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Reactions of Three Halogenated Organophosphorus Flame Retardants with Reduced Sulfur Species

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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

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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 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 extent 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 interaction reports an increased heterogeneous nucleophilic

transformation of a chloroactanilide (metolachlor) by HS^- on the surface of alumina (Wei et al., 2013).

Figure 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 Method

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 (Wartebury, 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 $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ (98%; EM Science, Gibbstown, NJ) using deoxygenated Milli-Q water as reported by Jans (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 $[(\text{H}_2\text{S})]_{\text{T}} = [\text{H}_2\text{S}] + [\text{HS}^-] + [\text{S}^{2-}]$, total thiophenol concentration $[(\text{PhSH})]_{\text{T}} = [\text{PhSH}] + [\text{PhS}^-]$, and total S(-II) concentration $[(\text{S}(-\text{II}))]_{\text{T}} = [\text{H}_2\text{S}]_{\text{T}} + [\text{H}_2\text{S}_n]_{\text{T}} = [\text{H}_2\text{S}]_{\text{T}} + [\text{S}_n^{2-}] + [\text{HS}_n^-] + [\text{H}_2\text{S}_n]$, $n = 2-5$ in polysulfides solutions were determined by iodometric titration using a starch endpoint (Skoog et al., 1999). An Accumet pH meter (Fisher Scientific, Pittsburgh, PA) with a Ross combination pH electrode (ThermoOrion, Beverly, MA) was used to measure pH in the reduced sulfur reaction solutions. Thiophenolate ion concentrations were calculated from the total thiophenol concentration and the measured pH values. The total concentrations of polysulfide dianions ($\Sigma[\text{S}_n^{2-}]$) were determined via speciation calculation from the measured $[\text{S}(-\text{II})]_{\text{T}}$ and pH values on the basis of the reported equilibrium constants (Schwarzenbach and Fischer, 1960; Giggenbach, 1972). The resulting values of $[\text{S}_n^{2-}]$ were used to compute the second-order rate constants $k''_{\text{S}_n^{2-}}$ for the reaction of these THAPs with polysulfides.

2.3 Experimental System

Unless otherwise stated, reaction solutions were prepared in an anaerobic glovebox. The reaction solutions were prepared in volumetric flasks and then transferred to 20 mL glass syringes equipped with a polycarbonate stopcock and PTFE needle tubing. The syringe contained three PTFE rings to facilitate mixing. All reactions contained 50 mM buffer sodium tetraborate (pH ≈ 9) and 100 mM NaCl was added to all solutions to hold the ionic strength relatively constant. The spiking solution of the THAPs was prepared by dissolving parent compounds in deoxygenated methanol. Reaction mixtures were maintained anoxic and incubated in a water bath at the selected temperatures. Polysulfide experiments were conducted at 25 °C while thiophenolate and bisulfide experiments were held at 50 °C. The kinetics was monitored by extracting aliquots (~ 1 mL) of the reaction mixture with 1 mL of ethyl acetate throughout the course of experiments. The resulting extracts were subjected to GC-FID. The kinetics were also monitored by adding one drop of glacial acetic acid into samples of 0.5 mL of the reaction solution and storing these samples immediately in the freezer until analysis by LC-MS-MS for the determination of BCPP or BDCPP concentration, respectively.

2.4 Chromatographic Analysis

GC-FID Analysis—Ethyl acetate extracts were analyzed on a Fisons GC 8000 equipped with an AS 800 autosampler, a FID-80 flame ionization detector (Carlo Erba Instrument, Milan, Italy), a split/splitless injector, and an ECTM-5 fused-silica capillary column (30 m $\times$ 0.25 mm $\times$ 0.25 μm film thickness; Alltech, Deerfield, IL). The carrier gas was helium (99.999 %). Injector and detector temperature for TCEP, TDCPP, and TCPP were set at 250 °C and 275 °C, respectively. The column temperature was held at 100 °C for one minute, then increased at a rate of 20 °C/min to 275 °C, and finally held constant at 275 °C for four minutes for TCEP. The column temperature for TDCPP was set at 150 °C for one minute, and then increased at a rate of 20 °C/min to 275 °C and held constant at 275 °C for 10 minutes. The column temperature was set at 100 °C for one minute, and then increased to 220 °C at a rate of 20 °C/min, to 225 °C at a rate of 1 °C/min, to 275 °C at a rate of 20 °C/min, and finally kept at 275 °C for 2 minutes for TCPP.

A product peak was observed in the ethyl acetate extracts of the experiment of TCP with thiophenolate. GC-MS analysis of this peak resulted in the mass spectrum shown in Figure 2a. The compound was assigned as bisphenylthio *iso*-propane (BPTiP). BPTiP is not commercially available. However, its isomer, bisphenylthio *n*-propane (BPTnP) is commercially available. The mass spectrum of BPTnP is shown in Figure 2b. Figure 2 illustrates that the mass spectrum of BPTiP and the mass spectrum of a BPTnP standard are similar as one would expect. Since a FID detector was used for the analysis of BPTiP, it is expected that BPTnP and BPTiP show almost identical responses. Therefore, BPTiP peaks were quantified using BPTnP standards.

LC-MS-MS Analysis—The formation of bis(chloropropyl) phosphate (BCPP) was monitored by LC (UFLC Shimadzu, Kyoto, Japan) and negative electrospray ionization tandem mass spectroscopy (ESI-MS-MS) (4000 Q Trap, Applied Biosystems MDS Sciex, Concord, Canada) operated in the negative ion mode for BCPP with multiple reaction monitoring (MRM). LC-MS-MS parameters for BCPP are the following: curtain gas: 240 kPa, ion spray voltage: – 4500 V, temperature: 350 °C, ion source gas 1: 140 kPa, ion source gas 2: 100 kPa. MRM transition monitored for BCPP were 249/35, 251/35, 249/37, 251/37. Since TCP has those same transitions, we also monitored 325/35 and 325/37. These two transitions are specific for TCP and were used to prevent that TCP is mistaken for BCPP. The chromatograms were examined using Analysis 1.4 software (Applied Biosystems). The 249/35 transition was used to integrate the peak areas and to quantify BCPP. A Zorbax eclipse XDB-C18 column (5 µm, 4.6 mm × 150 mm, Agilent Technology) was used for separating BCPP. LC conditions for BCPP were: flow rate 1.0 mL min⁻¹, mobile phase A: methanol/water (20/80) and mobile phase B: methanol/water (95/5), both containing 1 mM tributyl amine and 1 mM acetic acid. The gradient was as follows: 0.01 min, 40% B; 3 min, 48% B; 4 min, 100% B; 5 min, 100% B; 6 min, 40% B; 7 min, 40% B. The injection volume was 10 µL.

BCPP was synthesized by reacting sodium hydroxide with TCP at 100 °C (see Supplementary material for details). ¹H NMR spectra were recorded on a Varian Inova 500 NMR spectrometer. ¹H NMR spectra for BCPP are shown in Figure S1, Supplementary material). HRMS was obtained on an Agilent 6520 Q-TOF. The observed masses were 248.9847 and 500.8764 amu.

3. Results and Discussion

3.1 Kinetics of hydrolysis and substitution reaction with reduced sulfur nucleophiles

We have shown in our previous work that hydrolysis for TCEP is base-catalyzed and slow with an extrapolated half-life of about 2 years at pH 8 at 25 °C (Saint-Hilaire et al., 2011). Based on that observation, we assume that the hydrolysis of TDCPP and TCP is even slower than the hydrolysis of TCEP due to the larger side chain in their structure that increase steric hindrance. Since the hydrolysis is very slow, reactions of these THAPs with reduced sulfur species (bisulfide, polysulfides, and thiophenolate) might be relevant in the environment. The semilogarithmic plots for time courses of these investigated THAPs in the presence of excess sulfide species over 2–3 half-lives is indicative of first-order dependence in these THAPs (e.g., Supplementary material, Fig. S3). The slope in such semilogarithmic

plot yields a pseudo-first-order reaction rate constants (k'_{obs}). The expression for observed first-order rate constant for the reaction with bisulfide, polysulfides, and thiophenolate have been previously reported in (Saint-Hilaire et al., 2011). In short:

For the reaction with polysulfides the expression of the observed rate constant is

$$k_{\text{obs}} \approx k''_{\text{HS}^-} [\text{HS}^-] + k''_{\text{H}_2\text{S}} [\text{H}_2\text{S}] + \sum k''_{\text{HS}_n^-} [\text{HS}_n^-] + \sum k_{\text{S}_n^{2-}} [\text{S}_n^{2-}] \quad (1)$$

The speciation calculations for $\Sigma[\text{S}_n^{2-}]$ show that by choosing a pH greater than 8.5 and assuming that the solutions are saturated with elemental sulfur, $\Sigma[\text{S}_n^{2-}]$ will be present at much higher concentration than HS^- . The calculated values of $\Sigma[\text{S}_n^{2-}]$ were used to

compute the second-order rate constant ($k''_{\text{S}_n^{2-}}$) for the reaction of THAPs with polysulfide dianions (Lippa and Roberts, 2002). Under those assumptions the expression for the observed rate constant can be simplified

$$k_{\text{obs}} \approx \sum k''_{\text{S}_n^{2-}} [\text{S}_n^{2-}] \quad (2)$$

Kinetic equations for experiments with thiophenolate can be expressed accordingly.

The reactions of bisulfide, polysulfides, and thiophenolate with TCEP, TDCPP, and TCPP under anoxic conditions were investigated. Fig. 3 shows the concentration dependence of the observed first-order reaction rate constant versus the reduced sulfur species concentration. Second-order and relative rate constants of TCEP, TDCPP, and TCPP with bisulfide, polysulfides, and thiophenolate are reported in Table 1. The relative rate constants were obtained by dividing the individual second-order rate constant for the three THAPs by the second-order rate constant for TCPP (the smallest value of the three THAPs). The table shows that TCEP reacts the fastest with polysulfides while TCPP reacts the slowest with polysulfides.

Second-order and relative rate constants of TCEP, TDCPP, and TCPP with thiophenolate at 50 °C are also summarized in Table 1. It can be seen that TCEP is the fastest reacting compound with thiophenolate, while TCPP is the slowest reacting compound with thiophenolate at 50 °C. The relative rate constants of those three THAPs with thiophenolate are similar to those with polysulfides. Table 1 also shows the second-order and relative rate constants of those three THAPs with bisulfide at 50 °C. Those experiments were performed only once because of the extended time it took to reach 2 to 3 half-lives. The same relative reaction pattern for the reaction of bisulfide was observed with those three THAPs as for polysulfides and thiophenolate. TCEP is the fastest reacting compound with bisulfide, while TCPP is the slowest reacting compound with bisulfide at 50 °C.

3.2 Discussion of the relative rate constants in light of reactivity

Steric, electronic, and statistical factors are contributing to the reaction rate constants of TCEP, TDCPP and TCPP with thiophenolate, polysulfides, and bisulfide. All three factors have to be considered when attempting to explain the relative reactivity of the structurally

related THAPs towards reduced sulfur species. The discussion below considers a potential nucleophilic attack at the α - or β -carbon of the three THAPs and the expected relative reaction rate constant that are summarized in Table 1.

In a first step the nucleophilic attack at the α -carbon (carbon that is adjacent to the oxygen atom, see Figure 1) was evaluated. When considering steric effects TCEP is the least sterically hindered compound while TCPP with the additional methyl group and TDCPP with the additional chloromethyl group are sterically more demanding and therefore should have slower reaction rate constants. The expected difference in reactivity between TCPP and TDCPP based on steric hindrance should not be very large. When considering electronic effects in nucleophilic attack at the α -carbon one would expect TDCPP to be the fastest reacting compound followed by TCEP and TCPP. This is due to the fact that the additional chloromethyl group of TDCPP is electron-withdrawing and therefore is increasing the partially positive charge on the α -carbon and thus making the compound more susceptible to a nucleophilic attack compared to TCEP. In contrast, the additional methyl group in TCPP is an electron-donating group that is decreasing the positive charge of the reaction center and thus leading to a slower reaction rate constant for nucleophilic substitution compared to TCEP. The observed result of TCEP being the compound that reacts the fastest with reduced sulfur species, followed by TDCPP and TCPP being the slowest, suggest that a combination of the steric and electronic effects can lead to the observed relative reaction rate constants.

In a second step a potential nucleophilic attack at the β -carbon (see Figure 1) is evaluated. Steric considerations are much less important in an attack at the β -carbon compared to an attack at the α -carbon for the three compounds. Nevertheless, steric consideration would favor TCEP slightly over TCPP and TDCPP, since it has been reported that in a nucleophilic substitution an *iso*-propyl rest is sterically more demanding than a *n*-propyl substituent (Shorter, 1973). In addition, it is also likely that the three alkyl chains of a phosphoric acid triester affect each other. When considering electronic effects for a nucleophilic attack at the β -carbon, TDCPP would be expected to be the fastest reacting compound, followed by TCEP and then TCPP. The additional chloromethyl group of TDCPP is attached to the carbon that is adjacent to the β -carbon. It is increasing the partially positive charge of the β -carbon slightly and therefore electronic effects would lead to a slightly faster reaction rate constant for TDCPP compared to TCEP. The additional methyl group in TCPP is an electron donating-group that is one carbon removed from the nucleophilic center and therefore it will decrease the partially positive charge of the reaction center only slightly and leading to a slightly slower reaction rate constant for nucleophilic substitution of TCPP compared to TCEP. We should also note that a “statistical effect” has to be taken into consideration when comparing TDCPP to TCPP. Both chlorines of the dichloropropyl side chains in TDCPP can be replaced leading to the same product. Therefore, even without steric and electronic effects TDCPP would react twice as fast as TCPP. Again, it can be seen that a combination of the steric, electronic and statistical effects for a reaction at the β -carbon could explain the observed relative reactivity of the three THAPs. It can be concluded from this discussion that the observed relative reactivity trends of reduced sulfur species with the three investigated THAPs can potentially be explained with either an attack at α - or β -carbon.

3.3 Products of the reaction of THAP with sulfur nucleophiles

At first the product formation in the hydrolysis of TCPP was investigated. Fig S4 (Supplementary material) shows a time-course for the hydrolysis of TCPP at pH 13.00 and 50 °C. It can be seen that the TCPP concentration is decreasing with time while bis(monochloroisopropyl)phosphate (BCPP) is forming as the major product. The mass balance is actually increasing overtime, which could be explained with an over-estimation of the BCPP concentration due to impurities in the synthesized BCPP that was used to prepare BCPP standards. This finding is supported by the ^1H NMR of the synthesized BCPP, that shows some impurities (Fig. S1, Supplementary material). The reaction of TCPP with 18.2 mM thiophenolate at pH 9.35 and 50 °C is illustrated in Fig. 4. The figure shows that two products are formed. BCPP is formed at the highest concentration. Bisphenylthio *iso*-propylphosphate (BPTiP) is also formed and its concentration is significantly smaller than the concentration for BCPP. The mass balance remains high throughout the time-course. The formation of BPTiP can be explained either through an attack at the α -carbon or an attack at the β -carbon (see Fig. 5 for mechanism). Either of the two mechanisms would suggest that one BPTiP is formed for every BCPP. The fact that the BPTiP concentration is smaller than the BCPP concentration could be explained by the likelihood that the intermediate with the three-membered ring (I in Fig. 5) is not just reacting with thiophenolate but also with hydroxide ions leading to the formation of an additional product (phenylthiopropanol). We were able to quantify this corresponding product (phenylthioethanol) in the reaction of TCEP with thiophenolate since commercial standards for phenylthioethanol were available (Saint-Hilaire et al., 2011), however phenylthiopropanol is commercially not available.

Analogous experiments were undertaken with TDCPP to identify the products of the reaction of TDCPP with reduced sulfur experiments. Bis(dichloropropyl)phosphate was synthesized by large scale hydrolysis of TDCPP at high pH and elevated temperature (see Supplementary material). Bis(dichloropropyl)phosphate was detected as a major product in the reaction of TDCPP with polysulfide and thiophenolate.

4. Conclusions and environmental significance

The series of experiments indicate that the three reduced sulfur species (HS^- , S_n^{2-} , PhS^-) react with TCEP, TDCPP, and TCPP. TCPP reacts with these reduced sulfur species in a nucleophilic substitution reaction with BCPP being the major product. We could not draw a definite conclusion whether the nucleophilic attack occurs at the α - or β -carbon.

The environmental fate of TCEP, TDCPP, and TCPP is controlled by a number of abiotic and biotic processes. Our results suggest that HS^- , S_n^{2-} , PhS^- are sufficiently reactive as to control the fate of TCEP, TDCPP, and TCPP in anoxic and suboxic environments where reduced sulfur species are abundant. Half-lives for TCEP, TDCPP, and TCPP in marine porewater containing reduced sulfur species were calculated by multiplying the second-order rate constants by the maximum concentrations of HS^- and S_n^{2-} reported by MacCrehan (MacCrehan and Shea, 1995). (We did not consider any effect the pH might have on the speciation of HS^- for this calculation). The calculated half-lives of TCEP at pH 7.0, 5.6 mM HS^- , and 0.33 mM S_n^{2-} at 25 °C are 90 and 30 d, respectively while a half-life

of 2 years for hydrolysis of TCEP were reported in our previous work. (Activation energies of 50 kJ/mol were assumed for the bisulfide reactions and the hydrolysis reaction in order to extrapolate from the rate constants measured at 50 °C to 25 °C). The calculated half-life of TDCPP at pH 7.0, 5.6 mM HS⁻, and 0.33 mM S_n²⁻ at 25 °C are 180 and 74 d, respectively. The calculated half-life of TCPP at pH 7.0, 5.6 mM HS⁻, and 0.33 mM S_n²⁻ at 25 °C are 1800 and 402 d, respectively. Therefore, reduced sulfur species present at environmentally relevant concentrations can represent an important sink for TCEP, TDCPP, and TCPP in anoxic coastal marine environment. If abiotic transformation reactions (nucleophilic substitution) are dominating the degradation of THAPs in the environment, one could conclude that TCPP is less reactive and therefore potentially more persistent than TCEP. If TCEP will be banned a possible replacement that is considered is TCPP. However, a potential replacement of the TCEP by TCPP in consumer products could lead to a significant increase of the TCPP concentration in the environment. This increase would not just occur because more TCPP would be used, but also because its abiotic degradation is significantly slower than the degradation of TCEP.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Appendix A: Supplementary material

Supplementary data associated with this article can be found in the online version.

Fig 1.
Structures of investigated THAPs:

Figure 2.

a) MS spectrum of the product peak forming in the reaction of TCPP with 18.2 mM PhS^- , pH 9.35, reaction time 266 h, extracted with ethyl acetate b) MS spectrum of a 70 μM BPTnP standard in methanol.

Figure 3.

a) First-order rate constant of THAPs versus thiophenolate concentration at 50 °C, b) first-order rate constants of THAPs versus polysulfide concentration at 25 °C.

Figure 4.

Fig. 4. Reaction of 600 μM TCPP (♦) with 18.2 mM thiophenolate at pH 9.35 and 50 °C including BCPP (▲), BPTiP (■) as products and the phosphorus mass balance (TCPP + BPTiP) (●)

a) nucleophilic attack at an α -carbon of TCPP

b) nucleophilic attack at a β -carbon of TCPP

Figure 5.

The two possible reaction mechanisms of TCPP with thiophenolate that would explain the formation of BPTiP

Table 1

Second-order and relative rate constants of TCEP, TDCPP, and TCPP with polysulfides at 25 °C, thiophenolate, and bisulfide at 50 °C.

Flame retardant	TCEP	TDCPP	TCPP
$k''_{S_n^{2-}} \times (10^{-4} \text{ M}^{-1}\text{s}^{-1})^a$ 25 °C	5.0 ± 1.4	3.2 ± 0.43	0.61 ± 0.08
$k''_{PhS^-} \times (10^{-4} \text{ M}^{-1}\text{s}^{-1})^a$ 50 °C	34 ± 2.0	6.4 ± 1.4	1.8 ± 0.2
$k''_{HS^-} \times (10^{-4} \text{ M}^{-1}\text{s}^{-1})^b$ 50 °C	0.89	0.45	0.045
Relative rate constant for S_n^{2-}	8	5	1
Relative rate constant for PhS^-	19	4	1
Relative rate constant for HS^-	20	10	1

^a Stated uncertainties represent 95% confidence limits

^b No confidence interval is reported since the experiment was only performed at two different concentrations for TCEP and one concentration for TDCPP and TCPP.