Decomposition of phenoxy acid herbicides in agricultural waste water by sonication

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Abstract

The ultrasonic decomposition of phenoxy acid herbicide 2,4-D ($C_8H_6Cl_2O_3$) in aqueous solution was investigated and its comparison with that of another phenoxy acid herbicide MCPA ($C_9H_9ClO_3$) was made. It was found that MCPA and 2,4-D were fully decomposed after 180 minutes and most of the chlorine atoms were dissolved as HCl in solution after 270 minutes sonication at a frequency of 500kHz with a power of 21 W under argon atmosphere. During the ultrasonic decomposition of MCPA and 2,4-D, generation of the HCl was mainly responsible for decrease of pH. The total organic carbon (TOC) removal by sonication was about 40 % of the initial TOC concentration after 360 minutes. As the remaining organic compounds in the solution after sonication, organic acids such as acetic and formic acids were identified.

Keywords: ultrasound, MCPA, 2,4-D, cavitation, organic acids.

1 Introduction

Areas which have groundwater and soil polluted by organo-chlorine compounds continue to increase every year. These organo-chlorine compounds generally have high toxicity, thus, are resistant to destruction by biological treatment methods. Especially, phenoxy acid herbicides, commonly used in rice fields in Japan, have a relatively high toxicity that remains for a long period in the environment. Therefore it is necessary to effectively decompose the phenoxy

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acid herbicides and mineralize the chlorine group attached to the aromatic ring to remove the toxicity.

Recently, high power ultrasonic technique has attracted attention as a new method for the decomposition of organic chloride compounds in aqueous solution. It is said that the formation, growth and collapse of cavitation bubbles cause the chemical effect of ultrasound. The implosive collapse of the cavitation bubbles leads to the generation of the enormous local temperature and pressure field (hot spot). It is reported that the gas phase in the hot spot has temperatures as high as 5000 K and pressures near 1000 atm (Mason [1]). In the gas phase, it is presumed that volatile compounds are decomposed by direct pyrolysis. By the pyrolysis of molecules of water (H_2O) and volatile compounds, several reactive radicals such as hydroxyl radical are formed, leading to the degradation of the chemical species.

The application of ultrasound for the degradation of agricultural chemicals has been investigated and reported by several workers (Schramm and Hua [2], Hua and Pfalzer-Thompson [3], David *et al.* [4], Wayment and Casadonte [5]). In our previous study, the ultrasonic decomposition of 5.0×10^{-4} mol/L (4-chloro-2-methyl phenoxy) acetic acid (MCPA) in aqueous solution at the frequency of 500 kHz under the argon atmosphere was investigated and its probable mechanism was also reported (Fujita *et al.* [6]). It was found that MCPA in dilute aqueous solution was decomposed by ultrasonic irradiation to form acetic acid and formic acid through the formation of intermediates such as 4-chloro-2-methyl phenol (CMP), methylhydroquinone, 4-chlorocatecol, cresol and to lead to the reduction of total organic carbon (TOC).

In this study, we performed the ultrasonic degradation of (2,4-dichlorophenoxy) acetic acid (2,4-D) in aqueous solution at a frequency of 500 kHz and the power 21 W under an argon atmosphere. 2,4-D has two-chloride groups and has a relatively high toxicity (oral LD50=370 mg/L for rats) (The Society of Synthetic Organic Chemistry [7]). 2,4-D, once used as one of the constituents of the Agent Orange, has carcinogenic and teratogenic effects. The main purpose of this work is to investigate the decomposition mechanism of 2,4-D in water by ultrasonic irradiation by observing the behaviors of 2,4-D decomposition, dechlorination, TOC removal and byproducts produced during the 2,4-D decomposition process. By comparing the decomposition of 2,4-D with that of MCPA, which has one chloride group, we investigated the dependence of rate of decomposition and decomposition pathway on the number of chloride group in the compound.

2 Experimental

2.1 Samples

2,4-D ($C_8H_6Cl_2O_3$, 98% purity) of reagent grade (Wako) was used as a herbicide sample. An aqueous solution of 5.0×10^{-4} mol/L 2,4-D was prepared by dissolving in water. The water used in all experiments was degassed after deionization. In order to understand the 2,4-D decomposition pathway more clearly, the ultrasonic decomposition of 2,4-dichlorophenol (2,4-DCP), an intermediate having a similar structure to 2,4-D, was investigated. 2,4-DCP ($C_6H_4Cl_2O$, 98% purity) and 4-chloro-2-methyl phenol (CMP, C_7H_7ClO, 98% purity) of reagent grade (Tokyo Chemical Industry) were used. Aqueous solutions of 2,4-DCP and CMP (5.0×10^{-4} mol/L) were prepared in a similar manner as the 2,4-D solution. The structural formulas of 2,4-D and 2,4-DCP are shown in Fig. 1.

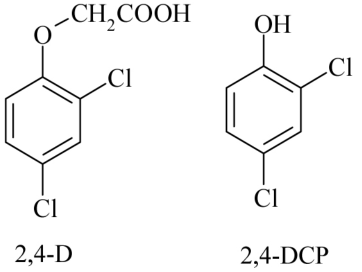

Figure 1: Structure of 2,4-D and 2,4-DCP.

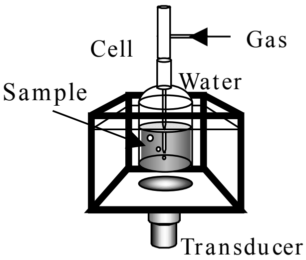

Figure 2: Block diagram of experimental apparatus.

2.2 Experimental procedure

A sonoreactor (HSR-301), made by Honda Electronics Co. Ltd., was used. The schematic diagram of experimental setup is shown in Fig. 2. Ultrasound was emitted at a frequency of 500 kHz from a planar PZT transducer (diameter 50mm) fixed on a stainless steel plate. A 50mmφ cylindrical glass vessel containing 100ml sample solution was placed 20mm above the transducer in a temperature-controlled water bath. The sample solution was kept at a constant temperature (298±1K). The power dissipated to the reaction system was determined by calorimetric technique, which is commonly used to measure the acoustic power. For this study, an acoustic power of 21.4 W was employed throughout the experiments. Bubbling of the sample solution with argon was performed for 20 minutes before ultrasonic irradiation, and was continued throughout the duration of the experiment.

2.3 Product analysis

The concentrations of 2,4-D, 2,4-DCP, CMP and products formed through the ultrasonic degradation process of 2,4-D were measured with a High Performance

Liquid Chromatograph (HPLC) (Shimadzu, UV-VIS detector type: SPD-10Avp, UV wavelength: 210nm). The HPLC was equipped with a C18 column (Shimadzu, Shim-pak VP-ODS, 250×4.6mm I.D.). The mobile phase constituted with 5.0×10^{-4} mol/L potassium phosphate (pH2.8): acetonitrile (10:11 v/v) mixture was used. Qualitative analysis of the 2,4-D solution after the sonication was performed on a GC-MS (Shimadzu, GC-17A gas chromatograph coupled to a QP5050 mass spectrometer), using capillary column (Shimadzu, ULBON HR-20M, 25 m × 0.25 mm × 0.1 μm). The temperature of the gas chromatograph column was raised from 333 K to 473 K at a constant heating rate of 10 K/min.

Concentrations of Cl^-, acetic acid and formic acid were determined using an Ion Chromatograph (IC) (Shimadzu, electroconductivity detector type: CDD-10Avp). The IC was equipped with a column (Tosoh, TSKgel IC-Anion-PW 6837, 50×4.6mmI.D.) Gluconate potassium (1.3×10^{-3} mol/L) + 4 sodium borate (1.3×10^{-3} mol/L) + boric acid (3.0×10^{-4} mol/L): acetonitrile: glycerin (89.5: 10: 0.5 v/v) mixture was used as mobile phase.

Total organic carbon (TOC) concentration was determined with a TOC analyzer (Shimadzu, TOC-V_{CSH}). The pH of the sample solution was measured using a portable pH meter (DKK-TOA, HM-21P).

The decomposition behaviors of 2,4-D, 2,4-DCP and CMP were described in terms of the decomposition ratio, X, dechlorination ratio, Y, and TOC removal ratio, Z. The decomposition ratio estimates the relative amount of 2,4-D, 2,4-DCP or CMP degraded by sonication. The extent of mineralization of chlorine from 2,4-D, 2,4-DCP, CMP and its sonication products was expressed as dechlorination ratio. Decomposition ratio and dechlorination ratio are defined as:

$$X\,[\text{-}] = (C_0 - C_t)/C_0, \tag{1}$$

$$Y\,[\text{-}] = [Cl^-]_t\,/\,(C_0\times(\text{number of chlorine groups in the sample structure})), \tag{2}$$

where C_0 and C_t are the initial concentrations and final concentrations, respectively, of 2,4-D, 2,4-DCP and CMP. $[Cl^-]_t$ is the concentration of chloride ion at the reaction time, t.

The ratio of total organic carbon in the solution before and after ultrasonic treatment is calculated as follows:

$$Z\,[\text{-}] = ([TOC]_0 - [TOC]_t)/\,[TOC]_0, \tag{3}$$

where $[TOC]_0$ and $[TOC]_t$ are the concentrations of TOC initially and at reaction time, t, respectively.

3 Results and discussion

3.1 Sonolysis of 2,4-D

Figure 3 shows the ultrasonic decomposition behavior of 2,4-D under an argon atmosphere. 2,4-D was fully decomposed after 180 minutes and most of its chlorine atoms were dissolved in solution after 270 minutes sonication. On the other hand, the TOC removal by sonication was about 40% of the initial TOC concentration after 360 minutes. Based on GC-MS analysis, some of the organic byproducts in the sample solutions after irradiation were identified as aromatic compounds such as 2,4-DCP, *o*-chlorophenol and *p*-chlorophenol. In the liquid phase, organic acids such as oxalic acid, succinic acid, acetic acid and formic acid were detected. In the gas phase, benzene, acetone, butane, CO and CO_2 were detected.

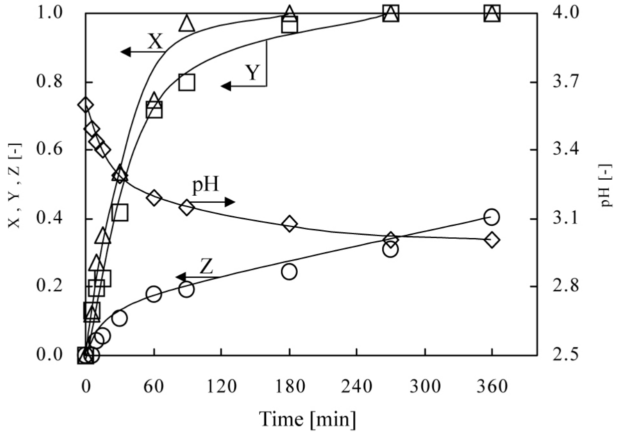

Figure 3: Ultrasonic decomposition of 2,4-D under argon atmosphere.

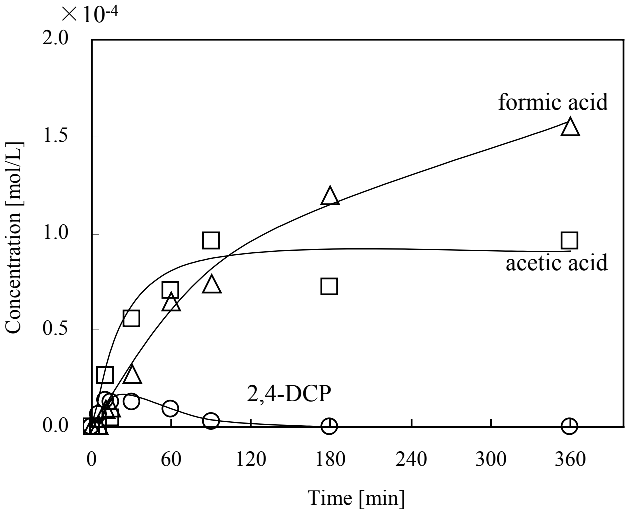

Figure 4: Byproduct concentration during sonication of 2,4-D.

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To obtain any information on the decomposition of sonolysis products, the concentrations of 2,4-DCP, acetic acid and formic acid in the solution were determined using HPLC and IC and the obtained results are shown in Fig.4. The concentration of 2,4-DCP increased during the early period of irradiation, reaching a maximum concentration of about 0.14×10^{-4} mol/L at 10 minutes followed by its decrease until 2,4-DCP was undetectable at 180 minutes. Similarly, the formation and decomposition of *o*- and *p*-chlorophenol were observed. These chlorophenols were completely decomposed after 180 minutes. On the contrary, organic acids remained in solution even after 360 minutes. Acetic acid concentration increased with irradiation time until 120 minutes, afterwards the concentration was constant about 0.83×10^{-4} mol/L. On the other hand, formic acid concentration was observed to increase during the duration of experiment.

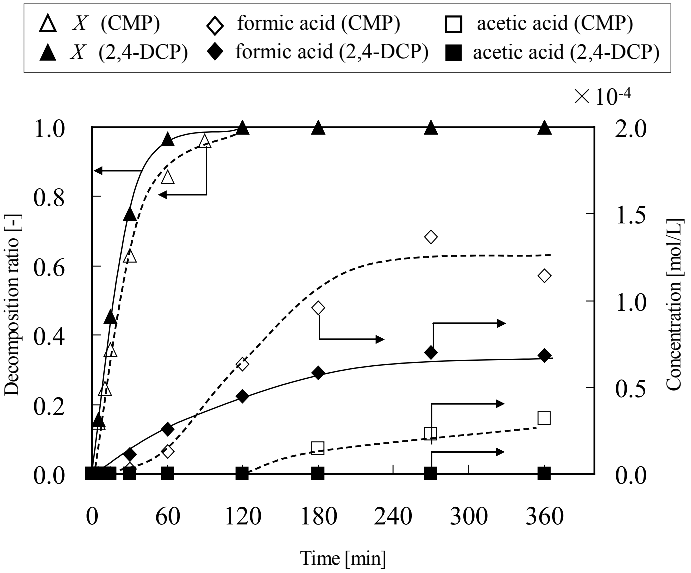

Figure 5: Decomposition and byproduct formation behaviors on CMP and 2,4-DCP under sonication.

3.2 Sonolysis of 2,4-DCP

We investigated the behavior of ultrasonic decomposition of 2,4-DCP, which was one of the high molecular intermediates and has a similar structure to 2,4-D, as shown in Fig.1. The time-variation of decomposition ratio ($X_{2,4\text{-DCP}}$) and concentrations of acetic and formic acids during the decomposition of 2,4-DCP are illustrated in Fig.5. As shown in Fig.5, the decomposition of 2,4-DCP proceeded with sonication time and was completely decomposed at 120 minutes. The concentration of formic acid increased with sonication time until 270 minutes. After 270 minutes, there was little change in the concentration and it was about 0.90×10^{-4} mol/L. The final concentration of formic acid generated by decomposition of 2,4-D was 2.4 times as high as that of 2,4-DCP. On the other hand, no acetic acid was detected during the experiment, though acetic acid was observed during the ultrasonic degradation of 2,4-D under identical experimental conditions.

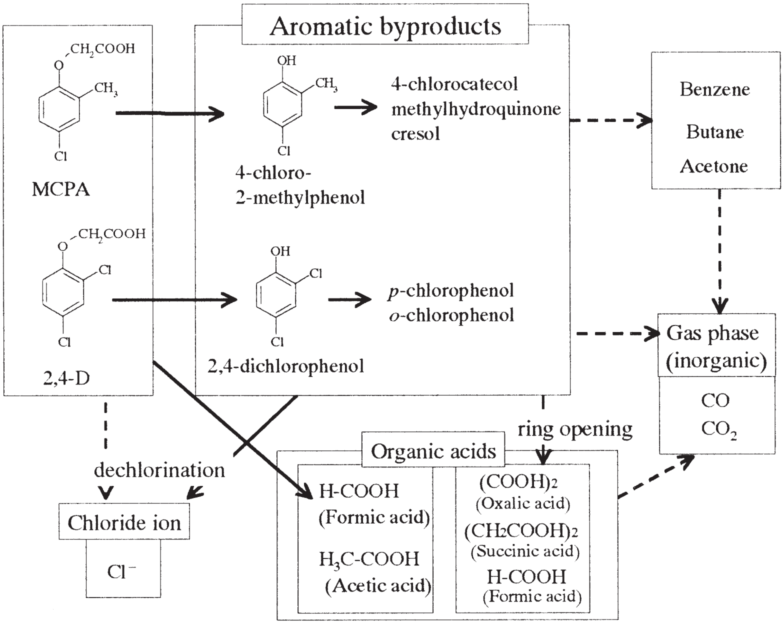

Figure 6: Mechanism of MCPA and 2,4-D decomposition under sonication.

3.3 Decomposition mechanism of 2,4-D and comparison with MCPA

The rate constants, *k*, was estimated by considering the time necessary to obtain a 60 % decomposition of MCPA, CMP, 2,4-D and 2,4-DCP were calculated. Their respective rate constants were 4.58×10^{-4} s^{-1}, 4.92×10^{-4} s^{-1}, 4.44×10^{-4} s^{-1} and 4.88×10^{-4} s^{-1}. We noted in our past paper that MCPA, which is a low volatile compound, was initially decomposed by radicals in the bulk solution (Fujita *et al.* [6]). Since CMP, 2,4-D and 2,4-DCP are also low volatile compounds, it is considered that these compounds were decomposed by radicals in the bulk solution. Moreover, the structures of MCPA, CMP, 2,4-D and 2,4-DCP differ only in the attached group on the aromatic ring. Their initial decomposition rate constants showed no significant difference.

Based on these data and our previous paper (Fujita *et al.* [6]), we proposed the 2,4-D decomposition mechanism by sonication and compared it with the decomposition of MCPA in Fig.6.

2,4-D was initially decomposed to 2,4-DCP, acetic acid and formic acid by the reaction with hydroxyl and hydrogen radicals. Zona *et al.* [8] performed studies on the radical decomposition of 2,4-D by gamma layer irradiation. They reported that 2,4-DCP was generated by the reaction of the $-CH_2-COOH$ group with hydroxyl radicals at the initial step of the decomposition of 2,4-D. In this study, it is assumed that in the next step of the decomposition pathway the reaction of the chloride group at the ortho and para positions of 2,4-DCP with hydroxyl radicals form *p*- and *o*-chlorophenols. These aromatic byproducts then decompose to chloride ion (HCl), CO, CO_2 and organic acids such as succinic and formic acids. On the other hand, it is assumed that volatile organic compounds such as benzene, acetone and butane detected in gas phase also exist in the sample solution. Some aromatic byproducts may decompose to CO and CO_2 by pyrolysis and reaction with radicals via the formation and decomposition of these volatile organic compounds.

Compared with the decomposition pathway of MCPA, the chloride ion concentration in the solution of 2,4-D after sonication was larger than that of MCPA. 2,4-D has two chlorine group attached aromatic ring while MCPA has only one. However, it was found based on the dechlorination ratio that the chlorine groups in MCPA and 2,4-D were mineralized by sonication independent of the number of chlorine groups in their structure. On the other hand, formic acid concentration by ultrasonic decomposition of MCPA was higher than that of 2,4-D at 360 minutes. In addition, the CMP decomposition ratio and concentrations of formic acid and acetic acid generated by the sonication of a 5.0×10^{-4} mol/L CMP solution were shown in Fig.5. Formic acid and acetic acid concentrations in CMP decomposition showed higher values than that of 2,4-DCP after 120 minutes. In the case of 2,4-DCP, the formation of acetic acid was inhibited. It is considered that the formation of formic and acetic acids is attributed to the presence of a methyl group attached to the aromatic ring of MCPA and CMP.

4 Conclusions

We investigated the ultrasonic decomposition of phenoxy acid herbicide 2,4-D under an argon atmosphere at 500 kHz and compared the sonolysis of 2,4-D with that of MCPA. The chloride ion was generated during the decomposition of 2,4-D and organo-chlorine byproducts by ultrasound. With the effective mineralization of the chloride group, it was considered that the toxicity of the compounds decreased. Comparison with the decomposition of MCPA, the decomposition rate constants were not much different. The initial decomposition of low volatile aromatic compounds was not dependent on the structure. On the other hand, the larger amount of organic acids was formed by phenoxy acid herbicides with methyl and $-O-CH_2-COOH$ groups attached to the aromatic ring.

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References

[1] Mason, T.J., *Sonochemistry: The Uses of Ultrasound in Chemistry*, Royal Society of Chemistry, Cambridge: England, pp.9-26, 1990.

[2] Schramm, J.D. & Hua, I., Ultrasonic irradiation of dichlorvos: Decomposition mechanism. *Water Research*, **35(3)**, pp. 665-674, 2001.

[3] Hua, I. & Pfalzer-Thompson, U., Ultrasonic irradiation of carbofuran: Decomposition kinetics and reactor characterization. *Water Research*, **35(6)**, pp. 1445-1452, 2001.

[4] David, B., Lhote, M., Faure, V. & Boule, P., Ultrasonic and photochemical degradation of chlorpropham and 3-chloroaniline in aqueous solution. *Water Research*, **32(8)**, pp. 2451-2461, 1998.

[5] Wayment, D.G. & Casadonte Jr., D.J., Frequency effect on the sonochemical remediation of alachlor. *Ultrasonics Sonochemistry*, **9**, pp. 251-257, 2002.

[6] Fujita, T., Ona, E.P., Kojima, Y., Matsuda, H., Koda, S., Tanahashi, N. & Asakura, Y., Ultrasonic Decomposition of (4-Chloro-2-Methyl)phenoxy Acetic Acid (MCPA) in Aqueous Solution. *Journal of Chemical Engineering of Japan.*, **36**, pp. 806-811, 2003.

[7] The Society of Synthetic Organic Chemistry, *Dictionary of Organic Compounds*, Kodansha Ltd.: Japan, p. 297, 1985.

[8] Zona, R., Solar, S. & Gehringer, P., Degradation of 2,4-dichlorophenoxyacetic acid by ionizing radiation: influence of oxygen concentration. *Water Research*, **36**, pp.1369-1374, 2002.

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