Micellar Effects upon Dephosphorylation by Amidoximes

Clifford A. Bunton,* Susan E. Nelson,[1] and Clifford Quan

Department of Chemistry, University of California, Santa Barbara, California 93106

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Micelles of cetyltrimethylammonium chloride (CTACl) only weakly speed the benzamidoximate-mediated dephosphorylation of *p*-nitrophenyl diphenyl phosphate (pNPDPP) at pH 10.7 because the amidoximate binds only weakly to CTACl and is only slightly deprotonated. Dephosphorylation by *p*-(hexyloxy)- or *p*-(dodecyloxy)benzamidoximate ion is speeded by CTACl, and the second-order rate constant for reaction of *p*-(hexyloxy)benzamidoximate in the micellar pseudophase of CTACl is slightly smaller than that for reaction of benzamidoximate ion in water. Oximate and amidoximate ions have similar reactivities toward pNPDPP in water and in the micellar pseudophase.

Oximate ions are effective dephosphorylating and deacylating agents.[2,3] The reactions are speeded by aqueous cationic micelles, and the rate–surfactant profiles have been studied by using both functional and nonfunctional micelles.[4-6]

Amidoximes (**1**) react nucleophilically in deacylation[7] and dephosphorylation,[8] and their effectiveness is sharply increased by conversion into amidoximate ion (**2**, eq 1).

$$\underset{\mathbf{1}}{RC(NH_2)=NOH} \rightleftharpoons \underset{\mathbf{2}}{RC(NH_2)=NO^-} + H^+ \quad (1)$$

However, the amidoximes, with pK_a s in the range 12–13,[7] are much less acidic than the otherwise similar oximes, so that reaction of the anion **2** is observed only at pH >10.5.

Benzamidoxime (**1**, R = Ph) is a poorer dephosphorylating agent than acetamidoxime (**1**, R = Me), but it is a stronger acid, and at pH >11 reaction is faster in benzamidoxime simply because of greater formation of benzamidoximate ion.[8]

The work described here involves reactions of *p*-nitrophenyl diphenyl phosphate (pNPDPP) with the anions of benzamidoxime or its *p*-alkoxy derivatives (**3a,b**, eq2) and comparison of reactivities of oximate and amidoximate ions. We also examined the effects of cationic micelles of cetyltrimethylammonium chloride (CTACl) on these reactions.

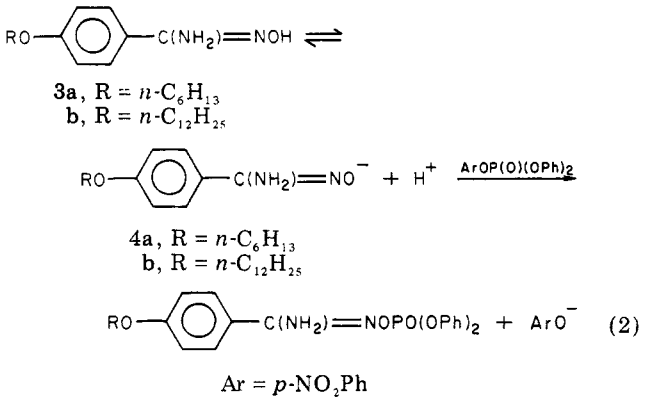

Table I. Effect of CTACl on Deprotonation of *p*-(Hexyloxy)benzamidoxime[a]

	[OH⁻], M	
10^3[CTACl]	0.01	0.1
1.5	0.75	0.87
2.0	0.76	
2.5	0.79	
3.0	0.80	
3.5	0.82	
4.0	0.85	0.94
5.0	0.89	
7.0	0.89	
8.0	0.79	
9.0	0.70	

[a] Fraction of deprotonation of 2.5×10^{-4} M amidoxime.

Our aim was to compare reactivities of oximate and amidoximate ions, because intramolecular catalysis is possible with an amidoxime,[7] and we also planned to test quantitative models of micellar rate enhancements of bimolecular reactions.[9]

Experimental Section

Materials. The substrate (pNPDPP) and CTACl were prepared by standard methods.[9,10] There was no minimum in a plot of surface tension against [CTACl], and the critical micelle concentration (cmc) in water was 1.27×10^{-3} M, in good agreement with literature values.[11] Benzamidoxime was prepared, as the hydrochloride, by the method of Lenaers, Eloy, and Moussebois.[12] The (hexyloxy)- and (dodecyloxy)benzamidoximes (**3a,b**) were prepared from the corresponding benzonitriles by heating them at 60 °C for 40 h with a slight excess of H_2NOH in EtOH. The solvent was removed by evaporation. In the preparation of **3a** the solid residue was washed twice with warm H_2O and was recrystallized twice from EtOH; mp 112–113 °C. In the isolation of **3b** the solid was washed with hexane, recrystallized three times from EtOH, and appeared to have a decomposition point from 107 to 112 °C. Further recrystallization from C_6H_6 did not change this range of decomposition. Both the *p*-alkoxy derivatives had the predicted mass numbers determined by high-resolution mass spectrometry.

Kinetics. The formation of *p*-nitrophenoxide ion from pNPDPP was followed spectrophotometrically.[9] We had a problem with the *p*-alkoxy benzamidoximates **3a,b** because the solutions tended to be cloudy, even in the presence of CTACl,

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Table II. Effect of OH^- on Deprotonation of p-(Hexyloxy)benzamidoxime[a]

$[OH^-]$, M	0.001	0.002	0.005	0.007	0.010	0.015	0.020
f[b]	0.52	0.58	0.61	0.74	0.81	0.92	0.94

[a] In 10^{-3} M CTACl with 5×10^{-4} M amidoxime. [b] Fraction of deprotonation.

Table III. Reaction with Benzamidoxime in CTACl[a]

10^3[CTACl], M	10^3k_ψ, s^{-1}	10^3[CTACl], M	10^3k_ψ, s^{-1}
0.44	4.92 (4.34)	4.40	4.56
0.88	5.24 (4.56)	8.00	(3.49)
1.76	4.99 (4.43)	8.81	3.98 (3.47)
4.00	(3.93)		

[a] At 25 °C, pH 10.7, 10^{-2} M carbonate buffer, and 10^{-3} M benzamidoxime. The values in parentheses are for reaction in the absence of benzamidoxime.

and the dodecyloxy derivative (**3b**) could be used only in very dilute solution. Because of these solubility problems reactions with **3a,b** were examined only in CTACl. The substrate concentration was typically 5×10^{-6} M, and substrate was added in MeCN so that the reaction solution contained 0.1–0.3% MeCN.

All the reactions were followed at 25.0 °C and the first-order rate constants, k_ψ, are in reciprocal seconds.

Deprotonation. The pK for deprotonation of benzamidoxime was determined spectrophotometrically by using a 5×10^{-4} M solution. The absorbance at 280 nm was monitored as a function of $[OH^-]$ up to 3 M where deprotonation is complete. The pK_a is 12.6 based on these experiments in 0.008–0.07 M NaOH and with no correction for activity effects.

The alkoxy derivatives were too insoluble for their deprotonation to be followed in water, but **3a** is deprotonated in CTACl/NaOH. The deprotonation was measured at 280 or 300 nm where the amidoxime aborbs weakly and the amidoximate ion strongly in CTACl solutions. The absorbance becomes constant at ca. 1 M NaOH and above 1.5×10^{-3} M CTACl, suggesting that deprotonation is complete in these solutions. The extent of deprotonation in NaOH and varying [CTACl] was obtained from the absorbance in these solutions relative to those in 1 M NaOH and CTACl. The deprotonation is ~80% complete (Tables I and II) so that we could neglect the contribution of the benzamidoxime to the absorbance. As expected, the extent of deprotonation of **3a** went through a maximum with increasing [CTACl].[10] In all these experiments at high pH, we used freshly prepared solutions to avoid decomposition of the benzamidoxime. Turbidity problems prevented our measuring the extent of deprotonation of **3b**.

Micellar Binding. The binding constant, K_s, of benzamidoxime to micellized CTACl was determined spectrophotometrically at 280 nm by following standard methods, and $K_s = 11$ M^{-1}.[13]

Results and Discussion

Reaction with Benzamidoximate Ion in the Absence of Surfactant. Benzamidoxime is a weak acid (pK_a = 12.6), and we used high pH to study reaction of the amidoximate ion and allowed for the contribution of the accompanying reaction of OH^-. We used 0.1 M benzamidoxime hydrochloride with 0.12 M NaOH, equivalent to 0.1 M amidoxime and 0.02 M NaOH. This solution had a pH of 11.8, and $k_\psi = 2.03 \times 10^{-2}$ s^{-1} for the overall reaction.

The contribution of reaction with OH^- to k_ψ was 3.1×10^{-3} s^{-1} on the basis of the pH of the solution,[14] so that of the rate constant of the benzamidoximate reaction was 1.7×10^{-2} s^{-1}. In calculating the second-order rate constant

Table IV. Effect of OH^- on the Reaction of p-(Hexyloxy)benzomidate Ion[a]

10^3[NaOH], M	1.0	2.0	7.0	10.0	15.0	20.0
k_ψ, s^{-1}	0.077	0.080	0.19	0.25	0.26	0.33

[a] At 25.0 °C with 10^{-3} M CTACl and 5×10^{-4} M **3a**.

Table V. Effect of CTACl on the Reaction of p-(Hexyloxy)benzamidate Ion[a]

10^3[CTACl], M	k_ψ, s^{-1}	k_{OH},[c] s^{-1}	k_ψ,[c] s^{-1}	k_M, s^{-1}
1.0	0.33[b]			
1.5	0.23	0.015	0.21	0.8
2.0	0.23	0.02	0.21	1.1
2.5	0.19	0.04	0.15	0.9
3.0	0.16	0.05	0.11	0.8

[a] At 25.0 °C with 10^{-2} M NaOH and 5×10^{-4} M **3a** unless specified. [b] 10^{-3} M **3a**. [c] Reference 19.

Table VI. Reaction of p-(Dodecyloxy)benzamidoximate Ion[a]

10^5[3b], M	10^4[CTACl], M	k_ψ, s^{-1}
0.25	0.21	0.0048
0.50	0.42	0.0050
1.30	1.10	0.011
2.50	2.10	0.026
5.00	4.20	0.16
13.0	11.0	0.10[b]

[a] At 25.0 °C with 10^{-2} M NaOH. [b] Turbid solution.

for this reaction, we used pK_a = 12.5, corrected for the ionic strength of ca. 0.1 by using the Davis equation,[15] and estimated a second-order rate constant of 0.9 M^{-1} s^{-1} for reaction of benzamidoximate ion. We also calculated the concentrations of OH^- and benzamidoximate from the stoichiometry of deprotonation and then estimated a second-order rate constant of 0.8 M^{-1} s^{-1} for reaction of benzamidoximate ion.

Reactions in CTACl–Benzamidoxime. Added CTACl increases k_ψ (Table III), but the contribution of reaction with benzamidoximate ion is relatively small, and at pH 10.7 there is a major contribution of reaction with OH^-. The small rate enhancement due to added benzamidoximate can be ascribed to the relatively high pK_a of benzamidoxime, and its weak binding to the micelle (Experimental Section).

***p*-Alkoxybenzamidoxime.** The *p*-alkoxy derivatives **3a,b** are almost completely insoluble in water, but reactions are relatively rapid in CTACl, where the amidoximates are deprotonated and should be extensively micellar bound. (Tables I and II.)

We could not follow the reactions over a wide range of [CTACl] or $[OH^-]$ because the solutions were cloudy, and we could use only dilute amidoxime. For reaction with **3a** and 10^{-3} M CTACl, k_ψ increases steadily with increasing $[OH^-]$. The reaction is much faster than in the absence of amidoxime (Table IV), and the rate increases with increasing formation of amidoximate ion. The reaction is very slow at low pH. With constant $[OH^-]$ k_ψ decreases with increasing [CTACl] (Table V). Under these conditions the substrate should be extensively micellar bound, and the decrease in k_ψ can be ascribed to two factors: (i) "dilution" of reactants in the micellar pseudophase and (ii) competition between OH^- and Cl^- for the micelle, which, with increasing [CTACl], will decrease the extent of deprotonation in the micellar pseudophase.[10] The

(13) The binding constant is given by $K_s = [S_M]/[S_w]([CTACl] - cmc)$, where S_M and S_w denote substrate in the micellar phase and aqueous pseudophase, respectively.

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Table VII. Effect of OH^- on the Reaction of *p*-(Dodecyloxy)benzamidoxime Ion[a]

10^3[NaOH], M	1.0	5.0	10.0	10.0	15.0	20.0
k_ψ, s^{-1}	0.028	0.032	0.083	0.10[b]	0.11	0.17

[a] At 25.0 °C with 2.1×10^{-3} M CTACl and 2.5×10^{-4} M **3b** unless specified. [b] 1.3×10^{-4} M **3b** and 1.1×10^{-3} M CTACl.

reactants are very hydrophobic and bind very strongly to the micelle, even in dilute CTACl, thus we did not observe the usual increase of k_ψ with increasing [surfactant].

Solutions were clear for most of the experiments with the dodecyloxy derivative (**3b**) shown in Table VI but were cloudy for all the experiments shown in Table VII, which complicated rate measurment. With a constant [**3b**] and [CTACl], k_ψ increased with increasing [OH^-] as expected (Table VII). The rate constants of reactions with **3b** were lower than those with **3a** because we were forced by solubility problems to use lower reagent concentrations.

We observed rate enhancements for these reactions of **4a,b** at well below the cmc of CTACl in water which are probably due to incorporation of the two hydrophobic reactants into aggregates of the surfactant,[6,8,16,17] generated by cooperative interaction of the three solutes. Reactions are often relatively rapid in these submicellar aggregates simply because the volume elements of reaction are small and the reactants are therefore in close proximity.[17] However, it is difficult to treat kinetics in these submicellar aggregates quantitatively, because of the difficulties in estimating the amounts of bound reactants and uncertainties regarding the structures of the aggregates.

Rate Constants with Bound Amidoximate. Reaction of benzamidoximate is only slightly speeded by surfactant (Table III), and it is not feasible to analyze quantitatively rate–surfactant relations for reaction of **4b**, because we could use only a very limited range of conditions.

However, we can use the rate constants for reaction with **4a** in CTACl to obtain an approximate value of the second-order rate constant of reaction in the micellar pseudophase.

We chose conditions so that both reactants are fully micellar bound and reaction occurs wholly in the micellar pseudophase. The binding constant of pNPDPP to CTABr is ca. 10^4 M^{-1} (based on the concentration of micellized surfactant[9]), so that the substrate should be almost fully bound in 3×10^{-3} M CTACl. Under these conditions, and in 10^{-2} M NaOH, approximately 80% of **3a** is deprotonated (Table I), and we assume, by analogy with similar systems, that all the amidoximate is micellar bound.[10]

If the substrate is fully micellar bound, the corrected first-order rate constant is given by[9] eq 3, where m_B^s is the

$$k_\psi^c = k_M m_B^s = k_M[B^-]/([CTACl] - cmc) \quad (3)$$

molar ratio of bound benzamidoximate (B^-) to micellized surfactant, [B^-] is the concentration of micellar-bound amidoximate ion, which is assumed to be the total concentration, and k_M is the related second-order rate constant. There is a problem in estimating the concentration of micellized CTACl under the kinetic conditions. Typically one assumes that the cmc gives the concentration of monomeric surfactant,[18] although this assumption is correct only at the cmc. However, we see rate effects in very dilute surfactant, well below the cmc in water, and, therefore, in estimating k_M we assume that the concentration of micellized CTACl is the total concentration.

There is a contribution from the reaction of pNPDPP with OH^-, which should be similar to that in CTABr.[19] The interpolated first-order rate constants, k_{OH}, for this reaction are given in Table V, and the corrected values of k_ψ are given by eq 4.

$$k_\psi^c = k_\psi - k_{OH} \quad (4)$$

In estimating k_M we allowed for incomplete deprotonation of **3a** (Table I), assuming that **3a** is 80% deprotonated under all our conditions. The estimated values of k_M are in Table V, and within the uncertainties of our data, $k_M \approx 1$ s^{-1}. This second-order rate constant is calculated in terms of the concentration of amidoximate ion expressed as a molar ratio of amidoximate ion to surfactant head groups and cannot be compared with second-order rate constants based on concentrations expressed as molarity. However, k_M (s^{-1}) can be converted into a second-order rate constant, k_2^m (M^{-1} s^{-1}) on the basis of the concentration of amidoximate ion expressed as moles per liter of micellar Stern layer, by estimating the molar volume of the Stern layer. Elsewhere we have taken this volume to be 0.14 L[20] for CTABr, so that here we obtain eq 5.

$$k_2^m = 0.14 k_M \quad (5)$$

We could instead base our conversion factor upon the total volume of the micelle,[4,21,22] which would approximately double k_2^m, but, at present, there seems to be no reason to believe that one approach is better than the other.

Rate Constants in Aqueous and Micellar Pseudophases. The micellar enhancement of the rate of reaction of benzamidoximate with pNPDPP is too small for us to estimate the rate constant, k_M, for reaction in the micellar pseudophase (Table III), although the rate constant for reaction in water can be determined. The situation is different for reaction of the *n*-hexyloxy derivative **4a** for which we can estimate a rate constant in the micellar but not in the aqueous pseudophase and where in micelles of CTACl, $k_2^m \approx 0.14$ M^{-1} s^{-1}. This value is similar in magnitude to the rate constant of 0.9 M^{-1} s^{-1} for reaction of benzamidoximate ion in water, despite possible substituent effects of the *p*-hexyloxy group in **4a**.

The nucleophilicities of the amidoximate ions toward pNPDPP can also be compared with those of oximate ions, e.g., 2-quinolinecarbaldoximate (**5**) or *p*-nitrobenzaldoximate (**6**). In water at 25 °C, the second-order rate constants for reactions of the oximate ions **5** and **6** are 1.87 and 1.38 M^{-1} s^{-1}, respectively,[6a] which are similar to that of 0.9 M^{-1} s^{-1} for reaction of benzamidoximate ion.

For reaction in CTABr the second-order rate constants, k_2^m, for reaction in the micellar pseudophase are 0.57 and 0.46 M^{-1} s^{-1} for reactions of **5** and **6**, respectively,[6c] and are similar to that of 0.14 M^{-1} s^{-1} for reaction of the amidoximate ion **4a** in CTACl micelles.

There are now many examples of reactions of nucleophilic anions for which second-order rate constants in the micellar pseudophase are similar to those in water, and the

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overall rate enhancements are due largely to concentration of the two reactants into the small volume of the micelles.[4,6b,c,9,20-22] For deacylation by oximate ion, Berezin and his co-workers concluded that second-order rate constants in the micellar pseudophase were slightly greater than those in water,[21] but for many reactions the reverse seems to be true. The comparisons depend slightly upon the assumed volume element of reaction and the method of estimating concentrations in the micellar pseudophase, so that exact agreement is not to be expected. In addition, the assumed volume element of reaction in the micelle should depend upon the specific reaction and the average location of reactants in the micelle. However, for dephosphorylations by amidoximate and oximate ion (**4–6**) the micellar rate enhancements are due almost wholly to concentration of the reactants into the small volume of the micellar pseudophase.

Intramolecular participation by the NH_2 moiety in deacylations and dephosphorylations has been suggested, because of the relatively high nucleophilicity of amidoximes,[7] but the similarity of the nucleophilicities of the oximate and amidoximate ions toward pNPDPP shows that participation is unimportant in reactions of the anions (cf. ref 8). However, undissociated amidoximes seem to be better nucleophiles than oximes.[7,8]

Although oximate and amidoximate ions have similar nucleophilicities, under practical conditions oximes are by far the more useful agent simply because with $pK_a \approx 10$ they give the reactive ion at relatively low pH, whereas amidoximes, with $pK_a \approx 12.6$, are deprotonated only in strongly alkaline solutions.

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Registry No. 1 (R = Ph), 613-92-3; **3a**, 80641-18-5; **3b**, 80641-19-6; **4a**, 80641-20-9; **4b**, 80641-21-0; *p*-hexyloxybenzonitrile, 66052-06-0; *p*-dodecyloxybenzonitrile, 29147-92-0; CTACl, 112-02-7; pNPDPP, 10359-36-1.

Ion Binding and Micellar Effects upon Reactions of Carboxylic Anhydrides and Carbonate Esters

Hamad Al-Lohedan and Clifford A. Bunton*

Department of Chemistry, University of California, Santa Barbara, California 93106

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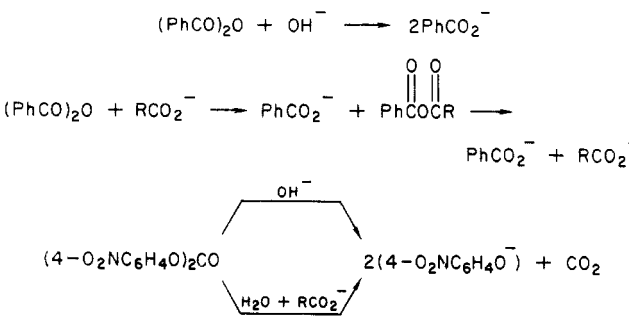
Cationic micelles speed reactions of benzoic anhydride and bis(4-nitrophenyl) carbonate with hydroxide and carboxylate ion. With micellized cetyltrimethylammonium bromide (CTABr) the variation of the first-order rate constant, k_ψ, with [CTABr] can be fitted to the pseudophase ion-exchange model, but this model fails when the counterion of the surfactant is OH^- or carboxylate ion. The variations of k_ψ with concentration of these reactive counterion surfactants fit a kinetic model in which the distribution of the nucleophilic anion between the aqueous and micellar pseudophases depends upon the concentration of nucleophilic ion. Despite the apparent differences between these two models, they predict similar values for the second-order rate constants of reaction of a given anion in the different types of micelles, and the implications of these findings to the interactions of micelles with counterions are discussed.

Micellar effects upon the reactions of nucleophiles with carboxylic esters have been extensively studied,[1] and the variations of rate constants with surfactant concentration have been explained quantitatively by considering the distribution of both reagents between aqueous and micellar pseudophases and the second-order rate constants in each pseudophase.[2-7]

Carboxylic anhydrides and diaryl carbonates are convenient substrates for study of micellar effects upon reaction rate because the reaction mechanisms are well understood,[8,9] and the reaction can be followed easily in dilute solution. We examined micellar effects upon reactions of benzoic anhydride or bis(4-nitrophenyl) carbonate with

Scheme I



OH^- or carboxylate ion in water (Scheme I). These substrates should bind readily to micelles.[10] The reagents were chosen so that the first step is followed kinetically. For example, in the reaction of benzoic anhydride with carboxylate ion we used formate ion, because the first-formed mixed anhydride goes readily to products.[11] Reaction of bis(4-nitrophenyl) carbonate with H_2O gives a short-lived intermediate carbonate, and carboxylate ions are general-base catalysts of water reaction.[9a]

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