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SHORT COMMUNICATION

A THREE STEP PHOTOCHEMICAL REACTION SCHEME FOR DECOMPOSITION OF WATER

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INTRODUCTION

The development of a practical system for decomposition of water into hydrogen and oxygen using sunlight is one of the most desired inventions. Although a great deal of experimentation[1-9] has been carried out on this subject during the past decade, practically viable systems are yet unavailable. Chemical reactions based on homogeneous or heterogeneous photocatalysts capable of decomposing water are documented.[1-9] However, the quantum and energy conversion efficiencies are not sufficient for commercial utilization. It is likely that new ideas are necessary for devising methods of photodecomposition of water. One of the most promising methods could be to adopt a series of light driven reactions where water is decomposed via a number of intermediate reactions. Instead of one step photodecomposition, a multi-step process has two distinct advantages. (1) Utilization of several photons for decomposition of one molecule of water, thereby making less energetic photons sensitive. (2) Back-reactions (i.e., recombination of hydrogen and oxygen in the active intermediate forms) are more easily suppressed in a multi-step process. In fact the most successful energy storing light reaction *viz.* photosynthesis, operates in this manner. The green plant photosynthetic apparatus consists of a two photosystems linked by a series of redox carriers. Earlier we have discussed several model systems for decomposition of water based on two photosystems.[10-12] In this work, we describe a three step process as a model system for photodecomposition of water.

METHODS AND MATERIALS

Copper (II) chloride, silver nitrate, sodium choloride, metallic copper (Aldrich) and hydrochloric acid (BDH) were used as the starting materials. Copper (I) chloride was prepared by boiling metallic copper with a solution of copper (II) chloride in dilute hydrochloric acid avoiding oxygen contamination. Silver chloride was prepared by double decomposition of silver nitrate and sodium chloride in aqueous solution and separation and washing without exposure to light. All photolysis experiments were conducted in a thermostatted (26^0C) photochemical reactor (Applied photophysics)

volume 300 ml and prior to irradiation solutions were purged with nitrogen (99.999%). The light source used was a 400 W medium pressure mercury lamp. A low pressure lamp (16W) was used to estimate the quantum yields and the photon flux was counted by ferrioxalate actinometry. Evolved gases were determined volumetrically at atmospheric pressure by gas chromatography (Shimadzu GC-9A gas chromatograph, column molecular sieve 5A, carrier gas Ar).

RESULTS AND DISCUSSION

The three steps are given below:

Step 1

A solution of copper (I) chloride in dilute hydrochloric acid liberates hydrogen upon UV irradiation with oxidation of copper (I) chloride to the copper (II) chloride [13], i.e.,

$$CuCl + HCl \xrightarrow{h\upsilon_1} CuCl_2 + \tfrac{1}{2}H_2 \quad (1)$$

Step 2

The irradiation of a suspension of particles of metallic silver in aqueous copper (II) chloride generates copper (I) chloride and silver chloride, ie.,

$$CuCl_2 + Ag \xrightarrow{h\upsilon_2} AgCl + CuCl \quad (2)$$

Step 3

An aqueous suspension of silver chloride when irradiated liberates oxygen, i.e.,

$$AgCl + \tfrac{1}{2}H_2O \xrightarrow{h\upsilon_3} Ag + HCl + \tfrac{1}{4}O_2 \quad (3)$$

The sum of reactions (1), (2) and (3) is

$\frac{1}{2}H_2O \longrightarrow \frac{1}{2}H_2 + \frac{1}{4}O_2$ and all them can be driven by light.

Figure 1 illustrates production of hydrogen upon irradiation of a (0.20 mol dm^{-3}) solutionof CuCl containing 0.25 mol dm^{-3} of HCl. After several hours of photolysis, the solution turns pale green owing to formation of copper (II) chloride. The initial quantum yield of H_2 production at 250 nm is ~ 63%.

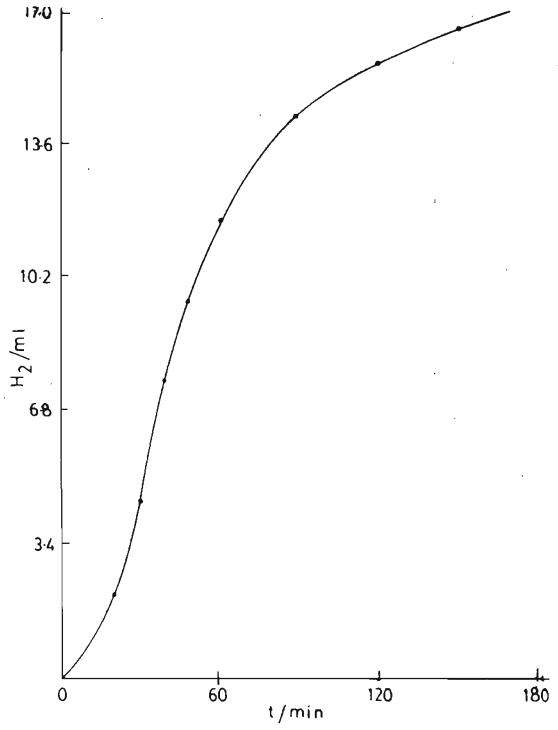

Figure 1: Hydrogen photogeneration from a 0.20M solution of CuCl in dilute HCl (0.25M).

A solution of copper(II) chloride when irradiated liberates detectable quantities of both hydrogen and oxygen via the following reactions (Figure 2).

$$CuCl_2 + \tfrac{1}{2}H_2O \xrightarrow{h\upsilon} CuCl + \tfrac{1}{4}O_2 + HCl \qquad (4)$$

$$CuCl + HCl \xrightarrow{h\upsilon} CuCl_2 + \tfrac{1}{2}H_2 \qquad (5)$$

In the presence of silver particles, the rates of hydrogen and oxygen evolution is increased (Figure 2 & 3) as a result of enhanced formation of CuCl via (2) and decomposition of AgCl via (3). The reaction (2) also occurs thermally: when silver dust is heated with a solution of copper (II) chloride, easily detectable quantities of copper (I) chloride are formed. We have found that, the rate of formation of copper (I) chloride in this reaction at 90^0C is increased by UV irradiation of the solution as an increase of temperature decreases[13] the photodecomposition of CuCl in HCl by the reaction 1.

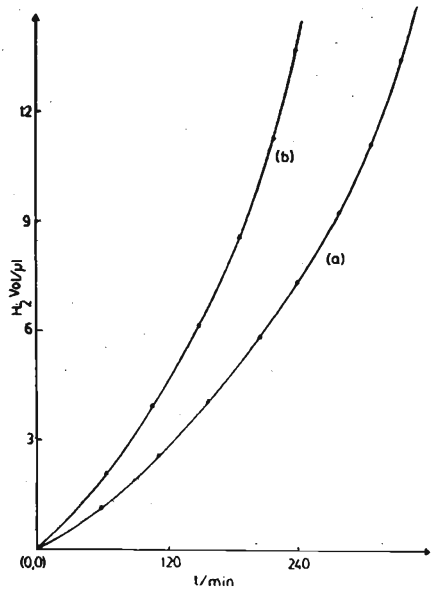

Figure 2: **Hydrogen photogeneration (the plot of volume of gas vs time) during photolysis of (a) 0.20M solution $CuCl_2$ containing HCl (0.25M) (b) 0.20M solution of $CuCl_2$ containing HCl (0.25M) in the presence of 5 mg of silver dust.**

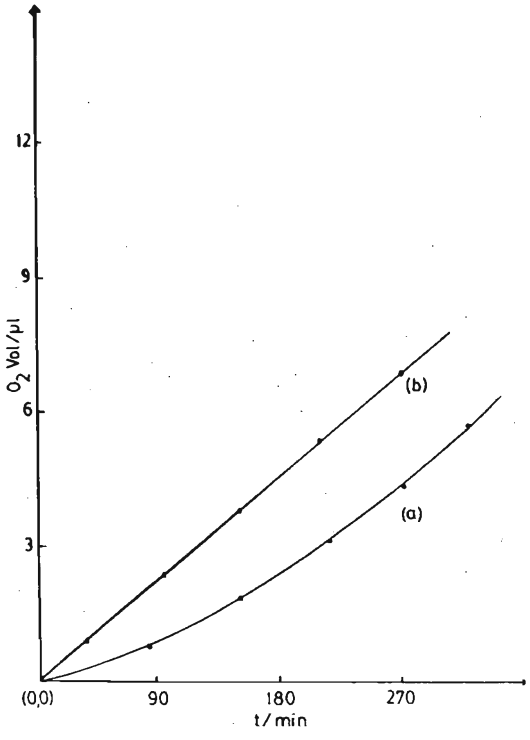

Figure 3: (a) Oxygen photogeneration during photolysis of a 0.20M solution (0.25M in HCl).
(b) Oxygen photogeneration from the same solution in the presence of 5mg of silver dust.

Figure 4 illustrates oxygen evolution in the photodecomposition of an aqueous suspension of silver chloride. The photodecomposition of silver chloride depends on its semiconductor property, i.e. the photogenerated electrons and holes participate in the following reaction, i.e.,

$$\tfrac{1}{2}H_2O + h^+ \longrightarrow H^+ + \tfrac{1}{4}O_2 \quad (6)$$

Valence band AgCl

$$AgCl + H^+ + e^- \longrightarrow HCl + Ag \quad (7)$$

Conduction band AgCl

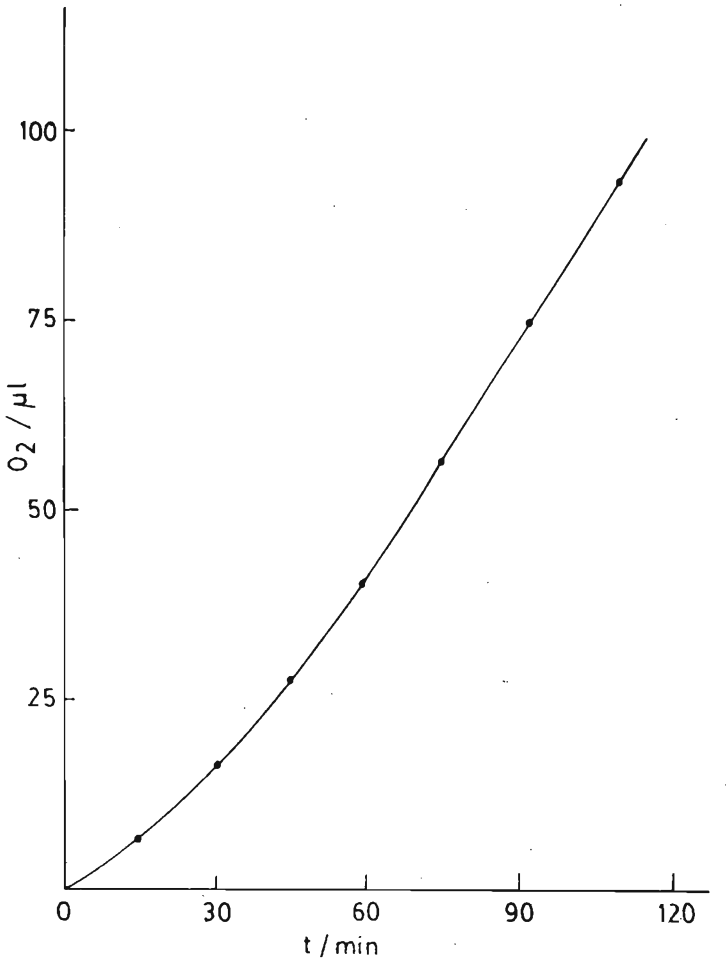

Figure 4: Oxygen evolution during photolysis of 50 mg AgCl in 200ml of water.

As a consequence of (1), (2) and (3), on prolonged photolysis, a solution of $CuCl_2$ containing Ag or AgCl generates both oxygen and hydrogen. If the reaction (2) is carried out thermally, AgCl can be separated from the CuCl containing solution and the reactions (1) and (3) carried out independently. Reactions (1) and (2) depend on charge transfer absorption in the complexes of CuCl and $CuCl_2$ with HCl (i.e. trichlorocuprate (I) and (II) ions) with absorption peaks near 275 and 250 nm respectively. Light of wavelength less than band gap radiation of AgCl (~390 nm) is responsible for reaction (3). Although the above reaction scheme is not practical at the moment, it gives much insight into the possibility of multi-step reactions for decomposing water into hydrogen and oxygen.

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