Preliminary Note

A new photosensitizer–catalyst for the photochemical cleavage of water

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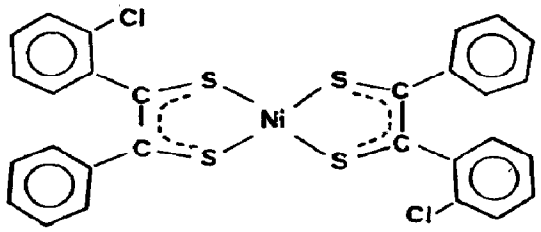
The information available on the photochemistry of 1,2-dithiolenes is extremely limited [1]. In particular there is no reference to any study that uses only visible light. In this note we report the photochemical cleavage of water by nickel(II) bis-2-chlorodithiobenzil (1) in the presence of a sacrificial reagent (ethylenediaminetetraacetic acid (edta)) and a relay (methyl viologen (MV^{2+})).



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This square planar member of the 1,2-dithiolene family and the monoanion derived from it act as photosensitizers in the visible region. However, what is perhaps more interesting is that these two species also act as catalysts for the formation of molecular hydrogen; there is no need for platinum [2] or any other catalyst for this process.

The neutral complex 1 was prepared [3] by a modification of the method described by Schrauzer *et al.* [4]. The monoanion can then be obtained readily by reduction with $LiAlH_4$, with zinc activated by dilute HCl or chromium(II) in stoichiometric amounts or with a 10:1 excess of hydrazine.

For solubility reasons the experiments were performed in a 70:30 acetone–water solution. All necessary blank experiments were performed to make sure that the acetone itself does not act as a donor. In one of the blanks we used deuterated acetone, ordinary water and edta. The gas obtained did not contain deuterium.

0047-2670/85/$3.30

In the mixed solvent the neutral complex 1 absorbs strongly at 840 nm ($\epsilon_{max} = 2.8 \times 10^4$ M^{-1} cm^{-1}) and also at 604 nm ($\epsilon_{max} = 2 \times 10^3$ M^{-1} cm^{-1}). The corresponding peaks for the monoanion 1^- lie at 920 nm and 504 nm (ϵ_{max} values of 1.3×10^4 M^{-1} cm^{-1} and 3×10^3 M^{-1} cm^{-1} respectively).

In the absence of added donors or acceptors 1 and 1^- are both thermally and photochemically stable, even under UV illumination. Some results obtained in the presence of edta and/or MV^{2+} are summarized in Table 1. Molecular hydrogen was measured chromatographically [5] or volumetrically under constant pressure [3].

The overall reactions are

$$C + \text{edta} + MV^{2+} \xrightarrow{h\nu} C^- + MV^{\cdot+} + P \quad (1)$$

$$C^- + \text{edta} + MV^{2+} \xrightarrow{h\nu} C^- + MV^{\cdot+} + P \quad (2)$$

$$MV^{\cdot+} + H^+ \xrightarrow{C,C^-} MV^{2+} + \tfrac{1}{2}H_2 \quad (3)$$

where C is the complex, C^- is its monoanion and P represents the products of the oxidation of edta. Reaction (3) is catalysed by C and C^-. This was shown independently by preparing $MV^{\cdot+}$ chemically, *e.g.* by reducing MV^{2+} with zinc.

TABLE 1

Photochemical behaviour of complex 1 in the presence or absence of methyl viologen and/or ethylenediaminetetraacetic acid in 70:30 acetone–water solution

Concentration (M)			*Wavelength range*[b] (nm)	*Observation*
Complex ($\times 10^{-5}$ M)	*MV*$^{2+}$ [a] ($\times 10^{-3}$ M)	*edta* ($\times 10^{-3}$ M)		
1.2	—	—	> 200	No change
1.2	2.55	—	> 200	No change
8.7	—	1.75	> 350	Formation of monoanion[c]
—	2.55	1.75	> 200	No change
4.3	2.38	0.95	> 350	Formation of H_2, monoanion and MV^+
4.3	2.38	0.95	> 350	Formation of H_2, monoanion and MV^+ [d]
2.9	2.14	0.71	593	Formation of monoanion and MV^+ [e]
2.9	2.14	0.71	840	Formation of monoanion

[a] The chloride salt of MV^{2+}.

[b] Without a filter the xenon lamp used (VIX-300) gives light with $\lambda > 200$ nm. Light with $\lambda > 350$ nm is cut off by a Corning CS 0-52 filter.

[c] Duration of illumination, 2 h. There is a slow thermal reaction between the complex and edta, but within the time of irradiation its effect is negligible.

[d] Colloidal platinum was added in this experiment (about 10^{-5} M).

[e] The intensity of monochromatic radiation was not high enough to allow the detection of any molecular hydrogen evolved.

The dependence on time of the volume of molecular hydrogen produced in the presence and absence of platinum is given in Fig. 1. In the presence of platinum the production of hydrogen is initially faster but soon stops and $MV^{+\cdot}$ starts to accumulate. In the absence of platinum the rate of formation of molecular hydrogen shows less levelling off.

Quantum yields for monoanion formation at three wavelengths are given in Table 2. It should be noted that 1^- is also formed at 840 nm, whereas $MV^{+\cdot}$ and molecular hydrogen are formed at 593 nm and not at 840 nm.

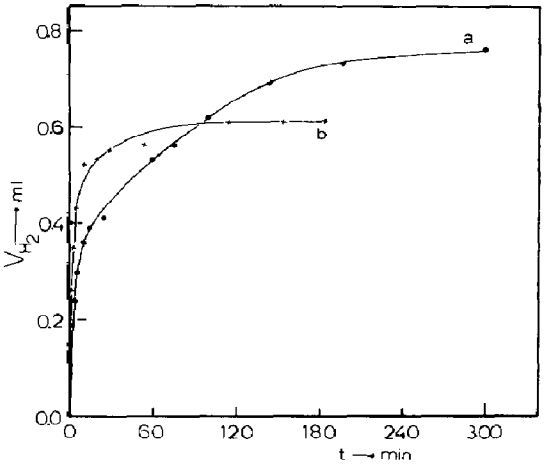

Fig. 1. The volume of molecular hydrogen formed as a function of time ($\lambda > 350$ nm); [1] = 4.3×10^{-5} M; [edta] = 9.5×10^{-4} M; [MV^{2+}] = 2.4×10^{-3} M; solution volume, 21 ml): curve a, without platinum; curve b, with platinum.

TABLE 2

Quantum yields Φ_{1^-} of the formation of the monoanion of nickel(II) bis-2-chlorodithiobenzil by irradiation with monochromatic light

Concentration			*Wavelength* (nm)	*Illumination time* (s)	Φ_{1^-}
Complex ($\times 10^{-4}$ M)	*edta* ($\times 10^{-4}$ M)	MV^{2+} ($\times 10^{-4}$ M)			
0.29	7.14	7.14	410	216	0.360
0.29	7.14	21.43	593	475	0.004
0.14	7.14	21.43	593	813	0.013
0.29	7.14	21.43	840	455	0.130

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