A Mechanistic Investigation of the Photoinduced Reduction of Carbon Dioxide Mediated by Tricarbonylbromo(2,2'-bipyridine)rhenium(I)

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Received February 15, 1985

A mechanistic study of the photoinduced reduction of carbon dioxide to carbon monoxide in the triethanolamine/dimethylformamide/$ReBr(CO)_3(bpy)$ (bpy is 2,2'-bipyridine) system is described. Continuous photolysis at 436 nm results in the highly specific formation of CO with a quantum yield, ϕ_{CO}, that reaches 0.15. The value of ϕ_{CO} decreases with increasing triethanolamine concentration in the range 0.75–3.8 M; addition of 10% water to the solvent medium also lowers ϕ_{CO}. Luminescence measurements reveal that triethanolamine reductively quenches the Re-to-bpy charge-transfer excited state of $ReBr(CO)_3(bpy)$ with a rate constant of 6×10^7 M^{-1} s^{-1}, whereas CO_2 undergoes no discernible interaction with the photoexcited complex. Formation and decay of the initial reduction product $[ReBr(CO)_3(bpy)]^-$ have been observed in flash photolysis experiments. The amount of $[ReBr(CO)_3(bpy)]^-$ produced correlates with the value of ϕ_{CO}, thereby implicating this 19e complex in the mechanism of CO_2 reduction. Evidence that $[ReBr(CO)_3(bpy)]^-$ reacts directly with CO_2 has been obtained, although the identity of the resulting product is unknown at present.

Introduction

Nonbiological systems capable of reducing carbon dioxide are of considerable interest as a means of transforming this abundant raw material into fuels and organic chemicals.[1-3] Recently, Lehn and co-workers reported[3c] that visible-light irradiation of $ReA(CO)_3(bpy)$ (A is Cl or Br; bpy is 2,2'-bipyridine) in a CO_2-saturated solvent mixture of triethanolamine (TEOA)/dimethylformamide (DMF) results in the reduction of carbon dioxide to carbon monoxide with high chemical specificity. It was proposed that reductive quenching of the lowest Re-to-bpy charge-transfer excited state of the complex by TEOA generates a species, $[ReA(CO)_3(bpy)]^-$, capable of mediating the two-electron process represented by eq 1.[4] While few

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

details concerning the nature of the interaction between this reduced species and CO_2 are currently available, it seems clear that a great deal of interesting and potentially useful chemistry is occurring at the Re center. We have undertaken a mechanistic investigation of the $ReBr(CO)_3(bpy)/TEOA/DMF/CO_2$ system and report here luminescence quenching, continuous photolysis, and flash photolysis data. Our results confirm the proposal concerning the initial photochemical act and also provide additional insight about the overall mechanism of CO_2 reduction.

Experimental Section

(a) Reagents. Dirhenium decacarbonyl (Aldrich) was purified by vacuum sublimation at 95 °C. Addition of a slight excess of bromine to a chilled (5 °C) methylene chloride solution of $Re_2(CO)_{10}$ yielded $ReBr(CO)_5$; evaporation of the solvent afforded the solid compound which was washed with distilled water and air-dried. Reaction of $ReBr(CO)_5$ and bpy according to the directions of Wrighton and Morse[5] gave $ReBr(CO)_3(bpy)$ (reported to be the facial isomer) in good yield. The purity of the product was established by spectroscopy (UV-visible and infrared) and elemental analysis.

Dimethylformamide (Aldrich Gold Label) and triethylamine (Baker reagent grade) were dried over potassium hydroxide and then distilled from calcium oxide. Triethanolamine (Aldrich) was used as received. The carbon dioxide (Selox) employed in the photochemical studies was found to be ≥99% pure by gas chromatography.

(b) Physical Measurements. Electronic absorption spectra were recorded on Cary 15 and 219 spectrophotometers. Infrared spectra were measured on a Perkin-Elmer 599B spectrometer. Luminescence spectra were taken with a Perkin-Elmer MPF-44B spectrofluorimeter and are uncorrected for photomultiplier response. Lifetimes were determined with an Ortec 9200 time-resolved spectrometer. Viscosities were measured with a Cannon viscometer.

(c) Continuous Photolysis Procedures. Photolyses at 436 nm were conducted with a 200-W high-pressure mercury-arc lamp (Illumination Industries) in conjunction with suitable interference and blocking filters. Incident light intensity was determined by Reineckate actinometry.[6] In a typical photochemical run, 3 mL of a TEOA/DMF solution containing $ReBr(CO)_3(bpy)$ was placed into a 1-cm rectangular quartz cell fitted with a rubber septum. The solution was bubbled for 15–30 min with either Ar or CO_2, placed in a thermostated cell holder, and then irradiated while being stirred. A known volume of gas from the headspace above

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(1) For reviews of transition metal–CO_2 chemistry, see: (a) Eisenberg, R.; Hendriksen, D. E. *Adv. Catal.* **1979**, *28*, 79. (b) Sneeden, R. P. A. in "Comprehensive Organometallic Chemistry"; Wilkinson, G., Ed.; Pergamon Press: Oxford, 1982; Vol. 8, Chapter 50.4. (c) Ito, T.; Yamamoto, A. In "Organic and Bio-organic Chemistry of Carbon Dioxide" Inoue, S., Yamazaki, N., Eds.; Wiley: New York, 1982; Chapter 3. (d) Darensbourg, D. J.; Kudaroski, R. A. *Adv. Organomet. Chem.* **1983**, *22*, 129.

(2) For recent studies of electrochemical CO_2 reduction, see: (a) Fischer, B.; Eisenberg, R. *J. Am. Chem. Soc.* **1980**, *102*, 7361. (b) Amatore, C.; Saveant, J.-M. *Ibid.* **1981**, *103*, 5021. (c) Tezuka, M.; Yajima, T.; Tsuchiya, A.; Matsumoto, Y.; Uchida, Y.; Hidai, M. *Ibid.* **1982**, *104*, 6834. (d) Kapusta, S.; Hackerman, N. *J. Electrochem. Soc.* **1983**, *130*, 607. (e) Lieber, C. M.; Lewis, N. S. *J. Am. Chem. Soc.* **1984**, *106*, 5033. (f) Hawecker, J.; Lehn, J.-M.; Ziessel, R. *J. Chem. Soc., Chem. Commun.* **1984**, 328.

(3) For recent studies of photochemical or photoelectrochemical CO_2 reduction, see: (a) Lehn, J.-M.; Ziessel, R. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 701. (b) Bradley, M. G.; Tysak, T.; Graves, D. J.; Vlachopoulos, N. A. *J. Chem. Soc., Chem. Commun.* **1983**, 349. (c) Hawecker, J.; Lehn, J.-M.; Ziessel, R. *Ibid.* **1983**, 536. (d) Halmann, M.; Katzir, V.; Borgarello, E.; Kiwi, J. *Sol. Energy Mater.* **1984**, *10*, 85. (e) Hawecker, J.; Lehn, J.-M.; Ziessel, R. *J. Chem. Soc., Chem. Commun.* **1985**, 56.

(4) The redox potential for the process given by eq 1 is –0.52 V vs. NHE in a pH 7 aqueous solution.

(5) Wrighton, M.; Morse, D. L. *J. Am. Chem. Soc.* **1974**, *96*, 998.

(6) Wegner, E.; Adamson, A. W. *J. Am. Chem. Soc.* **1966**, *88*, 394.

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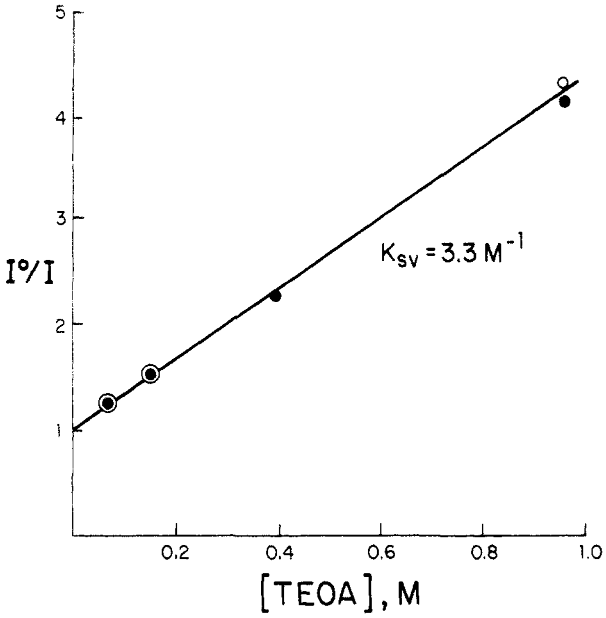

Figure 1. Stern–Volmer plot for quenching of the emissive excited state in $ReBr(CO)_3(bpy)$ by TEOA; I^0 and I denote luminescence intensity in the absence and presence of quencher, respectively: (●) solution bubbed with Ar; (○) solution bubbled with CO_2.

the photolyzed solution was removed with a syringe (inserted into the cell through the rubber septum) and analyzed for CO and H_2 by gas chromatography. The equipment and procedures employed in this analysis are described elsewhere.[7]

A systematic error occurs in the measurement of the quantum yield for CO production, since no account is taken of the CO that remains dissolved in the sample solution. The magnitude of this error can be estimated as follows. The solubility of CO in DMF at 25 °C and 1 atm gas pressure is 2.5×10^{-3} M,[8] and from the ideal gas law, the concentration in the gas phase under these conditions is 4.1×10^{-2} M. Thus the equilibrium constant for partitioning of CO between the two phases (eq 2) is 16.4. Given

$$CO(DMF) \rightleftharpoons CO(gas) \qquad (2)$$

that the sample solution and gaseous headspace in our photolysis cells are of comparable volume, a straightforward calculation shows that >94% of the CO produced during irradiation should reside in the gas phase. Consequently, the error in the quantum yield attributable to dissolved CO is minor (<6%) and has been neglected.

(d) Flash Photolysis Procedures. Since the apparatus employed in the majority of flash photolysis experiments has been described previously,[9] only a few important features will be summarized here. Pulses of polychromatic light having a duration of ~30 μs were obtained from two FP8-100C xenon flash lamps (Xenon Corp.) fired simultaneously at stored electrical energies of 40–250 J/pulse. The wavelength region ≥320 nm was isolated by means of a cutoff filter. Photogenerated transients were detected optically with an analyzing light beam directed through the sample cell. The output of the detector phototube, fed into an appropriate sample-hold circuit, was digitized and processed in a PDP-11/35 computer (Digital).

Transient absorption behavior at times shorter than 30 μs was probed with a Molectron 400 pulsed nitrogen laser. A description of this system is reported elsewhere.[9]

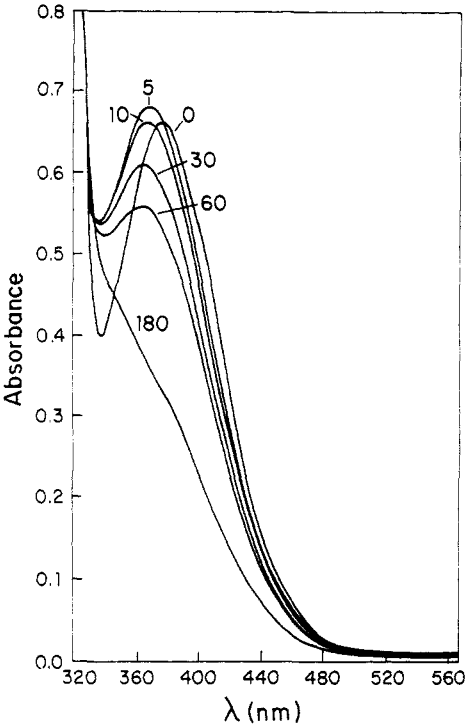

Figure 2. Spectral changes that occur upon 436-nm irradiation of $ReBr(CO)_3(bpy)$ in a TEOA (1.25 M)/DMF solvent mixture bubbled with CO_2. Indicated times of irradiation are in minutes.

Results and Discussion

(a) Luminescence Quenching Studies. A dimethylformamide solution of $ReBr(CO)_3(bpy)$ that has been thoroughly degassed by 3–4 freeze–pump–thaw cycles displays a broad luminescence with λ_{max} at 610 nm and a lifetime of 55 ns (25 °C). The emission originates from a Re-to-bpy charge-transfer excited state (hereafter designated as $ReBr(CO)_3(bpy)^*$) having substantial triplet character.[5] This state has an estimated reduction potential of ≥1.0 V vs. NHE,[10] and thus it should be susceptible to reductive quenching by TEOA ($TEOA^{+\cdot}/TEOA \approx 0.8$V vs. NHE[11]).[12] We monitored this quenching process (eq 3)

$$ReBr(CO)_3(bpy)^* + TEOA \xrightarrow{k_q} [ReBr(CO)_3(bpy)]^- + TEOA^{+\cdot} \qquad (3)$$

and find that it obeys typical Stern–Volmer kinetics. As seen in Figure 1, a plot of I^0/I vs. [TEOA] (I^0 and I represent the luminescence intensity in the absence and presence of quencher, respectively) is linear with a slope, the Stern–Volmer constant (K_{sv}), equal to 3.3 M^{-1}. Dividing this value by the excited-state lifetime in the absence of TEOA (55 ns) yields a bimolecular quenching rate constant, k_q, of $6 \times 10^7\ M^{-1}\ s^{-1}$. Significantly, identical quenching kinetics are observed for solutions bubbled with CO_2 (Figure 1). This observation establishes that CO_2 does not interact directly with $ReBr(CO)_3(bpy)^*$ but instead must react with some species (vide infra) produced by the quenching step.

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[7] King, A. D., Jr.; King, R. B.; Yang, D. B. *J. Am. Chem. Soc.* **1980**, *102*, 1028. King, A. D., Jr.; King, R. B.; Sailers, E. L., III *Ibid.* **1981**, *103*, 1867.

[8] (a) Linke, W. F. "Solubilities of Inorganic and Metal-Organic Compounds"; Van Nostrand: Princeton, NJ, 1958; Vol. 1, p 456. Since the solubility of CO in TEOA is only 4.8×10^{-4} M at 20 °C and 1 atm gas pressure,[8b] we neglect it in the analysis. (b) "Gmelins Handbuch der Anorganischen Chemie"; Verlag: Weinhein, 1970; Vol. 14C, part 1, p 282.

[9] Prasad, D. R.; Ferraudi, G. *Inorg. Chem.* **1982**, *21*, 4241.

[10] (a) The ground-state reduction potential of $ReBr(CO)_3(bpy)$ should be close to the value measured for the corresponding chloro complex,[10b] –1.1 V vs. NHE, while the excited-state energy can be estimated to be ≥2.1 eV from the emission spectrum. Addition of these two quantities yields an approximate value of the excited-state reduction potential. (b) Caspar, J. V.; Meyer, T. J. *J. Phys. Chem.* **1983**, *87*, 952.

[11] Kalyanasundaraman, K.; Kiwi, J.; Grätzel, M. *Helv. Chim. Acta* **1978**, *61*, 2720.

[12] Quenching of $ReBr(CO)_3(bpy)^*$ via energy transfer to TEOA can be discounted owing to the absence of low-energy electronic excited states in the amine.

Table I. Quantum Yields of CO Production Upon 436-nm Irradiation

run	soln compositn[a]	ϕ_{CO}[b,c]
A	3.8 M TEOA	0.038 ± 0.001
B	2.5 M TEOA	0.073 ± 0.002
C	1.9 M TEOA	0.11
D	1.5 M TEOA	0.11
E	1.2 M TEOA	0.13
F	0.83 M TEOA	0.14
G	0.75 M TEOA	0.15 ± 0.00
H	1.2 M triethylamine	0.051
I	2.2 M TEOA + 10% H_2O	0.038
J	2.5 M TEOA[d]	0.077
K	2.5 M TEOA[e]	0.044
L	2.5 M TEOA[f]	*f*
M	2.5 M TEOA[g]	0.073 ± 0.004

[a] Solution consisted of the indicated component(s) dissolved in DMF. [b] Unless indicated otherwise, the following conditions were employed in the photochemical runs: $[ReBr(CO)_3(bpy)] = 1 \times 10^{-3}$ M; $T = 25$ °C; solution saturated with CO_2; 30-min irradiation time. Where quoted, error limits represent mean deviation of two runs. [c] ϕ_{CO} is defined as (mol of CO produced/einsteins absorbed by $ReBr(CO)_3(bpy)$). The values of ϕ_{CO} have been corrected for the percent quenching of $ReBr(CO)_3(bpy)^*$ by TEOA. [d] Sample irradiated 15 min. [e] Sample irradiated 60 min. [f] Sample bubbled with Ar rather than CO_2; no CO detected. [g] Light intensity was half that used in run B.

Changes in solvent composition affect the charge-transfer luminescence of $ReBr(CO)_3(bpy)$. For example, the addition of 10% (by volume) water or absolute ethanol to a deaerated DMF solution of the complex enhances the emission intensity by ~15%. Higher concentrations of water cause further increases in intensity and a blue-shift of the emission maximum.[13]

(b) Continuous Photolysis Studies. In one large-scale photolysis experiment, 30 mL of a 9.4×10^{-4} M solution of $ReBr(CO)_3(bpy)$ in 1:2 (v:v) TEOA/DMF was placed in a Pyrex round-bottom flask, bubbled with CO_2 for 15 min, and then irradiated for 4.5 h with >340-nm light from a 200-W high-pressure Hg-arc lamp. Analysis of the gas above the solution revealed that 10.4 mL of CO had been produced, corresponding to a catalyst turnover of 15.[14] In contrast, no H_2 was detected. These results reproduce the essential findings communicated earlier by Lehn and coworkers.[3c]

Solutions of $ReBr(CO)_3(bpy)$ in CO_2-saturated TEOA/DMF undergo significant spectral changes upon continuous photolysis. As depicted in Figure 2, the Re-to-bpy charge-transfer absorption band at 375 nm experiences an apparent blue-shift accompanied by first an increase and then a decrease in intensity. The absence of isosbestic points is indicative of the formation of two or more absorbing products in relative amounts that vary during photolysis. These spectral characteristics of the system complicate the measurement of quantum yields owing to time-dependent changes in absorbance at the irradiating wavelength and possible secondary-photolysis effects. In an attempt to minimize these difficulties, we determined the quantum yield of CO formation (ϕ_{CO}) at short irradiation times.

Table I contains a compilation of quantum yield data obtained under a variety of experimental conditions. The key findings can be summarized as follows: (1) photoinduced reduction of carbon dioxide in the $ReBr(CO)_3(bpy)/TEOA/DMF/CO_2$ system occurs with a quantum efficiency that reaches 15%; (2) ϕ_{CO} decreases with increasing TEOA concentration within the range 0.75–3.75 M (runs A–G); (3) changing the reducing agent from TEOA to triethylamine causes a drop in ϕ_{CO} (runs E and H); (4) addition of 10% water to the solvent mixture lowers ϕ_{CO} (runs B and I); (5) ϕ_{CO} decreases with increasing time of irradiation (runs B, J, and K); (6) no CO is detected in a sample irradiated in the absence of CO_2 (run L); (7) ϕ_{CO} is independent of light intensity over a twofold range (runs B and M).

Reduction of carbon dioxide in the $ReBr(CO)_3(bpy)/TEOA/DMF$ system is surprisingly efficient given the multielectron nature of the process (eq 1) and the requirement that the metal complex functions as both photosensitizer and redox catalyst. The drop in ϕ_{CO} with increasing TEOA concentration (Table I, runs A–G) also is surprising when one considers that quenching of $ReBr(CO)_3(bpy)^*$ by the amine initiates the sequence of events that eventually results in CO formation. Evidently, some other effect of TEOA comes into play. Further discussion of this interesting behavior and the similar negative influence of water on CO production (Table I, runs B and I) will be presented in section d.

The decrease in ϕ_{CO} upon switching the reducing agent from TEOA to triethylamine (Table I, runs E and H) finds precedent in the behavior of a related CO_2 reduction system.[3a] Whether this disparity arises solely from a difference in the reducing properties of the two amines or involves additional factors (e.g., miscibility of CO_2) has not been established. Lastly, the drop in ϕ_{CO} at longer irradiation times (Table I, runs B, J, and K) suggests the presence of a process that degrades the catalytic system. While we have not investigated the details of this degradation path, it does not appear to involve photodissociation of CO from $ReBr(CO)_3(bpy)$ (Table I, run L).

(c) Flash Photolysis Studies. Flash photolysis of $ReBr(CO)_3(bpy)$ in an argon-bubbled TEOA/DMF solution induces a prompt (i.e., within the ~30 μs flash) increase in absorbance followed by a further growth at longer times (Figure 3a). The absorbance change attains its maximum value, ΔA_{max}, within ~300 μs and thereafter decays on a longer time scale (Figure 3b). The differential spectra determined at various times after the flash are identical (Figure 4), suggesting that they arise from a single absorbing product, X.

Further investigation of the initial, rapid stage in the formation of X was undertaken with a pulsed-laser system. Excitation of $ReBr(CO)_3(bpy)$ in DMF gives rise to a transient absorption attributable to the Re-to-bpy charge-transfer excited state.[15] Quenching of this state by TEOA generates a species that is readily identified as X by its spectral characteristics. The key finding is that no delay occurs between the disappearance of $ReBr(CO)_3(bpy)^*$ and the appearance of X. That is, within the time resolution of the pulsed-laser experiment (~10 ns), the reaction of $ReBr(CO)_3(bpy)^*$ and TEOA yields X directly.

The maximum yield of X (as measured by ΔA_{max}) varies linearly with flash intensity in the range 40–250 J/pulse. This yield initially rises and then drops with increasing TEOA concentration (Figure 4, insert a). Significantly, the ϕ_{CO} values determined in continuous photolysis studies show a similar TEOA dependence over a comparable concentration range (Figure 4, insert b). This close cor-

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[13] For a discussion of solvent effects on metal-to-ligand charge-transfer luminescence in a related system, see: Caspar, J. V.; Meyer, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 5583.

[14] Catalyst turnover is defined as mol of CO produced/mol of $ReBr(CO)_3(bpy)$.[3c]

[15] The assignment of this transient as $ReBr(CO)_3(bpy)^*$ is based upon (i) the similarity of its lifetime to the one obtained from excited-state luminescence decay measurements and (ii) its observed reactivity toward TEOA.

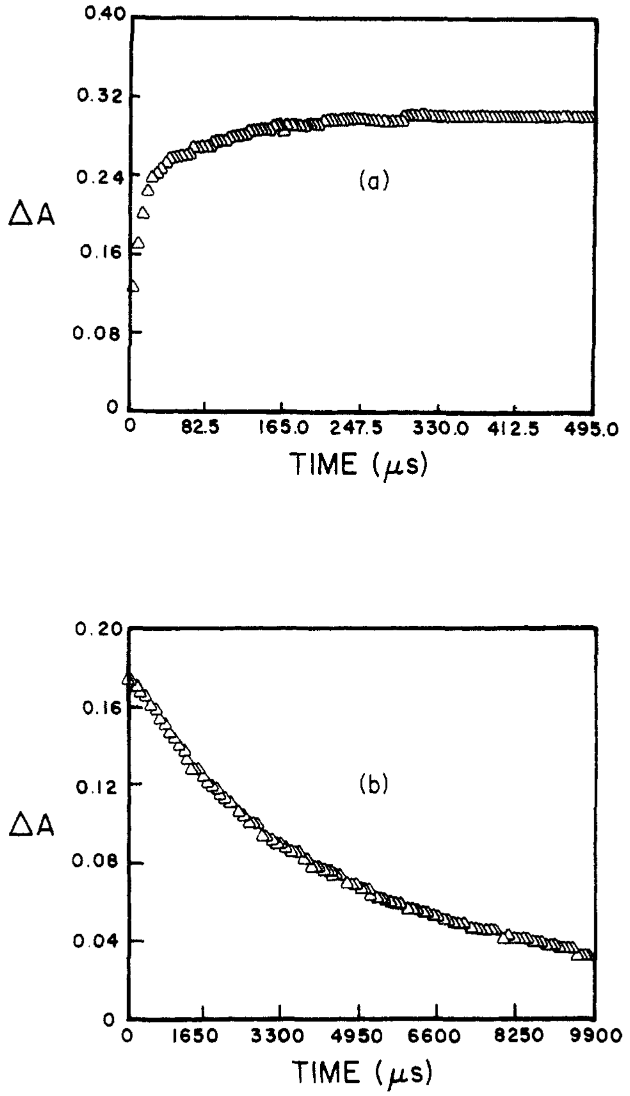

Figure 3. Growth (a) and decay (b) of transient absorption observed upon flash photolysis of $ReBr(CO)_3(bpy)$ in a TEOA (2.3 M)/DMF solvent mixture bubbled with Ar. Monitoring wavelength is 510 nm.

Table II. Viscosities of TEOA/DMF Solutions at 25 °C

soln compositn	viscosity,[a] cP	soln compositn	viscosity,[a] cP
DMF	0.73	2.5 M TEOA in DMF	2.81
0.75 M TEOA in DMF	1.02	3.8 M TEOA in DMF	7.71
1.5 M TEOA in DMF	1.83	TEOA	594

[a] Measurements are reproducible to ±1.5%.

respondence between ϕ_{CO} and the yield of X strongly suggests that the photogenerated intermediate is intimately involved in the mechanism of CO formation.

The effect of various additives on the yield of transient X was investigated. Three solutions containing identical concentrations of $ReBr(CO)_3(bpy)$ and the following solvent composition (percentages are by volume) were prepared: 20% TEOA/DMF, 20% TEOA/10% H_2O/DMF, and 20% TEOA/25% ethanol/DMF. Flash photolysis of these samples gave rise to transient X with relative yields 1:0.3:0.6, respectively.

The decay of X in Ar-saturated solutions (Figure 3b) follows the exponential rate law given by eq 4, where k_{obsd}, the observed rate constant, conforms to the expression in eq 5.

$$\Delta A = \Delta A_{max} e^{-k_{obsd} t} \tag{4}$$

$$k_{obsd} = \frac{0.025 + (0.076\Delta A_{max})^{-1}}{1 + (0.069\Delta A_{max})^{-1}} \tag{5}$$

This complex form for k_{obsd}, which was obtained from a curve-fitting analysis of the experimental data points (Figure 5), is consistent with a competition between first-order and second-order decay paths for X. Addition of excess bromide ion (5×10^{-6}–5×10^{-3} M) or carbonate ion (saturated solution) has no discernible effect upon the decay kinetics. The presence of 10% water or 25% ethanol, on the other hand, accelerates the decay rate.

Flash photolysis of $ReBr(CO)_3(bpy)$ in a TEOA/DMF solution saturated with CO_2 produces transient absorbance changes that, at times ≤75 μs, are similar to those observed in an Ar-bubbled solution (Figure 6). This result reveals that the photochemical formation of X is largely unaffected by the presence of CO_2. At longer times, however, the growth of a new absorption band at 475 nm and the decrease in intensity of the longer wavelength feature indicates that X reacts thermally with CO_2 to produce a new species, Y. Addition of excess Br^- does not affect the kinetic behavior of either X or Y.

(d) Mechanistic Interpretations. The dominant photochemical reaction of $ReBr(CO)_3(bpy)^*$ in TEOA/DMF solvent mixtures is reductive quenching by TEOA to produce $[ReBr(CO)_3(bpy)]^-$ (eq 3). There is ample precedent[16] to suggest that the added electron in this reduced complex resides in an orbital localized to a significant extent on the bpy ligand. Consequently, the reduced species can be viewed in a formal sense as a Re^I center bound to a 2,2′-bipyridine radical anion, that is, $Re^IBr(CO)_3(bpy^-)$. The absorption spectrum of the bpy^- moiety has been determined in a number of different chemical environments and found to posses a characteristic pattern.[16d] For example, bands arising from π^*–π^* transitions have been identified at 386 and 530–560 nm in the spectrum of Na^+bpy^- in tetrahydrofuran, whereas the corresponding transitions in $Ru(bpy)_3^+$ (formulated as $[Ru^{II}(bpy)_2(bpy^-)]^+$) occur at 342 and 500–530 nm. Since similar features are evident in the absorption spectrum of X (Figure 4), the transient observed in flash photolysis, we propose that this species be assigned as $[ReBr(CO)_3(bpy)]^-$.[17] This assignment is also consistent with the chemical properties of X. Thus the lack of reactivity toward the nucleophilic reagents Br^- and CO_3^{2-} seems quite reasonable for a 19e Re complex.[18]

The biphasic formation of $[ReBr(CO)_3(bpy)]^-$ (Figure 3) reflects the operation of two reaction paths. The prompt stage corresponds to the direct production of the reduced complex from $ReBr(CO)_3(bpy)^*$ via eq 3. The triethanolamine radial cation, $TEOA^{+\cdot}$, generated in this process can rapidly abstract a hydrogen atom from another TEOA molecule to produce the very reducing radical,

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[16] (a) Luong, J. C.; Faltynek, R. A.; Wrighton, M. S. *J. Am. Chem. Soc.* **1980**, *102*, 7892. (b) Summers, D. P.; Luong, J. C.; Wrighton, M. S. *Ibid.* **1981**, *103*, 5238. (c) Heath, G. A.; Yellowlees, L. J.; Braterman, P. S. *J. Chem. Soc., Chem. Commun.* 1981, 287. (d) Creutz, C. *Comments Inorg. Chem.* **1982**, *1*, 293.

[17] The alternative assignment of X as a species derived from $[ReBr(CO)_3(bpy)]^-$ via ligand dissociation (e.g., $Re(CO)_3(bpy)$), though not inconsistent with the spectral evidence, seems less tenable on kinetic grounds. Thus it would be necessary for ligand loss to be complete within the time of the flash (<10 ns in the case of the pulsed laser) in order for $[ReBr(CO)_3(bpy)]^-$ to escape detection by our flash photolysis equipment. Such lability is incompatible, however, with electrochemical evidence that indicates the initial one-electron reduction product of $ReCl(CO)_3(bpy)$ is relatively long-lived (i.e., ms or longer). Luong, J. C.; Nadjo, L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1978**, *100*, 5790.

[18] While added halide does not react directly with transient X, it reportedly causes a marked increase in the long-term stability of the CO_2 reduction system.[3c]

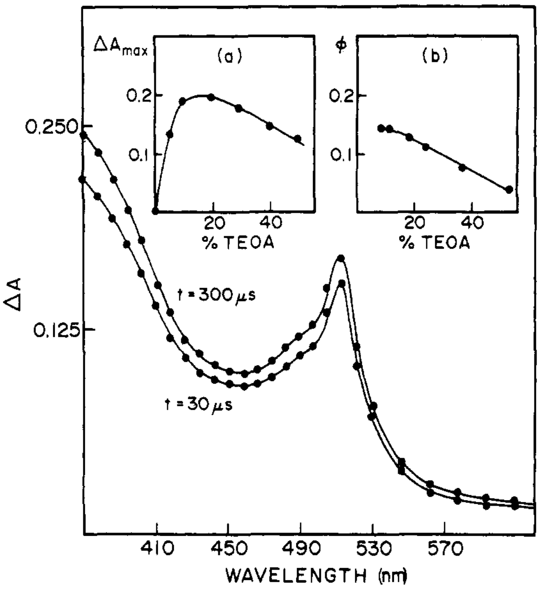

Figure 4. Transient difference spectrum determined at various times following flash photolysis of $ReBr(CO)_3(bpy)$ in a TEOA (2.3 M)/DMF solvent mixture bubbled with Ar. Insert a depicts the dependence of transient yield upon TEOA concentration. Insert b shows the dependence of ϕ_{CO} upon TEOA concentration.

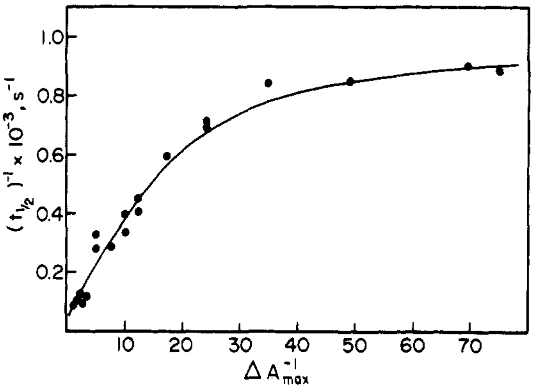

Figure 5. Dependence of the half-life of transient X upon its concentration (Ar-bubbled solution); points are experimentaly determined, whereas solid line is calculated from eq 5.

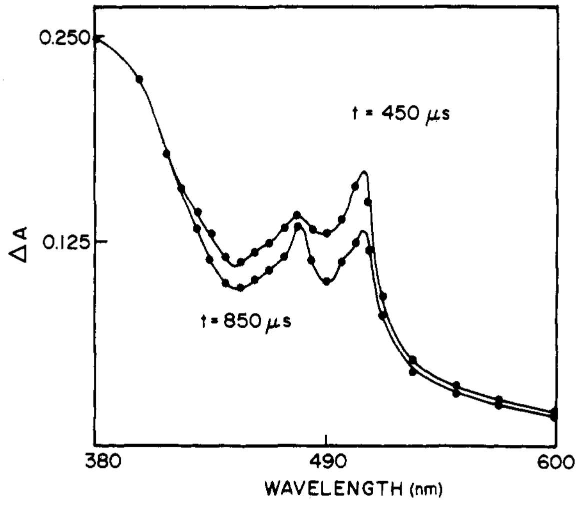

Figure 6. Transient difference spectra determined at various times following flash photolysis of $ReBr(CO)_3(bpy)$ in a TEOA (2.3 M)/DMF solvent mixture bubbled with CO_2.

TEOA′· (eq 6).[19] Subsequent reduction of ground-state $ReBr(CO)_3(bpy)$ by TEOA′· (eq 7) provides a plausible (though tentative[20]) explanation for the additional, slow formation of $[ReBr(CO)_3(bpy)]^-$.

$$TEOA^{+\cdot} + TEOA \rightarrow TEOAH^+ + TEOA'^{\cdot} \tag{6}$$

$$ReBr(CO)_3(bpy) + TEOA'^{\cdot} \rightarrow [ReBr(CO)_3(bpy)]^- + \text{products} \tag{7}$$

Perhaps the most significant finding of the present study is the correlation that exists between the amount of $[ReBr(CO)_3(bpy)]^-$ produced and the quantum yield of CO formation (Figure 4, inserts a and b). Such behavior strongly supports the view that reaction between the 19e Re species and the electrophilic CO_2 molecule activates the latter toward processes that ultimately result in the production of CO. It should be noted that our flash photolysis results provide the first direct observation of the reaction between CO_2 and a photogenerated Re-containing intermediate. While the resulting product Y presumably is a Re complex containing coordinated CO_2, we have no information at present concerning its composition, structure, or subsequent reactivity.[21] These aspects provide fertile areas for further study.

It was noted earlier that the addition of 10% water to the TEOA/DMF solvent system inhibits the photoreduction of CO_2 (Table I, runs B and I). This behavior can now be ascribed to the deleterious effects of water on the reduced complex $[ReBr(CO)_3(bpy)]^-$. Thus water decreases the initial yield of this species and enhances its rate of decay. Both processes reduce the effective concentration of this key intermediate and thereby lower the quantum yield of CO production. Interestingly, Lehn and coworkers reported[2f] that the electrochemical reduction of CO_2 to CO in the presence of $ReCl(CO)_3(bpy)$ as catalyst is enhanced upon the addition of 10% water. This disparity raises the interesting possibility that the photochemical and electrochemical processes differ in mechanistic detail.[22]

Finally, we can suggest two properties of TEOA that may contribute to the declines in ϕ_{CO} and the yield of transient X at high amine concentrations (Figure 4, inserts a and b): (1) the presence of hydroxyl groups,[23] (2) high viscosity.[24] Participation of the OH group is suggested by the similar declines observed for water (see preceding paragraph) and the finding that ethanol, a hydroxyl-containing compound which bears an obvious chemical resemblance to TEOA, also decreases the yield of X. Most importantly, the magnitude of this decrease corresponds closely to that caused by the equivalent amount (in terms of moles of OH groups) of TEOA. The influence of viscosity, on the other hand, can be inferred from the data in Table II which show that TEOA/DMF solutions become

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[19] Chan, S.-F.; Chou, M.; Creutz, C.; Matsubara, T.; Sutin, N. *J. Am. Chem. Soc.* **1981**, *103*, 369.

[20] While the redox potential for the TEOA′+/TEOA′· couple is unknown, TEOA′· has been reported[19] to reduce $Rh(bpy)_3^{3+}$ (Rh^{3+}/Rh^{2+} in aqueous solution is −0.5 V vs. NHE) with an estimated rate constant of $>10^7$ M^{-1} s^{-1}.

[21] (a) Both Re–hydride and Re–formate complexes have been cited as possible intermediates in the $ReA(CO)_3(bpy)$-mediated photoreduction of CO_2 to CO.[3c] In this regard we note with interest the recent report[21b] that CO_2 undergoes photoinduced insertion into the Re–H bond of $ReH(CO)_3(bpy)$ to yield $Re(O_2CH)(CO)_3(bpy)$. While this process accomplishes reduction of CO_2, no mention was made of CO formation. (b) Sullivan, B. P.; Meyer, T. J. *J. Chem. Soc., Chem. Commun.* **1984**, 1244.

[22] Although a common intermediate, $[ReA(CO)_3(bpy)]^-$, is purportedly generated in the electrochemical and photochemical processes, the *subsequent* reactions of this species need not be identical owing to differences in solution composition (e.g., TEOA is present only in the photochemical system)

[23] We thank a reviewer for this perceptive suggestion.

[24] A third possible factor, namely, lower concentrations of dissolved CO_2 in solutions containing increasing amounts of TEOA, can be ruled out by solubility measurements. Grutsch, P. A.; Kutal, C., unpublished results.

significantly more viscous as the amine content increases. Higher viscosity will tend to retard separation of the primary photoproducts formed in the reductive quenching step (eq 3) and thereby enhance the likelihood of unproductive back-electron transfer (eq 8). Additional information about the solution behavior of transient X will be required to decide which of these two properties of TEOA has greater importance.

$$[\mathrm{ReBr(CO)_3(bpy)}]^- + \mathrm{TEOA}^{+\cdot} \rightarrow \mathrm{ReBr(CO)_3(bpy)} + \mathrm{TEOA} \quad (8)$$

Summary

The results of the present study lead to several conclusions regarding the mechanism of CO_2 reduction in the $ReBr(CO)_3(bpy)/TEOA/DMF$ system. (1) The system is both efficient and specific for the photoinduced reduction of CO_2 to CO. Initial quantum yields reach 0.15 with 436-nm irradiation and may prove to be even higher when the optimum reaction conditions are established. (2) The initial photochemical step in the overall reaction sequence involves reductive quenching of photoexcited $ReBr(CO)_3(bpy)$ by TEOA. In contrast, the excited complex undergoes no discernible interaction with CO_2. (3) The reduced product of this quenching step, $[ReBr(CO)_3(bpy)]^-$, can be observed in the ns–μs time regime. In Ar-bubbled solutions, this species disappears via at least two pathways. (4) Scavenging of $[ReBr(CO_3(bpy)]^-$ by CO_2 leads to the appearance of a new species, Y. The identity of Y and its precise role in the mechanism of CO_2 reduction have yet to be ascertained.

Acknowledgment. We wish to thank Professor A. D. King, Mr. Neal Tonks, and Ms. Joan Corbin for valuable technical advice and assistance. We also acknowledge several fruitful discussions with Professor R. B. King. Financial support for this work was provided by the National Science Foundation (Grant CHE-8210558) and by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-2683 from the Notre Dame Radiation Laboratory.

Registry No. TEOA, 102-71-6; DMF, 68-12-2; $ReBr(CO)_3(bpy)$, 40231-87-6; $[ReBr(CO)_3(bpy)]^-$, 98577-53-8; CO_2, 124-38-9; CO, 630-08-0.

Cyclosiloxanes as Frameworks for Multimetallic Compounds. 4. Synthesis and Characterization of Some Tricarbonylchromium-Substituted Methylphenylcyclosiloxanes

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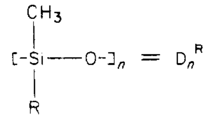
Received February 19, 1985

The cyclosiloxanes $D_n^{PhCr(CO)_3}$ (n = 3, cis,cis,cis and cis,trans,trans; n = 4, cis,trans,cis,trans and mixture of all possible isomers) have been prepared and characterized. Because the $Cr(CO)_3$ substituent renders the ortho and meta protons of the phenyl groups diastereotopic when the phenyl group is located on a chirotopic silicon atom, the structure of the pure n = 4 isomer can be unequivocally established by ^1H NMR. The catalytic properties of $D_3^{PhCr(CO)_3}$ for the hydrosilation of 1,3-pentadiene with triethoxysilane were compared to those of [(trimethoxysilyl)benzene]-, [(trimethylsilyl)benzene]-, and (benzene)chromium tricarbonyls. The lack of any significant difference in reactivity or specificity between the various catalysts supports the idea that catalysis is preceeded by dissociation of the $Cr(CO)_3$ from the arene ring. The absence of any significant specific intramolecular effects in the behavior of the cyclotrisiloxane catalyst is also mirrored in the mass spectral fragmentation behavior of the two cyclotrisiloxane isomers.

Introduction

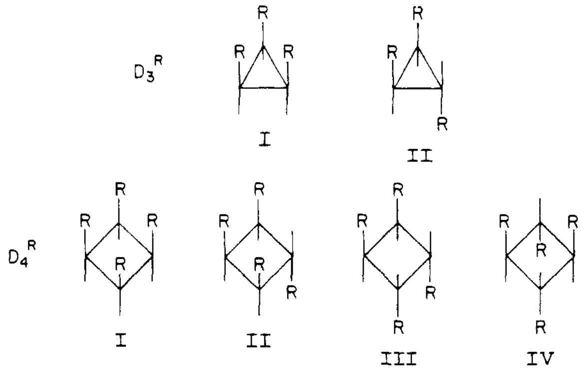
In the earlier papers of this series we described the preparation and characterization of some cyclosiloxanes of the general formula



$$[-\overset{\mathrm{CH_3}}{\underset{\mathrm{R}}{\mathrm{Si}}}\!-\!\mathrm{O}-]_n = D_n^R$$

where R is an organometallic function attached to the siloxane ring through a metal–Si bond.[1] These studies were directed toward exploring the suitability of the cyclosiloxane system as a framework for supporting catalytic functions in a closely defined spatial relationship to each other. In our initial studies we were mainly concerned with the stability of the cyclosiloxane ring system in the presence of organometallic functions and of developing methods for characterizing the different geometric isomers produced in the synthetic reactions. One of the main deficiencies of the systems studied was the failure to achieve complete separation of geometric isomers. Since the ultimate goal of this work is to take advantage of the

Chart I



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[1] (a) Pelletier, E.; Harrod, J. F. *Can. J. Chem.* **1983**, *61*, 762. (b) Pelletier, E. Harrod, J. F. *Organometallics* **1984**, *3*, 1064,1070.