C, 79.65; H, 7.86. Found: C, 79.52; H, 8.21; mol wt, 256 (mass spectrometry).

A mixture of XVa and XVb was prepared in a similar way from the mixture of dienes XVIa and XVIb.

Mixture of 4b-d_1- and 8,8-d_2-1,4,4a,4b,5,6,7,8,9,10,11,12,12a,12b-Tetradecahydrotriphenylene-1,4-dione (XI and XII). The mixture of dienes IX and X (300 mg) and freshly sublimed *p*-benzoquinone (200 mg) was allowed to stand at room temperature for 2 days. Trituration with methanol (2 ml) and recrystallization yielded the mixture of adducts XI and XII (200 mg), mp 110–112° (from methanol). The composition of the mixture was determined by mass spectrometry (see Discussion).

Micellar Effects upon Phosphorylation and Phosphate Ester Hydrolysis[1]

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Abstract: The reactions between hydroxide or fluoride ion and *p*-nitrophenyl diphenyl phosphate, catalyzed by micelles of cetyltrimethylammonium bromide, are inhibited by phenyl, diphenyl, and *p*-*t*-butylphenyl phosphate. With decreasing pH the reaction with hydroxide ion becomes unimportant, and micellar-catalyzed reactions between the substrate and inorganic phosphate ions and phenyl and *p*-*t*-butylphenyl phosphate dianions can be observed. Diphenyl phosphate monoanion is unreactive. For the micellar catalyzed reaction the reactivity sequence is $t\text{-BuC}_6\text{H}_4\text{OPO}_3{}^{2-} > \text{C}_6\text{H}_5\text{OPO}_3{}^{2-} > \text{HOP}_4{}^{2-}$ and depends upon the nonbonding interactions between the cationic micelle and the nucleophilic anion, rather than their inherent nucleophilicities. The second-order rate constants for the micellar-catalyzed reaction with hydroxide ion agree well with those calculated at low pH in borate buffer.

Cationic micelles are effective catalysts of reactions between uncharged substrates and nucleophilic anions, and the kinetic dependence upon detergent concentration can be explained in terms of reactions occurring in both the aqueous and micellar phases.[3–7] Both fluoride and hydroxide ions attack triaryl phosphates[8] and their reactions with *p*-nitrophenyl diphenyl phosphate are catalyzed by the cationic detergent cetyltrimethylammonium bromide (CTA), but retarded by the anionic detergent sodium lauryl sulfate (NaLS) and the uncharged polyether Igepal.[7] The catalysis by the cationic micelles is inhibited by added anions. We had earlier found that the catalyzed hydrolyses of the dianions of 2,4- and 2,6-dinitrophenyl phosphates were strongly inhibited by bulky anions, such as those of aryl phosphates,[9] and the present work had the twofold purpose of studying the inhibition of the micellar catalyzed reaction of hydroxide or fluoride ion with *p*-nitrophenyl diphenyl phosphate by aryl phosphate dianions and attempting to establish a micellar-catalyzed phosphorylation of an aryl phosphate dianion by *p*-nitrophenyl diphenyl phosphate (I). This system is very satisfactory for this purpose, because it is easy to make structural modifications of the aryl phosphate dianion, without affecting its nucleophilicity so far as reaction in water is concerned, by introducing bulky alkyl groups into the aryl group to increase the binding between the nucleophile and the micelle.

As well as examining the micellar-catalyzed reaction between *p*-nitrophenyl diphenyl phosphate and hydroxide ion of known concentration we also measured the reaction rate in buffers, so that we could compare the second-order rate constant calculated directly with that calculated from the hydroxide ion concentration estimated from the pH of the solution.

A number of workers have drawn analogies between micellar- and enzyme-catalyzed reactions.[3–7,9,10] The main similarities appear to be in the hydrophobic interactions between the substrate and catalyst; as in enzymic reactions chemically similar substrates can act either as a catalyst or an inhibitor, and the importance of phosphorylation in biological systems makes it useful to examine micellar-catalyzed phosphorylation. A few experiments were also carried out on the effects of detergents on the reactions between pyridine and *p*-nitrophenyl diphenyl or 2,4-dinitrophenyl phosphate,[11] but the rate enhancements were small and these reactions were not studied extensively.

Experimental Section

Materials. The preparation and purification of most of the reagents have been described.[6,7,9] Pyridine was redistilled before use.

Kinetics. The reactions were followed spectrophotometrically using a Gilford spectrophotometer with a water-jacketed cell compartment. Nucleophilic attack gives *p*-nitrophenoxide ion which can be detected spectrophotometrically.

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[1] Support of this work by the National Institute of Arthritis and Metabolic Diseases, U. S. Public Health Service, is gratefully acknowledged.

[2] University of Chile–University of California Cooperative Program Fellow, on leave from the Faculty of Chemistry and Pharmacy, University of Chile, Santiago.

[3] F. M. Menger and C. E. Portnoy, *J. Amer. Chem. Soc.*, **89**, 4698 (1967).

[4] L. R. Romsted and E. H. Cordes, *ibid.*, **90**, 4404 (1968).

[5] (a) T. C. Bruice, J. Katzhendler, and L. R. Fedor, *ibid.*, **90**, 1333 (1968); (b) C. Gitler and A. Ochoa-Solano, *ibid.*, **90**, 5004 (1968).

[6] C. A. Bunton and L. Robinson, *ibid.*, **90**, 5972 (1968).

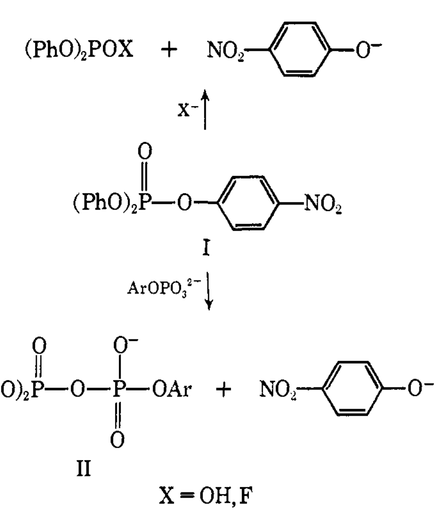
[7] (a) C. A. Bunton and L. Robinson, *J. Org. Chem.*, **34**, 773 (1969); (b) C. A. Bunton and L. Robinson, *ibid.*, **34**, 780 (1969).

[8] J. R. Cox and O. B. Ramsay, *Chem. Rev.*, **64**, 343 (1964).

[9] C. A. Bunton, E. J. Fendler, L. Sepulveda, and K-U. Yang, *J. Amer. Chem. Soc.*, **90**, 5512 (1968).

[10] D. G. Herries, W. Bishop, and F. M. Richards, *J. Phys. Chem.*, **68**, 1842 (1964).

[11] A. J. Kirby and A. G. Varvoglis, *J. Chem. Soc., B*, 135 (1968).



The only products of the reaction of I with phenyl phosphate dianion which we could detect were *p*-nitrophenol (spectrophotometrically) and diphenyl phosphate, which was detected by paper chromatography. The reaction solution contained 3×10^{-3} *M* CTA, 2×10^{-2} *M* phenyl phosphate, and 1.5×10^{-3} *M* *p*-nitrophenyl diphenyl phosphate at pH 7.5 in 0.015 *M* borate buffer. After complete reaction, the acidified solution was extracted several times with ether and chromatographed on Whatman No. 4 paper using 1-butanol-acetic acid-water (3:1:1) as developing solvent. *p*-Nitrophenol was identified directly and the phosphate esters were detected by spraying with acid molybdate and heating the chromatogram. The spots were *p*-nitrophenol (R_f = 0.97), diphenyl phosphate (R_f = 0.88), and phenyl phosphate (R_f = 0.17). In a larger scale experiment diphenyl phosphate was isolated. These observations suggest that the pyrophosphate (II) readily decomposed in the presence of a cationic detergent.

For kinetic runs the substrate concentration was *ca.* 10^{-5} *M* and in much lower concentration than the nucleophile so that the runs had a first-order kinetic form. (The units of the first-order rate constants, k_ψ, are sec^{-1}.) The pH specified for each run is that measured in the kinetic solution, with detergent, but without substrate, using a glass electrode.

The reaction with fluoride ion was followed with sodium fluoride in 0.015 *M* borate buffer, pH 9.0. The formation of nitrophenoxide ion in the reactions between pyridine and *p*-nitrophenyl diphenyl or 2,4-dinitrophenyl phosphate was also followed spectrophotometrically.

Spectral Measurements. The ultraviolet spectra of disodium phenyl and *p*-*t*-butylphenyl phosphates were examined in water and 0.01 and 0.02 *M* CTA, with 0.01 and 0.02 *M* phosphate using 1-mm cells. The detergent does not absorb in this region and Beer's law is obeyed by the phosphates.

Results

Most of the experiments were carried out using the cationic detergent cetyltrimethylammonium bromide (CTA), but a few experiments were done with the anionic detergent sodium lauryl sulfate (NaLS) or the uncharged detergent Igepal, which is a dinonylphenol condensed with 24 ethylene oxide units, and which we designate as DNPE. Both the anionic and uncharged detergents inhibit reaction of hydroxide and fluoride ions.[7]

Table I. Inhibition of Reactions of *p*-Nitrophenyl Phosphate in CTA[a]

C_{In}, *M*	NaOH	NaF
	542[b]	282
	551	351[e]
0.0025[c]	210[b]	
0.0025[d]	112[b]	
0.0025[d]	128	
0.005[c]	173[b]	
0.005[c]	153	117[e]
0.005[d]	79[b]	
0.005[d]	81	
0.020[c]	86[b]	
0.020[c]	76	68[e]

[a] Values of 10^4k_ψ, sec^{-1}, at 25.0°, with 0.01 *M* reagent and 0.0035 *M* CTA unless specified. [b] 0.003 *M* CTA. [c] $PhOPO_3Na_2$. [d] *p*-*t*-$BuC_6H_4OPO_3Na_2$. [e] 0.002 *M* CTA.

Table II. Inhibition by Anionic and Uncharged Detergents of the Hydrolysis of *p*-Nitrophenyl Diphenyl Phosphate[a]

Detergent C_D, *M*	NaLS	DNPE
0.001	5.68	
0.001	4.92[b]	
0.002	4.66	
0.002	2.19[b]	
0.003	1.07	0.51
0.003	0.48[b]	0.45[b]
0.004	0.35	0.46
0.004	0.26[b]	0.43[b]
0.006	0.16	0.41
0.006	0.14[b]	
0.008	0.09	
0.008	0.08[b]	

[a] Values of 10^5k_ψ at 25.0°; pH 9.0, 0.015 *M* borate buffer; in the absence of detergent $k_\psi = 5.7 \times 10^{-5}$ sec^{-1}. [b] With added 0.01 *M* $C_6H_5OPO_3Na_2$.

Phenyl and *t*-butylphenyl phosphate inhibit the attack of hydroxide or fluoride ions upon *p*-nitrophenyl diphenyl phosphate catalyzed by 0.003 and 0.0035 *M* CTA (Table I), and as expected the *t*-butyl group increases the effectiveness of the inhibitor. The inhibition is only slightly affected by small changes in the detergent concentration. A few experiments with NaLS and DNPE showed that these detergents inhibit the hydrolysis of the substrate at pH 9 (Table II), as had been found in more alkaline solutions.[7] Addition of disodium phenyl phosphate further inhibits the reaction at low detergent concentrations, probably by affecting the critical micelle concentration.

The inhibiting effect of inorganic phosphate and phenyl and *p*-*t*-butylphenyl phosphate ions (Table I and ref 7) upon the formation of *p*-nitrophenoxide ion disappears at low pH where these reagents actually assist instead of retarding the over-all hydrolysis (Figures 1–5). The results for inorganic phosphate are complicated by its ionization, because a change of pH from 7.5 to 10 generates some phosphate trianion which should be a better nucleophile than the dianion HPO_4^{2-}. (For phosphoric acid pK_2 = 6.82 and pK_3 ≈ 12.5.)[12] This complication is absent with the aryl phosphates, which exist wholly as dianions at the pH used in these experiments. (For phenyl phosphate pK_2 = 5.88,[13] and the value for *p*-*t*-butylphenyl phosphate should be similar.)

At pH 10 phenyl phosphate has almost no effect upon reaction rate in the presence of CTA, but with decreasing pH its rate-enhancing ability increases (although the over-all first-order rate constant, k_ψ, falls, because of the decreasing hydroxide ion concentration of the solution). This rate enhancement at low pH is even greater with the dianion of *p*-*t*-butylphenyl phosphate; *e.g.*, at pH 7.5 and 3×10^{-3} *M* CTA, 2×10^{-3} *M* *p*-*t*-butylphenyl phosphate increases the rate 15-fold, as opposed to 8-fold for 2×10^{-3} *M* phenyl phosphate and *ca.* 2-fold

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(12) W. D. Kumler and J. J. Eiler, *J. Amer. Chem. Soc.*, 65, 2355 (1943).

(13) J. D. Chanley and E. Feageson, *ibid.*, 77, 4002 (1955).

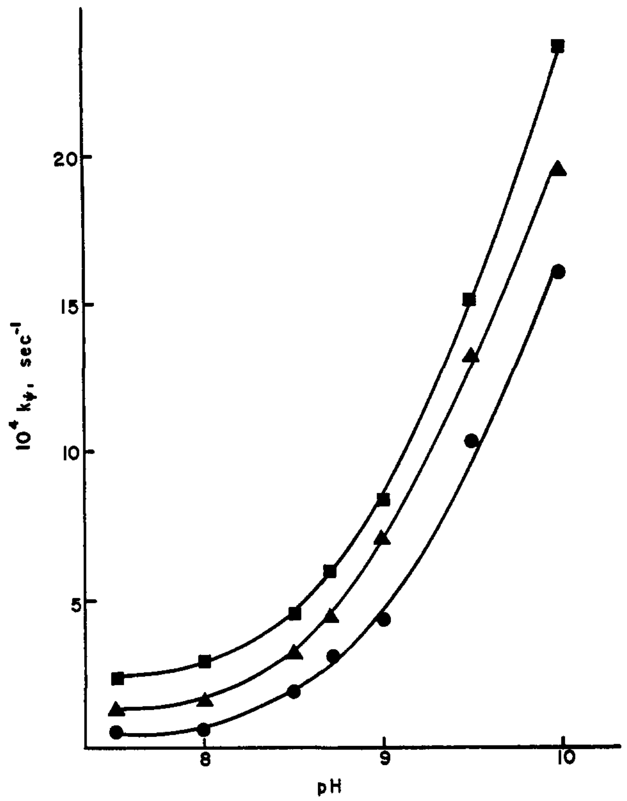

Figure 1. Effect of inorganic phosphate on the CTA-catalyzed reaction of *p*-nitrophenyl diphenyl phosphate in water at 25.0° with 3×10^{-3} *M* CTA and 0.015 *M* borate buffer: ●, no reagent; ▲, 0.003 *M* sodium phosphate; ■, 0.010 *M* sodium phosphate.

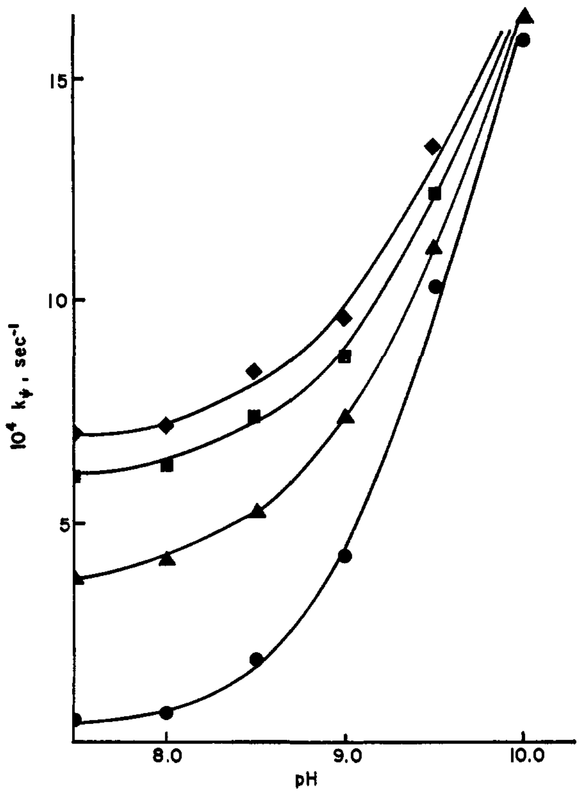

Figure 2. Effect of phenyl phosphate in the CTA-catalyzed reaction of *p*-nitrophenyl diphenyl phosphate in water at 25.0°, with 3×10^{-3} *M* CTA and 0.015 *M* borate buffer: ●, no reagent; ▲, 0.003 *M* phenyl phosphate; ■, 0.010 *M* phenyl phosphate; ◆, 0.020 *M* phenyl phosphate.

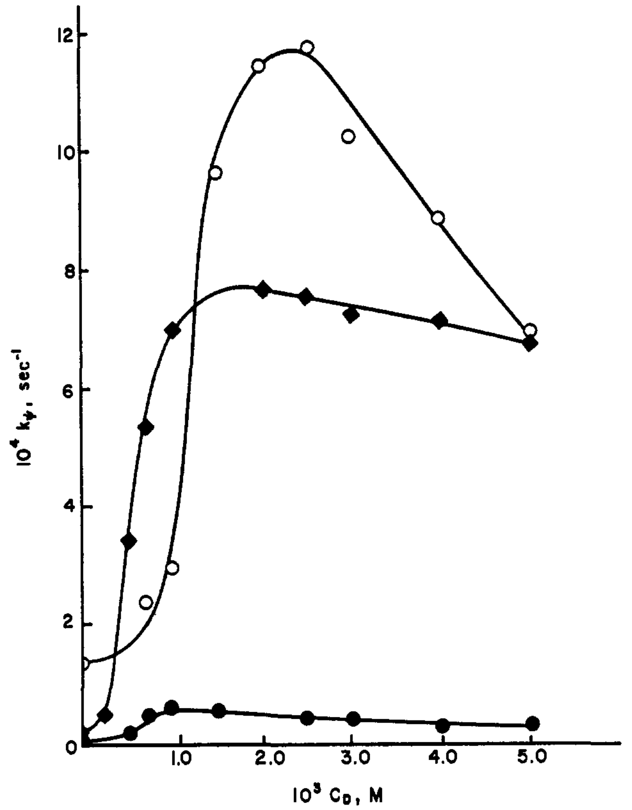

Figure 3. Effect of detergent concentration and pH on the CTA-catalyzed reaction of *p*-nitrophenyldiphenyl phosphate at 25.0° with 0.015 *M* borate buffer: ●, pH 7.5; ◆, pH 7.5 with 0.02 *M* phenyl phosphate; ○, pH 9.5.

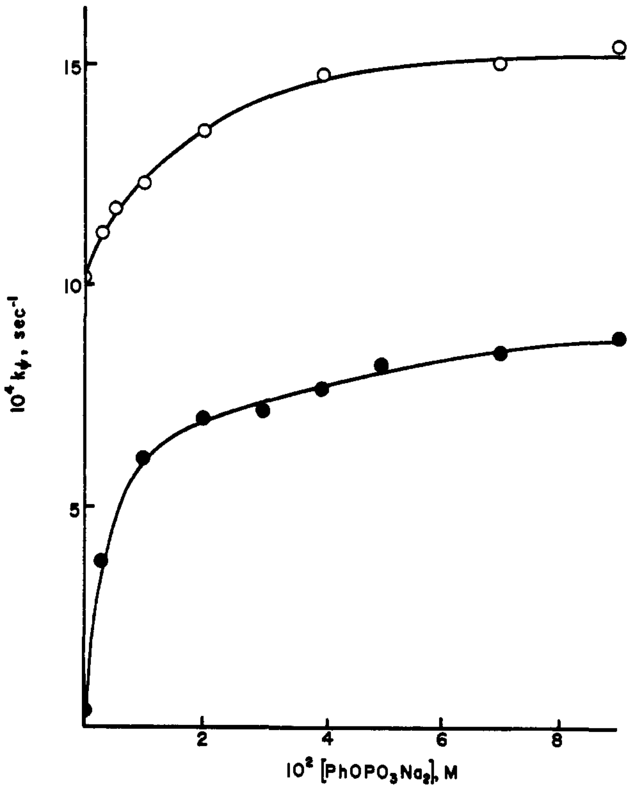

Figure 4. Effect of phenyl phosphate on the reaction of *p*-nitrophenyldiphenyl phosphate in 3×10^{-3} *M* CTA and 0.015 *M* borate buffer at 25.0°: ●, pH 7.5; ○, pH 9.5.

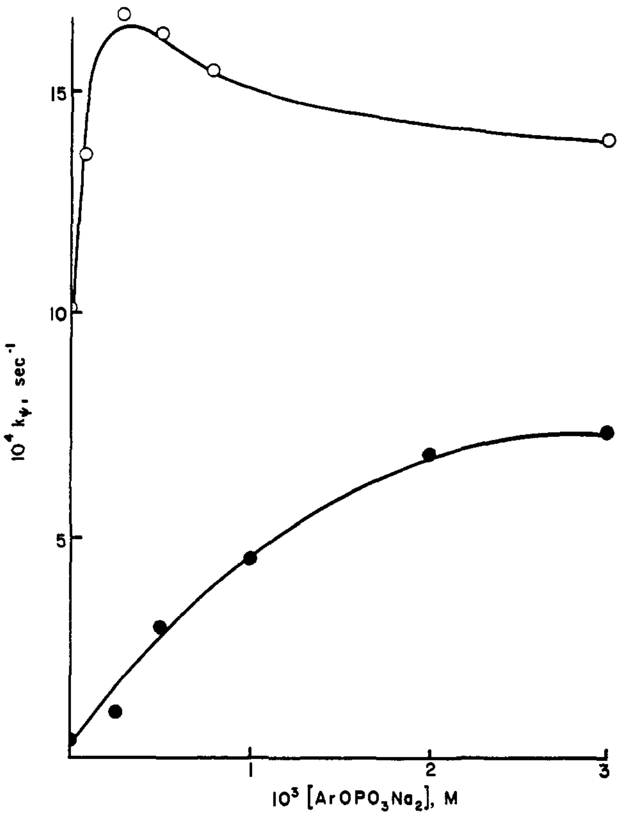

Figure 5. Effect of *t*-butylphenyl phosphate on the reaction of *p*-nitrophenyldiphenyl phosphate in 3 × 10^{-3} *M* CTA and 0.015 *M* borate buffer at 25.0°: ●, pH 7.5; ○, pH 9.5.

for 3 × 10^{-3} *M* inorganic phosphate dianion. However the monoanion of diphenyl phosphate is an effective inhibitor of the CTA-catalyzed hydrolysis at pH 9.5 (Table III).

Table III. Inhibition by Diphenyl Phosphate of the Hydrolysis of *p*-Nitrophenyl Diphenyl Phosphate[a]

[Ph_2PO_4Na], *M*	0.0	0.003	0.10
10^4k_ψ, sec^{-1}	10.2	1.70	0.48

[a] At 25.0° with 3 × 10^{-2} CTA in 0.015 borate buffer pH 9.5.

The variations of k_ψ with CTA concentration (Figure 3) show the typical rate maxima which are found for reactions between anionic nucleophiles and uncharged substrates in the presence of cationic micelles.[3-7] The rates reach maxima at 1–2 × 10^{-3} *M* CTA for reaction with hydroxide ion at pH 7.5 and 9.5 and reaction with phenyl phosphate at pH 7.5, although for this reaction the rate maximum is not very well marked. In these systems we are seeing attack by both hydroxide and aryl phosphate ion, and inhibition of the hydroxide ion reaction, and therefore there is no simple relation between k_ψ and detergent concentration. Either deactivation of the nucleophile[6] or inhibition by the counterion of the cationic detergent[4] could be responsible for these rate maxima.

At a constant detergent concentration k_ψ increases smoothly with increasing concentration of phenyl phosphate (Figure 4). At pH 7.50, the hydroxide ion reaction is relatively unimportant, and there is a steep increase of k_ψ which is followed by a levelling off as the micelles become saturated with the nucleophilic phenyl phosphate dianion. At pH 9.50 the rate increase is much smaller because the rate enhancement by phenyl phosphate acting as a nucleophile opposes its inhibition of the hydroxide ion reaction, which has become important at this pH.

The situation is more complex with *p*-*t*-butylphenyl phosphate dianion (Figure 5). At pH 7.50 the rate increases smoothly, and much more steeply than with phenyl phosphate (Figure 4). At pH 9.50 there is an initial sharp rate enhancement, which is followed by an inhibition of the hydroxide ion reaction, leading to a rate maximum at *ca.* 3 × 10^{-4} *M* *p*-*t*-butylphenyl phosphate (Figure 5).

The experiments on the reaction of pyridine with *p*-nitrophenyl diphenyl phosphate (Table IV) show that in the absence of detergent the rate enhancement by added amine is relatively small, in contrast to the high reactivity of the anionic nucleophiles. These observations confirm other observations of the relative unreactivity of amines toward phosphate esters.[8] This low reactivity of nitrogen as compared with oxygen nucleophiles or fluoride ions toward a phosphoryl compound accords with Pearson's classification of them as "hard" acids,[14] and is responsible for a basic aliphatic amine attacking the aryl rather than the phosphoryl group of *p*-nitrophenyl phosphate.[15]

Table IV. Micellar Effects upon the Reaction of *p*-Nitrophenyl Diphenyl Phosphate with Pyridine[a]

$C_{pyridine}$, *M*	10^4k_ψ, sec^{-1}
	0.57[b]
0.15	0.98[b]
0.30	1.43[b]
0.05	4.78
0.10	3.68
0.15	3.43
0.30	0.73[c]

[a] At 25.0° in 0.015 *M* borate buffer at pH 9 with 0.003 *M* CTA unless specified. [b] In the absence of detergent. [c] 0.001 *M* DNPE.

The detergent effects upon amine attack are also relatively small, and because of the problems in separating the spontaneous hydrolysis from that of the amine-promoted reactions we did not pursue this aspect of the problem. Richards and his coworkers have studied detergent effects upon the reaction between amines and 2,4-dinitrofluorobenzene, and did not find very large rate effects.[10] The reactions between *p*-nitrophenyl diphenyl phosphate and nucleophilic anions are markedly hindered by the neutral detergent DNPE, in contrast to what is found for most anion–molecule reactions, probably because the uncharged micelles absorb the substrate very strongly.[7] However they could also absorb the amine and the formally uncharged transition state, and their net kinetic effect upon the amine–phosphate reaction is therefore small.

The reaction between pyridine and the dianion of 2,4-dinitrophenyl phosphate is catalyzed by CTA, and almost unaffected by the uncharted detergent DNPE (Table V). Most micellar effects have been studied using an anionic nucleophile and an uncharged substrate in contrast to this system of an anionic substrate

(14) R. G. Pearson, *J. Amer. Chem. Soc.*, **85**, 3533 (1963).
(15) A. J. Kirby and W. P. Jencks, *ibid.*, **87**, 3217 (1965).

Table V. Micellar Effects upon the Reaction of Pyridine with 2,4-Dinitrophenyl Phosphate[a]

C_{pyridine}, M	C_{CTA}, M		
	0	0.003	0.01
0.05[b]	1.27	15.8	
0.30[c]	2.36	21.3	22.1

[a] Values of $10^5 k_\psi$, sec^{-1}, at 25.0° in 0.015 M borate buffer, and with 5×10^{-5} M substrate. [b] With 0.01 M DNPE $k_\psi = 1.43 \times 10^{-5}$ sec^{-1}. [c] With 0.01 M DNPE $k_\psi = 2.43 \times 10^{-5}$ sec^{-1}.

and an uncharged nucleophile, but the results are readily understandable in terms of simple electrostatic effects.[3-7]

The results of experiments on the reaction between p-nitrophenyl diphenyl phosphate and phosphate ions at pH 7.5 at 25.0° in the absence of detergent are given in Table VI. The values of k_ψ fit eq 1 (where k_2 is the

$$k_\psi = 0.43 \times 10^{-5} + k_2 C_{\text{X}^-} \qquad (1)$$

second-order rate constant for reaction between the anionic phosphate, X, and the substrate), with $k_2 = 1.1 \times 10^{-4}$ for phenyl phosphate and 4.5×10^{-4} l. mol^{-1} sec^{-1} for inorganic phosphate. These values show that in the absence of the detergent inorganic phosphate is a better nucleophile than phenyl phosphate at pH 7.5.

Table VI. Reaction between p-Nitrophenyl Diphenyl Phosphate and Phosphate or Phenyl Phosphate Ions[a]

[Reagent], M	Na_2HPO_4	$PhOPO_3Na_2$
0.02		0.55
0.05	2.28	0.90
0.10	9.04	2.69

[a] Values of $10^5 k_\psi$, sec^{-1}, at 25.0° and pH 7.5 in the absence of detergent. For the spontaneous reaction $10^5 k_\psi = 0.43$ sec^{-1}.

Ultraviolet Spectra. The extinction coefficients of the disodium salts of phenyl and p-t-butylphenyl phosphate in water are increased when 0.01 M CTA is added (Figure 6), suggesting that there is a strong interaction between the substrate and the cationic micelle.

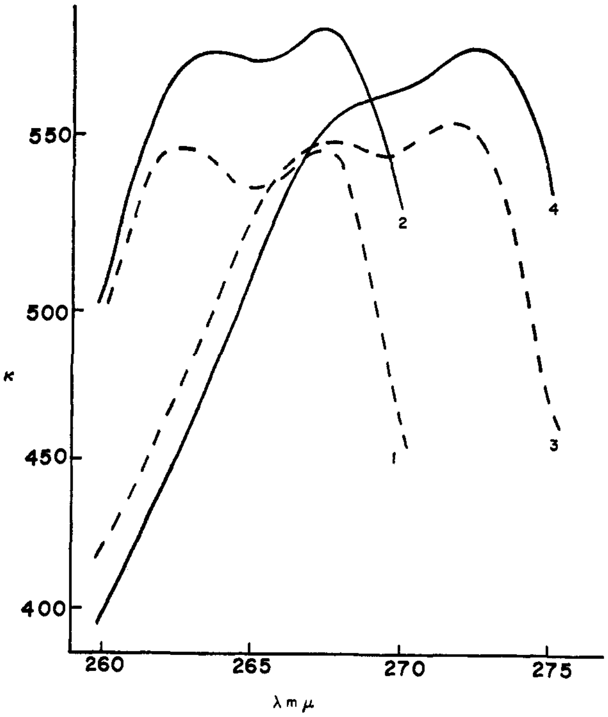

Figure 6. Variation of extinction coefficient with wavelength for phenyl phosphate (curves 1 and 2) and p-t-butylphenyl phosphate (curves 3 and 4). The broken lines are for aqueous solution and the solid lines for 0.01 M CTA.

Discussion

One of the problems in studying micellar effects upon reaction rate is that the detergent may change the autoprotolysis constant of water, and that the pH measured using a glass, or other, electrode in the solution may be different from that on the surface of the micelle where reaction is taking place.[16] For the reaction between p-nitrophenyl diphenyl phosphate and hydroxide ion, plots of k_ψ against C_{OH^-} are linear within the range pH 9–11 for reactions in the absence of detergent and in 3×10^{-3} M CTA. The value of C_{OH^-} is taken as antilog (14 − pH), where the pH is measured in the solution conventionally.

On the assumption that we can write: $k_\psi = k_1 + k_2 C_{\text{OH}^-}$, in the absence of detergent, and $k_\psi' = k_1' + k_2' C_{\text{OH}^-}$, in the presence of detergent, these plots give values of k_1 for the spontaneous hydrolysis of 4×10^{-5} sec^{-1} in the absence of detergent, and $k_1' = 4 \times 10^{-5}$ sec^{-1} in 3×10^{-3} M CTA. The second-order rate constants for attack of hydroxide ion, k_2 and k'_2, are 0.73 and 34.3 l. mol^{-1} sec^{-1} in 3×10^{-3} M CTA. The second-order rate constant in aqueous buffers and in the absence of detergent is larger than the value of 0.37 l. mol^{-1} sec^{-1} determined with 0.1 M sodium hydroxide in water–dioxane 5:95 v/v.[17,18] For the reaction between 0.01 M sodium hydroxide and p-nitrophenyl diphenyl phosphate in 3×10^{-3} M CTA the second-order rate constant is 44 l. mol^{-1} sec^{-1},[7] and the similarity of this directly determined value to that of 34.3 l. mol^{-1} sec^{-1} calculated from the variation of rate constant with pH suggests that the pH of a detergent solution gives a reasonably good measure of the hydroxide ion concentration in the solution, although it is possible that this agreement arises fortuitously as a result of opposing effects of the micelle upon the autoprotolysis constant of water and the response of the glass electrode. The detergent has no effect upon the spontaneous reaction between the substrate and water, as expected. These observations confirm existing evidence that micellar catalysis and inhibition depend upon direct interactions between the micelles and the reactants rather than upon indirect interactions through the solvent.[3-7,9,10] In addition they suggest that there are no major changes in the micellar structure over the pH range examined, and that the interactions between substrate and micelles are not markedly affected by the medium change.

The nucleophilic anions will tend to congregate in the neighborhood of cationic micelles, and detergent effects

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(16) G. S. Hartley and J. W. Roe, *Trans. Faraday Soc.*, **36**, 101 (1940); J. J. Davies and E. K. Rideal, "Interfacial Phenomena," Academic Press, New York, N. Y., 1961, p 94; J. L. Kurz, *J. Phys. Chem.*, 66, 2239 (1962).

(17) C. A. Bunton, S. Farber, and E. J. Fendler, *J. Org. Chem.*, **33**, 29 (1968).

(18) Qualitative solvent theory predicts the opposite result,[19] but initial state stabilization of the triaryl phosphate may be the determining factor in this system.

(19) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter VII.

upon indicator ionization led to the suggestion that the pH in the vicinity of a cationic micelle is considerably higher than in the bulk of the solution.[16,20] These differences were explained in terms of the high surface potential of the cationic micelle which attracted hydroxide to the surface. A simple electrostatic treatment predicts that the hydroxide ion concentration at the micellar surface, $C_{\text{OH}}{}^{\text{m}}$, can be related to the bulk concentration $C_{\text{OH}}{}^{\text{b}}$ by eq 2 (for low detergent concentrations the bulk concentration should be equal to the total concentration of hydroxide ions), where ψ is the

$$C_{\text{OH}}{}^{m} = C_{\text{OH}}{}^{\text{b}}e^{-\epsilon\psi/kT} \qquad (2)$$

surface potential, ϵ the electronic charge on the anion, and T the absolute temperature.

Equation 2 predicts the relation

$$\psi = 2.3(kT/\epsilon)\{\log (k_\psi' - k_1) - \log k_2 - \text{pH} + 14\} \qquad (3)$$

and from the value of $k_\psi' = 42 \times 10^{-5}$ sec^{-1} at pH 9.0 with 3×10^{-3} M CTA we calculate $\psi = 107$ mV, which is intermediate between the Gouy potential of 151 mV and the electrokinetic (ζ) potential of 81 mV at the slipping plane of the micelle.[16,21]

This general approach has also been used by Kurz and Mukerjee and Banerjee,[16,20] but although the rate enhancement gives a reasonably good value for the surface potential of the micelle there seem to be serious weaknesses to the simple electrostatic treatment. We should not assume that the rate constant on the micelle depends only upon the local concentration of anionic nucleophile, because the micelle may stabilize (or destabilize) the transition state relative to the reactants on its surface. In addition the theory does not predict that the efficiency of anions as reagents or inhibitors will be affected by their bulk, although such size effects are of great importance.[4-7,9]

In the same way indicator experiments do not prove that the pH at the surface of a cationic micelle is higher than in the bulk of the solution, because the equilibrium in the micellar phase

$$\text{OH}^- + \text{BH} \rightleftharpoons \text{B}^- + \text{H}_2\text{O}$$

will depend not only upon the local concentrations of the reagents, relative to the bulk solution, but upon their activity coefficients, which will be dependent upon the nature of the micelle.

Anion Inhibition. Added anions inhibit catalysis by cationic micelles for reactions between anionic nucleophiles and uncharged substrates,[3-7] and spontaneous hydrolyses of dinitrophenyl phosphate dianions.[9]

The inhibition is greatest for bulky ions of low charge density, *e.g.*, for nucleophilic attack upon *p*-nitrophenyl diphenyl phosphate in CTA the inhibition increases in the sequence (Table I and ref 7): $\text{CH}_3\text{SO}_3\text{Na}$, NaCl, $(\text{CH}_3)_4\text{NCl} < \text{Na}_2\text{SO}_4 < \text{NaBr} < \text{NaNO}_3 < \text{OC}_6\text{H}_4\text{(CO}_2\text{Na)}_2 < p\text{-C}_7\text{H}_7\text{SO}_3\text{Na} < \text{C}_6\text{H}_5\text{OPO}_3\text{Na}_2 < p\text{-}t\text{-BuC}_6\text{H}_4\text{OPO}_3\text{Na}_2 < 1\text{-C}_{10}\text{H}_7\text{SO}_3\text{Na}$ and the present work shows that the mono- and diaryl phosphates are better inhibitors (and nucleophiles) than inorganic phosphate ion.

The anion order is similar for the CTA-catalyzed hydrolysis of 2,4- and 2,6-dinitrophenyl phosphate dianions.[9] The effectiveness of phenyl and particularly *p-t*-butylphenyl phosphate dianions (Table I) provides further evidence for the importance of hydrophobic interactions between the cationic micelle and the anion.

Anion Catalysis. With decreasing pH the reaction of hydroxide ion with the substrate becomes unimportant for reactions in water and in aqueous CTA, and now attack of an aryl or inorganic phosphate ion upon the substrate can be observed. Several factors have to be considered in interpreting the results: (i) the extent of residual hydroxide ion reaction, whose importance will decrease sharply with decreasing pH; (ii) the nucleophilicity of the anions toward the substrate; (iii) their affinity to the cationic micelle.

The diphenyl phosphate monoanion is too weak a nucleophile to displace *p*-nitrophenoxide ion because its pK is probably *ca.* 1 (that of dimethyl phosphate is 1.6[22]), and it inhibits the residual hydroxide ion reaction at pH 9.5 (Table III). Phenyl and *p-t*-butylphenyl phosphate dianions should have similar nucleophilicities toward the substrate, but in low concentrations *p-t*-butylphenyl phosphate is more reactive than either phenyl or inorganic phosphate in the CTA-catalyzed reaction at pH <10 (Figures 4 and 5). At higher anion concentrations the rates increase to give approximately the same limiting rate constants which are reached when the cationic micelles are saturated by the anionic nucleophiles, and this limit is reached first with *p-t*-butylphenyl phosphate.

These results show that the *p-t*-butyl residue increases both the inhibiting ability and nucleophilicity so far as the CTA-catalyzed reactions are concerned. An anionic inhibitor plays a passive role in making it more difficult for the external nucleophile to attack a substrate which is attached to the micelle, and its orientation with respect to the substrate and the micelle should therefore not be critical. However reaction between an aryl phosphate dianion and the substrate either in the aqueous or micellar phases requires a precise orientation between them, and therefore it seems that the aryl phosphate dianion can take up various orientations relative to the substrate without seriously weakening its attachment to the micelle.

With decreasing pH phosphate trianion is converted into the dianion and the rate enhancement (in absolute terms) of the CTA-catalyzed hydrolyses by inorganic phosphate decreases in going from pH 10 to 7.5 (Figure 1). At high pH the inorganic phosphate will inhibit the reaction with hydroxide ion, and at the same time will catalyze hydrolysis because of attack of phosphate trianion. With decreasing pH the hydroxide ion reaction decreases, and therefore its inhibition will be less significant, but at the same time the phosphate trianion will be replaced by the less nucleophilic dianion, and it is this change in nucleophilicity which appears to be more important. In order to separate the factors which influence the reactivities of these phosphates in the detergent-catalyzed reactions, we have to take into account their nucleophilicities in the absence of detergent.

Differences in the inherent nucleophilicities of the phosphate anions in water are not responsible for the differences of rates in the micellar-catalyzed reactions

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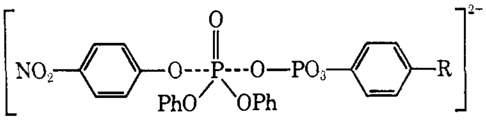
(Table VI), because these results show that phosphate is several times more reactive than the phenyl phosphate dianion, and therefore we are seeing a situation in which nucleophilicity in the micellar-catalyzed reaction is influenced strongly by nonbonding interactions. We could suppose that the greater efficiency of *p*-*t*-butylphenyl over phenyl phosphate as a nucleophile and inhibitor is caused by its more effective incorporation into the micellar phase. This explanation is completely satisfactory so far as the inhibition is concerned, but in considering nucleophilicity we must consider not only the concentrations of reactants in the micellar as compared with the aqueous phase but also their activity coefficients and that of the transition state (III) which is a bulky anion of low charge density. The results show that the aryl phosphate dianions and the substrate must be able to orient themselves so that they form the activated complex in the micellar phase without losing the hydrophobic and electrostatic bonding between the reagents and the cationic micelle. The enhancement of nucleophilicity caused by 0.003 *M* CTA is shown by the following second-order rate constants (l. mol^{-1} sec^{-1}) for the micellar catalyzed reactions: OH$^-$, 34.3 (0.73); HPO_4^{2-}, 2×10^{-2} (5×10^{-4}); $C_6H_5OPO_3^{2-}$, 10^{-1} (1×10^{-4}); *p*-*t*-$BuC_6H_4OPO_3^{2}$, 5×10^{-1}. The rate constants for the phosphates come from the results shown in Figure 1 for inorganic phosphate and from the initial slopes of the plots in Figures 2 and 3 for reactions at pH 7.5. The values in parentheses are for reaction in the absence of detergent.



III

The detergent enhances the nucleophilicity of hydroxide ion *ca.* 45-fold, of inorganic phosphate dianion *ca.* 40-fold, and of phenyl phosphate dianion *ca.* 1000-fold.

Experiments using spin-labled nitroxides have shown that the solute is not rigidly held to an anionic micelle of sodium lauryl sulfate, and can move freely from the hydrocarbon-like interior of the micelle to the water rich exterior.[23] If this behavior is general for solubilization in ionic micelles it would be easy for attack of an aryl phosphate dianion upon a triaryl phosphate in the micellar phase to be influenced strongly by hydrophobic interactions.

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Trapping Carbonium Ions in SbF_5–HSO_3F

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Abstract: Butyl, amyl, and hexyl cations have been generated by the solvolysis of alkyl halides in 2 *M* SbF_5–HSO_3F solutions and trapped by hydride transfer from methylcyclopentane both before and after reaching an equilibrium distribution of cations. Tertiary cations predominate at equilibrium in these systems. Under kinetic control tertiary ions may be trapped after little rearrangement but secondary and primary cations show increasing tendencies to isomerize. The data suggest that simple methyl group migrations occur *via* protonated cyclopropane intermediates rather than by direct methide shifts in the interconversion of methylpentyl and methylbutyl cations.

Many solutions containing antimony pentafluoride have been reported to be capable of stabilizing high concentrations of alkyl cations. The ions have generally been detected by spectral means, particularly nmr. This investigation has been concerned with studying the nature of the cations in 2 *M* SbF_5–HSO_3F solutions through the use of hydride transfer trapping experiments. This medium has previously been used both to generate stable alkyl ions[1] and to investigate calorimetrically the energetics of their rearrangement.[2] It has long been known that carbonium ion intermediates in strongly acidic systems can be trapped by reaction with a strong donor such as methylcyclopentane, but this powerful means of probing the nature of the intermediates in solutions containing SbF_5 has been relatively neglected.

The present investigation gives information about the equilibrium distributions of C_4, C_5, and C_6 ions and the ability of methylcyclopentane to trap ionic intermediates before equilibrium is attained. The *t*-butyl and *t*-amyl cations appear to be the stable C_4 and C_5 ions. The C_6 system yields a mixture of 2-methylpentyl, 3-methylpentyl, and 2,3-dimethylbutyl cations at low temperatures. The distribution shifts slightly with temperature but conditions leading to only the stable 2,3-dimethyl-2-butyl cation have not been found.

Rearrangements of ions originating from primary, secondary, or tertiary halides to the equilibrium mixtures are usually complete in less than 3 min at −50°. These rearrangements can be severely restricted by generating the ions in the presence of excess methylcyclopentane. In this case the initial ions or intermediates on the way to the equilibrium may be trapped and much information about mechanistic paths can be obtained. For example, *n*-butane is a major product of the reaction of 1-chlorobutane or 2-chlorobutane indi-

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