256. Hydrogen Evolution from Water by Visible Light, a Homogeneous Three Component Test System for Redox Catalysis

by **Kuppuswamy Kalyanasundaram**

The Royal Institution, London

and **John Kiwi** and **Michael Grätzel**

Institut de Chimie-Physique, Ecole Polytechnique Fédérale, CH-1015 Lausanne, Suisse

(29. VI. 78)

Summary

Irradiation by visible light of a neutral aqueous solution containing $Ru(bipy)_3^{2+}$ as a sensitizer, methylviologen (MV^{+2}) as an electron acceptor and triethanolamine or cysteine as an electron donor leads to the formation of stable methylviologen radical cation (MV^+). The kinetics and mechanism of the photoinduced reactions occurring in such a system were explored by laser photolysis technique. In the presence of *Adams* catalyst MV^+ is reoxidized by water under simultaneous evolution of hydrogen. Optimum conditions for the water reduction under continuous illumination are elaborated and implications for an energy conversion system discussed.

Introduction. – Considerable effort has recently been directed towards finding chemical processes that are capable of quantum storage of light energy [1]. An attractive system to consider is the photoredox reaction

$$A + S \underset{\Delta}{\overset{h\nu}{\rightleftarrows}} S^+ + A^- \tag{1}$$

where S stands for the photoactive sensitizer and A for the electron acceptor. The two components A and S may be selected such that in aqueous solution hydrogen and oxygen evolution becomes feasible.

$$A^- + H_2O \longrightarrow \tfrac{1}{2} H_2 + OH^- + A \tag{2}$$

$$2 D^+ + H_2O \longrightarrow 2 H^+ + \tfrac{1}{2} O_2 + D \tag{3}$$
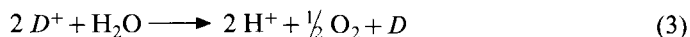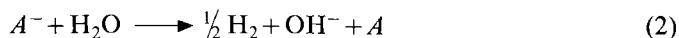
For kinetic and mechanistic reasons, these processes either do not occur spontaneously or they proceed at a very low speed. Furthermore, complications may arise from side reactions of A^- and D^+ resulting in a rapid deterioration of the

system. In these cases, suitable redox catalysts may preferably be added to the solution which are capable of mediating the complex electron transfer reactions leading to hydrogen and oxygen formation, respectively. *Shilov et al.* have shown [2] that the reduction of water *via* reaction (2) can be promoted by redox catalysts such as finely dispersed Pt. A similar mechanism has been claimed to be operative in a hydrogen evolution system described recently by *Lehn & Sauvage* [3] although in this case the oxidation state of the Pt catalyzing the decomposition of an intermediate hydride could not be specified. Recent investigations in our laboratory [4] have shown that oxygen evolution from water *via* reaction (3) can also be mediated by a suitable redox catalyst.

In the present work, we shall be concerned with the dye sensitized reduction of water using PtO_2 (*Adams* catalyst) as a redox catalyst. Tris(2,2'-bipyridine) ruthenium(II) ($Ru(bipy)_3^{2+}$) was employed as a sensitizer and methylviologen (MV^{2+}) as an electron acceptor. A third component (*DH*), *i.e.* triethanolamine or cysteine, was added to the solution which reduces the sensitizer cation according to

$$DH + S^+ \longrightarrow S + D + H^+ \tag{4}$$
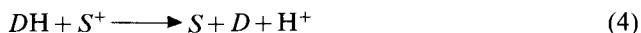
and thus prevents the thermal back transfer of an electron from A^- to D^+ (see eq. (1)). The purpose of this paper is to study, by means of laser and steady state photolysis techniques, the detailed nature of the redox events occurring in such a system in order to determine the optimum conditions for hydrogen evolution.

Experimental Part. – Ru(bipy)₃Cl₂ was kindly supplied to us by the institute 'G. *Ciamician*', Bologna, Italy. Methylviologen (*Ferak*, Berlin) was used without further purification. Deionized water was first distilled from alkaline permanganate and subsequently twice from a quartz still. '*Adams*' catalyst (PtO_2 for dehydrogenation) was obtained from *Fluka*. All other substances were analytical grade and were used as supplied by the vendor.

Continuous irradiation experiments were carried out using an *Osram* XBO-450 watt lamp as a light source. A 400 nm cut-off filter was placed in the beam to eliminate UV. wavelengths. A gas chromatographic method was employed for hydrogen detection. The instrument used was a *Becker* 419 (H.P.) chromatograph with a Carbosieve S (activated charcoal) 80/100 column supplied by *Supelco Inc.* (USA), which was run at 40°. A thermal conductivity detector was used for the identification of the gases.

Laser photolysis experiments were performed with a *J.K.* 2000 frequency doubled neodymium laser. The Q-switched pulse had a duration of 15 ns and an energy of *ca.* 100 mJ. Transient absorptions were detected by fast kinetic spectroscopy. The details of this method have been published elsewhere [5]. All samples were free from oxygen by flushing with helium.

Results and discussion. – i) *Laser Experiments.* The excitation of $Ru(bipy)_3^{2+}$ with the 530 nm light pulse leads to the formation of a *ML*-charge transfer excited state [6] which has triplet character ($Ru(bipy)_3^{2+*}$). This state exhibits strong reducing properties [7]. Thus, in acetonitrile solution, it is capable of reducing methylviologen [8] according to the equation

$$Ru(bipy)_3^{2+*} + MV^{++} \longrightarrow MV^+ + Ru(bipy)_3^{3+} \tag{5}$$
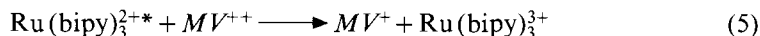
We shall now briefly examine the features of this redox process in aqueous solution. The kinetic analysis was performed by monitoring the characteristic

absorptions of MV^+ at 395 and 600 nm, the bleaching of $Ru(bipy)_3^{2+}$ ground state absorption at 452 nm and the luminescence of $Ru(bipy)_3^{2+*}$ at 615 nm. Oscilloscope traces illustrating the time course of these events are presented in *Figure 1*. The signal at 605 nm grows concomitantly with the 615 nm luminescence decay indicating that the quenching of excited states leads to the formation of reduced methylviologen as described by equation (5). Experiments performed with a series of MV^{++} concentrations showed that the kinetics of the quenching process are pseudo first order with respect to MV^{++}, the rate constant for the reduction of MV^{++} by excited $Ru(bipy)_3^{2+}$ being

$$k_5 = (5 \pm 0.4) \times 10^8 \text{ M}^{-1} \text{s}^{-1}$$

This value is somewhat lower than the rate constant $k_5 = 2.4 \times 10^9$ M^{-1}s^{-1} reported for the same reaction in acetonitrile [9].

The quantum efficiency of the methylviologen reduction by $Ru(bipy)_3^{2+}$ may be expressed as a product of three terms:

$$\eta = \phi_{CT} \cdot \eta_q \cdot \eta_{re} \tag{6}$$

where the symbols ϕ_{CT}, η_q and η_{re} refer to the quantum yield for the formation of CT. excited $Ru(bipy)_3^{2+}$ and the probabilities of the quenching and charge transfer events, respectively. The first parameter, ϕ_{CT}, has been determined to be practically unity [9]. The quenching probability of $Ru(bipy)_3^{2+*}$ by MV^{++} is defined by the kinetic expression

$$\eta_q = \frac{k_5[MV^{2+}]}{k_5[MV^{2+}] + k_o} \tag{7}$$

where $k_o = 1.6 \times 10^6$ s^{-1} designates the rate constant of the luminescence decay in the absence of the quencher. For a concentration of MV^{2+} of 10^{-2} M, which was employed throughout the experiments, we derive from eq. (7) a value of $\eta_q = 0.76$. The parameter η_{re} was evaluated according to a procedure described previously [10]. The bleaching signal immediately after the light pulse observed at 452 nm, ΔA_{452}, was compared to the transient absorption produced at 600 nm after completion of reaction (5), ΔA_{600}. ΔA_{452} contains a negative contribution from the removal of $Ru(bipy)_3^{2+}$ and a positive contribution from the formation of excited states

$$\Delta A_{452} = (-143000 + \varepsilon_{452}^*) C_o^*$$

Here, the number 143000 and the symbol ε_{452}^* represent the extinction coefficients for ground and excited state $Ru(bipy)_3^{2+}$ respectively, while C_o^* stands for the concentration of excited states produced during the laser pulse. The transient optical density produced at 600 nm, ΔA_{600}, arises exclusively from MV^+ formed in reaction (5):

$$\Delta A_{600} = 11300 \cdot C_{MV^+}$$

where 11300 is the extinction coefficient of reduced methylviologen at 600 nm [11]. If the quantum efficiency η_{re} is to be derived from the experimental quantities ΔA_{600} and ΔA_{452}, an assumption has first to be made regarding the magnitude of

ε^{*}_{452}. Using for this extinction coefficient an upper limit [12] of 7000 $\text{M}^{-1}\text{cm}^{-1}$, one obtains $\eta_{re}=0.17$. Alternatively, if we suppose that ε^{*}_{452} is small compared to 14300, a value $\eta_{re}=0.30$ is derived. Thus, under our experimental conditions, where $\eta_{q}=0.76$, the overall quantum yield for the reduction of methylviologen is contained within the limits 0.1 and 0.25.

From a comparison of the reduction potential of the two redox couples participating in reaction (5): $E_{o}(\text{Ru}(\text{bipy})_{3}^{3+}/\text{Ru}(\text{bipy})_{3}^{2+})=1.26$ V [13] and $E_{o}(MV^{++}/MV^{+})=-0.44$ V, it is apparent that this process is endoergic by 1.7 eV with respect to ground state $\text{Ru}(\text{bipy})_{3}^{2+}$. This energy difference provides the driving force for the back reaction:

$$MV^{+} + \text{Ru}(\text{bipy})_{3}^{3+} \longrightarrow MV^{++} + \text{Ru}(\text{bipy})_{3}^{2+} \tag{8}$$
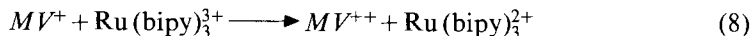
which therefore occurs spontaneously and at a high rate. Reaction (8) is illustrated by the lowest oscilloscope trace in *Figure 1*, which shows the long-time behaviour
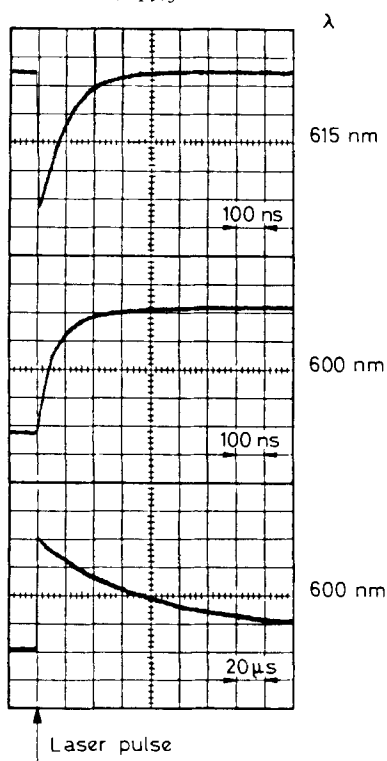

Fig. 1. *Oscilloscope traces obtained from the 530 nm laser photolysis of aqueous solutions containing $4 \cdot 10^{-5}$ M $\text{Ru}(\text{bipy})_{3}^{2+}$ and 10^{-2} M methylviologen*
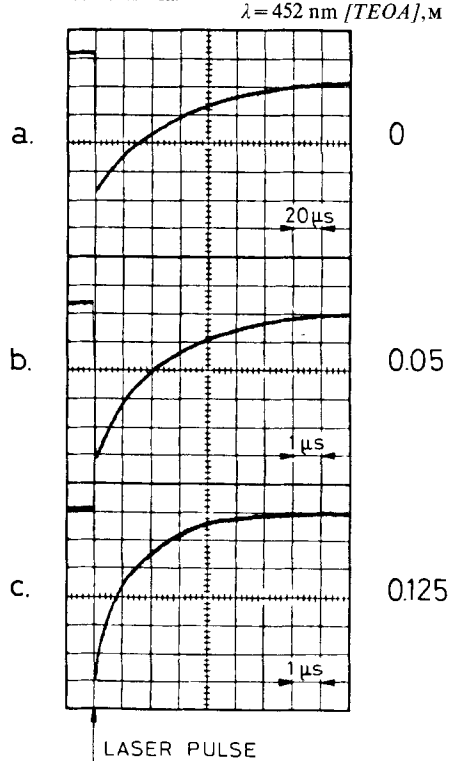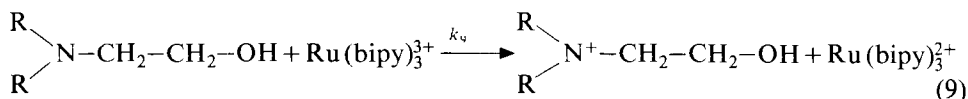
Fig. 2. *Oscilloscope traces showing the bleaching recovery of the $\text{Ru}(\text{bipy})_{3}^{2+}$ absorption at 452 nm in the absence and presence of triethanolamine ($\text{Ru}(\text{bipy})_{3}^{2+}$ $4 \cdot 10^{-5}$ M)*

of the MV^+ absorption at 600 nm. A gradual decay of the signal back to the original base line is noted in this time domain, which exhibits second-order characteristics. The kinetic evaluation yields:

$$k_8 = 2.4 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$$

The back reaction (8) may be prevented by adding a third component such as cysteine or triethanolamine to the solution which is capable of reducing $Ru(bipy)_3^{3+}$ back to the 2+ state (eq. 4). In the case of triethanolamine, equation (4) may be reformulated:

$$\underset{R}{\overset{R}{>}}N-CH_2-CH_2-OH + Ru(bipy)_3^{3+} \xrightarrow{k_9} \underset{R}{\overset{R}{>}}N^+-CH_2-CH_2-OH + Ru(bipy)_3^{2+} \tag{9}$$

This process manifests itself as an enhancement of the bleaching recovery at 452 nm which goes proportional with the TEOA concentration. For example, the lowest trace in *Figure 2* shows that in the presence of 0.125 M *TEOA* the signal returns to its original level within a period of only a few microseconds, while the return takes several hundred microseconds in the absence of TEOA. From a simple pseudo first-order analysis, we obtain for the rate constant of reaction (9) the value

$$k_9 = 6.5 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$$

In our three-component system *TEOA* might also interact directly with excited state $Ru(bipy)_3^{2+}$ via reductive quenching:

$$TEOA + Ru(bipy)_3^{2+*} \longrightarrow TEOA^+ + Ru(bipy)_3^+$$
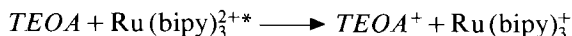
However, this possibility can be excluded from laser photolysis experiments with solutions containing only *TEOA* and $Ru(bipy)_3^{2+}$. Even at relatively high *TEOA* concentration (0.4 M) the lifetime of the excited state emission remains unchanged and the characteristic absorption of $Ru(bipy)_3^+$ at 510 nm does not appear after light excitation.

Turning now to the kinetic features of the MV^{2+} absorption at 600 nm, we note that in the three-component system, $MV^{2+}/Ru(bipy)_3^{2+}/TEOA$, these are crucially dependent on both the *TEOA* concentration and the pH of the solution. The effect of *TEOA* concentration for neutral conditions is illustrated in *Figure 3*. From the inserted oscilloscope traces it is seen that the 600 nm absorption decays in the microsecond time range until a plateau is attained. This remaining absorption in the absence of oxygen is stable over days giving the solution the characteristic blue color of MV^+. Upon admission of air to the solution, the blue color vanishes. The ratio of absorbances obtained in the plateau region to that initially present after the laser pulse, $\tau = A_p/A_o$, as well as the rate of the fractional decay increase with *TEOA* concentration, *Figure 3*. For example, at $[TEOA] = 0.125$ M, τ reaches the value 0.60, implying that under these conditions 60% of the MV^+ originally produced in the photoredox reaction escapes from reoxidation.

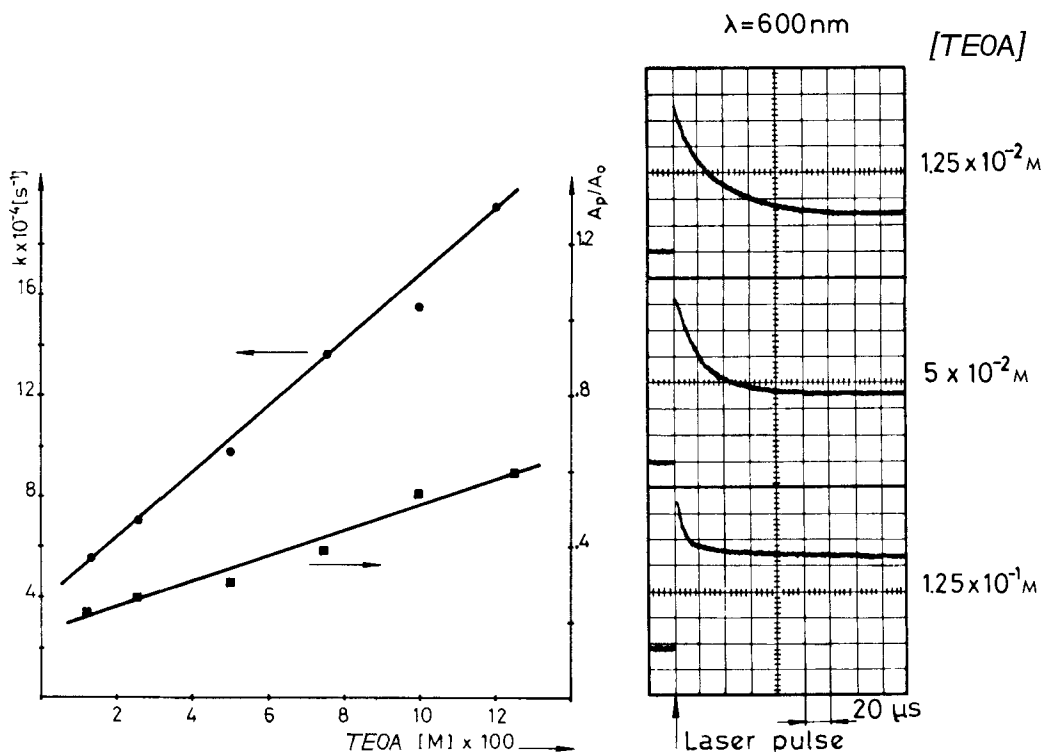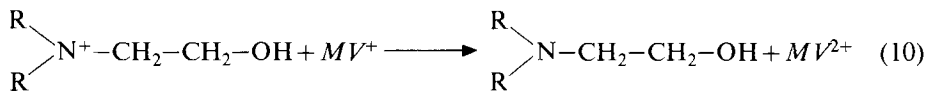The kinetic concept developed so far is not sufficient to account for these

Influence of *TEOA* Concentration on the *MV*+ Decay Kinetics

Fig. 3. *Effect of triethanolamine concentration on the behavior of the* MV+ *absorption at 600 nm.* Plot of the ratio of transient absorbances obtained in the plateau region and immediately after laser pulse as well as the rate of *MV*+ decay versus *TEOA* concentration. Representative oscilloscope traces are included in the figure

observations. Thus, the fractional decrease in the *MV*+ absorption cannot be solely attributed to a simple competition of reactions (8) and (9), *i.e.* the $Ru(bipy)_3^{3+}$ reduction by *MV*+ and *TEOA* respectively. At *[TEOA]* = 0.125 M the latter process should dominate and hence practically no *MV*+ reoxidation should occur. Also from a comparison of the oscilloscope traces 2c and 3c, it is apparent that under identical conditions of pH and *TEOA* concentration, the 452 nm bleaching recovery is considerably faster than the 600 nm absorption decay. Thus, at a time when $Ru(bipy)_3^{3+}$ has disappeared from the sphere of reaction, the reoxidation of *MV*+ to MV^{2+} continues to occur. This indicates that the second oxidant produced in solution, *i.e.* the cation radical of *TEOA* (*TEOA*+) is also capable of abstracting an electron from *MV*+:
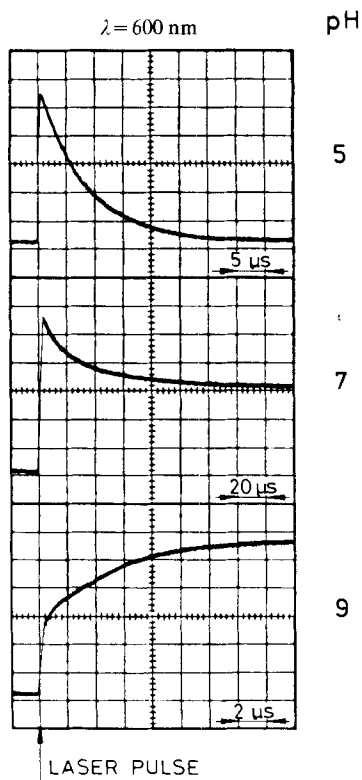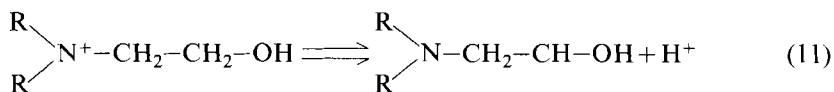
$$\begin{matrix} R \\ \\ R \end{matrix}\hspace{-0.3em}N^+\text{-}CH_2\text{-}CH_2\text{-}OH + MV^+ \longrightarrow \begin{matrix} R \\ \\ R \end{matrix}\hspace{-0.3em}N\text{-}CH_2\text{-}CH_2\text{-}OH + MV^{2+} \quad (10)$$

On the basis of the reduction potential of *TEOA*+, E_o *(TEOA*+/*TEOA)* = 0.82 V, reaction (10) is energetically favourable by 1.26 V and hence should occur

quantitatively. This, however, contradicts the experimental evidence shown in *Figure 3*, which indicates that a considerable fraction of MV^+ can escape from reoxidation by $Ru(bipy)_3^{3+}$ or $TEOA^+$ and remain stable in solution.

A rationale for this behaviour is provided by the effect of pH in the kinetic events. *Figure 4* shows the temporal behaviour of the 600 nm absorbance in solutions of different pH where the *TEOA* concentration was maintained at 0.05 M. In acid medium, the signal returns completely to the zero line indicating that all the MV^+ formed in the photoredox process (5) is reoxidized to MV^{2+}. Under steady state illumination, no blue color is produced. The features in neutral solution are characterized by a fractional decay of the MV^+ absorption as was discussed above. A drastic change is noted in alkaline medium where the 600 nm signal does not decay at all. On the contrary, the first and rapid rise of the absorption resulting from the formation of MV^+ *via* reaction (5) is followed here by a second and slower growth indicating additional MV^+ production.
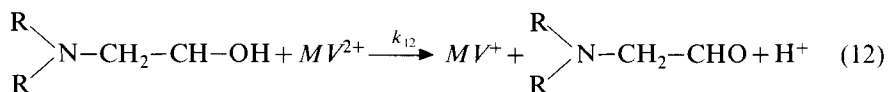
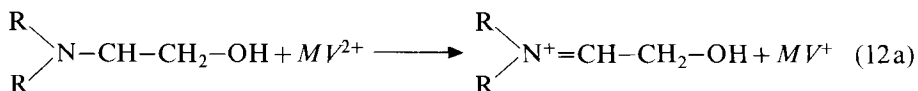These observations may be explained in terms of an acid base equilibrium of the *TEOA* cation:

$$\underset{R'}{\overset{R}{>}}N^+-CH_2-CH_2-OH \rightleftharpoons \underset{R'}{\overset{R}{>}}N-CH_2-CH-OH+H^+ \qquad (11)$$

$\lambda = 600$ nm   pH

Effect of pH on the MV^+ Kinetics
0.1 M *TEOA*, 4×10^{-5} M $Ru(bipy)_3^{2+}$, 10^{-2} M MV^{++}

5

5 µs

7

20 µs

9

2 µs

LASER PULSE

Fig. 4. *Effect of pH on the absorbance kinetics of* MV$^+$ *at 600 nm*

It appears that at pH 9 the cation $TEOA^+$ deprotonates to yield a neutral radical with the unpaired electron in a-position to either the amino or alcohol group. Such a species is expected to exhibit reducing instead of oxidizing properties [3]. Hence, after deprotonation of $TEOA^+$, the reoxidation of MV^+ can no longer occur. At pH 9, the proton loss seems to be rapid enough to dominate over the competing back electron transfer (10). Thus, practically all the MV^+ initially produced in the photoredox process remains in the reduced state. The strongly reducing properties of the neutral $TEOA$ radical manifests itself also through the fact that it is capable of transferring an electron to MV^{2+}:

$$\underset{R'}{\overset{R}{\diagdown}}N-CH_2-CH-OH + MV^{2+} \xrightarrow{k_{12}} MV^+ + \underset{R'}{\overset{R}{\diagdown}}N-CH_2-CHO + H^+ \quad (12)$$

If the a-amino radical is formed predominantly in the deprotonation step, an alternative reaction pathway may be conceived[1]), $i.e.$:

$$\underset{R'}{\overset{R}{\diagdown}}N-CH-CH_2-OH + MV^{2+} \longrightarrow \underset{R'}{\overset{R}{\diagdown}}N^+=CH-CH_2-OH + MV^+ \quad (12a)$$

The immonium form is expected to decompose according to:

$$H_2O + \underset{R'}{\overset{R}{\diagdown}}N^+=CH-CH_2-OH \longrightarrow \underset{R'}{\overset{R}{\diagdown}}NH + OHC-CH_2-OH \quad (12b)$$
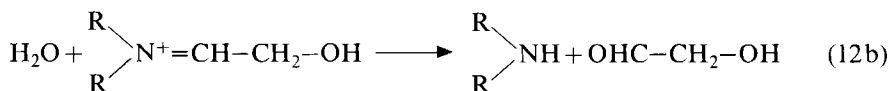
Reaction (12) or (12a) accounts for the second growth of the MV^+ absorption in *Figure 4c*. Its rate constant was determined as $k_{12} = 2.5 \times 10^6 \, M^{-1} s^{-1}$.

At pH 5, the equilibrium situation seems to favour the protonated form of the radical. As a consequence, the back reaction (10) can occur quantitatively, the system is cyclic, and no permanent chemical changes are induced by light.

In neutral solution, the protonated and unprotonated radical form coexist. Here the reactions (9), (10) and (11) occur simultaneously. As a result, only a fraction of the MV^+ initially produced can be preserved from reoxidation. As the deprotonation of $TEOA^+$ is a base catalyzed reaction, its rate will depend not only on the pH but also on the concentration of $TEOA$ which itself can act as a proton acceptor. This explains why in *Figure 3* the MV^+ decay is enhanced by increasing the $TEOA$ concentration while at the same time the fraction of MV^+ which is reoxidized decreases.

A final point which has to be dealt with when pH effects are being considered is the acide-base equilibrium of the $TEOA$ itself. As the pK value of this amine is within the pH range investigated, the protonated and neutral form coexists in the solution. The former should be a worse electron donor than the latter. As the relative proportions of the two species change with pH, it is expected that the rate constant k_9 for the reduction of $Ru(bipy)_3^{3+}$ by $TEOA$ is pH-dependent. Indeed, we find for pH 5,7 and 9 the values $k_g = 2.4 \times 10^5$, 6.5×10^6 and 4.7×10^7 indicating

---

[1])   We are grateful to the referee for suggesting this possibility.

that essentially only the unprotonated form of the amine is effective as a reducing agent. Similar conclusions have been reached by *Lehn & Sauvage* [3] who also employed *TEOA* as an electron donor in a hydrogen evolution system.

A few additional experiments were carried out with cysteine instead of *TEOA* as electron donor. In this case, the reduction of $Ru(bipy)_3^{3+}$ occurs with a specific rate of $3.7 \times 10^6 \, M^{-1} s^{-1}$. In analogy to the *TEOA* system, the deprotonation of the cysteine cation radical:

$$Cys\text{-}SH^+ \longrightarrow Cy\text{-}S\cdot + H^+ \tag{13}$$
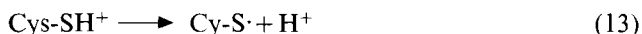
represents here also the crucial step through which the back reaction of $Cys\text{-}SH^+$ with reduced methylviologen is prevented. Thus, in neutral solution at $0.05\,M$ cysteine 35% of the MV^+ escapes from reoxidation while at pH 9, this fraction increases to almost 100%. The equivalent of reaction (12), *i.e.* reduction of MV^{++} by Cy-So does not occur in this system. The fate of the neutral cysteine radical is probably recombination under formation of cysteine:

$$2 \, Cys\text{-}S\cdot \longrightarrow Cys\text{-}S\text{-}S\text{-}Cys \tag{14}$$
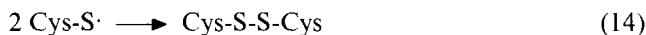
ii) *Continuous Irradiation Experiments. Redox Catalysis.* Upon irradiation of a neutral solution of $Ru(bipy)_3^{2+}/MV^{++}$ in the presence of *TEOA*, an intense blue color is produced corresponding to the MV^+ absorption spectrum. When such a solution is stirred with a few milligrams of PtO_2 (*Adams* catalyst), it resumes the yellow-orange color of the sensitizer. This cycle can be repeated many times. Spectral and gas chromatography evidence indicates that during the stirring process MV^+ is reoxidized to MV^{2+} while water is reduced to hydrogen:

$$2 \, MV^+ + H_2O \xrightarrow{\;PtO_2\;} 2 \, MV^{2+} + H_2 + 2 \, OH^- \tag{15}$$
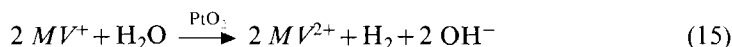
Apparently, *Adams* catalyst can mediate the water reduction by MV^+ which under standard conditions at pH 7 is exoergic by only a few tenths of an electron volt. The principle of such a catalytic action is illustrated in *Figure 5.* The PtO_2 particles
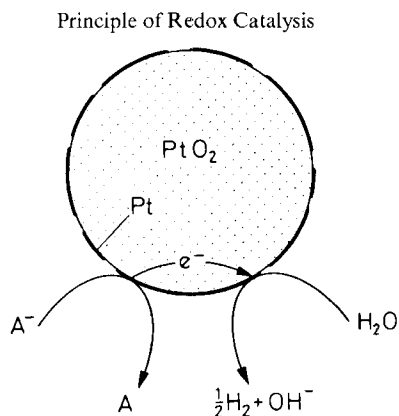
Principle of Redox Catalysis

Fig. 5. *Schematic illustration of the principle of redox catalysis.* The finely dispersed Pt on the surface of the PtO_2 particle mediates electron transfer from the reduced acceptor ion A to the water

in neutral aqueous solution are covered by a thin layer of platinum constituting the active part of the catalyst. Upon adsorption of reduced acceptor ions on the surface of the particles, a negative potential is imposed on the platinum which suffices to induce H_2 evolution from water. The low overpotential for the evolution characteristic for this metal insures that energy losses in the redox process (15) are minimal.

When illumination and stirring with the catalyst is carried out simultaneously, continuous production of H_2 is observed. In a typical experiment, 100 ml neutral solution containing 10^{-2} M MV^{2+}, 4×10^{-5} M $Ru(bipy)_3^{2+}$ and 0.05 M $TEOA$ was irradiated through a 400 nm cut-off filter with the Xe-lamp. During an irradiation time of 0.5 h, a quantity of 0.40 ml H_2 was produced. Within this period, no depletion of the sensitizer and the methylviologen could be detected. The donor $TEOA$, on the other hand, is used up through irreversible oxidation which manifests itself in a gradual darkening of the solution. The yield of H_2 was found to depend strongly on the pH of the solution. For example, at pH 5 no H_2 could be detected after illumination. This is explained by the results of the laser photolysis experiments which showed that MV^+ is rapidly reoxidized *via* reaction (10), and hence is not available for water reduction. In alkaline solution (pH 9), we also fail to observe hydrogen evolution. Through under these conditions the formation of MV^+ occurs with a high yield, the subsequent Pt-catalyzed reduction of water cannot take place. An irradiated solution maintains its blue color even after prolonged stirring with the catalyst. This is due to the fact that at pH 9 reaction (15) is energetically unfavorable since the reduction potential of water has shifted by 118 mV towards the negative side.

From these results, it is concluded that in the selection of the optimal conditions for light induced H_2 evolution a compromise has to be made with respect to the pH of the solution. Evidently, the yield of stable MV^+ from the photoreduction of methylviologen increases with pH while for energetic reasons the inverse trend holds for the efficacy of the redox catalysis. Therefore, a pH close to 7 appears to be a suitable choice, though under these conditions a considerable fraction of the MV^+ produced in the photochemical step is lost through reoxidation. We encounter here a problem that is typical for any homogeneous photoredox system to which a third component is added as an electron source to prevent thermal back reaction. The oxidation of this species leads to reactive intermediates which may undergo undesirable side reactions. For this reason, it appears preferable to restrict the number of reactive components to two, *i.e.* the donor and acceptor participating in the light reaction, and to employ suitable molecular organizations such as micelles or membranes in order to kinetically control the light and subsequent dark reactions.

In conclusion, the results obtained from the present investigation indicate the suitability of certain redox catalysts to mediate hydrogen evolution from water by reducing agents. We confirm here the recent observations made on similar three component systems [2]. By means of laser photolysis technique the detailed mechanism and the kinetics of the individual processes occurring in our test system were explored. The summarizing scheme given in *Figure 6* indicates that the overall mechanism induced by light is reduction of water and oxidation of the third
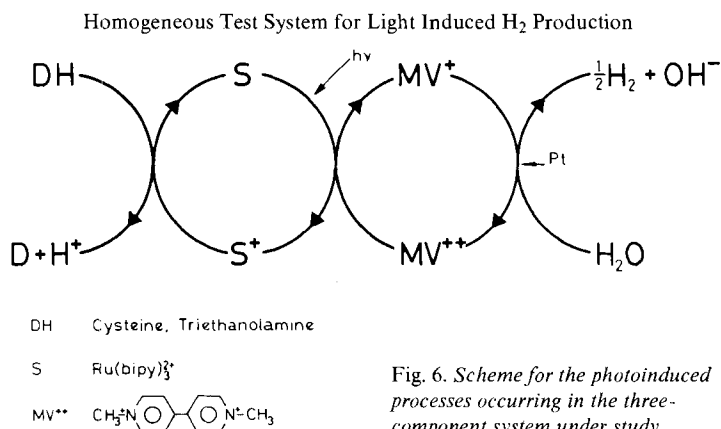
Homogeneous Test System for Light Induced H_2 Production

DH	Cysteine, Triethanolamine
S	$Ru(bipy)_3^{2+}$
MV⁺⁺	CH_3^+N⟨O⟩–⟨O⟩$N^+\text{-}CH_3$

Fig. 6. *Scheme for the photoinduced processes occurring in the three-component system under study*

component employed as an electron source. The understanding of the nature of redox catalysis and its application to photoprocesses in organized molecular aggregates such as functional micelles and vesicles should be of great value to resolve the problem of water cleavage by visible light.

REFERENCES

[1] (a) *G. Porter & M.D. Archer*, Interdisc. Sci. Rev. *1*, 119 (1976); (b) *M. Calvin*, Photochemistry Photo-biol. *23*, 425 (1976); (c) 'Solar Power and Fuels', J.R. Bolton, ed., Academic Press, N.Y. 1977.
[2] *B.V. Koryakin, T.S. Dzhabier & A.E. Shilov*, Dokl. Akad. Nauk, SRRR *238*, 620 (1977).
[3] *J.M. Lehn & J.P. Sauvage*, Nouveau J. Chim. *1*, 449 (1977).
[4] *J. Kiwi & M. Grätzel*, submitted for publication.
[5] *G. Beck, J. Kiwi, D. Lindenau & W. Schnabel*, Eur. Polym. J. *10*, 1069 (1974).
[6] (a) *H.D. Gafney & A.W. Adamson*, J. Amer. chem. Soc. *94*, 8238 (1972); (b) *I.N. Demos & I.W. Addington*, J. Amer. chem. Soc. *98*, 5800 (1976); (c) *V. Balzani, L. Maggi, M.F. Manfrin, F. Bolletta & G.S. Lawrence*, Co-ord. Chemistry Rev. *15*, 321 (1975) and references cited therein.
[7] *D. Meisel, M.S. Matheson & J. Rabani*, J. Amer. chem. Soc. *100*, 117 (1978).
[8] *R.C. Young, T.J. Meyer & D.G. Whitten*, J. Amer. chem. Soc. *98*, 286 (1976).
[9] *F. Boletta, M. Maestri & V. Balzani*, J. phys. Chemistry *80*, 2499 (1976).
[10] *M. Maestri & M. Grätzel*, Ber. Bunsenges. physik. Chem. *81*, 505 (1977).
[11] *P.A. Trudinger*, Analyt. Biochemistry *36*, 222 (1970).
[12] A reasoning is given in ref. [7].
[13] *C. Creutz & N. Sutin*, Proc. Nat. Acad. Sci. USA *72*, 2858 (1975).