

Hydrogen photogeneration from aqueous solutions of alcohols by the Fe^{3+} ion

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Abstract

Fe(III) chlorocomplex ions are found to generate hydrogen from aqueous solutions of aliphatic alcohols on photolysis with a medium pressure Hg lamp. The reaction mechanism is believed to involve the formation of reactive intermediates Cl^\cdot and H^\cdot , where H^\cdot abstracts hydrogen from the alcohol.

Introduction

Hydrogen production by photolysis of aqueous solutions or suspensions of organic compounds using homogeneous or heterogeneous catalysts continues to attract much attention. Aqueous suspensions of semiconductors (*e.g.* TiO_2) containing organic substances liberate hydrogen from water upon irradiation [1–13]. It is also known that the catalytic activity of semiconductor particles are enhanced by loading them with electron and/or hole transfer agents [1, 3]. Several homogeneous catalysts capable of photogenerating hydrogen from specific organic compounds have also been recorded. Benzophenone in the presence of colloidal platinum photogenerates hydrogen from aqueous solutions of 2-propanol [13, 14]. Complexes of rhodium (and related metals) [15–20] and dyes [21, 22] are also known to photocatalyse dehydrogenation of alcohols. We have found that the Fe^{3+} ion acts as a catalyst for photoproduction of hydrogen from aqueous solutions of alcohols. The reaction rate depends on anionic species present in the solution and the degree to which they form complexes with Fe^{3+} . The highest quantum yields are obtained when the anion in the solution is Cl^- .

Experimental section

Materials

$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{Fe}_2(\text{SO}_4)_3$ were purchased from BDH. Ferrous solutions free from the ferric ion were prepared by

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warming a solution of the ferrous salts containing the corresponding acid with pure metallic iron, avoiding exposure to air. Ferric solutions free from ferrous ions were prepared by adding hydrogen peroxide to the acidified solution of the ferric salt and boiling to decompose the excess hydrogen peroxide. Ferric perchlorate was made by the following method: NaOH was added to a solution of ferric chloride to precipitate hydrous ferric oxide. Hydrous ferric oxide separated by filtration was washed with sodium hydroxide followed by distilled water until the filtrate is free from Cl^{-1} ions. The precipitate was then dissolved in perchloric acid (Interchem). All the other chemicals were of the reagent grade and used as supplied by the vendor.

Apparatus

Photolysis experiments were carried out in a 300 ml cylindrical photochemical reactor (Applied Photophysics) with a 400 W medium pressure mercury lamp mounted inside an inner double-walled quartz cylinder which was water cooled (26 °C). The solution was contained in the annular region between the cylinders of thickness ~ 0.75 cm. Prior to irradiation, the solution was purged with nitrogen (99.999%) and during photolysis the solution was kept magnetically stirred. Evolved gases were detected volumetrically at atmospheric pressure by gas chromatography (Shimadzu GC 9AM gas chromatograph, column molecular sieve 5A, carrier gas Ar, thermal conductivity detector). Photolysis experiments were carried out using mixtures of water and alcohol of total volume 200 ml. In most experiments the iron salt added as the catalyst was initially in the ferric state (solutions of FeCl_3 , $\text{Fe}_2(\text{SO}_4)_3$ and $\text{Fe}(\text{ClO}_4)_3$ containing HCl, H_2SO_4 and HClO_4 respectively). Several experiments were also conducted using the corresponding ferrous salts. A 16 W low pressure mercury lamp fitted to the same reactor was used to estimate the quantum yields, and the photon flux was counted by ferrioxalate actinometry. The photolysed solution was analysed for the oxidation products of alcohols (aldehydes/ketones and acids) by gas chromatography. In the case of methanol, ethanol and 2-propanol the principal product was found to be formaldehyde, acetaldehyde and acetone respectively. The concentration of these ingredients was found to increase with the progress of photolysis. With methanol and ethanol, the corresponding organic acids were also detected. Separate experiments were conducted in the same reactor under same conditions and with a cut-off filter ($\lambda < 300$ nm) to monitor the time variation of $[\text{Fe}^{3+}]$ when the iron salt added was initially in the ferric state.

Results and discussion

Figure 1 illustrates photogeneration of hydrogen from a 0.43 M aqueous solution of ethanol 4.3 M in HCl at different $[\text{FeCl}_3]$. Initially the reaction rate increases with increasing $[\text{FeCl}_3]$ and then decreases. When the experiment was repeated with varying [ethanol] and [HCl], it was noted that the optimum $[\text{FeCl}_3]$ is largely independent of [ethanol] and [HCl]. Methanol and 2-

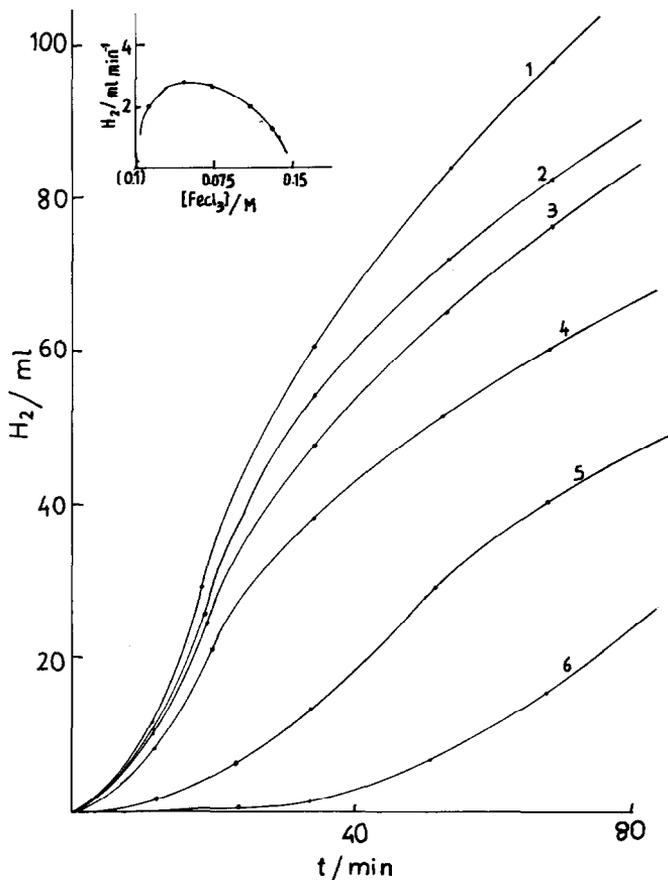


Fig. 1. Hydrogen generation in photolysis of 4.3 M aqueous solution of ethanol in the presence of (1) 0.05 M $FeCl_3$ + 4.3 M HCl, (2) 0.09 M $FeCl_3$ + 4.3 M HCl, (3) 0.02 M $FeCl_3$ + 4.3 M HCl, (4) 0.14 M $FeCl_3$ + 4.3 M HCl, (5) 0.03 M $Fe_2(SO_4)_3$ + 2.1 M H_2SO_4 , (6) 0.05 M $Fe(ClO_4)_3$ + 4.3 M $HClO_4$. Inset: Variation of the reaction rate (average during the first hour) with $FeCl_3$ concentration.

propanol behaved similarly, and corresponding optimum values of $[FeCl_3]$ were found to be nearly the same as that for ethanol. If the [alcohol] and the $[FeCl_3]$ are kept fixed, the reaction rates (for methanol, ethanol and 2-propanol) were found to be optimum when $[HCl] \approx 4.3$ M. Again this value is found to be nearly the same for all three alcohols. Figure 2 indicates the data for ethanol.

During irradiation of an alcohol-water mixture containing a ferric salt, the Fe^{3+} was found to be rapidly converted into the Fe^{2+} state. Figure 3 shows the progress of the depletion of Fe^{3+} under different conditions. the rate of depletion depends on the anions present, a faster rate being observed with Cl^- than with SO_4^{2-} or ClO_4^- . When a cut-off filter of wavelength < 300 nm is used, the reduction of Fe^{3+} to Fe^{2+} is still seen, however

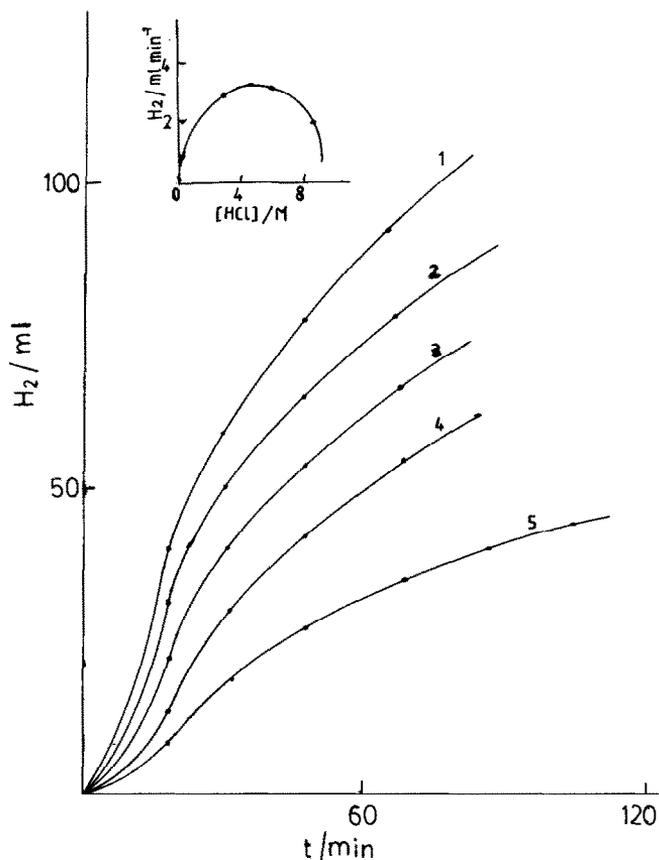


Fig. 2. Hydrogen photogeneration from 4.3 M aqueous solution of ethanol containing 0.05 FeCl₃ at HCl concentrations of (1) 5.8 M, (2) 3.5 M, (3) 7.5 M, (4) 0.29 M, (5) 0.00 M. Inset: Variation of the reaction rate (average during the first hour) with HCl concentration.

hydrogen evolution is hardly detectable. This observation suggests that the first step of the reaction is light-induced reduction of a ferric complex to the ferrous state. A possible reaction scheme is:



Of the several Fe³⁺ chlorocomplexes, FeCl²⁺ has stronger light absorption properties. The key reactive intermediates are Cl[·], H[·] and H-abstraction from alcohol by H[·] to give molecular hydrogen. It is known that UV irradiation (λ ≤ 240 nm) of Fe²⁺ in water liberates hydrogen [23–26] via the reactions:

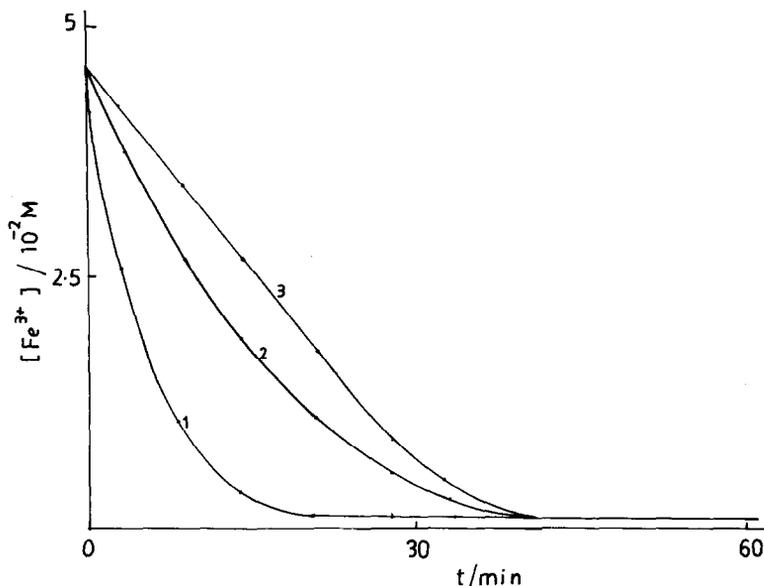


Fig. 3. The depletion of Fe^{3+} during irradiation (400 W medium pressure mercury lamp) of solutions initially containing (1) 0.05 M FeCl_3 + 4.6 M HCl + 4.3 M ethanol, (2) a solution of the same composition as (1) with a cut-off filter ($\lambda < 300$ nm), (3) 0.03 M $\text{Fe}_2(\text{SO}_4)_3$ + 2.3 M H_2SO_4 + 4.3 M ethanol.



or H^{\cdot} from (7) could participate in step (5).

Hydrogen evolution in the photolysis of Fe^{2+} in water is limited by the reverse of reaction (6), where H^{\cdot} recombines with a Fe^{3+} ion. However, in the presence of alcohol, Fe^{3+} rapidly reverts back to Fe^{2+} via the reactions (1)–(5), decreasing the probability of the reverse of (6). The drastic increase in hydrogen yield during the photolysis of Fe^{2+} in alcohol-containing aqueous solutions is shown in Fig. 4 (compare curves A and D with C). The initial value of $\phi[\text{H}_2]$ at 254 nm for a ferrous chloride solution (0.1 M in Fe^{2+} , 0.6 M in HCl) is $\sim 7 \times 10^{-3}$; in the presence of 4 M ethanol this increases to ~ 0.76 (Table 1).

The rates of hydrogen photogeneration from aqueous solutions of alcohols containing iron salts (initially as Fe^{2+} or Fe^{3+}) are also found to depend on the anionic species in the solution. Higher rates and quantum yields are obtained with Cl^- than from equivalent concentrations of SO_4^{2-} or ClO_4^- (Figs. 1 and 7, Table 1). In contrast, when Fe^{2+} is photolysed in the absence of a sacrificial reducing agent, $\phi[\text{H}_2]$ does not vary that significantly with the anion present (Table 1). The dependence of the rates of H_2 photogeneration from aqueous solutions of alcohols containing Fe ions on the anionic species in the solution results from their effect on the first step of the hydrogen-

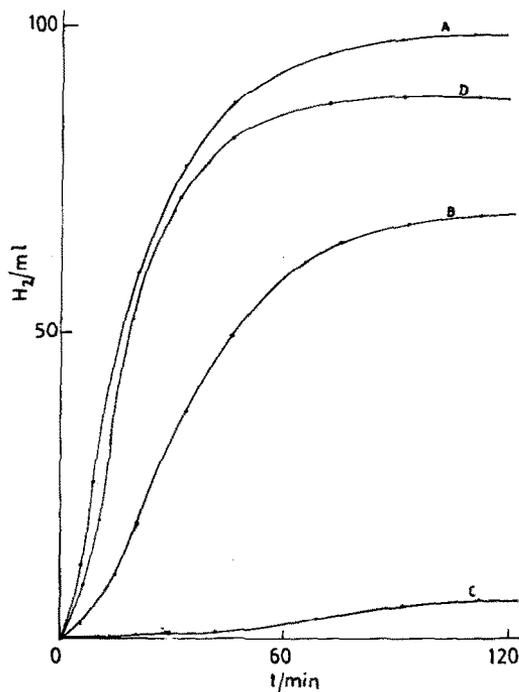


Fig. 4. Hydrogen photogeneration in the photolysis of solutions (A) 0.08 M FeCl₂ + 4.3 M ethanol + 4.6 M HCl, (B) 0.08 M FeSO₄ + 4.3 M ethanol + 2.0 M H₂SO₄, (C) 0.08 M FeCl₂ + 4.6 M HCl, (D) 0.08 M FeCl₂ + 3.3 M 2-propanol + 4.6 M HCl.

TABLE 1

The initial quantum yields of H₂ (computed from H₂ yield during first 45 min) at 254 nm in photolysis of aqueous Fe²⁺ at different solution compositions

| Solution | $\phi[\text{H}_2]$ |
|---|-----------------------|
| FeCl ₂ ([Fe ²⁺] = 0.1 M, [HCl] = 0.6 M) | 7×10^{-3} |
| FeSO ₄ ([Fe ²⁺] = 0.1 M, [H ₂ SO ₄] = 0.3 M) | 12.0×10^{-3} |
| Fe(ClO ₄) ₂ ([Fe ²⁺] = 0.1 M, [HClO ₄] = 0.6 M) | 7.0×10^{-3} |
| FeCl ₂ ([Fe ²⁺] = 0.1 M, [HCl] = 0.6 M, [ethanol] = 4 M) | 0.76 |
| FeSO ₄ ([Fe ²⁺] = 0.1 M, [H ₂ SO ₄] = 0.3 M, [ethanol] = 4 M) | 4.5×10^{-2} |
| Fe(ClO ₄) ₂ ([Fe ²⁺] = 0.1 M, [HClO ₄] = 0.6 M, [ethanol] = 4 M) | 6.7×10^{-3} |

producing reaction. This becomes evident when the rates of depletion of ferric ion in the presence of Cl⁻ and SO₄²⁻ are compared (Fig. 3). Irradiation reduce Fe³⁺ in alcoholic solutions more rapidly in the presence of Cl⁻ than SO₄²⁻ or ClO₄⁻. The primary photochemical event in reactions of type (1) is ligand to metal charge transfer in a ferric complex. Solutions of ferric salts contain hydroxy complexes [27] Fe(OH)²⁺, Fe(OH)₂⁺ and Fe(OH)₃,

together with species depending on other anions present. The chloride ion complexes strongly with Fe^{3+} to yield $[\text{27}] \text{FeCl}_2^+$, FeCl_2^+ , FeCl_3 and FeCl_4^- . Sulphate and perchlorate ions complex weakly with Fe^{3+} and consequently ferric sulphate and perchlorate solutions contain significant proportions of hydroxy complexes [27]. Both hydroxy and chloro complexes may initiate reactions similar to (1). The observation that the hydrogen photogeneration rates are higher in the presence of Cl^- indicates that the chloro complexes are more effective in initiating the first step of the reaction in which the alcohols are oxidised. Spectral characteristics and formation constants of ferric chloro complexes are well documented [27]. At the HCl and FeCl_3 concentrations at which the reaction rates are found to be highest, the predominant species that strongly absorbs light [28] is FeCl_2^{2+} . However, other chloro complexes may also be involved in reactions of the form (1)–(5). Although Fe(III) complex ions are regenerated, because of the complex chemistry the process may not be entirely catalytic. Furthermore, the sensitivity of the system, which is restricted to only the UV region makes it unsuitable for practical application.

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