Registry No.—1 (M = Na; Y = CH_3), 10486-08-5; 1 (M = H; Y = CH_3), 106-45-6; 1 (M = H; Y = Cl), 106-54-7; 1 (M = H, Y = H), 108-98-5; 1 (M = H; Y = OH), 637-89-8; 1 (M = H; Y = OCH_3), 696-63-9; 2 (X = 4-F), 319-03-9; 2 (X = 3-F), 652-39-1; 2 (X = 4-Cl), 118-45-6; 2 (X = 3-Cl), 117-21-5; 2 (X = 4-NO_2), 5466-84-2; 2 (X = 3-NO_2), 641-70-3; 2 (X = 4-Br), 86-90-8; 8, 103-19-5.

Supplementary Material Available. ^{13}C NMR assignments for the thiophenoxyphthalic anhydrides 5 (1 page). Ordering information is given on any current masthead page.

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Effect of Monoalkyl Phosphates upon Micellar-Catalyzed Dephosphorylation and Deacylation[1]

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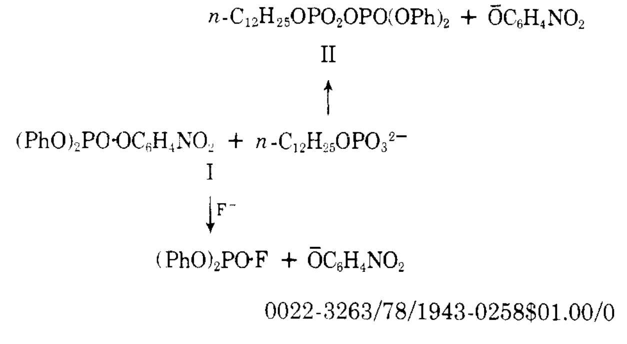
Received July 5, 1977

Disodium *n*-dodecyl phosphate (NaDodP) and to a lesser extent *n*-butyl phosphate are nucleophilic catalysts for the decomposition of *p*-nitrophenyl diphenyl phosphate (I) in cationic micelles, with up to 100-fold rate enhancement over the rate in water. Micelles of NaDodP are poor catalysts, even though they incorporate the substrate, suggesting a role for micellar charge in these reactions. Although *n*-butyl phosphate dianion weakly catalyzes deacylation of 2,4-dinitrophenyl 3-phenylpropionate, it and NaDodP inhibit the reaction in cationic micelles of cetyltrimethylammonium bromide by excluding hydroxide ion.

Micellar catalysis of bimolecular reactions involves concentration of the reagents at the micelle–water interface, in the so-called Stern layer.[3-6] Estimation of the rate constants at the interface depends on the volume element used in measuring concentration, but for a number of such reactions the second-order rate constants are apparently no larger at the interface than in water.[6,7] Functional micelles are often very effective catalysts because concentration of reagents minimizes the unfavorable entropy changes in forming a transition state from two or more reactants.[3-5,8] Many functional micelles are cationic or zwitterionic, and the role of the positive charge is not always obvious. For example, comicelles of acylhistidines and quaternary ammonium ions are excellent deacylating agents, whereas the acylhistidines alone are relatively ineffective,[9] but nonionic micelles of *n*-alkylamines and *n*-alkylimidazoles are often effective.[10]

The reaction of *p*-nitrophenyldiphenyl phosphate (I) with hydroxide ion is catalyzed by micelles of cetyltrimethylammonium bromide (CTABr).[11] At high pH this catalysis is reduced by phosphate and aryl phosphate ions, although at lower pH the nucleophilic attack by these ions becomes important.[12]

In order to obtain evidence on the role of micellar charge, we used micelles of disodium *n*-dodecyl phosphate (NaDodP) and examined its reactions with I giving initially II and its effect on dephosphorylation by fluoride ion.[11]



$$\begin{array}{c} n\text{-}C_{12}H_{25}OPO_2OPO(OPh)_2 + \bar{O}C_6H_4NO_2 \\ \text{II} \\ \uparrow \\ (PhO)_2PO\text{·}OC_6H_4NO_2 + n\text{-}C_{12}H_{25}OPO_3^{2-} \\ \text{I} \\ \downarrow F^- \\ (PhO)_2PO\text{·}F + \bar{O}C_6H_4NO_2 \end{array}$$

Although most work with nucleophilic micelles has been on deacylation, functional cationic micelles having hydroxyl or imidazole head groups are effective catalysts of dephosphorylation.[13] For purposes of comparison, we also examined the effect of NaDodP on the deacylation of 2,4-dinitrophenyl 3-phenylpropionate (III) in CTABr.

Experimental Section

Materials. *n*-Dodecyl- and *n*-butylphosphoric acid were prepared from the alcohols and $POCl_3$ by standard methods.[14] The phosphates were analyzed quantitatively for phosphorus and *n*-dodecylphosphoric acid had mp 58–60 °C (lit.[15] 58 °C). The preparation and purification of the other materials has been described.[11-15]

Kinetics. Reactions were followed spectrophotometrically at 403 and 358 nm for the *p*-nitrophenyl and 2,4-dinitrophenyl compounds, respectively, using a Gilford spectrophotometer with a water-jacketed cell compartment at 25.0 °C.[11-13] The first-order rate constants, k_ψ, are in s^{-1}. The pH of the reaction solution was measured in the presence of the surfactant, and the substrate concentrations were 1–2 $\times 10^{-5}$ M.

Critical Micelle Concentration. The critical micelle concentration (cmc) of disodium *n*-dodecyl phosphate (NaDodP) is 1.6×10^{-2} M at 22 °C in 0.02 M borate buffer, determined by surface-tension measurement. The cmc is considerably higher than that of sodium dodecyl sulfate ($NaDodSO_4$) of ca. 8×10^{-3} M,[16] because of the dianionic phosphate head group.

Products. The products of reaction of I with 2×10^{-3} M NaDodP in 4×10^{-3} M CTABr at pH 9.1 were separated by thin-layer chromatography using Eastman Kodak 6060 Si gel plates. After complete reaction, the pH was brought to 4 and the chromatogram was developed using MeOH-$CHCl_3$ (15:85, v/v). The surfactants did not move, and spots were observed at R_f 0.11 (of diphenyl phosphate) and 0.54 (of *p*-nitrophenol) plus a third spot with R_f 0.17 which we assume was that of the diphenyl *n*-dodecyl pyrophosphate (II). When reaction was done in the absence of NaDodP and it was added after complete reaction, this spot with R_f 0.17 was absent. The formation of diphenyl phosphate could have been due to reaction of OH^- with the substrate or to subsequent hydrolysis of the pyrophosphate (cf. ref 12).

We attempted to use the hydroxamic acid test in the detection of an acyl phosphate[17] as an intermediate in the reaction of *n*-dodecyl

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Table I. Reaction of *p*-Nitrophenyldiphenyl Phosphate with a Monoalkyl Phosphate Dianion[a]

	R	
10^2 [$ROPO_3^{2-}$], M	*n*-Bu	*n*-$C_{12}H_{25}$
0.18		5.25
1.35		5.64 (3.0)
1.80		5.60 (3.36)
2.70		10.90 (8.16)
4.50	5.85	
5.00	6.6	
7.50	7.1	
10.0	7.7	

[a] Values of $10^5 k_\Psi$, s^{-1} in 0.01 M borate buffer at pH 9.1 and 25.0 °C. The values in parentheses are k_M.

Table II. Inhibition of the Reaction of *p*-Nitrophenyldiphenyl Phosphate with Fluoride Ion[a]

10^2 [NaDodP], M	$10^4 k_\Psi$, s^{-1}
	9.65
0.40	7.14
0.75	6.35
1.00	5.75
1.50	5.60
2.00	4.48

[a] At 25.0 °C with 0.01 M NaF and borate buffer at pH 9.13.

phosphate dianion with III. The test was positive, but we can draw no conclusions from this observation because it was also positive with III under our experimental conditions, but in the absence of NaDodP.

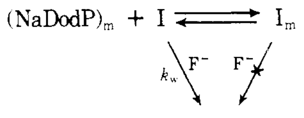
Results

Reaction of *p*-Nitrophenyldiphenyl Phosphate (I). Reaction of nucleophiles with I in the absence of cationic micelles is considered first. *n*-Butyl phosphate has a small effect upon the rate constant of decomposition of I which is ca. 5×10^{-5} s^{-1} in the absence of added reagent, showing that the alkyl phosphate dianion is a relatively ineffective nucleophile in water (Table I). (In this table, k_M is the first-order rate constant for reaction of NaDodP.) There is a linear relation between k_Ψ and the concentration of *n*-butyl phosphate, and the second-order rate constant is 4×10^{-4} M^{-1} s^{-1}, which is similar to the value for inorganic and phenyl phosphate.[12] Micelles of NaDodP (Table I) have two effects, (1) they inhibit reaction with hydroxide ion and (ii) they may speed reaction by attacking the substrate nucleophilically, and to separate these two effects we need to know how much substrate is incorporated into micelles of NaDodP.

We cannot examine incorporation directly, but the reaction with fluoride ion is inhibited by NaDodP (cf. ref. 11), which must therefore be incorporating the substrate (Table II). The reaction with fluoride ion is much faster than the other reactions, and we will neglect them.

Assuming that fluoride ion does not react with substrate in the dianionic micelles of NaDodP, we estimate the binding constant *K* in terms of micellized NaDodP[11] in Scheme I, where subscript m denotes micellized material and k_W is the rate constant in the absence of the micelle. (In earlier formulations, *K* was written as a binding constant to the micelle.) Scheme I gives eq 1.[11]

Scheme I



$$(k_W - k_\Psi) - 1 = K([\text{NaDodP}] - \text{cmc}) \qquad (1)$$

This treatment gives $K = 55$, which is very much smaller than the binding constants in CTABr or sodium lauryl sulfate.[11] It may be too low to the extent that we neglect reaction of NaDodP with the substrate, which would increase the value of k_Ψ. The kinetically estimated cmc is 4×10^{-3} M, which is much smaller than in water, showing that the hydrophobic substrate markedly reduces the cmc.[11]

We use this binding constant to separate the inhibiting and catalyzing effects of micelles of NaDodP, by assuming that micellar incorporated substrate will not react with hydroxide ion. The observed first-order rate constant is given by:

$$k_\Psi = k_W(1 - \alpha) + k_M\alpha \qquad (2)$$

where α is the fraction of substrate in the micelle and k_W and k_M are the first-order rate constants for reactions in the water and the micelle, respectively. The values of α are calculated using the binding constant of 55 and the cmc is determined from inhibition of the fluoride ion reaction, and we obtain the corrected values of the first-order rate constant, k_M, for reaction in micelles of NaDodP (Table I). These rate constants are approximate, but they show that micelles of NaDodP are not effective nucleophiles even though they incorporate the substrate. It is unfortunate that we were unable to use higher concentrations of NaDodP, but it readily forms liquid crystals under the reaction conditions.

The situation is different for reaction in the presence of CTABr or dodecyltrimethylammonium bromide (DodTABr), where there is considerable rate enhancement for attack of 0.002 M NaDodP or *n*-butyl phosphate. These phosphates have two effects: (i) as nucleophiles they attack the substrate and (ii) they inhibit the attack of hydroxide ion. This second effect is less important than the first, but our estimates of the rate enhancements by the alkyl phosphate dianions are low because of neglect of this inhibition.

The rate enhancements on addition of 0.002 M NaDodP are by factors of approximately 40 for DodTABr and 9 for CTABr, at pH 8.5, as compared with the maximum rate constants in the cationic micelles. These rate enhancements are similar to but larger than those obtained on addition of aryl phosphate dianions to CTABr.[12] For reactions with NaDodP the rate maxima are observed when the concentration of cationic surfactant is approximately twice that of NaDodP, i.e., when the charge of the ammonium ion approximately neutralizes that of the alkyl phosphate dianion. Earlier work shows that a hydrophobic substrate such as I should be almost completely micellar bound in 2–3 × 10^{-3} M CTABr,[11] so that under these conditions both the substrate and the alkyl phosphate should be in the micellar pseudophase.

For lower concentrations of cationic surfactant the micelle will have a net negative charge, and the results in Table I suggest that the rate constant should decrease as the micelle becomes anionic, but at concentrations of cationic surfactant greater than 4×10^{-3} M addition of further surfactant merely decreases the concentration of NaDodP in the micelle, so that the rate constant decreases (cf. ref 6 and 7).

This explanation presupposes that the hydrophobic *p*-nitrophenyldiphenyl phosphate is almost completely micellar bound at ca. 2×10^{-3} M cationic surfactant, but if NaDodP decreases the substrate binding this effect would contribute to the decrease of k_Ψ as the concentration of cationic surfactant (CD) is reduced below the optimum (Figure 1).

The binding constant of I to micellized CTABr is not known, but binding constants of greater than 10^4 have been estimated toward sodium lauryl sulfate,[11] so that it is probable that the bulk of the substrate is micellar bound under our reaction conditions.

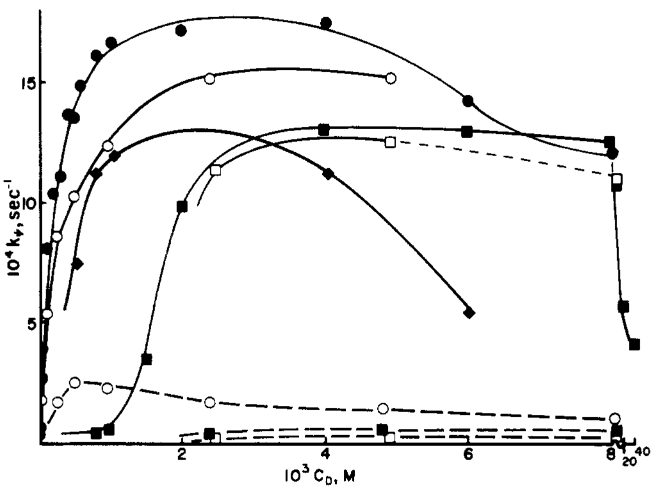


Figure 1. Micellar effects on the dephosphorylation of *p*-nitrophenyldiphenyl phosphate (I). The solid points are at pH 9.1 and the open points are at pH 8.5. The dashed lines denote reactions in the absence of alkyl phosphate. (●, ○) CTABr; (■, □) DDTABr; (◆) CTABr + 2 × 10^{-3} M *n*-BuOPO$_3$Na$_2$.

Table III. Reaction of 2,4-Dinitrophenyl 3-Phenylpropionate in Alkyl Phosphate Dianion[a]

10^2 [ROPO$_3^{2-}$], M	R: *n*-Bu	R: *n*-C$_{12}$H$_{25}$
0.5		1.26
0.8		1.28
0.9		1.30
1.8	4.21	
3.7		1.06
4.5	4.91	
10.0	5.71	

[a] Values of $10^3 k_\psi$, s^{-1} at 25.0 °C in 0.01 M borate buffer, pH 9.13; in the absence of added alkyl phosphate, $k_\psi = 1.7 \times 10^{-3}$ s^{-1}.

n-Butyl phosphate dianion is also an effective reagent when incorporated into micelles of CTABr, and its behavior is very similar to that of aryl phosphate dianions. It is not as effective a reagent as NaDodP, and the maximum rate is obtained with a lower concentration of CTABr than that required for NaDodP, which is understandable if the rate maximum is reached with an electrically neutral micelle, because *n*-butyl phosphate should bind less strongly than NaDodP.

Deacylation of 2,4-Dinitrophenyl 3-Phenylpropionate. The deacylation of 2,4-dinitrophenyl 3-phenylpropionate (III) is speeded up by added *n*-butyl phosphate (Table III), but the effect is small, as expected from the relatively low nucleophilicity of inorganic phosphate in deacylation.[18] However, added NaDodP slightly inhibits the reaction (Table III), suggesting that the substrate is being taken up into the anionic micelles which block attack by hydroxide ion, and this inhibition overcomes any catalysis by nucleophilic attack of the phosphate dianion.

Cationic micelles of CTABr effectively catalyze the deacylation (Table IV), and the 50-fold rate enhancement is similar to those found using *p*-nitrophenyl esters of hydrophobic alkane carboxylic acids,[3-5] and there is a rate maximum at 10^{-3} M CTABr which can be interpreted in terms of a distribution of reagents between water and micelle. This catalysis is reduced by both *n*-butyl and *n*-dodecyl phosphate dianion, with the latter being much more effective. Thus, in deacylation the phosphate dianions are such poor nucleophiles, relative to the hydroxide ion, that any nucleophilic contribution by them is more than offset by their inhibition of the reaction of hydroxide ion. In 10^{-2} M CTABr the value of k_ψ decreases sharply on the addition of a small amount of NaDodP and then remains approximately constant, suggesting that reaction with hydroxide ion has been largely suppressed and that we are following deacylation by the dodecyl phosphate dianion. If this hypothesis is correct, the nucleophilicity of NaDodP is enhanced by micellization (cf. Tables III and IV). However, in these buffered systems the micelles may introduce complications due to changes in buffer equilibria.

Other examples of inhibition of deacylation by micelles of weakly nucleophilic anions are reactions of *p*-nitrophenyl esters in the presence of *n*-alkyl carboxylate and bile salt micelles.[19] (Carboxylate ions are poorer nucleophiles than phosphates in deacylation.[18])

Discussion

Micellar Charge and Catalysis. Although phosphate dianions are effective nucleophiles toward phosphoryl groups, micelles and NaDodP are not particularly effective dephosphorylating agents. For example, under conditions in which I is over 50% micellar incorporated the first-order rate constant for dephosphorylation in the micelle is only 8 × 10^{-5} s^{-1} (Table I), but in comicelles of CTABr and NaDodP we observe an approximately 100-fold rate enhancement at pH 9.1 over the rate in water, and the rate constant is ca. 170 × 10^{-5} s^{-1} (Figure 1). This difference seems too large to be explained in terms of substrate incorporation in the micelles, suggesting that it is due in part to transition-state interactions.

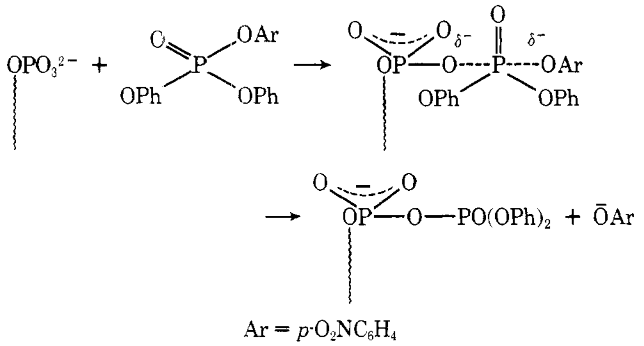
The transition state for dephosphorylation of *p*-nitrophenyldiphenyl phosphate is anionic, and because of its dispersed charge there should be strong coulombic attractions with the quaternary ammonium head groups in a cationic micelle, but the interactions will be unfavorable for reaction carried out in an anionic micelle of NaDodP (Scheme II).

Table IV. Reaction of 2,4-Dinitrophenyl 3-Phenylpropionate in CTABr and Monoalkyl Phosphate Dianion[a]

10^3 [CTACBr], M		10^3 [ROPO$_3^{2-}$], M: 5.0[b]	2.5[c]	5.0[c]	7.5[c]	10.0[c]
0.5	60.5	28.1				
0.75		39.7				
1.0	89.5	48.3		5.90		
1.5	82.7					
3.0				7.36		
5.0	53.7	33.4		9.64		
6.67				11.5		
10.0	43.2		11.9	12.0	11.3	11.2
15.0	43.1					
30.0				13.7		

[a] Values of $10^3 k_\psi$, s^{-1}, in 0.01 M borate buffer, pH 9.1; in the absence of CTABr, $k_\psi = 1.7 \times 10^{-3}$ s^{-1}. [b] *n*-BuOPO$_3^{2-}$. [c] *n*-C$_{12}$H$_{25}$OPO$_3^{2-}$.

Scheme II



The situation is different for deacylation in a micellized amine.[10] Reactions with nonmicellized amines are general base catalyzed, and both water- and amine-catalyzed reactions have been identified in reactions of micellized *n*-alkylamines with carboxylic esters, suggesting that a proton is transferred from nitrogen in the transition state and a micellized alkylamine could function very effectively as the base.

These observations suggest that micellar catalysis of bimolceular reactions depends on the bringing together of the reactants at the micellar surface prior to reaction, but that unfavorable coulombic interactions between the head groups and the transition state can prevent reaction, even though the reactants are taken up by the micelle. This conclusion should apply to reactions in both chemically inert and functional micelles, and it is consistent with the treatment of micelles as if they behave as a separate phase with their own solvent properties. We also note that micellar effects upon unimolecular reactions are wholly due to free-energy differences between initial and transition states.[20]

Registry No.—I, 10359-36-1; *n*-BuOPO$_3$Na$_2$, 64114-42-7; NaDodP, 7423-32-7; NaF, 7681-49-4; 2,4-dinitrophenyl-3-phenylpropionate, 23522-80-7; CTABr, 57-09-0; DodTABr, 1119-94-4.

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Photoinduced Decomposition of Peracetic Acid in Toluene

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Received February 28, 1977

A mixture of peracetic acid and toluene has been photolyzed at room temperature. The main products with 2537-Å light were carbon dioxide, methane, ethane, methanol, ethylbenzene, *o*-, *m*-, and *p*-xylenes, and bibenzyl together with smaller amounts of benzyl alcohol and *o*-, *m*-, and *p*-cresols. On the other hand, with light over 2900 Å, different yields of benzyl alcohol (a main product) and cresols (undetectably small) were observed. The effects of concentration of peracid on yields were studied, and the mechanism and reactivities of methyl and hydroxyl radicals were discussed.

The photolysis of a mixture of peracetic acid and toluene is of particular interest because of the possibility of reaction both with aliphatic and aromatic parts of the toluene molecule. The vapor-phase pyrolysis of peracetic acid in a stream of toluene was reported to involve both radical and wall reactions,[1b] while the thermolysis in liquid phase involves the two simultaneous reactions.[2] The photolysis of peracetic acid in cyclohexane gives cyclohexanol.[3]

As to the reaction of methyl radical with toluene both in the liquid and gas phases, evidences were presented for both addition to the ring and abstraction of hydrogen atom to form methane.[4–7] But there is little information on the yields of the other products besides gaseous products. The reaction of a hydroxyl radical with toluene gives cresols and bibenzyl.[8]

The present paper reports on the photolysis of peracetic acid in toluene. The mechanism of decomposition and the behavior of the produced radicals, i.e., $CH_3\cdot$ and $HO\cdot$ were discussed on the basis of the products analysis.

Results

The photolysis products from peracetic acid in toluene were carbon dioxide, methane, ethane, methanol, methyl acetate, ethylbenzene, xylenes, benzyl alochol, benzaldehyde, cresols, bibenzyl, and a trace of benzoic acid with quartz filter (2537-Å light). An almost similar distribution of products was also obtained with Pyrex-filtered light (>2900 Å), except for a marked decrease in the yield of cresols and an increase of the yield of benzyl alcohol.

0022-3263/78/1943-0261$01.00/0