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THE CATALYSIS OF HYDROGEN PHOTOGENERATION FROM SUGARS AND STARCH IN AQUEOUS MEDIUM BY COPPER(II) CHLORIDE

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Abstract—Aqueous solutions of sugars or dispersions of starch photogenerate hydrogen in the presence of copper(II) chloride and hydrochloric acid. The mechanism of catalysis is explained.

INTRODUCTION

Commercial hydrogen is produced from fossil fuels and to a lesser extent via electrolysis of water. Because of the depletion of fossil fuels, finding alternative sources of hydrogen is essential, notably for use in the fertilizer industry (ammonia manufacture). Furthermore, hydrogen is attracting much attention as a clean fuel. Recently photocatalytic hydrogen production from waste sugars, other carbohydrates and biomass is seriously considered and a number of heterogeneous and homogeneous catalysts (e.g. semiconductor particles, dyes, complexes of rhodium) are reported to be active [1–4]. We have found that the simpler substance copper(II) chloride in presence of hydrochloric acid acts as a catalyst for photogeneration of hydrogen from aqueous solutions of sugars or aqueous dispersions of starch.

EXPERIMENTAL

Copper(II) chloride free from copper(I) chloride was prepared by purging oxygen through a solution of copper(II) chloride in dilute HCl. The photolysis of aqueous solutions (200 ml) of D-glucose, sucrose and dispersions of starch containing copper(II) chloride and HCl were carried out in a thermostatted (26°C) photochemical reactor (Applied Photophysics) of volume 300 ml. The light source was 400 W medium pressure mercury lamp mounted at the central axis of the reactor. Evolved hydrogen was estimated volumetrically at atmospheric pressure by gas chromatography (Shimadzu gas chromatograph GC-9AM, column molecular sieve 5A, carrier gas Ar 1). Prior to irradiation solutions were purged with nitrogen (99.999%).

RESULTS AND DISCUSSION

At a given concentration of sugar, the hydrogen evolution rate increases and then decreases with the increase in concentration of $CuCl_2$ (Fig. 1). The optimum $[CuCl_2]$ (for both glucose and sucrose) being $\sim 1.25 \times 10^{-2}$ M. When $[CuCl_2]$ is kept fixed, the H_2 evolution rate is found to increase with the increase of sugar concentration. Reaction rates are slightly faster with glucose than sucrose and starch liberate relatively lesser amounts of H_2 (Fig. 2). The analysis of the photolysed solution indicated presence of gluconic acid in the case of glucose and gluconic acid and complex mixture of other acids in the case of sucrose. Undoubtedly products from further oxidation of these acids are also present. Trace quantities of carbon dioxide was detected by gas chromatography.

The reaction mechanism can be understood as follows. In the presence of excess HCl, Cu^{2+} exists mostly as trichlorocuprate(II) ions ($CuCl_3^-$). Upon on irradiation sugar gets oxidized with reduction of trichlorocuprate(II) to trichlorocuprate(I) ions ($CuCl_3^{2-}$), i.e.

$$\tfrac{1}{2}[CH_2OH(CHOH)_4CHO] + \tfrac{1}{2}H_2O + CuCl_3^- \xrightarrow{h\nu_1} CuCl_3^{2-} + \tfrac{1}{2}[CH_2OH(CHOH)_4CO_2H] + H^+. \quad (1)$$

It is known that trichlorocuprate(I) (i.e. CuCl in dil. HCl) in aqueous medium liberate hydrogen when irradiated with uv light [5], i.e.

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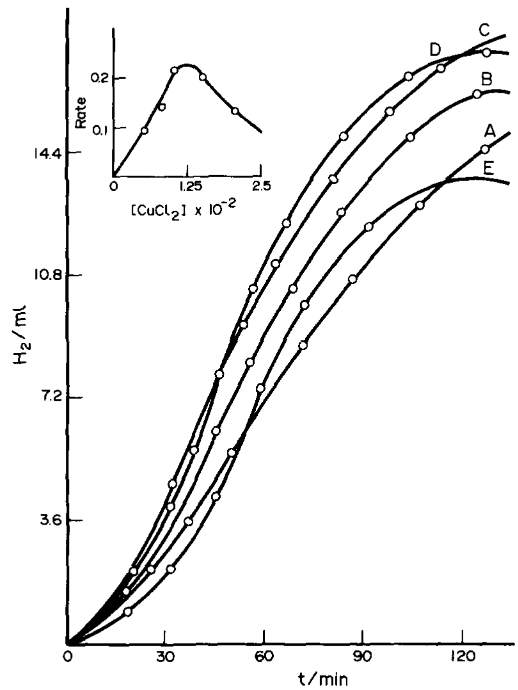

Fig. 1. Hydrogen photogeneration from a solution of sucrose (225 gl^{-1}) at concentrations (in 10^{-2} M), (A) 0.63, (B) 1.0, (C) 1.25, (D) 1.50, (E) 2.5 of $CuCl_2$ ([HCl] = 0.05 M). Inset: variation of the initial reaction rate (ml H_2 min^{-1}) with $CuCl_2$ concentration.

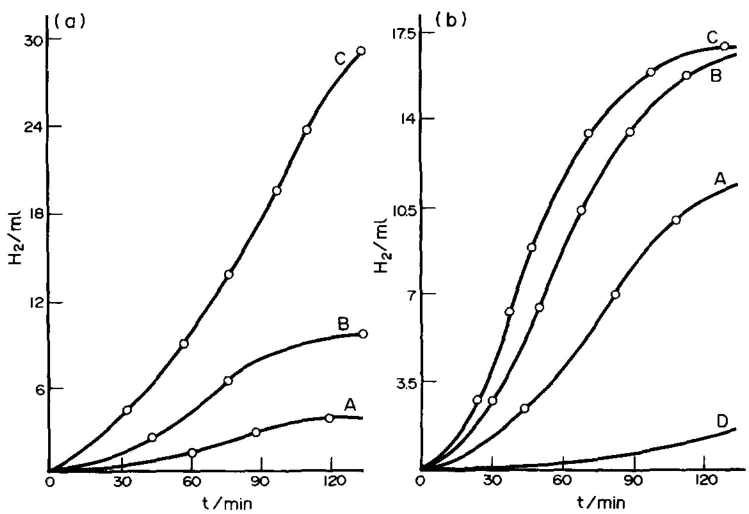

Fig. 2. (a) Photogeneration of H_2 from an aqueous solution of glucose at concentrations (gl^{-1}). (A) 50, (B) 100, (C) 165. (b) Photogeneration of H_2 from sucrose solutions of concentrations (gl^{-1}). (A) 100, (B) 150, (C) 225, (D) dispersion starch (50 gl^{-1}). In (a) and (b) [$CuCl_2$] and [HCl] kept fixed at 1.25×10^{-2} M, 0.05 M respectively.

$$CuCl_3^{2-} + H_2O \xrightarrow{h\nu_2} CuCl_3^- + \tfrac{1}{2}H_2 + OH^-. \quad (2)$$

The sum of reactions (1) and (2) is

$$\text{glucose} + H_2O \xrightarrow{h\nu_1 h\nu_2} \text{gluconic acid} + H_2. \quad (3)$$

Tricholorocuprate(II) ions acts as a catalyst. When the sugar concentration is high, $CuCl_3^{2-}$ can be detected spectrophotometrically in the photolysed solution, supporting the suggested reaction mechanism. Reactions (1) and (2) are caused by charge transfer absorption in $CuCl_3^-$ $CuCl_3^{2-}$ peaked at ~250, 275 nm respectively. The occurrence of an optimum $[Cu^{2+}]$ can be understood. Reaction rates depend on the number of photons captured which increases with $[Cu^{2+}]$. However, the reverse of the reaction (2) is also increased by an increase of $[Cu^{2+}]$. The two opposing factors give rise to an optimum concentration of the photocatalyst.

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