Photochemical generation of carbon monoxide and hydrogen by reduction of carbon dioxide and water under visible light irradiation

[artificial photosynthesis/solar-energy conversion/metal complex catalysis/tris(2,2'-bipyridine)ruthenium(II)/cobalt(II) system]

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Visible light irradiation of solutions of Ru(2,2'-ABSTRACT bipyridine)²⁺, cobalt(II) chloride, and carbon dioxide in acetonitrile/water/triethylamine generates simultaneously carbon monoxide and hydrogen. The reaction involves photoinduced reduction of CO₂ and H₂O, triethylamine serving as electron donor in the $Ru(2,2^{\overline{2}}-bipyridine)_3^{2+}/Co^{2+}$ system. The amount of gas (CO + H₂) produced and the selectivity ratio CO/H₂ depend markedly on the composition of the system. Addition of free bipyridine strongly decreases CO generation but increases H₂ production. With different tertiary amines, NR_3 , both the quantity (CO + H_2) and the ratio CO/H₂ increase markedly along the sequence R = methyl, ethyl, propyl. Higher selectivity for CO₂ reduction to CO in preference to water reduction occurs when triethanolamine is used instead of triethylamine. CoCl₂ is the most efficient mediator for both CO and H₂ generation and specifically promotes CO formation, whereas salts of other cations studied only yield H₂. The mechanism of the reaction may involve intermediate formation of Co(I) species. These processes represent an abiotic photosynthetic system allowing simultaneous generation of CO and H₂ and regulation of the CO/H₂ ratio. Mechanistic studies and explorations of other components that may increase efficiency and product selectivity should be carried out. The results obtained are also of significance for solar energy conversion with consumption of a pollutant, CO₂.

Photoinduced splitting of the water molecule and reduction of carbon dioxide are the basic reactions of natural photosynthesis. They represent a fascinating area of chemical research, from both the fundamental point of view-understanding the mechanism of the natural processes and devising artificial photosynthetic systems that perform these reactions in the laboratory-and the practical point of view-devising means for the photochemical conversion and storage of solar energy by producing fuels (hydrogen, carbon monoxide, methanol, methane, for instance).

The development of systems capable of catalyzing water photolysis has especially attracted attention in recent years (1-6). Our own work (7) has led us successively to devise systems that perform the photochemical reduction of water to hydrogen (8, 9), its photooxidation to oxygen (10), and its photosplitting with simultaneous generation of hydrogen and oxygen (11). (See also references to other work in this area in ref. 1-11.)

Other photochemical storage reactions (2-6, 12) are also of much interest but have been investigated comparatively little. In particular, there are only a few reports on the photochemical reduction of CO2, and most of the processes are very inefficient (12). Recent CO_2 reduction experiments involved irradiation of

aqueous solutions of metal ions (12-15) or of organic dyes (16), irradiation of semiconductor crystals (17) or powders (18), and photoelectrochemical processes (19-21).

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We now report a catalytic system that performs the photo-

reduction of CO_2 to CO under irradiation by visible light. The free energy ΔG^0 and the standard redox potential ΔE^0 per electron of the two-electron water-splitting (reaction 1) and CO₂-splitting (reaction 2) processes indicate that the latter stores slightly more energy than the former per mole of material (5, 6).

$$H_2O(1) \rightarrow H_2(g) + \frac{1}{2}O_2(g) \quad \Delta G^0 = 56.6 \text{ kJ/mol}$$

 $\Delta E^0 = 1.23 \text{ V}$ [1]

$$\operatorname{CO}_2(\mathbf{g}) \rightarrow \operatorname{CO}(\mathbf{g}) + \frac{1}{2} \operatorname{O}_2(\mathbf{g}) \quad \Delta G^0 = 61.4 \text{ kJ/mol}$$

$$\Delta E^0 = 1.33 \text{ V} \qquad [2]$$

The reduction potentials for the half-cell reactions at pH 7 in aqueous solution versus the normal hydrogen electrode (E^{0}) (20-22) are:

$$2 H^+ + 2 e^- \rightarrow H_2 E^{0\prime} = -0.41 V$$
 [3]

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O \quad E^{0\prime} = -0.52 V \quad [4]$$

$$CO_2 + 4H^+ + 4 e^- \rightarrow C + 2 H_2O \quad E^{0} = -0.20 V$$
 [5]

$$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH \quad E^{0} = -0.61 V$$
 [6]

 $CO_2 + 4H^+ + 4e^- \rightarrow HCHO + H_2O \quad E^{0\prime} = -0.48 V$ [7]

Because the direct monoelectronic reduction of CO₂ occurs at potentials as negative as about -2 V (23), it is advantageous on thermodynamic grounds to perform directly the polyelectronic (two to eight electrons) processes (4-9), which require much less energy per electron transferred.

The design of a system capable of performing these CO₂ reductions photochemically requires photogenerating species of sufficiently negative redox potentials and finding suitable catalysts for these polyelectronic processes.

In the course of our work on the photoreduction of water, we had observed that highly reducing Co(I) species are produced

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Abbreviations: bipy, 2,2'-bipyridine; NMe₃, NEt₃, and NPr₃, trimethyl-, triethyl-, and tripropylamine; $N(CH_2CH_2OH)_3$ triethanolamine; E^{0'}, redox potential at pH 7 in aqueous solution versus the normal hydrogen electrode.

on irradiation of solutions containing $CoCl_2$ and bipyridine in the presence of Ru(2,2'-bipyridine)₃ Cl_2 as photosensitizer and of an electron donor, such as a tertiary amine like triethanolamine $[N(CH_2CH_2OH)_3]$ (9).

On the other hand, metal complexes in general, and cobalt complexes in particular, are able to bind CO_2 (24–32) and to act as electrocatalysts for its reduction (33–36), for instance to CO by the overall reaction 4 (36).

Therefore, we decided to investigate CO₂ reduction by a system containing $\operatorname{Ru}(2,2'$ -bipyridine)³⁺₃ [Ru(bipy)³⁺₃] as the photosensitizer, a cobalt species as the reducing intermediate, and a tertiary amine as the electron donor, in aqueous acetonitrile solution. This system generates CO from dissolved CO₂ under irradiation with visible light. The reaction is accompanied by water reduction, so that it produces simultaneously CO and H₂ in proportions depending on the experimental conditions.

MATERIALS AND METHODS

Chemicals. All chemicals used were either high-purity commercial reagents or were prepared by standard methods.

Experiments and Analytical Methods. The irradiation experiments were conducted with a 1000-W Xe Müller lamp (XBO 1000/HS) or a 1000-W Xe/Hg ozone-free Oriel lamp, both equipped with a 400-mm cut-off filter (Schott filter GG 420). The temperature was that reached spontaneously by the irradiated sample (about 30°C).

Unless otherwise stated, all experiments were performed on 30 ml of a reference solution, designated RS, of Ru(bipy)₃Cl₂·6H₂O $(0.43 \text{ mM} \pm 10\%)$ and CoCl₂·6H₂O $(1.47 \text{ mM} \pm 10\%)$ in 60% acetonitrile/20% water/20% triethylamine (vol/vol), contained in a 50-ml round-bottom flask. All solutions were degassed under vacuum (0.1 mm of Hg), and a volumetrically measured amount of CO₂ (gas purity, 99.998%) was dissolved in the reaction mixture. A number of experiments were performed in the presence of added bipy ligand for complexing the cobalt ion. After irradiation the internal pressure was brought to atmospheric pressure by introducing NaOH (0.01 M) in the reaction vessel; the gas contained in the flask was sampled by a syringe and analyzed by gas-phase chromatography on a 5-Å-molecularsieve column at room temperature with methane as carrier gas as described (9). Known amounts of reference gases (CO, H_{2} , air) were injected for identification and quantitative analysis of the reaction gas. In a few cases, the gas was analyzed by mass spectrometry.

RESULTS

Some of the results obtained are listed in Table 1. The following data and comments may be added.

(*i*) Irradiation (Xe lamp) of RS containing bipy (4.41 mM; bipy per Co = 3) and CO₂ (700 ml) for 12 hr produced 0.28 ml (11.5 μ mol) of CO and 1.22 ml (51 μ mol) of H₂.

(*ii*) Kinetic experiments under the same conditions gave a linear increase in amounts of H_2 and CO generated as a function of time, yielding 25 μ mol of CO and 112 μ mol of H_2 after 26 hr of irradiation.

(iii) Addition of bipyridine to RS affected the total amount $(CO + H_2)$ of gas generated and especially decreased the CO/ H_2 ratio. (Table 1; runs 1–8). The first equivalent of bipy with respect to CoCl₂ had the strongest effect. Above ≈ 3 equivalents, the amounts of CO and H₂ formed respectively decreased and increased linearly with added bipy.

(iv) The nature of the tertiary amine markedly affected the gas produced (Table 1). When triethylamine (NEt₂) was re-

Table 1. Generation of CO and H_2 by photoreduction of CO_2 and H_2O as a function of system components*

Run [†]	Donor	bipy‡	CO, ml	H ₂ , ml	CO/H_2 §
1	NEt ₃	0	0.9	1.3	0.68 (7.86)
2	NEt ₃	0.3	0.53	1.13	0.47 (5.38)
3	NEt ₃	1	0.24	1.08	0.22 (2.55)
4	NEt ₃	2	0.24	1.24	0.19 (2.22)
5	NEt ₃	3	0.24	1.64	0.15 (1.68)
6	NEt ₃	5	0.18	2.04	0.09 (1.01)
7	NEt ₃	7.5	0.12	2.38	0.05 (0.58)
8	NEt ₃	10	0.07	2.72	0.02 (0.30)
9¶	NEt ₃	0	<10 ⁻⁵	0.07	<10-4
10¶	NEt ₃	0	<10 ⁻⁵	0.03	<10 ⁻⁴
11¶	NEt_3	0	<10 ⁻⁵	0.02	<10-4
12¶	NEt ₃	0	<10 ⁻⁵	0.33	<10 ⁻⁴
13	N(CH ₂ CH ₂ OH) ₃	0	2.93	0.12	24.9 (400)
14	NMe ₃	0	0.01	0.30	0.05 (0.79)
15	NEt ₃	0	0.10	1.04	0.10 (1.6)
16	NPr ₃	0	2.26	2.66	0.85 (13.6)

* Irradiation (22 hr) of 0.43 mM Ru(bipy)₃Cl₂ and 1.47 mM CoCl₂ in 30 ml of acetonitrile/donor/water, 3:1:1 (vol/vol).

[†] Runs 1–12: 700 ml of dissolved CO₂; Xe lamp. Run 13: 500 ml of dissolved CO₂; Xe lamp. Runs 14–16: 500 ml of dissolved CO₂; Xe/Hg lamp.

[‡] Equivalents of free bipyridine added with respect to CoCl₂.

[§] The CO/H₂ selectivity per mol of CO₂ and H₂O is given in parentheses. It is calculated by normalizing the amounts of CO and H₂ produced experimentally from dissolved CO₂ (700 ml = 0.029 mol or 500 ml = 0.0208 mol) and water (6 ml = 0.33 mol) to 1 mol of each reagent.

[¶]CoCl₂ was replaced by $1.47 \text{ mM} \pm 10\%$ of RhCl₃ (run 9), NiCl₂ (run 10), CuCl₂ (run 11), and K₂PtCl₄ (run 12).

placed by other NR₃ compounds, the quantity $(CO + H_2)$ and the ratio CO/H₂ increased along the series R = Me, Et, Pr. When NEt₃ was replaced by N(CH₂CH₂OH)₃, the dissolution of CO₂ (500 ml) yielded a two-phase system that, under irradiation with efficient stirring, generated preferentially CO.

(v) Experiments performed as a function of dissolved CO_2 showed that, as the concentration of CO_2 increased, the amounts of H_2 and CO that were produced respectively decreased and increased approximately in a linear fashion.

(vi) Control experiments were run by omitting one component of the system Ru(bipy)₃Cl₂/CoCl₂/CO₂ (700 ml)/bipy(bipy per Co = 3)/h ν (22 hr irradiation; Xe lamp) with the following results. In the absence of Ru(bipy)₃Cl₂, NEt₃, light, or water (nonaqueous solution was 60% CH₃CN/40% NEt₃), less than 0.01 μ l of H₂ and CO was produced. In the absence of CO₂, the solution turned dark blue-green with an absorption maximum at 620 nm, corresponding to the formation of the Co(I)(bipy)_n species (9, 37), and H₂ was produced (318 μ mol in 63 hr of irradiation; CO, <0.01 μ l). In the absence of both CO₂ and bipy, there was no color change and some H₂ was produced (10 μ mol in 22 hr irradiation; CO, <0.01 μ l). In the absence of both CoCl₂ and bipy, some H₂ (6.3 μ mol) and CO (2.1 μ mol) were formed [adding Ru(bipy)₂Cl₂ (1.45 mM) increased the amounts of H₂ (15.4 μ mol) and CO (6.2 μ mol) obtained].

(vii) When $CoCl_2$ in RS was replaced by another metal salt or complex, H_2 was produced more or less efficiently but no CO was detected (Table 1). With K_2PtCl_4 , particles of platinum apparently were formed.

DISCUSSION

The results lead to the following comments.

(*i*) The present system containing $\text{Ru}(\text{bipy})_3^{2+}/\text{Co}^{2+}/\text{NEt}_3$ as photosensitizer/mediator/donor, respectively, is capable of generating simultaneously CO and H₂ by reduction of CO₂ and

H₂O under irradiation with visible light. The process is catalytic because more of the quantity $(CO + H_2)$ is obtained than the amounts of metal species used; in experiment 16 (Table 1), the turnover numbers are 32 for $Ru(bipy)_3^{2+}$ and 9 for $CoCl_2$, by considering the total volume (CO + H_2) of gas produced and assuming a dielectronic reduction in each case.

(ii) That the CO generated comes from CO₂ agrees with the absence of CO formation when no CO2 is dissolved, whereas H₂ production still occurs.

(iii) CO is not produced by the initial generation of H₂ followed by a water gas shift reaction (Eq. 10) catalyzed by the components of the system:

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$
 [10]

Indeed, when RS is maintained in the dark for 22 hr under CO₂ + H₂ atmosphere, no CO is formed; under CO atmosphere, no H₂ is formed.

(iv) As indicated by the observations in the absence of CO₂, and by analogy with earlier experiments on irradiation of $\operatorname{Ru}(\operatorname{bipy})_{3}^{2+}/\operatorname{Co}(\operatorname{bipy})_{n}^{2+}$ mixtures (9, 38), a highly reducing $Co(bipy)_n^+$ species is probably produced in the presence of bipy. Irradiation of $\operatorname{Ru}(\operatorname{bipy})_3^{2+}$ in acetonitrile (39) or in aqueous acetonitrile (40) in the presence of electron donors like NEt₃ (40) yields Ru(bipy)₃⁺, which is able to reduce Co(bipy)₃²⁺ because $E^{0'} = -1.26$ V for Ru(bipy)₃^{2+/+} (41, 42) and -1.0 V for $Co(bipy)_3^{2+/+}$ (37). In the process, the organic electron donor is consumed, as is now well documented (8, 9, 38, 40). The nature of the reduced cobalt species formed in the absence of bipy is unknown at present.

(v) The efficiency of the system, taken as the total amount of $(CO + H_2)$ gas produced, increases on addition of bipy and along the series NMe3, NEt3, NPr3. Among the metal ions studied, Co^{2+} is by far the most efficient mediator.

(vi) The selectivity of the process may be defined by the ratio CO/H₂ of the amounts of CO and H₂ produced per mole of reagent (Table 1), with the assumption that the dielectronic reductions of CO2 and H2O have similar kinetic form. As seen from Table 1, the selectivity may be regulated by the choice of the components. Co(II) is an efficient and specific promoter of CO_2 reduction, whereas the other metal ions studied are not. The tertiary amine also influences CO/H_2 , which increases strongly (from 0.8 to 400) along the series NMe₃, NEt₃, NPr₃, $N(CH_2CH_2OH)_3$.

The dependence of the CO/H_2 ratio on the amount of bipy indicates that occupation of the coordination sites around the cobalt ion or the change in redox potential due to bipy coordination, or both, hinders CO₂ reduction but not H₂ formation. The marked effect of the tertiary amine suggests that it not only acts as donor but probably also influences the reaction processes by coordination to cobalt.

(vii) We have shown that H₂ is generated upon visible light irradiation of $Ru(bipy)_3^{2+}/Co(bipy)_n^{2+}$ in aqueous solution at pH 8.5–12.5 with $N(CH_2CH_2OH)_3$ as donor and in the presence of a Pt catalyst (9). The same complexes produce H_2 with ascorbic acid as donor at pH \approx 5.0 in the absence of catalyst (38). The involvement of intermediate Co(I) bipy species and hydride derivatives was proposed. It is probable that a similar mechanism is followed in the present case. The much lower yields of H_2 obtained when Co^{2+} is replaced by other ions (Table 1) is in agreement with other recent results (38).

(viii) The mechanism of CO formation is not clear at present. The dielectronic reduction (reaction 4) is thermodynamically feasible with $Co(bipy)_n^+$, as would be the formation and subsequent decomposition of formic acid (reaction 6) or oxalic acid (reaction 11) (22).

$$2 \operatorname{CO}_2 + 2\mathrm{H}^+ + 2\mathrm{e}^- \rightarrow (\operatorname{COOH})_2 \quad E^{0} = -0.90 \operatorname{V}.$$
 [11]

CO2 reacts with hydride complexes of Co(I) (29-32), and although CO could not be detected, its formation as an intermediate was envisaged (29). On the other hand, formate complexes were obtained (30-32) whose decomposition yielded CO and H_2 (44, 45). The mechanism of CO formation by the overall reaction 4 may be related to that of the electrocatalytic reduction of CO₂ to CO in the presence of macrocyclic cobalt complexes (36).

CONCLUSION

The present work describes a photochemical process which produces simultaneously CO and H_2 by reduction of CO_2 and H_2O . It represents a further step in the development of chemical systems capable of artificial photosynthesis and solar energy conversion and storage.

Further improvements in efficiency and in CO/H₂ selectivity may be realized by modification of the components, using other photosensitizers (such as other metal complexes, organic dyes, or semiconductors), other mediators (mono- or polynuclear cobalt complexes or other metal complexes), or other donors (organic or inorganic). Much work remains also to be done on the physicochemical and mechanistic aspects of the process discovered here.

Finally, one may note that the simultaneous reduction of CO_2 and H_2O produces in fact "synthesis gas" (CO + H_2), which is of interest for large scale industrial processes.

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