Photochemical Reduction of Carbon Dioxide to Carbon Monoxide in Water using a Nickel(II) Tetra-azamacrocycle Complex as Catalyst

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Visible-light illumination of a CO_2-saturated aqueous solution containing tris(2,2′-bipyridyl)-ruthenium(II) chloride as photosensitiser, ascorbic acid as electron donor, and 1,4,8,11-tetra-azacyclotetradecanenickel(II) chloride as catalyst results in the production of both carbon monoxide and hydrogen. The yields of both CO and H_2 are pH dependent. The production of CO is proposed to proceed *via* CO_2 insertion into the Ni–H bond that is formed upon reaction of the reduced nickel species with a proton. This is followed by dissociation to form CO and H_2O. The production of hydrogen is also proposed to proceed *via* the reaction of H^+ with the same Ni–H species. Some H_2 is also produced in the absence of catalyst, presumably by a photoreaction of the sensitiser. By a mechanism that is not yet understood, both CO_2 and CO enhance the photoproduction of H_2.

During the last ten years there has been much interest in the possibility of developing artificial photosynthetic systems that will be able to harvest solar energy and store it as chemical energy.[1–3] In particular, much attention has focused on the light-induced reduction of water to hydrogen.[2] Compared to water photolysis there have been few studies on the photoreduction of carbon dioxide.[2,4–8] It is therefore of interest to investigate the photochemical reduction of CO_2 to alternative organic fuels with the concomitant production of molecular oxygen.

The reduction of CO_2 *via* multi-electron-transfer reactions might produce formic acid, carbon monoxide, formaldehyde, methanol, or methane [equations (1)—(5); the reduction

$$CO_2 + 2H^+ + 2e^- \longrightarrow HCO_2H \qquad E^0 = -0.61\ \text{V} \quad (1)$$

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

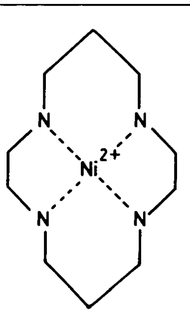
$$CO_2 + 4H^+ + 4e^- \longrightarrow HCHO + H_2O \qquad E^0 = -0.48\ \text{V} \quad (3)$$

$$CO_2 + 6H^+ + 6e^- \longrightarrow CH_3OH + H_2O \qquad E^0 = -0.38\ \text{V} \quad (4)$$

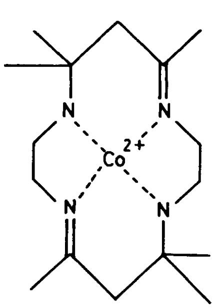
$$CO_2 + 8H^+ + 8e^- \longrightarrow CH_4 + 2H_2O \qquad E^0 = -0.24\ \text{V} \quad (5)$$

potentials, E^0, are thermodynamic values,[9] calculated from the half-cell reactions at pH 7 in aqueous solutions *vs.* n.h.e.]. These reactions require much less free energy per electron transferred than does the direct monoelectronic reduction of CO_2, producing the $CO_2^{\bullet-}$ radical anion, which has been estimated at approximately -2 V *vs.* n.h.e.[10–14] Hence it is advantageous to find catalysts capable of facilitating the two- to eight-electron-transfer processes [reactions (1)—(5)] at potentials close to the thermodynamic values.

In nature it has been shown that methanogenic bacteria (*i.e.* bacteria that catalyse the reduction of CO_2 to CH_4 under strict anaerobic conditions) require a nickel tetrapyrrole as one of six coenzymes in methanogenesis.[15] Several synthetic nickel (and cobalt) tetra-aza macrocyclic complexes[16] including porphyrins[17] as well as phthalocyanines[18,19] have been investigated and have been shown to function as electrocatalysts for the reduction of CO_2, in aqueous or mixed solvent systems at potentials between *ca.* -1.1 and -1.5 V *vs.* n.h.e. In such systems, CO is the major product but the selectivity for reduction of CO_2 *versus* that of H_2O is usually not very high and as a result the product ratio CO/H_2 is low.



(1)



(2)

Very recently, however, Beley *et al.*[20] achieved excellent results for the electrochemical reduction of CO_2 to CO in aqueous solution, using $[Ni(cyclam)]^{2+}$ (cyclam = 1,4,8,11-tetra-azacyclotetradecane), structure (**1**), as a homogeneous catalyst. In this system CO could be produced with great selectivity ($CO/H_2 = 10^2$—10^3) with almost 100% current efficiency and typical overall turnover number (mols product per mol of catalyst) of 100. In addition, Tinnemans *et al.*[7] have reported a system capable of reducing CO_2 *photochemically* in water, tris(2,2′-bipyridyl)ruthenium, $[Ru(bipy)_3]^{2+}$, as photosensitiser, ascorbate buffer as electron donor, and the cobalt(II) macrocycle (**2**) as catalyst. This system yields a mixture of CO and H_2, with much lower selectivity (CO/H_2 = 0.06—0.3, depending on the conditions used).

In this paper we investigate the photoreduction of CO_2 in a three-component system similar to that employed by Tinnemans *et al.*; $[Ru(bipy)_3]^{2+}$ is used as the photosensitiser and ascorbate buffer as the electron donor. However, in our system $[Ni(cyclam)]^{2+}$ is the catalyst. The results show that $[Ni(cyclam)]^{2+}$ functions as a homogeneous catalyst for the photochemical reduction of CO_2 to CO in water, as well as for the reduction of H^+ to H_2.

Table. Photochemical system for generation of CO and H_2 from $[Ru(bipy)_3]Cl_2{\cdot}6H_2O$ (5×10^{-4} mol dm^{-3}), $[Ni(cyclam)]Cl_2$ (2×10^{-3} mol dm^{-3}), ascorbate (pH 4), and CO_2, in water. Light source: xenon lamp, 1 000 W. Illumination time: 4 h

Run	$[Ru(bipy)_3]^{2+}$	$[Ni(cyclam)]^{2+}$	CO_2	Ar	Ascorbate	pH	Volume of product[a]/µl CO	 H_2
1	0	*	*	0	*	4		
2	*	*	*	0	0[b]	4		
3	*	0	0	*	*	4		180
4	*	0	*	0	*	4		295
5	*	*	0	*	*	4		675
6	*	*	0[c]	0	*	4	c	980
7	*	*	*	0	*	4	152	975
7a	*	1×10^{-4} mol dm^{-3}	*	0	*	4	357[d]	
8	*	*	*	0	*[e]	3	38	140
9	*	*	*	0	*[e]	5	132	160
10	*	*	*	0	*[e]	6	35	10

*, Present in reaction solution prior to photolysis; 0, absent from reaction solution prior to photolysis. [a] Lower detection limit for CO is 10 µl and for H_2 is 5 µl. [b] Ascorbate buffer replaced by acetate buffer. [c] Solution saturated with CO gas prior to photolysis. [d] Cumulative amount from repeated irradiation (see text). [e] The pH was changed by varying the relative amounts of acid and base. Total ascorbate concentration maintained at 1 mol dm^{-3}.

Results and Discussion

Visible light irradiation (4 h, 1 000 W) of an aqueous solution of $[Ru(bipy)_3]Cl_2{\cdot}6H_2O$ (5.0×10^{-4} mol dm^{-3}), $[Ni(cyclam)]Cl_2$ (2.0×10^{-3} mol dm^{-3}), and ascorbate buffer (pH 4) (total ascorbate 1 mol dm^{-3}) saturated with CO_2 produces both CO (152 µl) and H_2 (975 µl) (run 7, Table). The turnover numbers on nickel represented by these yields are 0.1 for CO and 0.7 for H_2. Using our standard conditions it was impractical to demonstrate higher turnovers. However, by reducing the nickel cyclam concentration to 1×10^{-4} mol dm^{-3} (run 7a) and by longer irradiation with replenished sensitiser and repeated purging with CO_2, we were able to obtain a turnover number for CO of 4.8. Moreover, absorption spectra between 800 and 900 nm[21] indicated that essentially all the nickel cyclam was still present at the end of the run. Taken together, these two facts show that cyclam acts as a catalyst.

Control experiments were performed by omitting one or more of the following components from the system: light, the ruthenium complex, $[Ni(cyclam)]^{2+}$, ascorbate buffer. In the absence of either light or $[Ru(bipy)_3]^{2+}$ (run 1) no CO or H_2 was detected. Also, when ascorbate buffer was replaced by an acetate buffer (run 2) neither H_2 nor CO was formed. When an argon-saturated solution (run 5) containing ruthenium sensitiser, $[Ni(cyclam)]^{2+}$, and ascorbate buffer was irradiated, no CO was formed but H_2 (675 µl) was produced. In the absence of $[Ni(cyclam)]^{2+}$ and the presence of CO_2 (run 4), H_2 (295 µl) was produced but no CO was detected. Similarly, in the absence of both $[Ni(cyclam)]^{2+}$ and CO_2 (run 3) only H_2 (180 µl) was formed. These results show that CO is produced only in the presence of $[Ni(cyclam)]^{2+}$. However, hydrogen is produced in the presence of $[Ni(cyclam)]^{2+}$ and in lower yields when only the ruthenium complex is present. The yield of H_2 is also enhanced in the presence of either CO_2 or CO as indicated in the Table by comparison of runs 4 and 3 with and without CO_2 and runs 6 and 5 with and without CO. Since the mechanism for the production of hydrogen *via* metal hydrides is reasonably well established, we will discuss this in some detail first before proceeding to the mechanism of CO formation. The reaction path for the production of H_2 in the absence of $[Ni(cyclam)]^{2+}$ is also discussed.

The Production of H_2 *in the Presence of* $[Ni(cyclam)]^{2+}$.—The steps proposed for this reaction are summarised in Scheme 1. In this scheme the short-lived excited state, $[^*Ru(bipy)_3]^{2+}$, is reductively quenched by ascorbate (HA^-) to yield the longer-lived, more strongly reducing ion, $[Ru(bipy)_3]^+$. The $[Ru(bipy)_3]^+$ reduces the $[Ni^{II}L]^{2+}$ complex which in turns reacts with H_3O^+ or H_2O to form the unstable hydride $[Ni^{III}H(L)]^{2+}$. The hydride then reacts with another proton and decomposes to yield H_2.

$$[Ru(bipy)_3]^{2+} \xrightarrow{h\nu} [^*Ru(bipy)_3]^{2+} \quad (6)$$

$$[^*Ru(bipy)_3]^{2+} + HA^- \longrightarrow [Ru(bipy)_3]^+ + HA^{\cdot} \quad (7)$$

$$HA^{\cdot} \longrightarrow H^+ + A^{\cdot -} \quad (8)$$

$$[Ru(bipy)_3]^+ + A^{\cdot -} \longrightarrow [Ru(bipy)_3]^{2+} + A^{2-} \quad (9)$$

$$H^+ + A^{2-} \longrightarrow HA^- \quad (10)$$

$$[Ru(bipy)_3]^+ + [Ni^{II}L]^{2+} \longrightarrow [Ru(bipy)_3]^{2+} + [Ni^{I}L]^+ \quad (11)$$

$$[Ni^{I}L]^+ + H^+ \longrightarrow [Ni^{III}H(L)]^{2+} \xrightarrow{H^+} [Ni^{III}L]^{3+} + H_2 \quad (12)$$

$$[Ni^{III}L]^{3+} + HA^- \longrightarrow [Ni^{II}L]^{2+} + HA^{\cdot} \quad (13)$$

Scheme 1.

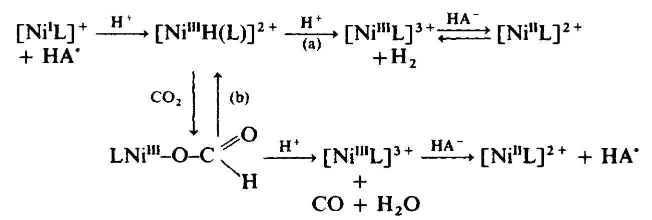
Creutz and co-workers have studied the $[Ru(bipy)_3]^{2+}$–ascorbate system *via* flash photolysis,[22] and also the photochemical evolution of H_2 in a similar system using complex (**2**) as catalyst.[23] Consequently, steps (6)—(10) have precedents. Using available electrochemical data we can show that in the present system, using a nickel(II) macrocycle, the reaction involved in step (11) is feasible. The one-electron reduction potential for $[Ni(cyclam)]^{2+}$ in an argon-degassed KNO_3 solution (pH 4.1) is −0.93 V *vs.* n.h.e.,[20] and for the $[Ru(bipy)_3]^{2+/+}$ couple is −1.3 V *vs.* n.h.e.[24] Hence the $[Ru(bipy)_3]^+$ ion is thermodynamically capable of reducing $[Ni(cyclam)]^{2+}$ to the corresponding nickel(I) complex. The stoicheiometry of step (12) has not been positively established; however, it is consistent with other studies involving various cobalt(I) complexes, including macrocycles,[25–28] which suggest that the proton transfer occurs *via* direct addition of H^+ to the $Co^{I}L$ complex, according to (14). Also, Tait *et al.*[29] have studied

$$Co^{I} + H^+ \longrightarrow [Co^{I}\text{–}H^+] \longrightarrow [Co^{II}\text{–}H] \longrightarrow [Co^{III}\text{–}H^-] \quad (14)$$

the reactivity of other nickel(I) 14-membered macrocyclic complexes in aqueous solution and proposed the formation of nickel(I) hydrido species in the same manner as the cobalt(II) analogues.

The principal mechanism for the production of hydrogen involves the nickel hydride in Scheme 1. However, some hydrogen is formed in the absence of $[Ni(cyclam)]^{2+}$ (runs 3 and 4). This has also been observed by Tinnemans *et al.*[7] and Krishnan and co-workers[30,31] in photolysis studies of the $[Ru(bipy)_3]^{2+}$–ascorbate system. Although a mechanism for the production of hydrogen in the absence of $[Ni(cyclam)]^{2+}$ has not been established, labelling experiments conducted by Krishnan *et al.*[31] suggest that the H_2 does not come from the reduction of water but, rather, from non-exchangeable H in the ascorbate.

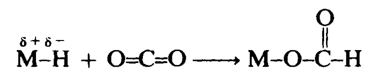
Production of CO *in the Presence of* $[Ni(cyclam)]^{2+}$.—The mechanism of CO formation is not yet clear. However, a possible reaction pathway is shown in Scheme 2. The initial



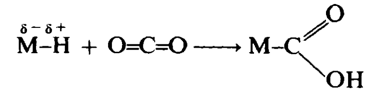
Scheme 2.

steps to form $[Ni^{I}L]^+$ are identical to steps (6)—(11) of the hydrogen-generating Scheme 1. In the above scheme both CO and H_2 are formed from the same metal hydride intermediate as in step (12) of the H_2-generating sequence (Scheme 1). The $[Ni^{III}H(L)]^{2+}$ species may react with a proton to generate hydrogen [step (a)] or, alternatively, react with CO_2 [step (b)]. The reaction of CO_2 with the hydride is proposed to proceed *via* CO_2 insertion into the Ni–H bond to yield a nickel(III) formate intermediate which decomposes to yield CO as well as $[Ni^{III}L]^{3+}$. The $[Ni^{III}L]^{3+}$ species then reacts with HA^- to regenerate the nickel(II) macrocycle, thus completing the cycle.

Very few cases of direct metal–CO_2 interactions have been reported. On the other hand, CO_2 insertion into metal–hydrogen (M–H) bonds is well known.[32,33] In general, two possible insertion reactions can occur, depending on the polarity of the metal–hydrogen bond. These are insertion to give a metal formate [reaction (15)], and reverse insertion producing a metallo-carboxylic acid species [reaction (16)]. The formation of metallo-carboxylic acids has rarely been observed,[33]



$$\overset{\delta+\,\delta-}{M\text{-}H} + O{=}C{=}O \longrightarrow M\text{-}O\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}H \qquad (15)$$



$$\overset{\delta-\,\delta+}{M\text{-}H} + O{=}C{=}O \longrightarrow M\text{-}C\begin{smallmatrix}{=}O\\ \text{-}OH\end{smallmatrix} \qquad (16)$$

indicating a lack of stability. The formation of formato complexes, however, has been reported for hydrido complexes of several metals, including cobalt,[34–36] iron,[37,38] ruthenium,[38,39] rhenium,[40] osmium,[41] iridium,[41] and platinum.[41] Since nickel complexes often behave in a similar manner to their cobalt analogues, we suggest that in this case the nickel formate complex may form *via* insertion of CO_2 into the Ni–H bond. The nickel formate species may decompose to produce CO and H_2O, or, alternatively, to generate formate (HCO_2^-) and free nickel complex. Perhaps a more likely source of the CO, however, is *via* the unstable metallo-carboxylic acid with concomitant production of OH^-. In the present system, photolysis of the $[Ru(bipy)_3]^{2+}$–ascorbate solution produces a number of organic products as shown by an h.p.l.c. analysis, but their identities have not yet been determined.

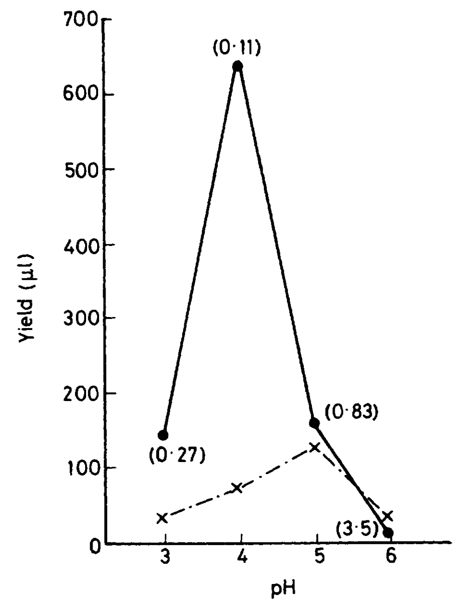


Figure 1. The pH dependence of the yields of CO (×) and H_2 (●) in the $[Ru(bipy)_3]^{2+}$–ascorbate–$[Ni(cyclam)]^{2+}$–CO_2 system. The CO/H_2 ratios are indicated in parentheses

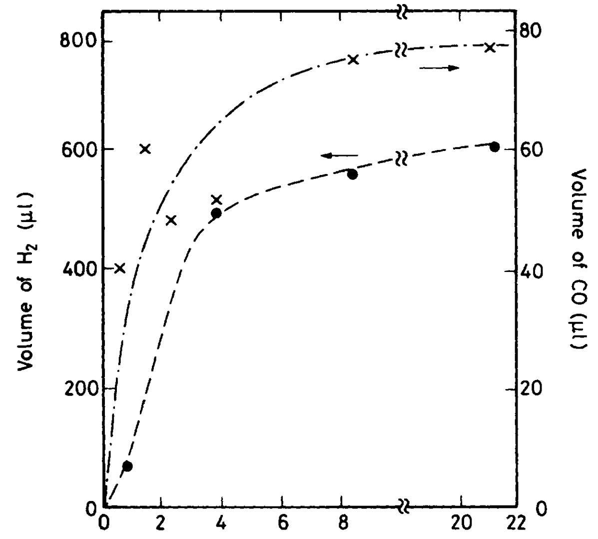


Figure 2. The volume of CO (×) and H_2 (●) produced as a function of illumination time for a solution containing 5×10^{-4} mol dm^{-3} $[Ru(bipy)_3]Cl_2 \cdot 6H_2O$, 2×10^{-3} mol dm^{-3} $[Ni(cyclam)]Cl_2$, ascorbate buffer (pH 4) (total ascorbate 1 mol dm^{-3}), saturated with CO_2

Optimization of CO *and* H_2 *Yields*.—In order to determine the optimum conditions, the production of H_2 and CO was studied as a function of both pH and illumination time. Figure 1 shows the variation in yields of CO and H_2 with pH, as well as the product ratio, CO/H_2, at each pH studied. The optimum pH for hydrogen formation is 4, maximum CO yield being achieved

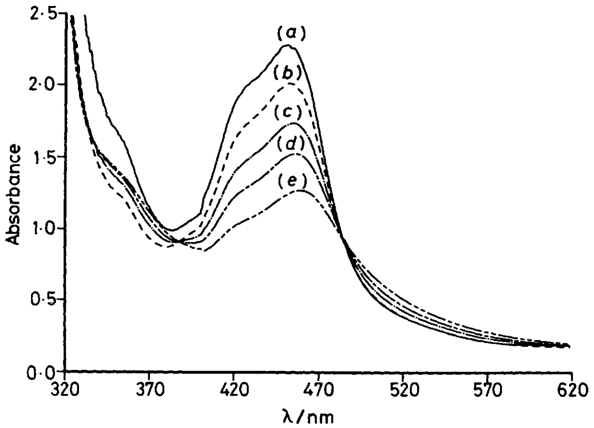


Figure 3. Absorption spectra of an aqueous solution containing 1.7×10^{-4} mol dm^{-3} $[Ru(bipy)_3]Cl_2{\cdot}6H_2O$, 2×10^{-3} mol dm^{-3} $[Ni(cyclam)]Cl_2$, ascorbate buffer (pH 4) (total ascorbate 1 mol dm^{-3}), saturated with CO_2. Illumination time, *t*: 0 (*a*); 20 (*b*); 50 (*c*); 80 (*d*); and 130 min (*e*)

at pH 5. The CO/H_2 ratio at pH 4 is 0.11, at pH 5 is 0.83, and at pH 6 is 3.5. Hence, in order to take advantage of both a high CO/H_2 ratio and high CO yield, the ideal operating condition would be pH 5.

The results of a typical kinetic experiment carried out on the present reaction system are shown in Figure 2. Initially, a rapid increase in the amounts of CO and H_2 generated with time is observed. However, the activity of the system decreases with long periods of irradiation, reaching a plateau after approximately 8 h. During photolysis, the absorption band of $[Ru(bipy)_3]^{2+}$ at 452 nm disappears with a concomitant increase in absorption in the region $\lambda < 350$ and <480 nm (Figure 3). On illumination for 22 h a new band at 472 nm is apparent, and there is a clear isosbestic point at 478 nm. Recent studies[42—47] of the photochemical stability of $[Ru(bipy)_3]^{2+}$ in various solvents and over a wide range of temperatures and pH values have shown that a bipy ligand may be lost from the complex and substituted by anionic species in solution. In most cases, this results in $Ru^{II}(bipy)_2$ species with maxima at 320—<370 and 440—<550 nm. Hence, the spectral changes during the photolysis experiment probably correspond to the photosubstitution of $[Ru(bipy)_3]^{2+}$, with the isosbestic points at 326, 387, and 478 nm indicating the conversion of $[Ru(bipy)_3]^{2+}$ into a $Ru(bipy)_2X_2$ species (where X is an anionic species in solution). Further studies are underway for a better understanding of the effect of CO_2 on $[Ru(bipy)_3]^{2+}$ and its degradation products.

An interesting feature of the present system is that both CO_2 and CO enhance the yield of H_2 (Table). This effect is large in the presence of the nickel(II) catalyst (*cf.* run 5 and runs 6 and 7), but also occurs when only $[Ru(bipy)_3]^{2+}$ is in solution (*cf.* runs 3 and 4). Kelly and Vos[48,49] have recently reported that H_2 is produced by the rapid decomposition of $[Ru(bipy)_2(CO)H]^+$ in weakly acidic solution. We suggest that an analogous ruthenium complex may be an active hydrogen-producing species in the present system in the absence of nickel(II) catalyst, with either CO or CO_2 as co-ordinating ligand. When the catalyst is present, CO is produced at the nickel centre and may function in a similar way further to enhance the production of H_2. This important observation is being investigated further.

Experimental

Materials.—1,4,8,11-Tetra-azacyclotetradecanenickel(II) chloride $[Ni(cyclam)]Cl_2$ was prepared from $NiCl_2{\cdot}6H_2O$ (Mallinckrodt) and 1,4,8,11-tetra-azacyclotetradecane (Strem Chemicals) in refluxing ethanol, according to the method of Bosnich *et al.*[50] The compound $[Ru(bipy)_3]Cl_2{\cdot}6H_2O$ was obtained from Strem Chemicals, sodium ascorbate from Sigma, and ascorbic acid from MCB Reagents. All chemicals were of reagent grade and were used without further purification. Water was distilled and further purified by passing it through a three-stage Millipore Q-Water System.

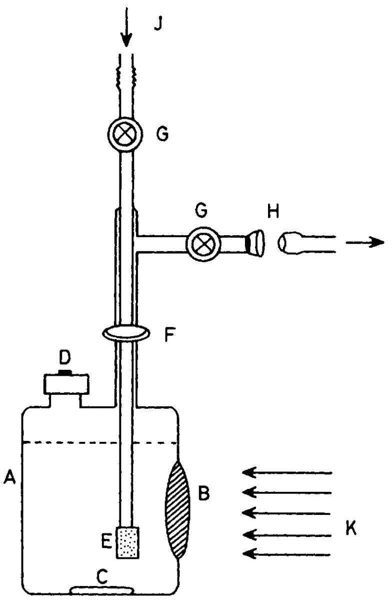


Figure 4. Photolysis cell used to degass the reaction solution, deliver product gases to the gas chromatograph for analysis, and contain calibration gases injected *via* syringe: A = glass photolysis cell; B = quartz window; C = stirrer bar; D = septum; E = medium frit; F = O-ring; G = stopcock; H = ball and socket; I = to gas chromatograph; J = Ar–CO_2; K = incident light

Continuous Photolysis.—The photolysis system consisted of a 1 000-W Oriel xenon lamp, i.r. cut-off filter ($CuSO_4$ solution, $\lambda < 600$ nm), water-filled vessel to prevent overheating of the photolysed solution, u.v. cut-off filter ($\lambda > 340$ nm), and photolysis vessel. The photolysis cell was custom-designed in order to allow degassing and irradiation of the solution, as well as analysis of the gas products (Figure 4). Unless otherwise stated, all experiments were performed on an aqueous solution (30 cm^3) of $[Ru(bipy)_3]Cl_2{\cdot}6H_2O$ (5.0×10^{-4} mol dm^{-3}), $[Ni(cyclam)]Cl_2$ (2.0×10^{-3} mol dm^{-3}), and ascorbate buffer (H_2A/HA^-, pH 4) (total ascorbate 1 mol dm^{-3}) contained in a cell (45 cm^3). All solutions were stirred continuously and irradiated after deaerating for 1 h with CO_2 (or argon).

Analytical Methods and Absorption Spectra.—Gas contained in the reaction vessel was sampled through a sample loop (250 μl) which was part of a six-valve system directly attached to a Varian 3700 gas chromatograph. Samples were analysed with thermal conductivity detection, using a two-column system. The inner column was packed with Porapak-Q for retention of CO_2, and the outer column was packed with molecular sieve 5 A for separation of CO and H_2. Carbon monoxide analysis was carried out at 60 °C, using helium as carrier gas, flow-rate 22 cm^3 min^{-1}. Hydrogen was determined using argon as carrier gas. The system was calibrated with known amounts of reference gases which were injected into a typical solution in the reaction vessel and were similarly sampled and analysed. Absorption spectra were measured both before and after illumination, in 1-mm cells using a Hewlett-Packard 8450A u.v.–visible diode-array spectrophotometer. Some product analysis was performed by h.p.l.c. using a Beckman model 100A chromatograph with a u.v. detector and a Bio-Rad Aminex HPX-87H ion-exclusion column.

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