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Reaction of Tris(2-chloroethyl)phosphate with Reduced Sulfur Species

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Abstract

Tris(2-chloroethyl)phosphates (TCEP) is a widely used flame retardant in the U.S. It has recently been identified as one of the most frequently detected contaminants in U.S. streams. This contaminant is 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-}), bisulfide (HS^-), and thiophenolate (PhS^-) present in anoxic subregions of coastal water bodies could have a significant impact on rates of removal of such a contaminant. The kinetics of reaction of reduced sulfur species with tris(2-chloroethyl)phosphate have been determined in well-defined aqueous solutions under anoxic conditions. Reactions were monitored at varying concentrations of reduced sulfur species to obtain the second-order rate constants from the observed pseudo-first order rate constants. The determined second-order rate constant for the reaction of TCEP with polysulfide at 25 °C is $5.0 (\pm 1.4) \times 10^{-4} M^{-1} s^{-1}$, with thiophenolate at 50 °C is $34 (\pm 2) \times 10^{-4} M^{-1} s^{-1}$ and with bisulfide at 50 °C is $0.9 \times 10^{-4} M^{-1} s^{-1}$, respectively. In addition, the degradation products of hydrolysis and the reactions with polysulfides, thiophenolate, and bisulfide with TCEP were studied with GC-FID and LC-MS-MS and were quantified.

Keywords

tris(2-chloroethyl)phosphate; bis(2-chloroethyl)phosphate; flame retardants; reduced sulfur species; bisulfide; polysulfide

1. Introduction

Phosphoric acid triesters that are used as organophosphorus flame retardants (OPFRs) and plasticizers are a class of chemicals with a high consumption volume (186,000 tons annually worldwide in 22001; Hartmann et al., 2004) and have been determined in many environmental samples (Carlsson et al., 1997; Fries and Püttmann, 2001; Kolpin et al., 2002; Meyer and Bester, 2004; Regnery and Püttmann, 2010). Tris(2-chloroethyl)phosphate

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(TCEP) is one of those OPFRs and is included in the European Commission second priority list (European Commission, 1995). It is also listed as an EU high production volume chemical together with other OPFRs such as triphenyl phosphate, tris(2-butoxyethyl)phosphate, and tributyl phosphate (IUCLID, 2000). The broad application range of OPFRs and the fact that they are utilized as additives may result in them spreading diffusely into the environment by volatilization, leaching, and abrasion (Marklund et al., 2005). Increasing standards for fire resistance along with legal restriction on competing products, such as the polybrominated diphenyl ethers, will likely lead to increases in the application of organophosphates as flame retardants (Hartmann et al., 2004).

OPFRs are of concern because they leach or diffuse out of the commercial products over the course of their product lifetime, with exposure to humans mainly through ingestion, inhalation of dust particles and dermal sorption (WHO, 1990; Hughes et al., 2001). Several studies demonstrated the potential for commercial products to emit OPFRs and their degradation products (Carlsson et al., 2000; Salthammer et al., 2003). Little is known about the toxicity of these compounds, although some studies indicate that some compounds like TCEP may be neuro and reproductive toxins as well as carcinogens (Tilson et al., 1990; Umezu et al., 1998; WHO, 1998). Many OPFRs and plasticizers have been found in various environments including indoor dust (Carlsson et al., 2000; Marklund et al., 2003; Salthammer et al., 2003; Takigami et al., 2009; Tollbäck et al., 2010) and outdoor air (Marklund et al., 2005), water (Ishihawa et al., 1995; Bester et al., 2008; Reemtsma et al., 2008; Benotti et al., 2009), sediments (Galassi et al., 1992; Chung and Ding, 2009), soils (David and Seiber, 1999; Kiersch et al., 2010), and landfill leachates (Yasuhara, 1999; Barnes et al., 2004). It has previously been suggested that OPFRs are subject to long-range air transportation (Ciccioli et al., 1994; Aston et al., 1996; Laniewski et al., 1998). In support of this suggestion, OPFRs have been detected in air samples collected in Antarctica (Ciccioli et al., 1994), pine needles in the Sierra Nevada Mountains, United States (Aston et al., 1996), as well as in precipitation in remote areas such as rainwater from Ireland, snow from Poland and Sweden (Laniewski et al., 1998), and rainwater collected in Germany (Fries and Püttmann, 2003). Maximum concentrations for TCEP of up to $0.5 \mu\text{g L}^{-1}$ are reported in urban rivers (Kolpin et al., 2002), $30 \mu\text{g L}^{-1}$ in wastewater treatment plant effluent (Fries and Püttmann, 2001), 1 ng g^{-1} in marine sediments (Chung and Ding, 2009), and 250 ng m^{-3} in indoor air (Carlsson et al., 1997).

To predict the environmental fate of these OPFRs, it is necessary to characterize their mobility and the rate of degradation under environmental conditions. OPFRs 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 4.7). It is also likely that some OPFRs 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 be replenished by mixing processes, microbial sulfate reduction can give rise to locally high concentrations 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 OPFRs can enter environmental compartments that contain high concentration of reduced sulfur species, the reaction of OPFRs 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 OPFRs. 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. TCEP was chosen in this study as a representative halogenated OPFRs, since it is the most water soluble halogenated OPFR. This allows experiments in water at concentrations that are high enough for an easy detection of TCEP and its degradation products. Fig. 1 shows the structure of the investigated TCEP. 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 and Jans, 2006; Wu et al., 2006). Such an attack at the α -carbon seems also likely in TCEP. However, TCEP also possesses chlorine atoms and it seems reasonable to also consider a nucleophilic substitution of a chloride by a reduced sulfur species (Loch et al., 2002; Zheng et al., 2006). Fig. 2 illustrates those two potential reaction pathways of TCEP reacting with thiophenolate. In pathway I, thiophenolate attacks TCEP at the β -carbon (carbon that is adjacent to the chlorine atom) to give O,O-dichloroethyl O-ethyl thiophenyl phosphate which potentially undergoes an intramolecular reaction to form 1-phenyl thiiranium chloride and bis(chloroethyl)phosphate (BCEP). Phenyl thiiranium chloride can react with another molecule of thiophenolate to give bis(phenylthio)ethane (BPTE). 1-Phenyl thiiranium chloride can also react with hydroxide ions to give 2-phenylthio ethanol (PTEA). Fig. 2 also shows proposed pathway II with thiophenolate attacking at the α -carbon (carbon that is adjacent to oxygen atom) to give 2-chloroethyl phenyl sulfide and BCEP. 2-Chloroethyl phenyl sulfide undergoes an intramolecular reaction to form 1-phenyl thiiranium chloride (Sedaghat-Herati et al., 1988). 1-Phenyl thiiranium chloride in return can react with another molecule of thiophenolate to give BPTE. However, 1-phenyl thiiranium chloride can also react with a hydroxide ion to form PTEA.

The primary purpose of this research was to explore the potential impact of polysulfides, thiophenolates, and bisulfide on the abiotic transformation of TCEP. The second-order rate constants were determined in well-defined systems. In addition, the formation of BPTE, PTEA, and BCEP from the reaction of TCEP with thiophenolate was quantified. BCEP was also quantified as a product in reactions of TCEP with polysulfides and bisulfide as well as in hydrolysis experiments at high pH.

2. Materials and method

2.1. Chemicals

All chemicals were used as received. TCEP (98.0%) was obtained from TCI (Portland, OR). All solvents were of analytical grade or equivalent. Ethyl acetate and methanol were of HPLC grade (J.T. Baker, Phillipsburg, NJ). All the reaction solutions were prepared inside a

controlled-atmosphere glovebox (96 % N₂, 4 % H₂, Pd catalyst; Coy Laboratory Products, Grass Lake, MI) using deionized water (Milli-Q, Millipore Corps, Milford, MA). Prior to use, Milli-Q water was purged with high purity argon or nitrogen and immediately brought into the glovebox. All glassware was soaked in 1 M HNO₃ 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/ methanol solution then rinsed several times with Milli-Q water prior to soaking in 1 M HNO₃.

2.2. Reduced sulfur solutions

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 (Na₂S₄, technical grade, 90+ %, H₂O 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 in polysulfides solutions $[S(-II)]_T = [H_2S]_T + [H_2S_n]_T = [H_2S]_T + [S_n^{2-}] + [HS_n^-] + [H_2S_n]$, $n = 2-5$ 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 the 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 ($\Sigma[S_n^{2-}]$) were determined via speciation calculations from the measured $[S(-II)]_T$ and pH values on the basis of reported equilibrium constants (Schwarzenbach and Fischer, 1960; Giggenbach, 1974). The resulting values of $\Sigma[S_n^{2-}]$ were used to compute the second-order rate constants $k''_{S_n^{2-}}$ for the reaction of these OPFRs 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 phosphate or sodium tetraborate) and 100 mM NaCl was included to all solutions to hold the ionic strength relatively constant. The spiking solution of TCEP was prepared by dissolving the parent compound in deoxygenated methanol. The initial concentration of TCEP was 50 or 500 μ M in these experiments. Reaction mixtures were maintained anoxic and incubated in a water bath at the selected temperatures. 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. In addition, the kinetics were also monitored by adding one drop of glacial acetic acid into 0.5 mL of reaction solution and storing the sample in the freezer until analysis by LC-MS-MS.

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), a split/splitless injector, and an ECTM-5 fused-silica capillary column (30 m × 0.25 mm × 0.25 μm; Alltech, Deerfield, IL). The carrier gas was helium (99.999 %). Injector and detector temperature 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⁻¹ to 275 °C, and finally held constant at 275 °C for four minutes.

LC-MS-MS Analysis—The formation of PTEA and BCEP was monitored by LC (UFLC Shimadzu, Kyoto, Japan) and electrospray ionization tandem mass spectroscopy (ESI-MS-MS) (4000 Q Trap, Applied Biosystems MDS Sciex, Concord, Canada) operated in the positive ion mode for PTEA and negative ion mode for BCEP with multiple reaction monitoring (MRM). LC-MS-MS parameters for PTEA are curtain gas: 140 kPa, ion spray voltage: +5500 V, ion source gas 1: 450 kPa, and ion source gas 2: 450 kPa. The ones for BCEP are 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 transitions monitored for PTEA and BCEP were 155/137 and 221/35, respectively. The chromatograms were examined using Analysis 1.4 software (Applied Biosystems). A Zorbax eclipse XDB-C₁₈ column (5 μm, 4.6 mm × 150 mm, Agilent Technologies) was used for separating PTEA and BCEP. LC conditions for PTEA were: flow rate 1.0 mL min⁻¹, mobile phase A water with 0.1 % (v/v) formic acid and 4 mM ammonium formate, mobile phase B methanol with 0.1 % (v/v) formic acid and 4 mM ammonium formate. The gradient was as follows: 0.01 min, 80 % B; 3 min, 95 % B; 4 min, 95 % B; 5 min, 80 % B; 6 min, 80 % B. The conditions for BCEP 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.

BCEP was synthesized in large-scale hydrolysis reactions of TCEP at high pH (Supplementary material for details). An internal standard, *p*-xylene, was used to confirm the identity of BCEP (see Fig. S7a and S7b, Supplementary material) by ¹H NMR. ¹H NMR spectra were recorded on a Varian Inova 500 NMR spectrometer.

3. Results and discussion

3.1 Kinetics of hydrolysis and substitution reactions with reduced sulfur nucleophiles

The pH dependence of the hydrolysis was investigated between pH 8 and 13 at 50 °C. A typical time-course for hydrolysis of TCEP at 50 °C and pH 9.20 is shown in Fig. S1a (Supplementary material). As expected the hydrolysis rate of TCEP increases with increasing pH (Fig. S1b and Table S1, Supplementary material). From a hydrolysis experiment of TCEP at 50 °C and pH 8, a half-life of approximately 2 years can be estimated for pH 8 and 25 °C (assuming an activation energy of 50 kJ mol⁻¹). Therefore, it can be concluded from these experiments that hydrolysis is a very slow pathway for degradation of TCEP under environmentally relevant conditions (WHO, 1998). Since the

hydrolysis is very slow, reactions of TCEP with reduced sulfur species (bisulfide, polysulfides, and thiophenolate) might be relevant in the environment. The semilogarithmic plot for the time-course of TCEP in the presence of excess sulfide species over 2–3 half-lives is indicative of first-order dependence in TCEP concentration (e.g., see Fig. S2, Supplementary material). The slope in such a semilogarithmic plot yields a pseudo-first-order reaction rate constant (k_{obs}). The observed first-order rate constant can be expressed in the following manner for the reaction with bisulfide:

$$k_{obs} \approx k''_{HS^-} [HS^-] + k''_{H_2S} [H_2S] \quad (1)$$

where k''_{H_2S} is the second-order reaction rate constant of hydrogen sulfide with TCEP and k''_{HS^-} is the second-order reaction rate constant of bisulfide with TCEP (second order rate constants are marked with the symbol "). The term $k''_{H_2S} [H_2S]$ is much smaller than $k''_{HS^-} [HS^-]$ at pH greater than 7, since most of the species are in HS^- form and since HS^- is a better nucleophile than H_2S . Therefore, at pH > 7 the expression can be simplified to

$$k_{obs} \approx k''_{HS^-} [HS^-] \quad (2)$$

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

$$k_{obs} \approx k''_{HS^-} [HS^-] + k''_{H_2S} [H_2S] + \sum k''_{HS_n^-} [HS_n^-] + \sum k''_{S_n^{2-}} [S_n^{2-}] \quad (3)$$

The speciation calculations for $\Sigma[S_n^{2-}]$ show that by choosing a pH greater than 8.5 and assuming that the solutions are saturated with elemental sulfur, $\Sigma[S_n^{2-}]$ will be present at much higher concentration than HS^- . The calculated values of $\Sigma[S_n^{2-}]$ were used to compute the second-order rate constant ($k''_{S_n^{2-}}$) for the reaction of TCEP with polysulfide dianions (Lippa and Roberts, 2002). Under those assumptions the expression for the observed rate constant can be simplified

$$k_{obs} \approx \sum k''_{S_n^{2-}} [S_n^{2-}] \quad (4)$$

The expression for the observed rate constant for the reaction of TCEP in the presence of thiophenolate is given by:

$$k_{obs} \approx k''_{PhS^-} [PhS^-] + k''_{PhSH} [PhSH] \quad (5)$$

For experiments at pH > 7 most of the thiophenol will be in the PhS^- form and the observed rate constant can be expressed as:

$$k_{obs} \approx k''_{PhS^-} [PhS^-] \quad (6)$$

The reactions of polysulfides with TCEP under anoxic conditions were investigated. A representative time-course profile for the reaction TCEP with 3.81 mM polysulfide at 25 °C and pH 9.29 is shown in Fig. S2 (Supplementary material). The second-order rate constant for the reaction of TCEP with polysulfides was determined by plotting k_{obs} vs. $[S_n^{2-}]$ (Fig. S3, Supplementary material). The determined second-order rate constant for the reaction of TCEP with polysulfides at 25 °C is $5.0 (\pm 1.4) \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$. The initial concentration of TCEP in these experiments was 50 μM . Linear regression analysis of $\log k_{obs}$ versus $\log[S_n^{2-}]$ yielded a slope equal to 1.10 ± 0.21 (where the stated uncertainties reflect the 95 % confidence limits). This result indicates that the reaction of TCEP with polysulfide is an overall second-order process, first-order both in polysulfide and in TCEP concentrations.

A representative time-course for the reaction of TCEP with 7.09 mM thiophenolate at 50 °C and pH 9.29 is shown in Fig. S4 (Supplementary material). Five experiments with varying thiophenolate concentrations were performed at 50 °C and the determined second-order rate constant is $34 (\pm 2) \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ (Fig. S5, Supplementary material). The initial concentration of TCEP in these experiments was 50 μM . Linear regression analysis of $\log k_{obs}$ versus $\log[PhS^-]$ yielded a slope equal to 1.37 ± 0.38 (where the stated uncertainties reflect the 95 % confidence limits). This result indicates that the reaction of TCEP with thiophenolate is an overall second-order process, first-order both in thiophenolate and in TCEP concentrations. Table 1 shows the second-order rate constants of TCEP with bisulfide at 50 °C. This experiment was performed only twice because of the extended time it took to reach 2 to 3 half-lives. From the rate constants summarized in Table 1, it can be seen that the second-order rate constant of TCEP at 50 °C with thiophenolate is higher than the second-order rate constant with bisulfide. This is in good agreement with the difference in reactivity that has been reported for nucleophilic substitution reactions at a carbon center (Schwarzenbach et al., 2003; Lipka and Roberts, 2005; Wu et al., 2006).

3.2. Products of the reaction of TCEP with sulfur nucleophiles

At first the hydrolysis of TCEP was investigated. Fig. 3 shows the time-course for hydrolysis of TCEP at pH 10.79 and 50 °C. It can be seen that the TCEP concentration is decreasing while the concentration BCEP is increasing with time. The figure also shows that TCEP is converted at a 1:1 ratio to BCEP. The mass balance is stable over the duration of the experiment indicating that BCEP is the sole and stable product of the hydrolysis of TCEP. The reaction of TCEP with 1.15 mM thiophenolate at pH 9.18 and 50 °C is illustrated in Fig. 4. The figure shows that three products are formed. BCEP is formed at the highest concentration. BPTE and PTEA are also formed and their concentrations are approximately half of the concentration of BCEP. 2-Chloroethyl phenyl sulfide, a potential intermediate in this reaction, was not observed (Fig. 2, pathway II). The mass balance remains high throughout the time-course indicating that the major degradation products for this reaction were quantified and that the products are stable over the course of the experiment.

Fig. 5 shows the time-course of the reaction of TCEP with 43.7 mM bisulfide at 50 °C and pH 9.70. BCEP is again detected to be the main product of this reaction. However, the mass balance declines with time indicating that not all products are detected. Possible reasons that no additional products were observed is that they might be charged or they might be thiols. Charged products and thiols are difficult to extract and analyze. Fig. 5 also includes fitted curves. The first-order rate constant for disappearance of TCEP and formation of BCEP were determined by simultaneously fitting the observed parent compound degradation data and degradation product formation data using Scientist (v.2.01; MicroMath, Inc). Scientist is software that is capable of determining rate constants and associated parameters by fitting experimental data to numerically integrated solutions of systems of differential rate expressions. The following model was used to fit the data

with k'_{TCEP} and k'_{BCEP} representing the pseudo-first order rate constants of the two sequential reactions.

Experiments starting with BCEP were also conducted in order to determine the stability of BCEP in bisulfide solutions. Two experiments of BCEP with 63.1 or 71.7 mM HS^- were performed. The first-order rate constants for the reaction of BCEP with 63.1 or 71.7 mM HS^- were determined to be $1.3 \times 10^{-6} \text{ s}^{-1}$ and $1.4 \times 10^{-6} \text{ s}^{-1}$, respectively. This corresponds to a second-order reaction rate constant of the reaction of BCEP with HS^- at 50 °C of $2.0 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ and $2.0 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$. In comparison, the second-order rate constant for the reaction of BCEP with bisulfide that was derived by fitting the data in Fig. 5 is $3.3 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$. One can see that the second-order rate constant for the reaction of BCEP with bisulfide obtained by fitting the TCEP and BCEP concentrations in Fig. 5 is almost 2 times larger than the rate constant directly determined in the experiments starting with BCEP. Such a discrepancy might be explained with the existence of a competing reaction between TCEP and HS^- that does not lead to the formation of BCEP. This competing reaction would have to contribute about 25% to the overall degradation of TCEP under the chosen conditions to explain the observed discrepancy in the rate constants. Nevertheless, we can conclude that the reaction of BCEP with HS^- to undetected products can explain the decrease in mass in Fig. 5.

Similar findings in regards to product formation were obtained with polysulfide as the nucleophile instead of bisulfide. Fig. 6 shows a time-course for the reaction of TCEP with 5.4 mM polysulfides at pH 9.18 and 25 °C. It can be seen that the TCEP concentration decreases while the BCEP concentration increases. It can also be seen that TCEP is almost converted in a 1:1 ratio to BCEP and therefore the mass balance is nearly constant. In order to elucidate the stability of BCEP in polysulfide solution an experiment of BCEP with S_n^{2-} was performed. A time-course for the reaction of BCEP with 8.05 mM polysulfides at pH 9.27 and 25 °C was measured. The first-order rate constant for the reaction of BCEP with 8.05 mM S_n^{2-} is $6.4 \times 10^{-7} \text{ s}^{-1}$ (Fig. S6, Supplementary material). This corresponds to a second-order reaction rate constant of the reaction of BCEP with S_n^{2-} of $7.8 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C. The first-order rate constant obtained by fitting the data in Fig. 6 is $3.1 (\pm 2.5) \times$

$10^{-5} \text{ M}^{-1} \text{ s}^{-1}$. Thus, the second-order rate constant for the reaction of BCEP with polysulfide that was derived by fitting the data in Fig. 6 is in the same order of magnitude as the rate constant determined by the direct experiment of BCEP with polysulfide. This finding suggests that all the major reactions of TCEP with polysulfide are accounted for.

3.3. 2-Chloroethyl phenyl sulfide, a potential intermediate of the reaction of TCEP with thiophenolate

2-Chloroethyl phenyl sulfide is proposed to be an intermediate in pathway II in Fig. 2, however it was not detected in experiments of TCEP with thiophenolate. In order to elucidate this observation the reactions of 2-chloroethyl phenyl sulfide were investigated. At first, the hydrolysis of 2-chloroethyl phenyl sulfide was studied. For the hydrolysis at 25 °C and pH 9.14, a first-order rate constant of $1.4 \times 10^{-4} \text{ s}^{-1}$ was obtained (Fig. S8, Supplementary material). Then, an experiment was repeated under similar conditions, however this time 5.2 mM thiophenolate was also added to the reaction solution (Fig. S9, Supplementary material). The first-order rate constant of this reaction of 2-chloroethyl phenyl sulfide at 25 °C, pH 9.14 and 5.2 mM thiophenolate was $1.7 \times 10^{-4} \text{ s}^{-1}$. It can be argued that the first-order rate constant of 2-chloroethyl phenyl sulfide is not significantly increased by the addition of 5 mM thiophenolate. This finding might indicate that the reaction of 2-chloroethyl phenyl sulfide is independent of nucleophiles such as thiophenolate. A proposed intramolecular attack could explain this observation. The products that were detected in the reaction of 2-chloroethyl phenyl chloride with 5.2 mM thiophenolate at 25 °C, pH 9.14 are shown (Fig. S10, Supplementary material). It can be seen that BPTE is formed as the main product. However the mass balance declines slightly with time. (PTEA was not quantified for this experiment.) A possible explanation for the fact that 2-chloroethyl phenyl sulfide could not be detected as an intermediate in the reaction of TCEP with thiophenolate could be the following pathway (Fig. S11, Supplementary material). 2-Chloroethyl phenyl sulfide would be formed from a slow reaction of TCEP with thiophenolate at 25 °C (the reaction rate constant in the presence of 5 mM thiophenolate is $1.4 \times 10^{-6} \text{ s}^{-1}$). The formed 2-chloroethyl phenyl sulfide then could undergo a much faster intramolecular attack to form the 1-phenyl thiiranium chloride ($(1.4 - 1.7) \times 10^{-4} \text{ s}^{-1}$) which is faster than the first step by a factor 100. The 1-phenyl thiiranium in return would react even faster with hydroxide or thiophenolate ion in the final step. In summary, in a reaction of TCEP with 5 mM thiophenolate 2-chloroethyl phenyl sulfide would potentially be formed 100 times slower than it reacts, therefore it does not accumulate at a concentration high enough that would allow its detection.

4. Conclusions and environmental significance

The series of experiments indicate that the three reduced sulfur species (HS^- , S_n^{2-} , PhS^-) react with TCEP in a nucleophilic substitution reaction with BCEP being the major product. The product formation can be explained by the proposed reaction pathway. However, our experiments are not conclusive in determining whether the nucleophilic attack occurs at the α -carbon or at the β -carbon of TCEP. The absence of 2-chloroethyl phenyl sulfide as intermediate does not necessarily favor pathway I over pathway II. Its absence can also be

explained with a sequence of reactions in pathway II that would not lead to an accumulation of 2-chloroethyl phenyl sulfide.

The environmental fate of TCEP 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 in anoxic and suboxic environments where reduced sulfur species are abundant. The half-lives for TCEP in marine porewater containing reduced sulfur species were calculated by multiplying the second-order rate constants by reported maximum concentrations of $[\text{HS}^-]$ and $\Sigma[\text{S}_n^{2-}]$ (MacCrehan and Shea, 1995). The results indicate that the calculated half-lives for TCEP at pH 7.0, 5.6 mM HS^- , and 0.33 mM S_n^{2-} at 25 °C are 90 and 30 days, respectively while a half-life of 2 years was estimated for hydrolysis of TCEP. Hence, our results demonstrate that significant degradation of TCEP can occur with polysulfides and bisulfide under anoxic conditions relative to hydrolysis. Therefore, reduced sulfur species present at environmentally relevant concentrations can represent an important sink for TCEP in anoxic coastal marine environment. Our experiments show that BCEP is the major product of the reactions of TCEP with reduced sulfur species. BCEP is significantly more water soluble than TCEP. Therefore, it will be predominantly present in aqueous environment and no accumulation in sediments and biota is expected.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Fig. 1.
Structure of investigated TCEP.

Fig. 2.
Possible pathways of the reaction of TCEP with thiophenolate.

Fig. 3.

Hydrolysis of TCEP (◆) at pH 10.80 and 50 °C including degradation product BCEP (△) and mass balance (■).

Fig. 4.

Reaction of TCEP (♦) with 1.15 mM thiophenolate at pH 9.18 and 50 °C including BCEP (△), BPTE (▲), PTEA (●) as product and the mass balance (■).

Fig. 5. Reaction of TCEP (♦) with 43.7 mM bisulfide at pH 9.18 and 50 °C including product BCEP (△). The lines represent model fits; the solid line without points represents the formation of an unknown compound (see reaction (7)).

Fig. 6.

Reaction of TCEP (◆) with 5.44 mM polysulfides at pH 9.18 and 25 °C including product BCEP (△). The lines represent model fits; the solid line without points represents the formation of an unknown compound (see reaction (7)).

Table 1

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

Second-order rate constant	TCEP
$k''_{S_n^{2-}} (25\text{ °C})^a$	$5.0 (\pm 1.4) \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$
$k''_{PhS^-} (50\text{ °C})^a$	$34 (\pm 2) \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$
$k''_{HS^-} (50\text{ °C})^b$	$0.89 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$

^a Stated uncertainties represent 95 % confidence limits.

^b No confidence interval is reported since the experiment was only performed at two different concentrations.