Proximity Effects in the Reactions of Surfactant *p*-Nitrophenyl Esters with Peroxide Nucleophiles

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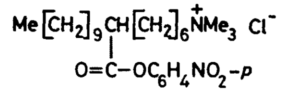
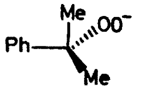
Summary Acyl-transfer reactions of surfactant esters (**1**) and (**2**) demonstrate the formation of hydrophobic ion-pairs and provide a striking example of association-prefaced catalysis.

The reactivity of chain-functionalised surfactants as nucleophiles has been reported previously.[1] We now describe the preparation of surfactant esters (**1**) and (**2**) and demonstrate how their reactivity towards peroxidic nucleophiles provides insight into some aspects of micellar catalysis. These esters are white crystalline solids† prepared from the corresponding carboxylic acids[2] *via* the acid chloride [$(COCl)_2$, $CHCl_3$, 20 °C] by reaction with sodium *p*-nitrophenolate (12 h, $CHCl_3$ suspension, 20 °C).

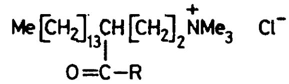


$\mathrm{Me[CH_2]_9\underset{O=C-OC_6H_4NO_2\text{-}p}{\underset{|}{CH}}[CH_2]_6\overset{+}{N}Me_3\ Cl^-}$

(1)



(3)



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

(2); R = $OC_6H_4NO_2$-*p*
(6); R = OO^-
(7); R = $O-\}_2-O$

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

(4)

$PhCH_2C(O)OC_6H_4NO_2$-*p*

(5)

Rate constants for their reactions with OH^-, O_2H^-, and the α-peroxycumyl anion (**3**) in aqueous buffer solution at pH 9·45 are recorded in Figure 1 which additionally demonstrates the effect of successively increasing concentrations of cetyltrimethylammonium chloride (**4**). In all cases added surfactant accelerates the reaction, but only to a rather minor extent, since the catalytic constant k_m/k_0 never exceeds 10, with no obvious trends relating to the structure of ester or nucleophile.

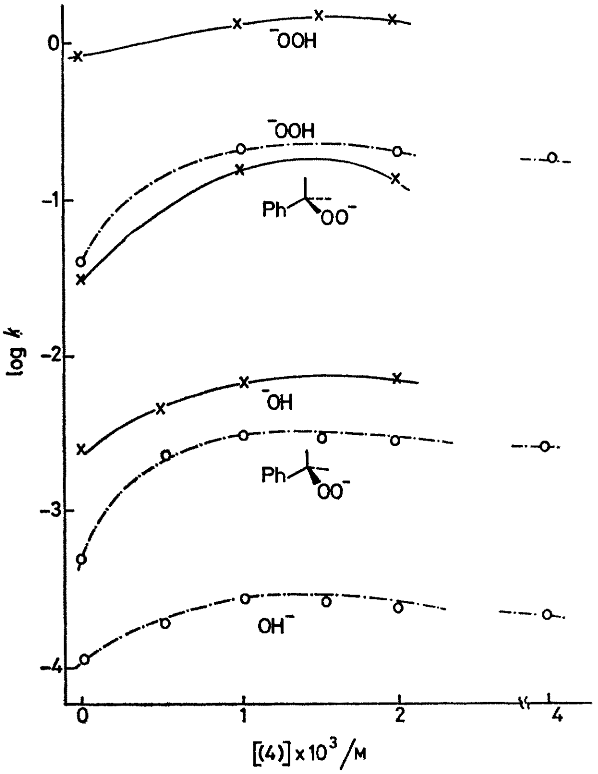


Figure 1. Reaction rates of surfactant esters (**1**) and (**2**) with nucleophiles in the presence and absence of (**4**). Conditions: 30·0 °C, pH 9·45, 0·05 M borate buffer, 5×10^{-5} M ester. A similar rate constant was observed for (**2**) in reaction with (**3**) at 1×10^{-5} M. Reactions were followed by stopped-flow spectrophotometry ($k \geqslant 10^{-1}\,s^{-1}$) or visible spectrometry, monitoring the absorbance of *p*-nitrophenoxide at 400 nm. ——, 3-ester; –·–·–, 7-ester.

It is instructive to compare the reactivities of (**1**) and (**2**) towards these nucleophiles with that of *p*-nitrophenyl phenylacetate (**5**) in the absence of surfactant. Towards OH^- and O_2H^-, (**1**) is less reactive than (**5**), reflecting the difference in inductive effects operating in phenylacetyl and secondary alkanoyl esters.[3] In addition, (**2**) is 20-fold more reactive than (**1**) towards these nucleophiles as a result of increased electrostatic stabilisation of the anionic transition state by the proximity of the quaternary ammonium head-group. What is most remarkable is the anomalously high reactivity of the hydrophobic nucleophile (**3**) towards both surfactant esters. Thus (**1**) reacts 27 times and (**2**) 80 times faster than expected on the basis of the reactivity of (**5**) in water. Although (**1**) and (**2**) are present at concentrations far below the expected critical micelle concentration, their inter-nucleophile selectivity resembles (**5**) under conditions of micellar catalysis.[4] This suggests that hydrophobic ion-pairs[5] are involved in their reactions with (**3**) so that the effective concentration of the anion is enhanced. It is significant that most of the catalysis conventionally associated with micelle formation is present in a non-aggregated state, demonstrating that simple model systems may suffice in the study of hydrophobic bonding and catalysis.

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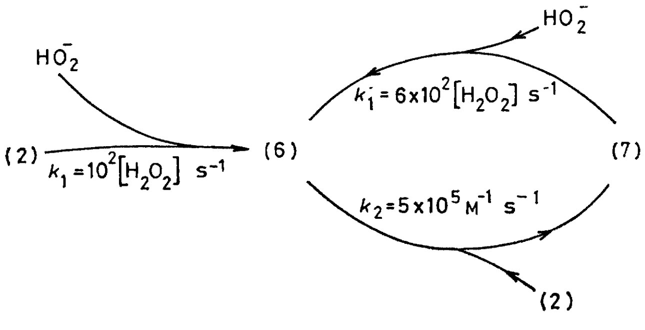
† Satisfactory spectral and analytical data were obtained for these compounds.

In all cases save the reaction of O_2H^- with (**2**) good first-order kinetics were observed for *p*-nitrophenoxide formation. In this last case, more complex kinetics were observed which may be simulated according to the mechanism shown in the Scheme. Thus the peracid (**6**) is formed in the first step of reaction, and will exist entirely in the ionised form at pH 9·45. Its anion then competes with O_2H^- for further (**2**) so that there is a build-up of the diacyl peroxide (**7**). This then reacts rapidly, according to precedent,[6] with hydroperoxide and thereby generates two moles of peracid. Computer simulation of the kinetic curves (Figure 2) gives the recorded rate constants. The reactivity of *p*-nitrophenyl acetate towards peracetate is unknown but may be extrapolated from data on other α-nucleophiles[7] to have a rate constant of $400\ \text{M}^{-1}\,\text{s}^{-1}$. Thus (**2**) reacts with (**6**) *ca.* $1{\cdot}2 \times 10^3$ faster than expected. We attribute this to association-prefaced catalysis and note that the rate enhancement is considerably greater than typical values[8] observed previously for a bimolecular reaction step. This demonstrates the orienting effect of the quaternary ammonium group and its ability to promote association at sub-micellar concentrations.[9]



SCHEME

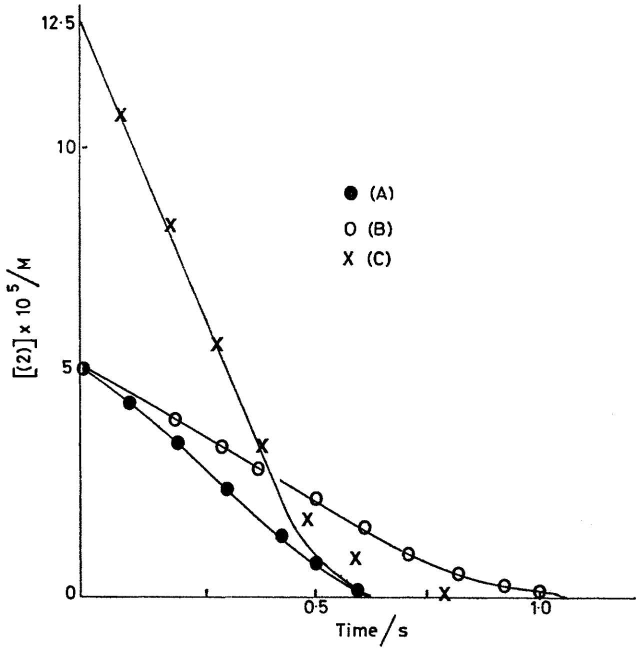


FIGURE 2. Reaction of (**2**) with hydrogen peroxide, pH 9·45, 0·05 M borate buffer, 5×10^{-5} M ester (A and B), $1{\cdot}25 \times 10^{-4}$ M ester (C) 10^{-2} M H_2O_2 (A and C), 5×10^{-3} M H_2O_2 (B). ● (A), ○(B), and × (C) are experimental points; lines are computer-derived according to the Scheme.

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