142. Hydrogen Generation by Visible Light Irradiation of Aqueous Solutions of Metal Complexes. An Approach to the Photochemical Conversion and Storage of Solar Energy[1])

by **Michèle Kirch, Jean-Marie Lehn** and **Jean-Pierre Sauvage**

Institut Le Bel, Université Louis Pasteur, 4, rue Blaise Pascal, F-67000 Strasbourg, France[2])

(20.III.79)

Summary

We describe a photochemical system for the generation of hydrogen by water reduction under visible light or sunlight irradiation of aqueous solutions containing the following components: a photosensitizer, the Ru(bipy)$_3^{2+}$ complex, for visible light absorption; a relay species, the Rh(bipy)$_3^{3+}$ complex, which mediates water reduction by intermediate storage of electrons *via* a reduced state; an electron donor, triethanolamine (TEOA) which provides the electrons for the reduction process and a redox catalyst, colloïdal platinum, which facilitates hydrogen formation. The conditions for efficient hydrogen production and the influence of the concentration of the components have been investigated; the metal complexes act as *catalysts* with high turnover numbers; excess bipyridine facilitates the reaction. The process contains two catalytic cycles: a *ruthenium cycle* and a *rhodium cycle.* The Ru cycle involves oxidative quenching of the *Ru(bipy)$_3^{2+}$excited state by Rh(bipy)$_3^{3+}$ forming Ru(bipy)$_3^{3+}$ which is converted back to Ru(bipy)$_3^{2+}$ by oxidation of the electron donor TEOA, which is thus consumed. The Rh cycle comprises a complicated set of transformations of the initial Rh(bipy)$_3^{3+}$ complex. The reduced rhodium complex formed in the quenching process undergoes a series of transformations involving the Rh(bipy)$_2^+$ complex and hydridorhodium-bipyridine species, from which hydrogen is generated by reaction with the protons of water. In view of the storage of two electrons in the reduced rhodium species, the process is formally a *dielectronic water reduction.* The properties and eventual participation of [Rh(III)(bipy)$_2$LL′]$^{n+}$(L, L′ = H_2O, OH^-) species are investigated. It is concluded that at neutral pH in presence of excess bipyridine, the cycle involving regeneration of the Rh(bipy)$_3^{3+}$ complex is predominant. A number of experiments have been performed with modified systems. Hydrogen evolution is observed with other photosensitizers (like proflavin), other relay species (like Rh(dimethylbipy)$_3^{3+}$ or Co(II)-bipyridine complexes), other donor species, or

---

[1]) Communicated in part at the 2nd International Conference on the Photochemical Conversion and Storage of Solar Energy, Cambridge, Great-Britain, August 10-12, 1978; for a preliminary report see [1].

[2]) E.R.A. No 265 of the C.N.R.S.

0018-019X/79/4/1345-40$01.00/0

in absence of the platinum catalyst. It also occurs in absence of photosensitizer by sunlight or UV. irradiation of $Rh(bipy)_3^{3+}$ or by visible light irradiation of iridium(III)-bipyridine complexes. These systems deserve further investigations. The present photochemical hydrogen generating system represents the reductive component of a complete water splitting process. Its role in solar energy conversion and in photochemical fuel production is discussed.

1. Introduction. - The search of processes for splitting the water molecule into oxygen and hydrogen under solar irradiation is attracting much well deserved attention, both for their fundamental interest, as new photochemical transformations and artificial models of photosynthesis, and for their potential applications as means for chemical storage of solar energy and fuel production [2-10]. The overall reaction may be divided into two half-systems, the reductive one producing hydrogen and the oxidative one producing oxygen, separated by a membrane permeable to electrons and protons.

The energy storage step resides in the direct or indirect photochemical production of a reduced species of strongly negative redox potential, whose reducing power may thereafter be used for preparing renewable fuels (hydrogen [2] [11] [12], but also other substances like methanol, *etc.*), for producing electricity in a rechargeable battery or in fuel cells *etc.* Ideally, the electrons needed in the generation of the reduced species should come from water itself. However, thermodynamically the photooxidation of any weak electron donor to produce a strong reductant amounts to light energy storage, and economically such a process may become of interest if the oxidized material is very cheap.

Our first goal was therefore to set up the reductive component of a complete water splitting system: *the catalytic generation, under irradiation with visible light, of a reduced species whose energy might be stored* (at least in part) *by production of hydrogen* via *water reduction.*

Such a process together with the previously described light driven transport of electrons and protons through artificial membranes containing suitable carrier molecules [13], represents in principle two components of a membrane separated water splitting cell, as schematically depicted in *Figure 1.* Of course one may envisage simultaneous production of hydrogen and oxygen in a single phase cell not involving a membrane, but at greater risks of 'short-circuits' and back transfer reactions between reduced and oxidized species.

Cells of the type shown in *Figure 1* may have several variants depending on which steps are thermal or photochemical. In particular, the oxidation and reduction reactions in which the water molecule is directly involved may be either both photochemical, one photochemical and one thermal, or both thermal. The photochemically activated transformation may thus not involve water directly but take place between species linked to the reactions involving water.

Among the numerous photochemical and photoelectrochemical processes which have been considered for solar energy conversion and/or hydrogen fuel production [2-12], most of them involve *transition metal cations* and *complexes with organic ligands,* whose photochemical and photocatalytic properties have been studied extensively

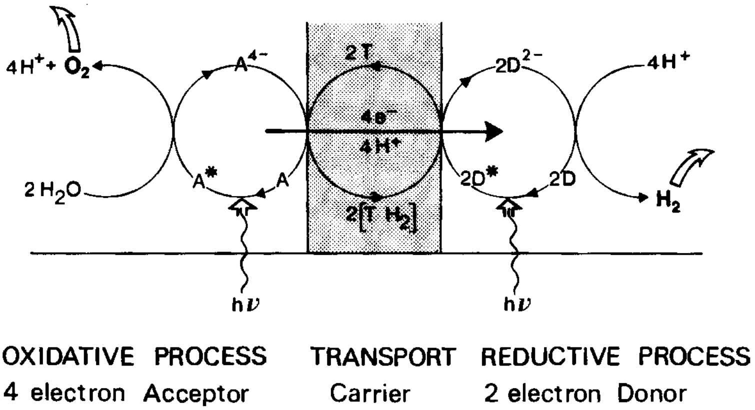


Fig. 1. *Schematic representation of a membrane separated photochemical water splitting system.* A is a photoactive species which is a strong oxidant in its excited state and a four-electron acceptor. T is a redox carrier rendering the membrane permeable to electrons and protons. D is a photoactive species which yields a reduced state capable of forming hydrogen from water in a dielectronic process. This is of course only one possible variant of such a system; several other schemes may be imagined

[14-17]. Solar energy conversion schemes for the formation of hydrogen by irradiation of aqueous solutions containing metal cations with UV. light have been investigated for instance with Ce(III) [18] [19], Eu(III) [20-23], Fe(II) [11a], [24-28], Cr(II) [29], Cu(I) [30] [31], Ru(II)[32] complex cations. Thus, irradiation of aqueous solutions of Eu(III) in the presence of organic H and OH scavengers yields Eu(II) which is photoactive and forms hydrogen with 5% quantum yield at 365 nm [23]. Hydrogen is produced by UV. (λ 254 nm) irradiation of aqueous acid solutions of binuclear Mo(II) species; direct evidence for the intermediate formation of hydrides has been presented [33] [34]. Visible light (λ 546 nm) irradiation of a bridged binuclear Rh(I) complex hydride $[Rh_2(bridge)_4H]^{3+}$ in 12 M HCl solution yields about one equivalent of H_2-gas [35] [36]. UV. photolysis of dihydro complexes of tungsten [37-39], iridium, ruthenium and molybdenum [40-42] results in generation of H_2. The elimination of H_2 from dihydridocobalt complexes is accelerated under UV. light [43]. Many recent studies were devoted to the interesting photochemical properties of the ruthenium(II)-tris (2,2'-bipyridyl) complex cation, $Ru(bipy)_3^{2+}$, whose excited state is thermodynamically capable of either oxidising or reducing water (see below) [44-66]. A report [67] on the photochemical splitting of water into H_2 and O_2 using monolayers of a lipophilic derivative of $Ru(bipy)_3^{2+}$ [68] [69] could not be reproduced by subsequent work in several laboratories [70-74].

The present account describes a *system generating hydrogen,* via *catalytic cycles, from aqueous solutions of metal complexes under continuous irradiation with visible light;* it involves the photochemical production of a reducing species which thermally reduces water. Preliminary results of this work have been reported earlier [1]. We now describe in detail: 1) the properties of the system together with substantially improved conditions for hydrogen generation; 2) mechanistic results on the nature of the species and of the reactions involved in the process; 3) a number of modifications of the system and related experiments. Several photochemical hydrogen evolving processes have been reported recently [75–78] (see also [79] for related studies). Systems involving biological materials like chloroplasts, hydrogenase, ferredoxin have been shown to produce small quantities of hydrogen under illumination (see for instance [80–84]).

2. Pathways for mediated photochemical reduction and oxidation of water. – The energy required for the dissociation of the water molecule into hydrogen and oxygen depends on the number of electrons involved in the process. The most favorable redox reactions of water³) are the dielectronic reduction (1) and the tetraelectronic oxidation (2):

$$2\,H^+ + 2\,e^- \rightarrow H_2 \qquad E_7 = -0.41\text{ V} \qquad (1)$$

$$2\,H_2O \rightarrow O_2 + 4\,H^+ + 4\,e^- \qquad E_7 = +0.82\text{ V} \qquad (2)$$

amounting to the overall dissociation reaction (3):

$$H_2O \rightarrow H_2 + \frac{1}{2}O_2 \qquad \Delta G = 1.23\text{ eV} \qquad (3)$$

where E_7 is the redox potential at pH 7 ([85]; see also *Fig. 2*) and ΔG is the free energy of the reaction *per electron*.

Monoelectronic reduction (4), oxidation (5) and dissociation (6) require a much higher energy:

$$H^+ + e^- \rightarrow H^\cdot \qquad E_7 \sim -2.5\text{ V} \qquad (4)$$

$$H_2O \rightarrow {}^\cdot OH + H^+ + e^- \qquad E_7 \sim +2.5\text{ V} \qquad (5)$$

$$H_2O \rightarrow H^\cdot + {}^\cdot OH \qquad \Delta G \sim 5\text{ eV} \qquad (6)$$

A redox couple having a potential more positive than +0.82 V is thermodynamically capable of oxidizing water at pH 7; conversely any couple having a redox potential more negative than −0.41 V is thermodynamically able to reduce water *(Fig. 2)*. It is clear that thermodynamic properties alone do not determine these reactions but kinetic and mechanistic features play a major role.

Photochemical dissociation of water by the monoelectronic process (6) requires photons of energy >5 eV *i.e.* of wavelength shorter than 250 nm since $\lambda(\text{nm}) \times E(\text{eV}) = 1240$, whereas light of $\lambda < 1000$ nm is sufficient if the tetraelectronic process (3) is followed. On the other hand, according to (1) and (2), *photochemical reduction* (7) or *oxidation* (8) of water can in principle be brought about if the excited state *PS of a photosensitizer PS has redox potentials

---

³) All redox potentials listed in the present work are given with respect to the normal hydrogen electrode (NHE) in aqueous solution unless stated otherwise.

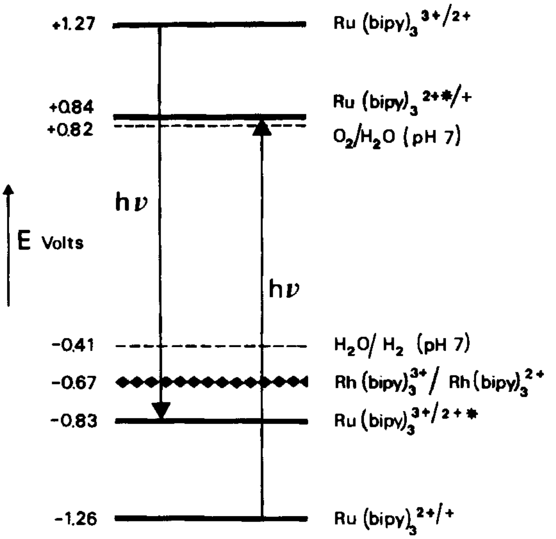


Fig. 2. *Redox potentials of ruthenium- and rhodium-tris(bipyridine)complexes and of water at pH 7.* The oxidizing and reducing properties of Ru(bipy)$_3^{2+}$ are both enhanced in the excited state by 2.10 V; for the Rh(bipy)$_3^{3+}$/Rh(bipy)$_3^{2+}$ redox potential see footnote[8]). Potentials are in volts, *versus* the normal hydrogen electrode (NHE) in aqueous solution

PS$^+$/*PS < -0.41 V or *PS/PS$^-$ $> +0.82$ V respectively, and reacts with water by *oxidative quenching* (7) or *reductive quenching* (8):

$$*PS + H^+ \rightarrow PS^+ + \frac{1}{2}H_2 \tag{7}$$

$$*PS + \frac{1}{2}H_2O \rightarrow PS^- + H^+ + \frac{1}{4}O_2 \tag{8}$$

If for mechanistic and for kinetic reasons, *PS itself is not able to perform the desired reaction(s), it may nevertheless be possible to use at least part of the excitation energy *via* electron transfer or energy transfer processes with a *quencher* Q which functions as a *relay species* mediating the reaction(s) with water. Three processes may be considered.

Oxidative quenching may occur:

$$*PS + Q_0 \longrightarrow PS^+ + Q_0^- \tag{9}$$

The thermal back-reaction (10)

$$PS^+ + Q_0^- \longrightarrow PS + Q_0 \tag{10}$$

may be prevented by fast reaction with an electron donor D:

$$PS^+ + D \longrightarrow PS + D^+ \tag{11}$$

The net reaction is then:

$$D + Q_0 \longrightarrow D^+ + Q_0^- \tag{12}$$

the PS species acting as a photocatalyst. The disproportionation (12) is strongly endothermic if the redox potential of the D^+/D couple is much higher than that of the Q_0/Q_0^- couple, so that D^+ and Q_0^- are only present during irradiation. The reverse, exothermic, recombination reaction will occur spontaneously and rapidly in the dark unless there is a kinetic barrier, or the D^+ and/or Q_0^- species undergo a fast irreversible transformation. For instance D^+ or Q_0^- may rapidly decompose (13) or react with water by *thermal* oxidation (14) or reduction (15):

$$D^+ \text{ or } Q_0^- \longrightarrow \text{decomposition products} \tag{13}$$

$$4\,D^+ + 2\,H_2O \longrightarrow 4\,D + O_2 + 4\,H^+ \tag{14}$$

$$2\,Q_0^- + 2\,H^+ \longrightarrow 2\,Q_0 + H_2 \tag{15}$$

In the case of *reductive quenching:*

$$^*PS + Q_r \longrightarrow PS^- + Q_r^+ \tag{16}$$

a parallel set of reactions may be written:

$$PS^- + Q_r^+ \longrightarrow PS + Q_r \tag{17}$$

$$PS^- + A \longrightarrow PS + A^- \tag{18}$$

$$A + Q_r \longrightarrow A^- + Q_r^+ \tag{19}$$

$$A^- \text{ or } Q_r^+ \longrightarrow \text{decomposition products} \tag{20}$$

$$2\,A^- + 2\,H^+ \longrightarrow 2\,A + H_2 \tag{21}$$

$$4\,Q_r^+ + 2\,H_2O \longrightarrow 4\,Q_r + O_2 + 4\,H^+ \tag{22}$$

where A is an electron acceptor.

A third process, *energy transfer* may take place

$$^*PS + Q \longrightarrow PS + {}^*Q \tag{23}$$

if ΔG (*PS, PS) is higher than ΔG (*Q, Q); thereafter, the excited quencher molecule *Q may react directly with water or enter a more complicated set of reactions.

Species Q_0^- in (15) and A^- in (21) play the role of an *electron relay* (R) mediating water reduction *via* intermediate storage and transfer of electrons. Species D^+ in (14) and Q_r^+ in (22) function similarly towards water oxidation.

Finally, a noble metal *redox catalyst* (C) should facilitate the establishment of the equilibria (1) and (2). In particular, such a heterogeneous catalyst, by taking up electrons and protons (at the solution-particle interface), may make the desired dielectronic pathway (1) available even for processes which involve only single electron transfers⁴).

---

⁴) The catalysis of metal cation oxidation (*e.g.* V^{2+} to V^{3+}), with hydrogen evolution, by platinum metal acting as a redox catalyst, is known since 1902 [86]. The analogy between biological systems and colloïdal palladium in the hydrogen formation equilibrium had already been noted in 1934 [87].

Focusing on water reduction, one may conclude that a suitable system for photochemical hydrogen generation may reside in the combination of a photosensitizer (PS) for light absorption, a relay species (R), an electron donor (D) for preventing the back reaction (10), and a redox catalyst (C). Such a chain of four components of suitable redox properties, PS/R/D/C, forms the basis of the present investigations[5]).

In the course of our work we arrived at a particular set of components which define our *reference system,* on which most of the studies described here have been performed, and with respect to which a number of modifications have been experimented.

3. Components of the reference system. - From the known redox potentials shown in *Figure 2* [54], the extensively studied $Ru(bipy)_3Cl_2$ complex appears to be a suitable *photosensitizer.* It presents a strong absorption covering a sizable region at the short wavelength end of the visible spectrum ($\lambda_{max} = 452$ nm, $\varepsilon = 14600$ in aqueous solution [46] [57]) and has a high excitation quantum yield [45] [66]. Although its excited state $^*Ru(bipy)_3^{2+}$ is thermodynamically capable of both oxidizing and reducing water at neutral pH, this has not been found to occur. Considering the redox properties of the Ru(I) and Ru(III) species [65] [66], $Ru(bipy)_3^{3+}$ is a strong oxidant and does oxidize water at pH 7 [51]; however, generation of the strong reductant $Ru(bipy)_3^+$ in neutral aqueous solution does not appear to cause water reduction [91] [92], but should be able to do so in suitable conditions.

A suitable *relay species* should have the following characteristics: i) be reduceable by $^*Ru(bipy)_3^{2+}$ and be itself able to reduce water at pH 7 or higher ($-0.83 < E_0 < -0.41$ V); ii) preferably accumulate two electrons at about the same reduction potential so as to potentially allow a dielectronic reduction (1); iii) show analogies with compounds which are able to combine with hydrogen, like homogeneous hydrogenation catalysts, to provide a pathway for hydrogen release from an intermediate hydride if supplied with two electrons and two protons. Whereas i) is a necessary (and may be a sufficient) requirement, ii) and iii) are not, but they may at least guide the search and improve efficiency. Rhodium(III) amine and bipyridine complexes have suitable properties: i) their first reduction step involves two electrons and lies in a suitable range of potentials [93-95] (see below); ii) they form hydrides [96] and are homogeneous hydrogenation catalysts [97] [98]. Finally, rhodium-bipyridine complexes have the further advantage of containing the same ligand as the $Ru(bipy)_2Cl_2$-PS.

As *donor,* triethanolamine (TEOA) is an attractive candidate since it has been used in photochemically induced reduction processes [90] and its pK_a ($=7.9$) is close to

---

[5]) A partial analogy of such a combination is found in the photoreduction of methylviologen (MV^{2+}) to the blue radical cation MV^+ by visible light irradiation of aqueous solution containing a photosensitizer, like proflavin (PF) or the $Ru(bipy)_3Cl_2$ complex, and EDTA as donor [47] [60] [89]. It had been noted earlier that the MV^{2+}-MV^+ interconversion, a useful redox indicator, may bring about the formation of hydrogen gas in presence of a catalyst like colloïdal platinum [87] [88]. Recent work has used the MV^{2+}-MV^+ couple to set up a photobattery [90] and to mediate light-driven electron transport across artificial membranes [13] as well as hydrogen formation [75-78].

neutrality [99]. Finally a noble metal catalyst (like colloïdal Pt formed by *in situ* reduction of a suitable salt) should facilitate hydrogen formation either by establishing the redox reaction (1) or from eventual intermediate metal hydrides (*cf.* the facilitated hydrogen formation from hydridocobalamin [100])[4])[5]).

In conclusion, our *reference system* contains the following components PS/R/D/C = $Ru(bipy)_3^{2+}$/$Rh(bipy)_3^{3+}$/TEOA/K_2PtCl_4[6]). We shall now describe and analyze the results obtained with this reference system.

4. Photochemical hydrogen generation experiments in visible light using the reference system. - 4.1. *Results.* When neutral aqueous solutions containing the $Ru(bipy)_3^{2+}$/$Rh(bipy)_3^{3+}$/TEOA/K_2PtCl_4 system are irradiated with visible light ($\lambda > 400$ nm) or sunlight, gas bubbles appear after a short induction period (from 10 seconds to a few minutes depending on the conditions); thereafter active gas generation is observed as long as irradiation is continued. The gas is collected and analyzed. Detailed descriptions are given in the experimental section. *Table 1* lists the results of a number of experiments (exper. 1-12). The rates of hydrogen production, the amounts produced and the number of catalytic cycles undergone by the ruthenium and rhodium complexes have been studied as a function of the concentrations of the various constituents and of experimental conditions (temperature, pH).

4.2. *Analysis of the gas generated.* The nature of the gas generated was monitored by gas phase chromatography (GPC.) in all experiments and by mass spectrometry in two cases. *Figures 3* and *4* display some analytical data. Quantitative composition of the gas was determined by comparison of the area of the GPC. peaks with reference curves given by known quantities of pure gases *(Fig. 3)*. The gas generated was pure (> 98%) hydrogen. When D_2O was used as solvent, the hydrogen gas contained about 94% D_2, 5% HD and 1% H_2 *(fig. 4)*[7]). In a similar experiment with EDTA as donor (see below) the percentages were respectively 94.5%, 5% and 0.5%.

4.3. *Turnover numbers. Number of catalytic cycles.* A very important parameter describing the efficiency of the system is the observed *turnover number* (*TO*) of the various components. For a given irradiation experiment, (*TO*) is defined as the ratio of the total amount of H_2 produced ($n(H_2)$ mol) to the amount of species *i* initially present ($n_0(i)$ mol), equation (24):

$$(TO)_i = n(H_2)/n_0(i) \qquad (24)$$

Since formation of a molecule of H_2 requires two electrons, the effective number of catalytic cycles undergone by species *i* is either equal to (*TO*) or to 2 (*TO*) depending on whether species *i* participates in a dielectronic or in a monoelectronic process.

---

[6]) In the preliminary description [1] the rhodium species was formed *in situ* and its nature was not specified. Indeed, as will be seen below, several rhodium complexes may be involved in the process.

[7]) Taking into account residual background signals, the amount of H_2 was below 1%.

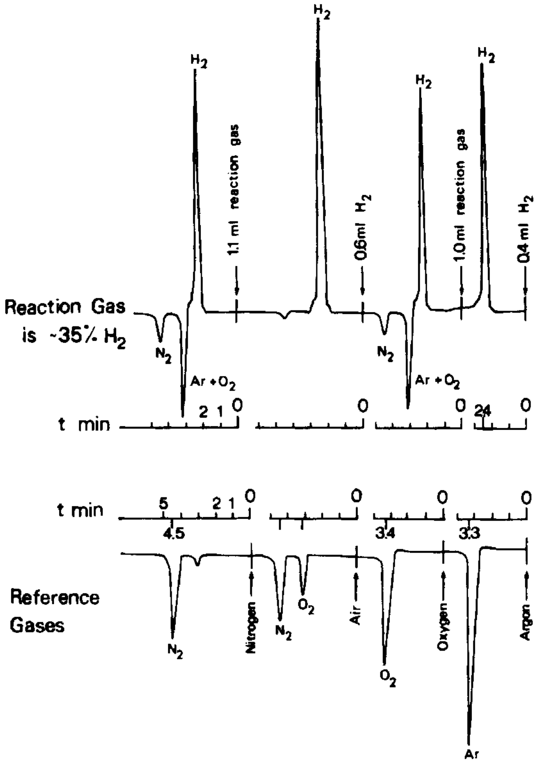


Fig. 3. *Quantitative analysis of the gases by gas chromatography. Bottom traces:* reference gases. *Top traces:* composition of the 'reaction gas' contained in the reaction flask after irradiation, and calibration with pure hydrogen; in the specific case shown here about 35% in volume of the gas is hydrogen generated by the reaction, the rest being other gases initially present in the set-up

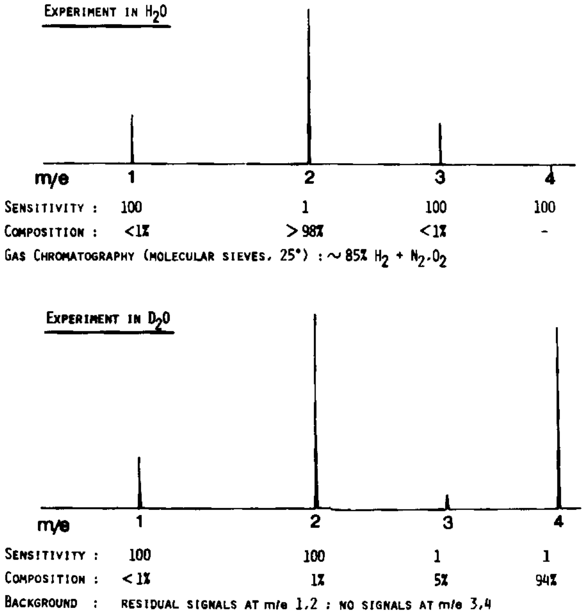


Fig. 4. *Mass-spectrometric analysis of the hydrogen gas generated. Top:* reaction performed in H_2O; *bottom:* reaction performed in D_2O. The sensitivity indicates the amplification factors used for the corresponding signals.

Another parameter of interest is the *extrapolated turnover number*, $(TO)_{ex}$, which indicates which turnover number may be expected for species i after all of i has been destroyed in the course of the reaction. The concentrations of $\mathrm{Ru(bipy)_3^{2+}}$, $\mathrm{Rh(bipy)_3^{3+}}$ (and other active rhodium species formed, see below) and (bipy) have been determined by electronic absorption spectroscopy after terminating exper. 11 and 12, *Table 1*. $(TO)_{ex}$ is obtained from (TO) for species i and from the initial and final concentrations of i, $(c_o)_i$ and $(c_f)_i$ respectively, by equation (25):

$$(TO)_{ex} = (TO)_i \times \frac{(c_o)_i}{(c_o)_i - (c_f)_i} \tag{25}$$

Table 1. *Hydrogen generation by visible light irradiation of the reference system:* $\mathrm{Ru(bipy)_3^{2+}/Rh(bipy)_3^{3+}/TEOA/K_2PtCl_4}$[a])

Experiment No	$\mathrm{Ru(bipy)_3^{2+}}$ conc. $10^4 \times$ M	$\mathrm{Rh(bipy)_3^{3+}}$ conc. $10^3 \times$ M	added (bipy) conc. $10^3 \times$ M	TEOA initial conc.	Rate of H_2 production ml/h[b])
1	9.1	1.95	3.1	0.083	0.66
2	9.1	1.95	3.1	0.42	3.1
3[c])	9.1	1.95	3.1	0.42	0.18
4	9.1	1.95	0	0.42	1.5
5	9.1	1.95	10	0.42	5.1
6	9.1	1.95	35	0.42	6.0
7	3.03	1.95	3.1	0.42	3.2
8	0.91	1.95	3.1	0.42	2.1
9	3.03	0.97	3.1	0.42	1.2
10	3.03	4.65	3.1	0.42	3.2
11[d])	3.03	1.95	0	0.42	0.8
(TO)	*500*	*80*	-	*37%*[f])	22.4(45)[e])
$(TO)_{ex}$	> *5000*[g])	[h])	-	-	
12[d])	3.03	1.95	3.1	0.42	1.7
(TO)	*750*	*110*	*75*	*54%*[f])	32.7(32)[e])
$(TO)_{ex}$	> *7500*[g])	> *1100*[g])	> *750*[g])	-	

[a]) Aqueous solutions containing $\mathrm{Ru(bipy)_3(SO_4) \cdot 6\,H_2O}$, $\mathrm{Rh(bipy)_3(SO_4)_{1.5} \cdot 7\,H_2O}$, $\mathrm{K_2PtCl_4}$, triethanolamine (TEOA) · H_2SO_4 at initial pH = 7.0. The experimental procedure is described in the experimental section. Each irradiation is carried out on a 6 ml sample of degassed solution containing 0.7 mg $\mathrm{K_2PtCl_4}$ except for run 3. The solutions are thermostated at 50° ± 1°, except for experiments 11 and 12 which were conducted at 15.0 ± 0.5°.

[b]) The rate of H_2 formation is constant over a period of time depending on the experimental parameters. The experiments are reproducible within ± 10%.

[c]) No platinum salt added.

[d]) For experiments 11 and 12, the (TO) and $(TO)_{ex}$ values are indicated as defined previously (see text, eq. 24 and 25).

[e]) Total volume (ml) of H_2 evolved and irradiation time (h) in parentheses.

[f]) Percentage of TEOA consumed calculated as the ratio of the total number of moles of H_2 produced to the number of moles of TEOA present × 100.

[g]) The initial and final concentrations measured by electronic spectroscopy are the same within the experimental error (± 10%).

[h]) The final solution contains a mixture of $\mathrm{Rh(bipy)_3^{3+}}$, $\mathrm{[Rh(bipy)_2(OH)_2]^+}$ and (bipy), the total concentration in rhodium(III) complexes being approximately (± 10%) equal to the initial concentration of $\mathrm{Rh(bipy)_3^{3+}}$.

From the results of *Table 1*, it is clear that (*TO*) is much higher than unity for all species except TEOA which is consumed. Thus these species are all *real catalysts*. Furthermore, for exper. 11 and 12, $(TO)_{ex}$ is much larger than (*TO*), indicating that the system would continue functioning for a much longer time if irradiation were continued and more donor substance TEOA were added when required. *Figure 5* represents graphically the experimental result for exper. 12, *Table 1*; no significant degradation (< 10%) of the catalytic complexes could be detected when the experiment was interrupted after 32.7 ml hydrogen had been produced under continuous irradiation for 32 hours.

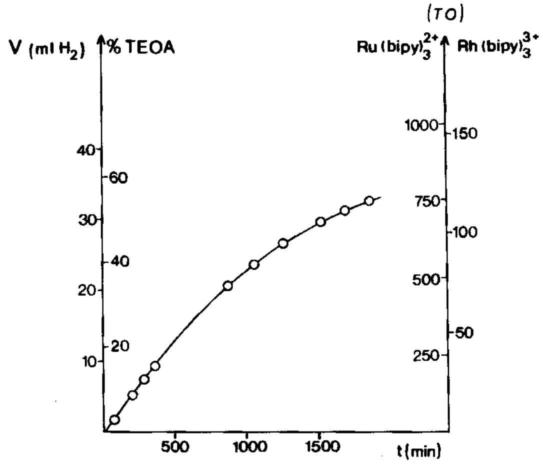


Fig. 5. *Graphical representation of the experimental results for experiment 12* (Table 1): volume of hydrogen evolved (in ml), fraction of TEOA consumed and observed turnover numbers (*TO*) for the $Ru(bipy)_3^{2+}$ and $Rh(bipy)_3^{3+}$ catalysts as a function of time

4.4. *Effect of experimental conditions.* The *nature of the anions* present in the system was found to play an important practical role, although they do not appear to participate in the chemical processes. In the initial experiments [1], the counter anions of the complexes $Ru(bipy)_3^{2+}$ and $Rh(bipy)_3^{3+}$ as well as those of the TEOA buffer were chlorides. Extensive precipitation of a dark brown insoluble material was observed as the reaction proceeded, and even more so with nitrate and perchlorate anions. The situation was greatly improved by using phosphate and sulfate anions for both the complexes and the adjustement of the TEOA buffer. The solutions remain clear throughout the irradiation experiments and hydrogen evolution is much more efficient. Thus, in the work described here, we have employed mainly the crystalline sulfates $Ru(bipy)_3SO_4 \cdot xH_2O$ and $Rh(bipy)_3(SO_4)_{1.5} \cdot 7\,H_2O$ obtained from the corresponding chlorides by anion exchange. The highly solvated multiply charged anions are expected to increase the solubility of intermediate rhodium complexes formed in the process (see below) and are less likely to coordinate to the metal cations.

The *pH* of the solution markedly influences the reaction. The optimum pH is about 7.5 ± 0.5 and the rate of hydrogen evolution decreases as the medium becomes either more acidic or more basic, being about five times slower at pH = 6.5 and 8.5 than at 7.5.

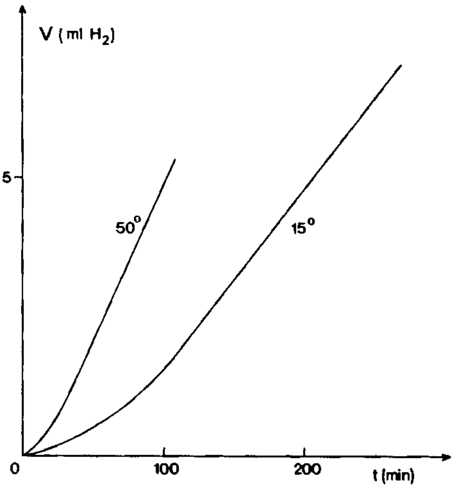


Fig. 6. *Hydrogen evolution (in ml) as a function of time at 50° (exp. 7,* Table 1) *and at 15° (exp. 12,* Table 1)

The influence of the *temperature* has been studied by performing exper. 7, *Table 1*, at 15°, 30°, 40° and 50° (see also *Fig. 6*). It is notable that the rate of hydrogen formation decreases only by a factor of about two between 50° and 15° (see discussion below). However the induction period is appreciably shorter at higher temperature. It appears that the reaction mixture is stable much longer at 15° than at 50°.

The reaction may be conducted in *air* as well as under inert gas.

4.5. *Effect of component concentrations on rates of hydrogen generation.* Experiments 1-10, *Table 1*, represent a limited exploration of the effect of the concentration of a given component on the rate of hydrogen formation while maintaining the other parameters constant. *Figure 7* gives a graphical representation of the data. *Saturation behaviour* is observed. For the components $Ru(bipy)_3^{2+}$, $Rh(bipy)_3^{3+}$, TEOA, as well as for addition of excess (bipy), the rate of hydrogen formation increases about linearly with concentration until a saturation concentration, c_s, is reached; beyond, the curve flattens out, indicating that the rate becomes limited by reactions other than those involving the species under study. Because of its high c_s value (> 0.4 M), TEOA must enter in a reaction with comparatively small rate constant (see below). The c_s values for the different species provide information about the optimal ratios of concentrations, about 1/10/50/ > 3000 for respectively $Ru(bipy)_3^{2+}/Rh(bipy)_3^{3+})$/excess (bipy)/TEOA at 50°. The addition of excess uncomplexed bipyridine strongly increases the rate of gas evolution, the total amount formed and the turnover of the complexes, while it does not appear to be consumed. The catalytic effect of this ligand may be related to the redox potentials involved as well as to mechanistic details of the process (see below).

5. Studies on the reaction mechanism. - *General considerations.* As pointed out above, the photochemical hydrogen generation process described here is catalytic with respect to the ruthenium and rhodium complexes introduced as well as with respect to the platinum and bipyridine species; it consumes an electron donor D

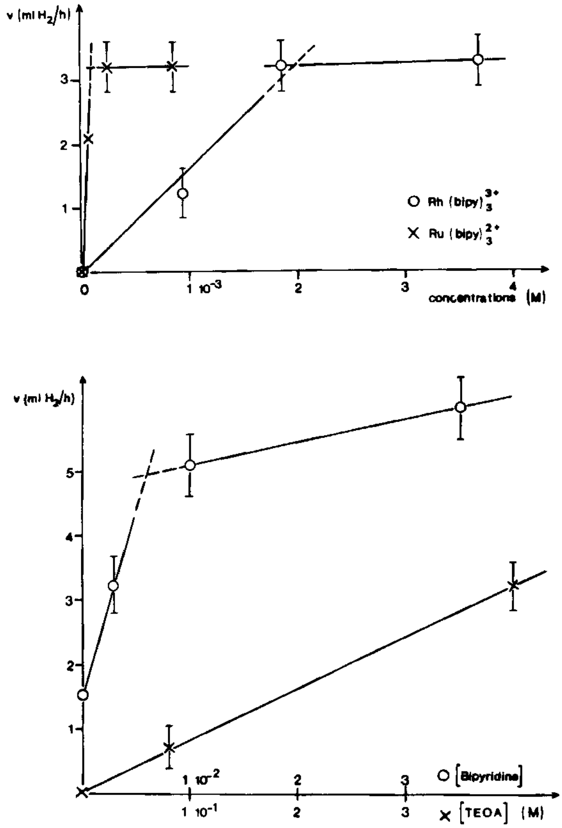


Fig. 7. *Dependence of the rate (v) of hydrogen generation (in ml/h) on the concentrations of the components of the system;* top: effect of the $Ru(bipy)_3^{2+}$ and $Rh(bipy)_3^{3+}$ concentrations; bottom: effect of the TEOA and bipyridine concentrations (see data in *Table 1*)

which provides the electrons necessary to the water reduction, protons from water (as shown by the experiment in D_2O) and visible light. The net reaction amounts to:

$$D + H^+ \xrightarrow{h\nu} D^+ + \frac{1}{2} H_2 \qquad (26)$$

The catalytic processes comprise two catalytic cycles: the photosensitizer ruthenium cycle and the relay rhodium cycle. The species involved and their transformations have been studied; a schematic representation of the overall process is given in *Figure 9* below. We shall now describe its components and analyze the data on which it is based.

5.1. *The Ruthenium cycle.* - 5.1.1. *Quenching process of the* $^*Ru(bipy)_3^{2+}$ *excited state.* The irradiation of $Ru(bipy)_3^{2+}$ with visible light leads to a $d\pi^*$ metal-to-ligand charge-transfer (MLCT) excited state [63] of about 2.1 eV higher energy, whose redox properties are shown in *Figure 2* [54] [64-66]. This excited state may luminesce or undergo electron transfer quenching by two paths:

- *oxidative quenching,* forming Ru(III), in the presence of an electron acceptor:

$$^*Ru(bipy)_3^{2+} + A \longrightarrow Ru(bipy)_3^{3+} + A^- \qquad (27)$$

- *reductive quenching*, forming Ru(I), when a suitable electron donor is present:

$$^{*}\mathrm{Ru(bipy)_3^{2+}} + \mathrm{D} \longrightarrow \mathrm{Ru(bipy)_3^{+}} + \mathrm{D^{+}} \qquad (28)$$

Oxidative quenching has been extensively studied [65] [66] and recent reports describe reductive quenching by organic donors like aromatic tertiary amines [65] [66] [92] [102-104].

The energy diagram of the relevant oxidation and electronic states of the $\mathrm{Ru(bipy)_3^{n+}} + \mathrm{Rh(bipy)_3^{m+}}$ system is represented in *Figure 8* (see also *Fig. 2*). The redox potentials of $^{*}\mathrm{Ru(bipy)_3^{2+}}$ are such that it may reduce $\mathrm{Rh(bipy)_3^{3+}}$ ($E_0(\mathrm{Rh(bipy)_3^{3+}/Rh(bipy)_3^{2+}}) = -0.67$ V [95])[8]) or oxidize TEOA ($E_0(\mathrm{TEOA^{+}/TEOA}) = +0.82$ V [78]).

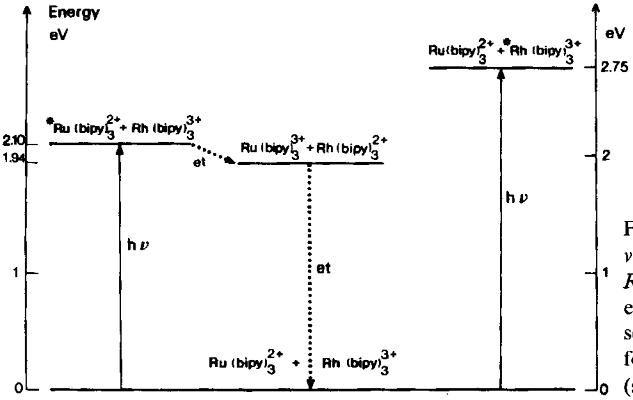


Fig. 8. *Energy diagram and interconversion paths of the* $\mathrm{Ru(bipy)_3^{2+}}$ + $\mathrm{Rh(bipy)_3^{3+}}$ *system*; hν: excitation; et: electron transfer; redox potentials: see *Figure 2;* excitation energies: 2.1 eV for $\mathrm{Ru(bipy)_3^{2+}}$, 2.75 eV for $\mathrm{Rh(bipy)_3^{3+}}$ (see text)

The other available path, *energy transfer* (equation (29)), is not expected to be followed since the frequency ν_0 of the $\mathrm{Rh(bipy)_3^{3+}}$ excitation ($\nu_0 = 22.25$ kK; 2.75 eV) is much higher than that of $\mathrm{Ru(bipy)_3^{2+}}$ ($\nu_0 = 17.23$ kK; 2.10 eV) [105]:

$$^{*}\mathrm{Ru(bipy)_3^{2+}} + \mathrm{Rh(bipy)_3^{3+}} \xrightarrow[0.65\ \mathrm{eV}]{} \mathrm{Ru(bipy)_3^{2+}} + {}^{*}\mathrm{Rh(bipy)_3^{3+}} \qquad (29)$$

$\mathrm{Ru(bipy)_3^{3+}}$ is able to oxidize TEOA but not $\mathrm{Rh(bipy)_3^{3+}}$, since E_0 ($\mathrm{Rh(bipy)_3^{4+}/Rh(bipy)_3^{3+}}$) > 2.0 V[9]); $\mathrm{Ru(bipy)_3^{+}}$ is able to reduce $\mathrm{Rh(bipy)_3^{3+}}$ but not TEOA (*Fig. 2*). Two ruthenium cycles may therefore be considered (free energy changes in eV, 1 eV = 23 kcal/mol):

the Ru(III) cycle (Fig. 9):

$$^{*}\mathrm{Ru(bipy)_3^{2+}} + \mathrm{Rh(bipy)_3^{3+}} \xrightarrow[-0.16\ \mathrm{eV}]{} \mathrm{Ru(bipy)_3^{3+}} + \mathrm{Rh(bipy)_3^{2+}} \qquad (30)$$

$$\mathrm{Ru(bipy)_3^{3+}} + \mathrm{TEOA} \xrightarrow[-0.45\ \mathrm{eV}]{} \mathrm{Ru(bipy)_3^{2+}} + \mathrm{TEOA^{+}} \qquad (31)$$

---

[8]) We use for the $\mathrm{Rh(bipy)_3^{3+}/Rh(bipy)_3^{2+}}$couple the potential $E_0 = -0.67$ V measured for reduction of $\mathrm{Rh(bipy)_3^{3+}}$ to $\mathrm{Rh(bipy)_2^{+}}$ in a two-electron wave at pH 10 [95].

[9]) Estimated by analogy with $E_0(\mathrm{Ir(bipy)_3^{4+}/Ir(bipy)_3^{3+}}) = +2.17$ V [66] [106].

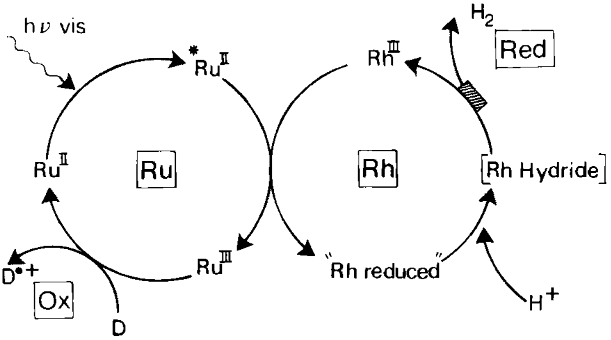


Fig. 9. *Schematic representation of the hydrogen generation process following the oxidative quenching Ruthenium cycle.* $\boxed{\mathrm{Ru}}$ and $\boxed{\mathrm{Rh}}$ represent the catalytic cycles undergone by the $Ru(bipy)_3^{2+}$ and $Rh(bipy)_3^{3+}$ complexes, 'Rh reduced' and [Rh hydride] designate the various reduced and hydrido rhodium species which may enter the cycle; **D** is the electron donor; the shaded block in the 'Red' component of the diagram stands for the platinum catalyst (see text for more details)

the Ru(I) cycle (Fig. 10):

$$^{*}\mathrm{Ru(bipy)_3^{2+} + TEOA} \xrightarrow[-0.02\ \mathrm{eV}]{} \mathrm{Ru(bipy)_3^{+} + TEOA^{+}} \tag{32}$$

$$\mathrm{Ru(bipy)_3^{+} + Rh(bipy)_3^{3+}} \xrightarrow[-0.59\ \mathrm{eV}]{} \mathrm{Ru(bipy)_3^{2+} + Rh(bipy)_3^{2+}} \tag{33}$$

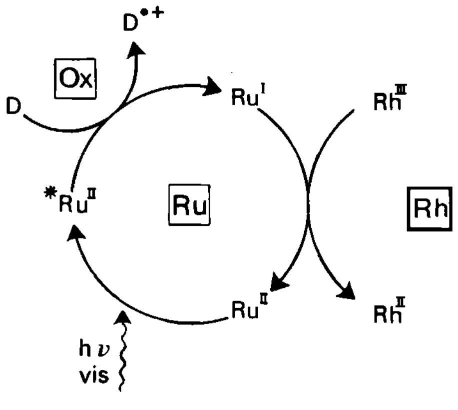


Fig. 10. *Schematic representation of the reductive quenching variant of the Ruthenium cycle* in the hydrogen generation process; the Rh cycle is the same as in *Figure 9*.

In order to distinguish between these two paths, quenching experiments have been performed. Whereas the luminescence of $^{*}Ru(bipy)_3^{2+}$ is unaffected by high concentrations of TEOA in aqueous solution, marked quenching of the emission is observed when $Rh(bipy)_3^{3+}$ is added instead. From a *Stern-Volmer* plot of the luminescence intensity changes on addition of increasing amounts of $Rh(bipy)_3^{3+}$ *(Fig. 11)*, the rate constant of the quenching reaction (30) is obtained:

$$k_{30} = 3.5 \pm 0.5 \times 10^{8}\,\mathrm{M^{-1}s^{-1}}\ \text{at}\ 25° \tag{34}$$

This rate constant is comparable to that measured for oxidative quenching of $^{*}Ru(bipy)_3^{2+}$ by methylviologen ($5 \times 10^{8}\,\mathrm{M^{-1}s^{-1}}$ [77a] [78]). Furthermore, laser

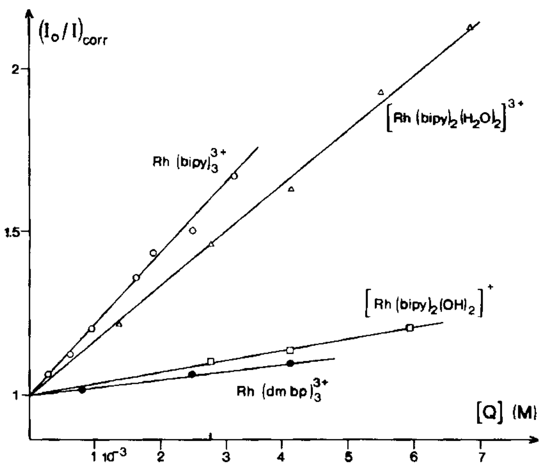


Fig. 11. Stern-Volmer *plots for the quenching of the luminescence of Ru(bipy)*$_3^{2+}$ *by the following complexes:* $Rh(bipy)_3^{3+}$, $Rh(dmbp)_3^{3+}$, $[Rh(bipy)_2(OH)_2]^+$ and $[Rh(bipy)_2(H_2O)_2]^{3+}$, at 25° in 0.5M phosphate buffer at pH 7.1 for the first three species and at pH = 3.0 for the last one; the emission data have been corrected for the absorption of the incident light by the quenchers (Q); the quenching rate constants are given in the text

flash experiments with solutions containing only $Ru(bipy)_3^{2+}$ and TEOA, in conditions similar to those used for hydrogen generation, gave no evidence for the formation of $Ru(bipy)_3^+$, since its characteristic absorption at 510 nm [91] [92] could not be observed after excitation (for similar results see also [77a] [78])[10].

In conclusion, the results obtained show that the present system follows the Ru(III) cycle (30) (31) as represented in *Figure 9.*

It has been noted above that the rate of H_2 generation decreases only weakly between 50° and 15°. This may be due, at least in part, to more efficient electron transfer (30) at lower temperature since the rate of autoquenching decreases with temperature and the measured luminescence lifetime of the $^*Ru^{2+}$ state is longer at 15° (0.67 μs) than at 50° (0.39 μs) [56].

5.1.2. *Regeneration of Ru(bipy)*$_3^{2+}$. In order for the ruthenium complex to act as a catalyst, $Ru(bipy)_3^{2+}$ must be regenerated from $Ru(bipy)_3^{3+}$ obtained after oxidative quenching (30). The latter complex is able to oxidize water [51] but the reaction appears not to be efficient enough to allow rapid regeneration of $Ru(bipy)_3^{2+}$ in competition with the highly exoenergetic thermal back transfer reaction (35):

$$Ru(bipy)_3^{3+} + Rh(bipy)_3^{2+} \xrightarrow[-1.94\ eV]{} Ru(bipy)_3^{2+} + Rh(bipy)_3^{3+} \qquad (35)$$

which should be very fast[11]. It is necessary to introduce an electron donor D reacting with $Ru(bipy)_3^{3+}$ faster than water:

$$Ru(bipy)_3^{3+} + D \longrightarrow Ru(bipy)_3^{2+} + D^+ \qquad (36)$$

---

[10] We thank Dr. *E. Amouyal* for performing these measurements.

[11] There might be a kinetic barrier to the back transfer reaction if loss of one (bipy) from $Rh(bipy)_3^{2+}$ (see below) is fast enough to compete with (35), so that the back reaction is not (35) but (37) which may be slower than (35) itself since additional ligand sites have to be occupied:

$$Ru(bipy)_3^{3+} + Rh(bipy)_2^{2+} \xrightarrow[2\,L]{e^-} Ru(bipy)_3^{2+} + Rh(bipy)_2L_2^{3+} \qquad (37)$$

When the tertiary amine TEOA is used as the donor D, its oxidation (31) regenerates $Ru(bipy)_3^{2+}$ at a fast enough rate for the ruthenium cycle to be operative at sufficiently high concentration of the donor. Similar conclusions hold in the case of the $Ru(bipy)_3^{2+}$/methylviologen/TEOA system [78].

5.2. *Role and fate of triethanolamine.* - TEOA is the donor substance providing the electrons which, together with the protons of water, yield the hydrogen gas generated. Its role is primordial from the point of view of both the net process and the kinetics of specific reactions. The key problem is to avoid the reoxidation of $Rh(bipy)_3^{2+}$, generated in reaction (30), by either $Ru(bipy)_3^{3+}$ (equation (35)) or by $TEOA^+$ produced in reaction (31) (equation 38).

$$Rh(bipy)_3^{2+} + TEOA^+ \xrightarrow[-1.49\ eV]{} Rh(bipy)_3^{3+} + TEOA \qquad (38)$$

Reactions (35) and (38) may be prevented or at least repressed 1) if (31) is sufficiently fast with respect to (35), and 2) if D^+, $TEOA^+$, undergoes very fast irreversible decomposition (see equation (13)) so that it disappears from the medium faster than it reacts with $Rh(bipy)_3^{2+}$, eq. (38).

Decomposition of the $TEOA^+$ radical cation follows probably the same scheme as that proposed for tertiary amines in general. Extensive studies of photochemical [107] and electrochemical [108] oxidation of tertiary amines indicate that, in aqueous solution, cleavage of the N–C bond occurs with hydrolysis and formation of a secondary amine and an aldehyde *via* an iminium salt. The mechanism may be written as a two-electron oxidation sequence:

$$R_2\ddot{N}-CH_2-R' \longrightarrow R_2\dot{N}^+-CH_2-R' + e^- \qquad (39)$$

$$R_2\dot{N}^+-CH_2-R' \longrightarrow R_2\ddot{N}-\dot{C}H-R' + H^+ \qquad (40)$$

$$R_2\ddot{N}-\dot{C}H-R' \longrightarrow R_2N^+=CH-R' + e^- \qquad (41)$$

$$R_2N^+=CH-R' + H_2O \longrightarrow R_2NH + R'-CHO + H^+ \qquad (42)$$

In the case of TEOA the rate of the oxidation reaction (31) has been determined [78]:

$$k_{31} = 6.5 \times 10^6 \text{M}^{-1}\text{s}^{-1} \qquad (43)$$

and the overall oxidative decomposition process (39)-(42) is:

$$N(CH_2CH_2OH)_3 + H_2O \longrightarrow HN(CH_2CH_2OH)_2 + CHO-CH_2OH + 2\,H^+ + 2\,e^- \qquad (44)$$

TEOA is thus a *two-electron donor*, in agreement with the result that *more* than half an equivalent of H_2 may be obtained per equivalent of TEOA present at the start of the reaction. The formation of glycolaldehyde has been confirmed by its characteristic colour reaction with diphenylamine (see Experimental Part). The pH effects also indicate that nitrogen is the preferred oxidation site rather than a terminal $-CH_2OH$ group.

One may note that the oxidation potential of TEOA (+0.82 eV) is about the same as that of water. That TEOA is a suitable donor but not H_2O should therefore be ascribed not to thermodynamic, but to mechanistic reasons. The critical step in the sequence (39)-(42) is probably the deprotonation (40). Loss of the proton prevents reoxidation of reduced rhodium species by $TEOA^+$ (38); furthermore, the neutral radical formed has reducing properties, making a second electron available (reaction (41)), a property which may explain the rapid generation of the Rh(I) species from $Rh(bipy)_3^{3+}$ (see reaction (53) below). The existence of a pH optimum for hydrogen generation, at about the pK_a of TEOA, agrees with the operation of opposite effects: at low pH, water reduction is easier, but the oxidation (31) (39) cannot occur when the amine is protonated and the deprotonation step (40) is slowed down. At high enough pH (for instance >10) the reduction potential of water is too low (< -0.6 V) and the proton loss (40) is fast enough to prevent back electron transfer (38), so that the red $Rh(bipy)_2^+$ species accumulates (see below).

At sufficient buffer consumption, the reaction medium is found to become more basic (see Experimental Part); this may arise from the formation of diethanolamine, eq. (44), which has an appreciably higher pK_a (= 9.0 [99]) than TEOA.

5.3. *The Rhodium cycle.* The transformations undergone by the $Rh(bipy)_3^{3+}$ complex form the rhodium cycle *(Fig. 9)* which is the key component of the present system. They are represented in a simplified fashion by *Figure 12* and will be discussed in the present section.

5.3.1. *Properties of* $Rh(bipy)_3^{3+}$. Rhodium(III)-bipyridyl complexes are best prepared by catalytic procedures employing alcohols or stronger reducing agents [109-112]. In the present work $Rh(bipy)_3Cl_3$ (λ_{max} = 305 nm, $\varepsilon \sim 36000$ and 318 nm,

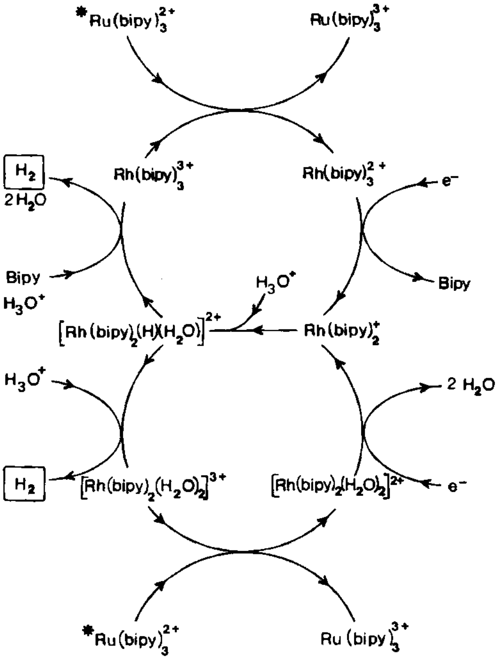


Fig. 12. *Schematic representation of the Rhodium cycle; top:* $Rh(bipy)_3^{3+}$ cycle; *bottom:* cycle of the rhodium-bis(bipy)-species; this is only a simplified diagram since a number of other transformations are not represented, like H_2 formation on Pt° catalyst, reactions (56) and (57); or regeneration of $Rh(bipy)_3^{3+}$ from the rhodium(bipy)$_2$ species, reaction (63); or the participation of the $[Rh(bipy)_2(OH)_2]^+$ species, *etc.* At neutral pH and in presence of excess bipyridine the process follows the top cycle (see text).

$\varepsilon \sim 38000$; *Fig. 14*) [112-114] has been obtained smoothly by heating aqueous $RhCl_3$ and bipyridine in presence of TEOA in air; under these conditions it forms even when there is a defect in ligand.

The *electrochemistry* of $Rh(bipy)_3Cl_3$ in acetonitrile shows the uptake of up to four electrons at -0.86, -1.00, -1.49 and -1.71 V *vs.* SCE; the first two steps are reversible and each is followed by a ligand elimination reaction [94]:

$$Rh(bipy)_3^{3+} \xrightarrow[-0.86\ V]{} Rh(bipy)_3^{2+} \tag{45}$$

$$Rh(bipy)_3^{2+} \xrightarrow[Y]{fast} Rh(bipy)_2Y^{2+} + bipy \tag{46}$$

$$Rh(bipy)_2Y^{2+} \xrightarrow[-1.00\ V]{} Rh(bipy)_2Y^{+} \tag{47}$$

$$Rh(bipy)_2Y^{+} \xrightarrow[fast]{} Rh(bipy)_2^{+} + Y \tag{48}$$

$$(\text{with } Y = CH_3CN)$$

Polarographic and coulometric measurements [95][12]) in aqueous solution at pH 10 indicate that $Rh(bipy)_3^{3+}$ sulfate undergoes a *dielectronic* reduction at -0.67 V giving a red solution ($\lambda_{max} = 520$ nm, $\varepsilon = 4800$). The reduction potential is the same at pH 7.0 but a brownish solution is obtained. These electrochemical results and other data (see below) indicate that the species formed is the complex $Rh(bipy)_2^+$.

$$Rh(bipy)_3^{3+} + 2\,e^- \xrightarrow[-0.67\ V]{} Rh(bipy)_2^{+} + (bipy) \tag{49}$$

$$(\lambda_{max} = 305{,}318\ nm \qquad 520\ nm \qquad 280\ nm)$$

The loss of a (bipy) ligand in reaction (49) is confirmed by the fact that the reduction potential becomes slightly more negative on addition of free bipyridine (by about 30 mV with a tenfold excess of ligand [95]).

Chemical reduction of $Rh(bipy)_3Cl_3$ and $[Rh(bipy)_2Cl_2]Cl$ yields $Rh(bipy)_2^+$, whose visible spectrum in aqueous methanol has been reported [115] to contain two bands at about 520 and 557 nm (see however below[13])). There is little evidence

---

[12]) We thank Prof. *M. Gross* and Dr. *J. P. Gisselbrecht* for performing these measurements.

[13]) There is no absorption band at 557 nm. However when the same experiment is performed in aqueous ethanol both 520 and 557 nm bands reported for $Rh(bipy)_2^+$ [115] are observed. When an aqueous TEOA/$Rh(bipy)_3Cl_3$ solution (pH 10) is irradiated with UV. light the solution becomes deep red and a dark violet film deposits on the cell wall. The visible spectrum contains two bands at 520 and 570 nm and is similar to the 520-557 nm spectrum published for the reported 'red violet solution' in 25% aqueous ethanol and attributed to $Rh(bipy)_2^+$ [115]. Contact with air regenerates the initial $Rh(bipy)_3^{3+}$ spectrum. Separation of the red solution and of the violet film shows that the solution absorbs at about 515 nm and the film at 570 nm. The shift of one band from 557 nm to 570 nm may be an effect of counterion, solvent, solid state *etc.* Violet crystals of $[Rh(bipy)_2]ClO_4, 2\,H_2O$ have been isolated [116a].

for Rh(II) complexes with bipyridine ligands [116b]. Rh-pyridine complexes first considered to be Rh(III) were shown to be in fact Rh(III) [110]. Rh(III) and Rh(I) bipyridine complexes are diamagnetic, whereas mononuclear Rh(II) species are expected to be paramagnetic.

5.3.2. *Photochemical reduction of Rh(bipy)$_3^{3+}$. Formation of Rh(bipy)$_2^+$ and of rhodium hydrides. At basic pH* (> 10), irradiation with visible light of aqueous solutions containing TEOA/Ru(bipy)$_3^{2+}$/Rh(bipy)$_3^{3+}$ leads to the appearance of an intense red colour within a few minutes (λ_{max} = 520 nm)[13]. Simultaneously one observes in the UV. spectrum the disappearance of Rh(bipy)$_3^{3+}$ (at 305 and 318 nm) and the formation of free bipyridine (characteristic absorption at 280 nm). The red species is very air sensitive; its formation and air oxidation with regeneration of the Rh(bipy)$_3^{3+}$ complex, can be repeated many times without any apparent decomposition *(Fig. 13)*.

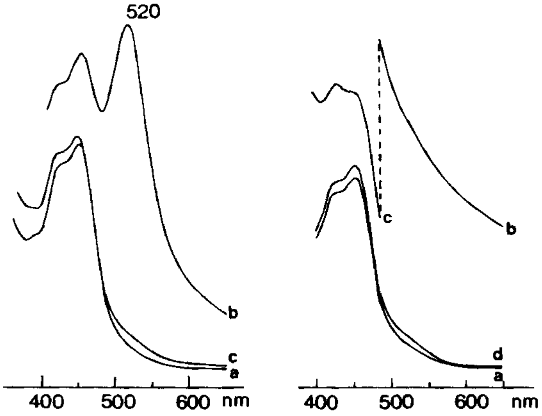


Fig. 13. *Photoreduction of the Rh(bipy)$_3^{3+}$ complex by visible light irradiation of aqueous triethanolamine solutions at pH = 10.5 (left) and 8.0 (right) in presence of Ru(bipy)$_3^{2+}$ as photosensitizer.* Visible absorption spectra in the following conditions, *left:* (a) initial spectrum, (b) after 3 min. irradiation; (c) after exposure of the irradiated solution (b) to air; *right:* (a) initial spectrum, (b), (c) after 5 min. irradiation, portion (c) displaced by − 0.5 in optical density; (d) after exposure to a stream of air. The absorptions at about 450 nm and 520 nm are due to the Ru(bipy)$_3^{2+}$ and Rh(bipy)$_2^+$ complexes respectively

The ^{1}H-NMR. spectrum of the red solution also indicates the formation of free bipyridine. These results together with the electrochemical data (see above) and studies on reduced rhodium-bipyridine complexes [115] lead to the conclusion that the red substance is a diamagnetic Rh(I) complex containing two ligand molecules, *i.e.* the tetracoordinated Rh(bipy)$_2^+$ species.

At neutral pH ~ *7-8,* the same irradiation experiment gives quite different results; the solution turns dark and a brown precipitate is formed which qualitatively ressembles the brown, insoluble products considered to be rhodium hydrides [97] [110] [111] [115]. The electronic spectrum of the mixture displays a broad absorption, rising below 500 nm into the UV., which is comparable to that described for the brown solutions of hydridorhodium species obtained by borohydride reduction of rhodium(III)-pyridine complexes [110]. On contact with air Rh(bipy)$_3^{3+}$ is regenerated quantitatively from the brown solution-suspension. When a photochemically generated basic solution of Rh(bipy)$_2^+$ is brought to pH ~ 7, the same brown mixture is obtained; it is unstable at this pH and decomposes slowly with formation of hydrogen gas.

These results support the idea that at neutral pH, the photochemical reaction yields *rhodium hydrides via* $Rh(bipy)_2^+$:

$$\begin{tikzcd}
Rh(bipy)_2^+ + H_3O^+ \arrow[r] & {[RhH(bipy)_2(H_2O)]^{2+}} \arrow[d, shift left, "-H^+"] & (50) \\
Rh(bipy)_2^+ + H_2O \arrow[r] & {[RhH(bipy)_2(OH)]^+} \arrow[u, shift left, "H^+"] & (51)
\end{tikzcd}$$

A further indication in favour of the occurence of rhodium hydrides comes from the observation that addition of base (pH ~ 11) to a brown suspension produces a red solution of $Rh(bipy)_2^+$, which may result from deprotonation of the hydride and loss of hydroxide ion. These changes in colour and in absorption spectrum can be produced reversibly on modification of the pH; they are best observed on the brown solutions obtained by UV. irradiation of $Rh(bipy)_3^{3+}$/TEOA (pH = 7.5) solutions (see below), rather than on those resulting from visible irradiation of solutions containing also $Ru(bipy)_3^{2+}$, whose colour and absorption bands obscure the changes to some extent[14]).

Finally, whereas polarographic reduction of $Rh(bipy)_3^{3+}$ to $Rh(bipy)_2^+$ occurs at the same potential at pH = 10.7 and 7.0, the third reduction step is markedly pH dependent being −1.15 V at pH = 10.7 and −0.90 V at pH = 7.0 [95], a result which again is indication for hydride formation.

Since the $Ru(bipy)_3^{2+}$-PS is a single electron transfer agent it is expected to generate first a rhodium (II) complex (reaction (30)). Therefore the formation of the Rh(I) species $Rh(bipy)_2^+$, involved in the reaction, requires a second electron. This may occur in several ways[15]):
from a second *PS species:

$$^*Ru(bipy)_3^{2+} + Rh(bipy)_2Y^{2+} \longrightarrow Ru(bipy)_3^{3+} + Rh(bipy)_2Y^+ \qquad (52)$$

from the radical formed in reaction (40):

$$Rh(bipy)_2Y^{2+} + R_2\ddot{N}-\dot{C}H-R' \longrightarrow Rh(bipy)_2Y^+ + R_2\overset{+}{N}=CH-R' \qquad (53)$$

by dismutation:

$$2\,Rh(bipy)_2Y^{2+} \longrightarrow Rh(bipy)_2Y^{3+} + Rh(bipy)_2Y^+ \qquad (54)$$

$Rh(bipy)_2Y^+$ is expected to rapidly loose $Y = H_2O$ forming $Rh(bipy)_2^+$, see eq. (48).

---

[14]) We were unable to detect the Rh-H group by either proton NMR. or IR. spectroscopy, even when more soluble brown compounds were prepared by repeating the experiments with Rh(batophen-S)$_3^{3-}$ in place of $Rh(bipy)_3^{3+}$(bathophen-S)(=4,7-diphenyl-1,10-phenanthroline-4',4''-disulfonate).

[15]) The species $Rh(bipy)_2Y^{2+}$ results from $Rh(bipy)_3^{2+}$, formed in the oxidative quenching reaction (30), by fast loss of a (bipy) unit and coordination of a solvent ($Y = H_2O$) molecule, by analogy with the electrochemical results in acetonitrile, equation (46). In the initial stage, $Rh(bipy)_3^{2+}$ might first form $[Rh(bipy)_2(bipy)_{sesqui}]^{2+}$ where $(bipy)_{sesqui}$ denotes a monodentate (bipy) ligand as found in iridium(III)-bipyridine chemistry [117].

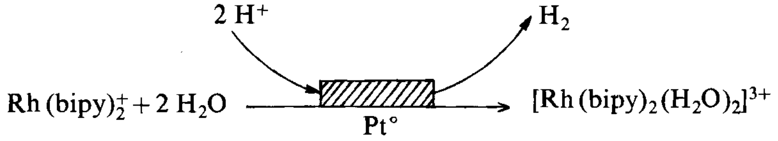
In view of the strong reducing character of the radicals obtained by reduction of iminium salts (about −1.5 V [119]) reaction (53) appears to be the preferred pathway, in agreement also with the fact that TEOA provides two electrons to the overall process (see above). Rates of dismutation (54) are not known but fast dismutation of Rh(II)-bipyridine complexes has been reported [115]. Contribution of reaction (52) would require sufficient stationary concentrations of the two species. Flash photolysis experiments could yield interesting data on the formation and fate of the Rh(II) complex in reaction (30).

5.3.3. *Pathways for hydrogen formation.* An important property of the $Rh(bipy)_3^{3+}$ complex is that it accumulates *two electrons* on reduction to $Rh(bipy)_2^+$. Thus, whereas the monoelectronic reduction of water, eq. (4), is thermodynamically forbidden for species with reduction potentials > -2.5 V, the formally dielectronic process (55) is allowed at pH 7:

$$Rh(bipy)_2^+ + 2\,H_3O^+ \xrightarrow[-0.26\,V]{} [Rh(bipy)_2(H_2O)_2]^{3+} + H_2 \qquad (55)$$

The fate of the $Rh(bipy)_2^+$ species may follow two paths:

i) discharging the two electrons at the Pt° redox catalyst where they combine with two protons and form hydrogen:



$$Rh(bipy)_2^+ + 2\,H_2O \xrightarrow[Pt^\circ]{2\,H^+ \;\to\; H_2} [Rh(bipy)_2(H_2O)_2]^{3+} \qquad (56)$$

ii) forming, *via* reactions (50) (51), an intermediate Rh(III) hydride which subsequently decomposes by reaction with H_3O^+ either in solution or at the Pt° surface:

$$[RhH(bipy)_2(H_2O)]^{2+} + H_3O^+ \xrightarrow[(Pt^\circ)]{} [Rh(bipy)_2(H_2O)_2]^{3+} + H_2 \qquad (57)$$

Equation (57) is mechanistically a true *dielectronic reduction* process since it formally involves the $H^- + H^+ \longrightarrow H_2$ reaction. In the Pt° catalyzed process (56), the successive addition of two protons may involve a short lived intermediate hydride type equivalent.

5.3.4. *Properties and role of $[Rh(III)(bipy)_2LL']^{n+}$ ($L, L' = H_2O, OH^-$) complexes.* Since both reactions (56) and (57) involve $[Rh(bipy)_2(H_2O)_2]^{3+}$ as an intermediate, its eventual participation in the rhodium cycle has been investigated. Heating $Rh(bipy)_3Cl_3$ in basic aqueous ethanol solution converts progressively the 305/318 nm UV. spectrum into a 301/311 spectrum with release of one bipyridine ligand (absorption at 280 nm) which may be extracted with ether (*Fig. 14*). That the 301/311 species thus obtained is a bis-hydroxo complex, is confirmed by the reversible, pH dependent spectral changes: 301/311 nm bands and yellow colour at basic pH; 304/317 nm bands and colourless solution at acid pH (see *Fig. 14*). The pK_a's for reactions (58) and (59) have been determined:

$$[Rh(bipy)_2(H_2O)_2]^{3+} \rightleftharpoons [Rh(bipy)_2(OH)(H_2O)]^{2+} + H^+ \qquad pK_a = 4.4 \qquad (58)$$

$$[Rh(bipy)_2(OH)(H_2O)]^{2+} \rightleftharpoons [Rh(bipy)_2(OH)_2]^+ + H^+ \qquad pK_a = 6.4 \qquad (59)$$

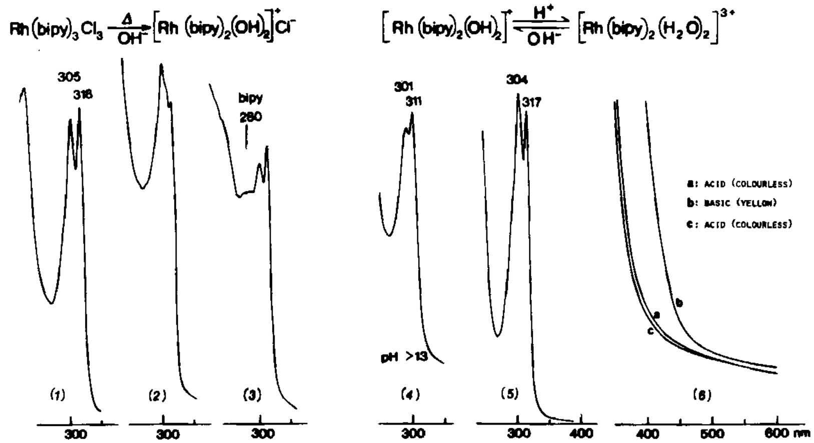


Fig. 14. *Spectroscopic observation of the formation of* $[Rh(bipy)_2(OH)_2]^+$ *from* $Rh(bipy)_3^{3+}$ in basic ethanol/water solution (pH > 13); (1): initial spectrum of $Rh(bipy)_3Cl_3$; (2), (3): spectra observed after heating solution (1) to 80° for 10 min and 30 min respectively, with formation of free bipyridine observed at 280 nm; (4): UV. spectrum of $[Rh(bipy)_2(OH)_2]^+$ after ether extraction of (bipy) from solution (3); (5): UV. spectrum of $[Rh(bipy)_2(H_2O)_2]^{3+}$ obtained by acidification of solution (4); (6): visible absorption spectra of the reversibly interconvertible aquo-hydroxo-rhodium$(bipy)_2$ species

The perchlorate of the (bis-aquo) and (bis-hydroxo) forms have been isolated, crystallized and characterized. Analogous pH dependence and spectral changes occur for the iridium complex $[Ir(bipy)_2(H_2O)_2]^{3+}$ ($pK_a = 3.9$ and 5.9) [117].

A *Stern-Volmer* study indicates that the quenching of the $^*Ru(bipy)_3^{2+}$ luminescence by $[Rh(bipy)_2(OH)_2]^+$, eq. (60), is much slower than quenching by $Rh(bipy)_3^{3+}$ (equations (30) and (34)):

$$^*Ru(bipy)_3^{2+} + [Rh(bipy)_2(OH)_2]^+ \longrightarrow Ru(bipy)_3^{3+} + [Rh(bipy)_2(OH)_2] \quad (60)$$

$$k_{60} = 5.2 \pm 0.7 \times 10^7 \text{M}^{-1}\text{s}^{-1} \text{ (at pH} = 7.1)$$

On the other hand, quenching by the bis(aquo) species $[Rh(bipy)_2(H_2O)_2]^{3+}$, eq. (61), and by $Rh(bipy)_3^{3+}$ occurs at about the same rate.

$$^*Ru(bipy)_3^{2+} + [Rh(bipy)_2(H_2O)_2]^{3+} \longrightarrow Ru(bipy)_3^{3+} + [Rh(bipy)_2(H_2O)_2]^{2+} \quad (61)$$

$$k_{61} = 3.2 \pm 0.5 \times 10^8 \text{M}^{-1}\text{s}^{-1} \text{ (at pH} = 3).$$

Visible light *irradiation of basic (pH ~ 10) solutions* containing $Ru(bipy)_3^{2+}$/$[Rh(bipy)_2(OH)_2]^+$/TEOA yields the red species $Rh(bipy)_2^+$ but the reduction is slower than with $Rh(bipy)_3^{3+}$ in the same conditions, in agreement with the respective quenching efficiencies of the two species.

In neutral solution, irradiation of the same system leads to the brown substances believed to be rhodium hydrides, but no hydrogen is detected even in presence of colloïdal Pt. However, the brown deposits do not form and hydrogen is evolved by irradiating $Ru(bipy)_3^{2+}/[Rh(bipy)_2(OH)_2]^+$ solutions: a) at slightly acidic pH (~5.5), with the donor EDTA (see below) instead of TEOA; b) at neutral pH with TEOA donor and in presence of *1 equivalent of (bipy)* with respect to the rhodium species. In case a), the lower pH makes water reduction easier. In case b), the rate of H_2 formation is about the same as when $Rh(bipy)_3^{3+}$ is used instead of the rhodium-bis(bipy) + (bipy) combination. This requirement for an additional (bipy) molecule points to the regeneration of the $Rh(bipy)_3^{3+}$ species by the overall reaction (62):

$$[Rh(bipy)_2L, L']^{n+} + (bipy) \longrightarrow Rh(bipy)_3^{3+} + L + L' \qquad (62)$$

Indeed, when $[Rh(bipy)_2(OH)_2]^+ClO_4^-$ is irradiated with visible light in presence of $Ru(bipy)_3SO_4$ sensitizer and excess bipyridine ligand in a TEOA-Phosphate buffer at pH 7.0 (*i.e.* in H_2-generating conditions except for the absence of Pt catalyst), the initial 301/311 nm spectrum changes to the 305/318 nm spectrum of $Rh(bipy)_3^{3+}$. This process may be similar to that by which $Rh(bipy)_3^{3+}$ is formed thermally in the presence of catalytic amounts of a reducing agent [109-112], which in the present case is photochemically generated; the take-up of the third (bipy) may occur through reduced rhodium intermediates, see eq. (60), (61) and (63).

The generation of hydrogen solely *via* rhodium-bis(bipy) species is represented schematically in the bottom cycle of *Figure 12*. However the above results show that this cycle requires acidic pH (< ~6.0) with EDTA as donor, and does not operate significantly at pH = 7 with TEOA.

5.3.5. *Role of bipyridine.* The results described in the previous section indicate the *requirement of at least three (bipy) units per rhodium cation* for efficient hydrogen generation at neutral pH, as is the case with the reference system. Addition of *excess (bipy)* markedly accelerates hydrogen generation at neutral pH *(Table 1; Fig. 7)* and allows operation at basic pH (~8.5). Thus the $Rh(bipy)_3^{3+}$ species represents the minimum requirement and excess (bipy) catalyzes the process.

In the hydrogen formation pathways (56) and (57), the $[Rh(bipy)_2(H_2O)_2]^{3+}$ complex produced may be converted back to $Rh(bipy)_3^{3+}$ by reaction (62). In presence of excess (bipy), hydrogen evolution could occur with simultaneous regeneration of $Rh(bipy)_3^{3+}$ according to the net reaction (63).

$$Rh(bipy)_2^+ + (bipy) + 2\,H_3O^+ \longrightarrow Rh(bipy)_3^{3+} + 2\,H_2O + H_2 \qquad (63)$$

It may proceed first through $[RhH(bipy)_2(H_2O)]^{2+}$ (equation (50)) followed by $[RhH(bipy)_2(bipy)_{sesqui}]^{2+}$ *via* ligand exchange[15]).

Furthermore, the addition of excess (bipy) renders the reduction potential of $Rh(bipy)_2^+$ more negative (see above), and thus facilitates water reduction for purely thermodynamic reasons.

The formation of hydrogen with regeneration of $Rh(bipy)_3^{3+}$ and catalysis by free (bipy) is described by the top cycle of *Figure 12*.

5.3.6. *Conclusion.* The various reactions discussed above are represented in a simplified fashion by the schematic rhodium catalytic process depicted in *Figure 12*. The two cycles shown may contribute and interfere depending on conditions (especially pH). However at neutral pH or above and in presence of excess free (bipy), hydrogen generation is most efficient and is expected to proceed almost exclusively *via* routes involving (bipy) as in the *top catalytic cycle* of *Figure 12.*

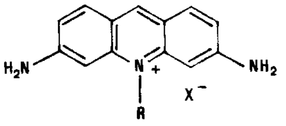
6. Role of the Platinum catalyst. - *In situ* reduction of K_2PtCl_4 during the induction period of the reaction is expected to give colloïdal platinum and accounts for the short induction period observed before hydrogen evolution occurs. $^*Ru(bipy)_3^{2+}$ itself or any of the reduced Rh(II) or Rh(I) species may effect this reduction since the redox potential is $E_0(PtCl_4^{2-}/Pt^\circ) = +0.73$ V [118]. The presence of this highly divided catalytic surface strongly accelerates hydrogen formation at $pH = 7.0$ (*exper. 2* and *3, Table 1;* acceleration factor of about 20). The rate is however little affected by the amount of Pt(II) salt added initially; in an experiment carried out with 2.5 times more platinum than experiment 1 *(Table 1)*, the other experimental conditions being identical, the observed rate of hydrogen formation was only ~25% higher than for experiment 1 itself.

Pt° may function as redox catalyst *via* reaction (56) or by facilitating the decomposition of intermediate rhodium hydrides (equation (57)). Other catalyst species like polymer bound platinum and gold [77a] or PtO_2 [78] may also be used for similar purposes[16].

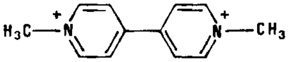
The hydrogen generation is however quite efficient *in absence of Pt°* at $pH < 5.5$ (see *Table 2*; exper. 19); since TEOA is protonated at low pH it no longer acts as electron donor and tertiary amines of lower pK_a like EDTA have to be used. At such pH the reduction potential of water is less negative (> -0.33 V) and protonation reactions like (50), (56), (57), (63) are faster.

7. Hydrogen generation with modified systems. - We have performed a number of modifications on the reference system $PS/R/D/C = Ru(bipy)_3^{2+}/Rh(bipy)_3^{3+}/$ TEOA/colloïdal Pt, replacing a given component by another one in order to uncover other hydrogen generating systems. A number of experiments are listed in *Table 2.* Although the data available are less detailed at present, we feel that, because of the routes which they indicate and the optimizations which may be conducted, it is desirable to describe briefly these results.

7.1. *Modified systems: Photosensitizers.* Whereas hydrogen is produced when $Ru(bipy)_3^{2+}$ is replaced by *Ru(phen)*$_3^{2+}$ (phen = ortho-phenanthroline) in the same conditions, this is not the case with *Os(bipy)*$_3^{2+}$[17].



R = H: PFH^+
R = CH_3: AF



MV^{2+}

---

[16] It has been noted that pieces of bright platinum markedly speed up the oxidation of Rh(I)-bipyridine complexes by ceric ammonium sulfate [115]; see also note 4.

[17] In view of the redox potentials, $E_0(Os(bipy)_3^{3+}/^*Os(bipy)_3^{2+}) = -1.02$ V and $Os(bipy)_3^{3+}/Os(bipy)_3^{2+} = +0.83$ V [66], oxidative quenching of $^*Os(bipy)_3^{2+}$ by $Rh(bipy)_3^{3+}$ should occur but reduction of $Os(bipy)_3^{3+}$ thus obtained by TEOA (*cf.* eq. (31)) may be too slow, so that the back reaction analogous to (35) dominates.

Table 2. *Hydrogen generation by irradiation*

Experiment No	Photosensitizer (conc. $10^4 \times$ M)	$Rh(bipy)_3^{3+}$ conc. $10^3 \times$ M	Added (bipy) conc. $10^3 \times$ M	K_2PtCl_4 conc. $10^4 \times$ M	Electron Donor (pH; conc. M)
13	$Ru(bipy)_3^{2+}$ (17.6)	2.05	53	4.8	TEOA (6.9; 0.4)
14	Proflavine (3.2)	0.85	52	3.6	TEOA (6.9; 0.4)
15	Proflavine (0.31)	0.47	48	4.8	TEOA (6.9; 0.4)
16	Proflavine (0.99)	1.03	1.33	1.0	TEOA (7.2; 0.2)
17	Acriflavine (15.4)	2.15	2.2	4.3	TEOA (6.9; 0.4)
18[d])	Proflavine (0.49)	0.42[d])	0.27[d])	2.6	TEOA (7.2; 0.1)
19	$Ru(bipy)_3^{2+}$ (4.4)	1.56	-	-	EDTA (5.2; 0.2)
20	$Ru(bipy)_3^{2+}$ (3.9)	1.57	3.2	7.2	EDTA (5.2; 0.2)
21[e])	-	4.3	5.1	4.8	TEOA (7.1; 0.16)
22[f])	-	5.7	7.7	4.8	EDTA (5.2; 0.2)
23[g])	$Ru(bipy)_3^{2+}$ (1.29)	0.65	2.0	1.44	TEOA (7.2; 0.1)

[a]) PS: photosensitizer; R: relay species, a $Rh(bipy)_3^{3+}$ type complex; D: electron donor, TEOA or EDTA; C: platinum redox catalyst. For experimental details, see experimental section.

[b]) See *Table 1*, note b).

[c]) The (*TO*) values are indicated as defined in the text, equation (24).

Acridine dyes like *proflavine* (PF) and *acriflavine* (AF), which have been extensively used in various photosensitisation reactions (photoreductions [89] [120-122], electrode processes [101], *etc.*), are also suitable PS-components. At low concentrations PF is a PS about *as efficient* as $Ru(bipy)_3^{2+}$ in terms of hydrogen evolution rates and turnover numbers (*Table 2*, exper. 14-16, compare to exper. 13). Acriflavine is much less satisfactory (*Table 2*, exper. 17).

According to literature reports, photoexcited proflavine oxidizes donors like EDTA [89] [120-122] or TEOA [90] forming $PFH^{\cdot}$, which reduces organic acceptors like methylviologen MV^{2+}; it may also reduce $Rh(bipy)_3^{3+}$ but probably not $Rh(dmbp)_3^{3+}$ (see below), unless sufficient $PFH^{\cdot}$ accumulates and/or PFH_2 is formed by further reduction[18]). On the other hand, photoexcited acridine orange has been shown to form either an oxidized or a reduced species depending on whether the irradiation is performed in presence of an electron acceptor or an electron donor respectively; proflavine may behave similarly [125]. Luminescence quenching and flash photolysis experiments should help clarifying the mechanism of the present process.

7.2. *Modified systems: Relay species.* - 7.2.1. *Rhodium complexes.* Hydrogen is evolved when $Rh(bipy)_3^{3+}$ is replaced by *Rh(phen)*$_3^{3+}$ but not when *Rh(dmbp)*$_3^{3+}$ is used in the reference conditions. The latter is more difficult to reduce than $Rh(bipy)_3^{3+}$ by about 0.2 V, E_0 ($Rh(dmbp)_3^{3+}/Rh(dmbp)_3^{2+}$) $= -0.90$ V [95][8,12]). A *Stern-Volmer* plot shows that quenching of $^*Ru(bipy)_3^{2+}$ by $Rh(dmbp)_3^{3+}$

---

[18]) Redox potentials: $E_0(PFH^+/PFH^{\cdot}) = -0.73$, $E_0(PFH^{\cdot}/PFH_2) = -1.06$ V [123], $E_0(MV^{2+}/MV^+) = -0.44$ V [89] [124].

of modified PS/R/D/C systems[a])

Volume of irradiated solution, ml (temperature)	Rate of H_2 formation (ml/h)[b])	Total volume of H_2 produced (ml) (irradiation time (h))	Turnover values (*TO*)[c])		
			Photosensitizer	$Rh(bipy)_3^{3+}$	added (bipy)
10 (50°)	13	11 (2.5)	26	22	0.9
10 (50°)	7	10.5 (3)	140	50	0.8
10 (40°)	2.3	16 (8)	2100	140	1.5
1250 (30°)	20	300 (24)	100	9.5	8
10 (50°)	1.5	3.1 (5)	8	6	6
10 (40°)	1.8	5.2 (5)	450	51[d])	80[d])
7 (30°)	1	1.6 (3)	22	6	-
10 (50°)	2	5.4 (3)	64	16	8
2.5 (30°)	0.2	0.85 (5)	-	3	~ 3
2.5 (25°)	0.25	0.4 (1.8)	-	~ 1	~ 1
10 (30°)	0.6	2.2 (6)	77	15	3

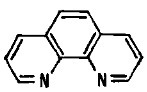
[d]) For experiment 18, 4,4′-dimethyl bipyridine (dmbp) is used instead of (bipy), the rhodium(III) complex being $Rh(dmbp)_3^{3+}$.

[e]) Irradiation with UV. light ($\lambda > 300$) in a quartz vessel.

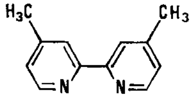
[f]) Irradiation with diffuse sunlight in a quartz vessel.

[g]) Irradiation with diffuse sunlight in a pyrex vessel.

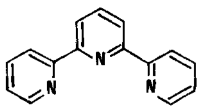
($k = 7 \pm 1 \times 10^7 M^{-1}s^{-1}$) is five times slower than quenching by $Rh(bipy)_3^{3+}$ (34). However, when $Rh(dmbp)_3^{3+}$ is used in conjunction with PF as sensitizer instead of $Ru(bipy)_3^{2+}$, efficient H_2 formation occurs (exper. 18, *Table 2*). Like in the PF/$Rh(bipy)_3^{3+}$ case above, the mechanism of the process is still unclear and further studies are required.



(phen)
ortho-phenanthroline



(dmbp)
4,4′-dimethyl-2,2′-bipyridine



(terpy)
2,2′,6′,2″-terpyridine

With *Rh(terpy)$_3^{3+}$* photoreduction occurs but no H_2 formation. One obtains a dark-blue, unidentified reduced species *(Fig. 15)* of low solubility, whose colour is not affected by pH and which regenerates the starting substance on air oxidation. The redox properties of the complex and/or the stronger coordination of (terpy) may be unsuitable for H_2 generation. The behaviour of $[Rh(bipy)_2(OH)_2]$ has been discussed above. *[Rh(bipy)$_2$Cl$_2$]$^+$* does not allow hydrogen generation unless it is transformed *in situ* into the bis-hydroxo species and excess (bipy) is present.

7.2.2. *Cobalt-bipyridine complexes.* Irradiation of a solution containing $Ru(bipy)_3^{2+}$, K_2PtCl_4, TEOA, $CoCl_2$ and 3 (bipy) at basic pH (> 10) yields a very air sensitive deep blue-green solution[19]). The electronic absorption spectrum contains bands at 520 and 640 nm *(Fig. 15)*; by analogy with literature data the latter may be attributed to $Co(bipy)_3^+$ [126] [127]; the former might be a $[Co(bipy)_2LL']^+$ species.

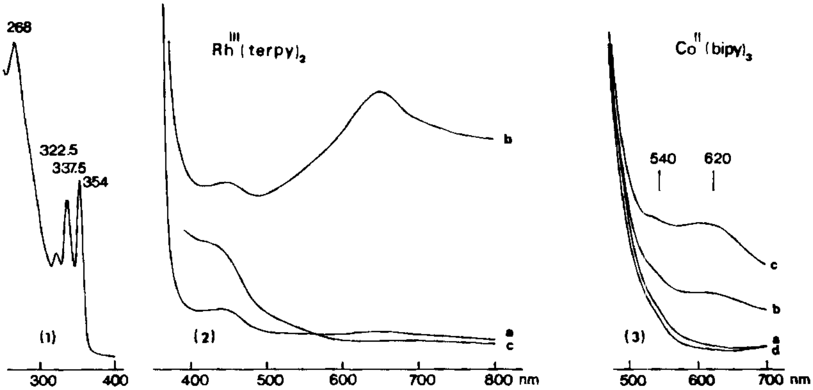


Fig. 15. *Absorption spectra and photoreduction of $Rh(terpy)_2Cl_3$ and Co(II)-bipyridine species;* (1): UV. spectrum of $Rh(terpy)_2Cl_3$ in aqueous triethanolamine solution. (2): Visible spectrum of solution (1); (a) initial; (b) after irradiation with visible light for 5 min; (c) after exposure of solution (b) to air. (3): visible spectrum of an aqueous triethanolamine solution containing $CoCl_2$, bipyridine (3 equiv.) and $Ru(bipy)_3Cl_2$ at pH = 10; (b), (c) spectra of solution (a) after 10 min and 20 min irradiation with visible light; (d) spectrum after exposure of solution (c) to air. The bands at 540 nm and 620 might correspond to Co(I)-$(bipy)_2$ and -$(bipy)_3$ species respectively.

In protic solution, Co(I) complexes are known to form hydrides [100] [126] whose decomposition to yield H_2 [128] is catalyzed by Pt° [100]. Indeed, when the same irradiation experiment as above is conducted in presence of K_2PtCl_4 at a pH between 8.5 and 12.5, hydrogen is produced. Thus with this system water reduction occurs *even at basic pH*; however, at present, the reaction is much less efficient and the number of catalytic cycles is much lower (a few units only) than when $Rh(bipy)_3^{3+}$ is used. Improvements in reaction conditions are being investigated.

7.2.3. *Cu(I)-bipyridine species* are obtained on irradiation of $Ru(bipy)_3^{2+}/CuCl_2$, 2 (bipy)/TEOA solutions at neutral or basic pH.

7.2.4. A number of experiments have also been performed with *methylviologen* MV^{2+} as acceptor, giving the blue radical cation MV^+. Like the formation of red $Rh(bipy)_2^+$, the blue MV^+ was used as a test for the occurrence of electron transfer, the accumulation of a reduced species (however of less negative potential than Rh(I)) and hydrogen generating capabilities. In view of the extensive work on the photosensitized reduction of MV^{2+} [13] [75–78] [89] only a few of our own results are briefly mentioned. Under irradiation with visible light and with the following substances as PS: PF, $Ru(bipy)_3^{2+}$, $Os(bipy)_3^{2+}$, meso-tetra (4-sulfonatophenyl)-

---

[19]) The complexes $Co(bipy)_2X_2$ and $Co(bipy)_3^{2+}$ form rapidly *in situ*.

porphine or its Zn(II) complex, MV^+ has been formed from donors like TEOA, EDTA (pH 5.0), $HSCH_2CH_2OH$ (pH 7.2), $HSCH_2COOH$ (pH 5.3), thiophenol in toluene (as a phase transfer experiment) etc.

7.3. Modified systems. Electron donors. Since the electron donor is consumed in the hydrogen generation process its role is of fundamental importance both for mechanistic as well as for practical reasons. The reduction of $Ru(bipy)_3^{3+}$ by D, eq. (36), should be thermodynamically feasible ($D^+/D < +1.2$ V) and kinetically fast enough, so as to overcome the return reaction (35). The back reactions due to D^+, *i.e.* oxidation of $^*Ru(bipy)_3^{2+}$ or of reduced rhodium-bipyridine species by accumulated D^+, may be prevented a) if D^+transforms rapidly into weaker oxidants; b) if there is a *kinetic barrier* to such processes, due for instance to the physical separation of the reaction species as in systems involving membrane [13] [129] or micellar [8] [130] phases, or solid state surfaces (electrodes) [6] [101]. A complete water photodissociation process would be realized if D^+ were reduced back to D by rapid oxidation of water with formation of O_2, equation (14).

Hydrogen generation with other donors than TEOA may be observed with tertiary amines of low pK_a like *N*-ethyl morpholine ($pK_a \sim 6.8$) or EDTA (see *Table 2*, exper. 19 and 20). Indeed, a sufficient amount of unprotonated nitrogen should be present at a pH where water reduction is feasible with the reduced rhodium species. With EDTA, hydrogen is evolved at pH 5.2 even in absence of platinum catalyst (*Table 2*, exper. 19). The oxidation of EDTA by $Ru(bipy)_3^{3+}$ probably follows a pathway similar to those proposed for its photooxidation by metal cations [131], methylene blue [132] or riboflavin [133].

Photoproduction of $Rh(bipy)_2^+$. Amines of high pK_a are only able to function as donors at high pH where they are substantially unprotonated. Visible light irradiation of solutions of $Ru(bipy)_3^{2+}$ and $Rh(bipy)_3^{3+}$ at pH ~ 10 in presence of donors leads to the rapid accumulation of the red $Rh(bipy)_2^+$ species; acidification of the solution then yields small quantities of hydrogen. The following donors were found to be suitable: TEOA, tertiary amines of high pK_a like NMe_3, NEt_3, *N*-methylpiperidine, *N*-methylpyrrolidine, dimethylaniline; secondary amines like $NHMe_2$ and (L)-proline methylester; *glucose*.

8. Photoreduction and hydrogen generation experiments in absence of photosensitizer. - 8.1. *Redox properties of* $Rh(bipy)_3^{n+}$ *species.* Photophysical studies of several rhodium(III)-bipyridine complexes have shown that excitation at $\lambda = 330$ nm yields a ligand centered (π-π^*) excited state which has a long lifetime at low temperature and luminescence at $\lambda_{max} = 450$ nm [63] [114]. With $\nu_0 = 22.25$ kK, the excited state is 2.75 eV higher in energy and 2.75 V more oxidant than the ground state, $E_0(^*Rh(bipy)_3^{3+}/Rh(bipy)_3^{2+}) = 2.1$ V (see footnote[8]) and *Fig. 2* and *8*). $^*Rh(bipy)_3^{3+}$ is thus a strong oxidant, much stronger than $^*Ru(bipy)_3^{2+}$ (*Fig. 2*), which is capable of reactions with compounds more difficult to oxidize than tertiary amines.

We have performed a number of irradiation experiments of $Rh(bipy)_3^{3+}$ solutions in absence of any PS.

8.2. *Photoreduction of* $Rh(bipy)_3^{3+}$ *by irradiation with UV. light.* Irradiation of aqueous solutions of $Rh(bipy)_3^{3+}$ with UV. light ($\lambda > 300$ nm) in presence of a donor rapidly leads to the formation of red solutions of the reduced complex $Rh(bipy)_2^+$ at pH > 10 and to brown 'hydride' solutions at pH = 7.5. The donors may be tertiary or secondary amines. Trimethoxybenzene may also be used despite its highly positive redox potential (+1.49 V in acetonitrile *vs.* SCE [134]), thus confirming the strong oxidizing character of $^*Rh(bipy)_3^{3+}$. With TEOA the first step is:

$$^*Rh(bipy)_3^{3+} + TEOA \xrightarrow[-1.28\ eV]{} Rh(bipy)_3^{2+} + TEOA^+ \qquad (64)$$

8.3. *Hydrogen generation by irradiation of* $Rh(bipy)_3^{3+}$ *solutions with UV. or sunlight.* Irradiation of aqueous TEOA solution of $Rh(bipy)_3^{3+}$ with UV. light ($\lambda > 300$ nm) at pH ~ 7-8 in presence of K_2PtCl_4 gives efficient hydrogen evolution (*Table 2*, exper. 21). Reductive quenching of the excited complex by TEOA (64) yields the $Rh(bipy)_3^{2+}$ species which is expected to undergo the same transformations as those extensively discussed above for the rhodium cycle (see equations (45)-(63) and *Fig. 9* and *12*). The reaction cycle is represented schematically in *Figure 16*.

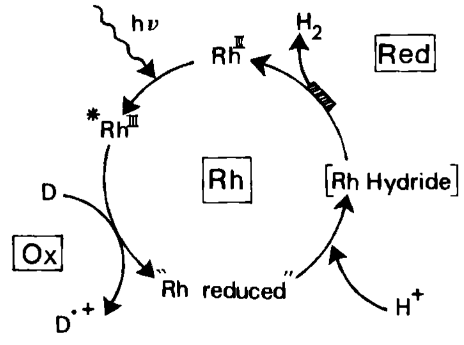


Fig. 16. *Schematic representation of the cycle for hydrogen generation by UV. irradiation of* $Rh(bipy)_3^{3+}$ *in aqueous solution in presence of a donor* **D**; the process involves reductive quenching of the excited state of the complex by the donor; see also *Figure 9* caption

Since sunlight contains a certain amount of UV. radiation (about 8% < 400 nm [2]), we performed some solar irradiations as described in *Table 2*, exper. 22 and 23. Appreciable hydrogen evolution is observed with the $Rh(bipy)_3^{3+}$/TEOA/(bipy) system (exper. 22), although the reaction is more efficient when the PS $Ru(bipy)_3^{2+}$ is also present (exper. 23). Modification of the Rh(III) ligands may allow shifting the absorption towards longer wavelength. For instance, $Rh(phen)_3^{3+}$ has still relatively strong absorption around 360 nm; indeed, irradiation of this complex in aqueous TEOA at pH ~ 10 with a halogen lamp ($\lambda > 350$ nm) leads to the rapid formation of the reduced species $Rh(phen)_2^+$.

8.4. *Hydrogen generation with iridium-bipyridine complexes.* $Ir(bipy)_3^{3+}$ has redox properties similar to $Rh(bipy)_3^{3+}$ 20), but contrary to what is observed with the rhodium complex, loss or substitution of a (bipy) ligand is slow or does not occur [135]. On the other hand, since Ir(III)-bipyridine complexes have still sizable

---

20) $E_0(Ir(bipy)_3^{3+}/Ir(bipy)_3^{2+}) = -0.76$ V; $E_0(^*Ir(bipy)_3^{3+}/Ir(bipy)_3^{2+}) = 2.05$ V [66].

absorption above 400 nm, although the maximum of the band is in the UV. (300-320 nm) [117] [136-138], they may be more suitable for setting up a hydrogen generating system which would be efficient even in absence of any PS.

Reaction of K_3IrCl_6 with bipyridine [113] yields a mixture of bis and tris (bipyridine)iridium-(III) complexes, which may be precipitated as perchlorates. Visible light irradiation of aqueous solutions containing this precipitate as well as TEOA and K_2PtCl_4 (pH = 7.8), yields hydrogen. In the same conditions, $Ir(bipy)_3^{3+}$, $[Ir(bipy)_2Cl_2]^+$ and $[Ir(bipy)_2(Cl)(OH)]^+$ [117] are inactive, whereas $[Ir(bipy)_2(H_2O)(bipy)_{sesqui}]^{3+}$ [117][15]) was found to produce hydrogen.

The ability of these complexes to function as photosensitizers in visible light has been stressed [137] [138]. Since $Ir(bipy)_3^{3+}$ is highly inert toward ligand substitution, even *via* a reductive process [117], it cannot play the same role as $Rh(bipy)_3^{3+}$ in hydrogen generation; however $[(bipy)_2]$ or $[(bipy)_2(bipy)_{sesqui}]$ derivatives may be suitable, as indeed the present data seem to indicate.

An attractive feature of the iridium complexes is that, depending on their nature, some may play the role of the PS $Ru(bipy)_3^{2+}$ and others may replace the relay species $Rh(bipy)_3^{3+}$. Further studies are in progress.

9. Conversion of light energy into chemical energy. - Photocatalytic systems may use light energy to drive a redox reaction in the non spontaneous direction, thus allowing conversion of light energy into chemical energy. In the present system, the initial photocatalytic step (30) converts 1.27 – (– 0.67) eV = 1.94 eV, corresponding to the reverse of reaction (35), into chemical energy. This amounts to about 90% of the excitation energy (2.1 eV, *Fig. 2*) and thus represents an efficient photochemical cycle for energy conversion. However, the back reaction (35) would occur immediately in absence of the other processes involving the fast reduction of $Ru(bipy)_3^{3+}$ by the donor. The net energy storage reactions are (65) and (66) depending on whether the reduced species accumulated is a rhodium complex or hydrogen:

$$TEOA + Rh(bipy)_3^{3+} \longrightarrow TEOA^+ + Rh(bipy)_3^{2+} \tag{65}$$

$$TEOA + H^+(pH = 7) \longrightarrow TEOA^+ + \frac{1}{2} H_2 \tag{66}$$

The $\Delta G°$ values for these reactions are $+0.82-(-0.67) = +1.49$ eV for (65) and $+0.82-(-0.41) = 1.23$ eV for (66), amounting respectively to 70% and 55% conversion of the excited state energy of $Ru(bipy)_3^{2+}$ into chemical energy.

$$N(CH_2CH_2OH)_3 + H_2O \longrightarrow H_2 + HN(CH_2CH_2OH)_2 + CHO{-}CH_2OH \tag{67}$$

Assuming that equation (67) represents the net chemical transformations in the process, the difference between the combustion energies of starting materials and products represents the energy gain (if any) in terms of materials consumed and generated. Furthermore, data on quantum and chemical yields of the reactions involved are required for assessing the chemical energy storage efficiency [7]. Such determinations are in progress.

Finally, in view of the extrapolated turnover numbers $(TO)_{ex}$ listed in *Table 1*, the energy storage per mol of precious metal catalyst consumed should exceed 10^3-10^4 times the amount stored for a single transformation (66) or (67).

10. Conclusion. - The process described in this report and analogous ones which may be devised following similar lines (see also [75-78]), represent schemes for the generation of *'photohydrogen'*, *i.e.* hydrogen produced *via* a photochemical process. Of course, the present state of affairs is still far from economic feasibility in large scale hydrogen production. However, if stability and turnover of the components can be further improved, such systems might well become of practical interest for the storage of solar energy and photochemical fuel production.

One may modify the photosensitizer or use mixtures of sensitizers (for instance organic dyes, acridines, phthalocyanines, porphyrins, *etc.*) so as to cover the visible spectrum as well as possible and increase the efficiency of light harvesting. Processes involving simultaneous pair excitation and higher excited states [139] [140] would be interesting alternatives. Of course, the 'photosensitizer' and 'relay' functions may be combined in a single species. For instance, in suitable conditions, hydrogen might be obtained directly with $Ru(bipy)_3^{2+}$ (*via* the Ru(I) cycle; see *Fig. 10*) or with PFH^+ (*via* $PFH^{\cdot}$) in absence of a relay species. Similarly, the results obtained with rhodium and iridium complexes in the absence of any sensitizer point to a notable simplification of the system if appropriate ligands are found which would confer to the complexes broad and strong absorption in the visible. By analogy with the studies on ruthenium-bipyridine monolayers [68] [72] [73], monolayers formed from surfactant rhodium-bipyridine complexes may display interesting properties. 'Relay' species like the cobalt complexes desserve special attention since they allow hydrogen generation at higher pH, *i.e.* in a region where water oxidation is easier. The storage of two electrons as in the $Rh(III) \rightarrow Rh(I)$ reduction, is an attractive feature which one may wish to retain; it makes available a *dielectronic* pathway for water reduction which circumvents the use of a noble metal redox catalyst required by the monoelectronic processes. Complexes of other cations, for instance of platinum or palladium, also appear suitable. A most important area of investigation concerns the electron donor. Using organic materials is of potential interest if they are cheap and available in large amounts, like disposable organic waste. Species capable of undergoing redox cycles (like hydroquinones, thiols, *etc.*) would allow coupling to electron carriers in membranes [13]. The use of water itself as the electron donor requires the development of a water oxidation system; together with a suitable water reduction process, it would form a complete water splitting cycle, generating both oxygen and hydrogen. Again, metal cation complexes are particularly attractive candidates for thorough investigation, especially polynuclear complexes if four electrons have to be exchanged (equation (2)). As pointed out earlier, binuclear or polynuclear cryptates might be suitable species [141], but simpler ligands may also be envisaged. Hybrid systems involving coupling with semi-conductor electrodes [2] [6] [142] provide another interesting area of research.

Finally, hydrogen need not be the sole product. The present process yields a strongly reducing intermediate which might be used to perform chemical reductions. Such systems would generate liquid fuels by chemical processes driven by the photochemically produced reductant. Whether and especially when sunlight driven processes will become of economic significance in providing fuels for abundant clean energy does however not merely depend on chemistry!

We thank Prof. *F. Gault*, Dr. *F. Garin*, Mr. *J.L. Schmitt* and Mrs. *S. Libs* for their help in the analysis of the gas by gas chromatography and mass spectrometry. We also thank Dr. *J.J. Daly* for preliminary crystal structure investigation of the rhodium-trisbipyridine complex and Prof. *M. Gross* and Dr. *J.P. Gisselbrecht* for measurement and discussion of the electrochemical properties. This work was supported by a grant from the *CNRS* and *PIRDES*.

Experimental Part

The solvents, reagents, metal salts and complexes were of commercial reagent grade purity and were used without further purification. The solutions were made of deionized water. Electronic spectra were obtained in aqueous solution on a *VARIAN-CARY* 118C Spectrometer (λ_{max} in nm and ε-values in parantheses). Abbreviation: RT. = room temperature, RV. = rotatory evaporator, i.V. = *in vacuo.*

Preparation of complexes. - *Rhodium(III)-tris(2,2'-bipyridine) trichloride, Rh(bipy)$_3$Cl$_3$ · 5 H$_2$O.* Rhodium trichloride (2.95 g; 10.5 mmol), bipyridine (4.8 g; 30.8 mmol) and *N*-ethyl morpholine (10 ml) are mixed in a 250 ml round bottomed flask. 120 ml aqueous ethanol 1:1 are added and the reaction mixture is heated in air at 80° with frequent shaking. A brown colour and dark brown suspensions develop as the reaction proceeds. The electronic spectrum of the solution is monitored and the mixture is cooled down as soon as the spectrum shows two peaks at 305 and 318 nm and no free bipyridine left at 280 nm. This usually requires 25 to 30 minutes. The reaction mixture is filtered over *Celite*, and the solvent is pumped off on a RV. The brownish solid obtained is recrystallized from ethanol/water/butanol 50:10:40. The pale yellow cristalline material is dried i.V. (15 Torr at 50° for 1 h) to yield 5.8 g (75%) of $Rh(bipy)_3Cl_3 \cdot 5\,H_2O$.

$C_{30}H_{34}Cl_3N_6O_5Rh$	Calc.	C 46.92	H 4.46	Cl 13.85	N 10.94	Rh 13.40%
(767.8)	Found.	„ 47.05	„ 4.29	„ 13.35	„ 11.02	„ 13.96%

Rhodium(III)-tris(2,2'-bipyridine)sulfate, Rh(bipy)$_3$(SO$_4$)$_{1.5}$ · 7 H$_2$O. A solution of $Rh(bipy)_3Cl_3 \cdot 5\,H_2O$ (1.5 g, 1.95 mmol) in 50 ml of distilled water is passed over an anion exchange column (*Dowex* 1×8, SO_4^{2-} form, 100 g of wet resin), the column being eluted by 200 to 300 ml of water. The end point can be determined by adding a concentrated baryum nitrate solution into an aliquot of eluate, the elution being stopped when the test shows that there is no more sulfate anion present. The glassy solid obtained after solvent evaporation is crystallized in methanol/water/butanol 40:10:50, to yield pale yellow, shiny crystals[21]) which are dried i.V. giving 1.3 g of $Rh(bipy)_3(SO_4)_{1.5} \cdot 7\,H_2O$. This compound is hygroscopic and is preferably stored under dry argon.

$C_{30}H_{38}N_6O_{13}RhS_{1.5}$ (841) Calc. C 42.81 H 4.55 N 9.99% Found. C 42.87 H 4.71 N 10.05%

UV. (H_2O, RT.): 242 (44100), 305 (43800), 318 (46700) (lit. for $Rh(bipy)_3(ClO_4)_3$ [113]: 240 (38800), 305 (33800), 318 (31600)).

---

[21]) The presence of small amounts of water is essential in order to get crystallization of these rhodium complexes and not the precipitation of glassy solids.

Rhodium(III)-tris(2,2'-bipyridine)phosphate, $Rh(bipy)_3(H_2PO_4)_3 \cdot x\, H_2O$. This compound can be prepared by anion exchange on a resin the same procedure as for the sulfate, the resin column being in the $H_2PO_4^-$ form. It can be crystallized from water/dimethylformamide.

Rhodium(III)-tris(phenanthroline)chloride, $Rh(phen)_3Cl_3 \cdot x H_2O$. Rhodium dichloride (0.27 g; 0.9 mmol), phenanthroline monohydrate (0.40 g; 2.3 mmol), and *N*-ethyl morpholine (3 g) are mixed in a 100 ml flask, 25 ml aqueous ethanol 1:1 were added, and the mixture was heated in air at 85° for 50 minutes. The reaction mixture is cooled down to RT. filtered over *Celite* and the solvent is pumped off on a RV. The brownish solid obtained is recrystallized from ethanol/2-propanol/toluene 30:30:40. The crystalline product is dried i.V. (15 Torr at 80° for 1 h) to yield 0.32 g of pale yellow $Rh(phen)_3Cl_3 \cdot xH_2O$. UV. ($H_2O$, RT.): 272 (91700), 302.5 (22200), 333 (5600), 350 (4200) (lit. for $Rh(phen)_3Cl_3$ [114b]: 279 (75500), 304 (20200), 314 (10400), 334 (4180), 351 (3080)).

Rhodium(III)-tris(4,4'-dimethyl-2,2'-bipyridine)chloride, $Rh(dmbp)_3Cl_3 \cdot 7\, H_2O$. Rhodium trichloride (0.9 g; 3.3 mmol), 4,4'-dimethyl-2,2'-bipyridine [72] [143] (dmbp) (1.84 g; 10 mmol) and *N*-ethylmorpholine (8 g) are dissolved in 80 ml of ethanol/water 1:1. After 30 min of stirring in air at 80°, the solvent is pumped off, the solid residue is redissolved in 20 ml of water and the solution is again evaporated i.V. The pale brown solid obtained is recrystallized as follows: it is dissolved in 20 ml of aqueous ethanol 1:10, and cold toluene is carefully added dropwise until the first crystals appear[21]). The rest of toluene is then added (total volume of toluene: 70 ml) and the mixture is kept at 0° for 1 h before filtration. The product is dried i.V. (15 Torr at 80° for 15 min) to yield 2.4 g (81%) of $Rh(dmbp)_3Cl_3 \cdot 7\, H_2O$.

$C_{36}H_{50}Cl_3N_6O_7Rh$ (888.0) Calc. C 48.68 H 5.67 N 9.46% Found. C 48.08 H 5.96 N 9.65%

Rhodium(III)-tris(4,4'-dimethyl-2,2'-bipyridine) sulfate, $Rh(dmbp)_3(SO_4)_{1.5} \cdot 5\, H_2O$. This compound is prepared by anion exchange from the previous complex, using the same procedure as for $Rh(bipy)_3(SO_4)_{1.5} \cdot 7\, H_2O$; it is recrystallized from methanol/butanol/toluene 10:20:70. The crystals are dried i.V. (0.5 Torr at 25° for 6 h).

$C_{36}H_{46}N_6O_{11}RhS_{1.5}$ (889.8) Calc. C 48.59 H 5.21 N 9.44% Found. C 48.24 H 5.51 N 9.43%

UV. (H_2O, RT.): 301 (42100), 313.5 (41800).

Rhodium(III)-bis(2,2',6',2''-terpyridine)chloride, $Rh(terpy)_2Cl_3 \cdot 5\, H_2O$. Rhodium trichloride (0.2 g; 0.67 mmol) and terpyridine (0.4 g; 1.71 mmol) are treated with *N*-ethyl-morpholine (2 g) and 10 ml of ethanol/water 1:1. After heating for 1.5 h at 90° in air, the solvent is evaporated and the brownish solid residue is recrystallized from ethanol/water 1:1 giving long needles. The compound is dried i.V. (0.5 Torr at RT. for 24 h) to yield 0.4 g of complex (65%).

$C_{30}H_{32}Cl_3N_6O_5Rh$ (765.9) Calc. C 47.04 H 4.21 N 10.97% Found. C 47.08 H 4.21 N 11.35%

UV./VIS. (H_2O, RT.): 324 (15400), 337 (23300), 354 (25600), 442 (85).

Rhodium(III)-bis(2,2'-bipyridine)bis-aquo perchlorate, $[Rh(bipy)_2(H_2O)_2](ClO_4)_3 \cdot 2\, H_2O$. $Rh(bipy)_3(SO_4)_{1.5} \cdot 7\, H_2O$ (0.55 g; 0.65 mmol) is dissolved in 10 ml of ethanol/water 2:1 and a solution of sodium hydroxide (0.11 g; 2.75 mmol) in H_2O (5 ml) is added. The solution is heated to 80° with vigorous shaking in air. The mixture becomes reddish as the reaction proceeds, the red colour disappearing when the solution is shaken in air. The electronic spectrum of the mixture is monitored; the starting solution contains two bands at 305 nm and 318 nm; as the reaction proceeds these two bands disappear to give rise to three new peaks at 280 nm (free bipyridine), 301 nm and 311 nm (bis(bipyridine)complex). As soon as the electronic spectrum does not change anymore (this usually requires about 10 min heating), the solution is cooled down to RT., in order to avoid further transformation which would occur by longer heating. The free bipyridine is extracted three times with 15 ml diethylether. The aqueous phase is acidified by sulfuric acid (pH ~ 1-2) and a lithium perchlorate solution (3 g in 5 ml H_2O) is added. The mixture is concentrated to about 5 ml i.V., giving a white precipitate which is redissolved by heating at 80°. The solution is left overnight at RT. to yield colourless crystals which are filtered off and dried i.V. (0.5 Torr at RT. for 8 h).

$C_{20}H_{24}Cl_3N_4O_{16}Rh$ (785.7) Calc. C 30.57 H 3.08 N 7.13% Found. C 30.45 H 2.58 N 7.30%

Solution of [Rh(bipy)$_2$(OH)$_2$]$^+$. The ClO_4^- counter-ion was exchanged for SO_4^{2-} by passing an aqueous solution of a weighed amount of [Rh(bipy)$_2$(H$_2$O)$_2$] (ClO$_4$)$_3$ over an anion exchange column (SO_4^{2-} form) as described previously, the pH of the final solution being adjusted at pH ~ 7 by addition of aqueous sodium hydroxyde. The [Rh(bipy)$_2$(OH)$_2$]$^+$ concentration is checked by optical density measurements at maximum absorption (311 nm). The two pK_a's were determined by conventional pH-metric measurements (eq. (58) and (59)). UV./VIS. (H$_2$O, RT.; see also *Fig. 14*): Rh(bipy)$_2$(H$_2$O)$_2^{3+}$ (at pH < 3): 304 (31800), 317 (30200) [ε (at 350 nm) = 100]; Rh(bipy)$_2$(OH)$_2^+$ (at pH > 7): 301 (27000), 311 (30900) [ε (at 350 nm) = 1400].

Ruthenium(II)-tris(2,2'-bipyridine) and ruthenium(II)-tris(1,10-phenanthroline) salts, Ru(bipy)$_3^{2+}$ and Ru(phen)$_3^{2+}$. The chlorides are prepared according to [144] by refluxing ruthenium trichloride (1 g; 3.5 mmol) plus the calculated amount of ligand in dimethylformamide (50 ml) for 3 h. The chloride anion is exchanged for sulfate or phosphate (HPO_4^{2-}) by the same method as for the rhodium complexes. For instance, 1 g of Ru(bipy)$_3$Cl$_2$ · 6 H$_2$O dissolved in 50 ml H$_2$O is passed over an anion exchange resin in its sulfate form; after evaporation, the solid complex is recrystallized from ethanol/toluene, to yield Ru(bipy)$_3$(SO$_4$) · xH$_2$O. - VIS. (H$_2$O, RT.): 452; (lit. [57]: 452).

Observation of photochemically produced air sensitive species. - The reduced species produced by UV. or visible light irradiation were observed either visually (colour change) or by electronic spectroscopy. The following procedure was used: in a glass *Schlenk* tube the starting reducible compound (MV^{2+}, [CuCl$_2$, 2 bipy], cobalt (II) or rhodium (III) complex) was dissolved in the appropriate phosphate buffer (0.5M); the other components, photosensitizer and/or electron donor (see text) were added. The concentrations normally used were in the range 10^{-4}M/10^{-3}-10^{-2}M/5.10^{-1}M, for respectively PS/R/D. For electronic spectroscopy measurements, the solution obtained was transfered into a quartz cell mounted on a *Schlenk* tube; when required, the initial optical path could be reduced from 5 mm to 0.1 or 0.5 mm by the use of a transparent insert. The solution was degassed and irradiated (as described below) and the photoreaction was monitored by recording the electronic spectrum (UV. and visible region) after given periods of irradiation time. The electronic spectrum of MV$^+$ was identical with that reported in [145]. The 435 nm band of Cu(bipy)$_2^+$ [146] was superimposed on the 450 nm band of the Ru(bipy)$_3^{2+}$-PS used.

Photochemical Hydrogen Generation Experiments. - *General Procedure.* The nature and the concentration of the various components used in each experiment are listed in *Tables 1* and *2*. In a small round bottomed *Schlenk* tube (~ 10 ml volume), the compounds were dissolved in a given volume of a buffer solution containing the tertiary amine (TEOA or EDTA) plus an inorganic acid (usually sulfuric acid). The reaction mixture was occasionally heated to 80° for a few minutes in order to insure the complete dissolution of the less soluble components. The mixture was then degassed as follows: the solution was boiled i.V. at RT. for ~ 1 min and argon was slowly introduced into the *Schlenk* tube, the mixture being shaken at the same time. This procedure was repeated twice and the final pressure was controlled by a mercury manometer. The *Schlenk* tube could be directly used for an irradiation experiment; the gas produced was analyzed after termination of the experiment when gas bubbles ceased to form. When kinetic measurements were to be performed, the *Schlenk* tube was connected to a water filled inverted burette over a water reservoir at atmospheric pressure. The spherical part of the *Schlenk* tube was then positioned in the light beam. The volume of gas produced was measured as a function of time. Analysis of the gas (see below) showed that it was pure hydrogen with TEOA as donor. EDTA also yields carbon dioxide on oxidation at acidic pH [132] [133].

Nature of the irradiation light. Visible light for experiments 1-20 *(Tables 1* and *2)* was provided by a *Rollei* slide projector (Type P35 A) fitted with a 150 W halogen lamp; the light beam was concentrated with a converging lens and its width was adjusted so as to cover entirely the part of the vessel containing the solution. For experiments 1-12 *(Table 1)* the light was filtered which a 400 nm cut-off filter (*Kodak-Wratten* 2B or *Oriel* G-772-3900). For experiment 21 *(Table 2)*, the light source was a 125 W high pressure mercury lamp (*Philips* HPK 125) used with a 300 nm cut-off filter (*Oriel* WG 320); the solution was positioned at approximately 10 cm from the lamp. Some of the experiments have been carried out in diffuse *sunlight* using either a quartz *Schlenk* tube in the absence of a coloured photosensitizer (experiment 22) or a pyrex *Schlenk* tube in presence of a photosensitizer (experiment 23).

For the experiments employing rhodium complexes, two types of experimental set-up have been used. Experiments 1-12 *(Table 1)* were performed with solutions prepared from stock solutions (total volume 6 ml), thermostated during irradiation using a double walled *Schlenk* tube and a temperature-controlled (±0.5°) water circulation. For experiments 13-23 *(Table 2)*, the solutions were pre-heated at 40-50° in order to roughly balance the pressure increase due to the increase in temperature during irradiation.

For the experiments with cobalt species, the complexes were prepared *in situ* by dissolution of the desired amounts of cobalt chloride and bipyridine in degassed water under argon. The ruthenium complex, K_2PtCl_4 and TEOA were then added and the pH was occasionally adjusted by addition of hydrochloric acid. The irradiation conditions were the same as for experiment 13 *(Table 2)*.

In a typical experiment, the following quantities were dissolved in 5 ml water: $CoCl_2 = 7.2$ mg; (bipy) = 55 mg; $Ru(bipy)_3Cl_2 \cdot 6\,H_2O = 16$ mg; $K_2PtCl_4 = 0.6$ mg; TEOA = 0.5 g; the initial pH of the solution as prepared was 9.2. 2.5 ml of hydrogen were produced in 15 h of irradiation at 50°.

Preparation of photochemically active iridium containing solutions. In an attempt to prepare $Ir(bipy)_3Cl_3$ from K_3IrCl_6 and (bipy) according to [113], a mixture of bis- and possibly tris(bipyridine)-iridium complexes was obtained instead of pure tris(bipyridine)complex. The crude product was dissolved in boiling water, and this solution was extracted with diethylether in order to remove free bipyridine. The mixture of iridium complexes was then precipitated by addition of saturated $NaClO_4$-solution to the aqueous phase and isolated by filtration. 10 mg of this crude solid and 1 mg K_2PtCl_4 were dissolved in 5 ml of a TEOA buffer solution (0.4M; pH = 7.8) and the solution obtained was degassed as described above. Visible light irradiation (experimental conditions as for exper. 13, *Table 2*) led to hydrogen production (in the range of several tenth's of a ml in a few hours). Small quantities of hydrogen were also obtained when the mixture of iridium complexes used above was replaced by a purified sample of $[Ir(bipy)_2H_2O(bipy)_{sesqui}]Cl_3$ [117] in the same experimental conditions.

Analysis of the gas generated. The amounts of hydrogen produced were determined by gas chromatography, injecting given volumes of the gas generated, diluted in argon, and comparing the traces to reference traces obtained from known quantities of pure hydrogen *(Fig. 3)*. A *Varian* Aerograph model 700 apparatus was used together with a molecular sieve 13X Mesh 42/60 *(Applied Science Laboratories Inc.)* column. The analysis were run at RT. with methane as carrier gas. In the isotopic experiments conducted in D_2O, the relative amounts of D_2, HD and H_2 were determined using a *Varian* CH7 mass spectrometer (ionisation voltage 70 eV) and focusing successively on each mass unit *(Fig. 4)*.

Characterisation of TEOA oxidation products. The formation of glycolaldehyde according to eq. (44) was checked by a previously reported specific color reaction [147]. After terminating an irradiation experiment (for instance, exper. 11 *(Table 1)*), addition of diphenylamine (20 mg in 2 ml acetic acid containing 0.01 ml H_2SO_4) to an aliquot of the final solution (0.5 ml), gave the green colour characteristic for glycolaldehyde ($\lambda_{max} = 660$ nm); this absorption was not observed with the initial PS/R/D/C reference solution kept in the dark. At sufficient levels of TEOA consumption the pH of the solution was found to increase; thus, in the case of experiment 16 *(Table 2)* the initial and final pH were respectively 7.2 and 7.8. This may be indication for the formation of the more basic diethanolamine, equation (44) (see also above).

Emission intensity measurements. – The emission spectra from ruthenium(II)tris(2,2'-bipyridine)-cation in non degassed aqueous solution at 25° were recorded on an absolute differential spectrofluorimeter *Fica* 55, equipped with a 450 W xenon lamp. $Ru(bipy)_2SO_4 \cdot 6\,H_2O$ (7.5×10^{-6}M) and quencher (TEOA or rhodium complex) were dissolved in a phosphate buffer (0.5M) at pH = 7.1 for TEOA, $Rh(bipy)_3^{3+}$, $Rh(dmbp)_3^{3+}$, $[Rh(bipy)_2(OH)_2]^+$, or at pH = 3.0 for $[Rh(bipy)_2(H_2O)_2]^{3+}$. The solutions were irradiated at the maximum absorbance of $Ru(bipy)_3^{2+}$ around 450 nm (with a slit width of 7.5 nm). The emission intensities were monitored around 600 nm. With TEOA, no quenching was observed over a wide concentration range up to 0.2M at pH = 7.1, *i.e.* 0.035M in free base. For quenching experiments with rhodium complexes, solutions containing only buffer and the rhodium complex were located in the reference beam. The emission data were corrected for the absorption of incident light by the quencher solution. No additional correction was needed, since these complexes have no absorption at the $Ru(bipy)_3^{2+}$ emission wavelength. The experiments were repeated at least twice for each complex and were reproducible within ±15%. *Stern-Volmer* plots were obtained, using the equation $(I_0/I)_{corr.} = 1 + k_q \tau_0 [Q]$, where $(I_0/I)_{corr.}$ is the corrected ratio of the emission intensities of Ru(bipy)$_3^{2+}$ in the absence and in the presence of a quencher at concentration [Q]; k_q is the rate constant for quenching; τ_0, the lifetime of the *Ru(bipy)$_3^{2+}$ excited state, was assumed to be 0.6 µsec at 25° [57]. The results are plotted in *Figure 11* and the rate constants calculated are given in the text.

REFERENCES

[1] *J.M. Lehn & J.P. Sauvage,* Nouv. J. Chimie *1,* 449 (1977).
[2] 'Solar Power and Fuels', *J.R. Bolton,* Ed., Academic Press, New-York 1977.
[3] *R.J. Marcus,* Science *123,* 399 (1956).
[4] *G. Stein,* Israel J. Chemistry *14,* 213 (1975).
[5] *V. Balzani, L. Moggi, M.F. Manfrin, F. Bolletta & M. Gleria,* Science *189,* 852 (1975).
[6] *M.D. Archer,* J. appl. Electrochem. *5,* 17 (1975).
[7] *J.R. Bolton,* J. solid State Chemistry *22,* 3 (1977); Science *202,* 705 (1978).
[8] *M. Calvin,* Accounts chem. Res. *11,* 369 (1978).
[9] *H. Gerischer,* Ber. Bunsenges physik. Chem. *80,* 1046 (1976); *M.S. Wrighton,* Technology Rev. *31,* May 1977.
[10] *E. Schumacher,* Chimia *32,* 193 (1978); *G. Calzaferri,* Chimia *32,* 241 (1978).
[11] a) *T. Ohta & T.N. Veziroglu,* Int. J. Hydrogen Energy *1,* 255 (1976); b) *P. Hagenmuller,* La Recherche *8,* 756 (1977).
[12] *J. O'M. Bockris,* Pure appl. Chemistry *47,* 25 (1976).
[13] *J.J. Grimaldi, S. Boileau & J.M. Lehn,* Nature *265,* 229 (1977).
[14] *V. Balzani & V. Carassiti,* 'Photochemistry of Coordination Compounds', Academic Press, New York 1970.
[15] *N. Uri,* Chem. Rev. *50,* 375 (1952).
[16] *M.S. Wrighton,* Topics Current Chemistry *65,* 37 (1976).
[17] *H. Hennig, P. Thomas, R. Wagener, D. Rehorek & K. Jurdeczka,* Z. Chem. *17,* 241 (1977).
[18] *L.J. Heidt & M.E. Smith,* J. Amer. chem. Soc. *70,* 2476 (1948); *L.J. Heidt,* Proc. Aur. Acad. Arts Sci. *79,* 228 (1951).
[19] *L.J. Heidt & A.F. McMillan,* Science *117,* 75 (1953); J. Amer. chem. Soc. *76,* 2135 (1954).
[20] *Y. Haas, G. Stein & M. Tomkiewicz,* J. phys. Chemistry *74,* 2558 (1970).
[21] *Y. Haas, G. Stein & R. Tenne,* Israel J. Chemistry *10,* 529 (1972).
[22] *D.D. Davis, K.L. Stevenson & G.K. King,* Inorg. Chemistry *16,* 670 (1970).
[23] *M. Brandys & G. Stein,* J. phys. Chemistry *82,* 852 (1978).
[24] *J. Weiss,* Nature *136,* 794 (1935); *E. Hayon & J. Weiss,* J. chem. Soc. 3866 (1960).
[25] *L.J. Heidt, M.G. Mullin, W.B. Martin, Jr., & A.M.J. Beaty,* J. phys. Chemistry *66,* 336 (1962).
[26] *J. Jortner & G. Stein,* J. phys. Chemistry *66,* 1258, 1264 (1962).
[27] *G.N. Schrauzer & T.D. Guth,* J. Amer. chem. Soc. *98,* 3508 (1976).
[28] *T. Ohta,* Chem. econ. Eng. Rev. *7,* 7 (1975).
[29] *E. Collinson, F.S. Dainton & M.A. Malati,* Trans. Faraday Soc. *55,* 2097 (1959); *M.W. Hershey, T.J. Vandernoot & C.H. Lanford,* Inorg. chim. Acta *29,* L233 (1978).
[30] *D.D. Davis, G.K. King, K.L. Stevenson, E.R. Birnbaum & J.H. Hageman,* J. solid State Chemistry *22,* 63 (1977).
[31] *G. Ferraudi,* Inorg. Chemistry *17,* 1370 (1978).
[32] *R.E. Hintze & P.C. Ford,* J. Amer. chem. Soc. *97,* 2664 (1975); *T. Matsubara & P.C. Ford,* Inorg. Chemistry *17,* 1747 (1978).
[33] *D.K. Erwin, G.L. Geoffroy, H.B. Gray, G.S. Hammond, E.J. Solomon, W.C. Trogler & A.A. Zagars,* J. Amer. chem. Soc. *99,* 3620 (1977).
[34] *W.C. Trogler, D.K. Erwin, G.L. Geoffroy & H.B. Gray,* J. Amer. chem. Soc. *100,* 1160 (1978).
[35] *K.R. Mann, N.S. Lewis, V.M. Miskowski, D.K. Erwin, G.S. Hammond & H.B. Gray,* J. Amer. chem. Soc. *99,* 5525 (1977).
[36] *V.M. Miskowski, G.L. Nobinger, D.S. Kliger, G.S. Hammond, N.S. Lewis, K.R. Mann & H.B. Gray,* J. Amer. chem. Soc. *100,* 485 (1978).
[37] *C. Giannotti & M.L.H. Green,* Chem. Commun. *1972,* 1114.

[38] *K. Elmitt, M.L.H. Green, R.A. Forder, I. Jefferson & K. Prout,* Chem. Commun. *1974,* 747.

[39] *L. Farrugia & M.L.H. Green,* Chem. Commun. *1975,* 416.

[40] *G.L. Geoffroy & R. Pierantozzi,* J. Amer. chem. Soc. *98,* 8054 (1976).

[41] *G.L. Geoffroy & M.G. Bradley,* Inorg. Chemistry *16,* 744 (1977).

[42] *G.L. Geoffroy & M.G. Bradley,* J. organometal. Chemistry *134,* C27 (1977). Inorg. Chemistry *17,* 2410 (1978).

[43] *A. Camus, C. Cocevar & G. Mestroni,* J. organometal. Chemistry *39,* 355 (1972).

[44] *D.M. Klassen & G.A. Crosby,* J. chem. Physics *48,* 1853 (1968).

[45] *J.N. Demas, E.W. Harris & R.P. McBride,* J. Amer. chem. Soc. *99,* 3547 (1977).

[46] *J.N. Demas & A.W. Adamson,* J. Amer. chem. Soc. *95,* 5159 (1973).

[47] *C.R. Bock, T.J. Meyer & D.G. Whitten,* J. Amer. chem. Soc. *96,* 4710 (1974).

[48] *G. Navon & N. Sutin,* Inorg. Chemistry *13,* 2159 (1974).

[49] *G.S. Lawrence & V. Balzani,* Inorg. Chemistry *13,* 2976 (1974).

[50] *C.R. Bock, T.J. Meyer & D.G. Whitten,* J. Amer. chem. Soc. *97,* 2909 (1975).

[51] *C. Creutz & N. Sutin,* Proc. Nat. Acad. Sci. USA *72,* 2858 (1975).

[52] *R.C. Young, T.J. Meyer & D.G. Whitten,* J. Amer. chem. Soc. *97,* 4781 (1975).

[53] *R.C. Young, T.J. Meyer & D.G. Whitten,* J. Amer. chem. Soc. *98,* 286 (1976).

[54] *C. Creutz & N. Sutin,* Inorg. Chemistry *15,* 496 (1976).

[55] *C.T. Lin & N. Sutin,* J. phys. Chemistry *80,* 97 (1976).

[56] *J. Van Houten & R.J. Watts,* J. Amer. chem. Soc. *98,* 4853 (1976).

[57] *C.T. Lin, W. Böttcher, M. Chou, C. Creutz & N. Sutin,* J. Amer. chem. Soc. *98,* 6536 (1976).

[58] *D. Meisel, M.S. Matheson, W.A. Mulac & J. Rabani,* J. phys. Chemistry *81,* 1449 (1977).

[59] *D. Meisel & M.S. Matheson,* J. Amer. chem. Soc. *99,* 6577 (1977).

[60] *J.K. Nagle, R.C. Young & T.J. Meyer,* Inorg. Chemistry *16,* 3366 (1977).

[61] *D. Meisel, M.S. Matheson & J. Rabani,* J. Amer. chem. Soc. *100,* 117 (1978).

[62] *N.E. Tokel-Tokvoryan, R.E. Hemingway & A.J. Bard,* J. Amer. chem. Soc. *95,* 6582 (1973).

[63] *G.A. Crosby,* Accounts chem. Res. *8,* 231 (1975).

[64] *T.J. Meyer,* Israel J. Chemistry *15,* 200 (1976/77).

[65] *T.J. Meyer,* Accounts chem. Res. *11,* 94 (1978).

[66] *V. Balzani, F. Bolletta, M.T. Gandolfi & M. Maestri,* Topics Current Chemistry *75,* 1 (1978).

[67] *G. Sprintschnik, H.W. Sprintschnik, P.P. Kirsch & D.G. Whitten,* J. Amer. chem. Soc. *98,* 2337 (1976).

[68] *D.G. Whitten, F.R. Hopf, F.H. Quina, G. Sprintschnik & H.W. Sprintschnik,* Pure appl. Chemistry *49,* 379 (1977).

[69] *P.J. DeLaive, J.T. Lee, H.W. Sprintschnik, H. Abruña, T.J. Meyer & D.G. Whitten,* J. Amer. chem. Soc. *99,* 7094 (1977).

[70] *S.J. Valenty & G.L. Gaines, jr.,* J. Amer. chem. Soc. *99,* 1285 (1977); *G.L. Gaines, jr., P.E. Behnken & S.J. Valenty,* in press.

[71] *A. Harriman,* Chem. Commun. *1977,* 777.

[72] *G. Sprintschnik, H.W. Sprintschnik, P.P. Kirsch & D.G. Whitten,* J. Amer. chem. Soc. *99,* 4947 (1977).

[73] *K.P. Seefeld, D. Möbius & H. Kuhn,* Helv. *60,* 2608 (1977).

[74] *L.J. Yellowlees, R.G. Dickinson, C.S. Halliday, J.S. Bonham & L.E. Lyons,* Austral. J. Chemistry *31,* 431 (1978).

[75] *B.V. Koriakin, T.S. Dzhabiev & A.E. Shilov,* Dokl. Akad. Nauk SSSR *233,* 620 (1977); *A.E. Shilov,* Le Bel Lectures, Strasbourg, May 1978.

[76] *A.I. Krasna,* Photochemistry Photobiol. *29,* 267 (1979); *A.I. Krasna,* in 'Biological Solar Energy Conversion', A. San Pietro and A. Mitsui Eds., Academic Press, New York 1977.

[77] a) *A. Moradpour, E. Amouyal, P. Keller & H. Kagan,* Nouveau J. Chimie *2,* 547 (1978); b) *I. Okura & N. Kim-Thuan,* reported at the 2nd Internat. Conf. on the Photochemical Conversion and Storage of Solar Energy, Cambridge, Great-Britain, August 10–12, 1978; submitted for publication.

[78] *K. Kalyanasundaram, J. Kiwi & M. Grätzel,* Helv. *61,* 2720 (1978).

[79] *P. Cappelle, M. de Backer, O. de Witte, G. Feuillade & G. Lepoutre,* C.r. hebd. Séances Acad. Sci. Série C *284,* 597 (1977); *Y. Larel & J. Manassen,* J. Amer. chem. Soc. *99,* 5817 (1977).

[80] 'Biological Solar Energy Conversion', A. San Pietro & A. Mitsui Eds., Academic Press, New York 1977.

[81] *H.D. Peck, Jr. & H. Gest,* J. Bacteriol. *71,* 70 (1956).

[82] *L. Yu & M.J. Wolin,* J. Bacteriol. *98,* 51 (1969).

[83] *J.R. Benemann, J.A. Berenson, N.O. Kaplan & M.D. Kamen,* Proc. Nat. Acad. Sci. USA *70,* 2317 (1973).

[84] *A.A. Krasnovskii, V.V. Nikandrov, G.P. Brin, I.N. Nogotov & V.P. Oshchepkov,* Dokl. Akad. Nauk SSSR *225,* 711 (1975); *I.V. Berezin, S.D. Varfolomeev & S.V. Saitzev,* Dokl. Akad. Nauk SSSR *229,* 94 (1976).

[85] *A.J. de Bethune & N.A.S. Loud,* ‘Standard Aqueous Potentials and Temperature Coefficients at 25°’, C.A. Hampel, Skokie, Ill., 1964.

[86] *A. Piccini & L. Marino,* Z. anorg. allg. Chem. *32,* 55 (1902).

[87] *D.E. Green & L.H. Stickland,* Biochem. J. *28,* 898 (1934).

[88] *L. Michaelis & E.S. Hill,* J. gen. Physiol. *16,* 859 (1933).

[89] *J.S. Bellin, R. Alexander & R.D. Mahoney,* Photochemistry Photobiol. *17,* 17 (1973).

[90] *N. Kanioya,* Kogyo Kagaku Zasshi *72,* 96 (1969).

[91] *J.H. Baxendale & M. Fiti,* J. chem. Soc. Dalton Trans. *1972,* 1995.

[92] *Q.G. Mulazzani, S. Emmi, P.G. Fuochi, M.Z. Hoffman & M. Venturi,* J. Amer. chem. Soc. *100,* 981 (1978).

[93] *R.D. Gillard, J.A. Osborn & G. Wilkinson,* J. chem. Soc. *1965,* 4107.

[94] *G. Kew, K. DeArmond & K. Hanck,* J. phys. Chemistry *78,* 727 (1974).

[95] *J.P. Gisselbrecht & M. Gross,* private communication.

[96] *G. Mestroni, G. Zassinovich & A. Camus,* J. organometal. Chemistry *140,* 63 (1977).

[97] *R.D. Gillard & G. Wilkinson,* J. chem. Soc. *1963,* 3594.

[98] *J.A. Osborn, F.H. Jardine, J.F. Young & G. Wilkinson,* J. chem. Soc. *1966,* 1711; *R.R. Schrock & J.A. Osborn,* J. Amer. chem. Soc. *98,* 2134 (1976).

[99] *J.F. Fischer & J.L. Hall,* Analyt. Chemistry *34,* 1094 (1962).

[100] *G.N. Schrauzer, E. Deutsch & R.J. Windgassen,* J. Amer. chem. Soc. *90,* 2441 (1968).

[101] *H. Gerischer & F. Willig,* Topics Current Chemistry *61,* 31 (1976).

[102] *C. Creutz & N. Sutin,* J. Amer. chem. Soc. *98,* 6384 (1976).

[103] *C.P. Anderson, D.J. Salmon, T.J. Meyer & R.C. Young,* J. Amer. chem. Soc. *99,* 1980 (1977).

[104] *M. Maestri & M. Grätzel,* Ber. Bunsenges. physik. Chem. *81,* 505 (1977).

[105] *G.A. Crosby & W.H. Elfring, Jr.,* J. phys. Chemistry *80,* 2206 (1976).

[106] *J.L. Kahl, K.W. Hanck & K. DeArmond,* J. phys. Chemistry *82,* 540 (1978).

[107] *S.G. Cohen, A. Parola & G.H. Parsons, jr.,* Chem. Rev. *73,* 141 (1973); *S.G. Cohen & R.J. Baumgarten,* J. Amer. chem. Soc. *87,* 2996 (1965).

[108] *P.J. Smith & C.K. Mann,* J. org. Chemistry *34,* 1821 (1969).

[109] *P. Poulenc,* Ann. Chim. *4,* 632 (1935); M. Delépine; C.r. hebd. Séances Acad. Sci. *236,* 559 (1953).

[110] *B.N. Figgis, R.D. Gillard, R.S. Nyholm & G. Wilkinson,* J. chem. Soc. *1964,* 5189.

[111] *R.D. Gillard, J.A. Osborn & G. Wilkinson,* J. chem. Soc. *1965,* 1951.

[112] *E.D. McKenzie & R.A. Plowman,* J. inorg. nucl. Chemistry *32,* 199 (1970).

[113] *B. Martin & G.M. Waind,* J. chem. Soc. *1958,* 4284.

[114] a) *D.H.W. Carstens & G.A. Crosby,* J. mol. Spectr. *34,* 113 (1970); b) *M.K. DeArmond & J.E. Hillis,* J. chem. Physics *54,* 2247 (1971).

[115] *B. Martin, W.R. McWhinnie & G.M. Waind,* J. inorg. nucl. Chemistry *23,* 207 (1961).

[116] a) *J.D. Miller & F.D. Oliver,* J. chem. Soc. Dalton *1972,* 2473; b) *H. Caldaru, K. DeArmond & K. Hanck,* Inorg. Chemistry *17,* 2030 (1978).

[117] *R.J. Watts, J.S. Harrington & J. Van Houten,* J. Amer. chem. Soc. *99,* 2179 (1977).

[118] *R. Lorenz & P.E. Spielmann,* Z. Elektrochem. *15,* 293 (1909).

[119] *C.P. Andrieux & J.-M. Savéant,* Bull. Soc. chim. France *1968,* 4671.

[120] *F. Millich & G. Oster,* J. Amer. chem. Soc. *81,* 1357 (1959); *G. Oster, J.S. Bellin, R.W. Kimball & M.E. Schrader,* J. Amer. chem. Soc. *81,* 5095 (1959).

[121] *P.S. Sweetzer,* Analyt. Chemistry *39,* 979 (1967).

[122] *K. Kikuchi & M. Koizumi,* Bull. chem. Soc. Japan *40,* 736 (1967).

[123] *B. Breyer, G.S. Buchanan & H. Duewell,* J. chem. Soc. *1944,* 360.

[124] *A.A. Krasnovskii & G.P. Brin,* Dokl. Akad. Nauk SSSR *16,* 761 (1965).

[125] *A. Kellmann,* Photochem. Photobiol. *20,* 103 (1974).

[126] *G.M. Waind & B. Martin,* J. inorg. nucl. Chemistry *8*, 551 (1958).

[127] *S. Margel, W. Smith & F.C. Anson,* J. electrochem. Soc. *125*, 241 (1978).

[128] *T.H. Chao & J.H. Espenson,* J. Amer. chem. Soc. *100*, 129 (1978).

[129] *W.E. Ford, J.W. Otvos & M. Calvin,* Nature *274*, 507 (1978).

[130] *S.A. Alkaitis & M. Grätzel,* J. Amer. chem. Soc. *98*, 3549 (1976); *J. Kiwi & M. Grätzel,* ibid. *100*, 6314 (1978).

[131] *P. Natarajan & J.F. Endicott,* J. phys. Chemistry *77*, 2049 (1973); J. Amer. chem. Soc. *95*, 2470 (1973); Canad. J. Chemistry *55*, 3132 (1977).

[132] *G. Oster & N. Wotherspoon,* J. Amer. chem. Soc. *79*, 4836 (1957); *J. Joussot-Dubien & G. Oster,* Bull. Soc. chim. France *1960*, 343.

[133] *K. Enns & W.H. Burgess,* J. Amer. chem. Soc. *87*, 5766 (1965).

[134] *C.K. Mann & K.K. Barnes,* 'Electrochemical Reactions in Non-aqueous Systems', Marcel Dekker, New York, N.Y. 1970.

[135] *J.L. Kahl, K.W. Hanck & K. DeArmond,* J. phys. Chemistry *82*, 540 (1978).

[136] *C.M. Flynn & J.N. Demas,* J. Amer. chem. Soc. *96*, 1959 (1974).

[137] *J.N. Demas, E.W. Harris, C.M. Flynn, jr., & D. Diemente,* J. Amer. chem. Soc. *97*, 3838 (1975).

[138] *J.N. Demas, E.W. Harris & R.P. McBride,* J. Amer. chem. Soc. *99*, 3547 (1977).

[139] *H.J. Schugar, E.I. Solomon, W.L. Cleveland & L. Goodman,* J. Amer. chem. Soc. *97*, 6442 (1975).

[140] *V.I. Korotkov, L.L. Basov & V.E. Colmogorov,* Dokl. Akad. Nauk SSSR *209*, 392 (1973).

[141] *J.M. Lehn, S.H. Pine, A.K. Willard & E.I. Watanabe,* J. Amer. chem. Soc. *99*, 6766 (1977); *A.H. Alberts, R. Annunziata & J.M. Lehn,* J. Amer. chem. Soc. *99*, 8502 (1977).

[142] 'Solid State Chemistry of Energy Conversion and Storage', J.B. Goodenough & M.S. Whittingham, Eds., Advances in Chem. Ser. n° 163, Amer. chem. Soc. 1977.

[143] *P.E. Rosevear & W.H.F. Sasse,* J. heterocycl. Chemistry *8*, 483 (1971).

[144] *J.N. Braddock & T.J. Meyer,* J. Amer. chem. Soc. *95*, 3158 (1973).

[145] *E.M. Kosower & J.L. Cotter,* J. Amer. chem. Soc. *86*, 5524 (1964).

[146] *B.R. James, M. Parris & R.J.P. Williams,* J. chem. Soc. *1961*, 4630.

[147] *Z. Dische & E. Borenfreund,* J. biol. Chemistry *180*, 1297 (1949).