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Sonolytic degradation of parathion and the formation of byproducts

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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/cm². The degradation rate increased proportionally with the increasing ultrasonic intensity from 0.10 to 0.69 W/cm². The parathion degradation was enhanced in the presence of dissolved oxygen due to formation of more '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_2^{2-} , HCO_2^{-} , and CI^- 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.

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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 ('OH) and hydrogen atoms ('H), as shown in Eq. (1), and where gas-phase pyrolysis and/or combustion reactions of volatile substances dissolved in water occur.

$$H_2 O \xrightarrow{\dots} H^{\cdot} + O H \tag{1}$$

~~~

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



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#### Table 1

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



 $Log K_{OH}$ : octanol-water partition coefficient.

 $W_{\rm s}$ : water solubility, mg L<sup>-1</sup> (20 °C).

 $V_{\rm p}$ : 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<sub>2</sub>. 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 DOW-EX 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  $25.0 \pm 1.0$  °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 ug/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<sub>3</sub>, NaBr or Na<sub>2</sub>CO<sub>3</sub>) 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:  $0.25 \,\mu\text{m}$ ; 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  $\mu$ L. 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<sup>-1</sup> gradient until 200.0 °C, 10.0 °C min<sup>-1</sup> until 220.0 °C, 30 °C min<sup>-1</sup> until 270.0 °C, and hold for 3 min. 4-Nitrophenol was analyzed by a Shimadzu



**Fig. 1.** Schematic diagram of the sonochemical reactors: (a) for the tests to investigate the effects of gases; and (b) for all the other tests (1: ultrasonic transducer; 2: stainless steel reaction vessel; 3: sample solution; 4: water bath; 5: cooling water inlet; 6: cooling water outlet; 7: ultrasonic generator; 8: gas inlet; 9: gas outlet; 10: sealed but operable sampling point).



Fig. 2. Effect of ultrasonic intensity on parathion sonolysis (initial parathion =  $2.9 \mu$ M; and ultrasonic frequency = 600 kHz).



**Fig. 3.** Effect of dissolved gas on parathion degradation (initial parathion =  $2.9 \mu$ M; ultrasonic frequency = 600 kHz; and ultrasonic intensity =  $0.69 \text{ W/cm}^2$ ).



**Fig. 4.** Effect of anions on parathion degradation and the paraoxon formation: (a) parathion degradation; (b) paraoxon formation) (initial parathion =  $2.9 \,\mu$ M; ultrasonic frequency =  $600 \,$ kHz; ultrasonic intensity =  $0.69 \,$ W/cm<sup>2</sup>).



**Fig. 5.** Effects of different components of dissolved natural organic matters on parathion degradation (initial parathion =  $2.9 \mu$ M; ultrasonic frequency = 600 kHz; ultrasonic intensity =  $0.69 \text{ W/cm}^2$ ).

LC-2010AHT HPLC equipped with a VP-ODS column (250 mm  $\times$  4.6 mm i.d.) and ultraviolet detector (UV wavelength = 318 nm). Elution was performed with a mobile phase composed of acetoni-trile/water/acetic acid (50:49.6:0.4, v/v/v). Dissolved organic car-

bon (DOC) was measured by Shimadzu TOC- $V_{CPH}$ . In order to calculate the actual ultrasonic intensity, the energy dissipated by the transducer of ultrasonic device was determined by calorimetry [18].

# 3. Results and discussion

#### 3.1. Effect of ultrasonic intensity on parathion degradation

The effect of ultrasonic intensity on parathion degradation with time is shown in Fig. 2. The degradation was pseudo 1st-order a reaction at various actual ultrasonic intensities  $(0.10-0.69 \text{ W/ cm}^2)$ . The degradation rate of parathion proportionally increased from 0.020 to 0.192 min<sup>-1</sup> with the increasing ultrasonic intensity from 0.10 to 0.69 W/cm<sup>2</sup> (as shown in Table 2). The positive effect was primarily due to the enhanced cavitational activity at higher ultrasonic intensity that increased the number and violence of bubble collapse. In addition, the mixing intensity was also enhanced with the increasing ultrasonic intensity due to the acoustic streaming generated by cavitational processes, in agreement with the previous findings about other Ops [19–21].

# 3.2. Effects of different dissolved gases on parathion degradation

The effects of different dissolved gases, O<sub>2</sub>, N<sub>2</sub>, and air, on parathion degradation are shown in Fig. 3. The degradation in the presence of O<sub>2</sub>, N<sub>2</sub>, or air was a pseudo 1st-order reaction. Among them, O<sub>2</sub> could achieve the highest rate constant of 0.288 min<sup>-1</sup>, followed by air  $(0.211 \text{ min}^{-1})$ , no gas addition  $(0.186 \text{ min}^{-1})$  and N<sub>2</sub>  $(0.123 \text{ min}^{-1})$  (as shown in Table 3). Owning to the little difference between their specific heats ( $O_2$ ,  $\gamma = 1.39$ ;  $N_2$ ,  $\gamma = 1.40$ ), the dissimilarity of the two gases in the impacts on parathion degradation is not related the well-known gas property that significantly influences the final collapse temperatures and pressures within the bubbles [22]. Under ultrasonic irradiation, water vapor can be pyrolyzed to  $\cdot$ OH and  $\cdot$ H, as shown in Eq. (1). After O<sub>2</sub> enters the vapor phase of the bubble, it can undergo pyrolysis (Eq. (2)), because the dissociative bond energies in the gas-phase for water and oxygen are both 119 kcal mol<sup>-1</sup> [23]. The formed highly active oxygen atom ('O') can react with water molecules to form 'OH, as shown in Eq. (3). Moreover,  $O_2$  can also combine abundant hydrogen atom ('H) inside the bubbles (Eq. (5)), or at the relatively cool interfacial region (Eq. (6)), to form additional 'OH [24]. Some 'OH can form H<sub>2</sub>O<sub>2</sub> through Eqs. (7) and (8). Wakeford et al. [22] reported that the formation rate of H<sub>2</sub>O<sub>2</sub> was much higher in O<sub>2</sub>- or air-saturated

Table 2

Pseudo 1st-order rate constants for the sonochemical degradation of parathion under different ultrasonic intensities.

| $k_{app}$ (min <sup>-1</sup> ) | $R^2$                                                                     |
|--------------------------------|---------------------------------------------------------------------------|
| 0.199                          | 0.992                                                                     |
| 0.108                          | 0.987                                                                     |
| 0.049                          | 0.997                                                                     |
| 0.020                          | 0.990                                                                     |
|                                | k <sub>app</sub> (min <sup>-1</sup> )<br>0.199<br>0.108<br>0.049<br>0.020 |

Table 3

Pseudo 1st-order rate constants for the sonochemical degradation of parathion under different dissolved gas conditions.

| Dissolved gas     | $k_{app}$ (min <sup>-1</sup> ) | $R^2$ |
|-------------------|--------------------------------|-------|
| 02                | 0.288                          | 0.997 |
| N <sub>2</sub>    | 0.123                          | 0.993 |
| Air               | 0.211                          | 0.998 |
| None gas addition | 0.186                          | 0.998 |

water than in N<sub>2</sub>-saturated water. Therefore, the positive impact of  $O_2$  on parathion sonolysis is due to the increase in 'OH production. On the other side, N<sub>2</sub> present in bubble can scavenge free radicals [25], as shown in Eqs. (9)–(14), and thus inhibit the parathion degradation. Yasui et al. [26] reported that 'OH and 'O' were rapidly consumed inside bubbles by oxidizing nitrogen when the temperature during the bubble collapse was higher than 7000 K.

| $O_2 \xrightarrow{)))} 2^{\circ}O^{\circ}$                                                                  | (2)  |
|-------------------------------------------------------------------------------------------------------------|------|
| $^{\cdot}O^{\cdot}+H_{2}O\rightarrow2^{\cdot}OH$                                                            | (3)  |
| $2{}^{\boldsymbol{\cdot}}OH \to {}^{\boldsymbol{\cdot}}O{}^{\boldsymbol{\cdot}} + H_2O$                     | (4)  |
| $0_2 + H^{\text{\cdot}} \rightarrow {}^{\text{\cdot}}OH + {}^{\text{\cdot}}O^{\text{\cdot}}$                | (5)  |
| $O_2 + H^{\textstyle \cdot} \rightarrow {\textstyle \cdot} O_2 H$                                           | (6)  |
| $2HO^{\boldsymbol{\cdot}} \to H_2O_2$                                                                       | (7)  |
| $2HO_2^{\textbf{\cdot}} \rightarrow O_2 + H_2O_2$                                                           | (8)  |
| $N_2 + {}^{\boldsymbol{\cdot}}OH \to NO_2 + H{}^{\boldsymbol{\cdot}}$                                       | (9)  |
| $N_2 + {}^{\boldsymbol{\cdot}}O^{\boldsymbol{\cdot}} \to NO^{\boldsymbol{\cdot}} + N^{\boldsymbol{\cdot}}$  | (10) |
| $0_2 + N^{\textstyle{\cdot}} \rightarrow N0^{\textstyle{\cdot}} + {\textstyle{\cdot}}0^{\textstyle{\cdot}}$ | (11) |
| $NO^{\textbf{\cdot}} + O^{\textbf{\cdot}} \rightarrow \textbf{\cdot}NO_2$                                   | (12) |
| $NO^{\boldsymbol{\cdot}} + {\boldsymbol{\cdot}}OH \to HNO_2$                                                | (13) |
| $\cdot \text{NO}_2 + \cdot \text{OH} \rightarrow \text{HNO}_3$                                              | (14) |
|                                                                                                             |      |

air–water interface and therefore react with 'OH to yield stable and long-lived radical anion,  $Br_2^-$  and inhibit the self-recombination of 'OH at the air–water interface (Eqs. (15)–(20)) [29]. Although the 'OH is consumed in the presence of  $Br^-$ , the total amount of radical increased at the interface region. Secondly, compared with 'OH, the non-recombined  $Br_2^-$  is more easy to diffuse out of the water cage into the bulk solution to react with parathion [30]. Moreover,  $Br_2^-$  has been demonstrated to be relatively more selective than 'OH in its reaction with organic sulfur compounds, including sulfides [31,32]. The reaction between parathion and  $Br_2^-$  is shown in Eq. (21).  $Br_2^-$  attacks P=S bond to finally form paraoxon (P=O) and re-release Br<sup>-</sup>.

$$Br^{-} + OH \rightarrow BrOH^{-}, \quad k = 1.06 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$$
 (15)

- $BrOH^{-} \rightarrow Br^{-} + OH^{-}, \quad k = 4.2 \times 10^{6} \text{ M}^{-1} \text{ s}^{-1}$  (16)
- $BrOH^{-} \rightarrow Br^{-} + OH, \quad k = (3.3 \pm 0.4) \times 10^{7} \text{ M}^{-1} \text{ s}^{-1}$  (17)
- $BrOH^{-} + Br^{-} \rightarrow Br_{2}^{-} + OH^{-}, \quad k = 1.9 \times 10^{8} \text{ M}^{-1} \text{ s}^{-1}$  (18)
- $Br^{-} + Br^{-} \to Br^{-}_{2}, \quad k \approx \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  (19)

$$^{\circ}OH + ^{\circ}OH \rightarrow H_2O_2, \quad k = 1.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$$
 (20)



#### 3.3. Effects of various anions on parathion degradation

Effects of different anions on parathion sonolysis are shown in Fig. 4(a). The pseudo 1st-order rate constants of parathion degradation with different anions additions are summarized in Table 4. The  $CO_3^{2-}$ ,  $HCO_3^{-}$ , and  $CI^-$  slowed the parathion degradation, and the degrees of their inhibiting effects followed the order of  $CO_3^{2-} > HCO_3^- > CI^-$ . However,  $Br^-$  exhibited a promoting effect to enhance the decomposition, and the promoting effect was increased with the increasing  $Br^-$  concentration.  $CO_3^{2-}$  and  $HCO_3^-$  have a well-known 'OH scavenging effect due to their high rate constants with 'OH in bulk solution  $(1.5 \times 10^7)$  and  $3.8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ , respectively) [27,28].

The promoting effect of Br<sup>-</sup> can be explained as follows: Firstly, Br<sup>-</sup> at sufficiently high concentration could be able to reach the

The formations of paraoxon in the presence of different anions under ultrasonic irradiation of parathion are shown in Fig. 4(b). The produced paraoxon had the highest level when  $Br^-$  was present thus supporting the enhanced hypothesis mentioned above.

#### Table 4

Pseudo 1st-order rate constants for the sonochemical degradation of parathion under different anion additions.

| Anion                                 | $k_{app}$ (min <sup>-1</sup> ) | $R^2$ |
|---------------------------------------|--------------------------------|-------|
| 0.010 M CO <sub>3</sub> <sup>2-</sup> | 0.138                          | 0.996 |
| 0.010 M HCO3                          | 0.166                          | 0.999 |
| 0.010 M Cl-                           | 0.186                          | 0.999 |
| 0.010 M Br <sup>-</sup>               | 1.080                          | 0.949 |
| 0.001 M Br <sup>-</sup>               | 0.388                          | 0.975 |
| None                                  | 0.199                          | 0.992 |
|                                       |                                |       |

To our knowledge, this is the first finding on the enhanced effect of Br<sup>-</sup> on sonolytic degradation. Kotronarou et al. reported a similar finding that another halogen ion I<sup>-</sup> could accelerate the sonolytic degradation of both carbon tetrachloride and H<sub>2</sub>S with a 3– 10-fold enhancement in overall reaction rate [33]. Among all anions studied, Cl<sup>-</sup> only slightly slowed down the degradation of parathion, as shown in Fig. 4(a). Although Cl<sup>-</sup>, as another halogen ion, can also react with 'OH to finally yield Cl<sup>-</sup><sub>2</sub>, the primary intermediate radical 'ClOH<sup>-</sup> itself is unstable so that formation Cl<sup>-</sup><sub>2</sub> is more difficult than the production of Br<sup>-</sup><sub>2</sub> (Eqs. (22) and (23)) [27,34].

$$Cl^{-} + OH \rightarrow ClOH^{-}, \quad k = 4.3 \times 10^{9} \text{ M}^{-1} \text{ s}^{-1}$$
 (22)

$$\cdot \text{ClOH}^- \to \text{Cl}^- + \cdot \text{OH}, \quad k = 6.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$$
 (23)

Thus, little difference in parathion degradation was observed with no addition of any anion and in the presence of  $Cl^-$ , as shown in Fig. 4(a). Moreover, the introduction of  $Cl^-$  did not significantly influence the formation rate of paraoxon, compared with that in the control (no additional anions), as shown in Fig. 4(b).

# 3.4. Effects of different components of dissolved natural organic matters on parathion degradation

The effects of different components of dissolved NOM on parathion are shown in Fig. 5. The pseudo 1st-order rate constants of parathion degradation with different components of dissolved natural organic matters are summarized in Table 5. Hydrophobic and hydrophilic NOM both slowed down the parathion degradation, but the inhibiting effect caused by hydrophobic component was more significant, particularly the strongly hydrophobic component. Since parathion is a strongly hydrophobic organic compound itself, the strongly hydrophobic NOM component with the similar

Table 5

Pseudo 1st-order rate constants for the sonochemical degradation of parathion under different components of dissolved natural organic matters additions.

| Components               | $k_{app}$ (min <sup>-1</sup> ) | $R^2$ |
|--------------------------|--------------------------------|-------|
| Strongly hydrophobic NOM | 0.127                          | 0.998 |
| Weekly hydrophobic NOM   | 0.156                          | 0.998 |
| Hydrophilic NOM          | 0.180                          | 0.996 |
| None                     | 0.199                          | 0.998 |
|                          |                                |       |

hydrophobic properties may have a stronger competition with parathion for reactive oxygen species, especially at the interface region of the cavitational bubbles [35].

# 3.5. The models of parathion degradation and the formation of paraoxon and 4-nitrophenol

A proposed mechanism of parathion sonolysis is showed in Fig. 6. The first step of parathion degradation under ultrasonic irradiation included: (1) Route I: the oxidative attack by 'OH on the P=S bond, which results in the formation of paraoxon; [36,37] (2) Route II: the decomposition of *p*-nitrophenoxy mainly caused by hydrolysis, which results in the formation of 4-nitrophenol and O,O-diethyl phosphorothioate [38,39]. (4) Route III indicates that the remainder of parathion is sonolyzed into some unknown products (e.g. small organic molecules formed by directly pyrolysis of parathion, a semi-volatile compound, inside the bubbles).

The continuous attack of 'OH on P=O bond of paraoxon (Routes I–I) and the hydrolysis of paraoxon (Route I–II) results in the formation of the 4-nitrophenol and O,O-diethyl phosphonic ester. Route I–III indicates that the remainder of paraoxon is sonolyzed into some unknown products. In each pathway, the sonolysis is a pseudo 1st-order degradation reaction [28]. Therefore, the overall parathion degradation is expressed as Eq. (24).

$$\frac{d[\text{parathion}]}{dt} = -(k_{\text{I}} + k_{\text{II}} + k_{\text{III}})[\text{parathion}] = -k_0[\text{parathion}] \quad (24)$$

where,  $k_{I}$ ,  $k_{II}$  and  $k_{III}$  are the pseudo 1st-order rate constants for each pathway of parathion degradation in Fig. 6, and  $k_0$  is the overall rate constant. Also, the formation of paraoxon and 4-nitrophenol can be expressed as Eqs. (24) and (25), respectively:

$$\frac{d[\text{paraoxon }]}{dt} = \eta_1 k_0 [\text{parathion }] - (k_{1-1} + k_{1-11} + k_{1-111}) [\text{paraoxon }]$$
$$= \eta_1 k_0 [\text{parathion }] - k_1 [\text{paraoxon }]$$
(25)

where,  $k_{1-1}$ ,  $k_{1-11}$  and  $k_{1-111}$  are the pseudo 1st-order rate constants for each pathway of paraoxon degradation in Fig. 6, and  $k_1$  is the overall rate constant for sonolytic degradation of paraoxon.

$$\frac{d[4 - \text{nitrophenol}]}{dt} = \eta_2 k_0 [\text{parathion}] + \eta_3 k_1 [\text{paraoxon}] - k_2 [4 - \text{nitrophenol}]$$
(26)



Fig. 6. The proposed reaction pathways for parathion sonolysis.



Fig. 7. The model of parathion degradation and the formation of paraoxon and 4-nitrophenol (ultrasonic frequency = 600 kHz; and ultrasonic intensity = 0.69 W/cm<sup>2</sup>, none gas.).

# Table 6 Estimated values of rate constants and fractions (ultrasonic frequency = 600 kHz; and ultrasonic intensity = 0.69 W/cm<sup>2</sup>, none gas).

| Constant                                     | Value ( $M^{-1} s^{-1}$ ) | Fraction coefficient | Value  |
|----------------------------------------------|---------------------------|----------------------|--------|
| $egin{array}{c} k_0 \ k_1 \ k_2 \end{array}$ | 0.1988                    | η <sub>1</sub>       | 0.2819 |
|                                              | 0.1458                    | η <sub>2</sub>       | 0.3292 |
|                                              | 0.0972                    | η <sub>3</sub>       | 0.6661 |

where  $\eta_1$  and  $\eta_2$  are the fraction coefficients ( $\eta_1 = k_{\rm I}/k_0$ ,  $\eta_2 = k_{\rm II}/k_0$ ) of parathion degradation via Routes I and II, respectively.  $\eta_3$  is the fraction coefficient ( $\eta_3 = (k_{\rm I-I} + k_{\rm I-II})/k_1$ ) of paraoxon degraded via Route I–I and I–II.  $k_2$  is the overall rate pseudo 1st-order rate constant for sonolytic degradation of 4-nitrophenol.

Integration and rearrangement of Eqs. (24)–(26) give Eqs. (27)–(29), which can be used to predict the concentrations of parathion, paraoxon and 4-nitrophenol as a function of time:

$$[\text{parathion}]_t = [\text{parathion}]_0 e^{-k_0 t} \tag{27}$$

$$[paraoxon]_{t} = \left(\frac{\eta_{1}k_{0}[parathion]_{0}}{k_{1} - k_{0}}\right) \left[\frac{e^{(k_{1} - k_{0})t} - 1}{e^{k_{1}t}}\right]$$
(28)

$$[4\text{-nitrophenol}]_{t} = \left(\frac{k_{0}[\text{parathion}]_{0}}{k_{1} - k_{0}}\right) \left\{ \left(\frac{\eta_{2}k_{1} + \eta_{1}\eta_{3}k_{1} - \eta_{2}k_{0}}{k_{2} - k_{0}}\right) \\ \times \left[\frac{e^{(k_{2} - k_{0})t} - 1}{e^{k_{2}t}}\right] - \left(\frac{\eta_{1}\eta_{3}k_{1}}{k_{2} - k_{1}}\right) \left[\frac{e^{(k_{2} - k_{1})t} - 1}{e^{k_{2}t}}\right] \right\}$$
(29)

The rate constants  $k_0$ ,  $k_1$ ,  $k_2$  and the fraction coefficients  $\eta_1$ ,  $\eta_2$ ,  $\eta_3$  were determined by the least-square method via the Matlab 2008a program (MathWorks, Inc.), as shown in Fig. 7.

The observed data well fit the modeled data from Eqs. (27)–(29) as shown in Table 6. Under ultrasonic irradiation, 28.19% of the parathion was degraded into paraoxon (Route I), and 32.92% of parathion was transformed to 4-nitrophenol (Route II). In addition, 66.61% of paraoxon produced was degraded into 4-nitrophenol (Route I–I and Route I–II).Of note, the degradation of parathion into paraoxon (Route I) was regarded as the predominant pathway for photolysis or photocatalysis of parathion [36,37]. However, our observation indicates that parathion is decomposed by sonolysis in a different fashion. Three parallel pathways explain the parathion degradation, including paraoxon formation (Route I), 4-nitrophenel formation (Route II), and production of unknown species

(Route III), among which any one cannot be overlooked. Moreover, hydrolysis contribute the transformation of parathion to 4-nitrophenel in Route II. Several previous studies [20,40,41] showed that ultrasonic irradiation can accelerate the hydrolysis of ester due to formation of a hot water shell at the cavitation bubble interface.

# 4. Conclusions

This paper provides a full picture of parathion degradation under ultrasonic irradiation. In this study, 99.6% of 2.9 µM parathion was decomposed at neutral conditions within 30 min under 600 kHz ultrasonic irradiation. Dissolved oxygen greatly enhanced the degradation, while nitrogen gas slowed down the reactions due to its free radical scavenging effect in vapor phase within the cavitational bubbles. Thus, air bubbling of parathion-containing solution may be a method to increase the treatment efficiency of sonolysis in practice. Moreover,  $CO_3^{2-}$ ,  $HCO_3^{-}$ , and  $Cl^{-}$  were found to have inhibiting effects on parathion degradation, and their inhibition degrees followed the order of  $CO_3^{2-} > HCO_3^{-} > CI^{-}$ , implying that removal of alkalinity prior to sonolysis is another potential pre-treatment process. Differently, Br<sup>-</sup> enhanced the parathion degradation, and the promoting effect was further enhanced with the increasing Br<sup>-</sup> concentration. Both the hydrophobic and hydrophilic natural organic matters slowed the parathion degradation rate, but the inhibiting effect caused by hydrophobic component was greater. Based on the proposed pathways of parathion sonolysis, kinetics models could be established to well predict the concentrations of parathion, paraoxon and 4-nitrophenol as a function of time. Under ultrasonic irradiation, the first step of parathion degradation includes three parallel pathways: (1) formation of paraoxon; (2) formation of 4-nitrophenol; and (3) unknown species production. The fractions of the parathion decomposed via the three pathways were 28.19%, 32.92%, and 38.89%, respectively. This observation indicates that the primary mechanism of parathion sonolysis is different from photo-degradation of parathion, in which the first pathway is the dominant one. In addition, 66.61% of paraoxon produced was degraded into 4-nitrophenol. To sum up, our results demonstrate that ultrasonic irradiation is an effective treatment for control of aqueous parathion.

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#### References

- [1] K.V. Ragnarsdottir, Journal of the Geological Society 157 (2000) 859-876.
- [2] Z. Zhang, H. Hong, X. Wang, et al., Marine Pollution Bulletin 45 (2002) 397-402.
- [3] M. Liess, R. Schulz, M.H.D. Liess, et al., Water Research 33 (1999) 239-247.
- [4] EPAUS EPA RED Facts, Ethyl-parathion, 2000.
- [5] AM China, No. 199 Announcement of the Ministry of Agriculture, China, 2007.
- [6] F. Tian, X. Wu, H. Pan, et al., Neurotoxicology 28 (2007) 843-849. [7] F. Monnet-Tschudi, M. Zurich, B. Schilter, et al., Toxicology and Applied Pharmacology 165 (2000) 175-183.
- [8] K. Ohno, T. Minami, Y. Matsui, et al., Water Research 42 (2008) 1753-1759.
- [9] J. Wu, D.A. Laird, Environmental Toxicology and Chemistry 22 (2003) 261-264.
- [10] C. Wu, K.G. Linden, Water Research 42 (2008) 4780-4790.
- [11] M. Inoue, Y. Masuda, F. Okada, et al., Water Research 42 (2008) 1379–1386.
- [12] W. Song, K.E. O'Shea, Water Research 41 (2007) 2672-2678 [13] M. Goel, H. Hongqiang, A.S. Mujumdar, et al., Water Research 38 (2004) 4247-4261.
- [14] C. Vassilakis, A. Pantidou, E. Psillakis, et al., Water Research 38 (2004) 3110-3118
- [15] O. Hamdaoui, E. Naffrechoux, Ultrasonics Sonochemistry 15 (2008) 981-987. [16] A. Kotronarou, G. Mills, M.R. Hoffmann, Environmental Science and
- Technology 26 (1992) 1460-1462. [17] C. Berthe, E. Redon, G. Feuillade, Journal of Hazardous Materials 154 (2008)
- 262-271
- [18] T. Kimura, T. Sakamoto, J. Leveque, et al., Ultrasonics Sonochemistry 3 (1996) S157-S161.
- [19] J. Wang, W. Sun, Z. Zhang, et al., Journal of Molecular Catalysis A: Chemical 272 (2007) 84-90.
- [20] J.D. Schramm, I. Hua, Water Research 35 (2001) 665-674.
- [21] J. Wang, Z. Pan, Z. Zhang, et al., Ultrasonics Sonochemistry 13 (2006) 493-500. [22] C.A. Wakeford, R. Blackburn, P.D. Lickiss, Ultrasonics Sonochemistry 6 (1999) 141-148
- [23] Inez Hua, M.R. Hoffmann, et al., Environmental Science and Technology 31 (1997) 2237-2243.

- [24] R.A. Torres, C. Petrier, et al., Environmental Science and Technology 41 (2007) 297\_302
- [25] V. Mišík, P. Riesz, Journal of Physical Chemistry 100 (1996) 17986-17994.
- [26] K. Yasui, T. Tuziuti, T. Kozuka, et al., Journal of Chemical Physics 127 (2007)
- 154502-154509 [27] G.V. Buxton, C.L. Greenstock, W.P. Helman, et al., Journal of Physical and Chemical Reference Data 17 (1988).
- J. Kang, M.R. Hoffmann, Environmental Science and Technology 32 (1998) [28] 3194-3199
- [29] D. Zehavi, J. Rabani, The Journal of Physical Chemistry 76 (1972) 312-319.
- [30] R. Das, B. Dutta, V. Maurino, et al., Environmental Chemistry Letters 7 (2009) 337-342.
- [31] R. Bouillon, W.L. Miller, Environmental Science and Technology 39 (2005) 9471-9477
- [32] G.E. Adams, R.H. Bisby, J.L. Redpath, et al., Radiation Research 49 (1972) 290.
- [33] A. Kotronarou, California Institute of Technology, California, 1992.
- [34] P. Neta, R.E. Huie, A.B. Ross, Journal of Physical and Chemical Reference Data 17 (1988) 1027-1234.
- [35] M.R. Hoffmann, I. Hua, R. Höchemer, Ultrasonics Sonochemistry 3 (1996) S163-S172.
- E. Moctezuma, E. Leyva, G. Palestino, et al., Water Research 186 (2007) 71-84. [37] E. Evgenidou, I. Konstantinou, K. Fytianos, et al., Catalysis Today 124 (2007)
- 156 162[38] K.V. Ragnarsdottir, Journal of the Geological Society, London 157 (2000) 859-
- 876 [39] J.J. Yao, N.Y. Gao, C. Li, et al., Journal of Hazardous Materials 175 (2010) 138-
- 145.
- [40] B. Yim, Y. Nagata, Y. Maeda, The Journal of Physical Chemistry A 106 (2002) 104-107.
- [41] M. Sakakura, M. Takayama, Ultrasonics Sonochemistry 16 (2009) 367-371.
- [42] US Epa, Health Effects Assessment for Parathion. EPA/600/8-88/047. Environmental Criteria and Assessment Office, Office of Health and Environmental Assessment, Office of Research and Development, Cincinnati, OH. 1988.
- [43] J. Wang, Z. Pan, Z. Zhang, et al., Ultrasonics Sonochemistry 13 (2006) 493-500.
- [44] J. Wang, W. Sun, Z. Zhang, et al., Journal of Molecular Catalysis A: Chemical 272 (2007) 84-90.