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# Micelles of an Oxime-Functionalized Imidazolium Surfactant. Reactivities at Phosphoryl and Sulfonyl Groups

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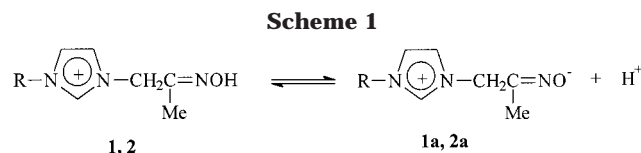
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Micelles of deprotonated 1-cetyl-3-(2-oximopropyl)imidazolium chloride strongly accelerate displacements of 4-nitrophenoxide ion from 4-nitrophenyl diethyl phosphate and 4-nitrophenyl tosylate. The first-order rate constants of reactions of fully bound substrates are similar to those predicted from second-order rate constants of reactions of deprotonated 1-methyl-3-(2-oximopropyl)imidazolium chloride in water and a reasonable value of the molar volume of the micellar interfacial region.

Cationic micelles accelerate reactions of anionic nucleophiles and bases with micellar-bound substrates due largely to concentration of the two reactants in the small volume of the micellar interfacial region.<sup>1</sup> Functional micelles with a nucleophile bound covalently to the headgroup strongly accelerate reactions at acyl and phosphoryl groups.<sup>1c,d,2</sup> We have examined oximolysis of 4-nitrophenyl diethyl phosphate (NPDEP) and 4-nitrophenyl tosylate (NPOTos) in functional micelles of an imidazolium derived surfactant, **1a**, (R = *n*-C<sub>16</sub>H<sub>33</sub>) and related the rate constants to those of the short-chain, monomeric derivative **2a** (R = Me) in water (Scheme 1).<sup>3</sup>

Oximate ions are effective nucleophiles at acyl, phosphoryl, and sulfonyl centers and are potentially useful decontaminants of toxic phosphonates.<sup>5,6</sup> Some functional surfactants are sparingly water soluble and are therefore comicellized with inert surfactants, but **1**, **1a**, is



sufficiently soluble to be used at concentrations that give complete binding of NPDEP and NPOTos.

First-order rate constants,  $k_{\text{obs}}$ , for reactions with **1a** were measured at 25.0 °C and pH 12.9, where deprotonation is complete and  $k_{\text{obs}}$  is pH independent. They increase very sharply in dilute **1a** and become approximately constant with fully bound substrate (Figure 1). In these conditions, reactions of OH<sup>−</sup> in water are relatively slow, and first-order rate constants,  $k'_{\text{OH}}$ , are  $7.6 \times 10^{-4}$  and  $6.4 \times 10^{-4} \text{ s}^{-1}$  for reactions of NPDEP and NPOTos, respectively. Reactions of OH<sup>−</sup> are inhibited by zwitterionic micelles,<sup>7</sup> and with micellar-bound substrate can be neglected, except in very dilute surfactant. Reactions with monomeric **1a** are relatively unimportant, because second-order rate constants for reactions of **2a** in water at pH 12.9 are  $8.4 \times 10^{-3}$  and  $1.5 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ , for NPDEP and NPOTos, respectively, and the critical micelle concentration (cmc) is very low. Values of  $k_{\text{obs}}$  for the reaction of NPOTos increase monotonically below the cmc of **1a** in water (Figure 1) due to reaction in premicelles or substrate-induced micellization.<sup>8</sup> The cmc of **1a** at pH 12.9 is  $2.5 \times 10^{-4} \text{ M}$ .

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(1) (a) Martinek, K.; Yatsimirsky, A. K.; Levashov, A. V.; Berezin, I. V. In *Micellization, Solubilization and Microemulsions*; Mittal, K. L., Ed.; Plenum Press: New York, 1977; Vol. 2, p 489. (b) Romsted, L. S. In *Micellization, Solubilization and Microemulsions*; Mittal, K. L., Ed.; Plenum Press: New York, 1977; Vol. 2, p 509. (c) Romsted, L. S. In *Surfactants in Solution*; Mittal, K. L., Lindman, B., Eds.; Plenum Press: New York, 1984; Vol. 2, p 1015. (d) Bunton, C. A.; Savelli, G. *Adv. Phys. Org. Chem.* **1986**, *22*, 213. (e) Bunton, C. A.; Nome, F.; Quina, F. H.; Romsted, L. S. *Acc. Chem. Res.* **1991**, *24*, 357.

(2) (a) Bunton, C. A.; Hamed, F. H.; Romsted, L. S. *J. Phys. Chem.* **1982**, *86*, 2103. (b) Bunton, C. A.; Scrimin, P.; Tecilla, P. *J. Chem. Soc., Perkin Trans. 2* **1996**, 419. (c) Scrimin, P.; Ghirlanda, G.; Tecilla, P.; Moss, R. A. *Langmuir* **1996**, *12*, 6235. (d) Scrimin, P.; Tecilla, P.; Tonellato, U.; Bunton, C. A. *Colloids Surf., A* **1998**, *144*, 71.

(3) The imidazolium ions were prepared from the *N*-alkylimidazoles by the general method of Poziomek et al.,<sup>4</sup> and structures were confirmed by elemental analysis and the <sup>1</sup>H NMR spectra. The cmc of **1a** was determined by using fluorescein. The  $pK_a$  of **2** of 10.7 was determined potentiometrically and from the dependence of  $k_{\text{obs}}$  on pH. Formation of 4-nitrophenoxide ion at 25.0 °C was followed spectrophotometrically (400 nm) with  $<5 \times 10^{-5} \text{ M}$  substrate.

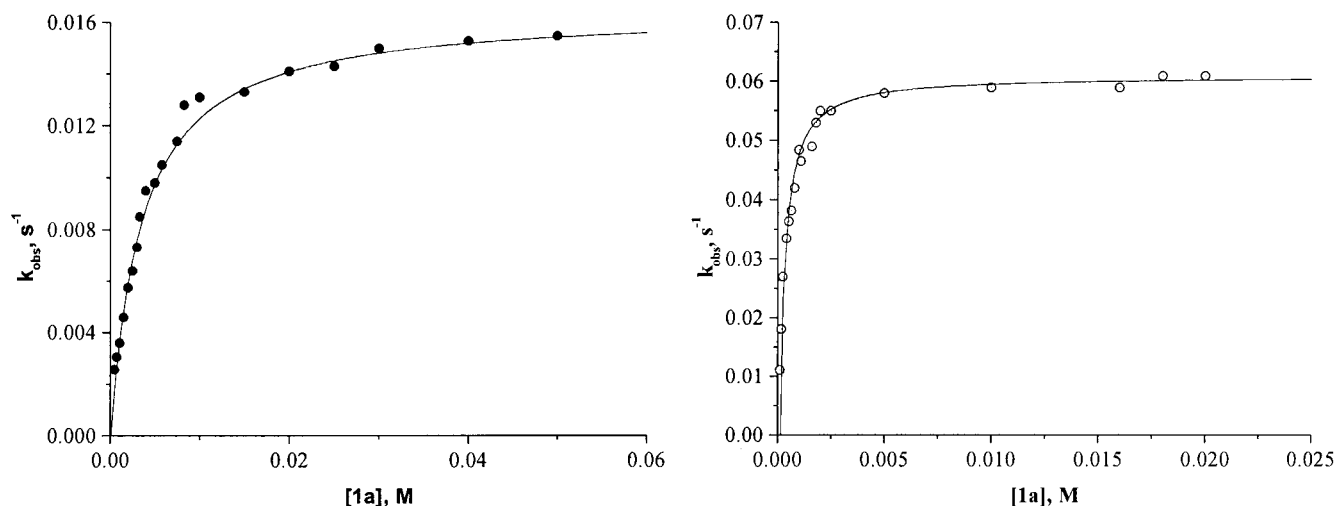
(4) Poziomek, E. J.; Hackley, B. E.; Steinberg, G. M. *J. Org. Chem.* **1958**, *23*, 714.

(5) (a) Epstein, J.; Kaminski, J. J.; Bodor, N.; Enever, R.; Sowa, J.; Higuchi, T. *J. Org. Chem.* **1978**, *43*, 2816. (b) Fornasier, R.; Tonellato, U. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 1302. (c) Bunton, C. A.; Foroudian, H. J.; Gillitt, N. D. *Langmuir* **1999**, *15*, 1067.

(6) (a) Yang, Y.-C.; Baker, J. A.; Ward, J. R. *Chem. Rev.* **1992**, *92*, 1729. (b) Yang, Y.-C. *Chem. Ind. (London)* **1995**, 334.

(7) (a) Bunton, C. A.; Mhala, M. M.; Moffatt, J. R. *J. Org. Chem.* **1987**, *52*, 3832. (b) Bunton, C. A.; Mhala, M. M.; Moffatt, J. R. *J. Phys. Chem.* **1989**, *93*, 854.

(8) (a) Drennan, C. E.; Hughes, R. J.; Reinsborough, V. C.; Soriyan, O. O. *Can. J. Chem.* **1998**, *76*, 152. (b) Brinchi, L.; Di Profio, P.; Germani, R.; Giacomini, V.; Savelli, G.; Bunton, C. A. *Langmuir* **2000**, *16*, 222.



**Figure 1.** Variations of  $k_{\text{obs}}$  with concentration of **1a** at pH 12.9: left, NPDEP; right, NPOTos.

Except in very dilute surfactant variations of  $k_{\text{obs}}$  with  $[1a]$  are fitted by eq 1.<sup>9</sup>

$$k_{\text{obs}} = (K'_{\text{OH}} + k_2^{\text{m}} K_{\text{S}} ([1a]_{\text{M}} / V_{\text{M}})) / (1 + K_{\text{S}} [1a]_{\text{M}}) \quad (1)$$

where  $k_2^{\text{m}}$  is the second-order rate constant, M<sup>-1</sup> s<sup>-1</sup>, for reaction with the oximate, **1a**, in the micellar interfacial reaction region with concentration of **1a** as local molarity, which is  $1/V_{\text{M}}$ , where  $V_{\text{M}}$  is the molar volume of this region, and  $K_{\text{S}}$ , M<sup>-1</sup>, is the substrate association constant in terms of micellized **1a** and  $[1a]_{\text{M}} = [1a]_{\text{T}} - \text{cmc}$ . Quantities in square brackets are concentrations in terms of total solution volume. Reactions with OH<sup>-</sup> in the zwitterionic micelle are neglected in eq 1, as is reaction of monomeric **1a** in the aqueous pseudophase. Equation 1 can be linearized in a double reciprocal form,<sup>9</sup> which gives rate and equilibrium constants that fit the rate-surfactant profiles.

The lines in Figure 1 are predicted by using parameters from eq 1 in the double reciprocal form<sup>9</sup> (eq 2), but without data in very dilute surfactant where there is reaction at [surfactant] < cmc.

$$1/(k_{\text{obs}} - K'_{\text{OH}}) = 1/((k_2^{\text{m}}/V_{\text{M}}) - K'_{\text{OH}}) + 1/(K_{\text{S}}((k_2^{\text{m}}/V_{\text{M}}) - K'_{\text{OH}})([1a] - \text{cmc})) \quad (2)$$

For NPDEP  $K_{\text{S}} = 280 \text{ M}^{-1}$  and  $k_2^{\text{m}}/V_{\text{M}} = 0.0165 \text{ s}^{-1}$ , and for NPOTos  $K_{\text{S}} = 4 \times 10^3 \text{ M}^{-1}$  and  $k_2^{\text{m}}/V_{\text{M}} = 0.061 \text{ s}^{-1}$ . The cmc in kinetic conditions is taken as  $2.5 \times 10^{-4}$  and  $10^{-4} \text{ M}$  for reactions of NPDEP and NPOTos, respectively.

With fully bound substrate, eq 1 gives

$$k_{\text{obs}} = k_2^{\text{m}}/V_{\text{M}} \quad (3)$$

For many reactions of nucleophilic anions values of  $k_2^{\text{m}}$  are similar to, or slightly lower than, second-order rate constants in water,  $k_{\text{W}}$ ,<sup>1c-e</sup> depending on the nature of the reaction and the value of  $V_{\text{M}}$ , which for trimethylammonium micelles is generally assumed to be in the range  $0.14\text{--}0.37 \text{ M}^{-1}$ ; cf. ref 1. However,  $V_{\text{M}}$  may depend on the headgroup, and a value of  $0.5 \text{ M}^{-1}$  was used in fitting data for reactions in metallomicelles because of their bulky headgroups.<sup>2d</sup> We use this value here because the extended headgroup structure of **1**, **1a**, indicates that the interfacial region will be larger than that in a trimethylammonium micelle, although we do not know how these headgroups pack at the micellar surface. The spread of values of  $V_{\text{M}}$  gives an uncertainty of ca. 3 in  $k_2^{\text{m}}$ .<sup>1e</sup>

With  $V_{\text{M}} = 0.5 \text{ M}^{-1}$ , and provided that second-order rate constants in water are the same for reactions with **1a** and **2a**, cf. ref 10, values of  $k_2^{\text{m}}/k_{\text{W}}$  are 1 and 2 for reactions of NPDEP and NPOTos, respectively. They are close to unity within the approximations of our treatment<sup>1e</sup> and a possible dependence of  $V_{\text{M}}$  on headgroup and substrate structures. The relative values of  $K_{\text{S}}$  indicate that NPOTos is more hydrophobic than NPDEP, and if it locates deeper in the interfacial region, our value of  $V_{\text{M}} = 0.5 \text{ M}^{-1}$  will be too high, as will  $k_2^{\text{m}}$  for NPDEP. These results are qualitatively consistent with the conclusion that the high concentration of oximate moiety in the interfacial region is the major source of the rate enhancements.<sup>1,2,5</sup> This generalization fits extensive data on nucleophilic reactions in functional micelles and comicelles, although for the latter allowance has to be made for dilution by inert surfactant and in some cases for incomplete deprotonation.<sup>2</sup>

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(9) Menger, F. M.; Portnoy, C. E. *J. Am. Chem. Soc.* **1967**, *89*, 4698.

(10) Guthrie, J. P. *Can. J. Chem.* **1973**, *51*, 3494.