Hydrogen production in the photolysis of tetrahydroxostannate(II) ions in an aqueous medium

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Abstract

The photolysis of aqueous tetrahydroxostannate(II) ions in an aqueous medium is found to liberate hydrogen with the formation of hexahydroxostannate(IV). Colloidal platinum increases the rate of the reaction.

1. Introduction

Some inorganic ions in an aqueous medium when photolysed liberate hydrogen with the oxidation of the ions. In all reported cases [1-9] (Fe²⁺, Ce²⁺, Eu²⁺, Sr²⁺ and V²⁺), the oxidation state changes by one unit and the reaction mechanism is believed to be associated with light-induced transfer of an electron to the solvent which is scavanged by the H⁺ ions [10, 11], *i.e.*

$$\mathbf{X}^{n+} \longrightarrow \mathbf{X}^{(n+1)+} + \mathbf{e}^{-} \tag{1}$$

$$H^+ + e^- \longrightarrow H \tag{2}$$

$$H + H \longrightarrow H_2$$
 (3)

The quantum yield of H_2 formation in this process depends on several factors such as the nature of light absorption by the ion, $X^{(n+1)+}-X^{n+}$ oxidation-reduction potential, the concentration of X^{n+} and the pH of the solution [12]. The electron detachment from ions and molecules in aqueous solution is generally monophotonic [13]. As molecular hydrogen generation requires a transfer of two electrons, the above severely limits the quantum yield of hydrogen generation in the photolysis. Although there is extensive literature on the photochemistry of coordination compounds of transition metals [1-12], studies on the complexes of the main group have been somewhat neglected. In this note we report our observations on the photolysis of aqueous tetrahydroxostannate(II) ion, which is found to liberate hydrogen with concomitant oxidation to hexahydroxostannate(IV) ion, *i.e.*

$$[Sn(OH)_4]^{2-} + 2H_2O \xrightarrow{h\nu} [Sn(OH)_6]^{2-} + H_2$$
(4)

The above is a rare example of a system where the oxidation state of the ion changes by two units during photolysis.

2. Experimental details

The tetrahydroxostannate(II) solution was prepared by the addition of excess sodium hydroxide to a solution of tin(II) chloride (Aldrich) when tin(II) hydroxide dissolved in excess sodium hydroxide to form $[Sn(OH)_4]^{2-}$ ions. pH adjustments were made by altering the amount of sodium hydroxide added. Photolysis experiments were carried out in a 300 cm³ cylindrical reactor (Applied Photophysics) with a 400 W medium pressure mercury lamp (Germilamp) mounted inside an inner double-walled quartz cylinder which is water cooled (26 °C). In all experiments the volume of the solution was 200 ml. The thickness of the solution layer between the cylinders in the reactor was about 0.75 cm. Prior to irradiation, the solution was purged with nitrogen



Fig. 1. Hydrogen photogeneration in the photolysis of a 0.02 M solution of $[Sn(OH)_4]^{2-}$: curve 1, pH 10; curve 2, pH 14; curve 3, pH 12.5; curve 4, pH 12.5 containing 2×10^{-5} g pt 1^{-1} .



Fig. 2. Absorption spectrum of $[Sn(OH)_4]^{2-}$ solution.

(99.99%) and during photolysis it was kept magnetically stirred. The evolved hydrogen was detected by gas chromatography (Shimadzu GC 9AM gas chromatograph; column molecular sieve 5A; carrier gas, argon; thermal conductivity detector). The presence of Sn^{4+} ions in the photolysed solution was confirmed by the following method [14]. The addition of ammonium sulphide precipitates both tin(II) and tin(IV) sulphides; however, only tin(IV) sulphide is soluble in excess Na₂S. Consequently, when excess Na₂S is added, the precipitate formed is tin(II) sulphide from unreacted hydroxostannate(II) which is filtered off; the presence of tin in the filtrate confirmed the formation of hydroxostannate(IV) during photolysis. Chloroplatinic acid, added to tin(II) chloride, is reduced to colloidal platinum. When the resulting solution is treated with excess sodium hydroxide, a hydroxostannate(II) solution containing colloidal platinum is formed. This solution was used to study the effect of colloidal platinum on the photogeneration of hydrogen. To determine quantum yields, a 16 W low pressure lamp (Germilamp) was used. The photon flux was measured by ferrioxalate actinometry [15]. The ferrioxalate solution was agitated by bubbling nitrogen (99.999%) and Fe^{2+} was estimated spectrophotometrically using phenanthroline.

3. Results and discussion

Curves 1-3 in Fig. 1 show the rate of photogeneration of hydrogen from aqueous tetrahydroxostannate(II) solution (0.02 M in Sn^{2+}) at different pH values. With an increase in pH, the reaction rate increased and then decreased. The rate was found to be optimum when the pH was about 12.5. The quantum yield of H_2 at 254 nm $([Sn^{2+}]=0.02 \text{ M}; \text{ pH } 12.5)$ was found to be about 1.1×10^{-2} . When the pH was about 10 or less, hydrogen is generated but instead of hydroxostannate(IV) a precipitate of tin(IV) hydroxide is formed. The experiment is complicated by the deposition of stannic hydroxide on the walls of the reactor. Under acidic conditions (*i.e.* a solution of $SnCl_2$). detectable quantities of H_2 are produced but the yield is very much smaller. Here the oxidation product is almost entirely tin(IV) hydroxide; Sn⁴⁺ ions were not detectable in the solution. The observed pH variation can be understood as follows. The species that undergoes rapid photolysis is $[Sn(OH)_4]^{2-}$, the concentration of which increases with increase in pH. However, the hydrogen production via consumption of H^+ ions is favoured at low pH values. The two opposing factors leads to an optimum pH. Aqueous tetrahydroxostannate(II) shows optical absorption (Fig. 2) with a peak at about 230 nm. The primary reaction mechanism is unclear; presumably the excitation is associated with electron transfer to the solvent. In the presence of colloidal platinum, the yield of hydrogen is greatly increased (Fig. 1, curve 4). As expected, this results from catalysing the formation of molecular hydrogen [16]. The quantum yield of H_2 at 254 nm in the presence of about 0.5 mg pt l^{-1} is about 0.15 compared with about 1.1×10^{-2} in the absence of p^t (the quantum yield in the presence of colloidal p^t could be slightly higher than the above value, because colloidal p^t absorbs light).

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