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ENHANCED HYDROGEN GENERATION IN PHOTOLYSIS OF FERROUS IONS IN THE PRESENCE OF FLUORIDE

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Abstract : The quantum yield of hydrogen in photolysis of ferrous ions in an aqueous medium is found to be greatly enhanced in the presence of the fluoride ions.

1. Introduction

The photolysis of ferrous ions in aqueous medium is known to liberate hydrogen with oxidation of ferrous to the ferric state.[1,2,3,5,6,8] This is an example of a simple up-hill chemical reaction initiated by light . The reaction mechanism is believed to be creation of a solvated electron.[1,2,4,5,7] Which is scavanged by the H^+ ions, ie,

$$Fe^{2+} \xrightarrow{h\upsilon} Fe^{3+} + e^- \qquad (1)$$

$$H^+ + e^- \longrightarrow H \qquad (2)$$

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

Reaction steps (1) – (3) is equivalent to

$$Fe^{2+} + H_2O \xrightarrow{h\upsilon} Fe^{3+} + OH^- + \tfrac{1}{2}H_2 \qquad (4)$$

We have found that the yield of H_2 from (4) is greatly enhanced by fluoride ion.

2. Experimental

Photolysis experiments were carried out in a double–walled thermostatted (26^0C) photochemical reactor (Applied Photophysics) of volume 300 ml fitted with a 400 w medium pressure mercury lamp at the central axis. Ferrous solutions free from ferric ions were prepared by reducing acidified solutions of ferrous chloride and ferrous sulphate with metallic iron. Ferrous ion concentrations were determined by standard techniques. Sodium fluoride was used as the sorce of fluoride ion. Prior to photolysis all solu-

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tions were purged with nitrogen (99.999%). Photogenerated hydrogen was estimated volumetrically by gas chromatography (Shimadzu GC–9AM, column MS 5A, Carrier gas Ar).

3. Results and Discussion

Figure 1 illustrates photogeneration of hydrogen from acidified (HCl) ferrous chloride solution containing varying amounts of fluoride. It is seen that the yield of H_2 increases with the increase of the fluoride concentration. The maximum $[F^-]$ permitted by the solubility of FeF_2 is ~ 0.6M and the highest yield of H_2 is obtained at this concentration. When the experiment was repeated with ferrous sulphate (acidified with H_2SO_4) results obtained were almost identical to that of $FeCl_2$ containing equivalent amounts of Fe^{2+} (Figure 1)

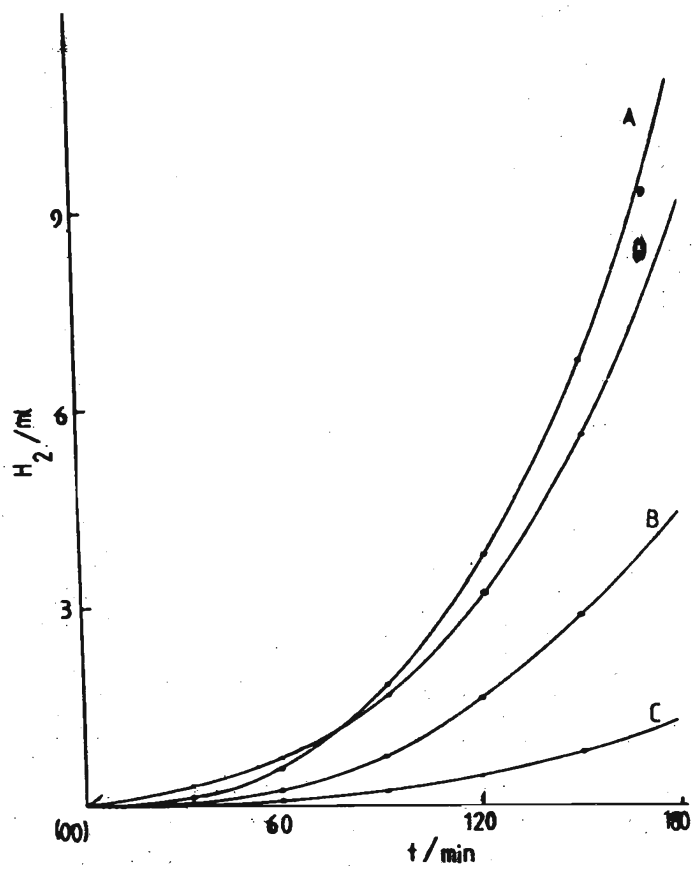

Figure 1: Photogeneration of hydrogen from 0.1M $FeCl_2$ solution (0.16M in HCl) (A) $[F^-]$ = 0.60M (B) $[F^-]$ = 0.35M (c) $[F^-]$ = 0. (d) $[F^-]$ = 0.60M, $[FeSO_4]$ = = 0.1M.

It is easy to understand the mechanism involved in the enhancement of the hydrogen yield by the fluoride. Hydrogen production via (4) is largely inhibited by the reverse of step. (1), where the photogenerated electrons are scavanged by the ferric ions. Ferric ions form a highly stable complex anion[4] $[FeF_5 (H_2O)]^{2-}$ with the F^- ions. The complex anion is less effective in scavenging photogenerated electrons as combination of repulsive partners is less probable.

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