



Carbon and hydrogen stable isotope analysis for characterizing the chemical degradation of tributyl phosphate

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HIGHLIGHTS

- Quantification of ²H and ¹³C isotope enrichment factors of TBP.
- Comparison of isotope fractionation patterns upon hydrolysis and radical oxidation.
- Characterizing the C–O, C–H bond cleavage of TBP using apparent kinetic isotope effect.

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ABSTRACT

Tributyl phosphate (TBP) belongs to the group of trialkyl substituted organophosphate esters. Its chemical reactivity depends on the stability of various chemical bonds. TBP was used as a model compound for the development of a concept using stable isotope fractionation associated with bond cleavage reactions for better understanding the fate of TBP in the environment. Carbon isotope enrichment factors (ϵ_C) of TBP hydrolysis were found to be pH dependent ($-3.8 \pm 0.3\%$ at pH 2, $-4.6 \pm 0.5\%$ at pH 7, $-2.8 \pm 0.1\%$ at pH 9, no isotope fractionation at pH 12), which is in accordance with the mode of a S_N2 hydrolytic bond cleavage. Hydrogen isotope fractionation was negligible as no H bond cleavage is involved during hydrolysis. The apparent carbon kinetic isotope effect ($AKIE_C$) ranged from 1.045 to 1.058. In contrast to hydrolysis, both carbon and hydrogen isotope fractionation were observed during radical oxidation of TBP by $\cdot OH$ and $SO_4^{\cdot -}$, yielding ϵ_C from $-0.9 \pm 0.1\%$ to $-0.5 \pm 0.1\%$ and ϵ_H from $-20 \pm 2\%$ to $-11 \pm 1\%$. $AKIE_C$ and $AKIE_H$ varied from 1.007 to 1.011 and from 1.594 to 2.174, respectively. The correlation of ²H and ¹³C isotope fractionation revealed Δ values ranging from 17 ± 1 to 25 ± 6 . Results demonstrated that the correlation of ²H and ¹³C isotope fractionation of TBP allowed to identify radical reactions and to distinguish them from hydrolysis. The presented dual isotope analysis approach has diagnostic value for characterizing the chemical transformation of TBP in the environment.

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1. Introduction

Tributyl phosphate (TBP) is an organophosphorus compound widely used as flame retardant, plasticiser, anti-foamer, component

of herbicides and hydraulic fluids (Regnery et al., 2011). In addition, it was extensively used as a solvent for plutonium/uranium redox extraction (PUREX) for nuclear fuel reprocessing (Mincher et al., 2008). The production of commercially used TBP is about 3000–5000 tons/year in Europe (Nancharaiyah et al., 2015). Due to its extensive use, TBP is frequently detected in the aquatic environment of many countries, including Germany (Fries and Püttmann, 2003; Regnery and Püttmann, 2010), Austria (Martinez-Carballo et al., 2007), Italy (Bacaloni et al., 2008), Spain (Rodil et al., 2012), Korea (Lee et al., 2016), and China (He et al., 2014; Shi et al., 2016).

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TBP can inhibit the enzyme acetylcholine esterase (AChE), resulting in cholinergic toxicity of the autonomic system and can thus lead to respiratory paralysis and even death (Bergman et al., 2012; Greget et al., 2016). Given these adverse effects, TBP has been an environmental concern for decades, especially in aquatic systems. The main degradation pathways are hydrolysis, indirect photo-oxidation or microbial degradation (Berne et al., 2005; Watts and Linden, 2009; Nanchaiah et al., 2015; Su et al., 2016). These are probably the key processes how TBP is degraded or attenuated in the environment. Direct chemical oxidation is effective for the removal of organic contaminants in waste water. In particular, chemicals, such as hydrogen peroxide, persulfate, permanganate and ozone, have been applied for *in situ* chemical oxidation (ISCO) for the treatment of subsurface TBP or similar contamination (Watts and Teel, 2006). Hydroxyl radicals ($\cdot\text{OH}$) are an effective oxidant with redox potential of 1.7–2.8 V and are frequently used for wastewater remediation (Waclawek et al., 2017). Similar to $\cdot\text{OH}$, the sulfate radical ($\text{SO}_4^{\cdot-}$) with a redox potential of 2.5–3.1 V is efficient for the oxidation of many organic compounds (Neta et al., 1988). $\text{SO}_4^{\cdot-}$ can be generated for example from peroxydisulfate ($\text{S}_2\text{O}_8^{2-}$, PS) or peroxymonosulfate (HS_2O_5) salts by the activation of the persulfate anion ($\text{S}_2\text{O}_8^{2-}$, $E_0 = 2.01$ V) using light (Herrmann, 2007; Yang et al., 2017) or heat (House, 1962; Liang and Su, 2009). Over the past ten years, considerable attention has been paid to potassium peroxydisulfate (KPS) because of its lower cost compared to H_2O_2 or O_3 and the high efficiency for organic mineralization (Lau et al., 2007; Waclawek et al., 2017).

Conventionally, degradation pathways are chemically analyzed by measuring the concentrations decrease of reactants and the appearance of degradation products. However, this approach often has large uncertainties in field studies because of the influence of physical processes (such as dilution, volatility and sorption), the challenges of detecting unknown products and the difficulties to establish mass balances. As an alternative technology, compound specific isotope analysis (CSIA) making use of isotope fractionation processes of degradation reactions can be used for the qualitative characterisation and quantitative estimation of processes involved in organic compound degradation in the environment. This technique is becoming a routine and practical approach in biogeochemistry and environmental science (Elsner, 2010; Thullner et al., 2012; Nijenhuis and Richnow, 2016; Vogt et al., 2016).

For better understanding of the transformation mechanisms, the kinetic isotope effect (KIE) based on chemical bond change reactions can be analyzed. The KIE characterizes the rate limitation of a bond change reaction posed by isotopologues. The rate limitation is equivalent to the stability of heavy and light isotope substituted bonds and characterizes the transition state of a chemical reaction (Northrop, 1981; Wolfsberg et al., 2009). The apparent kinetic isotope effect (AKIE) can be calculated to normalize the isotope enrichment factor (ϵ) for non-reacting positions and intermolecular competition to compensate for “dilution” of the isotope composition in reacting isotopologues. The AKIE can be used to compare the kinetic isotope effect of bond cleavage reactions of different molecules. Multi-element isotope fractionation analysis correlating the isotope fractionation of two (or more) elements can be used to evaluate the degradation pathways (Gray et al., 2002; Elsner et al., 2005). Previous studies demonstrated the potential use of stable isotope fractionation for characterizing the transformation mechanisms of organophosphorus compounds, such as dichlorvos, dimethoate, methyl parathion, parathion and tris(2-chloroethyl) phosphate (Wu et al., 2014, 2017, 2018a).

In the present study, we systematically examined the carbon and hydrogen isotope fractionation upon hydrolysis of TBP under acidic, neutral and alkaline conditions to characterise the reaction

pathways. The isotope fractionation patterns of TBP by radical oxidation ($\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$) were also examined. The objectives of this study were to (1) investigate the kinetic reaction rate constant k_{obs} of hydrolysis and radical oxidation; (2) characterise the stable carbon and hydrogen isotope fractionation of TBP during hydrolysis and radical oxidation; (3) distinguish different mechanisms by using the AKIE values and correlating ^2H and ^{13}C isotope fractionation to obtain Δ values, which may be used diagnostically for tracing TBP degradation in the field.

2. Materials and methods

A detailed description of the analytical methods is provided in the [Supplementary Information \(SI\)](#).

2.1. Chemicals

All chemicals were of analytical grade quality and used without further purification. Tributyl phosphate (TBP, 99% purity) and dibutyl phthalate (DBP, >99% purity) were purchased from Xiya Company (China). Dichloromethane (DCM) was supplied by Carl Roth GmbH + Co. KG (Karlsruhe, Germany). Potassium peroxydisulfate ($\text{K}_2\text{S}_2\text{O}_8$), hydrogen peroxide (30% H_2O_2), di-potassium hydrogen phosphate (K_2HPO_4), potassium dihydrogen phosphate (KH_2PO_4), sodium hydrogen carbonate (NaHCO_3), sodium hydrate (NaOH), and disodium hydrogen phosphate (Na_2HPO_4) were supplied by Merck (Guaranteed reagent quality, Darmstadt, Germany). Solutions and pH buffers were prepared in ultrapure water obtained by a Milli-Q System (Millipore GmbH, Germany).

2.2. Hydrolysis and radical oxidation experiments

The following buffer solutions were used to obtain hydrolysis at different pH conditions: KCl–HCl (50 mM for pH 2), K_2HPO_4 – KH_2PO_4 (100 mM for pH 7), NaHCO_3 – NaOH (45.5 mM for pH 9), and Na_2HPO_4 – NaOH (32.5 mM for pH 12).

Hydrolysis experiments: TBP is hydrolyzed with very slow reaction rates at room temperature under neutral to acidic conditions but rapidly hydrolyzed under strong alkaline condition (Su et al., 2016). In order to adjust the hydrolysis rates in the same order of magnitude for a better comparison of the isotope fractionation patterns associated with different reaction pathways, hydrolysis experiments were carried out at 80 °C to accelerate the hydrolysis rate at pH 2, pH 7 and pH 9, respectively. Hydrolysis experiments at pH 12 were performed at 35 °C to slow down the reaction. All experiments were conducted in 40 mL buffer solutions in 150-mL serum bottles with 100 mg L⁻¹ TBP as initial concentration. At different time intervals, the reaction solutions were extracted by adding 1 mL DCM containing 1000 mg L⁻¹ DBP as internal standard and shaking for at least 4 h at 10 °C. Extracts were stored at 4 °C prior to analysis. The extraction recovery and effect of the extraction procedure on carbon and hydrogen isotope signature were evaluated as described in [Section 3 of the Supplementary Information](#).

Potassium peroxydisulfate (KPS) oxidation: For KPS oxidation experiments a molar ratio of TBP to KPS of 1:20 was used. The KPS oxidation reaction was not conducted at pH 2 due to the exclusive formation of secondary radicals and complicating subsequent reactions. At pH 2, the $\text{SO}_4^{\cdot-}$ reacts exclusively with the Cl^- from the HCl/KCl buffer to produce a Cl atom, which will subsequently react to form $\text{Cl}_2^{\cdot-}$, a dichloride radical anion (Herrmann, 2003). Therefore, the KPS oxidation reactions were only conducted at pH 7, pH 9 and pH 12, respectively. The initial concentration of TBP was 100 ppm. Buffer solutions with different pH values were prepared as described above. All KPS oxidation reactions were carried out at

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