

TEMPERATURE EFFECT ON THE PHOTOINDUCED REDUCTION OF METHYL VIOLOGEN WITH SEVERAL SENSITIZERS AND THE EVOLUTION OF HYDROGEN FROM WATER

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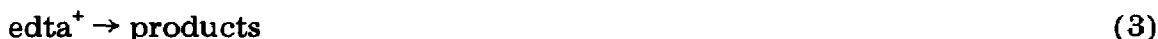
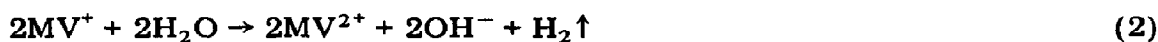
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Summary

Irradiation by visible light of an aqueous solution containing a photosensitizer, methyl viologen (MV^{2+}) and ethylenediaminetetraacetic acid leads to the formation of the reduced form of methyl viologen (MV^+). The quantum yield for the formation of MV^+ depends strongly on the time during which the formation is observed owing to the reaction of MV^+ with oxidative products and its reduction to MV^0 . Proflavin, acridine yellow and ruthenium(II)tris(2,2-bipyridyl) were used as photosensitizers and showed the same ability to promote hydrogen evolution. When CdS was used as a sensitizer a factor of 10 less hydrogen was obtained than when the dyes were used. The redox catalysts platinum, Pt-TiO₂-RuO₂ and Pt-CdS in colloidal systems showed approximately the same activity towards the reduction of water. The reduction of MV^{2+} and the evolution of hydrogen were enhanced at higher temperatures (70 °C). The optimum conditions for water reduction on redox catalysts in colloidal systems under continuous illumination are analysed.

1. Introduction

In recent years there has been considerable interest in the photodecomposition of water to molecular hydrogen and oxygen induced by visible light [1 - 7]. The production of hydrogen from water is well documented and numerous studies have been reported which utilize various sensitizers (S), the electron donor ethylenediaminetetraacetic acid (edta) and methyl viologen (MV^{2+}) as an acceptor relay for the hydrogen evolution sequence



In all these systems the evolved gas was produced at the expense of consuming edta so that the system can be termed "sacrificial".

In this study the formation of MV^+ with irradiation time was observed in the 0.1 s time scale in order to determine the initial quantum yield of MV^+ . The sensitizers ruthenium(II)tris(2,2-bipyridyl) ($Ru(bpy)_3^{2+}$) [3, 4, 7 - 10], proflavin [5, 11], acridine yellow [1, 12] and CdS [13 - 15] were used to initiate reaction (1) and the quantum yields of MV^+ and hydrogen were compared. The chemical reactions in these systems are well known and colloidal catalysts suitable for hydrogen evolution have been investigated earlier [9, 10, 16, 17]. We undertook a comparison of the quantum yields of MV^+ and hydrogen produced under the same conditions in order to obtain more information about hydrogen evolution activities for various systems since the data for quantum yields in the literature are very scarce. Hydrogen evolution was investigated at elevated temperatures and reduced pressures in order to determine the optimum conditions for hydrogen evolution.

2. Experimental details

All the reagents used were commercial products of the highest purity available. CdS (Fluka, 99.999%) was used as supplied. The solutions were prepared with triply distilled water and oxygen was removed by bubbling argon through them. The solution pH was adjusted using H_2SO_4 , NaOH or phosphate buffers.

Colloidal platinum was prepared by the reduction of K_2PtCl_6 with sodium citrate [18] followed by mixing with an ion exchange resin to remove the citrate ions. The liquid contained small particles of colloidal platinum (average size, 3 nm (measured by electron microscopy)). Colloidal platinum-poly(vinyl alcohol) (Pt-PVA) was prepared according to the method described by Kiwi and Grätzel [9].

The colloidal catalyst Pt-TiO₂ was prepared according to a procedure described elsewhere [16]. The doping of Pt-TiO₂ with RuO₂ was achieved by suspending the powder in an aqueous acid solution of $RuCl_3 \cdot 3H_2O$ and heating for several hours at 95 °C to give a deposit of RuO₂. A yellow sol of CdS was prepared from solutions of $Cd(NO_3)_2$ and CH_3CSNH_2 at pH 0.75 in the presence of PVA.

The cell employed in photoelectrochemical experiments was similar to that described by Durham *et al.* [19]. The anode compartment (platinum gauze of dimensions 2 cm × 2 cm) contained 5×10^{-5} mol proflavin dm^{-3} , 5×10^{-3} mol MV^{2+} dm^{-3} , 1×10^{-2} mol edta dm^{-3} , 1×10^{-1} mol $NaClO_4$ dm^{-3} and the phosphate buffer (pH 5). The cathode compartment (platinized platinum foil of dimensions 2 cm × 2 cm) contained 1 mol HCl dm^{-3} . The salt bridge consisted of 1×10^{-1} $NaClO_4$. Both the anode and the cathode compartments were deaerated by bubbling argon through them.

Continuous production of hydrogen was observed when the solution was illuminated with an Osram XBO 150 lamp. A 400 nm cut-off filter was

placed in the beam to eliminate UV radiation. Each irradiation was carried out on a sample of argon-saturated solution of volume 8 cm³. The light intensity was measured by potassium ferrioxalate actinometry to be 1.2×10^{-6} einsteins min⁻¹. The wavelength of the incident light was limited to 420 - 480 nm by using a k-45 Balzers interference filter. The hydrogen was detected by gas chromatography using a 154D Perkin-Elmer instrument with a silica gel column at 50 °C.

Kinetic spectrometry was used to determine the quantum yield of MV⁺ in time ranges below 1 s. The spectrometer consisted of an Osram XBO 450 W xenon lamp, an OPTON MM12 double monochromator and an RCA 1P28 photomultiplier tube coupled directly to a Tektronix 454 oscilloscope. All the optical equipment was constructed of Suprasil silica glass. The light intensity was 9.5×10^{-8} einsteins s⁻¹.

3. Results and discussion

3.1. Formation of MV⁺ ions

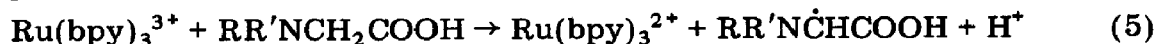
MV⁺ was produced by the steady state photolytic reaction of the photosensitizer (Ru(bpy)₃²⁺, proflavin, acridine yellow or CdS) with MV²⁺ (reaction (1)). The nature and absorption spectrum of the MV⁺ stable radical ($\lambda_{\text{max}} = 605$ nm; $\epsilon_{605} = 8.6 \times 10^3$ mol⁻¹ cm⁻¹) have been established previously [5]. edta was added to the solution to donate electrons to the photosensitizer.

Figure 1 shows the absorbance of MV⁺ obtained in Ru(bpy)₃²⁺, MV²⁺ and edta solutions as a function of the irradiation time. The quantum yield of MV⁺ in solution at pH 4.8 increases from 0.4 to 0.8 for short irradiation times. A typical kinetic spectrometry output trace is given in the inset to Fig. 1. The quantum yield of MV⁺ is time dependent and is linear only for short irradiation times ($t < 0.7$ s). The value of 0.8 is slightly higher than the value of 0.3 for $\Phi(\text{MV}^+)$ estimated previously [3] for the reaction



taking into account the formation of the excited triplet state of Ru(bpy)₃²⁺, the probability of quenching the excited triplet state and the separation of the product from the solvent cage ion pair [3, 10].

It was assumed that the radical RR'N $\dot{\text{C}}\text{HCOOH}$ formed during the photoinduced oxidation of edta [20] reacts with MV²⁺:



In our previous work [17] we have found by pulse radiolysis that the RR'N $\dot{\text{C}}\text{HCOOH}$ radical formed in the reaction of edta with OH and H reduces MV²⁺ to MV⁺ with a rate constant k_6 of 1.4×10^9 dm³ mol⁻¹ s⁻¹ at pH 5.

The rate of MV⁺ formation is dependent on the pH of the solution (Table 1). This effect can be explained by the change in the rate constant of

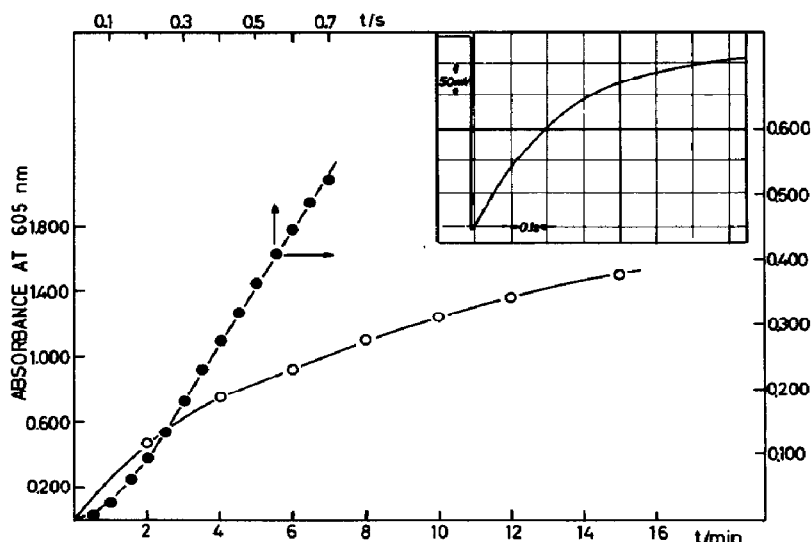


Fig. 1. Photoreduction of MV^{2+} (5×10^{-3} mol dm $^{-3}$) by edta (1×10^{-2} mol dm $^{-3}$) and $Ru(bpy)_3^{2+}$ (1×10^{-4} mol dm $^{-3}$). The abscissa represents the time scale in minutes (1.7×10^{-6} einsteins min $^{-1}$) which gives $\Phi(MV^+) = 0.4$ (○) and in seconds (9.5×10^{-8} einsteins s $^{-1}$) which gives $\Phi(MV^+) = 0.8$ (●). The oscilloscope trace shows MV^+ absorption at 605 nm.

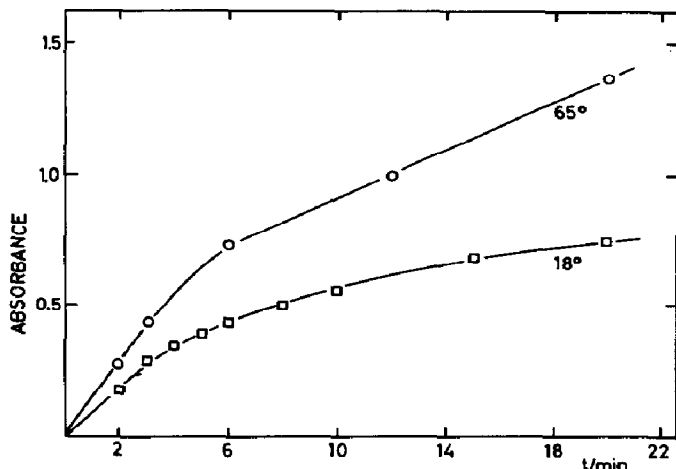
the reaction of $Ru(bpy)_3^{3+}$ with edta (eqn. (5)) which decreases over 200-fold between pH 7 ($k = 2 \times 10^6$ mol $^{-1}$ s $^{-1}$ dm 3) and pH 4 ($k = 8 \times 10^3$ mol $^{-1}$ s $^{-1}$ dm 3) [21]. At pH 4, edta becomes protonated and reacts more slowly with $Ru(bpy)_3^{3+}$. The time dependence of MV^+ formation is a result of competition between the reaction of $Ru(bpy)_3^{3+}$ with edta and the back reaction of $Ru(bpy)_3^{3+}$ with MV^+ .

Figure 2(a) shows the absorbance of MV^+ in proflavin, MV^{2+} and edta solutions as a function of the irradiation time at two different temperatures. The formation of MV^+ is not linear on the minute time scale and extensive photolysis leads to its gradual disappearance, probably by further reduction to MV^0 . However, it is linear for the first 0.5 s and a value of 0.9 was obtained for $\Phi(MV^+)$ using kinetic spectrometry. MV^+ is formed more effectively at elevated temperatures. Since reaction (1), in which MV^+ is formed, is very fast [11], the increase in temperature probably only affects the reduction of MV^+ to MV^0 . The addition of MV^{2+} ions to an air-free solution of MV^+ leads to an increase in the MV^+ concentration of about 10% probably because of the oxidation of MV^0 to MV^+ .

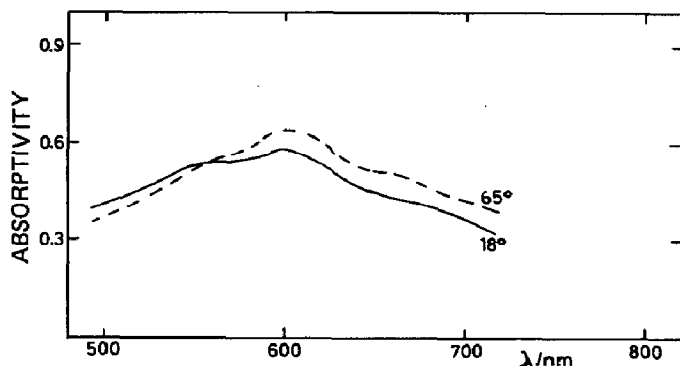
The absorption spectra of MV^+ at 18 and 65 °C are presented in Fig. 2(b). There is only a slight difference in the molar absorptivity but the shape of the spectrum is changed probably owing to the dissociation of small amounts of $(MV^+)_2$ formed according to the reaction



for which $K = 2.6 \times 10^{-3}$ [22]. This dimerization process takes place at room



(a)



(b)

Fig. 2. (a) Photoreduction of MV^{2+} (5×10^{-3} mol dm^{-3}) by edta (1×10^{-2} mol dm^{-3}) and proflavin (5×10^{-5} mol dm^{-3}); (b) difference in the absorption spectra of MV^+ ions (10^{-4} mol dm^{-3}) measured in two similar photolysed solutions one of which was heated to 65 °C.

temperature and high MV^+ concentrations (above 10^{-4} mol dm^{-3}), and the spectrum of $(MV^+)_2$ is shifted to shorter wavelengths ($\lambda_{max} = 550$ nm).

3.2. Temperature effect

MV^+ radicals on a platinum catalyst reduce water according to eqn. (2). In order to ensure that the hydrogen formation step is fast the electron transfer from MV^+ to the catalyst has to compete with reactions in which MV^+ disappears, *i.e.* the back reaction of MV^+ with S^+ , the reduction of MV^+ to MV^0 and the hydrogenation of MV^+ on platinum [23, 24]. It has previously been found that fast electron transfer from MV^+ to platinum takes place in platinum, Pt-TiO₂ [9, 16] and Pt-CdS colloids.

The hydrogen quantum yields (Table 1) depend strongly on temperature. The increase in the temperature probably favours the evolution of

TABLE 1
Evolution of hydrogen from aqueous solutions containing various sensitizers under the action of visible light^a

Photosensitizer	Catalyst	pH	$\Phi(MV^+)$ ^b at 20 °C		$\Phi(H_2)$		$2\Phi(H_2)/\Phi(MV^+) \times 100$
			20 °C	70 °C	20 °C	70 °C	
Ru(bpy) ₃ ²⁺		2 - 4.2	0.08 - 0.60				
		4.7	0.8 ^c				
		5.3 - 8.7	1.4 - 1.5				
Proflavin	Pt (citric acid) colloid ^d	4.7		0.07 ^e	-0.20	50	
	Pt-TiO ₂ -RuO ₂ colloid ^f	4.7		-	0.33	82	
Proflavin, CdS ^h	-	4.7 - 5	0.90				
	Pt black powder ^g			0.03	0.06	13	
	TiO ₂ powder ^g			0.04	0.04	9	
	Pt-PVA colloid ^d			0.18	0.30	67	
	Pt (citric acid) colloid ^d			0.15	0.25	55	
Acridine yellow	Pt (citric acid) colloid ^d	4.8	0.9	-	-	78	
	Pt-PVA colloid ^d			0.17	0.25	55	
CdS powder ^j CdS colloid ^l Pt-CdS powder ^m		6.2	0.1 - 0.2 ^k	0.15	0.26	57	
						0.03	

^a The experimental procedure is described in Section 2. Each irradiation was carried out on a sample of volume 8 cm³ saturated with argon. The value reported for hydrogen evolution is the average of two to four determinations with an error of 20%. Experimental conditions: 1 × 10⁻⁴ mol⁻¹ dm³ S; 5 × 10⁻³ mol MV²⁺ dm⁻³; 0.1 mol edta dm⁻³.

^b Initial quantum yield of MV⁺ production obtained in time range 0.1 - 1 s; absorbed light intensity 9.5 × 10⁻⁸ einsteins s⁻¹.

^c Values of 0.30 have been reported earlier [9].
^d 10 mg Pt dm⁻³.
^e 40 mg Pt dm⁻³; 110 mg CdS dm⁻³; 5 × 10⁻³ mol MV²⁺ dm⁻³; 0.1% PVA.
^f 100 mg CdS dm⁻³; 5 × 10⁻³ mol MV²⁺ dm⁻³; 0.2 mol edta dm⁻³.

^g A value of 0.13 has been reported for Pt-PVA [9].

^h 40 mg Pt dm⁻³; 1 g TiO₂ dm⁻³; 8 mg RuO₂ dm⁻³.

ⁱ Catalyst content, 120 mg dm⁻³.

^j The solution contained 1 g CdS dm⁻³.

^k Obtained from the slope after the induction period.
^l 110 mg CdS colloid dm⁻³; 5 × 10⁻³ mol MV²⁺ dm⁻³; 0.2 mol edta dm⁻³.
^m 40 mg Pt dm⁻³; 1 g CdS dm⁻³; 0.2 mol edta dm⁻³.

hydrogen because of increases in the rates of the processes on the catalyst. All the dyes used show approximately the same activity towards hydrogen evolution. For all colloidal catalysts (platinum, Pt-PVA, Pt-TiO₂-RuO₂ and Pt-CdS) the quantum yields of hydrogen evolution differ by only about 20%. Colloidal platinum hydrosol stabilized with citrate ions shows better reproducibility and a smaller loss of activity than the Pt-PVA. The pulse radiolysis experiment showed that the reaction



has a pseudo-first-order rate constant of $1.2 \times 10^4 \text{ s}^{-1}$ for the solution containing $110 \text{ mg CdS dm}^{-3}$ and 40 mg Pt dm^{-3} . This rate constant is the same order of magnitude as that for the platinum hydrosols [17] and one order of magnitude lower than that for the Pt-TiO₂ colloid [16]. In the presence of hydrogen, which is a real condition in the case of the continuous evolution of hydrogen from water, electron transfer from MV⁺ to platinum decreases markedly. In our previous work it was shown that the rate of reaction with platinum at a concentration of $2.5 \times 10^{-5} \text{ mol Pt dm}^{-3}$ in a hydrogen-saturated solution was 0.6 s^{-1} [17]. This is three orders of magnitude lower than that in an argon-saturated solution. The inhibition of electron transfer to platinum in the presence of hydrogen probably reflects the formation of some products which are strong platinum poisons. The temperature appears to increase the rate of this reaction markedly. The maximum yield was obtained at an elevated temperature and a reduced gas pressure in the cell (Table 1, proflavin as sensitizer, 70 °C and $7.6 \times 10^4 \text{ Pa}$). Under these conditions the hydrogen evolution is approximately 80% of the stoichiometric formation in the reaction of MV⁺ with water.

3.3. CdS suspensions

CdS suspensions have previously been shown to photosensitize the reduction of MV²⁺ by edta [14]. CdS has a band gap of 2.4 eV and absorbs light strongly at wavelengths below 510 nm. A dispersion of CdS in water which was produced by sonication was irradiated in the presence of $5 \times 10^{-3} \text{ mol MV}^{2+} \text{ dm}^{-3}$ and $0.1 \text{ mol edta dm}^{-3}$ and the reduction of MV²⁺ was observed. The reduction was very pronounced and in a solution of $0.1 \text{ g CdS dm}^{-3}$ which was transparent enough to enable the absorbance of MV⁺ at 605 nm to be observed a maximum quantum yield of 0.20 for MV⁺ was determined assuming that all the light energy was absorbed in the system. However, the real yield was even higher as this amount of CdS was not sufficient to absorb all the photons [25]. The reproducibility of the results for the reduction of MV²⁺ was poor because the dispersion in the samples was not the same and the quantum yield of MV⁺ differed by 50% (Table 1). The formation of MV⁺ at 20 and 60 °C is shown in Fig. 3 as an illustration. The rate of MV⁺ formation was lower at elevated temperatures probably because of the decrease in MV²⁺ absorption on the CdS surface. After stirring a solution of $10^{-5} \text{ mol MV}^{2+} \text{ dm}^{-3}$ with 1 mg CdS ml^{-1} at room temperature the concentration of MV²⁺ was reduced to 35% of its original value which means

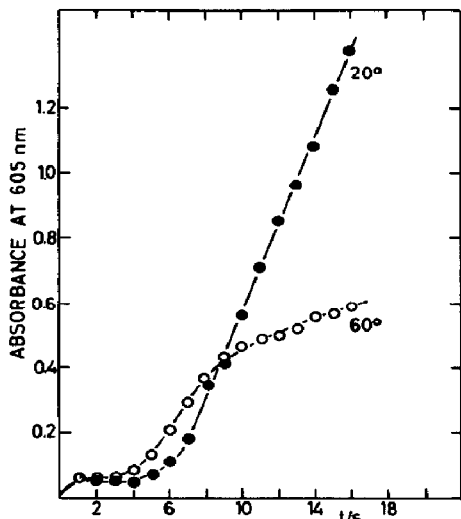


Fig. 3. Photoreduction of MV^{2+} (5×10^{-3} mol dm^{-3}) by edta (0.2 mol dm^{-3}) and CdS (1 mg ml^{-1}) measured by kinetic spectrometry.

that MV^{2+} ions were adsorbed on the CdS surface. Hydrogen formation was observed in the Pt-CdS solution in the absence of MV^{2+} . In this case the quantum yield increased with increasing temperature. The maximum quantum yield of hydrogen was 0.03 at 70 °C (Table 1) for Pt-CdS prepared under our working conditions. The high quantum yield of MV^+ shows that MV^{2+} which is adsorbed on CdS has a high electron-withdrawing power, exceeding even that of platinum deposited on CdS.

3.4. Photoelectrochemical cells

The experimental results obtained with the photoelectrochemical cell are shown in Fig. 4. The cell was similar to that described by Durham *et al.* [19]. The anode compartment contains an illuminated solution of proflavin, MV^{2+} and edta (pH 5). Electron transfer from MV^+ to platinum gauze rather than to platinum hydrosol particles occurred:



The electron produced is used to drive hydrogen evolution on a platinized platinum electrode immersed in an acid solution in the cathode compartment:



Within 10 min the current rises to 130 μA which is sustained throughout the subsequent irradiation period. The quantum efficiency of the cell in terms of the current produced per photon added to the system calculated on the basis of the maximum steady state current is 0.06 at pH 6.5. The addition of Pb^{2+} ions strongly increases the current intensity and a value of 0.26 was obtained for $\Phi(e^-)$ in the presence of 1×10^{-3} mol Pb^{2+} dm^{-3} . Pb^{2+} ions adsorb

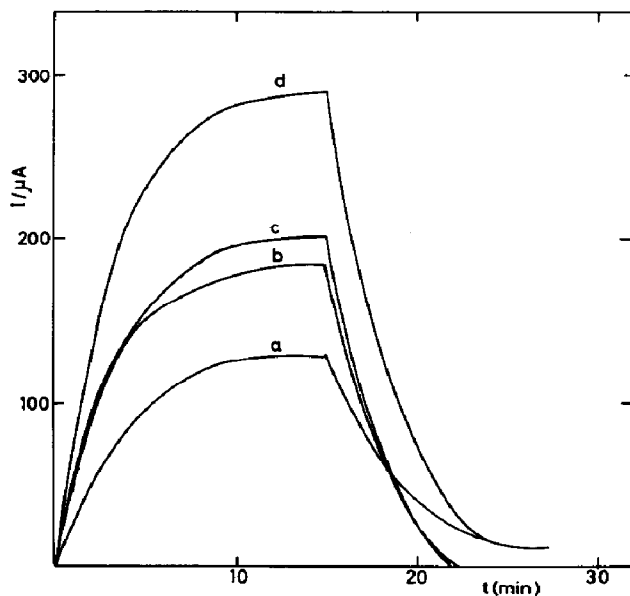


Fig. 4. The effect of the concentration of Pb^{2+} in the anode compartment on the photocurrent vs. time curves for a cell containing proflavin ($5 \times 10^{-5} \text{ mol dm}^{-3}$), MV^{2+} ($5 \times 10^{-3} \text{ mol dm}^{-3}$) and edta ($2 \times 10^{-2} \text{ mol dm}^{-3}$) at pH 6.5 in $0.1 \text{ mol NaClO}_4 \text{ dm}^{-3}$: curve a, without Pb^{2+} ; curve b, $1 \times 10^{-5} \text{ mol Pb}^{2+} \text{ dm}^{-3}$; curve c, $1 \times 10^{-4} \text{ mol Pb}^{2+} \text{ dm}^{-3}$; curve d, $1 \times 10^{-3} \text{ mol Pb}^{2+} \text{ dm}^{-3}$.

strongly on the platinum surface and modify the catalytic properties of platinum [26] which changes the mechanism of the electron transfer reaction from MV^+ to platinum.

When a platinum hydrosol is employed as the catalyst we find a maximum quantum yield corresponding to 82% of the stoichiometric conversion ($2\Phi(\text{H}_2)/\Phi(\text{MV}^+) \times 100$) at 70°C (36% conversion was obtained at 20°C). The efficiency decreases sharply to 26% (in the presence of $10^{-3} \text{ mol Pb}^{2+} \text{ dm}^{-3}$) when the platinum electrode is used for electron transfer and hydrogen production. The efficiency is even lower (about 13%) when platinum black powder is used as the catalyst (Table 1). When the electrode size is decreased to the dimensions of colloidal particles the electron transfer reaction from MV^+ to platinum, which is a rate-determining step in the hydrogen generation process, is substantially enhanced. When MV^{2+} is used as an electron relay in the presence of hydrogen the nature of the platinum surface is changed and the electron transfer to platinum is inhibited. The temperature appears to influence this transfer, probably by decreasing the adsorption of some products which are strong platinum poisons and facilitating electron transfer to platinum.

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