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DEPHOSPHORYLATION BY PEROXYANIONS IN MICELLES AND MICROEMULSIONS

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Dephosphorylation of *p*-nitrophenyl diphenylphosphate (pNPDPP) by OH^- in aqueous cationic micelles of cetyltrimethylammonium hydroxide (CTAOH) is inhibited by *tert*-butyl hydroperoxide (t-BuO_2H), which reduces the binding of OH^-, and whose anion is a relatively ineffective nucleophile. Reaction is faster in microemulsions of CTACl, *n*-octane and OH^-, with t-BuO_2H as cosurfactant, than in otherwise similar microemulsions with *t*-butyl alcohol as cosurfactant. Dephosphorylation by *m*-chloroperoxybenzoate ion is slower in microemulsions of cetyltrimethylammonium mesylate or benzenesulfonate, with *n*-octane and *tert*-butyl alcohol, than in cationic micelles, but a wide range of concentrations can be examined. The reaction rates qualitatively follow the concentration of peroxy acid relative to surfactant, and inert anions slow the reaction. Dephosphorylation by peroxyphthalate dianion in micelles of CTACl fits a pseudophase kinetic model, except in very dilute surfactant where reaction is faster than predicted.

INTRODUCTION

Peroxyanions are effective α-nucleophiles[1] and hydroperoxide and *m*-chloroperoxybenzoate ion react readily with *p*-nitrophenyl diphenylphosphate (pNPDPP). The course of these nucleophilic reactions of peroxyanions has been discussed.[2] These reactions and deacylation by peroxyanions are speeded by cationic micelles.[3,4]

Oil-in-water (o/w) microemulsions of cationic surfactants, oil and alcohol cosurfactants solubilize high concentrations of hydrophobic solutes and are much more effective than aqueous micelles in this respect.[5] This high solubilizing power makes microemulsions useful as reaction media. However, the overall reaction rates are typically lower than in micelles[5,6] because for a given overall concentration of reagent local concentrations in microemulsion droplets are lower than in micelles, and alcohol or other cosurfactants reduce the surface charge density of the droplet and its ability to attract reactive counterions coulombically.[7] The factors that govern reactivity in aqueous micelles also apply to o/w microemulsions and both micelles and microemulsion droplets can be regarded as pseudophases that act as reaction media distinct from bulk solvent.[7] Quantitative treatments of rate effects of aqueous micelles are reasonably straightforward because surfactant concentrations are usually low. The bulk medium is not materially perturbed by the surfactant and it is reasonable to define concentrations in this aqueous pseudophase in terms of molarities. The situation is more complicated for microemulsions or alcohol-modified micelles which are multicomponent systems. Solute concentrations are often high and cosurfactants are generally partitioned between bulk solvent and the microemulsion droplets so that is often difficult to define concentrations in these pseudophases in any simple way and qualitative discussions are often based on overall rate effects as a function of total concentrations of reagents and inert solutes.[4,5]

Reactions of pNPDPP with various nucleophilic anions have been examined in both aqueous micelles of cationic surfactants and o/w microemulsions with alcohol cosurfactants or alcohol-modified cationic micelles,[4–6] but dephosphorylation by peroxyanions has not been examined in microemulsions. The aim of this work was to extend comparisons of micelles and microemulsions as reaction media to dephosphorylation by peroxyanions:

$$RO_2^- + (PhO)_2POOC_6H_4NO_2 \rightarrow RO_2PO(OPh)_2 + {}^-OC_6H_4NO_2$$

$$R = H,\ t\text{-Bu},\ m\text{-}ClC_6H_4CO,\ o\text{-}OCC_6H_4CO_2^-$$

We examined the dephosphorylation of pNPDPP by *tert*-butyl hydroperoxide (t-BuO_2H) in aqueous cationic micelles and in microemulsions at high pH, because t-BuO_2H should act as a cosurfactant without addition of a medium-chain-length alcohol.[5] We also examined the reaction of *m*-chloroperoxybenzoate ion ($MCPBA^-$) in microemulsions and reactions of the *o*-peroxyphthalate

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ion (PPA^{2-}) in cationic micelles of cetyltrimethylammonium chloride, mesylate and benzenesulfonate (CTACl, CTAOMs, CTAOBzs), to complement earlier work on the dephosphorylation by MCPBA in cationic micelles.[3]

RESULTS

Reaction with *tert*-butyl hydroperoxide

Dephosphorylation of pNPDPP by OH$^-$ in aqueous micelles of CTACl is slowed by addition of t-BuO$_2$H,[3] even though it, and its anion, should bind strongly to cationic micelles. This system is complicated by competition between OH$^-$ and Cl$^-$, which should decrease the deprotonation of t-BuO$_2$H.[8,9] We eliminated this competition by using cetyltrimethylammonium hydroxide (CTAOH),[10] but reaction was still inhibited by t-BuO$_2$H over a wide range of concentration (Table 1). The increasing inhibition with increasing t-BuO$_2$H concentration arises from a decrease in counterion concentrations at the micellar surface due to a decrease in surface charge density[11] and competition between t-BuO$_2^-$ and OH$^-$.[8,9]

The pK_a of t-BuO$_2$H is 12·8 in water,[12] so it should be partially deprotonated in CTAOH (Table 1). The bulky alkyl group should sterically hinder reaction so t-BuO$_2^-$ is a weak nucleophile and its reaction with p-NPDPP does not offset the inhibition due to exclusion of OH$^-$ from the micelle. Consistently reaction in water (containing 3 vol-% acetonitrile) at pH 10·5 or 12 (0·075 M carbonate buffer, 25·0 °C) is not speeded by t-BuO$_2$H (data not shown).

Table 1. Dephosphorylation in CTAOH[a]

$10^2[t\text{-BuO}_2\text{H}]$ (M)	[CTAOH](M)			
	0·001	0·0025	0·004	0·005
—			16·0	17·0
5		15·2		
8	3·8		13·8	
10	3·7	12·0		13·4
15		8·2		
16	3·6	6·5	10·6	10·4
30	1·8	6·8	8·4	
35		4·7		
40		4·8	4·4	3·7
48		2·6	3·9	
50	1·1	2·0		3·6
60			3·5	2·5
70			1·4	1·8
80			1·1	2·3
90				0·9
100				0·5

[a]Values of $10^2 k_\psi$ (s^{-1}) at 25·0 °C; in 0·009 M CTAOH, $10^2 k_\psi = 23$, 9·5 and 5·0 s^{-1} in 0,[10] 0·3 and 0·5 M t-BuO$_2$H, respectively.

Although t-BuO$_2^-$ is an ineffective nucleophile in water and in aqueous cationic micelles, microemulsions with t-BuO$_2$H as cosurfactant are effective dephosphorylating agents at high pH. Reaction in microemulsions of CTACl and n-octane with t-BuO$_2$H is much faster than in those containing *tert*-butyl alcohol (Tables 2 and 3). *tert*-Butyl alcohol and its alkoxide ion are ineffective nucleophiles[13] and slow the reaction of pNPDPP with OH$^-$ by decreasing the charge density and binding of OH$^-$ at the surface of the microemulsion droplet.[7,8,11] In microemulsions, reaction with OH$^-$ is slow, because so little OH$^-$ binds to the droplet, and reaction with t-BuO$_2^-$ then becomes important. Therefore, by using the reagent as cosurfactant we obtain reaction of t-BuO$_2^-$ in microemulsions, but not in aqueous micelles (Table 1).

Rate constants of the reaction of t-BuO$_2^-$ increase sharply with increasing water and OH$^-$ content of the microemulsion (Tables 2 and 3). This effect is due to increased deprotonation of t-BuO$_2$H by OH$^-$ and a decrease in the total volume of the microdroplets, which increases the reagent concentrations in the droplet pseudophase.[8] Addition of *tert*-butyl alcohol slightly slows the reaction by decreasing the charge density and deprotonation of t-BuO$_2^-$ at the droplet surface.

Table 2. Dephosphorylation by *tert*-butyl hydroperoxide: effect of microemulsion composition[a]

CTACl[b]	t-BuO$_2$H[b]	t-BuOH[b]	n-Octane[b]	H$_2$O (wt-%)	$10^5 k_\psi$ (s^{-1})
2	0	2	1	60	1·7
2	1	1	1	60	169
2	1	1	1	70	292
2	1	1	1	80	635
2	1	0	1	70	411
2	1	0	1	80	768
2	1	0	0	80	724

[a]At 25·0 °C with 0·01 M KOH in the aqueous component.
[b]Weight ratios of the organic components.

Table 3. Dephosphorylation by *tert*-butyl hydroperoxide in microemulsions: effect of water[a]

H$_2$O (wt-%)	KOH[b](M)	
	0·005	0·01
45		79·8
50	22·3	
60	44·8	141·0
70	93·5	243·0
80	219·0	533·0

[a]Values of $10^5 k_\psi$ (s^{-1}) at 25·0 °C with CTACl–t-BuO$_2$H–n-octane (2:2:1, w/w/w).
[b]Molarity in terms of the aqueous component.

Removal of *n*-octane has little effect on the rate, which shows that even the very hydrophobic substrate pNPDPP does not enter the oil-rich region of the droplet. Similar observations have been made in other systems and generally the reaction rates are similar at surfaces of alcohol-modified micelles and corresponding o/w microemulsions with oil in the interior.[5,6,8c,13]

Reaction with *m*-chloroperoxybenzoate ion

Dephosphorylation of *p*-NPDPP by $MCPBA^-$ was followed in microemulsions of CTAOBzs or CTAOMs, *t*-BuOH and *n*-octane (Figures 1 and 2). At a given microemulsion composition, first-order rate constants, k_ψ, increase with increasing pH of the aqueous component and become constant at pH ≈ 11 (Figure 2). At pH 11.4 reaction is speeded by 10^{-3} M $MCPBA^-$ by a factor of ca 240 and k_ψ has half its maximum value at an apparent pH of 9·2, i.e. $pK_a = 9{\cdot}2$, whereas in water $pK_a = 7{\cdot}8$.[14] This dissociation constant is an apparent value because the pH in micelles or microemulsion droplets is different from that in the aqueous medium;[8,9,11] however, an alcohol cosurfactant decreases the binding of counterions and deprotonation of a weak peroxy acid. Reaction of $MCPBA^-$ is slower in microemulsions than in micelles of CTACl, where $k \approx 10 k_\psi\ s^{-1}$ under optimum conditions, i.e. with the maximum concentration of MCPBA relative to that of CTACl.[3] This difference is similar to those for other anion reactions.[5,6,13]

Competition between reactive peroxyanion and inert benzenesulfonate ion is important and for a given pH and microemulsion composition k_ψ decreases monotonically with increasing $PhSO_3Na$ concentration (Table 4). However, considerable amounts of added salt were needed to obtain a sizable rate decrease, whereas only small amounts of inert counterion are needed for inhibition of ionic reactions in aqueous micelles.[3,8] These differences in salt effects in micelles and microemulsion droplets are due to the lower affinity of the droplets for counterions.[6–8,11]

The microemulsions were made up so that concentrations of MCPBA and buffer in the aqueous component were kept constant and the water content was varied. For given relative concentrations of surfactant, cosurfactant and oil, rate constants increased monotonically with increasing water content (Tables 5 and 6). This increase is due in part to an increase in the concentration of $MCPBA^-$ relative to those of the inert contents of the droplets, i.e. surfactant, cosurfactant and oil, but it is steeper than the increase in the relative concentration of $MCPBA^-$. An increase in water content decreases the amount of *tert*-butyl alcohol in the droplets, which increases their charge density and concentration of peroxy anion at the droplet surface. The pH of the aqueous medium was high enough to ensure complete deprotonation of the peroxy acid, and the increase in rate with increasing water content and the $[MCPBA^-]/[CTAOMs]$ or $[MCPBA^-]/[CTAOBzs]$ ratio seems to be general for these microemulsions (Figure 1 and Tables 5 and 6). Similar conclusions can be drawn from the dependence of k_ψ on the concentration of MCPBA relative to the sum of the concentrations of surfactant, cosurfactant and oil.

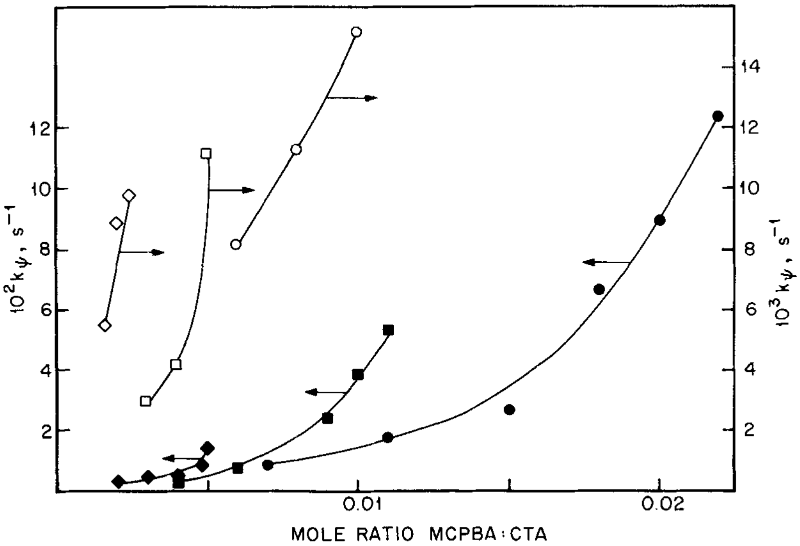

Figure 1. Dephosphorylation by MCPBA in microemulsions of CTAOMs (open symbols) and CTAOBzs (solid symbols). ◇, ◆, 0·00125; □, ■, 0·0025; ○, ●, 0·005 M MCPBA in aqueous component. Conditions are specified in Tables 5 and 6

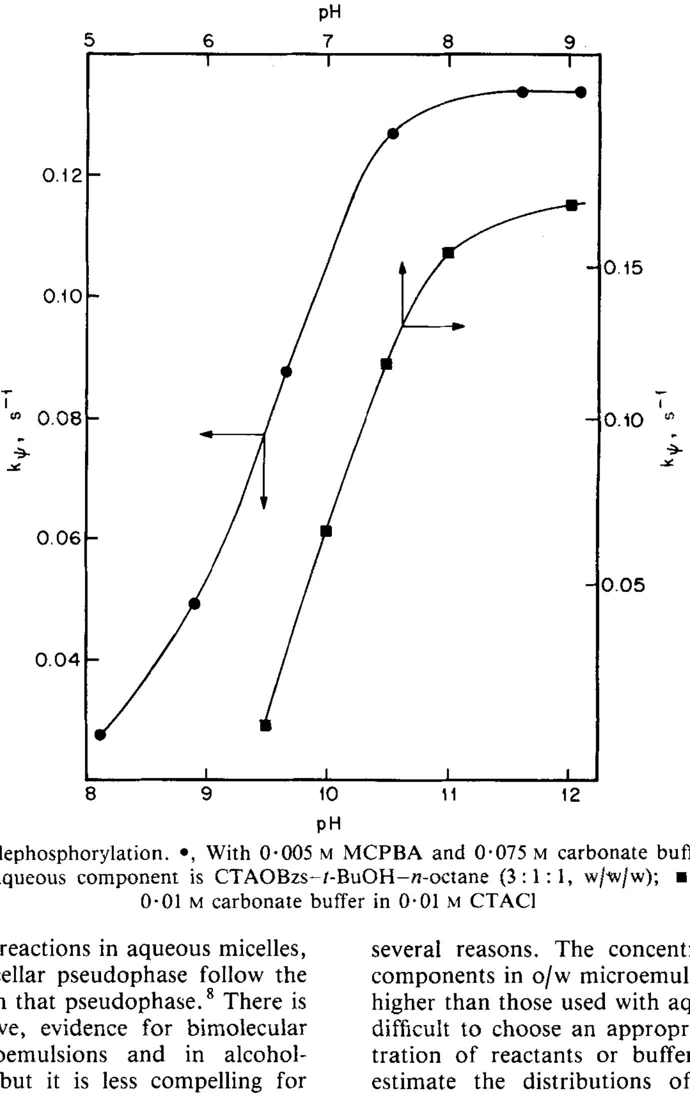

Figure 2. Effect of pH on dephosphorylation. ●, With 0·005 M MCPBA and 0·075 M carbonate buffer in aqueous component, which is 81% (w/w), non-aqueous component is CTAOBzs–*t*-BuOH–*n*-octane (3 : 1 : 1, w/w/w); ■, with $8{\cdot}8 \times 10^{-5}$ M PPA, 0·01 M carbonate buffer in 0·01 M CTACl

For many bimolecular reactions in aqueous micelles, reaction rates in the micellar pseudophase follow the reactant concentrations in that pseudophase.[8] There is similar, but less extensive, evidence for bimolecular reactions in o/w microemulsions and in alcohol-modified micelles,[5–7,8c] but it is less compelling for several reasons. The concentrations of non-aqueous components in o/w microemulsions are typically much higher than those used with aqueous micelles, and it is difficult to choose an appropriate measure of concentration of reactants or buffer. It is also difficult to estimate the distributions of reagents between the microemulsion droplet and the aqueous part of the medium because the cosurfactant usually has some

Table 4. Inhibition by sodium benzenesulfonate of dephosphorylation[a]

$PhSO_3$ (wt%)	10^2k_ψ(s^{-1})	$PhSO_3Na$ (wt-%)	10^2k_ψ(s^{-1})
0	12·4	2·38	4·61[b]
0·78	8·12	5·70	3·72
1·27	8·00	5·70	3·72
1·84	6·80	5·70	3·23[b]
2·38	4·90	5·70	3·35[c]

[a] At 25·0 °C with 0·005 M MCPBA and 0·0375 M carbonate buffer (pH 10·5) in aqueous component; microemulsion contains 81% H_2O, with CTAOBzs–*t*-BuOH–*n*-octane (3 : 3 : 1, w/w/w).

[b] 0·034 M carbonate buffer.

[c] 0·0375 M carbonate buffer (pH 10·2).

Table 5. Effect of microemulsion composition on dephosphorylation in CTAOBzs[a]

[MCPBA][b] (M)	H_2O(wt-%)					
	58·8	68·2	74·1	78·1	79·7	81·1
0·00125	0·30	0·78	0·43	0·82	1·40	
0·0025	0·27	0·77	0·96	2·39	3·84	5·34
0·005	0·83	1·77	2·63	6·68	8·92	12·4

[a] Values of 10^2k_ψ (s^{-1}) at 25·0 °C in microemulsion with CTAOBzs–*t*-BuOH–*n*-octane (3 : 3 : 1, w/w/w), pH 10·5, 0·075 M carbonate in aqueous component.

[b] In aqueous component.

Table 6. Effect of microemulsion composition on dephosphorylation in CTAOMs[a]

	H_2O(wt-%)		
[MCPBA][b](M)	58·8	64·1	68·2
0·00125	0·55	0·89	0·98
0·0025	0·30	0·42	1·12
0·005	0·82	1·13	1·52

[a] Values of $10^2 k_\psi$ (s^{-1}) at 25 °C in microemulsions with CTAOMs-*t*-BuOH-*n*-octane (3:3:1, w/w/w), pH 10·5, 0·75 M carbonate in aqueous component.
[b] In aqueous component.

solubility in water and is partitioned between it and droplets, so that the composition of the bulk pseudophase is not constant.

Micellar structures do not change rapidly with changes in surfactant or electrolyte concentration, at least in low concentration, because the packing of monomers is governed largely by the dimensions of the hydrophobic alkyl groups of the surfactant.[15] However, these requirements are relaxed in a multicomponent microemulsion and the properties of the droplet surface may be sensitive to composition. Second-order rate constants in microemulsion droplets probably depend on the properties of the surfaces and, although the assumption of constant second-order rate constants is reasonably satisfactory for micelles,[8] it may be less so for microemulsions. Our experiments were carried out in solvents of high water content so that o/w droplets should be present, and most conclusions regarding rates of ionic reactions in microemulsions have been drawn from experiments under these conditions.[5,6,8c] It appears that the pseudophase model of micellar rate effects, including ion exchange, is applicable, qualitatively, to reactions in o/w microemulsions.

Reaction with peroxyphthalate dianion

Dephosphorylation by the peroxyphthalate dianion (PPA^{2-}) was followed in aqueus CTACl. The rate constants for reaction in 0·01 M CTACl increase with increase pH and level off at ca pH 9 (Figure 2). The value of k_ψ is half that of the maximum at pH ≈ 7, i.e. the apparent pK_a of the hydroperoxy group is ca 7 in CTACl. In water the pK_a of the carboxyl and hydroperoxy groups are 2·96 and 8·2, respectively.[16] Reactions in the micelles were followed at pH 9, where deprotonation should be complete. First-order rate constants increase sharply with increasing CTACl concentration, even at concentrations below the critical micelle concentration (cmc) which is ca 1.3×10^{-3} M in water,[17] and pass through maxima with increasing CTACl concentration (Figure 3). There are precedents for large rate effects of very dilute surfactants in reactions of peroxy anions.[3,4]

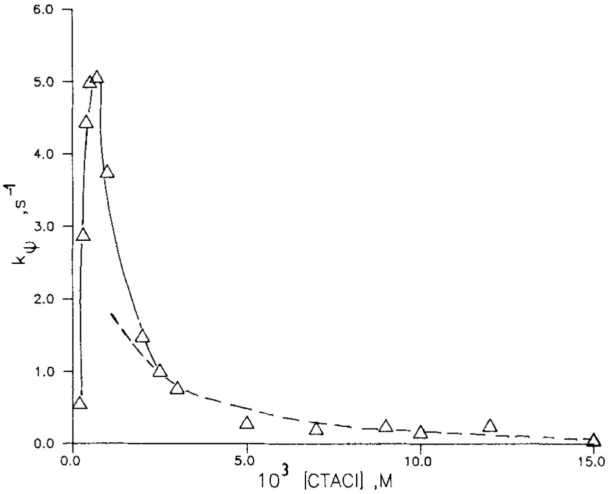

Figure 3. Dephosphorylation by $8 \cdot 8 \times 10^{-5}$ M peroxyphthalate dianion in CTACl micelles and 0·01 M carbonate buffer (pH 9·0). Broken line, values calculated from equation (1). The solid line is meant to guide the eye

Rate maxima with increasing surfactant concentration are typical of bimolecular reactions and are treated quantitatively by estimating the concentration of each reactant at the micellar surface.[8] It is difficult to apply this treatment if the reactants induce micellization or react in submicellar aggregates, because it is based on the assumption that reaction occurs in the aqueous pseudophase or in fully formed micelles whose properties are unaffected by the reactants,[8,18] and the cmc is generally taken to be the concentration of monomeric surfactant. We treated the data for reaction at higher CTACl concentrations on the assumption that PPA^{2-} is fully bound, because dianions interact strongly with cationic micelles. The binding constant of pNPDPP to micellized surfactant is ca 10^4 l mol^{-1} so that binding should be essentially complete for [CTACl] > 10^{-3} M.[9,19] The first-order rate constant is then given by

$$k_\psi = k_M[PPA_M^{2-}]/[CTACl] \qquad (1)$$

where k_M is the second-order rate constant in the micellar pseudophase with concentration written as a mole ratio of PPA^{2-} relative to micellized CTACl [equation (1)]. Rates increase at such low CTACl concentrations that we neglect the concentration of monomeric surfactant.

From values of k_ψ in 0·002–0·015 M CTACl (Figure 3) we estimate $k_M \approx 28\ s^{-1}$. The broken line in Figure 3 is calculated from equation (1) and this value of k_M. The fit is fair above 2×10^{-3} M CTACl, and some of the deviations at higher CTACl concentrations are probably due to adventitious decomposition of PPA. This problem is worst for the slower reactions (see Experimental).

On the assumption that reaction occurs in a region at the micellar surface whose molar volume is 0·14 l,[8a,c] the second-order rate constant in terms of molarity in this region is $k_2^m \approx 4\,\mathrm{l\,mol^{-1}}$. The corresponding value for reaction of $\mathrm{MCPBA^-}$ is ca $2\,\mathrm{l\,mol^{-1}\,s^{-1}}$.[2] These rate constants are similar to those of 1·2 and $1{\cdot}1\,\mathrm{l\,mol^{-1}\,s^{-1}}$ for $\mathrm{MCPBA^-}$ (Ref. 3) and $\mathrm{PPA^{2-}}$, respectively, in water–acetonitrile (97 : 3, v/v) at 25·0 °C (see Experimental), so that charge and structural effects are small for these reactions of peroxyanions. An increased reactant concentration at the micellar surface is the major source of the rate enhancement. This simple treatment should overpredict values of k_ψ in dilute CTACl where the reactants may not be fully bound, but the observed values are higher than those predicted (Figure 3). There is probably reaction in submicellar aggregates which is faster than in normal micelles because of the close proximity of the reactants.[20] Brown and Darwent[4] observed very large rate enhancements by very dilute CTACl in deacylations by cumyl hydroperoxide, and ascribed them to reaction in submicellar aggregates. There are many other examples of rate enhancements with surfactant concentrations below the cmc,[7,18a,21,22] typically for reactions of hydrophobic reactants. The $\mathrm{PPA^{2-}}$ dianion could bind to, and stabilize, submicellar clusters, but with increasing surfactant concentration normal micelles will form and equation (1) then fits the data.

EXPERIMENTAL

Materials. The preparation and purification of most of the materials has been described.[3] Peroxyphthalic acid (PPA) was used as the magnesium salt (Interox) and contained 85% of the peroxy salt; the remainder was largely magnesium phthalate. The specified concentration takes into account this inactive material and we assumed that the (low) concentration of phthalate ion would not materially affect the rate and $\mathrm{Mg^{2+}}$ should not materially affect reactions in cationic micelles.

Kinetics. Reactions were followed spectrophotometrically at 25·0 °C in Gilford, Hewlett-Packard diode-array or Durrum stopped-flow spectrometers,[3,10] at the $\lambda_{\max}$ for 4-nitrophenoxide ion (400 nm). A few reactions at pH < 7 were followed at the isosbestic point between the phenol and phenoxide ion (347 nm). The concentration of pNPDPP was ca 10^{-5} M, and it was added in acetonitrile so that, except where specified, the reaction solution contained ca 0·2 vol.-% acetonitrile. For reactions in aqueous micelles, reagent concentrations are specified in terms of total solution volume, but the specified pH is that of the aqueous solution before addition of surfactants, which will slightly change the pH in the aqueous component of the solution.

Microemulsion solutions of $t\text{-BuO}_2\text{H}$ were prepared by weight and the molarity of KOH is that in the aqueous component, so that the total amount of $\mathrm{OH^-}$ increases with increasing water content. A similar approach was used for reaction of $\mathrm{MCPBA^-}$ in microemulsions. The pH and concentrations of buffer, $\mathrm{MCPBA^-}$ and salt, where added, refer to the aqueous component of the microemulsion, and the amount of $\mathrm{MCPBA^-}$, in particular, increases with increasing water content. Decomposition of MCPBA is faster in micelles and microemulsions than in water, so solutions were prepared immediately before reaction.

Decomposition of $\mathrm{PPA^{2-}}$ was a major problem[16] and, although the salt is reasonably stable as a solid, it decomposes readily in micelles or microemulsions. One mode of decomposition involves attack of a peroxy anion on the peroxy acid[14] and it should be assisted by colloidal species which bind both reactants. There is less decomposition at higher pH where the hydroperoxy group is deprotonated, and we generally followed reactions at pH 9 or higher with freshly prepared dilute solutions. The problem is less serious in micelles than in microemulsions where dephosphorylation is slow and therefore we did not follow rate constants for reaction of $\mathrm{PPA^{2-}}$ in microemulsions.

All reactions were followed at 25·0 °C. First-order rate constants, k_ψ, are in reciprocal seconds. The second-order rate constant for reaction of pNPDPP with $\mathrm{PPA^{2-}}$ is $1.1\,\mathrm{l\,mol^{-1}\,s^{-1}}$ in the absence of surfactant in water–acetonitrile (97:3, v/v) and 0·03 M carbonate buffer (pH 10·5).

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REFERENCES

1. (a) W. P. Jencks, *Catalysis in Chemistry and Enzymology*, Chap. 2. McGraw-Hill, New York (1969); (b) C. D. Ritchie, *J. Am. Chem. Soc.*, **97**, 1170 (1975); (c) E. Buncel, H. Wilson and B. Chuaqui, *J. Am. Chem. Soc.* **104**, 4896 (1982).
2. L. Horner and A. Parg, *Justus Liebigs Ann. Chem.* **61** (1977).
3. C. A. Bunton, M. M. Mhala, J. R. Moffatt, D. Monarres and G. Savelli, *J. Org. Chem.* **49**, 426 (1984).
4. J. M. Brown and J. R. Darwent, *J. Chem. Soc., Chem. Commun.* 166 (1969).
5. R. A. Mackay, *Adv. Colloid Interface Sci.* **15**, 131 (1981).
6. (a) R. A. Mackay, *J. Phys. Chem.* **86**, 4756 (1982); (b) R. A. Mackay, F. R. Longo, B. L. Knier and H. D.

Durst, *J. Phys. Chem.* **91**, 861 (1987); (c) B. A. Burnside, L. L. Szafranie, C. B. L. Knier, H. D. Durst, R. A. Mackay and F. R. Longo, *J. Org. Chem.* **53**, 2009 (1988).

7. (a) J. W. Larsen and L. B. Tepley, *J. Colloid Interface Sci.* **49**, 113 (1974); (b) R. Zana, *J. Colloid Interface Sci.* **78**, 330 (1980); (c) C. A. Bunton and F. de Buzzaccarini, *J. Phys. Chem.* **86**, 5010 (1982).
8. (a) L. S. Romsted, in *Surfactants in Solution*, edited by K. L. Mittal and B. Lindman, Vol. 2, p. 1015. Plenum Press, New York (1984); (b) F. H. Quina and H. Chaimovich, *J. Phys. Chem.* **83**, 1844 (1979); (c) C. A. Bunton and G. Savelli, *Adv. Phys. Org. Chem.* **22**, 213 (1986).
9. (a) L. S. Romsted, *J. Phys. Chem.* **89**, 5107, 5113 (1985); (b) L. S. Romsted and D. Zanette, *J. Phys. Chem.* **92**, 4690 (1988).
10. C. A. Bunton, L.-H. Gan, J. R. Moffatt, L. S. Romsted and G. Savelli, *J. Phys. Chem.* **85**, 4118 (1981).
11. C. A. Bunton and J. R. Moffatt, *J. Phys. Chem.* **89**, 4166 (1985); **92**, 2896 (1988).
12. A. J. Everett and G. J. Minkoff, *Trans. Faraday Soc.* **49**, 410 (1953).
13. C. A. Bunton, F. de Buzzaccarini and F. H. Hamed, *J. Org. Chem.* **48**, 2457 (1983).
14. E. Koubek, M. L. Haggett, C. J. Battaglia, K. M. Ibne-Rasa, H. Y. Pyun and J. O. Edwards, *J. Am. Chem. Soc.* **85**, 2263 (1963).
15. (a) K. A. Dill, D. E. Koppel, R. S. Cantor, J. D. Dill, D. Benededouch and S.-H. Cheng, *Nature* (London) **309**, 42 (1984); (b) D. W. R. Gruen, *Prog. Colloid Polym. Sci.* **70**, (1985).
16. (a) R. E. Ball, J. O. Edwards, M. L. Haggett and P. Jones, *J. Am. Chem. Soc.* **89**, 2331 (1967); (b) P. Jones, M. L. Haggett, D. Holden, P. J. Robinson, J. O. Edwards, S. J. Bachofer and Y. T. Hayden, *J. Chem. Soc., Perkin Trans. 2* 443 (1989).
17. P. Mukerjee and K. J. Mysels, *Critical Micelle Concentrations of Aqueous Surfactant Systems.* National Bureau of Standards, Washington, DC (1971).
18. (a) L. R. Fisher and D. G. Oakenfull, *Chem. Soc. Rev.* **6**, 25 (1977); (b) F. M. Menger and C. E. Portnoy, *J. Am. Chem. Soc.* **89**, 4698 (1967).
19. C. A. Bunton and L. Robinson, *J. Org. Chem.* **34**, 773 (1969).
20. C. A. Bunton, Y. S. Hong, L. S. Romsted and C. Quan, *J. Am. Chem. Soc.* **103**, 5788 (1981).
21. D. Piskiewicz, *J. Am. Chem. Soc.* **99**, 1550, 7695 (1977).
22. C. A. Bunton and R. Bacaloglu, *J. Colloid Interface Sci.* **115**, 288 (1987).