

## Hydrophobic Effects in the Micellar Reactions of Peroxide Nucleophiles

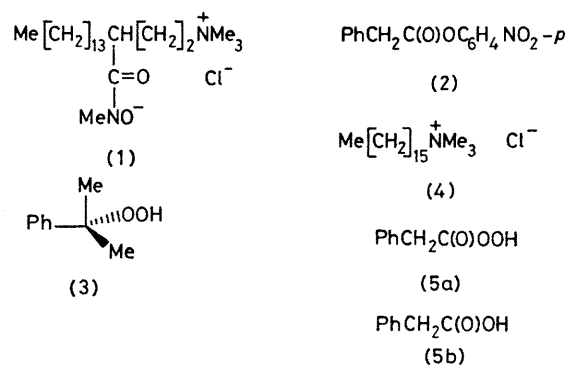
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**Summary** Acyl-transfer reactions of hydroperoxide and  $\alpha$ -peroxycumyl anions with *p*-nitrophenyl phenylacetate demonstrate hydrophobic effects in micellar catalysis.

ONE of the most intensively studied micelle-catalysed reactions is the hydrolysis of *p*-nitrophenyl esters by aqueous base.<sup>1</sup> 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.<sup>2</sup> A range of functional surfactants such as (1), where the oxide nucleophile is an integral part of the micelle, show considerably greater catalysis.<sup>3</sup>

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<sup>-</sup>, O<sub>2</sub>H<sup>-</sup> and  $\alpha$ -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<sup>-</sup> 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.<sup>4</sup> Acyl-transfer to O<sub>2</sub>H<sup>-</sup> is always the dominant mechanism of ester decomposition in  $5 \times 10^{-3}$  M H<sub>2</sub>O<sub>2</sub> at pH 9.4 and the micellar effect is slightly greater than for OH<sup>-</sup> ( $k_m/k_0 = 91$ ). The rate of the micelle-catalysed reaction is linearly dependent

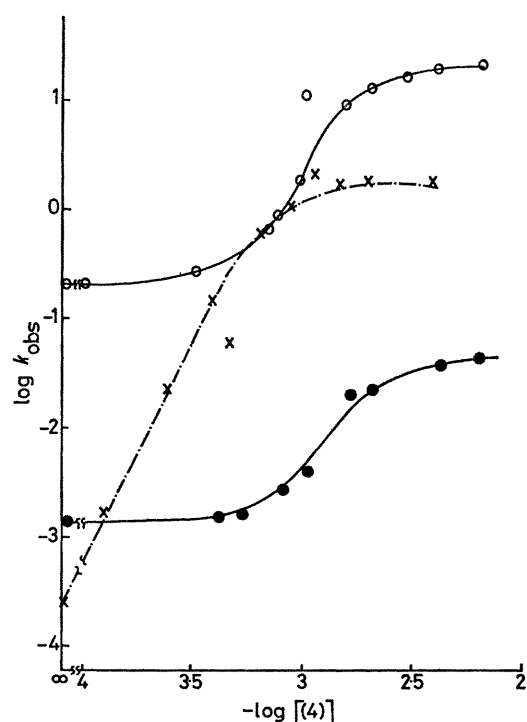


FIGURE 1. Reaction of *p*-nitrophenyl phenylacetate (2) with nucleophiles at 30 °C in 0.05 M borate buffer at pH 9.45.  $\text{H}_2\text{O}_2$  and (3) were present at  $5 \times 10^{-3}$  M. Reactions were followed by stopped-flow spectrophotometry ( $k > 10^{-1} \text{ s}^{-1}$ ) or visible spectrometry, monitoring the absorbance of *p*-nitrophenoxide at 400 nm. ●,  $\text{OH}^-$ ; ○,  $\text{OOH}^-$ ; ×, (3).

on  $[\text{OH}^-]$  over the pH range 8.8–10.0. The  $\alpha$ -peroxycumyl anion behaves quite differently, however. In the absence of surfactant,  $5 \times 10^{-3}$  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  $0.25 \times 10^{-3}$  M surfactant. The limiting rate enhancement ( $k_m/k_0 = 9 \times 10^3$ ) 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  $1 \times 10^{-3}$  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).<sup>5</sup> Nucleophiles  $\text{OH}^-$  and  $\text{O}_2\text{H}^-$  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 ( $1.0 \times 10^{-3}$  M) in pure water. The kinetic c.m.c. for reactions of (3) is  $5.5 \times 10^{-4}$  M and this is corroborated by the value deter-

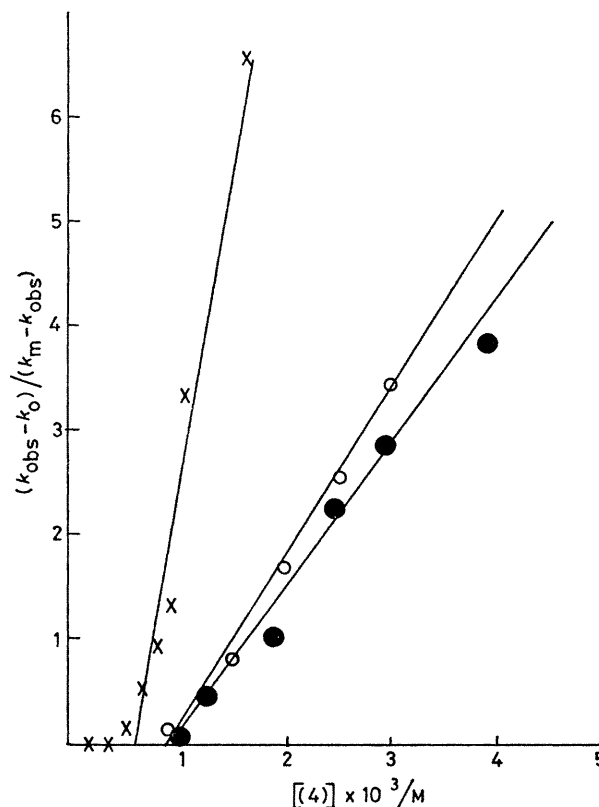


FIGURE 2. Treatment of the data in Figure 1 according to ref. 5. ●,  $\text{OH}^-$  ( $K' = 1360$ ); ○,  $\text{OOH}^-$  ( $K' = 1620$ ); ×, (3) ( $K' = 7500$ ).  $K' = K/N$ .

mined as above ( $7.2 \times 10^{-4}$  M). This presumably reflects co-micellisation of (3) and (4).<sup>6</sup> 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,<sup>5</sup> the linearity of the plots demonstrates that the extent of catalysis depends only on the concentration of micelles. The  $\text{p}K_a$  values of (3) and  $\text{H}_2\text{O}_2$  were not significantly altered by the presence of the surfactant (4).<sup>†</sup>

The ester (2) was treated with  $\text{O}_2\text{D}^-$ – $\text{O}_2\text{D}_2$  in borate buffer at pD 9.2 and the solution examined immediately by 270 MHz n.m.r. spectroscopy.<sup>7</sup> The dominant species after 75 s was (5a) [ $\delta$  3.74 ( $\text{CH}_2$ ), by comparison with an authentic sample<sup>8</sup>] but this decayed quite rapidly to the corresponding acid (5b) ( $\delta$  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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<sup>†</sup>  $\text{p}K_a$  measurements were carried out with conditions and concentrations analogous to the kinetic experiments, with (3) at  $8 \times 10^{-3}$  M and (4) at  $10^{-2}$  M.

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