

PHOTOGENERATION OF HYDROGEN FROM AQUEOUS SOLUTIONS OF HYPOPHOSPHORIC AND PHOSPHORIC ACIDS

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Abstract – U.v. photolysis of an aqueous solution of H_3PO_2 and H_3PO_3 generates detectable quantities of hydrogen. A dramatic increase in the quantum yields are observed if Eu^{3+} , Cu^{2+} and/or colloidal Pt is added to the solution. The reaction mechanisms are discussed.

INTRODUCTION

Hydrogen generation in photolysis of aqueous solutions or suspensions of organic and inorganic substances using homogeneous or heterogeneous catalysts has attracted much attention [1-10]. The original motivation for these studies was solar energy conversion and use of hydrogen as a nonpolluting renewable fuel [1-10]. Of homogeneous systems, certain metal complexes, transition metal ions and dyes were identified as active catalysts [5-10]. Most extensively studied heterogenous systems utilized semiconductor particles [1, 3, 4] (e.g. TiO₂, CdS) as the photocatalyst. In both homogeneous and heterogenous systems, colloidal Pt [1, 11, 12] (and other Pt group metals) were found to enhance hydrogen evolution. In this paper, we describe our observations on hydrogen evolution in photolysis of aqueous solutions of reducing hypophosphoric and phosphoric acids in the presence of transition metal ions and colloidal Pt. Transition metal cations, notably Eu^{3+} and Cu^{2+} are highly effective in photogenerating hydrogen from aqueous solutions of the above acids. The reaction rates are further enhanced by colloidal Pt.

EXPERIMENTAL

All chemicals were used as purchased from the vendor $[EuCl_3, CuCl_2 (Aldrich); H_3PO_2, H_3PO_3 and hexa$ chloroplatinic acid (BDH)]. Photolysis experiments wereconducted in an immersion-well-type photochemicalreactor (Applied Photophysics) of volume 350 ml. Thewater-cooled double-walled vessel housing the 400 Wmedium-pressure mercury lamp was made from quartz. $300 ml of the solution (i.e. H_3PO_2 or H_3PO_3 containing$ transition metal ions and other catalysts) was rapidlypurged with pure Ar (99.99%) to remove dissolved oxygen, the purging rate was kept constant at a reduced rate of 10 ml min⁻¹ and the lamp was switched on. Hydrogen in the outgoing gas was detected by gas chromatography (Shimadzu GC 9AM gas chromatograph, molecular sieve 5A column, thermal conductivity detector). Under a given set of conditions, the experiment was repeated three times and the results were found to be reproducible. Photolysed solutions were qualitatively analysed to determine the types of phosphoric acids present.

The photon flux passing through the solution was determined by ferrioxalate actinometry. When a volume of ferrioxalate solution equal to the volume of the photolysed solution was placed in the reactor, the counted photon flux was 8.7×10^{18} photons s⁻¹. When a borosilicate glass sleeve that cuts off of light of wavelength < 300 nm was included, hydrogen evolution from H₃PO₂ and H₃PO₃ solutions was completely stopped. The photon flux determined by ferrioxalate actinometry in the presence of the filter was 9.8×10^{-6} einstein s⁻¹.

RESULTS AND DISCUSSION

The net reactions occurring in hydrogen production with H_3PO_2 and H_3PO_3 are:

$$H_{3}PO_{2} + H_{2}O \xrightarrow{h\nu} H_{3}PO_{3} + H_{2}, \Delta G^{0}$$
$$= 48.2 \text{ kJ mol}^{-1}, \qquad (1)$$

$$H_{3}PO_{3} + H_{2}O \xrightarrow{h\nu} H_{3}PO_{4} + H_{2}, \Delta G^{0}$$
$$= 26.6 \text{ kJ mol}^{-1}. \qquad (2)$$

When a solution of H_3PO_2 or H_3PO_3 is irradiated with u.v. light, detectable amounts of hydrogen are evolved



Fig. 1. Hydrogen generation in photolysis of (a) 0.025M H_3PO_2 , (b) 0.025M H_3PO_3 , (c) 0.025M $H_3PO_3 + 97 \mu M$ Pt, (d) 0.025M $H_3PO_2 + 97 \mu M$ Pt aqueous solutions.

(Fig. 1, curves a and b). The reaction mechanisms involved here are probably:

$$H_2PO_2^- + H_2O \xrightarrow{hv} H_2PO_2^- + e_{eq}^-$$
 (3)

$$\rightarrow$$
 H₂PO₂ + H[•] + OH⁻, (4)

$$H_2PO_2^{\bullet} + H_2O \longrightarrow H_2PO_3^{-} + H^{\bullet} + H^{+}.$$
 (5)

The primary photochemical step is formation of a solvated electron which is scavenged by hydrogen ions to yield hydrogen free radicals (i.e. step 4). At low pHs where this reaction is carried out, the solvated electron is undetectable and reaction (4) may be regarded as the primary step. The reaction of $H_3PO_2^{\cdot}$ with water results in the formation of hydrogen free radicals. Diffusion-controlled combination of hydrogen free radicals yields molecular hydrogen. The analogous reactions for H_3PO_3 are:

$$H_2 PO_3^- + H_2 O \xrightarrow{h\nu} H_2 PO_3^- + e_{eq}^-, \tag{6}$$

$$\longrightarrow$$
 H₂PO'₃ + H' + OH⁻, (7)

$$H_2PO_3^{-} + H_2O \longrightarrow H_2PO_4^{-} + H^{+} + H^{+}.$$
 (8)

Colloidal Pt (when chloroplatinic acid is introduced into the hypophosphoric or phosphoric acid solution, it is quickly reduced to colloidal Pt) increases the rate of hydrogen evolution ($R[H_2]$). The effect of Pt is undoubtedly to collect atomic hydrogen and catalyse the formation of molecular hydrogen. (Hydrogen evolution was not detected in the dark when chloroplatinic acid was introduced.)

We also noted that transition metal ions (notably Eu^{3+} , Cu^{2+}) have a dramatic effect upon the photogeneration of H₂ from H₃PO₂ and H₃PO₃. The reaction

mechanism involved here is:

$$X^{q+1} + H_3 PO_2 + H_2 O \xrightarrow{h\nu_1} X^q + H_3 PO_3 + H^+ + H^*, \quad (9)$$

$$X_{eq}^{q} + H_2O \xrightarrow{hv_2} X^{q+1} + H^{\bullet} + OH^{-}, (1)$$

where X^{q+1} , X^{q} denote the oxidised and reduced forms of the transition metal ions. Similar equations can be written for the case of H_3PO_3 . Both the reactions (9) and (10) are light induced; in reaction (9), the primary mechanism is charge transfer from solvent to ion, whereas in reaction (10), the charge transfer is from ion to the solvent. Figure 2 shows the variation of $R[H_2]$ with Eu³⁺ concentration. Initially $R[H_2]$ (rate of purging X% H₂ in the outgoing gas, volumes are measured at atmospheric pressure and 26°C) increases with the increase of [Eu³⁺], reaches an optimum and then begins to decrease when $[Eu^{3+}]$ is further increased. The above observation can be understood as follows: with the increase of $[Eu^{3+}]$, the rate of the forward reaction (9) is increased; however, the increase of $[Eu^{3+}]$ will also increase the rate of the back reaction (10), where H' is consumed. The two opposing effects give rise to an optimum value of $[Eu^{3+}]$. This optimum value depends on the concentration of H_3PO_2 (or H_3PO_3 as the case may be). Figure 3 shows the pH variation of $R[H_2]$ from H_3PO_2 at the optimum Eu³⁺ concentration. Decrease of pH increases R[H2] as expected, because low pHs favour reaction (10). The presence of colloidal Pt enhances the effect of Eu³⁺. A plot of $R[H_2]$ vs time in the presence of Eu³⁺, as well as colloidal Pt, is shown in Fig. 4. The Cu²⁺ ion also shows photocatalytic activity in hydrogen production from aqueous solutions of H_2PO_2 and H_3PO_3 and is superior to Eu³⁺. (Strong solutions of Cu²⁺ and H₃PO₂ slowly precipitate CuH which decomposes to liberate H₂. At Cu^{2+} concentrations used in this experiment, $R[H_2]$



Fig. 2. Photogeneration of hydrogen from an aqueous solution H_3PO_2 (0.025M) containing (a) 0M Eu³⁺, (b) 0.025M Eu³⁺, (c) 0.04M Eu³⁺, (d) 0.05M Eu³⁺, (e) 0.06M Eu³⁺, (f) 0.075M Eu³⁺, (g) 0.1M Eu³⁺.



Fig. 3. pH Variation of the rate of hydrogen evolution from a 0.025M solution of H_3PO_2 in the presence of 0.05M Eu³⁺ (a) pH = 0.6, (b) pH = 1.0, (c) pH = 1.7, (d) pH = 3, (e) pH = 5.3.



Fig. 4. Plot of rate of hydrogen evolution vs time from (a) $0.025M H_3PO_2$, (b) $0.025M H_3PO_3$ in the presence 97 μ M Pt.

from this mechanism was barely detectable.) Figure 5 compares $R[H_2]$ with catalysts Eu^{3+} and Cu^{2+} ; the effect of colloidal Pt is also indicated. The catalytic activity of a transition metal ion depends on the X^{q+1}/X^q redox potential and the charge transfer optical absorbance of ions X^{q+1} and X^q . Both the above factors are favourable for the Cu²⁺ ion. Analysis of the photolysed solution indicated that the transition metal ion remained almost completely in the oxidised form at the end of photolysis suggesting that reaction (10) is much faster than reaction (9). Again it was confirmed that photolysis of H₃PO₂ yields H₃PO₃ and photolysis of H₃PO₃ yields H_3PO_4 . Absorption spectra of Cu^{2+} and Eu^{3+} in the presence and absence of phosphorus were similar suggesting that aquo-ions (i.e. not complexes with the acids) are responsible for the reaction.

In all experiments, $R[H_2]$ initially increases, reaches a stationary value and then decreases. Photogenerated hydrogen is partly carried over by the Ar current and partly dissolved in water. The subsequent decrease results from consumption of the reactants. U.v. radiation of



Fig. 5. Plot of rate of hydrogen evolution vs time from a 0.025M aqueous solution of H_3PO_2 containing (a) 0.004M CuCl₂ (b) 0.004M CuCl₂ + 97 μ M Pt.

 Table 1. Polychromatic quantum yields measured in the stationary region

| System | Quantum yield |
|---|----------------------|
| 0.025M H ₂ PO ₂ | 3.1×10^{-3} |
| 0.025M H ₃ PO ₃ | 3.7×10^{-3} |
| 0.025M H ₃ PO/Pt | 0.20 |
| 0.025M H ₃ PO ₃ /Pt | 0.10 |
| $0.025M H_{3}PO_{2}(0.05M Eu^{3+} (pH 7))$ | 0.05 |
| $0.025M H_{3}PO_{2}^{2}/0.05M Eu^{3+}$ (pH 0.6) | 0.12 |
| $0.025M H_{3}PO_{2}^{-}/0.05M Eu^{3+}/Pt$ | 0.40 |
| $0.025M H_{3}PO_{2}/Cu^{2+}$ | 0.53 |
| $0.025M H_{3}PO_{2}^{2}/Cu^{2+}/Pt$ | 0.60 |

the Hg lamp is predominantly in 365-366 nm region, with smaller amounts at 265, 297, 304, 313 and 334 nm, and significant amounts in the visible at 404-408, 436, 546 and 577-579 nm. In the presence of the borosilicate filter, hydrogen evolution was completely suppressed indicating that the active photon flux in the wavelength range 265-297 nm is 2.9×10^{18} photons s⁻¹. The polychromatic quantum yields (i.e. no. of molecules of H₂ produced/no. of photons in the wavelength range 265-297 nm that are absorbed) measured in the stationary region are given in Table 1.

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