# Hydrogen Evolution from Aqueous Alkaline Solution of Titanium(III)

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Recently, Wagner and Somorjai [1] have shown that the photocatalytic decomposition of water into hydrogen and oxygen takes place on metal-free $SrTiO_3$ crystals in aqueous alkaline solution. Under illumination the formation of surface $Ti^{3+}$ ions has been demonstrated by spectroscopic techniques [2] and the rate of hydrogen photogeneration was found to increase with increasing concentration of hydroxide ion in aqueous solution [1]. Van Damme and Hall [3] have proposed that the surface $Ti^{3+}$ ions are responsible for the generation of hydrogen. However, the role of hydroxide in the photocatalytic decomposition of water is open to discussion. In connection with the mechanism of photocatalytic hydrogen production from water over $SrTiO_3$ crystals, we wish to report a strong effect of hydroxide concentration on the rate of hydrogen evolution from aqueous alkaline solution of $Ti^{3+}$ ions.

An aqueous solution of $Ti^{3+}$ was prepared by dissolving $TiCl_3$ in carefully deoxygenated water. The concentration of $Ti^{3+}$ in the solution was determined by titration with $KMnO_4$ solution. A typical experimental procedure for $H_2$ evolution is as follows. A 20 $cm^3$ portion of deoxygenated aqueous NaOH solution of 0.011 to 5.0 *M* introduced into a reaction flask of 98 $cm^3$ total capacity with a magnetic stirrer, and was kept at 30 °C under an atmosphere of argon or acetylene. To initiate the reaction, 0.5 $cm^3$ of 0.46 *M* aqueous solution of $Ti^{3+}$ was injected through a side arm sealed with silicon rubber. Samples of the gases above the reaction solution were withdrawn at intervals by a syringe and analyzed by gas chromatography, using a 2 m column of active carbon for $H_2$ analysis and a 2 m column of Porapak N for hydrocarbon analysis.

The addition of $Ti^{3+}$ into aqueous alkaline solution resulted in the evolution of $H_2$ and the formation of $TiO_2$, as originally described by Jorgensen [4]. Figure 1 shows the time dependence of $H_2$ yield at 30 °C under an argon atmosphere. The initial rate of $H_2$ evolution increases with increasing concentration of NaOH added. At $[OH^-]/[Ti^{3+}]$ ratios above 4.0, the total yield of $H_2$ was confirmed to reach 50 mol% of $Ti^{3+}$, corresponding to 100% of the theoretical electron transfer efficiency. Figure 2 shows the initial

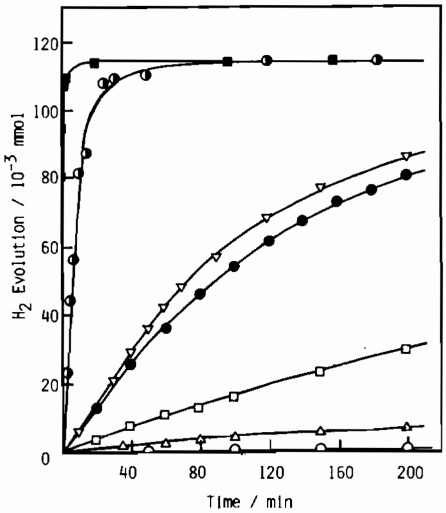

Fig. 1. Time dependence of $H_2$ evolution from aqueous alkaline solution of $TiCl_3$ in different concentrations of NaOH at 30 °C under argon. Reaction conditions: $TiCl_3$ = 0.011 *M* (0.23 mmol), total aqueous solution = 20.5 $cm^3$, and (○) NaOH = 0.011 *M*; (△) NaOH = 0.022 *M*; (□) NaOH = 0.033 *M*; (●) NaOH = 0.044 *M*; (▽) NaOH = 0.056 *M*; (○) NaOH = 0.49 *M*; (■) NaOH = 5.0 *M*.

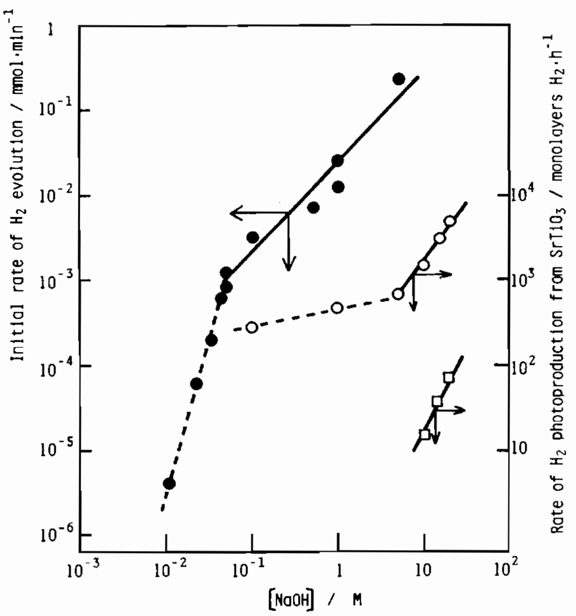

Fig. 2. Rates of $H_2$ evolution as a function of NaOH concentration. (●); Initial rate of $H_2$ evolution from aqueous alkaline solution of $TiCl_3$ at 30 °C observed in the present work. (○, □); Rates of $H_2$ photoproduction from prereduced platinized (○) and metal-free (□) $SrTiO_3$ crystals in aqueous alkaline solution at 44 °C under UV illumination, as reported by Wagner and Somorjai [1].

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rate of $H_2$ evolution from aqueous alkaline solution of $Ti^{3+}$ as a function of NaOH concentration, which is quite similar to the hydroxide dependence on the rate of $H_2$ photogeneration on $SrTiO_3$ crystals observed by Wagner and Somorjai [1]: see Fig. 2. This parallel kinetic behavior, as can be seen from Fig. 2, seems to indicate a direct participation of hydroxide ions in the rate-limiting step of $H_2$ formation over $Ti^{3+}$ ions in both systems. In the presence of acetylene molecules, the reduction of acetylene to ethylene competed with the $H_2$ evolution in the aqueous alkaline solution of $Ti^{3+}$ at 30 °C, as shown in Fig. 3. This result may be comparable to the photoreduction of acetylene to ethylene observed on $TiO_2$ powders containing chemisorbed water [5, 6].

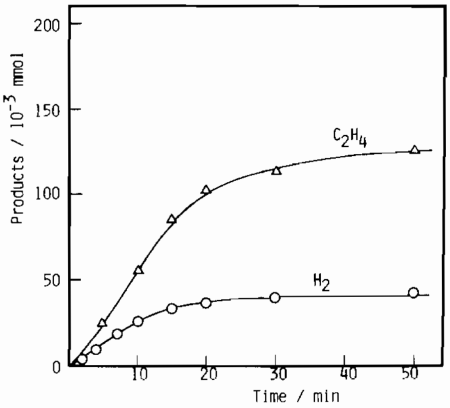

Fig. 3. $C_2H_4$ production of $H_2$ evolution from aqueous alkaline solution of $TiCl_3$ at 30 °C under 1.0 bar of $C_2H_2$. Reaction condition: $TiCl_3$ = 0.017 *M* (0.36 mmol), NaOH = 0.5 *M*, and total aqueous solution = 21 $cm^3$.

The absorption spectrum of a violet aqueous solution of $TiCl_3$ showed a distinct double structure of 17400 $cm^{-1}$ ($\epsilon$ 2.7) and 20300 $cm^{-1}$ ($\epsilon$ 4.0) in the visible region, which is consistent with that of the complex formulated in solution as $Ti(H_2O)_6^{3+}$ [7]. The addition of NaOH into the violet aqueous solution of $Ti^{3+}$ resulted in rapid formation of a dark violet-brown precipitate at $[OH^-]/[Ti^{3+}]$ ratios above 3.0. The formation of a dark violet brown precipitate, which has been formulated as $Ti_2O_3 \cdot xH_2O$ by Allen *et al.* [8], was apparently complete within a few minutes, even at the $[OH^-]/[Ti^{3+}]$ ratio of 3.0 where the rate of $H_2$ evolution was relatively slow. The $Ti_2O_3 \cdot xH_2O$ obtained was found to be inert in pure water, but it rapidly oxidized to form white $TiO_2$ and $H_2$ when immersed in a concentrated aqueous alkaline solution of 1.0 *M*. From these results, we have concluded that hydroxide ions are directly involved in a rate-limiting step, as expressed by eq (1).

$$Ti_2O_3(H_2O)_x + OH^- \longrightarrow 2TiO_2 + H_2 + (x-1)H_2O + OH^- \qquad (1)$$

Such a direct kinetic role for the hydroxide ion appears to account for the strong dependence of hydroxide concentration on the rate of $H_2$ photogeneration observed on the $SrTiO_3$ crystals under UV illumination.

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