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HYDROGEN PRODUCTION FROM A TWO STEP PROCESS BASED ON BROMIDES OF COPPER

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Abstract—A solution of cuprous bromide containing hydrobromic acid is photo-decomposed to cupric bromide and hydrogen upon irradiation. Cupric bromide readily undergoes thermal decomposition into cuprous bromide and bromine. A model cyclic system for hydrogen production based on this effect is described.

INTRODUCTION

Photochemical hydrogen production continues to attract much attention as an ideal way of storing solar energy [1–3]. The literature on the subject is extensive and can be divided into the following categories. (1) Methods that photo-decompose water into hydrogen and oxygen in one step [3–6]. These systems have very low quantum and energy conversion efficiencies. Furthermore, since hydrogen and oxygen are obtained as a mixture which is explosive, additional techniques are needed for separation. (2) Sacrificial systems where water is photo-reduced to hydrogen with concomitant oxidation of an electron donor [7–10]. Here, although the quantum efficiencies are high, irreversibility leads to severe constraints on the practical utility (unless a vast reserve of the sacrificial agent is available). (3) Reactions consisting of two steps. In one step, water is reduced to hydrogen with concomitant oxidation of an electron donor and in a second step, water photo-oxidation takes place with reduction of the oxidized donor to the original state [11–14]. Two step reactions have several distinct advantages: (i) the highly reactive primary oxidation and reduction products of water are generated in sites separated in space, preventing the back reactions; (ii) each step can function independently of the other for a limited duration of time; (iii) hydrogen and oxygen could be collected into separate compartments; (iv) if both steps are photochemical reactions, each electron transfer involves two photons, thus less energetic photons can be utilized; and (v) in some cases one step could be a light reaction and the other a thermal reaction.

In our earlier work a model two step process for water photodecomposition based on cuprous chloride was discussed [13]. This system depends on the following reactions.

Step 1

The u.v. irradiation of a solution of cuprous chloride in HCl liberates hydrogen, i.e.

$$\mathrm{CuCl + HCl \rightarrow CuCl_2 + H} \qquad (1)$$

$$\mathrm{H + H \rightarrow H_2}. \qquad (2)$$

Step 2

A solution of cupric chloride when irradiated in the presence of TiO_2, generates O_2, i.e.

$$\mathrm{CuCl_2 + \tfrac{1}{2}H_2O \xrightarrow{TiO_2/h\nu} CuCl + HCl + \tfrac{1}{4}O_2}. \qquad (3)$$

Reactions (1) and (3) are equivalent to decomposition of water. Step 1 proceeds almost towards completion with a high quantum yield [15] (the initial quantum yield at 254 nm ~80%). However, reaction (3) does not move very far in the forward direction, owing to occurrence of the back reaction at a significant rate. An alternative possibility is to modify step 2 in the following manner. On heating, $CuCl_2$ decomposes into chlorine and CuCl (decomposition temperature ≃993°C), i.e.

$$\mathrm{CuCl_2 \rightarrow CuCl + \tfrac{1}{2}Cl_2}. \qquad (4)$$

Chlorine can react photocatalytically with water to produce oxygen and HCl, i.e.

$$\mathrm{Cl_2 + H_2O \xrightarrow{TiO/h\nu} 2HCl + \tfrac{1}{2}O_2}. \qquad (5)$$

The analogous system with copper bromides instead of chlorides has a distinct advantage as the decomposition temperature of $CuBr_2$ is much lower (243°C). The present paper describes a system for hydrogen production based on copper bromides, i.e.

Step 1

$$\mathrm{CuBr + HBr \xrightarrow{h\nu} CuBr_2 + \tfrac{1}{2}H_2}$$

$$\Delta G = -14.2\ \mathrm{kcal\ mol^{-1}} \qquad (6)$$

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Step 2

$$CuBr_2 \xrightarrow{\text{Thermal}} CuBr + \tfrac{1}{2}Br_2$$

$$\Delta G = -10.7\ \text{kcal mol}^{-1} \quad (7)$$

$$Br_2 + H_2O \xrightarrow{\text{Thermal or photocatalytic}} 2HBr + \tfrac{1}{2}O_2$$

$$\Delta G = -33.3\ \text{kcal mol}^{-1} \quad (8)$$

2. EXPERIMENTAL

The starting materials used were cupric bromide (Aldrich) and hydrobromic acid (BDH). Cuprous bromide was prepared by heating cupric bromide in a stream of nitrogen (reaction 7). The decomposition temperature of CuBr was accurately determined by differential thermal analysis (Fig. 1). Photolysis of CuBr solutions in dil. HBr was carried out using a thermostatted photochemical reactor of volume 300 ml (Applied Photophysics). The light source was a medium pressure 400 W mercury lamp mounted at the central axis of the reactor. Prior to photolysis all solutions were purged with nitrogen (99.999%). Liberated hydrogen was estimated volumetrically using a gas chromatograph (Shimadzu 90-AM). The progress of hydrogen evolution during photolysis is illustrated in the Fig. 2. Quantum yields were determined using a 16 W low pressure mercury lamp.

3. DISCUSSION

Just as in the cuprous chloride system, step 1 proceeds quite considerably in the forward direction. The quantum yield of H_2 production at 254 (number of moles of H_2 produced/number of photons absorbed by the solution) during the initial phase of the reaction was found to be ~78%. The active species involved in reaction (6) [15] is the tribromocuprate (I), i.e. $CuBr_3^{2-}$ ion which has an absorption peak at 280 nm. Presumably, the primary photochemical event is the formation of a solvated electron [15] which is scavenged by H^+ ions. The reaction may be represented by,

$$CuBr_3^{2-} \rightarrow CuBr_3^{-} + e \quad (9)$$

$$H^+ + e \rightarrow H.$$

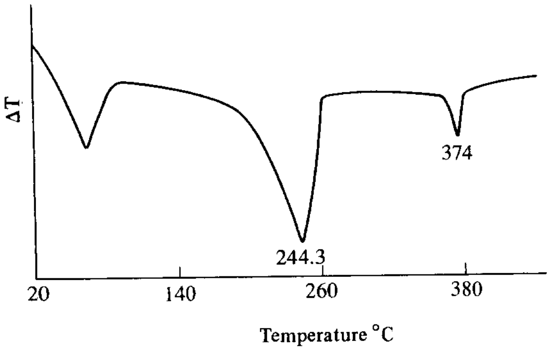

Fig. 1. Differential thermal analysis curve for cupric bromide (ΔT = temperature change when the heating the rate is 2°C min^{-1}). The endothermic peak at 244.3°C is due to thermal decomposition. The peak at 374°C originates from a phase change in CuBr.

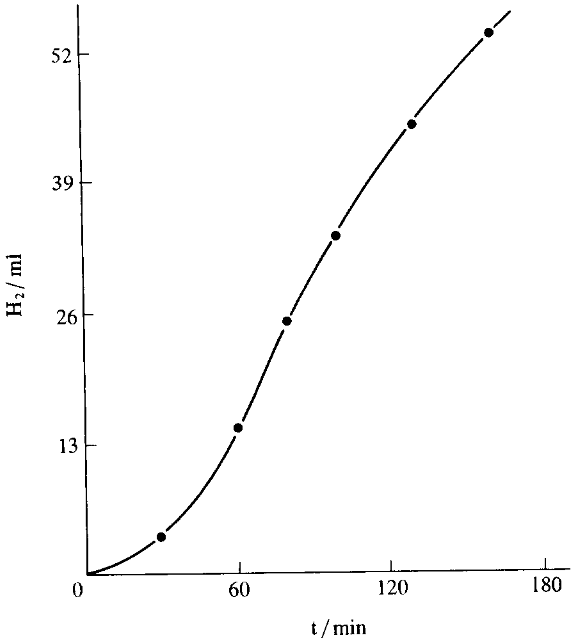

Fig. 2. Hydrogen photogeneration (ml per 275 ml of solution) from aqueous CuBr in dilute HBr (0.02 M in Cu^{2+}, 0.4 M in HBr).

A disadvantage of the process is that step 1 is sensitive mostly to u.v. light (quantum yields are negligibly small in the visible region). Again to carry out step 2, the solution used from the step 1 will have to be evaporated. Instead of carrying out reaction (8), hydrogen from (6) and bromine from (7) may be recombined in a fuel cell to recover energy: this process is also cyclic. Although, as at present, the systems of this type are not practically viable, two step processes are one of the promising ways of achieving photochemical solar energy conversion based on hydrogen.

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