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Photoinduced Direct Synthesis of Formic Acid and Methyl Formate from Methanol in the Presence of Hydrogen Peroxide

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Formic acid and methyl formate were directly synthesized by UV irradiation of the oxygen-saturated methanol containing hydrogen peroxide. The formations of formic acid and methyl formate were affected by H_2O_2 feeding rate. The combined selectivity of formic acid and methyl formate formations was 99%.

The direct transformation of methanol into more valuable compounds is very important from a viewpoint of effective utilization of organic resources. The direct synthesis of methyl formate from methanol has been investigated using supported copper or metal carbide such as WC catalysts[1,2] and recently has been carried out industrially, but the lifetime of the catalysts is very short and reaction temperature is high. Also, formic acid is produced by a two-step process.[3] We report here a method for the photoinduced direct and selective synthesis of formic acid and methyl formate from methanol containing H_2O_2 and O_2.[4]

Experimental methods were the same as those used in the previous paper. Methanol bubbled with O_2 (100 ml min^{-1}) in the presence of H_2O_2 was irradiated internally with a 120 W low pressure mercury lamp at 25 °C. Formic acid was analyzed by ion chromatography (Yokogawa IC-100).

When the O_2-saturated methanol was irradiated with UV light in the presence of H_2O_2, formic acid and methyl formate were produced as major products and ethylene glycol and acetaldehyde were produced as minor products. Figure 1 shows the effect of H_2O_2 feeding rate on formic acid and methyl formate formations. The quantities of formic acid and methyl formate increased with H_2O_2 feeding rate and reached the maximum at 5 ml h^{-1}, and those of ethylene glycol and acetaldehyde were less than about 2.7 mmol. Small quantities of formic acid and methyl formate were formed even in the absence of H_2O_2, and the ratios of the quantities of formic acid and methyl formate in

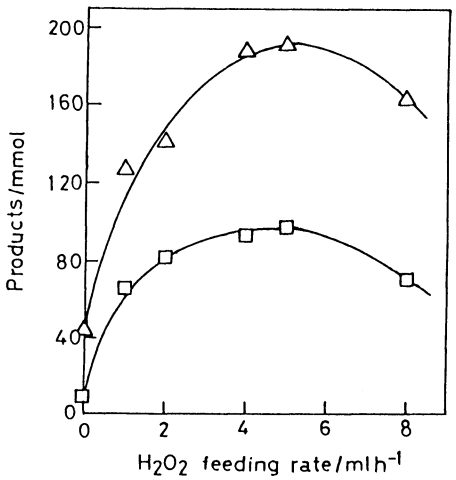

Fig. 1. Effect of H_2O_2 feeding rate on formic acid and methyl formate formations. △: Formic acid, □: Methyl formate. CH_3OH: 225 ml, Irradiation time: 7 h, Irradiation temp: 25 °C.

the absence of H_2O_2 to those at 5 ml h^{-1} of H_2O_2 feeding rate were 0.23 and 0.09, respectively. The quantum yields of formic acid and methyl formate at 5 ml h^{-1} were 1.36 and 0.69, respectively. Such high quantum yields indicate that the formations of formic acid and methyl formate proceed efficiently in this system. The combined selectivity of formic acid and methyl formate formations was 99% at 5 ml h^{-1}. These results indicate that formic acid and methyl formate are directly and selectively synthesized by UV irradiation of the O_2-saturated methanol containing H_2O_2.

As described in the previous paper,[4] hydroxyl radical formed by the photolysis of H_2O_2 is the initiating species in this system. It is known that in the presence of O_2, hydroxymethyl radical, which is formed by the abstraction of α-hydrogen atom of methanol,[5] reacts rapidly with O_2 to form hydroxymethyldioxy radical.[6] It is also known that hydroxymethyldioxy radical abstracts hydrogen atom from methanol to form hydroperoxyhydroxymethane which is decomposed photochemically or thermally to formic acid and water.[7] The formation of formaldehyde was hardly observed. When formic acid was added to methanol, the formation of methyl formate was observed even without UV irradiation.

It can be presumed from these facts that formic acid is mainly formed through the reactions(1)-(5) and methyl formate through the reaction(6).

$$H_2O_2 \xrightarrow{h\nu} 2\cdot OH \quad (1)$$

$$CH_3OH + \cdot OH \longrightarrow \cdot CH_2OH + H_2O \quad (2)$$

$$\cdot CH_2OH + O_2 \longrightarrow \cdot O_2CH_2OH \quad (3)$$

$$\cdot O_2CH_2OH + CH_3OH \longrightarrow HO_2CH_2OH + \cdot CH_2OH \quad (4)$$

$$HO_2CH_2OH \xrightarrow{h\nu\ (\text{or wall})} HCOOH + H_2O \quad (5)$$

$$HCOOH + CH_3OH \longrightarrow HCOOCH_3 + H_2O \quad (6)$$

Scheme 1.

As can be seen in Fig. 1, the quantities of formic acid and methyl formate decreased at higher H_2O_2 feeding rate. Methyl formate was hardly decomposed by UV irradiation. In addition, because the quantities of CO_2 and CO evolved in this system were small, the decomposition of formic acid would be small. On the other hand, hydrogen peroxide is a scavenger of hydroxyl radical.[8] It can therefore be presumed that the decrease in formic acid and methyl formate formations at higher H_2O_2 feeding rate is mainly attributed to the scavenging of hydroxyl radical by hydrogen peroxide.

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