Ultrasonics Sonochemistry 17 (2010) 802–809

Contents lists available at ScienceDirect

Ultrasonics Sonochemistry

journal homepage: www.elsevier.com/locate/ultsonch

Sonolytic degradation of parathion and the formation of byproducts

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ARTICLE INFO

Article history:
Received 19 August 2009
Received in revised form 30 December 2009
Accepted 31 January 2010
Available online 4 February 2010

Keywords:
Parathion
Ultrasonic irradiation
Paraoxon
4-Nitrophenol
Kinetics model

ABSTRACT

Ultrasonic degradation of parathion has been investigated in this study. At a neutral condition, 99.7% of 2.9 μM parathion could be decomposed within 30 min under 600 kHz ultrasonic irradiation at ultrasonic intensity of 0.69 W/cm^2. The degradation rate increased proportionally with the increasing ultrasonic intensity from 0.10 to 0.69 W/cm^2. The parathion degradation was enhanced in the presence of dissolved oxygen due to formation of more $^{\cdot}OH$, but was inhibited in the presence of nitrogen gas owning to the free radical scavenging effect in vapor phase within the cavitational bubbles. CO_3^{2-}, HCO_3^-, and Cl^- exhibited the inhibiting effects on parathion degradation, and their inhibition degrees followed the order of $CO_3^{2-} > HCO_3^- > Cl^-$. But Br^- had a promoting effect on parathion degradation, and the effect increased with the increasing Br^- level. Moreover, both the hydrophobic and hydrophilic natural organic matters (NOM) could slow the parathion degradation, but the inhibiting effect caused by hydrophobic component was greater, especially the strongly hydrophobic NOM. The three reaction pathways of parathion sonolysis were proposed, including formation of paraoxon, formation of 4-nitrophenol, and unknown species products. The kinetics tests showed that anyone of these pathways could not be overlooked, and the fractions of the parathion decomposed in the three pathways were 28.19%, 32.92% and 38.89%, respectively. In addition, 66.61% of paraoxon produced was degraded into 4-nitrophenol. Finally, kinetics models were established to adequately predict the concentrations of parathion, paraoxon and 4-nitrophenol as a function of time.

1. Introduction

Massive applications of organophosphorus pesticides (Ops) in agriculture and forestry have been causing great concerns about the environment pollution due to their non-specific inhibiting effects on enzyme acetylcholinesterase (AChE) in human nervous system. The pollution may greatly degrade the quality of surface water and groundwater [1–3]. As one of the representative Ops, parathion has been listed as "extremely hazardous" by the World Health Organization. Although, parathion has been banned in many countries (e.g. USA) [4], it is still being used in other countries. For example, in China, parathion is legally used for forestry and crops other than vegetables, fruits, teas or herbal medicines [5]. The chemical structure and physical properties of parathion containing phosphorus–sulfur double bound (P=S) is shown in Table 1. When parathion is applied in agricultural activities or transports into surface water, it is readily oxidized to paraoxon (P=O), a more potent AChE inhibitor, by the oxidants naturally present [6,7]. During water chlorination, ozonization and UV irradiation processes, the transformation from parathion to paraoxon is more rapid and completes [8–10].

Recently, ultrasonic irradiation, an advanced oxidation process, has received increasing attention for the degradation of various organic pollutants in water [11–15]. Application of ultrasound to aqueous solutions forms cavitation bubbles, which will undergo transient collapse events. Quasi-adiabatic compression of transient bubbles generates average vapor temperatures near 5000 K and pressures up to 10,000 bar. In aqueous solution, three different reaction zones have been postulated: (i) interiors of bubbles where water vapor is pyrolyzed to hydroxyl radicals ($^{\cdot}OH$) and hydrogen atoms ($^{\cdot}H$), as shown in Eq. (1), and where gas-phase pyrolysis and/or combustion reactions of volatile substances dissolved in water occur.

$$H_2O \xrightarrow{)))} H^{\cdot} + {}^{\cdot}OH \qquad (1)$$

(ii) Water-bubble interfaces where 600–1000 K temperature with a high gradient exists, and where locally condensed $^{\cdot}OH$ has been reported. A thin shell of transiently supercritical water exists in this region. (iii) Bulk solution at ambient temperature where reactions with $^{\cdot}OH$ or $^{\cdot}H$ that migrates from the interface occur.

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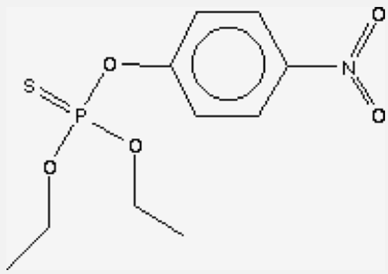
doi:10.1016/j.ultsonch.2010.01.016

Table 1
Chemical structure and physical properties of ethyl parathion [10,42].

Compound	Structure	MW	Log K_{OH}	V_p	W_s
Parathion		291.26	3.83	3.78×10^{-5}	11

Log K_{OH}: octanol–water partition coefficient.
W_s: water solubility, mg L^{-1} (20 °C).
V_p: vapor pressure, mm Hg (20 °C).

Sonolysis of parathion was reported first by Kotronarou et al. [16] who identified the final products and proposed a simple degradation pathway. They proposed that the hydrolysis of parathion by supercritical water at the water-bubble interface is dominant pathway for sonolytic degradation of parathion. However, the quantitative of byproducts was not done to prove their supposition. Wang et al. [43,44] reported the sonocatalytic degradation of parathion in the presence of heterogeneous sonocatalysts TiO_2. However, little literature has been available to explore the effect of environmental factors on parathion degradation and the formation model of byproducts by ultrasonic irradiation alone.

The objectives of this study are to: (i) evaluate the effect of irradiation intensity, dissolved gasses, anions, and natural organic matters, on parathion sonolysis; and (ii) establish kinetic models of the degradation of parathion and the formation of paraoxon and 4-nitrophenol (two major highly toxic byproducts of parathion) based on our proposed reaction pathways.

2. Materials and methods

2.1. Chemicals

Parathion (99%, purity) and paraoxon (99%, purity) were purchased from Dr. Ehrenstorfer GmbH (German). Acetonitrile (HPLC grade), dichloromethane (PESTANAL grade), 4-nitrophenol standard solution, triphenylphosphate (>99%) as internal standard (I.S.), Supelite DAX-8 resin, Amberlite XAD-4 resin, Amberlystra-26(OH) anion-exchange resin and DOWEX 50WX4-50 cation-exchange resin were obtained from Sigma–Aldrich (USA). All the other reagents are analytical grade except as noted. All the solutions were prepared using the water purified by a Milli-Q Gradient water purification system. Natural organic matters (NOMs) were extracted from a natural surface water (Yangtze River, Shanghai, China) by 0.45 μm polyether sulfone membrane filtration and subsequent nanofiltration membrane (NF-90, Toray Co., Japan) in the state key laboratory of pollution control and resources reuse laboratory at Tongji University (Shanghai, China). The different components of NOM were fractionated by Supelite DAX-8 and Amberlite XAD-4 [17]. All the component solution passed through the DOWEX 50WX4-50 cation-exchange resin and Amberlystra-26(OH) anion-exchange resin subsequently before use.

2.2. Experiments

All the experiments were conducted in the sonochemical reactors shown in Fig. 1. The ultrasonic generator provided a fixed frequency of 600 kHz with an electric power output up to 100 W (SF600, Shanghai Acoustics Laboratory, Institute of Acoustics, Chinese Academy of Sciences, China). A cylindrical stainless steel reaction vessel (i.d. 100 mm, and volume 600 mL) was directly connected to an ultrasonic transducer (SF600, Shanghai Acoustics Laboratory, Institute of Acoustics, Chinese Academy of Sciences, China) with flanges and a flexible Teflon O-ring for sealing. The vessel was immersed in a water bath to control the reaction temperature at a constant level. In the tests to investigate the effects of gases, the vessel was sealed with a special stainless steel lid via flanges, and the gases were introduced into the solution through a Teflon tube, as shown in Fig. 1(a). In all the other tests, the vessel was open to the air, as shown in Fig. 1(b).

All tests were performed at 25.0 ± 1.0 °C and under atmospheric pressure. In all experiments, 300 mL of parathion solution was prepared daily and then stored into the reaction vessel. The solution pH was adjusted to 7.0 ± 0.05 with 1.0 M HCl and 1.0 M NaOH, and remained uncontrolled during the ultrasonic irradiation, except in the experiments to investigate the effect of anions in which the initial pH was not adjusted. The reactions were initiated by turning on the ultrasonic transducer. At each sampling time, 5 mL sample was pipetted to a 10 mL glass bottle with 200 μg/L internal standard addition and extracted by 1 mL dichloromethane immediately. The extract was collected and subsequently analyzed by GC–MS. All the experiments were carried out at least in duplicates. The standard deviations of duplicate experiments were less than 10%. The symbols in Figs. 2–5 showed the mean values of the duplicate experiments. In the experiments to investigate effect of dissolved gases, the gas investigated was introduced into the solution for 30 min with the flow rate of 0.5 L/min prior to the reaction. In the experiments to investigate effect of anions, a certain amount of salt (NaCl, $NaHCO_3$, NaBr or Na_2CO_3) was added to form designated initial concentration of the corresponding anion before the reaction.

2.3. Analysis

Parathion and paraoxon in the samples were extracted by dichloromethane, and quantified by a Shimadzu GC/MS-QP2010s gas chromatograph–mass spectrometer equipped with a 30 m RTX-5MX column by RESTEK (film thickness: 0.25 μm; i.d. 0.25 mm). Helium (purity >99.999%) was used as the carrier gas, with a flow rate of 1.5 mL/min. The injection volume of each extract was 1.0 μL. SIM mode was used with a dwell time of 50 ms for each ion. The GC oven temperature program was: initial temperature at 40 °C, hold for 1 min, 25.0 °C min^{-1} gradient until 200.0 °C, 10.0 °C min^{-1} until 220.0 °C, 30 °C min^{-1} until 270.0 °C, and hold for 3 min. 4-Nitrophenol was analyzed by a Shimadzu