Further Studies of the Photoinduced Reduction of Carbon Dioxide Mediated by Tricarbonylbromo(2,2'-bipyridine)rhenium(I)

Charles Kutal,*[†] A. Joan Corbin,[†] and Guillermo Ferraudi*[‡]

Department of Chemistry, University of Georgia, Athens, Georgia 30602, and Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana 46556

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Reported are mechanistic studies of the photoinduced reduction of carbon dioxide to carbon monoxide mediated by $ReBr(CO)_3(bpy)$ (bpy is 2,2'-bipyridine). Water, ethanol, and perchlorate ion enhance the intensity of luminescence from the Re-to-bpy charge-transfer excited state, whereas bromide ion and triethylamine (TEA) quench this emission. In the case of the amine, the quenching process leads to prompt formation of $[ReBr(CO)_3(bpy)]^-$. Additional, slower production of this 19e species by reduction of the parent complex by a TEA-derived radical is unimportant. Water and ethanol lower the quantum efficiency of CO formation, whereas Br^- has little effect. Reduction of bicarbonate ion to CO can be excluded as an important pathway in the system. Postirradiation spectral changes occur over several hours, but the chemistry responsible for this behavior is unrelated to CO formation.

Introduction

Interest in the chemical fixation of carbon dioxide has been stimulated in recent years by the desire to convert this plentiful C_1 resource into fuels and industrial feedstocks.[1,2] Several reduction reactions of CO_2 are attractive on thermodynamic grounds in that the energy requirement per electron transferred is rather modest; the process described by eq 1, for example, possesses a redox potential

$$CO_2 + 2H^+ + 2e^- = CO + H_2O \qquad (1)$$

of −0.52 V vs. NHE in pH 7 aqueous solution. In practice, however, direct electrochemical reduction of CO_2 occurs at considerably more negative potentials owing to the presence of a substantial kinetic barrier (overvoltage).[3] Consequently, a viable CO_2 reduction system requires the use of one or more redox catalyst(s) to mediate these multielectron processes and provide low-energy pathways to the desired products.

Several transition-metal complexes have been reported to function in this catalytic role; examples include macrocyclic complexes of cobalt and nickel,[4,5] iron-sulfur clusters,[6] $ReCl(CO)_3(bpy)$[7] (bpy is 2,2'-bipyridine), $Rh(diphos)_2Cl$ (diphos is 1,2-bis(diphenylphosphino)ethane),[8] and polypyridine complexes of ruthenium and rhodium.[9] Typically, the metal complex undergoes initial electrochemical reduction at the surface of an electrode. Subsequent reaction of the reduced species with the electrophilic CO_2 molecule then activates the latter toward processes that ultimately result in the production of CO (e.g., eq 1) or some other reduction product.

An alternative though less-explored approach to CO_2 reduction involves the photochemical generation in homogeneous solution of electron-rich transition-metal species that can serve as redox catalysts. Lehn et al. described the first examples of this strategy,[10] and, very recently, we reported a detailed mechanistic investigation of CO_2 photoreduction mediated by $ReBr(CO)_3(bpy)$ in triethanolamine (TEOA)/dimethylformamide (DMF) solvent mixtures.[11] Equations 2–5 summarize the essential findings of this latter study.

$$ReBr(CO)_3(bpy)^* + TEOA \rightarrow [ReBr(CO)_3(bpy)]^- + TEOA^{\cdot +} \qquad (2)$$

$$TEOA^{\cdot +} + TEOA \rightarrow TEOAH^+ + TEOA'^{\cdot} \qquad (3)$$

$$ReBr(CO)_3(bpy) + TEOA'^{\cdot} \rightarrow [ReBr(CO)_3(bpy)]^- + \text{products} \qquad (4)$$

$$[ReBr(CO)_3(bpy)]^- + CO_2 \rightarrow Y \qquad (5)$$

Reductive quenching of the emissive Re-to-bpy charge-transfer excited state (denoted with an asterisk) by the sacrificial reagent TEOA in eq 2 occurs with a bimolecular rate constant (k_q) of 6×10^7 M^{-1} s^{-1} in *both* Ar-bubbled and CO_2-bubbled solutions. This observation establishes that CO_2 does not interact directly with $ReBr(CO)_3(bpy)^*$ but instead must react with some species produced by the quenching step. Continuous irradiation (436 nm) of a CO_2-saturated solution of $ReBr(CO)_3(bpy)$ in TEOA/DMF results in the highly specific formation of CO with a quantum yield, ϕ_{CO}, that reaches 0.15. The value of ϕ_{CO} depends upon a variety of factors including the nature and concentration of the reducing agent, time of irradiation, and the presence of additives such as water. The kinetic behavior of $[ReBr(CO)_3(bpy)]^-$ can be monitored in the nanosecond–microsecond time regime by flash photolysis techniques. Prompt formation (within 10 ns)

[†] University of Georgia.

[‡] Notre Dame Radiation Laboratory.

(1) Rodenberger, C. A., Baen, S. R., Eds. *Basic Research Opportunities for Lasting Fuel Supplies from Inorganic Resources*; Gas Research Institute: Chicago, 1983.

(2) For a thorough review of metal–CO_2 chemistry, see: Palmer, D. A.; van Eldik, R. *Chem. Rev.* 1983, *83*, 651.

(3) Amatore, C.; Saveant, J. M. *J. Am. Chem. Soc.* 1981, *103*, 5021.

(4) Fischer, B.; Eisenberg, R. *J. Am. Chem. Soc.* 1980, *102*, 7361.

(5) Lieber, C. M.; Lewis, N. S. *J. Am. Chem. Soc.* 1984, *106*, 5033.

(6) Tezuka, M.; Yajima, T.; Tsuchiya, A.; Matsumoto, Y.; Uchida, Y.; Hidai, M. *J. Am. Chem. Soc.* 1982, *104*, 6834.

(7) Hawecker, J.; Lehn, J.-M.; Ziessel, R. *J. Chem. Soc., Chem. Commun.* 1984, 328.

(8) Slater, S.; Wagenknecht, J. H. *J. Am. Chem. Soc.* 1984, *106*, 5367.

(9) Bolinger, C. M.; Sullivan, B. P.; Conrad, D.; Gilbert, J. A.; Story, N.; Meyer, T. J. *J. Chem. Soc., Chem. Commun.* 1985, 796.

(10) (a) Lehn, J.-M.; Ziessel, R. *Proc. Natl. Acad. Sci. U.S.A.* 1982, *79*, 701. (b) Hawecker, J.; Lehn, J.-M.; Ziessel, R. *J. Chem. Soc., Chem. Commun.* 1983, 536.

(11) Kutal, C.; Weber, M. A.; Ferraudi, G.; Geiger, D. *Organometallics* 1985, *4*, 2161.

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of this reduced species occurs via eq 2, while much slower production is thought to result from eq 4. In the latter process, ground-state $ReBr(CO)_3(bpy)$ accepts an electron from the strongly reducing $TEOA'^{\bullet}$ radical ($(OHCH_2CH_2)_2N(CH_2\dot{C}HOH)$ or $(OHCH_2CH_2)_2N(\dot{C}HCH_2OH)$) generated in eq 3. Most importantly, the amount of $[ReBr(CO)_3(bpy)]^-$ produced in the flash experiment correlates with the value of ϕ_{CO} measured in continuous photolysis. Such behavior strongly supports the view that reaction between the 19e reduced Re complex and CO_2 initiates a sequence of events that culminates in production of CO. Direct observation of this initial reaction has, in fact, been achieved, but the identity of the resulting long-lived transient, Y in eq 5, and its precise role in the mechanism of CO_2 reduction have yet to be elucidated.

Since the abiotic photoreduction of CO_2 is of both intrinsic interest and potential industrial importance, we have undertaken additional studies of the $ReBr(CO)_3(bpy)$/TEOA/DMF model system with the goal of gaining a better understanding of the photophysical and photochemical processes involved. Reported below are photoluminescence, continuous photolysis, and flash photolysis results, the significance of which are considered within the mechanistic framework provided by eq 2–5.

Experimental Section

(a) Reagents. Analytically pure $ReBr(CO)_3(bpy)$ was prepared as described previously.[11] Dimethylformamide (Aldrich, >99%) and triethylamine (Eastman, 99%) were dried over potassium hydroxide for 1.5 h, refluxed with calcium oxide for 2 h, and finally distilled under nitrogen. Triethanolamine (Fisher, 99.1%, 0.2% water) was used as received. Reagent grade sodium bicarbonate (Baker) and triethylammonium perchlorate (Eastman) were used as received, while tetraethylammonium bromide (Eastman) was recrystallized from absolute ethanol, washed with ice cold hexane, and dried over phosphorus pentoxide in an evacuated dessicator. High purity nitrogen, argon, and carbon dioxide (>99.9% by gas chromatography) were employed in the luminescence and photochemical experiments.

(b) Measurements. Electronic absorption spectra were recorded on a Cary 219 spectrophotometer, while luminescence spectra were measured on a Perkin-Elmer MPF-44B spectrofluorimeter. Flash photolyses, continuous photolyses, and analyses of gaseous products were performed by using equipment and procedures identical to those reported earlier.[11]

Results and Discussion

(a) Luminescence and Flash Photolysis Studies. Addition of 10% (by volume) water or 20% absolute ethanol to a deaerated DMF solution of $ReBr(CO)_3(bpy)$ enhances the intensity of the charge-transfer luminescence by 15–20% with little or no alteration in peak position.[12] Qualitatively similar behavior occurs in the presence of 1×10^{-2} M $(C_2H_5)_4N^+(ClO_4)^-$. Such increases in intensity presumably reflect the sensitivity of metal-to-ligand charge-transfer excited states to changes in solvent polarity or hydrogen bonding ability.[13,14]

In contrast to the behavior just described, millimolar quantities of bromide ion (as the $(C_2H_5)_4N^+$ salt) quench the luminescence of $ReBr(CO)_3(bpy)$. Conventional Stern–Volmer analysis of the emission intensity as a function of anion concentration affords a k_q value, 9×10^8 M^{-1} s^{-1}, which is appreciably higher than that observed for TEOA.[15] Accordingly, in systems containing both the amine and added bromide ion, competitive quenching by the latter species should be taken into account.

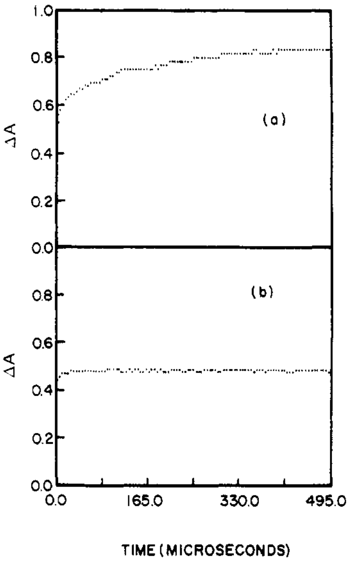

Figure 1. Transient absorbance changes observed upon flash photolysis of $ReBr(CO)_3(bpy)$ in N_2-bubbled (a) TEOA (2.3 M)/DMF and (b) TEA (2.2 M)/DMF. Monitoring wavelength was 510 nm.

Energetics militate against complete electron transfer from Br^- to the charge-transfer excited state of $ReBr(CO)_3(bpy)$ (eq 6) as the mechanism of quenching; this

$$ReBr(CO)_3(bpy)^* + Br^- \rightarrow [ReBr(CO)_3(bpy)]^- + Br^{\bullet} \quad (6)$$

process possesses an estimated endoergicity of ~1 V[16] and thus should be of relatively little consequence. In accord with this expectation, we find no evidence for the formation of the reduced Re complex upon flash photolyzing a DMF solution of the two components. Partial electron transfer or enhanced spin–orbit coupling (i.e., a type of heavy-atom effect) within a $ReBr(CO)_3(bpy)^*/Br^-$ exciplex[17] could promote radiationless decay of the emissive excited state, but at present we have insufficient data to judge the importance of these quenching pathways.

Our earlier investigation of photoinduced CO_2 reduction in the $ReBr(CO)_3(bpy)$/TEOA/DMF system[11] revealed that ϕ_{CO} drops by ~60% upon changing the reducing agent from triethanolamine to triethylamine (TEA). To gain some insight concerning the origin of this effect, we monitored the quenching of $ReBr(CO)_3(bpy)^*$ by TEA (eq 7) in DMF solution. Stern–Volmer treatment of the data

$$ReBr(CO)_3(bpy)^* + TEA \rightarrow [ReBr(CO)_3(bpy)]^- + TEA^{\bullet +} \quad (7)$$

yields a bimolecular quenching rate constant, 6.7×10^7 M^{-1} s^{-1}, which is essentially identical with that found for TEOA. Consequently, the disparity in ϕ_{CO} values for the two amines cannot be attributed to different rates of the initial reductive quenching step (eq 2 and 7).

Additional information bearing on this issue was obtained from a flash photolysis study of $ReBr(CO)_3(bpy)$

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[12] Higher percentages of water cause further increases in intensity and a gradual blue-shift of the emission maximum. In contrast, raising the ethanol content to 40% enhances luminescence intensity without changing the peak position.

[13] Caspar, J. V.; Meyer, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 5583.

[14] Manuta, D. M.; Lees, A. J. *Inorg. Chem.* **1983**, *22*, 3825.

[15] No new features are evident in the absorption spectrum of 2.3×10^{-4} M $ReBr(CO)_3(bpy)$ in DMF upon addition of 2.8×10^{-3} M bromide ion, thereby supporting the treatment of the quenching as a dynamic process.

[16] (a) This estimate is based upon the reduction potentials for the couples $Br^{\bullet}/Br^-$ (2.06 V vs. NHE in H_2O[16b]) and $ReBr(CO)_3(bpy)^*/[ReBr(CO)_3(bpy)]^-$ (~1.1 V vs. SCE in CH_3CN[11]). (b) Woodruff, W. H.; Margerum, D. W. *Inorg. Chem.* **1973**, *12*, 962.

[17] Slama-Schwok, A.; Gershuni, S.; Rabani, J.; Cohen, H.; Meyerstein, D. *J. Phys. Chem.* **1985**, *89*, 2460.

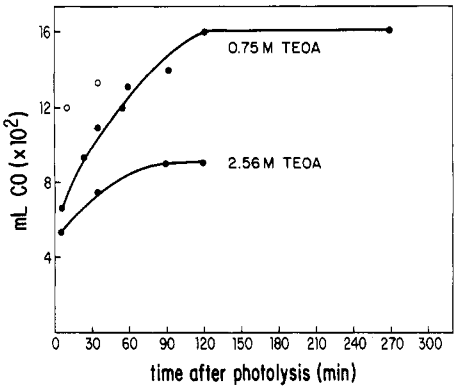

Figure 2. Time profile of CO evolution from CO_2-saturated solutions of $ReBr(CO)_3(bpy)$ in TEOA/DMF: (●) Samples were irradiated at 436 nm for 700 s and then left to sit undisturbed in the dark for varying periods prior to analysis; (○) samples were irradiated as above, but stirring was continued in the dark prior to analysis.

in N_2-bubbled TEA/DMF solution. Excitation of the complex induces an absorbance increase that rapidly attains its maximum value and thereafter decays on a much longer time scale (Figure 1b). The transient responsible for this behavior is readily identified as $[ReBr(CO)_3(bpy)]^-$ by its spectral characteristics.[11] The prompt appearance of this species suggests that it originates predominately from the reductive quenching process described by eq 7. Furthermore, the relative yield of $[ReBr(CO)_3(bpy)]^-$ in this system approximately matches that observed for reductive quenching by TEOA (eq 2) under equivalent conditions (compare ΔA values at zero time in Figure 1a,b). This latter finding and the luminescence results reported above establish that TEA and TEOA undergo very similar interactions with the photoexcited Re complex.

In contrast, a clear distinction exists between the reactivities of radical species derived from the two amines. Examination of Figure 1a,b reveals that the additional, slow production of $[ReBr(CO)_3(bpy)]^-$ via eq 3 and 4 in the TEOA-containing sample is unimportant in the corresponding TEA system.[18] Since this postirradiation thermal reduction process increases the overall yield of the key 19e Re intermediate, it is the most likely cause for the disparity in the ϕ_{CO} values of TEOA and TEA.

(b) Continuous Photolysis Studies. Initial attempts to reproduce the quantum yield data reported in our earlier study of CO_2 reduction in the $ReBr(CO)_3(bpy)$/TEOA/DMF system resulted in ϕ_{CO} values that were generally low and frequently irreproducible. Systematic examination of these difficulties revealed that samples irradiated with stirring for 700 s and then left to sit undisturbed in the dark continued to release CO for 1–2 h.[19] Typical results for two different concentrations of TEOA are illustrated in Figure 2 (filled circles). Since the amount of CO evolved (and therefore the magnitude of ϕ_{CO}) depends upon the length of the postirradiation period,[20] all quantum yields reported below are based upon CO analyses performed 1 h after the cessation of photolysis. Although the values of ϕ_{CO} obtained via this procedure may be systematically low (20–25% for [TEOA] = 0.75 M; see Figure 2), relative comparisons within a series of samples should be valid.

Table I. Quantum Yields of CO Production

run	soln compositn[a]	ϕ_{CO}[b,c]
A	0.75 M TEOA	0.13
B	0.75 M TEOA + 10% H_2O	0.079
C	0.75 M TEOA + 20% C_2H_5OH	0.11
D	0.75 M TEOA + 10% H_2O + 1 × 10^{-2} M HCO_3^-	0.0015
E	0.75 M TEOA + 1 × 10^{-2} M Br^-	0.14[d]

[a] Solution consisted of the indicated components and 1 × 10^{-3} M $ReBr(CO)_3(bpy)$ dissolved in DMF; T = 25 °C; sample bubbled with CO_2 for 35 min; irradiation time of 700 s. [b] ϕ_{CO} is defined as (mol of CO produced/einsteins absorbed by $ReBr(CO)_3(bpy)$). Values of ϕ_{CO} have been corrected for incomplete quenching of $ReBr(CO)_3(bpy)^*$ by TEOA. [c] Values of ϕ_{CO} may be systematically low by 20–25%; see text. [d] Value of ϕ_{CO} also corrected for unproductive quenching by Br^-.

Enhancements in the luminescence intensity of $ReBr(CO)_3(bpy)$ resulting from the addition of water or ethanol (vide supra) are not mirrored in the effect of these hydroxyl-containing compounds on the quantum yields of CO production. As summarized in Table I (runs A–C), 10% water decreases ϕ_{CO} by 40% whereas 20% ethanol causes an 18% drop. Flash photolysis studies[11] reveal that yields of the primary reduction product $[ReBr(CO)_3(bpy)]^-$ (e.g., eq 2) experience parallel declines (i.e., in a 2:1 ratio) in the presence of these additives. The close correspondence between these two sets of data once again illustrates the direct involvement of the 19e Re species in the mechanism of CO_2 reduction.

Electrochemical evidence led Tazuke et al.[21] to postulate the existence of a complex between TEOA and CO_2 in aqueous solution (eq 8). Since this species can be plausibly

$$CO_2 + N(CH_2CH_2OH)_3 + H_2O \rightarrow HOCO_2NH(CH_2CH_2OH)_3 \quad (8)$$

formulated as a bicarbonate (i.e., $HCO_3^-(CH_2CH_2OH)_3NH^+$), we investigated the possibility that HCO_3^- rather than CO_2 was undergoing reduction in the $ReBr(CO)_3(bpy)$/TEOA/DMF system.[22] As seen in Table I (runs b and d), the efficiency of CO production for a solution containing 10^{-2} M $NaHCO_3$[23] is less than 3% of that in a CO_2-saturated solution. This result and the previous finding that water adversely affects ϕ_{CO} argue against the importance of eq 8 in the production of CO.

Some photodegradation of the catalytic system occurs as evidenced by the trend toward smaller ϕ_{CO} values with time of irradiation.[11] The data of Lehn et al.[10b] suggest that addition of bromide ion retards this undersirable pathway and results in enhanced production of CO over long time periods. This stabilizing effect is somewhat surprising in view of our finding that Br^- quenches the photoactive excited state of $ReBr(CO)_3(bpy)$. As seen in Table I (runs a and e), the anion has relatively little effect on ϕ_{CO}, at least for short irradiation times. We conclude from this result that added Br^- plays no direct role (other than as an unproductive quencher) in the mechanism of CO_2 reduction. Most likely, its effect on the longevity of

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[18] (a) Whether this behavior reflects a weaker reducing ability of $(C_2H_5)_2N(\dot{C}HCH_3)^{18b}$ (formed in a process analogous to eq 3) relative to $TEOA'^{\cdot}$ or involves some other factor cannot be determined from our results. (b) For a discussion of the properties of this type of radical, see: DeLaive, P. J.; Foreman, T. K.; Giannotti, C.; Whitten, D. G. *J. Am. Chem. Soc.* **1980**, *102*, 5627.

[19] This postirradiation effect was traced to the sluggishness of CO release from solution. Control experiments reveal that stirring a sample after photolysis enhances the rate of escape of the dissolved gas (see Figure 2, open circles).

[20] Since quantum yields calculated from data in the plateau regions of Figure 2 agree rather well (10–15%) with the values reported previously,[11] we infer that photolyzed samples in the earlier study fortuitously were left to sit unstirred in the dark for 1–2 h before analysis.

[21] Kitamura, N.; Kazami, S.; Tazuke, S., Abstracts of 5th International Conference on Photochemical Conversion and Storage of Solar Energy, Osaka, Japan, Aug 1984, p 330.

[22] Anhydrous triethanolamine is extremely difficult to obtain; the small amount (0.2%) of water present in our sample could lead to the formation of bicarbonate via eq 8.

[23] Addition of 10% water to the solvent was required to dissolve $NaHCO_3$.

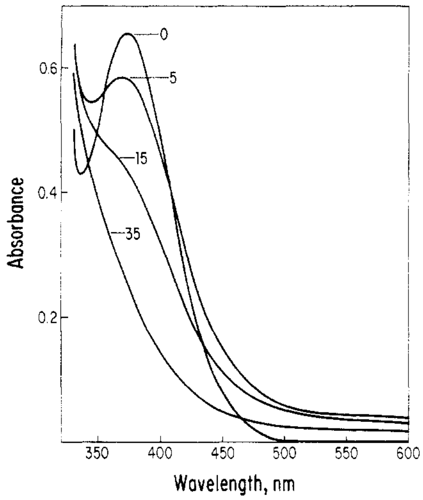

Figure 3. Spectral changes resulting from 436-nm irradiation of ReBr(CO)$_3$(bpy) in a TEOA (1.5 M)/DMF solution bubbled with Ar. Indicated times of irradiation are in minutes.

the catalytic cycle arises from the ability to regenerate some Re-containing catalyst or catalyst precursor (e.g., ReBr(CO)$_3$(bpy)). Such a role also accounts for the effect of added chloride ion on the ReCl(CO)$_3$(bpy)-mediated electrochemical reduction of CO$_2$.[7]

(c) Electronic Absorption Spectral Studies. It was noted previously[11] that solutions of ReBr(CO)$_3$(bpy) in CO$_2$-saturated TEOA/DMF undergo marked spectral changes upon continuous irradiation at 436 nm. As photolysis proceeds, the Re-to-bpy charge-transfer absorption band at 375 nm experiences a blue-shift accompanied by first an increase and then a decrease in intensity. As displayed in Figure 3, quite different behavior occurs for an Ar-bubbled sample under comparable photochemical conditions. The charge-transfer band drops steadily and develops a tail at longer wavelengths. This disparity between CO$_2$- vs. Ar-saturated solutions is not unexpected in view of flash photolysis results that reveal that the initial photoreduction product [ReBr(CO)$_3$(bpy)]$^-$ follows different reaction pathways depending upon the dissolved gas in the system.[11]

We were surprised, however, by the discovery that the spectral changes observed during continuous photolysis experiments continue for extended periods in the dark. Figure 4 depicts this behavior for a CO$_2$-bubbled sample that had been irradiated for 35 min and then left to sit in the dark for up to 3 h. Small but reproducible increases in absorbance during the postirradiation period establish that one or more species undergo(es) thermal chemistry on an exceedingly long time scale. Argon-saturated samples also exhibit spectral changes well after the cessation of photolysis (Figure 5). Here again, the pattern of these changes differs from those seen in CO$_2$-containing samples.

Further studies are needed to characterize the processes giving rise to these slow spectral changes.[24] Nevertheless, it appears that the reactions occurring on this time scale (i.e., several hours) do not contribute substantially to the formation of CO. We base this assertion on the finding that the spectral changes continue well beyond the time at which CO production ceases. In one particularly convincing demonstration of this point, postirradiation stirring liberated 75% of the total CO produced in a sample within 10 min while the spectral changes continued for up to 22 h.

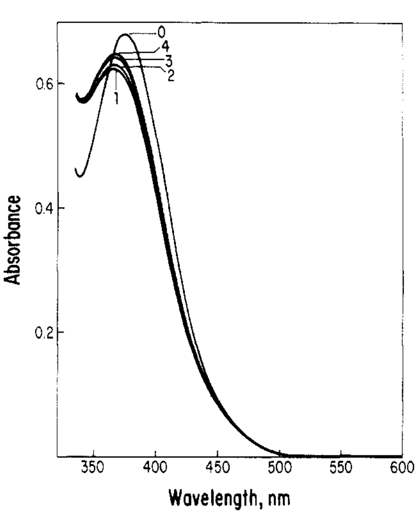

Figure 4. Postirradiation spectral changes exhibited by a CO$_2$-bubbled solution of ReBr(CO)$_3$(bpy) in TEOA (1.5 M)/DMF. Spectrum 0 corresponds to an unphotolyzed solution, while spectra 1–4 were measured 2 min, 25 min, 2 h, and 3 h, respectively, after photolysis at 436 nm for 2100 s.

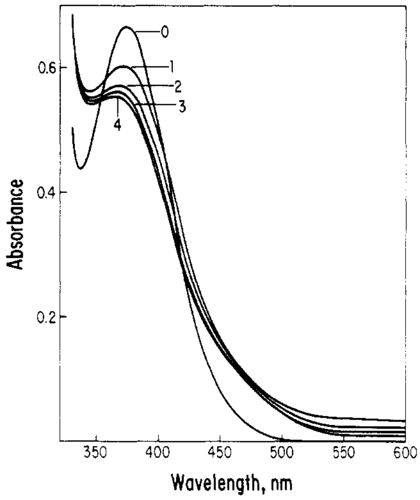

Figure 5. Postirradiation spectral changes exhibited by an Ar-bubbled solution of ReBr(CO)$_3$(bpy) in TEOA (1.5 M)/DMF. Spectrum 0 corresponds to an unphotolyzed solution, while spectra 1–4 were recorded 2 min, 25 min, 1 h, and 2 h, respectively, after photolysis at 436 nm for 300 s.

Concluding Remarks

The present study clarifies certain aspects of our earlier work on the mechanism of the ReBr(CO)$_3$(bpy)-mediated photoreduction of CO$_2$ and, in addition, reveals some interesting behavior that previously went unnoticed. Several points are worthy of mention. (1) Water, ethanol, and perchlorate ion enhance luminescence from the Re-to-bpy charge-transfer state by altering the solution environment of the Re complex. Bromide ion, on the other hand, quenches this emission by a process of unknown origin. (2) Triethanolamine and triethylamine are equally effective in the generation of [ReBr(CO)$_3$(bpy)]$^-$ via reductive quenching of the photoexcited Re complex. Radicals derived from the former amine cause additional reduction of the ground-state complex. The absence of this latter pathway for TEA accounts for its substantially lower ϕ_{CO} value. (3) Like water, ethanol decreases the quantum efficiency of CO formation. This apparently general property of hydroxyl-containing compounds arises from

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(24) One possibility is ReH(CO)$_3$(bpy) which has been reported to undergo a slow thermal reaction with CO$_2$ to yield the corresponding formate complex.[24b] In Ar-saturated solution, the hydride would necessarily react via a different route (compare Figures 4 and 5). (b) Sullivan, B. P.; Meyer, T. J. *J. Chem. Soc., Chem. Commun.* **1984**, 1244.

their adverse effect upon the formation and decay of the primary photoreduction product $[ReBr(CO)_3(bpy)]^-$ (eq 2). (4) While bromide ion has been reported to increase the long-term stability of the catalytic system, it appears to play no direct role in the production of CO. Likewise, reduction of bicarbonate ion (rather than CO_2) to CO can be discounted as a significant process. (5) Thermal chemistry continues to occur for several hours after the cessation of photolysis. The available evidence suggests that such behavior arises from processes unrelated to the formation of CO.

Further advances in understanding the mechanism of CO_2 reduction in this system await characterization of catalytically active Re-containing intermediates. Efforts directed along these lines are underway in this laboratory.

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Reactions of Organotin Hydrides with Lithium Diisopropylamide and Organolithiums. Reactivities of the Intermediates and of the Lithium Hydride Produced

Werner Reimann, Henry G. Kuivila,* Dan Farah, and Theodorus Apoussidis

Department of Chemistry, State University of New York at Albany, Albany, New York 12222

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Equimolar lithium diisopropylamide (LDA) and trimethyltin hydride (TMTH) react in tetrahydrofuran (THF) to form diisopropylamine and (trimethylstannyl)lithium, but in diethyl ether or hexanes 2 mol of TMTH is required for complete reaction and the products are diisopropylamine, hexamethylditin, and lithium hydride. When organic halides are present in this reacting system, reduction to alkane or substitution to form the trimethylalkyltin may occur depending on the nature of the halide. These and other observations suggest that (trimethylstannyl)lithium is formed as an intermediate yielding the tetraalkyltin. Studies on the products and stoichiometries of the reductions of alkyl bromides in ether and hexanes suggest that three reducing agents may be involved: TMTH, $[Me_3Sn(H)N\text{-}i\text{-}Pr_2]^-$, and $[Me_3SnSn(H)Me_3]^-$. The latter predominates in ether, and either or both of the others predominate in hexanes. Formation of methylcyclopentane from 1-bromo-5-hexene suggests involvement of a free radical mechanism. When methyllithium is used instead of LDA in the reaction with TMTH, the products are tetramethyltin and lithium hydride. This reaction can also be diverted to reduction by the presence of primary bromides. Aryl bromides react in both systems, but the yields of either substitution or reduction products are low. The lithium hydride formed in these reactions is extremely reactive as a base as shown by a brief study of its reaction with weak carbon acids and amines and as a nucleophile by its reaction with hexamethylditin to form (trimethylstannyl)lithium in THF.

Studies on the mechanisms of reactions of (triorganostannyl)alkalis with organic halides have revealed significant effects of solvent and donor addends on the competition between the S_N2 and electron-transfer mechanisms. For example, both mechanisms are observed in the reaction of (trimethylstannyl)sodium with 2-bromooctane in tetrahydrofuran (THF) and the S_N2 component increases upon addition of 18-crown-6.[1] This component disappears when the solvent is an 80:20 ether/THF mixture. Furthermore, 1-bromo-5-hexene yields no cyclized product (by way of 5-hexenyl radicals) in THF, but about 10% is formed in the ether/THF mixtures.[1,2] Observations such as these suggest that useful structure/reactivity information could be obtained if the reactions could be conducted in very poor donor solvents. Then studies could be made in a wide range of donor solvent systems by introduction of suitable donor addends. The method which has been used for the preparation of (organostannyl)alkalis in most mechanistic studies involves the reaction of the metal with hexalkylditin; however, this method is unsatisfactory in poor donor solvents such as ethyl ether. Therefore, it was decided to explore use of an alternative method that did not involve reduction by the alkali metal.

Lithium Diisopropylamide

The method of Still[3] that involves the reaction of the triorganotin hydride with lithium diisopropylamide (LDA) (eq 1) and provides essentially quantitative yields of (trialkylstannyl)lithium in THF was explored.

$$Me_3SnH + i\text{-}Pr_2NLi \rightarrow Me_3SnLi + i\text{-}Pr_2NH \quad (1)$$

When equimolar amounts of the reactants of eq 1 were mixed in cyclohexane or diethyl ether at 0 °C and allowed to stand, a white precipitate formed and NMR showed the presence of hexamethylditin and equal amounts of LDA and diisopropylamine. The presence of the unreacted LDA suggested that the stoichiometry of the reaction which occurred was that of eq 2, and this was confirmed by its

$$2Me_3SnH + i\text{-}Pr_2NLi \xrightarrow[\text{hexanes}]{\text{ether or}} (Me_3Sn)_2 + i\text{-}Pr_2NH + LiH \quad (2)$$

absence in the reaction product mixture when this stoi-

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[3] Still, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 1481.

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