

Photoinduced reduction of water by diacetyl

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Abstract

The irradiation of diacetyl ($\lambda \geq 385$ nm) in the presence of the methylviologen ion (MV^{2+}), colloidal platinum catalyst, and sacrificial electron donors yields hydrogen. Such electron donors include EDTA, formaldehyde, some ethanolamines and trialkylamines. The highest hydrogen amounts are achieved with EDTA, followed by formaldehyde and triethanolamine. No hydrogen was obtained with trimethylamine as electron donor. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Diacetyl; Photoinduced water reduction; Formaldehyde; Triethanolamine

1. Introduction

The photoinduced decomposition of water for conversion and storage of solar energy has been the subject of intensive research over several decades [1–5]. Numerous systems have been studied. To utilize visible light it has been necessary to add sensitizers absorbing in a suitable range. In the past, the sensitizer has usually been tris(2,2-bipyridyl)ruthenium(II) ($Ru(bpy)_3^{2+}$), but porphyrins have also been employed. In these systems the reaction starts, together with other processes, with the transfer of an electron from the excited dyestuff to an electron carrier, e.g. methylviologen (MV^{2+}), which transfers this electron to water. To repeat the cycle, the oxidized dyestuff has then to be reduced by a sacrificial electron donor (e.g. EDTA), which by this is irreversibly degraded to different products (Fig. 1). It can be assumed that it is oxidized by oxygen, but the oxygen species involved have not been identified. A quantum yield of $\Phi(H_2) \approx 0.13$ has been obtained in a system consisting of MV^{2+} , $Ru(bpy)_3^{2+}$, EDTA, and Pt [6]. Great attention has been paid to the platinum catalyst in this reaction. It has been found that platinum catalysts stabilized with polyvinyl alcohol (PVA) are particularly effective [7,8].

Formerly, we have been able to demonstrate that a simple diketone, such as diacetyl (DA), can function as the sensitizer during the reduction of water [9]. Quantum yields of up to 0.5 (H_2) have been achieved with a novel platinum

catalyst. The oxidizing power of DA can be explained on the basis of the energy of the excited state. The triplet energy of DA^* amounts to 2.38 V. From the Rehm–Weller equation [10]

$$E_{(DA^*/DA^-)} \approx E_T + E_{1/2} \approx 2.38 \text{ V} - 0.57 \text{ V}$$

a redox potential of ca. 1.81 V can be obtained for ${}^3DA^*$. The potential is even higher (2.12 V) in the excited singlet state ($E_s = 2.69$ V). The higher reactivity of diacetyl in the singlet state [11] has been attributed to its more ionic character. However, this does not necessarily mean that the electron transfer reactions occur primarily from the singlet state. The singlet state lifetime of diacetyl is 3.6×10^4 times shorter than that of the triplet [12]. Furthermore, the quantum yield in water for the singlet state is only 0.00011 compared with 0.86 ± 0.07 for phosphorescence [12]. Investigations of the kinetics of electron transfer and hydrogen abstraction by other groups have shown that DA possesses electrophilic properties in the triplet state [13], in contrast to many other dyestuffs that have been used for this purpose. It has been established that the irradiation of DA in the presence of proton donors leads to proton uptake by DA and its reduction [14–16]. Isopropyl alcohol, phenol, primary and secondary amines have already been employed as proton donors. On the other hand, reversible electron transfer reactions without subsequent reduction are observed with tertiary and aromatic amines [14]. These are far more interesting in the connection with the use of DA as a catalyst for water reduction, not only because of the cyclic reaction of DA, but also because tertiary and aromatic amines are known to

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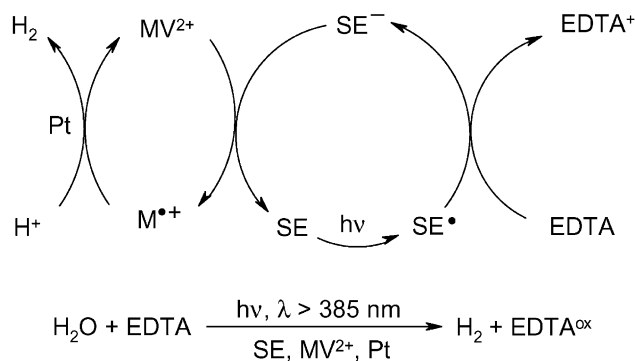


Fig. 1. Mechanism proposed for the catalyzed photoinduced decomposition of water by a sensitizer (SE), methylviologen (MV^{2+}), and EDTA with platinum as catalyst.

form stable positive ions which may not be destroyed by re-reduction. With these amines, the rates of the electron transfer reactions were greater in polar solvents, such as acetonitrile and ethanol, than they were in non-polar ones (e.g. benzene). Nevertheless, the most efficient electron donor known till now still is EDTA. For a possible employment in microheterogeneous systems, we screened the electron donor properties of some other tertiary amines (trialkylamines), ethanolamines, and, of a nonamine, formaldehyde.

2. Experimental details

2.1. Materials

Diacetyl (Fluka) was distilled once before use. Ethylenediaminetetracetic acid disodium salt (EDTA, Merck), methylviologen chloride (MV^{2+} , Fluka), hexachloroplatinic acid (Merck), formaldehyde (Fluka, 36%, stabilized with 10% methanol), triethanolamine (TEOA), *N*-methyldiethanolamine (NMDEOA), *N*-ethyldiethanolamine (NEDEOA), *N,N*-dimethylethanolamine (NNDMEOA), *N,N*-diethylethanolamine (NNDEOA), trimethylamine (TMA, 30% in water), triethylamine (TEA), tributylamine (TBA), tripropylamine (TPA, Fluka), acetic acid, sulphuric acid, sodium hydroxide, $\text{RuO}_2 \cdot \text{H}_2\text{O}$ (Merck), and PVA ($M_w = 72,000$, Fluka) were used without further purification. Triply distilled water was employed as solvent. Irradiations were carried out in pyrex glass vessels with a capacity of 36 ml. A typical irradiation solution (30 ml) contained $1.2 \times 10^{-2} \text{ mol l}^{-1}$ DA, $3.0 \times 10^{-3} \text{ mol l}^{-1}$ MV^{2+} , $5.0 \times 10^{-2} \text{ mol l}^{-1}$ EDTA, and $5.1 \times 10^{-5} \text{ mol l}^{-1}$ Pt (catalyst *a*). Catalyst *b* was used for formaldehyde-free irradiations. The pH was adjusted to 4.5 with sulphuric acid or sodium hydroxide solution. All solutions for irradiation were flushed with nitrogen for 20 min before photolysis. The light source was a 300 W Osram Vitalux lamp. To eliminate the IR portion of the radiation, a 15 cm long water filter thermostatted to 20°C was used. The UV portion was removed by means of a Schott GG 385

glass filter. The solutions were vigorously stirred by means of a magnetic stirrer during irradiation. After the irradiation, the volume of the gas space over the liquid was determined by filling the irradiation vessel with water. Hydrogen was determined by means of a GC equipped with a thermal conductivity detector. The column, which was packed with activated carbon (35–50 mesh ASTM, from Merck), was 2 m long and 2 mm in internal diameter. The carrier gas was nitrogen with a flow rate of 40 ml min^{-1} . $\text{p}K_a$ values of ethanol amines used are only approximative; they were obtained by measuring the pH of 50 ml of 0.2 mol l^{-1} base solutions after adding 50 ml of 0.1 mol l^{-1} HCl solution.

2.2. Preparation of the Pt catalysts

2.2.1. With formaldehyde

Forty milligrams of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and 100 mg of PVA were dissolved in 85 ml of water and 10 ml of formaldehyde solution added. After this, the pH of this solution was adjusted to 9.3 with 1 mol l^{-1} NaOH solution and the solution filled up with water to 100 ml. While being protected from light and oxygen, the solution was stirred for 1–2 days with a magnetic stirrer until it became dark. Then the solution was stored in the dark at -10°C . A 2 ml aliquot of it was used for each irradiation.

2.2.2. With hydrogen

Forty milligrams of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and 100 mg of PVA were dissolved in 95 ml water, the pH adjusted to 8 as above and the solution filled up with water to 100 ml. Then hydrogen was passed through the solution under exclusion of light until the colour changed from yellowish to black. The passing through of the hydrogen was continued for another 30 min. Then the solution was stored in the dark at 4°C . A 2 ml aliquot of it was used for each irradiation.

2.3. Determination of redox potentials

The oxidation potentials of the amines were measured in dimethylformamide (DMF). Tetraethylaminotetrafluoroborate was used as conduction salt with a concentration of 0.1 mol l^{-1} . A saturated calomel electrode (Metrohm) was used as reference electrode. The working electrode was a dropping mercury electrode (drop rate, $11 \text{ drops min}^{-1}$). The counter electrode was a platinum wire (thickness, 0.5 mm; length, 1 cm) which was fused into the glass. Oxygen was removed with argon. The measured half wave potentials were corrected with respect to the NHE according to the equation

$$E_{1/2}^0 = E_{1/2} + E_{\text{calomel}}$$

3. Results and discussion

Sacrificial electron donors investigated, H_2 yields, and redox potentials are listed in Table 1. The effect of various

Table 1
Electron donors investigated for the H₂ evolution during photoinduced water reduction

Electron donor	H ₂ yield (μl)	pK _a	E _{1/2} ^a	C _(amine) /C _(amine-H⁺)
TEOA ^b	400	7.91	0.97	3.8 × 10 ⁻⁴
NMDEOA ^b	315	8.76	0.93	5.0 × 10 ⁻⁵
NEDEOA ^b	135	9.00	0.98	2.7 × 10 ⁻⁵
NNDMEOA ^b	76	9.46	0.97	1.0 × 10 ⁻⁵
NNDEEOA ^b	5	10.05	0.98	2.8 × 10 ⁻⁶
TMA ^c	–	9.76 [18]	1.29 [17]	5.0 × 10 ⁻⁶
TEA ^c	0.50	10.65 [18]	1.19 [17]	7.0 × 10 ⁻⁷
TPA ^c	0.15	10.65 [18]	1.02 [17]	7.0 × 10 ⁻⁷
TBA ^c	0.15	10.89 [18]	1.02 [17]	4.0 × 10 ⁻⁷
EDTA ^d	830	2.8; 6.1 [19]	0.47 [21]	
Formaldehyde ^e	620	13.85 [20]	0.58 [22]	

^a Half-wave potential versus NHE.

^b pH = 4.7, C_{donor} = 1.4 mol l⁻¹.

^c pH = 4.5, C_{donor} = 0.12 mol l⁻¹.

^d pH = 4.5, C_{donor} = 0.05 mol l⁻¹.

^e pH = 3.5, C_{donor} = 2.5 mol l⁻¹; irradiation time generally 1 h.

cations on the H₂ yield is shown in Table 2. None of the substances tested was as effective as EDTA, although some of them gave hydrogen yields of nearly 50–75% of that of EDTA. The highest hydrogen yields were obtained with formaldehyde (620 μl h⁻¹) and TEOA (400 μl h⁻¹). Whether the electron donors were degraded during the irradiation period could not be decided under the experimental conditions. Nevertheless, theoretical considerations concerning the electron transfer reactions and, probably, the final electron donor for the re-reduction of the amines can be made. Former studies showed that the solvent also influences the reaction; the rate constants for the phosphorescence quenching of DA with amines were higher in polar solvents than in benzene [11]. Contrary to this, the proton transfer was inhibited with increasing polarity of the solvent. Therefore, electron transfer reactions should predominate in water.

Whether the redox potential of excited DA (2.1 V for singlet and 1.81 V for triplet) remains constant with changing pH or not has not been tested, but no influence of it could be observed during these experiments. Therefore, it can be assumed that it is always above those of the sacrificial electron donors. The potential of DA⁻ is -0.57 V and, therefore, well

below that of MV²⁺ (E_{1/2}^{red} = -0.44 V) which is relatively constant over a wide range of pH [23]. The potentials of H⁺ and of the sacrificial electron donor both vary in dependence on the pH of the solution, but with the most pronounced differences in the potential of H⁺. Consequently, the production of H₂ mainly depends on the difference between the potentials of MV²⁺ and H⁺ at the actual pH. Because the electron donors tested in these experiments are weak acids or bases, the actual pH of the solution is determined by the dissociation constants of the sacrificial electron donor.

In Fig. 2, H₂ production is plotted against pH for EDTA, TEOA, and formaldehyde. The peaks of yield with EDTA and TEOA are close to each other between pH 4.5 and 4.7 while the activity of formaldehyde is highest at pH 3.5. The redox potential of H⁺ at a given pH can be obtained from the Nernst equation

$$E_{1/2} \approx 0.059 \log[\text{H}^+],$$

and the actual pH of an EDTA solution can be approximately calculated from

$$\text{pH} \approx -\log\sqrt{K_2 K_3}.$$

EDTA is a weak acid with the dissociation constants K₁ = 1.0 × 10⁻², K₂ = 1.6 × 10⁻³, K₃ = 7.9 × 10⁻⁷, and K₄ = 6.3 × 10⁻¹¹, and a solution of 0.05 mol l⁻¹ EDTA (E_{1/2}^{ox} = 0.47 V at pH 3.7, [24]) results in a pH of about 4.5 and a potential of H⁺ E_{1/2} = -0.27 V. According to Fig. 2, this is the pH at which the H₂ production is highest in the presence of EDTA. Therefore, the difference in potential between MV^{•+} and H⁺ is sufficiently great for the electron transfer from MV^{•+} to H⁺, the reaction is exergonic and, indeed, should be so up to a pH of 7.45, when the difference in potential becomes 0.

On the other hand, despite of a dissociation constant of 1.4 × 10⁻¹⁴ at 0°C for formaldehyde [20], the pH of the solution is determined by the formic acid present in the

Table 2
Influence of various cations on the activity of EDTA

EDTA-M ^a	H ₂ yield (μl)
Na ⁺	830
TEOA ⁺	810
TEA ⁺	680
Li ⁺	660
K ⁺	580
NH ₄ ⁺	500
Ca ²⁺	70

^a EDTA-M was obtained from ethylenediaminetetraacetic acid and the corresponding base.

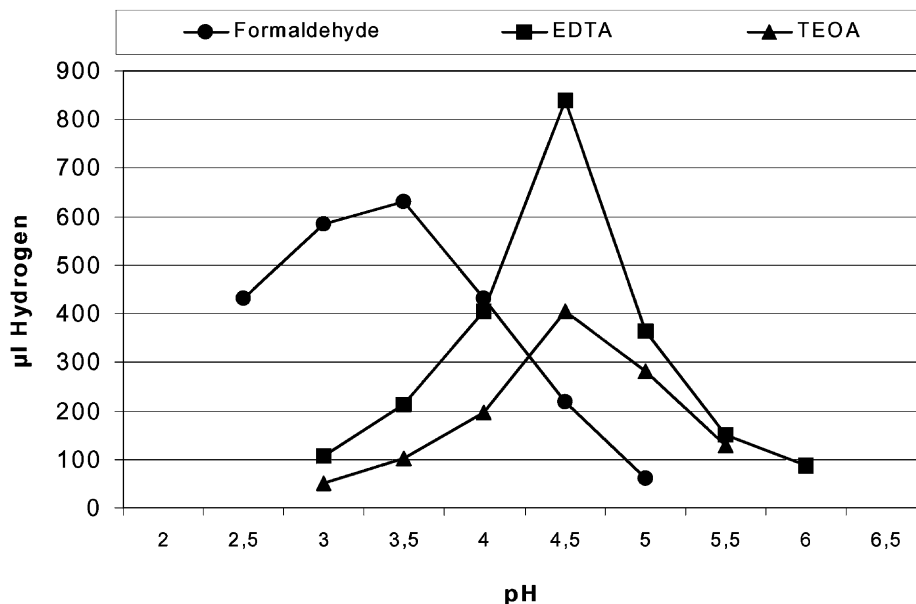
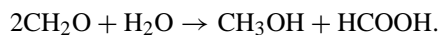


Fig. 2. Dependence of H₂ yield on pH for EDTA, TEOA, and formaldehyde.

formaldehyde solution ($pK_a = 2.75$), formed, for example, by the disproportionation of formaldehyde



For a solution of formaldehyde of 0.2 mol l^{-1} with a measured pH of 3.5, the calculated formic acid concentration is ca. $3.7 \times 10^{-4} \text{ mol l}^{-1}$. Although the difference between the redox potentials of formaldehyde and its oxidation product formic acid ($E_{1/2}(\text{CH}_2\text{O}) = 0.58 \text{ V}$, $E_{1/2}(\text{HCOOH}) = 0.55 \text{ V}$) is minimal [24], the electron donor should be mainly the aldehyde because of the extreme low concentration of formic acid compared to that of the aldehyde. The formaldehyde concentration had to be raised to more than 0.2 mol l^{-1} to obtain hydrogen yields comparable to those of EDTA, even though the reduction of H^+ at pH 3.5 rather than at 4.5 should be energetically more favourable by 0.118 V.

On the other hand, the redox potential of methanol which is present in commercial formaldehyde up to 10%, also differs only slightly from that of formaldehyde. In our experiments, it was not possible to decide whether or not the presence of methanol affected the reduction of water. However, no hydrogen was obtained in the presence of methanol and the absence of formaldehyde, i.e. methanol obviously cannot serve as a sacrificial electron donor.

In contrast to EDTA and formaldehyde, TEOA is a base and the pH of a 0.14 mol l^{-1} solution is ca. 11. The redox potential of H^+ at this pH ($E_{1/2} = -0.65 \text{ V}$) is far below that of MV^{2+} . Therefore, it was not possible to reduce H^+ with $\text{MV}^{\bullet+}$ at this basic pH, although a blue coloration of the solution was observed as the result of the production of the $\text{MV}^{\bullet+}$ radical, indicating the electron transfer from TEOA ($E_{1/2} = 0.97 \text{ V}$) to DA^* ($E_{1/2} = 1.8$ or 2.1 V) and

from DA^- ($E_{1/2} = -0.57 \text{ V}$) to MV^{2+} ($E_{1/2}^{\text{red}} = -0.44 \text{ V}$). The reactivities of the other various ethanolamines differed considerably, although the half wave oxidation potentials of the free amines ($E_{1/2} = 0.93\text{--}0.98 \text{ V}$) are comparable to those of TEOA. Contrary to this, there is a striking correlation between pK_a values and hydrogen yields. The pH of the solutions of these amines has been adjusted to 4.5 to allow comparison of the H₂ production. In the acidic range, the protonated form dominates; for example, the proportion of free NNDMEOA is ca. 0.001%, compared to ca. 0.04% of free TEOA. The half-life potentials of the salt forms have not been determined, but amines in the form of their salts are electrophilic in character and cannot be oxidized by the excited diacetyl.

In addition to ethanolamines, some trialkylamines were also studied as possible sacrificial electron donors. The hydrogen yields were either extremely low or, as in the case of TMA, below detection limit. The proportion of nondissociated amine in TMA is higher than that of the other trialkylamines, but this amine also possesses the highest oxidation potential ($E_{1/2} = 1.29 \text{ V}$). This is still below the potential of excited DA, and other factors may attribute to the failure to detect any H₂ production. TPA has been reported to have a higher luminescence extinction constant for DA than TEA [14]; in our investigations, however, the H₂ yield of TEA was always higher than that of TPA. The low yields with TBA can also be explained with its low solubility. The concentration of TBA (0.12 mol l^{-1}) was considerably lower than those of the ethanolamines.

Since EDTA is present in anionic form, a further investigation was made on the influence of the cation on the production of H₂ (Table 2). When Na^+ ions were replaced by K^+ ions, the hydrogen yield dropped significantly. No

explanation can be offered by now for this effect. As expected, the lowest activity was obtained with Ca^{2+} as cation because of the complex formation with EDTA. The expectation, that the presence of TEOA in addition to EDTA would lead to a lower hydrogen yield by competition, was confirmed, although the effect was not very pronounced. The difference in yield was greater when TEA or NH_3 was added.

4. Conclusions

The investigations with tertiary amines described above resulted in no improvement of the catalysis of photoinduced water reduction. None of the amines tested gave H_2 yields higher than EDTA or showed improved stability, although the second point remains to be confirmed. Furthermore, to achieve a cyclic decomposition of water, in analogy to the photosystems of plants and bacteria, oxygen has to be produced along with hydrogen. Oxygen has a redox potential of 0.83 V at pH 7. Since, apart from EDTA, all the amines investigated possess higher oxidation potentials and, with the exception of TMA, are oxidized by DA^* , it should be possible to produce molecular oxygen. However, all attempts, for instance by adding RuO_2 as catalyst without EDTA, did not yield detectable quantities of hydrogen or oxygen. Probably, the life time of $^3\text{DA}^*$ is not long enough to allow the transfer of an electron from the oxygen atom in water to $^3\text{DA}^*$. Nevertheless, some aromatic tertiary amines might be suitable as an electron carrier that catalyzes the transfer from O^{2-} to DA^* in analogy to MV^{2+} . Particularly some triphenylamines with Cl, CH_3 , and Br substituents in the para-position have been found in electrochemical investigations to yield very stable cation radicals [25]. The stability or rather half-life of such a radical is of particular importance because, for the oxygen side, there has not yet been found an effective catalyst like platinum for H^+/H_2 so that the energy barrier for the oxidation of oxygen in water is too

high. Further screening is necessary. Probably, the efficiency of the photochemical decomposition of water could be further increased by covalent binding of MV^{2+} and $\text{N}(\text{Ar})_3$ to diacetyl. However, other reactions, such as that between the $\text{MV}^{\bullet+}$ radical and O_2 , have to be taken into account in such a system.

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