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Laser-induced Highly Selective Synthesis of Ethylene Glycol from Methanol in the Presence of Hydrogen Peroxide

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Ethylene glycol was highly selectively synthesized in high quantum yield by KrF-laser irradiation of the N_2-saturated methanol containing hydrogen peroxide.

In the previous paper,[1)] we reported that ethylene glycol (EG) was directly and selectively synthesized by mercury lamp irradiation of the N_2-saturated methanol (MeOH) containing H_2O_2. For the purpose of highly selective synthesis of EG, we have attempted to induce selectively the dimerization of hydroxymethyl radical formed in high density by the reaction of MeOH with hydroxyl radical using a KrF laser with high intensity.

MeOH (56 - 64 ml) and aqueous 30% H_2O_2 (5.9 - 20.0 vol%) were placed in a Pyrex cylindrical vessel (volume: 91.5 ml, diameter: 35.5 mm, length: 70 mm) with a Suprasil window for the incidence of laser beam and well-bubbled with nitrogen. The N_2-saturated MeOH solutions were stirred magnetically (500 rpm), and irradiated with the KrF laser (Lumonics Hyper EX-460, 248 nm, energy: 300 mJ per pulse, intensity: 3.75×10^{17} photons per pulse, frequency: 16 Hz, pulse duration (FWHM): 12 - 15 ns, beam shape: 9 × 34 mm) at room temperature. Analytical technique was the same as that in the previous paper.[1)]

When the N_2-saturated MeOH containing H_2O_2 was irradiated with the KrF laser, EG was produced as a major product and formic acid and methyl formate were produced as minor products. The quantity of EG increased gradually with number of photon up to about 1.5×10^{20} photons ml^{-1} and linearly above it in 5.9 - 20.0 vol% of H_2O_2. Organic products were hardly produced in the absence of H_2O_2.

Figure 1 shows the effects of H_2O_2 concentration on the quantum yield of EG formation and the selectivity. The quantum yield of EG formation decreased with increasing H_2O_2 concentration and the high quantum yield (Φ = 0.78 - 0.94) was obtained in 5.9 - 13.5 vol% of H_2O_2. Such the high quantum yield indicates that EG formation proceeds efficiently in this system. The selectivity of EG formation was 96 - 98% in 5.9 - 20.0 vol% of H_2O_2. 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 containing H_2O_2 below 13.5 vol%.

As described in the previous paper,[1)] in mercury lamp irradiation, EG is produced through the dimerization of hydroxymethyl radicals which are formed by the abstraction of a hydrogen atom from MeOH by hydroxyl radical formed by the photolysis of H_2O_2.[2-4] The light intensity is about 10^7 times larger with the KrF laser than with the mercury lamp. It is therefore considered that in KrF-laser irradiation, hydroxyl radical would be formed in high density, and the abstraction of a hydrogen atom from MeOH occurs more efficiently, followed by the effective dimerization of hydroxymethyl radicals.

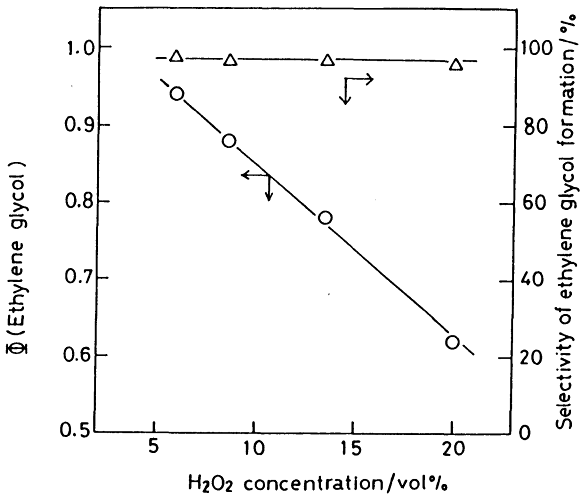

Fig. 1. Effects of H_2O_2 concentration on the quantum yield of ethylene glycol formation (Φ) and the selectivity. Number of photon: 3.5×10^{20} photons ml^{-1} (8.6, 13.5, 20.0 vol%), 2.6×10^{20} photons ml^{-1} (5.9 vol%).

As described above, the high quantum yield of EG formation ($\Phi = 0.78 - 0.94$) was obtained in lower H_2O_2 concentration by KrF-laser irradiation. In this case, assuming the quantum yield of hydroxyl radical formed by the photolysis of H_2O_2 is 2.0,[5] 78 - 94% of hydroxyl radical formed is consumed to form EG. This suggests that most of hydroxyl radicals formed are very efficiently consumed by the reaction with MeOH. It is therefore considered that such high quantum yield of EG formation in lower H_2O_2 concentration by KrF-laser irradiation is attributed to the effective dimerization of hydroxymethyl radical formed in high density. Also, EG hardly has the absorption band at 248 nm. It is therefore presumed that the decrease in the quantum yield of EG formation in higher H_2O_2 concentration is mainly attributed to the scavenging of hydroxyl radical by H_2O_2.[6] Furthermore, since the absorption coefficient of H_2O_2 at 248 nm is about 40 times larger than those of formic acid and methyl formate, those decomposition by KrF-laser irradiation would be negligible small in the presence of H_2O_2. Therefore, the high selectivity of EG formation in higher H_2O_2 concentration would be mainly attributed to the suppression of the reaction of hydroxymethyl radical with hydroperoxy radical, that is, subsequent reactions which induce the formations of formic acid and methyl formate,[7] by the recombination of hydroperoxy radicals[8] formed through the reaction of hydroxyl radical with H_2O_2.[6]

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