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Laser-induced Direct Synthesis of Butanediol and Acetaldehyde from Ethanol in the Presence of Hydrogen Peroxide

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Butanediols and acetaldehyde were directly synthesized by KrF-laser irradiation of the N_2-saturated ethanol (EtOH) containing H_2O_2.

As reported already,[1)] we found that ethylene glycol was directly and highly selectively synthesized via the effective dimerization of hydroxymethyl radicals formed by the reaction of methanol with the OH radical formed in high density by the laser-photolysis of H_2O_2. On the basis of this finding, we have attempted to synthesize directly butanediol, which is manufactured by a multi-step process using butene, butadiene or acetaldehyde obtained in petrochemical industry,[2)] from EtOH using a KrF laser.

Experimental apparatus and analytical method were the same as those used in the previous papers.[1)] The N_2-saturated EtOH was stirred magnetically and irradiated with the KrF laser (248 nm, energy: 430 mJ per pulse, intensity: 4.15×10^{17} photons per pulse, frequency: 16 Hz, pulse duration: 12 - 15 ns) at room temperature. At the same time with irradiation, the aqueous 30% H_2O_2 was added to EtOH by using a micro feeder.

When the N_2-saturated EtOH containing H_2O_2 was irradiated with the KrF laser, 2,3-, 1,3-butanediols and acetaldehyde were produced as major products together with 1,4-butanediol and ethylene glycol as minor products. The quantities of these products increased linearly with number of photon up to about 4.2×10^{20} photons ml^{-1}. Figure 1 shows the effects of H_2O_2 feeding rate (f) on the quantities of 2,3-, 1,3-, 1,4-butanediols and acetaldehyde. The quantities of butanediols decreased with increasing f, while that of acetaldehyde increased. In the case of f=3.4 ml h^{-1}, the quantities of 2,3-, 1,3-, 1,4-butanediols and acetaldehyde were 20.2, 5.8, 1.2, and 19.2×10^{-2} mmol ml^{-1} at irradiation of 4.0×10^{20} photons ml^{-1}, respectively, and the selectivities were 42, 12, 4, and 40%. The combined selectivity of butanediols and acetaldehyde was 92 - 98% in f=3.4 - 14.7 ml h^{-1}. Also, the quantum yields of 2,3-, 1,3-, 1,4-butanediols and acetaldehyde were 0.31, 0.09, 0.02, and 0.29, respectively, and the combined quantum yield was about 0.71 in f=3.4 - 14.7 ml h^{-1}. On the other hand, in the case of UV light irradiation of 4.0 × 10^{20} photons ml^{-1} (low pressure mercury lamp, mainly 253.7 nm, 3.38 × 10^{18} photons s^{-1}), the quantities of 2,3-, 1,3-, 1,4-butanediols and acetaldehyde were 11.6, 0.3, 0.7, and 24.7 × 10^{-2} mmol ml^{-1}, respectively, and the selectivities were 29, 1, 2, and 62%. It was found that the quantity of butanediol was much larger in KrF-laser irradiation than in UV light irradiation. These results indicate that butanediols were directly synthesized in high efficiency by KrF-laser irradiation of the N_2-saturated EtOH containing H_2O_2.

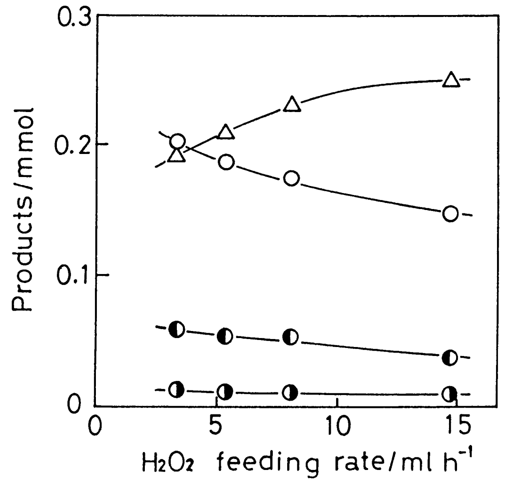

Fig. 1. Effects of H_2O_2 feeding rate on the quantities of 2,3- (○), 1,3- (◐), 1,4-(◑) butanediols and acetaldehyde (△). Number of photon: 4.0 x 10^{20} photons ml^{-1}.

The OH radical formed in high density by the laser-photolysis of $H_2O_2$1) abstracts competitively α- or β-H atom in EtOH to form α- or β-hydroxyethyl radical.3) It is therefore considered that 2,3- and 1,4-butanediols are produced by the dimerization of α- and β-hydroxyethyl radicals, respectively, and that 1,3-butanediol is produced by the recombination between α- and β-hydroxyethyl radicals. It is also presumed that acetaldehyde is produced by the disproportionation of α-hydroxyethyl radicals in competition with the dimerization.3)

The quantity of products formed via α-hydroxyethyl radical was much larger than via β-hydroxyethyl radical. The ratio was about 9.1 at f=3.4 ml h^{-1}. This value is in excellent agreement with that (9.0) obtained by the radiation-induced oxidation of aqueous EtOH solution.3) This supports the mechanism for the formation of butanediols and acetaldehyde proposed above. The increase of acetaldehyde in higher H_2O_2 feeding rate may also be attributed to the promotion of the disproportionation due to the ease of dehydrogenation in oxidative condition,4) inferring from the higher acidity of the solution after the reaction (lowering from pH=3.75 at f=3.4 ml h^{-1} to pH=3.15 at f=14.7 ml h^{-1}).

References

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