Hydrogen generation in photolysis of aqueous solutions of acetic acid in the presence of copper(II) chloride



K. Tennakone^{*}, U.S. Ketipearachchi, S. Punchihewa, W. A. C. Perera and R. Tantrigoda

Institute of Fundamental Studies, Hantana, Kandy (Sri Lanka)

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Introduction

Photogeneration of hydrogen from organic compounds (alcohols, organic acids, sugars etc.) in the presence of homogeneous or heterogeneous catalysts is discussed in a large number of literature reports [1-10]. Aqueous suspensions of semiconductor dispersions containing organic substances liberate hydrogen from water upon irradiation, with oxidation of the organic material [1-7]. Several homogeneous catalysts capable of photogenerating hydrogen from specific organic compounds have also been recorded [8–10]. Complexes of rhodium (and related metals) or organic sensitizers are known to dehydrogenate alcohols [8–10]. The authors have found that the Cu²⁺ ion in the presence of HCl acts as a catalyst in the photogeneration of hydrogen from aqueous solutions of acetic acid.

Experimental

Reagent grade acetic acid, HCl and CuCl₂ were used in all experiments. CuCl₂ dissolved in dil. HCl was purged with oxygen to convert any CuCl present into CuCl₂. Mixtures consisting of acetic acid, water, CuCl₂ and HCl were irradiated with a 400 W medium pressure mercury lamp (producing $\sim 5 \times 10^{19}$ photons s⁻¹, predominantly in the wavelength range 365–366 nm) in a thermostatted (26 °C) photochemical reactor (Applied Photophysics) of 300 ml volume. In every experiment, 200 ml of the solution was placed in the reactor and degassed with nitrogen (99.999%). Evolved hydrogen was detected volumetrically by gas chromatography (Shimadzu gas chromatograph GC-9AM, column MS 5A, carrier gas Ar). The only other gas detected was carbon dioxide (gas chromatography using an activated charcoal column). Analysis of the photolyzed solution revealed the presence of dissolved carbon dioxide, and when the acetic acid concentration was high small quantities

^{*}Sumanasekara Professor of Natural Science; also affiliated with the Department of Physics, University of Ruhuna, Matara, Sri Lanka.

of Cu^{1+} ion were also detected. There was no evidence (gas chromatography) for volatile compounds in the solution, other than unreacted acetic acid. Chemical analysis did not reveal the presence of any other organic acid.

Results and discussion

Figure 1 illustrates the photogeneration of hydrogen from aqueous acetic acid solution when [CH₃COOH] is varied at constant [Cu²⁺]. The rate of H₂ evolution increases initially with increasing [CH₃COOH] and then decreases. The H₂ evolution rate is maximum when [CH₃COOH] ~0.12 M. At a given [CH₃COOH] the reaction rate was found to depend on [Cu²⁺]. Here again when [CH₃COOH] is kept constant, the H₂ liberation rate initially increases and then decreases with [Cu²⁺] (Fig. 2). At all [CH₃COOH], the [Cu²⁺] corresponding to the maximum reaction rate was found to be 1.25×10^{-2} M. In all experiments [HCl] was kept fixed at 0.05 M and the reaction rate was largely independent of [HCl], provided it was in excess.

The above observations can be explained as follows: the initial reaction step is the oxidation of acetic acid with reduction of Cu^{2+} to Cu^{1+} , *i.e.*

$$CH_{3}COOH + 8CuCl_{3}^{-} + 2H_{2}O \xrightarrow{\mu\nu} 2CO_{2} + 8H^{+} + 8CuCl_{3}^{2-}$$
(1)

In the presence of excess Cl^- , Cu^{2+} and Cu^{1+} exist in the form of trichlorocuprate ions (II) and (I) (*i.e.* CuCl_3^- , CuCl_3^{2-}) respectively. It is known that trichlorocuprate(I) ions in aqueous solution liberate hydrogen upon UV irradiation with a high quantum yield [11, 12] (80% at 290 nm) via the reaction:



Fig. 1. Photogeneration of hydrogen from acetic acid solutions (0.05 M in HCl) of concentrations (M) (1) 0.12, (2) 0.15, (3) 0.18, (4) 0.08 when the Cu^{2+} concentration is 1.25×10^{-2} M.



Fig. 2. Photogeneration of hydrogen from acetic acid 0.12 M (0.05 M in HCl) when the Cu²⁺ concentrations (M) are (1) 1.25×10^{-2} , (2) 0.63×10^{-2} (3) 1.87×10^{-2} , (4) 3.1×10^{-2} , (5) 5×10^{-2} .

The reaction steps (1) and (2) are equivalent to:

$$CH_3COOH + 2H_2O \longrightarrow 2CO_2 + 4H_2$$
(3)

and trichlorocuprate(II) ions act as a catalyst. In contrast to the present system, in the photolysis of acetic acid with semiconductor catalysts, reaction (3) occurs only at alkaline pH. When the pH is acidic, reaction modes (4) and (5) are possible [2, 3]:

$$CH_3COOH \longrightarrow CH_4 + CO_2$$
 (4)

 $2CH_3COOH \longrightarrow C_6H_6 + 2CO_2 + H_2$

(4) being the most dominant. The occurrence of steps (1) and (2) is supported by detection of CuCl_3^{2-} ions in the photolyzed solution spectrophotometrically, when [CH₃COOH] in the solution is high. Under these conditions, detectable quantities of photogenerated CuCl_3^{2-} ions remain undecomposed via step (2). The mechanism of photo-oxidation of CuCl_3^{2-} (*i.e.* reaction (2)) is well understood. On absorption of UV radiation (CuCl_3^{2-} has a CT absorption peak at ~280 nm⁸) a solvated electron is generated which is scavenged by H⁺ ions, *i.e.*,

$$CuCl_{3}^{2-} \longrightarrow CuCl_{3}^{-} + e^{-}$$

$$H^{+1} + e^{-} \longrightarrow H^{0}$$

$$H^{0} + H^{0} \longrightarrow H_{2}$$
(6)

The extraction of an electron from OH^- during charge transfer excitation (~250 nm) of $CuCl_3^-$ is presumably the primary act responsible for step (1). Before CO_2 formation, a number of unstable intermediates could be

(5)

formed. It is possible that the Cu^{2+} or Cu^{1+} complex with acetic acid affects the reaction rates. The formation of a more unstable complex of Cu^{1+} would explain the observed increase in the rate of H_2 production with the progress of photolysis. When $CuSO_4$ and H_2SO_4 were used instead of $CuCl_2$ and HCl, there was no change in the reaction rate suggesting that species such as Cl^0 of Cl_2^- are not playing a role in the photochemical reaction. The occurrence of an optimum [CH_3COOH] can be understood from the fact that both CH_3COOH and H_2O are reactants in (3). A maximum in [Cu^{3+}] occurs probably because the rate of (1) increases with increasing [Cu^{2+}], whereas that of (2) has the opposite behavior. The authors have found that other organic materials in aqueous medium also undergo photo-oxidation in the presence of $CuCl_3^-$ with concomitant reduction of water. The present system is not practically useful, as H_2 yields are very small.

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