of the anions of the

Table V. Influence of electrolytes on catalysis by MNBZ in the hydrolysis of 2,4-DNPP[a]

Electrolyte	$k \times 10^4$, 1/sec
—	5.3
NaCl	5.1
Na₂SO₄	3.9
Phthalic acid	3.5
3-Nitrophthalic acid	3.2
4-Nitrophthalic acid	1.9
3,6-Dinitrophthalic acid	1.0
3,5-Dinitrobenzoic acid	4.3
3,4-Dinitrobenzoic acid	3.7

[a] 25°C; [2,4 DNPP], $0.718 \times 10^{-4} M$; [borate buffer]; $10^{-2} M$; pH, 9; [MNBZ], 10^{-4} equiv/l; [electrolyte], $2 \times 10^{-4} M$.
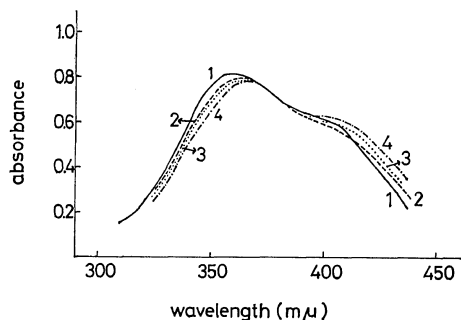
Figure 6. Spectral changes of 2,4-dinitrophenoxide ions induced by addition of MBZ: [Phenoxide], $5.5 \times 10^{-5} M$; pH, 9. MBZ concn (equiv/l): curve 1, 0; curve 2, 1.17×10^{-4}; curve 3, 5×10^{-4}; curve 4, 3.5×10^{-3}.
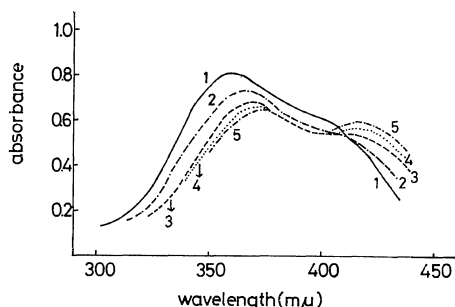

Figure 7. Spectral changes of 2,4-dinitrophenoxide ions induced by addition of MNBZ: [Phenoxide], $5.5 \times 10^{-5} M$; pH, 9. MNBZ concn (equiv/l): curve 1, 0; curve 2, 3.3×10^{-5}; curve 3, 1.17×10^{-4}; curve 4, 5×10^{-4}; curve 5, 3.5×10^{-3}.

third electrolytes and the substrate dianions with polycations. It is seen that divalent anions are more effective retarders than the monovalent anions. Furthermore, the more nitro groups the phthalic acid derivatives contain, the more strongly the acceleration is diminished. This indicates that, in addition to the electrostatic and hydrophobic interactions, van der Waals interactions are important to the catalysis by MNBZ.

Finally mention should be made on the changes in the spectra of 2,4-dinitrophenoxide ions by the presence of MBZ and MNBZ. When MBZ is added, the absorbance at $358 \, m\mu$ was slightly decreased, and the absorption maximum redshifted by a few $m\mu$. The shift became larger

with increasing polyelectrolyte concentration. For MNBZ, these changes were more distinct than for MBZ. When the polyelectrolyte concentration is high, a new maximum appeared at $415 \, m\mu$. On the other hand, no change was observed for DM and DE in a concentration range 10^{-4}—3.5×10^{-3} equiv/l. We should note here that the addition of trimethylbenzylammonium chloride and methyl-p-nitrobenzyldillyl-ammonium chloride (a monomeric substance of MNBZ) did not influence the spectra even at electrolyte concentration of 3.5×10^{-3} equiv/l. Though it was not possible to observe any change in the spectra of 2,4-DNPP because of the overlapping with those of the polyelectrolytes, it is interesting that the magnitude of polyelectrolyte catalysis is in parallel with the spectral change by polyelectrolyte addition, which is probably due to the metachromasis.

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