114. Photogeneration of Carbon Monoxide and of Hydrogen *via* Simultaneous Photochemical Reduction of Carbon Dioxide and Water by Visible-Light Irradiation of Organic Solutions Containing Tris(2,2′-bipyridine)ruthenium(II) and Cobalt(II) Species as Homogeneous Catalysts

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CO and H_2 are photogenerated simultaneously by visible-light irradiation of systems containing a *photosensitizer*, the $[Ru(bpy)_3]^{2+}$ complex, *Co(II) species* as homogeneous catalysts, which mediate CO_2 and H_2O reduction by intermediate formation of Co(I), a tertiary amine as *electron donor*, which provides the electrons for the reduction, and an organic solvent which also facilitates dissolution of CO_2. The efficiency of ($CO + H_2$) gas production and the selectivity CO/H_2 markedly depend upon the composition of the medium, the nature of the tertiary amine, the solvent, and the ligand of the Co ions. 2,9-Dimethyl-1,10-phenanthroline is particularly effective in promoting CO and H_2 formation, giving a quantum yield of 7.7% in ($CO + H_2$) (1.2% for CO and 6.5% for H_2). The process consists of two catalytic cycles: a photocatalytic cycle for the Ru complex and a double dark reaction pathway for the Co species; oxidative and/or reductive quenching of the excited state of the photosensitizer lead to the formation of Co(I) species which reduce either CO_2 or H_2O to CO or H_2, respectively.

Introduction. – Although there is considerable interest in the development of CO_2 chemistry (for recent reviews on CO_2 activation, see [1]) [2], little research has been devoted to the photoreduction of CO_2. Reported experiments involve irradiation of aqueous solutions of transition metal ions [2a] [3] or of organic dyes [4], irradiation of semiconductor crystals [5a] or powders [5b] as well as photoelectrochemical means of reducing CO_2 [6].

Over the last years, we have described three homogeneous catalytic systems which perform photochemical CO_2 reduction [7]: the first allows the simultaneous reduction of CO_2 and H_2O into CO and H_2, respectively, based on $[Ru(bpy)_3]Cl_2$ (bpy = 2,2′-bipyridine) as photosensitizer and Co(II) ions or Co(II) complexes as catalyst [8], the second is highly efficient and selective for the reduction of CO_2 into CO and based on a single complex *fac*-$[Re(bpy)(CO)_3]X$ (X = Cl, Br) acting both as photosensitizer and as catalyst [9], and the third, based on Ru complexes, performs the photochemical reduction of CO_2 to formate [10]. In our initial reports [8] [9], we described the simultaneous photogeneration of a 'synthesis gas' mixture ($CO + H_2$) with a system containing a photosensitizer ($[RuL_3]^{2+}$, L = 2,2′-bipyridine, 1,10-phenanthroline or derivatives thereof), a CO_2-reduction catalyst (solvated Co(II) ions or Co(II) complexes) and a tertiary amine as electron donor; this system catalytically reduced CO_2 to CO *via* a photogenerated Co(I) species with an efficiency ($CO + H_2$) and a selectivity (CO/H_2) dependent upon experi-

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[1]) UA 422 of the CNRS.

Table 1. *Generation of CO and H_2 by Photoreduction of CO_2 and H_2O in Presence of Different Tertiary Alkylamines and Different Amounts of CO_2*[a])

Exper.	Tertiary amine[b])	Volume of CO_2 dissolved [ml]	Volume of CO produced [ml]	Volume of H_2 produced [ml]	CO + H_2 [μmol]	CO/H_2
1	Et_3N	800[c])	0.13	0.05	7.5	2.4
2	Et_3N	–[d])	–	0.82	34.2	–
3	Et_3N	–	–	0.17	7.1	–
4[e])	Et_3N	800[c])	0.05	0.15	8.3	0.3
5[f])	Et_3N	800[c])	0.15	0.37	21.7	0.4
6[g])	Pr_3N	620[c])	2.36	1.12	145	2.1
7	Me_3N	200[c])	–	0.06	2.5	–
8[g])	Bu_3N	320[c])	0.43	0.28	29.3	1.5
9[g])	$(Pentyl)_3N$	260[c])	0.12	0.05	6.8	2.4
10	Et_3N	200	–	1.04	43.2	–
11[g])	Pr_3N	200	0.28	0.79	44.5	0.4
12[g])	Bu_3N	200	0.07	0.36	17.9	0.2
13[g])	$(Pentyl)_3N$	200	0.08	0.10	7.5	0.8
14[g])	Bu_3N	140	–	0.46	1.9	–
15[g])	$(i\text{-}Bu)_3N$	140[c])	–	0.43	1.8	–
16	$(i\text{-}Bu)_2NEt$	660[c])	0.33	2.20	105	0.2
17	TMEDA	200	0.01	1.92	80.3	–

[a]) Irradiation was carried out at 30° during 16 h with a 1000-W Xe-Hg lamp. The soln. (30 ml) contained $[Ru(bpy)_3]^{2+}$ (4.7×10^{-4}M), $CoCl_2 \cdot 6H_2O$ (1.5×10^{-3}M), MeCN/tertiary amine/H_2O 3:1:1.

[b]) TMEDA: *N,N,N',N'*-tetramethyl-ethylenediamine.

[c]) Soln. saturated with CO_2.

[d]) Formal pH adjusted to 8.6 with conc. HCl.

[e]) Control exper. performed without Co salt.

[f]) 1.45 mM $[Ru(bpy)_2]Cl_2$ added in place of $CoCl_2 \cdot 6H_2O$.

[g]) In these experiments, the mixture separated into two phases after saturation with CO_2.

mental parameters. To investigate the factors which influence the reaction of CO_2 with reduced species (generated photochemically or electrochemically), we have undertaken a systematic study of the effects of changing the Co complex, the tertiary-amine donor, the photosensitizer and the medium composition (see *Tables 1* and *2*). Results on the mechanistic aspects of the processes occurring in this system have also been obtained.

Photoreduction Experiments. – Our studies were carried out using two main systems. The first contained a photosensitizer $[Ru(bpy)_3]^{2+}$, a mediator $CoCl_2 \cdot 6H_2O$, and an electron donor, Et_3N. The solvent was an aquo-organic medium, MeCN/Et_3N/H_2O 3:1:1 saturated with CO_2. The second contained $[Ru(bpy)_3]^{2+}$, a Co(II) complex such as $[Co(bpy)_3]^{2+}$, 'triethanolamine' ($(HOCH_2CH_2)_3N$), and the solvent was either purely organic or an aquo-organic mixture (dimethylformamide (DMF)/H_2O 3:2 or DMF/H_2O/$(HOCH_2CH_2)_3N$ 3:1:1) saturated with CO_2.

Irradiation of both systems with visible light ($\lambda > 400$ nm) catalytically produced H_2 and CO. The gas formed was analysed by GC, after calibration with samples of the pure gases (see *Fig. 1*). To determine the origin of the CO produced, some experiments were run with labelled $^{13}CO_2$ (90.5% enriched) and the gaseous products analysed by GC/MS. The results clearly showed that the *CO produced came from the CO_2 introduced (Fig. 2).* Both *Exper. 1* and *23* gave 90% ^{13}CO when labelled CO_2 was used. In *Fig. 2a,* the peaks at mass 29 correspond to ^{15}NN and ^{13}CO present in natural abundance. The low-intensity

Table 2. *Generation of CO and H_2 by Photoreduction of CO_2 and H_2O in Presence of Different Tertiary Hydroxylated Amines and Different Amounts of CO_2*[a])

Exper.	Tertiary amine	Volume of CO_2 dissolved [ml]	Volume of CO produced [ml]	Volume of H_2 produced [ml]	CO + H_2 [µmol]	CO/H_2
18	$(HOCH_2CH_2)_3N$	200	0.71	0.1	33.7	7.4
19	$(HOCH_2CH_2)_2NMe$	200	0.09	1.32	58.5	0.1
20	$(HOCH_2CH_2)NMe_2$	200	–	0.06	2.4	–
21	$(CH_3CH(OH)CH_2)_3N$	200	0.55	0.03	24.3	19.3
22	$(HOCH_2CH_2)_3N$	150[b])	0.05	0.20	10.4	0.3
23	$(HOCH_2CH_2)_3N$	150[b])	2.2	9.2	475	0.2
24[c])	$(HOCH_2CH_2)_3N$	150[b])	0.04	0.35	16.3	0.1
25[d])	$(HOCH_2CH_2)_3N$	–	–	9.8	408	–
26[e])	$(HOCH_2CH_2)_3N$	180[b])	4.3	3.0	304	1.4
27[f])	$(HOCH_2CH_2)_3N$	150[b])	2.7	5.8	354	0.5
28[e])[f])	$(HOCH_2CH_2)_3N$	120	4.7	4.2	371	1.1
29	$(HOCH_2CH_2)_2NMe$	200[b])	2.4	6.4	366	0.4
30	$(HOCH_2CH_2)_3N$	160[b])	3.7	11.9	650	0.3
31	$(HOCH_2CH_2)_3N$	160[b])	8.6	18.9	1146	0.5
32[e])	$(HOCH_2CH_2)_3N$	160[b])	0.8	9.9	445	0.1
33	$(HOCH_2CH_2)_3N$	150[b])	2.35	1.15	146	2.0
34	$(HOCH_2CH_2)_3N$	150[b])	2.7	1.85	190	1.5

[a]) *Exper. 18–21* contained in 30 ml of soln.: $[Ru(bpy)_3]^{2+}$ (4.7×10^{-4} M), $CoCl_2 \cdot 6H_2O$ (1.5×10^{-3} M), MeCN/tertiary amine/H_2O 3:1:1; the one-phase soln. was irradiated at 30° during 16 h with a 1000-W Xe-Hg lamp. *Exper. 22–29* contained in 30 ml of solution: $[Ru(bpy)_3]^{2+}$ (4.7×10^{-4} M), $[Co(bpy)_3]Cl_2 \cdot 6H_2O$ (1.5×10^{-3} M), DMF/tertiary amine 2:1; the one-phase solution was irradiated at 30° during 15 h (except for *Exper. 22* and *24* which were irradiated during 3 h and for *Exper. 29* which was irradiated during 6 h), with a 1000-W Xe-Hg lamp. *Exper. 30–32* contain: $[Ru(bpy)_3]^{2+}$ (4.7×10^{-4} M); $CoCl_2 \cdot 6H_2O$ (1.5×10^{-3} M) and 3 equiv. of 2,9-dimethyl-1,10-phenanthroline in DMF/$(HOCH_2CH_2)_3N$ 2:1; irradiation time: *Exper. 30*, 3 h and *Exper. 31*, 15 h at 30° with a 1000-W Xe-Hg lamp. *Exper. 33* and *34* contain: $[Ru(bpy)_3]^{2+}$ (4.7×10^{-4} M); $CoCl_2 \cdot 6H_2O$ (1.5×10^{-3} M) and 3 equiv. of 4,4',6,6'-tetramethyl-2,2'-bipyridine in DMF/$(HOCH_2CH_2)_3N$ 2:1; irradiation time: *Exper. 33*, 3 h and *Exper. 34*, 15 h at 30° with a 1000-W Xe-Hg lamp.

[b]) Solution was saturated with CO_2.

[c]) Control exper. performed without Co ions of complexes.

[d]) Formal pH adjusted to 8.9 with conc. AcOH.

[e]) 20% H_2O added to the soln. (DMF/$(HOCH_2CH_2)_3N$/H_2O 3:1:1).

[f]) 3 equiv. of bpy, with respect to the Co complex, added to the medium.

peak of mass 30 in *Fig. 2b* is that of $^{13}C^{17}O$. The MS determinations were performed on gases from which all $^{13}CO_2$ had been removed, in order to avoid any contribution to the ^{13}CO peak from the decomposition of $^{13}CO_2$ itself in the mass spectrometer (see *Exper. Part*).

A series of control experiments was performed to confirm that the presence of each component was essential. Both system showed no activity (< 1 µl H_2 and CO), when either the photosensitizer, the tertiary amine, or light were omitted. In the absence of MeCN, the system containing $[Ru(bpy)_3]^{2+}$, $CoCl_2$, and H_2O/Et_3N 3:2, produced only a few µl of H_2. Irradiation experiments performed without CO_2 gave exclusively H_2 (*Exper. 3* and *Exper. 25*); in these cases, the formal pH was adjusted to that obtained in the presence of CO_2 by addition of conc. HCl to the aquo-organic solution (MeCN/H_2O), or of conc. AcOH to the purely organic DMF medium. When the acidity was not adjusted in the case of the MeCN/H_2O medium, less H_2 was evolved (*Exper. 2* and *3*). When the catalytic species Co^{2+} or $[Co(bpy)_3]^{2+}$ were not added, only small quantities of

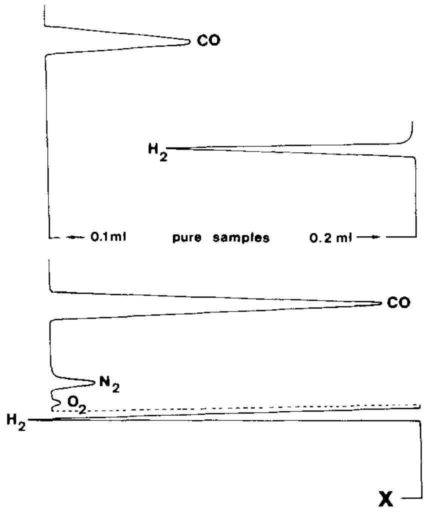

Fig. 1. *GC Analysis of photogenerated (CO + H_2) gas* (0.5 ml) (bottom, see X). Pure CO (0.1 ml) and H_2 (0.2 ml) were used as references.

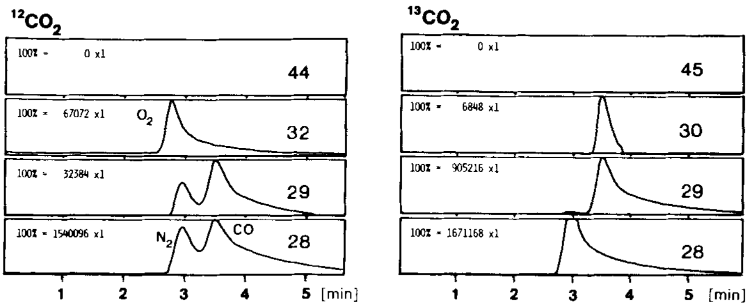

Fig. 2. *GC/MS Analysis of photogenerated CO.* Gas obtained from photoreduction of $^{12}CO_2$ (left) and $^{13}CO_2$ (right); the mass peaks are recorded at very different sensitivities, indicated by the figure for 100% (= height of strongest peak) at left and decreasing from top to bottom (for example CO at mass 29 on left is natural abundance ^{13}CO); abscissa: GC retention time in min.

H_2 and CO were detected (*Exper. 4* and *Exper. 24*). In accord with recent results obtained using (bipyridine)ruthenium complexes in the photoreduction of CO_2 to formate [10], one may suspect bis(bipyridine)ruthenium complexes (obtained by photolabilization of a bpy ligand from the starting complex) to be the active species in these reactions. ^{13}C-NMR studies performed in $MeCN/H_2O$ or DMF, in the presence of 90.5% labelled CO_2, did not reveal other reduction products such as formate, formaldehyde, MeOH, or coupling products. Recent kinetic and mechanistic studies have described the reduction of HCO_3^- to CO by $[Co(bpy)_3]^+$ in aqueous media [11]. However, traces of formate were detected in the absence of Co ions or complexes (*Exper. 4* and *Exper. 24*).

To confirm the catalytic nature of our system and to investigate its stability, we performed some kinetic experiments. The photochemical gas production (CO and H_2)

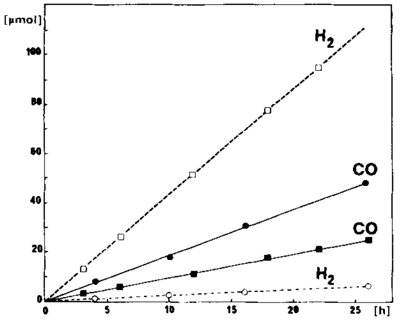

Fig. 3. *Photogeneration of CO and H_2 as a function of time by photoreduction of CO_2 and H_2O.* ●, ○: Conditions of *Exper. 18, Table 2,* with solution saturated with CO_2. ■, □: Conditions of *Exper. 1, Table 1,* using $[Co(bpy)_3]Cl_2$ instead of $CoCl_2 \cdot 6H_2O$.

was linear during at least 26 h irradiation under the conditions described in *Fig. 3.* This was true whether a Co^{2+} salt, isolated $[Co(bpy)_3]^{2+}$ or *in-situ* prepared (bipyridine)cobalt complexes were used. One notes an inversion of CO/H_2 selectivity, when no bpy was used to complex the Co ions. The following turnovers were obtained by dividing the number of moles of ($CO + H_2$) by the number of moles of species used: *Exper. 6:* $[Ru(bpy)_3]^{2+}$, 21, and Co^{2+}, 3; *Exper. 31:* $[Ru(bpy)_3]^{2+}$, 164, and (2,9-dimethyl-1,10-phenanthroline)cobalt complex, 26. The homogeneous character of the system was checked by ultracentrifugation (15 h at 20000 rpm) of the irradiated main systems (*Exper. 6* and *31*); no deposit was detected during or after photolysis, and subsequent irradiation of the same sample showed the same efficiency.

The results described here clearly demonstrate that CO_2 and H_2O were *reduced photocatalytically, homogeneously,* and with *good efficiency,* into CO and H_2. To improve empirically efficiency and selectivity, and to investigate the mechanism of these processes, we have studied the influence of various parameters of the system. The composition of the medium (H_2O and CO_2 contents, proportions of tertiary amine, and of organic solvent), the nature of the tertiary amine and of the organic solvent used, and the presence of specific ligands for Co ions may be expected to influence the process by various means: coordination with Co ions, stabilization of reduced species and reactive intermediates, availability of protons, amount and nature of dissolved CO_2, *etc.*

Effects of Medium Composition and of Nature of the Tertiary Amine. A number of variations were studied mainly for two systems.

1) *System $[Ru(bpy)_3]^{2+}$, $CoCl_2$, R_3N, $MeCN/H_2O$.* With the proportion of H_2O arbitrarily fixed at 20%, an optimal efficiency in the photochemical generation of ($CO + H_2$) was obtained using 20% Et_3N, at CO_2 saturation. Similar variation in efficiency was observed on varying the relative proportions of H_2O (optimum at ~20%) and tertiary amine, while maintaining the proportion of MeCN at 60%. In the absence of H_2O (medium composition $MeCN/Et_3N$ 3:2), the efficiency of the system decreased drastically. The optimum composition was about $MeCN/Et_3N/H_2O$ *ca.* 3:1:1.

Addition of up to 1 equiv. of bpy had a marked effect on CO generation *(Fig. 4)* [8]. On further addition, the quantities of CO and H_2 formed decreased and increased, respectively, linearly with added bpy.

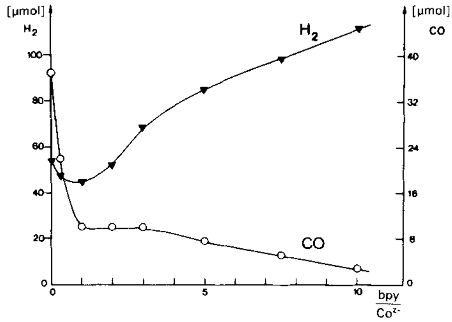

Fig. 4. *Effect of addition of increasing amounts of bpy* (equivalents with respect to Co^{2+} ions) *on CO and H_2 photogeneration*. Conditions of *Exper. 1, Table 1*.

Two main types of tertiary amines have been tested: *alkylamines* such as Me_3N, Et_3N *(Table 1)*, and *hydroxylated amines* such as 'triethanolamine' ($(HOCH_2CH_2)_3N$), ($(CH_3CH(OH)CH_2)_3N$), 'diethanolmethylamine' ($(HOCH_2CH_2)_2NMe$), or 'dimethylethanolamine' ($(HOCH_2CH_2)NMe_2$) *(Table 2)*. In the first class, at CO_2 saturation, Pr_3N gave by far the most efficient system *(Exper. 6)*. When the volume of dissolved CO_2 was maintained constant (at 200 ml), the efficiency sequence was: $Pr_3N \approx Et_3N > Bu_3N > (pentyl)_3N > Me_3N$. Using either Bu_3N *(Exper. 14)* or $(i\text{-}Bu)_3N$ *(Exper. 15)*, with 140 ml of CO_2 dissolved in the solution (saturation volume for $(i\text{-}Bu)_3N$), no CO but the same amounts of H_2 was obtained, whereas saturation of the Bu_3N medium with 320 ml of CO_2 *(Exper. 8)* gave significant CO generation.

It is clear that, in addition to the nature of the tertiary amine, the volume of CO_2 dissolved in the medium also plays an important role. With Et_3N as donor, the photochemical generation of CO and H_2 increased and decreased, respectively, linearly with increasing amounts of dissolved CO_2 *(Fig. 5a)*. At the same time, the selectivity increased until 600 ml of CO_2 were dissolved and then levelled off *(Fig. 5b)*; a similar curve of acid-base-titration type has previously been reported [12]. However, although at saturation Pr_3N dissolved less CO_2 than Et_3N (*Exper. 1* and *6*), the efficiency in CO formation was 18 times higher. Similarly, Pr_3N and $(i\text{-}Pr)_2NEt$ (*Exper. 6* and *16*) both dissolved at saturation the same amount of CO_2, but showed different CO and H_2 generation activi-

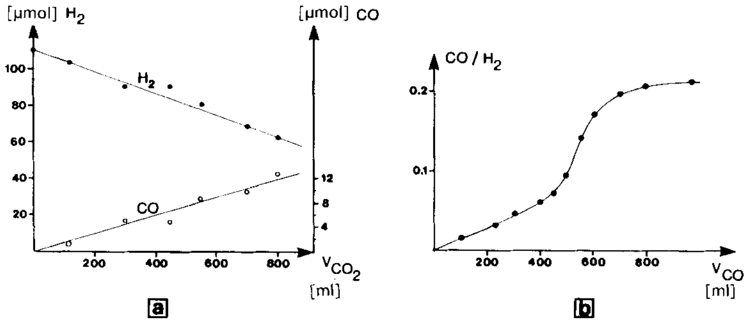

Fig. 5. *Efficiency of CO and H_2 photogeneration* (left) *and of CO/H_2 selectivity* (right) *as a function of the volume of CO_2 dissolved in the medium*. Conditions of *Footnote a, Table 1*, with $[Co(bpy)_3]Cl_2$ instead of $CoCl_2 \cdot 6H_2O$.

ties. *N,N,N',N'*-Tetramethylethylenediamine (TMEDA) may, in addition, act as chelating ligand for the Co(II) ions *(Exper. 17)*. By comparison with Me_3N *(Exper. 7)* or Et_3N *(Exper. 10)* CO generation was not affected, while H_2 production increased from Me_3N to Et_3N and to TMEDA. Coordination of the tertiary amine with the Co(II) ions yields complexes which, when reduced, may exhibit different reactivities towards CO_2 and H_2O. Aromatic tertiary amines such as *N,N*-dimethylaniline or *N,N,N',N'*-tetramethylbenzidine were not active as donors, presumably because their reversible oxidation does not allow accumulation of reduced species in the medium.

With the second class of electron donors, the *hydroxylated amines*, photoreduction was appreciably more efficient in general *(Table 2)*. A marked decrease in CO_2 reduction was observed when a hydroxylated chain of $(HOCH_2CH_2)_3N$ was replaced by an alkyl group (*Exper. 18* and *19*); with $(HOCH_2CH_2)_2NMe$, CO_2 reduction was strongly inhibited, but a large quantity of H_2 was generated. With $HOCH_2CH_2NMe_2$, formation of both CO and H_2 was very slow *(Exper. 20)*, as with Me_3N *(Exper. 7)*. For the amines tested, the following activity sequences were obtained: $(HOCH_2CH_2)_3N$ > $(CH_3CH(OH)CH_2)_3N$ > $(HOCH_2CH_2)_2NMe \approx Me_3N$ and $(HOCH_2CH_2)_2NMe$ > $(HOCH_2CH_2)_3N$ > $(HOCH_2CH_2)NMe_2 \approx Me_3N$ > $(CH_3CH(OH)CH_2)_3N$ for CO_2 and H_2O reduction, respectively. With *N*-ethyl- or *N*-methylmorpholine as donors, neither CO nor H_2 could be detected.

Another interesting feature of these hydroxylated tertiary amines is the inhibition of Co(II) oxidation to Co(III) species. The blue solution (λ_{max} 650 nm) obtained on complexation of the Co^{2+} ion by an alkylamine in the presence of MeCN and H_2O gave, on contact with air, an insoluble brown solid attributed to (amine)cobalt(III) species. This precipitate disappeared on reduction in the present photochemical system. By contrast, the pink-violet colour (λ_{max} 570 nm) obtained with hydroxylated amine and Co(II) salts, was stable during several hours, in air. Despite the formation of weak $Co^{2+}/(HOCH_2CH_2)_3N$ complexes in H_2O ($pK = 1.7$ [13]), (hydroxylated amine)cobalt(I) complexes may be weaker reductants than the (alkylamine)cobalt(I) complexes.

The pK_a values of alkylamines are much higher than those of hydroxylated amines (pK_a 10.7 and 7.9 for Et_3N and $(HOCH_2CH_2)_3N$, respectively [13]). At saturation, the former dissolved more CO_2 than the latter (800 ml for Et_3N and 400 ml for $(HOCH_2CH_2)_3N$), the apparent pH of the final solution being approximatively the same (~ 8.6). The pK for the CO_2/HCO_3^- equilibrium is 10.3 in H_2O, so that the solution contained free CO_2 and HCO_3^-, as was confirmed by ^{13}C-NMR measurements using labelled CO_2. However, the nature of the active species during reduction by the Co(I) complex is as yet unknown. Since the oxidation potential $E'^0(D^{+\cdot}/D)$ of the amines used all fall in a narrow range (+0.75 to 0.85 V[2]) [14]), the effects observed should arise from ligating ability rather than difference in reductive power.

2) *System* $[Ru(bpy)_3]^{2+}$, $[CoL'_n]^{2+}$, *DMF*/$(HOCH_2CH_2)_3N$ *or DMF*/$(HOCH_2CH_2)_3N/H_2O$ (L' = bpy, 4,4',6,6'-tetramethyl-2,2'-bipyridine, or 2,9-dimethyl-1,10-phenanthroline). In these experiments, preformed Co(II) complexes were used instead of Co(II) ions. With bipyridine as ligand, the efficiency of the photochemical reaction was enhanced by a factor of 50 (*Table 2, Exper. 22* and *23*). Addition of 20% of H_2O increased CO formation and decreased H_2 generation (*Exper. 23* and *26*). Excess free

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[2]) All redox potentials listed in the present work are given *vs.* the normal hydrogen electrode (NHE).

bipyridine slightly affected CO_2 and H_2O reduction (*Exper. 23, 27,* and *28*). By far, the best results were those obtained with (2,9-dimethyl-1,10-phenanthroline)cobalt complexes in purely organic medium *(Exper. 31)*; addition of H_2O decreased CO generation by a factor of 10 *(Exper. 32)*. This behaviour might be related to the instability of the (2,9-dimethyl-1,10-phenanthroline)cobalt complex in the presence of H_2O; the blue colour observed in DMF disappeared instantaneously on addition of a few drops of H_2O. The system was unstable under prolonged irradiation in some experiments (*Exper. 30, 31,* and *34*). The linearity observed in *Fig. 3* with $[Co(bpy)_3]^{2+}$ in $MeCN/(HOCH_2CH_2)_3N/H_2O$ 3:1:1 was only maintained for generation of rather small quantities of gases. Such unstability was also found previously for an homogeneous H_2-producing system [12]. Photodecomposition of the photosensitizer in DMF solution [15] as well as in other solvents [16] and formation of a secondary amine, a strong ligand, from the consumption of the electron donor, could be the main factors responsible for the loss of efficiency with time. The marked effect observed between $(HOCH_2CH_2)_3N$ and $(HOCH_2CH_2)_2NMe$ in the Co^{2+} system (*Exper. 18* and *19*) was not found with (bipyridine)cobalt complexes

Table 3. *Photogeneration of CO and H_2 as a Function of the Solvent and Co Ligand*[a])

Exper.	Solvent	Co ligand[b])	Volume of CO_2 dissolved [ml]	Volume of CO produced [ml]	Volume of H_2 produced [ml]	CO + H_2 [μmol]	CO/H_2
34	Ethylene glycol dimethyl ether	–	200	1.65	0.67	96.7	2.5
35	DMF	–	180	0.56	1.13	70.4	0.5
36	MeCN[c])	–	400	0.18	0.04	9.2	4.5
37	Diethoxydiethylene glycol	–	400	0.005	0.01	–	–
38	THF[c])	–	270	0.43	0.13	22.3	3.5
39	Dioxane[c])	–	200	0.86	0.38	51.3	2.3
40	$CHCl_3$[c])	–	400	0.06	0.02	3.5	3.4
41	Tetramethylurea[c])	–	150	0.37	0.62	41.2	0.6
42	DMF	bpy	150	0.65	1.17	76.0	0.6
43	DMF	dm-phen	150	2.00	13.0	625	0.2
44	DMF	phen	150	0.20	0.41	26.7	0.5
45	DMF	dph-phen	150	0.40	0.004	16.7	–
46	DMF	dmdph-phen	150	0.05	12.8	535	–
47	DMF	bathophen-S_2	150	0.35	0.11	19.2	3.3
48	DMF	bathocup-S_2	150	0.70	6.36	293	0.1
49	DMF	bpy-R_2	150	0.73	1.78	105	0.4
50	DMF	bpy-R_4	150	1.80	1.25	127	1.5
51[d])	DMF	bpy-R'_2	150	< 1 μl	1.48	61.7	–
52	DMF	vitamin B_{12}	150	0.58	0.16	30.8	3.6

[a]) All experiments contained: $[Ru(bpy)_3]^{2+}$ (4.7×10^{-4}M), $CoCl_2 \cdot 6H_2O$ (1.5×10^{-3}M), in 30 ml of soln. *Exper. 34–41* contained: 20% $(HOCH_2CH_2)_3N$ and 20% of H_2O and were irradiated at 30° during 15 h with a 1000-W Xe-Hg lamp. *Exper. 42–52* contained: $DMF/(HOCH_2CH_2)_3N$ 2:1 and were irradiated at 30° during 15 h with a 1000-W Xe-Hg lamp.

[b]) Complexes prepared *in situ* by addition of 3 equiv. of ligand (4.5×10^{-3}M); bpy: 2,2'-bipyridine; phen: 1,10-phenanthroline; dm-phen: 2,9-dimethyl-phen ('neocuproine'); dph-phen; 4,7-diphenyl-phen; dmdph-phen: 2,9-dimethyl-4,7-diphenyl-phen ('bathocuproine'); bathophen-S_2: disodium, 4,7-diphenyl-phen-4',4''-disulfonate; bathocup-S_2: disodium, 2,9-dimethyl-4,7-diphenyl-phen-4',4''-disulfonate; bpy-R_2: 4,4'-dimethyl-bpy; bpy-R_4: 4,4',5,5'-tetramethyl-bpy; bpy-R'_2: 3,3'-dimethyl-bpy.

[c]) Two phases formed on saturation with CO_2.

[d]) The same results were obtained with 6 equiv. of β-picoline (= 3-methylpyridine; 9.5×10^{-3}M).

(*Exper. 23* and *29*). This confirms that the environment of the Co ion is an important factor in the reduction of CO_2, the amine effect being less pronounced when a ligand such as bpy or 2,9-dimethyl-1,10-phenanthroline (= 'neocuproine') was used.

Influence of the Solvent. In homogeneous catalysis, the solvent often plays a critical role, in particular by its ligating abilities [17]. As seen above, the results were markedly dependent upon the nature of the solvent (MeCN or DMF). Therefore, we tested a series of different solvents using Co^{2+} as the relay species, $(HOCH_2CH_2)_3N$ as the electron donor, in the presence of H_2O and at CO_2 saturation. Efficiency and selectivity were clearly solvent dependent, and the best results were obtained with monoglyme (ethylene glycol dimethyl ether) and DMF (*Table 3, Exper. 34* and *35*). The selectivity was highest with MeCN. Both CO_2 and H_2O photoreductions were inhibited with a solvent such as diethoxydiethylene glycol *(Exper. 37)*. It is unlikely that this strong effect is related to changes in the reduction potential of the Co ions or in the excited state lifetime of $[Ru(bpy)_3]^{2+}$ as a function of solvent. The Co(II)/Co(I) couple was in the range of -1.25 V to -1.23 V in different solvents (DMF, MeCN, monoglyme, and diethoxydiethylene glycol with $(HOCH_2CH_2)_3N$ added) as compared to -1.0 V for $[Co(bpy)_3]^{2+}$ [18]. No large changes in the excited-state life-time of $[Ru(bpy)_3]^{2+}$ were found when measured in the following solvents: MeCN (780 ns), THF (590 ns), DMF (670 ns), monoglyme (650 ns), dioxane (510 ns), and diethoxydiethylene glycol (800 ns)[3]).

Effect of the Nature of the Co Ligand. As discussed above, the results depended strongly upon whether Co(II) ions or Co complexes were used. The stability of $[Co(bpy)_3]^{n+}$ (n = 2 or 1) complexes in the $MeCN/Et_3N/H_2O$ or $DMF/(HOCH_2CH_2)_3N$ medium may explain at least in part the differences observed. CO_2 activation requires at least one vacant coordination site at the Co center. Since this may be achieved only by ligand labilization, the effect of changing the ligand was investigated *(Table 3)*. Me substituents increase the reductive properties of the Co(I) complex, which may facilitate reduction of CO_2 and H_2O. A small increase in efficiency was observed on increasing the number of Me substituents on the bipyridine ligand (*Exper. 42, 49,* and *50*). With 4,4′,5,5′-tetramethyl-2,2′-bipyridine, the selectivity was 2.5 times higher than with bpy itself. 3,3′-Dimethyl-2,2′-bipyridine gave the same result as 6 equiv. of β-picoline, no CO being produced in either case *(Exper. 51)*. Highest efficiency was obtained using α-substituted phenanthrolines such as 2,9-dimethyl-1,10-phenanthroline *(Exper. 43)* or 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline *(Exper. 46)*. In contrast, 1,10-phenanthroline or derivatives with no Me substituents in the α-position gave significantly less CO and H_2 than bpy. Chelating and non-chelating phosphines such as Ph_3P, 1,2-diphenylphosphinoethane, or 1,2-diphenylphosphinoethylene gave poor yields of CO and H_2. The high stability of (phosphine)cobalt(I) complexes may explain their low reactivity. With the Co cation complexed by dimethylglyoxime, CO_2 reduction was totally inhibited, while H_2 formation was strongly enhanced [12]. Complexing Co(II) ions with various macrocyclic ligands also led to photochemical reduction of both H_2O and CO_2 to H_2 and CO, respectively [12] [19].

Of biological interest was the use of cobalamin (vitamin B_{12}) as relay. Turnover was low *(Exper. 52)*, but a labelled experiment with $^{13}CO_2$ (90.5%) confirmed the reduction of CO_2 giving 90% of ^{13}CO.

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[3]) We thank Dr. *A. Harriman* of the Royal Institution, London, for performing these measurements.

Table 4. *Photogeneration of CO and H_2 as a Function of Photosensitizer*[a])

Exper.	Photosensitizer/ Co species[b])	τ_0 [μs][c])	Absorption λ_{max} [nm]	Volume of CO produced [ml]	Volume of H_2 produced [ml]	$CO + H_2$ [μmol]	CO/H_2
53	$[Ru(bpy)_3]^{2+}/Co^{2+}$	0.78	452	0.71	0.11	34.3	6.2
54	$[Ru(bpy)_3]^{2+}/Co^{2+}$/2 equiv. bpy	0.78	452	0.41	0.66	44.6	0.6
55	$[Ru(bpy\text{-}R_2)_3]^{2+}/Co^{2+}$	0.33	460	< 1 μl	0.16	6.7	–
56	$[Ru(bpy\text{-}R_2)_3]^{2+}/Co^{2+}$/2 equiv. bpy	0.33	460	0.20	0.31	21.2	0.6
57	$[Ru(bpy\text{-}R_4)_3]^{2+}/Co^{2+}$	0.77	457	< 1 μl	< 1 μl	–	–
58	$[Ru(phen)_3]^{2+}/Co^{2+}$	0.81	447	< 1 μl	0.14	5.8	–
59	$[Ru(phen)_3]^{2+}/Co^{2+}$/2 equiv. bpy	0.81	447	0.25	0.34	24.6	0.7
60	$[Ru(bathophen\text{-}S_2)_3]^{4-}/Co^{2+}$	3.4	454	0.09	0.22	12.8	0.4
61	$[Ru(phen)_2(CN)_2]/Co^{2+}$	1.1	475	< 1 μl	< 1 μl	–	–

[a]) All experiments contain $[RuL_3]^{2+}$ or $[RuL_3]^{4-}$ (4.7×10^{-4}M), $CoCl_2 \cdot 6H_2O$ (1.5×10^{-3}M), dissolved in 30 ml of $MeCN/(HOCH_2CH_2)_3N/H_2O$ 3:1:1 and containing 400 ml of CO_2 (*Exper. 53, 55, 57, 58, 60,* and *61*) or in 30 ml of $DMF/(HOCH_2CH_2)_3N/H_2O$ 3:1:1 and containing 140 ml of CO_2 (*Exper. 54, 56,* and *59*). Irradiation was carried out at 30°, during 15 h with a 1000-W Xe-Hg lamp.

[b]) bpy: 2,2′-bipyridine, bpy-R_2: 4,4′-dimethyl-2,2′-bipyridine, bpy-R_4: 4,4′,5,5′-tetramethylbipyridine, phen: 1,10-phenanthroline, bathophen-S_2: disodium 4,7-diphenyl-phen-4′,4″-disulfonate.

[c]) Lifetime of the excited state determined in MeCN for $[Ru(L)_3]^{2-}$ and in H_2O for $[Ru\,L_4]^{4-}$.

Effect of the Nature of the Photosensitizer. The photosensitizer was modified in order to investigate the effect of variations in excited-state life-time, redox potential of the ground and excited states, and complex stability *(Table 4)*. No correlation was found between the excited-state life-time of $[RuL_3]^{2+}$ complexes and the efficiency of the photochemical system. The redox potentials play a major role in different steps of the process. For all the photosensitizers studies, $[RuL_3]^+$ is reductive enough to produce from Co(II) the Co(I) species necessary for reduction of CO_2 and H_2O. However, the limiting factor may be the oxidizing potential (III)/(II)* of the ruthenium excited state. Thus, the excited states of $[Ru(phen)_2(CN)_2]$ and $[Ru(bpy\text{-}R_4)_3]^{2+}$ (bpy-R_4 = 4,4′,5,5′-tetramethyl-2,2′-bipyridine) cannot be quenched by $(HOCH_2CH_2)_3N$: $E'^0([Ru(phen)_2(CN)_2]^{*0/-}) = +0.4$ V [20], $E'^0([Ru(bpy\text{-}R_4)]^{*2+/+}) = +0.67$ V[4]), $E'^0((HOCH_2CH_2)_3N^{+\cdot}/(HOCH_2CH_2)_3N) = 0.82$ V [22]. No trace of CO or H_2 was detected in either cases (*Exper. 57* and *61*). Apart from these thermodynamic factors, the most important effect of modifying the photosensitizer lies in ligand photolabilization. Whereas the $[Ru(bpy)_3]^{2+}/Co^{2+}$ system *(Exper. 53)* was quite efficient, $[Ru(bpy\text{-}R_2)_3]^{2+}/Co^{2+}$ *(Exper. 55)* produced very little CO. However, addition of 2 equiv. of free bpy to both systems (*Exper. 54* and *56*) resulted in the same selectivity ($CO/H_2 = 0.6$) and gave similar efficiencies. Addition of 2 equiv. of bpy to $[Ru(phen)_3]^{2+}$ *(Exper. 59)* also gave similar efficiency and selectivity. This suggests that the active (bipyridine)cobalt complex was the same in all three cases, and that the Ru complex acted effectively as a photosensitizer. When UV light ($\lambda > 300$ nm; 1000-W Xe-Hg lamp) was used with no Ru photosensitizer present, 0.23 ml of CO and 1.36 ml of H_2 were produced after 15 h. Excited Co ions may oxidize H_2O [23] or the tertiary amine [24]. The resulting species could mediate the reductions of CO_2 and H_2O to CO and H_2.

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[4]) This value has been obtained by adding the estimated zero-zero transition energy from photoemission measurements (~ 2.15 eV) to the ground-state redox potential [21].

H-Atoms have been identified by EPR studies during the UV irradiation of Co^{2+} complexes of organic acids [23]. Photosensitizers such as proflavin and Co-phthalocyanine did not afford any reduction products.

Temperature Effect and Quantum Yield. Photochemical CO generation doubled on raising the temperature by 10°, while the H_2 yield remained stable *(Fig. 6)*. This temperature dependence for the formation of CO agrees with the decomposition of a Co intermediate in the CO_2-reduction cycle, whereas the very fast protonation of a Co-hydride species is practically independent of temperature [25].

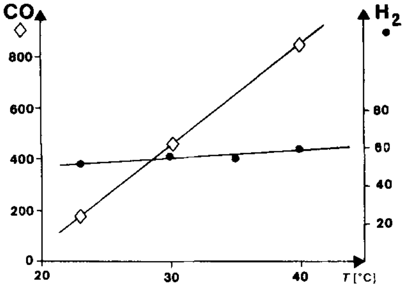

Fig. 6. *Efficiency of CO and H_2 photogeneration as a function of temperature.* Conditions of *Exper. 18, Table 2,* at saturation with CO_2 and irradiating with a 1000-W Xe lamps for 16 h.

Using as actinometer, a published homogeneous hydrogen generation system having a quantum yield of 13% [26], the photochemical system $[Ru(bpy)_3]^{2+}$, (2,9-dimethyl-1,10-phenanthroline)cobalt, and $DMF/(HOCH_2CH_2)_3N$ 2:1, gave under the same experimental conditions ($\lambda = 450 \pm 20$ nm) *quantum yields of 1.2 and 6.5% for CO_2 and H_2O photoreduction,* respectively.

Mechanistic Components of the CO_2 and H_2O Photoreduction Processes. – As stated above, the photochemical CO- and H_2-generation processes are catalytic with respect to the Ru and Co complexes. They consume a tertiary-amine donor (D), which provides the electrons required for CO_2 and H_2O reduction. The protons involved in these reductions may come from either the oxidized amine ($D^{+\cdot}$) or from H_2O present in the medium.

$$2D + \left\{\begin{matrix} CO_2 + 2H^+ \\ 2H^+ \end{matrix}\right. \xrightarrow[\text{Ru, Co catalysts}]{h\nu} 2D^{+\cdot} + \left\{\begin{matrix} CO + H_2O \\ H_2 \end{matrix}\right. \tag{1}$$

The net reactions may be expressed as given in *Eqn. 1.* The process comprises two catalytic cycles: a photochemical cycle involving tris(bipyridine)ruthenium and a thermal cycle based on the Co complex. Before discussing in more detail the mechanism of the reactions occurring, it is necessary to establish the sequence of overall steps which leads to the products CO and H_2.

Photochemical Ruthenium Cycle. The pathway for quenching of the excited state of (polypyridyl)ruthenium(II) complexes by $[CoL_3]^{2+}$ complexes, (reductive, oxidative, or energy-transfer) depends on the nature of the ligand and on the sensitizer-quencher combination [11] [28] [29]. Possible pathways for quenching of $^*[RuL_3]^{2+}$ and generation of Co(I) are described by *Eqns. 2–4.*

Reductive quenching:

$$^*[\mathrm{RuL_3}]^{2+} + D \longrightarrow [\mathrm{RuL_3}]^{+} + D^{+\cdot} \qquad (2)$$

ΔG[5]) ≈ 0 eV (L = bpy), +0.15 eV (L = 4,7-dimethyl-1,10-phenanthroline), $D = (\mathrm{HOCH_2CH_2})_3\mathrm{N}$.

$$[\mathrm{RuL_3}]^{+} + [\mathrm{CoL'_3}]^{2+} \longrightarrow [\mathrm{RuL_3}]^{2+} + [\mathrm{CoL'_3}]^{+} \qquad (3)$$

$\Delta G = -0.33$ eV (L = L' = bpy), 0 eV (L = bpy, L' = solvent).

Oxidative quenching:

$$^*[\mathrm{RuL_3}]^{2+} + [\mathrm{CoL'_3}]^{2+} \longrightarrow [\mathrm{RuL_3}]^{3+} + [\mathrm{CoL'_3}]^{+} \qquad (4)$$

$\Delta G = +0.11$ eV (L = L' = bpy), +0.41 eV (L = bpy, L' = solvent), +0 eV (L = 4,7-dimethyl-1,10-phenanthroline, L' = bpy).

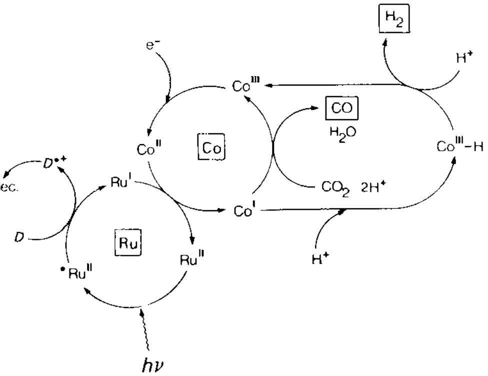

Fig. 7. *Schematic representation of the process occurring in the simultaneous and competing generation of CO and H_2 by photoinduced reduction of CO_2 and H_2O using the system $[Ru(bpy)_3]^{2+}/Co(II)/$donor* (D) *and following a pathway of reductive quenching of the excited state of the ruthenium photosensitizer.* Only heterolytic formation of H_2 by protonation of a cobalt-hydride is shown; see also text; the ligands of the metal ions are not indicated.

It is clear that oxidative quenching of the $[\mathrm{Ru(bpy)_3}]^{2+}$ excited state is thermodynamically unfavourable, but, in view of recent kinetic studies [29], it cannot be excluded (see below). *Fig. 7* gives a schematic representation of the photocatalytic reduction of CO_2 and H_2 by $[\mathrm{Ru(bpy)_3}]^{2+}$ and Co complexes *via* a *reductive quenching mechanism*. Reductive quenching according to *Eqn. 2* has been reported with organic donors such as aromatic tertiary amines [19] [30], ionic donors such as dithioanions [31] [32], Eu(II) [32] [33], sulfite [34], Ti(III) [35], or metal complexes such as $[\mathrm{Ru(NH_3)_6}]^{2+}$ [32], $[\mathrm{Os(CN)_6}]^{4-}$ [36], or $[\mathrm{Fe(CN)_5L}]^{3-}$ [37]. Flash photolysis of $[\mathrm{Ru(bpy)_3}]^{2+}$ in the presence of an electron donor such as $\mathrm{Et_3N}$ in MeCN [38] gave the Ru(I) species. With 25% of H_2O added, no accumulation of the reduced metal complex was observed, but a fast reaction with H_2O occurred [39]. Reductive quenching of $^*[\mathrm{Ru(bpy)_3}]^{2+}$ by a (macrocycle)cobalt(II) complex or by $[\mathrm{Co(bpy)_3}]^{2+}$ was observed, when the electron donor was Eu(II) [40] or sodium ascorbate [26], respectively. In our work, on the photochemical reduction of CO_2 to formate [10], the reduced species was generated by reductive quenching of $^*[\mathrm{Ru(bpy)_3}]^{2+}$ by a tertiary amine. However, reductive quenching of $^*[\mathrm{Ru(bpy)_3}]^{2+}$ by $(\mathrm{HOCH_2CH_2})_3\mathrm{N}$ in an organic solvent was difficult to detect and was an inefficient process. *Stern-Volmer*

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[5]) ΔG is the free-energy change for the reaction in eV (1 eV = 23 kcal/mol).

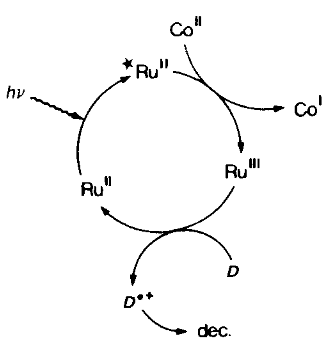

Fig. 8. *Modification of the scheme of Fig. 7 for the case of oxidative quenching of the excited state of the* $[Ru(bpy)_3]^{2+}$ *photosensitizer*

plots obtained with $(HOCH_2CH_2)_3N$ as quencher in DMF were linear and gave a quenching rate constant of 1.7×10^5 $M^{-1}s^{-1}$, at the limit of the method.

Fig. 8 is a schematic representation of the *oxidative quenching process*. Although thermodynamically unfavourable with $[Ru(bpy)_3]^{2+}$ (see above), it has been observed in the case of $*[Ru(4,7-(CH_3)_2phen)_3]^{2+}$ and $[Co(bpy)_3]^{2+}$ [29], where the excited state of the photosensitizer is more reducing by 170 mV than $*[Ru(bpy)_3]^{2+}$. Consequently, ΔG for this reaction *(Eqn. 4)* is near 0 eV. Quenching rate constants were reported as 7.4×10^7 $M^{-1}s^{-1}$ for $[Ru(4,7-(CH_3)_2phen)_3]^{2+}$ and $[Co(bpy)_3]^{2+}$ and 2.8×10^7 $M^{-1}s^{-1}$ for $[Ru(bpy)_3]^{2+}$ and $[Co(bpy)_3]^{2+}$ in aqueous medium [29]. We have determined a rate constant of 7.1×10^7 $M^{-1}s^{-1}$ for quenching of $*[Ru(bpy)_3]^{2+}$ by $CoCl_2$ in $MeCN/(HOCH_2CH_2)_3N/H_2O$ 3:1:1 under Ar and of 5×10^6 $M^{-1}s^{-1}$ for the same reaction in $MeCN/(CH_3CH(OH)CH_2)_3N/H_2O$ 3:1:1 under a CO_2 atmosphere[6]. However, no detectable quenching of $*[Ru(bpy)_3]^{2+}$ by $[Co(bpy)_3]^{2+}$ was observed in $DMF/(HOCH_2CH_2)_3N$ 2:1 under CO_2. Quenching mechanism and rate constant depend on the reaction medium and the nature of ligand used to complex Co and Ru. As mentioned previously, no CO and H_2 were produced, when the excited state of the photosensitizer was less oxidising than $*[Ru(bpy)_3]^{2+}$ (*e.g.* $*[Ru(phen)_2(CN)_2]$ and $*[Ru(bpy\text{-}R_4]^{2+})$, despite the fact that it was reducing enough to reduce $[Co(bpy)_3]^{2+}$. Conceivably, both mechanisms may participate in the photochemical process. It appears also that the rate of quenching may be a limiting factor in our photochemical system. The use of a single complex acting both as photosensitizer and as CO_2-activation catalyst would clearly simplify the mechanism and probably increase the efficiency of the photochemical reaction. This is the case with *fac*-$[Re(bpy)(CO)_3X]$ whose excited state is efficiently quenched by $(HOCH_2CH_2)_3N$ in an organic medium[7] [9]. In the present case ($*[RuL_3]^{2+}$ + $[CoL'_3]^{2+}$), both oxidative and reductive mechanisms yield the same net reaction:

$$[CoL'_3]^{2+} + D \xrightarrow[{[RuL_3]^{2+}}]{h\nu} [CoL'_3]^{+} + D^{+\cdot} \tag{5}$$

Fast irreversible decomposition of the radical cation ($D^{+\cdot}$) allows the accumulation in solution of the reduced species and further reaction of this species with CO_2 and H_2O. The

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[6] Correction was made for absorption of the incident excitation light at 452 nm by the Co complexes.

[7] $(HOCH_2CH_2)_3N$ in DMF quenches *fac*-$*[Re(bpy)(CO)_3Br]$ with a rate constant of 3.4×10^7 $M^{-1}s^{-1}$ at 25° under a CO_2 atmosphere.

role and fate of $(HOCH_2CH_2)_3N$ or other tertiary amines has been discussed in detail in [27] [39].

Catalytic Cobalt Cycle: CO_2 and H_2O Reduction by Co(I) Complexes. When $[Ru(bpy)_3]^{2+}$ and $[Co(bpy)_3]^{2+}$ were irradiated in DMF/$(HOCH_2CH_2)_3N$ 2:1 in the absence of CO_2, the initial orange-red solution turned blue-green. The VIS spectrum showed a new band at 620 nm *(Fig. 9c)*, corresponding to the formation of (bipyridine)cobalt(I) species [18] [27]. When this blue-green solution was stored under CO_2 in the dark, the initial orange colour was restored after 3 h, and appreciable quantities of CO and H_2 were obtained (51 % in total with respect to Co(I) complex formed photochemically; selectivity $CO/H_2 = 0.5$). The concentration of (bipyridine)cobalt(I) was determined from the VIS absorbance at 620 nm.

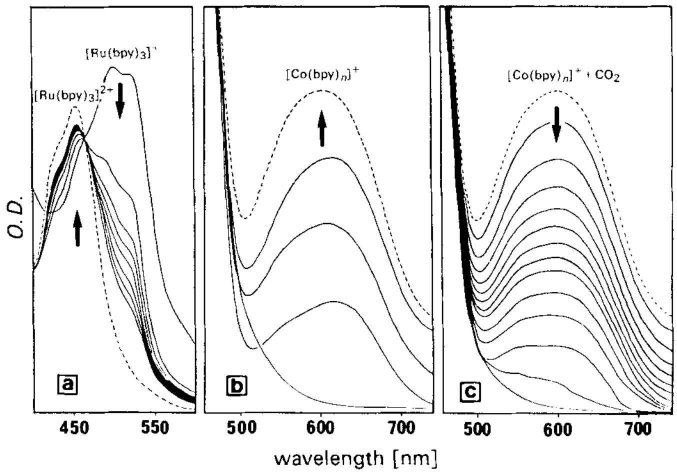

Fig. 9. *Spectroscopic observation of the redox changes leading to generation of CO by reduction of CO_2. a)* Formation of $[Ru(bpy)_3]^{2+}$ on addition of $[Co(bpy)_3]^{2+}$ to a soln. of electrochemically generated $[Ru(bpy)_3]^+$ in DMF; the broken line is the absorption of $[Ru(bpy)_3]^{2+}$ and was obtained after addition of 1.2 equiv. of $[Co(bpy)_3]^{2+}$ with respect to $[Ru(bpy)_3]^+$. *b)* Observation of $[Co(bpy)_3]^+$ formation corresponding to the changes shown in *a*, but at higher concentration and higher sensitivity of the spectrometer. *c)* Disappearance of the $[Co(bpy)_n]^+$ band in presence of CO_2; the reduced Co complex was produced photochemically by irradiation of a soln. of $[Ru(bpy)_3]^{2+}$, $[Co(bpy)_3]^+$ and $(HOCH_2CH_2)_3N$ in DMF in absence of CO_2; gas analysis indicated formation of CO and H_2 in *ca.* 51 % yield ($CO/H_2 = 0.5$), see *Text.*

Chemical reduction of $[Co(bpy)_3]^{2+}$ with Na-Hg [41] or $NaBH_4$ [42] afforded a deep blue $[Co(bpy)_3]^+$ complex, which was precipitated by addition of a large excess of $NaClO_4$ and was recrystallised from EtOH. Addition of this air-sensitive complex as a dark-blue solid, to a degassed solution of DMF/$(HOCH_2CH_2)_3N$ 2:1, gave a dark-blue solution whose absorption spectrum ($\lambda_{max} = 620$ nm) was identical to that obtained photochemically *(Fig. 9c)*. Deep blue solutions of $[Co(bpy)_3]^+$ in DMF or MeCN with Et_4NClO_4 as supporting electrolyte, were also generated quantitatively[8]) by controlled potential electrolysis on a Hg cathode at −1.2 V under Ar. In the absence of CO_2 and O_2, the deep blue solution was stable for at least 7 days. After that time, only traces of H_2 (< 1 % with

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[8]) During the electropreparation of the reduced complex, 0.98 F per mol of $[Co(bpy)_3]^{2+}$ were consumed.

respect to the quantity of $[Co(bpy)_3]^+$ used) could be detected by GC. However, in the presence of CO_2 and in DMF/H_2O 4:1, the deep blue colour of the solution (containing 54 µmol of $[Co(bpy)_3]^+$) disappeared within 5 h *(Fig. 9c)*. Concomitantly, appreciable yields of CO (11.4 µmol, 21%[9]) and H_2 (22.8 µmol, 42%[9]) were obtained. This large increase in H_2 generation was probably due to a pH effect, as confirmed by the fact that around 50% H_2 with respect to $[Co(bpy)_3]^+$ was obtained in MeCN, in the absence of CO_2, when the formal pH was adjusted to ~ 5 with HCl.

$[Ru(bpy)_3]^+$ was generated [43] in DMF/Et_4NClO_4 (controlled potential at −1.4 V on a Hg electrode; 0.97 F consumed per mol of $[Ru(bpy)_3]^{2+}$, under Ar) as a highly air-sensitive red complex with a characteristic λ_{max} at 510 nm [44] *(Fig. 9a)*. When an Ar-degassed solution of $[Co(bpy)_3]^{2+}$ in DMF/H_2O 4:1 was gradually added to this $[Ru(bpy)_3]^+$ solution, the colour changed from red to green and then to blue-green, as two new absorption bands appeared in the VIS spectrum (*Fig. 9a* and *b*). The bands at 452 and 620 nm are characteristic of $[Ru(bpy)_3]^{2+}$ and $[Co(bpy)_n]^+$ complexes, respectively. This clean (isosbestic point) transformation is complete after addition of 1.2 equiv. of $[Co(bpy)_3]^{2+}$. On storing this blue-green reaction mixture under CO_2 for several hours, the original orange colour, characteristic of $[Ru(bpy)_3]^{2+}$ was restored, while CO and H_2 were formed in yields comparable with those obtained using performed $[Co(bpy)_3]^+$. The reported rate for the exergonic reduction of $[Co(bpy)_3]^{2+}$ by $[Ru(bpy)_3]^+$ is 4×10^8 $M^{-1}s^{-1}$ [26a]. Yields of both CO and H_2 were the same when the above experiments were carried out in presence of $(HOCH_2CH_2)_3N$, suggesting that the tertiary amine acts only as electron donor. Irradiation of a blue solution of $[Co(bpy)_3]^+$ in DMF under CO_2 atmosphere did not increase the yield of CO or H_2, indicating that only the Ru cycle is photochemically activated.

These experiments confirm that the present process resulting in the generation of CO and H_2 involves a sequence of three steps: *1)* photoactivation of $[Ru(bpy)_3]^{2+}$, *2)* the latter produces reduced Co(I) species, which *3)* reduce catalytically CO_2 and H_2O. Since the reduction potential of the Co(I) species may be estimated as about −1.2 V, *dielectronic* reduction of both H_2O to H_2 and CO_2 to CO are thermodynamically feasible.

Mechanism of CO and H_2 Formation. H_2 Formation in homogeneous systems using Rh [27] [45] or Co [12] [26] [40] [46] complexes, proceeds *via* formation and subsequent protonation of a metal hydride. By analogy, the generation of H_2 in the photochemical process described here, may arise from the formation of a (bipyridine)cobalt(III)-hydride species *(Eqn. 6)* followed by protonation *(Eqn. 7)*, which represents overall the dielectronic H_2 generation reaction *(Eqn. 8)*.

$$[Co^{I}(bpy)_n]^+ + H^+ \longrightarrow [Co^{III}H(bpy)_n]^{2+} \quad (6)$$

$$[Co^{III}H(bpy)_n]^{2+} + H^+ \longrightarrow [Co(bpy)_n]^{3+} + H_2 \quad (7)$$

$$H^- + H^+ \longrightarrow H_2 \quad (8)$$

Because of the lability of the bpy ligand, the exact nature of the active species could not be determined. In recent studies on the thermal reduction of hydrogencarbonate and H_2O using $[Co(bpy)_3]^+$, a possible intermediate was formulated as $[Co(bpy)_2(H_2O)H]^{2+}$ [11].

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[9] If $[Ru(bpy)_3]^+$ and $[Co(bpy)_3]^+$ are considered as monoelectronic and dielectronic reagents, respectively, and since CO_2 and H_2O reduction are dielectronic processes, 1 mol of $[Ru(bpy)_3]^+$ produces ½ mol of CO or H_2, whereas $[Co(bpy)_3]^+$ produces 1 mol of CO or H_2. This introduces a factor of 2 in the calculation of the yield, when $[Ru(bpy)_3]^+$ is used as reductant.

Two mechanisms may be envisaged for the *CO_2-reduction process* if one excludes, as previously discussed [8a], the operation of the H_2O gas shift reaction in which CO_2 would be reduced to CO by initially formed H_2. The first involves the insertion of CO_2 into a cobalt-hydride bond of an intermediate also involved in the H_2O reduction, and the second consists in direct reaction of CO_2 with a Co(I) complex. In light of recent studies on *fac*-[Re(bpy)$(CO)_3$Cl] [9] [47], other Re complexes [48] [49] and Ru complexes [10], CO_2 insertion into a metal-hydride bond should yield coordinated or free formate. Decomposition of these (formate)metal complexes does not readily occur under mild conditions, and the reverse process of CO_2 extrusion to form metal hydrides has been observed for complexes of Mo, W [50], Os [51], and Re [48] [49]. Thermolysis in a high-boiling alcohol gave carbonyl hydrides in good yield [52]. Decomposition of free formate yielded CO_2 and H_2 but never CO [53]. In some cases, metal-carbonyl species were formed but these reactions were not cyclic with respect to the metal [49a] [54]. We did not observe in any case photochemical decomposition of formate to CO on irradiation of solutions containing $[RuL_3]^{2+}$, $[CoL'_3]^{2+}$, and HCOONa in DMF or MeCN/$(HOCH_2CH_2)_3N/H_2O$ 3:1:1. Clearly, CO was not produced by the photodecomposition of free or coordinated formate. In our studies on a Ru-based system which efficiently reduced CO_2 to formate [10], only negligible amounts of CO were detected.

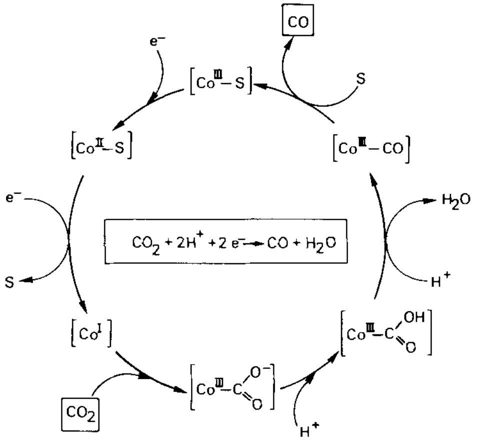

Fig. 10. *Schematic representation of a possible catalytic Co cycle for reduction of CO_2 to CO* via *direct reaction of Co(I) with CO_2 to give a Co(III)-carboxylate intermediate.* The electrons are provided by the added electron donor *via* the photochemical Ru cycle *(Fig. 7)*; the dielectronic CO_2 to CO reduction shown as insert has a potential of −0.52 V [8] and is, therefore, thermodynamically feasible *via* Co(I) complexes (see *Text*); S: solvent or other ligand molecule.

Taken together, the available data suggest that the reduction of CO_2 to CO might arise from direct nucleophilic attack of the Co(I) complex on the electrophilic C-atom of the CO_2 molecule *(Fig. 10)*. Reaction of CO_2 with Co(I) complexes to yield a C-metal bond has been reported [55]. Subsequent CO formation may involve reactions similar to, but in the reverse direction of, those described for the Co-catalyzed oxidation of CO [56]. The decomposition of a carboxylic intermediate by protonation would lead to the formation of H_2O and a labile (carbonyl)cobalt(III)species *(Fig. 10)*. Formation of this intermediate by direct insertion of CO_2 into a cobalt(III)-hydride bond cannot be totally excluded, although such reactions have only been observed rarely [1]. Several metal carboxylates such as $[IrCl_2(COOH)(CO)(PMe_2Ph)_2]$ [57] and $[Re(\eta^5{-}C_5H_5)(CO)(p{-}N_2C_6H_4R)(COOH)]$ [58] have been obtained recently by direct attack of H_2O [57] or NaOH [58] on coordinated CO.

The above considerations agree with the schematic formulation of CO_2 reduction to CO by Co(I) species shown in *Fig. 10*. It also finds analogy in the reverse of the proposed photochemical H_2O gas shift reaction catalysed by $[Ru(bpy)_2(CO)Cl]^+$ [59]. Further mechanistic details of CO_2 reduction to CO by Co(I) complexes and the reasons why only CO and not formate is produced, remain to be investigated.

Conclusion. – Photosynthetic systems which use light to drive a redox reaction in the non-spontaneous direction allow conversion of light energy into chemical energy. With $(HOCH_2CH_2)_3N$ as electron donor, the net reactions occurring in the system described here, are given in *Eqns. 9* and *10*.

$$(HOCH_2CH_2)_3N(l) + CO_2(g) \xrightarrow{PS, h\nu} (HOCH_2CH_2)_2NH(s) + CO(g) + HCO{-}CH_2OH(s) \qquad (9)$$

$$(HOCH_2CH_2)_3N(l) + H_2O(l) \longrightarrow (HOCH_2CH_2)_2NH(s) + HCO{-}CH_2OH(s) + H_2(g) \qquad (10)$$

The $\Delta G°$ values for these reactions are +1.34 eV for *Eqn. 9* and +1.23 eV for *Eqn. 10*, amounting to about 65% and 55% conversion of the excited-state energy of $[RuL_3]^{2+}$ into chemical energy, respectively, assuming that *Eqns. 9* and *10* represent the overall chemical transformations in this photochemical system. The difference between the combustion energies of the starting materials and products represents the energy gain in terms of materials consumed and generated. Based on the following data: $\Delta H_f^\circ((HOCH_2CH_2)_3N(l)) = 664.2$ [60], $\Delta H_f^\circ((HOCH_2CH_2)_2NH(s)) = 493.8$ [60]; $\Delta H_f^\circ(CO_2(g)) = 393.5$ [61], $\Delta H_f^\circ(CO(g)) = 110.5$ [61], $\Delta H_f^\circ(CHO{-}CH_2OH(s)) = 387$ kJ-mol^{-1} [60] at T = 298.15 K, we estimate that *ca.* 66 kJmol^{-1} are stored in *Reaction 9*. The reported experimental value for *Reaction 10* is 69 kJmol^{-1} stored energy [60].

The photochemical system described here produces a 'synthesis gas' mixture ($CO + H_2$) with an efficiency and a selectivity (CO/H_2) depending upon the nature of the Co and Ru complexes used, the composition of the medium, the concentration of CO_2 in solution, the temperature, *etc.* The catalytic reduction of CO_2 to CO by Co(I) species formed as intermediates, represents a new CO_2-activation reaction.

In both the CO and H_2 generation processes, an organic donor molecule is consumed. Ultimately, the electron-donor molecule should be the H_2O molecule along the global *Reaction 11:*

$$CO_2 + H_2O \longrightarrow CO + H_2 + O_2 \qquad (11)$$

This equation amounts to the separate formation of the components CO and H_2 of formaldehyde H_2CO, which represents the lowest homolog ($n = 1$) in the conversion of CO_2 into carbohydrates by natural photosynthesis, see *Eqn. 12*.

$$n CO_2 + n H_2O \longrightarrow C_nH_{2n}O_n + n O_2 \qquad (12)$$

To achieve *Reaction 11*, the catalytic system must provide pathways for generation of both CO and H_2. This is the case for the homogeneous Co-catalyzed process described above.

Further developments in photochemical and chemical systems performing CO_2 fixation processes involve *inter alia* the search for new photocatalysts, where the function of both photosensitizer and CO_2 reduction catalyst are combined in the same species (*e.g.* *fac*-[Re(bipy)(CO)$_3$Cl] [9]) and new chemical and electrochemical catalysts for the reduction of CO_2 to CO, $HCOO^-$, CH_2O, CH_3OH, CH_4, or higher C-homologues.

Experimental Part

General. All commercially avalaible chemicals employed were reagent-grade and used without further purification, unless stated otherwise. Irradiations: 1000-W Xe-Hg lamp or 1000-W Hg lamp. The light beam was concentrated with a converging lens and its width was adjusted so that the entire soln. was irradiated. The light was filtered by a 400-nm cut-off filter *(Schott GG420)*, having 0% transmission at 395 nm. GC: *Varian Aerograph 700* apparatus, 5-Å molecular sieve column (13 × mesh 42/60, *Applied Science Laboratories Inc.*), at r.t. using CH_4 as the carrier gas [27]; when labelled CO_2 was used, the gas was analysed by GC/MS using a *R 10/10 Ribermag* GC/MS apparatus. Emission measurements: *Perkin-Elmer*, model *MPF-3* spectrofluorimeter equipped with a 150-W Xe lamp. Quantum yields: 1000-W Hg lamp and a *Schöffel* model *GM 250* monochromator (450 ± 20 nm). Light intensities: by $[Ru(bpy)_3]^{2+}$, $[Co(NH_3)_5Cl]Cl_2$ actinometry [45]; typically 1.8×10^{-9} einstein sec^{-1} cm^{-2}. Electrochemical measurements: were made *vs.* the saturated calomel electrode (SCE) at r.t. and were uncorrected for junction potentials effects. Cyclic-voltametry studies: *PRT 20-2X Tacussel* potentiostat, *GSATP2 Tacussel* pilot scanner, *ADTP3 Tacussel* current potential converter, and *IF 3802 IFELEC XY* recorder. UV/VIS spectra: *Cary 118* or *219* spectrophotometer, quartz cell mounted on a *Schlenk* tube; when required, the optical path-length could be reduced from 5 to 0.5 mm by the use of a transparent insert; molar extinction coefficients were obtained from absorbance measurements on at least two different concentrations of complex. ^{13}C-NMR spectra: ***Bruker*** *SY-200* spectrometer at 50.3 MHz, solvent ((D_7)DMF or MeCN) as internal standard; reactions monitored by ^{13}C-NMR spectroscopy were performed in sealed NMR tubes under $^{13}CO_2$ atmosphere (90.5% enriched).

Photochemical CO and H_2 Generation Experiments. The nature and the concentration of the various components used in each experiment are listed in *Tables 1–4*. The solns. (30 ml) of the compounds (in a round bottomed *ca.* 60-ml *Schlenk* tube) were degassed at 0.1 Torr, and a volumetrically measured amount of CO_2 (purity 99.995%) was dissolved in the mixture. Blank experiments were carried out under vacuum in the absence of CO_2. After irradiation, the internal pressure was brought to atmospheric pressure by cooling down the flask in dry ice and by introducing 1M NaOH. The gas contained in the flask was sampled by syringe and analysed by GC.

Preparation of the Complexes. The Ru complexes were prepared according to [62]. $[Ru(phen)_2(CN)_2]$ [63] and $[Co(bpy)_3]^{2+} \cdot Cl_2 \cdot 6H_2O$ [64] were synthetized as described in the lit. Solns. of reduced complexes such as $[Ru(bpy)_3]^+$ [43] or $[Co(bpy)_3]^+$ [18] were prepared coulometrically using a Hg working electrode, a Pt wire as auxiliary electrode, and a SCE as reference. The solns. were deaerated using Ar and transferred by standard *Schlenk* techniques. The reactivity of these reduced species towards CO_2 and H_2O was observed either visually (colour change) or by UV/VIS spectroscopy.

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