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Polymer Effects under Pressure. III. Hydrolysis of Normal Alkyl Acetate Catalyzed by Dodecyl Hydrogensulfate Micelle

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Measurements of the rates of hydrolysis of methyl, ethyl, propyl, and butyl acetates have been made to 2 kbar in water catalyzed by dodecyl hydrogensulfate (DSA) micelle at 40 °C. The rate of hydrolysis decreases with compression up to approximately 1 kbar and then increases above 1 kbar; methyl acetate differs in these respects. The inversion phenomenon under pressure has been explained by the incorporation of both the H_3O^+ ion and ester molecules into the micellar phase. The observed value of the over all activation volume at 1 atm ΔV^* is -5.3 ± 1 cm^3/mol for methyl, 0.40 ± 1 cm^3/mol for ethyl, 9.7 ± 1 cm^3/mol for propyl, and 20 ± 1 cm^3/mol for butyl acetate, respectively. From the activation volumes of HCl and DSA micellar catalysts, the volume change accompanying the incorporation of the esters into the micellar phase $\Delta\Delta V_{\mathrm{micelle}}$, has been estimated to be 4.0 ± 1 cm^3/mol for methyl, 9.8 ± 1 cm^3/mol for ethyl, 18.7 ± 1 cm^3/mol for propyl, and 27.9 ± 1 cm^3/mol for butyl acetate, respectively. The values above have been explained in terms of the contribution to the hydrophobic interaction between the ester molecule and the micelle.

Recently, there have been a large number of publications dealing with the enzyme and enzyme-model reactions as polymer and micellar effects;[1-3] the micellar catalyzed reaction being one of the polymer effects. The incorporation of substrates into the micellar phase is brought about by secondary forces such as the electrostatic and hydrophobic interactions between substrates and micelles. The rate of hydrolysis of esters is recognized to be markedly accelerated above the critical micelle concentration (CMC) and is expected to be retarded under pressure since the volume change accompanying each bond formation is positive. In a previous study,[4] the rate of hydrolysis of alkyl acetates catalyzed by sulfonated polystyrene (PSS) accompanying the hydrophobic incorporation of esters into the polymer domain was shown to be retarded by compression up to about 2 kbar.

It is well documented that hydrophobic interactions participate in micelle formation[5] and a maximum appears in the CMC *vs.* pressure plots at about 1 kbar.[6-13] In the present study, we measured the rate of the hydrolysis of methyl ethyl, propyl, and butyl acetates by dodecyl hydrogensulfate micelle as an acid catalyst up to 2 kbar. The reaction mechanism under pressure is discussed from the activation volume ΔV^* for the micellar catalyzed reaction.

Experimental

Materials. Sodium dodecyl sulfate (SDS) was prepared by the reaction of chlorosulfuric acid and 1-dodecanol, which was fractionally distilled three times and analyzed by gas chromatography. The reaction mixture was neutralized with sodium hydroxide. The crude SDS was extracted three times with petroleum ether in a Soxhlet apparatus for 50 h, and finally recrystallized from methanol. The CMC value of 8.3×10^{-3} mol/kg agrees with those of Hamann[6] and Kaneshina *et al.*[10] A DSA solution was prepared from the SDS solution using an ion exchange resin (Amberlite IR-120). The CMC value was 1.8×10^{-3} mol/kg at atmospheric pressure and 40 °C. An ester was distilled prior to use.

Apparatus and Procedures. The high pressure apparatus for measuring the hydrolysis of the ester has been described in detail elsewhere.[4] Under these experimetal conditions, the rate of hydrolysis of DSA was negligibly smaller than that of the alkyl acetates from the blank test for 3 h, which was compared with the data of Kurz.[14] Analysis of the acetic acid formed was conducted by titration using 1/20 M NaOH solution. The rate constant k_a was obtained by dividing the first-order rate constant by the concentration of acid at atmospheric pressure and 40 °C.

Results

At atmospheric pressure, the catalytic effects of the DSA micelle were greater than that of HCl as shown in Fig. 1. The k_a values for the HCl catalyst are almost identical for all esters, however, those for the micellar catalyst increase with increasing carbon number, *i.e.*, the hydrophobicity of the esters. For example the rates are 2.57, 4.31, 6.87, and 10.2×10^{-2} M^{-1} min^{-1} for methyl, ethyl, propyl, and butyl acetate at 40 °C, respectively. The accelerating effect is similar to that previously reported for PSS catalysts.[4]

Under high pressure, as shown in Fig. 2, the rates showed a minima at approximately 1 kbar, the ex-

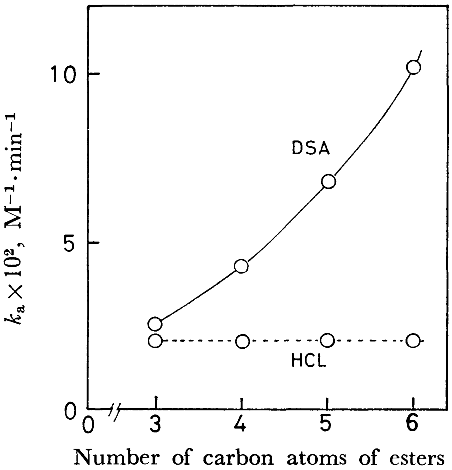

Fig. 1. Plots of k_a *vs.* number of ester carbon atoms for hydrolysis reactions catalyzed by HCl and DSA micelle at 1 atm and 40 °C. Each ester, HCl, and DSA catalysts concentrations are 2×10^{-2} M, 2×10^{-2} M, and 8.3×10^{-3} M.

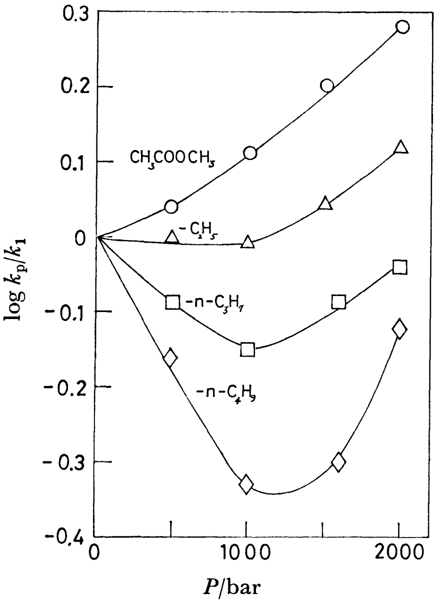

Fig. 2. Plots of $\log k_p/k_1$ *vs.* pressures for hydrolysis reactions catalyzed by DSA micelle at 40 °C. Each ester and DSA catalyst concentrations are 2×10^{-2} M and 8.3×10^{-3} M.

TABLE 1. OBSERVED ACTIVATION VOLUME (ΔV^*) FOR ESTER HYDROLYSIS REACTIONS BY DSA MICELLE AT 40 °C

Catalyst	CH$_3$COO-R, $\Delta V^*\pm1.0$ cm^3/mol			
	-CH$_3$	-C$_2$H$_5$	-n-C$_3$H$_7$	-n-C$_4$H$_9$
HCl	−9.3[a)]	−9.4[a)]	−9.0	−7.9[a)]
DSA	−5.3	0.40	9.7	20

a) Ref. 4.

ception being methyl acetate, and the pressure effects were larger with longer esters. The inversion phenomena corresponded to the appearance of the maximum of the CMC of DSA at 1 kbar.[12)] The observed activation volume ΔV^* is defined by

$$(\partial \ln (k_p/k_1)/\partial P)_T = -\Delta V^*/RT, \tag{1}$$

where R is the gas constant and T the absolute temperature. From the initial slope of the plot of log (k_p/k_1) *vs.* pressure, the ΔV^* values determined graphically have been summarized in Table 1, and compared with previous data for HCl,[4)] in addition to the data of propyl acetate catalyzed by HCl.

Discussion

The acid-catalyzed reaction of carboxylic esters in water is generally accepted to occur by an A-2 mechanism,[15,16)]

$$H_3O^+ + RCOOR' \overset{K}{\rightleftharpoons} RCO\overset{+}{O}HR' + H_2O \tag{2}$$

$$RCO\overset{+}{O}HR' + H_2O \xrightarrow{k} R'OH + RCO\overset{+}{O}H_2 \tag{3}$$

$$RCO\overset{+}{O}H_2 + H_2O \xrightarrow{\text{fast}} RCOOH + H_3O^+ \tag{4}$$

at dilute ester concentration. The rate is given by the equation:

$$(\text{rate})_{\text{HCl}} = K\cdot k\cdot C_{\text{ester}}\cdot C_{\text{H}_3\text{O}^+} \tag{5}$$

where C_{ester} and $C_{\text{H}_3\text{O}^+}$ are the ester and H_3O^+ concentrations. In the micelle catalyst, $C_{\text{H}_3\text{O}^+}$ is not uniform throught out the solution but is higher near the micellar anion and C_{ester} is also concentrated in the micellar region through hydrophobic interaction. Assuming that $K\cdot k$ in Eq. 5 is approximately independent of the electric field, the rate of acid hydrolysis in the micelle is given by

$$(\text{rate})_{\text{micelle}} = K\cdot k\langle C_{\text{ester}}\cdot C_{\text{H}_3\text{O}^+}\rangle, \tag{6}$$

where $\langle C_{\text{ester}}\cdot C_{\text{H}_3\text{O}^+}\rangle$ are the concentrations of the ester and H_3O^+ incorporated into the micellar phase.

A strong acid such as DSA is completely ionized and the counterions are distributed closely to the micellar anion by electrostatic interaction. The effect of added salts on the CMC of SDS surfactants at high pressure was reported by Kaneshina *et al.*,[10)] where it was suggested that the ratio of the number of counterions to surfactant in micelles decreases initially with an increase in pressure and then slightly increases with pressure *via* a minimum at 1.5 kbar. This suggests that compression at low pressure causes dissociation of the counterions from the micelle and that compression at higher pressure causes association of the ions to the micelle. If this tendency is the same as for the DSA micelle, the incorporation of the H_3O^+ ion into the micellar phase would show a minimum at approximately 1 to 1.5 kbar independent of the carbon number of the ester.

The driving force of the incorporation of the ester molecules into the micellar phase is expected to be a hydrophobic from Fig. 1. That the rate catalyzed by the DSA micelle increases with increasing carbon number in the ester, indicates a great degree of incorporation of the longer alkyl chain esters into the micellar phase. The methyl acetate, however, would be poorly incorporated into the micelle since the rate catalyzed by DSA is approximately the same as that of the HCl catalyst. Therefore, the rate of methyl acetate catalyzed by DSA micelle under pressure may be expected to increase linearly independently of the behaviour of the micelle under pressure in a similar manner of HCl. The behaviour of the mixed micelle of DSA and ester molecules would be similar to that of the DSA micelle under pressure. From a study of the pressure effect on the CMC of SDS and dodecyltrimethylammonium bromide (DTAB) in water–organic solvent mixtures,[17)] the maximum in the CMC–pressure plots gradually shifts to higher values as the alcohol content of the solvent increases, and the effect of 1-butanol is larger than that of methanol. This agrees with the minimum pressure on the rate of hydrolysis for esters having longer alkyl chains under pressure which increase (Fig. 2). Therefore, the inversion phenomena in the rate of hydrolysis for esters having long alkyl chain under pressure has been attributed to the joint effects of the incorporation of the H_3O^+ ion and ester molecules into the micellar phase under pressure in Eq. 6.

Table 2 shows the micellar effects on ΔV^*, $\Delta\Delta V_{\text{micelle}}$

Table 2. Micellar effect on ΔV^* for ester hydrolysis compared with PSS polymer effect at 40 °C

Catalyst	CH_3COO-R, $\Delta\Delta V_{\text{micelle}} \pm 1.0$ cm^3/mol			
	$-CH_3$	$-C_2H_5$	$-n-C_3H_7$	$-n-C_4H_9$
DSA	4.0	9.8	18.7	27.9
PSS(100)[a]	3.4	8.6		10.0
PSS(60)[a]	6.6	12.5		15.5

a) Ref. 4.

compared with the PSS polymer effect. The increase of $\Delta\Delta V_{\text{micelle}}$ with increase in the carbon number of the esters needs consideration. The results correspond to the order of the incorporation of the esters into the micelle, and may be explained by the volume increase accompanying rupture of the hydrophobic hydration around the hydrocarbon part of the esters. It has been reported that the volume change for the formation of hydrophobic interaction is 1, 5, and 8 cm^3/mol for methyl, ethyl, and propyl groups, respectively.[18] The value of 1—2 cm^3/mol per methyl group accompanying the breaking down of hydrophobic hydration is supported by Noguchi,[19] Kaneshina *et al.*,[10] Corkill *et al.*,[20] and Friedman *et al.*[21] For butyl acetate the expected value accompanying the hydrophobic incorporation of ester molecules into the micelle is approximately half the $\Delta\Delta V_{\text{micelle}}$ suggesting additional contributions to $\Delta\Delta V_{\text{micelle}}$ accompanying a strong hydrophobic atmosphere *e.g.*, the dehydration of H_2O molecules from the carbonyl oxygen atom of the esters for hydrophobic incorporation, which accompanies a positive volume change of 5 to 7 cm^3/mol.[22—25] Also, the exclusion of water molecules by strong hydrophobic atmosphere may change the A-2 mechanism into an A-1 mechanism in the *t*-butyl acetate system. Assuming such a development, the ΔV_{HCl} in Eq. 1 becomes small and positive or zero.[26] The $\Delta\Delta V_{\text{micelle}}$ for the butyl acetate system is 20 cm^3/mol, which is a reasonable value. Further studies are necessary to confirm the A-1 mechanism in the micelle.

References

1) K. J. Laidler and P. S. Bunting, "The Chemical Kinetics of Enzyme Action," 2nd ed, Oxford University Press, London (1973).

2) J. H. Fendler and E. J. Fendler, "Catalysis in Micellar and Macromolecular Systems," Academic Press, New York, N. Y. (1975).

3) "Reaction Kinetics in Micelles," ed by E. H. Cordes, Plenum Press, New York, N. Y. (1973), p. 25.

4) Y. Taniguchi, N. Sugiyama, and K. Suzuki, *J. Phys. Chem.*, **82**, 1231 (1978).

5) C. Tanford, "The Hydrophobic Effect: Formation of Micelles and Biological Membranes," Wiley, New York, N.Y. (1973).

6) S. D. Hamann, *J. Phys. Chem.*, **66**, 1359 (1962).

7) R. F. Tuddenham and A. E. Alexander, *J. Phys. Chem.*, **66**, 1839 (1962).

8) J. Osugi, M. Sato, and N. Ifuku, *Rev. Phys. Chem. Jpn.*, **35**, 32 (1965).

9) J. Osugi, M. Sato, and N. Ifuku, *Rev. Phys. Chem. Jpn.*, **38**, 58 (1968).

10) S. Kaneshina, M. Tanaka, T. Tomida, and R. Matuura *J. Colloid Interface Sci.*, **48**, 450 (1974).

11) M. Ueno, M. Nakahara, and J. Osugi, *Rev. Phys. Chem. Jpn.*, **47**, 25 (1977).

12) K. Suzuki, Y. Taniguchi, and M. Tsuchiya, 6th International Conference on High Pressure, Boulder, July 1977.

13) Recently, from a study of the pressure effect on CMC using naphthalene as a probe, it was found that the CMC of SDS does not invert up to about 5 kbar. See, S. Rodriguez and H. Offen, *J. Phys. Chem.*, **81**, 47 (1977).

14) The rate constants of H^+ catalyzed hydrolysis for sodium alkyl sulfate is 82×10^{-5} to 198×10^{-5} mol^{-1} s^{-1} at 90 °C. See, J. L. Kurz, *J. Phys. Chem.*, **66**, 2239 (1962).

15) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," 2nd ed, Cornell University Press, Ithaca N.Y. (1967), p 1098.

16) K. J. Laidler, "Chemical Kinetics," 2nd ed, McGraw-Hill, London (1965) p. 88.

17) S. Kaneshina, M. Tanaka, and R. Matuura, *Mem. Fac. Sci. Kyushu Univ., Ser. C*, **9**, 71 (1974).

18) K. Suzuki, Y. Taniguchi, and T. Watanabe, *J. Phys. Chem.*, **77**, 1918 (1973).

19) H. Noguchi, *Prog. Polym. Sci.*, **8**, 191 (1975).

20) J. M. Corkill, J. F. Goodmann, and T. Walker, *Trans. Faraday Soc.*, **63**, 768 (1967).

21) M. E. Friedman and H. A. Scheraga, *J. Phys. Chem.*, **69**, 3795 (1965).

22) E. Fishman and H. G. Drickamer, *J. Chem. Phys.*, **24**, 548 (1956).

23) K. Suzuki and M. Tsuchiya, *Bull. Chem. Soc. Jpn.*, **48**, 1701 (1975).

24) Y. Taniguchi and K. Suzuki, *J. Phys. Chem.*, **78**, 759 (1974).

25) K. Suzuki, M. Tsuchiya, and M. Kadono, *Bull. Chem. Soc. Jpn.*, **43**, 3083 (1970).

26) A. R. Osborn and E. Whalley, *Can. J. Chem.*, **39**, 1094 (1961).