Polyelectrolyte Catalysis of the Alkaline Hydrolysis of Neutral and Anionic Esters [1]

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Alkaline hydrolysis of *p*-nitrophenyl acetate (PNPA), 4-acetoxy-3-nitrobenzoic acid (NABA), and 4-acetoxy-3-nitrobenzenearsonic acid (NABAA), has been carried out in the presence of cationic polyelectrolytes of varying degree of hydrophobic character or micelles. Ion–molecule and ion–ion reactions are accelerated by cationic polyelectrolytes, and the acceleration becomes larger with increasing hydrophobic character of the esters and/or polyelectrolytes. Polyelectrolyte catalysis is analysed in terms of saturation kinetics, and the equilibrium association constant and the rate coefficients of the polyelectrolyte–ester complex are calculated. The relative catalytic contributions of the electrostatic and hydrophobic interactions is discussed.

It is well known that the rate of various kinds of chemical reactions are strikingly influenced by polyelectrolytes [2] or micelles.[3] However, a clearcut elucidation of the mechanism of the catalytic action of polyelectrolytes has not been achieved.† We reported previously [6] data on the effect of polyelectrolytes on the hydrolysis of *p*-nitro-

† The term ' polyelectrolyte catalysis ' is used in this paper with its customary meaning. However, we do not imply that the polyelectrolytes are really catalysts as defined by Ostwald.[4,5]

[1] Presented at the 31st Annual Meeting of the Chemical Society of Japan, Sendai, 1974.

[2] For reviews of polyelectrolyte catalysis, see (*a*) H. Morawetz, *Accounts Chem. Res.*, 1970, **3**, 354; (*b*) N. Ise, ' Polyelectrolytes and Their Application,' eds. E. Selegny and A. Rembaum, Reidal, Dordrecht, 1975, p. 71.

[3] For reviews of micellar catalysis see (*a*) E. J. Fendler and J. H. Fendler, *Adv. Phys. Org. Chem.*, 1970, **8**, 271; (*b*) E. H. Cordes and C. Gitler, *Progr. Bio-org. Chem.*, 1973, **2**, 1.

[4] W. Ostwald, *Phys. Z.*, 1902, **3**, 313.

[5] T. Okubo and N. Ise, *J. Amer. Chem. Soc.*, 1973, **95**, 4031.

[6] T. Okubo and N. Ise, *J. Org. Chem.*, 1973, **38**, 3120.

phenyl esters in strongly alkaline media using a stopped-flow technique. In the present paper, we add data for weakly alkaline media. Furthermore, we also report results for the alkaline hydrolyses of negatively charged esters. The main purpose of this work is to discuss the contribution of electrostatic and hydrophobic interactions to the relationship between a substrate and a polymer catalyst.

EXPERIMENTAL

Materials.—*p*-Nitrophenyl acetate (PNPA) (Nakarai Chemicals Co.) was further purified by recrystallization

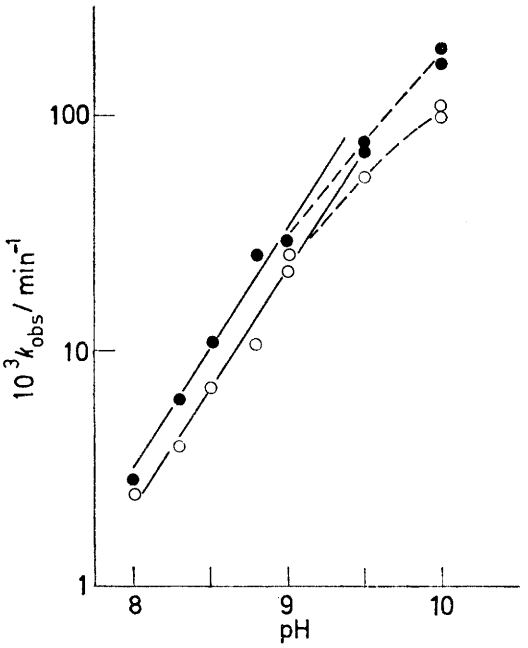

FIGURE 1 First-order rate constants for the hydrolysis of PNPA and NABA plotted as a function of pH at 30°: ●, [PNPA] = 5mM in 10% EtOH–H_2O, [KCl] = 25mM; ○, [NABA] = 2.5mM in H_2O, [KCl] = 25mM

until it was nearly colourless, m.p. 78°. 4-Acetoxy-3-nitro-benzoic acid (NABA) and -benzenearsonic acid (NABAA) were prepared by the methods of Letsinger *et al.*[7] and Overberger *et al.*,[8] respectively. The preparation of the polymers poly-4-vinyl-*N*-ethylpyridinium bromide (C_2PVP), poly-4-vinyl-*N*-propylpyridinium bromide (C_3-PVP), poly-4-vinyl-*N*-n-butylpyridinium bromide (C_4PVP), and the copolymer of 4-vinyl-*N*-benzylpyridinium chloride (95%) and 4-vinyl-*N*-n-cetylpyridinium bromide (5%) (C_{16}BPVP) were described previously.[9] Diethyldiallylammonium chloride–sulphur dioxide copolymer (DECS), a strongly basic polyelectrolyte, was synthesised by the method of Harada *et al.*[10] Cetyltrimethylammonium bromide (CTABr) and cetyldimethylbenzylammonium chloride (CDBACl) were commercially available. Deionised water was distilled for the preparation of solutions of ester and polymer.

Kinetic Measurements.—Reaction rates were obtained from the change in absorbance at 400—410 nm due to the release of phenoxide ion, or from the amount of acid released. Fast reactions were followed using a Union stopped-flow spectrophotometer (RA 1100) with a Hitachi Memoriscope (model V-018). The details of the apparatus are described elsewhere.[11] Slow reactions were monitored using a Hiranuma pH stat titrator (Rat 101). For duplicate or repeated runs, k_{obs}, k_1, and k_2 are accurate to within 10%, K to within 25%.

RESULTS

The first-order rate constants for the hydrolysis of PNPA and NABA were measured as a function of pH (Figure 1). A straight line with slope unity (solid line) was obtained for pH 8—9, indicating that the rates of ester hydrolysis are quantitatively accounted for by the equation $k_{obs} = k_{OH^-}[OH^-]$. This linearity was also observed for NABAA.

The first-order rate constants of the hydrolyses of the neutral ester, PNPA, at pH 8.0 in the presence of polyelectrolytes and micelles are shown in Figure 2. It is apparent that cationic polyelectrolytes containing highly hydrophobic groups accelerate hydrolysis. This is due to hydrophobic interactions between the esters and polymers, and to the electrostatic attractive forces between OH^- and the cationic polymers. The highest acceleration factor for the hydrolysis of PNPA at pH 8.0 was *ca.* 6, which is quite similar to that at pH *ca.* 12 (*ca.* 5, see ref. 6).

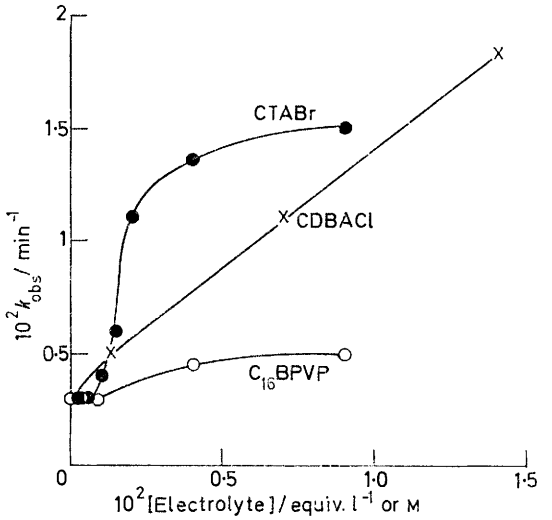

FIGURE 2 Alkaline hydrolysis of PNPA in the presence of CTABr, CDBACl, and C_{16}BPVP at 30°: pH = 8.0, [PNPA] = 1mM in H_2O

Figure 3 gives the influence of polyelectrolytes on the alkaline hydrolysis of NABA (a univalent anionic ester). The observed first-order rate constants, k_{obs}, were increased by

[7] R. Letsinger and T. J. Savereide, *J. Amer. Chem. Soc.*, 1962, **84**, 114.
[8] C. G. Overberger, T. St. Pierre, N. Vorchheimer, J. Lee, and S. Yaroslavsky, *J. Amer. Chem. Soc.*, 1965, **87**, 296.
[9] T. Okubo and N. Ise, *J. Amer. Chem. Soc.*, 1973, **95**, 2293.
[10] Y. Negi, S. Harada, and O. Ishizuka, *J. Polymer Sci. A1*, 1967, **5**, 1951.
[11] N. Ise, T. Okubo, H. Kitano, and S. Kunugi, *J. Amer. Chem. Soc.*, 1975, **97**, 2882.

the addition of polyelectrolytes or micelles. As it is an interionic process between univalent anionic species, the

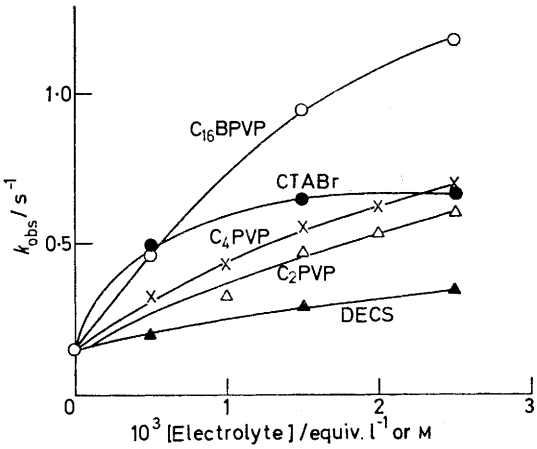

FIGURE 3 Alkaline hydrolysis of NABA in the presence of CTABr, DECS, C_2PVP, C_4PVP, and C_{16}BPVP at 25°: [NaOH] = 12.5mM, [NABA] = 0.1mM in H_2O

reaction was highly accelerated by the cationic polyelectrolytes as was observed for a variety of interionic reactions.[2,5,9,12] The order of acceleration produced by the cationic polyelectrolytes in Figure 3 is as follows: DECS < C_2PVP < C_4PVP < C_{16}BPVP.

Polyelectrolyte and micelle effects on the alkaline hydrolysis of a divalent anionic ester, NABAA are shown in Figure 4. Cationic polyelectrolytes accelerated the hydro-

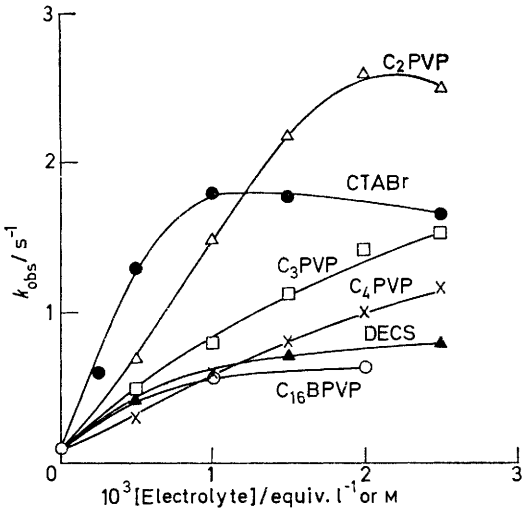

FIGURE 4 Alkaline hydrolysis of NABAA in the presence of CTABr, C_2PVP, C_3PVP, C_4PVP, DECS, and C_{16}BPVP at 35°: [NaOH] = 12.5mM, [NABAA] = 55.2μM

lyses. As the hydrophobic character of the polycation was strengthened, the degree of acceleration increased (DECS < C_2PVP), passed a maximum, and then decreased (C_2PVP > C_3PVP > C_4PVP > C_{16}BPVP). Presumably, the attractive forces between NABAA and the catalyst polymer are so strong as a result of both electrostatic and hydrophobic interactions that attack by hydroxide ions on NABAA is sterically hindered.*

DISCUSSION

We discuss the alkaline hydrolyses in terms of saturation kinetics. If ester–polymer complex formation

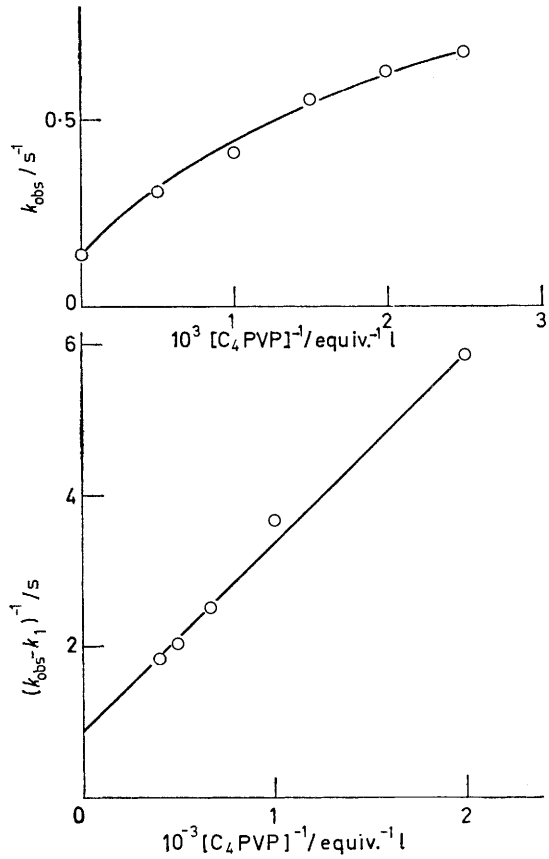

FIGURE 5 Kinetic analysis for the hydrolysis of NABA in the presence of C_4PVP at 25°: [NaOH] = 12.5mM, [NABA] = 0.1mM in H_2O

occurs prior to hydrolysis by hydroxide ions, reaction (2) is applicable, where K is the equilibrium association

$$\begin{array}{ccc} \mathrm{PE} + \mathrm{S} & \overset{K}{\rightleftharpoons} & \mathrm{PE,S} \\ {\scriptstyle +OH^-}\downarrow{\scriptstyle k_1} & & {\scriptstyle +OH^-}\downarrow{\scriptstyle k_2} \\ \mathrm{P} & & \mathrm{P} \end{array} \qquad (2)$$

constant of polyelectrolyte (PE) and ester (S), and k_1 and k_2 the first-order rate coefficients. PE,S And P indicate the polyelectrolyte–ester complex and the product, respectively. Equation (2) seems to be correct, the saturation-type acceleration having often been observed for alkaline hydrolysis in the presence of polyelectrolytes (see Figures 2—4 and ref. 6).

* Similar steric effects have been reported for reactions between two ions with charges of the same sign by us [9] and by Brückner *et al.*[13]

[12] N. Ise and F. Matsui, *J. Amer. Chem. Soc.*, 1968, **90**, 4242.
[13] B. Brückner, V. Crescenzi, and F. Quadrifoglio, *J. Chem. Soc.* (*A*), 1970, 1168.

Under the condition of [PE] ≫ [PE,S], the rate equation (3) is obtained by the method adopted for micellar catalysis.[3a] k_{obs} Is the observed first-order rate

$$\frac{1}{k_{obs} - k_1} = \frac{1}{k_2 - k_1} + \frac{n}{k_2 - k_1}\frac{1}{K}\frac{1}{[PE]} \quad (3)$$

constant in the presence of a polyelectrolyte and n indicates the number of binding sites of polyions complexing with ester molecules. The n values for the univalent anionic ester NABA and for the divalent anionic ester NABAA are 1 and 2, respectively. The n value of the neutral ester PNPA cannot be determined by kinetic measurements only. We assume $n = 1$ for the neutral ester in this paper.

Typical plots of equation (3) are shown in Figure 5 for the hydrolyses of NABA with C_{16}BPVP. The values of K, k_1, and k_2 for various reaction systems are compiled in the Table. It was found that saturation kinetics held for hydrolysis of NABA in the presence of all the cationic polyelectrolytes and micelles studied. As is apparent from the Table, the K values of NABAA decreased with increasing hydrophobic character of the polyelectrolyte. The hydrolysis rate of NABA in the presence of C_{16}BPVP, however, was not explained by reaction (2) which implies that NABAA is bound to C_{16}BPVP too strongly by both electrostatic and hydrophobic forces to react with hydroxide ion. This interpretation is self-consistent with the observation of decreasing values of k_2 with increasing hydrophobic character of the polyelectrolyte in the hydrolysis of NABAA (see Table).

Reaction (2) holds for hydrophobic neutral esters, *i.e.*, *p*-nitrophenyl valerate (PNPV), caprolate (PNPC), laurate (PNPL), and palmitate (PNPP) in the presence of hydrophobic polycations or micelles such as BPVP, C_{16}BPVP, or CTABr. In these reaction systems, both K and k_2 increased with increasing hydrophobicity of polyion or ester. The hydrolysis of weak hydrophobic esters such as PNPA and *p*-nitrophenyl proponate (PNPPR), however, does not satisfy reaction (2), which indicates that the attractive forces between ester and polyelectrolyte are weak.

Parameters of equation (3) for the hydrolyses of phenyl esters in the presence of polyelectrolytes and micelles [a]

Ester	Catalyst	K/l mol^{-1}	k_1/s^{-1}	k_2/s^{-1}
NABA [b] ($n = 1$)	DECS	210	0.14	0.8
	C_2PVP	260	0.14	1.2
	C_4PVP	330	0.14	1.3
	C_{16}BPVP	330	0.14	3.2
NABA [c] ($n = 1$)	DECS	30	5.4×10^{-5}	7.2×10^{-4}
	C_2PVP	90	5.4×10^{-5}	2.6×10^{-4}
	C_{16}BPVP	65	5.4×10^{-5}	3.3×10^{-4}
	CTABr	160	5.4×10^{-5}	8.7×10^{-5}
NABAA [d] ($n = 2$)	DECS	900	0.08	0.8
	C_2PVP	1 300	0.08	2.6
	C_3PVP	200	0.08	6.3
	CTABr	5 100	0.08	1.7
PNPV [e] ($n = 1$)	C_{16}BPVP	520	0.20	1.0
PNPC [f] ($n = 1$)	BPVP	260	0.11	0.22
	CTABr	500	0.11	1.8
PNPL [g] ($n = 1$)	BPVP	640	0.016	0.21
	C_{16}BPVP	700	0.016	0.30
	CTABr	1 100	0.016	2.0
PNPP [h] ($n = 1$)	C_4PVP	2 400	1.1×10^{-4}	6.7×10^{-4}
	BPVP	850	1.1×10^{-4}	0.022
	C_{16}BPVP	2 600	1.1×10^{-4}	0.015

[a] The rate coefficients of NABA and NABAA were obtained from this work and those of neutral esters from ref. 6. [b] [NABA] = 10^{-4}M, [OH$^-$] = 0.0125M, at 25° in H_2O. [c] [NABA] = 2.5×10^{-3}M, pH = 8.0, [KCl] = 2.5×10^{-2}M, at 30° in H_2O. [d] [NABAA] = 5.52×10^{-5}M, [OH$^-$] = 0.0125M, at 35° in H_2O. [e] [PNPV] = 5×10^{-5}M, [OH$^-$] = 0.025M, at 30° in H_2O. [f] [PNPC] = 5×10^{-5}M, [OH$^-$] = 0.025M, at 25° in 15% EtOH–H_2O. [g] [PNPL] = 5×10^{-5}M, [OH$^-$] = 0.025M, at 25° in 22.5% EtOH–H_2O. [h] [PNPP] = 4×10^{-5}M, [OH$^-$] = 0.001M, at 30° in 30% EtOH–H_2O.

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