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Hydrogen generation in the photolysis of aqueous solutions of alcohol in the presence of copper(II) sulfate

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Abstract

Ethanol or methanol and water mixtures containing copper(II) sulfate are found to liberate hydrogen upon UV irradiation with partial reduction of copper sulfate to the metallic copper.

Introduction

Photodehydrogenation of alcohols has been achieved with heterogeneous as well as homogeneous catalysts [1–10]; semiconductor powder dispersions, notably TiO_2 and CdS liberate hydrogen from water alcohol mixtures upon illumination [1–3, 10]. As homogeneous systems, the complexes of rhodium (or related metals) and organic sensitizers are known to photocatalyze dehydrogenation of alcohols [4, 7, 8]. Although the reaction is not catalytic, we have found that copper(II) sulfate sensitizes photodehydrogenation of hydrogen from ethanol and methanol water mixtures with partial reduction of copper(II) sulfate to metallic copper.

Experimental

Reagent grade (Analar) copper sulfate was used without purification. Acidified (H_2SO_4) copper sulfate solution, alcohol and water mixtures (total volume 200 ml) were irradiated in a thermostatted (26 °C) photochemical reactor (Applied Photophysics) of volume 300 ml. The light source was a 400 W medium pressure mercury lamp, mounted at the central axis of the reactor (IR is cut-off by a circulating water filter). Prior to irradiation, the solution was purged with nitrogen. Quantum yield measurements were carried out using a 16 W low pressure mercury lamp and the photon flux was counted by ferrioxalate actinometry. Evolved hydrogen was estimated volumetrically at atmospheric pressure by gas chromatography (Shimadzu GC-9AM, column MS 5A, carrier gas Ar). Except for small quantities of CO_2, the only gas detected was hydrogen. During photolysis, a chocolate brown precipitate was formed in the solution. The precipitate was separated by filtration. Chemical analysis and X-ray diffractometry (Shimadzu XD-7A diffractometer) confirmed that the precipitate is metallic copper. The analysis of the filtrate by standard techniques revealed the presence of acetaldehyde and a small quantity of acetic acid in the case of ethanol, and formaldelyde and formic acid in the case of methanol.

Results and discussion

Figures 1 and 2 illustrate the photogeneration of hydrogen from ethanol and methanol in the presence of copper sulfate. The reaction rate depends on alcohol water mixing ratios and the concentration of copper(II) sulfate. The composition corresponding to the maximum rate of H_2 evolution and the quantum yields of H_2 and Cu are given in Table 1.

The formation of both hydrogen and copper during photolysis can be explained by the following reaction mechanism. Presumably, the initial reaction step is light induced oxidation of alcohol with reduction of copper(II) sulfate to copper(I) sulfate, i.e.

$$CH_3OH + 2CuSO_4 \xrightarrow{h\nu} Cu_2SO_4 + H_2SO_4 + HCHO \quad (1)$$

$$C_2H_5OH + 2CuSO_4 \xrightarrow{h\nu} Cu_2SO_4 + H_2SO_4 + CH_3CHO \quad (2)$$

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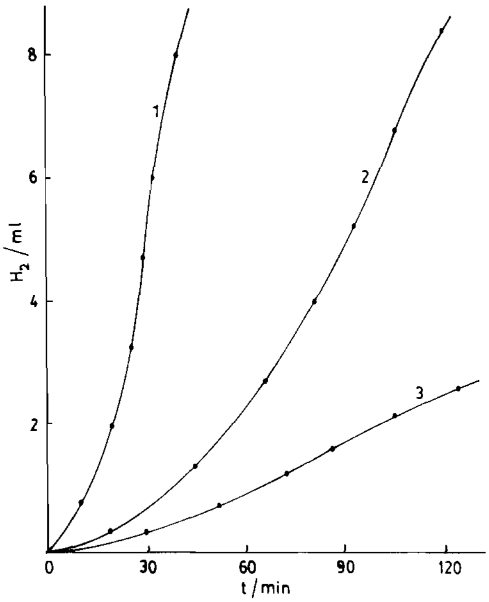

Fig. 1. Photogeneration of hydrogen from aqueous solutions of (1) 8.7 M ethanol, (2) 4.3 M ethanol and (3) 6.6 M acetic acid containing 0.2 M H_2M H_2SO_4 and 0.04 M $CuSO_4$.

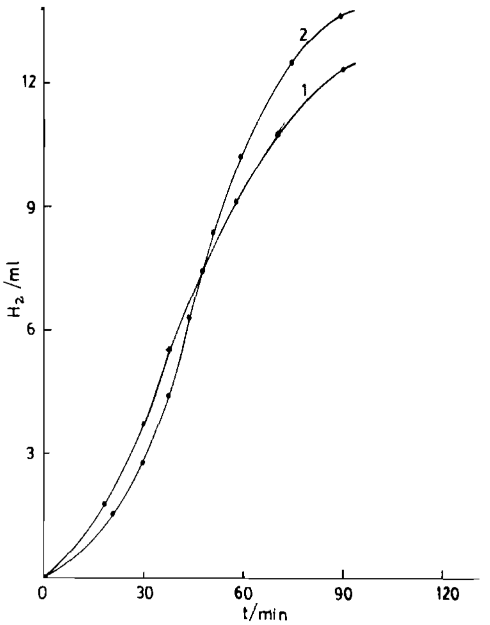

Fig. 2. Photogeneration of hydrogen from aqueous solutions of (1) 9.5 M methanol and (2) 13.0 M formaldehyde containing 0.04 M $CuSO_4$ and 0.2 M H_2SO_4.

Copper(I) sulfate disproportionates into metallic copper and copper(II) sulfate in the presence of water, i.e.

$$Cu_2SO_4 \longrightarrow Cu + CuSO_4 \qquad (3)$$

TABLE 1. Quantum yields of H_2 and Cu at 254 nm at different compositions of the alcohol water, $CuSO_4$ mixture (H_2SO_4 concentration kept fixed at 0.2 M). The first row gives the composition giving the optimum H_2 quantum yield for ethanol

[Alcohol] (M)	[$CuSO_4$] (M)	$\phi[H_2]$	ϕ[Cu]
Ethanol 8.7	0.04	0.36	0.41
Ethanol 8.7	0.01	0.19	0.26
Ethanol 4.3	0.04	0.08	0.40
Methanol 6.6	0.04	0.27	0.38

Undoubtedly, metallic copper is formed by this dark reaction. The hydrogen generating photo-reaction is probably the following:

$$Cu_2SO_4 + H_2SO_4 \xrightarrow{h\nu} 2CuSO_4 + H_2 \qquad (4)$$

The stability of copper(I) sulfate is increased in non-aqueous solvents (e.g. alcohol, acetic acid). As expected, the quantum yield of H_2 compared to Cu is enhanced when the concentration of alcohol is increased (Table 1). (Because of the unstability of Cu_2SO_4 in aqueous H_2SO_4 we have not succeeded in assessing the reaction independently.) Formic and acetic acids are formed by subsequent oxidation of the aldehydes via the following reactions, i.e.

$$HCHO + H_2O + 2CuSO_4 \xrightarrow{h\nu} Cu_2SO_4 + HCOOH \qquad (5)$$

$$CH_3CHO + H_2O + 2CuSO_4 \xrightarrow{h\nu} Cu_2SO_4 + H_2SO_4 + CH_3COOH \qquad (6)$$

Copper(I) sulfate produced in eqns. (5) and (6) participates in the reactions (3) and (4) to yield metallic copper and hydrogen. Carbon dioxide is formed by further oxidation of the acids, i.e.

$$HCOOH + 2CuSO_4 \xrightarrow{h\nu} Cu_2SO_4 + H_2SO_4 + CO_2 \qquad (7)$$

$$CH_3COOH + 2H_2O + 8CuSO_4 \xrightarrow{h\nu} 4Cu_2SO_4 + 2CO_2 + 4H_2SO_4 \qquad (8)$$

In a separate experiment we have confirmed the photo-oxidation of formaldehyde and acetic acid by copper sulfate. (During photolysis of acetic acid in the presence of $CuSO_4$, carbon dioxide, hydrogen and small quantities of ethane were detected by gas chromatography.)

All the above reactions are initiated only by UV light (an experiment with a filter indicates $\lambda \leqslant 300$ nm). The charge transfer (CT) absorption in Cu^{2+} and Cu^+ is responsible for the oxidation and reduction reactions. The CT absorption in Cu^{2+} aquo-ion $[Cu(H_2O)_6]^{2+}$ is peaked at ≈ 250 nm. We have not succeeded in determining the absorption spectrum of the transitory Cu^+ species (i.e. Cu_2SO_4) produced during the photolysis. Generally the CT absorption in Cu^{2+} complexes is in the range 230–290 nm [10].

Aqueous solutions of alcohols are also photodehydrogenated in the presence of copper(I) chloride and hydrochloric acid. Although the quantum yields are somewhat smaller, the reaction in this case is catalytic with respect to copper(II) chloride. Alcohols are oxidized with reduction of copper(II) chloride to copper(I) chloride. A solution of copper(I) chloride in dilute hydrochloric acid is rapidly photo-oxidized to copper(II) chloride with liberation of hydrogen [10, 11].

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