The catalysis of hydrogen photogeneration from electron-donor ions in aqueous medium by the iodide ion

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Abstract

Iodide ion is found to catalyse the photogeneration of hydrogen from aqueous electron-donor ions. As examples, the photolysis data of aqueous Fe^{2+} , Ti^{3+} , SO_3^{2-} and $H_2PO_2^{-}$ ions in the presence and absence of I^- ion are given. The reaction mechanisms are discussed.

1. Introduction

Several inorganic electron-donor ions, when photolysed (UV light), liberate hydrogen with an increase in the oxidation state of the ion [1-11]. If X^q denotes an ion of charge q, the primary photochemical step is the formation of a solvated electron which is scavenged by the hydrogen ion, *i.e.*

$$X^{q} + H_{2}O \xrightarrow{h\nu} X^{q+1} + e_{aq} \xrightarrow{}$$
(1)
$$\longrightarrow X^{q+1} + H^{*} + OH^{-}$$
(2)

At low pH values, the creation of the solvated electron is undetectable and reaction (2) may be regarded as the primary step [12]. Hydrogen evolution results from diffusioncontrolled combination of hydrogen free radicals. The best known examples of cations which behave in this manner during photolysis are Cr^{2+} , Eu^{2+} , Fe^{2+} , Ce^{2+} , V^{2+} and Ti^{3+} [1–11]. Of the electron-donor anions we note that sulphite (SO₃²⁻), sulphide (S²⁻) [13] and hypophosphite (H₂PO₂⁻) liberate detectable quantities of hydrogen when irradiated. Hydrogen evolution during the photolysis of cations and anions is severely limited by the recombination of H to yield the initial products and by the low molar extinction coefficient associated with the transition. We have observed that iodide ion, which absorbs strongly in the UV region, catalyses the photogeneration of hydrogen in the above reactions. As examples, data on the photolysis of Fe²⁺, Ti^{3+} , SO₃²⁻ and H₂PO₂⁻ in the presence and absence of I⁻ are presented and the reaction mechanisms are discussed.

2. Experimental details

2.1. Preparation of materials

 $FeCl_2$ free from Fe^{3+} was prepared by digestion of $FeCl_2$ (Aldrich) solution with iron filings. Titanium metal (Aldrich, 99.99%) was dissolved in concentrated hydrochloric

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acid (purged with nitrogen to avoid oxygen contamination) to obtain a solution of TiCl₃. Hypophosphite solutions of different pH values were prepared by mixing hypophosphorus acid (BDH) and sodium hydroxide. Sodium sulphite was used as supplied by BDH. Adjustments of pH were carried out using sulphuric acid and sodium hydroxide.

2.2. Apparatus

Photolysis experiments were carried out in an immersion well photochemical reactor (500 cm^3) (Applied Photophysics) with a double-walled, water-circulated (26 °C) quartz inner jacket. A 400 W medium pressure mercury lamp was housed in the central axis of the inner jacket. The solution (450 cm³) placed inside the reactor was rapidly purged with argon (99.99%) to remove dissolved oxygen. The lamp was switched on and the purging was continued at a slower rate (7.5 cm³ min⁻¹). Hydrogen in the outgoing gas was monitored by gas chromatography (Shimadzu GC 9AM; molecular sieve 5A column; thermal conductivity detector). The absorption spectra of the solutions were obtained using a Shimadzu UV 3000 spectrophotometer.

3. Results and discussion

Figures 1 and 2 illustrate the hydrogen evolution in the absence and presence of iodide from aqueous solutions of Fe²⁺, Ti³⁺, SO₃²⁻ and H₂PO₂⁻. It is clear that, in all cases, the rate of hydrogen evolution (R_{H_2}) is increased significantly in the presence of the I⁻ ion. It is known that the iodide ion strongly absorbs UV radiation (Fig. 3) around 240 nm generating a solvated electron [14, 15], which is scavenged



Fig. 1. Rate of hydrogen evolution (R_{H_2}) in the presence (0.0074 M) (A) and absence (B) of I⁻ for solutions containing (a) Fe²⁺ (0.0074 M), (b) Ti³⁺ (0.0074 M) and (c) SO₃²⁻ (0.50 M). pH values are indicated on each curve.



Fig. 2. Rate of hydrogen evolution (R_{H_2}) for H_3PO_2 (0.042 M) solution with: (a) I⁻ (0.0 M), pH 7.0; (b) I⁻ (0.0074 M), pH 7.0; (c) I⁻ (0.0074 M), pH 2.0; (d) I⁻ (0.0074 M), pH 10.4.



Fig. 3. Absorption spectra of aqueous solutions of (a) I^- and (b) Ti^{3+} .

by H⁺ to yield hydrogen and iodine free radicals, *i.e.* H₂O+I⁻ $\xrightarrow{h\nu}$ I⁺+e_{aq}⁻ (3) \longrightarrow I⁺+H⁺+OH⁻ (4)

Highly reactive I can accept electrons from a donor (X^q) to generate I⁻, *i.e.*

$$X^{q} + I^{\bullet} \longrightarrow X^{q+1} + I^{-}$$

The removal of I prevents the recombination of the products to yield H₂O and I⁻ and facilitates combination of H to yield molecular hydrogen. Equations (1)-(5) give the mechanism of catalysis by I⁻ of hydrogen photoproduction from inorganic cations such as Fe²⁺ and Ti³⁺ (in the case of Ti³⁺, Ti⁴⁺ generated via eqn. (5) is unstable and undergoes rapid hydrolysis to give TiO₂ [11]).

In the case of anions SO_3^{2-} and $H_2PO_2^{-}$, the reaction of I will be

$$SO_3^{2-} + I \longrightarrow SO_3^{-} + I^{-}$$

$$SO_3^{-} + H_2O \longrightarrow SO_4^{2-} + H^+ + H^*$$
(6)
(7)

$$H_2PO_2^- + I^- \longrightarrow H_2PO_2^+ + I^-$$
(8)

$$H_2PO_2 + H_2O \longrightarrow H_2PO_3 + H^+ + H^-$$
(9)

In the absence of I^- , sulphite and hypophosphite solutions liberate small but detectable quantities of hydrogen. The mechanisms involved here are

$$SO_3^{2-} + H_2O \longrightarrow SO_3^{-} + e_{aq}^{-}$$
 (10)

$$\longrightarrow SO_3^{-} + H^{+} + OH^{-} \tag{11}$$

$$SO_3^{-} + H_2O \longrightarrow SO_4^{2-} + H^+ + H^-$$
 (12)

and

$$H_2PO_2^- + H_2O \longrightarrow H_2PO_2^+ + e_{aq}^-$$
(13)

$$\rightarrow H_2 PO_2 + H + OH^-$$
(14)

$$H_2PO_2^{\bullet} + H_2O \longrightarrow H_2PO_3^{-} + H^{\bullet} + H^+$$
(15)

Here the free radicals SO_3^{-} and $H_2PO_2^{-}$ are not rapidly removed and the recombination of free radicals suppresses the hydrogen yield.

The rate of reaction (4) increases with a decrease in pH, as expected; the rates of the above catalytic reactions also increase with a decrease in pH. In addition to the catalytic reaction, a non-catalytic reaction which liberates iodine is possible. At lower pH values iodine liberation is detectable. The decrease in $R_{\rm H_2}$ with time at lower pH values (e.g. Fig. 1(c)) is due to this effect. When a Pyrex filter is used, hydrogen evolution is drastically suppressed indicating that UV absorption by I^- is responsible for the reaction.

References

- 1 J. Weiss, Nature, 136 (1935) 794.
- 2 R. H. Potterill, J. O. Walker and J. Weiss, Proc. R. Soc. London, Ser. A, 156 (1936) 561.
- 3 F. S. Dainton and G. L. James, J. Chem. Phys., 48 (1951) C17.
- 4 L. J. Heidt, M. G. Mullin, W. B. Martin, Jr. and A. M. J. Beatly, J. Phys. Chem., 66 (1962) 336.
- 5 L. J. Heidt and A. F. McMillan, J. Am. Chem. Soc., 76 (1954) 2135.
- 6 D. L. Douglas and D. M. Yost, J. Chem. Phys., 17 (1949) 1345.

- 7 D. D. Davis, K. L. Stevenson and G. K. King, Inorg. Chem., 16 (1977) 670.
- 8 E. Collinson, F. S. Dainton and M. A. Malati, Trans. Faraday Soc., 55 (1959) 2097.
- 9 M. W. Rophael and M. A. Malati, J. Inorg. Nucl. Chem., 37 (1975) 1326.
- 10 K. Tennakone and U. S. Ketipearachchi, Chem. Phys. Lett., 167 (1990) 524.
- 11 K. Tennakone, W. D. W. Jayatilaka and U. S. Ketipearachchi, Chem. Phys. Lett., 167 (1990) 524.
- 12 J. W. T. Spinks and K. J. W. Woods, An Introduction to Radiation Chemistry, Wiley, New York, 1976.
- 13 H. Kisch, A. Fernandez and R. Millini, Chem. Ber., 119 (1986) 3473.
- 14 J. Frank and R. L. Platzman, Z. Phys., 138 (1954) 411.
- 15 G. Stein and A. Treinin, Trans. Faraday Soc., 54 (1958) 338.