

Photocatalytic Synthesis of Ethane from Acetic Acid. Kolbe Reaction at a Gas–Solid Interface under U.V.-illumination

Shinri Sato

Research Institute for Catalysis, Hokkaido University, Sapporo 060, Japan

Photocatalytic decarboxylation of gaseous acetic acid over u.v.-illuminated, platinized titania gave predominantly ethane when gaseous water was present in the system.

Although electrochemical reactions are usually carried out in solutions, the present paper shows an example of a process analogous to an electrochemical reaction which occurs at a gas–solid interface without an applied voltage. The process

is decarboxylation of gaseous CH_3COOH over u.v.-illuminated platinized titania powder (Pt-TiO_2) giving the same products as in the Kolbe electrolysis of CH_3COOH . The product selectivity and the reaction rate were found to be sensitive

to reaction conditions. In a similar reaction carried out in the liquid phase, the products were almost exclusively CH_4 and CO_2 , independent of reaction conditions.¹

In a typical experiment, 0.3 g of Pt-TiO₂ catalyst were spread on the flat bottom of a quartz reaction cell. The cell was then connected to an evacuable circulation system (212 ml) and the catalyst was outgassed at 200 °C in a vacuum of less than 3×10^{-6} Torr. Glacial CH_3COOH , which had been outgassed at about -100 °C, was introduced in the gas phase into the reaction system at a desired pressure and the reaction was started by illuminating the catalyst with a 500 W ultra-high-pressure Hg lamp. The reaction products were analysed by a mass spectrometer.

A typical time dependence of the reaction products is shown

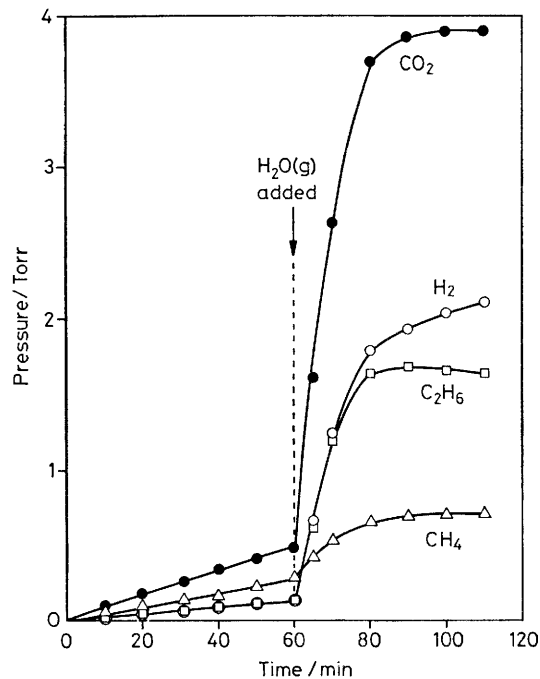


Figure 1. Time dependence of the products in the photodecomposition of gaseous CH_3COOH (initial pressure ca. 4 Torr) over Pt-TiO₂. After 60 min gaseous H_2O (ca. 20 Torr) was added.

in Figure 1. No other product (such as O_2) was detected and no reaction took place without the catalyst or in the dark. Figure 1 indicates that two reactions (1) and (2) are involved,



as in the Kolbe electrolysis, because the product composition exactly satisfies the stoichiometry of these reactions while CH_3COOH is present. A remarkable feature in the present process is that addition of gaseous H_2O to the system leads to a marked increase in the decarboxylation rate, especially in the rate of formation of C_2H_6 . As shown in Figure 1, C_2H_6 formation was accelerated from 1.5 to 74 $\mu\text{mol/h}$ and CH_4 formation from 3 to 17 $\mu\text{mol/h}$. The degree of acceleration depends on the amount of H_2O introduced. Addition of gaseous CH_3OH instead of H_2O did not accelerate the reaction. Although the photo-decarboxylation of gaseous CH_3COOH occurs slowly over TiO₂ alone, H_2O had no effect on its rate.

Figure 1 also shows that the amounts of CO_2 and H_2 still increase and that of C_2H_6 slightly decreases after the consumption of CH_3COOH owing to the photocatalytic reaction of C_2H_6 with H_2O over Pt-TiO₂, which yields CO_2 and H_2 as reported before.²

Since a fairly large amount of gaseous CH_3COOH is adsorbed on Pt-TiO₂, the surface would be covered with more than one monolayer of adsorbed CH_3COOH even at low pressure. The mechanism of the present process, therefore, may be basically the same as that of the liquid phase reaction,¹ *i.e.*, a photoanodic oxidation of CH_3COOH takes place on TiO₂ and each Pt-TiO₂ particle is thought to act as a short-circuited Pt-TiO₂ photoelectrochemical cell.^{1,3} The role of H_2O in the gas phase reaction, however, has not yet been elucidated but OH radicals formed from H_2O may give rise to CH_3 radicals.

Received, 24th August 1981; Com. 1026

References

- 1 B. Kraeutler and A. J. Bard, *J. Am. Chem. Soc.*, 1978, **100**, 2239, 5985.
- 2 S. Sato and J. M. White, *Chem. Phys. Lett.*, 1980, **70**, 131.
- 3 S. Sato and J. M. White, *J. Phys. Chem.*, 1981, **85**, 592.