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Photoinduced Selective Synthesis of Ethylene Glycol from Methanol in the Presence of Hydrogen Peroxide

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Ethylene glycol was selectively synthesized by UV irradiation of the nitrogen-saturated methanol containing hydrogen peroxide. The concentration of ethylene glycol and the selectivity were affected markedly by a H_2O_2 feeding rate.

The direct synthesis of ethylene glycol from methanol has been investigated in the presence of organic peroxides such as di-t-butyl peroxide,[1,2] but the selectivity is not satisfactory. On the other hand, photochemical reaction of methanol using rhodium complex gave high selectivity for ethylene glycol formation,[3] however, very expensive photocatalyst is required. We report here a method for the photoinduced selective synthesis of ethylene glycol from methanol in the presence of hydrogen peroxide.

Methanol (225 ml; 5.6 mol) was placed in a Pyrex vessel and well-bubbled with nitrogen (99.9%). The N_2-saturated methanol was stirred magnetically (500 rpm), and irradiated internally with a 120 W low pressure mercury lamp (Eikosha EL-J-120, mainly 253.7 nm) at 25 °C. Under these conditions, aqueous 30% hydrogen peroxide (1 - 8 ml h^{-1}, 0.01 - 0.10 mol h^{-1}) was gradually added to the methanol with a micro feeder. Products were analyzed by gas chromatography (Shimadzu GC-7A: Porapak Q column, GC-4C: Porapak N column, and GC-3BT: Molecular sieve 5A column).

Analysis of reaction mixture showed ethylene glycol is produced as a major product and methyl formate, ethanol, acetaldehyde, formaldehyde, formic acid, hydrogen, carbon dioxide, carbon monoxide and methane are formed as minor products. Figure 1 shows the concentrations of main organic products as a function of irradiation time. The concentration of ethylene glycol increased with irradiation time and was much larger than those of other products. The concentration of ethylene glycol was 102.1 mmol and those of other products were less than about 7 mmol on irradiation for 7 h. On the other hand, organic products were hardly produced even on irradiation for 7 h in the absence of hydrogen peroxide.

The concentration of ethylene glycol produced increased with H_2O_2 feeding rate, and became the maximum at 5 ml h^{-1}. The selectivity of ethylene glycol formation decreased from 97.8% at 1 ml h^{-1} to 79.5% at 8 ml h^{-1}. At the maximun concentration of ethylene glycol, the selectivity was ca. 90.9%. Thus, the concentration of ethylene glycol and the selectivity were affected markedly by H_2O_2 feeding rate. These results show ethylene glycol is selectively synthesized

by UV irradiation of N_2-saturated methanol containing hydrogen peroxide. The quantum yield of ethylene glycol formation increased with H_2O_2 feeding rate and became the maximum (Φ = 0.73) at 5 ml h^{-1}.

It is well known that hydrogen peroxide is easily decomposed by UV irradiation to form hydroxyl radical.[4] The effect of thiocyanate ion, which is an efficient scavenger of hydroxyl radical,[5] on ethylene glycol formation has been examined. Ethylene glycol formation was almost perfectly suppressed by the addition of 0.02 mmol of potassium thiocyanate. It is concluded from these facts that hydroxyl radical is an initiating species of ethylene glycol formation. It is also known that hydroxyl radical reacts rapidly with methanol to form hydroxymethyl radical,[6] which is rapidly dimerized to form ethylene glycol in the absence of oxygen.[7] Therefore, it can be considered that the ethylene glycol formation proceeds efficiently through the quick dimerization of hydroxymethyl radicals formed by the abstraction of α-position hydrogen of methanol by hydroxyl radical.

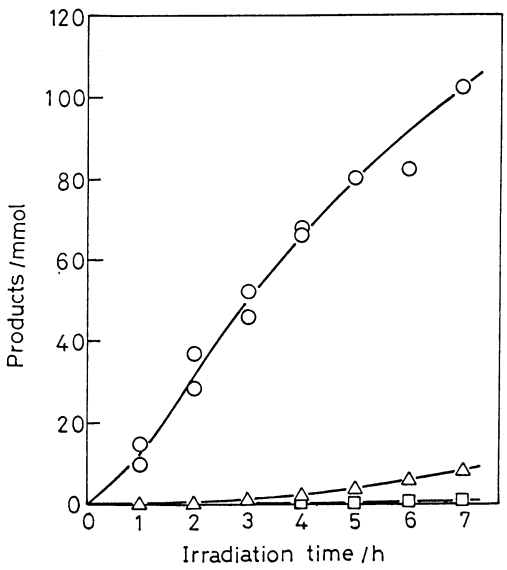

Fig. 1. Concentration of main organic products as a function of irradiation time. ○: Ethylene glycol, △: Methyl formate, □: Ethanol. CH_3OH: 225 ml, H_2O_2 feeding rate: 5 ml h^{-1}, Irradiation temp , 25 °C.

The decrease in ethylene glycol formation in higher H_2O_2 feeding rate may be mainly attributed to the scavenzing of hydroxyl radical by hydrogen peroxide.[8] It should be noted as a new method for direct synthesis of ethylene glycol from methanol that ethylene glycol is selectively synthesized by UV irradiation of the N_2-saturated methanol containing hydrogen peroxide.

References

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