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Study on Ozone Treatment of Water-Soluble Polymers. I. Ozone Degradation of Polyethylene Glycol in Water

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Synopsis

Polyethylene glycol (molecular weight 8000) was degraded by ozone in 1% aqueous solution of pH 12. Chemical oxygen demand of the solution decreased with increasing ozone consumed. Intrinsic viscosity of the solution lowered exponentially as a result of the ozonization. The number of breaks calculated from the viscosity indicated that two molecules of ozone were consumed for one cleavage of the polymer chain. The molecular weight distribution obtained by gel permeation chromatography was very broadened and molecular weight was lower as well, and the polymer chain was found to be cleaved randomly by ozone. The production of formic ester, ethylene glycol, diethylene glycol, triethylene glycol, and hydrogen peroxide was confirmed by IR, NMR, gas chromatography, and chemical analysis. These observations could be accounted for by electrophilic attack of ozone on the ether bond.

INTRODUCTION

In recent years, the treatment of waste polymer has been studied from the point of a protection against environmental pollution. Much excellent work concerning the degradation of water-insoluble polymers has been published, while little attention has been paid to degradation of water-soluble polymers such as polyethylene glycol, polyacrylamide, and poly(vinyl alcohol). These polymers are widely used as water-treatment agents or food additions in spite of hardness of their degradation in nature. They are abundantly exhausted and accumulated as environmental pollutants. Therefore, these water-soluble polymers have to be removed or to be treated in order to enable them to be degraded in nature in case of abundance.

So far as the previous investigators are concerned, poly(vinyl alcohol) is known to be utilized by *Pseudomonas* sp.,[1] and can be treated using activated sludge.[2] The polyethylene glycol (PEG) of low molecular weight (approximately less than 400) is also utilized by *Pseudmonas* sp.,[3] but PEG of high molecular weight can never be completely utilized. Therefore, it is very important to carry out chemical degradation in order to enable it to be utilized by microorganisms.

This investigation was undertaken to obtain information on the degradation of polyethylene glycol by ozone in water, and to determine if the ozone treatment of PEG could be a suitable method for the purpose described above.

The reaction of ozone with ethers have been reported by many workers. In 1964, the course of ozonization of simple ethers was reported by Price and Tumolo,[4] and the reaction was explained by electrophilic attack of ozone on the ether bond. Also, the ozonization of PEG in chloroform was dealt with briefly by them in another report.[5] However, the details of the ozonization products were not revealed.

In this report, the ozone degradation of PEG in water was studied by measurement of chemical oxygen demand and molecular weight variation and analysis of products.

EXPERIMENTAL

Polyethylene glycol was obtained from Union Carbide Chemical Company. The molecular weight was 8000 (by gel permeation chromatography). The ozonization of the PEG was carried out in 1% aqueous solution which was prepared to pH 12 with 1*N* sodium hydroxide. The apparatus used for the ozonization is shown in Figure 1. The ozonator used in this research was a Nippon Ozone Model 0-1-2 laboratory ozonator. The ozone source was air, and the evolution rate of ozone was 9.1 mg per minute. The residual ozone was absorbed in the absorber with 2% aqueous solution of potassium iodide and determined by an iodometry. The amount of ozone consumed in the reactor was calculated from the difference between the residual ozone and the evolved ozone. The amount of ozone consumed was described in terms of value per liter of PEG solution (1%).

The chemical oxygen demand (COD) of the ozonized solution was measured by the oxidation method with potassium dichromate.

The intrinsic viscosity of the ozonized PEG was measured in water at 30°C with an Ubbelohde viscometer. Although not strictly accurate for degraded PEG, the following equation[6] concerning PEG was used to estimate weight-average molecular weight:

$$[\eta] = 12.5 \times 10^{-5} \mathrm{Mw}^{0.78}$$

The number of breaks of PEG polymer chain was estimated according to the method of Sakurada.[7]

The ozonized solution was lyophilized, and the molecular weight distribu-

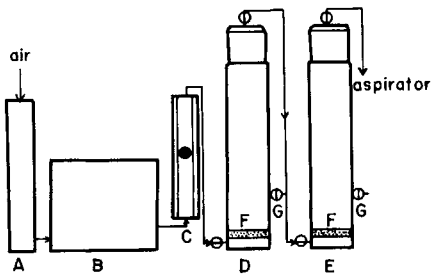


Fig. 1. Apparatus of ozonization: (A) drying tube packed with silica gel and sodium hydroxide for the purpose of removal of CO_2 and H_2O; (B) ozonator (evolution rate, 9.1 mg/min); (C) flowmeter; (D) ozonization reactor (solution volume 250 ml); (E) ozone absorber (2% KI aqueous solution); (F) gas dispersion plate; (G) sampling cock.

tion of the dried samples were measured by gel permeation chromatography (GPC) with a Waters GPC 200. Tetrahydrofuran was used as the solvent.

The IR spectra of the dried samples were observed by the KBr disk method with a Hitachi 225 infrared spectrophotometer.

The NMR spectra of the dried samples were obtained in carbon tetrachloride solution at room temperature with a JNM-4H 100 Mc/sec NMR spectroscope. Chemical shifts were given in τ-values.

The ester group in the ozonized PEG was determined colorimetrically by hydroxamic acid formation using ethyl formate as standard.[8]

The peroxide in the ozonized solution was determined by iodometry.

A Shimazu Model GC-3B gas chromatograph equipped with a hydrogen flame ionization detector was used for the quantitative and qualitative analysis of the ozonization products. A stainless steel column of 2 m × 3 mmϕ packed with 20% PEG 20M on 60 to 80 mesh acid-washed Chromosorb G was used. The column temperature was 180° and 220°C. The carrier gas was nitrogen with a flow rate of 30 ml/min, and other gases were hydrogen at a flow rate of 30 ml/min and air at a flow rate of 800 ml/min. Identification was performed in comparison with the elution time of unknown compounds to that of authentic compounds. Those compounds were determined by gas chromatograph peak areas using triethylene glycol dimethyl ether as internal standard.

RESULT AND DISCUSSION

Decrease of COD by Ozonization

In order to know the effect of pH on the ozonization of PEG aqueous solution, the ozonization was carried out in acidic (pH 2) and basic (pH 12) solu-

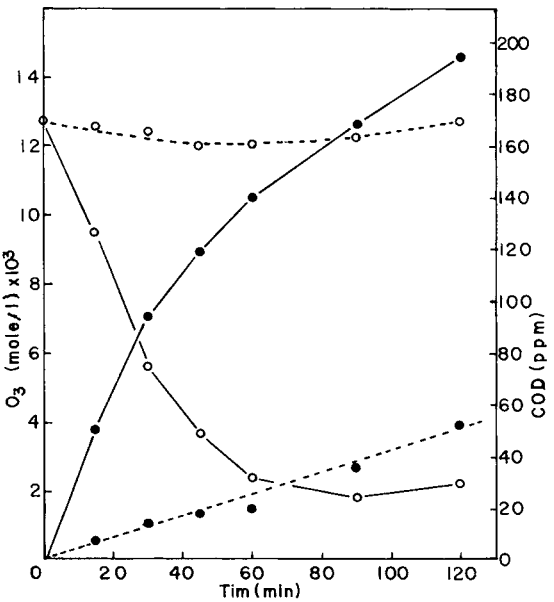


Fig. 2. Effect of pH on ozonization: full line, pH 12; dashed line, pH 2; (●) amount of ozone consumed; (○) COD of solution (0.01%).

TABLE I
COD of Ozonized PEG Solution (1%)

Reaction time, min	Ozone consumed, (moles/l.) × 10^3	COD, mg/l.	Oxygen uptake,[a] (moles/l.) × 10^3	O/O_3 ratio[b]
0	0	17,690	0	—
15	11.46	17,316	23.4	2.0
30	23.19	16,869	51.3	2.2
45	35.24	16,682	63.0	1.8
60	47.69	16,234	91.0	1.9
90	73.56	15,413	142.3	1.9
120	99.73	15,003	167.9	1.7

[a] Oxygen atom used for oxidation of PEG.
[b] Molar ratio of oxygen uptake to ozone consumed.

tion of 0.01%. The extent of oxidation was confirmed by the measurement of COD. As shown in Figure 2, the ozone oxidation was found to proceed little in acidic solution. Therefore, the following experiments were carried out at pH 12.

The value of COD of PEG solution which was not ozonized was approximately equal to the calculated value of oxygen required to oxidize completely the PEG to CO_2 and H_2O. Accordingly, oxygen uptake into the PEG by ozonization can be calculated from the decrease in COD. Naturally, the value includes the oxygen incorporated to CO_2 or H_2O. Table I shows the reaction time, the ozone consumed, the COD, and the oxygen uptake in the ozonization of 1% PEG solution at pH 12. The molar ratio of the oxygen uptake to

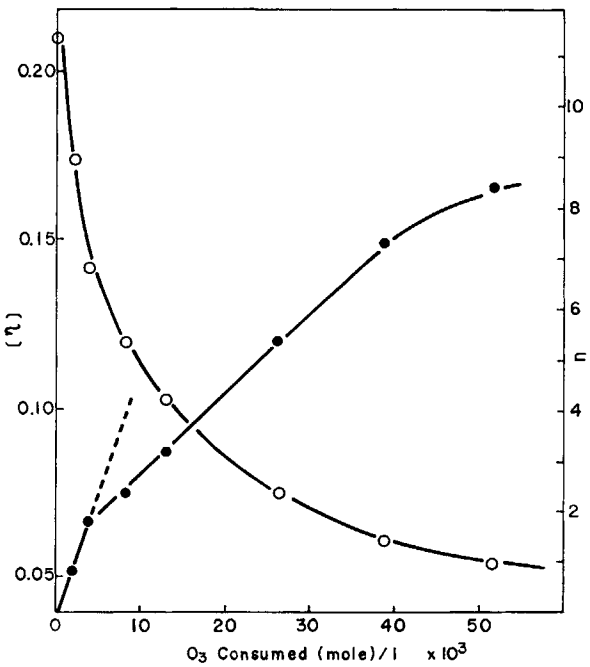


Fig. 3. Relationship between ozone consumed and intrinsic viscosity or number of breaks: (○) intrinsic viscosity; (●) number of breaks.

TABLE II
Molecular Weight Distribution of Ozonized PEG

Reaction time, min	Ozone consumed, (moles/l.) × 10^3	M_w	M_n	M_w/M_n
0	0	8000	7800	1.03
2.5	2.0	5400	3700	1.46
60	43.9	1400	700	2.00

the ozone consumed is shown in the last column. These results indicate that the ozone oxidation proceeds in proportion to the ozonization time or the ozone consumed. From the O/O_3 ratio, the two oxygen atoms of one ozone molecule are found to be used for the oxidation of PEG.

Variation of Molecular Weight

The intrinsic viscosity of the ozonized solution was measured in order to evaluate the lowering of molecular weight caused by the ozonization. Also, the number of breaks of the polymer chain was calculated from the viscosity according to the method of Sakurada. The results were plotted against the ozone consumed per liter of the PEG solution (1%) as shown in Figure 3. The intrinsic viscosity was lowered exponentially with increasing ozone consumed. The plot of the number of breaks against the ozone consumed did not give a single straight line. This phenomenon seems to be due to the production of such low molecular weight compounds which do not affect the viscosity.

Actually, a considerable quantity of ethylene glycol and diethylene glycol was confirmed, which will be described later. The initial slope of the plots, which may not be influenced by those compounds, indicates that about two molecules of ozone are consumed for one cleavage of the PEG chain.

Figure 4 shows the elution pattern of the ozonized PEG by gel permeation chromatography. In this case, the following relation existed between the elution volume V and the molecular weight M with respect to standard PEG:

$$\log M = -0.2V + 8.3.$$

From the equation and the elution pattern in Figure 4, the weight-average molecular weight and the number-average molecular weight of the ozonized PEG were calculated according to the method of Cazes,[9] and the M_w/M_n ratio, which is an indication of a molecular weight distribution, was determined.

The calculated values are shown in Table II. From the data it was found that the original PEG was a monodispersed polymer and that the molecular weight distribution was very broadened and the molecular weight lowered as a result of the ozonization. The above-mentioned results suggest that the polymer chain of PEG is cleaved randomly by ozone.

Ozonization Products

Figure 5 shows the IR spectra of the original PEG and the ozonized PEG, which have been lyophilized. The ozonized PEG had a broad spectrum over the whole range compared with the original PEG. However, at the wave

number of the main absorption peak, except the absorption band at 1720 cm^{-1}, no remarkable difference was observed. This phenomenon may be due to the production by the ozonization of various molecules with a similar structure. The new absorption band was assigned to carbonyl stretching vibration, and the absorption intensity increased with ozonization time.

The NMR spectra of the same samples were observed in carbon tetrachloride solution. For the original PEG, the single signal arising from equivalent methylene proton was observed at 6.5τ. But the signal of terminal hydroxyl proton was not detected. On the other hand, the spectrum of the ozonized PEG had a singlet at 2.0τ, a triplet at nearly 5.8τ, and a singlet at 5.95τ, besides the signal of the equivalent methylene proton as shown in Figure 6. Also a triplet appeared to the left shoulder of the methylene peak. The singlet at 5.95τ alone disappeared by adding heavy water to the solution, and hence the signal was assigned to a hydroxyl proton. The singlet at 2.0τ was assigned to the aldehyde proton adjacent to ether oxygen (—O—CHO, namely, formic ester) on the basis of the fact that coupling was not observed and that the resonance was shifted to high field compared with a general aldehyde, while no other signal corresponding to a general aldehyde or a carboxyl group was observed even at further low field. The triplet at nearly 5.8τ and the triplet of the left shoulder of the methylene peak at 6.5τ and the same coupling constant of 5.0 c/sec. Also, the intensity of the triplet at 5.8τ was

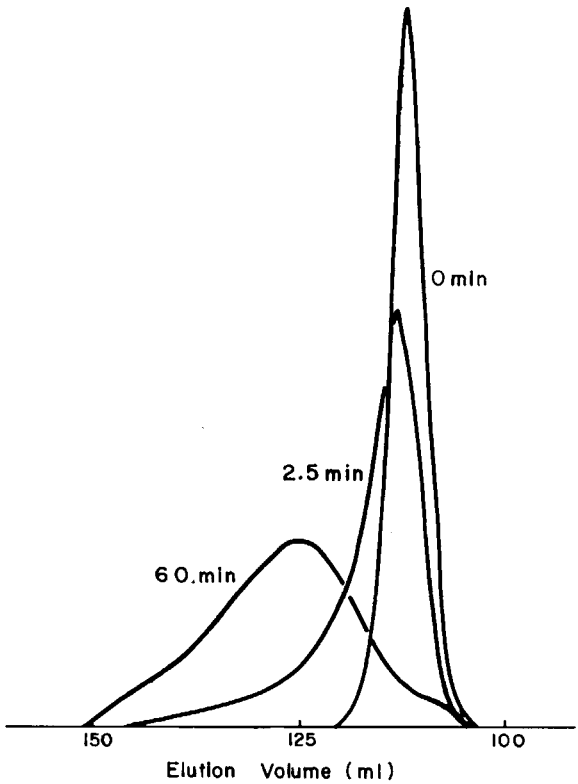


Fig. 4. Variation of GPC elution pattern of PEG by ozonization. Figures in each pattern show ozonization time.

TABLE III
Ozonization Products of PEG

Reaction time, min	Ozone consumed, (moles/l.) × 10^3	Formic ester (moles/l.) × 10^3	Formic ester mole-%[a]	H_2O_2 (moles/l.) × 10^4	H_2O_2 mole-%[a]	pH
0	0	0	0	0	0	12.0
2.5	2.0	1.0	50	0.8	4	11.8
5	3.4	2.2	65	2.5	7	11.6
10	7.6	5.1	67	4.2	6	9.9
15	12.4	8.3	67	4.0	3	8.5
30	24.6	16.0	65	3.7	2	7.7
45	35.3	20.9	59	4.8	1	7.6

[a] Mole percentage per mole ozone consumed.

about two times that of the aldehyde signal. From these result, the triplet at nearly 5.8τ was assigned to α-methylene to the formic ester, and the triplet of the left shoulder of the peak at 6.5τ was assigned to β-methylene to the ester ($-\overset{\beta}{O}CH_2\overset{\alpha}{C}H_2OCHO$). These observations indicate that the formic ester was freshly produced by the ozonization. Consequently, it can be concluded that the absorption band of carbonyl at 1720 cm^{-1} on the IR spectrum arises from the formyl group.

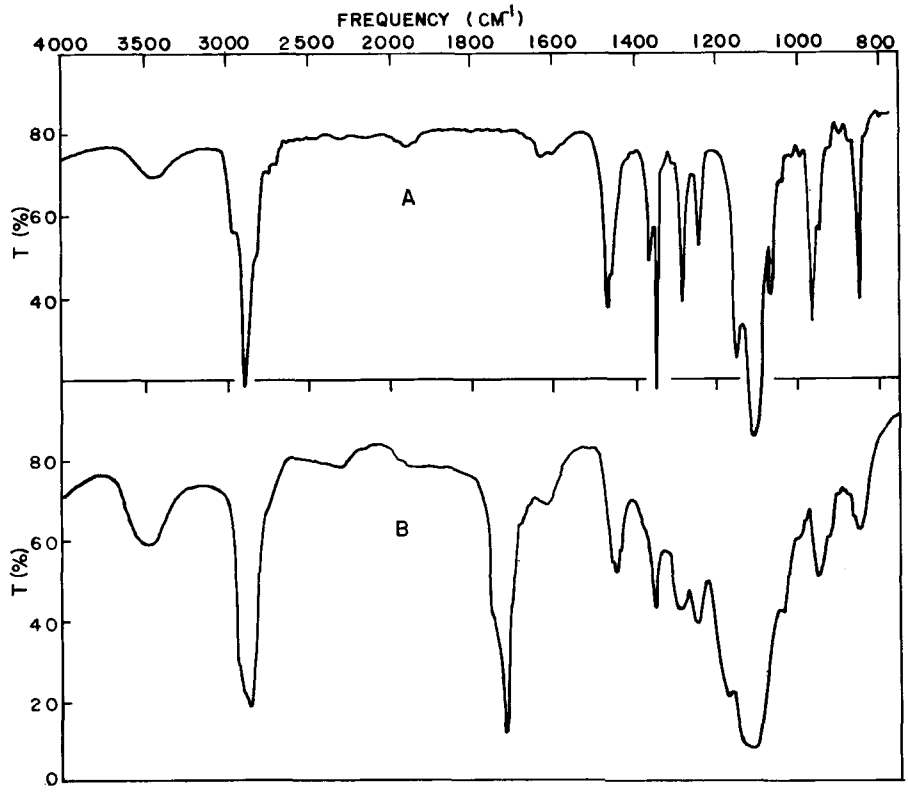


Fig. 5. IR spectra of ozonized PEG (KBr disk): (A) original PEG; (B) ozonized PEG.

Next, the formic ester was determined colorimetrically by hydroxamic acid formation. The results are shown in Table III together with the ozone consumed, the hydrogen peroxide, and the pH of the ozonized solution. The amount of ester produced was 60–70 mole-% of the ozone consumed, and was approximately constant.

On the other hand, the production of the carboxyl group was expected from the decline in pH of the ozonized solution. Therefore, the carboxyl group in the same sample was esterified with ethylene glycol, and then the ester was determined again. But the analytical results were about the same as the values in Table III. Consequently, the production of carboxyl group seems to be small.

The hydrogen peroxide in the ozonized solution was ascertained by the purple coloration with potassium dichromate[10] and determined by iodometry.

The gas chromatogram of the ozonized solution is shown in Figure 7. The aqueous solution was injected directly into the column. The column temperature was at 180°C and then at 220°C, which was the limiting temperature of the column packed with PEG–Chromosorb. In the gas chromatogram of Figure 7, the individual distinct peaks were confirmed to be ethylene glycol (EG), diethylene glycol (DEG), and triethylene glycol (TEG), respectively, in comparison with the elution time of the peak to that of each authentic compound.

The amounts of EG and DEG in the ozonized solution were determined by the peak area of the gas chromatogram. The results are shown in Table IV. Both EG and DEG increased in proportion to the reaction time or the amount of ozone consumed. The amount of EG produced was 8 mole-% of

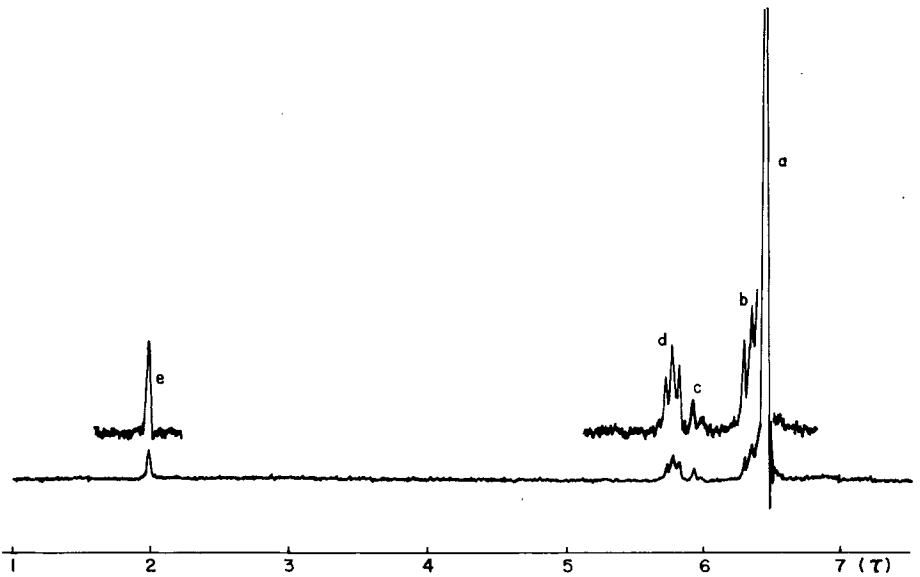


Fig. 6. NMR spectrum of ozonized PEG: (a) singlet at 6.5τ; (b) triplet at shoulder of (a), coupling const. 5 c/sec; (c) singlet at 5.95τ, disappeared upon addition of D_2O; (d) triplet at 5.8τ, coupling const. 5 c/sec; (e) singlet at 2.0τ.

TABLE IV
EG and DEG Produced by Ozonization of PEG

Reaction time, min	Ozone consumed, (moles/l.) × 10^3	EG (moles/l.) × 10^3	EG mole-%[a]	DEG (moles/l.) × 10^3	DEG mole-%[a]
15	11.3	1.58	14	—	—
30	22.7	1.75	8	—	—
45	34.5	2.37	7	1.35	4
60	46.5	3.54	8	1.53	3
90	70.9	5.88	8	2.40	3
120	97.2	7.84	8	3.39	3

[a] Mole percentage per mole ozone consumed.

the ozone consumed, and was about two times that of the DEG. This result suggests that a hydroxyl group resists the attack of ozone, and hence many compounds with terminal hydroxyl groups other than EG, DEG, or TEG may be freshly produced although such compounds could not be detected in the column condition.

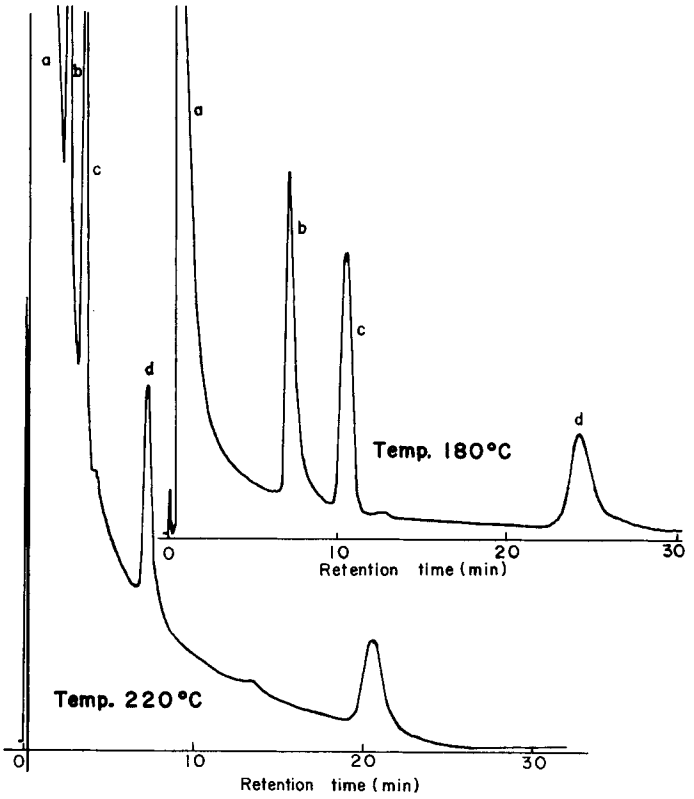
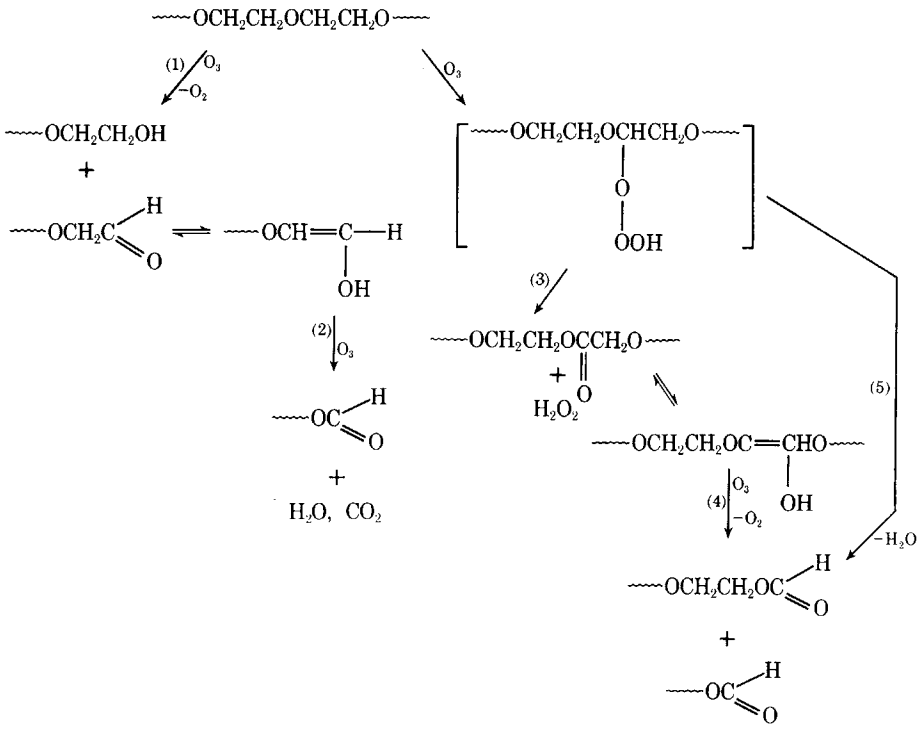


Fig. 7. Gas chromatogram of ozonized PEG solution: column condition, stainless steel column 2 m × 3 mmϕ packed with 20% PEG 20M on 60 to 80 mesh acid-washed Chromosorb G; (a) water; (b) EG; (c) internal standard of triethylene glycol dimethyl ether; (d) DEG; (e) TEG.

Degradation Mechanism

As mentioned above, it was found that the PEG chain was cleaved randomly by ozone and that compounds with a terminal hydroxyl group and formic esters were formed as the chief products of the ozonization. These observations can be accounted for by electrophilic attack of ozone on the ether bond, as Price and Tumolo proposed for the ozonization of simple ethers. The degradation course is shown in the following scheme by reference to their proposal:



The aldehyde produced in reaction (1) and the ester produced in reaction (3) contain the methylene activated by both ether and carbonyl, and hence seem to show tautomer-like behaviors as shown in the scheme. In the enolic form, the double bonds may be readily attacked by ozone and lead to a formic ester, reactions (2) and (4). With this postulate, it is possible to interpret the fact that such an aldehyde is not observed in the NMR spectrum. In the ozonization of PEG, consequently, it is found that the formic ester is produced in every reaction.

On the other hand, the oxygen uptake in each reaction is one atom in reactions (1) and (4), two atoms in reaction (3), and three atoms in reactions (2) and (5). Therefore, the data of COD can be accounted for by reactions (1) and (2). This information on COD and the production of the EG, DEG, and TEG suggest that reactions (1) and (2) are the main reactions in the ozone degradation of PEG. Also reaction (3) seems to be a few per cent per ozone consumed, judging from the amount of hydrogen peroxide produced.

Consequently, the ozone consumed apparently for one cleavage of PEG

chain is two molecules. This agrees with the value estimated from the viscosity.

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