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Heterogeneous kinetics of the OH-initiated degradation of fenthion and parathion

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ABSTRACT

Fenthion and parathion are two representative kinds of organophosphorus pesticides and widely used in agriculture. They are directly or indirectly released into the atmosphere by spraying or volatilization processes. However, their heterogeneous reactivity toward OH radicals has not yet been well understood. Therefore, this work investigated the heterogeneous kinetics of the OH-initiated degradation of surface-bound fenthion and parathion using a flow reactor. The results showed that OH radicals played an important role in the atmospheric degradation of fenthion and parathion. Their average rate constants were $(7.20 \pm 0.77) \times 10^{-12}$ and $(10.40 \pm 0.60) \times 10^{-12} \text{ cm}^3/(\text{mol} \cdot \text{sec})$ at a relative humidity (RH) and temperature of 35% and 20 °C, respectively, suggesting that they have relatively short lifetimes in the atmosphere. In addition, a negative RH dependence and a positive temperature dependence of the rate constants were observed. The Arrhenius expressions of fenthion and parathion were $k_2 = (1.34 \pm 0.48) \times 10^{-9} \exp[-(1432.59 \pm 105.29)/T]$ and $k_2 = (1.96 \pm 1.38) \times 10^{-9} \exp[-(1619.98 \pm 222.02)/T]$, respectively, and their overall activation energy was estimated to be (11.88 ± 0.87) and $(13.48 \pm 1.83) \text{ kJ/mol}$. The experimental results will update the kinetic data of fenthion and parathion in the atmosphere and be helpful to further understand their atmospheric transportation processes.

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Introduction

Organophosphorus pesticides (OPPs) are widely used in agriculture for crop protection with the aim to improve production and quality (Avino et al., 2011). The amount of pesticides used

in the world is approximately 2 million tons every year (Li and Niu, 2021), and the amount of OPPs accounts for approximately 38% of the total pesticides (Marrs et al., 2007), which is equal to about 0.8 million tons every year. During the application process, up to 90% of pesticides cannot effectively reach the targeted crops, the specific fraction of which is depen-

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dent on their physical properties, application methods, and meteorological conditions (Gil and Sinfort, 2005; Bouya et al., 2015). In addition, approximately 15%–40% of pesticides are directly or indirectly released into the atmosphere by spraying or volatilization processes (Sinfort et al., 2009; Yates et al., 2015), the amount of which is about 0.3–0.8 million tons every year. The removal channels of pesticides in the atmosphere mainly include dry and wet depositions, and chemical reactions with gas-phase oxidants during transportation process (Van Den Berg et al., 1999; Hu et al., 2013). Through the chemical oxidation of the P=S bond to the P=O bond, the formed oxon products of OPPs are always higher toxic than their parent compounds (Raina et al., 2010). Thus, the environmental health and safety problems caused by OPPs and their degradation products should be seriously considered.

The current widely-used pesticides including OPPs are semi-volatile and can be present in both gas and particle phases in the atmosphere, the distribution fractions of which mainly depend on their physicochemical characteristics and environmental conditions (Munoz et al., 2011). In recent years, the atmospheric degradation kinetics, products, and mechanisms of pesticides have attracted increasing attention from academic community (Borras et al., 2015a, 2015b, 2017; Bouya et al., 2015; Vera et al., 2015; Yang et al., 2015; Socorro et al., 2016; Mattei et al., 2018, 2019a, 2019b, 2019c; Murschell and Farmer, 2019; Rokbani et al., 2019), with the aim to provide crucial information for understanding their environmental chemical behaviors and potential risk to non-targets. Due to the semi-volatile property, most pesticides partly adsorb on the surface of atmospheric aerosols (Socorro et al., 2016). Thus, the heterogeneous degradation of pesticides should reasonably play an important role during their atmospheric transportation processes. Previous studies have studied the heterogeneous reactions of some pesticides by O_3 , OH radicals, and NO_3 radicals, suggesting that the heterogeneous degradation of pesticides by OH radicals and NO_3 radicals are important pathways due to their fast rate constants (Bouya et al., 2015; Socorro et al., 2016; Mattei et al., 2018, 2019a, 2019b, 2019c; Rokbani et al., 2019). In addition, pesticide concentration, relative humidity (RH), and substrate type have significant impacts on heterogeneous degradation of pesticides (Mattei et al., 2018, 2019a, 2019c). However, very limited studies has investigated the heterogeneous reactions of OPPs with atmospheric gas-phase oxidants though OPPs are still widely used in agriculture (Liu et al., 2012, 2015).

Fenthion (O,O-dimethyl O-[3-methyl-4-(methylthio)phenyl] phosphorothioate) and parathion (O,O-diethyl O-(4-

nitrophenyl) phosphorothioate) are two typical kinds of OPPs and cause the death of target organisms from respiratory failure due to the inhibitory activity to acetylcholinesterase (Cheke and Sidatt, 2019). Their chemical structures are shown in Fig. 1. Parathion has been banned for production, sale, and use in China in 2020 due to its high toxicity (Ministry of Agriculture and Rural Affairs of the People's Republic of China, 2020), but it is still widely used in agriculture in some countries (Calaf et al., 2021; Tao et al., 2021). In the atmosphere, they exist in both gas and particle phases due to their low vapor pressures of approximately 10^{-3} Pa at 25 °C (US EPA, 2012). According to a simple gas-particle partitioning model proposed by Kroll and Seinfeld (2008), the fractions of fenthion and parathion adsorbed on atmospheric particles are approximately 20% and 28% at a temperature and an annual organic aerosol (OA) mass loading of 25 °C and $40 \mu\text{g}/\text{m}^3$ (Huang et al., 2017), respectively, and these fractions can be approximately 50% when the OA mass loading is over $100 \mu\text{g}/\text{m}^3$ in the polluted days (Guo et al., 2014; Huang et al., 2014). The rate constants for the gas-phase reactions of fenthion and parathion with OH radicals can be obtained by the Atmospheric Oxidation Program for Microsoft Windows (AOP WIN) model or theoretical calculation. But, it has been demonstrated that the rate constants for the heterogeneous reactions of organophosphate compounds with OH radicals are much lower than those for their gas-phase reactions (Liu et al., 2014b, 2014c). The widely accepted reason for this is the inaccurate representation of the electronic effects of the functional groups on the reactivity during the calculation process of the AOP WIN model (Lauraguais et al., 2012). Therefore, the experiments are necessary to measure the heterogeneous kinetics of fenthion and parathion due to their relatively significant particle-phase fractions. Previous studies have investigated the heterogeneous reactivity of fenthion and parathion toward NO_3 radicals and reported their degradation products and kinetics (Liu et al., 2012, 2015). However, their heterogeneous degradation by OH radicals has not yet been reported though OH radicals are widely taken as an important oxidant for the atmospheric degradation of organic pollutants (Atkinson, 1986). Therefore, the kinetics of the heterogeneous reactions of OH radicals with fenthion and parathion adsorbed on quartz plates was investigated in a flow reactor in this work. The impacts of RH and temperature on their rate constants were also investigated. The obtained rate constants were compared to those of other pesticides with gas-phase oxidants. The experimental results will update kinetic data of the heterogeneous degradation of

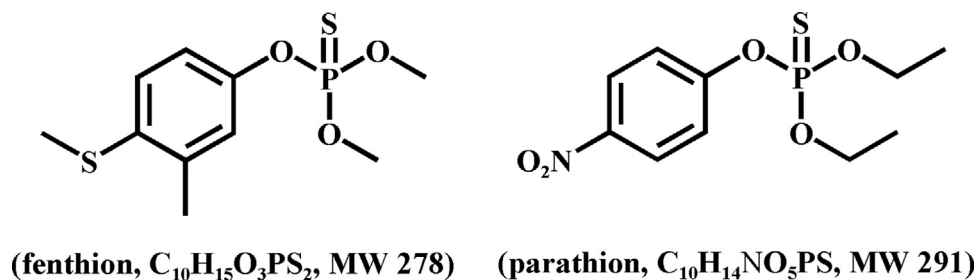


Fig. 1 – Chemical structures of fenthion and parathion.

these two OPPs and be helpful in further understanding their chemical behaviors in the atmosphere.

1. Materials and methods

1.1. Chemicals

All chemicals were used as received from suppliers. They are listed as follows: methanol ($\geq 99.9\%$) and H_2O_2 (30%) from Sinopharm Chemical Reagent Co., Ltd., China; fenthion ($\geq 98\%$), parathion ($\geq 98\%$), and salicylic acid ($\geq 99\%$) from Sigma-Aldrich, Germany; and dichloromethane (chromatographic grade) from J. T. Baker Co., USA; N_2 (99.99%) and O_2 (99.99%) were from Pangang and Messer gas products Co., Ltd., China.

1.2. Experimental procedures

A schematic diagram of the experimental setup is shown in Fig. S1, the detailed descriptions of which have been described in our previous study (Liu and Zeng, 2018). Thus, only a brief introduction is presented herein. OH radicals were formed in the single quartz tube via H_2O_2 photolysis by 254 nm UV lamp (Jelight Co., Inc., USA). The reactor is made of stainless steel and has a volume of 30 cm^3 (6 cm (length) \times 5 cm (width) \times 1 cm (high)), the inner walls of which are coated by Teflon and are inert. A quartz plate with a surface area of 12 cm^2 (4 cm (length) \times 3 cm (width)) coated with pesticide sample was put in the reactor center and used for kinetic study. The reliability of this system used for kinetic studies of the OH-initiated heterogeneous reactions has been verified by previous studies (Ma et al., 2010; Lai et al., 2014; Liu and Zeng, 2018; Liu et al., 2020).

The coating process of pesticide on quartz plates was that 1 mL of 1 mg/L pesticide/dichloromethane solution was firstly transferred on the quartz plate and then gently dried by the N_2 flow. Lastly, a surface-bound film containing 1 μg pesticide was formed on the quartz plate. During the reaction process, the concentration of OH radicals and the flow (500 mL/min) of a mixture air were invariable. The mean residence time of OH radicals in the reactor was approximately 3.6 sec, which was estimated by the ratio of the reactor volume to the mixture air flow. The mixture air was composed of the bubbled H_2O_2 flow and the simulated air. The RH in the reactor ranged from 20% to 80%, which was achieved by controlling the ratio of dry N_2 flow to wet N_2 flow and was determined at the reactor outlet using a humidity temperature meter (HMP110, Beijing Epoch-tech Science & Technology Co., Ltd., China). The dry N_2 flow bubbled the deionized water to produce the wet N_2 flow. The temperature in the reactor ranged from 5 to 35 °C with an uncertainty of below 0.5 °C, which was realized by a circulation water bath (HX-105, Beijing Changliu Scientific Instruments Co., Ltd., China).

As shown in Fig. S1, it is clear that the quartz tube for the production of OH radicals is independent, thus the degradation of pesticide coated on quartz plates in the reactor is reasonably caused by OH radicals. To measure the evaporation of pesticides and the possible degradation by gaseous H_2O_2 , the control experiments were carried out at 35% RH in a temperature range of 5–35 °C in the dark using the same mixture air flow and H_2O_2 flow as those in the oxidation experiments.

The results showed that the decreases in the concentrations of fenthion and parathion in a temperature range from 5 to 35 °C were lower than 16% and were considered in the correction of kinetic data. When the reaction proceeded to a preset reaction time, the reaction was stopped with the air flow and UV lamp turned off. Meanwhile, the quartz plate was taken out from the reactor and used for pretreatment. For each RH and each temperature, the oxidation experiments were performed for at least 3 times at a preset reaction time. After reaction, the quartz plates were firstly extracted for 3 times and pretreated for the gas chromatography-mass spectrometry (GC-MS) analysis. The detailed descriptions of this process are described in Supplementary material because they have been introduced in detail elsewhere (Liu and Zeng, 2018). For GC-MS analysis, the selected ion monitoring mode was used. The quantification ions of fenthion and parathion were at m/z 278 and 291, respectively. The GC temperature settings for the determination of fenthion and parathion were in line with those reported by Tsakirakis and Machera (2007) and Giordano et al. (2006), respectively. The concentrations of fenthion and parathion were calculated by calibration curves obtained using the external standard method. The recovery rates were more than 94% for fenthion and parathion, suggesting that this method was reliable.

1.3. Determination of OH radicals

OH radicals were formed in an independent quartz tube via H_2O_2 photolysis by 254 nm UV light. The concentration was controlled by adjusting the ratio of N_2 flow to H_2O_2 flow. The determination of OH radicals are described in detail in Supplementary material because this process have been introduced in detail elsewhere (Lai et al., 2014; Liu and Zeng, 2018). Thus, a brief introduction is shown herein. First, the surface-bound film of salicylic acid on quartz plates was prepared according to the same method abovementioned for pesticides. Second, salicylic acid coated quartz plate was put in the reactor center for heterogeneous degradation by OH radicals. At last, the production yields of 2,3-dihydroxybenzoic acid and 2,5-dihydroxybenzoic acid were applied for the determination of the near-surface concentration of OH radicals. In order to achieve reliable results, the ratio of N_2 flow to H_2O_2 flow in the quartz tube used to achieve a specific concentration of OH radicals was the same as that used for the heterogeneous degradation of pesticides. Each OH concentration was measured for 6 times, the standard deviation of which was below 10%. In this work, 3 near-surface concentrations of OH radicals were applied for heterogeneous kinetic studies, which were $(1.8 \pm 0.1) \times 10^7$, $(3.5 \pm 0.1) \times 10^7$, and $(5.4 \pm 0.2) \times 10^7 \text{ mol/cm}^3$, respectively.

2. Results and discussion

2.1. Degradation kinetics

The OH-initiated reactions of fenthion and parathion adsorbed on quartz plates were considered as the second-order reactions in this work. Thus, the kinetic data can be obtained using the equation $\ln(C/C_0) = -k_2[\text{OH}]t$ (Lai et al., 2014), where C and C_0 are the residual and initial concentrations

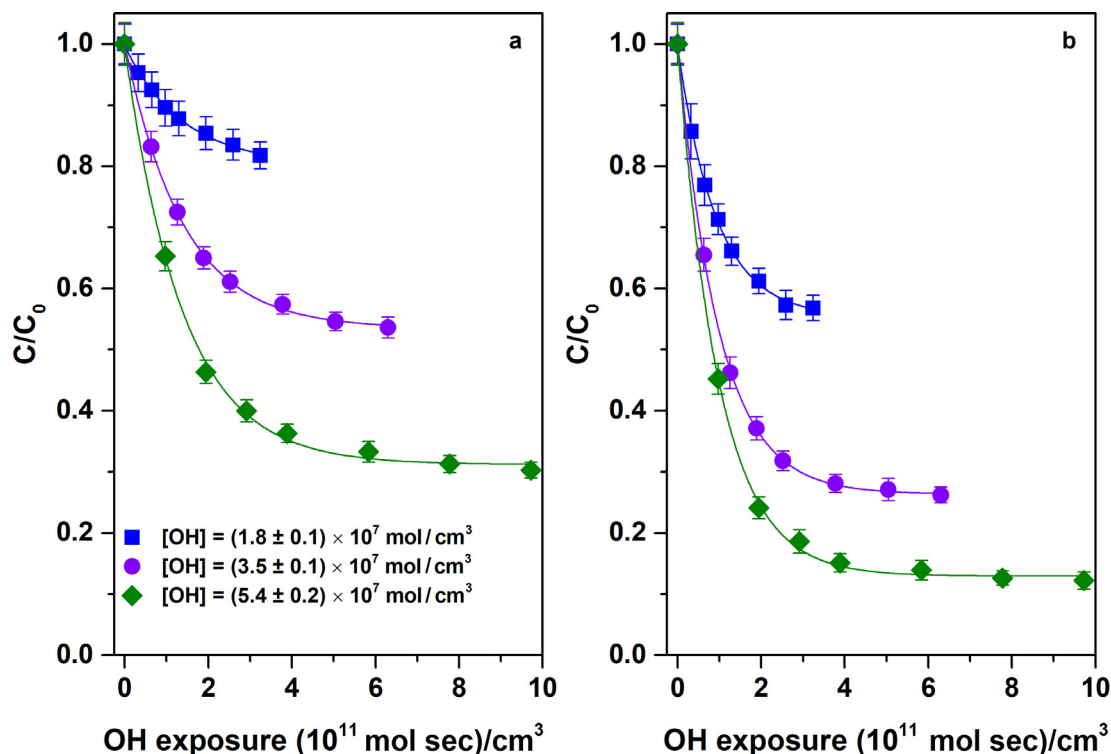


Fig. 2 – Degradation of fenthion (a) and parathion (b) as a function of OH exposure at 3 different concentrations of OH radicals (RH = 35% and temperature = 20 °C).

of pesticide, respectively, k_2 is the second-order rate constant ($\text{cm}^3/(\text{mol} \cdot \text{sec})$), $[\text{OH}]$ is the near-surface concentration of OH radicals ($\text{molecules}/\text{cm}^3$), and t is the reaction time (sec).

The heterogeneous degradation of pesticide at different concentrations of OH radicals was carried out at a RH and temperature of 35% and 20 °C, respectively. As shown in Fig. 2, the pesticide concentrations were well fitted by an exponential decay function ($C = C_0 + \exp^{-k_2[\text{OH}]t}$), and the k_2 could be obtained according to the fitted parameter (Lai et al., 2014). It is clear that increasing OH concentration was favorable for enhancing the degradation of pesticide. The possible reason for this might be that more OH radicals diffused into the surface-bound pesticide at higher concentration of OH radicals when some products formed in the surface were further oxidized into higher volatile products, leading to the possible reaction sites for OH radicals (Lai et al., 2015a). In addition, Fig. 2 shows that the plateaus are present regardless the concentration of OH radicals, which should be reasonably resulted from the hindered diffusion of OH radicals caused by the oxidation products formed in the surface (Lai et al., 2015b). This phenomena were also widely reported in the heterogeneous reactions of organic compounds with OH radicals, NO_x radicals, and O_3 (Esteve et al., 2004; Miet et al., 2009; Liu et al., 2017).

As illustrated in Table 1, the rate constants for fenthion or parathion at three different OH concentrations are in agreement, suggesting that this experimental system used in this work is reliable and repeatable. The average values of k_2 for fenthion and parathion were $(7.20 \pm 0.77) \times 10^{-12}$ and $(10.40 \pm 0.60) \times 10^{-12} \text{ cm}^3/(\text{mol} \cdot \text{sec})$, respectively, and their lifetimes in the atmosphere were estimated to be

(1.08 ± 0.12) and (0.74 ± 0.04) days, at a typical OH concentration of $1.5 \times 10^6 \text{ molecules}/\text{cm}^3$ (Mao et al., 2009). These rate constants were much lower than those calculated by the AOP WIN model (US EPA, 2012). Similar comparison results between the AOP WIN model and laboratory measurement were also widely observed (Lai et al., 2014, 2015a, 2015b; Liu and Zeng, 2018; Rokbani et al., 2019; Liu et al., 2020). In other word, the experiments are necessary to measure the rate constants of the heterogeneous reactions of fenthion and parathion with gas-phase oxidants because their atmospheric lifetimes will be significantly underestimated if calculated by the rate constants from the AOP WIN model.

Table 2 shows a brief summary of the kinetic data of the heterogeneous degradation of pesticides by atmospheric gas-phase oxidants. The rate constants for the heterogeneous reactions of pesticides toward O_3 are in a range of 10^{-17} – $10^{-20} \text{ cm}^3/(\text{mol} \cdot \text{sec})$, which are in the ranges of 10^{-11} – 10^{-14} and 10^{-12} – $10^{-15} \text{ cm}^3/(\text{mol} \cdot \text{sec})$ toward OH radicals and NO_3 radicals, respectively. Therefore, the heterogeneous degradation of pesticides by OH radicals and NO_3 radicals should be the predominant pathways. In addition, the reactions of pesticides with OH radicals and NO_3 radicals have similar mechanisms including the electrophilic addition and H-abstraction (Mattei et al., 2019b). As listed in Table 2, the average rate constants of fenthion and parathion obtained in this work are in accordance with those of other pesticides with OH radicals, while are higher than that $((2.97 \pm 0.13) \times 10^{-12})$ for the heterogeneous reaction of NO_3 radicals with parathion adsorbed on suspended azelaic acid particles (Liu et al., 2015).

Table 1 – Summary of rate constants for the heterogeneous reactions of surface-bound fenthion and parathion with OH radicals.

Experimental conditions		Second-order rate constant (k_2 , 10^{-12} cm ³ (mol·sec))		Atmospheric lifetimes ^a (days)	
		fenthion	parathion	fenthion	parathion
OH concentration (molecules/cm ³)	1.8×10^7	7.20 ± 1.10	10.80 ± 0.84	1.08 ± 0.17	0.72 ± 0.06
	3.5×10^7	7.14 ± 0.49	10.22 ± 0.27	1.08 ± 0.07	0.75 ± 0.02
	5.4×10^7	7.24 ± 0.72	10.17 ± 0.68	1.07 ± 0.11	0.76 ± 0.05
	average	7.20 ± 0.77	10.40 ± 0.60	1.08 ± 0.12	0.74 ± 0.04
AOP WIN model (US EPA, 2012)		71.09	92.08	0.11	0.08
RH (%)	20	7.89 ± 0.69	11.00 ± 1.16	0.98 ± 0.09	0.71 ± 0.08
	35	7.14 ± 0.49	10.22 ± 0.27	1.08 ± 0.07	0.75 ± 0.02
	50	6.46 ± 0.63	9.49 ± 0.70	1.20 ± 0.12	0.82 ± 0.06
	65	5.64 ± 0.70	8.76 ± 0.71	1.38 ± 0.17	0.88 ± 0.07
	80	5.12 ± 0.76	7.86 ± 0.59	1.53 ± 0.23	0.98 ± 0.07
temperature (°C)	5	4.74 ± 0.90	7.47 ± 0.77	1.67 ± 0.32	1.04 ± 0.11
	10	5.10 ± 0.42	8.12 ± 1.16	1.52 ± 0.13	0.96 ± 0.14
	20	7.14 ± 0.49	10.22 ± 0.27	1.08 ± 0.07	0.75 ± 0.02
	30	7.65 ± 1.23	11.67 ± 0.98	1.02 ± 0.17	0.66 ± 0.06
	35	8.18 ± 1.20	12.10 ± 0.97	0.96 ± 0.14	0.64 ± 0.05

^a Atmospheric lifetime was calculated using the equation $\tau = 1/k_2[\text{OH}]$, where $[\text{OH}]$ is the typical OH concentration of 1.5×10^6 molecules/cm³ in the atmosphere (Mao et al., 2009).

2.2. Effect of humidity on kinetics

It has been pointed out that the heterogeneous degradation of pesticides can be significantly affected by the RH (Mattei et al., 2018, 2019c). Therefore, the influence of the RH on heterogeneous kinetics was carried out at 20% RH, 35% RH, 50% RH, 65% RH, and 80% RH at a constant temperature and OH concentration of 20 °C and $(3.5 \pm 0.1) \times 10^7$ molecules/cm³, respectively. As shown in Fig. 3, increasing humidity was not favorable for the heterogeneous degradation of fenthion and parathion, suggesting a negative RH dependence of the rate constants. The rate constants of fenthion and parathion were $(7.89 \pm 0.69) \times 10^{-12}$ and $(11.00 \pm 1.16) \times 10^{-12}$ cm³/(mol·sec) at 20% RH, respectively, which significantly decreased to $(5.12 \pm 0.76) \times 10^{-12}$ and $(7.86 \pm 0.59) \times 10^{-12}$ cm³/(mol·sec) at 80% RH (Table 1). Thus, the humidity has a greater impact on the degradation of parathion than fenthion. The similar results about the heterogeneous degradation of other pesticides were also observed (Mattei et al., 2018, 2019c). For example, the rate constant for the heterogeneous degradation of deltamethrin by OH radicals declined from $(2.88 \pm 0.27) \times 10^{-12}$ to $(5.54 \pm 0.53) \times 10^{-13}$ cm³/(mol·sec) when the RH increased from 0 to 70% (Table 2); the rate constants of permethrin, pendimethalin, and cyprodinil also have the similar decreasing trends with the increase in humidity (Mattei et al., 2019c).

Goodman et al. (2001) have indicated that the number of water layers on particles increases with the increase in the RH. Therefore, increasing humidity can enhance the adsorption rate of water on surface-bound pesticide and then result in a shielding effect toward OH radicals. According to the Estimation Programs Interface Suite™ (US EPA, 2012), fenthion and parathion both have a very low solubility in water, indicating that the adsorbed water cannot fully soften the surface-bound pesticide. The lower rate constants of fenthion and parathion obtained at higher RH suggested that the degradation of pes-

ticide was significantly hindered because of the steric constraints and the slow diffusion of OH radicals through water layers (Slade and Knopf, 2014; Mattei et al., 2019c). In addition, it should be noted that if water is necessary and participates in the degradation reaction of pesticide, water will also have an effect on the degradation kinetics because different reaction mechanisms will occur in the presence or absence of water (Mattei et al., 2019c).

2.3. Effect of temperature on kinetics

Temperature is widely known to be one of important parameters influencing the degradation kinetics of organic compounds. Therefore, the influence of temperature on the degradation kinetics of pesticide was conducted at 5 °C, 10 °C, 20 °C, 30 °C, and 35 °C at a constant RH and OH concentration of 35% and $(3.5 \pm 0.1) \times 10^7$ molecules/cm³, respectively. As depicted in Fig. 4, increasing temperature was in favor of the heterogeneous degradation of fenthion and parathion, suggesting a positive dependence of the rate constants. Their rate constants were $(4.74 \pm 0.90) \times 10^{-12}$ and $(7.47 \pm 0.77) \times 10^{-12}$ cm³/(mol·sec) at 5 °C (Table 1), respectively, which increased to $(8.18 \pm 1.20) \times 10^{-12}$ and $(12.10 \pm 0.97) \times 10^{-12}$ cm³/(mol·sec) at 35 °C. This results indicated that an activation energy existed for the production of the transition intermediate, the production rate of which could be enhanced significantly at higher temperature. The similar phenomena were also observed (Lai et al., 2014, 2015b; Liu and Zeng, 2018; Liu et al., 2020), which pointed out that the rate constants for the heterogeneous reactions of OH radicals with the potential tracers of biomass-burning emissions had a significant increasing trend with the increase of temperature. Considering that pesticides are always used in different seasons, the effect of temperature at different seasons on the atmospheric degradation of pesticides is necessarily paid more attention.

Table 2 – Rate constants for the heterogeneous reactions of other pesticides with atmospheric gas-phase oxidants.

Oxidant	Pesticide	Conditions	Substrate	Second-order rate constant (k_2 , cm ³ /mol·sec)	Atmospheric lifetimes ^a (days)	References
O ₃	bupirimate	T = (19 ± 1) °C	quartz plaques	(5.4 ± 0.3) × 10 ⁻²⁰	3.06 × 10 ²	(Bouya et al., 2015)
	difenoconazole	T = 29 °C	quartz plaques	(2.6 ± 0.4) × 10 ⁻²⁰	6.36 × 10 ²	(Al Rashidi et al., 2011)
	folpet	T = (20 ± 2) °C	quartz plaques	(1.7 ± 0.5) × 10 ⁻¹⁹	97.26	(Al Rashidi et al., 2013)
	Z-dimethomorph	T = (20 ± 2) °C	quartz plaques	(2.6 ± 0.2) × 10 ⁻¹⁹	63.59	(Al Rashidi et al., 2013)
	tebuconazole	T = (25 ± 2) °C	quartz plaques	(0.5 ± 0.2) × 10 ⁻²⁰	3.31 × 10 ³	(Rokbani et al., 2019)
	diniconazole	T = (25 ± 2) °C	quartz plaques	(1.4 ± 0.2) × 10 ⁻¹⁹	1.18 × 10 ²	(Rokbani et al., 2019)
	pendimethalin	T = (20 ± 1) °C, RH = 5–80%	hydrophilic silica	(4.1 ± 0.4) × 10 ⁻¹⁸ to (3.3 ± 0.8) × 10 ⁻¹⁹	4.03 to 50.10	(Mattei et al., 2018)
	cyprodinil	T = (20 ± 1) °C, RH = 30–80%	Arizona dust	(0.9 ± 2.2) × 10 ⁻¹⁷ to (2.3 ± 0.1) × 10 ⁻¹⁹	1.84 to 71.89	(Mattei et al., 2018)
OH radicals	bupirimate	T = (25 ± 1) °C	quartz plaques	(1.06 ± 0.82) × 10 ⁻¹²	7.28	(Bouya et al., 2015)
	difenoconazole	T = 29 °C	quartz plaques	(7.1 ± 0.8) × 10 ⁻¹⁴	1.09 × 10 ²	(Al Rashidi et al., 2011)
	folpet	T = (29 ± 2) °C	quartz plaques	(2.0 ± 1.1) × 10 ⁻¹⁴	3.86 × 10 ²	(Al Rashidi et al., 2014)
	Z-dimethomorph	T = (29 ± 2) °C	quartz plaques	(1.6 ± 0.9) × 10 ⁻¹³	48.23	(Al Rashidi et al., 2014)
	tebuconazole	T = (20 ± 2) °C	quartz plaques	(1.7 ± 0.2) × 10 ⁻¹³	45.39	(Rokbani et al., 2019)
	diniconazole	T = (20 ± 2) °C	quartz plaques	(1.74 ± 1.21) × 10 ⁻¹²	4.43	(Rokbani et al., 2019)
	deltamethrin	T = (25 ± 1) °C, RH = 0–70%	silica particles	(2.88 ± 0.27) × 10 ⁻¹² to (5.54 ± 0.53) × 10 ⁻¹³	2.68 to 13.93	(Mattei et al., 2019c)
	permethrin	T = (25 ± 1) °C, RH = 0–70%	silica particles	(2.57 ± 0.09) × 10 ⁻¹² to ≤ 10 ⁻¹³	3.00 to ≤ 77.16	(Mattei et al., 2019c)
	pendimethalin	T = (25 ± 1) °C, RH = 0–70%	silica particles	(4.08 ± 0.27) × 10 ⁻¹² to ≤ 10 ⁻¹³	1.89 to ≤ 77.16	(Mattei et al., 2019c)
	cyprodinil	T = (25 ± 1) °C, RH = 0–70%	silica particles	(2.50 ± 0.14) × 10 ⁻¹² to ≤ 10 ⁻¹³	3.09 to ≤ 77.16	(Mattei et al., 2019c)
	terbuthylazine	T = 27 °C, RH = 42–50%	silica particles	(1.1 ± 0.2) × 10 ⁻¹¹	0.70	(Palm et al., 1997)
	simazine	T = 25 °C, RH = 25–40%	hydrophilic silica	1.1 × 10 ⁻¹¹	0.70	(Palm et al., 1998)
	NO ₃ radicals	chlorpyrifos	T = ~15 °C, RH = ~40%	azelaic acid	(3.4 ± 0.2) × 10 ⁻¹²	6.81 × 10 ⁻³
parathion		T = ~20 °C, RH = ~5%	azelaic acid	(2.97 ± 0.13) × 10 ⁻¹²	7.79 × 10 ⁻³	(Liu et al., 2015)
phosmet		T = ~20 °C, RH = ~5%	azelaic acid	(2.80 ± 0.16) × 10 ⁻¹²	8.27 × 10 ⁻³	(Liu et al., 2015)
fenvalerate		T = ~25 °C, RH = ~5%	azelaic acid	(1.86 ± 0.04) × 10 ⁻¹²	1.24 × 10 ⁻²	(Wang et al., 2013)
phenothrin		T = ~25 °C, RH = ~5%	azelaic acid	(1.61 ± 0.03) × 10 ⁻¹²	1.44 × 10 ⁻²	(Wang et al., 2013)
resmethrin		T = ~25 °C, RH = ~5%	azelaic acid	(5.54 ± 0.14) × 10 ⁻¹²	4.18 × 10 ⁻³	(Wang et al., 2013)
pyrimicarb		T = ~25 °C, RH = ~10%	azelaic acid	(7.5 ± 0.3) × 10 ⁻¹³	3.09 × 10 ⁻²	(Wang et al., 2012)
pirimophos-methyl		T = ~25 °C, RH = ~10%	azelaic acid	(9.9 ± 0.3) × 10 ⁻¹²	2.34 × 10 ⁻³	(Wang et al., 2012)
ametryn		T = ~25 °C, RH = ~5%	azelaic acid	8.4 × 10 ⁻¹³	2.76 × 10 ⁻²	(Liu et al., 2014a)
deltamethrin		T = (25 ± 1) °C, RH = (40 ± 2)%	hydrophobic silica	(2.08 ± 0.51) × 10 ⁻¹⁵	11.13	(Mattei et al., 2019b)
permethrin		T = (25 ± 1) °C, RH = (40 ± 2)%	hydrophobic silica	(3.73 ± 0.52) × 10 ⁻¹⁵	6.21	(Mattei et al., 2019b)
pendimethalin		T = (25 ± 1) °C, RH = (40 ± 2)%	hydrophobic silica	(1.99 ± 0.42) × 10 ⁻¹⁵	11.63	(Mattei et al., 2019b)
cyprodinil		T = (25 ± 1) °C, RH = (40 ± 2)%	hydrophobic silica	(2.87 ± 0.32) × 10 ⁻¹⁵	8.07	(Mattei et al., 2019b)
tetraconazole		T = (25 ± 1) °C, RH = (40 ± 2)%	hydrophobic silica	(4.22 ± 0.69) × 10 ⁻¹⁵	5.49	(Mattei et al., 2019b)

^a Atmospheric lifetime was calculated using the equation $\tau = 1/k_2[\text{oxidant}]$, where [oxidant] is the typical concentration of gas-phase oxidant in the atmosphere. The concentrations of O₃, OH radicals, and NO₃ radicals are 7 × 10¹¹ molecules/cm³ (Logan, 1985), 1.5 × 10⁶ molecules/cm³ (Mao et al., 2009), and 5 × 10⁸ molecules/cm³ (Atkinson, 1991), respectively.

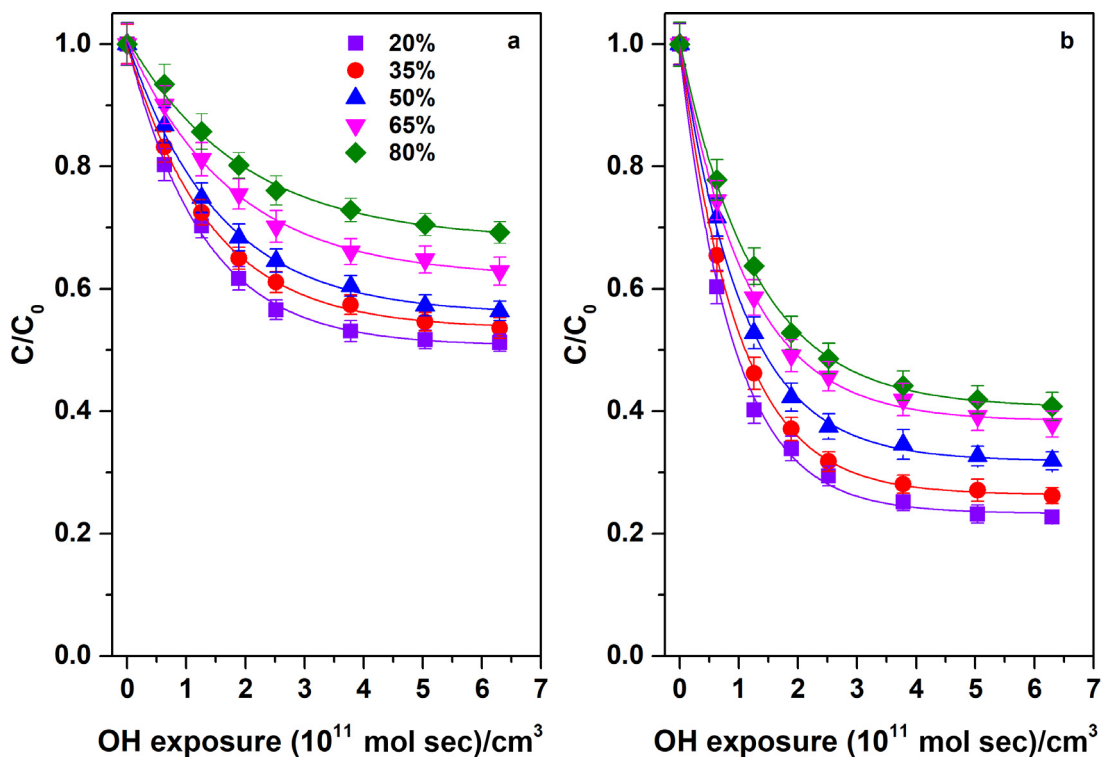


Fig. 3 – Effects of the RH on the degradation of fenthion (a) and parathion (b) as a function of OH exposure (temperature = 20 °C and $[\text{OH}] = (3.5 \pm 0.1) \times 10^7 \text{ molecules}/\text{cm}^3$).

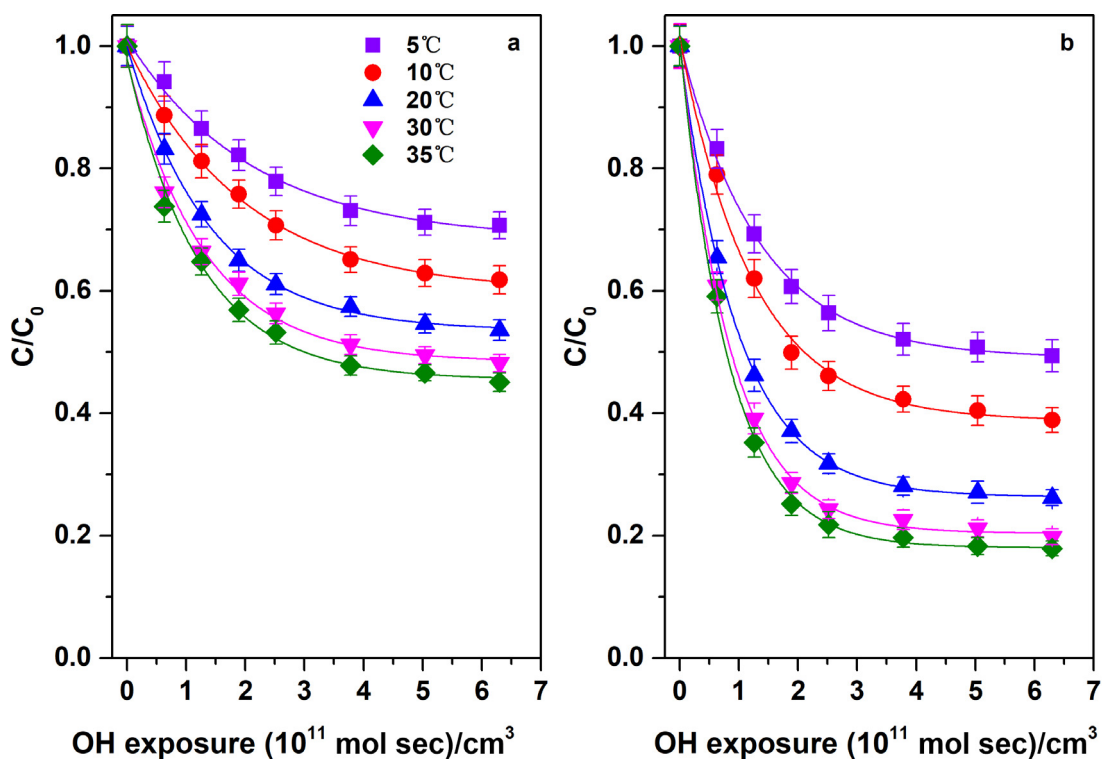


Fig. 4 – Effects of the temperature on the degradation of fenthion (a) and parathion (b) as a function of OH exposure (RH = 35% and $[\text{OH}] = (3.5 \pm 0.1) \times 10^7 \text{ molecules}/\text{cm}^3$).

The Arrhenius plots of the rate constants for the heterogeneous degradation of pesticides by OH radicals are shown in Fig. S2. Using the linear fitting, the Arrhenius expressions of fenthion and parathion were calculated to be $k_2 = (1.34 \pm 0.48) \times 10^{-9} \exp[-(1432.59 \pm 105.29)/T]$ and $k_2 = (1.96 \pm 1.38) \times 10^{-9} \exp[-(1619.98 \pm 222.02)/T]$, respectively. The overall activation energy of the OH-initiated heterogeneous reactions of fenthion and parathion was estimated to be (11.88 ± 0.87) and (13.48 ± 1.83) kJ/mol, respectively. The positive temperature dependence of the rate constants for the degradation of organic pollutants including pesticides has been widely observed in previous studies (Castillo and Torstensson, 2007; Lai et al., 2014, 2015b; Liu and Zeng, 2018; Liu et al., 2020, 2022). The possible reason for this is that improving temperature is favorable for increasing the proportion of activation molecules, consequently leading to increase the rate constant. However, the negative temperature dependence of the rate constants for the OH-initiated degradation of organic pollutants has also been reported previously (An et al., 2019, 2020), the reason for which is that increasing temperature leads to the falloff impacts on the rate constants of electrophilic addition and H-abstraction reactions of OH radicals. The different impacts of temperature on the rate constant are mainly ascribed to the different chemical structures of organic compounds, because increasing temperature will result in different responses of the different functional groups to the electrophilic addition and H-abstraction reactions of OH radicals (An et al., 2019, 2020; Liu et al., 2022).

2.4. Atmospheric implications

OH radicals are an important gas-phase oxidant for the atmospheric degradation of pesticides, thus the OH-initiated reactions of pesticides play an important role in their atmospheric degradation. As shown in Table 1, the atmospheric lifetimes of fenthion and parathion are (1.08 ± 0.12) and (0.74 ± 0.04) days, respectively, calculated using their average rate constants obtained at different OH concentrations and a typical atmospheric OH concentration of 1.5×10^6 molecules/cm³ in the atmosphere (Mao et al., 2009). Except for OH radicals, fenthion and parathion could also be degraded by NO₃ radicals and O₃. Thus, fenthion and parathion have relatively short lifetimes in the atmosphere. Compared to the atmospheric lifetimes calculated using their gas-phase rate constants, the results are much longer, indicating that the heterogeneous degradation of pesticides will be overestimated by the AOP WIN model. At different RH (20%–80%) and temperatures (5–35 °C), the atmospheric lifetimes of fenthion and parathion were in ranges from (0.96 ± 0.14) and (0.64 ± 0.05) to (1.67 ± 0.32) and (1.04 ± 0.11) days, respectively. The results showed a negative RH dependence and a positive temperature dependence of their rate constants. These kinetic data of fenthion and parathion will be favorable for further understanding their chemical behaviors in the atmosphere.

The fast degradation of fenthion and parathion by OH radicals suggested that the oxidation products can be formed rapidly, which might be partitioned into particle phase and lead to the formation of secondary organic aerosols. In recent years, Borrás et al. (2015a, 2017) indicated that the OH-initiated reactions of chlorpyrifos and pirimiphos-methyl (two repre-

sentative kinds of OPPs) had significant aerosol formation potentials, the average yields of which were higher than 20%. The results suggested that a considerable fraction of the oxidation products with lower volatility and higher oxidation level were partitioned into particle phase. Therefore, the aerosol formation of the atmospheric oxidation of OPPs and the subsequent effects on climate and air quality should be paid more attention. In addition, previous studies have widely indicated that the oxidation products of OPPs especially the oxon products show higher toxic than their parent chemicals (Raina et al., 2010; Liu et al., 2012). Therefore, the toxicity assessment of the oxidation products of fenthion and parathion should be systematically carried out in future work.

3. Conclusions

The rate constants for the heterogeneous reactions of fenthion and parathion adsorbed on quartz plates with OH radicals were investigated using a flow reactor. The results showed that OH radicals played an important role in the atmospheric degradation of fenthion and parathion. The average rate constants for fenthion and parathion at a RH and temperature of 35% and 20 °C were $(7.20 \pm 0.77) \times 10^{-12}$ and $(10.40 \pm 0.60) \times 10^{-12}$ cm³/(mol·sec), respectively. A negative RH dependence and a positive temperature dependence of the rate constants were observed. The Arrhenius expressions of fenthion and parathion were $k_2 = (1.34 \pm 0.48) \times 10^{-9} \exp[-(1432.59 \pm 105.29)/T]$ and $k_2 = (1.96 \pm 1.38) \times 10^{-9} \exp[-(1619.98 \pm 222.02)/T]$, respectively, and their overall activation energy was estimated to be (11.88 ± 0.87) and (13.48 ± 1.83) kJ/mol. Under different conditions, the atmospheric lifetimes of fenthion and parathion were in ranges of (0.96 ± 0.14) and (0.64 ± 0.05) to (1.67 ± 0.32) and (1.04 ± 0.11) days, respectively, suggesting that they have relatively short lifetimes in the atmosphere. These rate constants for fenthion and parathion obtained in this work will update their kinetic data in the atmosphere and be favorable for further understanding their atmospheric chemical behaviors.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A Supplementary data

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jes.2022.05.040.

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