## PHOTOCATALYTIC DEHYDROGENATION OF ETHANOL BY THE Cu<sup>2+</sup> ION

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## Summary

 $Cu^{2+}$  ion is found to photocatalyse hydrogen generation from aqueous solutions of ethanol. The reaction rate was found to be optimum when the concentrations of  $Cu^{2+}$  and ethanol are 0.01 M and 25% v/v respectively.

The photodehydrogenation of alcohols has been accomplished with heterogeneous [1-4] as well as homogeneous [5-7] catalysts. Although a wide variety of semiconductors act as effective catalysts in dehydrogenating alcohols, the homogeneous systems reported in the literature are based almost exclusively on complexes of rhodium (and related metals) or organic sensitizers. We have found that the much simpler material copper(II) chloride is a stable and efficient catalyst for the photodehydrogenation of alcohols.

Photolysis experiments were conducted using a thermostatted (26 °C) double-walled photochemical reactor (Applied Photophysics) of volume 300 ml fitted with a 400 W mercury lamp at the central axis. In determining quantum yields, a low pressure 15 W lamp was used. Copper(II) chloride dissolved in HCl (0.25 M CuCl<sub>2</sub>, 0.25 M HCl) was purged with oxygen to convert any copper(I) chloride present to copper(II) chloride. Mixtures consisting of water, ethanol, copper(II) chloride and HCl (total volume 200 ml) were irradiated and the evolved hydrogen estimated volumetrically at atmospheric pressure by gas chromatography (Shimadzu GC-9AM gas chromatograph, column MS 5A, carrier gas Ar). Prior to irradiation all solutions were purged with nitrogen (99.999%). The only gas detected was  $H_2$ , and analysis of the solution by standard techniques revealed the presence of acetaldehyde and small quantities of acetic acid.

Figure 1 illustrates  $H_2$  photogeneration at different ethanol concentrations (ECs) when CuCl<sub>2</sub> concentration is kept fixed. It is seen that the rate of  $H_2$  production initially increases with increasing EC and then decreases. When the EC is very high (85% v/v or more), little  $H_2$  is produced and the photolysed solution is found to contain acetaldehyde and copper(I) chloride.

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Fig. 1. Photogeneration of  $H_2$  at ethanol concentrations (1) 12.5% (2) 25% (3) 50% (4) 87.5% ([Cu<sup>2+</sup>] kept fixed at 0.01 M).

The above observation indicates that the primary step in the dehydrogenation reaction is the reduction of  $Cu^{2+}$  to  $Cu^+$ , with concomitant oxidation of ethanol to acetaldehyde upon irradiation, i.e.:

$$\frac{1}{2}C_{2}H_{5}OH + CuCl_{3}^{-} \xrightarrow{h\nu} \frac{1}{2}CH_{3}CHO + CuCl_{3}^{2-} + H^{+}$$
(1)

Acetaldehyde is not produced via (1) in a dark reaction. In the presence of excess HCl,  $Cu^{2+}$  and  $Cu^+$  exists as trichlorocuprate ions (II) and (I) (i.e.  $CuCl_3^-$ ,  $CuCl_3^{2-}$ ) respectively. It is known that  $CuCl_3^{2-}$  in aqueous solution (i.e. CuCl in HCl) undergoes rapid photo-oxidation to  $CuCl_3^-$  with the liberation of hydrogen [8,9], *i.e.*:

$$\operatorname{CuCl}_{3}^{2-} + \mathrm{H}^{+} \xrightarrow{h\nu} \operatorname{CuCl}_{3}^{-} + \mathrm{H}$$

$$\tag{2}$$

(3)

$$H + H \rightarrow H_2$$

When the EC is not excessively high, the hydrogen photogeneration which proceeds via steps (1)-(3) is essentially catalytic. On replacement of water by D<sub>2</sub>O, at low ECs, the photoproduced gas is mostly D<sub>2</sub>. However, at high ECs, a mixture of H<sub>2</sub>, HD and D<sub>2</sub> is obtained. Nevertheless, this observation cannot be taken as clear evidence that the hydrogen originates from water, because D<sub>2</sub>O exchanges rapidly with the hydroxylic hydrogen atom of ethanol. The H<sub>2</sub> evolution rate initially increases and then rapidly diminishes as the Cu<sup>2+</sup> concentration is increased (Fig. 2). The optimum [Cu<sup>2+</sup>] = 0.01 M and this value is nearly independent of the EC. Obviously this effect originates from enhancement of the rate of back reaction (-2) with the [Cu<sup>2+</sup>]. For all values of [Cu<sup>2+</sup>], the H<sub>2</sub> evolution rate becomes maximum when EC = 25% v/v. Thus the reaction rate is highest when [Cu<sup>2+</sup>] = 0.01 M, EC = 25% v/v. Under these conditions the quantum efficiency of H<sub>2</sub> production at 254 nm in the initial irradiation interval 40–100 min is 0.03. Reaction



Fig. 2. (a) Photogeneration of  $H_2$  at different [Cu<sup>2+</sup>] (ethanol concentration = 25%) (1) 0.00 M (2)  $1.0 \times 10^{-2}$  M (3)  $5 \times 10^{-3}$  M (4)  $2 \times 10^{-3}$  M (5)  $2 \times 10^{-2}$  M. (b) Variation of the initial reaction rate with [Cu<sup>2+</sup>] (ethanol concentration = 25%).

(2) is initiated by charge transfer (CT) absorption in  $CuCl_3^{-}$ , which exhibits a peak at 273 nm [8].  $CuCl_3$  has a CT peak at ~250 nm. The excitation at this wavelength and possibly also the free radical generation by absorption in ethanol is responsible for the reaction (1). (Upon UV irradiation, ethanol undergoes detectable dehydrogenation even in the absence of a catalyst, Fig. 2 curve 1). Other alcohols also photodehydrogenate in the presence of  $Cu^{2+}$ . Furthermore, the photodehydrogenation of aliphatic aldehydes and acids is also catalysed by the  $Cu^{2+}$  ion. The dismutation of  $Cu^+$  to Cu was not detected. Energetically this is less favourable than reduction of  $Cu^{2+}$  in the complexed or uncomplexed forms.

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