that of the pendant carbon atom, which ought to have a greater amount of vibrational motion and hence a larger vibrational ellipsoid. This is physically unreasonable and suggest that too much electron density has been assigned to the atom called O(61). By calling it a carbon atom, C(6), which is the only chemically acceptable alternative, we obtain the physically satisfying result already shown in Figure 5, where the two capping atoms, O(1) and C(6), have thermal ellispoids of essentially equal size, with that of the terminal carbon atom C(61) being much larger.

If we change the OCH_3^- to CCH_3^{3-}, we then raise the mean oxidation number of molbydenum to +4. This leaves only 18 - 12 = 6 electrons to be placed in cluster molecular orbitals, and these suffice exactly to provide the three Mo-Mo single bonds. Thus, the electronic structure difficulty is resolved. Further, it is a lot easier to imagine CCH_3^{3-} (formally) as a reduction product of the acetic acid than OCH_3^-. Also, the final, refined C-CH_3 bond length of 1.51 (1) Å is entirely acceptable.

Finally, there is a fifth form of evidence favoring the O,CCH_3 model. Having changed the crystallographic model, albeit modestly, by introducing the carbon atom for the oxygen atom, we observed a decrease in R values from 0.033 and 0.043 to 0.032 and 0.041 for R_1 and R_2, respectively. Concurrently, there was an improvement in the goodness-of-fit parameter from 1.43 to 1.38.

These arguments, together with the evidence that in related compounds there were also μ_3-CCH_3 groups, left no real doubt that we were dealing with a μ_3-CCH_3 group. However, direct evidence was deemed necessary and this was provided by the ^{13}C NMR spectrum, as shown in Figure 2. In addition to the signals for the other five types of carbon atom, that would be present for the O,OCH_3 formulation, we find an additional signal in a region where the CCH_3 resonance might reasonably be expected.

The CCH_3-capping group, or similar C-X capping groups, have been observed often in the past.[20,24] However, in all these previous cases, the compounds have been of the metal carbonyl and/or organometallic types that characteristically have a nonaqueous chemistry and are more or less unstable toward water, air, and oxidizing agents. The remarkable characteristics of the compound described here, and related ones with CCH_3 capping groups, is that they are prepared and handled in aqueous, oxidizing conditions.

Acknowledgment. We are grateful to the Robert A. Welch Foundation, The National Science Foundation, and the U.S.-Israeli Binational Science Foundation for financial support. B.W.S.K. was the recipient of a NATO Postdoctoral Fellowship from the Natural Sciences and Engineering Research Council of Canada, 1979-1981. We are grateful to Professor B. L. Shapiro and Drs. R. Willson and D. Holecek of Shell Research Laboratories for their help with the NMR spectra.

Supplementary Material Available: A table of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

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Micellar Catalysis of Dephosphorylation by Benzimidazolide and Naphth-2,3-imidazolide Ions

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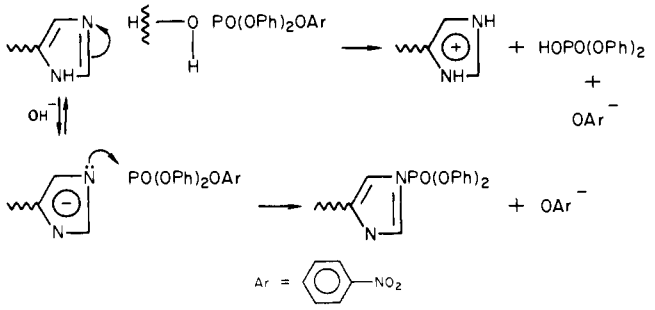
Abstract: The reactions of *p*-nitrophenyl diphenyl phosphate (*p*-NPDPP) with benzimidazolide and naphth-2,3-imidazolide ion are strongly catalyzed by micelles of cetyltrimethylammonium bromide (CTABr). The maximum rate enhancements are 2.5×10^3 and ca. 1.5×10^4 for benzimidazole and naphth-2,3-imidazole, respectively. The first-order rate constants go through maxima with increasing [CTABr], and for [CTABr] > 10^{-3} M the rate-surfactant profile is accommodated by a pseudophase model which relates rates in the micelles to the concentrations of micellar bound reactants, with the second-order rate constants in the micelle being similar to those in water. The imidazolide ions are phosphorylated by *p*-NPDPP and the phosphoryl intermediates can react with *p*-nitrophenoxide ion, regenerating starting material, or can go forward to product.

Imidazole derivatives are effective deacylating agents,[2] and their reactions with carboxylic esters are speeded by micellized surfactants.[3] The rate enhancements are especially large when the imidazole moiety is covalently bound to the surfactant head group, and these systems have been studied intensively.[3b,c]

Scheme I



Imidazole mediated dephosphorylation has not been studied widely, in either the absence or presence of micelles. Imidazole

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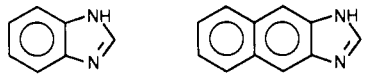
and *N*-methylimidazole are nucleophilic catalysts of nonmicellar hydrolysis of tetrabenzyl pyrophosphate, as shown by trapping experiments.[4] However 2,6-lutidine is a general base catalyst of this hydrolysis.[5] Cationic micelles of imidazole-derived surfactants speed hydrolysis of *p*-nitrophenyl diphenyl phosphate (*p*-NPDPP).[6] It was suggested that the nonionic imidazole moiety acts as a general-base catalyst, but there is an indication that the imidazolide anion acts as a nucleophile (Scheme I).[7]

The aim of the present work was to examine micellar effects upon dephosphorylation of *p*-NPDPP in the presence of an areneimidazole and to determine the mechanism of the reactions.

Benzimidazole (BI) is not a particularly effective deacylating



BI NI

agent,[3a] but it is deprotonated in dilute alkali, giving the reactive benzimidazolide anion, and deacylation by this anion is strongly catalyzed by cationic micelles. Berezin and his co-workers concluded that second-order rate constants in the micelle were larger than those in water, by about 1 order of magnitude, but that most of the rate enhancement was due to increased reactant concentrations in the micelles.[3a]

There is general agreement that miecllar effects on reactivity fit the assumption that micelles behave as if they were a separate phase, so that reaction can occur in either the aqueous or micellar pseudophase, and it is possible to measure the relevant rate constants.[3,8]

Cationic micelles are effective catalysts of the reaction of *p*-NPDPP with phenoxide and oximate ions and, except at low surfactant concentration, the rate–surfactant profiles can be explained in terms of the distribution of both reactants between aqueous and micellar pseudophases.[9,10] The second-order rate constants *in the micellar pseudophase* are only slightly dependent upon the hydrophobicity of the phenols and are similar to those in water, but an increase in hydrophobicity increases incorporation in the micelles so that the more hydrophobic phenoxide ions are better dephosphorylating agents in surfactant. These observations are consistent with recent kinetic studies on other reactions.[3a,8,11]

Experimental Section

Materials. The preparation or purification of most of the reagents has been described.[9] Naphth-2,3-imidazole was prepared by standard methods[12] and had a melting point of 216 °C (lit. 218 °C).

Kinetics. The formation of *p*-nitrophenoxide ion was followed spectrophotometrically in aqueous solution at 25.0 °C.[9] The first-order rate constants for the overall reaction, k_ψ, are in reciprocal seconds.

Areneimidazoles are weak acids, and at the relatively high pH needed for their ionization there is a contribution from reaction with OH^-. We assume that reactions of hydroxide and imidazolide ion are independent, and k_ψ for the overall reaction is corrected for the contribution of the hydroxide ion reaction (1) (where k_1' and k_{OH}' are respectively the

$$k_\psi = k_1' + k_{OH}' \quad (1)$$

first-order rate constants for reaction with the imidazole and OH^-. We use a prime superscript to denote a first-order rate constant, and a subscript I to denote reaction with an areneimidazole).

The experiments in CTABr were made in 0.01 M carbonate buffer (pH 10.7 or 11 in the absence of surfactants). The contribution of the hydroxide ion reaction was measured in CTABr in absence of the imidazole and presence of buffer.

The concentrations of both substrate and areneimidazole were low to minimize perturbation of micellar structure, and we generally used 0.1 or 0.12 mM areneimidazole and 3×10^{-6} M *p*-NPDPP. Use of these low concentrations of areneimidazole allowed us to measure the concentration of micellar bound ion directly. In experiments with NI a decrease in [*p*-NPDPP] did not affect k_ψ.

Acid-Dissociation Constants of the Areneimidazoles. The acid-dissociation constants for deprotonation in water of the conjugate acid of benzimidazole, pK_{a1}, and of benzimidazole itself, pK_{a2}, have been reported.[13a,b] There are discrepancies (Table I), and we remeasured pK_{a2} for benzimidazole,[13c] and pK_{a1} and pK_{a2} for naphth-2,3-imidazole. (Table I). We used the following wavelengths: benzimidazole, pK_{a2}, 283 nm, naphth-2,3-imidazole, pK_{a1}, 339 nm, pK_{a2}, 354 nm. Some of the differences in reported values of pK_{a2} for benzimidazole may arise from activity corrections which were applied in some experiments. We did not apply activity corrections to our results which were obtained in solutions of low ionic strength. However, Hisano and Ichikawa worked at 243 nm,[13a] and when we attempted to use this wavelength, we calculated a lower pK_a than at 283 nm (Table I).

Deprotonation and Micellar Binding in CTABr. The concentration of micellar bound areneimidazolide ion was determined directly spectrophotometrically by using a Beckman spectrophotometer. Benzimidazolide ion was monitored at 289 nm ($\epsilon = 4170$) and naphth-2,3-

Table I. Acid-Dissociation Constants

	pK_{a1}	pK_{a2}
benzimidazole	5.5[a]	11.25,[b] ca. 12.5,[a] 12.8[c]
naphth-2,3-imidazole	5.2[d]	12.3[e]

[a] Reference 13b. [b] Reference 13a. [c] Reference 13c. [d] In 0.02 M succinate buffer. [e] In dilute NaOH.

Table II. Reaction in the Absence of Surfactant[a]

imidazole	$10^3 \times$ [imidazole], M	$10^4 k_\psi$, s^{-1}	k_I^w, M^{-1} s^{-1}
		2.60	
BI	2	2.69	
BI	4	2.96	1
BI	8	3.23	0.9
NI	1	2.78[b]	0.7
NI	2	2.87[c]	0.5

[a] In water at 25.0 °C at pH 10.7, 0.01 M carbonate buffer; k_I^w is the second-order rate constant with respect to areneimidazole ion. [b] In 15 vol % EtOH. [c] 30 vol % EtOH.

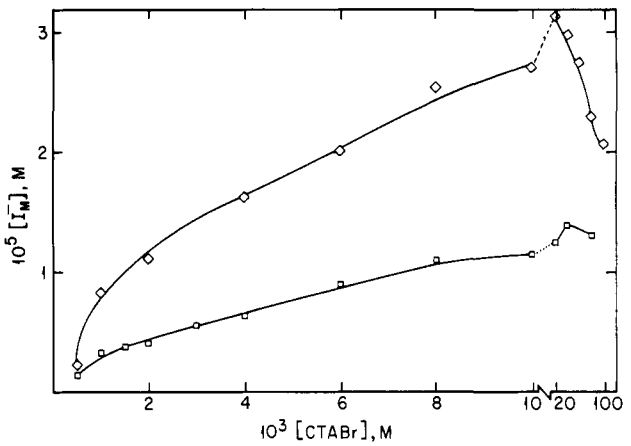


Figure 1. Micellar effects upon the deprotonation of benzimidazole in carbonate buffer: □, 10^{-4} M benzimidazole, pH 10.7; ◇, 1.2×10^{-4} M benzimidazole, pH 11.

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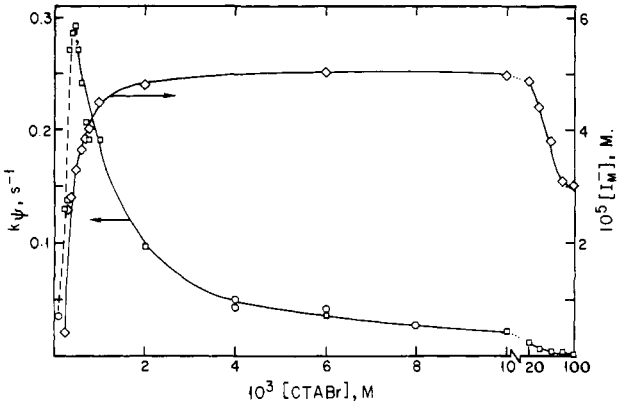

Figure 2. Micellar effects at pH 10.7 upon the deprotonation of naphth-2,3-imidazole (◇) and upon dephosphorylation mediated by 10^{-4} M naphth-2,3-imidazole (□, ○). The circles refer to experiments with 2×10^{-6} M *p*-NPDPP.

imidazolide ion at 364 nm (ϵ = 4250).[13c,d] These wavelengths do not correspond to absorbance maxima but were chosen because of low absorbance by the areneimidazoles. The binding of undissociated areneimidazole to CTABr has been determined.[3a,13c,d] The general methods for determining the micellar binding of conjugate bases of weak acids have been described.[9,10,13c,d]

We could not measure [areneimidazolide] in the experiments with added phenols because of the strong absorbance of the phenoxide ions.

Results and Discussion

Reaction with the Areneimidazoles in the Absence of Surfactant. In the absence of surfactant the imidazoles are only slighly deprotonated at pH 10.7, and there is a relatively small contribution from reaction with imidazolide ion (Tables I and II). From the rate constants and pK_{a2} = 12.8 and 12.3 for BI and NI, respectively, we estimate second-order rate constants of approximately 1 and 0.6 M^{-1} s^{-1} for reaction with benzimidazolide and naphth-2,3-imidazolide ion, BI^- and NI^-, respectively (Table II). These second-order rate constants are only approximate because of the small incremental rate. The value for NI is the less reliable because we had to add EtOH to solubilize the nucleophile (Table II).

Reaction in CTABr Solutions. Benzimidazolide and naphth-2,3-imidazolide ion are very effective reagents for dephosphorylation of *p*-NPDPP in CTABr (Figures 2 and 3). The first-order rate constants in CTABr in the absence of areneimidazole are in Figure 3.

The values of k_ψ reach a maximum with increasing [CTABr]. Such rate maxima are typical of micellar catalyzed bimolecular reactions, and the rise in rate constant followed by a gradual decrease is characteristic of reactions of hydrophobic substrates.[3a,8-11] The rate enhancements at the optimum [CTABr] are large, being by factors of 2.5×10^3 and ca. 1.5×10^4 for reactions with BI and NI, respectively, at pH 10.7 (Table II and Figures 2 and 3). Cationic micelles increase deprotonation,[13c,d] but the rate enhancements are much too large to be explained solely in these terms.

The contribution of the hydroxide ion reaction in the presence of CTABr cannot be neglected (Figure 3 and ref 14), and in the following discussion we use rate constants for reaction with the areneimidazole ion corrected for reaction with OH^- (eq 1). However, reactions in the micellar solutions are so much faster than those in water (Table II) that we can neglect the contribution of reaction in the aqueous pseudophase.

Analysis of the Rate–Surfactant Profiles. The corrected first-order rate constants, k_1', for reaction in solutions of CTABr mediated by areneimidazolide ion can be written as eq 2,[8b,9,10]

$$k_1' = k_M' K_S(([\text{CTABr}] - \text{cmc})/(1 + K_S[\text{CTABr}] - \text{cmc})) \quad (2)$$

where K_S is the binding constant of *p*-NPDPP,[15] expressed in terms

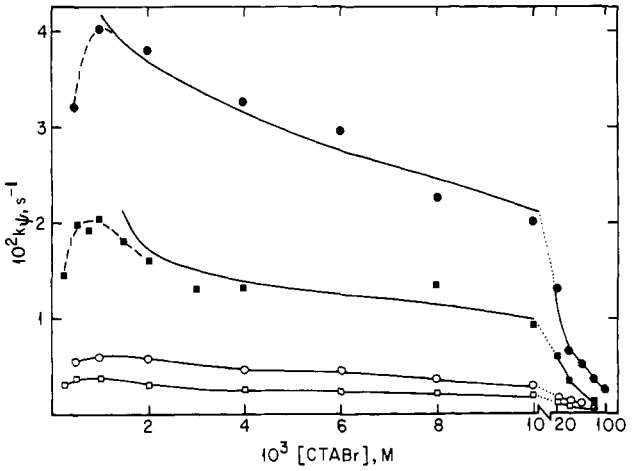

Figure 3. Micellar effects upon dephosphorylation mediated by benzimidazole (solid points). The open points are for dephosphorylation in the absence of benzimidazole: □, pH 10.7; ○ pH 11; ■, 10^{-4} M benzimidazole, pH 10.7; ●, 1.2×10^{-4} M benzimidazole, pH 11. The solid lines are calculated, see text.

of micellized surfactant, and cmc is the critical micelle concentration.[16] The first-order rate constant for reaction in the micellar pseudophase, k_M' is given by eq 2,[8b,9] where m_N^S is the mole ratio

$$k_M' = k_M m_N^S = k_M[I_M^-]/([\text{CTABr}] - \text{cmc}) \quad (3)$$

of nucleophile to micellized surfactant, $[I_M^-]$ is the concentration of micellar bound imidazolide ion, expressed in terms of the total solution volume, and k_M is the appropriate second-order rate constant in the micellar pseudophase.

Equations 2 and 3 give

$$k_1' = k_M K_S[I_M^-]/\{1 + K_S([\text{CTABr}] - \text{cmc})\} \quad (4)$$

Equation 4 can be rearranged to

$$[I_M^-]/k_1' = 1/k_M K_S + ([\text{CTABr}] - \text{cmc})/k_M \quad (5)$$

The reciprocal form, eq 5, is very useful in that it allows estimation of k_M from the slope of a plot of $[I_M^-]/k_1'$ against surfactant concentration.[17] Plots of $[I_M^-]/k_1'$ against [CTABr] were linear, and we estimate k_M = 7 and 4 s^{-1} for reaction with BI^- and NI^-, respectively. The binding constant, K_S, is ca. 16 000 M^{-1} for *p*-NPDPP in CTABr,[9,14] and the intercept in eq 5 is close to zero. A similar situation has been found for other micellar catalyzed reactions of *p*-NPDPP.[9,10]

We can use our kinetic parameters and values of $[I_M^-]$ (Figures 1–3) and eq 4 to predict the variation of reaction rate with [CTABr]. In order to do this, we have to allow for the contribution of the reaction with OH^- (Figure 3) and we assume a value of 3×10^{-4} M for the cmc of CTABr in the reaction solution. The value is lower than that of 8×10^{-4} M in water,[16] because of lowering of the cmc by the solutes, and we treat it as a disposable parameter. Similar low values fit the data for other reactions in CTABr.[9,10,18]

The treatment fails in very dilute [CTABr] (Figures 2 and 3), and it does not correctly predict the position of the rate maximum.

(14) Bunton, C. A.; Robinson, L. *J. Org. Chem.* **1969**, *34*, 773.

(15) The binding constant is given by $K_s = [S_M]/\{[S_W]([\text{CTABr}] - \text{cmc})\}$ where $[S_M]$ and $[S_W]$ are the concentrations of solute in the micellar and aqueous pseudophases, expressed in terms of the total volume of solution.

(16) Mukerjee, P.; Mysels, K. J. "Critical Micelle Concentrations of Aqueous Surfactant Systems"; National Bureau of Standards: Washington, D.C., 1971.

(17) The experimental data can be fitted to eq 5 without the value of the cmc being known. This is important because solutes often change the value of the cmc. It is necessary however to assume that the concentration of monomers, which is assumed to be given by the cmc, does not change markedly with surfactant concentration; cf. ref 18.

(18) Bunton, C. A.; Carrasco, N.; Huang, S. K.; Paik, C. M.; Romsted, L. S. *J. Am. Chem. Soc.* **1978**, *100*, 5420.

Table III. Rate Constants in Micellar and Aqueous Pseudophases[a]

imidazole ion	k_I^W, M^{-1} s^{-1}	k_M, s^{-1}	k_2^m, M^{-1} s^{-1}
benz-	ca. 1	7	1
naphth-2,3	ca. 0.6	4	0.6

[a] At 25.0 °C in 0.01 M carbonate buffer, pH 10.7.

These failures are common with micellar catalyzed reactions of very hydrophobic reactants and have been ascribed to solute-induced micellization reaction in submicellar aggregates.[10,18,19] The question is considered in the accompanying paper.

There are now many examples of reactions in which second-order rate constants in the micellar pseudophase are very similar to those in water.[3a,8b,11] Some investigators have estimated the rate constants in terms of the total volume of the micelle, others in terms of estimated volumes of the Stern layer. We estimated an approximate volume of the Stern layer in 1 mol of micellized CTABr as 0.14 L.[3b,9] On this basis the second-order rate constant, k_2^m, calculated in terms of molarity of a reactant in 1 L of Stern layer is given by eq 6.

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

The values of k_M, k_2^m, and the second-order rate constant in water, k_1^W, are compared in Table III. The good agreement between k_2^m and k_1^W is fortuitous, because the values of k_1^W are approximate (see Results). However, the results show that the micellar effects upon dephosphorylation by these imidazoles depend on increased deprotonation and concentration of the reactants in the micellar pseudophase. They also show that the higher reactivity of NI over BI in solutions of CTABr (Figure 2 and 3) is simply the result of greater incorporation of the nucleophile, not of a larger second-order rate constant in the micellar pseudophase, cf. ref 10.

Although we find agreement between the second-order rate constants in the micellar pseudophase and water (Table III), Berezin and his co-workers found that for deacylation by BI^- the second-order rate constants in micelles of CTABr are larger than those in water by approximately 1 order of magnitude.[3a] These differences are in part due to different methods of calculating the concentration of BI^- in the micelle, because Berezin and his co-workers estimated the concentration indirectly from the effect of CTABr on pK_{a2},[3a] and also they based their calculation on the total volume of the micelle rather than that of the Stern layer. However, in these, and other systems, it is evident that concentration of reactants into the small volume of the micelles is the major source of the rate enhancement.[3a,8,11]

Mechanism of the Reaction. The rate surfactant profiles (Figures 2 and 3) can be analyzed regardless of reaction mechanism, but it is important to distinguish between the areneimidazolide ion acting as a general base or as a nucleophile (cf. Scheme I).

The effects of added phenoxide ions upon dephosphorylation by areneimidazolide ion in CTABr allow us to distinguish between the two mechanisms. If the areneimidazolide anions were acting as general bases, the only effect of a phenoxide ion would be to exclude other anions, e.g., OH^-, from the cationic micelle and this inhibitory effect should not be strongly dependent on the nature of the phenoxide ion. But nucleophilic attack gives a phosphorylated intermediate (**1**) which might react with *p*-nitrophenoxide ion to regenerate substrate (Scheme II); it could also react with another phenoxide ion, $Ar'O^-$, giving a new triaryl phosphate (**2**), but we would not detect this reaction, because we follow formation of *p*-nitrophenoxide ion.

We used *p*-cyano- and 2,4-dichlorophenoxide ions to test for the competitive effect of an added phenoxide ion. The phenols are fully ionized in our reaction conditions, and all three phenoxide ions should be similar in their interactions with cationic micelles and should therefore be similarly effective in excluding OH^- from the micelle. This competition effect is not very important, and *p*-nitrophenoxide ion is a very effective inhibitor, because it can attack the phosphorylated intermediate (**1**) and return it to reactant (Scheme II).[20] Thus the areneimidazolide ions in CTABr are acting as nucleophiles toward *p*-NPDPP, and general-base catalysis is apparently unimportant.

Scheme II

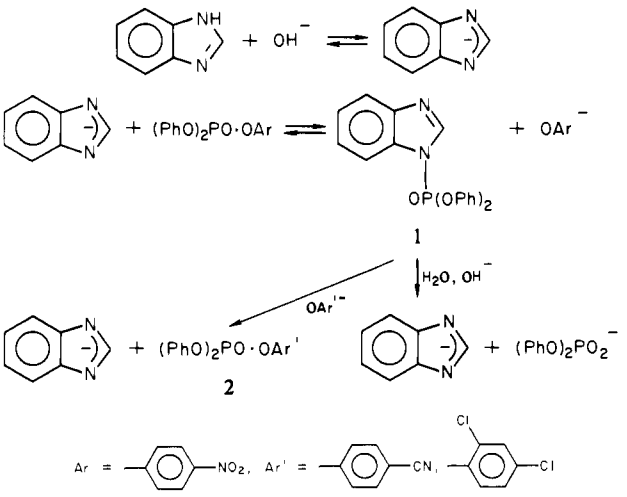

Table IV. Inhibition by *p*-Nitrophenoxide Ion[a]

imidazole	$10^4 \times$ [OAr^-], M	$10^3 \times k_I'$, s^{-1}	k_{-1}/k_2	k_{-1}/k_2[OAr^-],[b] M^{-1}
benz-		10.3		
benz-	0.25	8.0	0.25	10^4
benz-	0.5	7.0	0.47	9×10^3
benz-	1.0	5.0	1.06	1.1×10^4
benz-	1.5	4.6	1.24	8×10^3
naphth-2,3-		49		
naphth-2,3-	0.5	41	0.25	4×10^3
naphth-2,3-	1.0	25	1.0	10^4
naphth-2,3-	2.0	14	2.5	1.3×10^4

[a] At 25.0 °C in 4×10^{-3} M CTABr, 10^{-4} M total areneimidazole, and 0.01 M carbonate buffer, pH 10.7. [b] [ArO^-] is the total concentration of *p*-nitrophenoxide ion.

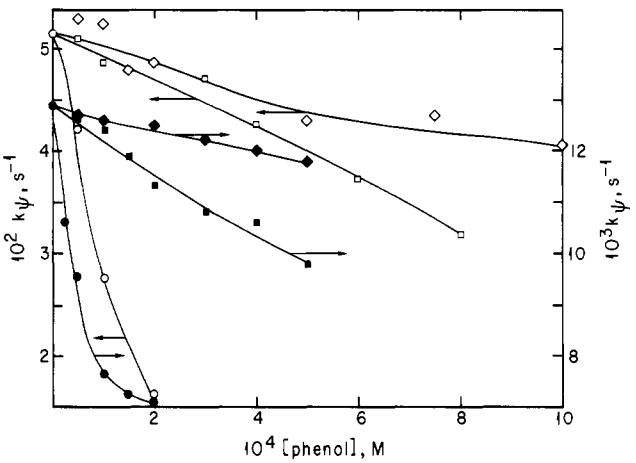

Figure 4. Effect of phenoxide ions upon dephosphorylation in 4×10^{-3} M CTABr, pH 10.7: solid points, 10^{-4} M naphth-2,3-imidazole; open points, 10^{-4} M benzimidazole; ○ and ●, *p*-nitrophenol; ◇ and ◆, *p*-cyanophenol; □ and ■, 2,4-dichlorophenol.

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(20) In the absence of added *p*-nitrophenoxide ion return of **1** to reactants does not compete with its hydrolysis at the low substrate concentrations which are used.

In principle these trapping experiments can be treated quantitatively in terms of Scheme II, which gives the rate equation (7).

$$p\text{-NPDPP} + I^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 1 + OAr^- \xrightarrow[OH^-]{k_2} \text{product}$$

$$k_1' = k_1k_2/(k_{-1} + k_2) \quad (7)$$

In eq 7 k_1' is the observed first-order rate constant for reaction with areneimidazolide ion, and k_1, k_{-1}, and k_2 are first-order rate constants for the individual steps. We assume that k_1 is given by k_1' in the absence of added *p*-nitrophenoxide ion,[20] and k_1, k_{-1} and k_2 will depend on the concentrations of nucleophilic ions in the micellar pseudophase. The values of k_{-1}/k_2 are given in Table IV. There are several approximations in eq 7; for example it neglects competition between the various anions for the micelle, and retardation by *p*-cyano- and 2,4-dichlorophenoxide ions (Figure 4) shows that these effects are present. However, $k_{-1}/k_2[ArO^-]$ is reasonably constant for reaction of a given areneimidazolide ion (Table IV), which is reasonable because phenoxide ions bind very strongly to cationic micelles.[21] Thus in view of the complexities of micellar catalyzed reactions the relative rate constants (Table IV) fit the proposed reaction scheme satisfactorily, especially for reaction with BI^-.

An important aspect of this trapping study is that it would be very difficult to do the experiments in nonmicellar systems, because in water reactions of the areneimidazolide ions are small contributors to the overall rate (Table II). In addition trapping of the intermediate by *p*-nitrophenoxide ion is much more effective in a cationic micelle than in water because phenoxide ions bind much more strongly than hydroxide ions to cationic micelles.[13c]

Micelles appear to catalyze or inhibit reactions without materially changing mechanism, and our trapping experiments show how micelles can be used to develop mechanistic probes which may not be available for reactions in water or similar solvents.

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Catalysis by Hydrophobic Tetraalkylammonium Ions. Dephosphorylation of *p*-Nitrophenyl Diphenyl Phosphate

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Abstract: The phase-transfer agents tri-*n*-octylethylammonium bromide and mesylate (TEABr and TEAMs, respectively) strongly catalyze the reaction of *p*-nitrophenyl diphenyl phosphate (*p*-NPDPP) with benzimidazolide ion (BI^-) and naphth-2,3-imidazolide ion (NI^-). In dilute TEABr and TEAMs reactions are of greater than first order with respect to substrate, areneimidazole, and TEABr or TEAMs, suggesting that reaction is occurring in small aggregates of the three solutions. The reaction of *p*-NPDPP with OH^- is not catalyzed by TEABr. The solubility of TEAMs allows study of the catalysis up to 2×10^{-2} M, and the first-order rate constants, k_ψ, for reaction of the areneimidazoles with *p*-NPDPP go through maxima with increasing [TEAMs]. The constants depend upon [*p*-NPDPP] at low [TEAMs] but not at high. The rate maxima can be explained in terms of incorporation of both *p*-NPDPP and BI^- in aggregates of TEAMs, and the rate constants of reaction in the aggregates can be estimated and are similar to that for reaction in micelles of cetyltrimethylammonium bromide (CTABr). The reactions of areneimidazolide ions with *p*-NPDPP are catalyzed by CTABr at concentrations below the critical micelle concentration (cmc) in water. Under these conditions the order with respect to *p*-NPDPP is less than 1 and catalysis appears to be due to induced micelle formation.

Micellar effects upon reaction rates in aqueous solution have generally been analyzed in terms of a pseudophase model,[2-4] assuming reactants are distributed between the aqueous solvent and the micelles, with reaction occurring in either pseudophase. It was first applied to micellar inhibited bimolecular reactions[5] and then to micellar catalyzed unimolecular reactions[6] and has been extended to bimolecular micellar catalyzed reactions.[3,4,7-9]

It is implicit in these treatments that reactants do not perturb micellar structure and do not bind cooperatively to the micelle. These assumptions are reasonable, provided that surfactant is in large excess over reactants. However the quantitative treatments sometimes fail for [surfactant] close to the critical micelle concentration (cmc), especially with hydrophobic reactants which may interact strongly with micelles or premicelles.[10,11]

Piskiewicz has developed an alternative model in which rate–surfactant profiles are explained by an equation similar to the Hill equation of enzyme kinetics,[11] which stresses cooperative binding. Kunitake and co-workers found that the phase-transfer catalyst tri-*n*-octylmethylammonium chloride (TMAC) strongly accelerates deacylation of *p*-nitrophenyl acetate by hydrophobic hydroxamates or imidazoles in water.[12] The reactions in TMAC were faster than in micellized cetyltrimethylammonium bromide (CTABr), showing that nonmicellar aggregates could be catalytically active and that rate effects in very dilute surfactant might also be due to formation of submicellar aggregates. The rate enhancements

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