Quantitative Treatment of Micellar Catalysis of Reactions Involving Hydrogen Ions[1]

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At concentrations of sodium lauryl sulfate (NaLS) greater than 10^{-2} M the acid benzidine rearrangement of 1,2-diphenylhydrazine (1) is second order in micellar bound hydrogen ions and first order in bound substrate, whereas the acid hydrolysis of *p*-nitrobenzaldehyde diethyl acetal (4) is first order with respect to each micellar bound reactant. The kinetic binding constant of 1 to the micelle agrees with that determined spectrophotometrically. Although the pseudophase distribution model is successful at moderately high concentrations of NaLS, it fails at very low concentrations probably because of the formation of submicellar aggregates.

Micellar catalysis of reactions in aqueous solution is generally explained in terms of a distribution of reactants between water and the micelles, with reactions occurring in both environments.[3] It should be possible therefore to treat the rate–surfactant profiles in terms of the concentrations of reactants in the aqueous and micellar pseudophases and the rate constants in each pseudophase. This approach has been applied to micellar catalyzed reactions of nonionic substrates with nonionic nucleophiles[8,9] and to reactions of hydrophobic anionic nucleophiles by estimating nucleophile concentrations in the micellar pseudophase.[8]

Except for reactions involving the hydrogen ion, this experimental approach has not been used for reactions of hydrophilic ions, although Romsted has shown how rate–surfactant profiles can be rationalized in terms of such a model[10] and a similar model has been used to treat micellar catalysis of nucleophilic addition to carbocations.[11]

The distribution of hydrogen ions between water and anionic micelles of sodium lauryl sulfate (NaLS) has been determined by several independent methods,[12] and under conditions in which the substrate was extensively micellar bound the rate–surfactant profiles for acetal hydrolysis depend on the concentrations of micellar bound hydrogen ions rather than on total concentration or activity.[13] The rate–surfactant profiles for the acid hydration of dihydropyridines in aqueous NaLS have also been interpreted in terms of the concentrations of micellar bound substrate and hydrogen ion, but in these systems there is a complication due to the formation of an unreactive conjugate acid by unproductive protonation.[14]

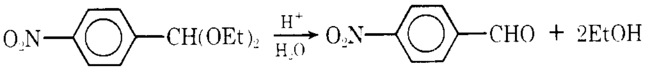
The acid benzidine rearrangement is a very convenient reaction for testing quantitative treatments of micellar catalysis because the reaction of 1,2-diphenylhydrazine (1) is second order in hydrogen ions in dilute acid.[15,16]

$$\underset{\mathbf{1}}{\mathrm{PhNH\text{-}NHPh}} \rightleftarrows \underset{\mathbf{2}}{\mathrm{PhN^+H_2NHPh}} \xrightarrow{H^+} \mathrm{H_2NC_6H_4{\cdot}C_6H_4NH_2}$$

The mechanism of this intramolecular rearrangement has been extensively studied, and N–N scission has been shown to be part of the rate limiting step.[17]

The catalysis of anionic micelles of sodium lauryl sulfate (NaLS) is large for two-proton rearrangements, with a maximum rate enhancement of ca. 2000 for the rearrangement of 1 and of ca. 4300 for the two-proton rearrangement of 1,2-ditolylhydrazine (3), whereas for one-proton rearrangements it is ca. 50.[18] These results are understandable if micellar catalysis depends strongly upon concentrations of reactants in the Stern layer at the water–micelle interface. There are sharp maxima in the rate–surfactant profiles, and at high surfactant concentrations there is dilution of hydrogen ions in the micellar pseudophase and the rate constants for reactions of 3 become smaller than in water. The aim of the present work was to interpret these profiles in terms of the concentrations of substrate and hydrogen ion in the micellar pseudophase. The distribution of 1 between water and the anionic micelles was estimated spectrophotometrically, and that of hydrogen ions had already been determined. [12,13]

In addition, we examined the rate–surfactant profiles of the hydrolysis of *p*-nitrobenzaldehyde diethyl acetal (4) in a similar way.[13]



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Because the rearrangement of 1,2-diphenylhydrazine (1) is second order with respect to hydrogen ions, its micellar catalysis provides a more sensitive test of the pseudophase distribution model than does the acetal hydrolysis.

Experimental Section

Surfactants. There are reports of the difficulties in obtaining samples of NaLS of purity such that they do not show surface tension minima.[19] In our present experience the only commercial material which did not exhibit such minima after purification was supplied by Atomergic. We also prepared material by treating lauryl alcohol (0.5 mol) with freshly distilled $ClSO_3H$ (1 mol) in Et_2O under reflux for several days under N_2. The mixture was then neutralized (NaOH), and volatiles and Na_2SO_4 were removed. Both samples were purified by several recrystallizations (EtOH), and we found no surface tension minima. The cmc of the Atomergic sample was 0.007 M, and that of our sample was 0.0076 M at 23 °C, in reasonable agreement with literature values of ca. 0.008 M.[20]

Although both of our samples of NaLS had no minima in plots of surface tension against log [NaLS], we found small (1–2 dyn) minima with mixtures of HCl and NaLS. The surface tensions of NaLS solutions are sensitive to small amounts of surface active impurities, e.g., dodecanol.[19] Micellization speeds the acid-catalyzed hydrolysis,[21] but there should have been very little hydrolysis in the time required for measurement of the surface tension. It is difficult to explain these minima, unless a monolayer of undissociated lauryl sulfuric acid forms at the air–water interface.

These minima make it difficult to estimate the cmc by the surface tension method, but the approximate values of the cmc in the presence of HCl are 0.0055, 0.0045, and 0.0035 M in 0.001, 0.003, and 0.01 M HCl, respectively. These values are similar to those in solutions of NaCl, and therefore in treating the kinetics we estimated the cmc by interpolation of literature values for mixtures of NaCl and NaLS[20,22] and used the following values for the benzidine rearrangement: 0.006, 0.006, 0.005, 0.0045, and 0.004 M for 0.00099, 0.00165, 0.00198, 0.0052, and 0.0098 M HCl, respectively. For the acetal hydrolyses we used cmc values of 0.006, 0.0045, 0.004, and 0.0028 M for 0.001, 0.00316, 0.01, and 0.03 M HCl, respectively.

Incorporation of 1,2-Diphenylhydrazine (1). The binding of 1 to NaLS was determined spectrometrically.[14,23] Freshly prepared deoxygenated solutions were used, and 0.1 mL of a stock solution of 1.3×10^{-3} M 1 in 40:60 $EtOH-H_2O$ was added to 2 mL of the surfactant solution through a septum cap under N_2. The absorbance at 250 nm was immediately measured.

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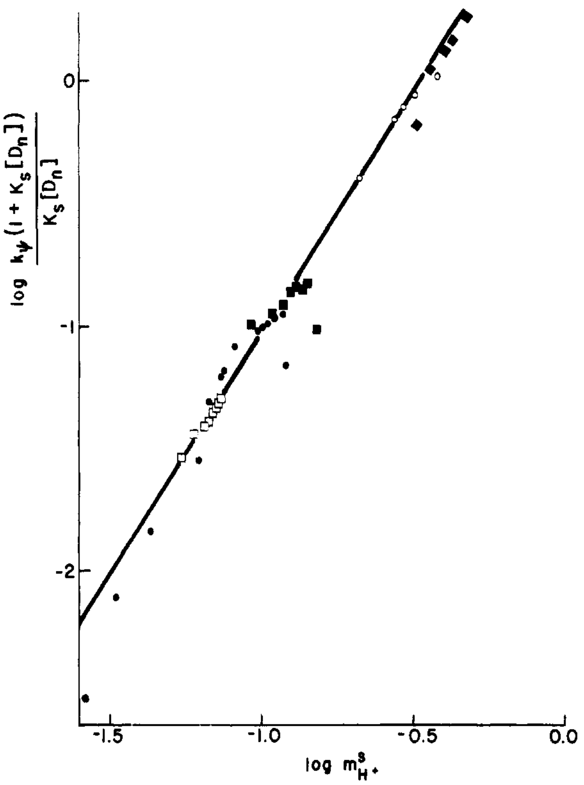


Figure 1. Determination of the kinetic order for the rearrangement of 1,2-diphenylhydrazine in solutions of NaLS at 25.0 °C: (□) 0.000992, (●) 0.00165, (■) 0.00198, (○) 0.0052, and (♦) 0.0098 M HCl.

The fraction, f, of micellar bound substrate at various surfactant concentrations was estimated from the absorbances, A:[14] $f = (A - A_0)/(A_\infty - A_0)$. The subscripts o and ∞ denote absorbances in water and with fully bound 1.

A plot of $f/(1 - f)$ against [NaLS] is linear up to 0.02 M NaLS with a slope $K_s = 220\ M^{-1}$ for both samples of NaLS. The intercept gives a cmc of 0.0075 M, in reasonable agreement with that in the absence of solute.

Results

Quantitative Treatment of Micellar Catalysis. The first-order rate constant, k_ψ, for reaction in the presence of micelles is given by eq 1,[24] where k_W' and k_M' are first-order

$$k_\psi = (k_W' + k_M' K_s[D_n])/(1 + K_s[D_n]) \qquad (1)$$

rate constants in the aqueous and micellar pseudophases, respectively, [D] is the concentration of surfactant (detergent), and K_s is the binding constant of the substrate to the micelles written in terms of micellized surfactant. The concentration of micellized surfactant $[D_n]$ is that of the surfactant less that of the monomeric surfactant, which is assumed to be constant and given by the cmc.

Equation 1 is derived on the assumption that the relation between the concentration of the micellar bound substrate, $[S_M]$, and the total concentration, $[S_T]$, is given by eq 2.

$$[S_M]/[S_T] = K_s[D_n]/(1 + K_s[D_n]) \qquad (2)$$

Equation 2 is valid only if there is negligible perturbation of the micelles by reactants, which requires that their concentrations must be much smaller than that of the surfactants.

The concentration of hydrogen ions in micelles of NaLS containing HCl and in the absence of added salt is written in terms of the mole ratio of hydrogen ions to micellized surfactant, $m_{H^+}{}^s$, which is given by eq 3.[12]

$$m_{H^+}{}^s = 0.82([H^+{}_T]/[H^+{}_T] + [Na^+{}_T]) \qquad (3)$$

In this empirical relation, total concentrations of $H^+{}_T$ and $Na^+{}_T$ are used, and in applying it to our kinetics we assumed that it is unaffected by micellar incorporation of the substrate. The dimensionless concentration $m_{H^+}{}^s$ can be converted into molarity in the micellar pseudophase using an appropriate volume element.[11,14]

Benzidine Rearrangement. The micellar catalysis of the two-proton benzidine rearrangement is so large that we can neglect reaction in the aqueous pseudophase, except in very dilute surfactant solutions.[18] Provided that there is no build up of monoprotonated substrate, the first-order rate constant, k_M', is given by eq 4, where k_M is a third-order rate constant, s^{-1}.

$$k_M' = k_M(m_{H^+}{}^s)^2 \qquad (4)$$

Equation 1 reduces to eq 5. If eq 5 is obeyed, a plot of log

$$k_\psi = \frac{k_M K_s (m_{H^+}{}^s)^2 [D_n]}{1 + K_s[D_n]} \qquad (5)$$

$k_\psi(1 + K_s[D_n])/K_s[D_n]$ against log $m_{H^+}{}^s$ should be linear with a slope of 2.

Several assumptions are made in this treatment. (i) The binding constant, K_s, to NaLS is assumed to be unaffected by dilute HCl. (ii) The value of monomeric surfactants is assumed to be given by the cmc in the presence of dilute HCl. (iii) The bindings of hydrogen ions and substrate to the micelle are assumed to be independent parameters. (iv) It is assumed that there is no buildup of monoprotonated substrate under the experimental conditions, which is reasonable because 1 is weakly basic.[18]

Assumptions i–iii are reasonable provided that the surfactant concentration is considerably above the cmc and [HCl], because then the counterions in the Stern layer are primarily sodium rather than hydrogen, and uncertainties in the value of the cmc become unimportant. However, there are serious problems in assigning values of the cmc under reaction conditions because there is extensive catalysis below the cmc of NaLS in water.[18]

In treating the data, we took $K_s = 220\ M^{-1}$, measured in NaLS in the absence of acid (Experimental Section), but nonetheless the results fit eq 5 reasonably well (Figure 1) over a tenfold range of $[HCl_T]$ considering the approximations in the treatment and in the estimation of $m_{H^+}{}^s$ and k_ψ.[25] The values of k_ψ are from ref 18, and from the intercept in Figure 1 we estimated k_M as 10 s^{-1}.

Equation 5 can be rearranged to give eq 6. The major

$$(m_{H^+}{}^s)^2/k_\psi = 1/(k_M K_s[D_n]) + 1/k_M \qquad (6)$$

problem in using an equation of this form is the sensitivity to the value of the cmc, especially at low surfactant concentrations. However, for the runs at the higher concentrations of acid, where the cmc is low, the data fit reasonably well, even for surfactant concentrations as low as 0.007 M (Figure 2). The scatter is not unreasonable, especially considering the uncertainties in the cmc under the reaction conditions and the dependence of rate on $(m_{H^+}{}^+)^2$.

From the slope and intercept, we estimate $k_M = 10\ s^{-1}$ and $K_s = 160\ M^{-1}$, which are in reasonable agreement with $K_s = 220\ M^{-1}$ in the absence of acid (Experimental Section). The agreement between the values of k_M determined using equations 5 and 6 is fortuitous because of the scatter in the data; but the differences in K_s may be significant because of the different conditions of the measurements, and there may be systematic deviations due to differences in [HCl] in the various reaction solutions.

Hydrolysis of *p*-Nitrobenzaldehyde Diethyl Acetal. In aqeous dilute acid this reaction is first order with respect to hydrogen ion concentration,[26] and provided that this is also true for reaction in the micellar pseudophase, eq 1 gives eq 7,

$$k_\psi = \frac{k_W[H^+{}_W] + k_M K_s m_{H^+}{}^s [D_n]}{1 + K_s[D_n]} \qquad (7)$$

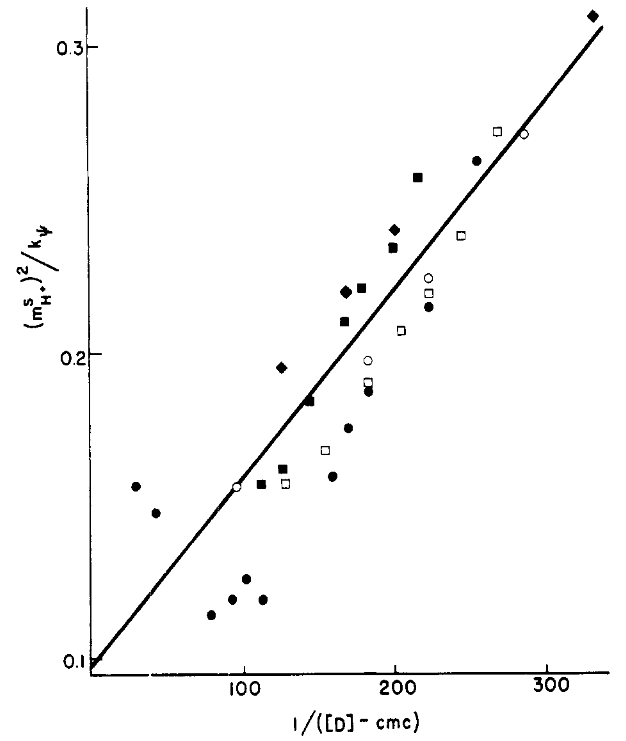


Figure 2. Determination of k_M and K_s for the rearrangement of 1,2-diphenylhydrazine in solutions of NaLS. The symbols are the same as in Figure 1.

where k_W, the second-order rate constant in water,[13] is 0.29 $M^{-1} s^{-1}$ and k_M, s^{-1}, is the second-order rate constant in the micellar pseudophase.

The concentration of hydrogen ions in the aqueous pseudophase, $[H^+_W]$, can be written in terms of the total hydrogen ion concentration, $[H^+_T]$, by eq 8 so that eq 7 gives eq 9.

$$[H^+_W] = [H^+_T] - m_{H^+}{}^s[D_n] \qquad (8)$$

$$(k_\psi - k_W[H^+_T])/m_{H^+}{}^s[D_n] = K_s k_M - k_W - k_\psi K_s/m_{H^+}{}^s \qquad (9)$$

Equation 9 can be treated graphically (Figure 3). (The values of k_ψ are from ref 13.) We did not use the results for experiments in which $m_{H^+}{}^s$ is much greater than 0.5 because eq 3 fails under these conditions.[12]

The results fit eq 7 reasonably well, and from the slope and intercept we obtain $K_s = 100\ M^{-1}$ and $k_M = 0.11\ s^{-1}$. (This value of k_M is, as expected, close to that estimated earlier from rate constants obtained under conditions in which the substrate is fully bound to the micelle.[13]) The value of K_s is in the expected range, for example, for the binding of methyl orthobenzoate to micelles of NaLS it is 73 M^{-1},[27] and we have estimated kinetically a value of $K_s = 73\ M^{-1}$ for the binding of the acetal 4 to micelles of tetradecanesulfonic acid.

Discussion

Reactivity in the Micellar Pseudophase. The rearrangement of 1,2-diphenylhydrazine is first order in substrate and second order in hydrogen ion concentration in the micellar pseudophase, and as in other systems[13,14] the rates do not depend directly on the overall hydrogen ion concentration or activity.

The value of k_M, s^{-1}, calculated using equations 5 and 6 cannot be compared directly with the usual form of the third-order rate constants, $M^{-2} s^{-1}$, in dilute strong acid, but comparison can be made by choosing a volume element for reaction in the micelles and so calculating the acid molarity in the micellar pseudophase. Following Stigter's model of micelles of NaLS,[28] we estimate the volume of the Stern layer in 1 mol of micellized surfactant as 140 mL.[29]

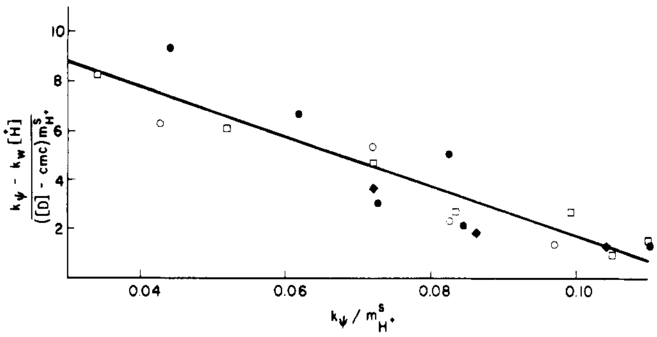


Figure 3. Determination of k_M and K_s for the acid hydrolysis of *p*-nitrobenzaldehyde diethyl acetal in solutions of NaLS at 25.0 °C: (○) 0.001, (□) 0.00316, (●) 0.01, and (♦) 0.03 M HCl.

On this basis the molarity of hydrogen ions in the Stern layer of micelles of NaLS is given by $m_{H^+}{}^s/0.14$, so that the third-order rate constant $k_3{}^m$, $M^{-2} s^{-1}$, is $0.14^2 k_M$. The value of $k_3{}^m$ for rearrangement of 1 is 0.2 $M^{-2} s^{-1}$, which is considerably smaller than the third-order rate constant of 16 $M^{-2} s^{-1}$ for rearrangement in dilute HCl.[18]

The value of k_M, s^{-1}, for the hydrolysis of *p*-nitrobenzaldehyde diethyl acetal can be converted into the usual form of the second-order rate constant $k_2{}^m = 0.015\ M^{-1} s^{-1}$. This rate constant is smaller than that of 0.29 $M^{-1} s^{-1}$ for reaction in dilute aqueous HCl.[13]

It appears therefore that both of these hydrogen ion catalyzed reactions are slower in the Stern layer of the micelle than in water if we estimate rate constants in terms of concentrations measured in moles per liter. This behavior is not unusual; for example, second-order rate constants for molecule–molecule reactions are generally smaller in the micellar pseudophase than in water,[8,9] as are those for the reaction of Malachite Green with 1-benzyldihydronicotinamide[11] and for the acid hydration of dihydropyridines.[14] The only reported exceptions appear to be deacylations by some imidazole anions in cationic micelles where the conclusions depend upon indirect estimates of the extent of micellar binding of the anionic nucleophiles.[8]

The effects of micelles on these second- and third-order rate constants are qualitatively akin to solvent effects because the reactions are slowed by the addition of organic solvents to water[13,15,18,26] and the Stern layers of micelles appear to be less polar than water.[4] The organic substrates have lower free energies in both micelles and organic solvents than in water, and this rate-retarding effect is apparently not offset by effects on the free energies of the hydrogen ion and the cationic transition state. In addition, micellized laurylsulfuric acid may not be strong (cf. ref 21), which would in effect reduce the acidity of micellar bound hydrogen ions. Therefore, as in so many other micellar catalyzed reactions, the rate enhancement is derived largely from concentration of reactants into a small volume.

The dependency of reaction rates upon the concentration of micellar bound hydrogen ion rather than on the total concentration or activity suggests that reaction rates and equilibria in other macromolecular systems, such as polyelectrolytes (cf. ref 30) and enzymes, should also be considered in terms of bound rather than total hydrogen ions.

Validity of the Pseudophase Model. For surfactant concentrations well above the cmc, the pseudophase distribution model (equations 1, 2, and 5) is reasonably satisfactory and the observed and predicted values of log k_ψ for the benzidine rearrangement of 1 (Figure 4) are in reasonable agreement, especially considering the sensitivity of log k_ψ to changes in $m_{H^+}{}^s$. But for the rearrangement of 1, values of k_ψ calculated from k_M and K_s using eq 5 do not agree with experiment values at low surfactant concentration. For example, in 1.65

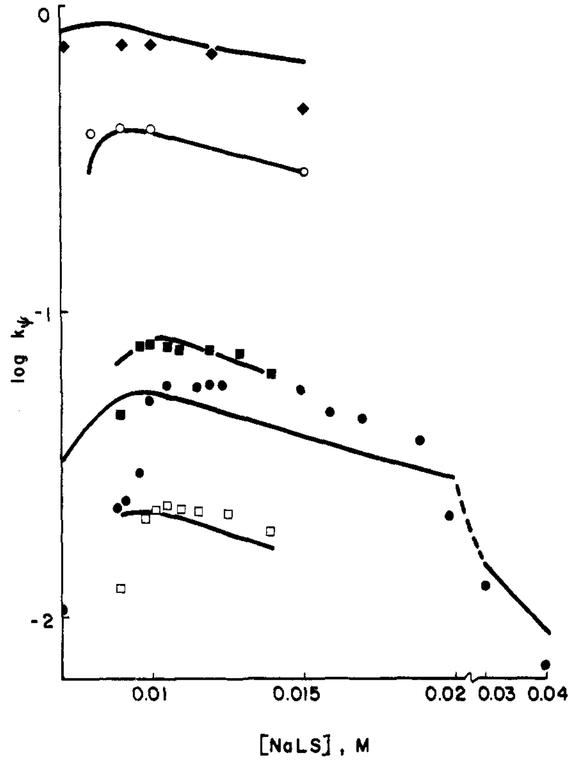


Figure 4. Comparison of observed and calculated values of the first-order rate constant, k_ψ, for rearrangement of 1,2-diphenylhydrazine. The lines are calculated using eq 5. The symbols are the same as in Figure 1.

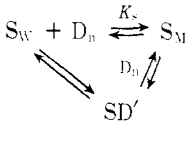
$\times 10^{-3}$ M HCl the predicted maximum value of k_ψ agrees reasonably well with the experiment value, but eq 5 does not predict the very rapid decrease of k_ψ at [NaLS] $< 10^{-2}$ M for reaction in 1.65×10^{-3} M HCl (Figure 4).

Equations 1–3 are derived on the assumption that the properties of the micelles are essentially unaffected by the reactants and that all of the surfactant is present either as monomers or as micelles. These conditions appear to be met at higher NaLS concentrations but not at low concentrations. Part of the problem lies in our method of estimating the concentration of monomeric surfactants, and even if we take the cmc as an adjustable parameter it is not possible to choose a value which fits a complete rate–surfactant profile for rearrangement of **1**.[18] (Problems of measurement of the cmc are noted in the Experimental Section.)

There are several problems with the assumption that the monomer concentration over a range of surfactant concentration is given by the cmc. Increase of ionic concentration decreases the cmc,[31] and presumably the monomer concentration. But only 70–80% of the head groups in ionic micelles are neutralized by counterions so that their concentrations in the aqueous pseudophase increase with increasing surfactant concentration,[10] and therefore the concentration of monomers should decrease, regardless of the presence of added solutes.[32] Added solutes complicate the situation because the relative concentration of surfactant to solute, e.g., substrate or hydrogen ions, changes with surfactant concentration. In addition, the micelles in our kinetic solvents can have both sodium and hydrogen ions as counterions in the Stern layer.

Failure of the assumption that the cmc gives the concentration of monomers under all conditions causes no (numerical) problem when the surfactant concentration is much larger than the cmc, but NaLS in relatively low concentration effectively catalyzes the rearrangement of **1**,[18] so it is understandable that the model fails under these conditions.

Scheme I



Many workers have noted failures of equations akin to eq 1 at low surfactant concentration and have ascribed them to induced micellization or the formation of submicellar aggregates rather than to an inherent failure of the assumptions made in deriving eq 1.[4–7,34,35]

Induced micellization does not appear to be of great importance here; for example, **1** only slightly reduces the cmc of NaLS (Experimental Section). However, submicellar aggregates must be considered (cf. ref 34–36). Such aggregates may well bind organic solutes, e.g., **1**, although not as well as a fully formed micelle. They would probably be ineffective at binding counterions, e.g., hydrogen ions, and thus would be poorer catalysts than a fully formed micelle. However, little appears to be known about the detailed structures of such aggregates, so that approaches invoking premicellar aggregates to explain these results are highly speculative.

Equation 2 describes the relation between free and bound substrate (S_W and S_M, respectively) in terms of a binding constant, K_s (Scheme I). In Scheme I, SD′ represents a submicellar–substrate complex, and if such complexes exist at low surfactant concentrations, the concentrations of S_M will be less than predicted by the usual treatment (eq 2). The relative importance of SD′ will decrease as the surfactant concentrations are increased.

It might be possible to describe the rate–surfactant profiles for reactions in very dilute NaLS in terms of equilibrium and rate constants involving SD′, but we see no way of doing this except by introducing adjustable parameters whose values could not be estimated by independent methods. The pseudophase distribution model, based on the concentration of micellar bound hydrogen ions, appears to be generally satisfactory, although we see no simple way of applying it quantitatively at low surfactant concentrations or under conditions in which reactants materially perturb micellar structures.

Registry No.—**1**, 122-66-7; **4**, 2403-62-5; NaLS, 151-21-3.

References and Notes

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Role of the Furan Ring in the Formation of Meisenheimer-Type Adducts

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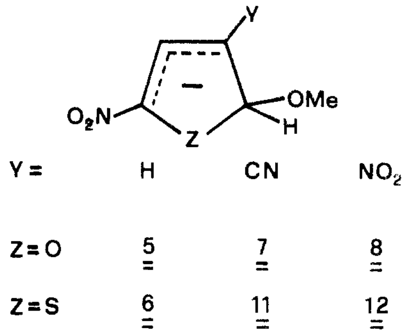
The rate and equilibrium constants for the formation of Meisenheimer adducts from 2-nitrofuran and 4-cyano-2-nitrofuran have been measured in methanol at 25 °C. Kinetic measurements have also been made for the formation of a related adduct from 2,4-dinitrofuran. The comparison of these data with those previously observed for the formation of adducts from the corresponding thiophene derivatives shows an accelerating and stabilizing effect of the furan ring in the formation of adducts. On the other hand, an increased lability of the adducts is also observed in the furan series.

The quantitative aspects of the reactivity of the furan ring in nucleophilic aromatic substitution have been recently compared with those of the thiophene ring.[1–3] The activating effect of the former is stronger than that of the thiophene ring. As to the reaction mechanism, an addition–elimination mechanism via the formation of an anionic intermediate σ complex is well established in the case of thiophene derivatives.[4]

A main piece of evidence in favor of the addition–elimination mechanism is the actual detection or isolation of Meisenheimer-type adducts from several electron-deficient thiophene compounds and nucleophilic reagents.[5–9] Rate and equilibrium constants for the formation of some of these adducts have also been reported, particularly in view of a comparison between adducts formed from benzene and thiophene derivatives.[6,7]

Similar information was lacking as to the formation of Meisenheimer adducts from furan derivatives. Therefore, we have become interested in investigating the following points: (i) whether adducts could be detected or isolated in the interaction between electron-deficient furans and methoxide ion or other nucleophiles; and (ii) to what extent the furan ring, in comparison with the thiophene ring, would affect the equilibrium and rate constants in the formation of adducts.

Following a preliminary communication,[10] where we showed that 2-nitrofuran (**1**) and 2-nitrothiophene (**2**) undergo addition of methoxide ion at the hydrogen-bearing α positions, yielding Meisenheimer adducts **5** and **6**, respectively, we report here kinetic and equilibrium data for these reactions in methanol. Moreover, we describe the formation of adducts upon interaction of methoxide ion with 4-cyano-2-nitrofuran (**3**) and 2,4-dinitrofuran (**4**). It was expected that the presence of two electron-withdrawing groups should provide a greater stabilization of the resulting adducts and give more general information on the role of the furan ring.



Experimental Section

Melting points are uncorrected. UV–vis, NMR, and mass spectral characterizations of the products were made as described in ref 5b.

Materials. 2-Nitrofuran was obtained according to an optimized procedure.[11] **2-Nitrothiophene,** free from 3-nitrothiophene, was obtained by decarboxylation of 5-nitrothienoic acid.[12]

3-Cyanofuran. The amide of 3-furoic acid was converted to the title compound by a standard procedure. After the usual workup, a solid (mp 24–26 °C) was obtained upon reduced pressure distillation (3-cyanofuran had been previously reported[13] as a liquid); IR (ν_{CN} 2250 cm^{-1}) and NMR data [(in $CDCl_3$) δ 6.60 (m, 1 H), 7.46 (m, 1 H), 7.91 (m, 1 H)] were in accordance with the structure of the compound (yield 73%).

4-Cyano-2-nitrofuran (3). A solution of 3.0 g of 3-cyanofuran in 7 g of acetic anhydride was slowly added to a well-stirred nitrating mixture made up from 20.1 g of 99% HNO_3 and 32 g of acetic anhydride at a temperature lower than 10 °C. At the end of the addition, the reaction mixture was poured onto ice and extracted repeatedly with ethyl ether. The residue on evaporation of ether was an oil containing **3** and at least another product. Upon chromatography on silica