JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 4, 618–628 (1991)

MICELLAR RATE EFFECTS ON REACTIONS OF HYDROXIDE ION WITH PHOSPHINATE AND THIOPHOSPHINATE ESTERS

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Cationic micelles of cetyltrimethylammonium chloride, bromide and mesylate (CTACl, CTABr, CTAOMs) speed reactions of OH^- with phosphinate and thiophosphinate esters: $Ph_2PO.OPh$ (1a), $Ph_2PO.OC_6H_4NO_2$-*p* (1b), Ph(*i*-Pr)$PO.OC_6H_4NO_2$-*p* (1c), $Ph_2PO.SEt$ (2a), $Ph_2PO.SPh$ (2b), $(EtO)_2PO.SPh$ (2c) and $(EtO)_2PS.OC_6H_4NO_2$-*p* (Parathion, 3). First-order rate constants go through maxima with increasing [surfactant]. The rate–surfactant profiles are fitted quantitatively in terms of a kinetic model that treats the distribution of OH^- between aqueous and micellar pseudo-phases in terms of coulombic and non-coulombic ion–micelle interactions. Second-order rate constants at the micellar surface are lower than in water by factors that range from 0·035 for 1a to 0·7 for 1c. The thiophenyl derivative (2b) is more reactive than the corresponding phenoxy derivative (1a) and it is more reactive than the corresponding thioethyl derivative (2a). Parathion (3) is the least reactive substrate in both water and micelles.

INTRODUCTION

Reactions of OH^- with phosphinate and thiophosphinate esters have been extensively examined in aqueous organic solvents.[1–4] Reactions of the thiophosphinates are faster than those of the corresponding phosphinates, reflecting the higher leaving abilities of thiolate as compared to the corresponding oxide residues. Thiols and thiophenols are considerably stronger acids than the corresponding oxy acids. Nucleophilic attack on phosphorus (V) esters is often written as an addition–elimination reaction involving a trigonal bipyramidal intermediate with groups entering and leaving apically.[3,4] However, Williams and coworkers have suggested that these reactions are probably concerted, based on analysis of substituent effects in terms of Brønsted linear free energy relations.[5]

Reactions of phosphate and phosphinate esters with anionic nucleophiles are speeded by a variety of colloidal assemblies, e.g. micelles[6–9] and microemulsion droplets.[10–12] These rate enhancements can be treated quantitatively in terms of pseudo-phase models that provide estimates of second-order rate constants at surfaces of colloidal assemblies by calculating concentrations of both reagents at the surfaces.[13–22] These models show that both cationic and zwitterionic micelles speed reactions in aqueous solution, not by increasing rate constants but by concentrating reagents into the small volume of the colloidal pseudo-phase. Second-order rate constants for reactions of various anionic nucleophiles with phosphate and phosphinate esters at micellar surfaces are slightly lower than those in water.[8b,9,16,17] This result is typical of bimolecular non-solvolytic reactions in micelles, microemulsion droplets and vesicles. We planned to test these quantitative treatments for substrates with different leaving groups because to date most of the work has involved the nitrophenoxide leaving group. Relative second-order rate constants of reactions of carboxylic esters and hydroxide ion in aqueous and micellar pseudo-phases are dependent upon electronic effects of substituents and electron withdrawal favors the micellar reaction.[21]

We examined reactions of OH^- with a series of phosphinates and thiophosphinates. The substrates were:

$R'R''PO.OR$ (1a) $R' = R'' = R = Ph$
(1b) $R' = R'' = Ph$, $R = C_6H_4NO_2$-*p*
(1c) $R' = Ph$, $R'' = (CH_3)_2CH$, $R = C_6H_4NO_2$-*p*

$R'_2PO.SR$ (2a) $R' = Ph$, $R = Et$
(2b) $R' = R = Ph$
(2c) $R' = OEt$, $R = Ph$

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0894–3230/91/100618–11$05.50

Received 25 March 1991
Revised 24 June 1991

We also examined a thione derivative, Parathion (**3**):

$(EtO)_2\ PS.OC_6H_4NO_2$-*p*

Reactions were followed both in water and at micellar surfaces. Rate constants of reaction at micellar surfaces can be estimated by calculating concentrations of OH$^-$ at those surfaces by solution of the Poisson–Boltzmann equation (PBE). This treatment considers both coulombic and specific ion–micelle interactions.[17,22] To date it has been applied to reaction of OH$^-$ with *p*-nitrophenyl diphenyl phosphate (pNPDPP),[17] but not to reactions of other phosphorus (v) esters in cationic micelles.

RESULTS AND DISCUSSION

Reactions in the absence of surfactant

When necessary second-order rate constants, k_w, in water, were estimated by extrapolating rate constants of reaction in aqueous acetonitrile. All the reactions were overall second order and examples of the solvent effects upon reactions of the thiol and thione derivatives are given in the Experimental Section. Rate constants decrease with decreasing water content of the solvent. Many reactions of nucleophilic or basic anions are speeded by a decrease in water content because dehydration of the anions increases their reactivities.[23] However, organic solvents decrease activity coefficients of phosphorus esters. This stabilization of the substrate more than offsets the rate increase due to destabilization of OH$^-$, probably because there is extensive hydration of anionic residues in the transition state. The rate of reaction of OH$^-$ with pNPDPP decreases with decreasing water content of a mixed solvent,[24] and phosphinate esters behave similarly (Ref. 3 and Experimental Section).

The effects of structure upon reactivity are as expected.[1-4] Reaction rates increase in changing from a phenoxide to a *p*-nitrophenoxide leaving group (**1a**/**b**) or from a thioethyl to a thiophenyl leaving group (**2a**/**b**) (Table 1 and 2). Reactivity increases slightly in going from a phenoxide to a thiophenoxide leaving group (**1a**/**2b**). Alkoxy groups at phosphorus inhibit reaction (**2b**/**c**), the thione derivative (**3**) is relatively unreactive and a phosphinate is more reactive than the corresponding phosphate (**1b** and pNPDPP[8a,17]). These differences are probably due to p–d or d–d interactions that reduce the positive character at phosphorus (v). An isopropyl group at the reaction center inhibits reaction (**1b**/**c**), probably due to a combination of steric and electronic effects.

Micellar reaction

We used cetyltrimethylammonium surfactants ($C_{16}H_{33}NMe_3X$, X = Cl, Br, OMs; CTACl, CTABr, CTAOMs) and a range of dilute OH$^-$. First-order rate constants increase sharply with increasing [surfactant] and go through maxima, and are lower when the surfactant counterion is Br$^-$ rather than Cl$^-$ or OMs$^-$. The overall reaction is less than first order in stoichiometric [OH$^-$] (Figures 1–8). (Concentrations of OH$^-$ are shown in each figure with the plots). These kinetic features are general for micellar-assisted bimolecular reactions of counterions with hydrophobic substrates

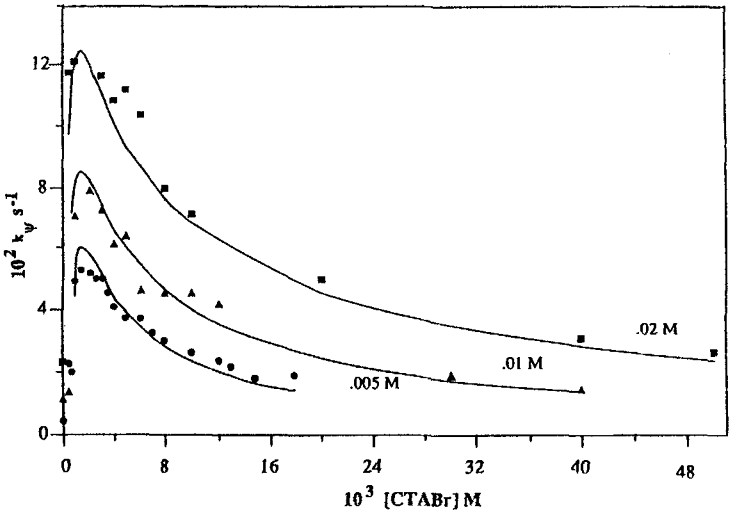

Figure 1. Reaction of OH$^-$ with $Ph_2PO.OPh$ (**1a**) in solutions of CTABr. Here and elsewhere concentrations of OH$^-$ are shown with each plot, unless specified in the caption

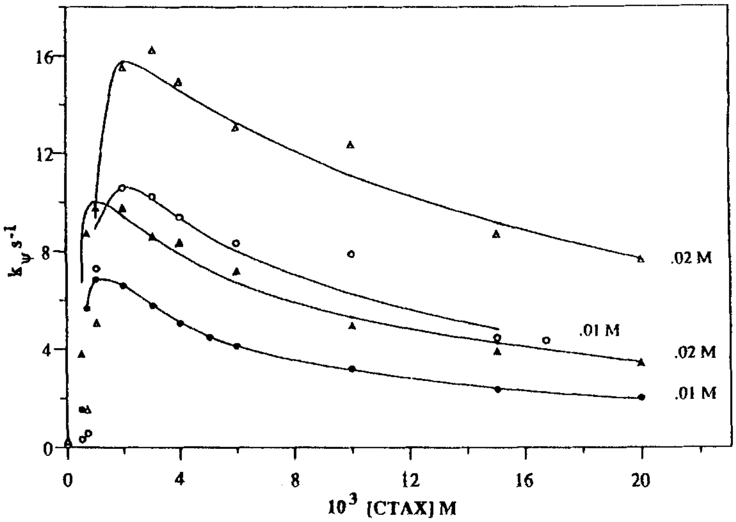

Figure 2. Reaction of OH^- with $Ph_2PO.OC_6H_4NO_2$-*p* (**1b**) in solutions of CTABr (solid points) and CTACl (open points)

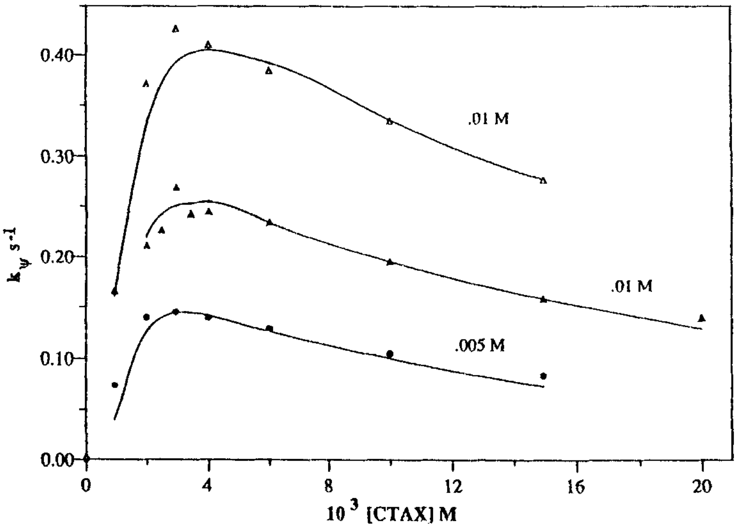

Figure 3. Reaction of OH^- with Ph(*i*-Pr)PO.$OC_6H_4NO_2$-*p* (**1c**) in solutions of CTABr (solid points) and CTACl (open points)

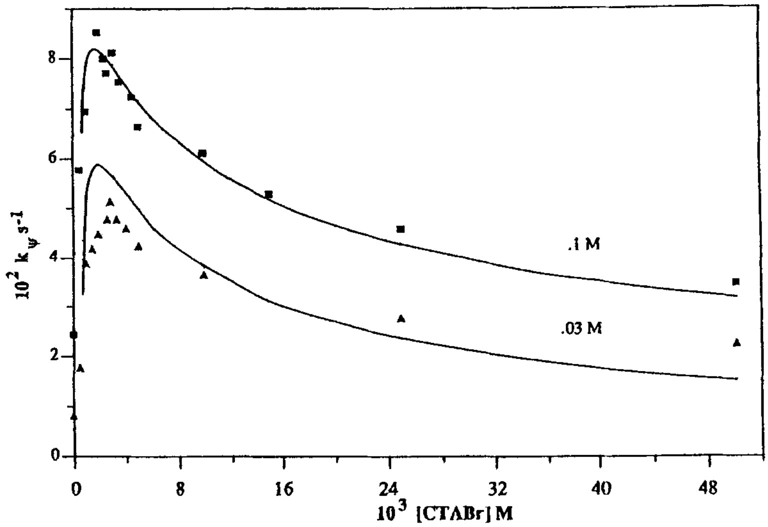

Figure 4. Reaction of OH⁻ with $Ph_2PO.SPEt$ (**2a**) in solutions of CTABr

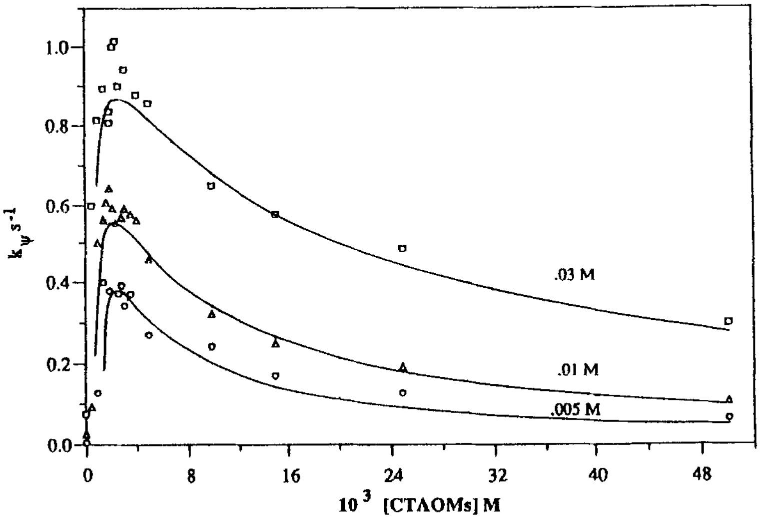

Figure 5. Reaction of OH⁻ with $Ph_2PO.SPh$ (**2b**) in solutions of CTAOMs

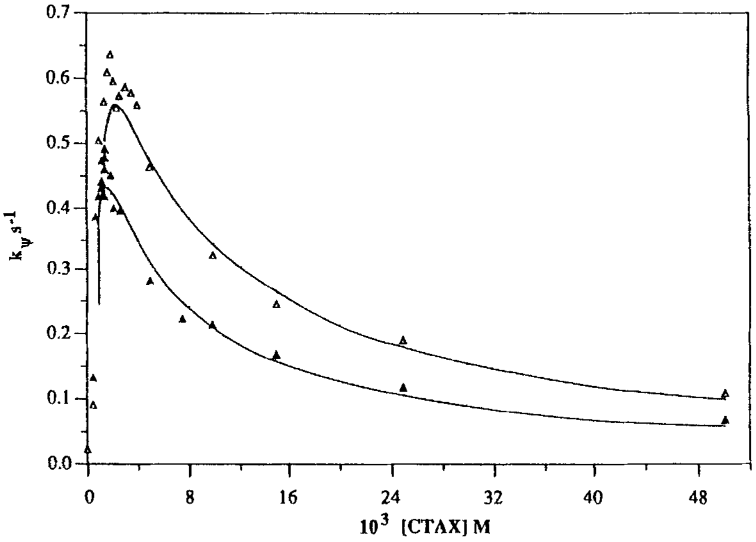

Figure 6. Reaction of 0·01 M OH^- with $Ph_2PO.SPh$ (**2b**). Comparative effects of CTAOMs (open points) with CTABr (solid points)

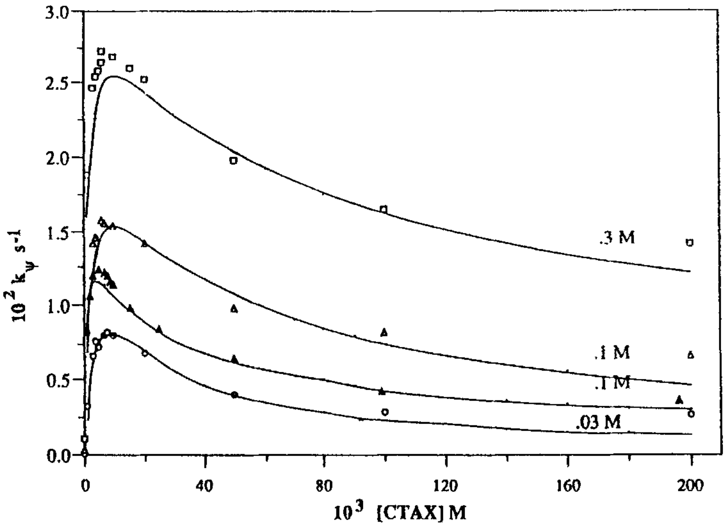

Figure 7. Reaction of OH^- with $(EtO)_2PO.SPh$ (**2c**) in solutions of CTAOMs (open points) and CTABr (solid points)

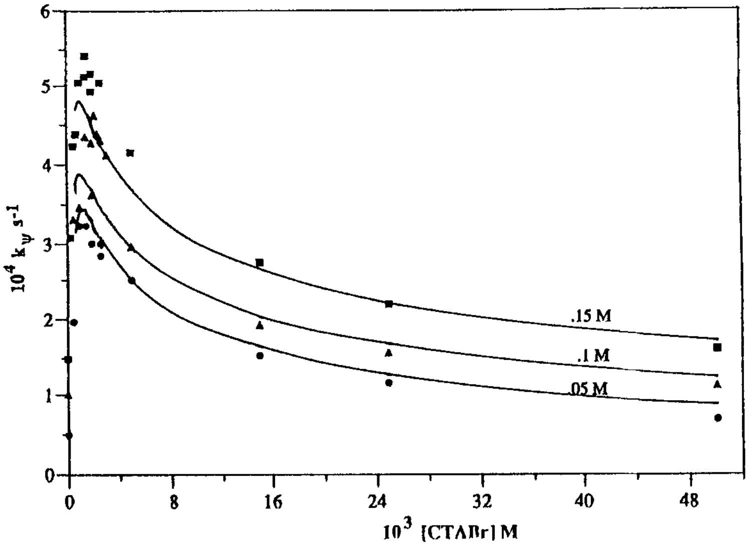

Figure 8. Reaction of OH⁻ with Parathion (3) in solutions of CTABr

and are explained by pseudo-phase models that consider the distribution of both reactants between water and micelles.[14-18] The concentration of OH^- at the micellar surface depends upon competition with the inert counterion and this competition can be treated quantitatively by various ion exchange equations. We treated the data by using a treatment that includes both non-specific, coulombic and ion-specific interactions between the anions and micelles. This treatment has been applied to reaction of pNPDPP + OH^- in solutions of cationic micelles.[17]

Quantitative treatments of micellar rate effects

Most quantitative models treat micelles and water as separate reaction media, so it is necessary to calculate concentrations of both OH^- and substrate (S) in the aqueous and micellar pseudo-phases, although for the hydrophobic phosphorus (v) esters reaction is largely in the micellar pseudo-phase.

The distribution of dilute S between water and micelles is generally considered to be given by Scheme 1 and equations (1) and (2),[13-18,25]

$$\begin{array}{c} S_W + D_n \rightleftharpoons S_M \\ \searrow \quad \swarrow \\ \text{Products} \end{array}$$

Scheme 1

$$[S_M]/[S_T] = K_s[D_n]/(1 + K_s[D_n]) \tag{1}$$

$$[S_W]/[S_T] = 1/(1 + K_s[D_n]) \tag{2}$$

where subscripts T, M and W denote, respectively, the total concentration and those in the micellar and aqueous pseudo-phases, K_S is a binding constant and D_n is micellized surfactant (detergent). The concentration of monomeric surfactant is assumed to be the critical micelle concentration (cmc) under the kinetic conditions.

We assume that reaction occurs in a shell of width, Δ, at the micellar surface, so that the first-order rate constant, with respect to substrate, is given by:[17]

$$k_\psi = \frac{k_W[OH_W^-] + k_2^M K_s[D_n][OH^-]_\Delta}{1 + K_s[D_n]} \tag{3}$$

Second-order rate constants k_W and k_2^M($l\ mol^{-1} s^{-1}$) in the aqueous and micellar pseudo-phases, respectively, have the same dimensions and can be compared directly and $[OH^-]_\Delta$ is the local molarity integrated over the reaction region, width Δ.

We used the cell model of solution and calculated distributions of co- and counter-ions between the micellar surface, radius *a*, and the cell wall by solving the PBE in spherical symmetry,[26] but with an added term that considers specific, non-coulombic, ion–micelle interactions.[17] Each cell contains one micelle, so the cell radius is governed by the concentration of micellized surfactant and the micellar aggregation number, *N*. Ions can interact with micelles specifically as well as coulombically and the specific attractions will be largest for the most polarizable, low-charge density, anions, e.g. Br^-. The interaction is written in terms of a Volmer isotherm with the assumption that OH^- interacts only coulombically with micelles.[17]

The fraction of head groups (*f*) that are neutralized by a specifically bound counterion, X^-(Cl^-, Br^- or

OMs$^-$) is given by:

$$f = \frac{\delta_X \exp(-f/(1-f))[X_{\bar{w}}]}{1 + \delta_X \exp(-f/(1-f))[X_{\bar{w}}]} \qquad (4)$$

The interactions can also be written in terms of Langmuir isotherms, although the Volmer isotherm is probably better when ion coverage is high,[17b,c] as is the case here.

We assume that specifically bound counterions neutralize the charge of an equal number of cationic head groups and in fitting the rate data we assign a specificity parameter, δ_X (equation 4), to each anion with $\delta = 0$ for very hydrophilic anions, e.g. OH^-.

Values of N for CTA^+ micelles are known, or can be estimated by analogy with known values. The radius, a, to the charged interface is lower than the hydrodynamic radius (R_h) because R_h includes organic residues in the head group and associated counterions and water molecules. The specificity parameters, δ_X, are independent of concentrations of surfactants and electrolytes and for Cl^- and Br^- fit data for reactions in which these ions are inert inhibitors and also for reactions in which they are reactants.[17c] We took $\Delta = 2{\cdot}4$ Å in fitting rate data for anion reactions in solutions of CTA^+ surfactants,[17] but satisfactory fits can be obtained with other values of Δ.

The binding constants, K_s, can be estimated by analogy with known values, but for very hydrophobic substrates fits are insensitive to variations in K_s. Second-order rate constants, k_2^M, are disposable parameters, but our fitting procedure requires that they do not depend significantly upon changes in concentrations of surfactants or electrolytes.

Micelles tend to grow with added electrolyte[27] and it appears that fits improve if the aggregation number, N, increases on addition of electrolyte, although we assume that N is independent of [surfactant]. For reactions of the most hydrophobic substrate, Parathion (**3**), we get better fits if N for CTABr micelles is slightly larger than when the other substrates are present. The quality of the fits is only slightly impaired by taking the values of N used in fitting data for the other substrates.

The theoretical fits to the data are shown in Figures 1–8. They are based on the rate constants given in Tables 1 and 2. The other fitting parameters are given in the Experimental Section. For reactions of the thiol and thione derivatives we obtained acceptable fits with values of k_2^M that were independent of $[OH^-]$, because micellar rate enhancements are small (Figures 4–8). As a result fits are insensitive to small variations in k_2^M.

Most simulations based on pseudo-phase models neglect changes in micellar properties due to incorporation of substrate, which may be a problem in very dilute surfactant close to the cmc.[13–18] The treatments also neglect contributions of reactions in submicellar aggregates, even though hydrophobic substrates may

Table 1. Reactions of phosphinate esters[a]

Substrate	$[OH^-]$ (M)	X	k_2^M, (l mol^{-1} s^{-1})	k_2^M/k_W
(**1a**) $Ph_2PO.OPh$	0·005	Br	0·042	0·035
(**1a**) $Ph_2PO.OPh$	0·01	Br	0·040	0·033
(**1a**) $Ph_2PO.OPh$	0·02	Br	0·043	0·036
(**1b**) $Ph_2PO.OC_6H_4NO_2$-*p*	0·01	Br	3·0	0·17
(**1b**) $Ph_2PO.OC_6H_4NO_2$-*p*	0·02	Br	3·3	0·18
(**1b**) $Ph_2PO.OC_6H_4NO_2$-*p*	0·01	Cl	3·5	0·19
(**1b**) $Ph_2PO.OC_6H_4NO_2$-*p*	0·02	Cl	3·8	0·21
(**1c**) Ph(*i*-Pr)$PO.OC_6H_4NO_2$-*p*	0·005	Br	0·21	0·70
(**1c**) Ph(*i*-Pr)$PO.OC_6H_4NO_2$-*p*	0·01	Br	0·23	0·77
(**1c**) Ph(*i*-Pr)$PO.OC_6H_4NO_2$-*p*	0·01	Cl	0·22	0·73

[a] Values of k_W are: 1·2, 18·0 and 0·30 l mol^{-1} s^{-1} for reactions of **1a**, **1b** and **1c**, respectively, at 25·0 °C; values of K_s are: 5×10^3, 10^4 and 600 l mol^{-1} for **1a**, **1b** and **1c**, respectively, in CTAX.

Table 2. Reactions of thiol and thione esters of phosphorus(V)[a]

Substrate	k_W (l mol^{-1} s^{-1})	k_2^M (l mol^{-1} s^{-1})	k_2^M/k_W
(**2a**) $Ph_2PO.SEt$	0·27	0·034	0·13
(**2b**) $Ph_2PO.SPh$	2·5	0·33[b]	0·13
(**2c**) $(EtO_2)_2PO.SPh$[c]	0·037	0·005[b]	0·14
(**3**) $(EtO)_2PS.OC_6H_4NO_2$-*p*	0·001	$1{\cdot}3 \times 10^{-4}$	0·08

[a] In CTABr at 25·0 °C with $K_s = 3 \times 10^3$, 5×10^3 and 5×10^4 l mol^{-1} for **2a**, **2b** and **3**, respectively.
[b] Also followed in CTAOMs.
[c] $K_s = 300$ and 500 l mol^{-1} in CTAOMs and CTABr, respectively.

interact with monomeric surfactant or hydrophobic ion or small clusters of them and form substrate–ion complexes that generate overall reaction.[28,29] Pseudo-phase models predict that k_ψ should go through a maximum with increasing [surfactant],[9–18] but we observed double maxima in plots of k_ψ against [surfactant] in reactions of **2a–c** and **3**. It is very easy to miss double rate maxima unless a large number of data points are taken near the rate maximum, and they are not always evident on large-scale plots.

We have not seen double maxima for reactions of **1a–c** and pNPDPP with OH$^-$ and so far as we know they have not been seen in reactions of pNPDPP with other nucleophiles. However, they are very evident in some reactions of dinitronaphthalene derivatives with nucleophiles mediated by cationic micelles.[30] They have also been seen in the spontaneous decarboxylation of 6-nitrobenzisoxazole-3-carboxylate ion in solutions of didodecyldimethylammonium ion.[31]

Double rate maxima probably arise from reaction in submicellar aggregates of substrate and surfactant and evidence for their existence will be given elsewhere. However, the possible existence of submicellar species complicates simulation of rate data in very dilute surfactant so fitting is relatively unsatisfactory in this region. The simulations are, as noted, poorest at the rate maxima because of the assumption in the pseudo-phase model that reaction is either in the aqueous or micellar pseudo-phase.

Overall rate constants depend upon the nature of the surfactant counterion, because its competition with OH$^-$ is ion-specific, but second-order rate constants, k_2^M, at the micellar surface are almost unaffected, as predicted by other pseudo-phase models.[14–18] The lower overall rate constants in CTABr as compared with CTACl or CTAOMs (Figures 2–7) are due to the high affinity of Br$^-$ for cationic micelles. Values of k_2^M are only slightly affected by changes in [OH$^-$], but for the overall reaction the order is less than first in [OH$^-$], as predicted by pseudo-phase treatments.[14–18]

Reactivities in aqueous and micellar pseudo-phases

Second-order rate constants, k_W, in water are consistently higher than those in the micellar pseudo-phase, as for reaction of OH$^-$ with pNPDPP.[9a,17] This lower reactivity in micelles seems to be typical of reactions of hydrophilic anions with esters of phosphorus (V) acids and of carboxylic acids[14,16] and is consistent with the decrease of rates of the non-micellar reactions as the polarity and water content of the solvent are decreased. Water activity at a micellar surface is lower than in bulk water,[32] as is polarity, based on spectrometric probes.[33] For reactions of carboxylic esters values of k_2^M/k_W increase with increasing electron withdrawal by substituents[21] and we see this effect in comparing values of k_2^M/k_W for reactions of phenyl and *p*-nitrophenyl diphenylphosphinate (**1a/b**) (Table 1). Micellar rate enhancements of reactions of OH$^-$ with carboxylic and phosphorus (V) esters are typically small, e.g. within a factor of ten, for two reasons. (i) Values of k_2^M/k_W are low and (ii) OH$^-$ does not compete effectively with bromide, chloride or mesylate ions at micellar surfaces.[14–18,21b] Overall micellar rate enhancements are larger for reactions of less hydrophilic nucleophilic anions that bind strongly to micelles and have larger values of k_2^M/k_W.[8a,9a,14,16]

Most values of k_2^M/k_W are in the approximate range 0·1–0·2, except, as noted, for reaction of **1a**, and for reaction of **1c** where replacement of phenyl by isopropyl at phosphorus increases k_2^M/k_W from 0·19 to 0·7. The value of $K_s = 600\ \mathrm{l\,mol^{-1}}$ used in fitting data for the micellar reaction of **1c** is much lower than values of $K_s \approx 10^4\ \mathrm{l\,mol^{-1}}$ for most of the other esters. This difference suggests that **1c** stays in a very water-rich region of the micellar surface, whereas the other more hydrophobic esters move more into the micellar surface and away from the very hydrophilic OH$^-$.

Substrate orientation may also influence values of k_2^M/k_W even for reactions of chemically similar substrates, although there is conflicting evidence on this question.[34,35] All our reactions are overall second order in water and in micelles, which is consistent with a trigonal bipyramidal intermediate in steady state, or a concerted substitution.

Regardless of mechanistic details bond breaking does not seem to be very extensive in the transition state, because although a *p*-nitro group increases the acidity of a phenol by a factor of *ca* 5×10^2, reactivities of **1a/b** differ by a factor of only 15 in water, although the rate difference is larger in cationic micelles (Table 1). Similarly, although thiophenols and thiols are much more acidic than their oxygen analogs, **2b** is only slightly more reactive than **1a** and reactivities of **2a/b** differ only by a factor of *ca* 10 despite very different acid strengths of EtSH and PhSH. These, and similar comparisons for micellar and non-micellar reactions,[1–4,8,9,17] suggest that bond making is more important than bond breaking in both water and micelles. This conclusion is consistent with the lower reactivity of a phosphate (pNPDPP) and a thionephosphate (Parathion, **3**) as compared with phosphinates (**1**) due to pd orbital overlap in phosphates and dd overlap in P=S compounds.

Relative second-order rate constants in aqueous and micellar pseudo-phases depend on electronic effects of substituents (Refs. 1–5, Tables 1 and 2), but the differences are surprisingly small. Values of k_W range from $10^{-3}\ \mathrm{l\,mol^{-1}\,s^{-1}}$ for reaction of **3** to $18\ \mathrm{l\,mol^{-1}\,s^{-1}}$ for reaction of **1b**, a difference of almost 2×10^4, but values of k_2^M/k_W range from 0·035 for reaction of **1a** to 0·7 for reaction of **1c** and if we limit our comparison to phenyl and ethoxy phosphinates and thiophosphinates the maximum value of k_2^M/k_W is 0·2

9. (a) C. A. Bunton, M. M. Mhala and J. R. Moffatt, *J. Phys. Chem.* **93**, 854 (1989). (b) C. A. Bunton, M. M. Mhala and J. R. Moffatt, *J. Phys. Chem.* **93**, 7851 (1989).
10. (a) R. A. Mackay, *Adv. Colloid Interface Sci.* **15**, 131 (1981). (b) R. A. Mackay, *J. Phys. Chem.* **86**, 4756 (1982).
11. B. A. Burnside, B. L. Knier, R. A. Mackay, H. D. Durst and F. R. Longo, *J. Phys. Chem.* **92**, 4505 (1988).
12. C. A. Bunton, F. de Buzzaccarini and F. H. Hamed, *J. Org. Chem.* **48**, 2457 (1983).
13. K. Martinek, A. K. Yatsimirski, A. V. Levashov and I. V. Berezin, in *Micellization, Solubilization and Microemulsions*, edited by K. L. Mittal, Vol. 2, p. 489. Plenum Press, New York (1977).
14. (a) L. S. Romsted, in Ref. 13, p. 509. (b) L. S. Romsted, in *Surfactants in Solution*, edited by K. L. Mittal and B. Lindman, Vol. 2, p. 1015. Plenum Press, New York (1984).
15. C. A. Bunton, *Cat. Rev. Sci. Eng.* **20**, 1 (1979).
16. C. A. Bunton and G. Savelli, *Adv. Phys. Org. Chem.* **22**, 213 (1986).
17. (a) C. A. Bunton and J. R. Moffatt, *J. Phys. Chem.* **89**, 4166 (1985). (b) C. A. Bunton and J. R. Moffatt, *J. Phys. Chem.* **90**, 538 (1986). (c) C. A. Bunton and J. R. Moffatt, *J. Phys. Chem.* **92**, 2896 (1988).
18. F. H. Quina and H. Chaimovich, *J. Phys. Chem.* **83**, 1844 (1979).
19. J. H. Fendler and W. Hinze, *J. Am. Chem. Soc.* **102**, 5439 (1981).
20. I. M. Cuccovia, F. H. Quina and H. Chaimovich, *Tetrahedron* **38**, 917 (1982).
21. (a) E. H. Cordes and C. Gitler, *Progr. Bioorg. Chem.* **2**, 1 (1973). (b) V. R. Correia, I. M. Cuccovia and H. Chaimovich, *J. Phys. Org. Chem.* **4**, 13 (1991).
22. E. Rodenas and F. Ortega, *J. Phys. Chem.* **91**, 837 (1987).
23. T. H. Lowry and K. S. Richardson, *Mechanism and Theory in Organic Chemistry*, 3rd edn, Chap. 4.4. Harper and Row, New York (1987).
24. C. A. Bunton, S. J. Farber and E. J. Fendler, *J. Org. Chem.* **33**, 29 (1968).
25. F. M. Menger and C. E. Portnoy, *J. Am. Chem. Soc.* **89**, 4698 (1967).
26. (a) M. Mille and G. Vanderkooi, *J. Colloid Interface Sci.* **59**, 211 (1977). (b) G. Gunnarsson, B. Johnsson and H. Wennerstrom, *J. Phys. Chem.* **84**, 3114 (1980).
27. (a) R. Dorshow, J. Briggs, C. A. Bunton and D. F. Nicoli, *J. Phys. Chem.* **86**, 2388 (1982). (b) T. Imae and S. Ikeda, *J. Phys. Chem.* **90**, 5216 (1986). (c) F. Quinon and L. Magid, *J. Phys. Chem.* **90**, 5435 (1986).
28. (a) Y. Okahata, R. Ando and T. Kunitake, *J. Am. Chem. Soc.* **99**, 3067 (1977). (b) T. Kunitake, Y. Okahata, R. Ando, S. Shinkai and S. Hirakawa, *J. Am. Chem. Soc.* **102**, 7877 (1980).
29. (a) C. A. Bunton, Y.-S. Hong, L. S. Romsted and C. Quan, *J. Am. Chem. Soc.* **103**, 5788 (1981). (b) G. Biresaw, C. A. Bunton, C. Quan and Z.-Y. Yang, *J. Am. Chem. Soc.* **106**, 7178 (1984).
30. C. A. Bunton and R. Bacaloglu, *J. Colloid Interface Sci.* **115**, 288 (1987).
31. R. Germani, P. P. Ponti, G. Savelli, N. Spreti, A. Cipiciani, G. Cerichelli and C. A. Bunton, *J. Chem. Soc., Perkin Trans. 2*, 1767 (1989).
32. A. D. Angeli, A. Cipiciani, R. Germani, G. Savelli, G. Cerichelli and C. A. Bunton, *J. Colloid Interface Sci.* **121**, 43 (1988).
33. (a) K. A. Zachariasse, N. V. Phuc and B. Kosankiewicz, *J. Phys. Chem.* **85**, 2672 (1981). (b) C. Ramachandran, R. A. Pyter and P. Mukerjee, *J. Phys. Chem.* **86**, 3198 (1982).
34. T. J. Broxton, J. R. Christie and R. P. T. Chung, *J. Org. Chem.* **53**, 3081 (1988).
35. G. B. van der Langkruis and J. B. F. N. Engberts, *J. Org. Chem.* **49**, 4152 (1984).
36. H. Chaimovich, R. M. V. Aleixo, I. M. Cuccovia, D. Zanette and F. H. Quina, in *Solution Behavior of Surfactants*, edited by K. L. Mittal and E. J. Fendler, Vol. 2, p. 949. Plenum Press, New York (1982).
37. C. A. Bunton, L.-H. Gan, J. R. Moffatt, L. S. Romsted and G. Savelli, *J. Phys. Chem.* **85**, 4118 (1981).
38. C. A. Bunton, L.-H. Gan, F. H. Hamed and J. R. Moffatt, *J. Phys. Chem.* **87**, 336 (1983).
39. (a) E. Rodenas and S. Vera, *J. Phys. Chem.* **89**, 513 (1985). (b) F. Ortega and E. Rodenas, *J. Phys. Chem.* **90**, 2408 (1986).
40. R. Germani, P. Ponti, G. Savelli, N. Spreti, C. A. Bunton and J. R. Moffatt, *J. Chem. Soc., Perkin Trans. 2*, 401 (1989).
41. (a) T. J. Broxton and D. B. Sango, *Aust. J. Chem.* **36**, 711 (1983). (b) T. J. Broxton, J. R. Christie and S. Wright, *J. Phys. Org. Chem.* **3**, 677 (1990).
42. (a) F. Nome, A. F. Rubira, C. Franco and L. G. Ionescu, *J. Phys. Chem.* **86**, 1881 (1982); (b) E. Stadler, D. Zanette, M. C. Rezende and F. Nome, *J. Phys. Chem.* **88**, 1892 (1984).
43. C. A. Bunton, C. P. Cowell, F. Nome and L. S. Romsted, *J. Phys. Org. Chem.* **3**, 239 (1990).
44. (a) B. Miller, *Tetrahedron* **20**, 2069 (1964); (b) R. Jentzsch, P. Schneider and G. W. Fischer, *J. Prakt. Chem.* **319**, 871 (1977).