Hydrophobic Effects in the Micellar Reactions of Peroxide Nucleophiles

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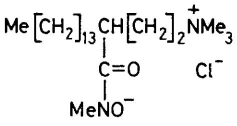
Summary Acyl-transfer reactions of hydroperoxide and α-peroxycumyl anions with *p*-nitrophenyl phenylacetate demonstrate hydrophobic effects in micellar catalysis.

One of the most intensively studied micelle-catalysed reactions is the hydrolysis of *p*-nitrophenyl esters by aqueous base.[1] The rate enhancements observed with simple cationic surfactant micelles are generally quite small, unless mechanisms other than direct nucleophilic attack at carbonyl carbon are involved.[2] A range of functional surfactants such as (**1**), where the oxide nucleophile is an integral part of the micelle, show considerably greater catalysis.[3]

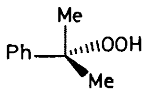


$$\mathrm{Me[CH_2]_{13}\underset{\underset{\underset{MeNO^-}{|}}{C=O}}{\overset{|}{CH}}[CH_2]_2\overset{+}{N}Me_3\quad Cl^-}$$

(1)

$\mathrm{PhCH_2C(O)OC_6H_4NO_2\text{-}}p$

(2)



(3)

$\mathrm{Me[CH_2]_{15}\overset{+}{N}Me_3\quad Cl^-}$

(4)

$\mathrm{PhCH_2C(O)OOH}$

(5a)

$\mathrm{PhCH_2C(O)OH}$

(5b)

We have been interested in the generation of reactive oxidising species in micelles and have studied the reaction of *p*-nitrophenyl phenylacetate (**2**) with OH^-, O_2H,$^-$ and α-peroxycumene (**3**) in borate buffer solutions at pH 9·4 containing varying amounts of the surfactant (**4**). The results are recorded in Figure 1. It will be seen that the OH^- catalysed reaction follows normal trends although the extent of catalysis ($k_m/k_0 = 31$) is higher than normal for aliphatic esters, possibly due to a favourable secondary interaction of the benzyl group with the quaternary ammonium centre at the transition-state.[4] Acyl-transfer to O_2H^- is always the dominant mechanism of ester decomposition in 5×10^{-3} M H_2O_2 at pH 9·4 and the micellar effect is slightly greater than for OH^- ($k_m/k_0 = 91$). The rate of the micelle-catalysed reaction is linearly dependent

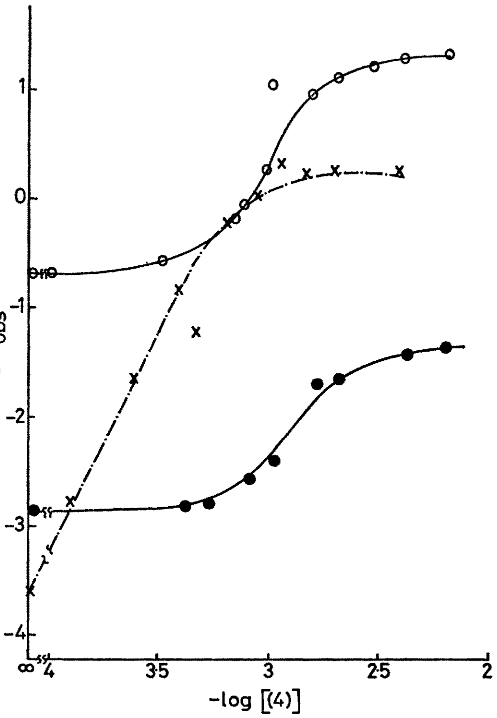


FIGURE 1. Reaction of p-nitrophenyl phenylacetate (**2**) with nucleophiles at 30 °C in 0·05 M borate buffer at pH 9·45. H_2O_2 and (**3**) were present at 5 × 10^{-3} M. Reactions were followed by stopped-flow spectrophotometry ($k > 10^{-1}$ s^{-1}) or visible spectrometry, monitoring the absorbance of p-nitrophenoxide at 400 nm. ●, OH^-; ○, OOH^-; ×, (**3**).

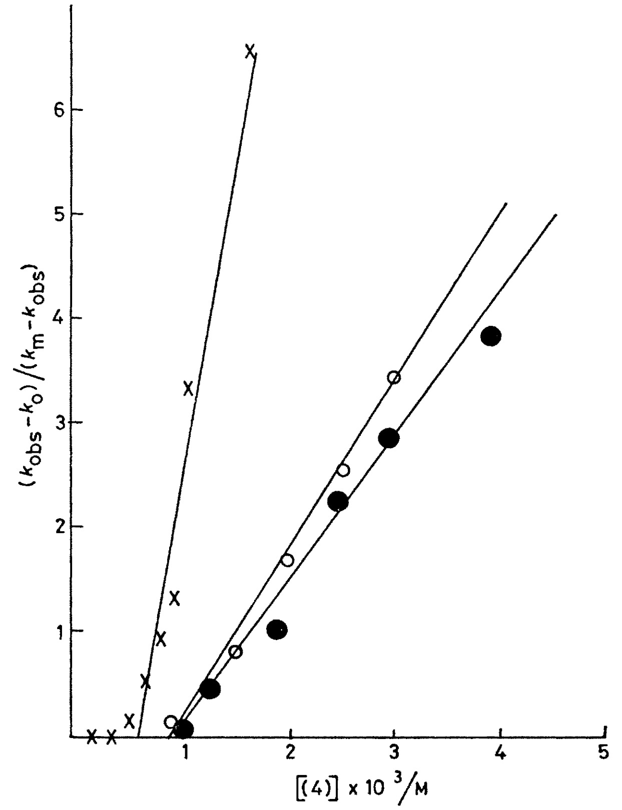


FIGURE 2. Treatment of the data in Figure 1 according to ref. 5. ●, OH^- (K' = 1360); ○, OOH^- (K' = 1620); ×, (**3**) (K' = 7500). $K' = K/N$.

on [OH^-] over the pH range 8·8—10·0. The α-peroxycumyl anion behaves quite differently, however. In the absence of surfactant, 5 × 10^{-3} M (**3**) has almost no effect on the rate of formation of p-nitrophenoxide. Very low concentrations of (**4**) are effective in promoting the peroxycumyl anion pathway with an estimated 100-fold enhancement of its rate at 0·25 × 10^{-3} M surfactant. The limiting rate enhancement (k_m/k_0 = 9 × 10^3) is reached at a considerably lower surfactant concentration than in the other two cases. Thus in water at pH 9·45 the ratio of reactions occurring *via* (**3**) and lyate ion is 1 : 6·5 but in the presence of 1 × 10^{-3} M surfactant their relative reactivities are 440 : 1.

The origin of this selectivity is clarified by treatment of the kinetic data according to the standard procedures (Figure 2).[5] Nucleophiles OH^- and O_2H^- behave rather similarly, the kinetic critical micelle concentration (c.m.c.) in both cases being within experimental error of that determined by chloride-ion potentiometry (1·0 × 10^{-3} M) in pure water. The kinetic c.m.c. for reactions of (**3**) is 5·5 × 10^{-4} M and this is corroborated by the value determined as above (7·2 × 10^{-4} M). This presumably reflects co-micellisation of (**3**) and (**4**).[6] The apparent binding constant K/N is considerably greater for (**3**)-catalysed reactions due to enhanced substrate-binding to the perturbed mixed aggregate. Given the assumptions inherent in the data treatment,[5] the linearity of the plots demonstrates that the extent of catalysis depends only on the concentration of micelles. The pK_a values of (**3**) and H_2O_2 were not significantly altered by the presence of the surfactant (**4**).†

The ester (**2**) was treated with O_2D^-–O_2D_2 in borate buffer at pD 9·2 and the solution examined immediately by 270 MHz n.m.r. spectroscopy.[7] The dominant species after 75 s was (**5a**) [δ 3·74 (CH_2), by comparison with an authentic sample[8]] but this decayed quite rapidly to the corresponding acid (**5b**) (δ 3·55). Peracid decomposition was always faster in the presence of (**4**) than in its absence but this reaction may have been accelerated under our conditions by the presence of trace metal ions.

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† pK_a measurements were carried out with conditions and concentrations analogous to the kinetic experiments, with (**3**) at 8 × 10^{-3} M and (**4**) at 10^{-2} M.

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