Photoinduced Organic Transformation. Selective Synthesis of Ethylene Glycol or Formic Acid and Methyl Formate from Methanol in the Presence of Hydrogen Peroxide

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The photoinduced transformation of methanol (MeOH) has been investigated in the presence of H_2O_2. Ethylene glycol (EG) was selectively produced by UV light irradiation of the N_2-saturated MeOH and the selectivity was 85—94% below 3 ml h^{-1} of H_2O_2 feeding rate (f). The quantity of EG reached the maximum at f=5 ml h^{-1} and the quantum yield was 0.73. EG was produced through the dimerization of hydroxymethyl radicals formed by the abstraction of hydrogen atom from MeOH by hydroxyl radical which was formed by the photolysis of H_2O_2. On the other hand, formic acid (FA) and methyl formate (MF) were selectively produced by UV light irradiation of the O_2-bubbled MeOH and the combined selectivity was about 99% in the f range of 1—8 ml h^{-1}. The quantities of FA and MF reached the maximum at f=5 ml h^{-1} and their quantum yields were 1.36 and 0.69, respectively. FA was mainly produced through the decomposition of hydroperoxyhydroxymethane formed by the abstraction of hydrogen atom from MeOH by hydroxymethyldioxy radical which was formed by the reaction of hydroxymethyl radical with oxygen, and MF through the reaction of MeOH with FA formed.

The direct transformation of methanol (MeOH) into more valuable compounds is very important from a viewpoint of effective utilization of organic resources. Ethylene glycol (EG), present-day produced from ethylene by a two-step method, is very important as a raw material for the industrial production of polyester synthetic fiber and polyester resin, and also as antifreezing agent and so on. The direct synthesis of EG from MeOH, not from petrochemicals, has been investigated in the presence of organic peroxides such as di-*t*-butyl peroxide,[1,2] but the selectivity is not satisfactory. The photochemical reaction of MeOH using rhodium complex gave high selectivity for EG formation,[3] but very expensive photocatalyst was required for the acceleration of this reaction. On the other hand, the direct synthesis of methyl formate (MF) from MeOH has been investigated using supported copper or metal carbide such as WC catalysts,[4,5] and recently has been carried out industrially, but the lifetime of the catalysts is very short and the reaction temperature is high. Also, formic acid (FA) is produced through a two-step process.[6]

In the previous papers,[7,8] we reported that EG or FA and MF were directly and selectively synthesized by UV light irradiation of the N_2-saturated or O_2-bubbled MeOH containing H_2O_2. In this paper, we report in further detail with regard to the photoinduced synthesis of EG or FA and MF from MeOH and to discuss the reaction mechanism.

Experimental

Materials. All chemicals were of reagent grade. MeOH was purchased from Tokyo Kasei Kogyo Co., Ltd. and was used without further purification. The aqueous 30% hydrogen peroxide was purchased from Santoku Chemical Industries Co., Ltd. N_2 and O_2 used were of high purity grade of above 99.9%.

Apparatus and Procedures. The photoreactions were carried out in an inner source typed Pyrex glass reaction vessel (volume: 500 ml). 225 ml of MeOH was placed in the reaction vessel and well-bubbled with nitrogen in order to remove oxygen or with oxygen. The N_2-saturated or O_2-bubbled MeOH was stirred magnetically (500 rpm), and irradiated internally with a 120 W low pressure mercury lamp (Eichosha EL-J-120, mainly 253.7 nm). At the same time with irradiation, the aqueous 30% H_2O_2 was added to MeOH with the feeding rate (f) from 1 to 8 ml h^{-1} (H_2O_2 successive addition) by using a micro feeder (Atto Corp., AC-2120). The MeOH solution was controlled at 25 °C by using a Yamato-Komatsu Coolnics (TE-24W). In some experiments MeOH solution containing a given quantity of H_2O_2 at the beginning (simultaneous addition) was irradiated.

Actinometry. The quantity of light from the lamp was determined by using a potassium tris(oxalato)ferrate(III) actinometer. The quantity of light was 3.38×10^{18} photons s^{-1}.

Analysis. Products were analyzed by gas chromatography (Shimadzu GC-7A: Porapak Q column, GC-4C: Porapak N column, and GC-3BT: Molecular sieve 5A column) and ion chromatography (Yokogawa IC-100: SAX 1 column).

Results and Discussion

N_2-Saturated Methanol. When the N_2-saturated MeOH containing H_2O_2 was irradiated with UV light, EG was produced as a major product and FA, MF, acetaldehyde, ethanol, formaldehyde, hydrogen, carbon dioxide, carbon monoxide, and methane were produced as minor products. Figure 1 shows the quantities of main products as a function of irradiation time in the case of the H_2O_2 successive addition of 3 ml h^{-1}. The quantities of EG, FA, and MF increased with irradiation time. The quantity of EG was about 7 times that of

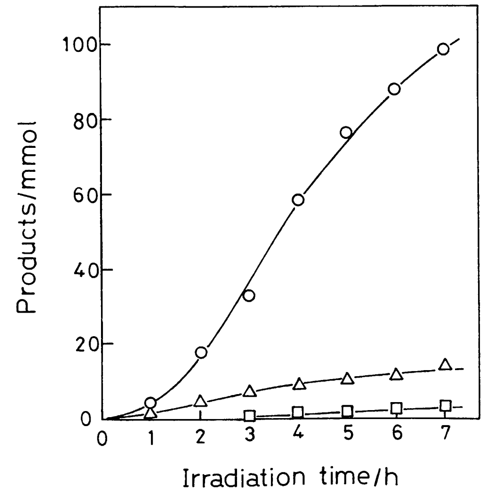

Fig. 1. Plots of the quantity of main products as a function of irradiation time in the N_2-saturated methanol. Aqueous 30% H_2O_2 feeding rate: 3 ml h^{-1}. ○: Ethylene glycol, △: formic acid, □: methyl formate.

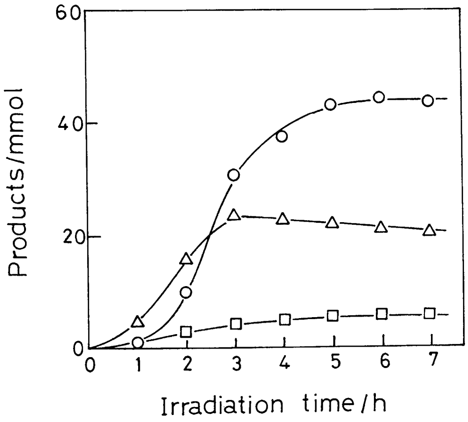

Fig. 2. Plots of the quantity of main products as a function of irradiation time in the N_2-saturated methanol. Amount of added aqueous 30% H_2O_2: 21 ml. Symbols are the same as in Fig. 1.

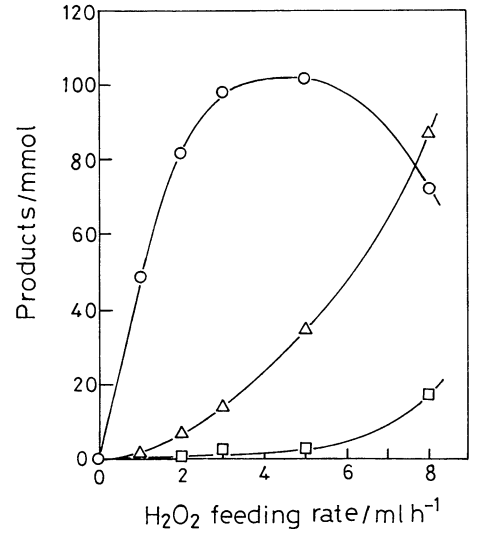

Fig. 3. Effect of H_2O_2 feeding rate on the quantity of main products in the N_2-saturated methanol. Irradiation time: 7 h. Symbols are the same as in Fig. 1.

FA, and the sum of the quantities of other products were less than about 3 mmol after 7 h irradiation. The selectivity of EG formation was about 85% after 7 h irradiation. EG formation was hardly affected by the irradiation temperatures from 10 to 40 °C. Also, when the N_2-saturated MeOH alone was irradiated in the absence of H_2O_2, organic products were hardly produced even after 7 h irradiation. These results indicate that EG is selectively synthesized by UV light irradiation of the N_2-saturated MeOH containing H_2O_2.

The quantities of EG, FA, and MF produced in the case of the H_2O_2 simultaneous addition were examined. The amount of H_2O_2 (21 ml) added in this case corresponds to that in the case of the H_2O_2 successive addition of 3 ml h^{-1} for 7 h. Figure 2 shows the quantities of main products as a function of irradiation time. The quantity of EG increased with irradiation time and became almost constant after about 5 h. The quantities of FA and MF increased with irradiation time up to about 3 h and became almost constant thereafter. The quantity of EG was about twice that of FA and about 8 times that of MF, and the sum of the quantities of other products were less than about 1 mmol after 7 h irradiation. The selectivities of EG and FA formations were about 62 and 29% after 7 h irradiation, respectively. It was apparent from these results that EG formation and the selectivity were much larger in the H_2O_2 successive addition than in the H_2O_2 simultaneous addition. Subsequent experiments were carried out with the H_2O_2 successive addition.

Figure 3 shows the effects of H_2O_2 feeding rate on the quantities of EG, FA, and MF produced by UV light irradiation for 7 h. The quantity of EG increased with H_2O_2 feeding rate and reached the maximum at f=5 ml h^{-1}. The quantity of FA increased gradually up to f=3 ml h^{-1} and steeply thereafter, and that of MF increased steeply in the range of $f>5$ ml h^{-1}. The quantity of FA was larger than that of EG in the range of $f>8$ ml h^{-1}. The quantum yields of EG, FA, and MF at the maximum of EG were 0.73, 0.25, and 0.02, respectively. Such a high quantum yield of EG indicates that EG formation proceeds efficiently in this system. Table 1 shows the effect of H_2O_2 feeding rate on the selectivity of EG formation. The selectivity of EG formation decreased with increasing H_2O_2 feeding rate and was 85—94% below 3 ml h^{-1}. It was found from these results that the selectivity of EG formation were affected markedly by H_2O_2 feeding rate

Table 1. Effect of H_2O_2 Feeding Rate on the Selectivity of Ethylene Glycol Formation[a)]

H_2O_2 feeding rate ml h^{-1}	Selectivity %
1	94
2	90
3	85
5	72
8	40

a) Irradiation time: 7 h.

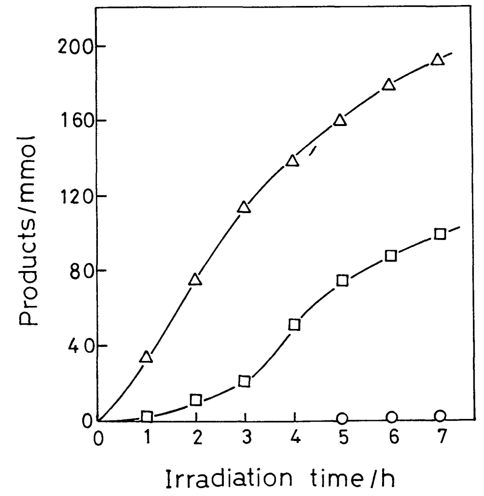

Fig. 4. Plots of the quantity of main products as a function of irradiation time in the O_2-bubbled methanol. Aqueous 30% H_2O_2 feeding rate: 5 ml h^{-1}, O_2 flow rate: 100 ml min^{-1}. Symbols are the same as in Fig. 1.

and EG was selectively synthesized in lower H_2O_2 feeding rate ranges.

O_2-Bubbled Methanol. When the O_2-bubbled MeOH containing H_2O_2 was irradiated with UV light, FA and MF were produced as major products and EG, acetaldehyde, ethanol, formaldehyde, hydrogen, carbon dioxide, carbon monoxide, and methane were produced as minor products. Figure 4 shows the quantities of main products as a function of irradiation time in the case of the H_2O_2 successive addition. The quantities of FA and MF increased with irradiation time. EG was hardly produced even after 3 h irradiation. The quantity of FA was about twice that of MF, and the sum of the quantities of other products was less than about 2.7 mmol after 7 h irradiation. The combined selectivity of FA and MF formations was about 99% after 7 h irradiation. These results indicate that FA and MF are selectively produced by UV light irradiation of the O_2-bubbled MeOH containing H_2O_2. Thus, it should be noted that main products in the O_2-bubbled MeOH differ entirely from those in the N_2-saturated one.

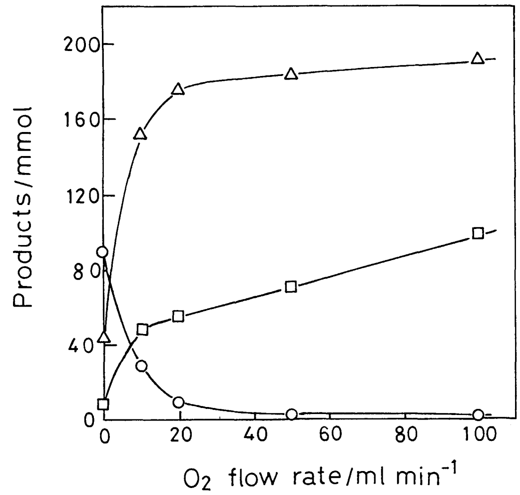

Fig. 5. Effect of O_2 flow rate on the quantity of main products in the O_2-bubbled methanol. Aqueous 30% H_2O_2 feeding rate: 5 ml h^{-1}. Irradiation time: 7 h. Symbols are the same as in Fig. 1.

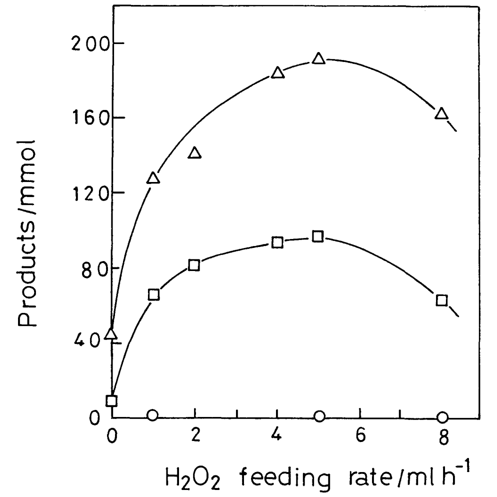

Fig. 6. Effect of H_2O_2 feeding rate on the quantity of main products in the O_2-bubbled methanol. O_2 flow rate: 100 ml min^{-1}. Irradiation time: 7 h. Symbols are the same as in Fig. 1.

Figure 5 shows the effects of O_2 flow rate (f_o) on the quantities of FA, MF, and EG produced by UV light irradiation for 7 h. The quantity of FA increased steeply in the $f_o<20$ ml min^{-1} range and was almost constant at $f_o>50$ ml min^{-1}. The quantity of MF increased steeply in the $f_o<20$ ml min^{-1} range and gradually thereafter. On the contrary, the quantity of EG decreased steeply from 89.6 mmol to 8.8 mmol at $f_o=20$ ml min^{-1} and was less than 3.2 mmol at $f_o>$ 50 ml min^{-1}. These results indicate that O_2 flow rate above about 50 ml min^{-1} is necessary for the effective formations of FA and MF.

Figure 6 shows the effects of H_2O_2 feeding rate on the quantities of FA, MF, and EG produced by UV light irradiation for 7 h. The quantities of FA and MF increased with H_2O_2 feeding rate and reached the maximum at f=5 ml h^{-1}. EG was hardly produced in the f range of 1—8 ml h^{-1}. The dependences of H_2O_2 feeding rate on FA and MF formations were similar to that of EG formation in the N_2-saturated MeOH. The quantum yields of FA and MF at the maximum of FA were 1.36 and 0.69, respectively. Such high quantum yields of FA and MF indicate that FA and MF formations proceed efficiently in this system. The combined selectivity of FA and MF formation was about 99% in the f range of 1—8 ml h^{-1}. These results indicate that FA and MF are selectively synthesized by UV light irradiation of the O_2-bubbled MeOH in the wide range of H_2O_2 feeding rate. Also, small quantities of FA and MF were produced even in the absence of H_2O_2, and the ratios of the quantities of FA and MF in the absence of H_2O_2 to those at f=5 ml h^{-1} were 0.23 and 0.09, respectively. This suggests that most of FA and MF are produced through the decomposition of H_2O_2 by UV light irradiation.

Ethylene Glycol, Formic Acid, and Methyl Formate Formation. It is well known that H_2O_2 is easily decomposed by UV light irradiation to form hydroxyl radical (Eq. 1).[9] The effect of thiocyanate ion, which is an efficient scavenger of hydroxyl radical,[10] on EG or FA and MF formations has been examined. EG formation was almost perfectly suppressed by the addition of 0.02 mmol of potassium thiocyanate. Similar result was also obtained for FA and MF formations. It is concluded from these results that hydroxyl radical formed by the photolysis of H_2O_2 is an initiating species of EG or FA and MF formations in these systems.

Also, as can be seen from Figs. 1 and 4, EG formation was almost perfectly suppressed by oxygen. This fact suggests that EG formation proceeds through the radical reaction.

In the absence of oxygen, the hydroxyl radical reacts rapidly with MeOH to form hydroxymethyl radical (Eq. 2),[11] which is rapidly dimerized to form EG (Eq. 3).[12] Therefore, it is considered that in the N_2-saturated MeOH EG is produced through the quick dimerization of hydroxymethyl radicals formed by the abstraction of α-position hydrogen of MeOH by hydroxyl radical as follows:

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

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

$$2\cdot CH_2OH \longrightarrow (CH_2OH)_2 \qquad (3)$$

As described already, in the N_2-saturated MeOH the quantum yield at the maximum of EG (Fig. 3) was 0.73. Since a molecule of EG is formed by the consumption of two hydroxyl radicals, the quantum yield of hydroxyl radical consumed to form EG is 1.46. Assuming the quantum yield of hydroxyl radical formation is 2.0,[13] about 73% of hydroxyl radical formed is consumed to form EG. This suggests that in the N_2-saturated MeOH most of hydroxyl radical is consumed by reaction (2).

As shown in Fig. 3, in higher H_2O_2 feeding rate ranges, the quantity of EG decreased while that of FA increased. It is known that hydroxyl radical is scavenged by H_2O_2 to form hydroperoxy radical and H_2O as reaction (4).[14]

$$H_2O_2 + \cdot OH \longrightarrow \cdot O_2H + H_2O \qquad (4)$$

It is also known that the hydroxymethyl radical formed by reaction (2) reacts rapidly with hydroperoxy radical to form hydroperoxyhydroxymethane which is decomposed photochemically or thermally to FA and H_2O as reactions (5) and (6).[15]

$$\cdot CH_2OH + \cdot O_2H \longrightarrow HO_2CH_2OH \qquad (5)$$

$$HO_2CH_2OH \xrightarrow{h\nu \text{ or wall}} HCOOH + H_2O \qquad (6)$$

It is considered from these facts that reaction (4) would occur predominantly in higher H_2O_2 concentration. It is therefore presumed that a considerable increase in the quantity of FA on higher H_2O_2 feeding rate is attributed to an enhancement in the formation of FA by reactions (4)—(6). In fact, as shown in Fig. 2, in the presence of a large quantity of H_2O_2 from the beginning, FA was produced in large quantity even in the N_2-saturated MeOH. Consequently, it is concluded that in the N_2-saturated MeOH EG was produced through reactions (1)—(3) on lower H_2O_2 feeding rate, and EG and FA through reactions (1)—(3) and (4)—(6) on higher H_2O_2 feeding rate, respectively.

In the presence of O_2, the hydroxymethyl radical formed by reaction (2) reacts rapidly with O_2 to form hydroxymethyldioxy radical (Eq. 7)[16] which abstracts a hydrogen atom from MeOH to form hydroperoxyhydroxymethane (Eq. 8), followed by reaction (6).[15] The formation of formaldehyde was hardly observed. Also, when UV light irradiated MeOH was kept at 25 °C, the quantity of FA decreased gradually while those of MF and H_2O increased. The sum of the quantities of FA and MF was almost constant. Furthermore, when FA was added to MeOH, the formations of MF and H_2O were observed even without UV light irradiation. Consequently, it is concluded that in the O_2-bubbled MeOH FA is mainly produced through reactions (1), (2), (6)—(8) in addition to reactions (4) and (5) and MF through reaction (9).

$$\cdot CH_2OH + O_2 \longrightarrow \cdot O_2CH_2OH \qquad (7)$$

$$\cdot O_2CH_2OH + CH_3OH \longrightarrow HO_2CH_2OH + \cdot CH_2OH \qquad (8)$$

$$HCOOH + CH_3OH \longrightarrow HCOOCH_3 + H_2O \qquad (9)$$

As shown in Figs. 3 and 6, the quantities of EG or FA and MF decreased in higher H_2O_2 feeding rate ranges. EG and MF were hardly decomposed by UV light irradiation. Also, since the quantities of CO_2 and CO evolved by UV light irradiation of the O_2-bubbled MeOH were small, the decomposition of FA would be small in these systems. As described already, hydroxyl radical is scavenged by H_2O_2.14) It is therefore presumed that the decrease in EG or FA and MF formations on higher H_2O_2 feeding rate is mainly attributed to the scavenging of hydroxyl radical by H_2O_2 as reaction (4).

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