analyzed as described above. Results of these experiments are presented in Tables I and III.

(C) *trans*-α-Methyl-γ-mesitylallyl Acetate (8-OAc). These experiments were carried out as described above for *exo*-3-OAc except that the reaction time was 1.5 h at 0 °C, and only a 2-fold excess of $LiCuMe_2$ was used.

Alkylation of Allylic Carboxylates with LiCu(CN)Me. (A) *endo*- and *trans*-5-Methyl-2-cyclohexenyl Acetate (1-OAc). In a typical experiment a flask equipped with a stirrer and septum was charged with 1.79 g (20 mmol) of CuCN and 30 mL of dry ether. After the mixture was cooled to 0 °C, 16.2 mL of 1.23 M MeLi was added, and the mixture was stirred 45 min at room temperature to obtain a homogeneous solution. The resulting solution was cooled to 0 °C, and 1.16 g (7.5 mmol) of *cis*-1-OAc was added dropwise to the stirred solution. The mixture gradually became a suspension of a yellow precipitate, after 23 h at 0 °C the solution became clear, and a gummy green-black precipitate coated the flask. The reaction was quenched with 15 mL of saturated aqueous NH_4Cl, and the precipitate was removed by filtration and washed well with ether. The ether layers were combined, dried (brine followed by $MgSO_4$), and carefully concentrated by fractional distillation. Yields and product distributions were determined by capillary GC (230-ft column, UCON LB-550-X).

Reactions of α- and γ-D-*cis*-1-OAc were carried out in the same way. The product (2) was isolated from the concentrated reaction mixture by preparative GC (10 ft × $^3/_8$ in. column, 20% UCON LB-550-X on Chromosorb W).

(B) *exo*-Bicyclo[3.2.1]oct-3-en-2-yl Acetate (*exo*-3-OAc). The procedure was the same as described above for 1-OAc except that a 5-fold excess of LiCu(CN)Me was used, and the reaction was stirred for an additional 10 h at room temperature. In addition to the black precipitate, a copper mirror was formed on the sides of the flask. Isolation and analysis were the same as described above for alkylation of *exo*-3-OAc with $LiCuMe_2$. The results of the experiments are included in Tables I and II.

(C) *endo*-Bicyclo[3.2.1]oct-3-en-2-yl Mesitoate (*endo*-3-OTMB). In a typical experiment a flask equipped with stirrer and septum was charged with 0.69 g (8 mmol) of CuCN, 0.12 g (1 mmol) of mesitylene (internal standard), 15 mL of dry ether, and 6.4 mL of 1.26 M MeLi. The mixture was stirred for 45 min at room temperature after which the homogeneous solution was cooled to 0 °C, and a solution of 0.27 g (1 mmol) of *endo*-3-OTMB in 5 mL of dry ether was added. After being stirred 1 h at 0 °C, the mixture was stirred for 4 days at room temperature. Analysis (capillary GC) showed the reaction had stopped at 50% conversion. An additional 5 mmol of ethereal LiCu(CN)Me was added and stirring continued 6 days at room temperature. The reaction was quenched, worked up, and analyzed as described for reaction of *endo*-3-OTMB with $LiCuMe_2$. Results for these experiments are included in Tables I and III.

(D) *trans*-α-Methyl-γ-mesitylallyl Acetate (8-OAc). The procedure was the same as for 1-OAc, and product distributions were determined by capillary GC (94 ft column, UCON LB-550-X).

Acknowledgment. This work was supported by the National Science Foundation (Grant GHE 8108535).

Registry No. *cis*-1-OAc, 61221-47-4; *trans*-1-OAc, 61221-48-5; α-*d*-*cis*-1-OAc, 88158-64-9; γ-*d*-*cis*-1-OAc, 73964-42-8; *cis*-**2**, 17516-95-9; *trans*-**2**, 56021-63-7; *endo*-**3**-OH, 32222-49-4; *exo*-**3**-OH, 4802-43-1; (+)-*exo*-**3**-OH, 68629-26-5; α-*d*-*endo*-**3**-OH, 88158-59-2; γ-*d*-*endo*-**3**-OH, 88158-60-5; *exo*-**3**-OAc, 4802-37-3; *endo*-**3**-OAc, 39762-77-1; (+)-*exo*-**3**-OAc, 79027-20-6; *exo*-**3**-OTMB, 88158-52-5; *endo*-**3**-OTMB, 88158-53-6; α-*d*-*endo*-**3**-OTMB, 88158-54-7; γ-*d*-*endo*-**3**-OTMB, 88158-55-8; (±)-*exo*-**4**, 88199-20-6; *endo*-**4**, 88199-21-7; (+)-*exo*-**4**, 88199-22-8; *exo*-**4**-*2*-*d*, 88158-56-9; *exo*-**4**-*4*-*d*, 88158-57-0; *trans*-**8**-OH, 84473-23-4; **8**-OAc, 88158-58-1; **9**, 16204-62-9; (*E*)-**10**, 84473-25-6; (*Z*)-**10**, 84473-26-7; **11**, 74457-38-8; (*E*)-3-methyl-1-phenyl-1-butene, 15325-61-8; (*E*)-4-phenyl-2-pentene, 42461-65-4; (*Z*)-4-phenyl-2-pentene, 76807-04-0; γ-*d*-bicyclo[3.2.1]oct-3-en-2-one, 88158-61-6; 2-methylbicyclo[2.2.1]-hept-2-ene-*3*-*d*, 88158-62-7; *cis*-3-acetylcyclopentanecarboxaldehyde-α-*d* dimethyl acetal, 88158-63-8; bicyclo[3.2.1]oct-3-en-2-one, 3212-77-9; $LiCuMe_2$, 15681-48-8; LiCu(CN)Me, 41753-78-0; CuCN, 544-92-3; MeLi, 917-54-4.

Micellar Effects upon Dephosphorylation by Peroxy Anions

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Received August 5, 1983

Dephosphorylation of *p*-nitrophenyl diphenyl phosphate (pNPDPP) by the anions of hydrogen peroxide or *m*-chloroperoxybenzoic acid (MCPBA) is markedly speeded by cationic micelles of the cetyltrimethylammonium ion. For reaction with H_2O_2 in cetyltrimethylammonium chloride (CTACl) in dilute OH^- (10^{-4} to 2.5×10^{-3} M), first-order rate constants, k_ψ, go through maxima with increasing [CTACl] and increase with increasing [OH^-] but decrease on addition of Cl^-. Added borate ion markedly speeds reaction, but carbonate ion has little effect. Reaction with *m*-chloroperoxybenzoate ion is rapid in CTA^+ micelles with chloride, mesylate, or benzenesulfonate counterion. The micellar rate enhancement is reduced by added *m*-chlorobenzoate or *p*-toluate ion. *tert*-Butylperoxy anion is an ineffective nucleophile in either water or micellized CTACl. These peroxy anion reactions were examined at high pH, and reaction with [OH^-] was studied for comparison. The rate data over a wide range of [OH^-] were fitted quantitatively to the pseudophase ion-exchange model, but this model fitted the rate data only qualitatively for reactions of the peroxy anions.

Peroxy anions are effective α-effect nucleophiles and their reactions with a variety of electrophiles have been studied mechanistically.[3] Large micellar effects upon acylation were observed by Brown and Darwent,[4] even at submicellar concentration of cetyltrimethylammonium

(1) Supported by the Apprenticeship Program of the U.S. Army Research Office administrated by the Academy of Applied Sciences.

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chloride with the hydrophobic peroxycumyl anion.

Hydroperoxide ion is an effective dephosphorylating agent in water,[5] and we have examined micellar and buffer effects upon reactions of peroxy anions with *p*-nitrophenyl diphenyl phosphate (pNPDPP). As surfactants we used cetyltrimethylammonium chloride, mesylate, and benzenesulfonate (CTACl, CTAOMs, and CTAOBez, respectively). Reactions of peroxy anions were followed at high pH so that we must also consider reaction with OH^-. This reaction has been examined in solutions of bromide ion surfactants[6] but not in CTACl, so the effect of this surfactant was examined. The results were fitted to equations that describe the distribution of both reactants between aqueous and micellar pseudophases.[6-11]

Experimental Section

Materials. Preparation and purification of the substrate and surfactants have been described.[12] *m*-Chloroperoxybenzoic acid (Aldrich) and *tert*-butyl hydroperoxide (Aldrich) were purified by standard methods.[13] Freshly prepared solutions were used in all experiments, and concentrations of the peroxides were determined by standard methods.[14]

Kinetics. Reactions were carried out in CO_2-free solutions saturated with N_2 and then degassed. Formation of *p*-nitrophenoxide ion was followed spectrophotometrically at 402 nm, in Beckman or Gilford spectrophotometers for the slower and a Durrum stopped-flow spectrophotometer for the faster reactions. For some reactions with half-lives in the range 2–4 s we used both Gilford and Durrum spectrophotometers and obtained satisfactory agreement between the rate constants.

Reactions of hydrogen peroxide and *tert*-butyl hydroperoxide were followed in solutions of NaOH or KOH, but for reactions of H_2O_2 in borate or carbonate buffer and MCPBA in carbonate buffer, the pH was adjusted in the reaction solution.

Bubble formation, due to peroxide decomposition, was a problem, but it was minimized by degassing. Reactions were followed at 25.0 °C, and the first-order rate constants, k_ψ, are in reciprocal seconds. Reactions followed in Gilford or Beckman spectrophotometers were started by adding substrate in MeCN so that the reaction solution typically contained 2×10^{-5} M substrate and 1% MeCN.

Decomposition of *m*-Chloroperoxybenzoic Acid. The decomposition of MCPBA, followed at 260 nm, in solutions of CTACl, is much slower than reaction with pNPDPP. For example, with 3.3×10^{-4} M MCPBA and 0.07 M carbonate buffer, pH 10.1, $k_\psi = 7 \times 10^{-5}$ s^{-1} in 0.025 and 0.04 M CTACl at 25.0 °C. In a similar buffer, at pH 8.4, in 10^{-3} M CTACl and 3.3×10^{-4} M MCPBA, reaction did not have an integral order, but $t_{1/2} \approx 1500$ s at 25.0 °C.

Results

Reaction of Hydroperoxide Anion. Hydroperoxide anion is a better nucleophile than OH^- toward pNPDPP in water,[3,4] and in 2.5×10^{-3} M NaOH, $k_\psi = 0.020$ and 0.026 s^{-1} in 0.02 and 1 M H_2O_2, respectively. For reaction with OH^- the second-order rate constant is 0.5 M^{-1} s^{-1} at 25 °C,[6] so added H_2O_2 is speeding reaction by a factor of approximately 20-fold. This high nucleophilicity of HO_2^-, is typical of the behavior of α-effect nucleophiles,[3] and the second-order rate constant is 11 M^{-1} s^{-1}, based on $pK_A = 11.65$ for H_2O_2.[15]

Micellar effects upon the reaction of pNPDPP with HO_2^- were examined with various concentrations of added NaOH in CTACl. The first-order rate constants, k_ψ, go through maxima with increasing [CTACl] at fixed [H_2O_2] and [OH^-] (Figure 1), as is typical of micellar-assisted

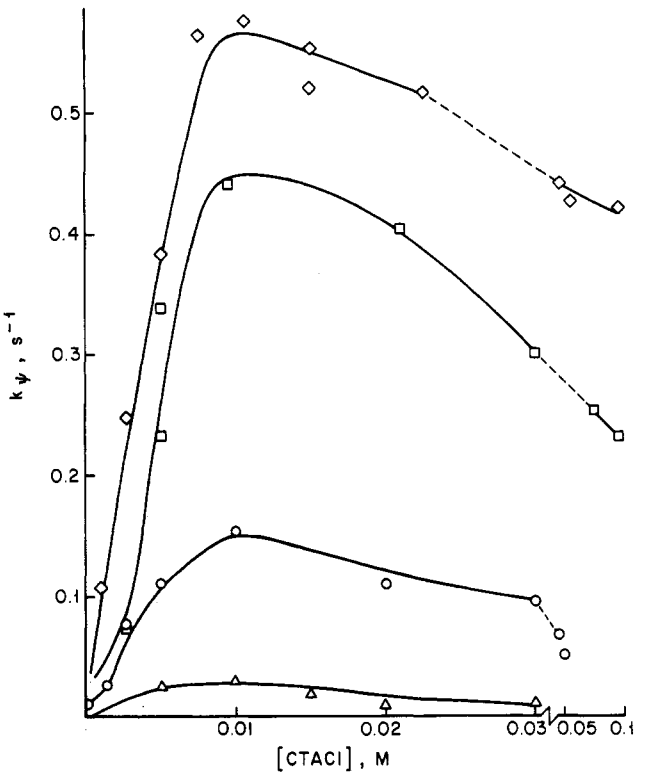

Figure 1. Reaction of pNPDPP with H_2O_2 in micellized CTACl: (△) 0.03 M H_2O_2, 10^{-4} M OH^-; (○) 0.01 M H_2O_2, 5×10^{-4} M OH^-; (□) 0.02 M H_2O_2, 2.5×10^{-3} M OH^-; (◇) 1 M H_2O_2, 2.5×10^{-3} M OH^-.

Table I. Inhibition of Reaction of Hydroperoxide Ion by Chloride Ion[a]

	reaction medium[b]		
10^3[KCl], M	1	2	3
	0.11	0.578	0.525
0.5	0.11	0.524	
1.0	0.103		
2.5	0.108	0.487	
5.0			0.385
10.0	0.015		0.270
20.0	0.0063	0.184	0.250
30.0	0.0056		0.210
50.0			0.170
100			0.149
250			0.083

[a] Values of k_ψ, s^{-1}, at 25.0 °C. [b] 1, 0.01 M H_2O_2, 5×10^{-4} M KOH, 0.02 M CTACl; 2, 1 M H_2O_2, 2.5×10^{-3} M KOH, 0.01 M CTACl; 3, 1 M H_2O_2, 2.5×10^{-3} M KOH, 0.02 M CTACl.

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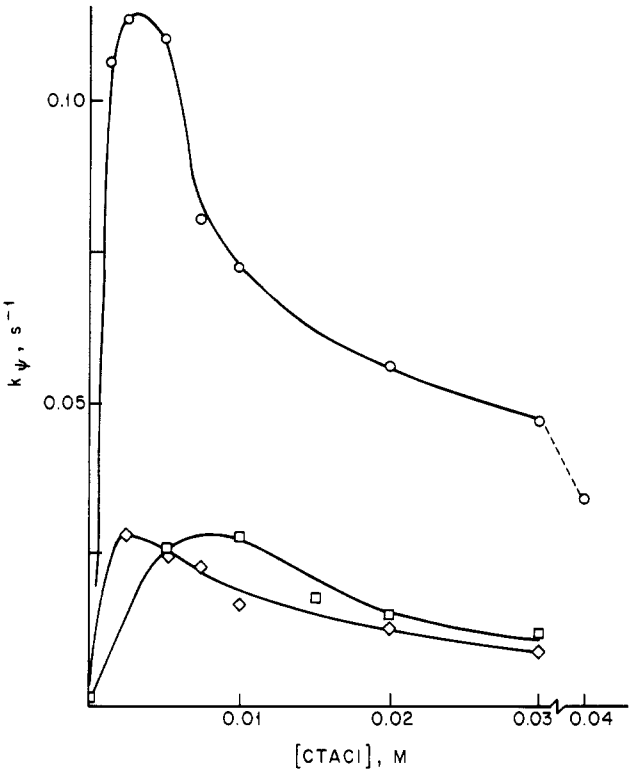

Figure 2. Buffer effects on reaction of pNPDPP with 0.01 M H_2O_2 in CTACl: (□) 10^{-4} M OH^-; (◇) 0.015 M carbonate buffer, pH 10.1; (○) 0.031 M borate buffer, pH 10.

Table II. Effect of Borate Buffer on Reaction with H_2O_2[a]

	reaction medium[b]	
10^2[borate], M	1	2
0.25	5.15	2.40
0.75		2.24
1.00	2.41	2.34
1.40	2.21	1.59
1.80	1.68	1.22
2.33	0.64	0.96
3.88	0.52	0.48
7.00	0.32	
7.36		0.20

[a] Values of k_ψ, s^{-1}, at 25.0 °C and pH 10. [b] 1, 0.1 M H_2O_2 and 0.0075 M CTACl; 2, 0.1 M H_2O_2 and 0.02 M CTACl.

bimolecular reactions.[6-13,16] Increases in $[H_2O_2]$ and $[OH^-]$ speed reactions, and the rate enhancements over reactions in aqueous OH^- are by factors of up to 500.

Inhibition of Reaction with H_2O_2. Added chloride ion inhibits reaction of HO_2^- in CTACl (Table I), probably due to competition for the micelle between reactive and unreactive counterions.[6,7,9,10,16]

Buffer Effects on Reaction with H_2O_2. The maximum values of k_ψ for reaction of H_2O_2 in solutions of CTACl are similar in carbonate buffer (pH 10.1) and in 10^{-4} M OH^-, although optimum [CTACl] is lower in the buffer (Figure 2). This difference is probably due to a decrease of the critical micelle concentration, cmc, in carbonate buffer[17] and to a salt effect that should increase micellar binding of the substrate.[18]

Table III. Effect of pH upon Reaction with *m*-Chloroperoxybenzoic Acid[a]

pH	8.41	8.77	9.05	9.52	10.0	10.7	12.1
k_ψ, s^{-1}	2.26	2.71	2.91	3.38	3.48	3.43	3.38

[a] At 25.0 °C with 10^{-3} M MCPBA in 0.075 M carbonate buffer and 10^{-2} M CTACl.

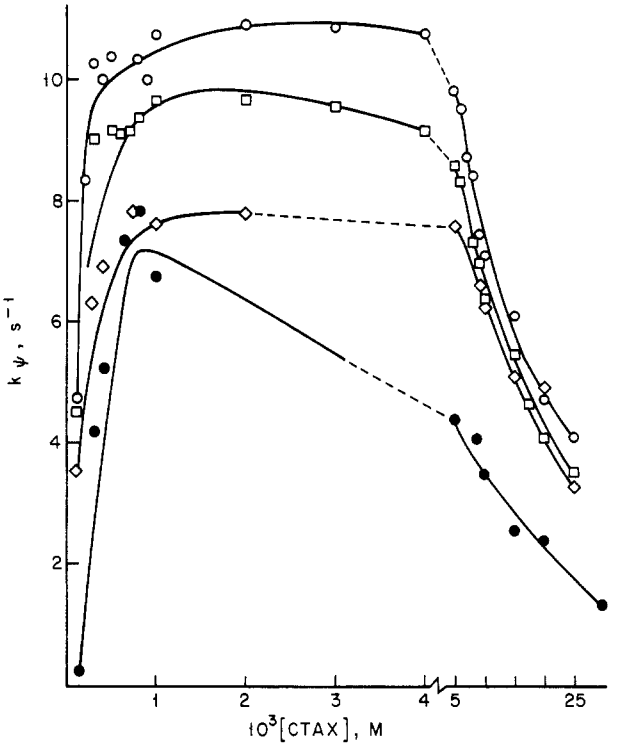

Figure 3. Reaction of pNPDPP with *m*-chloroperoxybenzoate ion at pH 10.5: Open points, 0.005 M MCPBA, 0.0375 M carbonate buffer; solid points, 0.001 M MCPBA, 0.075 M carbonate buffer. Counterions (○), ●: □; ◇); Cl^-, $MeSO_3^-$, $PhSO_3^-$, respectively.

Added borate ion speeds reaction in the presence and absence of CTACl. In aqueous 0.01 M H_2O_2 at pH 10, k_ψ = 3.75 × 10^{-3} s^{-1} in 0.031 M borate and 1.0 × 10^{-3} s^{-1} in 10^{-4} M NaOH. The rate differences in CTACl are shown in Figure 2. These rate increases are probably due to formation of a peroxyborate ion,[19] which should bind readily to the micelle and may itself be an effective nucleophile.

In micelles the dependence of k_ψ upon [borate] is complex (Table II). We cannot compare rate constants in a buffer directly with those in unbuffered 10^{-4} M OH^- (nominal pH 10), but the data in Figure 1 show that dilute borate ion markedly speeds reaction. Further addition of borate ion decreases k_ψ but not to the value in the absence of borate ion. Probably borate ion speeds reaction by generating peroxyborate ion, but this effect is partially offset by competition between borate and peroxyborate ion for the micelle. With 0.031 M borate ion, reaction in the micelles is faster than that in water by a factor of ca. 30 (Figure 2).

Reactions with *m*-Chloroperoxybenzoate Ion. The first-order rate constant for reaction of pNPDPP in 10^{-3} M MCPBA and 0.075 M carbonate buffer, pH 10.5, is 1.3 × 10^{-3} s^{-1} at 25.0 °C, and allowing for reaction with OH^-,[20]

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Table IV. Effect of Carboxylate Ions on Reaction of MCPBA[a]

10^4[RCO_2Na], M	p-$MeC_6H_4CO_2Na$	m-$ClC_6H_4CO_2Na$
0.1	3.79	(3.38)
1.0	3.16	4.04 (2.98)
4.0	3.21	3.29 (2.72)
10	2.78	2.93 (2.41)

[a] Values of k_ψ, s^{-1}, at 25.0 °C with 10^{-3} M MCPBA in 2.5×10^{-3} M CTACl, pH 10.5, 0.075 M carbonate buffer. In the absence of added salt, $k_\psi = 4.68\ s^{-1}$. Values in parentheses are in 5×10^{-3} M CTACl; in the absence of added salt, $k_\psi = 4.39\ s^{-1}$.

we estimate the second-order rate constant for reaction of m-chloroperoxybenzoate ion to be 1.2 $M^{-1}\ s^{-1}$. This ion is therefore an α-effect nucleophile in dephosphorylation.

In water the pK_A of peroxybenzoic acid is 7.8,[21] and the m-chloro substituent in MCPBA should slightly increase acidity. The rate constants for reaction of MCPBA with pNPDPP in CTACl are independent of pH >9.5 (Table III).

Cationic micelles sharply speed dephosphorylation by m-chloroperoxybenzoate ion. Values of k_ψ go through maxima with increasing [surfactant], and rate–surfactant profiles depend slightly upon the nature of the surfactant counterion (Figure 3). Rate enhancements are observed in surfactant well below the cmc in water (Figure S1 (Supplementary Material)). The reactants promote micellization or bind to submicellar aggregates (cf. ref 4, 24). Under optimum conditions micellar rate enhancement are by factors of ca. 10^2.

m-Chlorobenzoate or p-toluate ion inhibit reaction of MCPBA in CTACl (Table IV) because of competition between inert carboxylate ion and peroxy anion for the micelle (cf ref. 6–9, 26). Carboxylate ions bind readily to cationic micelles,[25] and solutions of CTACl become viscous on addition of arenecarboxylate ion.

Reaction in Solutions of *tert*-Butyl Hydroperoxide. In water, *tert*-butylperoxy ion is a poor dephosphorylating agent, and at pH 10.5 and 12 (0.075 M carbonate buffer) reaction is not speeded by 0.1 M t-BuO_2H. This low reactivity is not due to limited deprotonation, because alkyl hydroperoxides are only slightly weaker acids than H_2O_2.[15] Probably the bulky *tert*-butyl group is slowing reaction.

tert-Butyl hydroperoxide and pNPDPP should bind readily to aqueous micelles, but in solutions of CTACl k_ψ *decreases* with increasing [t-BuO_2H] (Figure 4), and reaction is slower than in corresponding solutions of OH^-. (The variation of k_ψ with [CTACl] for reaction in solution containing t-BuO_2H (Figure 4) is estimated by interpolation of rate data for higher and lower [OH^-].) Nonionic solutes reduce binding of counterions to micelles[27] and *tert*-butylperoxy anion is an ineffective dephosphorylating agent in cationic micelles, as in water.

Reaction with Hydroxide Ion. Reaction of pNPDPP with OH^- in CTABr or CTACl (Figure S2 and S3) is considerably slower than with hydroperoxide or m-chloroperoxybenzoate ion.

Discussion

Quantitative Treatment of Micellar Rate Enhancements. Micellar rate effects on biomolecular reactions can generally be treated quantitatively in terms of the distribution of reactants between aqueous and micellar pseudophases and second-order rate constants in each pseudophase.[6-12,28,29]

The first-order constant for the overall reaction is given by eq 1, where k_W' and k_M' are first-order rate constants

$$k_\psi = \frac{k_W' + k_M' K_s[D_n]}{1 + K_s[D_n]} \quad (1)$$

in aqueous and micellar pseudophases, respectively, D_n is micellized surfactant, and K_s is a binding constant.

The distribution of reactive (N^-) and unreactive (X^-) counterions between aqueous and micellar pseudophases is assumed to follow the ion-exchange eq 2.[7,10]

$$K_X^N = [N_W^-][X_M^-]/[N_M^-][X_W^-] \quad (2)$$

The first-order rate constants, k_W' and k_M', are written in terms of second-order rate constants, k_W and k_M:

$$k_W' = k_W[N_W^-] \quad (3)$$

$$k_M' = k_M m_s^N = k_M[N_M^-]/[D_n] \quad (4)$$

where m_s^N is concentration of reactive ion in the micelle, written as a mole ratio.

The overall first-order rate constant is given by

$$k_\psi = \frac{k_W[N_W^-] + k_M K_s[N_M^-]}{1 + K_s[D_n]} \quad (5)$$

The concentrations of ionic reagent in aqueous and micellar psedophase, $[N_W^-]$ and $[N_M^-]$, respectively, can be related to the total concentration of N^-. Typically the ion-exchange constant K_X^N is taken as a disposable parameter, and β, the fraction of micellar head groups neutralized by counterions, is assumed to be constant and allows application of the mass-balance relationship.

The value of K_s is taken as $10^4\ M^{-1}$, but fitting of the rate data is insensitive to the precise value.[12a] The "kinetic" cmc is treated as a disposable parameter and will be smaller than the cmc in water because of the effects of added solutes. Parameters such as K_X^{OH} and β should be unaffected by the nature of the substrate, and K_s and k_M should be relatively insensitive to the nature of the surfactant counterion.

The variation of k_ψ with [CTABr] or [CTACl] for reaction in 0.001–0.05 M OH^- with pNPDPP (Figures S2 and S3) can be fitted to eq 3–6 with the parameters given in Table V. As in generally found,[9,10,30] various combinations of the parameters fit the data equally well, but the values in Table V are consistent with literature values.[9-11,25,31,32] The agreement is satifactory over a 50-fold range of [OH^-], which is much wider than that generally used.

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(26) When inhibition by carboxylate ion was examined in very dilute CTACl ($<4 \times 10^{-4}$ M), we could not obtain consistent results. In some experiments reaction was faster than in the absence of carboxylate ion, perhaps because added inert salts promoted formation of aggregates that assisted reaction.
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Table V. Quantitative Treatment for Reaction of OH^- [a]

medium	cmc, M	K_X^{OH}	β	k_M, s^{-1}
CTABr, 0.05 M OH^-	2×10^{-4}	15.5	0.8	0.55
	3×10^{-4}	12	0.75	0.55
CTABr, 0.03 M OH^-	3×10^{-4}	12	0.8	0.48
CTABr, 0.01 M OH^-	5×10^{-4}	12	0.8	0.38
CTABr, 0.001 M OH^-	6×10^{-4}	14	0.8	0.35
CTACl, 0.03 M OH^-	5×10^{-4}	4	0.72	0.54
CTACl, 0.01 M OH^-	9×10^{-4}	4	0.72	0.54
CTACl, 0.001 M OH^-	10^{-3}	4	0.75	0.43

[a] At 25.0 °C with $K_s = 10^4$ M^{-1}. The results in 0.05 M OH^- are from ref 6b.

Values of k_M cannot be compared directly with second-order rate constants in water because of different dimensions. Comparison can be made if the molar volume element of reaction in the micellar pseudophase is estimated, based on the volume of the micellar Stern layer so that[10]

$$k_2^m = 0.14k_M \quad (6)$$

where k_2^m is the second-order rate constant, with concentration as molarity in the Stern layer. Values of k_2^m range from 0.05 to 0.08 and are lower than that of the second-order rate constant in water, which is ca. 0.5 M^{-1} s^{-1}. The rate constants in the micelles appear to decrease with decreasing $[OH^-]$ (Table V), but the differences are within the uncertainties of the treatment.[33] Reaction is consistently faster in aqueous CTACl than in aqueous CTABr, because Br^- competes more effectively than Cl^- with OH^- for cationic micelles, not because of differences in k_M.

Quantitively the variations of k_ψ with [surfactant] for reactions of H_2O_2 and MCPBA (Figures 1, 3, and 4) follow the pseudophase model. We could not fit the rate–surfactant profiles for reaction of MCPBA quantitatively to the pseudophase ion exchange for *different* concentrations of *m*-chloroperoxybenzoate ions (Figure 3) in terms of competition only between the peroxy anion and micellar counterion. The problem is partly due to the presence of carbonate ion, which also competes with the peroxy anion. An additional problem in treating the data in Figure 3 quantitatively is that the rate maxima are observed in very dilute surfactant, at concentrations close to the cmc in water, which makes it impossible to define the concentration of micellized surfactant.

The form of the plots in Figure 3 suggests that both reactants bind very strongly to the micelles, because k_ψ is only slightly increased by a fivefold increase in [MCPBA]. We estimate a *minimum* value for k_M by assuming that pNPDPP is fully micellar bound and that, in dilute surfactant and 5×10^{-3} M MCPBA, micelles of CTACl, for example, are saturated with peroxy anion. Equation 5 then reduces to

$$k_\psi = k_M[N_M^-]/[D_n] = k_M\beta \quad (7)$$

If $\beta \approx 0.8$, the value of k_ψ (max) = 11 s^{-1} in CTACl (Figure 3) gives $k_M \approx 15$ s^{-1} and $k_2^m \approx 2$ M^{-1} s^{-1}, which is similar to the second-order rate constant of 1.2 M^{-1} s^{-1} in water. Therefore, as is often found, the rate enhancement is due largely to increased reactant concentration in the micellar pseudophase. Reaction is slightly slower in cetyltrimethylammonium benzenesulfonate than in the chloride or mesylate (Figure 3), probably because benzenesulfonate competes with the peroxy anion for the micelle.[12b]

(33) There is evidence that rate constants increase in the micelle at high OH^-.[11]

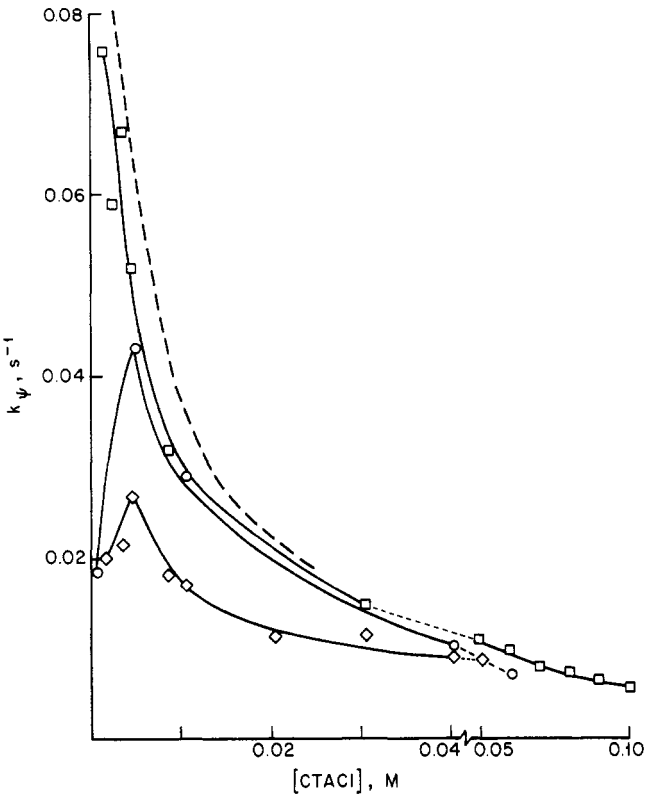

Figure 4. Reaction of pNPDPP in *t*-BuO_2H in 0.0025 M OH^- (□, ○, ◇): 0.095, 0.19, and 0.258 M *t*-BuO_2H, respectively. The dashed line is for reaction of OH^-.

We did not attempt to treat quantitatively the variation of k_ψ with [surfactant] for reaction of H_2O_2 (Figures 1 and 2). The postulated formation of peroxyborate (Figure 2) complicates analysis in solutions containing borate buffer. Ionic micelles bind H_2O_2 and other peroxides,[34] although binding of H_2O_2 is not strong and we have no evidence on micellar effects upon deprotonation of H_2O_2. Micellar effects upon acid–base equilibria have been examined but without additional data on the equilibria attempts to fit these micellar effects involve too many adjustable parameters.

Alkaline H_2O_2 is a better dephosphorylating agent than OH^- and in 0.02 and 1 M H_2O_2 (Figure 1) the maximum values of k_ψ in CTACl are similar, which is consistent with $[HO_2^-]$ being approximately the same as the stoichiometric concentration of OH^-.

The α-effect of the hydroperoxide ion is evident in both water and cationic micelles, cf. ref 4, which is consistent with an aqueous micellar environment, because the effect is absent in gas-phase reactions.[3d]

Acknowledgment. Support of this work by the U.S. Army Office of Research and the North Atlantic Treaty Organization is gratefully acknowledged.

Registry No. pNPDPP, 10359-36-1; CTACl, 112-02-7; CTAOMs, 65060-02-8; CTAOBez, 17322-67-7; MCPBA, 937-14-4; CTABr, 57-09-0; MCPBA anion, 64235-64-9; *m*-$ClC_6H_4CO_2^-$, 16887-60-8; *p*-$CH_3C_6H_4CO_2^-$, 5118-31-0; $B(OH)_4^-$, 15390-83-7; HO_2^-, 14691-59-9.

Supplementary Material Available: Figures of variation of k_ψ for reaction of pNPDPP with *m*-chloroperoxybenzoate ion in dilute CTACl and CTABr (4 pages). Ordering information is given on any current masthead.

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