



Characterizing chemical transformation of organophosphorus compounds by ^{13}C and ^2H stable isotope analysis \star



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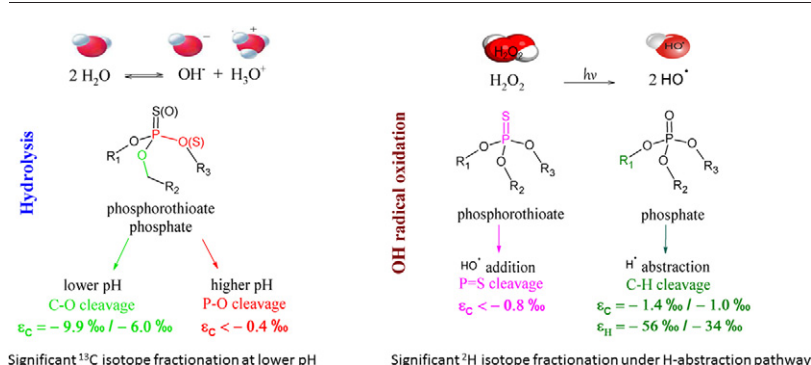
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HIGHLIGHTS

- Concept using C and H isotope fractionation to analyze degradation of OPs is developed.
- Isotope fractionation patterns upon hydrolysis and radical oxidation are compared.
- Dependence of isotope fractionation patterns on the chemical structure of OPs.
- Isotope fractionation pattern has potential to study the OPs in the environment.

GRAPHICAL ABSTRACT



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ABSTRACT

Continuous and excessive use of organophosphorus compounds (OPs) has led to environmental contaminations which raise public concerns. This study investigates the isotope fractionation patterns of OPs in the aquatic environment dependence upon hydrolysis, photolysis and radical oxidation processes. The hydrolysis of parathion (EP) and methyl parathion (MP) resulted in significant carbon fractionation at lower pH (pH 2–7, $\epsilon_{\text{C}} = -6.9 \sim -6.0\text{‰}$ for EP, $-10.5 \sim -9.9\text{‰}$ for MP) but no detectable carbon fractionation at higher pH (pH 12). Hydrogen fractionation was not observed during any of the hydrolysis experiments. These results indicate that compound specific isotope analysis (CSIA) allows distinction of two different pH-dependent pathways of hydrolysis. Carbon and hydrogen isotope fractionation were determined during UV/ H_2O_2 photolysis of EP and tris(2-chloroethyl) phosphate (TCEP). The constant $\delta^2\text{H}$ values determined during the OH radical reaction of EP suggested that the rate-limiting step proceeded through oxidative attack by OH radical on the P=S bond. The significant H isotope enrichment suggested that OH radical oxidation of TCEP was caused by an H-abstraction during the UV/ H_2O_2 processes ($\epsilon_{\text{H}} = -56 \pm 3\text{‰}$). Fenton reaction was conducted to validate the H isotope enrichment of TCEP associated with radical oxidation, which yielded ϵ_{H} of $-34 \pm 5\text{‰}$. Transformation products of OPs during photodegradation were identified using Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS). This study

\star All authors declare that there is no conflict of interest.

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highlights that the carbon and hydrogen fractionation patterns have the potential to elucidate the transformation of OPs in the environment.

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1. Introduction

Organophosphorus compounds (OPs) are often used as pesticides, warfare agents, flame retardants, plasticizers, or flotation agents. The OPs discussed in the present study are esters of phosphoric acids, thiophosphoric acids and dithiophosphoric acids forming a wide variety of phosphates, phosphorothioates, or phosphorodithioates (Fig. S1 in Supplementary material (SM)), each of them has different reactivity towards hydrolysis, oxidation and biodegradation (Pehkonen and Zhang, 2002; Singh and Walker, 2006). Many OP derivatives are associated with acute toxicity by inhibiting acetylcholinesterase (AChE) in the nervous system, hence they are used as pesticides for control of insects and other higher organisms (Colovic et al., 2013). OP pesticides are less persistent in the environment when compared with organochlorine pesticides and thus have been widely used throughout the world. However, continuous and excessive use of OPs has led to environmental contaminations which raise public concerns (EPA US, 2006).

Parathion (*O,O*-diethyl *O*-(4-nitrophenyl) phosphorothioate), also known as ethyl parathion (EP), was one of the most widely applied organophosphorus insecticides in agriculture in the past decades, and was primarily used as an insecticide on fruit, cotton, wheat, vegetables, and nut crops (FAO, 1990b). The average half-life time of EP during hydrolysis, degradation in aerobic soil and anaerobic soil are 302 days, 58 days and 21 days respectively (Kegley et al., 2016b), which leads to a huge potential for EP and its metabolic products to contaminate surface water and groundwater. Its use is banned or restricted in many countries but continues in many other developing countries including China and India, where the application is still legal for crops.

Methyl parathion (*O,O*-dimethyl-*O*-(4-nitrophenyl) phosphorothioate, MP) is structurally very similar to EP and less persistent in the environment, with an average half-life time during hydrolysis, degradation in aerobic soil and anaerobic soil of 45 days, 12 days and 1 day, respectively (Kegley et al., 2016a). Due to its severe hazardous potential classified by the Rotterdam Convention, MP is not allowed for sale and import in nearly all countries around the world (Rotterdam Convention, 2004).

Tris(2-chloroethyl) phosphate (TCEP) is an anthropogenic organic compound used as flame retardant, plasticizer, and viscosity regulator in various types of polymers, and is commonly listed among a class of emerging contaminants associated with wastewater pollution of freshwater resources (Andresen et al., 2004; Stackelberg et al., 2007). TCEP is considered as almost non-biodegradable and not expected to hydrolyze significantly under environmental conditions, thus advanced oxidation processes (AOP), such as Fenton reaction and UV/H₂O₂, have been studied as a possible remediation strategy (Ou et al., 2017; Watts and Linden, 2008; Watts and Linden, 2009; Yuan et al., 2015).

Compound specific stable isotope analysis (CSIA) can provide additional information on the organic pollutants' transformation pathways in complex environments (Elsner et al., 2005; Hofstetter and Berg, 2011; Thullner et al., 2012). Previous studies have shown the potential use of stable isotope fractionation to characterize transformation mechanisms of organic compounds (Elsner, 2010; Elsner and Imfeld, 2016; Elsner et al., 2012; Nijenhuis and Richnow, 2016; Vogt et al., 2016; Wu et al., 2014), as this approach is a valuable tool to analyze the rate-limiting step in reaction mechanisms such as the mode of chemical bond cleavage (Northrop, 1981).

Hydrolysis is one pathway controlling the fate of OPs in the environment and react by a common mechanism, where H₂O and OH⁻ act as nucleophiles in a bimolecular nucleophilic substitution mechanism (S_N2 mechanism) (Pehkonen and Zhang, 2002). The esters of phosphates, phosphorothioates, and phosphorodithioates can be hydrolyzed

under acidic and alkaline conditions by two different pathways but the relative contribution of each hydrolysis pathway is pH-dependent. Photodegradation and chemical oxidation are other important degradation processes. Several studies investigated the reaction mechanisms of OPs during photodegradation, in which simultaneous pathways including oxidation of P=S to P=O, elimination of nitro group, remethylation and oxidation of the alkyl substituent were proposed (Araújo et al., 2007; Durand et al., 1994; Kanmoni et al., 2012; Sakellarides et al., 2003; Santos et al., 2005; Wu and Linden, 2008). Although several types of transformation products were typically determined, it is difficult to confirm photodegradation pathways via identified transformation products, as short-lived intermediates could be missed.

Previous studies reported OPs contamination in natural waters (Pehkonen and Zhang, 2002) and atmosphere (Kawahara et al., 2005). OP residues have been found in rain, snow, fog and air samples (Aston and Seiber, 1996). Oxidation of OPs by OH radical is likely in surface water and atmosphere (aerosols). OH radical can be generated by natural presented photosensitizers such as humic substances (Zhang et al., 2015). The photosensitizers promoted indirect photolysis is a naturally occurring degradation process. It may be an important factor governing the fate of organic contaminants in the environment. The multi-isotope fractionation pattern allows characterize the bond cleavage mechanisms of photosensitization, and is thus a valuable tool for studying the fate of OPs in surface waters and atmospheric media containing photosensitizers.

The main objective of this study is to evaluate the carbon and hydrogen isotope fractionation patterns associated with hydrolysis and photolysis which are considered to be important chemical transformation reactions of OPs in the environment. We selected EP, MP and dimethoate (Wu et al., 2017) as model compounds of phosphorothioates and phosphorodithioates representing typical esters of phosphoric acids and analyzed the carbon and hydrogen isotope fractionation patterns upon hydrolysis at various pH values to study the different mode of hydrolysis by CSIA. Radical oxidation and photolysis of EP (model of phosphorothioates) were investigated to compare isotope fractionation patterns with those obtained from hydrolysis. In addition, OH radical oxidation of TCEP (model of phosphate) by Fenton reaction (the iron catalyzed hydrogen peroxide) and via indirect photolysis (UV/H₂O₂) was performed to understand the isotope fractionation associated by an H-abstraction step. The transformation products were further identified using Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS) to analyze the transformation mechanisms.

2. Materials and methods

2.1. Chemicals

Parathion (*O, O*-diethyl *O*-(4-nitrophenyl) phosphorothioate, purity >99.7%), methyl parathion (*O, O*-dimethyl-*O*-(4-nitrophenyl) phosphorothioate; purity > 99.8%), TCEP (tris(2-chloroethyl) phosphate, purity > 97.0%) and dichlorvos (2,2-dichlorovinyl dimethyl phosphate, purity >98.8%) were purchased from Sigma-Aldrich (Munich, Germany) and used without further purification. Tributyl phosphate (TBP, purity 99%) was purchased in Xiya Company in China. Hydrogen peroxide (30% w/w) was supplied by Merck (Darmstadt, Germany).

2.2. Hydrolysis experiment

Hydrolysis of EP and MP were carried out at up to 60 °C (to reduce the reaction time) in 100 mM phosphate buffer solution at pH 2, pH 5, pH 7,

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