Photoproduction of Hydrogen from Water Catalysed by Metal Sulfur Chelates

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Metal dithiolenes and other sulfur containing metal complexes catalyse the photoproduction of hydrogen from water in the presence of tetrahydro- or dihydrofurans.

Catalysed photochemical generation of hydrogen from water in homogeneous solution is known to occur only in the presence of a reducing agent and a multicomponent catalyst system composed of a sensitizer, e.g. tris(2,2'-bipyridine)Ru$^{2+}$, an electron relay species, e.g. N,N'-(dimethyl-4,4'-bipyridinium-chloride, and of a redox catalyst like colloidal platinum [1–6]. The two latter components may be omitted on the expense of catalytic activity [7]. We recently discovered simple and very efficient catalytic systems consisting of a metal dithiolene catalyst and a reducing agent only [8a]. In the present communication we report on the ability of a large number of metal sulfur chelates to catalyse the photoproduction of hydrogen from water in homogeneous solution [8b].

In a typical experiment 0.06 mmol of the zinc complex of type I (Fig. 1) (I: M = Zn, R = CN, n = 2, z = —2, n-Bu$_4$N$^+$ as the counter ion) were dissolved in 60 ml of tetrahydrofurane (THF) followed by addition of 60 ml of water. After 20 h of irradiation (immersion lamp apparatus, lamp: Philips HPK 125 W, $\lambda \geq 254$ nm) 200 ml of hydrogen were formed; if THF is replaced by 2,5-dihydrofuran, the rate of $H_2$-evolution is enhanced by a factor of ten and the formerly homogeneous solution turns into an emulsion. Under the latter reaction conditions the catalyst is active during four to five days and up to five liters of hydrogen are obtained; maximum turnover numbers are in the range of 2000 mmol $H_2$/mmol catalyst. The cleavage of water was demonstrated by using D$_2$O for the same kind of experiment and the composition of the gas evolved was determined to be 87% D$_2$, 10% HD and 3% $H_2$.

Fig. 1 summarizes the types of complexes investigated [9], metal dithiolenes (I) exhibit the best catalytic properties. Among the numerous compounds of type I studied - M = Ti, V, Cr, Mo, W, Mn, Re, Fe, Os, Co, Ni, Pd, Pt, Cu, Au, Zn, Cd; R = H, CH$_3$, Ph, CN; R-R = CS, C$_2$O$_2$; n = 2, 3; z = 0, —1, —2 - we found that the zinc complexes give the highest activities and the best D$_2$/HD/$H_2$ ratios. All other complexes show either no (III: M = W, M' = Ni; V, VI) or strongly reduced activity (II: M = Fe, Co; III: M = W, M' = Fe; IV: R = PhNH, M = Cr, Fe, Co, Zn; R = o-CH$_3$-C$_6$H$_4$, M = Ni, Cu) and generate predominantly HD if irradiated in D$_2$O/THF. The zinc complex I was therefore used to study the mechanism of $H_2$-production.

The UV-VIS spectrum of I in ethanol at room temperature exhibits two broad absorption bands at 267 ($\varepsilon = 23,620$) and 383 nm ($\varepsilon = 21800$). Excitation at each of these wavelengths gives rise to a very weak emission at room temperature and a rather strong one at 77 K, both centered at 446 nm in ethanol. This is the first time that emission has been observed from a metal dithiolene.
UV-VIS absorption spectroscopy reveals that 1 is transformed at early reaction stages to species absorbing at higher energy than the starting complex. This conversion easily occurs upon irradiation at 267 nm whereas other products are formed if 1 is excited at 383 nm. A similar wavelength dependence is found for the quantum yield of \( \Phi(H_2) \approx 0.03 \) at 267 nm, \( \leq 10^{-5} \) at 366 nm [10].

THF is essential for the catalytic system and seems to be the reducing agent since dihydrofurans and furan are detected by gas chromatography of the liquid reaction phase. The use of open chain aliphatic ethers instead of THF prevents catalytic \( H_2 \)-production. Air has no influence on the rate of \( H_2 \)-evolution whereas CO gives rise to a long induction period. This points to competition of CO, THF and/or \( H_2O \) for an empty coordination site.

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[8] a) R. Henning, W. Schlamann, and H. Kisch, Angew. Chem. 92, 664 (1980);
[10] In THF/H\(_2\)O = 2/1.