Hydrolysis of 2,4-dinitrophenyl phosphate in normal and reverse micelles

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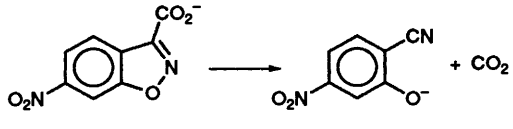
The rate of spontaneous hydrolysis of the 2,4-dinitrophenyl phosphate dianion ($DNPP^{2-}$) is strongly increased by aqueous cationic micelles of cetyltrialkylammonium bromides (alkyl = Me, Pr, Bu) and tetradecylquinuclidinium bromide. First order rate constants reach limiting values in dilute surfactant where $DNPP^{2-}$ is fully micellar bound. Rate enhancements increase with increasing bulk of the head group and are associated with decreases in activation enthalpies. Betaine sulfonate micelles ($C_{14}H_{29}N^+R_2[CH_2]_3SO_3^-$, R = Me, Et, Pr, Bu) also speed hydrolysis, but first order rate constants continue to increase even up to 0.2 mol dm^{-3} surfactant, because $DNPP^{2-}$ is not strongly bound. Reverse micelles of cetyltrialkylammonium bromide (alkyl = Me, Bu) in dichloromethane give rapid hydrolysis, but rate constants decrease on addition of water approximately to the value observed with aqueous cationic micelles as 'water pool' reverse micelles of CTABr are formed. *N,N*-Dimethylhydroxylamine increases the rate of hydrolysis in water, but not in reverse micelles, and a (hypothetical) phosphoramidate is not trapped by F^-.

Effects of aqueous colloidal self assemblies, *e.g.*, micelles, microemulsion droplets or vesicles upon rates of spontaneous reactions are consistent with the surfaces of these assemblies being less polar than water, in agreement with spectrometric estimates of surface polarity.[1] For example, spontaneous S_N reactions of alkyl halides and sulfonic esters are inhibited by a decrease in solvent polarity and water content and are slower at micellar surfaces than in water.[2] Spontaneous hydrolyses of acyl or aryl phosphate dianions are faster at micellar surfaces than in water and consistently reaction rates increase with a decrease in solvent polarity.[3,4] Solvent and micellar effects upon these phosphate ester hydrolyses are similar to those upon anionic decarboxylation, *e.g.*, of 6-nitrobenzisoxazole-3-carboxylate ion (**1**).[5,6]



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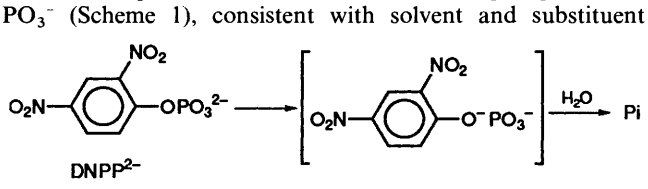
There are some significant differences between phosphate ester hydrolyses and decarboxylations, *e.g.*, hydrolysis involves at least one water molecule in the overall reaction. Hydrolysis of dianionic 2,4-dinitrophenyl phosphate ($DNPP^{2-}$) has been written as spontaneous elimination of metaphosphate ion PO_3^- (Scheme 1), consistent with solvent and substituent



Scheme 1

effects on rates of reaction. However free PO_3^- is not an intermediate, because there is complete inversion of configuration at phosphorus[7] and tertiary amines catalyse hydrolysis by generating a transient phosphoramidate.[3d,8] Therefore it appears that reaction involves nucleophilic attack on $DNPP^{2-}$, but PO_3^- has been detected in reaction in an aprotic solvent.[9]

The behaviour of an aqueous micelle as a submicroscopic reaction medium depends upon the nature of the head group. For example, in a series of trialkylammonium surfactants rates of decarboxylation of **1** at micellar surfaces increase with increasing head group bulk, probably because the surface becomes less polar.[10] Replacement of a cationic by a zwitterionic head group also speeds decarboxylation of **1**.[6] We therefore planned to examine the way in which aqueous dephosphorylation of $DNPP^{2-}$ is affected by changes in the micellar surface, *e.g.* by a change from an ammonium to a sulfobetaine head group and by changes in head group bulk.

A second part of the study involved dephosphorylation in solutions of cationic surfactants in dichloromethane. Addition of cationic surfactants to nominally dry dichloromethane increases the rate of decarboxylation of **1**, but rates decrease sharply as 'water-pool' reverse micelles form on addition of water.[11] However, even at the highest possible concentration of water decarboxylation at the (interior) surface of a reverse micelle is faster than at the (exterior) surface of an aqueous cationic micelle. We therefore examined dephosphorylation of $DNPP^{2-}$ in moist dichloromethane solutions of cationic surfactants.

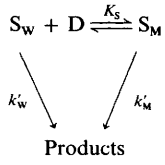
Tertiary amines catalyse hydrolysis of $DNPP^{2-}$ and transient phosphoramidates can be trapped by fluoride ion.[3b,8] The catalysis is insensitive to amine basicity and we examined the effect of *N,N*-dimethylhydroxylamine, an effective nucleophile, on the rate of dephosphorylation in water and in reverse micelles in dichloromethane.

We used hexadecyltrialkylammonium bromide (cetyltrialkylammonium bromide, $C_{16}H_{33}NR_3Br$, R = Me, CTABr; R = Pr, CTPABr; R = Bu, CTBABr) and tetradecylquinuclidinium bromide (TDQBr) because the hexadecyl derivative is sparingly soluble in water. We used tetradecylsulfobetaines ($C_{14}H_{29}N^+R_2[CH_2]_3SO_3^-$; R = Me, SB3-14; R = Et, SBEt3-14; R = Pr, SBPr3-14; R = Bu, SBBu3-14), because of the low solubilities of the hexadecyl derivatives.

Results and discussion

Reaction in normal cationic micelles

The rate effects of aqueous micelles are described by a pseudophase model (Scheme 2) where substrate, S, reacts in the aqueous or micellar pseudophase designated by subscripts W and M respectively.[1]



Scheme 2

The first order rate constant is given by eqn. (1), where k'_W

$$k'_{obs} = \frac{k'_W + k'_M K_S[D]}{1 + K_S[D]} \quad (1)$$

and k'_M are first order rate constants and K_S is the binding constant of S to micellized surfactant (detergent), D, whose concentration is taken as the total concentration less the critical micelle concentration, CMC, under kinetic conditions.[1,12] At surfactant concentrations well below the CMC the rate constant is assumed to be similar to that in water but, as micelles form, and incorporate the substrate, rates increase (or decrease) and become constant when the substrate is essentially fully micellar bound. In these conditions $k'_M \approx k_{obs}$ for spontaneous reactions.[4] For many reactions rates increase with [surfactant] below the CMC in water because reactants induce micellization or premicelles which are kinetically effective.[1] We see this situation for reaction of $DNPP^{2-}$. When the head group bulk of the surfactant is increased rate constants increase sharply on initial addition of cationic surfactant (CTABr, CTPABr, CTBABr and TDQBr) and reach constant values characteristic of complete substrate binding. The CMC values of trialkylammonium ion surfactants decrease modestly with increasing head-group bulk (Experimental section), but for reactions in aqueous CTPABr, CTBABr and TDQBr rate constants increase at [surfactant] well below the CMC in water, unlike the behaviour in CTABr.[4a] Added electrolytes decrease the CMC, but with very dilute NaOH the decrease should be small, and the rate increases with submicellar surfactants (Fig. 1) are probably due to formation of catalytically effective complexes of dianionic substrate with monomeric surfactant cation or small clusters of it. Trioctylalkylammonium salts do not form micelles but speed the hydrolysis of $DNPP^{2-}$.[4c,13]

As [surfactant] increases and micelles form they 'dissolve' premicellar assemblies and the rate–surfactant profiles are then characteristic of micellar-assisted reactions.[1] Rate constants in the micellar pseudophase increase modestly with increasing head group bulk (Table 1) which reduces polarity at the micellar surface.[10] Hydrolysis in aqueous CTABr was followed over a limited range of [surfactant] but earlier work showed that k_{obs} did not increase at higher [CTABr].[4b]

Because of complications due to possible interactions between $DNPP^{2-}$ and submicellar surfactant we base our rate comparisons on data in conditions such that $DNPP^{2-}$ is fully micellar bound and rate constants are independent of [surfactant]. These values of k'_M are in Table 1 and values over a range of [surfactant] are in Fig. 1 and as supplementary† material (Table 1S). The values at 25.0 °C agree with earlier data.[4a] The binding constants, K_S, at 25.0 °C calculated by using values of k_{obs} (Fig. 1) are in Table 2.

Variations of k_{obs} with temperature in water and in CTABr or CTBABr follow the Eyring equation and values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ obtained from values of k'_W and k'_M (Table 1) are in Table 3. The micellar rate enhancements are due largely to a decrease in the enthalpy of activation, which comes from a favourable interaction of the cationic micellar head groups and the charge delocalized transition state,[2-6] and a possible decrease in initial state hydration. Indeed, initial state hydration of the OPO^{2-} residue inhibits reaction, but in the transition state the negative charge moves to the aryloxy residue and interacts with the 'soft' cationic head group. This favourable enthalpy change is only partially offset by a decrease in the entropy of activation.

† For details of the supplementary publications scheme, see 'Instructions for Authors (1995),' *J. Chem. Soc., Perkin Trans. 2*, 1995, Issue 1 (Supp. Pub. No. 57074 (5 pp.)].

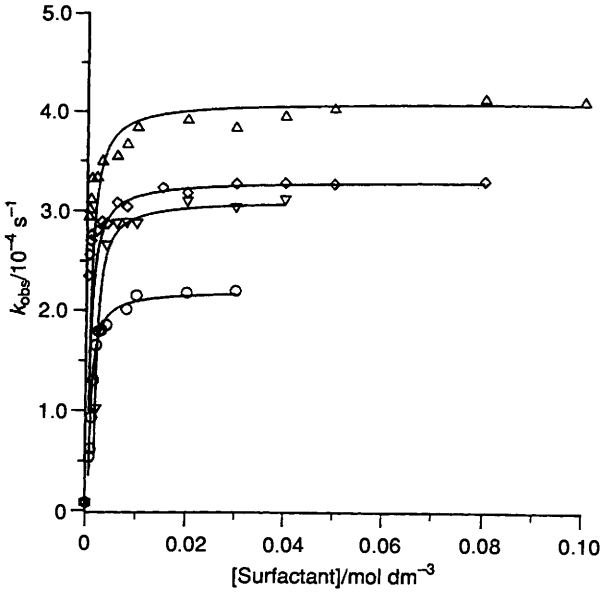


Fig. 1 Effect of head group size of cationic surfactants on reactivity in aq. 10^{-4} mol dm^{-3} NaOH. Surfactants: (○) CTABr, (◇) CTPABr, (△) CTBABr, (▽) TDQBr. Curves are predicted.

Table 1 Temperature effects on the hydrolysis of 2,4-dinitrophenyl phosphate dianion[a]

T/°C	H_2O	CTABr	CTBABr
25.0	0.086	2.20	4.11
30.0	0.163	4.94	9.85
40.0	0.827	15.8	29.4
50.0	4.17	56.5	115
60.0	16.6	175	385

[a] Values of $10^4 k'_W$ in water and $10^4 k'_M$/s^{-1} in aq. CTABr and CTBABr 10^{-4} mol dm^{-3} NaOH.

Table 2 Micellar binding and rate constants of 2,4-dinitrophenyl phosphate dianion[a]

Surfactant	K_S/dm^3 mol^{-1}	$k'_M/10^{-4}$ s^{-1}
CTABr	2×10^3	2.20
CTPABr	2×10^3	3.30
CTBABr	2×10^3	4.11
TDQBr	2×10^3	3.10
SB3–14	20	2.75
SBEt3–14	13	2.75
SBPr3–14	10	3.20
SBBu3–14	11	3.60

[a] At 25.0 °C.

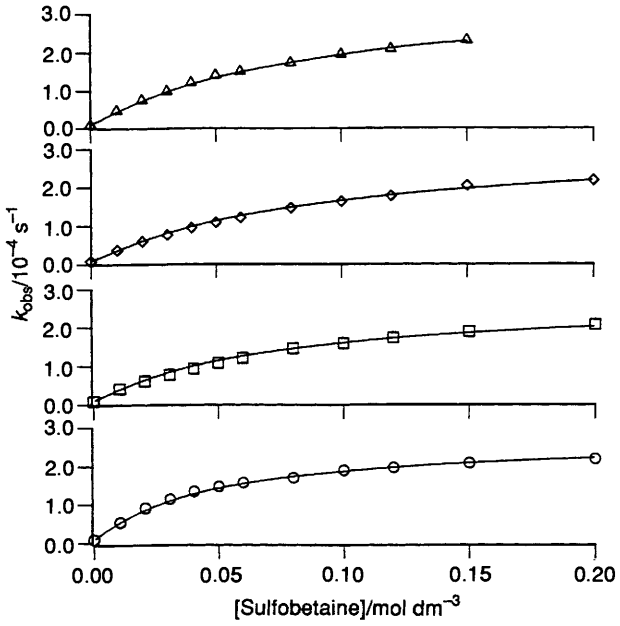


Fig. 2 Effect of head group size (indicated) of tetradecylsulfobetaines in reactivity in 0.05 mol dm^{-3} NaOH. Surfactants: (○) SB3–14, (□) SBEt3–14, (◇) SBPr3–14, (△) SBBu3–14. Curves are predicted.

Reaction in sulfobetaine micelles

Micellized sulfobetaine surfactants increase rates of spontaneous hydrolysis of $DNPP^{2-}$. Most of the rate constants were measured in 0.05 mol dm^{-3} NaOH (Fig. 2) but a few values were obtained in 0.01 mol dm^{-3}. They are not shown in Fig. 2 because they almost coincide with the other values, but are given as Supplementary material (Table 1S). First order rate constants increase with increasing [surfactant] as in cationic micelles, but the increase is much more gradual and we do not reach constant values of k_{obs}, even at high [sulfobetaine] (Fig. 2). Cationic micelles strongly bind $DNPP^{2-}$, $K_S > 10^3$ mol dm^{-3}, so that k_{obs} becomes constant, due to quantitative binding in relatively dilute surfactant. The binding is much weaker in sulfobetaine than in cationic micelles because of decreased electrostatic interactions in sulfobetaine micelles which are formally uncharged.

The dependence of k_{obs} on [sulfobetaine] is fitted by eqn. (1) but in dilute surfactant $1 \gg K_S[D]$ and eqn. (1) gives eqn. (2), so

$$k_{obs} = k'_W + k'_M K_S[D] \quad (2)$$

the fitting gives only the product $k'_M K_S$. The values of k'_M and K_S given in Table 2 are based on data with higher [surfactant] and fit the data. Values of K_S are very much lower in sulfobetaine than in cationic micelles, but those of k'_M appear to be higher in sulfobetaine than in cationic micelles and increase modestly with increasing head group bulk (Tables 1 and 2).

Decarboxylation of **1** is faster in betaine carboxylate than in cationic micelles,[10a,11] and this behaviour is understandable because unfavourable interactions between negative charges in **1** or $DNPP^{2-}$ and on the carboxylate or sulfate residues in the betaine surfactants decrease in the transition state as negative charge moves into the organic moieties. These 'charge' effects[2,14] make a modest contribution to overall rate effects at micellar surfaces. The lower polarities of micelles, relative to water, and decreased hydration, seem to be the main factors in micellar rate effects on dephosphorylation and decarboxylation.

Dephosphorylation in dichloromethane

Solutions of CTABr in dichloromethane tolerate significant amounts of water[11] and we used up to 0.8 mol dm^{-3} water with 0.06 mol dm^{-3} CTABr, although with 0.06 mol dm^{-3} CTBABr we could only use up to 0.275 mol dm^{-3} water. Dephosphorylation of $DNPP^{2-}$ is much faster in organic solvents than in water,[3b,d] and was too fast to follow in solutions of CTABr or CTBABr in nominally dry CH_2Cl_2, but addition of water sharply decreases the rate as shown for data at [surfactant] = 0.06 mol dm^{-3} (Table 4). For a fixed $[H_2O] = 0.125$ mol dm^{-3}, k_{obs} increases with increasing [CTABr] (Table 5). All these solutions contained 1.68×10^{-3} mol dm^{-3} tetrabutylammonium hydroxide, TBAOH, to deprotonate the substrate. Decarboxylation of 6-nitrobenzisoxazole-3-carboxylate ion in dichloromethane in the absence of surfactant is speeded by tetrabutylammonium bromide,[11] but addition of this salt (1.68×10^{-3} mol dm^{-3}) to solutions of 0.06 mol dm^{-3} CTABr has little effect on k_{obs} for reaction of $DNPP^{2-}$ within our experimental error of ± 5%.

Structures of the surfactant assemblies in CH_2Cl_2 depend upon $w = [H_2O]/[\text{surfactant}]$. At high w typical 'water-pool' reverse micelles form,[15] but at low w the surfactants exist as 'ion-pair' clusters solvated by water molecules. The structure of

Table 3 Activation parameters for hydrolysis of 2,4-dinitrophenyl phosphate dianion[a]

Medium	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J mol^{-1} K^{-1}
H_2O	126	7.9
CTABr	103	3.3
CTBABr	103	3.8

[a] Calc. from values of k'_M (Table 1).

Table 4 Effects of water on dephosphorylation in dichloromethane[a]

$[H_2O]$/mol dm^{-3}	CTABr	CTBABr	w
0.078	111	> 300	1.30
0.090	22.3	> 300	1.50
0.10	11.8	*ca.* 280	1.67
0.125	4.94	148	2.08
0.15	2.40	58.1	2.5
0.175	1.34	25.8	2.94
0.20	0.643	8.66	3.33
0.225		7.75	3.75
0.25	0.540	5.77	4.17
0.275	0.482	5.15	4.55
0.30	0.413		5.0
0.40	0.251		6.25
0.50	0.224		8.25
0.60	0.217		10.0
0.80	0.207		13.3

[a] Values of 10^3 k_{obs}/s^{-1} at 25.0 °C and 0.06 mol dm^{-3} surfactant with 2×10^{-5} mol dm^{-3} $DNPP^{2-}$ and 1.68×10^{-3} mol dm^{-3} Bu_4NOH.

Table 5 Dephosphorylation in dichloromethane with variation of [surfactant][a]

[Surfactant]	CTABr 0.125 H_2O	CTABr 0.25 H_2O	CTBABr 0.20 H_2O
0.04	4.83 (3.13)		
0.05	5.11 (2.5)	0.40 (5.0)	
0.06	4.94 (2.08)	0.54 (4.17)	8.66 (3.33)
0.07	7.68 (1.79)	0.54 (3.57)	9.81 (2.86)
0.08	9.04 (1.56)	0.54 (3.13)	12.3 (2.5)
0.10	11.5 (1.39)	0.85 (2.5)	21.2 (2.0)

[a] Values of 10^3 k_{obs}/s^{-1} at 25.0 °C with 2×10^{-5} $DNPP^{2-}$ and 1.68×10^{-5} mol dm^{-3} Bu_4NOH. Values of w in parentheses and concentrations in mol dm^{-3}.

Table 6 Effect of *N,N*-dimethylhydroxylamine on hydrolysis of 2,4-dinitrophenyl phosphate[a]

	$[Me_2NOH]$/mol dm^{-3}			
	0.1	0.3	0.5	0.7
$k_{obs}/10^{-5}$ s^{-1}	4.22, 3.01[b]	6.92, 7.43, 7.8[c]	10.8, 11.7, 11.9[c]	17.7, 19.5[c]

[a] At 25.0 °C with aq 0.7 mol dm^{-3} NaCl + 10^{-2} NaOH unless specified; without amine $10^5 k_{obs} \approx 1.4$ s^{-1}. [b] Free amine + 10^{-2} mol dm^{-3} NaOH. [c] [NaCl] = $[Me_2NOH]$.

these clusters, which are almost certainly polydisperse, should depend upon the surfactant concentration as well as upon w, and, as in decarboxylation,[11] 'ion-pair' clusters are better catalysts than 'water-pool' reverse micelles. This structural change with concentrations of water and CTABr is shown by changes in the ^{1}H NMR chemical shifts of H_2O which, at high w, become very similar to those of water and micellized CTABr.[11]

Rate increases by CTBABr are much larger than those by CTABr (Tables 4 and 5). It is difficult for the large Bu_3N^+ head group to be accommodated at the surface of a water microdroplet in a reverse micelle of CTBABr so that it will be largely in 'ion pair' clusters which are catalytically more effective than 'water-pools'.[11] The dianionic substrate will pair with ammonium ions and the bulky butyl groups will tend to exclude water molecules from the substrate, which will increase hydrolysis rates and values of k_{obs} at relatively high [surfactant] increase significantly with decreasing values of w (Tables 4 and 5). There is no simple relation between k_{obs}, w and [surfactant], probably because the colloidal particles are highly polydisperse and their sizes change markedly over the conditions that we examined, although in the limit of high w the 'water pool' description seems to be correct and k_{obs} falls to a limiting value with [CTABr] at high w (Table 4). We did not observe this situation with CTBABr in dichloromethane because of phase separation at high w.

For solutions of CTABr at high w, the phosphate dianion will be located at the interior interfacial region of the water microdroplet in contact with Me_3N^+ head groups. Apart from the difference in curvature, this interfacial region of a reverse micelle should be very similar to the surface of a normal cationic micelle in water, and consistently the value of k_{obs} 0.2 s^{-1} in 0.06 mol dm^{-3} CTABr in CH_2Cl_2 and $w > 10$ (Table 4) is only slightly higher than that in aqueous CTABr where the first order rate constant at the micellar surface, $10^3 k'_M = 0.18$ s^{-1} (Table 1). It appears that to a first approximation interfacial regions are similar in aqueous micelles of CTABr and its 'water pool' reverse micelles at high w.

Catalysis by tertiary amines

Spontaneous hydrolyses of $DNPP^{2-}$ and dianionic acyl phosphates in water are catalysed by tertiary amines which generate intermediate phosphoramidates. Second order rate constants of these dephosphorylations are only slightly dependent upon amine basicities.[3a,b,d,8] Tertiary amines also increase rates of dephosphorylation of $DNPP^{2-}$ in cationic micelles.[4c]

We examined catalysis by aqueous *N,N*-dimethylhydroxylamine, an α-effect nucleophile, in reverse micelles of CTACl in CH_2Cl_2 (Table 6). There might be a minor rate enhancement, because reaction is slightly inhibited by addition of an equivalent amount of LiCl which is formed from LiOH + Me_2NOH·HCl (Table 7). However, other tertiary amines have little effect on dephosphorylation in reverse micelles of CTABr in CH_2Cl_2 (Table 7). The reaction with added Me_2NOH was made in CTACl, so that Cl^- was the common anion, and without added solute, reaction was slightly faster with CTACl than with CTABr (Tables 4 and 7). The lack of amine catalysis

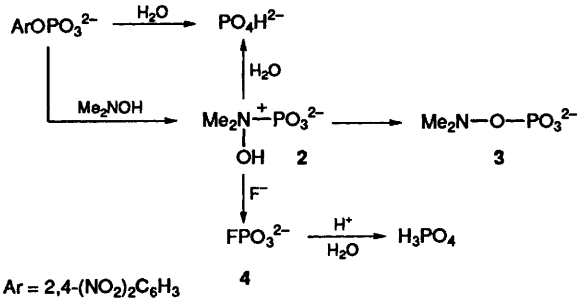
Table 7 Effects of tertiary amines on reaction in dichloromethane[a]

	10^2 [Amine]/mol dm^{-3}			
	0.17	0.34	1.68	2.50
Me_3N	2.00	2.16	2.20	
$N(HOCH_2CH_2)_3$	2.11	2.08	1.80	
Me_2NOH[b]				6.90

[a] Values of $10^4 k_{obs}$/s^{-1} at 25.0 °C with 0.06 mol dm^{-3} CTABr, 0.6 mol dm^{-3} H_2O and 1.68×10^{-3} mol dm^{-3} Bu_4NOH unless specified. Without amine $10^4 k_{obs} = 2.17$ s^{-1}. [b] With 0.06 mol dm^{-3} CTACl, 0.025 mol dm^{-3} Me_2NOH·HCl + 0.025 mol dm^{-3} and 0.3 mol dm^{-3} H_2O; without amine and with 0.025 mol dm^{-3} LiCl, $10^4 k_{obs} = 5.52$ and 4.89 s^{-1}, respectively.

in CH_2Cl_2 may simply be due to the amine residing largely in the organic solvent, for example Me_2NOH is readily soluble in diethyl ether (Experimental section). We did not examine reactions of these hydrophilic amines either in aqueous micelles, because of their high solubility in water, or in CH_2Cl_2 with no surfactant, where rates are very sensitive to small changes in solvent polarities and added electrolyte.

The hydrolysis in water is effectively catalysed by Me_2NOH (Table 6) and the rate enhancement is similar to that given by pyridine,[4c] which is slightly less basic than the hydroxylamines and is not an α-effect nucleophile. Thus, the α-effect seems to be unimportant in these amine-catalysed dephosphorylations. *N,N*-Dimethylhydroxylamine could attack the phosphoryl group of $DNPP^{2-}$ and generate phosphoramidate (**2**) which could either react with water to give inorganic phosphate, rearrange to **3**, or react with added fluoride ion to give fluorophosphate ion which is stable at high pH but is hydrolysed in acid[3a,b,d] (Scheme 3). However, reaction in the presence or



Scheme 3

absence of F^- gives only inorganic phosphate, based on colourimetric analysis and identification of inorganic phosphate by ^{31}P NMR spectroscopy (Experimental section).

These observations show that a phosphoramidate (**2**), if formed, must have a very short life, so that it is not trapped even by 0.5 mol dm^{-3} F^- and it does not rearrange. Rearrangement of **2** to **3** requires front-side attack on phosphorus, whereas intermolecular nucleophilic attack occurs with inversion of configuration,[7,8] so that rearrangement should be disfavoured. However, the inability of F^- to trap **2** was unexpected in view of results with other aqueous tertiary amines.[3b,d,8]

Table 8 Effect of *N,O*-dimethylhydroxylamine on hydrolysis of 2,4-dinitrophenyl phosphate[a]

	[MeHNOMe]/mol dm^{-3}			
	0.1	0.3	0.5	0.7
$10^5 k_{obs}$/ s^{-1}	1.12, 1.87[b]	1.45, 2.24[b]	1.48	1.63, 2.76[b]

[a] At 25 °C with 0.01 aq mol dm^{-3} NaOH. [b] Added 0.7 mol dm^{-3} NaCl.

The rate enhancement by Me_2NOH in water is qualitatively similar to those observed by Jencks, Kirby and co-workers,[3b,d,8] although experiments were at different temperatures. Jencks has postulated a compensation between effects of amine basicity on nucleophilicity and amine desolvation in order to explain the low sensitivity of reactivity to amine basicity.[8] Based on consideration of three-dimensional free energy diagrams[16] the transition state for amine catalysed dephosphorylation should involve little bond making between amine and the phosphoryl centre, consistent with insensitivity of catalysis to amine basicity. In agreement with earlier evidence on amine participation we saw only a small rate enhancement by *N,O*-dimethylhydroxylamine, which could have been due to the positive salt effect on hydrolysis (Table 8).

Experimental

Materials

2,4-Dinitrophenyl phosphate was prepared as the lutidinium salt by the method of Rawji and Milburn.[17] The mp of 155–157 °C was higher than those reported for other preparations, probably because of differences in water of crystallization (Found: C, 42.1; H, 4.0; N, 11.45. Calc. for the anhydrous form: C, 42.06; H, 3.80; N, 11.32%). The cationic surfactants were prepared and purified by standard methods.[18,19] and SBEt3–14, SBPr3–14 and SBBu3–14 were prepared from propanesultone and the tertiary amine as described for SB3–14.[18] The melting points and analyses are as follows. SBEt3–14, 187 °C [Calc. (found): C, 64.40 (64.5); H, 11.58 (11.5); N, 3.85% (3.8)]. SBPr3–14, 160 °C [Calc. (found): C, 65.82 (65.8); H, 11.77 (11.75); N, 3.34% (3.3)]. SBBu3–14, 125 °C [Calc. (found): C, 67.06 (67.0); H, 11.93 (11.9); N, 3.13% (3.1)]. There were no minima in plots of surface tension *vs.* concentration. The critical micelle concentrations, mmol dm^{-3}, are: CTABr, 0.9; CTPABr, 0.56; CTBABr, 0.24; TDQBr, 2.57; SB3–14, 0.29; SBEt3–14, 0.26; SBPr3–14, 0.20; SBBu3–14, 0.10. Dichloromethane was dried over P_2O_5 and distilled. The free amines were isolated from the hydrochlorides and extracted (Et_2O).

Kinetics

Formation of 2,4-dinitrophenoxide ion was followed spectrophotometrically at 358 nm with 2×10^{-5} mol dm^{-3} of substrate in Beckman or HP diode array spectrophotometers[4] and the pH was controlled with NaOH, LiOH or Bu_4NOH.

Trapping by fluoride ion

The general procedure was that of Kirby, Jencks and co-workers,[3a,b,d] except that the experiments were at 25.0 °C and the concentrations of inorganic phosphate were determined by Allen's method.[20]

NMR experiments

Hydrolyses of $DNPP^{2-}$ were carried out in three sets of conditions: 0.024 mol dm^{-3} $DNPP^{2-}$, with (*i*) 0.7 NaCl, 0.3 mol dm^{-3} Na_2CO_3; (*ii*) 0.7 Me_2NOH·HCl, 0.7 NaOH, 0.3 mol dm^{-3} Na_2CO_3; (*iii*) 0.7 Me_2NOH·HCl, 0.7 NaOH, 0.3 Na_2CO_3, 0.5 mol dm^{-3} NaF. The ^{31}P NMR spectra of these solutions (H_2O) were monitored on a GN 500 spectrometer during hydrolysis, with D_2O as an external lock. The only additional ^{31}P signal was that of inorganic phosphate ion formed by hydrolysis. After complete hydrolysis the solutions were diluted and the absorbance due to 2,4-dinitrophenoxide ion was measured at 358 nm, inorganic phosphate was monitored by Allen's method,[20] at 780 nm. The ratios of absorbances at 358 and 780 nm were within 1% for the three solutions. Solution (*iii*) was then heated with HCl to hydrolyse any fluorophosphate without change in the amount of inorganic phosphate.

Simulation of micellar rate effects

The rate data were fitted to eqn. (1),[4a] although it was derived for reactions for non-ionic substrates.[1,12] Simulations were insensitive to small changes in the fitting parameters, and eqn. (1) involves the implicit assumption that K_S and k'_M are unaffected by changes in [surfactant] or in the aqueous medium. Modest changes in [OH^-] did not affect values of k_{obs} and for reactions in the sulfobetaines we measured k_{obs} in *ca.* 0.1 mol dm^{-3} surfactant at 0.01 and 0.05 mol dm^{-3} OH^-.

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