

Ozone Treatment of Water-Soluble Polymers. V. Ultraviolet Irradiation Effects on the Ozonization of Polyacrylamide

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Synopsis

Polyacrylamide was ozonized in aqueous solution (at pH 2, 7, and 11) under UV irradiation with a low-pressure mercury lamp. The breakage of the polymer chains by ozone was strongly accelerated by UV irradiation under acidic and neutral conditions. Formaldehyde was produced characteristically in the UV ozonization. From the correlation between the amount of formaldehyde and the number of breaks of polymer chains, it was presumed that one molecule of formaldehyde resulted from the chain breakage, at least under acidic conditions. The intensity of the UV absorption peak at 266 nm (285 nm in the UV ozonization at pH 2), which was presumed to be due to the carbonyl groups, namely, ketone and terminal aldehyde produced by ozonization, was very much stronger than that in simple ozonization. Oxamic acid and oxamide as end products were observed in the solution which was ozonized exhaustively under UV irradiation.

INTRODUCTION

Recently, UV irradiation has been ascertained to be effective for wastewater treatment and the oxidation of organic material by ozonization. Horikawa et al. reported the ozone treatment of many organic compounds, glucose, starch, etc., under UV irradiation.¹ Nakayama found that the UV ozonization was especially effective for the oxidation of carboxylic acids, e.g., sodium acetate.² UV ozonization of 2-propanol, acetic acid, and oxalic acid was reported by Kuo³ et al., and that of phenol was reported by Wakao.⁴ Only recently Nakayama et al. stated that the UV irradiation effect on the ozonization of organic materials is due to OH radicals produced by the photolysis of ozone in water.⁵

On the other hand, it was reported in the previous paper⁶ that both the rate and the efficiency of the ozonization of polyacrylamide (PAA) were poor. Under acidic and neutral conditions, particularly, the direct attack of ozone was not observed, and the degradation of PAA was restricted by the self-decomposition of ozone. Hoigne and Bader reported that OH radicals are the principal oxidizing intermediates formed in the decomposition of ozone catalyzed by hydroxide ions in water.⁷ If the acceleration of ozonization by UV irradiation is due to OH radicals, the UV irradiation is expected to be also effective for the ozonization of such refractory polymers.

Accordingly, investigating the UV ozonization of refractory polymer (PAA) is significant for evaluating the availability of UV irradiation upon ozone treatment of PAA and also for elucidating the mechanism of the UV irradiation effect upon ozonization. In this work, PAA was ozonized both with and without UV irradiation, and the UV irradiation effects were studied.

EXPERIMENTAL

Polyacrylamide was the same sample as that used in the previous paper,⁶ whose viscosity-average molecular weight was 280,000. The ozonization and UV ozonization of PAA was carried out in 0.1% (distilled water solution) and 1% aqueous solutions that were prepared to pH 2, 7, and 11 with the prescribed buffer solution. The ozonization apparatus is illustrated in Figure 1. The reactor was equipped with a 15-W low-pressure mercury germicidal lamp (Toshiba GL-15) for the UV ozonization study. The ozone feed to the reactor had a flow rate of 8 mg/min. The other ozonization techniques were the same as those described previously.⁸

The number of breaks in the PAA chain was estimated according to the method described previously⁸ on the basis of the intrinsic viscosity measured in 1.0M NaNO₃ aqueous solution.

The molecular weight distributions of the ozonized samples were measured by gel filtration chromatography with Sephadex G-25 (column size 2.6φ × 100 cm). Phosphate buffer (0.5M, pH 7) was used as solvent. The other chromatography conditions were as previously described.⁹ The total organic carbon (TOC) of the solutions was measured with a Shimadzu TOC analyzer.

The formaldehyde produced by ozonization was determined colorimetrically by using 4-amino-3-hydrazino-5-mercapto-1,2,4-triazol,¹⁰ which is a specific coloration reagent for formaldehyde in case potassium periodate is used as an oxidation reagent. The other aldehyde groups were determined colorimetrically by the 3-methyl-2-benzothiazolinone hydrazone method¹¹ using formaldehyde as standard. However, this method was applicable only up until the sample was completely ozonized, because PAA precipitated in acetone when used as analytical solvent. Carbonyl groups (aldehyde and ketone) were determined colorimetrically by the vanillin method¹² using cyclohexanone as standard. In this method, the color is not developed by formaldehyde.

Acids in the ozonized solution were separated and identified preliminarily by paper chromatography using ether:acetic acid:water (13:3:1) as solvent and bromophenol blue (0.04% ethanol solution, pH 6.7) as color reagent.¹³

The UV spectra of the ozonized solutions were obtained with a Hitachi 323 recording spectrophotometer.

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

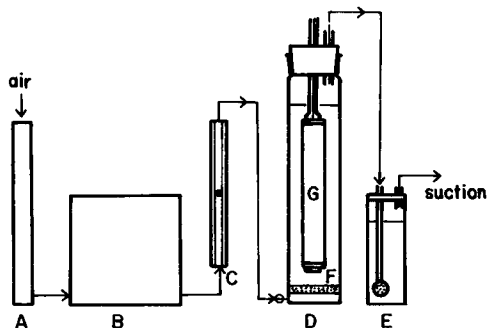


Fig. 1. Apparatus for ozonization: (A) drying tube packed with silica gel and sodium hydroxide for the purpose of removal of CO₂ and H₂O; (b) ozonator (evolution rate, 8 mg/min); (C) flowmeter; (D) ozonization reactor (solution volume, 450 ml); (E) ozone absorber (2% KI aqueous solution); (F) gas dispersion plate; (G) low-pressure mercury germicidal lamp (Toshiba GL-15).

RESULTS AND DISCUSSION

Effects of UV Irradiation

Ozone has an absorption maximum¹⁴ at 260 nm and is activated by UV irradiation. The values shown in Table I are the decomposition rates of ozone in the reactor with and without UV irradiation. Under neutral and acidic conditions the decomposition of ozone was found to be strongly accelerated by UV irradiation, although no such UV effect was observed under basic conditions.

Table II shows the rate of chain breakage and the amount of ozone consumed per one breakage of polymer chain calculated from the decrease of intrinsic viscosity and the amount of ozone consumed. It can be seen from these data that the rate of chain breakage is very much accelerated by UV irradiation at pH 2 and 7, in analogy with the decomposition rate of ozone. It is noteworthy that PAA is degraded markedly under UV irradiation even in acidic solution. The amount of ozone consumed per one break of the polymer chain, that is, the breakage efficiency of the chain by ozone, was much increased under acidic conditions. The accelerations of the rate of chain breakage is explicable by the acceleration of ozone decomposition, but the improvement of the breakage efficiency of the chain is not always explicable.

An important characteristic in the UV ozonization of PAA was the production of a large amount of formaldehyde, which was scarcely produced in simple ozonization. The largest amount of formaldehyde was produced under acidic conditions. In addition, a correlation was observed between the amount of formaldehyde and the number of chain breaks. Figure 2 shows the correlation under respective pH conditions. The total breakage number was calculated from the following equation:

$$T = nC/M_0$$

where T is the total breakage number (mole/liter), n is the number of breaks in the polymer chain,⁸ C is the concentration of PAA (g/liter), and M_0 is the molecular weight of the original PAA. As can be seen from Figure 2, the amount of formaldehyde produced at pH 2 is approximately equal to the total breakage number. This fact indicates that one molecule of formaldehyde arises from one

TABLE I
Self-Decomposition Rate of Ozone

	Rate, mg/min		
	pH 2	pH 7	pH 11
Ozonization	1.07	1.14	3.12
UV Ozonization	4.81	5.35	3.28

TABLE II
Rate and Efficiency of Chain Breakage by Ozonization

	Rate of chain breakage, hr ⁻¹			Ozone consumed per break, moles		
	pH 2	pH 7	pH 11	pH 2	pH 7	pH 11
Ozonization	0.6	3.6	24.6	322.6	21.2	12.8
UV Ozonization	40.2	28.8	33.0	12.4	20.9	11.2

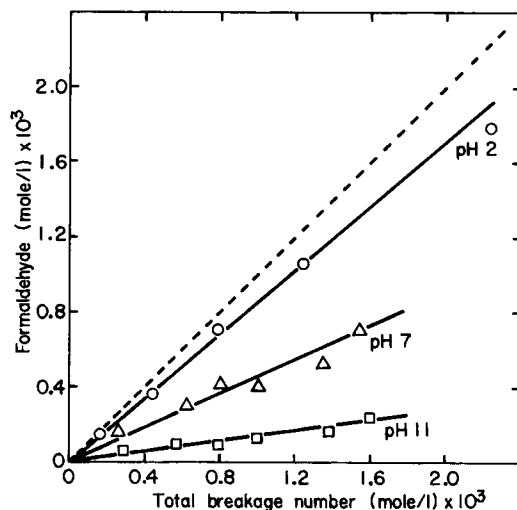


Fig. 2. Correlation between amount of formaldehyde produced by UV ozonization and the number of breaks of PAA chains: broken line shows the correlation in which the amount of formaldehyde is equal to the total breakage number; total breakage number (T) was calculated from the equation $T = nC/M_0$ (C , concentration of original PAA; n , number of breaks of PAA chain; M_0 , molecular weight of original PAA).

breakage of the polymer chain. On the other hand, the amount of formaldehyde in neutral and basic solutions was less than the total breakage number. Such results seem to be caused by the fact that formaldehyde is liable to be oxidized by ozone under neutral and basic conditions.

It was reported in the previous paper⁹ that a strong absorption peak appeared newly at 266 nm when PAA was ozonized. This same absorption peak was observed also in ozonization with UV irradiation under basic and neutral conditions. Under acidic conditions, the absorption peak was scarcely observed in the ozonized solution but appeared clearly when the ozonized solution was basified by addition of strong base (0.5N NaOH). The wavelength of the absorption maximum, however, was 285 nm, unlike that (266 nm) under neutral and basic conditions. Figure 3 shows the plots of the absorbance (266 nm at pH 7 and 11, and 285 nm at pH 2) against the ozonization time. The absorbance in neutral and acidic solution is the value measured after 0.5N NaOH was added into the solution. The absorbance in UV ozonization under acidic and neutral conditions is found to be much larger than that in simple ozonization. There was no difference in the absorbance both in ozonization and UV ozonization at pH 11.

Figure 4 shows the gel filtration pattern (G-25) of the solution ozonized under UV irradiation at pH 2 for 120 min, depicted on the basis of the TOC and the absorbance at 285 nm in respective fractions. The absorbance at 285 nm was observed under basic conditions after 0.5N NaOH was added to each fraction. The intensity of the pattern based on the UV method tends to be stronger than that of the pattern based on the TOC method in the large effluent volume, i.e., the low molecular weight region. This result indicates that a terminal group of ozonized PAA is involved in the UV absorption band at 285 nm. Such apparent deviation of the gel filtration pattern based on UV absorbance (at 266 nm) from the TOC pattern was not observed in the samples ozonized at pH 7 and 11. However, both absorption bands at 266 and 285 nm behaved similarly upon

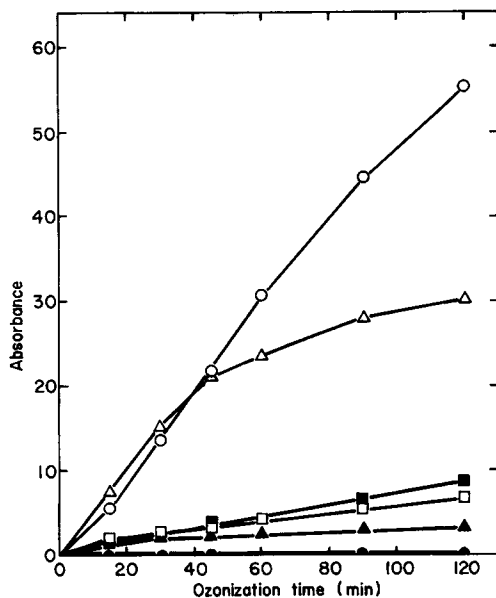


Fig. 3. Variation in absorbance at 266 nm (pH 7, 11) or 285 nm (pH 2) by ozonization: (O) UV ozonization at pH 2; (●) ozonization at pH 2; (Δ) UV ozonization at pH 7; (▲) ozonization at pH 7; (□) UV ozonization at pH 11; (■) ozonization at pH 11.

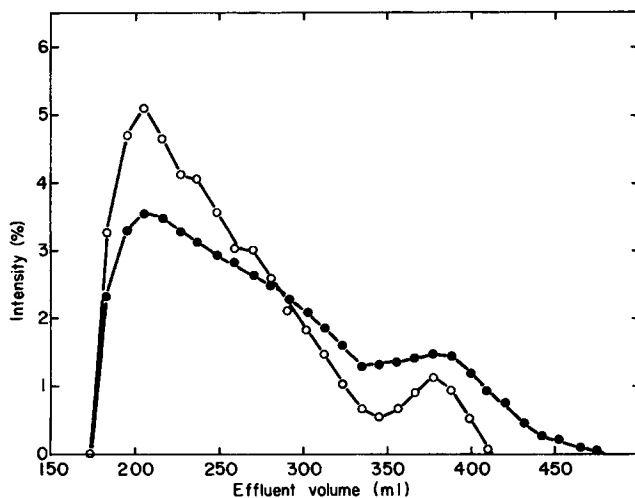


Fig. 4. Gel filtration pattern (Sephadex G-25) of the solution ozonized for 120 min at pH 2 under UV irradiation: (O) pattern based on the TOC of each fraction; (●) pattern on the absorbance at 285 nm of each fraction basified.

addition of acid (they disappear) or base (they appear) to the solution.⁹ Accordingly, those UV absorptions seem to be caused by similar molecular structure. These phenomena are explicable on the assumption that a certain ring structure is formed between the amide group and the ketone or terminal aldehyde, as described in the previous paper.⁹

As described above, the changes of PAA by the UV ozonization are similar to those by simple ozonization, especially under neutral and basic conditions, although there are definite differences in the degradation rate. Consequently,

it is reasonable to presume a radical reaction initiated by OH radicals both in ozonizations with and without UV irradiation. The differences in the degradation rate can be accounted for by the ease of OH radical formation by photolysis of ozone in water. The delicate differences in the chemical changes under pH conditions may be attributed to the change in attack position of OH radicals.

End Products in UV Ozonization

In order to elucidate the degradation process of PAA by UV ozonization, 0.1% PAA solution (distilled water solution) was exhaustively ozonized under UV irradiation. The variations in TOC, the absorbance at 266 nm, the carbonyl group, the formaldehyde, and the other aldehyde groups during the UV ozonization are shown in Figure 5. The TOC in the solution decreased linearly with reaction time. The absorption intensity at 266 nm reached a maximum after 2 hr of UV ozonization, and then the intensity decreased gradually. The amounts of formaldehyde and other aldehyde groups (the total aldehyde based on the 3-methyl-2-benzothiazolinone hydrazone method minus the formaldehyde) reached a maximum after 1 hr of UV ozonization. On the other hand, the variation in carbonyl groups based on the vanillin method coincided perfectly with that of the absorbance at 266 nm. This result supports the previous assumption concerning the cause of the UV absorption band.

In order to find the origin of the absorption band at 266 nm and the end products in the UV ozonization, two samples that were ozonized under UV irradiation for 2.5 hr and for 7.5 hr were lyophilized, and the IR spectra of the dry

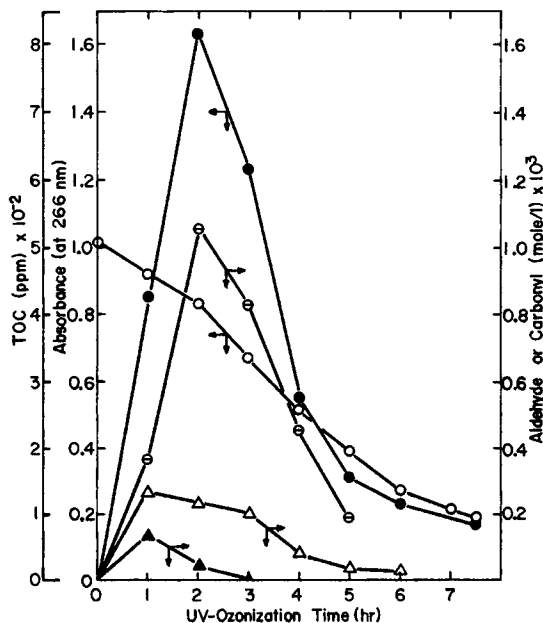


Fig. 5. Variations in TOC (○), absorbance at 266 nm (●), carbonyl group (⊖), formaldehyde (▲), and aldehyde groups other than formaldehyde (△) in the exhaustive UV ozonization of 0.1% PAA solution.

samples were observed. As can be seen from Figure 6, the IR spectra changed greatly after exhaustive ozonization under UV irradiation. The sample ozonized for 2.5 hr has a broad spectrum over the whole wavelength range, but most of the absorption peak in the spectrum agreed with the absorption peak of oxamic acid (spectrum (b) in Fig. 6). The broadening of the spectrum seems to be caused by the presence of low molecular weight PAA, aldehyde, and ketone. The spectrum ozonized for 7.5 hr is relatively sharp and also has the same absorption peak as oxamic acid. The strong absorption band near 1400 cm^{-1} in the spectra of both the 2.5-hr and the 7.5-hr samples is attributable to the nitrate resulting from the oxidation of amide groups: red coloration was observed by adding concentrated H_2SO_4 solution of brucine into the dry samples. A part of the dry 7.5-hr sample was not redissolved in water, and the IR spectrum (e) of the insoluble parts shown in Figure 6 coincides exactly with that of oxamide. This result is due to the sparing solubility of oxamide in water and indicates that a small amount of oxamide was present in the ozonized solution. However, the oxamide was not detected by other means in the ozonized solution owing probably to the low concentration, while the oxamic acid was confirmed by paper chromatography. Although oxamic acid and oxamide were observed as end products in UV ozonization of PAA, neither compound had an absorption band at 266 or 285 nm. No other compound contributing to the UV absorption band was separated or identified in the solution ozonized for 2.5 or 7.5 hr. These results indicate also that the origin of the UV absorption band is the aldehyde or the ketone produced in the course of the ozonization process of PAA and not a single compound.

These end products seem to be formed through the radical chain reaction initiated by the abstraction of the tertiary hydrogen atom from the PAA chain with

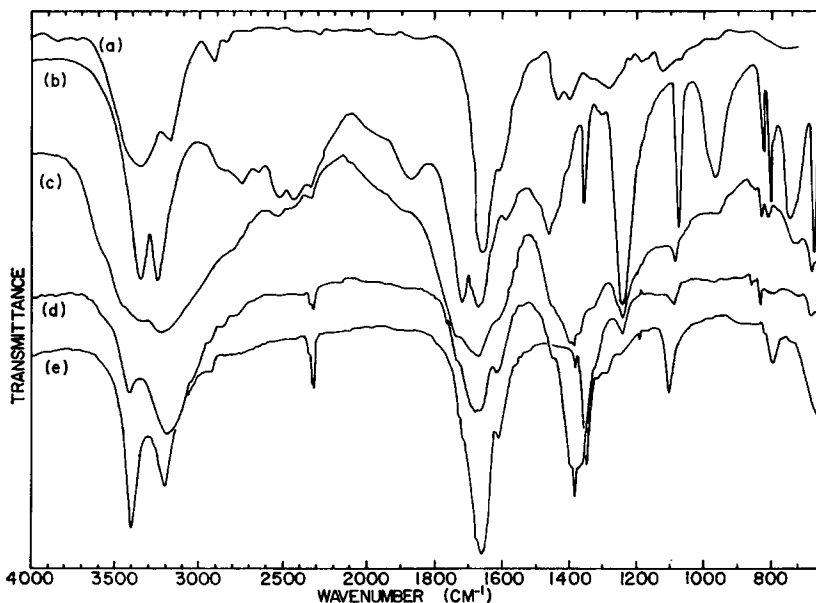


Fig. 6. IR spectra of original PAA (a), oxamic acid (b), and lyophilized samples of the solution ozonized for 2.5 hr (c) and 7.5 hr (d) under UV irradiation, and the water-insoluble parts of the dry sample of the 7.5-hr sample (e).

OH radical. However, the details of the reaction mechanism could not be completely elucidated in this study.

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