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Effects of Pressure on Hydrolysis of *p*-Nitrophenyl Acetate in Aerosol OT Reversed Micelles

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Synopsis. Kinetic studies were made on imidazole-catalyzed hydrolysis of *p*-nitrophenyl acetate in Aerosol OT (AOT) reversed micelles (AOT/H_2O/heptane) at high pressure. The rate of the reaction was found to increase with increase in the size of the aqueous core in the reversed micelles and with increase in pressure. Micellar effects on the hydrolysis are discussed in relation with the activation parameters of the reaction.

The hydrolyses of carboxylic acid esters in micelles have often been used as examples of chemical reactions in micellar systems that are similar to enzyme reactions. Studies on micelle catalysts are important because many hydrolyses catalyzed by nucleophiles or enzymes occur in biosystems. Aerosol OT forms stable reversed micelles that can contain large amounts of water as an aqueous core, and these reversed micelles are of biochemical interest because their molecular assembly is similar to that of water pockets in bioaggregates (biomembranes, mitochondria,[1] etc.).

We have studied the effects of pressure on some chemical reactions in micellar systems.[2–6] In the present paper we report the effects of pressure on the hydrolysis of *p*-nitrophenyl acetate in AOT reversed micelles. Micellar effects on the hydrolysis are discussed in relation with activation parameters of the reaction.

Experimental

Sodium salt of bis(2-ethylhexyl) sulfosuccinate (Aerosol OT, AOT) was obtained from Tokyo Kasei. It was dissolved in methanol and filtered, and then the solvent was removed under vacuum. *p*-Nitrophenyl acetate (Tokyo Kasei) was recrystallized twice from ethanol. Imidazole (Wako) was used without further purification.

A high-pressure vessel with quartz optical windows was used to follow the reaction at high pressure directly. Sample solutions were charged into a sliding cell (inner quartz cell) to prevent contamination of the solution by the metal body and packing of the vessel. The high-pressure vessel was set in a Hitachi 100-60 UV-visible spectrophotometer and the reaction product, *p*-nitrophenol, was determined by measuring its absorbance at 400 nm. Pressures were generated by a hand-operated hydraulic pump (Hikari KP-5B) and measured with a Heise Bourdon gauge.

The reaction solution was prepared by mixing 3 wt% AOT in heptane with aqueous 5.0×10^{-2} mol dm^{-3} imidazole solution in various ratios. *p*-Nitrophenyl acetate (8.0×10^{-5} g) was added to 4 cm^3 samples of the AOT/H_2O/imidazole/heptane solutions and the mixtures were stirred for 10 min. Reaction rates in water were used as standards in evaluating micellar effects.

Results and Discussion

Pseudo-first-order rate constants (k) were deter-

Table 1. Effects of Pressure and Temperature on the Pseudo-First-Order Rate Constants of the Hydrolysis of *p*-Nitrophenyl Acetate in Aerosol-OT Reversed Micelles[a] and Water[b]

R=[H_2O]/[AOT]	k/10^{-4} s^{-1}								
	P/MPa=0.1	10	20	30	60	70	80	90	100
				T/K=288.15					
5.0	0			0	0				0
12.1	1.14		1.22		1.41				1.76
23.4	1.54			1.72	2.07				2.55
aq. soln[b]	1.52			1.84	2.26				3.03
				T/K=298.15					
1.1	0			0	0				0
5.8	0			0	0				0
11.2	1.50			1.54	1.62	2.09	2.71	2.89	2.87
12.9	2.26			2.46	2.67				3.48
23.7	2.59			3.01	3.12				4.03
35.2	2.92			3.36	4.05				5.17
38.7	2.97			3.53	4.18				5.51
39.9	2.90			3.48	4.16				5.53
aq. soln[b]	3.48			3.99	4.66				5.55
				T/K=308.15					
5.0	0			0	0				0
12.2	1.95	1.88	2.06	2.31	3.24				3.32
24.6	2.79			3.20	3.60				4.29
34.4	3.52			4.32	5.63		6.29		
aq. soln[b]	5.74			7.29	8.44				

a) [Imidazole]=5.0×10^{-2} mol dm^{-3} (AOT systems). b) [Imidazole]=5.0×10^{-4} mol dm^{-3} (aq. soln).

mined by the Guggenheim method⁷⁾ and are presented in Table 1. Water contents are shown as molar ratios of water to AOT (R=[H_2O]/[AOT]). The hydrolysis of *p*-nitrophenyl acetate was strongly dependent on the properties of the reaction fields and pressure. For example, the reaction did not occur when the water content was less than 6 (R<6). This is because at R< 6 almost all the water molecules in the reversed micelles are strongly bound to the polar heads of AOT or to sodium ions (counter ions),⁸⁻¹⁰⁾ and so hydrolysis does not readily occur. At $R > 10$, there is a free water phase and the hydrolysis occurs. Thus we can conclude that the hydrolysis of *p*-nitrophenyl acetate proceeds only in the presence of free water. The size of the aqueous core also affected the reaction rate: the rate increased with increase in the size of the water pool. Over a range of water contents of $10 < R < 30$, the rate of *p*-nitrophenyl acetate hydrolysis was an almost linear function of R ([H_2O]/[AOT]) at both atmospheric and high pressures.

Pressure also promoted the hydrolysis of *p*-nitrophenyl acetate in AOT reversed micelles. In general, acid- and base-catalyzed hydrolyses of esters are promoted by pressure, because partial electric charges or bonds are formed during the reactions. Apparent activation volumes ($\Delta V^{\ddagger}_{\mathrm{ap}}$) were calculated by the equation:

$$(\partial \ln k/\partial P)_T = -\Delta V^{\ddagger}_{\mathrm{ap}}/RT$$

where R, T, and P are the gas constant, the absolute temperature and the pressure, respectively. The apparent activation volumes of the hydrolysis of *p*-nitrophenyl acetate are shown in Table 2. These volumes depend greatly on the nature of the reaction field. The large and irregular variations of the values from −3.2 (R=11.2) to −16.0 cm³ mol⁻¹ (R=39.9) suggest that not only the nature of the water pool, but also micellar size are closely related to the effects of pressure on the reaction rate. In particular, the $\Delta V^{\ddagger}_{\mathrm{ap}}$ is found to decrease rapidly at $R \approx 30$. Fluorescence polarization studies of AOT reversed micelles at high pressures¹¹⁾ showed that the micelles aggregated and formed polydisperse syslems at $R \approx 30$ and that these changes of micellar size were greatly enhanced by pressure. This aggregation of the micelles can be considered as one reason for the increase in reaction rates with increase in pressure at $R \geqq 30$. The activation volume in the aqueous solution (−11.8 cm³ mol⁻¹) coincided exactly with that at this water content $R \approx 30$ (Fig. 1).

Table 2. Apparent Activation Volumes of the Hydrolysis of *p*-Nitrophenyl Acetate in AOT Reversed Micelles^a)^ and Water^b)^ at Atmospheric Pressure and 298.15 K

R=[H_2O]/[AOT]	$\Delta V^{\ddagger}_{\mathrm{ap}}$/cm³mol⁻¹
11.2	−3.2
12.9	−6.4
23.7	−10.4
35.2	−14.4
38.7	−15.2
39.9	−16.0
aq. soln^b)^	−11.8

a) [Imidazole]=5.0×10⁻² mol dm⁻³ (AOT systems).
b) [Imidazole]=5.0×10⁻⁴ mol dm⁻³ (aq. soln).

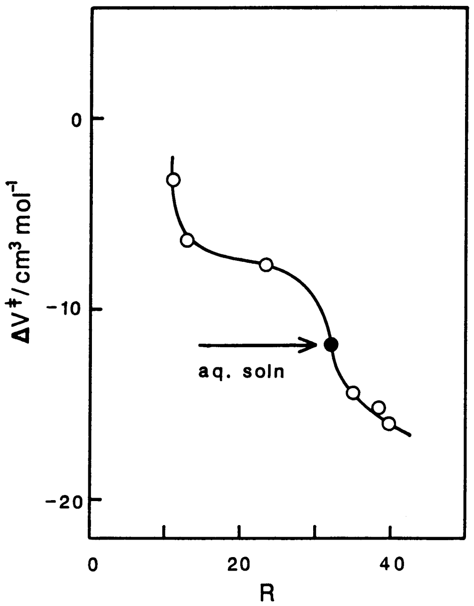

Fig. 1. Activation volumes for the hydrolysis of *p*-nitrophenyl acetate in AOT reversed micellar systems and aqueous solution at atmospheric pressure and 298.15 K. R=[H_2O]/[AOT].

The base-catalyzed hydrolyses of esters in water usually have activation volumes in the range of −5 to −10 cm³ mol⁻¹.¹²⁾ These values are explained as follows. The coordination of OH^- ions to esters should be associated with volume reduction due to formation of new chemical bonds, although loss of electrostriction by dispersion of electric charges may result in some increase in volume. In imidazole-calalyzed hydrolysis of *p*-nitrophenyl acetate in AOT reversed micelles, the imidazole molecule presumably acts as a nucleophile rather than a general base as in aqueous solutions.¹³⁾

As imidazole is insoluble in dry AOT/heptane solutions, it must be present exclusively in the water pool of AOT/H_2O/heptane reversed micelles. When *p*-nitrophenyl acetate is added to the AOT/H_2O/imidazole/heptane system, hydrolysis of the ester occurs in the water pool. Therefore, the partition of the ester between the heptane phase and the water phase across the surfactant boundary becomes important.¹⁴⁾ Accordingly, when determining reaction rates at high pressure the effect of pressure on partition coefficients should be considered. The volume change ΔV for the transfer of *p*-nitrophenyl acetate from the heptane to water phase can be expressed as

$$-RT\,(\partial \ln K/\partial P)_T = \Delta V = V_{\mathrm{W}} - V_{\mathrm{H}}$$

$$K = x_{\mathrm{W}}/x_{\mathrm{H}}$$

where K is the partition coefficient, V_{W} and V_{H} are the partial molar volumes of *p*-nitrophenyl acetate in the water and heptane phases, and x_{W} and x_{H} are the mole fractions in these systems. In general, esters have smaller partial molar volumes in water than in alkanes (ΔV<0). This means that pressure increases

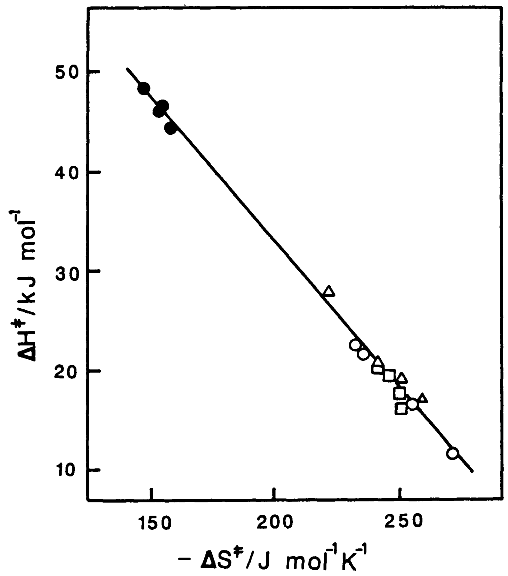

Fig. 2. Linear relationship between activation enthalpies and entropies for the hydrolysis of *p*-nitrophenyl acetate in AOT reversed micellar systems and aqueous solution at atmospheric pressure and 298.15 K.
Water contents (R): △: 12, □: 24, ○: 35, ●: aq. soln.

the partition coefficient and promotes the hydrolysis. This is another reason for acceleration of the reaction by increase in pressure. This effect is more pronounced at higher water contents ($R > 30$).

Figure 2 shows the relationship between the activation enthalpies and entropies of the hydrolysis of *p*-nitrophenyl acetate at 298.15 K. Good compensation effects between the enthalpies and the entropies are observed in the water and AOT systems. Although the activation enthalpies and entropies for the aqueous solution have much larger values than those for AOT systems, the linear relationship is very good.

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