

## The Reactivity of 1,2-Diketones during the Photoinduced Reduction of Water in Microheterogeneous Systems

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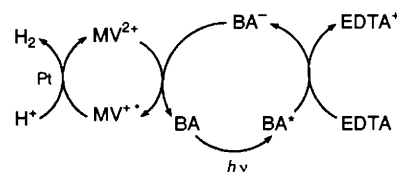
Efficient light-induced reduction of water and evolution of hydrogen with a quantum yield of 1.0 has been achieved by use of negatively charged 1,2-diketone radicals.

The photoinduced decomposition of water into hydrogen and oxygen has become the subject of intensive research on account of the increasing scarcity of conventional energy sources.<sup>1</sup> Microheterogeneous systems, with the reactants not being compartmentalised, are primarily employed for this purpose. The redox processes that thereby take place are light-induced electron transfers where the absorbed energy is stored in the form of energy-rich molecules.<sup>2</sup> Suitable organometallic dyestuffs are employed for the primary electron transfer; many research groups have used the tris(2,2'-bipyridine)ruthenium(II) dication, [Ru(bpy)<sub>3</sub>]<sup>2+</sup>,<sup>3</sup> as it fulfils the conditions for efficient reduction of water on account of its strong charge transfer absorption ( $\epsilon > 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) and its photoredox potential of  $-0.86 \text{ V}$ .

During our investigations we have been able to establish that simple organic compounds, such as 1,2-diketones, are also suitable for this purpose. In contrast to [Ru(bpy)<sub>3</sub>]<sup>2+</sup>, which donates an electron to the acceptor, the excited diketones take possession of an electron from the donor [ethylenediaminetetraacetic acid (EDTA)] in their incompletely filled low energy orbital. There can, in principle, also be a hydrogen abstraction instead of an electron transfer. However, such a step can be neglected when EDTA is the donor, since it possesses a favourable fluorescence-phosphorescence-quenching constant ratio ( $K_q^f/K_q^p$ ) (Table 1) and low oxidation potential ( $E_{1/2}^{p/p^+} = 0.44 \text{ V}$ ). Investigations with other amines as electron donors have revealed that only triethylamine as a tertiary alkylamine leads to a reduction of water, while aromatic amines such as aniline ( $E_{1/2}^{p/p^+} = 1.20 \text{ V}$ ), diphenylamine ( $E_{1/2}^{p/p^+} = 1.07 \text{ V}$ ) and triphenylamine ( $E_{1/2}^{p/p^+} = 1.16 \text{ V}$ ) do not.

If the simplest 1,2-diketone, biacetyl (BA), with a phosphorescence lifetime of  $0.229 \times 10^{-3} \text{ s}$ <sup>5</sup> and a redox potential of  $-0.57 \text{ V}$ , is used as the dyestuff, it reacts in an electron-transfer reaction to yield the negatively charged radical (BA<sup>•-</sup>), which is very effective in reducing water to hydrogen in the presence of methylviologen (MV<sup>2+</sup>), EDTA and active Pt surfaces (Scheme 1). The use of various catalysts make it possible to increase the yield of hydrogen even more. Platinum catalysts stabilized with polyvinyl alcohol are particularly effective, producing quantum yields for hydrogen production  $\Phi_p(\text{H}_2)$  of up to  $0.49 \pm 0.01$  ( $\lambda = 436 \pm 5 \text{ nm}$ ) (Table 2). If the product quantum yield is based on hydrogen atoms (H<sup>0</sup>) rather than hydrogen molecules (H<sub>2</sub><sup>0</sup>), then the value of  $\Phi_p(\text{H}) = 1.00$  is achieved. This result suggests a value of unity for  $\Phi(\text{BA}^{\bullet-})$ . A value of unity for  $\Phi(\text{BA}^{\bullet-})$  is possible, if each of the following terms is unity.

- $$\Phi(\text{BA}^{\bullet-}) = \Phi(\text{BA}^*) \times f \times \gamma$$
- $\Phi(\text{BA}^*)$  = quantum yield for the formation of the excited state
  - $f$  = quenched fraction of BA\*
  - $\gamma$  = cage escape yield for the formation of the redox products.



Scheme 1

Table 1 Blocking biacetyl luminescence with various amines and possible quenching mechanisms

Compound	$10^{-10} K_q^f/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$10^{-9} K_q^p/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$K_q^f/K_q^p$	Probable quenching mechanism
PhNH <sub>2</sub> <sup>a</sup>	0.93	1.50	6.20	Reversible e abstraction
Ph <sub>2</sub> NH <sup>a</sup>	1.20	2.80	4.28	Reversible e abstraction
Ph <sub>3</sub> N <sup>a</sup>	1.20	1.60	7.50	Reversible e abstraction
Et <sub>3</sub> N <sup>a</sup>	0.30	0.27	11.11	Irreversible H or e abstraction
EDTA <sup>b</sup>	0.024	0.0082	29.26	Irreversible H or e abstraction

<sup>a</sup>  $K_q^f$  and  $K_q^p$  were calculated from the Stern-Volmer quenching constants  $K_q^{f,f}$  and  $K_q^{p,p}$  values, determined in acetonitrile, and lifetimes  $\tau_f = 8.2 \times 10^{-9} \text{ s}$  and  $\tau_p = 0.2 \times 10^{-3} \text{ s}$ .<sup>4b</sup>  $K_q^f$  and  $K_q^p$  were calculated from  $K_q^{f,f}$  and  $K_q^{p,p}$  values (determined in triply distilled H<sub>2</sub>O), using the lifetimes  $\tau_f = 6.3 \times 10^{-9} \text{ s}$  and  $\tau_p = 0.229 \times 10^{-3} \text{ s}$ .<sup>5</sup>

**Table 2** Half-wave potentials ( $E_{1/2}^{p/p^-}$  vs. normal hydrogen electrode, NHE), quantum yields  $\Phi_p$  ( $H_2$ ) and yields of hydrogen ( $H_2$ ) for 1,2-diketones as a function of the type of platinum catalyst employed

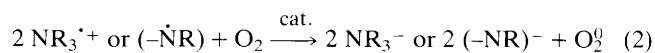
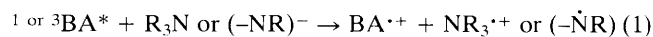
Compound	$E_{1/2}^{p/p^-}$ vs. NHE	Catalyst <sup>a</sup>	$\Phi_p$ ( $H_2$ ) <sup>c/f</sup> Einstein mol <sup>-1</sup>	$H_2$ production <sup>d/</sup> ml h <sup>-1b</sup>
Biacetyl	-0.57	I	0.390	0.875
		II	0.127	0.278
		III	0.490	1.097
Hexane-2,3-dione	-0.59	III	0.004	0.010
Hexane-3,4-dione	-0.62	III	0.065	0.160
Benzil	-0.51	III	<10 <sup>-4</sup>	0.004
p-Tolil	-0.58	III	<10 <sup>-4</sup>	0.002

<sup>a</sup> I: catalyst from  $H_2PtCl_6$  reduced with hydrogen and stabilized with polyvinyl alcohol;<sup>8</sup> II:  $H_2PtCl_6$  reduced with trisodium citrate;<sup>9</sup> III:  $H_2PtCl_6$  reduced with formaldehyde and stabilized with polyvinyl alcohol. All catalysts were  $TiO_2$ -free. <sup>b</sup> 30 ml of triply distilled  $H_2O$  outgassed with  $N_2$  containing: EDTA (50 mmol dm<sup>-3</sup>);  $MV^{2+}$  (3 mmol dm<sup>-3</sup>); Pt (0.051 mmol dm<sup>-3</sup>); diketone (13.5 mmol dm<sup>-3</sup>). <sup>c</sup>  $436 \pm 5$  nm. <sup>d</sup>  $\lambda > 385$  nm.

The present results indicate that a nearly ideal situation has been achieved for all three key steps. Such high product quantum yields have not been achieved in aqueous solution using  $[Ru(bpy)_3]^{2+}$  or other photosensitizers. In contrast, the other 1,2-diketones investigated do yield hydrogen but their efficiencies [ $\Phi_p$  ( $H_2$ ) of  $1.0 \times 10^{-4}$  to  $6.5 \times 10^{-2}$ ] are less than that of biacetyl. The same applies to  $[Ru(bpy)_3]^{2+}$  under the experimental conditions employed, with the measured  $\Phi_p$  ( $H_2$ ) value of  $0.08 \pm 0.01$  ( $\lambda = 436 \pm 5$  nm) and a lifetime of only  $6.24 \times 10^{-7}$  s<sup>10</sup> in the excited state, which, in contrast to that of biacetyl, is not long enough for an effective quenching of  $MV^{2+}$  ( $k_q = 1.03 \times 10^9$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>).<sup>11</sup> In addition, a comparison of the reduction potentials for the conversion of  $[Ru(bpy)_3]^{3+}$  to  $[Ru(bpy)_3]^{2+}$  and of  $MV^{2+}$  to  $MV^{+}$  reveals that the quenching is 1.70 eV endergonic with respect to the ground state of  $[Ru(bpy)_3]^{2+}$ . This difference in potential and the blockage of rapid charge separation dependent on the solvation shell of the inner ion pair both favour the thermal back reaction<sup>12</sup> whose rate constant is  $2.4 \times 10^9$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>.

The redox potentials of the excited states of biacetyl are of particular interest in this context. On the basis of the Rehm–Weller equation they have a value of  $E_{1/2}(^1p^*/p^-) =$

2.10 V for the singlet and  $E_{1/2}(^3p^*/p^-) = 1.81$  V for the triplet excited state, respectively.<sup>13</sup> This means that the excited states of biacetyl are able to oxidize water. A suitable electron relay analogous to  $MV^{2+}$  for the oxygen side is not yet available. This could, for instance, consist of tertiary amines ( $R_3N$ ) or negatively charged nitrogen bases ( $-NR^-$ ), whose oxidized forms ( $R_3N^{+}$  and  $-NR$ ) should possess sufficiently high potentials to oxidize water in the presence of suitable catalysts [eqns. (1) and (2)]. If these were available, it would be quite possible that an efficient cyclic light-induced decomposition of water by 1,2-diketones could be feasible.



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