Decomposition of Ketones in Water by Ozone Treatment and UV Irradiation

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There is a possibility that aliphatic ketones are contained in waste from chemical laboratories, painting factories and so on. Therefore, the polluted water must be treated in order to remove them.

In this report each 5 mM ketone in the 0.05 M phosphate buffer (pH 7.0) was treated by ozone alone, UV irradiation alone or ozone + UV irradiation, and their degradation pathways were investigated from the decomposition products. Sample ketones were very rapidly decomposed by ozone + UV, and the main pathway was considered to have released a longer side-chain prior to the other shorter chain. Released alkyl chains were oxidized to aldehydes and fatty acids, and they were decomposed according to each decomposition pathway. The other pathway was production of keto acids by oxidation at the terminal methyl group.

Ketones themselves were decomposed slowly by ozone alone, but decomposition by UV alone occurred more rapidly than by ozone alone. The reason was considered ketones have UV absorption about 254 nm which is the irradiation wavelength of a low pressure mercury lamp.

The ketones having a longer side-chain were decomposed faster than a short side-chain like acetone. But total organic carbon (TOC) removal (%) was lowered in ketones having side-chains of larger carbon numbers.

Key words — ozone treatment ; UV irradiation ; ketone ; acetone ; methyl ethyl ketone

Introduction

There is a possibility of aliphatic ketones being present in the waste from chemical laboratories used as extraction solvents in chemical experiments. Solvents like benzene were detected in the effluents from college laboratories.¹⁾ Ketones may be also contained in paint thinner,²⁾ and waste from painting factories and so on.³⁻⁵⁾ We presume that ketones will be produced as intermediate products, when branched fatty acids are decomposed by treatment with ozone and UV irradiation.

The precursor of produced trihalomethane by chlorination had ketone structure,⁶⁻⁸⁾ and β -diketones were used as model compounds.⁹⁾ The trihalomethane could be considerably decreased, when the water

containing their compounds was previously treated by ozone.^{10,11)} In this way, ketone related compounds are contaminated in various water sources, and it seems to be necessary to remove them. But there are few reports on the decomposition of ketones by ozone/UV. Niki *et al.*¹²⁾ reported the decomposition of carbonyl compounds by ozone alone, but the amount of decomposed substances was only a little except in a very alkaline solution, and the detail consideration on degradation pathway was not described.

We reported that the aliphatic carboxylic acids contained in the water were not decomposed by the treatment of UV irradiation alone, and they were decomposed only very slowly by the treatment of ozone alone.¹³⁾ But the simultaneous treatment of ozone and UV irradiation could rapidly de-

compose them. Further we reported degradation pathway of fatty acids¹⁴⁾ and keto acids¹⁵⁾ as intermediate products of the decomposed fatty acids. In this report, the decomposition products and the degradation pathway of ketones by simultaneous treatment with ozone and UV irradiation were described.

Materials and Methods

Materials — Acetone, methyl ethyl ketone and diethyl ketone were obtained from Wako Pure Chemical Industries (Osaka). Methyl propyl ketone, *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (PFBOA) and *N*-methyl-*N*-(*tert*-butyldimethylsilyl)-trifluoroacetamide (MTBSTFA) were obtained from Tokyo Kasei Kogyo (Tokyo). All other reagents were guaranteed reagent grade as described previously.¹⁴⁾

Apparatus — Ozonizer : Nippon Ozon O-1-2. Photochemical reaction apparatus: Reaction vessel of Shigemistandard Co., Ltd. and 15 W low pressure mercury lamp. High performance liquid chromatography (HPLC) : Toso CCPD pump, Toso UV-8000 spectrophotometer and Shimadzu C-R4A integrator. Gas chromatography (GC) : Shimadzu GC-14A gas chromatograph with FID. Gas chromatograph-mass spectrometry (GC-MS) : Hewlett Packard HP-5890 Series II gas chromatograph and JEOL AX-500 mass spectrometer. Total organic carbon (TOC) apparatus : Shimadzu TOC-5000.

Decomposition Procedure — As the sample solutions, 250 ml of 5 mM ketone in 0.05 M phosphate buffer (pH 7.0)¹³⁾ were treated by UV irradiation, ozone alone or simultaneous treatment with ozone and UV irradiation (ozone/UV). An average ozone production rate was 4 mg/200 ml gas / min. The reaction solution was stirred with a magnetic stirrer in order to contact well with ozone in the reaction vessel. An aliquot of the sample solution was withdrawn at each time interval. The reaction solutions were determined by each method of analysis after replacing the dissolved ozone with nitrogen gas.

Analysis of Ketones and Aldehydes by GC

— According to the method as described previously,¹⁴⁾ the derivatization of ketones and aldehydes in reaction solutions was performed as follows. One ml of 0.1% PFBOA aqueous solution was added to 1 ml of the reaction solution or the standard solution. The reaction was allowed to proceed over night at room temperature. The reaction mixture was saturated with 0.8 g of sodium chloride and 2 drops of 18 N sulfuric acid were added, and the mixture was extracted with 0.4 ml of hexane containing 0.01% *p*-chlorobenzyl chloride as an internal standard for 30 s. After the excess of sodium chloride and the aqueous layer were removed, the hexane layer was dried with a small quantity of anhydrous sodium sulfate, and was analyzed by GC.

The column used was HP-1 (100% dimethylpolysiloxane (Gum), coating film thickness 2.65 μ m, 0.53 mm i.d. $\times$ 10 m, Hewlett-Packard Co.). The gas chromatographic conditions were as follows: injection temperature, 280°C; column temperature, 60–250°C; program rate, 20°C/min; initial time, 3 min; final hold time, 5 min; flow rate, 30 ml/min (He); injection mode, splitless.

Analysis of Keto Acids and Fatty Acids by HPLC — Twenty μ l of the reaction solution were applied to HPLC. The HPLC conditions were as follows: the columns, connection with Shim-pack SCR-101H (8 mm i.d. $\times$ 300 mm, Shimadzu Co.) and Shodex Ionpack KC-811 (8 mm i.d. $\times$ 300 mm, Showa Denko Co.); eluent, 0.1% phosphoric acid; column temperature, 60°C; wavelength setting of UV detector, 210 nm.

Analysis of Keto Acids and Dicarboxylic Acids by GC — The derivatization of keto acids and dicarboxylic acids was as follows. An aliquot of the reaction solution was extracted with an automatic ether extractor for 5 h. The ether extract was evaporated to dryness under reduced pressure and was allowed to stand for 1 h at 40°C after adding 0.1 ml of acetonitrile and 0.1 ml of MTBSTFA reagent. This solution was analyzed by GC. The gas chromatographic conditions were as follows: the column, HP-1; column tempera-

ture, 70–245°C; program rate, 15°C/min; initial time, 1 min; final hold time, 10 min; flow rate, 30 ml/min (He); injection mode, splitless.

The GC-MS conditions were as follows: the column, HP-1 (100% dimethylpolysiloxane (Gum), coating film thickness 2.65 μ m, 0.53 mm i.d. $\times$ 5 m, Hewlett-Packard Co.); flow rate, 8 ml/min (He); injection mode, splitless; ionizing voltage, EI at 70 eV, and temperature conditions were set the same as GC method.

Results and Discussion

Decomposition and Degradation Pathway of Acetone

In the first instance, we experimented with acetone as the most simple ketone. We described 0.05 M phosphate buffer (pH 7.0) adequate for preparing sample solution in previous paper.¹³⁾ A concentration of acetone as a starting material was adjusted to 5 mM in order to detect most of the intermediate products. Figure 1 shows the time course of acetone decomposition and the intermediate products formed by the simultaneous treatment with ozone/UV from acetone in water. Acetone had a half life of about 15 min, and disappeared after about 150 min. A large quantity of acetic acid was produced by the decomposition of acetone, and reached the maximum level at 75 min. Glyoxylic acid and oxalic acid were produced by the decomposition of acetic acid. Small quantity of methylglyoxal and pyruvic acid were detected, and hence acetic acid would be produced by the decomposition of them.

From the above results, the degradation pathway of acetone in water was considered as follows. One methyl group was released and decomposed finally to carbon dioxide *via* formic acid after the production of formaldehyde by oxidation as the main pathway. Acetic acid was produced through the formation of acetaldehyde by oxidation on the residue group. On the side pathway, pyruvic acid was produced from methylglyoxal which had been produced by the oxidation of either

methyl group on acetone. As described previously pyruvic acid was decomposed to acetic acid by oxidative decarboxylation through the pathways¹⁵⁾ (Fig. 2). Further, we reported the effect of pH (2, 7 and 10) on the decomposition of caproic acid by ozone/UV, and the results were almost the same.¹³⁾ Therefore the sample solution was only used at pH 7 in this

Fig. 1. Decomposition of 5 mM Acetone by Ozone + UV Irradiation

0.05 M phosphate buffer solution (pH 7.0). ●, acetone; □, formic acid; ■, acetic acid; ○, oxalic acid; ▢, glyoxylic acid; △, pyruvic acid; ◇, methylglyoxal; ▲, formaldehyde.

Fig. 2. Degradation Pathway of Acetone in Water by Ozone + UV Irradiation

[], not detected; →, simultaneously CO_2 produced; →, CO_2 not produced; [A], degradation pathway of acetic acid; [V], degradation pathway of pyruvic acid.

experiment.

Decomposition and Degradation Pathway of Methyl Ethyl Ketone

Only 2.6 mM of methyl ethyl ketone

Fig. 3. Decomposition of 5 mM Methyl Ethyl Ketone by Ozone + UV Irradiation

0.05 M phosphate buffer solution (pH 7.0). ●, methyl ethyl ketone; □, formic acid; ■, acetic acid; □, oxalic acid; ○, propionic acid; ▲, formaldehyde; △, acetaldehyde.

remained after 15 min, and it disappeared after 120 min by ozone/UV. A very large quantity of acetic acid was produced by the decomposition of methyl ethyl ketone, and the produced acetic acid was about 2.5 times what was obtained from acetone by ozone/UV. A small quantity of propionic acid was detected from the initial stage (Fig. 3).

From the results on the behavior of intermediate products, the degradation pathway of methyl ethyl ketone by ozone/UV is proposed as shown in Fig. 4. The main pathway was considered to be the released ethyl group which had a longer alkyl chain, and the ethyl group was oxidized to acetic acid through the formation of acetaldehyde. On the other hand, acetic acid was produced from the residue group at the same time. Very large quantity of acetic acid was produced temporary and it was considered due to the two production routes. In the second pathway, propionic acid was produced from residue group releasing the methyl group as formaldehyde. But this pathway might be a little, because the concentration of propionic acid was very low. As the third pathway, 3-ketobutyric acid (identified by GC-MS) was produced by oxidation of an

Fig. 4. Degradation Pathway of Methyl Ethyl Ketone in Water by Ozone + UV Irradiation

→, simultaneously CO₂ produced; →, CO₂ not produced; *, identified by GC-MS; [], not detected; [A], degradation pathway of acetic acid; [B], degradation pathway of 3-ketobutyric acid; [M], degradation pathway of malonic acid; [P], degradation pathway of propionic acid; [V], degradation pathway of pyruvic acid.

ethyl group on methyl ethyl ketone.

Next, methyl ethyl ketone as an example of ketones was treated by ozone alone or UV irradiation alone in order to compare their decompositions. The time course of methyl ethyl ketone decomposition and the intermediate products formed by each treatment was experimented.

The decomposition of methyl ethyl ketone itself by ozone alone was degraded

very slowly. Low concentrations of decomposed products were determined, because these intermediates also could be decomposed by ozone during treatment. On the other hand, methyl ethyl ketone itself was degraded somewhat faster by UV irradiation alone. But acetic acid, acetaldehyde and others remained even after 180 min. These results show that the main intermediate products as fatty acids could not be decomposed

Fig. 5. Decomposition of 5 mM Methyl Ethyl Ketone by Ozone Alone or UV Irradiation Alone

A: ozone alone, B: UV irradiation alone. ●, methyl ethyl ketone; □, formic acid; ■, acetic acid; ◻, oxalic acid; ▲, formaldehyde; △, acetaldehyde.

Fig. 6. Decomposition of 5 mM Methyl Ethyl Ketone by Ozone Alone, UV Irradiation Alone or Ozone + UV Irradiation

A: decomposition of methyl ethyl ketone, B: TOC removal (%). ○, ozone alone; ▲, UV irradiation alone; ●, ozone + UV irradiation.

easily as described previously¹³⁾ (Fig. 5).

The behavior of methyl ethyl ketone itself by each treatment method was compared. Degradation speed was most rapid by ozone/UV, the second was by UV irradiation alone. Because ketones themselves as methyl ethyl ketone has UV absorption at about 254 nm¹⁶⁾ which is the main irradiation wavelength of a low pressure mercury lamp. On the other hand, it was degraded only by half after 180 min by ozone alone.

Then TOC removal rates of their reaction solutions by each treatment method were compared as shown in Fig. 6B. TOC removal rates by ozone/UV were reached about 85% after 180 min. The rates by ozone alone were higher than that of UV irradiation alone. These results were different ranking at decomposition rate of methyl ethyl ketone itself in Fig. 6A. It seemed that the intermediate products as acetic acid, acetaldehyde and others, which have no UV absorption about 254 nm, were almost not decomposed. Therefore methyl ethyl ketone itself was decomposed somewhat faster by UV irradiation

Fig. 7. Decomposition of 5 mM Methyl Propyl Ketone by Ozone + UV Irradiation

0.05 M phosphate buffer solution (pH 7.0). ●, methyl propyl ketone; □, formic acid; ■, acetic acid; □, oxalic acid; ▤, glyoxylic acid; △, pyruvic acid; ○, propionic acid; ×, *n*-butyric acid; ■, 4-ketovaleric acid; ▲, formaldehyde; ▼, acetaldehyde.

tion alone, but the TOC removal rate was low.

Decomposition and Degradation Pathway of Methyl Propyl Ketone

Five mM of methyl propyl ketone in phosphate buffer (pH 7.0) was treated by ozone/UV. Only about 1 mM remained after 15 min, and a large quantity of acetic acid was produced from the methyl ethyl ketone (Fig. 7). Small quantities of 4-ketovaleric acid, propionic acid and *n*-butyric acid were detected. The next time, a concentration of methyl propyl ketone as a starting material was adjusted to 10 mM in order to identify a slight amount of intermediate products, and the HPLC chart of reaction solution by ozone/UV after 120 min is shown in Fig. 8. Hydroxyacetic acid at peak 4, 4-ketovaleric acid at peak 7 and other slight amount of intermediate products could be detected.

The degradation pathway of methyl propyl ketone which was considered with the behavior of intermediate products is shown in Fig. 9. As the main pathway, a propyl group as the longer side-chain was released and decomposed to acetic acid through the formation of propionic acid. The residue group was oxidized to acetic acid. In the second pathway, a small quantity of *n*-butyric acid was produced from the residue group when the methyl group as a shorter side-chain was released as formaldehyde. The *n*-butyric acid was decomposed to smaller carbon chain products through propionic acid. In another pathway, 4-ketovaleric acid (identified by HPLC and GC-MS) was produced by the oxidation of the terminal carbon of propyl group on methyl propyl ketone. It was decomposed to malonic acid and acetic acid as described previously.¹⁰⁾

Decomposition and Degradation Pathway of Diethyl Ketone

Only about 0.7 mM of diethyl ketone remained after 15 min by ozone/UV. As intermediate products, a large quantity of acetic acid was produced similar to that mentioned above, and a comparative quantity of

Fig. 8. HPLC Chromatogram of 10 mM Methyl Propyl Ketone by Ozone + UV Irradiation for 120 min

Operating conditions: detector λ , 210 nm; column, Shim-Pack SCR-101(H) + Shodex Ionpack KC-811; mobile phase, 0.1% phosphoric acid; flow rate, 1.0 ml/min; column temp., 60°C. (1), pyruvic acid; (2), malonic acid or glyoxylic acid; (3), succinic acid; (4), hydroxyacetic acid; (5), formic acid; (6), acetic acid; (7), 4-ketovaleric acid; (8), propionic acid; (9), *n*-butyric acid.

Fig. 9. Degradation Pathway of Methyl Propyl Ketone in Water by Ozone + UV Irradiation

→, simultaneously CO_2 produced; →, CO_2 not produced; *, identified by GC-MS; [], not detected; $\boxed{\text{A}}$, degradation pathway of acetic acid; $\boxed{\text{P}}$, degradation pathway of propionic acid; $\boxed{\text{R}}$, degradation pathway of 4-ketovaleric acid; $\boxed{\text{S}}$, degradation pathway of succinic acid.

Fig. 10. Decomposition of 5 mM Diethyl Ketone by Ozone + UV Irradiation

0.05 M phosphate buffer solution (pH 7.0). ●, diethyl ketone; □, formic acid; ■, acetic acid; □, oxalic acid; ▢, glyoxylic acid; △, pyruvic acid; ○, propionic acid; ▲, formaldehyde; ▼, acetoaldehyde.

propionic acid was determined after 30 min characteristically. It seemed that propionic acid was certainly produced from the residue group after releasing either ethyl group (Fig. 10).

The decomposition pathway was shown in Fig. 11. As the main pathway, an ethyl group was released as acetic acid, and the

residue group produced propionic acid. In the second pathway, 3-ketovaleric acid was produced by oxidation of either ethyl group on diethyl ketone. The degradation pathways of 3-ketovaleric acid were considered to decompose glyoxylic acid and propionic acid, acetic acid and malonic acid, or 2-ketobutyric acid (identified by GC-MS) by oxidative decarboxylation. The other degradation pathway of 3-ketovaleric acid might be the decomposition to 3-ketoglutaric acid by oxidation at the terminal methyl group.

Decomposition and TOC Values of Ketones

The behavior of the decomposition of these four ketones themselves and TOC values by ozone/UV were compared. It was found that the decomposition of the ketones themselves occurred much later in acetone (Fig. 12), and the compounds containing longer alkyl carbon such as the ethyl group or the propyl group were decomposed faster. On the other hand, TOC removal rate of acetone was about 100% after 180 min. The rates of compounds containing a large amount of carbon such as methyl ethyl ketone, methyl propyl ketone and diethyl ketone were somewhat lower, although their TOC were more efficiently removed than methyl ethyl ketone

Fig. 11. Degradation Pathway of Diethyl Ketone in Water by Ozone + UV Irradiation

→, simultaneously CO₂ produced; →, CO₂ not produced; [], not detected; *, identified by GC-MS; [A], degradation pathway of acetic acid; [M], degradation pathway of malonic acid; [O], degradation pathway of oxalacetic acid; [P], degradation pathway of propionic acid.

Fig. 12. Decomposition of 5 mM Ketones by Ozone + UV Irradiation

A: decomposition of 5 mM ketones, B: TOC values as a function of decomposition time. ○, acetone; ●, methyl ethyl ketone; □, diethyl ketone; ■, methyl propyl ketone; —, TOC (mg/l); ----, TOC removal (%).

by ozone alone or UV irradiation alone.

Conclusion

Each 5 mM ketone in the 0.05 M phosphate buffer (pH 7.0) was treated by ozone alone, UV irradiation alone or ozone + UV irradiation, and their degradation pathways were investigated from the products of decomposition. Sample ketones were very rapidly decomposed by ozone + UV, and the main pathway was considered to have released a longer side-chain prior to the other shorter chain. Released alkyl chains were decomposed finally to carbon dioxide through the formation of acetic acid together with the residue group when the shorter side-chain was the methyl group, and a part of acetic acid was decomposed to formic acid by oxidative decarboxylation. In the other pathway, keto acids were produced by the oxidation at the terminal methyl group.

Ketones themselves were decomposed slowly by ozone alone. The decomposition of them by UV alone was more rapid than by

ozone alone. The reason was that they have UV absorption about 254 nm which is the irradiation wavelength of a low pressure mercury lamp.

The ketones having a longer side-chain were decomposed faster than a short side-chain ketones like acetone. But TOC removal (%) was lowered in ketones having a side-chain of larger carbon numbers.

Ketones may be expected to be produced as intermediate products from branching fatty acids, or mingled with waste used as solvents. Compounds containing ketone structure are known to lead to trihalomethane by chlorination. Therefore, it is considered that decomposition of ketones or related substances by ozone and UV irradiation will be adopted for water treatment in the future.

In the present study, aliphatic ketones in water could be decomposed rapidly by the simultaneous treatment of ozone and UV irradiation, and the productions and disappearance of intermediate products were also ascertained.

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