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(7) That only dipolar intermediates are represented in this scheme is purely a consequence of our focus on the electrophilically available pathways for reaction of **1**. Depending on the nature of the π-electrophile and the preponderance of evidence concerning its mode of nonconcerted, e.g. (2 + 2), cycloaddition, diradical intermediates may be preferable.

(8) The implication that the first ionic intermediate of path b has a classical secondary structure is for the purposes of discussion only and should not be construed as having any supportive basis. In fact the evidence from the acid-catalyzed ring opening of **1** in methanol,[2] as well as the TCNE results presented here, strongly argue against a classical intermediate at this stage of the reaction.

(9) The complex proton spectrum was partially unraveled with the help of decoupling experiments and inspection of molecular models. The assigned long-range coupling constants are of the W-type. The subscripts a (anti), s (syn), x (exo), and n (endo) stereolabel the respective methylene bridge protons at C9 and C10 in accordance with accepted practice for bicyclo[3.2.1]oct-2-ene derivatives.

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Merle A. Battiste,* James M. Coxon, Robert G. Posey
Roy W. King, M. Mathew, Gus J. Palenik
Department of Chemistry, University of Florida
Gainesville, Florida 32611

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Transition Metal Carbonyl Substitution via a Radical Chain Pathway[1]

Sir:

Recognized pathways for substitution at a transition metal carbonyl center include rate-determining CO dissociation, displacement of CO in an associative step, and ligand migration.[2,3] We report here the first evidence for a heretofore unrecognized radical chain pathway for substitution, which may prove to be of considerable generality and importance.

Although substitution of $HRe(CO)_5$ by triphenylphosphine (PPh_3) and other similar ligands has been reported,[4] no kinetics studies have been reported. We found that it was exceedingly difficult to obtain reproducible kinetics results. Under the most rigorous attainable conditions of solvent and reagent purity, with exclusion of light, the thermal reaction in hexane, under N_2, of 10^{-3} *M* $HRe(CO)_5$ with $\sim 10^{-2}$ *M* tributylphosphine, $P(n\text{-}C_4H_9)_3$, exhibited no reaction after 60 days at 25°. Thus $HRe(CO)_5$ is extraordinarily inert toward substitution via CO dissociation or hydride migration pathways, in comparison with $HMn(CO)_5$.[5] Exposure to light, failure to exhaustively purify the reagents, and various other circumstances caused the reaction to go to completion at widely varying rates to yield $HRe(CO)_4L$ and $HRe(CO)_3L_2$. With PPh_3, $HRe(CO)_4L$ was formed at similarly erratic rates. Similar results were obtained in THF as solvent, except that the reactions were generally much faster. Exposure to air or hydroquinone in low concentration retards reaction. Contrary to an earlier report,[6] $HRe(CO)_5$ alone in either solvent does not react with dissolved oxygen at room temperature.

These observations suggest a radical pathway involving adventitious radicals as initiators. The following mechanism accounts for the observations.

$$R + HRe(CO)_5 \longrightarrow RH + Re(CO)_5 \qquad (1)$$

$$Re(CO)_5 + L \longrightarrow Re(CO)_4L + CO \qquad (2)$$

$$Re(CO)_4L + L \longrightarrow Re(CO)_3L_2 + CO \qquad (3)$$

$$Re(CO)_4L + HRe(CO)_5 \longrightarrow Re(CO)_5 + HRe(CO)_4L \qquad (4)$$

$$Re(CO)_3L_2 + HRe(CO)_5 \longrightarrow Re(CO)_5 + HRe(CO)_3L_2 \qquad (5)$$

$$Re(CO)_{5-n}L_n + Re(CO)_{5-m}L_m \longrightarrow Re_2(CO)_{10-n-m}L_{n+m} \qquad (6)$$

Chain termination steps involving formation of $RRe(CO)_5$, $Re_2(CO)_9L$, and $Re_2(CO)_8L_2$ (but probably not $Re_2(CO)_6L_4$[7]) are all possible.

The following results support the proposed mechanism. A solution containing 10^{-3} *M* $HRe(CO)_5$ with 10^{-2} *M* $P(n\text{-}C_4H_9)_3$ in hexane was irradiated with a 1000-W mercury-xenon lamp filtered through an interference filter centered at 311 nm. There resulted a slow substitution to form initially $HRe(CO)_4L$. After 2 hr the reaction was only about 10% complete. Continued irradiation yielded $HRe(CO)_3L_2$ in addition to $HRe(CO)_4L$. After 12 hr of irradiation the reaction was only about 66% complete. Substitution in this system is presumably due to CO photodissociation from $HRe(CO)_5$ and later from $HRe(CO)_4L$.

Our proposed mechanism requires that $Re(CO)_5$ be labile toward substitution, since it probably has a rather short lifetime in solution. The absorption of $Re_2(CO)_{10}$ at 310 nm is ascribed to the σ-σ^* transition of the Re-Re bond.[8,9] Photochemical studies suggest that irradiation of $Re_2(CO)_{10}$ at this wavelength produces $Re(CO)_5$ radicals.[10] A 5×10^{-4} *M* solution of $Re_2(CO)_{10}$ with excess $P(n\text{-}C_4H_9)_3$ in hexane does not undergo substitution at room temperature over a period of several hours. Irradiation at 311 nm for a period of 150 min results in about 15% loss of $Re_2(CO)_{10}$, with $Re_2(CO)_9P(n\text{-}C_4H_9)_3$ and $Re_2(CO)_8[P(n\text{-}C_4H_9)_3]_2$ as products along with several other as yet unidentified substitution products. These results are suggestive of a rapid substitution of (probably) diffusively separated $Re(CO)_5$ radicals, followed by recombination of substituted radicals.[11,12]

A hexane solution containing 10^{-3} *M* $HRe(CO)_5$, $\sim 10^{-2}$ *M* $P(n\text{-}C_4H_9)_3$, and 10^{-4} *M* $Re_2(CO)_{10}$ shows no evidence of reaction in the dark over a period of several hours. The reaction solution was irradiated at 311 nm. Typically, the parent hydride disappeared very slowly during the first 6–10 min, during which time only $HRe(CO)_4L$ was formed as product. After this initial induction period,[13] the reaction proceeds very rapidly under irradiation; reaction is essentially complete after about 5–6 min. Both $HRe(CO)_4L$ and $HRe(CO)_3L_2$ are formed concurrently, in roughly 3:1 ratio.[14,15]

In all the above experiments the flux of 311 nm photons is constant. The results thus indicate that, whatever the quantum yield for photosubstitution of $Re_2(CO)_{10}$, the quantum yield for substitution of $HRe(CO)_5$ with photocatalysis by $Re_2(CO)_{10}$ or $Mn_2(CO)_{10}$ is enormously higher, consistent with the proposed mechanism.

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.

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(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.
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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

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