# Photo-enhanced Production of Hydrogen by Liquid-phase Catalytic Dehydrogenation of Propan-2-ol with Rhodium–Tin Chloride Complexes

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*Summary* Photo-irradiation of a homogeneous solution in propan-2-ol of a rhodium–tin chloride catalyst markedly enhanced the endothermic reaction rate to produce acetone and hydrogen, an energy conversion efficiency as large as 23% being attained.

LIQUID-PHASE dehydrogenation of propan-2-ol to acetone by a rhodium–tin chloride catalyst has been studied by Charman.[1] We have found that the rate of reaction (1) is considerably enhanced under irradiation from low-pressure mercury lamps.

$$Me_2CHOH \rightarrow Me_2CO + H_2 \quad (1)$$

Hydrogen was evolved at a rate of 144 ml h$^{-1}$ (6·0 mmol h$^{-1}$), in a reaction vessel containing 3 low-pressure 24 W Hg lamps inside the vessel, from a refluxing solution of $RhCl_3 \cdot 3H_2O$ (2·0 mM), $SnCl_2 \cdot 2H_2O$ (7·1 mM), and LiCl (5·9 mM) in refluxing Pr$^i$OH (200 ml). An equimolar amount of acetone, relative to the hydrogen produced, was formed, as shown by n.m.r. spectroscopy. The quantum yield was estimated as 1·7.

An appreciable amount of the incident photon energy is recovered, since reaction (1) is endothermic ($\Delta U$ 15·0 kcal mol$^{-1}$) and the quantum yield, $\phi$, is larger than unity. The energy conversion efficiency, $\eta$, was calculated as 23%, according to equation (2),

$$\eta = \alpha\phi\Delta U/h\nu \quad (2)$$

where the absorbance, $\alpha$, is 1·0, since the radiation from the low-pressure Hg lamp (112·2 kcal mol$^{-1}$) was absorbed completely by the rhodium complexes under these conditions.

For a more dilute solution of the catalyst (0·20 mM concentration of $RhCl_3 \cdot 3H_2O$), the rates under irradiation were 3·5 mmol h$^{-1}$ at 82 °C and 1·62 mmol h$^{-1}$ at 33 °C, respectively, with an activation energy of 3·5 kcal mol$^{-1}$. Interruption of the irradiation, including a period overnight, had no influence on the reaction rates (Figure 1).

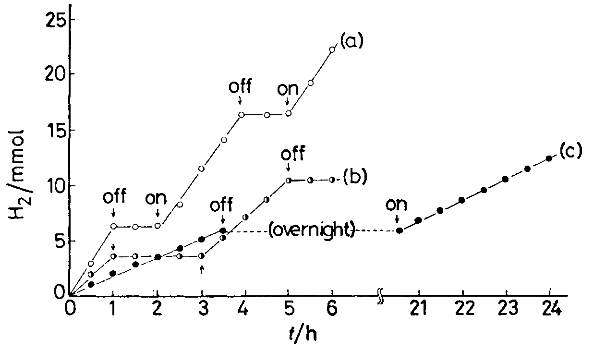

FIGURE 1. Photo-irradiation effects on the rates of the liquid-phase catalytic dehydrogenation of propan-2-ol. Catalyst composition: (a) $RhCl_3 \cdot 3H_2O$ (2·0 mM), $SnCl_2 \cdot 2H_2O$ (7·1 mM), and LiCl (5·9 mM); (b) and (c) $RhCl_3 \cdot 3H_2O$ (0·20 mM), $SnCl_2 \cdot 2H_2O$ (0·71 mM), and LiCl (0·59 mM); temperature: (a) and (b) 82 °C; (c) 33 °C; solvent, propan-2-ol.

The fact that the quantum yield is larger than unity and the distinct temperature dependence suggest that photo-induced ligand elimination activates the catalyst.[2]

The catalyst solution exhibited strong absorption bands at $\lambda_{max}$ 208 nm ($\epsilon$ 2·95 × 10$^4$ l mol$^{-1}$ cm$^{-1}$) and 270 nm ($\epsilon$ 1·02 × 10$^4$ l mol$^{-1}$ cm$^{-1}$), accompanied by a broad, weak absorption in the visible region (Figure 2). It was ascertained in a spectrophotometric reaction vessel that visible photons of up to *ca.* 570 nm wavelength were also effective for the rate enhancement.

Photochemical applications of transition-metal complexes for solar energy storage have been reported.[3] The present reaction seems to be particularly interesting for the following reasons. (i) The limit of 100% in energy conversion efficiency can be surpassed for the input photon, because the quantum yield is determined by the turnover numbers of the photo-activated catalyst, and (ii) the thermal region in the solar spectrum is also useful, because the higher the reaction temperature, the greater the rate of hydrogen production.

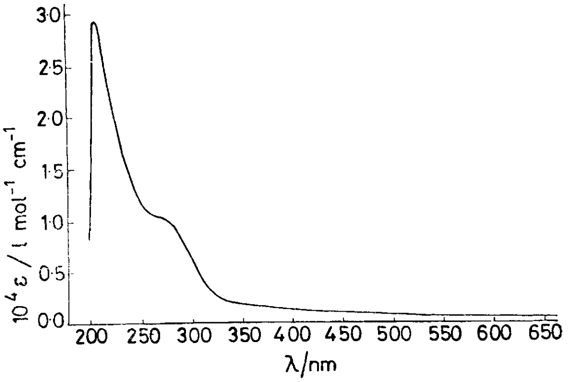

FIGURE 2. Electronic absorption spectrum of the catalyst solution, composition as in Figure 1, (b) and (c).

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