Kinetic Consequences of Molecular Aggregation in the Hydrolysis of *p*-Nitrophenyl Carboxylates

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Alkaline hydrolysis of *p*-nitrophenyl carboxylates was investigated in mixed aqueous–organic solvents. Esters with a long alkyl chain tend to aggregate by intermolecular hydrophobic interaction above the critical concentration. Among acetate, hexanoate, decanoate, dodecanoate, and hexadecanoate, the last showed the lowest critical concentration, while acetate and hexanoate did not demonstrate any detectable aggregation even in 1.0% (v/v) aqueous dioxan. The reactivity of monomeric esters decreased with increasing alkyl-chain length, due to the self-coiling behaviour of the alkyl chain which acts to mask the ester bond from hydroxide attack. The critical concentration for dodecanoate decreased in the reaction medium order: 10.9% (v/v) dioxan > 10.9% (v/v) acetonitrile ≃ 1.0% (v/v) dioxan > 10.9% (v/v) ethanol. The rate increase observed for hydrolysis of monomeric dodecanoate by increasing the organic content of a solvent was attributed to elongation or decoiling of the monomeric ester. As for the effect of hydroxide ion concentration on aggregation behaviour, the monomer fractions of dodecanoate and of hexadecanoate above their critical concentrations were found to decrease with increasing [OH^-] due to the structure-making ability of hydroxide ion. Urea acted to raise somewhat the critical concentrations of the esters and to decrease their aggregation numbers as exemplified by the alkaline hydrolysis of dodecanoate. The salting-out effects of inorganic salts gave a reduction in the fraction of monomeric ester and hence in the overall hydrolysis rate.

p-NITROPHENYL esters of aliphatic monocarboxylic acids with a long alkyl chain provide a convenient kinetic probe for hydrophobic interactions in aqueous media. The deacylation rates of these substrates are moderately to significantly enhanced by well designed functional micelles [1] and paracyclophanes.[2-5] Substrate–catalyst association *via* hydrophobic interaction is undoubtedly responsible for the observed rate enhancements. It is important to note, however, that the spontaneous alkaline hydrolysis rates of these substrates, to which rate accelerations are usually referred, are surprisingly small relative to that of a simple substrate such as *p*-nitrophenyl acetate. The hydrolysis rates of *p*-nitrophenyl octanoate,[6] decanoate,[6,7] and dodecanoate [8] have been shown to increase as their initial concentrations were lowered. These results have been cited as evidence for self-aggregation of these esters at normal spectroscopic concentrations, but their micelle-forming behaviour has not been commented on in any critical sense. The effects of a limited number of additives (urea, n-butylurea, dioxan, and tetramethylammonium bromide) on the aggregation of *p*-nitrophenyl dodecanoate have also been investigated, but the corresponding change in micelle-forming behaviour has not been clarified at all. In view of the general use of these esters as substrates, it is highly desirable to shed more light on the aggregation phenomena. Employing a wider variation in alkyl-chain length, we have investigated the effects of several factors on aggregation from the kinetic viewpoint with the emphasis on the following: (i) micelle-forming

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equilibria as affected by the alkyl-chain length by reference to the aggregation behaviour of non-ionic surfactants, and reactivity of monomeric and polymeric ester species; (ii) the effects of organic co-solvents on the critical concentration for micelle formation of esters as well as on the self-coiling behaviour of monomeric ester species in mixed aqueous–organic solvents; (iii) the effects of a wide range of ionic additives as well as urea on the molecular aggregation of esters by reference to the behaviour of a simple carboxylic ester, *p*-nitrophenyl acetate. Consequently, this work provides a sound basis for evaluation of hydrophobic contributions in the catalytic deacylation of carboxylic esters bearing a long alkyl chain.

EXPERIMENTAL

Materials.—*p*-Nitrophenyl acetate, hexanoate, decanoate, and dodecanoate were prepared by condensation of the corresponding acid chlorides with *p*-nitrophenol. *p*-Nitrophenyl hexadecanoate was from Merck. The esters were identified by elemental analyses and spectral measurements before use.

Kinetic Measurements.—Rates of *p*-nitrophenol liberation from *p*-nitrophenyl acetate and hexanoate were measured at 400 nm with a Hitachi 124 recording spectrophotometer. Rates of liberation of *p*-nitrophenol from *p*-nitrophenyl decanoate, dodecanoate, and hexadecanoate were measured in a similar manner with a Union Giken SM-401 high sensitivity spectrophotometer with the following conditions; response 2 s, and sensitivity 0.02—0.5 OD/full scale. Each run was initiated by adding 30 μl of a stock solution of *p*-nitrophenyl carboxylate dissolved in an appropriate organic solvent to 3 ml of a buffer medium [borate–carbonate, 0.01M; μ 0.10 (KCl)], which was pre-equilibrated at 40.0 ± 0.1 °C in a thermostatted cell set in the spectrophotometer. The upper limits of the ester concentrations for kinetic runs were carefully set by referring to the solubility properties of the esters, and the esters were completely soluble in the specified solvent systems over the concentration ranges employed here.

Surface Tension Measurements.—Measurements were performed at room temperature with a Kyowa DIGI-O-MATIC ESB-IV electro-surface balance assembled by the Wilhelmy principle for solutions of *p*-nitrophenyl decanoate (6.0×10^{-7}—1.0×10^{-5}M) in 1.0% (v/v) aqueous dioxan maintained at pH 7.0 and μ 0.10 (KCl). The platinum blade was repeatedly washed with distilled water and heated to incandescence in the flame of an alcohol lamp after each measurement.

Determination of Hydroxide Ion Concentrations.—pH Measurements were carried out with a Beckman expandomatic SS-2 pH meter equipped with a Metrohm EA-125 combined electrode after calibration with a combination of appropriate standard buffers. The pH values of kinetic solutions were converted to the hydroxide ion concentrations by referring to those of solutions containing known amounts of sodium hydroxide under identical kinetic conditions.

RESULTS AND DISCUSSION

Effects of Initial Ester Concentration on Hydrolysis Rate.—Alkaline hydrolysis of *p*-nitrophenyl acetate, hexanoate, decanoate, and dodecanoate was investigated at pH 10.3, 40.0 ± 0.1 °C, and initial ester concentrations of 2.0×10^{-7}—2.0×10^{-5}M in 1.0% (v/v) aqueous dioxan. Even in the hydrolysis of decanoate and dodecanoate at the highest initial concentration range, the pseudo-first-order plots were linear at least up to 50% conversion. The second-order rate constants derived from the corresponding pseudo-first-order constants are shown in Figure 1 as a function of initial ester concentration. In contrast to the cases of acetate and hexanoate, the hydrolysis rates for decanoate and dodecanoate decrease drastically beyond the critical concentrations. This reduction in rate at higher concentrations is readily attributed to self-aggregation of the carboxylate molecules.[6-8] In order to confirm further the intermolecular aggregation behaviour of *p*-nitrophenyl carboxylates bearing a long alkyl chain, surface tension measurements were carried out for solutions of decanoate in 1.0% (v/v) aqueous dioxan. As shown in Figure 2, the decanoate system shows clearly a break-point characteristic of micelle formation, and the critical concentration at the break-point is *ca.* 3×10^{-6}M. This is in good agreement with the kinetically determined value (2×10^{-6}M, see Table). Below the critical concentration, the esters must be monomeric and the hydrolysis rates are independent of their concentrations. The critical concentration decreases as the alkyl chain is elongated (Table).

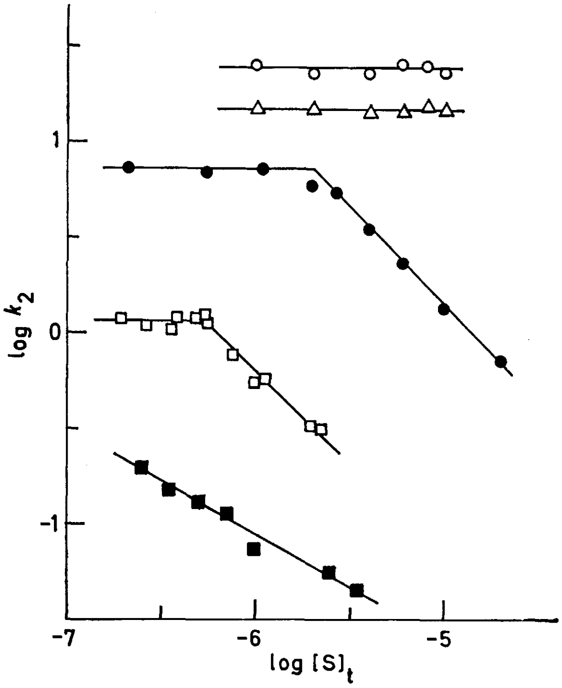

FIGURE 1 Correlations of second-order rate constant k_2 with initial ester concentration $[S]_t$ for hydrolysis of *p*-nitrophenyl carboxylates: acetate (○), hexanoate (△), decanoate (●), dodecanoate (□), and hexadecanoate (■) at 40.0 ± 0.1 °C and μ 0.10 (KCl) in 1.0% (○, △, ●, □) and 10.9% (v/v) aqueous dioxan (■)

p-Nitrophenyl carboxylates with a sufficiently long alkyl chain may form micelles with a certain aggregation

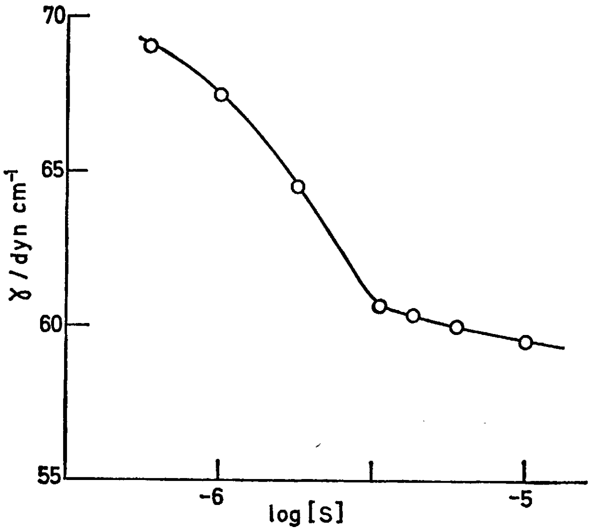

FIGURE 2 Correlation of surface tension γ with ester concentration [S] for solutions of *p*-nitrophenyl decanoate in 1.0% (v/v) aqueous dioxan at pH 7.0, μ 0.10 (KCl), and 20 °C

Second-order rate constants (k_2) for hydrolysis of monomeric *p*-nitrophenyl carboxylates and their critical concentrations for aggregation [a]

p-Nitrophenyl carboxylate	Medium [b]	k_2/l mol^{-1} s^{-1}	Critical concentration (M)
Acetate	1.0% (v/v) D	23.8	
Hexanoate	1.0% (v/v) D	14.5	
Octanoate	3.3% (v/v) A		1.0×10^{-5} [c]
Decanoate	1.0% (v/v) D	7.1	2.0×10^{-6} [d]
Dodecanoate	1.0% (v/v) D	1.1—1.2	5×10^{-7}
	10.9% (v/v) D	6—6.5	9×10^{-7}
	10.9% (v/v) A	4.5—5	$\sim 5 \times 10^{-7}$
	10.9% (v/v) E	$\gtrsim 6$	$\lesssim 2 \times 10^{-7}$
	30.7% (v/v) E	11	
Hexadecanoate	10.9% (v/v) D		$< 2.5 \times 10^{-7}$

[a] At 40.0 ± 0.1 °C and μ 0.10 (KCl). [b] Aqueous solution containing the indicated amount of organic solvent: D, dioxan; A, acetonitrile; E, ethanol. [c] See ref. 6. [d] Similar values have been reported: 1.6×10^{-6}M,[6] 2×10^{-6}M.[7]

number above their critical concentrations, which is characterised by their thermodynamic stabilities in a given medium, as observed for non-ionic surfactants.[1] On this basis, the linear correlation between the logarithm of the second-order rate constant (log k_2) and total ester concentration (log $[S]_t$) observed beyond the critical concentration for decanoate and dodecanoate are analysed as follows. Suppose that the self-aggregate (S_n) is composed of n molecules of the monomeric ester with equilibrium constant K [equations (1) and (2)]. If the

$$nS \rightleftharpoons S_n \qquad (1)$$

$$[S_n]/[S]^n = K \qquad (2)$$

aggregation number n is sufficiently large, only the monomeric species is reactive in hydrolyses. Then, the rate expression is given by equation (3), where $[S]_t$ and [S] represent stoicheiometric concentrations of all ester species and monomer, respectively; k_m and f stand for second-order rate constant for hydrolysis and fraction of monomeric species [equation (4)], respectively. Thus,

$$-d[S]_t/dt = k_m[OH^-][S] = k_m[OH^-]f[S]_t \qquad (3)$$

$$f = [S]/[S]_t \qquad (4)$$

the apparent second-order rate constant k_2 is correlated with k_m by equation (5). Combination of equations (2)

$$k_2 = k_m f \qquad (5)$$

and (4) results in equation (6), provided $[S_n] = ([S]_t - [S])/n$.

$$(1 - f)f^{-n} = nK[S]_t^{n-1} \qquad (6)$$

It seems reasonable to assume that the variation of the $(1 - f)$ value $(0 < f < 1)$ is sufficiently small relative to that of f^n such that $(1 - f)$ can be taken as a constant, n being sufficiently large. Thus, equation (6) is converted into (7). With reference to equations (5) and (6), the

$$f^n[S]_t^{n-1} = \text{constant} \qquad (7)$$

correlation between log k_2 and log $[S]_t$ is established by equation (8) which is further simplified to equation (9) if $n \simeq n - 1$.

$$\log k_2 = -\frac{(n-1)}{n}\log [S]_t + \text{constant} \qquad (8)$$

$$\log k_2 = -\log [S]_t + \text{constant} \qquad (9)$$

The theoretical correlation between rate and ester concentration expressed by equation (9) is observed experimentally as shown in Figure 1 for decanoate and dodecanoate. The agreement between the theoretical treatment and the experimental data seems to indicate the validity of the assumptions made in deriving equation (9). Consequently, two important comments can be made here. (i) Over the whole concentration range studied the reactive species for hydrolysis is the monomeric ester and the reduced rate above the critical concentration is ascribed to decrease in the monomer fraction upon aggregate formation. (ii) The micelle-forming behaviour with a significantly large aggregation number is analogous to that observed for non-ionic surfactants.

The rate–concentration correlation for *p*-nitrophenyl hexadecanoate in 10.9% (v/v) aqueous dioxan is shown in Figure 1. The rate constant regularly increases with decreasing ester concentration over the whole concentration range studied, and hence the critical concentration of this ester is indeterminably small under the present conditions. We must comment on the slope which is much smaller than unity for the linear log k_2 — log$[S]_t$ correlation. As the slope decreases from unity [equation (8)], the aggregation number is lowered accordingly. Thus, qualitatively speaking, the aggregation number for hexadecanoate * seems to be much smaller than those for

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* It is not justified to evaluate the aggregation number of hexadecanoate directly from the slope [see equation (8)] since the derivation of equation (8) is based on the assumption that n is sufficiently large.

decanoate and dodecanoate. Long hydrocarbon chains in water tend to undergo self-coiling by intramolecular hydrophobic interaction,[9] which leads to reduction in the intermolecular aggregation number. Such intramolecular coiling must be more extensive for hexadecanoate than for decanoate and dodecanoate.

The reactivity of monomeric ester decreases with increasing alkyl-chain length as shown in the Table. Similar effects have also been noted elsewhere without detailed discussion.[6,10,11] The extent of self-coiling of the alkyl chain is undoubtedly reflected in the decrease in the hydrolysis rate, which is caused by masking the ester bond from hydroxide attack by both hydrophobic and steric effects. The intramolecular coiling effect may be particularly significant for carboxylic esters having an alkyl chain longer than that of dodecanoate. The hydrolysis rate decreases sharply on going from decanoate to dodecanoate even though the two esters differ only by two methylene units. It has been recognized that esters with a bulky acyl substituent are subject to considerable retardation in hydrolysis.[12-17] A rough comparison of the present results with the existing data [12-15] indicates that the effective size of the alkyl portion of monomeric dodecanoate in aqueous media is greater than that of the isopropyl but smaller than that of the t-butyl group.

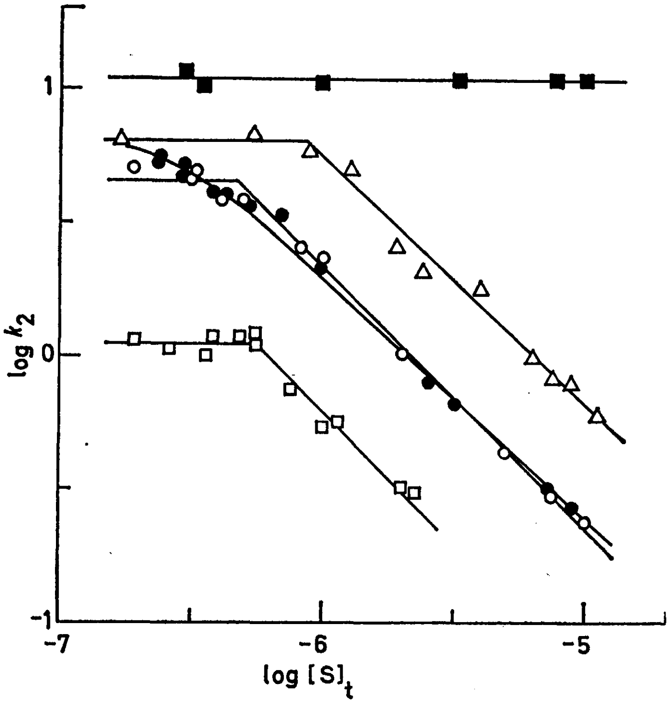

FIGURE 3 Correlations of second-order rate constant k_2 with initial ester concentration $[S]_t$ for hydrolysis of *p*-nitrophenyl dodecanoate at 40.0 ± 0.1 °C and μ 0.10 (KCl) in 1.0% (v/v) aqueous dioxan (□), 10.9% (v/v) aqueous ethanol (●), 10.9% (v/v) aqueous acetonitrile (○), 10.9% (v/v) aqueous dioxan (△), and in 30.7% (v/v) aqueous ethanol (■)

Effects of Organic Co-solvents on Aggregation Behaviour.—Figure 3 shows the correlations between second-order rate and ester concentration for dodecanoate in 1.0% (v/v) aqueous dioxan, in 10.9% (v/v) aqueous ethanol, acetonitrile, and dioxan, and in 30.7% (v/v) aqueous ethanol. All three systems containing 10.9% (v/v) organic solvent show similar overall features. The rate-descending portions in the log k_2—log $[S]_t$ correlations at higher ester concentrations have a slope of —0.9 to —1.0, which is related to the aggregation number [equation (8)]. Hence, the aggregation behaviour of dodecanoate is the same in the three different media. The critical concentration, on the other hand, is sensitive to the nature of the particular medium employed (Table). Aqueous 10.9% ethanol gives the lowest critical concentration among reaction media employed for dodecanoate, since the rate still increases somewhat with further reduction in the ester concentration even in its critical concentration range (Figure 3). The critical concentration decreases in the reaction medium order: 10.9% (v/v) dioxan > 10.9% (v/v) acetonitrile ≃ 1.0% (v/v) dioxan > 10.9% (v/v) ethanol. The critical concentration is one way of evaluating the extent of hydrophobic interaction of solute molecules in a given solvent system. Thus, the intermolecular hydrophobic interaction of dodecanoate molecules is strengthened, little affected, and weakened in 10.9% (v/v) ethanol, 10.9% (v/v) acetonitrile, and 10.9% (v/v) dioxan, respectively, relative to 1.0% (v/v) dioxan and probably pure water. Hydrophobic interaction is related to the hydrogen-bonded structure of water,[18] and it is tempting, therefore, to present the discussion in the light of the effects of organic solvents on water structure. It has been generally recognized that the fraction of structured water in a mixed aqueous–organic solvent system reaches a maximum and falls as the organic content increases from 0 to 100%.[19-23] The organic content of a solvent at the maximum fraction of structured water is highly dependent on the nature of the particular solvent employed. Ethanol has been claimed to facilitate more structuring than dioxan.[22] It must be emphasized, however, that a strict correlation between the water structure and the strength of hydrophobic interactions of apolar solutes

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has not been established, and that the mode of hydrophobic interaction in mixed solvents differs from one case to another. For example, water is more structured in 1M- [*ca.* 8.5% (v/v)] dioxan than in pure water according to measurements of the dielectric relaxation time of water,[21] while the present results clearly indicate that 10.9% (v/v) dioxan acts to weaken the hydrophobic interaction of dodecanoate relative to 1.0% (v/v) dioxan. The strength of hydrophobic interaction in aqueous ethanol has been claimed to have a maximum at 0.1 mole fraction [*ca.* 26% (v/v)] of ethanol from a conductometric study of decyltrimethylammonium carboxylates.[23] Our present results show, however, that 10.9% (v/v) ethanol tends to strengthen the hydrophobic interaction on one hand relative to 1.0% (v/v) dioxan on the basis of critical concentration data, but 30.7% (v/v) ethanol destroys it completely on the other (Figure 3).

The Table shows the second-order rate constants for hydrolysis of monomeric dodecanoate in various solvent systems. The rate constant in aqueous media containing 10.9% (v/v) organic solvent is rather insensitive to the nature of the solvents employed and is *ca.* 5-fold larger than that in 1.0% (v/v) aqueous dioxan. The reaction rate is even larger in 30.7% (v/v) aqueous ethanol. The increase in rate upon increasing the organic content of a solvent is presumably due to elongation or decoiling of the monomeric ester, since the second-order rate constant for hydrolysis of *p*-nitrophenyl acetate underwent only a minor change by replacement of 1.0% (v/v) with 10.9% (v/v) dioxan.*

The discussion and conclusions above allow an interpretation of the rate perturbation induced by added organic co-solvents at higher ester concentrations. For example, dodecanoate hydrolysis is enhanced in 10.9% (v/v) relative to that in 1.0% (v/v) dioxan (Figure 3). This rate acceleration is partly attributed to the increase in reactivity of the monomeric ester (see Table) and partly to the increase in critical concentration which gives accordingly the increase in monomer fraction at any given ester concentrations.

Effect of Hydroxide Ion Concentration on Aggregation Behaviour.—The plots of the logarithm of the pseudo-first-order rate constant ($k_1 = k_m[OH^-]f$) *versus* pH for hydrolysis of hexanoate and decanoate in 1.0% (Figure 4) and decanoate in 10.9% (v/v) aqueous dioxan (Figure 5) provide linear correlations with a slope of unity or near unity. A similar plot for dodecanoate in 10.9% (v/v) aqueous dioxan (Figure 5) gives a straight line but the slope is less than unity. This trend is even more pronounced for the hexadecanoate system, the slope being 0.6 (Figure 5). These results cannot be taken as evidence that the hydrolysis rates for dodecanoate and hexadecanoate are not first order in [OH⁻] since the monomeric dodecanoate at a concentration of 3.3×10^{-7}M exhibits the expected linear log k_1—pH correlation with a slope of unity (Figure 4). Therefore, the monomer fractions of dodecanoate and, to a greater extent, hexadecanoate decrease with increasing [OH⁻] due to the structure-making ability of hydroxide ion towards water.[24]

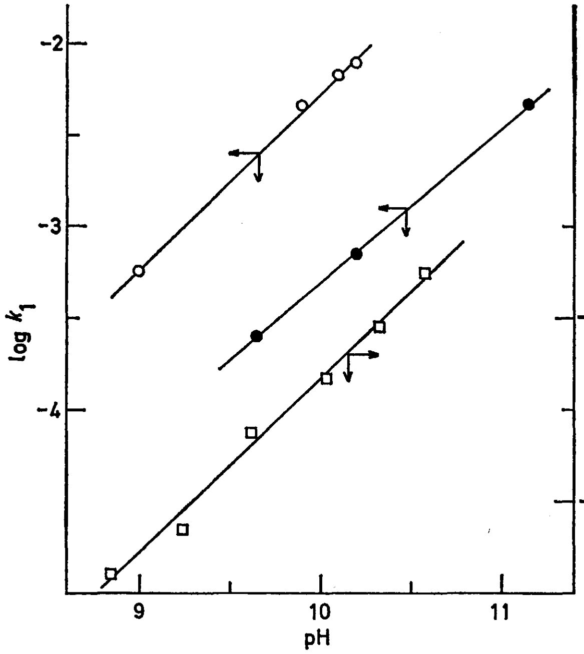

FIGURE 4 pH–k_1 Correlations for hydrolysis of *p*-nitrophenyl hexanoate (1.0×10^{-5}M; ○), decanoate (1.0×10^{-5}M; ●), and dodecanoate (3.3×10^{-7}M; □) at 40.0 ± 0.1 °C and μ 0.10 (KCl) in 1.0% (v/v) aqueous dioxan

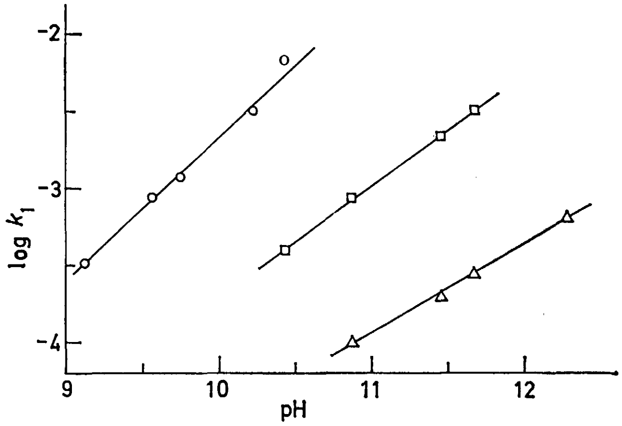

FIGURE 5 pH–k_1 Correlations for hydrolysis of *p*-nitrophenyl decanoate (1.0×10^{-5}M; ○), dodecanoate (1.0×10^{-5}M; □), and hexadecanoate (1.0×10^{-5}M; △) at 40.0 ± 0.1 °C and μ 0.10 (KCl) in 10.9% (v/v) aqueous dioxan

Effects of Additives on Aggregation Behaviour.—The effect of added urea (5M) on the hydrolysis of 1.0×10^{-5}M-dodecanoate in 10.9% (v/v) aqueous dioxan is shown in Figure 6. Urea acts to raise somewhat the critical concentration of the ester and to decrease the

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* Menger and Portnoy reported that the second-order rate constant for hydrolysis of *p*-nitrophenyl acetate was retarded by *ca.* 1.7-fold upon addition of 1.05M-[9% (v/v)] dioxan.[8]

[24] W. B. Danklicker and V. A. de Saussure, in ' The Chemistry of Biosurfaces,' ed. M. L. Hair, Marcel Dekker, New York, 1971, vol. 1, ch. 1.

aggregation number [equation (8)] in the manner observed for surfactant micellar systems.[25]

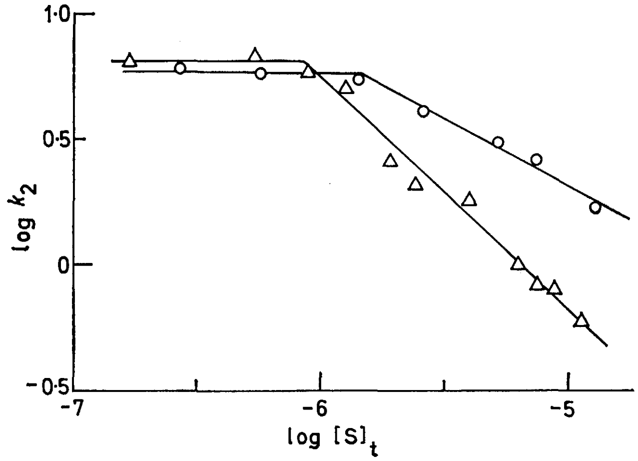

FIGURE 6 Correlations of second-order rate constant k_2 with initial ester concentration $[S]_t$ for hydrolysis of *p*-nitrophenyl dodecanoate in the absence (△) and presence of 5M-urea (○) at 40.0 ± 0.1 °C and μ 0.10 (KCl) in 10.9% (v/v) aqueous dioxan

Molecular aggregation should in principle be influenced by added salts. In fact, the pseudo-first-order rate constant for hydrolysis of *p*-nitrophenyl acetate (1.0×10^{-5}M), which does not show any significant molecular aggregation in 1.0% (v/v) aqueous dioxan at pH 9.69 ± 0.01 and 40.0 °C increases in the following order with respect to added salts (0.5M): NaSCN (0.97×10^{-3}) < $(CH_3)_4NBr$ (1.2×10^{-3}) $\simeq$ $NaClO_4$ (1.2×10^{-3}) $\simeq$ KCl (1.2×10^{-3}) < NaBr (1.4×10^{-3}) $\simeq$ NaCl (1.4×10^{-3}) < Na_2SO_4 (1.5×10^{-3} s^{-1}). On the other hand, the pseudo-first-order rate constant for hydrolysis of decanoate (1.0×10^{-5}M) in 1.0% (v/v) aqueous dioxan at pH 10.47 ± 0.01 increases in the following order with respect to added salts (0.5M): Na_2SO_4 (4.3×10^{-4}) < KCl (8.1×10^{-4}) ~ NaCl (8.2×10^{-4}) ~ NaBr (8.3×10^{-4}) < NaSCN (1.0×10^{-3}) < $NaClO_4$ (1.3×10^{-3}) < $(CH_3)_4NBr$ (1.7×10^{-3} s^{-1}). Practically reversed correlations were established for acetate and decanoate. The latter sequence of salt effects presumably reflects the aggregation behaviour of the carboxylic esters since a similar order of salt effects has been noted for denaturation of protein and also for salting-out of benzene and its derivatives,[26-28] even though the effectiveness of the alkylammonium salt in protein denaturation is not established and SCN$^-$ is often claimed to be a better protein denaturant than ClO_4^-. The present kinetic salt effects can be interpreted in the following manner. The salts which are effective in salting-out benzene are also effective in salting-out the monomeric ester and promote ester aggregation. The consequence of this effect is the reduction in the fraction of monomer and hence in the overall rate of hydrolysis of carboxylic esters bearing a long alkyl chain.

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