

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  $\text{H}_2\text{O}_2$  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<sup>1,2)</sup> 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.<sup>3)</sup> We report here a method for the photoinduced direct and selective synthesis of formic acid and methyl formate from methanol containing  $\text{H}_2\text{O}_2$  and  $\text{O}_2$ .<sup>4)</sup>

Experimental methods were the same as those used in the previous paper.<sup>4)</sup> Methanol bubbled with  $\text{O}_2$  ( $100 \text{ ml min}^{-1}$ ) in the presence of  $\text{H}_2\text{O}_2$  was irradiated internally with a 120 W low pressure mercury lamp at  $25^\circ\text{C}$ . Formic acid was analyzed by ion chromatography (Yokogawa IC-100).

When the  $\text{O}_2$ -saturated methanol was irradiated with UV light in the presence of  $\text{H}_2\text{O}_2$ , 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  $\text{H}_2\text{O}_2$  feeding rate on formic acid and methyl formate formations. The quantities of formic acid and methyl formate increased with  $\text{H}_2\text{O}_2$  feeding rate and reached the maximum at  $5 \text{ ml h}^{-1}$ , and those of ethylene glycol and acetaldehyde were less than about  $2.7 \text{ mmol}$ . Small quantities of formic acid and methyl formate were formed even in the absence of  $\text{H}_2\text{O}_2$ , and the ratios of the quantities of formic acid and methyl formate in

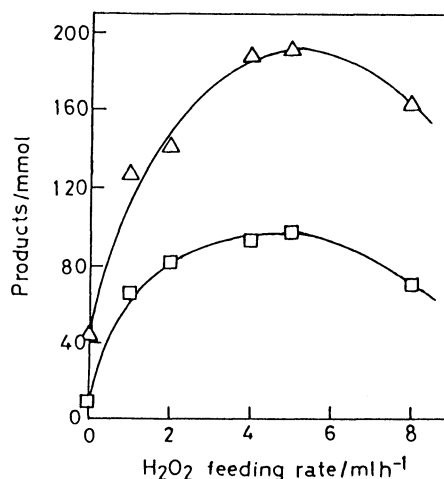
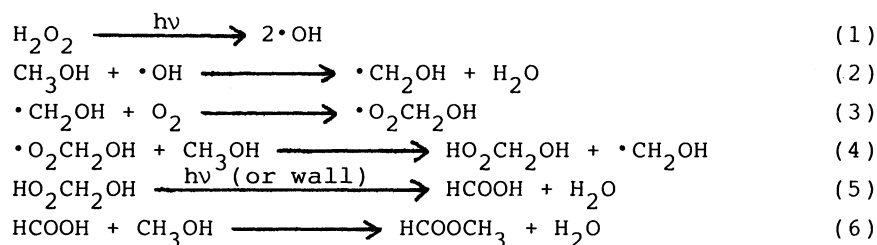


Fig. 1. Effect of  $\text{H}_2\text{O}_2$  feeding rate on formic acid and methyl formate formations.  $\Delta$ : Formic acid,  $\square$ : Methyl formate.  $\text{CH}_3\text{OH}$ :  $225 \text{ ml}$ , Irradiation time:  $7 \text{ h}$ , Irradiation temp:  $25^\circ\text{C}$ .

the absence of  $\text{H}_2\text{O}_2$  to those at  $5 \text{ ml h}^{-1}$  of  $\text{H}_2\text{O}_2$  feeding rate were 0.23 and 0.09, respectively. The quantum yields of formic acid and methyl formate at  $5 \text{ ml h}^{-1}$  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  $5 \text{ ml h}^{-1}$ . These results indicate that formic acid and methyl formate are directly and selectively synthesized by UV irradiation of the  $\text{O}_2$ -saturated methanol containing  $\text{H}_2\text{O}_2$ .

As described in the previous paper,<sup>4)</sup> hydroxyl radical formed by the photolysis of  $\text{H}_2\text{O}_2$  is the initiating species in this system. It is known that in the presence of  $\text{O}_2$ , hydroxymethyl radical, which is formed by the abstraction of  $\alpha$ -hydrogen atom of methanol,<sup>5)</sup> reacts rapidly with  $\text{O}_2$  to form hydroxymethyldioxy radical.<sup>6)</sup> 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.<sup>7)</sup> 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).



Scheme 1.

As can be seen in Fig. 1, the quantities of formic acid and methyl formate decreased at higher  $\text{H}_2\text{O}_2$  feeding rate. Methyl formate was hardly decomposed by UV irradiation. In addition, because the quantities of  $\text{CO}_2$  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.<sup>8)</sup> It can therefore be presumed that the decrease in formic acid and methyl formate formations at higher  $\text{H}_2\text{O}_2$  feeding rate is mainly attributed to the scavenging of hydroxyl radical by hydrogen peroxide.

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