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Reactions of three halogenated organophosphorus flame retardants with reduced sulfur species

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HIGHLIGHTS

- Reactions of tris(chloropropyl)phosphates and tris(dichloropropyl)phosphate with reduced sulfur species were investigated.
- TCEP is more reactive than TDCPP, which is more reactive than TCPP.
- Major degradation product of TCPP in these reactions is bis(chloropropyl)phosphate.
- Sulfur species are sufficiently reactive as to control fate of TCPP and TDCPP in anoxic environments.

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ABSTRACT

Tris(haloalkyl)phosphates (THAPs) are among the most widely used flame retardants in the U.S. They have been identified as one of the most frequently detected contaminants in U.S. streams. These contaminants are of toxicological concern in sensitive coastal ecosystems such as estuaries and salt marshes. It is likely that reactions with reduced sulfur species such as polysulfides (S_n^{2-}) and bisulfide (HS^-), present in anoxic subregions of coastal water bodies could have a significant impact on rates of removal of such contaminants, especially since no significant degradation reactions in the environment (e.g., hydrolysis, biological degradation) is reported for these compounds. The kinetics of the reaction of reduced sulfur species with three structurally related THAPs have been determined in well-defined aqueous solutions under anoxic conditions. Reactions were monitored at varying concentrations of reduced sulfur species to obtain second-order rate constants from the observed pseudo-first order rate constants. The degradation products were studied with GC–FID and LC–MS. The reactivity of S_n^{2-}, thiophenolate, and HS^- were compared and steric, as well as electronic factors are used to explain the relative reactivity of the three THAPs with these three sulfur species.

1. Introduction

Flame retardants and plasticizers are widely used and found in common items in the home and at the workplace, including plastics, polyurethane foams, coatings, and textiles (Ellis et al., 2007). Despite the high production volume and wide application of halogenated trisalkyl phosphates (THAPs) as flame retardants, knowledge is limited on their environmental fate. Currently available environmental studies of THAPs have mainly focused on abiotic compartments (air, dust, water, sediments), whereas little is known regarding wildlife and human exposure. THAP have entered the water cycle in urban environment and the compounds are detected in groundwater, rainwater, and surface water (Fries and Püttmann, 2001; Bester et al., 2008). Tris(1,3-dichloropropyl)phosphate (TDCPP) and tris(monochloroisopropyl)phosphate (TCPP) are present in polyurethane foam collected from baby products (Stapleton et al., 2011). And all three compounds (tris(2-chloroethyl)phosphate (TCEP), TDCPP, TCPP) are reported at similar median concentration in house dust samples from California (Dodson et al., 2012). Only a few studies are available that investigate the bioaccumulation potential of THAPs in environmental biota. A recent report describes the detection of TCEP and TCPP in herring gull eggs from Lake Huron (Chen et al., 2012) suggesting that bioaccumulation might occur. The evaluation of neurotoxicity of TCEP, TDCPP, and TCPP shows that THAPs have the potential to cause developmental neurotoxicity in a manner similar to organophosphorus insecticides, a class of compounds widely recognized to damage the developing brain (Dishaw et al., 2011). TCEP has been the compound of the three THAPs (TCEP, TCPP, and TDCPP) that has been detected at the highest concentrations in aqueous environmental samples (Kolpin et al., 2002). However, TCEP is undergoing

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detailed review by the U.S. Environmental Protection Agency (EPA) in 2013 and 2014 (Hogue, 2012) and as a consequence of this review current applications of TCEP might be replaced by other compounds.

To predict the environmental fate of these THAPs, it is necessary to characterize their mobility and the rate of degradation under environmental conditions. THAPs that are present in surface water may associate with particles and settle out to the sediment phase ($\log K_{ow}$ values range from 1.7 to 3.8) (Sasaki et al., 1982). It is also likely that some THAP are transported into salt marshes and into the bottom layers of estuaries where anoxic conditions are typically prevalent. Anoxic conditions can give rise to high concentrations of reduced sulfur species. When oxygen is consumed more rapidly than it can replenish by mixing processes, microbial sulfate reduction can give rise to locally high concentration of hydrogen sulfide species (H_2S and HS^-) and polysulfides ions (S_n^{2-}). Reduced sulfur species are capable of reacting with a wide array of pollutants, including organic contaminants that undergo nucleophilic substitution reactions (Lippa et al., 2004; Bondarenko et al., 2006). Since it is likely that THAPs can enter environmental compartments that contain high concentration of reduced sulfur species, the reaction of THAPs with reduced sulfur species is of interest. In addition to HS^- and S_n^{2-}, thiophenolate (PhS^-) was chosen in this study as a model for aromatic sulfur nucleophiles in the degradation of these THAPs. Aromatic sulfur nucleophiles can form when natural organic matter (NOM) reacts with reduced sulfur species (e.g., H_2S, HS^-) (Mopper and Taylor, 1986). In addition, use of thiophenolate has the advantage that the products formed by nucleophilic substitution reactions are neutral and therefore they can be more easily isolated and analyzed than corresponding products of the reaction with bisulfide or polysulfides. Several studies have shown S_n^{2-} to be the considerably more reactive nucleophile than HS^- to the extend that although S_n^{2-} are typically present at a lower concentration than HS^-, their contribution to the overall rates of nucleophilic substitution reactions can exceed that of HS^- at pH > 7 (Haag and Mill, 1988; Roberts et al., 1992). A recent study investigating the degradation of chloroacetanilide pesticides in sediment porewater, nicely showed that HS^- and S_n^{2-} were the major contributors to the observed degradation of the insecticides that were added to the porewater (Zeng et al., 2011). An additional factor that might play an important role in the degradation of contaminants in sediments is the role of the mineral surfaces. At this point very little is known whether the interaction of dissolved reduced sulfur nucleophile to mineral surfaces in sediments could enhance the reactivity of the nucleophile and therefore the degradation of contaminants such as THAPs in sediments. One study investigating such interactions reports an increased heterogeneous nucleophilic transformation of a chloroacetanilide (metolachlor) by HS^- on the surface of alumina (Wei et al., 2013).

Fig. 1 shows the structure of the three investigated THAPs: TCEP, TCPP, and TDCPP. From previous studies investigating the reaction of organophosphorus insecticides with reduced sulfur species, it is known that reduced sulfur species attack the insecticides at the α-carbon of ethoxy and methoxy groups and not at the phosphorus atom (Wu et al., 2006; Wu and Jans, 2006). Such an attack seems also likely in the compounds investigated here. However, the chosen compounds of this study also possess chlorine atoms and it seems reasonable to also consider a nucleophilic substitution of a chloride by a reduced sulfur species. Those two potential reaction pathways of TCEP reacting with thiophenolate have been investigated previously. However, no conclusion could be reached on which of the pathways is dominating under those conditions (Saint-Hilaire et al., 2011).

The primary purpose of this research was to explore the potential impact of polysulfides, thiophenolates, and bisulfide solution on the abiotic transformation of TCEP and its structural analogues TDCPP and TCPP. The second-order rate constants were determined in well-defined systems. Some degradation products were identified. The relative reactivity of TCEP, TDCPP, and TCPP with polysulfides, thiophenolates, and bisulfides is compared. And relative reactivity of TCEP, TCPP, and TDCPP is discussed considering their structures.

2. Materials and methods

2.1. Chemicals

All chemicals were used as received. TCEP (98.0%), TDCPP (95.0%) were obtained from TCI America (Portland, OR). TCPP (97%) was purchased from Pfaltz and Bauer (Warterbury, CT). 1,3-Bis(phenylthio)propane (BPTnP) was received from Acros Organics. All solvents were analytical grade or equivalent. Ethyl acetate and methanol were HPLC grade (J.T. Baker, Phillipsburg, NJ). All the reaction solutions were prepared inside a controlled-atmosphere glovebox (96% N_2, 4% H_2, Pd catalyst; Coy Laboratory Products, Grass Lake, MI) using deionized water (Milli-Q, Millipore Corps, Milford, MA). Prior to use, Milli-Q water and methanol was purged with high purity argon or nitrogen and immediately brought into the glovebox. All glassware was soaked in 1 M HNO_3 overnight and rinsed several times with Milli-Q water prior to use. Glassware, having prior contact with sulfur species, was first rinsed in 1 M NaOH in methanol solution then rinsed several times with Milli-Q water prior to soaking in 1 M aqueous HNO_3.

2.2. Reduced sulfur solutions

Na_2S stock solutions were prepared under argon from $Na_2S{\cdot}9H_2O$ (98%; EM Science, Gibbstown, NJ) using deoxygenated Milli-Q water as reported by Jans and Miah (2003). Thiophenol stock solutions were prepared by dissolving thiophenol (99%, Lancaster Synthesis, Inc., Pelham, NH) in deoxygenated methanol. Polysulfide stock solutions were prepared by dissolving the toluene-washed sodium tetrasulfide (Na_2S_4, technical grade, 90+%, H_2O 5% max, Alfa Aesar, Ward Hill, MA) in 100 mM sodium tetraborate buffer. The reaction solutions were prepared by dilution of reduced sulfur stock solution into 50 mM tetraborate buffer and 100 mM NaCl. The total hydrogen sulfide concentration $[(H_2S)]_T = [H_2S] + [HS^-] + [S^{2-}]$, total thiophenol concentration $([PhSH])_T = [PhSH] + [PhS^-]$, and total S(-II) concentration $([S(\text{-}II)])_T =$

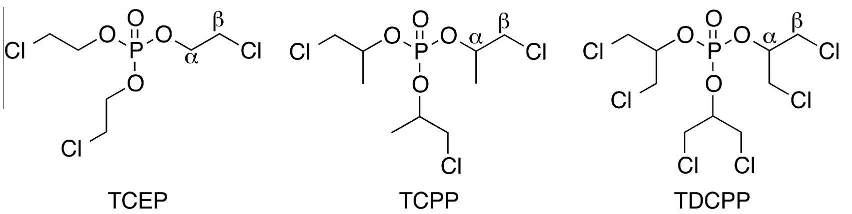

Fig. 1. Structures of investigated THAPs.