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# Water Photolysis with Copper(I) Chloride

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A deaerated suspension of copper(I) chloride in dilute HCl has been found to photogenerate  $H_2$  efficiently when irradiated with u.v. light, oxidising itself into copper(II) chloride. Aqueous copper(II) chloride can be photoreduced to copper(I) chloride using SrTiO<sub>3</sub>, TiO<sub>2</sub> or WO<sub>3</sub>, oxidising water concomitantly. The practical limitations of such a system are discussed.

Heterogeneous photocatalysis with semiconductors is receiving much attention as one of the most promising methods for chemical storage of solar energy.<sup>1</sup> Now it is well known that semiconductor particulate dispersions possess the ability to photoreduce or photo-oxidise water in the presence of a sacrificial electron donor or an acceptor.<sup>2-10</sup> The sacrificial systems employing familiar reducing or oxidising agents are irreversible and it is highly desirable to search for systems where the oxidised electron donor resulting from photoreduction of water can be used as the electron acceptor to photo-oxidise water in another reaction.

We have investigated the photocatalytic properties of  $Cu^1$  chloride, which is a p-type semiconductor of band gap 3.31 eV<sup>11</sup> and have found that in principle a water-cleavage process consisting of two photosystems can be based on this material.

#### Photosystem I

A suspension of CuCl in dilute HCl is found to generate  $H_2$  efficienctly when irradiated with u.v. light. CuCl acts as the sensitizer as well as the sacrificial agent, *i.e.* 

$$4CuCl+4HCl \rightarrow 4CuCl_2+2H_2, \qquad \Delta G = 216.8 \text{ kJ} \quad (\text{pH 7}). \tag{1}$$

#### Photosystem II

An aqueous solution of  $CuCl_2$  is found to photogenerate  $O_2$  from water in the presence of sensitizers  $SrTiO_3$ ,  $TiO_2$  or  $WO_3$  via the reaction

$$4\operatorname{CuCl}_2 + 2\operatorname{H}_2\operatorname{O} \rightarrow 4\operatorname{CuCl} + 4\operatorname{HCl} + \operatorname{O}_2, \qquad \Delta G = 255.2 \text{ kJ} \quad (\text{pH 7}). \tag{2}$$

The sum of reactions (1) and (2) is equivalent to photodecomposition of  $H_2O$  into  $H_2$  and  $O_2$ .

#### Experimental

CuCl was prepared from CuCl<sub>2</sub> (analytical grade) and metallic copper by the method described in ref. (12). Commercial CuCl (analytical grade), purified by washing with deaerated dilute HCl was also used in some experiments and identical results were obtained. Anatase TiO<sub>2</sub> (99.9%) and tungsten oxide (99.9%) were purchased from Aldrich.

The light source used was a 90 W medium-pressure Hg lamp. Light intensities were measured with an International light IL 700 radiometer. An Applied Photophysics water-cooled (26  $^{\circ}$ C) reaction cell (volume 35 cm<sup>3</sup>) equipped with a Clark-type calibrated



Water Photolysis with CuCl

Fig. 1. H<sub>2</sub> photoproduction from 10 mg of CuCl. HCl concentration/mol dm<sup>-3</sup>: (a) 0.2, (b) 0.3, (c) 0.6, (d) 1.1.

membrane polarographic detector monitored the H<sub>2</sub> and O<sub>2</sub> concentrations in the irradiated solution. An Applied Photophysics monochromator and 200 W high-pressure Hg lamp were used to estimate the quantum yields. As a check on measurements with the monochromator, reaction (1) was also carried out under irradiation with a u.v. lamp (LCE-450 Q, Allen & Co.), which transmits a band peaked near 370 nm, and the photon flux was estimated by ferrioxalate actinometry. All solutions were degassed with purified argon (O<sub>2</sub> content *ca.* 10 ppm) until the residual O<sub>2</sub> concentration was *ca.*  $8 \times 10^{-7}$  mol dm<sup>-3</sup>.

CuCl in the reaction product of eqn (2) was estimated as follows. The catalyst containing CuCl was filtered off, washed with air-free water and digested in dilute ammonia. The extract was aerated to convert  $Cu(NH_3)_4^+$  into  $Cu(NH_3)_4^{2+}$  ions, which were estimated spectrophotometrically.

#### **Results and Discussion**

Fig. 1 shows  $O_2$  photogeneration from 10 mg of CuCl suspended in 35 cm<sup>3</sup> dilute HCl. It is seen that the initial reaction rate and the equilibrium concentration of  $O_2$  rapidly increase as the concentration of HCl is increased. When the HCl concentration is *ca*. 1 mol dm<sup>-3</sup>, the initial quantum yield of  $\frac{1}{2}H_2$  (corrected for transmittance of the solution estimated spectrophotometrically) at 370 nm is *ca*. 51%. In direct sunlight, bubbling of H<sub>2</sub> from deaerated solutions is seen at the same concentration of HCl. Fig. 2 gives O<sub>2</sub> photoproduction from 0.1 mol dm<sup>-3</sup> aqueous CuCl<sub>2</sub> (pH 6.7) in the presence of catalysts SrTiO<sub>3</sub>, TiO<sub>2</sub> and WO<sub>3</sub>. Here the reaction rates decrease rapidly as the pH is decreased.



Fig. 2.  $O_2$  photoproduction from a 0.1 mol dm<sup>-3</sup> solution of CuCl<sub>2</sub>. Catalysts (10 mg): (a) WO<sub>3</sub>, (b) TiO<sub>2</sub>, (c) SrTiO<sub>3</sub>.

With SrTiO<sub>3</sub>, which is found to be the most effective catalyst for initiating this reaction, ca. 1.2% stoichiometric amount of O<sub>2</sub> expected from reaction (2) is produced in reaching the equilibrium (the reaction cell which was initially deaerated was kept closed). It is noted that the CuCl yield is somewhat smaller than the corresponding stoichiometric quantity. This can be understood because CuCl<sub>2</sub> can also be reduced to Cu with concomitant oxidation of water. In fact the residual catalyst from reaction (2) contains detectable amounts of Cu in addition to CuCl.

Reaction (2) does not proceed very far in the forward direction because the rate of the back reaction, *i.e.* oxidation of CuCl to CuCl<sub>2</sub> by C<sub>2</sub>, is quite high. Fig. 3 shows O<sub>2</sub> uptake by a suspension of CuCl in 0.7 mol dm<sup>-3</sup> HCl. There are no significant differences in dark and illuminated uptake rates. If argon is bubbled at a rate *ca*. 0.5 dm<sup>-3</sup> min<sup>-1</sup>, the maximum yield of CuCl from the forward reaction (2) increases to *ca*. 8.0% of the stoichiometric amount. Bubbling argon (containing 10 ppm O<sub>2</sub>) at this rate would deliver 7.0  $\mu$  mol O<sub>2</sub> in 30 min. These O<sub>2</sub> molecules will also assist the back reaction (2).

The very rapid photoreduction of water is an indication that the conduction band of CuCl is well above the  $H_2O/H_2$  redox level. Photogenerated electrons reduce water and holes are consumed in oxidising CuCl itself into CuCl<sub>2</sub>. When the same material acts as the sensitizer and the hole scavenger, such very high quantum yields of  $H_2$  can be expected because there is no necessity for holes to be transferred into another substance. We have noted that in the presence of SrTiO<sub>3</sub>, TiO<sub>2</sub> or WO<sub>3</sub> in contact with CuCl (*i.e.* CuCl ground with these powders) the photogeneration of  $H_2$  via reation (1) is almost completely suppressed. Clearly the suppression of reaction (2). It is very



Fig. 3.  $O_2$  uptake by a suspension of 10 mg CuCl in 0.7 mol dm<sup>-3</sup> HCl containing dissolved  $O_2$ .

likely that  $TiO_2$  and CuCl in contact behave as minature photoelectrochemical cells with p-type CuCl and n-type  $TiO_2$  forming photocathodes and photoanodes, respectively. As hole tunnelling to the solution now occurs at the  $TiO_2$  surface, the oxidation of CuCl is prevented and water oxidation takes place instead with the reduction of CuCl<sub>2</sub>.

As reaction (2) cannot be made to move very far in the forward direction without spending additional energy, in practice the system cannot be recycled using light as the only source of energy. There are other complications: CuCl produced by reaction (2) has to be separated from the catalyst to initiate the photoreduction reaction and this operation will also consume energy. However, the possibility remains that these extra energy requirements may also be derived from the sun.

Previous authors<sup>13</sup> have observed photoreduction of HCl by Cu<sup>+</sup> dissolved in acid. Here the maximum quantum efficiency (*ca.* 80%) occurs at a much shorter wavelength,<sup>13</sup> 265 nm. The solubility of CuCl in HCl increases progressively with increasing concentration of HCl and the contribution to the quantum yield of hydrogen from this effect at 370 nm is *ca.* 4.0%.

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