Efficient Photochemical Reduction of CO_2 to CO by Visible Light Irradiation of Systems containing Re(bipy)$(CO)_3$X or Ru(bipy)$_3^{2+}$–Co^{2+} Combinations as Homogeneous Catalysts

Jeannot Hawecker, Jean-Marie Lehn,* and Raymond Ziessel

E.R.A. No 265 au C.N.R.S., Institut Le Bel, Université Louis Pasteur, 4 Rue Blaise Pascal, 67000 Strasbourg, France

Efficient photogeneration of either (CO + H_2) simultaneously, or CO selectively, occurs on visible light irradiation of CO_2 solutions in $(HOCH_2CH_2)_3N$–dimethylformamide containing, respectively, Ru(bipy)$_3^{2+}$–Co^{2+} combinations or the single component Re(bipy)$(CO)_3$X (X = Cl, Br) as homogeneous catalysts.

Carbon dioxide fixation is the basic reaction by which natural photosynthesis produces organic matter. A major goal of research in artificial photosynthesis is to discover abiotic photocatalytic systems capable of producing reduced species by photochemical reduction of CO_2. The development of such systems is of interest from three points of view, *viz.*, finding catalysts for CO_2 activation, devising means for conversion and storage of solar energy by production of fuels and organic raw materials, and setting up models of natural photosynthesis.

Compared to water photolysis[1] little research has been devoted to the photoreduction of CO_2 (refs. 2—4 and references therein), which may yield a variety of products by reactions proceeding most easily *via* polyelectronic processes.[2,3] It requires the photochemical generation of species of sufficient reducing power and the discovery of suitable catalysts for these reactions.

Extending our earlier work on the photoreduction of water,[5] we have recently shown[3] that visible light irradiation of CO_2 solutions in aqueous acetonitrile, containing Ru(bipy)$_3^{2+}$ as photosensitizer, Co^{II} ions as catalyst, and a tertiary amine as electron donor, yields a mixture of CO and H_2 (synthesis gas) by simultaneous photoreduction of CO_2 and H_2O. We now report results on (i) marked improvements of this Ru(bipy)$_3^{2+}$/Co^{II} system and (ii) a 'single component' system using Re(bipy)$(CO)_3$X both as photosensitizer and as catalyst for the $CO_2 \rightarrow CO$ photoconversion.

Extensive modifications of the Ru(bipy)$_3^{2+}$/Co^{II} process[3] were performed in order to improve its (CO + H_2) photogeneration efficiency as well as to control its CO/H_2 selectivity. Marked effects have been found by varying the nature of the solvent, of the tertiary amine donor, and of the photosensitizer, allowing efficiencies much higher than those reported previously[3] to be achieved.[6] Thus, visible light irradiation (2 h, 250 W, halogen lamp, 400 nm cut-off filter) of a solution containing Ru(bipy)$_3^{2+}$ (10 mg), $CoCl_2.6H_2O$ (8 mg), 2,9-dimethyl-1,10-phenanthroline (17 mg) as ligand for the cobalt ions, and CO_2 (160 ml) dissolved in a mixture of $(HOCH_2CH_2)_3N$ (5 ml) and dimethylformamide (DMF) (25 ml), gave 2 ml of CO and 4.5 ml of H_2. Irradiation for 15 h with a 1000 W Xe lamp gave 8 ml of CO and 19 ml of H_2.

That the CO formed comes from the dissolved CO_2 was confirmed by isotope labelling experiments which gave ^{13}CO (90% enriched) from 90% enriched $^{13}CO_2$ [coupled gas chromatography-mass spectrometry (g.c.-m.s.) analysis].

The overall CO_2 reduction reaction may be represented by equation (1).

$$CO_2 + 2H^+ + 2e^- \rightleftharpoons CO + H_2O \quad E^{0\prime} = -0.52 \text{ V} \qquad (1)$$

Electrochemical results give insight into the mechanism of the process. Addition of CO_2 to Ru(bipy)$_3^+$ produced electrochemically in acetonitrile solution, gave only little CO. Addition of Co(bipy)$_3^{2+}$ to Ru(bipy)$_3^+$ in DMF gave Co^I

Table 1. Generation of CO by photoreduction of CO_2 *via* visible light irradiation of solutions containing $Re(L)(CO)_3X$ and CO_2 in $(HOCH_2CH_2)_3N$–DMF.[a]

Expt.	Complex	Additive [b]	Irradiation time/h	Vol. of CO produced/ml	Turnover number [c]
1	$Re(bipy)(CO)_3Cl$	0	1	6.5	11
2	"	0	2	9.7	16
3	"	0	4	16.8	27
4	"	NEt_4Cl	2	14.5	23
5	"	NEt_4Cl	4	30.0	48
6	"	NEt_4ClO_4	2	6.4	10
7	"	NEt_4Cl[f]	2	14.0	22
8	$Re(bipy)(CO)_3Br$	0	2	7.6	14
9	"	0	4	11.4	20
10	"	NBu_4Br	2	12.0	21
11	"	NBu_4Br	4	16.0	28
12	$Re(Br\text{-}phen)(CO)_3Br$	0	2	2.7	5
13	"	NBu_4Br	2	3.7	9
14[d]	$Re(bipy)(CO)_3Br$	0	3.5	0.08	—
15[e]	$Re(bipy)(CO)_3Br$	0	6	0.04	—

[a] $Re(bipy)(CO)_3Cl \times 8.710^{-4}$M; $Re(bipy)(CO)_3Br$ 7.9×10^{-4}M; $Re(Br\text{-}phen)(CO)_3Br$ 6.6×10^{-4}M; Br-phen = 5-bromo-1,10-phenanthroline. 30 ml of solution containing $Re(L)(CO)_3X$ and 160 ml CO_2 (99.8% purity) dissolved in dimethylformamide–$(HOCH_2CH_2)_3N$ (5 : 1) were irradiated with a 250 W halogen lamp (slide projector) fitted with a 400 nm cut-off filter (Schott GG 420). [b] NEt_4Cl 2×10^{-2}M; NBu_4Br 10^{-2}M. [c] Obtained by dividing the number of moles of CO produced by the number of moles of $ReL(CO)_3X$. [d] Experiment carried out without CO_2; formal pH of the solution adjusted to 9.5; 1.1 ml of H_2 generated. [e] Same conditions as in experiment 14 but adjusted to 'pH' 8.5; 1.3 ml of H_2 generated. [f] And 25 equiv. of bipy.

species (as indicated by electronic absorption spectroscopy); subsequent dissolution of CO_2 into the mixture afforded CO in 55% yield with respect to Ru^I. These results favour a CO_2 photoreduction mechanism involving (i) photoproduction of $Ru(bipy)_3^+$ *via* reductive quenching of the excited species $^*Ru(bipy)_3^{2+}$ by the tertiary amine, (ii) reduction of the Co^{II} ions to Co^I by $Ru(bipy)_3^+$, (iii) reduction of dissolved CO_2 to CO by the Co^I species. The mechanism of the latter process, which represents a CO_2 activation reaction,[7] is not known at present; it might, for instance, involve steps similar, but in the opposite sequence of, those described for Co^I-catalysed oxidation of carbon monoxide.[8]

$Re(L)(CO)_3X$ (L = 2,2′-bipyridine or 1,10-phenanthroline; X = Cl, Br) complexes[9–11] have photophysical, electron transfer, and redox properties[10,11] which should make them suitable for use as photosensitizers in place of $Ru(bipy)_3^{2+}$. Furthermore, metal carbonyls are known to be homogeneous catalysts for the water gas shift reaction,[12] and might therefore also be able to catalyse CO_2 to CO reduction. Thus, it appeared of interest to investigate the photocatalytic properties of such rhenium complexes.

Visible light irradiation (1000 W Xe lamp) of a solution of $Re(bipy)(CO)_3Br$ (13.3 mg), $Co(bipy)_3^{2+}$ (13.7 mg), and CO_2 (160 ml) in a mixture of $(HOCH_2CH_2)_3N$ (10 ml) and DMF (20 ml) for 17 h gave H_2 (0.3 ml) and an especially large amount of CO (11.4 ml). Similar irradiations conducted *in the absence* of $Co(bipy)_3^{2+}$, led to efficient generation of *only* CO. A number of experiments were then performed in order to investigate the features of this reaction and some of the results obtained are listed in Table 1.

(i) The present $Re(L)(CO)_3X/(HOCH_2CH_2)_3N$ system performs a *photocatalytic CO_2 reduction process*, in which the rhenium complex must act *both as photosensitizer and as homogeneous catalyst*. It also represents a novel CO_2 activation reaction.[7] No CO is detected when the irradiation is conducted in the absence of the complex.

(ii) When $^{13}CO_2$ (90.5% enriched) is used, only ^{13}CO (88% enriched) is obtained as indicated by g.c.–m.s. analysis and also observed by ^{13}C n.m.r. spectroscopy.

(iii) The system displays *high efficiency* giving high turnover numbers (Table 1) and producing more reduced product than even the most active $Ru(bipy)_3^{2+}/Co^{II}$ combinations (see above and ref. 6).

(iv) The process has *very high CO/H_2 selectivity*, generating only CO and no detectable amount of H_2, although H_2 is formed in the absence of CO_2 (Table 1, experiments 14 and 15). Addition of $Co(bipy)_3^{2+}$ provides a pathway for simultaneous H_2 formation, presumably *via* cobalt hydrides (see above and refs. 3, 5, 13).

(v) Kinetic experiments indicate that the activity of the system decreases slowly with time. This may be due to labilization of ligand species. Whereas no improvement occurs on addition of an excess of bipyridine or perchlorate (compare runs 2 and 6, 4 and 7, Table 1), addition of chloride or bromide anions to the corresponding $Re(bipy)(CO)_3X$ (X = Cl, Br) complex leads to a marked increase in *stability*, producing appreciably more CO in experiments over long time periods (compare runs 2 and 4, 3 and 5, 8 and 10, 9 and 11, Table 1).

(vi) The *mechanism* of the process involves a *photocatalytic rhenium cycle*. Visible light absorption by the $Re(bipy)(CO)_3X$ complex (λ_{max} 385, 392 nm; ϵ 3100, 2680 dm^3 mol^{-1} cm^{-1}; X = Cl, Br) yields the excited state $^*Re^I$ which, by analogy with the corresponding (phen) complexes,[11] may undergo either oxidative or reductive electron transfer quenching, depending on the redox potential of the quencher. Assuming that the redox potential $^*Re^I(bipy)(CO)_3X/[Re^0(bipy)(CO)_3X]^-$ is similar to that in the (phen) series [*ca.* +1.25 V *vs.* normal hydrogen electrode (N.H.E.)][11], reductive quenching by $(HOCH_2CH_2)_3N$ (E^0 *ca.* +0.8 V) may occur and has been confirmed by quenching experiments. The $[Re^0(bipy)(CO)_3X]^-$ species thus formed should have a Re^I/Re^0 redox potential close to that of the corresponding (phen) species (−1.05 V *vs.* N.H.E.)[11] and should therefore be able to reduce CO_2 to CO *via* equation (1).

(vii) The *CO_2 activation and reduction* sequence must involve co-ordination of CO_2 to the metal. The effect of added anions (see above) may indicate that loss of the halide ligand provides a free co-ordination site; indeed, under the conditions of Table 1, anion exchange in the rhenium complex (*e.g.* between Cl^- and Br^-) occurred readily. Loss of a single nitrogen co-ordination to a *sesqui*-bipy ligand as proposed in other cases (see for instance ref. 14) might also be envisaged, but would be difficult with (phen) as ligand (Table 1, experiments 12 and 13).

Recent examples of CO_2 co-ordination to reduced transition metal sites[7] involve for instance cobalt,[15] tungsten,[16] and rhenium[17] complexes. In particular, CO_2 is reduced to co-ordinated CO *via* complexes with metal carbonylate dianions such as $[W(CO)_5]^{2-}$.[16] Reaction of CO_2 with a species derived from the photogenerated $[Re^0(bipy)(CO)_3X]^-$ complex, would present analogies with such a process. ^{13}C N.m.r. and i.r. data show that, when $^{13}CO_2$ is used, all carbonyl groups of the initial $Re(bipy)(CO)_3X$ complex become labelled on irradiation.

The formation of hydrogen in the absence of CO_2 (Table 1, experiments 14 and 15) is expected to proceed *via* a rhenium hydride. Insertion of CO_2 into Re–H bonds yields formate complexes;[18] photolysis apparently gives a mixture containing a carbonyl complex.[18b] It also would find analogies in the reverse sequence of the steps proposed for the photochemical water gas shift reaction catalysed by $[Ru(bipy)_2(CO)Cl]Cl$.[19] When the irradiation was performed without addition of excess of anion (under conditions similar to expts. 1—3, Table 1), the formate complex $Re(bipy)(CO)_3(O_2CH)$ was isolated and characterized; its role in CO formation is being investigated.

The results described above lead to several conclusions. (i) They represent new processes of artificial photosynthesis and light energy storage, (ii) they involve new CO_2 activation reactions by homogeneous catalysts, which may also be of use in electroreduction of CO_2[20] as has indeed been found,[21] (iii) the single component process involving the $Re(bipy)(CO)_3X$ complexes is simpler, more efficient, and much more selective for CO_2 *vs.* H_2O reduction than the combined $Ru(bipy)_3^{2+}/Co^{II}$ system, and (iv) metal carbonyl complexes might also act as photosensitizer and catalyst for other photoinduced reactions, in particular for reduction of CO_2 beyond CO.

We thank Mr. Y. Guilbert for performing the g.c.–m.s. analyses.

Received, 3rd March 1983; Com. 286

References

1 'Photochemical Conversion and Storage of Solar Energy,' ed. J. S. Connolly, Academic Press, New York, 1981.

2 B. Åkermark in 'Solar Energy-Photochemical Conversion and Storage,' eds. S. Claesson and L. Engström, National Swedish Board for Energy Source Development, NE 1977:6, 1977, ch. 6.

3 J. M. Lehn and R. Ziessel, *Proc. Natl. Acad. Sci. USA*, 1982, **79**, 701.

4 'Organic and Bioorganic chemistry of Carbon Dioxide,' eds. S. Inoue and N. Yamazaki, Kodansha Ltd., Tokyo, Wiley, New York, 1982.

5 J. M. Lehn and J. P. Sauvage, *Nouv. J. Chim.*, 1977, **1**, 449; M. Kirch, J. M. Lehn, and J. P. Sauvage, *Helv. Chim. Acta*, 1979, **62**, 1345; J. Hawecker, J. M. Lehn, and R. Ziessel, *Nouv. J. Chim.*, 1983, in the press; J. M. Lehn, ch. 6 in ref. 1.

6 J. Hawecker, J. M. Lehn, and R. Ziessel, unpublished results; R. Ziessel, Doctorat ès-Sciences, Université Louis Pasteur, Strasbourg, 1982.

7 M. E. Vol'pin and I. S. Kolomnikov, *Pure Appl. Chem.*, 1975, **33**, 567; R. Eisenberg and D. E. Hendriksen, *Adv. Catal.*, 1979, **28**, 70; J. A. Ibers, *Chem. Soc. Rev.*, 1982, **11**, 57.

8 J. E. Bercaw, L.-Y. Goh, and J. Halpern, *J. Am. Chem. Soc.*, 1972, **94**, 6534.

9 E. W. Abel and G. Wilkinson, *J. Chem. Soc.*, 1959, 1501; F. Zingales, M. Graziani, F. Faraone, and U. Belluco, *Inorg. Chim. Acta*, 1967, **1**, 172; D. Vitali and F. Calderazzo, *Gazz. Chim. Ital.*, 1972, **102**, 587.

10 M. Wrighton and D. L. Morse, *J. Am. Chem. Soc.*, 1974, **96**, 998.

11 J. C. Luong, L. Nadjo, and M. S. Wrighton, *J. Am. Chem. Soc.*, 1978, **100**, 5790.

12 P. C. Ford, *Acc. Chem. Res.*, 1981, **14**, 31.

13 C. V. Krishnan and N. Sutin, *J. Am. Chem. Soc.*, 1981, **103**, 2141; C. V. Krishnan, C. Creutz, D. Mahajan, H. A. Schwarz, and N. Sutin, *Isr. J. Chem.*, 1982, **22**, 98.

14 R. C. Angelici and J. R. Graham, *J. Am. Chem. Soc.*, 1965, **87**, 5586; M. S. Wrighton and D. L. Morse, *J. Organomet. Chem.*, 1975, **97**, 405.

15 G. Fachinetti, C. Floriani, P. F. Zanazzi, and A. R. Zanzari, *Inorg. Chem.*, 1979, **18**, 3469.

16 J. M. Maher and N. J. Cooper, *J. Am. Chem. Soc.*, 1980, **102**, 7604; J. M. Maher, G. R. Lee, and N. J. Cooper, *ibid.*, 1982, **104**, 6797.

17 K. W. Chiu, C. G. Howard, H. S. Rzepa, R. N. Sheppard, G. Wilkinson, A. M. R. Galas, and M. B. Hursthouse, *Polyhedron*, 1982, **1**, 441.

18 (a) G. La Monica, S. Ceinini, F. Porta, and M. Pizzoti, *J. Chem. Soc., Dalton Trans.*, 1976, 1777; (b) M. G. Bradley, D. A. Roberts, and G. L. Geoffroy, *J. Am. Chem. Soc.*, 1981, **103**, 379.

19 D. Choudhury and D. J. Cole-Hamilton, *J. Chem. Soc., Dalton Trans.*, 1982, 1885.

20 B. Fischer and R. Eisenberg, *J. Am. Chem. Soc.*, 1980, **102**, 7361; M. Tezuka, T. Yajima, A. Tsuchiya, Y. Matsumoto, Y. Uchida, and M. Hidai, *ibid.*, 1982, **104**, 6834.

21 J. Hawecker, J. M. Lehn, and R. Ziessel, unpublished results.