

Decomposition of toxic organics by boron-doped diamond electrode

Soo-Gil Park, Yasuaki Einaga*, Akira Fujishima**
Dept. of Industrial Chemical Eng., School of Process Eng.,
Chungbuk Nat'l Univ.,

San 48, Kaeshin, Heungduk, Cheongju, Chungbuk, Korea
*Dept. of Chemistry, Faculty of Science and Technology, Keio
University, Japan

**Dept. of Applied Chemistry, School of Eng., The University of
Tokyo, Japan

Organic phosphate pesticides are of great environmental concern primarily because they are toxic to mammals and birds, and are relatively soluble in water to contaminate surface water and groundwater [1,2]. In this study, the decomposition of phorate, a widely used organic phosphate insecticide, in aqueous solutions by Boron doped diamond (BDD) electrode was examined. The LD50 of phorate was reported to be 1.1.2.3 mg/L, depending on the pathway of intake [3-8]. Photolytic ozonation (UV/O₃) process is considered to an advanced oxidation process that applies ozonation and UV irradiation simultaneously to the target compounds, and converts these compounds completely to simple inorganic species, such as carbonate and water, if the reaction is taking long enough for completion. Photolytic ozonation thus has the potential for being an environmental clean process for treating organic contaminants and has attracted attention at present for a wide range of environmental applications. However, the initial and operating costs of photolytic ozonation are still relatively expensive comparing to traditional treatment technologies. Therefore, the determination of optimum operational conditions is one of the primary concerns for the future development and potential application of photolytic ozonation process. The objective of this research was to investigate the effect of various experimental parameters on the temporal decomposition behavior of phorate in aqueous solutions by photolytic ozonation. The reaction rate and kinetic behavior of phorate and some intermediate reacting species were characterized using an empirical kinetic model.

Phorate and other chemicals employed in this experiment were reagent grade. All experiments were conducted in a continuously sparged stirred-tank cylindrical reactor (3-L total volume, 2.4-L effective liquid volume) made of borosilicate glass. A double-walled immersion well made of quartz was inserted in the centerline of the reactor with an air-tight joint at top for housing an low-pressure mercury-vapor UV lamp (UVP, model xx-15s) rated at 15 W. The output of the UV lamp is primarily at 254nm and the UV intensity on the inner surface of the reactor was determined to be 31.2W/m² by a digital radiometer (Spectroline, DRC-100X with a DIX-254 sensor). The experimental solution containing 20 mg/l phorate was taken into the annular space of the reactor and was aerated by continuously sparging 50 L/h of ozonecontaining gas generated from dry oxygen with a Fischer 500 ozone generator. A UV spectrometric ozone analyzer (Seki, model SQZ-6000) was used to determine the ozone content in the inlet and outlet gaseous streams. The pH level of experimental solution was kept at desired levels by the addition of 0.1N sodium hydroxide and/or hydrochloric acid solutions using a Kyoto APB-118-20B autotitrator. The reactor system was water-jacketed to keep the solution temperature at 25°C. For experiments conducted under different operating conditions, aliquots of 15-mL reaction solution were withdrawn at desired time intervals from the reactor for further analyses. The total solution volume sampled was kept below 10% of the initial solution volume in the reactor. The dissolved ozone concentration of reaction solution was determined by the indigo blue method. Phorate concentration in the reaction solution was analyzed by a Spectra-Physics P1000 HPLC equipped with a UV detector. The carbonate and total organic carbon (TOC) concentration was measured using an OIC model 700 TOC analyzer. The anion concentrations, including phosphate and sulfate, were analyzed by an ion chromatograph (Dionex, model DX-100). For certain experiments, the reaction intermediates were determined using a

gas chromatograph (HP, model G-1800A GCD) equipped with an electron ionization detector (EID).

Almost complete decomposition of phorate in aqueous solution by BDD ozonation can be accomplished in 20 min for most experiments conducted in this research. The sulfur groups of phorate were released early during the course of decomposition reaction, followed by the mineralization of organic intermediates to form phosphate, and carbonate ions by the indirect oxidation of hydroxyl free radicals. The decomposition rate of phorate by photolytic ozonation was relatively independent of the solution pH value, but increased linearly with ozone concentration in the inlet gaseous stream. The increase in ozone dosage does increase the reaction rate and does not decrease the utilization of ozone indicating that the oxidation of phorate was more favorable in solutions containing higher dissolved ozone concentrations. The simplified kinetic model could be adequately applied to describe the temporal behavior of the decomposition of phorate in aqueous solution by photolytic ozonation.

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REFERENCES

- [1] Foster DM, Rachwal AJ, White SL. Advanced treatment for removal of atrazine and other pesticides. *Water Supply* 1992;10:133-9.
- [2] Reynolds G. Pesticides: a review. *Ozone Sci. Eng* 1989;11:339-412.
- [3] Budavare S, O'Neil MJ, Smith A. *The Merck Index: an encyclopedia of chemicals, drugs, and biological*, 12th ed. Rahway, NJ, USA:Merck & Co.Inc., 1996.
- [4] Beltran FJ, Garcia-Araya JF, Acede B. Advanced oxidation of atrazine in water- II. Ozonation combined with ultraviolet radiation. *Water Res* 1994;28:2165-73.
- [5] Biltran FJ, Ovejero G, Garacia-Araya JF, Rivas J. Oxidation of polynuclear aromatic hydrocarbons in water. 2. UV radiation and ozonation in presence of UV radiation. *Ind. Eng. Chem. Res.* 1995;34:1607-15.
- [6] Esplugas S, Yue PL, Perves MI. Degradation of 4-chlorophenol by photolytic oxidation. *Water Res* 1994;28:1323-8.
- [7] Hayashi JI, Ikeda J, Kusakabe K, Morooka S. Decomposition rate of volatile organochlorines by ozone and utilization efficiency of ozone with ultraviolet radiation in bubble-column contactor. *Water Res* 1993;27:1091-101.
- [8] Ku Y, Su WJ, Shen YS. Decomposition of phenols in aqueous solution by UV/O₃ process. *Ozone Sci Eng* 1996;8(5):443-60.