

## THE CATALYSIS OF HYDROGEN PHOTOGENERATION FROM AQUEOUS SOLUTIONS OF ALCOHOLS BY THE SAMARIUM(III) AND EUROPIUM(III) IONS

K. TENNAKONE <sup>a,b,1</sup> and U.S. KETIPEARACHCHI <sup>a</sup>

<sup>a</sup> *Institute of Fundamental Studies, Hantana, Kandy, Sri Lanka*

<sup>b</sup> *University of Ruhuna, Matara, Sri Lanka*

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$\text{Sm}^{3+}$  and  $\text{Eu}^{3+}$  ions are found to catalyse photogeneration of hydrogen from aqueous solutions of alcohols. The reaction mechanism is discussed.

### 1. Introduction

Hydrogen needed for industrial processes, notably the fertilizer industry, is manufactured from fossil fuels. With the depletion of fossil deposits, it became essential to find alternative sources of hydrogen. An attractive possibility is generation of hydrogen from organic waste products using sunlight [1,2]. Heterogeneous as well as homogeneous catalysts have been adopted for the production of hydrogen from alcohols, organic acids, carbohydrates, biomass, etc. [3-6]. Semiconductor catalysts (e.g.  $\text{TiO}_2$ ,  $\text{CdS}$ ) are known to liberate hydrogen from aqueous solutions or suspensions of organic materials upon irradiation, and the best known homogeneous catalysts are complexes of rhodium [5,6]. We have found that samarium(III) and europium(III) ions act as catalysts in photogeneration of hydrogen from aqueous solutions of alcohols.

### 2. Experimental

Photolysis experiments were carried out in a thermostatted (26°C) photochemical reactor (Applied Photophysics) of volume 300 ml mounted with a 400 W medium pressure mercury lamp at the central axis. 200 ml of water-alcohol mixtures (methanol, ethanol and propane-2-ol were used) containing samar-

ium(III) or europium(III) chlorides and hydrochloric acid were irradiated. Prior to irradiation, the solutions were purged with nitrogen (99.999%). The evolved gases were estimated volumetrically at atmospheric pressure by gas chromatography (Shimadzu GC-9AM gas chromatograph, column molecular sieve 5A, carrier gas Ar). The photolysed solution analysed by chromatography and chemical tests (e.g. Tollen's test for aldehydes) showed the presence of oxidation products of alcohols, i.e. corresponding aldehydes or ketones with small quantities of organic acids and carbon dioxide.

### 3. Results and discussion

Figs. 1 and 2 illustrate photogeneration of hydrogen from aqueous solutions of methanol, ethanol and propane-2-ol. The reaction rates are found to increase in the order propane-2-ol > ethanol > methanol.  $\text{Eu}^{3+}$  is slightly more active than  $\text{Sm}^{3+}$ . Hydrogen evolution continued for more than 24 h with a slight decrease in the reaction rate possibly as a result of depletion of alcohol and accumulation reaction products. Hydrogen production is not detected in the dark. When photolysis is carried out in the absence of the catalyst, hydrogen is detectable but the yield is smaller by a factor of  $\approx 50$ . A significant increase in the hydrogen yield is observed (figs. 1 and 2, curves 4) when chloroplatinic acid ( $\approx 2 \times 10^{-3}$  M) is added to the solution. Within a few minutes

<sup>1</sup> Sumanasekara Professor.

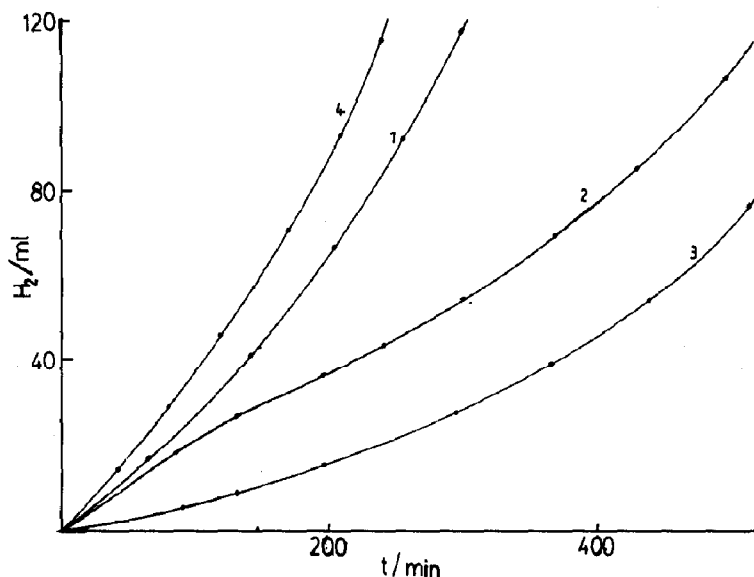


Fig. 1. Photogeneration of hydrogen from 25% v/v solution of (1) propane-2-ol, (2) ethanol, (3) methanol, (4) ethanol+0.3 mg g<sup>-1</sup> of colloidal platinum, in the presence of  $4.0 \times 10^{-2}$  M of SmCl<sub>3</sub> and 0.01 M HCl.

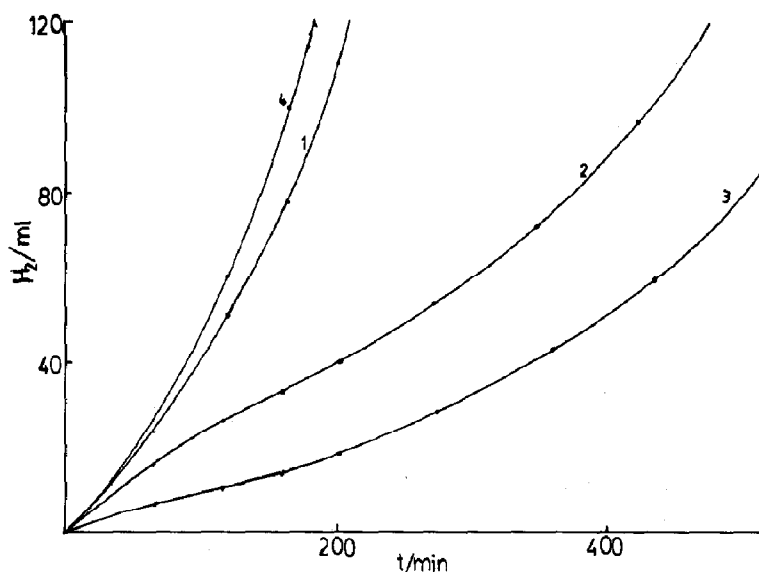


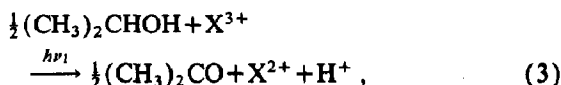
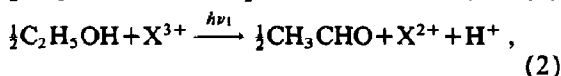
Fig. 2. Photogeneration of hydrogen from 25% v/v solution of (1) propane-2-ol, (2) ethanol, (3) methanol, (4) ethanol+0.3 mg g<sup>-1</sup> of colloidal platinum, in the presence of  $2.5 \times 10^{-2}$  M of EuCl<sub>3</sub> in 0.01 M HCl.

of irradiation, chloroplatinic acid is reduced to colloidal platinum.

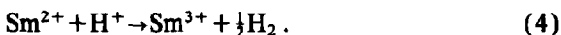
The mechanism of catalysis can be understood as follows. The primary step is oxidation of alcohol with

reduction of  $X^{3+}$  ( $X = \text{Sm}$  or  $\text{Eu}$ ) to  $X^{2+}$  as a result of light-assisted solvent to ion electron transfer. The formation of transient  $\text{Sm}^{2+}$  ions has been detected when SmCl<sub>3</sub> solution is irradiated with a KrF exci-

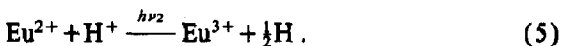
mer laser [7,8]. For methanol, ethanol and propane-2-ol the reactions are



the oxidation products being formaldehyde, acetaldehyde, and acetone, respectively.  $\text{Sm}^{2+}$  ion is unstable in water and "instantaneously" oxidises into  $\text{Sm}^{3+}$  with reduction of water, i.e.



$\text{Eu}^{2+}$  is stable in an aqueous medium, it is, however, readily photodecomposed [9–11] into  $\text{Eu}^{3+}$  and hydrogen, i.e.



It is believed that (5) proceeds via photogeneration of a solvated electron which is scavenged by hydrogen ions, i.e.



Colloidal platinum catalyses generation of molecular hydrogen as observed. Hydrogen evolution is not seen when  $\text{EuCl}_3$  or  $\text{SmCl}_3$  dissolved in pure ethanol is irradiated showing that the  $\text{H}^+$  ion is necessary for the occurrence of the reaction. When the  $\text{XCl}_3$  concentration is increased, the reaction rate initially increases and then decreases, the optimum being  $\approx 4 \times 10^{-2}$  and  $2.5 \times 10^{-2}$  M for  $\text{SmCl}_3$ ,  $\text{EuCl}_3$  respectively. This effect can be easily understood. Reaction rates increase with the increase in  $[\text{X}^{3+}]$ . However, the rates of the reverse reactions (4) and (5) are also increased by the increase in  $[\text{X}^{3+}]$ . The two opposing factors result in an optimum concen-

tration. A slight increase in the hydrogen yield with pH is observed, possibly because reactions (4) and (5) are favoured by an increase of pH. Organic acids arise from further oxidation of the aldehyde by the same mechanism. Dehydrogenation of alcohols are energy storing processes (e.g.  $\Delta G^0 = 32 \text{ kJ mol}^{-1}$  for the propane-2-ol reaction [12]). Unfortunately, the light absorption by  $\text{Sm}^{3+}$  and  $\text{Eu}^{3+}$  in aqueous medium responsible for the reactions (1)–(3) is peaked in the 200–230 nm region. The energy conversion efficiency at 254 nm is found to be  $\approx 2\%$ . Although the efficiency is certainly much higher in the 200–230 nm region, the system is unsuitable for solar energy conversion because of the lack of sensitivity to the visible spectrum. One possibility is to look for stable complexes of  $\text{Sm}^{3+}$ ,  $\text{Eu}^{3+}$  or other transition metals that undergo reactions of the types of (1)–(3) and (4) or (5).

## References

- [1] A. Harriman and M.E. West, eds., *Photogeneration of hydrogen* (Academic Press, New York, 1983).
- [2] P. Pichat, J.M. Herman, J. Disdier, H. Courbon and M.N. Mozzanega, *Nouv. J. Chim.* 5 (1981) 627.
- [3] F.H. Hussein and R. Rudham, *J. Chem. Soc. Faraday Trans. I* 80 (1984) 2817.
- [4] C.G. Griggs and D.J.H. Smith, *J. Organomet. Chem.* 273 (1984) 105.
- [5] R. Irie, X. Li and Y. Saito, *J. Mol. Catal.* 23 (1984) 17.
- [6] B. Hubsch and B. Mahieu, *Polyhedron* 4 (1985) 669.
- [7] T. Donohue, in: *Rare earths in modern science and technology*, Vol. 3, eds. G.J. McCarthy, H.B. Silber and J.J. Rhybe (Plenum Press, New York, 1982) p. 223.
- [8] J.C.G. Bunjli, in: *Handbook on physics and chemistry of rare earths*, Vol. 9, eds. K.A. Gschneider and L. Eyring (North-Holland, Amsterdam, 1987).
- [9] D.L. Douglas and D.M. Yost, *J. Chem. Phys.* 17 (1949) 1345.
- [10] Y. Hass, G. Stein and R. Tenne, *Isr. J. Chem.* 10 (1972) 529.
- [11] D.D. Davis, K.L. Stevenson and G.K. King, *Inorg. Chem.* 16 (1977) 670.
- [12] K. Chandrasekaran and D.G. Whitten, *J. Am. Chem. Soc.* 102 (1980) 5119.