Role of Solvation and Desolvation in Polymer "Catalysis". 7. The Influence of High Pressures on the Alkaline Hydrolyses of Neutral and Cationic Esters Catalyzed by Macroions¹

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The alkaline hydrolyses of electrically neutral esters and positively charged esters are influenced by macroions under high pressures up to 2000 bar. The polyelectrolytes used are sodium poly(styrenesulfonate) (NaPSS) and poly(trimethylvinylbenzylammonium chloride) (PMVA). All of the volumes, enthalpies, and entropies of activation of the reactions examined increase on the addition of hydrophobic macroanions (NaPSS), whereas they decrease on the addition of the hydrophobic and cationic macroions (PMVA). The significant role of the hydrophobic hydration effects of macroions, i.e., the formation of the "iceberg" water structure around the hydrophobic reactants and macroions, is demonstrated for the observed rate acceleration and deceleration with PMVA and NaPSS, respectively.

Introduction

Remarkable catalytic influence of synthetic polyelectrolytes on various chemical reactions has been reported.² The catalysis by macroions of interionic reactions has been accounted for in terms of the Bronsted equation and the transition-state theory.³⁻⁶

The strong electrostatic potential of macroions influences the free energies (activities) of reactants and/or activated complexes and hence the reaction rates. Recently, a substantial contribution of the electrostatic dehydration effects by macroions upon reactant ions and/or activated complexes was found by high-pressure measurements.⁷⁻⁹ The volume of activation (ΔV^*) of cation-cation or anion-anion reactions increased strikingly by addition of anionic or cationic macroions, respectively. For example, an increase of 81 mL mol⁻¹ was observed for the Ag⁺-induced aquation of $Co(NH_3)_5Br^{2+}$ in the presence of sodium poly(styrenesulfonate). On the other hand, ΔV^* of cation-anion reactions always decreased with addition of macroions.

A type of hydration different from the electrostatic one, i.e., hydrophobic hydration, has first been discussed by us for the alkaline fading reactions of triphenylmethane dyes, e.g., ethylviolet.¹⁰ The hydrophobic hydration of reactants and macroions in aqueous media creates the "iceberg" water structure¹¹ and decreases the molar volume and

entropy levels of reactants. A similar situation is expected to occur with activated complex and macroions, and the reaction rates will be influenced by this interaction. In the present article, we discuss further the hydrophobic hydration effects of macroions in the hydrolysis reactions between neutral esters and OH^- (eq 1) and between pos-



itively charged esters and OH^- (eq 2). The important contributions of the intrinsic changes in the volumes of the solute and of the electrostatic hydration effects have been discussed in the hydrolysis reactions of various esters under high pressures.¹²⁻¹⁶ The present reaction systems are convenient for discussion of the hydrophobic effects in macroion "catalysis".

⁽¹⁾ Presented at the 2nd International Kyoto Conference on New Aspects of Organic Chemistry, Kyoto, Japan, Aug 1982.

⁽²⁾ For a convenient review of previous work, see: Ise, N.; Okubo, T.;
Kunugi, S. Acc. Chem. Res. 1982, 15, 171.
(3) Ise, N. Adv. Polym. Sci. 1971, 7, 536.
(4) Ise, N. "Polyelectrolytes and Their Applications"; Rembaum, A.,

Selegny, E., Eds.; D. Reidel: Dordrecht, The Netherlands, 1975; p 71.
 (5) Ise, N.; Okubo, T. Macromolecules 1978, 11, 439.

⁽⁶⁾ Ise, N. Makromol. Chem., Suppl. 1981, 5, 107.

⁽⁷⁾ Ise, N.; Maruno, T.; Okubo, T. Proc. R. Soc. London, Ser. A 1980, 370, 485

⁽⁸⁾ Okubo, T.; Maruno, T.; Ise, N. Proc. R. Soc. London, Ser A 1980, 370. 501.

 ⁽⁹⁾ Ise, N.; Okubo, T.; Yamamura, Y. J. Phys. Chem. 1982, 86, 1694.
 (10) Maruno, T.; Okubo, T.; Ise, N. Ber. Bunsenges. Phys. Chem. 1981, 85.667.

⁽¹¹⁾ See, for example: (a) Frank, H. S.; Wen, W. Y. Discuss, Faraday Soc. 1957, 24, 133. (b) Kauzmann, W. Adv. Protein Chem. 1959, 14, 1.
(c) Nemethy, G.; Sheraga, H. A. J. Chem. Phys. 1962, 36, 3382, 3401. (d) Nemethy, G.; Sheraga, H. A. J. Phys. Chem. 1962, 66, 1773. (e) Wen, W. Y.; Saito, S. *Ibid.* **1964**, *68*, 2639. (f) Ise, N.; Okubo, T. J. Am. Chem. Soc. **1968**, *90*, 4527. (g) Jencks, W. P. "Catalysis in Chemistry and Enzymology", Part II; McGraw-Hill: New York, 1969.

⁽¹²⁾ Laidler, K. J.; Chen, D. Trans. Faraday, Soc. 1958, 54, 1026. (13) Andersen, B.; Grönlund, F.; Olsen, J. Acta Chem. Scand. 1969, 23. 2458.

⁽¹⁴⁾ Lockyer, G. D.; Owen, D.; Crew, D.; Neuman, R. C. J. Am. Chem. Soc. 1974, 96, 7303.

⁽¹⁵⁾ Neuman, R. C.; Lockyer, G. D.; Marin, J. J. Am. Chem. Soc. 1976, 98.6975

⁽¹⁶⁾ Taniguchi, Y.; Makimoto, S.; Suzuki, K. J. Phys. Chem. 1981, 85, 2218, 3469.



Figure 1. Alkaline hydrolyses of PNPV in the presence of PMVA (O) and NaPSS (X) at 20 °C. [PNPV] = 2.5×10^{-5} M, [NaOH] = 1.0×10^{-3} M.

TABLE I: Influence of Macroions on Reaction Rates, ΔH^{\ddagger} , ΔV^{\ddagger} , and ΔS^{\ddagger}

macroions	PMVA	NaPSS
reaction rate	acceleration	deceleration
$\Delta H^{\ddagger}, \Delta V^{\ddagger}, \Delta S^{\ddagger}$	decrease	increase
$\Delta H^{\ddagger}_{h}, \Delta V^{\ddagger}_{h}, \Delta S^{\ddagger}_{h}$	decrease	increase

Experimental Section

Materials. p-Nitrophenyl acetate (PNPA, n = 1), valerate (PNPV, n = 5), and laurate (PNPL, n = 11) were commercially available from Sigma. These were further purified by recrystallization. 3-Acetoxy- (ANTI, n = 1), 3-octanoyloxy- (ONTI, n = 7), and 3-decanoyloxy-N-trimethylanilinium iodide (DENTI, n = 9) were prepared and purified by the method of Overberger et al.^{17,18}

The solubilities of PNPA and PNPV in water were much higher than 2.5×10^{-5} M, at which the experiments were conducted. However, that of PNPL was lower than this concentration, and 10% of ethanol was added for all reaction solutions of this ester. The cationic esters were readily soluble in water at 2.5×10^{-4} M. Poly(trimethylvinylbenzylammonium chloride) (PMVA, a cationic hydrophobic polymer) was purchased from Polyscience and further purified by dialysis against deionized water for 1 week. Sodium poly(styrenesulfonate) (NaPSS, molecular weight = 5×10^{-5}) was obtained from Polyscience and further purified by dialysis. For the preparation of solutions, water was deionized with ion-exchange-resin columns and then distilled.

Kinetic Measurements. The hydrolysis rates were followed by an absorption increase at 400 nm for the neutral esters, and at 295 nm for the cationic ones on a high-sensitivity spectrophotometer (SM401, Union Engineering, Hirakata) at atmospheric pressure. A highpressure spectrophotometer made by the same manufacturer was used, following the same procedures described earlier⁷ at elevated pressures (1-2000 bar).

Results

Typical examples of the macroion effects on the hydrolysis reaction rates of the neutral and cationic esters are shown in Figures 1 and 2, for PNPV and DENTI, respectively. At atmospheric pressure, (1) the reactions of the neutral and cationic esters were accelerated more or less by the strongly hydrophobic cationic macroions, i.e.,



Figure 2. Alkaline hydrolyses of DENTI in the presence of PMVA (O) and NaPSS (X) at 20 °C. [DENTI] = 2.5×10^{-5} M, [NaOH] = 1.0×10^{-3} M.



Figure 3. Pressure influences on the alkaline hydrolyses of PNPV in the presence of PMVA (O) and NaPSS (\bullet) and in their absence (X). [PNPV] = 2.5×10^{-5} M, [NaOH] = 1.0×10^{-3} M, [PMVA] = 2.0×10^{-4} M, [NaPSS] = 0.018 M.

PMVA, and (2) they were retarded by the strongly hydrophobic anionic macroions (NaPSS) (Table I). The rate-enhancing or -retarding influence seems to be more significant for more strongly hydrophobic esters and/or macroions. Result 1 may be due to the fact that hydrophobic esters and OH⁻ are attracted to the hydrophobic cationic macroions by electrostatic and hydrophobic forces, especially for cationic esters, in spite of the electrostatic repulsion between the esters and the macroion.¹⁹ Result 2 is explained by the attraction between the esters and the anionic macroions, and by the electrostatic repulsion between OH⁻ and the anionic macroions.

The pressure influence on the reaction rates is shown in Figure 3 for PNPV. The results are as follows: (i) The reaction without macroions was enhanced with increasing

⁽¹⁷⁾ Overberger, C. G.; Salamone, J. C.; Yaroslavsky, S. J. Am. Chem. Soc. 1967, 89, 6231.

⁽¹⁸⁾ Overberger, C. G.; Podsiadly, C. J. Bioorg. Chem. 1974, 3, 35.

TABLE II: Volume of Activation and Other Thermodynamic Parameters for the Alkaline Hydrolyses of Neutral Esters at $25 \,^{\circ}C^{\alpha}$

ester	macroion	[macroion], mol L ⁻¹	∆G‡, kJ mol⁻¹	$\Delta H^{\ddagger}, \mathrm{kJ} \mathrm{mol}^{-1}$	$\Delta S^{\ddagger}, \mathbf{J} \mathbf{K}^{-1} \mathbf{mol}^{-1}$	ΔV^{\ddagger} , mL mol ⁻
PNPA	none	0	68.2 ± 0.3	45.2 ± 1.0	-75 ± 8	$-3 \pm 1, -3^{c}$
	PMVA	$1.5 imes10^{-4}$	66.9	36.4	-105	-8
	NaPSS	$1.8 imes10^{-2}$	70.7	77.4	21	- 3
PNPV	none	0	69.0	51.9	- 59	-5
	PMVA	$2.0 imes10^{-4}$	66.1	46.0	- 67	-8
	NaPSS	$1.8 imes10^{-2}$	71.5	59.8	- 38	-2
$PNPL^{b}$	none	0	80.3	88.3	25	-11
	PMVA	$6.0 imes10^{-5}$	67.8	49.8	59	-13
	NaPSS	$1.8 imes10^{-2}$	81.2	95.8	50	-7
a [PNPA] = [PN]	[PV] = [PNPL]	$] = 2.5 \times 10^{-5} \text{ M},$	$[NaOH] = 1.0 \times 1$	10 ⁻³ M. ^b In 10%	C,H,OH-H,O.	^c From ref 15.

TABLE III: Volume of Activation and Other Thermodynamic Parameters for the Alkaline Hydrolyses of Cationic Esters at 25 $^\circ {\rm C}^a$

ester	macroion	[macroion], mol L ⁻¹	$\Delta G^{\ddagger}, \mathrm{kJ} \mathrm{mol}^{-1}$	$\Delta H^{\ddagger}, \mathrm{kJ} \mathrm{mol}^{-1}$	$\Delta S^{\ddagger}, \mathbf{J}$ $\mathbf{K}^{-1} \mathbf{mol}^{-1}$	ΔV^{\ddagger} , mL mol ⁻
ANTI	none	0	66.9 ± 0.3	36.8 ± 1.0	-100 ± 8	-5 ± 1
	PMVA	$3.5 imes10^{-3}$	66.5	30.5	-121	- 9
	NaPSS	$3.1 imes10^{-3}$	72.4	45.2	-92	-4
ONTI	none	0	67,8	36.0	-109	-7
	PMVA	$3.0 imes10^{-3}$	67.4	30.1	-126	-8
	NaPSS	$7.8 imes10^{-4}$	77.0	43.1	-113	- 3
DENTI	none	0	68.2	34.7	-113	-7
	PMVA	$3.0 imes10^{-3}$	67.8	30.5	-126	-10
NaPS	NaPSS	$7.8 imes 10^{-4}$	76.1	73.6	- 8	- 5

pressure. In other words, ΔV^* was negative. The value observed for PNPA, i.e., -3 mL mol⁻¹, agreed well with the value reported by Neuman et al.,^{14,15} though the latter was obtained in a Tris buffer. (ii) In the presence of PMVA, the rate increase with rising pressure was more significant than that without polymer; i.e., ΔV^* decreased by PMVA addition. (iii) On the other hand, ΔV^* increased by addition of NaPSS. The macroion effects on the volume of activation are shown in Tables II and III. It is to be noted that the entropy of activation (ΔS^*), which is evaluated from the temperature dependence of reaction rates, also shows in most cases changes similar to those in ΔV^* . Clearly, there exists a close correlation between the two parameters, as was pointed out earlier for reactions of ions or fairly strong dipoles, and even for enzyme reactions.^{7,8,20,21}

Discussion

The volume of activation (ΔV^*) and the entropy of activation (ΔS^*) are convenient parameters to show the role of hydration for ionic reactions as discussed earlier.²⁰⁻²³ In previous work,¹⁰ we assumed that both ΔV^* and ΔS^* are composed of three contributions:

$$\Delta V^* = \Delta V^*_{int} + \Delta V^*_e + \Delta V^*_h \tag{3}$$

$$\Delta S^* = \Delta S^*_{\text{int}} + \Delta S^*_{e} + \Delta S^*_{h} \tag{4}$$

where ΔV^*_{int} and ΔS^*_{int} are the contributions from the changes of the intrinsic volume and entropy in the course of activation. The terms ΔV^*_e and ΔS^*_e are due to the electrostatic hydration ("electrostriction"). The ΔV^*_h and ΔS^*_h terms denote changes in hydrophobic hydration.

First, let us discuss ΔV^* in the absence of macroions. According to the earlier work on the ester hydrolyses,¹²⁻¹⁶ the molar volume of the tetrahedral activated complex should be smaller than the sum of those of the reactants (ester and OH⁻), since the activated complex involves bonding between two previously discrete molecular species. In other words, ΔV^*_{int} is negative. On the other hand, water molecules, hydrating to OH⁻, would be released in the course of activation due to charge dispersion in the activated complex, i.e., $\Delta V^*_e > 0$. For cationic esters the activated complex would also be neutral and therefore $\Delta V^*_e > 0$ holds, because of dehydration of the complex.

The ΔV_{h}^{*} term would be positive for the hydrolyses of neutral esters and negative for cationic ones, because the anionic or neutral activated complex is supposed to be surrounded by smaller or larger iceberg structures than those of the reactants, respectively. It is assumed here that the iceberg structure around the hydrophobic moiety of the solute would be, at least in part, destroyed by the electric charge on the solute species.¹⁰ Thus, the negative values obtained for ΔV^* suggest that a decrease in ΔV_{int}^* is much more significant than increases in ΔV_{int}^* and ΔV_{h}^* for the neutral esters and that decrease in ΔV_{int}^* are more important than an increase in ΔV_{e}^* for the cationic esters.

Next, we consider the macroion effects on the volume of activation (Table I). The intrinsic term, ΔV^*_{int} , would be insensitive to the polyelectrolyte addition if the reaction mechanism were not influenced by macroions. The ΔV^*_{e} is expected to decrease by the addition of cationic macroions for the hydrolyses of both neutral and cationic esters, because OH⁻ is attracted to the vicinity of the cationic macroions and can be more easily dehydrated by the latter compared with the charge-dispersed activated complex.⁷⁻⁹ This is especially true for the cationic esters which can be repelled by the cationic macroions. On the other hand, the anionic macroions would be ineffective with regard to ΔV^*_{e} of neutral ester hydrolyses, since there exists no electrostatic attraction between the ester and the anionic macroions. The reaction of cationic esters is one

⁽²⁰⁾ Laidler, K. J. "Chemical Kinetics", 2nd ed.; McGraw-Hill: London, 1965; Chapter 5.
(21) Laidler, K. J.; Bunting, P. S. "The Chemical Kinetics of Enzyme

 ⁽²¹⁾ Laidler, K. J.; Bunting, P. S. "The Chemical Kinetics of Enzyme Action", 2nd ed.; Clarendon Press: Oxford, 1973.
 (22) Hamann, S. D. "Physico-Chemical Effects of Pressures"; Butter-

⁽²²⁾ Hamann, S. D. "Physico-Chemical Effects of Pressures"; Butterworth: London, 1957.

⁽²³⁾ Weale, K. E. "Chemical Reactions at High Pressures"; E. and F. N. Spon Ltd.: London, 1967.



Figure 4. Schematic description of the hydrophobic hydration in the alkaline hydrolyses of neutral esters (A) and cationic esters (B). \angle indicates water molecules and their ordered arrangement reflects the iceberg structure. The region covered by \angle indicates the iceberg structure of water.

of the interionic reactions between oppositely charged species. Thus, the anionic macroions would increase ΔV_e^* in this case, as was found earlier.⁸

Now, we discuss the ΔV_{h}^{*} and ΔS_{h}^{*} terms. As is shown schematically in Figure 4, the term ΔV_{h}^{*} with PMVA would be negative, because the cationic macroions and the negatively charged (for eq 1) or neutral (eq 2) activated complex stabilize the large iceberg structure more than the reactant esters. For example, for the hydrolyses of neutral esters, an attraction between a hydrophobic anionic activated complex and a hydrophobic cationic macroion would be stronger than that between a neutral ester and a cationic macroion in the reactant state. This is because there exist both electrostatic and hydrophobic interactions for the former combination, whereas there are only hydrophobic forces for the latter. The underlying ideas are that (1) the stronger the hydrophobicities of reactants and macroions, the larger the iceberg structure, and (2) the stabilization of the iceberg structure contributes toward a decrease in the partial molar volume and the entropy.¹⁰ In the presence of NaPSS, the attraction of the anionic macroions toward neutral or cationic ester is much stronger than that toward the activated complex, because the neutral esters in reaction 1 are more strongly attracted by

The changes in the ΔH^* term on addition of the macroions seem to demonstrate also the important role of the hydrophobic hydration. Tables II and III show that the polyelectrolyte influence is enthalpy controlled; namely, the rate acceleration or deceleration with macroions is caused by the decrease or increase in the enthalpy of activation. These observations are the same as those reported previously for the alkaline hydrolyses of hydrophobic triphenylmethane dyes,¹⁰ but are in contrast to the entropy-controlled reaction systems, for which only electrostatic interactions are important.^{7,8} These dependences of ΔH^* are believed to be accounted for as follows with the assumption that $\Delta H^* = \Delta H^*_{int} + \Delta H^*_e + \Delta H^*_h$. In the presence of PMVA, the iceberg formation is enhanced in the course of activation as is seen in Figure 4, and the enthalpy level of the activated complex is lower than that of the reactant. Thus, the ΔH^* would be smaller than that in the absence of polymer. On the contrary, the addition of NaPSS stabilizes the iceberg structure more strongly for the reactant than the activated complex. Thus, the ΔH_{h}^{*} would increase. The intrinsic quantity ΔH_{int}^{*} is indifferent to the polymer addition. Furthermore, the ΔH^*_{e} term is assumed to be unimportant for the reactions under consideration. The ΔH^* should therefore decrease or increase with PMVA or NaPSS addition.

Acknowledgment. We thank the Grant-in-Aid administered by the Ministry of Education, Science, and Culture, and the Yamada Science Foundation for their generous support of this work.

Registry No. PNPA, 830-03-5; PNPV, 1956-07-6; PNPL, 1956-11-2; ANTI, 17427-00-8; ONTI, 84649-53-6; DENTI, 84649-54-7; PMVA, 9017-80-5; NaPSS, 9080-79-9.

Chemisorption of Cyclohexene on Nickel. A Volumetric and Neutron Inelastic Spectroscopy Study

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Absorption of cyclohexene on Raney nickel was studied at different surface coverages by using neutron inelastic spectroscopy and volumetric methods. At high coverage, hydrogen, benzene, and cyclohexane are detected on the surface. At low coverage, only hydrogen and benzene are present on the nickel.

Hydrogenation of aromatic molecules on transition metals is a well-studied reaction. The detailed mechanism and the limiting steps are now rather clear¹ and the spectroscopic studies concerning the structure of adsorbed benzene^{2,3} have explained why the reaction rate is comparatively low.

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⁽¹⁾ J. P. Candy, P. Fouilloux, and B. Imelik, Nouv. J. Chim., 2, 45 (1978).

⁽²⁾ H. Jobic and A. Renoupresz, Surf. Sci., 111, 53 (1981).

⁽³⁾ A. Renouprez, G. Clugnet, and H. Jobic, J. Catal., 74, 296 (1982).