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$Ru(bpy)_3^{2+}$ Photosensitized Oxidation of Ascorbic Acid and Hydrogen Evolution on TiO_2

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Light driven redox reactions, coupled with redox catalysts, have been investigated as a possible route for the generation of fuels by visible light [1–3]. Extensive studies with transition metal complexes containing ligands such as αα-bipyridyl, phenothraline, *o*-phenanthroline and organic dyes have shown their potential utility as photosensitizers in the photochemical conversion of solar energy [4–6]. The ability of $Ru(bpy)_3^{2+}$ to act as a photosensitizer, an electron donor [7] or an electron acceptor [8] has led to a recent interest in its possible role in the photochemical production of hydrogen from water.

The kinetics and mechanism of the oxidation of ascorbic acid catalyzed by Ru(III) ion has recently been reported [9] by us. In this paper we report the photochemical oxidation of ascorbic acid to dehydroascorbic acid using Pt loaded TiO_2 in an aqueous solution of $Ru(bpy)_3^{2+}$. The system uses ascorbic acid as a sacrificial agent for the efficient evolution of H_2. The mechanism of the reaction is given in eqns. (1)–(6) and depicted in Scheme 1.

$$Ru(bpy)_3^{2+} \xrightarrow{h\nu} Ru^*(bpy)^{2+} \quad (1)$$

$$^*Ru(bpy)_3^{2+} + TiO_2 \longrightarrow Ru(bpy)_3^{3+} + TiO_2(e^-_{cB})$$

$$(e^- \text{ in conduction band}) \quad (2)$$

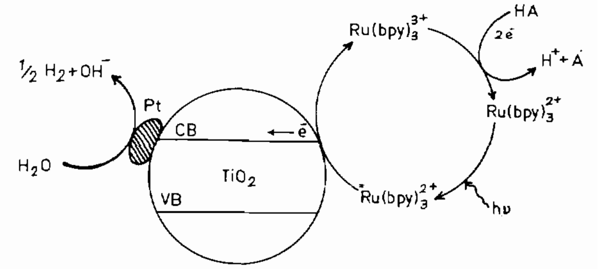
$$TiO_2(e^-_{cB}) + H^+ \xrightarrow{Pt} \tfrac{1}{2}H_2 + TiO_2 \quad (3)$$

$$H_2A \longrightarrow HA^- + H^+ \quad (4)$$

$$Ru(bpy)_3^{3+} + HA^- \longrightarrow Ru(bpy)_3^{2+} + HA^{\bullet} \quad (5)$$

$$Ru(bpy)_3^{3+} + HA^{\bullet} \longrightarrow Ru(bpy)_3^{2+} + H^+ + A \quad (6)$$

Photoexcitation of $Ru(bipy)_3^{2+}$ by visible light (510 nm) gives an electron to the vacant conduction band of TiO_2 (eqns. (1) and (2)). Transfer of the photoelectron to a proton from water through platinum (eqn. (3)) causes the evolution of hydrogen.



Scheme 1. Mechanism for photosensitized oxidation of ascorbic acid and hydrogen evolution.

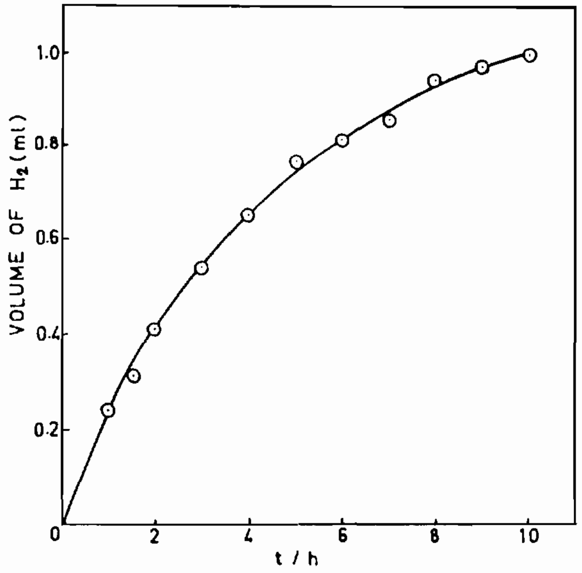


Fig. 1. Plot of hydrogen produced *vs.* time.

At pH 3 of the reaction ascorbic acid exists in the monoprotonated form, HA^- ($K_a = 5.4 \times 10^{-5}$ at 25 °C) [10]. In eqns. (5) and (6) fast reduction of $Ru(bipy)_3^{3+}$ to $Ru(bpy)_3^{2+}$ takes place by HA^-, the ascorbate anion. Sutin [11] has reported a rate constant 2.96×10^6 M^{-1} s^{-1} for this reaction at 25 °C.

It may be seen from Fig. 1 that the amount of H_2 produced in the reaction is 130 μl/h which is much higher than the earlier reported [12, 13] values of 25–30 μl of H_2 per hour with the use of TEA [12] or EDTA [13] as sacrificial agents. The higher rate of evolution of H_2 is due to a rapid [11] rate of reduction of $Ru(bipy)_3^{3+}$ by ascorbic acid. Further, unlike TEA or EDTA the reaction does not involve the oxidative degradation of the reductant.

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