Hydrogen Peroxide-catalyzed Ozonation of Refractory Organics. I. Hydroxyl Radical Formation

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Synopsis. The kinetics of hydrogen peroxide-catalyzed ozonation was studied in aqueous solutions of various lower alcohols containing ethanol as a reference. The relative rates of degradation of alcohols obtained support the initiation of the reaction by hydroxyl radicals formed in the reaction between ozone and hydrogen peroxide.

The use of ozone for water treatments has been growing steadily in responce both to increasing requirement for environmental protection and to recent improvement in the efficiency of ozone generator.[1] Ozone is known to be efficient in decolorization of effluents containing organics, but believed generally to be ineffective toward removal of COD (Chemical Oxygen Demand) and TOC (Total Organic Carbon). This may be ascribed to the characteristics of ozone which reacts very rapidly with unsaturated compounds but slowly with saturated ones.

The authors have been studying catalytic ozonation to remove COD and TOC in effluents containing refractory organics, and developed several ozonation methods, *i.e.*, high-pH ozonation,[2] UV-irradiated ozonation[3] and hydrogen peroxide (H_2O_2)-catalyzed ozonation.[4] Of these methods, H_2O_2-catalyzed ozonation is the most practical because of its simplicity and economic advantage, and was commercialized to remove COD in the effluent from an electrodeposition process.

In a series of investigations on the reaction mechanism of H_2O_2-catalyzed ozonation, the authors found that hydroxyl radical is formed and acts as an initiator for the oxidation of refractory organics. The present paper reports an experimental result supporting the OH radical formation.

Experimental

Ozonation was carried out at room temperatures (22—27 °C) by using an apparatus shown in Fig. 1. Ozone was generated from oxygen (99.98%) in a Mitsubishi OS-1 ozonizer (max. capacity, 2 g-O_3/h). The stream of ozonized oxygen from the ozonizer, containing 20 g/m^3 ozone, was passed at a constant flow rate of 1000 cm^3/min through a 1000 cm^3 gas absorption bottle (6.5 cm I.D.) filled with various solutions for ozonation. An ozone monitor was set up for measuring ozone concentration in the inlet and outlet gas stream.

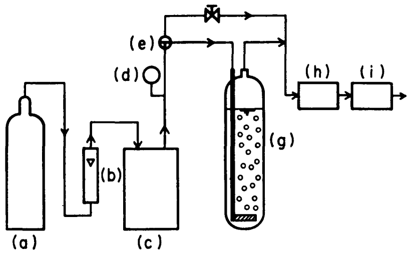

Fig. 1. Apparatus. (a): O_2-cylinder, (b): flow meter, (c): ozonizer, (d): pressure gauge, (e): three-way cock, (f): needle valve, (g): gas absorption bottle (reactor), (h): ozone monitor, (i): activated carbon column.

Aqueous solutions (*ca.* 1—10^{-1} mol/m^3) of methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, 2-butanol, and 2-methyl-2-propanol were used for the ozonation. All chemicals were of commercially available reagent grade. H_2O_2 was added to the solution just before the ozonation. The pH of the solution was kept 7.5 during the ozonation by dosing sodium hydroxide; otherwise, the pH decreased gradually with the reaction time.

The concentrations of alcohols and the reaction products were measured by a gas chromatograph with a flame ionization detector and 2 m packed columns of PORAPAK-Q, -N and TENAX-GC. H_2O_2 concentration was measured by means of iodometry using ammonium molybdate.

Results and Discussion

The degradation of ethanol by ozone (feeding rate, 20 mg/min) in the presence of H_2O_2 (initial concentration, 5×10^{-1} mol/m^3) is shown in Fig. 2. The effect of H_2O_2 on enhancement of the degradation of alcohols is remarkable. Figure 3 shows a typical reaction profile of H_2O_2-catalyzed ozonation: ethanol disappeared rapidly in the early stage of the reaction consuming about equimolar amount of ozone and acetaldehyde and acetic acid were formed in the later stage. TOC was also decreased after an induction period. The molar ratio of consumed H_2O_2 to consumed ozone was about 1/20. The amount of organics fleeing from the bottle during the ozonation was confirmed to be negligible. These results indicate clearly that H_2O_2 accelerates ozone

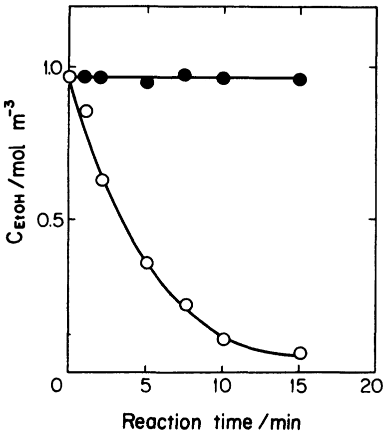

Fig. 2. Effect of H_2O_2 on the degradation of ethanol in water.
Temp: 25 °C, pH: 7.5, —○—: $[H_2O_2]_i=5\times10^{-1}$ mol/m^3, —●—: $[H_2O_2]_i=0$ mol/m^3.

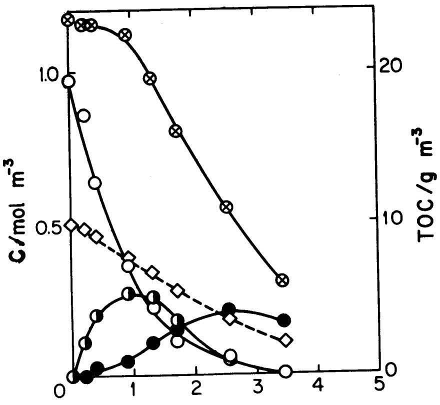

Fig. 3. H_2O_2-catalyzed ozonation of ethanol in water. Temp: 25 °C, pH: 7.5, —○—: ethanol, —◑—: acetaldehyde, —●—: acetic acid, —⊗—: TOC, --◇--: H_2O_2.

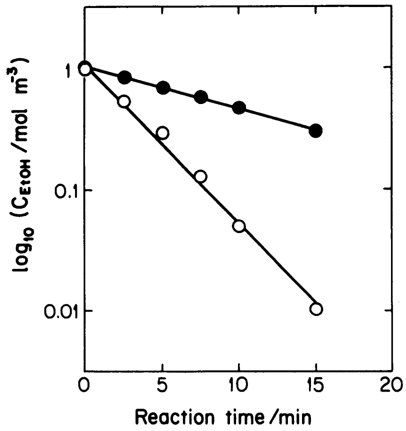

Fig. 4. Competitive degradation of ethanol and 2-methyl-2-propanol in water by H_2O_2-catalyzed ozonation.
Temp: 25 °C, pH: 7.5, —○—: ethanol, —●—: 2-methyl-2-propanol.

TABLE 1. RELATIVE DEGRADATION RATE CONSTANTS OF LOWER ALCOHOLS IN WATER BY H_2O_2-CATALYZED OZONATION AND HO RADICAL

Compound	k_{rel}	k_{ROH}/k_{EtOH} [a]
Methanol	0.40	0.46
Ethanol	1	1
1-Propanol	1.51	1.48
2-Propanol	1.17	1.10
1-Butanol	2.12	2.19
2-Methyl-1-propanol	1.93	1.80—1.91
2-Butanol	1.53	1.31—1.69
2-Methyl-2-propanol	0.28	0.28

a) Calculated value from Ref. 6.

oxidation of ethanol.

The mechanism of the acceleration may be attributed to HO radical formation by the reaction of H_2O_2 with ozone, as was suggested by Taube and Bray.[5] In order to comfirm the assumption, the relative rate constants for the degradation of several lower alcohols were determined by competition kinetic measurements, and compared with the literature values.[6] Solutions containing two kinds of alcohols, with ethanol being the reference, were ozonized in the presence of H_2O_2, and relative rate constants were obtained, by assuming first order reaction rate with respect to concentration of alcohol, from the following equation:

$$k_{rel} = \frac{\ln([C_1]_f/[C_1]_i)}{\ln([C_2]_f/[C_2]_i)},$$

where C_1 and C_2 are the concentrations of objective alcohol and ethanol, respectively, the subscripts i and f denoting the conditions before and after the reaction, respectively. Figure 4 shows a typical profile of competitive degradation obtained with a mixed solution of ethanol and 2-methyl-2-propanol. The values of k_{rel} obtained are shown in Table 1 together with those obtained for the reactions between alcohols and HO radical.[6] It should be noted that both values agree quite well with each other, which means that the oxidation of alcohols is initiated by HO radical in the H_2O_2-catalyzed ozonation.

References

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