Inhibition of the reaction by dissolved O_2 is consistent with the proposed mechanism. Formation of O_2 complexes of carbonyl radicals has been demonstrated in ESR experiments with $Co(CO)_4$ and $Mn(CO)_5$.[16] In $Re(CO)_5O_2$ the unpaired spin could be localized on O_2, as suggested by the ESR hyperfine data for $Mn(CO)_5O_2$, so that the metal possesses a coordinatively saturated (i.e., 18 e^-) configuration. The metal is thus probably not substitutionally labile nor capable of hydrogen abstraction from $HRe(CO)_5$.

Additional tests of the radical chain hypothesis are in progress. The radical chain process for substitution should be applicable to many other transition metal systems. Extension to other metal hydride systems is especially appealing. Deliberate photochemical initiation with $Re_2(CO)_{10}$ or other suitable source of radicals may provide a convenient route to substituted hydrides, both mononuclear and polynuclear. Radical chain processes may be of importance in cobalt carbonyl hydride chemistry. Studies of this and several other systems, including metal carbonyl halides and other substituted metal carbonyl compounds susceptible to radical attack, are also in progress.

References and Notes

(1) This research was supported by the National Science Foundation through Contract DMR-7203026 with the Materials Research Laboratory, University of Illinois, and research Grant MPS 71-03201.

(2) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, 1967, Chapter 7.

(3) (a) D. A. Brown, *Inorg. Chim. Acta Rev.*, **1**, 35 (1967); (b) R. J. Angelici, *Organomet. Chem. Rev.*, **3**, 173 (1968); (c) H. Werner, *Angew. Chem., Int. Ed. Engl.*, **7**, 930 (1968).

(4) N. Flitcroft, J. M. Leach, and F. J. Hopton, *J. Inorg. Nucl. Chem.*, **32**, 137 (1970); R. W. Harrill and H. D. Kaesz, *Inorg. Nucl. Chem. Lett.*, **2**, 69 (1966).

(5) A. Berry and T. L. Brown, *J. Organomet. Chem.*, **33**, C67 (1971).

(6) V. W. Beck, W. Hieber, and G. Braun, *Z. Anorg. Allg. Chem.*, **308**, 23 (1961).

(7) (a) J. T. Moelwyn-Hughes, A. W. B. Garner, and N. Gordon, *J. Organomet. Chem.*, **26**, 373 (1971); (b) E. Singleton, J. T. Moelwyn-Hughes, and A. W. B. Garner, *J. Organomet. Chem.*, **21**, 449 (1970); (c) F. Nyman, *Chem. Ind.*, **21**, 449 (1965).

(8) R. A. Levenson, H. B. Gray, and G. P. Ceasar, *J. Am. Chem. Soc.*, **92**, 3653 (1970).

(9) M. Wrighton, *Chem. Rev.*, **74**, 401 (1974).

(10) M. Wrighton and D. Bredesen, *J. Organomet. Chem.*, **50**, C35 (1973).

(11) The substitution lability of $Mn(CO)_5$ produced by irradiation of $Mn_2(CO)_{10}$ has been demonstrated by Wrighton and Ginley.[12]

(12) M. S. Wrighton and D. S. Ginley, *J. Am. Chem. Soc.*, in press.

(13) We attribute the induction period to traces of radical chain inhibitors, notably O_2, present in low concentrations even in carefully purified systems.

(14) Using 10^{-5} M $Mn_2(CO)_{10}$ in place of $Re_2(CO)_{10}$, and irradiating with monochromatic radiation at 350 nm, caused the reaction to proceed to completion after less than 2 min of irradiation. The products in this instance were $HRe(CO)_4L$ and $HRe(CO)_3L_2$ in 2.5:1 ratio. Presumably in this instance photochemically generated $Mn(CO)_5$ radicals act as reaction initiators.

(15) Irradiation of 10^{-3} M $HRe(CO)_5$, 10^{-2} M PPh_3, and 10^{-5} M $Re_2(CO)_{10}$ in hexane at 311 nm results in almost complete reaction to form $HRe(CO)_4PPh_3$ after only 70 sec. The interpretation of these results is complicated by intense absorption of 311 nm radiation by PPh_3. The ligand may in this case be acting to sensitize the $Re_2(CO)_{10}$ dissociation.

(16) S. A. Fieldhouse, B. W. Fullam, G. W. Neilson, and M. C. R. Symons, *J. Chem. Soc., Dalton Trans.*, 567 (1974).

Blaine H. Byers, Theodore L. Brown*

Materials Research Laboratory and
School of Chemical Sciences
University of Illinois
Urbana, Illinois 61801

Received November 8, 1974

Fast Proton Transfer at a Micelle Surface

Sir:

Micellar chemistry has been developed mainly through studies of reactive additives adsorbed into or onto the micelles.[1-3] Although "kinetic probes" have provided useful information, doubt concerning the location of the adsorption sites has complicated interpretation of the rate data. We report here an investigation of NH-proton exchange of micellar long-chain amine salts (e.g., dimethyldodecylammonium ion). Several considerations prompted this work. (1) Since proton transfer involves the surfactant "heads," the reaction would unquestionably proceed at the micelle surface (the most unique portion of the micelle). (2) By measuring the reactivity of the micelle components themselves, we can avoid probes which perturb micellar structure.[4] (3) Dynamic NMR can be used to determine rates of proton transfer in solutions *at equilibrium*. Thus, we could avoid systems with a time-dependent composition. (4) As has been pointed out repeatedly,[1-3] micelles constitute an important model for enzymes and membranes. Proton transfer at micelle surfaces, therefore, warrants considerable attention.

Rates of NH-proton exchange of *N,N*-dimethylhexylamine ($C_6NHR_2^+$), *N,N*-dimethyldecylamine ($C_{10}NHR_2^+$), and *N,N*-dimethyldodecylamine ($C_{12}NHR_2^+$) in acidic aqueous solutions were deduced from the slow-passage NMR signal of the *N*-methyl protons. Since proton exchange rates of amines decrease with decreasing pH,[5] the CH_3 signal transforms from a singlet to a doublet when the pH is lowered sufficiently. NMR spectra were recorded with a Jeol-JNM-MH-100 spectrometer equipped with a variable temperature probe. Temperatures, calculated by the equation of Van Geet,[6] were measured frequently during a series of runs and are believed to be accurate to ±0.6°. Four to nine spectra were traced for each sample, and the resulting rate constants were averaged. An optimum constant homogeneity was achieved by adjusting the resolution control prior to each run while observing a component of the methylene multiplets. Natural line widths were measured under conditions of fast exchange (e.g., pH 6 for $C_6NHR_2^+$ and pH 2 for $C_{12}NHR_2^+$). Coupling constants, J, were obtained under conditions of slow exchange. Since $C_{12}NHR_2^+$ displayed only partial splitting even in concentrated HCl, its J was evaluated by an extrapolation method. J = 5.19, 5.08, and 5.24 Hz for $C_6NHR_2^+$, $C_{10}NHR_2^+$, and $C_{12}NHR_2^+$, respectively. Spectra were traced using an rf field of 0.1 mG, sweep width of 108 Hz, sweep time of 250 sec, and filter band width of 10 Hz. Rate constants were calculated with the aid of an RCA Spectra 70/55 computer which adjusted τ (the reciprocal of k_{obsd}) so as to minimize deviations between experimental and theoretical line widths or peak-to-valley ratios.[7,8]

At 0.20 M (well above its CMC of ca. 0.02 M[9]) *N,N*-dimethyldodecylammonium ion exchanges protons much faster than a nonaggregating analog, *N,N*-dimethylhexylammonium ion. Thus, the pH necessary to bring the observed rates into the NMR "window" is 3 units lower for $C_{12}NHR_2^+$ tlhan for $C_6NHR_2^+$ (Table I). Although instrumental limitations prevented examination of $C_{12}NHR_2^+$ at concentrations below its CMC, this was possible for $C_{10}NHR_2^+$ (Figure 1). The k_{obsd} rises sharply near the expected CMC[10] of $C_{10}NHR_2^+$, indicating that the fast proton transfer is micellar in origin.

All known nonmicellar ammonium salts transfer protons to water by the mechanism shown in eq *1*.[5] Three species in addition to water were found to accept protons from $C_6NHR_2^+$ at pH 3-4: unprotonated amine (k_2), hydroxide

$$\begin{aligned}
R_3N\mathit{H}^+\cdot\cdot OH_2 + H_2O &\underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} R_3N\cdot\cdot\mathit{H}OH + H_3O^+ \\
R_3H\cdot\cdot\mathit{H}OH &\xrightarrow{k_H} R_3N + \mathit{H}OH \qquad (1) \\
R_3N + H_3O^+ &\xrightarrow{\text{fast}} R_3NH^+
\end{aligned}$$

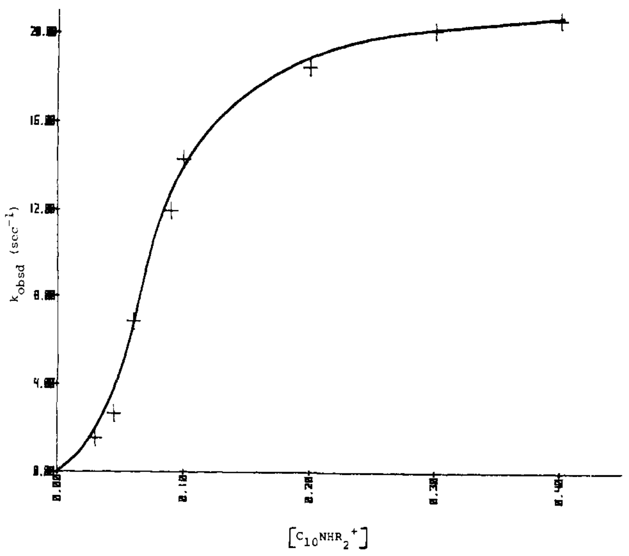

Figure 1. Observed rate constants for proton exchange of *N,N*-dimethyldecylammonium ion at 25° and pH 1.00 as a function of the concentration of the surfactant.

Table I. Rate Constants for NH-Proton Exchange at 25° in Aqueous Solutions[a]

[Amine], *M*	pH	k_{obsd}, sec^{-1}
	N,N-Dimethylhexylamine[b]	
0.15	3.25	4.4
0.30	3.26	6.2
0.45	3.26	7.8
0.15	3.66	7.9
0.30	3.66	11.5
0.45	3.66	16.1
	N,N-Dimethyldodecylamine[c]	
0.20	0.00[d]	6.2
0.20	0.00[d]	6.8
0.20	0.00[d]	6.9
0.20	0.16	8.8
0.20	0.40	12.9
0.20	0.70	20.3

[a] This table lists only a portion of the collected rate data. A detailed report of all the results is planned. [b] 0.01 *M* tartrate buffer. [c] Aqueous HCl solutions. [d] Repeat runs performed on three different days.

ion (k_b), and buffer.[11] Values of the parameters are k_a = 1.3 sec^{-1}, k_{-a} = 1.7 × 10^{10} M^{-1} sec^{-1}, k_2 = 7.3 × 10^7 M^{-1} sec^{-1}, and k_b = 3.4 × 10^{10} M^{-1} sec^{-1}. It was not possible to extract k_H from the raw data, but a value of 3 × 10^9 sec^{-1} is reasonable on the basis of previous work with aliphatic amines.[12]

Micellar $C_{12}NHR_2^+$ was examined at a high acidity (Table I) where catalysis by hydroxide ion and buffer does not contribute to the exchange rate. In contrast to its nonaggregating analog, $C_{12}NHR_2^+$ has a k_{obsd} which is independent of the amine concentration (0.1–0.3 *M*). We found that k_a = 40 sec^{-1} and $k_H K_a$ = 6.4 *M* sec^{-1}, both of which are 30-fold larger than the corresponding values for $C_6NHR_2^+$. If one assumes that the rate of diffusion-controlled k_{-a} reaction in eq 1 is identical for micellar and nonmicellar systems, then the large $k_H K_a$ for $C_{12}NHR_2^+$ can be ascribed solely to a modified K_a. This follows from the fact that k_a and $k_H K_a$ increase by the same factor and that $K_a = k_a/k_{-a}$. Therefore, the enhanced $C_{12}NHR_2^+$ exchange at the micelle surface stems primarily from an abnormally fast Grotthus proton transfer (k_a) rather than an abnormally fast amine desolvation (k_H).

An apparent pK_a for $C_{12}NHR_2^+$ was calculated from its log k_a and the linear log k_a vs. pK_a plot for four amines studied by Grunwald.[5] The pK_a so obtained equals 8.7 (1.4 units less than the pK_a of $C_6NHR_2^+$). Likewise, inserting a "normal" k_H of 3 × 10^9 sec^{-1} into $k_H K_a$ = 6.4 *M* sec^{-1} provides an apparent micellar pK_a of 8.7.

Close proximity of the ammonium groups at the micelle surface could conceivably lead to efficient proton transfer from one surfactant "head" to another (similar to the bimolecular exchange observed with $C_6NHR_2^+$ at pH 3–4). Transfer of this type is *not* necessarily excluded by the independence of k_{obsd} on the $C_{12}NHR_2^+$ concentration above its CMC. Nevertheless, the reaction mode appears unlikely because mixed micelles composed of *N,N,N*-trimethyldodecylammonium bromide and $C_{12}NHR_2^+$ in a 2:1 molar ratio have a k_{obsd} only 29% less than micelles of pure $C_{12}NHR_2^+$. Diluting the $C_{12}NHR_2^+$ by a large quantity of bulky nonreactive surfactant would have diminished k_{obsd} to a much larger extent if bimolecular exchange were important. We conclude that the fast proton transfer takes place primarily between the micellar ammonium groups and the interfacial water.[13]

Acknowledgment. This work was supported by a grant from the National Science Foundation (GP-42919X) and from the National Institutes of Health (GM-20336 and GM-21457).

References and Notes

(1) E. H. Cordes and R. B. Dunlap, *Acc. Chem. Res.*, **2**, 329 (1969).
(2) E. J. Fendler and J. H. Fendler, *Adv. Phys. Org. Chem.*, **8**, 271 (1970).
(3) E. H. Cordes, Ed., "Reaction Kinetics in Micelles," Plenum Press, New York, N.Y., 1973.
(4) J. W. Larsen, L. J. Magid, and V. Payton, *Tetrahedron Lett.*, 2663 (1973).
(5) E. Grunwald and E. K. Ralph, *Acc. Chem. Res.*, **4**, 107 (1971).
(6) A. L. Van Geet, *Anal. Chem.*, **42**, 679 (1970).
(7) F. M. Menger and G. Saito, *J. Am. Chem. Soc.*, **95**, 6838 (1973).
(8) The reliability of our methods was demonstrated by duplicating to within 15% rates derived by "total" line-shape analysis.
(9) The CMC values of dodecylammonium and *N,N,N*-trimethyldodecylammonium ions are 0.013 and 0.022 *M*, respectively. I. J. Lin and A. Metzer, *J. Phys. Chem.*, **75**, 3000 (1971); R. A. Parker and S. P. Wasik, *ibid.*, **63**, 1921 (1959).
(10) The CMC of decylammonium ion is 0.054 *M*. H. W. Hoyer and A. Greenfield, *J. Phys. Chem.*, **61**, 818 (1957.
(11) The overall rate expression is

$$k_{obsd} = \frac{k_a k_H}{k_H + k_{-a}[H^+]} + \frac{k_2 K_a [R_3NH^+]}{[H^+]} + \frac{k_b K_w}{[H^+]}$$

where k_{obsd} is the observed rate constant corrected for the buffer reaction, K_w is the autoprotolysis constant for water, and K_a is the acidity constant for the ammonium ion. See D. E. Leyden and W. R. Morgan, *J. Phys. Chem.*, **73**, 2924 (1969).
(12) See Figure 2 in ref 5.
(13) Surprisingly, neither inorganic salts nor solubilized benzene appreciably affect the fast rate of micellar proton transfer. The effects of these and other additives will be discussed in the full report.
(14) Recipient of a Camille and Henry Dreyfus Teacher-Scholar Grant and a National Institutes of Health Research Career Development Award.

F. M. Menger,*[14] J. L. Lynn
Department of Chemistry, Emory University
Atlanta, Georgia 30322

Received September 20, 1974

Stereoselective Alkylation of 1-Lithiocyclopropyl Bromides

Sir:

The synthetic application of the title carbenoids (I) has been limited to intramolecular reactions leading to allenes and/or bicyclobutanes.[1] As this is mainly due to the thermal lability, the carbenoids generated at sufficiently low temperatures do react with aldehydes, ketones, and diethyl carbonate to provide otherwise difficultly accessible com-