The Alkaline Hydrolyses of *p*-Nitrophenyl Esters in the Presence of Polyelectrolytes[1]

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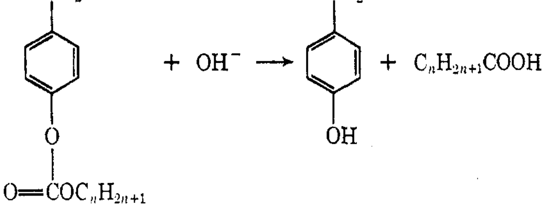
The rapid hydrolyses of *p*-nitrophenyl esters in a strongly alkaline media were followed using the stopped-flow technique in the presence of polyelectrolytes and in their absence. The esters used were *p*-nitrophenyl acetate, propionate, valerate, caprylate, laurate, and palmitate. The polyelectrolytes were poly(4-vinylpyridine) quaternized with ethyl, butyl, and benzyl halides, copolymer of 4-vinyl-*N*-benzylpyridinium chloride and 4-vinyl-*N*-cetylpyridinium bromide, and copolymer of diallyldiethylammonium chloride and sulfur dioxide. Cationic and anionic surfactants (cetyltrimethylammonium bromide and sodium lauryl sulfate) were also used. The ion-molecule reactions were accelerated with the hydrophobic cationic polyelectrolytes, and the strength of the acceleration increased with increasing hydrophobicity of esters and/or polyelectrolytes. The free energy, enthalpy, and entropy of activation were decreased by addition of the polyelectrolytes. The relative catalytic contributions of the electrostatic and hydrophobic interactions were discussed.

It is now well recognized that the reaction rates of many kinds of organic and inorganic reactions are strikingly influenced by polyelectrolytes.[2] The important contributions of hydrophobic interactions in a large number of organic reactions in solutions containing polyelectrolytes or micelle electrolytes have also been pointed out.[3-6]

In the present paper, we report additional data on the hydrophobic effects of polyelectrolytes using an ion-molecule reaction.



In this reaction, attractive interactions between the *p*-nitrophenyl ester and polyelectrolyte would be *hydrophobic.* On the other hand, those between hydroxide ions and macroion are certainly *electrostatic.* The relative magnitudes of the two kinds of interactions, therefore, may be compared by studying the reaction. We can also examine the hydrophobic interactions more systematically by changing n of the substrate ester (from 1 to 15 in the present study). Salts of poly(4-vinylpyridine) quaternized with alkyl halides of various numbers of methylene groups and polystyrene sulfonate were used as synthetic hydrophobic polyelectrolytes.

Results and Discussion

The hydrolyses were performed in aqueous media for *p*-nitrophenyl acetate (PNPA, $n = 1$), propionate (PNPPR, $n = 2$), and valerate (PNPV, $n = 4$). Those of *p*-nitrophenylcaprylate (PNPC, $n = 7$), laurate (PNPL, $n = 11$), and palmitate (PNPP, $n = 15$) were carried out in aqueous ethanol. The second-order rate constants, k_2, of the hydrolyses of PNPA, PNPV, and PNPP in the presence of various amounts of poly- or micelle electrolyte are portrayed in Figures 1-3. The k_2 values in the absence of polyelectrolytes or micelles were also plotted in the figures for the reader's convenience. The concentrations of the esters and the hydroxide ions are $4 \times 10^{-5} \sim 5 \times 10^{-5}\, M$ and $10^{-3} \sim 2.5 \times 10^{-2}\, M$, respectively, and those of electrolytes $10^{-6} \sim 10^{-1}$ equiv l.$^{-1}$. The changes of pH during the reaction were not observed under the present experimental conditions. The results of PNPPR, PNPC, and PNPL were similar to those of the other esters and are not given here in order to save space.

Several important results were derived. First, the cationic polyelectrolytes having hydrophobic groups accelerated the hydrolyses, whereas those having no hydrophobic groups did not show such effects; *i.e.*, the accelerating effect of the polymer increases with increasing hydrophobicity of the polymer. The rate-enhancing actions are in the following order except for the PNPP system: DECS < C2PVP < C4PVP < BzPVP < C16BzPVP < CTABr, where DECS, C2PVP, C4PVP, BzPVP, and C16BzPVP indicate the copolymer of diethyldiallylammonium chloride and sulfur dioxide, poly(4-vinyl-*N*-ethylpyridinium bromide), poly(4-vinyl-*N*-butylpyridinium bromide), poly(4-vinyl-*N*-benzylpyridinium chloride), and copolymer of 4-vinyl-*N*-benzylpyridinium chloride (95%) and 4-vinyl-*N*-cetylpyridinium bromide (5%), respectively. In the case of PNPP, the rate-enhancing action of CTABr below $5 \times 10^{-3} M$ is not so large as that of cationic polysoaps such as C16BzPVP and BzPVP. The order is clearly the same as that of the hydrophobicity of the polyelectrolyte, and the same inequality was found to hold for the alkaline fading reactions of triphenylmethane dyes.[6] The hydroxide ions are attracted to the cationic polymer by the electrostatic attractive forces and the hydrophobic esters are also accumulated around the polymer by the hydrophobic attractive interactions. Thus, the cationic, hydrophobic polymer promotes the hydrolysis. Similar findings were observed for ester hydrolysis by using polysulfonic acid,[4] micelle-forming cationic detergents of various hydrophobicities,[7,8] and polyethylenimine derivatives.[9,10]

Second, hydrophobic polyelectrolyte was effective

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(1) Presented at the 21st Annual Meeting of the Society of High Polymers, Tokyo, Japan, May 1972.

(2) See, for example, H. Morawetz, *Accounts Chem. Res.*, **3**, 354 (1970); N. Ise, *Advan. Polym. Sci.*, **7**, 536 (1970).

(3) (a) E. H. Cordes and R. B. Dunlop, *Accounts Chem. Res.*, **2**, 329 (1969); (b) E. J. Fendler and J. H. Fendler, *Advan. Phys. Org. Chem.*, **8**, 271 (1970).

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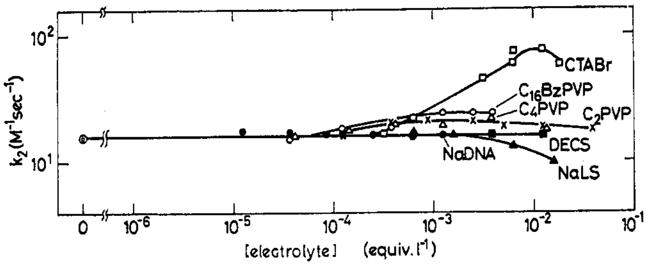

Figure 1.—Polyelectrolyte effect on the alkaline hydrolysis of PNPA at 30°: [PNPA] = 5×10^{-5} *M*, [NaOH] = 2.5×10^{-2} *M*.

in accelerating the reaction even in dilute concentration regions compared with surfactants; CTABr accelerated the reaction in the concentration above 10^{-4} *M*, whereas polyelectrolyte was effective at $10^{-6} \sim 10^{-5}$ equiv l.$^{-1}$ as is clearly shown in Figure 3. This is quite understandable because the charges and the hydrophobic groups are fixed to the main chain in the case of polyelectrolytes and cannot be separated by dilution from each other. The cmc of CTABr ($\sim 10^{-3}$*M* in pure water) would be expected to decrease upon the addition of a hydrophobic ester.[3b] Hence, one would expect CTABr to begin to catalyze the reaction at lower concentrations as the esters become more hydrophobic, which agrees with the observations.

Third, the strength of the rate-enhancing action of the polyelectrolytes is most marked for the hydrolysis of PNPP and least for PNPA with the order PNPA < PNPPR < PNPV < PNPC < PNPL < PNPP. This feature has already been demonstrated for the hydrolyses in the presence of surfactant, in which the concentration of hydroxide ions was extremely low compared with that in the present work.[11,12] The relative strength of the rate enhancement by C16BzPVP of the hydrolysis is shown in Table I, where k_{20} is the rate constant without the polyelectrolyte. As is clear in the table, the larger the *n* values of esters, the stronger the rate enhancement. The maximum acceleration factor for the hydrolysis of PNPP is about 150, whereas that for PNPA is only 1.5. The factor for PNPP probably would become much larger if the reaction could be carried out in pure water, since ethanol is considered to be a breaker of the hydrophobic bonds between ester and catalyst.

TABLE I

RATE ENHANCEMENT BY C16BzPVP OF THE ALKALINE HYDROLYSES OF *p*-NITROPHENYL ESTERS

Concn of C16BzPVP, equiv l.$^{-1}$	k_2/k_{20}					
	$n = 1^a$	2^a	4^a	7^b	11^c	15^d
1.25×10^{-5}	1.00	1.15	1.40			15.0
1.25×10^{-4}	1.12	1.15	1.58	1.63	2.95	43.9
3.75×10^{-4}	1.14	1.38	1.96	2.39	5.32	80.2
1.25×10^{-3}	1.34	1.57	2.47	3.98	21.4	135
3.75×10^{-3}	1.46	1.59	3.57	16.9	112	140

[a] [Ester] = 5×10^{-5} *M*, [OH$^-$] = 2.5×10^{-2} *M*, at 30°, in pure water. [b] [Ester] = 5×10^{-5} *M*, [OH$^-$] = 2.5×10^{-2} *M*, at 25°, in 15% EtOH–H_2O. [c] [Ester] = 5×10^{-5} *M*, [OH$^-$] = 2.5×10^{-2} *M*, at 25°, in 22.5% EtOH–H_2O. [d] [Ester] = 4×10^{-5} *M*, [OH$^-$] = 10^{-3} *M*, at 30°, in 30% EtOH–H_2O.

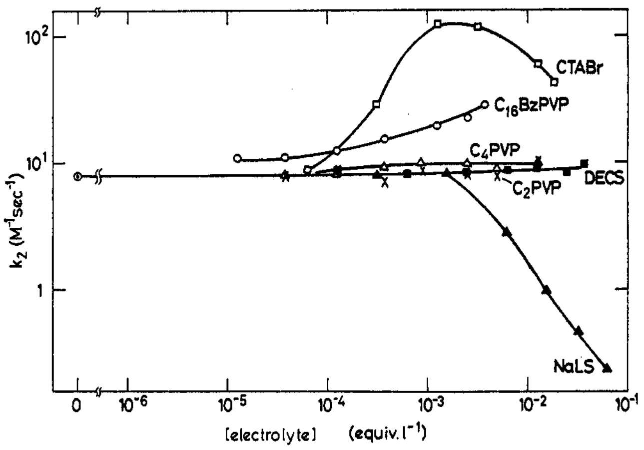

Figure 2.—Polyelectrolyte effect on the alkaline hydrolysis of PNPV at 30°: [PNPV] = 5×10^{-5} *M*; [NaOH] = 2.5×10^{-2} *M*.

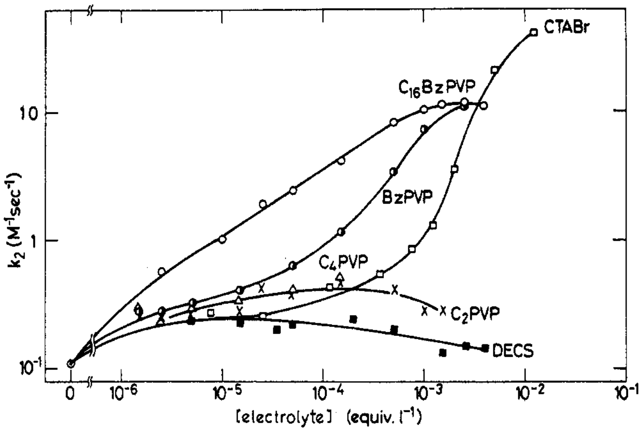

Figure 3.—Polyelectrolyte effect on the alkaline hydrolysis of PNPP at 30° in 30% ethanol-H_2O: [PNPP] = 4×10^{-5} *M*, [NaOH] = 10^{-3} *M*.

The activation parameters, namely the free energy ($\Delta G^{\ddagger}$), enthalpy ($\Delta H^{\ddagger}$), and entropy ($\Delta S^{\ddagger}$) of activation, are given in Table II for the alkaline hydrolysis of PNPL in the presence of C16BzPVP and CTABr and in their absence. As was usually found,[13] the $\Delta S^{\ddagger}$ values are strongly negative. All three parameters were decreased by the electrolytes. It should be noted that the $\Delta H^{\ddagger}$ was sharply decreased by the electrolyte, as was the case for interionic reactions in the presence of polyelectrolytes.[2,14] The decrease in $\Delta S^{\ddagger}$ suggests that the acceleration is due to the enthalpic loss.

TABLE II

ACTIVATION PARAMETERS FOR THE ALKALINE HYDROLYSIS OF PNPL IN 22.5% ETHANOLIC AQUEOUS SOLUTION AT 30° [a]

Electrolyte	Concn of electrolyte, equiv l.$^{-1}$	$\Delta G^{\ddagger}$, kcal mol^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal deg^{-1} mol^{-1}
None	0	18.0	10.9	−23
C16BzPVP	1.67×10^{-3}	14.7	5.3	−31
CTABr	2.5×10^{-3}	14.6	4.8	−32

[a] [PNPL] = 5×10^{-5} *M*, [NaOH] = 2.5×10^{-2} *M*.

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Experimental Section

Materials.—PNPA obtained from Nakarai Chemicals Co., Kyoto, Japan, was further purified by recrystallization until it was nearly colorless (mp 78°). PNPPR, PNPV, PNPC, and PNPL obtained from Sigma Chemicals Co. were used without further purification. PNPP was a guaranteed reagent from Nakarai Chemicals Co. The details about the preparation of the polymers, namely C2PVP, C4PVP, BzPVP, C16BzPVP, and DECS, were described in the preceding paper.[6] The degree of polymerization of the parent poly(4-vinylpyridine) is 3800. The characterization of NaDNA was also described before.[6] NaLS and CTABr were commercially available. Deionized water was used for the preparation of the solutions of esters and polymer catalysts.

Kinetic Measurements.—Reaction rates were obtained from the change in absorbance at 400 nm owing to release of *p*-nitrophenoxide ion. The rapid reaction was followed using a Hitachi stopped-flow spectrophotometer, Model RSP-2, with a Hitachi memoriscope Model V-018. The slow ractions were monitored using a Hitachi spectrophotometer Model EPS-3T.

Registry No.—PNPA, 830-03-5; PNPPR, 1956-06-5; PNPV, 1956-07-6; PNPC, 1956-10-1; PNPL, 1956-11-2; PNPP, 1492-30-4; C2PVP, 25619-82-3; C4PVP, 25703-28-0; BzPVP, 30109-97-8; C16BzPVP, 40780-43-6; DECS, 27577-32-8; CTABr, 57-09-0; NaLS, 151-21-3.

Proton Nuclear Magnetic Resonance Spectra of 1-Substituted Acenaphthenes and Other Systems of Well-Defined Geometry[1a]

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The pmr spectra of 22 1-substituted acenaphthenes were analyzed and the published nmr data for series of hexachlorobicyclo[2.2.1]heptenes, oxiranes, 1,1-dichlorocyclopropanes, and dibenzobicyclo[2.2.2]octadienes were extended by the analysis of the parent compound using ^{13}C satellites. The above data enable us to derive the following conclusions. (1) For the common range of functional groups, the dependence of vicinal and geminal coupling constants on the "electronegativity" of the substituent X is complex. However, it appears likely that empirical "substituent effects" can be used predictively. (2) A wide variety of substituents shield the vicinal protons eclipsed by them relatively to those trans to them. With some substituents ($-COCH_3$, $-COOH$, $-COOMe$, $-CONH_2$, $-N^+Me_3$, $-CHO$) the opposite effect may be observed. (3) By comparison with unsubstituted compounds, trans vicinal protons and geminal protons are deshielded by all substituents encountered here, except $-SiMe_3$. The cis vicinal protons may be either shielded or deshielded. (4) No encompassing theoretical analysis of the observed shifts was possible. However, by restricting the data to selected substituents it has been shown that the shift of the geminal hydrogen induced by a given substituent depends on the substrate. A Hammett-type relationship has been proposed which should prove useful for estimation of chemical shifts. An interpretation of this observation in terms of the inductive effect is presented. (5) For substituents limited to first-row elements, both vicinal hydrogens are shifted to about the same extent, consistent with either electric field or inductive effects. In addition, the eclipsed vicinal hydrogen shows a substantial upfield shift which is not explicable by any current theory. A new interpretation in terms of backbonding and a Karplus type relationship is suggested.

To explore the influence of substituents on chemical shifts and coupling constants, it is necessary to use molecules of reasonably well-defined stereochemistry. System **1** represents one class of compounds where H_A and H_C are approximately eclipsed and X is any substituent of interest in proton magnetic resonance studies. Clearly, system **1** can be incorporated only into flat, rigid rings and extensive systematic studies have so far been confined to hexachlorobicyclo[2.2.1]heptenes (**2**)[2a] and their 7,7-difluoro derivatives,[2b] 1,1,dichlorocyclopropanes (**3**),[3] oxiranes (**4**),[3] cyclopropanes (**5**),[4,5] and norbornenes (**6**).[6] A fairly large collection of data is also available[7] for dibenzobicyclo[2.2.2]octadienes (**7**), and some general studies dealing with the effects of substituents on coupling constants[8] are pertinent.

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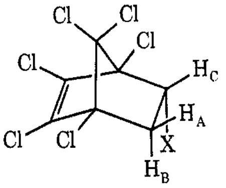

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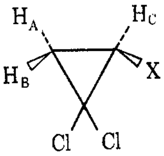

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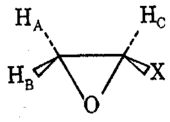

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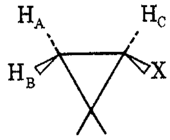

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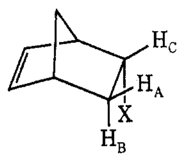

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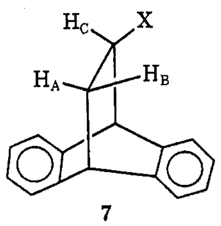

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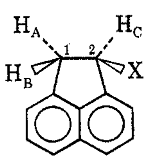

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This work deals with the nmr parameters for fragment **1** in 22 1-substituted acenaphthenes (**8**) and with the extension of data for systems **2**, **3**, **4**, and **7** by the analysis of the nmr spectra of the parent compounds (X = H) for each series. The principal purpose of the present study was the exploration of previously pro-

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[1] (a) Abstracted in part from the Ph.D. thesis of P. W. Westerman, University of Sydney, 1970; (b) University of Sidney; (c) Purdue University; (d) Varian Associates.

[2] (a) K. L. Williamson, *J. Amer. Chem. Soc.*, **85**, 516 (1963); (b) K. L. Williamson and J. C. Fenstermaker, *ibid.*, **90**, 342 (1968).

[3] K. L. Williamson, C. A. Lanford, and C. R. Nicholson, *ibid.*, **86**, 762 (1964).

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