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# Photosensitized Reduction of $CO_2$ to $CH_4$ and $H_2$ Evolution in the Presence of Ruthenium and Osmium Colloids: Strategies To Design Selectivity of Products Distribution[1]

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**Abstract:** Photoreduction of $CO_2$ to methane and higher hydrocarbons is accomplished in aqueous solutions by using visible light and Ru or Os colloids as catalysts. One system is composed of Ru(II) tris(bipyridine), $Ru(bpy)_3^{2+}$, as photosensitizer, triethanolamine, TEOA, as electron donor, and one of the following bipyridinium charge relays: *N*,*N'*-dimethyl-2,2'-bipyridinium, $MQ^{2+}$ (**1**), *N*,*N'*-trimethylene-2,2'-bipyridinium, $TQ^{2+}$ (**2**), *N*,*N'*-tetramethylene-2,2'-bipyridinium, $DQ^{2+}$ (**3**), or *N*,*N'*-bis-(3-sulfonatopropyl)-3,3'-dimethyl-4,4'-bipyridinium, $MPVS^0$ (**4**). Illumination of these systems under $CO_2$ in the presence of Ru or Os colloids results in the formation of methane and ethylene and in $H_2$ evolution. In the second system, illumination of an aqueous solution under $CO_2$ that includes Ru(II) tris(bipyrazine) as sensitizer, TEOA as electron donor, and the Ru colloids leads to the formation of methane, ethylene, and ethane, and no $H_2$-evolution occurs. The reduction process of $CO_2$ proceeds via electron transfer of metal-activated $CO_2$ rather than through a hydrogenation route. Detailed studies show that the $H_2$-evolution process can be inhibited by the addition of bipyrazine, while $CO_2$ reduction is inhibited in the presence of added thiols. Methanation of $CO_2$ by hydrogen proceeds in the dark in the presence of Pt and Ru or Os colloids and in the presence of $MQ^{2+}$ (**1**). The need for the electron relay implies that the methanation process occurs through an electron-transfer mechanism.

Photosensitized cleavage of water to hydrogen and oxygen and reduction of $CO_2$ to organic fuels are of substantial interest for the solar light-induced conversion of abundant materials to novel fuels.[2,3] Extensive efforts have been directed in recent years toward the development of photoinduced $H_2$-evolution systems.[4-7] Homogeneous photosensitizers such as Ru(II) tris(bipyridine), $Ru(bpy)_3^{2+}$, or Zn porphyrins have been applied to photosensitize the reduction of various relay compounds that mediate $H_2$ evolution from aqueous solutions. For example, photoreduced *N*,*N'*-dialkyl-4,4'-bipyridinium radicals (viologen radicals), Co(III) sepulchurate, or $Rh(bpy)_3^{3+}$ mediate $H_2$ evolution from aqueous solutions in the presence of heterogeneous metal colloids such as Pt or Rh.[8-10] $H_2$ evolution has also been accomplished with semiconductor particles suspended in aqueous media in the form of powders or microheterogeneous colloids.[11,12] In these systems metals such as Pt or Rh immobilized on the particles catalyze $H_2$ evolution by conduction band electrons formed by excitation of the semiconductor. Several cyclic systems for the photocleavage of water have been reported,[13,14] although other studies questioned the cyclic activity of the systems.[15] Recent efforts were also directed toward the photoreduction of $CO_2$ to organic fuels.[16-21] Reduction of $CO_2$ might proceed to various products (eq 1-8).

$$2H^+ + 2e^- \rightarrow H_2 \qquad E° = -0.41\ V \tag{1}$$

$$CO_2 + 1e^- \rightarrow CO_2^{\bullet -} \qquad E° = -2\ V \tag{2}$$

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O \qquad E° = -0.52\ V \tag{3}$$

$$CO_2 + 4H^+ + 4e^- \rightarrow C + 2H_2O \qquad E° = -0.20\ V \tag{4}$$

$$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH \qquad E° = -0.61\ V \tag{5}$$

$$CO_2 + 4H^+ + 4e^- \rightarrow HCHO + H_2O \qquad E° = -0.48\ V \tag{6}$$

$$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O \qquad E° = -0.38\ V \tag{7}$$

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \qquad E° = -0.24\ V \tag{8}$$

The standard redox potentials of these reactions at pH 7 are given in the respective equations[16,22] and compared to that of $H_2$ evolution. It can be seen that, while the single-electron reduction potential of $CO_2$ (eq 2) exhibits an extreme value, the multielectron reduction potentials of $CO_2$ to CO, formate, formaldehyde, and methanol exhibit comparable values to that of the $H_2$-evolution process. Furthermore, the reduction potential of $CO_2$ to $CH_4$ is thermodynamically more feasible than that required to reduce protons to $H_2$. Nevertheless, despite the thermodynamic feasibility to reduce $CO_2$, we anticipate kinetic difficulties in accomplishing

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these processes due to the need to pursue multielectron reduction processes. Thus, reduction of $CO_2$ in aqueous solutions is expected to be accompanied, or eventually obscured, by the kinetically favored $H_2$ evolution.

Several recent studies have explored the photoinduced fixation of $CO_2$. Photoreduction of $CO_2$ to CO (eq 3) has been reported by Lehn and co-workers[16] in two different systems using $Re(bpy)(CO)_3Cl$ as photocatalyst or using Ru(II) tris(bipyridine), $Ru(bpy)_3^{2+}$, as sensitizer and cobalt(II) chloride as electron relay. In the latter system $H_2$ evolution is accompanied by $CO_2$ reduction. Photoreduction of $CO_2$ to formate (eq 5) has been claimed by Tazuke,[17] but later studies questioned the formation of formate by $CO_2$ reduction.[18] Reduction of $CO_2$ to $HCO_2^-$ has been reported by Lehn[19] using $Ru(bpy)_3^{2+}$ as photosensitizer in a dimethylformamide–triethanolamine–aqueous medium that contains $CO_2$.

Fixation of $CO_2$ to various organic fuel products in very low yields has been reported by use of semiconductors.[20] We have recently reported on the specific photosensitized fixation of $CO_2$ into organic acids or formate using enzymes as specific $CO_2$-fixation catalysts.[21] Similarly, in a primary note we have exemplified the application of Ru colloids as catalysts for the photoreduction of $CO_2$ to methane.[1]

Here we describe the photosensitized fixation of $CO_2$ to $CH_4$ and higher hydrocarbons using visible light. In these systems Ru and Os colloids act as $CO_2$-fixation catalysts. We discuss two different systems for the reduction of $CO_2$ to $CH_4$. One system involves the primary photosensitized reduction of *N,N'*-bipyridinium charge relays that mediate $CO_2$ reduction and $H_2$ evolution in the presence of Ru and Os colloids. The second system involves the selective reduction of $CO_2$ to $CH_4$ by using photogenerated Ru(I) tris(bipyrazine) and a Ru metal catalyst. We also provide means to control the selectivities of $CO_2$ reduction vs. $H_2$ evolution by proper additives. As far as we are aware, these systems are the first examples for the photoinduced reduction of $CO_2$ to $CH_4$.

## Experimental Methods

Absorption spectra were recorded with a Uvikon-860 (Kontron) spectrophotometer. Gas chromatography analyses were performed with a Packard 427 instrument (thermal conductivity detector) for $H_2$ analysis and Tracor 540 gas chromatograph (flame ionization detector) for methane, ethane, and ethylene analysis. For $H_2$ separation a 5-Å MS column and argon as the carrier gas were used. For hydrocarbon analyses a Porapak T-column and nitrogen as the carrier gas were used. Size and shape of Ru and Os colloids were determined with a Jeol 200 CX electron microscope. Elementary composition of particles was determined with a Link 860 energy-dispersion system. Atomic absorption measurements were carried out with a Perkin-Elmer 403 spectrophotometer. Continuous illuminations were performed with 150-W xenon arc lamps (PTI). Laser flash experiments were performed on a DL 200 (Molectron) dye laser pumped by a UV-IU nitrogen laser (Molectron). Flashes were recorded on a Biomation 8100, and pulse collection was carried out with a Nicolet 1170.

**Preparation of Metal Colloids.** Colloids were prepared by the reduction of the respective metal salts with citrate as reducing agent:[23] A 0.1% sodium citrate solution, 100 mL, that contains $RuCl_3$, 16 mg, or $OsO_4$, 15 mg, was heated to 100 °C overnight. The resulting colloid suspensions were centrifuged and dialyzed. Metal content of colloid suspension was determined by atomic absorption to be 60 mg $L^{-1}$ for Ru colloid and 95 mg $L^{-1}$ for Os colloid. The mean diameter of colloid particles was estimated by EM to be 400 Å for Ru colloid and 50 Å for Os colloid. An alternative procedure for the preparation of the Ru colloid involves the photochemical reduction of $K_3RuCl_6$. This colloid exhibits improved catalyst activity toward reduction of $CO_2$ to $CH_4$: A 3-mL bicarbonate aqueous solution, pH 7.8, that includes Ru(II) tris(bipyrazine), $Ru(bpz)_3^{2+}$, $1 \times 10^{-4}$ M, $K_3RuCl_6$, $2 \times 10^{-4}$ M, and triethanolamine, 0.1 M, was illuminated for 20 min with a 150-W xenon lamp. To the resulting suspension a mixed-bed ion exchanger (Amberlite MB-1) was added to exclude all ions, and the colloid was filtered off. The mean diameter of the resulting colloid is estimated by EM to be 100 Å.

*N,N'*-Dimethyl-2,2'-bipyridinium, $MQ^{2+}$ (**1**), *N,N'*-trimethylene-2,2'-bipyridinium, $TQ^{2+}$ (**2**), and *N,N'*-tetramethylene-2,2'-bipyridinium, $DQ^{2+}$ (**3**), were prepared according to literature procedures.[24] *N,N'*-Bis(3-sulfonatopropyl)-3,3'-dimethyl-4,4'-bipyridine, $MPVS^0$ (**4**), was prepared by the reaction of 3,3'-dimethyl-4,4'-bipyridine with 1,3-propanesultone. To 100 mg of 3,3'-dimethyl-4,4'-bipyridine[25] was added 390 mg of 1,3-propanesultone. The resulting mixture was heated to 120 °C for 15 min without solvent under nitrogen. To the resulting semisolid was added 5 mL of DMF, and heating at 120 °C was continued for 3 h. After cooling, the white precipitate of **4** was filtered and washed three times with acetone; yield 89%. The product gave satisfactory elementary analysis.

Continuous-illumination experiments were performed in a glass cuvette equipped with a valve and stopper. Samples of 3 mL each contained a ruthenium or osmium colloid, 20 mg/L; TEOA, $1.0 \times 10^{-1}$ M; $NaHCO_3$, $5.0 \times 10^{-2}$ M; $Ru(bpz)_3^{2+}$, $1.0 \times 10^{-4}$ M or $Ru(bpy)_3^{2+}$, $1.4 \times 10^{-4}$ M; and one of the electron relays ($MQ^{2+}$, $TQ^{2+}$, $DQ^{2+}$, or $MPVS^0$), $1.4 \times 10^{-3}$ M; at pH 7.8 under a $CO_2$ atmosphere. Gas samples were taken out from the cuvette at time intervals of illumination and analyzed by the respective gas chromatography analyses.

Methane and hydrogen inhibition experiments were performed in similar cuvettes on 3-mL samples containing the ruthenium colloid, 20 mg/L; EDTA, $3.3 \times 10^{-2}$ M; $NaHCO_3$, $5.0 \times 10^{-2}$ M; $Ru(bpy)_3^{2+}$, $1.4 \times 10^{-4}$ M; and $MQ^{2+}$, $1.0 \times 10^{-3}$ M; at pH 6.0 under a $CO_2$ atmosphere. The rates of formation of methane and hydrogen were followed at different bipyrazine or 1,4-dimercapto-2,3-butanediol, dithiothreitol (DTT), concentrations.

Dark reduction of $CO_2$ was performed in a glass pressure-resistant reaction flask connected through a pressure gauge to a manifold enabling accurate control of the gaseous atmosphere composition. In a typical experiment, a solution containing Ru and Pt colloids, 20 mg/L each, $NaHCO_3$, $5.0 \times 10^{-2}$ M, and $MQ^{2+}$, $1.0 \times 10^{-2}$ M, was stirred under 0.75 atm of $CO_2$ and 0.75 atm of $H_2$. Under these conditions methane and ethylene were formed as assayed by GC analysis. Exclusion of the relay from the reaction yielded no products.

## Results and Discussion

Photoreduction of *N,N'*-dialkylbipyridinium salts[8,26] in the presence of $Ru(bpy)_3^{2+}$, metalloporphyrins, and organic dyes[27] in the presence of sacrificial electron donors and the subsequent evolution of $H_2$ with metal colloids[8-10] have been studied extensively. Various organometallic complexes such as Co(II) porphyrins[28] or Co and Ni macrocyclic complexes[29] exhibit catalytic activity in the electrochemical reduction of $CO_2$. Nevertheless, the electrocatalytic potentials are usually far from being adequate to be applied in the photosensitized reduction of $CO_2$. Ruthenium and osmium metals are used[30,31] as heterogeneous catalysts in the methanation of $CO_2$ (eq 9). Although this process proceeds at

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \tag{9}$$

elevated temperatures and pressures, it suggests that these metals activate $CO_2$ toward reduction. Recent electrochemical studies by Frese[32] have revealed that Ru electrodes catalyze the electrochemical reduction of $CO_2$ to $CH_4$ (eq 8). In these studies $CO_2$ reduction to $CH_4$ has been accomplished in aqueous solutions (pH 4.2–6.8) at electrode potentials ($E°$) as low as −0.55 V vs. SCE. Together with $CO_2$ reduction to $CH_4$, hydrogen evolution is observed as well as reduction of $CO_2$ to CO. Thus, we have decided to examine the photosensitized reduction of $CO_2$ to methane in the presence of Ru and Os colloids.

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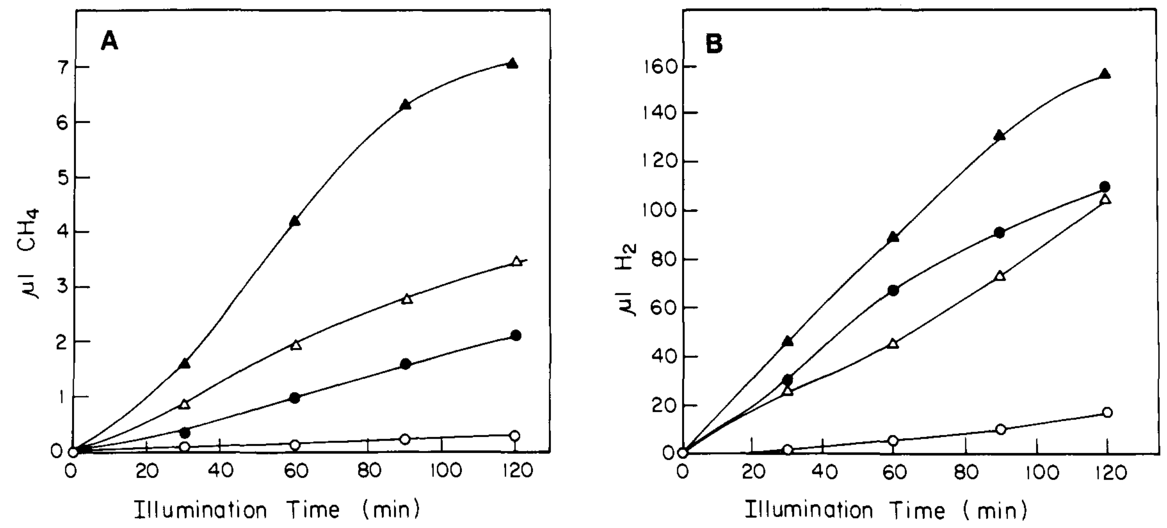
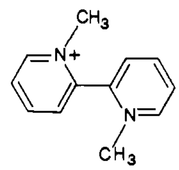


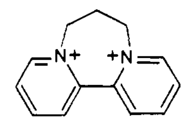
Figure 1. Rate of photosensitized $CH_4$ formation (A) and $H_2$ evolution (B) in the presence of the various charge relays and Ru colloid: $[Ru(bpy)_3^{2+}] = 1.4 \times 10^{-4}$ M, [relay] $= 1.4 \times 10^{-3}$ M, [TEOA] $= 1.0 \times 10^{-1}$ M, $[NaHCO_3] = 5.0 \times 10^{-2}$ M, [Ru colloid] = 20 mg/L, pH 7.8 under $CO_2$ atmosphere. Key: (△) $MQ^{2+}$; (●) $DQ^{2+}$; (○) $TQ^{2+}$; (▲) $MPVS^0$.

**Photosensitized $H_2$ Evolution and $CO_2$ Reduction Using Bipyridinium Electron Relays.** The reduction potentials for $H_2$ evolution and $CO_2$ reduction depend on the pH of the aqueous media. Both of the processes are thermodynamically favored as the pH of the aqueous solution decreases. Yet, the reduction potentials for $H_2$ formation decline to more positive values sharper than those of $CO_2$ as the pH of the solution decreases.[33] Thus, to thermodynamically favor $CO_2$ reduction over $H_2$ evolution, it is advantageous to perform the reactions in basic aqueous media. However, since $CO_2$ in aqueous solutions exhibits complex equilibria with $HCO_3^-$ and $CO_3^{2-}$ (eq 10) that are strongly affected by the pH, one is limited to the region employed. We have examined the photosensitized reduction of $CO_2$ in aqueous solutions at pH 7.8 where $CO_2$ consists of 3% of the total carbon dioxide introduced that corresponds to 11.2 μM.[34]

$$CO_{2(aq)} + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \rightleftharpoons 2H^+ + CO_3^{2-} \quad (10)$$

We have studied the $CO_2$-reduction and $H_2$-evolution processes in aqueous solutions where photosensitized electron-transfer reactions result in reduced bipyridinium radical relays. In these systems Ru(II) tris(bipyridine) is used as photosensitizer and triethanolamine, TEOA, as sacrifical electron donor. As charge relays we have applied *N*,*N*′-dimethyl-2,2′-bipyridinium, $MQ^{2+}$ (**1**), *N*,*N*′-trimethylene-2,2′-bipyridinium, $TQ^{2+}$ (**2**), *N*,*N*′-tetramethylene-2,2′-bipyridinium, $DQ^{2+}$ (**3**), or *N*,*N*′-bis(3-sulfonatopropyl)-3,3′-dimethyl-4,4′-bipyridinium, $MPVS^0$ (4).


$MQ^{2+}$ (1)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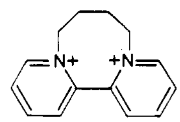
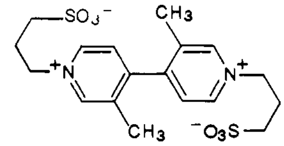

$DQ^{2+}$ (3)


$MPVS^0$ (4)

One of the colloids, Os or Ru, is included in the systems as a $CO_2$-reduction or a $H_2$-evolution catalyst. These charge relays were selected since their reduced forms exhibit more negative reduction potentials than *N*,*N*′-dialkyl-4,4′-bipyridinium (viologen) radicals. Previous studies have indicated that the reduction potentials of bipyridinium salts $[E°(V^{•-}/V^{2+})]$, are strongly affected by steric interactions in the molecular structure.[35] Reduction of the bipyridinium salts tends to bring the two pyridine rings into a planar structure to gain effective $\pi$–$\pi$ overlap and resonance delocalization. Hence, substitution of the ortho positions in the bipyridine structure distorts the two rings from planarity. Consequently, their reduction is more difficult, and the reduced form exhibits more negative reduction potentials as compared to the sterically unhindered relays. For example, the reduction potential of *N*,*N*′-bis(3-sulfonatopropyl)-4,4′-bipyridinium, PVS (**5**), corresponds[36] to $E°(PVS^{•-}/PVS^0) = -0.41$ V, and introduction of the two methyl groups in the ortho positions to obtain the relay **4** introduces sufficient steric hindrance to decrease the reduction potential to the value of $E°(MPVS^{•-}/MPVS^0) = -0.79$ V. The reduction potentials of the various relays used in our studies are summarized in Table I.

Illumination of these systems with visible light ($\lambda > 400$ nm) under a gaseous atmosphere of $CO_2$ results in the formation of methane and ethylene, $C_2H_4$, as well as the evolution of $H_2$. Figure 1 shows the rates of $CH_4$ formation and $H_2$ evolution by the different relays and Ru colloid as catalyst for the reaction. Figure 2 exemplifies the rates of formation of $CH_4$ and $C_2H_4$ as a function of illumination time with MPVS as relay and Os as catalyst. The quantum yields for the formation of the various products with the different electron relays and the Os and Ru colloids as catalysts are summarized in Table I. It is evident that the yields of $H_2$-evolution and $CO_2$-reduction products increase as the reduction potentials of the relay is more negative. For example, by using the Ru colloid and MPVS as relay ($E°' = -0.79$ V), the quantum yields for $H_2$ evolution and $CH_4$ formation are $\phi(H_2) = 2.6 \times 10^{-3}$ and $\phi(CH_4) = 5.7 \times 10^{-4}$, while with the relay TQ ($E°' = -0.55$ V) the respective quantum yields correspond to $\phi(H_2) = 2.8 \times 10^{-4}$ and $\phi(CH_4) = 2.0 \times 10^{-5}$. When argon is used as the gaseous atmosphere instead of $CO_2$, only $H_2$ evolution is observed. The quantum yields for $H_2$ evolution in the presence of the different relays and metal catalysts are also summarized in Table I. Control experiments reveal that all of the components included in the systems are essential for $H_2$ evolution as well as for $CO_2$ reduction. Exclusion of either the electron donor, charge relay, or catalysts prohibits any photoproduct formation. Furthermore,

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**Table I.** Quantum Yields for $H_2$ Evolution and Hydrocarbon Formation in the Presence of Different Relays and Ru or Os Colloids as Catalysts[a]

| relay | $E°'$, V vs. SHE[b,c] | Ru colloid catalyst | | | Os colloid catalyst | | |
|---|---|---|---|---|---|---|---|
| | | $10^3\phi(H_2)$ | $10^4\phi(CH_4)$ | $10^5\phi(C_2H_4)$ | $10^3\phi(H_2)$ | $10^4\phi(CH_4)$ | $10^5\phi(C_2H_4)$ |
| $MPVS^0$ | -0.79 | 2.6 (80)[d] | 5.7 (4.3) | 1.9 (0.1) | 1.9 (58) | 2.1 (1.6) | 1.04 (0.05) |
| $MQ^{2+}$ | -0.72 | 1.7 (51) | 2.3 (1.7) | 0.73 (0.03) | 3.0 (91) | 0.52 (0.4) | 0.29 (0.014) |
| $DQ^{2+}$ | -0.65 | 1.8 (56) | 1.4 (1.1) | 1.08 (0.05) | 9.2 (270) | 0.61 (0.5) | 0.67 (0.03) |
| $TQ^{2+}$ | -0.55 | 0.28 (8) | 0.20 (0.15) | 0.18 (0.01) | 0.64 (19) | 0.12 (0.1) | 0.15 (0.008) |

[a] In all systems $[Ru(bpy)_3^{2+}] = 1.4 \times 10^{-4}$ M, [TEOA] = $1 \times 10^{-1}$ M, [relay] = $1.4 \times 10^{-3}$ M, aqueous 0.1 M bicarbonate solution under $CO_2$, pH 7.8. [b] Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 159–244. [c] Furlong, D. N.; Johansen, O.; Launikonis, A.; Loder, J. W.; Mau, A. W.-H.; Sasse, W. H. F. *Aust. J. Chem.* **1985**, *38*, 363–367. [d] In parentheses volume (μL) of products formed per hour.

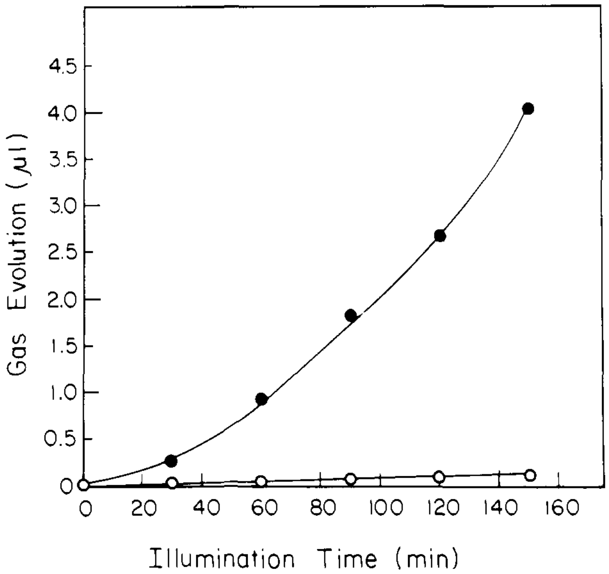

**Figure 2.** Yield of methane and ethylene formation as a function of illumination time with $MPVS^0$ as relay and Os colloid as catalyst: $[Ru(bpy)_3^{2+}] = 1.4 \times 10^{-4}$ M, [MPVS] = $1.4 \times 10^{-3}$ M, [TEOA] = $1.0 \times 10^{-1}$ M, $[NaHCO_3] = 5.0 \times 10^{-2}$ M, [Os colloid] = 20 mg/L, pH 7.8 under $CO_2$ atmosphere. Key: (●) methane; (○) ethylene.

other metal catalysts such as Pt or Pd are inactive toward the reduction of $CO_2$, and only $H_2$ evolution is observed. Also, substitution of the charge relays by *N*,*N*′-dimethyl-4,4′-bipyridinium (methylviologen, $MV^{2+}$) does not yield the reduction of $CO_2$, and the blue radical cation ($MV^{\bullet+}$) is accumulated. The lack of $H_2$ evolution and $CH_4$ formation with $MV^{2+}$ as charge relay suggests that the reduced relay $MV^{\bullet+}$ does not exhibit the reduction potential required to evolve $H_2$ from the basic aqueous medium (pH 7.8) or to reduce metal-activated $CO_2$.

The results clearly indicate that the photosensitized electron-transfer reaction leads to the reduction of $CO_2$ to methane and higher hydrocarbons. Thus, Ru and Os colloids are indeed heterogeneous catalysts that activate $CO_2$ toward the reduction. Nevertheless, the reduction of $CO_2$ in the aqueous media is nonspecific, and substantial amounts of $H_2$ are evolved. In fact $H_2$ evolution is the predominant product in the photosensitized transformations.

The mechanism that leads to $H_2$ evolution is well established.[8,9] It involves the oxidative quenching via electron transfer of the excited sensitizer $Ru(bpy)_3^{2+}$ by the relay ($R^{2+}$), followed by charge separation (eq 11 and 12). Oxidation of the electron donor

$$Ru^*(bpy)_3^{2+} + R^{2+} \rightarrow Ru(bpy)_3^{3+} + R^{\bullet+} \qquad (11)$$

$$Ru(bpy)_3^{3+} + TEOA \rightarrow Ru(bpy)_3^{2+} + TEOA^{\bullet+} \qquad (12)$$

TEOA by the oxidized sensitizer recycles the light-active compound, and the reduced relay is accumulated. Electron transfer from the reduced relay to the metal catalyst charges the colloid, and in the presence of protons, metal-bound H atoms are formed and their dimerization leads to $H_2$ evolution.[37] Figure 3 schematically represents the $H_2$-evolution process. The fact that Ru or Os colloids are essential catalysts for the reduction of $CO_2$ clearly indicates that $CO_2$ interacts with the metal surface and that it is activated toward the reduction process. The reduction might proceed via two alternative mechanisms: (i) hydrogenation of metal-activated $CO_2$ via in situ generated H atoms that lead to the methanation process (eq 9) [Similar photoinduced hydrogenation reactions and utilization of in situ generated hydrogen atoms have been exemplified with unsaturated substrates, i.e. ethylene and acetylene, and heterogeneous Pt or Pd colloids.[37]] and (ii) direct reduction of metal-activated $CO_2$ via electron transfer from the charge relay, independent to the $H_2$-evolution system (Figure 3).

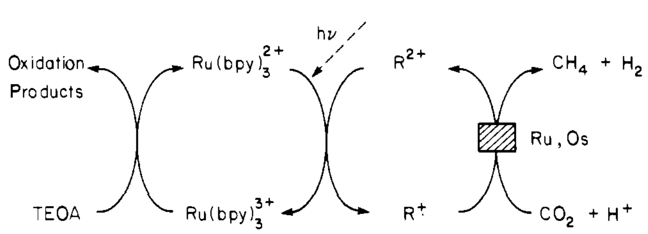

**Figure 3.** Schematic cycle for photosensitized $H_2$ evolution and $CO_2$ reduction using bipyridinium electron relays ($R^{2+}$).

Dark experiments exclude the hydrogenation pathway as the mechanistic route for the reduction of $CO_2$ to $CH_4$ and imply that the reduction process proceeds through electron transfer from the reduced relay. In these experiments an aqueous bicarbonate solution (pH 7.8) that included the Ru or Os colloid was stirred in a sealed flask under a gaseous atmosphere that included $H_2$ (0.75 atm) and $CO_2$ (0.75 atm), and no hydrocarbons have been detected. Similarly, addition of the charge relay $MQ^{2+}$ to the system did not lead to any hydrocarbon products. Yet, addition of a Pt colloid to the system that included either Ru or Os colloid and the charge relay, $MQ^{2+}$, resulted in the formation of methane and ethylene ($C_2H_4$). In a control experiment where $MQ^{2+}$ was excluded from the system, and Ru or Os and Pt colloids were present, no reduction of $CO_2$ occurred. Similarly, when the Ru or Os colloids were excluded and the Pt colloid and $MQ^{2+}$ were present, only $MQ^{\bullet+}$ was formed and no $CO_2$-reduction products were formed. This set of dark experiments clearly indicate that the reduction of $CO_2$ to hydrocarbons proceeds via electron transfer rather than through the hydrogenation route. The primary step involves the Pt-catalyzed reduction of the charge relay $MQ^{2+}$ (eq 13). The generation of the reduced relay, $MQ^{\bullet+}$, allows the subsequent reduction of Ru or Os metal-activated $CO_2$ to methane and higher hydrocarbons (eq 14).

$$H_2 + 2MQ^{2+} \xrightarrow{Pt} 2H^+ + 2MQ^{\bullet+} \qquad (13)$$

$$8MQ^{\bullet+} + CO_2 + 8H^+ \xrightarrow{\text{Ru or Os}} CH_4 + 2H_2O + 8MQ^{2+} \qquad (14)$$

It should be noted that these control dark reactions suggest a new important route for the methanation process of $CO_2$ (eq 9). At present, the reaction conditions using $H_2$ and $CO_2$ require high pressures and elevated temperatures.[30,31] Our results indicate that addition of an electron relay and proper electron-transfer mediating catalysts affects the process at an ambient temperature and low pressure.

**Photoreduction of $CO_2$ with $Ru(bpz)_3^{2+}$ as Photosensitizer.** The results discussed until now demonstrate that $H_2$ evolution occurs concomitantly to $CO_2$ reduction and the former process is the

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(37) Degani, Y.; Willner, I. *J. Chem. Soc., Perkin Trans. 2* **1986**, 37–41.

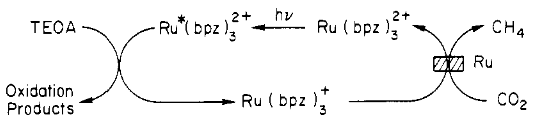

**Figure 4.** Schematic cycle for photosensitized reduction of $CO_2$ to $CH_4$ using $Ru(bpz)_3^{2+}$ as sensitizer.

**Table II.** Quantum Yields and Turnover Numbers (TN) for Hydrocarbon Formation Using $Ru(bpz)_3^{2+}$

| system[a] | $\phi(CH_4)$ | $\phi(C_2H_4)$ | $\phi(C_2H_6)$ | $TN[Ru(bpz)_3^{2+}]$ |
|---|---|---|---|---|
| I | $2.5 \times 10^{-5}$<br>(0.15)[b] | $3.5 \times 10^{-6}$<br>(0.014) | $2 \times 10^{-6}$<br>(0.008) | 1.8 |
| II | $4.0 \times 10^{-4}$<br>(2.4) | $7.5 \times 10^{-5}$<br>(0.36) | $4 \times 10^{-5}$<br>(0.18) | 15 |

[a] System components: $[Ru(bpz)_3^{2+}] = 1.0 \times 10^{-4}$ M, [TEOA] = $1 \times 10^{-1}$ M, [Ru colloid] = 20 mg $L^{-1}$, $[NaHCO_3] = 0.05$ M. Systems: I, aqueous solution; II, water–ethanol, 2:1. [b] In parentheses volume (μL) of products formed per hour.

predominating reaction. Assuming that $CO_2$ reduction does not proceed through a hydrogenation mechanism suggests that specificity toward $CO_2$ reduction might be designed. A strategy to induce selectivity into the process and favor $CO_2$ reduction over $H_2$ evolution will involve the design of a couple composed of a reduced relay–catalyst system that exhibits a kinetic barrier toward $H_2$ evolution but still allows $CO_2$ reduction. Ru(II) tris(bipyrazine), $Ru(bpz)_3^{2+}$, is a photosensitizer that absorbs in the visible region ($\lambda_{max} = 443$ nm, $\epsilon = 15000$ $M^{-1}$ $cm^{-1}$) and exhibits a long excited-state lifetime ($\tau = 1.04$ μs).[38,39] It is reductively quenched via electron transfer by various electron donors, i.e. triethanolamine, TEOA (eq 15). The reduced photoproduct,

$$Ru(bpz)_3^{2+} + TEOA \xrightarrow{h\nu} Ru(bpz)_3^{+} + TEOA^{\cdot +} \qquad (15)$$
$$\hookrightarrow \text{dec products}$$

$Ru(bpz)_3^{+}$, is a powerful reducing agent ($E° = -0.86$ V vs. SCE) capable thermodynamically to evolve $H_2$ as well as to reduce $CO_2$ to $CH_4$. Nevertheless, it has been reported that $Ru(bpz)_3^{+}$ does not mediate $H_2$ evolution at pH 7.8 in the presence of heterogeneous catalysts such as Pt colloid.[40] Thus it exhibits the kinetic barrier for $H_2$ evolution and meets the basic requirements to design selective $CO_2$ reduction.

We therefore examined the reduction of $CO_2$ in an aqueous system that includes $Ru(bpz)_3^{2+}$ as photosensitizer, TEOA as electron donor, and the Ru colloid as $CO_2$ reduction catalyst. Illumination of this system (pH 7.8, $\lambda > 400$ nm) results in the reduction of $CO_2$ to $CH_4$ and the formation of oligomerated hydrocarbons ethylene and ethane (Figure 4). No $H_2$ formation is observed in these systems, and $CO_2$-reduction products are the sole products. Table II summarizes the quantum yield for the formation of the various hydrocarbons and the turnover numbers of the photosensitizer.

Control experiments reveal that indeed $CO_2$ is photoreduced to methane, ethylene, and ethane. Illumination of a system that includes the colloids under argon instead of $CO_2$ does not lead to any hydrocarbon products. Also, exclusion of the $Ru(bpz)_3^{2+}$ from the system does not yield upon illumination under $CO_2$ any hydrocarbon products. Thus, it is evident that a photosensitized electron-transfer reaction in the visible absorption region leads to the reduction of $CO_2$.

A hydrogenation mechanism of $CO_2$ to the hydrocarbons in these systems can be excluded since no $H_2$ evolution occurs either in the presence of $CO_2$ or under argon. That $CO_2$ is reduced via electron transfer is evident from laser flash experiments as well as steady-state illumination. Excitation of an aqueous solution that includes $Ru(bpz)_3^{2+}$ and TEOA under argon by a light pulse ($\lambda_{exc} = 440$ nm) results in the trace displayed in Figure 5a. It corresponds to the reductive quenching of $Ru(bpz)_3^{2+}$ to form $Ru(bpz)_3^{+}$ (eq 15). The trace shows an initial decay for ca. 80 μs and afterward a steady-state accumulation of $Ru(bpz)_3^{+}$. The initial decay is due to a recombination of $Ru(bpz)_3^{+}$ with $TEOA^{\cdot +}$, but since $TEOA^{\cdot +}$ is simultaneously decomposed, a net steady-state accumulation of $Ru(bpz)_3^{+}$ is observed. Addition of $CO_2$ (instead of argon) does not alter the trace obtained upon flashing. Thus, no electron transfer from $Ru(bpz)_3^{+}$ to $CO_2$ occurs. Addition of the Ru colloid to the system under argon results in the decay of $Ru(bpz)_3^{+}$ ($\tau = 170$ μs), implying that electron transfer from $Ru(bpz)_3^{+}$ to the metal colloid occurs. In turn, flashing the system in the presence of $CO_2$ and the Ru colloid results in the trace displayed in Figure 5b. It is evident that under these conditions a rapid decay ($\tau = 50$ μs) of the photogenerated $Ru(bpz)_3^{+}$ occurs and $Ru(bpz)_3^{2+}$ is regenerated. Namely, photogenerated $Ru(bpz)_3^{+}$ is capable of affecting the electron transfer to Ru-activated $CO_2$, a process that ultimately yields the hydrocarbon products.

It is established that $Ru(bpz)_3^{+}$ can be photogenerated upon steady-state illumination of an aqueous ethanol solution that contains the photosensitizer $Ru(bpz)_3^{2+}$ and TEOA.[40] This accumulation of $Ru(bpz)_3^{+}$ in ethanol solutions is presumably due

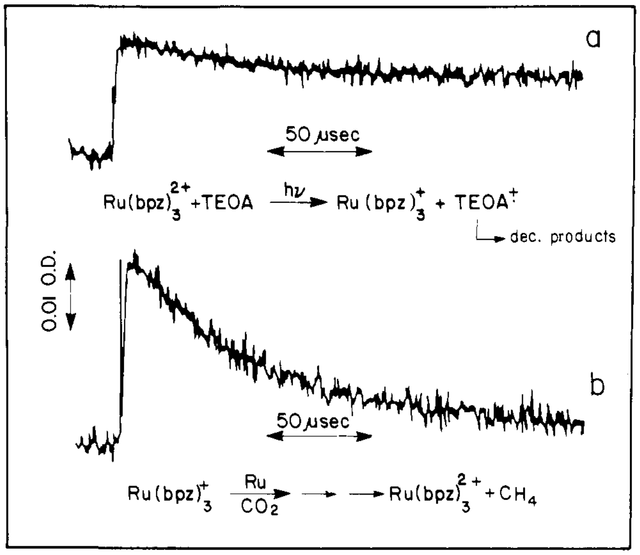

**Figure 5.** Transient spectra formed upon illumination of $Ru(bpz)_3^{2+}$, $2.2 \times 10^{-5}$ M, and TEOA, 0.17 M solution, pH 9.5. Systems are flashed at $\lambda = 440$ nm and product, $Ru(bpz)_3^{+}$, is followed at $\lambda = 500$ nm: (a) under argon or $CO_2$; (b) in the presence of Ru colloid (20 mg/L) under $CO_2$.

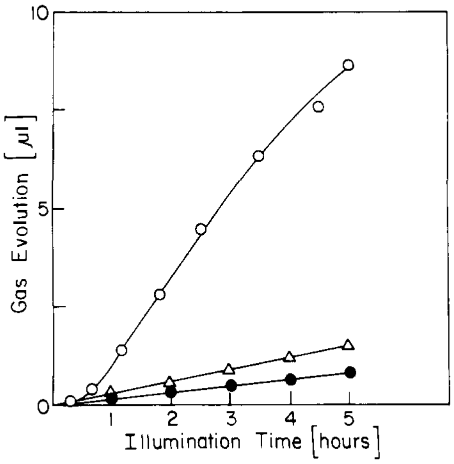

**Figure 6.** Rate of hydrocarbon formation as a function of illumination time in the $Ru(bpz)_3^{2+}$ system: $[Ru(bpz)_3^{2+}] = 1.0 \times 10^{-4}$ M, [TEOA] = $1.0 \times 10^{-1}$ M, $[NaHCO_3] = 5.0 \times 10^{-2}$ M, [Ru colloid] = 20 mg/L, pH 7.8, water–ethanol (2:1) solution under $CO_2$ atmosphere. Key: (○) methane; (△) ethylene; (●) ethane.

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(40) (a) Dürr, H.; Dörr, G.; Zengerle, K.; Curchod, J.-M.; Braun, A. M. *Helv. Chim. Acta* **1984**, *66*, 2652–2655. (b) Dürr, H.; Dörr, G.; Zengerle, K.; Mayer, E.; Curchod, J.-M.; Braun, A. M. *Nouv. J. Chim.* **1985**, *9*, 717–720.

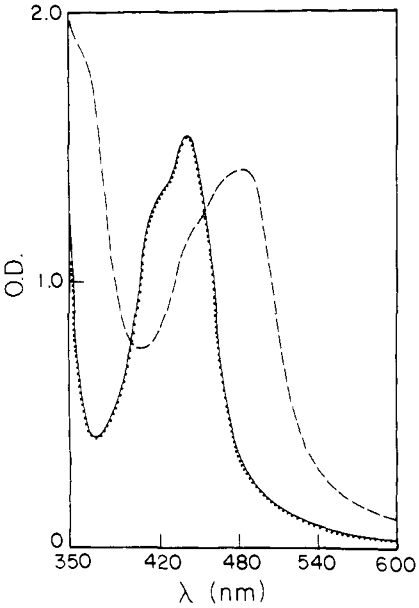

**Figure 7.** Effects of added $CO_2$ on photogenerated $Ru(bpz)_3^+$. Absorption Spectra: (—) $Ru(bpz)_3^{2+}$, $1.0 \times 10^{-4}$ M in water–ethanol (2:1) under argon; (- - -) photogenerated $Ru(bpz)_3^+$ prepared by illumination of $Ru(bpz)_3^{2+}$ in the presence of TEOA, $1.0 \times 10^{-1}$ M; (···) obtained upon injection of $CO_2$ to photogenerated $Ru(bpz)_3^+$. In all samples [Ru colloid] = 20 mg/L.

to the rapid irreversible decomposition of $TEOA^{\bullet+}$ in this medium (eq 15). Thus, the effective photogeneration of $Ru(bpz)_3^+$ in ethanol solutions suggests that enhanced quantum yields for $CO_2$ reduction to $CH_4$ could be accomplished in this medium. We have examined the photosensitized reduction of $CO_2$ to $CH_4$ in a water–ethanol (2:1) mixture using $Ru(bpz)_3^{2+}$ as sensitizer, TEOA as electron donor, and the Ru colloid as catalyst. Illumination of this system under $CO_2$ results in the formation of $CH_4$ and higher hydrocarbons. The rate of $CH_4$ formation (Figure 6) corresponds to a quantum yield of $\phi = 4.0 \times 10^{-4}$. This value is 16-fold higher than the quantum yield for $CH_4$ formation in pure aqueous solutions and is mainly attributed to the effective photogeneration of $Ru(bpz)_3^+$ in the ethanol–water solution. Steady-state illumination experiments on this system in the absence and presence of $CO_2$ and the Ru colloid support the electron-transfer mechanism for reduction of $CO_2$. Illumination of the ethanol–water solution that includes TEOA and the photosensitizer $Ru(bpz)_3^{2+}$ results in the photoreduction of $Ru(bpz)_3^{2+}$ to $Ru(bpz)_3^+$, $\lambda_{max} = 470$ nm (Figure 7, eq 15). Upon addition of the Ru colloid or $CO_2$ the photogenerated $Ru(bpz)_3^+$ is unaffected. Addition of both of the components, the Ru colloid and $CO_2$, results in the reoxidation of $Ru(bpz)_3^{2+}$ and evolution of $CH_4$, implying that the photosensitizer is recycled in the photosensitized evolution of $CH_4$ as well as supporting the electron-transfer mechanism. It should be noted that illumination of this system is performed in the region of $\lambda = 420$–$450$ nm. We find that illumination of the system with light of $\lambda > 400$ nm results in poor stability of the photosensitizer. The absorption spectra of $Ru(bpz)_3^{2+}$ and $Ru(bpz)_3^+$ (Figure 7) show that the two components exhibit an overlap in their absorption bands. The poor stability of the photosensitizer, under conditions where $Ru(bpz)_3^+$ is also excited, suggests that the photoproduct $Ru(bpz)_3^+$ is itself photoactive and transforms to a product inactive for $CO_2$ reduction. The relatively limited turnover number (TN) of the system, TN = 15, is thus attributed to the residual absorbance of $Ru(bpz)_3^+$ in the excitation region ($\lambda = 420$–$450$ nm) that causes photoconsumption of $Ru(bpz)_3^{2+}$. We anticipate that development of $Ru(bpz)_3^{2+}$ derivatives where the 2+/1+ oxidation states exhibit distinct nonoverlapping absorption properties might increase the stability of the system toward $CO_2$ reduction.

**Selectivity in $CO_2$-Reduction and $H_2$-Evolution.** The two systems discussed for $CO_2$ reduction demonstrate that those systems that include a relay yield a mixture of $H_2$ and hydrocarbons while the system that includes $Ru(bpz)_3^{2+}$ is specific for $CO_2$ reduction only. The laser flash studies (Figure 5) reveal that $Ru(bpz)_3^+$ exhibits a kinetic barrier toward $H_2$ evolution. We have speculated that the coordination sites on the ligands of $Ru(bpz)_3^{2+}$ might interact with the heterogeneous catalyst and consequently deactivate the catalyst toward the $H_2$-evolution process. We thus examined the $H_2$-evolution process under argon using $Ru(bpy)_3^{2+}$ as sensitizer, $MQ^{2+}$ as charge relay, $Na_2EDTA$ as electron donor, and the Ru colloid as catalyst in the presence and absence of bipyrazine. Figure 8 shows the quantum yield for $H_2$ evolution upon addition of the bipyrazine ligand. It is evident that $H_2$ evolution is retarded as the bipyrazine concentration increases, and at a concentration of $1 \times 10^{-3}$ M, no $H_2$ evolution occurs. Thus we conclude that $H_2$ evolution is prohibited by the bipyrazine ligand. It should be noted that no inhibitory effect in $H_2$ evolution is observed with 2,2′-bipyridine or 3,3′-bipyridine as additives. Under $CO_2$ the inhibition profile of $H_2$ evolution with added bipyrazine is similar to that observed under argon. Yet, also $CO_2$ reduction is inhibited to some extent by the addition of bipyrazine, and at [bipyrazine] = $1 \times 10^{-3}$ M $H_2$ evolution is totally blocked while the quantum yield of $CO_2$ reduction to $CH_4$ decreases to 30% of its value in the absence of bipyrazine.

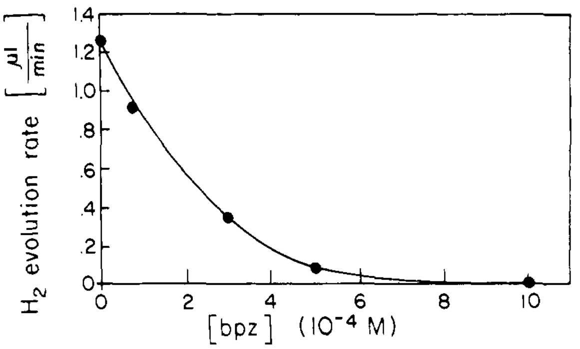

**Figure 8.** $H_2$-Evolution rate as a function of bipyrazine concentration: $[Ru(bpy)_3^{2+}] = 1.4 \times 10^{-4}$ M, $[MQ^{2+}] = 1.0 \times 10^{-3}$ M, $[Na_2EDTA] = 3.3 \times 10^{-2}$ M, $[NaHCO_3] = 5.0 \times 10^{-2}$ M, [Ru colloid] = 20 mg/L, pH 6.0 under $CO_2$ atmosphere.

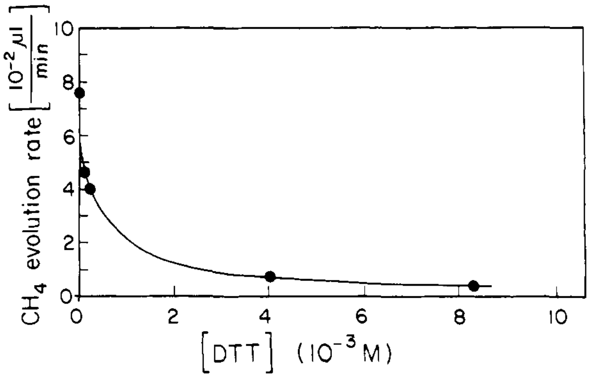

**Figure 9.** $CH_4$-Evolution rate as a function of dithiothreitol concentration: $[Ru(bpy)_3^{2+}] = 1.4 \times 10^{-4}$ M, $[MQ^{2+}] = 1.0 \times 10^{-3}$ M, $[Na_2EDTA] = 3.3 \times 10^{-2}$ M, $[NaHCO_3] = 5.0 \times 10^{-2}$ M, [Ru colloid] = 20 mg/L, pH 6.0 under $CO_2$ atmosphere.

Similarly, specificity toward $H_2$ evolution can be designed. $CO_2$ reduction can be eliminated in the two systems by the addition of thiols. In the presence of these additives $H_2$ evolution is not affected. We have examined the photosensitized reduction of $CO_2$ and $H_2$ evolution in a system composed of $Ru(bpy)_3^{2+}$ as sensitizer, $MQ^{2+}$ as electron relay, $Na_2EDTA$ as electron donor, and the Ru colloid as catalyst. Figure 9 shows the rates of $CO_2$ reduction to $CH_4$ at different concentrations of added dithiothreitol (DTT). It should be noted that the added thiols do not inhibit $H_2$ evolution. Furthermore, with DTT the quantum yield for $H_2$ reduction is slightly increased. It is evident that the added thiol inhibits $CO_2$ reduction and at $8 \times 10^{-3}$ M DTT $CO_2$ reduction to methane is prohibited while the $H_2$ evolution yield is unaffected.

This deactivation of the Ru colloid by thiols toward $CO_2$ reduction is general, and cysteine or mercaptoethanol show similar inhibition effects. We thus conclude that thiols prevent the reduction of $CO_2$, and selective $H_2$ evolution can be accomplished. Added bipyrazine shows inhibitoric effects toward $H_2$ evolution as well as $CO_2$ reduction although the deactivation is more pronounced toward the former process. We anticipate that other ligands might show higher selectivity in the degree of deactivation of these reactions. Also, the possibility to control the selective $CO_2$-reduction or $H_2$-evolution process suggests that on the Ru colloid exist distinct and different catalytic sites for the two reactions.

## Conclusions

We have discussed the novel application of Ru and Os colloids as catalysts for the photosensitized $CO_2$ reduction to $CH_4$. The fixation of $CO_2$ to $CH_4$ in aqueous solutions is accompanied by the kinetically favored $H_2$-evolution process. Our results emphasize that selectivity toward $CO_2$ reduction might be accomplished by proper design of a relay–catalyst configuration that exhibits overpotential properties toward $H_2$ evolution. In this respect we find that bipyrazine acts as an inhibitor that eliminates $H_2$ evolution. Similarly, thiols eliminate $CO_2$ reduction but do not affect evolution of $H_2$. The multielectron fixation of $CO_2$ to $CH_4$ that involves eight electrons is certainly a stepwise process that involves various intermediates. We emphasize that no other reduction products of $CO_2$, i.e. formate, formaldehyde, or methanol, could be detected in the photosensitized transformation. We have shown that $C_2$ hydrocarbons (ethane and ethylene) are also formed during the photoreduction of $CO_2$. The formation of these products suggests that $Ru{=}CH_2$ (or $Os{=}CH_2$) and $Ru{-}CH_3$ act as intermediates along the photoreduction of $CO_2$ since ethylene would be formed by the dimerization of the carbene species while ethane is anticipated to originate from dimerization of the metal–methyl intermediate. It should be noted that similar intermediates have been suggested[41] in the methanation process of $CO_2$.

Our study has emphasized that photoreduction of $CO_2$ occurs via electron transfer followed by protonation steps rather than by a hydrogenation mechanism. The control experiments that were applied to elucidate the mechanistic aspects of the photoreduction of $CO_2$ revealed that the photochemically generated reduced relays $Ru(bpz)_3^+$ or the bipyridinium radicals mediate the reduction of $CO_2$ to $CH_4$ in the presence of Ru or Os colloids. Since bipyridinium radicals can be produced by $H_2$ and heterogeneous catalysts, we might envisage routes to develop novel methanation reactions or electrocatalyzed methanation processes that proceed at ambient temperatures and atmospheric pressure via an electron-transfer pathway. Further attempts to characterize mechanistic aspects involved in the photoreduction of $CO_2$ to methane, development of other $CO_2$-reduction catalysts, and the development of the dark electron-transfer reduction processes of $CO_2$ are now under way in our laboratory.

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**Registry No. 1**, 41491-80-9; **2**, 7325-63-5; **3**, 16651-68-6; **4**, 86690-04-2; TEOA, 102-71-6; $CO_2$, 124-38-9; $Ru(bpy)_3^{2+}$, 15158-62-0; Ru, 7440-18-8; Os, 7440-04-2; Pt, 7440-06-4; $H_2$, 1333-74-0; tris(bipyrazine)ruthenium(II), 75523-96-5; ethylene, 74-85-1; ethane, 74-84-0; methane, 74-82-8; dithiothreitol, 3483-12-3; 3,3′-dimethyl-4,4′-bipyridine, 4479-73-6; 1,3-propanesultone, 1120-71-4.

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# Cyclobutene Photochemistry. Nonstereospecific Photochemical Ring Opening of Simple Cyclobutenes

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*Contribution from the Department of Chemistry, McMaster University, Hamilton, Ontario, Canada L8S 4M1.* *Received December 15, 1986*

**Abstract:** The photochemistry of bicyclo[3.2.0]hept-6-ene, bicyclo[4.2.0]oct-7-ene, and *cis*- and *trans*-3,4-dimethylcyclobutene has been investigated in hydrocarbon solution with monochromatic far-ultraviolet (185 and 193 nm) light sources. All of these simple cyclobutene derivatives undergo ring opening to yield the isomeric 1,3-dienes, and the latter three open nonstereospecifically to yield mixtures of the possible geometric isomers. The isomeric 3,4-dimethylcyclobutenes yield different mixtures of the three 2,4-hexadiene isomers, and in each case the mixtures are weighted in favor of the orbital symmetry forbidden isomer(s). Attempts have been made to analyze the relative isomeric diene yields from ring opening of bicyclo[4.2.0]octene and the isomeric 3,4-dimethylcyclobutenes within the context of the purely disrotatory, adiabatic ring-opening mechanism that recent ab initio calculations suggest should be possible. While the results for the former compound are consistent with this mechanism, analysis of the relative yields of the isomeric 2,4-hexadienes from photolysis of the latter two compounds indicates that photochemical ring opening by the formally forbidden, conrotatory pathway may compete to some extent with disrotatory ring opening.

In spite of the central role that the thermal[2,3] and photochemical[3b,4,5] interconversions of cyclobutene and 1,3-butadiene play in our understanding of pericyclic reactions,[6] there are few reported examples that illustrate the photochemical electrocyclic ring-

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