Laser-Induced Organic Transformation. Direct and Selective Synthesis of Diols from Methanol, Ethanol, and Their Mixture in the Presence of Hydrogen Peroxide

Yuichi SHIMIZU,* Shun'ichi SUGIMOTO, Shunichi KAWANISHI, and Nobutake SUZUKI
Osaka Laboratory for Radiation Chemistry, Japan Atomic Energy Research Institute, 25-1 Mii-minami, Neyagawa, Osaka 572
(Received August 12, 1991)

The laser-induced transformation of methanol (MeOH), ethanol (EtOH), and MeOH–EtOH mixture have been investigated in the presence of H_2O_2. Ethylene glycol (EG) was highly selectively produced in high quantum yield (ϕ=0.94) by KrF-laser irradiation of the N_2-saturated MeOH and the selectivity was 94% at 3.2 ml h^{-1} of H_2O_2 feeding rate (f). Butanediol (BD) and acetaldehyde (AA) were directly and selectively produced by KrF-laser irradiation of the N_2-saturated EtOH. The quantum yields of BD and AA were 0.42 and 0.29, respectively, and the combined selectivity was 97% at f=3.4 ml h^{-1}. Also, propanediols (PD) were directly produced by KrF-laser irradiation of the N_2-saturated MeOH–EtOH mixture. The quantity of 1,2-PD reached the maximum at about 64 mol% of MeOH content. EG is produced through the dimerization of hydroxymethyl radicals formed by the abstraction of a hydrogen atom from MeOH by hydroxyl radical formed in high density by the laser-photolysis of H_2O_2. Similarly, 2,3-BD is produced by the dimerization of 1-hydroxyethyl radicals formed by the abstraction of α-hydrogen atom from EtOH by hydroxyl radical and 1,2-PD is produced by the recombination between hydroxymethyl radical and 1-hydroxyethyl radical.

The direct transformation of alcohols, which are not petrochemicals, into more valuable compounds is very important from a viewpoint of effective utilization of organic resources. Ethylene glycol (EG), butanediols (BD), and propanediols (PD), present-day manufactured by a multistep process using ethylene, butene, acetaldehyde, and propylene etc. obtained in petrochemical industry,[1] are very important as raw materials for the industrial production of polyester synthetic fiber and polyester resin, and also as antifreezing agent and so on.

In the previous paper,[2,3] we reported that EG was directly and selectively synthesized by steady state UV (low-pressure mercury lamp) irradiation of the N_2-saturated MeOH containing H_2O_2. For the purpose of highly selective synthesis of EG, we have attempted to proceed more efficiently the reaction of MeOH with H_2O_2 using a KrF laser with high intensity. We found that EG was highly selectively synthesized by KrF-laser irradiation of the N_2-saturated MeOH containing H_2O_2.[4] Also, we found that BD and acetaldehyde (AA) were directly and selectively synthesized by KrF-laser irradiation of N_2-saturated EtOH containing H_2O_2.[5]

In this paper, we report in further detail with regard to the laser-induced direct synthesis of EG and BD from MeOH and EtOH, respectively, and discuss the reaction mechanism. Furthermore, we report the laser-induced direct synthesis of PD from MeOH–EtOH mixture containing H_2O_2.

Experimental

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

Apparatus and Procedures. The laser-induced reactions were carried out in a Pyrex glass cylindrical reaction vessel (volume: 91.5 ml, diameter: 35.5 mm, length: 70 mm) with a Suprasil window for the incidence of laser beam. MeOH, EtOH, and MeOH–EtOH mixture (56—64 ml) were placed in the reaction vessel, respectively, and well-bubbled with nitrogen in order to remove oxygen. The N_2-saturated MeOH, EtOH, and MeOH–EtOH mixture were stirred magnetically (500 rpm), and irradiated with the KrF laser (Lumonics Hyper EX-460, wavelength: 248 nm, pulse energy: 350 mJ per pulse, frequency: 16 Hz, pulse duration: 12—15 ns, beam shape: 9×34 mm) at room temperature. At the same time with irradiation, the aqueous 30% H_2O_2 was added to MeOH, EtOH, and MeOH–EtOH mixture with the feeding rate (f) from 3.2 to 16.0 ml h^{-1} by using a microfeeder (Atto Corp., AC-2120). For the purpose of comparison, some experiments were carried out using a steady state UV (low-pressure mercury lamp, wavelength: mainly 253.7 nm, quantity of light: 3.38×10^{18} photons s^{-1}).

Actinometry. The quantity of light from the laser was determined by using a calorimeter (Scientech 38-4UV5). The calorimeter was also placed behind the reaction vessel to determine precisely the quantity of light absorbed by alcohol–H_2O_2 mixture during the laser irradiation. The quantity of light was 4.38×10^{17} photons per pulse.

Analysis. Products were analyzed by gas chromatography (Shimadzu GC-7A: Porapak Q column, GC-4C: Porapak N or Chromosorb 101 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 the KrF laser, EG was produced as a major product together with formic acid (FA), methyl formate (MF), formaldehyde, hydrogen, carbon dioxide, carbon monoxide, and methane as minor products. Figure 1 shows the quantities of EG, FA, and MF as a function of number of photon at f=3.2 ml h^{-1}. The quantity of EG increased linearly with number of photon up to about 4.1×10^{20} photons ml^{-1}. The quantities of EG, FA, and MF were 43.3, 0.4, and 0.4×10^{-2} mmol ml^{-1}, respectively, and the sum of the quantities of other products was less than 0.1×10^{-2} mmol ml^{-1} at irradiation of 4.0×10^{20} photons ml^{-1}. The quantum yield of EG formed and the selectivity were 0.94 and 94%, respectively, at irradiation of 4.7×10^{19} photons ml^{-1}. Such high quantum yield and selectivity indicate that the formation of EG proceeds efficiently in this system. Also, when the N_2-saturated MeOH alone was irradiated in the absence of H_2O_2, organic products were hardly produced even after irradiation of about 4.1×10^{20} photons ml^{-1}.

On the other hand, in the case of steady state UV irradiation, the quantum yield of EG formed was 0.73 and the selectivity was 85% at irradiation of 3.7×10^{20} photons ml^{-1}.[3] It was found from these results that the quantum yield of EG formed and the selectivity were much larger in KrF-laser irradiation than in steady state UV one. This indicates that the KrF-laser irradiation is favorable for the effective formation of EG.

Figure 2 shows the effects of H_2O_2 feeding rate on the quantities of EG, FA, and MF. The quantity of EG decreased with increasing H_2O_2 feeding rate in the range of f=3.2—14.4 ml h^{-1}. This indicates that the H_2O_2 feeding rate is an important factor for the efficient formation of EG, and that the efficient formation of EG is favorable in lower H_2O_2 feeding rate. The sum of the quantities of FA and MF was less than 1×10^{-2} mmol ml^{-1} at f=14.4 ml h^{-1}. Table 1 shows the effects of H_2O_2 feeding rate on the quantum yield of EG formed and the selectivity. The quantum yield of EG formed decreased with increasing H_2O_2 feeding rate, that is, from 0.94 at f=3.2 ml h^{-1} to 0.56 at f=14.4 ml h^{-1}. The selectivity of EG formation was 94—97% in the wide range of f=3.2—14.4 ml h^{-1}. It was found from these results that EG was highly selectively synthesized in high quantum yield by KrF-laser irradiation of the N_2-saturated MeOH in lower H_2O_2 feeding rate ranges.

N_2-Saturated Ethanol. When the N_2-saturated EtOH containing H_2O_2 was irradiated with the KrF laser, 2,3-, 1,3-BD, and AA were produced as major products together with 1,4-BD, hydrogen, carbon dioxide, carbon monoxide, and methane as minor products. Figure 3 shows the quantities of 2,3-, 1,3-, 1,4-BD, and AA as a function of number of photon at f=3.4 ml h^{-1}. The

Table 1. Effects of H_2O_2 Feeding Rate on the Quantum Yield of Ethylene Glycol Formed and the Selectivity in the Case of KrF-Laser Irradiation of N_2-Saturated Methanol

H_2O_2 feeding rate	Number of photon	Ethylene glycol	
ml h^{-1}	10^{20} photons ml^{-1}	ϕ	Selectivity/%
3.2	0.5	0.94	94
5.3	2.5	0.68	97
8.9	1.6	0.62	97
14.4	1.6	0.56	96

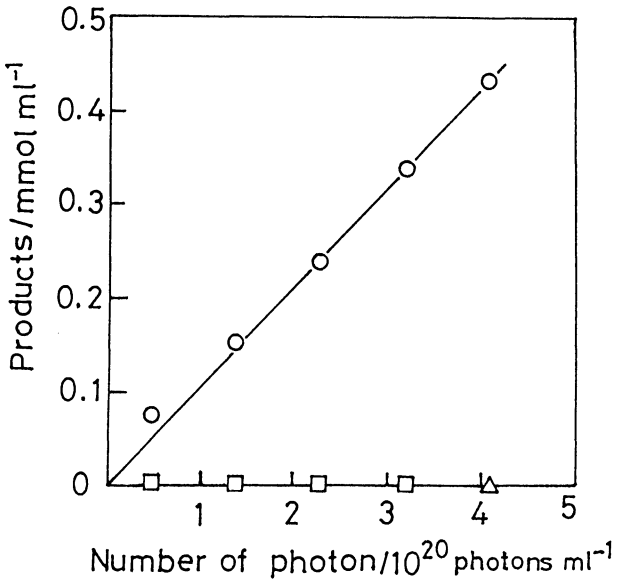

Fig. 1. Plots of the quantities of main products as a function of number of photon in the case of KrF-laser irradiation of N_2-saturated methanol.
○: Ethylene glycol, □: Methyl formate, △: Formic acid. Aqueous 30% H_2O_2 feeding rate: 3.2 ml h^{-1}.

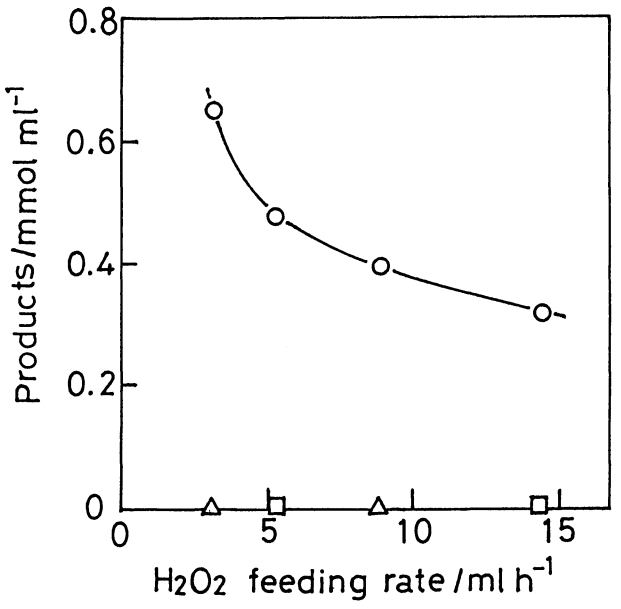

Fig. 2. Effects of H_2O_2 feeding rate on the quantities of main products in the case of KrF-laser irradiation of N_2-saturated methanol.
Symbols are the same as in Fig. 1. Number of photon: 2.8×10^{20} photons ml^{-1}.

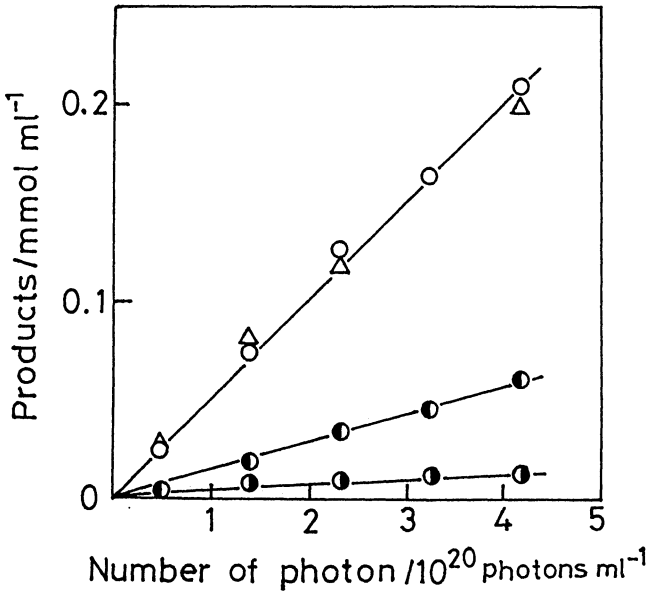

Fig. 3. Plots of the quantities of main products as a function of number of photon in the case of KrF-laser irradiation of N_2-saturated ethanol.
○: 2,3-Butanediol, ◐: 1,3-Butanediol, ◑: 1,4-Butanediol, △: Acetaldehyde. Aqueous 30% H_2O_2 feeding rate: 3.4 ml h^{-1}.

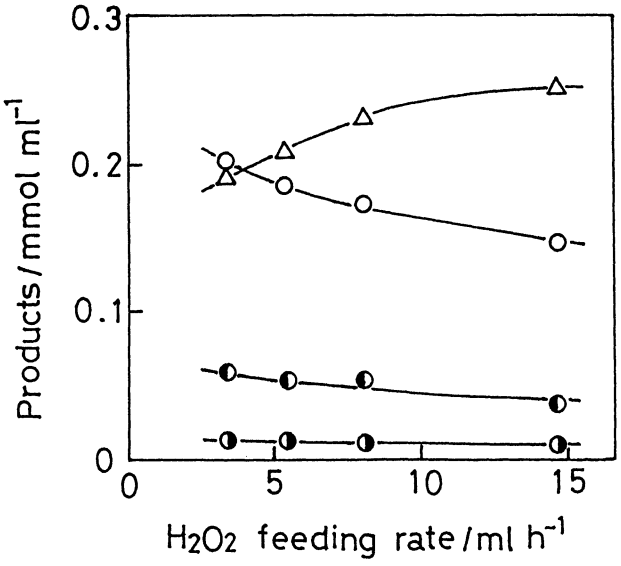

Fig. 4. Effects of H_2O_2 feeding rate on the quantities of main products in the case of KrF-laser irradiation of N_2-saturated ethanol.
Symbols are the same as in Fig. 3. Number of photon: 4.0×10^{20} photons ml^{-1}.

quantities of 2,3-, 1,3-, 1,4-BD, and AA increased linearly with number of photon up to about 4.2×10^{20} photons ml^{-1}. The quantities of 2,3-, 1,3-, 1,4-BD, and AA were 20.2, 5.8, 1.2, and 19.2×10^{-2} mmol ml^{-1}, respectively, and the sum of the quantities of other products was less than 1.6×10^{-2} mmol ml^{-1} at irradiation of 4.0×10^{20} photons ml^{-1}. The quantum yields of 2,3-, 1,3-, 1,4-BD, and AA formed were 0.31, 0.09, 0.02, and 0.29, respectively, and the selectivities were 42, 12, 3, and 40%. Also, when the N_2-saturated EtOH alone was irradiated in the absence of H_2O_2, organic products were hardly produced even after irradiation of about 4.2×10^{20} photons ml^{-1}.

On the other hand, in the case of steady state UV irradiation, the quantities of 2,3-, 1,3-, 1,4-BD, and AA were 11.6, 0.3, 0.7, and 24.7×10^{-2} mmol ml^{-1}, and the selectivities were 29, 1, 2, and 62%, respectively, at irradiation of 4.0×10^{20} photons ml^{-1}. It was found from these results that the quantity and the selectivity of BD were much larger in KrF-laser irradiation than in steady state UV one. This indicates that the KrF-laser irradiation is favorable for the effective formation of BD.

Figure 4 shows the effects of H_2O_2 feeding rate on the quantities of 2,3-, 1,3-, 1,4-BD, and AA. The quantities of BD decreased with increasing H_2O_2 feeding rate, while that of AA increased. The sum of the quantities of 2,3-BD and AA was almost constant (40×10^{-2} mmol ml^{-1}) in the wide ranges of f=3.4—14.7 ml h^{-1}. The quantity of BD was much larger than that of AA in lower f ranges, on the contrary, in higher f ranges the

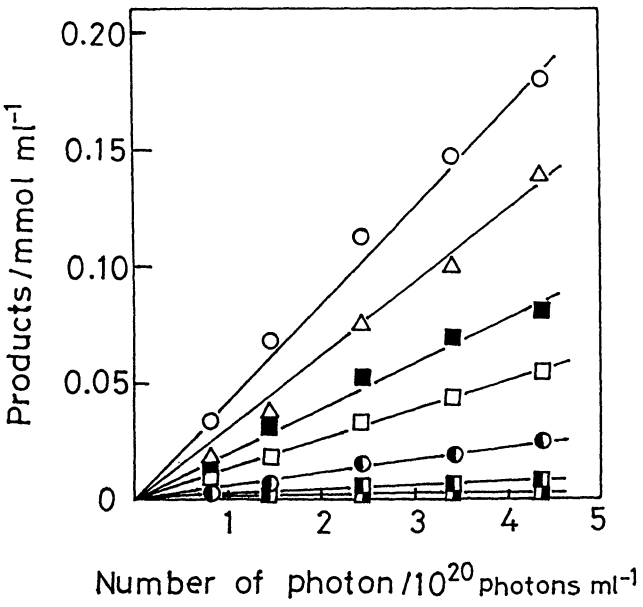

Fig. 5. Plots of the quantities of main products as a function of number of photon in the case of KrF-laser irradiation of N_2-saturated methanol–ethanol mixture.
○: 1,2-Propanediol, ◐: 1,3-Propanediol, □: 2,3-Butanediol, ◧: 1,3-Butanediol, ◨: 1,4-Butanediol, △: Ethylene glycol, ■: Acetaldehyde. Aqueous 30% H_2O_2 feeding rate: 3.6 ml h^{-1}. Methanol content: 66.7 mol%.

former was smaller than the latter. The quantum yields of BD and AA formed were 0.42 and 0.29, respectively, at f=3.4 ml h^{-1}. The combined quantum yield of BD and AA formed and the combined selectiv-

ity were 0.70—0.71 and 92—97%, respectively, in the wide f ranges. It was found from these results that BD and AA were directly and selectively synthesized by KrF-laser irradiation of the N_2-saturated EtOH containing H_2O_2. Such high combined quantum yield and selectivity indicate that the formations of BD and AA proceed efficiently in this system.

N_2-Saturated Methanol-Ethanol Mixture. When the N_2-saturated MeOH–EtOH mixture containing H_2O_2 was irradiated with the KrF laser, 1,2-PD, EG, 2,3-BD, and AA were produced as major products together with 1,3-PD, 1,3-BD, 1,4-BD, hydrogen, carbon dioxide, carbon monoxide, and methane as minor products. Figure 5 shows the quantities of main products as a function of number of photon at f=3.6 ml h^{-1}. The quantities of 1,2-PD, EG, 2,3-BD, 1,3-PD, 1,3-BD, 1,4-BD, and AA increased linearly with number of photon up to about 4.4×10^{20} photons ml^{-1}. The quantities of 1,2-PD, EG, 2,3-BD, 1,3-PD, 1,3-BD, 1,4-BD, and AA were 16.8, 12.8, 5.2, 2.2, 0.8, 0.3, and 7.8×10^{-2} mmol ml^{-1}, respectively, and the sum of the quantities of other products was less than 0.3×10^{-2} mmol ml^{-1} at irradiation of 4.0×10^{20} photons ml^{-1}.

On the other hand, in the case of steady state UV irradiation, the quantities of 1,2-PD, EG, 2,3-BD, and AA were 10.2, 9.4, 2.6, and 12.7×10^{-2} mmol ml^{-1}, respectively, at irradiation of 4.0×10^{20} photons ml^{-1}. It was found from these results that the quantities of PD, EG, and BD were much larger in KrF-laser irradiation than in steady state UV one. This indicates that the KrF-laser irradiation is favorable for the effective formation of PD, EG, and BD.

Figure 6 shows the effects of H_2O_2 feeding rate on the quantities of 1,2-PD, EG, 2,3-BD, and AA. The quantities of 1,2-PD, EG, and 2,3-BD decreased linearly with increasing H_2O_2 feeding rate, while that of AA increased. The quantities of 1,2-PD and EG were much larger than that of AA in lower f ranges, on the contrary, in higher f ranges the formers were smaller than the latter. This result indicates that the efficient formation of diols is favorable in lower f ranges.

Figure 7 shows the effects of MeOH content on the quantities of 1,2-PD, EG, 2,3-BD, and AA at f=3.6 ml h^{-1}. The quantity of 1,2-PD increased with MeOH content and reached the maximum at about 64 mol% of MeOH content. The quantity of EG increased linearly with MeOH content, while those of 2,3-BD and AA decreased. In the case of 64 mol% of MeOH content, the quantum yields of PD, EG, BD, and AA were 0.30, 0.17, 0.11, and 0.14, respectively, and the combined quantum yield was 0.72. The selectivities of 1,2-PD, EG, 2,3-BD, and AA were 36, 24, 13, and 19%, respectively, and the combined selectivity of diols and AA formation is 99%. It was found from these results that PD was directly synthesized by KrF-laser irradiation of the N_2-saturated MeOH–EtOH mixture containing H_2O_2. Such high combined quantum yield and selectivity indicate that the formation of diols such as PD, EG, and BD and AA proceeds efficiently in this system.

Reaction Mechanism. As described in the previous paper,[3] in the case of steady state UV irradiation of N_2-saturated MeOH containing H_2O_2, EG was produced

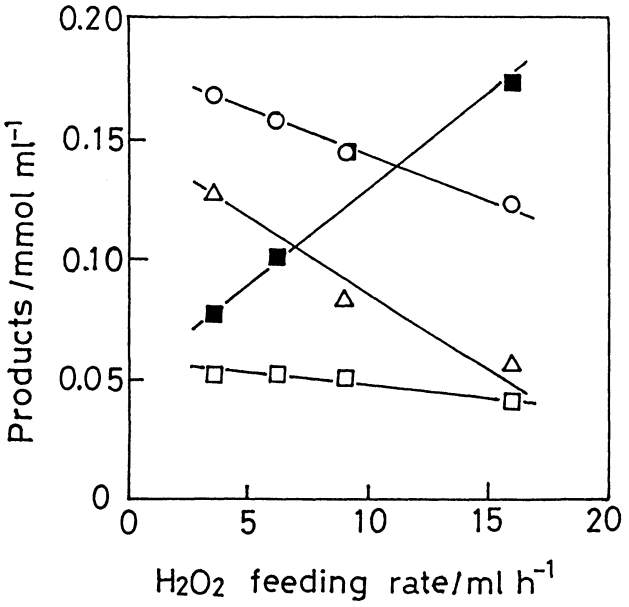

Fig. 6. Effects of H_2O_2 feeding rate on the quantities of main products in the case of KrF-laser irradiation of N_2-saturated methanol–ethanol mixture.
Symbols are the same as in Fig. 5. Number of photon: 4.0×10^{20} photons ml^{-1}. Methanol content: 66.7 mol%.

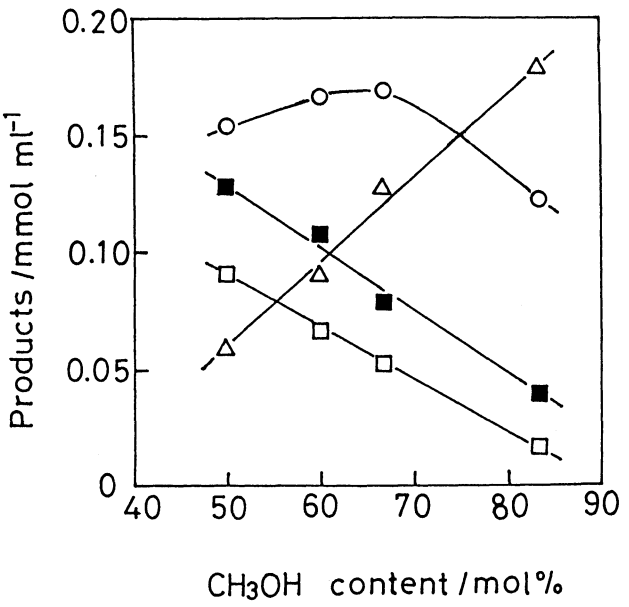

Fig. 7. Effects of methanol content on the quantities of main products in the case of KrF-laser irradiation of N_2-saturated methanol–ethanol mixture.
Symbols are the same as in Fig. 5. Aqueous 30% H_2O_2 feeding rate: 3.6 ml h^{-1}. Number of photon: 4.0×10^{20} photons ml^{-1}.

through the dimerization of hydroxymethyl radicals which were formed by the abstraction of a hydrogen atom from MeOH by hydroxyl radical formed by the photolysis of H_2O_2 as the reactions (1)—(3).

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

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

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

The UV absorption spectrum of H_2O_2 gives a strong and very broad absorption band in the wavelength range of UV and vacuum UV regions below 300 nm. The absorbance of H_2O_2 at the wavelength of KrF laser (248 nm) is about 1.3 times that at the wavelength of steady state UV (253.7 nm). In analogy with the case of steady state UV irradiation,[6] H_2O_2 is very efficiently decomposed to form hydroxyl radicals by the laser irradiation. It can therefore be considered that in the case of KrF-laser irradiation of the N_2-saturated MeOH, EG would be produced through the reactions (1)—(3). As described already, quantum yield of EG formed was much larger in the KrF-laser irradiation than in steady state UV irradiation. The light intensity is about 10^7 times larger with the KrF laser than with the low-pressure mercury lamp. It is therefore considered that in KrF-laser irradiation, hydroxyl radical would be formed in high density (Eq. 1), and the abstraction of a hydrogen atom from MeOH occurs more efficiently (Eq. 2), followed by the effective dimerization of hydroxymethyl radicals (Eq. 3).

As shown in Table 1, the high quantum yield of EG formed was obtained in lower f ranges. In the case of f=3.2 ml h^{-1}, assuming the quantum yield of hydroxyl radical formed by the reaction (1) is 2.0,[6] 94% of hydroxyl radical formed is consumed to form EG. This indicates that most of hydroxyl radicals formed are very efficiently consumed by the reaction (2). It is therefore considered that such high quantum yield of EG formed in lower f ranges by KrF-laser irradiation is attributed to the effective dimerization of hydroxymethyl radical formed in high density. Also, in higher f ranges, the quantum yield of EG formed decreased. Since EG hardly has the absorption band at 248 nm, it is considered that the decrease of EG formation in higher f ranges is mainly attributed to the scavenging of hydroxyl radical by H_2O_2 to form hydroperoxyl radical (Eq. 4).[7]

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

The hydroperoxyl radical formed by the reaction (4) reacts mainly with hydroxyl radical to form H_2O and O_2.[8]

In the case of KrF-laser irradiation of the N_2-saturated EtOH, the hydroxyl radical abstracts competitively α- or β-hydrogen atom from EtOH to form 1- or 2-hydroxyethyl radical (Eqs. 5 and 6).[9] It is therefore considered that 2,3- and 1,4-BD are produced by the dimerization of 1- and 2-hydroxyethyl radicals (Eqs. 7 and 8), respectively, and that 1,3-BD is produced by the recombination between 1- and 2-hydroxyethyl radicals (Eq. 9).

$$CH_3CH_2OH + \cdot OH \longrightarrow CH_3\dot{C}HOH + H_2O \quad (5)$$

$$CH_3CH_2OH + \cdot OH \longrightarrow \cdot CH_2CH_2OH + H_2O \quad (6)$$

$$2CH_3\dot{C}HOH \longrightarrow (CH_3CHOH)_2 \quad (7)$$

$$2\cdot CH_2CH_2OH \longrightarrow (CH_2CH_2OH)_2 \quad (8)$$

$$CH_3\dot{C}HOH + \cdot CH_2CH_2OH \longrightarrow CH_3CHOHCH_2CH_2OH \quad (9)$$

It is also considered that AA is mainly produced by the disproportionation of 1-hydroxyethyl radicals in competition with the dimerization (Eq. 10).[9,10]

$$2CH_3\dot{C}HOH \longrightarrow CH_3CHO + CH_3CH_2OH \quad (10)$$

The quantities of 2,3-, 1,3-BD, and AA formed via 1-hydroxyethyl radical were much larger than that of 1,4-BD formed via 2-hydroxyethyl radical. In the case of irradiation of 4.0×10^{20} photons ml^{-1}, the percentage of the quantity of products formed via 1-hydroxyethyl radical to that formed via 1- and 2-hydroxyethyl radicals was 91% at f=3.4 ml h^{-1}. This value is in excellent agreement with that (90%) obtained by the radiation-induced oxidation of aqueous EtOH solutions.[9] This supports the reaction mechanism for the formations of BD and AA in lower f ranges proposed above.

On the other hand, as shown in Fig. 4, the quantity of AA increased in higher f ranges. Assuming AA is produced by the reaction (10), the percentage of the quantity of products formed via 1-hydroxyethyl radical to that formed via 1- and 2-hydroxyethyl radicals was 94% at f=14.7 ml h^{-1} in the case of irradiation of 4.0×10^{20} photons ml^{-1}. This value is larger than that (91%) at f=3.4 ml h^{-1} described above. It is known that 1-hydroxyethyl radical reacts with H_2O_2 to form AA (Eq. 11).[9]

$$CH_3\dot{C}HOH + H_2O_2 \longrightarrow CH_3CHO + H_2O + \cdot OH \quad (11)$$

Assuming AA is produced by the reaction (11), the percentage of the quantity of products formed via 1-hydroxyethyl radical to that formed via 1- and 2-hydroxyethyl radicals was 91% at f=14.7 ml h^{-1} in the case of irradiation of 4.0×10^{20} photons ml^{-1}, and was in good agreement with the value (90%)[9] in reference. It is therefore considered from these results that AA is preferentially produced by the reaction (11) in higher f ranges.

In the case of KrF-laser irradiation of the N_2-saturated MeOH–EtOH mixture, the hydroxyl radical reacts with MeOH and EtOH to form hydroxymethyl, 1-, and 2-hydroxyethyl radicals. It is therefore considered that 1,2- and 1,3-PD are produced by the recombination between hydroxymethyl radical and 1-and 2-hydroxyethyl radicals (Eqs. 12 and 13), respectively.

$$\cdot CH_2OH + CH_3\dot{C}HOH \longrightarrow CH_3CHOHCH_2OH \quad (12)$$

$$\cdot CH_2OH + \cdot CH_2CH_2OH \longrightarrow HOCH_2CH_2CH_2OH \quad (13)$$

As shown in Fig. 7, the quantity of 1,2-PD reached a maximum at about 64 mol% of MeOH content. The ratio (1.7) of MeOH to EtOH at the maximum of 1,2-PD is in good agreement with the ratio ($k_{EtOH}/k_{MeOH}=1.5$)[11] of the rate constant of the abstraction of hydrogen atoms from MeOH and EtOH by hydroxyl radical. Also, the percentage of the quantity of 1,2-PD to that of total PD was 86% at irradiation of 4.0×10^{20} photons ml^{-1}. This value is close to the relative probability (90%)[9] of the abstraction of a hydrogen atom from α-position to that from β-position of EtOH by hydroxyl radical. These results support the reaction mechanism of the PD formation proposed above. Also, EG and 2,3-BD are produced by the dimerization of hydroxymethyl and 1-hydroxyethyl radicals, respectively, (Eqs. 3 and 7). AA is mainly produced by the disproportionation of 1-hydroxyethyl radicals in lower f ranges (Eq. 10) and the reaction of 1-hydroxyethyl radical with H_2O_2 in higher f ranges (Eq. 11).

References

1) "10889 No Kagaku Shohin," ed by the Kagaku Kogyo Nippo Sha, Tokyo (1989), p. 339, 416, 421; "Kagaku Binran, Oyo Kagaku," ed by the Chemical Society of Japan, Maruzen, Tokyo (1986), Part 1, p. 514.

2) Y. Shimizu, S. Sugimoto, and N. Suzuki, *Chem. Lett.*, **1989**, 333.

3) Y. Shimizu, S. Sugimoto, S. Kawanishi, and N. Suzuki, *Bull. Chem. Soc. Jpn.*, **63**, 97 (1990).

4) Y. Shimizu, S. Sugimoto, S. Kawanishi, and N. Suzuki, *Chem. Lett.*, **1989**, 2153.

5) Y. Shimizu, S. Sugimoto, S. Kawanishi, and N. Suzuki, *Chem. Lett.*, **1991**, 35.

6) F. S. Dainton and J. Rowbottom, *Trans. Faraday Soc.*, **49**, 1160 (1953).

7) L. F. Keyser, *J. Phys. Chem.*, **92**, 1193 (1988).

8) J. K. Thomas, *J. Phys. Chem.*, **67**, 2593 (1963).

9) C. E. Burchill and I. S. Ginns, *Can. J. Chem.*, **48**, 2628 (1970).

10) C. Anastasi, V. Simpson, J. Munk, and P. Pagsberg, *J. Phys. Chem.*, **94**, 6327 (1990).

11) "Kagaku Binran, Kiso" ed by the Chemical Society of Japan, Maruzen, Tokyo (1984), Part II, p. 423.