# CATALYSIS OF WATER PHOTOLYSIS BY TRICHLOROCUPRATE IONS

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# Summary

Irradiation of an aqueous solution of trichlorocuprate(I) ions liberates hydrogen with oxidation of trichlorocuprate(I) to trichlorocuprate(II). Irradiation of trichlorocuprate(II) ions liberates oxygen with reduction to trichlorocuprate(I). Thus continuous water photolysis is possible with trichlorocuprate ions. Quantum yields are measured under various conditions.

# 1. Introduction

It is known that some inorganic ions (e.g.  $Fe^{2+}$ ,  $Cr^{2+}$ ,  $Ce^{3+}$ ) photoreduce water to hydrogen with concomitant oxidation of the ion [1-12]. In rare cases, the oxidized ion has the ability to photo-oxidize water reverting back to the original state. Such ions catalyse the photodecomposition of water and their photolysis releases detectable amounts of hydrogen and oxygen. The best known example is the  $Ce^{3+}-Ce^{4+}$  system; UV irradiation of a solution of cerous ions generates minute quantities of oxygen and hydrogen. We have found that  $CuCl_3^{2-}-CuCl_3^{-}$  behaves in the same manner. Photolysis of a solution of cuprous chloride in HCl (containing the trichlorocuprate(I) ion,  $CuCl_3^{2-}$ ) liberates hydrogen with a very high quantum yield [13], *i.e.* 

$$\operatorname{CuCl_3}^{2-} + \operatorname{H_2O} \xrightarrow{h\nu_1}{k_1} \operatorname{CuCl_3}^{-} + \frac{1}{2}\operatorname{H_2}^{+} + \operatorname{OH}^{-}$$
(1)

Irradiation of a solution of cupric chloride in HCl (containing the trichlorocuprate(II) ion) liberates oxygen, *i.e.* 

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$$\operatorname{CuCl}_{3}^{-} + \frac{1}{2}\operatorname{H}_{2}\operatorname{O} \xrightarrow{h\nu_{2}}{k_{2}} \operatorname{CuCl}_{3}^{2-} + \frac{1}{2}\operatorname{O}_{2} + \operatorname{H}^{+}$$
(2)

As a consequence of reactions (1) and (2), the photolysis of a solution initially containing only trichlorocuprate(II) ions liberates detectable quantities of both hydrogen and oxygen.

#### 2. Experimental details

Photolysis experiments were conducted with solutions initially containing only cupric or cuprous ions. Cupric chloride solution (0.6 M in  $Cu^{2+}$ ) was prepared by dissolving cupric chloride (BDH) in dilute HCl (0.5 M). To ensure that the cupric solution was free from cuprous ions, the acidified cupric chloride solution was purged with oxygen. Cuprous chloride solution was prepared by prolonged boiling of a solution of cupric chloride in HCl with copper powder. (To prevent the entry of air, the mixture was boiled in a closed flask with the steam outlet tube dipped into water.) During dilution and transfer of the solution air contamination was avoided.

Photolysis experiments were carried out in a double-walled, watercooled (26 °C) photochemical reactor (volume, 310 ml) (Applied Photophysics) mounted with a 400 W medium pressure mercury lamp at the central axis. The solution was contained in the annular region between two cylinders; the thickness of the solution layer was approximately 0.7 cm. During photolysis the solution was magnetically stirred. A low pressure 15 W mercury lamp was also used for the determination of the quantum yields. Prior to photolysis all solutions were purged with nitrogen (99.999%). The volume of solution used for photolysis in each experiment was 200 ml. The photon flux was counted by ferrioxalate actinometry.

Photogenerated hydrogen and oxygen were estimated by injecting samples of residual gas in the reactor, collected (through a septum valve) at intervals, into a gas chromatograph (Shimadzu, Porapak column, argon as the carrier gas). The total volume of each gas evolved was ascertained by taking into account the amount dissolved in the solution. Although extreme precautions were taken to prevent the entry of air into the apparatus, a blank experiment showed that small quantities of atmospheric oxygen entered at a nearly constant rate. Photochemically generated oxygen was calculated by subtracting the atmospheric oxygen. As a double check on oxygen photogeneration, photolysis was also carried out in a reaction vessel provided with a polarographic oxygen detector (Applied Photophysics). The rates of oxygen evolution measured by both methods were found to be comparable.

## 3. Results and discussion

Figure 1 illustrates the photogeneration of hydrogen and oxygen from a solution which initially contained only cupric ions. On prolonged



Fig. 1. Time development of hydrogen (full line) and oxygen (broken line) during photolysis of trichlorocuprate(II) (0.6 M in  $Cu^{2+}$ ; 0.5 M in HCl).

photolysis, hydrogen and oxygen are liberated continuously at nearly constant rates: the hydrogen evolution rate is approximately equal to twice the oxygen evolution rate.

The photogeneration of hydrogen from a solution of cuprous chloride in HCl (cuprous chloride dissolves in excess HCl to form trichlorocuprate(I) ions with a little admixture of dichlorocuprate(I) ions) is shown in Fig. 2. Here the initial rate of hydrogen evolution is much faster than that of the solution which initially contained the same concentration of cupric ions. Oxygen evolution is not detectable initially. However, after about 4 h, when the concentration of cupric ions is sufficiently high, oxygen can be detected simultaneously with hydrogen. At equilibrium, both systems (*i.e.* solutions which initially contained either Cu<sup>2+</sup> or Cu<sup>+</sup>) behave identically.

 ${\rm CuCl_3}^{2-}$  has a charge transfer band centred around 273 nm and the photolysis is most effective when  $\lambda \leq 273$  nm. The charge transfer band



Fig. 2. Photogeneration of hydrogen from a solution of trichlorocuprate(I) (0.6 M in  $Cu^+$ ; 0.5 M in HCl).

in CuCl<sub>3</sub><sup>-</sup> peaks near 245 nm. The initial quantum yield of hydrogen production during photolysis of CuCl<sub>3</sub><sup>-</sup> (0.6 M in Cu<sup>+</sup>) at 254 nm is approximately 0.78. The equilibrium water photolysis rate as calculated for the data presented in Fig. 1 is  $\phi(H_2) \approx 2\phi(O_2) \approx 10^{-3}$ .

The primary step involved in the photolysis of  $\text{CuCl}_3^{2-}$  is probably the formation of a primary pair  $\text{CuCl}_3^{-}\cdot\text{e}^-$ , where the repulsive partners (CuCl}\_3^{-} and e^-) separate and undergo reactive scavenging leading to hydrogen formation [13], *i.e.* 

$$\operatorname{CuCl}_{3}^{-} + e^{-} + H^{+} \longrightarrow \operatorname{CuCl}_{3}^{-} + H^{*}$$
(3)

$$H' + H^+ + CuCl_3^{2-} \longrightarrow H_2 + CuCl_3^{-}$$
(4)

Presumably charge transfer excitation of  $CuCl_3$  or related halide complexes of  $Cu^{2+}$  is responsible for the photolysis leading to the formation of oxygen; the exact mechanism is not clear. If the solutions are kept continuously purged, the back reactions (1) and (2) are suppressed and the water photolysis rate is enhanced.

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