Positronium Reactions in Micellar Systems[1]

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Abstract: The rate constants for Ps reactions with nitrobenzene and $CuCl_2$ in various micellar systems such as sodium dodecyl sulfate, sodium octyl sulfate and sulfonate, hexadecyltrimethylammonium bromide and chloride, hexadecylpyridinium chloride, and tergitol were measured. The results show that in most cases the Ps reactivity toward nitrobenzene is significantly reduced when the latter is located in the micellar phase as compared to the homogeneous aqueous phase. On the other hand, the observed reaction constants do not coincide with the constants measured for Ps-nitrobenzene in the corresponding alkanes either, with the exception of sodium octyl sulfate and sulfonate. Since Ps-nitrobenzene reaction rate constants were found to be sensitive to the environment in which they occur, these results may suggest that the nitrobenzene probe molecule is located in the Stern layer where it forms complexes with the various head groups, in which form its reactivity toward Ps will be decreased. An exception could be the sodium octyl sulfate system, where nitrobenzene may be in an aqueous environment, or the sodium octyl sulfonate where the nitrobenzene may reside in a hydrocarbon-like environment. In micellar solutions containing Cu^{2+} ions, no change in the Ps rate constants is observed in the case of the neutral tergitol or the cationic hexadecylpyridinium chloride micellar systems, whereas in the presence of the anionic micelles, sodium dodecyl sulfate or sodium octyl sulfate or sulfonate, which easily adsorb Cu^{2+} ions, the rate constants drastically drop.

Surface active compounds are frequently used to solubilize molecules which otherwise would not be soluble in water. The mechanism of this solubilization involves the formation of aggregates of surfactant molecules which are called micelles and in which the solubilizate is contained. Because of the great practical importance of the micellar chemistry in detergency processes as well as for its relationship to the natural aggregation of hydrophobic moieties which form biomembranes this area of chemistry has been under active investigation in the recent past and several reviews describing micelles and micellar phenomena have been published.[2]

While the structure of a micelle is fairly well understood in terms of a spherical entity with a viscous hydrocarbon-like core and a polar exterior containing the charged head groups of the surfactant molecule, still more detailed information is needed about the location of the solubilizate in the micelle as well as about the dynamics of the solubilization process.

Several techniques such as NMR, ESR, and fluorescence probes have been employed to define the location of the solubilizate in the micelle.[2]

By comparing the spectral characteristics of probe molecules observed in the presence of micellar systems with those which the probe molecules display in a homogeneous aqueous solution or in an alkane, which would resemble the hydrocarbon-like core of the micelle, conclusions have been reached as to the position of the probe molecules in the micelle.[2]

Since micellar systems catalyze many reactions extensive studies were made to evaluate the influence of the micelle on the course of reaction by comparing reactions in micellar and homogeneous solutions. These studies involved among others the external quenching of the fluorescence of probe molecules and the reactions of hydrated electrons. In the latter case a clear dependence of the reaction rates on the micellar charge was observed.[2]

In the following the results of a study shall be reported in which the reactions of positronium with probe molecules in micellar systems were investigated as a potential new tool for the determination of the location of a probe molecule in the micelle and the effect of micelles on the chemical reaction process.

A positron may combine with an electron to form an electron–positron bound state, the positronium atom (Ps). This species has a lifetime of about 10^{-7}–10^{-9} s, which is too short for its reactions to be followed by conventional product analysis. The chemical reactions of positronium can be studied by observing changes in its average lifetime and decay modes which are dependent on the chemical reactivity and physical composition of its environment.[3]

By using these methods Ache et al.[4] have been able to show that Ps undergoes reversible molecular complex formation in solutions with compounds which are known in conventional chemistry as strong complex formers, such as nitrobenzene, benzoquinone, etc. Temperature studies were carried out which resulted in an assessment of the kinetics and the activation parameters of these processes.

Furthermore, these authors were able to show that these Ps molecules complexes are stabilized to various degrees in different solvent,[4,5] a fact which is reflected in the measured overall reaction rate constants. Thus the comparison of the rate constants obtained for Ps interaction with probe molecules in micellar systems with those observed in the aqueous solution or in an appropriate alkane should provide information about the location of the probe molecule in the micelle, since Ps reactions are fast in relation to the time to transfer the probe molecule from a micellar to an aqueous environment. Positronium, being a neutral species, should not be repelled by the charges on the micelle surface and should be able to effectively penetrate into the micelle.

Thus, the Ps reaction rate constants with nitrobenzene and $CuCl_2$ were determined in micellar solutions of seven surfactants (Table I). While the reactivity of nitrobenzene toward Ps is reduced in each of the micellar systems with respect to its reactivity in water or the corresponding alkane, neutral and cationic micelles have relatively little or no effect on the Ps reactivity toward Cu^{2+}. The results will be discussed by assuming that nitrobenzene molecules are preferentially located in the Stern layer[2] and that Cu^{2+} ions are attracted by the negatively charged micelles, immobilizing the Cu^{2+} ions or reducing their reactivity when absorbed on the surface of the micelle.

Experimental Section

A. Purity of Compounds. Sodium dodecyl sulfate (NaLS), obtained from Aldrich Co., was recrystallized in 95% ethanol and dehydrated in a desiccator (with P_2O_5) under vacuum.[6] The purification process was repeated until subsequent melting point measurements agreed with literature values within ±1.0 °C. Hexadecyltrimethylammonium bromide (CTAB) and hexadecylpyridinium chloride (CPyCl) were obtained from Pfaltz-Bauer, Inc., and purified in a similar way by carrying out the recrystallization in methanol. Sodium octyl sulfonate (NaOSO) was obtained from Pfaltz-Bauer, Inc., and was purified in the same way as NaLS. Hexadecyltrimethylammonium chloride (CTACl) and sodium octyl sulfate (NaOSA) were purchased from

Table I. Properties of Surfactants Used in This Study[a]

	Mol wt	cmc, M	Aggregation Number (N)
Anionic			
NaLS (sodium dodecyl sulfate)	288.3	8×10^{-3}	62
NaOSA (sodium octyl sulfate)	232.3	1.3×10^{-1}	<40
NaOSO (sodium octyl sulfonate)	216.2	1.5×10^{-1}	28
Cationic			
CTAB (hexadecyltrimethylammonium bromide)	364.5	9.2×10^{-4}	61
CTACl (hexadecyltrimethylammonium chloride)	320.0	$\simeq 10^{-3}$	
CPyCl (hexadecylpyridinium chloride)	340.0	$\simeq 8 \times 10^{-4}$	95
Nonionic			
TGT (tergitol NPX) p-$C_9H_{19}C_6H_4O$—$(CH_2CH_2O)_{10.5}$—H	683	$\simeq 8.3 \times 10^{-5}$	$\simeq 50$

[a] From ref 2b.

Pfaltz-Bauer, Inc. The source of tergitol NPX was Union Carbide Co. All these latter compounds were of highest purity available (>99%) and were dehydrated by the addition of molecular sieves to the liquid compound. The water used in this investigation was demineralized and triple distilled with a purity better than 99.8%.

B. Preparation of the Positron Source. A positron source consisting of 3-5 μCi of ^{22}Na incorporated into a thin glass foil was used throughout all positron lifetime measurements. The glass was made of soda lime glass (density 2.47, softening point 695 °C, from Corning Glass Co.) and had the dimensions 0.8 cm × 1.5 cm × 0.01 mm. This source was prepared by depositing 3-5 mCi of $^{22}NaHCO_3$ solution, carrier free (obtained from Amersham Searle Co.), in the center of the glass foil, which was subsequently sandwiched between two layers of graphite and annealed in an oven at 585 °C for 24 h, a process by which ^{22}Na diffused into the glass. ^{22}Na activities remaining on or close to the surface were removed placing the foil into water until the positron activity remained constant. It was found that about 90% of ^{22}Na was embedded in the glass. The amount of positron annihilation occurring in the glass was found to be less than 2%.

C. Positron Lifetime Measurements and Preparation of Sample. Positron lifetime measurements were carried out by the usual delayed coincidence method as previously described.[7] The resolution of the system, as measured by the fwhm of the prompt coincidence spectrum of a ^{60}Co source without changing the 1.27 and 0.511 MeV bias, was found to be less than 0.36 ns fwhm. Specially designed cylindrical sample vials (Pyrex glass 100 mm long and 10 mm i.d.) were used. About 2 mL of the appropriate solution was placed into the tube with the positron glass source being centered in the liquid sample. The solution was degassed under vacuum by a freeze-thaw technique to remove oxygen and the vials subsequently sealed off. All measurements were carried out at 20 °C.

Results and Discussion

1. General Method of Data Analysis. As discussed in a previous paper[4] the interaction between thermal ortho Ps atoms and organic molecules can be interpreted in terms of a mechanism which involves the reversible formation of Ps-molecule complexes.

In subsequent papers[8,9] it was demonstrated how kinetic data can be obtained from the measurement of the time-dependent two-photon annihilation for two components in a solution when their reactivity toward Ps is significantly different. Such differences in the reactivity toward Ps, however, are not only observed when molecules of a different nature react with Ps (Table II) but also when the same type of molecule is dissolved in various types of solvents.[5] As pointed out in the introduction, such a situation may exist in micellar solutions, where the solubilizate could be located in a quite different environment, depending on whether the solubilizate is located in the hydrocarbon-like core of the micelle, in the Stern layer, or in the homogeneous aqueous phase.[2] Thus in analogy to the previously discussed case[8,9] of a solution composed of the solvent and two reactive solutes which are in equilibrium, one can set up a kinetic scheme as shown in Figure 1, where Ps reacts with the solubilizate present in the two different phases at different rate constants.

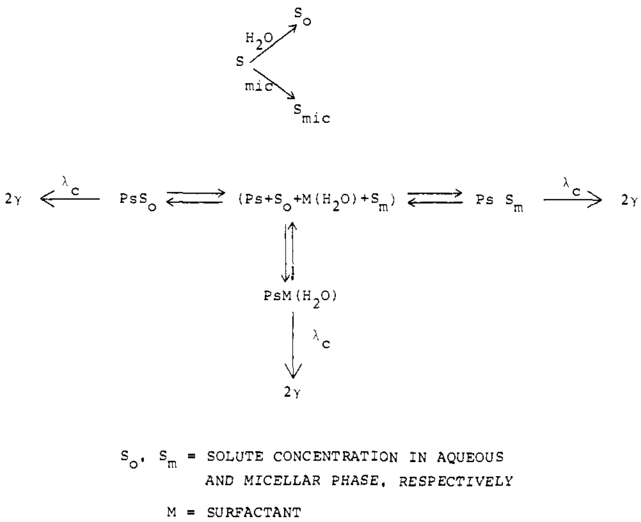

Figure 1. Ps interactions with solute in micellar systems.

Table II. Rate Constants for Ps-Nitrobenzene Interactions in Various Solvents

$$[\mathrm{Ps} + \mathrm{NB}]_{\mathrm{solv}} \underset{k_2}{\overset{k_1}{\rightleftarrows}} [\mathrm{PsNB}]_{\mathrm{solv}} \xrightarrow{\lambda_c} 2\gamma$$

$$k_{\mathrm{obsd}} = \frac{k_1 \lambda_c}{k_2 + \lambda_c}$$

Solvent	K_{obsd} (10^{10} s^{-1}) (at 22 °C)	Solvent	K_{obsd} (10^{10} s^{-1}) (at 22 °C)
Benzene	2.55	1-Heptane	0.34
Toluene	2.58	1-Octane	0.69
H_2O	1.05	1-Decane	1.19
Propanol	1.00	1-Dodecane	1.28
1-Pentanol	0.86	1-Hexadecane	1.15
1-Hexane	0.30		

From this kinetic scheme an equation can be obtained which correlates λ_2, the slope of the long-lived component in the lifetime, with the rate constants for Ps reactions with the probe molecule (S) in the micellar phase (K_{mic}) and in the homogeneous aqueous phase (K^0_{obsd}) and the annihilation constant of the Ps in the solvent containing the surfactant $K_{\mathrm{mic}(H_2O)}$ as well as with the concentrations $[S_m]$, $[S_0]$, and $[M(H_2O)]$, respectively.

$$\lambda_2 = K_{\mathrm{mic}(H_2O)}[M(H_2O)] + K_{\mathrm{mic}}[S_m] + K^0_{\mathrm{obsd}}[S_0] \quad (1)$$

The first term of this equation can be obtained from the measurement of λ_2 without solubilizate present, i.e., $([S_m] + [S_0]) = 0$.

$$\lambda_2{}^0 = K_{\mathrm{mic}(H_2O)}[M(H_2O)] \quad (2)$$

Thus

$$\lambda_2 - \lambda_2{}^0 = K_{\mathrm{mic}}[S_m] + K^0_{\mathrm{obsd}}[S_0] \quad (3)$$

or K_{obsd}

$$\frac{\lambda_2 - \lambda_2{}^0}{[S_t]} = \frac{K_{\mathrm{mic}}[S_m]}{[S_t]} + K^0_{\mathrm{obsd}} \frac{[S_0]}{[S_t]} \quad (4)$$

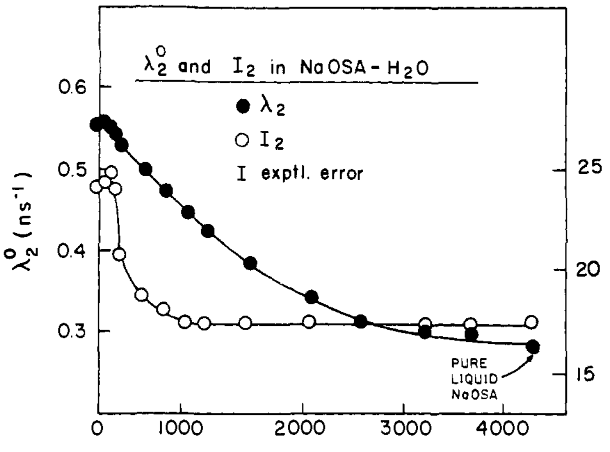

Figure 2. λ_2 and I_2 vs. surfactant concentration in NaOSA-H_2O (room temperature).

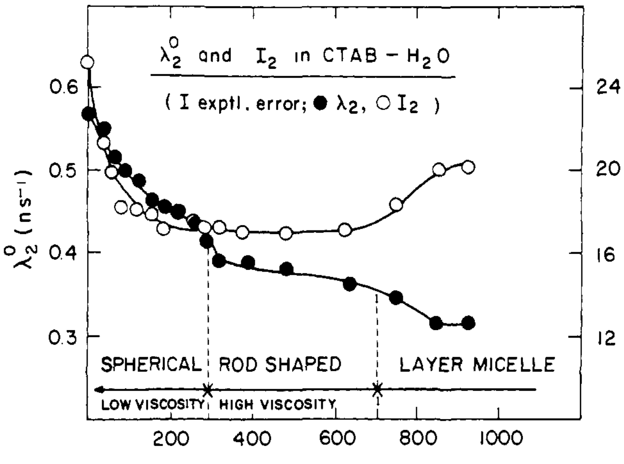

Figure 3. λ_2 and I_2 vs. surfactant concentration in CTAB-H_2O (room temperature).

At high surfactant concentrations one can assume that the probe molecule is completely located in the micellar phase; therefore $[S_0] \rightarrow 0$ and $[S_m]$ becomes equal to the total solute concentration $[S_t]$. Therefore

$$\lambda_2 - \lambda_2{}^0 = K_{\mathrm{mic}}[S_t] \tag{5}$$

or

$$(\lambda_2 - \lambda_2{}^0)/[S_t] = K_{\mathrm{mic}} \tag{6}$$

With no surfactant present one obtains from eq 4 with $[S_m] = 0$, $\lambda_2 = \lambda_{H_2O} + K^0_{\mathrm{obsd}}[S_0]$ where λ_{H_2O} is the Ps annihilation rate in H_2O.

2. Ps Reactions in Micelle Solutions with No Probe Molecules Present. One of the conditions for a successful application of the positron annihilation technique to the study of the reaction of probe molecules inside the micelle is that the micelle itself shows no extensive reactivity toward the Ps. This was studied by measuring the positron lifetimes in the aqueous micellar solutions of each of the surfactants employed in this study. From these results $\lambda_2{}^0$ (see above) was determined. A typical plot of $\lambda_2{}^0$, and I_2, which is the intensity of the component associated with $\lambda_2{}^0$, as a function of surfactant is shown in Figure 2 for NaOSA.

While in this system $\lambda_2{}^0$ decreases smoothly with increasing NaOSA concentration, a more structured behavior is evident in the CTAB system (Figure 3) which seems to reflect changes in the micellar shape, that is to say that the Ps reactivity is affected by the form and size of the micelles, a structure effect which has previously been observed, e.g., in liquid crystals.[10]

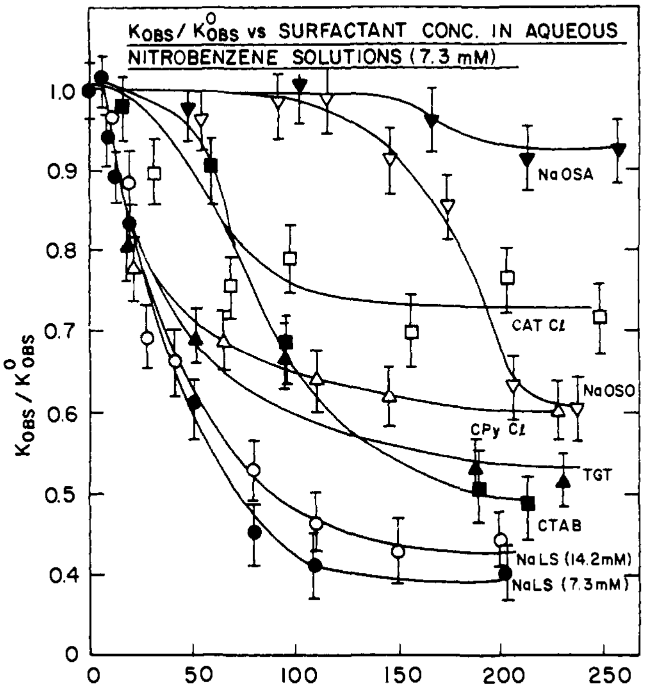

Figure 4. $K_{\mathrm{obsd}}/K^0_{\mathrm{obsd}}$ vs. surfactant concentration in aqueous nitrobenzene solutions (room temperature).

3. Ps Reactions with Nitrobenzene in Micellar Solutions. In Figure 4 the relative rate constants $K_{\mathrm{obsd}}/K^0_{\mathrm{obsd}}$ (where K^0_{obsd} is the observed rate constant with no surfactant present, see eq 4) are plotted for micellar solutions of the various surfactant to which a small amount of the probe molecule (nitrobenzene, 7.3 or 14.3 mM) was added.

They all show the same feature, namely, a decrease of the ratio $K_{\mathrm{obsd}}/K^0_{\mathrm{obsd}}$ with increasing surfactant concentration, leveling off at values characteristic for each individual micellar system. It should also be pointed out that $K_{\mathrm{obsd}}/K^0_{\mathrm{obsd}}$ does not start to drop before the critical micelle concentration (cmc), i.e., the concentration at which the surfactant forms micelles, is reached, as it is clearly depicted in the NaOSA and NaOSO systems, where the cmc is fairly large, 1.3×10^{-1} or 1.5×10^{-1} M, respectively.

From Figure 5, where $K_{\mathrm{obsd}}/K^0_{\mathrm{obsd}}$ is plotted vs. the surfactant (NaOSA) concentration over the whole concentration range, i.e., reaching from the pure solvent to the pure (liquid) surfactant, it can be seen that the first plateau, which we want to interpret as the micelle concentration at which the solubilizate has completely associated itself with the micelles, is followed by a second plateau at still higher concentration. We assume that the $K_{\mathrm{obsd}}/K^0_{\mathrm{obsd}}$ value in this range corresponds to the relative reactivity of Ps toward the nitrobenzene probe molecule now completely dissolved in the (almost) homogeneous liquid surfactant.

On the basis of these assumptions and by using eq 4 and 5 the relative concentration of the nitrobenzene in the micellar phase and the homogeneous solvent phase can be evaluated as shown in Figure 6. Assuming an aggregation number of about 5^{2b} it appears that an actual micelle concentration of 20 mM micelles is sufficient to completely dissolve 7.3 mM of nitrobenzene or 3 micelles per 1 nitrobenzene. This is further confirmed by the results shown in Figure 7 where λ_2 is plotted as a function of nitrobenzene concentrations and where no significant deviations from K_{obsd} could be observed up to 13

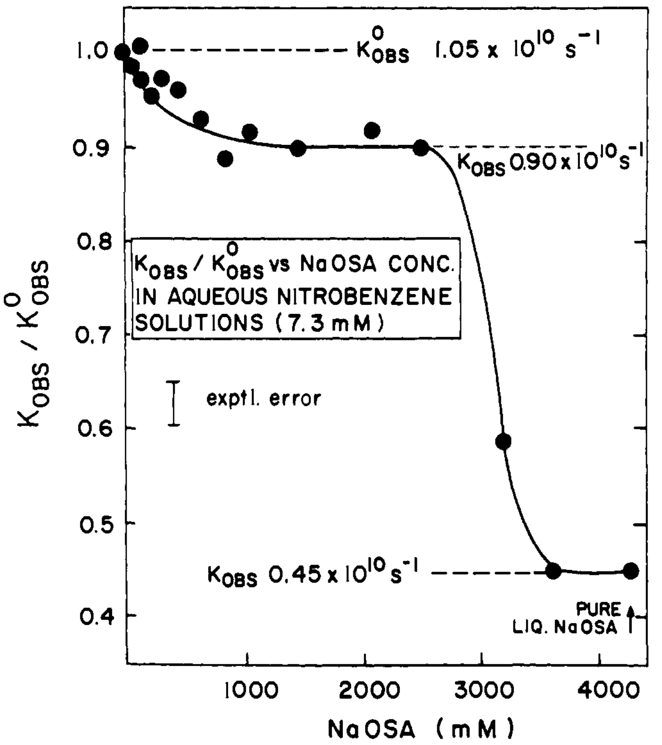

Figure 5. K_{obsd}/K^0_{obsd} vs. NaOSA concentration in aqueous nitrobenzene (7.3 mM) solution (room temperature).

Table III. Rate Constants for Ps-Nitrobenzene Interactions in Aqueous Micellar Systems (K_{mic}) in the (Pure) Liquid Surfactant (K_{surf}) and in the Corresponding n-Alkane (K_{alk})[a]

Surfactant	K_{mic}, 10^{10} s^{-1}	K_{surf}, 10^{10} s^{-1}	K_{alk}, 10^{10} s^{-1}
NaLS	0.41		1.28 (C_{12})
NaOSA	0.90	0.47	0.69 (C_8)
NaOSO	0.60		0.69 (C_8)
CTAB	0.48		1.15 (C_{16})
CTACl	0.73	0.39	1.15 (C_{16})
CPyCl	0.60		1.15 (C_{16})
TGT	0.53	0.13	

K^0_{obsd} in aqueous nitrobenzene 1.05 × 10^{10} s^{-1}

[a] All values at 22 °C.

mM in a solution containing 199 mM surfactant or 50 mM in a 900 mM solution of NaLS, respectively.

As pointed out above, the K_{obsd}/K^0_{obsd} of the plateau region corresponds to a complete association to or solution of the probe molecule in the micelle. Thus at this surfactant concentration [S_0] approaches zero and eq 6 applies from which K_{mic} can be extracted.

By using the kinetic approach as described in detail in ref 2b,c one obtains a correlation between the observed rate constants at different surfactant concentrations K_{obsd} and K_c, the equilibrium constant for complexing the solubilizate in the micelle (N, aggregation number; C, surfactant concentration):

$$\frac{K_{obsd} - K^0_{obsd}}{K_{mic} - K_{obsd}} = \frac{K_c(C - \text{cmc})}{N} \qquad (7)$$

Such an evaluation of the nitrobenzene-NaLS system results in a K_c of about 3000 M^{-1}, which is of the same order of magnitude as K_c for similar systems for which literature values are available.[2b]

Of special interest as far as the location of the nitrobenzene in the micelle is concerned is a comparison of K_{mic} observed in the various micellar systems, obtained from K_{obsd}/K^0_{obsd} in Figures 4 and 5, and the corresponding values K_{alk} observed in solutions of nitrobenzene in pure alkanes and K_{surf} observed for Ps interaction with nitrobenzene in the pure surfactant.

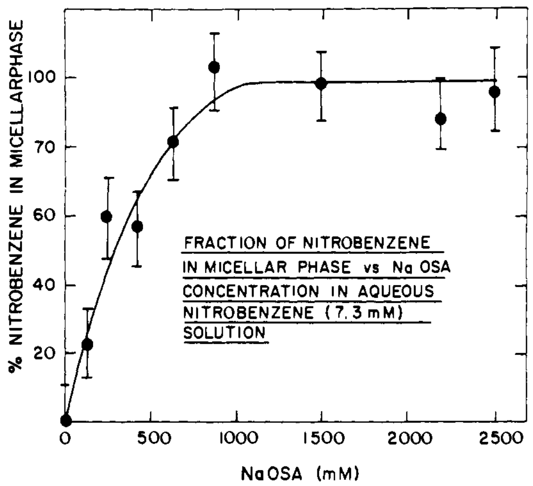

Figure 6. Fraction of nitrobenzene in micellar phase vs. NaOSA concentration in aqueous nitrobenzene (7.3 mM) solution (room temperature).

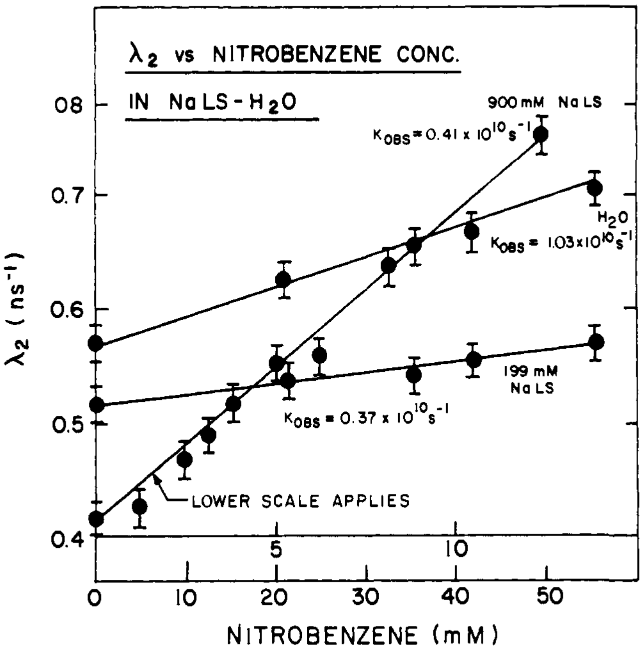

Figure 7. λ_2 vs. nitrobenzene concentrations in NaLS-H_2O at various surfactant concentrations (room temperature).

It is quite obvious from Table III, where these values are listed, that in each case K_{mic} is smaller than the rate constant observed in the homogeneous aqueous phase. The values listed in Table III also show that with the exception of the NaOSA and NaOSO systems, the reactivity of the Ps toward nitrobenzene is reduced with respect to its reactivity toward nitrobenzene if dissolved in an n-alkane with a number of carbon atoms which equals those in the hydrocarbon chain of the surfactant molecule. Primarily two factors will have to be considered which could be responsible for this decrease in Ps reactivity. Firstly, the nitrobenzene probe occupies a position in the micelle with an environment which neither reflects the homogeneous aqueous environment outside the micelle nor the hydrocarbon-like environment in the core of the micelle. Secondly, the reduced reactivity is due to the fact that the Ps is hindered by the micelle structure to approach the probe molecule or that the mobility of the latter is decreased in the

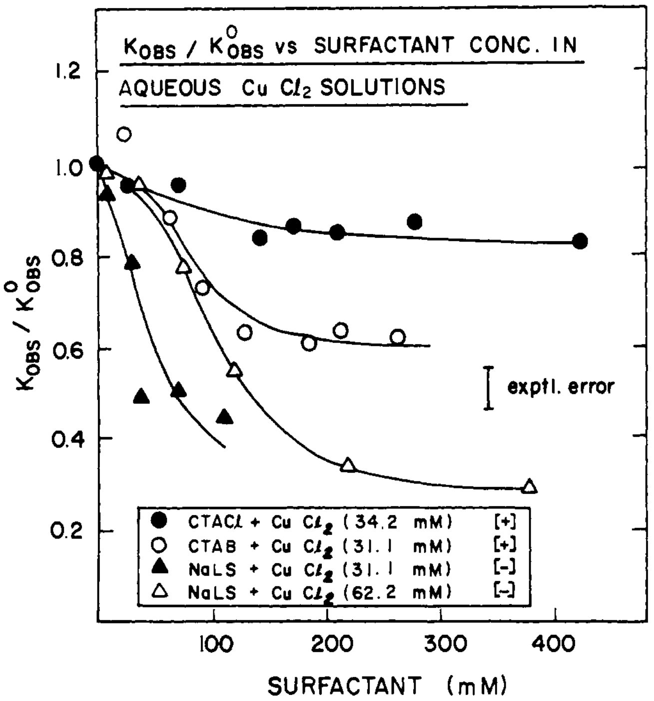

Figure 8. K_{obsd}/K^0_{obsd} vs. surfactant concentrations in aqueous $CuCl_2$ solutions of CTACl, CTAB, and NaLS (room temperature).

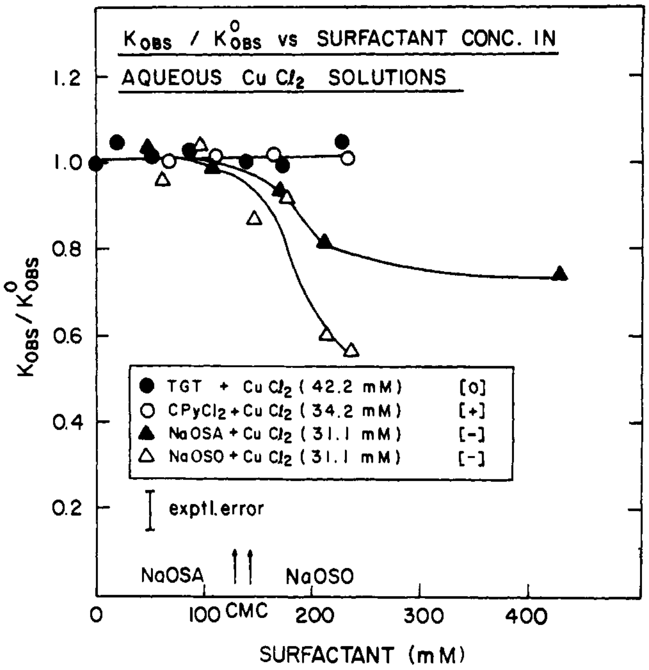

Figure 9. K_{obsd}/K^0_{obsd} vs. surfactant concentrations in aqueous $CuCl_2$ solutions of TGT, CPyCl, NaOSA, and NaOSO (room temperature).

micellar phase compared with the homogeneous aqueous phase.

If one adopts the first explanation the experimental results would suggest that in the NaLS, CTAB, CTACl, and CPyCl micellar system the nitrobenzene is not deeply embedded in the hydrocarbon-like core of the micelle but most likely in the Stern layer, where the nitrobenzene molecules may have formed molecular complexes with the head groups of the surfactant molecules. As a result of this interaction their reactivity toward Ps is reduced. This is in agreement with previous findings which showed that if an acceptor like nitrobenzene forms a conventional molecule complex with a donor, its reactivity toward Ps is severely limited. It is interesting to note that even in the CTAB and CTACl micellar systems where the head groups are identical K_{mic} assumes substantially different values which points to the effect of the two different counterions Br^- vs. Cl^- on K_{mic}. In the case of the NaOSO where K_{mic} is very similar to that in the corresponding alkane K_{alk}, one would have to assume that the nitrobenzene molecule is more deeply embedded in the micelle core, whereas in the NaOSA the opposite seems to be the case, since K_{mic} resembles closely K^0_{obsd} observed in aqueous nitrobenzene solutions, thus suggesting an aqueous environment, which necessarily would have to be on the surface of the micelle.

At the present time, no explanation for the parameters which lead to this distinctly different behavior of the probe molecule in the various micellar systems can be given. It should be pointed out, however, that similar observations have been made by utilizing the NMR techniques and fluorescent probes.[2b]

In order to explain the different values of K_{mic} in the various micellar systems in terms of a hindered approach of the Ps to the probe molecule in the micelle or a reduced mobility of the latter in the micellar phase, one would have to consider the fact that Ps is a neutral species which has been shown to diffuse rapidly in all matter. Thus, unlike the case of the e_{aq}^-[2a,11] which is repelled by the negative charge on certain micelles, one would expect the Ps to penetrate easily the micelle walls. On the other hand, the mobility of the nitrobenzene in the micelle will definitely be reduced; however, since we have been able to show[12] that Ps reactions with nitrobenzene are not diffusion controlled, the somewhat reduced mobility of the probe molecule will only slightly affect the rate constants and cannot explain the magnitude of the observed effects.

Thus, we prefer to explain the effects of micelles on the rates of Ps reactions in terms of the differences in reactivity of the substrate in the micellar phase and in the bulk solution. The environmental effect on the reactivity of the probe molecule probably originates from the various degrees of stabilization which the environment can provide for the Ps-nitrobenzene molecule complex.

4. Ps Reactions with $CuCl_2$ in Micellar Solutions. The results of the reactions of Ps with Cu^{2+} ions in various micellar systems are shown in Figures 7 and 8, where K_{obsd}/K^0_{obsd} is plotted as a function of surfactant concentration.[13]

Cu^{2+} ions are are generally more soluble in the aqueous phase than in the micellar phase and one would expect to see that micelle formation has only a minor effect on the rate constants unless Cu^{2+} becomes associated to the micelle surface by some electrostatic attraction to the (negatively) charged surface.

This is clearly borne out in the case of the neutral TGT (Figure 9) where there are no electrostatic forces on the micelle surface which would lead to an attachment of the Cu^{2+} ions and where the rate constant for Ps reactions with Cu^{2+} remains unchanged. The same is true for the CPyCl system where the positively charged micelle surface repels Cu^{2+}. On the other hand, in the case of anionic micelles Cu^{2+} ions should become easily associated with the oppositely charge micellar surface and the rate constants should drop significantly due to a reduced reactivity of the Cu^{2+} which becomes in some way attached to the micelle surface, toward Ps, as it is observed for NaOSA, NaOSO, and NaLS. In the case of NaOSA and NaOSO the shape of the plot of k_{obsd}/k^0_{obsd} vs. surfactant concentration clearly shows the onset of micelle formation at the cmc as the point where the rate constants sharply drop.

Although in the CTAB and CTACl systems where the micelles are positively charged no effect on the k_{obsd}/k^0_{obsd} would be expected, these ratios decrease at increasing surfactant concentrations. This behavior parallels that previous observed for e_{aq}^- reactions with Cu^{2+} in this micellar system (CTAB).[11]

Thus it appears that in spite of the positive micelle charge Cu^{2+} ions which would normally be repelled become complexed on the micelle surface. Atlernatively the possibility exists that the high Cl^- or Br^- ion concentration at the surface of the micelle leads first to the formation of $CuCl_2$ or $CuBr_2$, followed by a complexation of these compounds by the micelle. In either case the observable effect would be an apparent reduction of the interaction between Ps and the copper species.

References and Notes

(1) Work partially supported by the U.S. Energy Research and Development Administration and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

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Potential Surfaces for the Unimolecular Reactions of Organic Ions: $C_2H_6N^+$ and $C_2H_5O^+$

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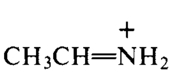
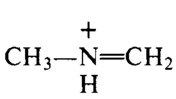
Abstract: The isomeric ions $CH_3CH{=}N^+H_2$ (**1**) and $CH_3N^+H{=}CH_2$ (**2**) are shown to decompose over the same potential surface through loss of H_2 and C_2H_2 in slow unimolecular (metastable) transitions. Deuterium labeling data, appearance potential measurements, and metastable peak widths are presented to show that **2** isomerizes to **1** in a process which has energy requirements similar to those for unimolecular dissociations of **1**. The potential energy surface for reactions of $C_2H_6N^+$ ions is compared and contrasted with the corresponding surface for $C_2H_5O^+$ ions; the approach naturally accommodates the independent behavior of $CH_3CH{=}O^+H$ and $CH_3{}^+O{=}CH_2$.

In discussing the unimolecular chemistry of species of a given chemical formula, an ultimate aim must be to describe the complete potential surface, or surfaces, over which the species can react. As a result of several years work in numerous laboratories, it is now evident that many details of the potential surfaces for unimolecular ionic reactions can be obtained by examining the slow (metastable) reactions taking place in a conventional magnetic sector mass spectrometer. The main criteria are as follows: (1) in many cases the energy levels of reactants and products can be obtained from known heats of formation, or appearance potential measurements; (2) the transition state energies for isomerization or dissociation of a reactant can be obtained from appearance potential measurements; (3) information on direct dissociation of a reactant, or isomerization prior to dissociation, can be obtained from isotope, usually ^2H or ^{13}C, labeling; and (4) reaction of species, initially generated as isomeric structures, over the same surface (or surfaces) at the same internal energies will be indicated by the same, or very similar, channeling among two or more slow (metastable) decomposition pathways.[2a] In addition, we now possess an unambiguous criterion to establish which of a set of isomeric ions are in potential wells, as opposed to those which may isomerize without activation energy to other structures, through the consideration of collision-induced dissociations.[2b] Finally, the heats of formation of species which may lie on the potential surface, but not correspond to potential energy minima, may be estimated by an isodesmic substitution procedure.[3] We now apply these criteria to a study of the potential surface for $C_2H_6N^+$ ions, which can be conveniently generated as the isomeric species **1** and **2**, both of which exist in potential wells.[2b]


$CH_3CH{=}\overset{+}{N}H_2$

1


$CH_3{-}\underset{H}{\overset{+}{N}}{=}CH_2$

2

Results and Discussion

In the present work, the two major decay pathways of $C_2H_6N^+$ ions observed in metastable transitions are loss of acetylene and molecular hydrogen. The former process, which is evidenced by the appearance of a metastable peak at *m/e* 7.36, dominates. Other reactions (e.g., loss of hydrogen radical or methane) are of negligible intensity, being responsible for only ca. 1% of the total metastable ion current.

The ratios of the metastable peak areas for C_2H_2 and H_2 loss from $C_2H_6N^+$ ions, produced from a variety of amines, are shown in Table I. Two conclusions are evident from the data; first, that the $C_2H_6N^+$ ions, irrespective of the precursor, undergo C_2H_2 and H_2 losses in similar ratios, thus suggesting at least partial equilibration of the two isomeric structures prior