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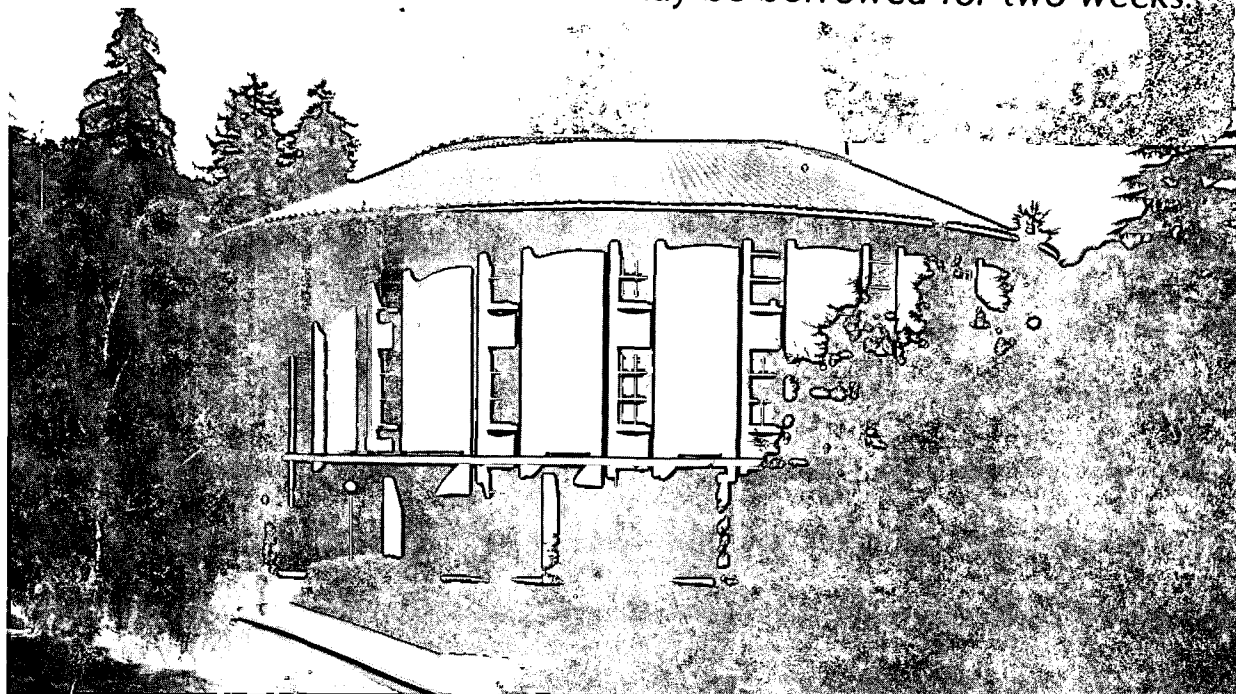
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J.L. Grant, K. Goswami, L.O. Spreer, J.W. Otvos,
and M. Calvin

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The Photochemical Reduction of Carbon Dioxide to Carbon Monoxide
in Water Using a Ni(II)Tetra-azamacrocyclic Complex As Catalyst

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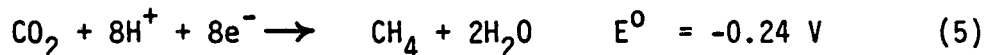
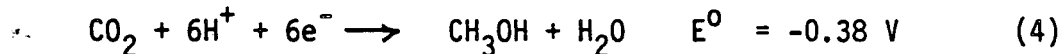
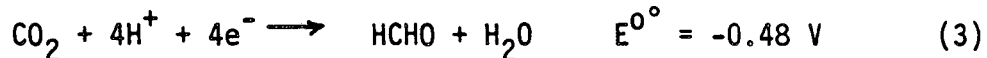
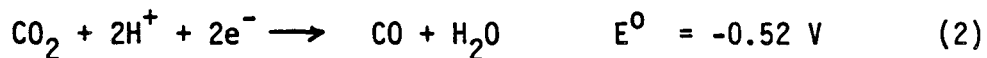
Summary

Visible light illumination of a CO₂-saturated aqueous solution containing tris(2,2'-bipyridyl) Ru(II) chloride as photosensitizer, ascorbic acid as electron donor, and 1,4,8,11-tetraazacyclotetradecane Ni(II) chloride, [Ni(II)cyclam · Cl₂], catalyst results in the production of both carbon monoxide and hydrogen. The yields of both CO and H₂ are pH dependent. The production of CO is proposed to proceed via CO₂ 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 H₂O. The production of hydrogen is also proposed to proceed via the reaction of H⁺ with the same Ni-H species. Some H₂ is also produced in the absence of catalyst, presumably by a photoreaction of the sensitizer. By a mechanism that is not yet understood, both CO₂ and CO enhance the photoproduction of H₂.

Introduction

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 (pp 507-530), 4-8 It is therefore of interest to investigate the photochemical reduction of CO₂ to alternative organic fuels with the concomitant production of molecular oxygen.

The reduction of CO₂ via multi-electron transfer reactions might produce formic acid, carbon monoxide, formaldehyde, methanol, or methane.



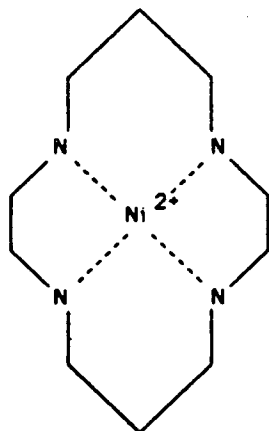
(The reduction potentials, E° , are thermodynamic values⁹, calculated from the half-cell reactions at pH 7 in aqueous solution vs NHE.)

These reactions require much less free energy per electron transferred than does the direct monoelectronic reduction of CO₂, producing the CO₂^{-•} radical-anion, which has been estimated at approximately

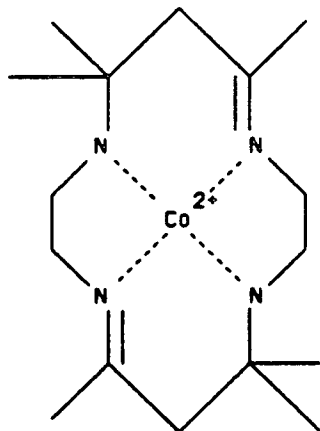
$-2 V_{\text{NHE}} \cdot 10^{-14}$ Hence it is advantageous to find catalysts capable of facilitating the 2 to 8 electron transfer processes [reactions (1)-(5)] at potentials close to the thermodynamic values.

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 complexes¹⁶ including porphyrins¹⁷ 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. $-1.1 V_{\text{NHE}}$ and $-1.5 V_{\text{NHE}}$. 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.

Very recently, however, Beley²⁰ and co-workers achieved excellent results for the electrochemical reduction of CO_2 to CO in aqueous solution, using $[\text{Ni}(\text{II})\text{cyclam}]^{2+}$ (1,4,8,11-tetraazacyclotetradecane-Ni(II)), $(\text{C}_{10}\text{H}_{24}\text{N}_4\text{Ni})$ (Structure I) as homogeneous catalyst. In this system CO could be produced with great selectivity ($\text{CO}/\text{H}_2 = 10^2$ to 10^3) with almost 100% current efficiency and typical overall turnover number of 100 (mols product/mole of catalyst). In addition, Tinnemans et al.⁷ have reported a system capable of reducing CO_2 photochemically in water, using ruthenium trisbipyridyl, $\text{Ru}(\text{bipy})_3^{2+}$, as photosensitiser, ascorbate buffer as electron donor, and the Co(II) macrocycle $[\text{Co}(\text{II})\text{Me}_6[14]-4,11\text{-dieneN}_4]^{2+}$ (Structure II), $(\text{C}_{16}\text{H}_{30}\text{N}_4\text{Co})$ as catalyst. This system yields a mixture of CO and H_2 , with much lower selectivity ($\text{CO}/\text{H}_2 = 0.06$ to 0.3 , depending on the conditions used).



(I)



(II)

In this paper we investigate the photoreduction of CO_2 in a three-component system similar to that employed by Tinnemans and co-workers; $\text{Ru}(\text{bipy})_3^{2+}$ is used as the photosensitiser and ascorbate buffer as the electron donor. However, in our system $[\text{Ni}(\text{II})\text{cyclam}]^{2+}$ is the catalyst. The results show that $[\text{Ni}(\text{II})\text{cyclam}]^{2+}$ 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 .

Results and Discussion

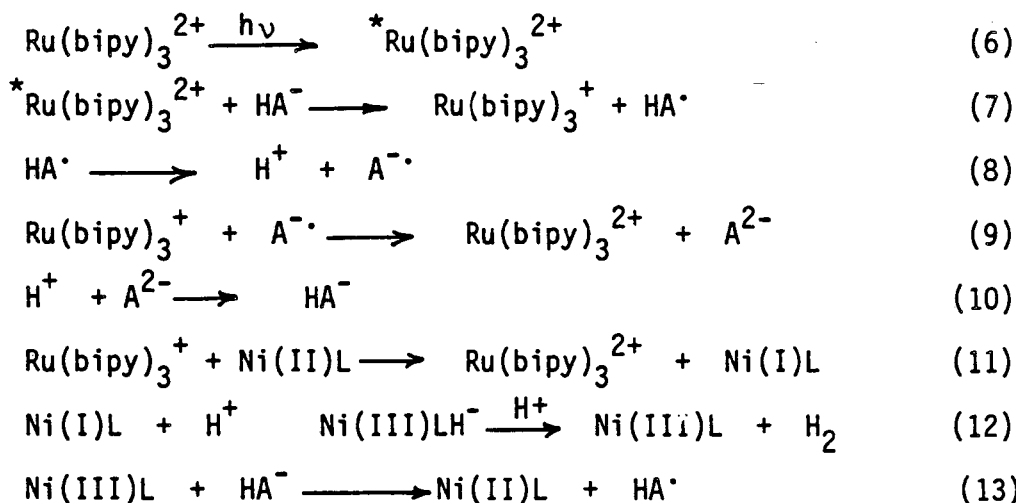
Visible light irradiation (4 hours, 1000 W) of an aqueous solution of $\text{Ru}(\text{bipy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ (5.0×10^{-4} M), $\text{Ni}(\text{II})\text{cyclam} \cdot \text{Cl}_2$ (2.0×10^{-3} M), and 0.5M/0.5M ascorbate buffer (pH 4) saturated with CO_2 produces both CO (152 μl) and H_2 (975 μl) (Run 6, Table 1). A number of experimental runs were carried out on this system in order to investigate the features of the reaction, and the results are presented in Table 1. Control experiments were performed by omitting one or more of the following components from the system: light, the ruthenium complex, $[\text{Ni}(\text{II})\text{cyclam}]^{2+}$, ascorbate buffer. In the absence of either light or $\text{Ru}(\text{bipy})_3^{2+}$ (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, $[\text{Ni}(\text{II})\text{cyclam}]^{2+}$, and ascorbate buffer was irradiated, no CO was formed but H_2 (675 μl) was produced. In the absence of $[\text{Ni}(\text{II})\text{cyclam}]^{2+}$ 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 $[\text{Ni}(\text{II})\text{cyclam}]^{2+}$ and CO_2 (Run 3) only H_2 (180 μl) was formed. These results show that CO is produced only in the presence of $[\text{Ni}(\text{II})\text{cyclam}]^{2+}$. However, hydrogen is produced in the presence of

$[\text{Ni(II)cyclam}]^{2+}$ 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 . There is evidence to

suggest that a nickel hydride species is actually a common intermediate for both CO production and the formation of H_2 . Since the mechanism for the production of hydrogen via metal-hydrides is reasonably well established,²¹ 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 $[\text{Ni(II)cyclam}]^{2+}$ is also discussed.

The production of H_2 in the presence of $[\text{Ni(II)cyclam}]^{2+}$. - The steps proposed for this reaction are summarised in Scheme 1.

Scheme 1



In this scheme the short-lived excited state, ${}^*\text{Ru(bipy)}_3^{2+}$, 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 complex which in turns reacts with H_3O^+ or H_2O to form the unstable

hydride Ni(III)LH^- . The hydride then reacts with another proton and decomposes to yield H_2 .

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 $[\text{Co(II)Me}_6[14]-4,11\text{-dieneN}_4]^{2+}$ as catalyst.²³ Consequently, steps (6)-(10) have precedents. Using available electrochemical data we can show that in the present system, using a Ni(II) macrocycle, the reaction involved in step (11) is feasible. The one-electron reduction potential for $[\text{Ni(II)cyclam}]^{2+}$ in an argon-degassed KNO_3 solution (pH 4.1) is $-0.93 \text{ V}_{\text{NHE}}$ ²⁰, and the $\text{Ru(bipy)}_3^{2+/+}$ couple is $-1.3 \text{ V}_{\text{NHE}}$.²⁴ Hence the Ru(bipy)_3^+ ion is thermodynamically capable of reducing $[\text{Ni(II)cyclam}]^{2+}$ to the corresponding Ni(I) complex. The stoichiometry of step (12) has not been positively established; however, it is consistent with other studies involving various Co(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



Also, Tait²⁹ has studied the reactivity of other Ni(I) 14-membered macrocyclic complexes in aqueous solution and has proposed the formation of Ni(I) hydrido species in the same manner as the Co(I) analogues.

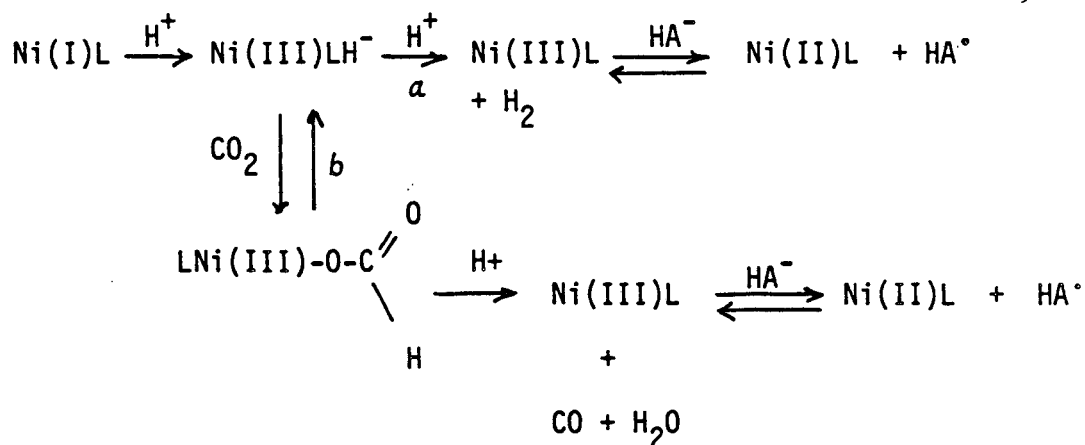
The principal mechanism for the production of hydrogen involves the nickel hydride in Scheme 1. However, some hydrogen is formed in the absence of $[\text{Ni(II)cyclam}]^{2+}$ (Runs 3 and 4). This has also been observed by Tinnemans et al.⁷ and Krishnan et al.^{30,31} in photolysis studies of the Ru(bipy)_3^{2+} -ascorbate system. Although a mechanism for the production of hydrogen in the absence of $[\text{Ni(II)cyclam}]^{2+}$ has not been established, labelling experiments conducted by Krishnan et al.³¹ suggest

that the H₂ does not come from the reduction of water but, rather, from nonexchangeable H in the ascorbate.

Production of CO in the presence of [Ni(II)cyclam]²⁺. -

The mechanism of CO formation is not yet clear. However, a possible reaction pathway is shown in Scheme 2. The initial steps to form Ni(I)L are identical to steps (6)-(11) of the hydrogen generating Scheme 1.

Scheme 2



In the above scheme both CO and H₂ are formed from the same metal-hydride intermediate as in step (12) of the H₂ generating sequence (Scheme 1). The Ni(III)LH⁻ species may react with a proton to generate hydrogen (step_a) or, alternatively, react with CO₂ (step_b). The reaction of CO₂ with the hydride is proposed to proceed via CO₂ insertion into the Ni-H bond to yield a Ni(III)formate intermediate which decomposes to yield CO as well as Ni(III)L. The Ni(III)L species then reacts with HA⁻ to regenerate the Ni(II) macrocycle, thus completing the cycle.

Very few cases of direct metal-CO₂ interaction have been reported. On the other hand, CO₂ 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 The formation of formate 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 Ni-formate complex may form via insertion of CO₂ into the Ni-H bond. The nickel-formate species may catalytically decompose to produce CO and H₂O, or, alternatively, decompose to generate formate (HCO₂⁻). In the present system, photolysis of the Ru(bipy)₃²⁺-ascorbate solution produces a number of organic products as shown by an HPLC chromatographic analysis, but their identities have not yet been determined. Further work is currently being carried out in our laboratory to determine the nature of other products of the CO₂ reduction process.

Optimization of CO and H₂ Yields.- In order to determine the optimum conditions, the production of H₂ and CO was studied as a function of both pH and illumination time. Figure 1 shows the variation in

yields of CO and H₂ with pH, as well as the product ratio, CO/H₂, at each pH studied. The optimum pH for hydrogen formation is 4, with maximum CO yield being achieved at pH 5. This probably reflects the fact that at higher pH values the concentration of H⁺ decreases and the competition between CO₂ and H⁺ for the Ni(III)LH⁻ intermediate (Scheme 2) shifts in favour of CO₂. The CO/H₂ 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/H₂ ratio and high CO yield, the ideal operating condition would be pH 5.

The results of a typical kinetic experiment carried out on the Ru-ascorbate-Ni reaction system are shown in Figure 2. Initially, a rapid increase in amounts of CO and H₂ generated with time is observed. However, the activity of the system decreases with long periods of irradiation, reaching a plateau after approximately 8 hours. The decrease in activity of the system with time is readily explained since the ruthenium sensitiser is destroyed upon prolonged illumination (see Figure 3). During photolysis the Ru(bipy)₃²⁺ absorption band at 452 nm disappears with a concomitant increase in absorption in the region $\lambda < 350$ nm and $\lambda > 480$ nm. On illumination for 22 hours a new band at 472 nm is apparent, and there is a clear isosbestic point at 478 nm. Recent studies⁴²⁻⁴⁷ of the photochemical stability of Ru(bipy)₃²⁺ 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 nm and 440->550 nm. Hence, the spectral changes during the photolysis experiment probably correspond to the photosubstitution of Ru(bipy)₃²⁺, with the isosbestic

points at 326 nm, 387 nm and 478 nm indicating the conversion of $\text{Ru}(\text{bipy})_3^{2+}$ to a $\text{Ru}(\text{bipy})_2\text{X}_2$ species (where X is an anionic species in solution). From the spectral results we can conclude that total yields of CO and H_2 are limited by bipy loss from the $\text{Ru}(\text{bipy})_3^{2+}$ complex. This loss could be inhibited by the addition of excess bipy to the solution to maintain the $\text{Ru}(\text{bipy})_3^{2+}$ level.³¹

An interesting feature of the present system is that both CO_2 and CO enhance the yield of H_2 (Table 1). This effect is large in the presence of the Ni^{2+} catalyst (c.f. Run 5 and Runs 6 and 10), but also occurs when only $\text{Ru}(\text{bipy})_3^{2+}$ is in solution (c.f. Runs 3 and 4). Kelly and Vos^{48,49} have recently reported that H_2 is produced by the rapid decomposition of $[\text{Ru}(\text{bipy})_2(\text{CO})(\text{H})]^+$ 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 Ni^{2+} catalyst, with either CO or CO_2 as coordinating ligand. When the Ni catalyst is present, CO is produced at the nickel center and may function in a similar way to further enhance the production of H_2 . This important observation is being investigated further.

Experimental Section

Materials.- 1,4,8,11-tetraazacyclotetradecane Ni(II) chloride $[\text{Ni}(\text{II})\text{cyclam}\cdot\text{Cl}_2]$ was prepared from $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (Mallinckrodt) and 1,4,8,11-tetraazacyclotetradecane (Strem Chemicals) in refluxing ethanol, according to the method of Bosnich⁵⁰. $\text{Ru}(\text{bipy})_3\text{Cl}_2\cdot 6\text{H}_2\text{O}$ was obtained from Strem Chemicals, sodium ascorbate from Sigma, and the 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 3-stage Millipore Q-Water System.

Continuous Photolysis. - The photolysis system consisted of a 1000-W Oriel xenon lamp, i.r. cutoff filter (CuSO_4 solution, λ 600 nm), water-filled vessel to prevent overheating of the photolysed solution, u.v. cutoff 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 30 ml of an aqueous solution of $\text{Ru}(\text{bipy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ (5.0×10^{-4} M), $\text{Ni}(\text{II})\text{cyclam} \cdot \text{Cl}_2$ (2.0×10^{-3} M), and 0.5M/0.5M ascorbate buffer ($\text{H}_2\text{A}/\text{HA}^-$, pH 4) contained in a 45 ml cell. All solutions were stirred continuously and irradiated after deaerating for one hour with CO_2 (or argon).

Analytical Methods and Absorption Spectra. - Gas contained in the reaction vessel was sampled through a 250 μl sample loop which was part of a 6-valve system directly attached to a Varian 3700 gas chromatograph. Samples were analysed with TC detection, using a 2-column system. The inner column was packed with Porapak-Q for CO_2 retention, and the outer column was packed with molecular sieve 5 \AA for separation of CO and H_2 . Carbon monoxide analysis was carried out at 60°C , using helium carrier gas, flow rate 22 ml 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 UV/VIS diode array spectrophotometer. Some product analysis was performed by HPLC using a Beckman

Model 100A with a u.v. detector and a Bio-Rad Aminex Ion Exclusion column HPX-87H.

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Table 1

Photochemical system for generation of CO and H₂ from:
 Ru(bipy)₃Cl₂·6H₂O (5x10⁻⁴M), Ni(II)cyclam·Cl₂ (2x10⁻³M), ascorbate
 (pH 4), CO₂, in H₂O

Light source = Xe lamp, 1000 W. Illumination time = 4 hrs

Run	Ru(bipy) ₃ ²⁺	[Ni(II)cyclam] ²⁺	CO ₂	Ar	Ascorbate	pH	CO ^a (μl)	H ₂ ^a (μl)
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	*	4	152	975
7	*	*	*	0	* ^c	3	38	140
8	*	*	*	0	* ^c	5	132	160
9	*	*	*	0	* ^c	6	35	10
10	*	*	0 ^d	0	*	4	d	980

* - 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 H₂ is 5 μl.

b - Ascorbate buffer replaced by acetate buffer.

c - pH changed by varying the relative amounts of acid and base. Total ascorbate concentration maintained at 1M.

d - Solution saturated with CO gas prior to photolysis.

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Figure Captions

Figure 1. The pH dependence of CO and H₂ yields in the Ru(bipy)₃²⁺-ascorbate-[Ni(II)cyclam]²⁺-CO₂ system. The CO/H₂ ratios are indicated in parentheses.

Figure 2. The volume of CO and H₂ produced as a function of illumination time for a solution containing 5x10⁻⁴M Ru(bipy)₃Cl₂·6H₂O, 2x10⁻³M Ni(II)cyclam·Cl₂, 0.5M/0.5M ascorbate buffer (pH 4), saturated with CO₂.

Figure 3. Absorption spectra of an aqueous solution containing 1.7x10⁻⁴M Ru(bipy)₃Cl₂·6H₂O, 2x10⁻³M Ni(II)cyclam·Cl₂, 0.5M/0.5M ascorbate buffer (pH 4), saturated with CO₂. (a) illumination time, t = 0; (b) t = 20 min; (c) t = 50 min. (d) t = 80 min; (e) t = 120 min.

Figure 4. Photolysis cell used to degass the reaction solution, deliver product gases to g.c. for analysis, and contain calibration gases injected via syringe.

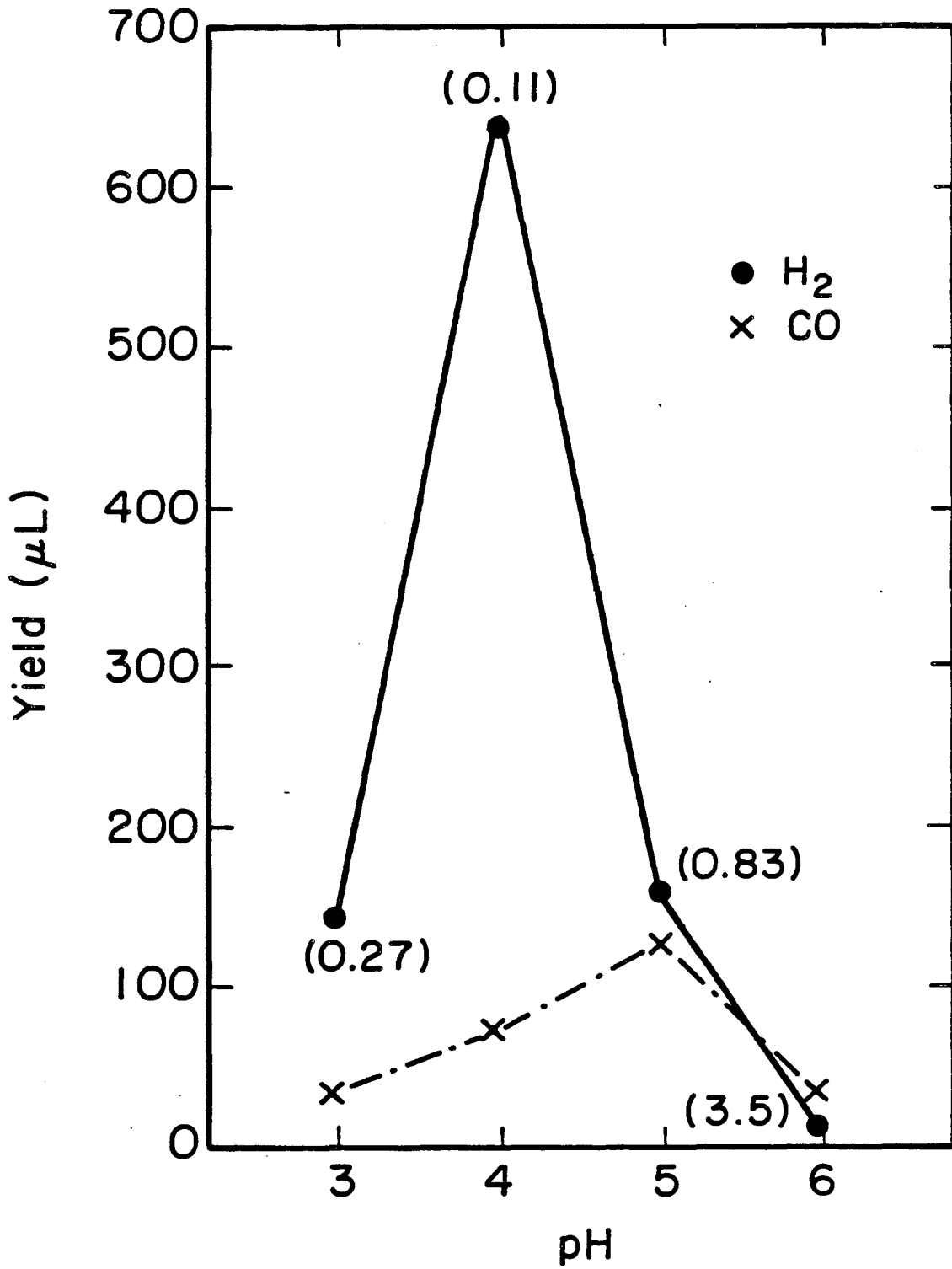


Fig. 1

XBL 867-2592

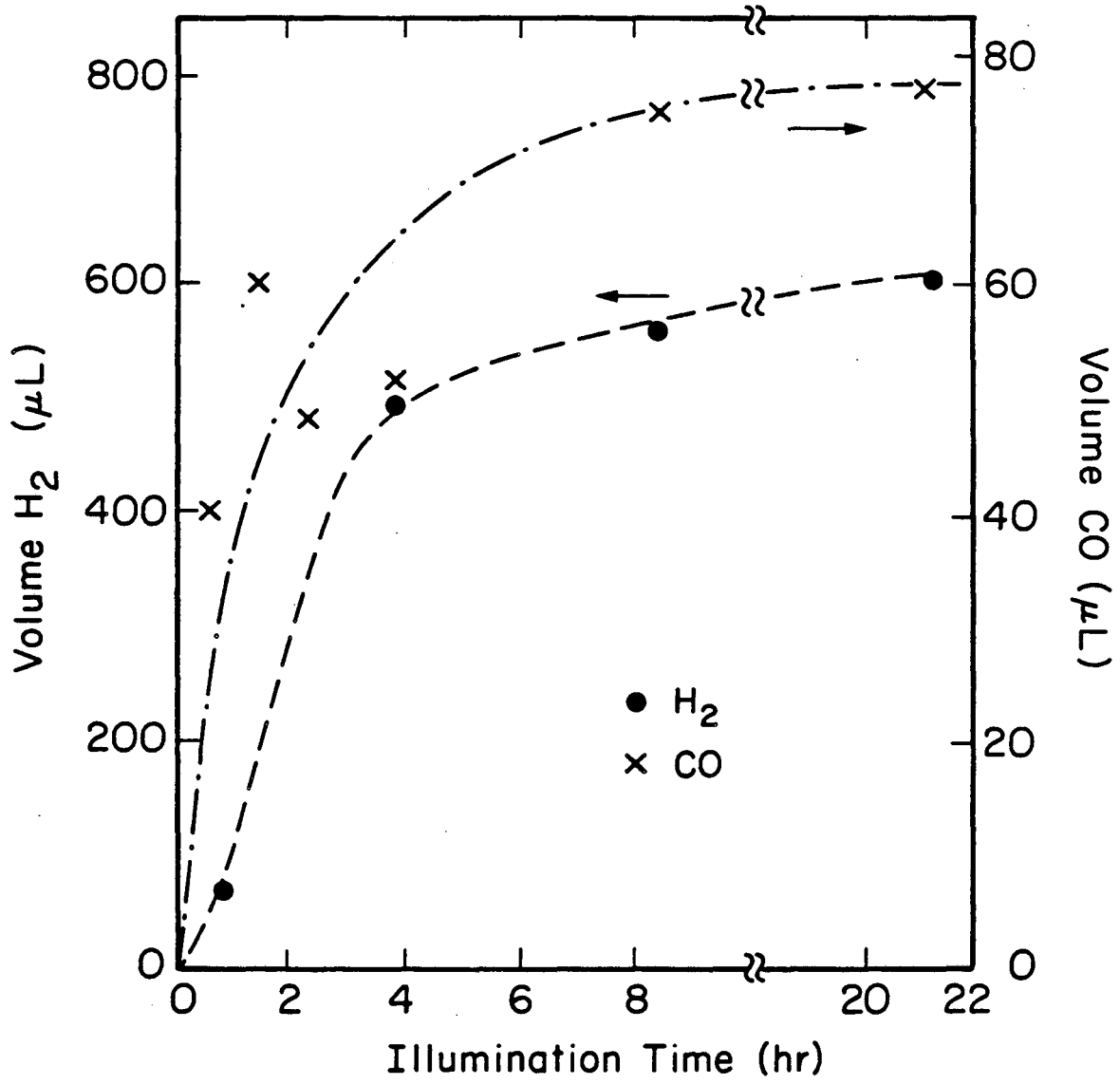


Fig. 2

XBL 867-2591

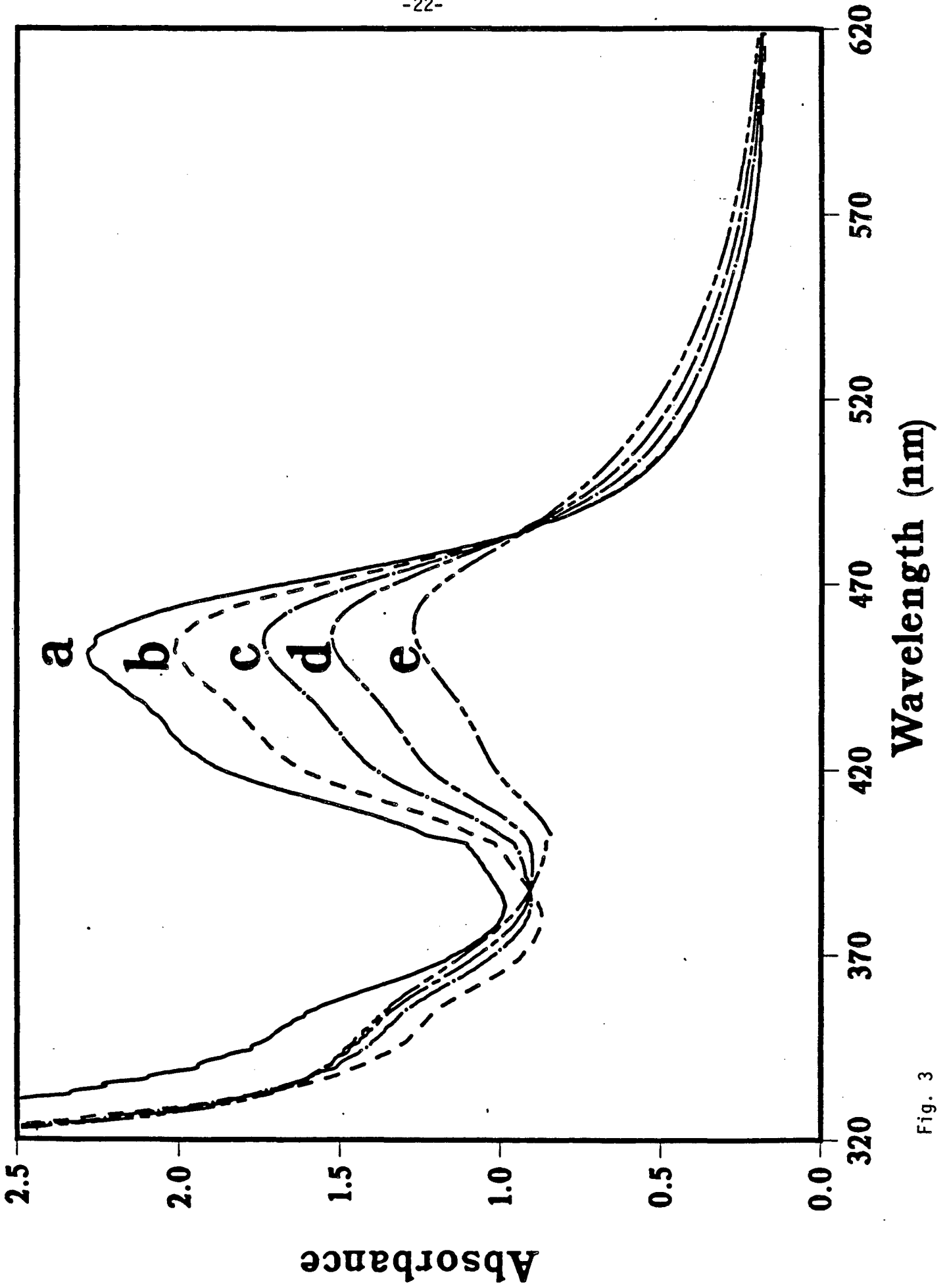
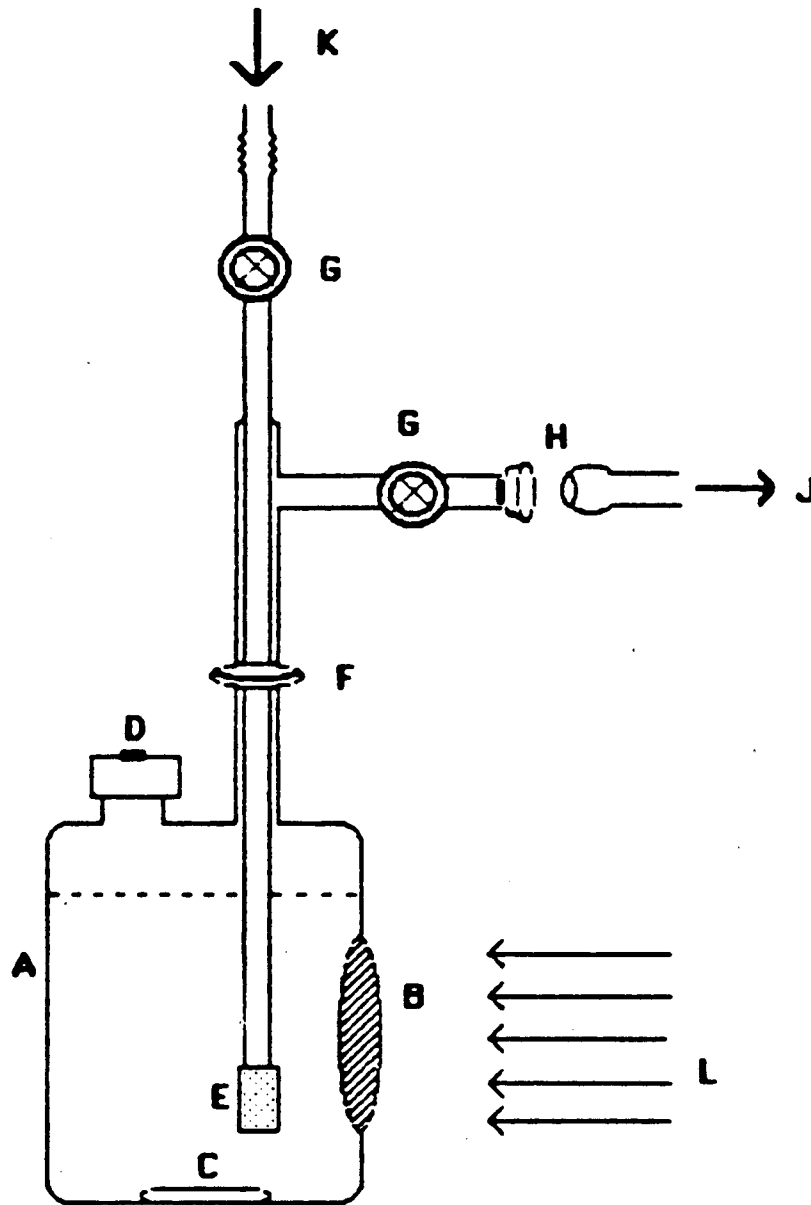


Fig. 3



A - Glass photolysis cell

B - Quartz window

C - Stirrer bar

D - Septum

E - Medium frit

F - O-ring

G - Stopcock

H - Ball and socket

J - To g.c.

K - Ar/CO₂

L - Incident light

Fig. 4

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