Insights into the Atmospheric Chemistry of Polybrominated Diphenyl Ethers

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Introduction.
Polybrominated diphenyl ether (PBDE) flame-retardants are persistent organic pollutants that have been found globally in the environment. PBDEs are prone to undergo long-range atmospheric transport to regions where they were never used, e.g., the Arctic. During their dispersion through the atmosphere, PBDEs may be destructively removed from the atmosphere through photolysis and by reactions with atmospheric oxidants such as hydroxyl (OH) radicals. We report here a systematic determination of gas-phase hydroxyl radical rate constants of eight brominated diphenyl ethers with 0–2 bromines. These data provide insight into the effect of substitution on OH reactivity and allow us to evaluate the accuracy of current structure activity relationships in predicting OH rate constants for other PBDEs. We also studied the photolysis of some of the more volatile congeners in an attempt to derive photolysis quantum yields for PBDE photolysis in the gas phase. These data, combined with our measurements of solution phase spectra of PBDEs containing 1–10 bromines, allow us to estimate atmospheric photolysis lifetimes for these compounds. The estimates are used to evaluate the importance of OH radical reactions and photolysis in determining the atmospheric fate of PBDEs. Our conclusions are discussed in light of the congener pattern of PBDE contamination found in sediments collected from the bottom of a lake on Isle Royale National Park, a pristine island in Lake Superior, where the only source of pollution is atmospheric deposition.

Materials and Methods.
Kinetics Experiments. Hydroxy radical reactions and photolysis decays were measured in a 160 cm^3 quartz reaction chamber located in a Hewlett-Packard 5890 gas chromatograph oven (for temperature control). The reactor was coupled via a 45 cm long stainless steel (or fused SiO_2) capillary to a Hewlett-Packard 5989A quadrupole mass spectrometer operated in electron impact mode. Irradiation of the reaction chamber was provided by a 200 W Hg(Xe) arc lamp, the light from which was filtered to eliminate infrared radiation. Hydroxyl radicals were generated by irradiation of He/air/isopropyl nitrite (i-C_3H_7ONO) mixtures at wavelengths greater than 320 nm. Photolysis decays of PBDEs were measured in He in the presence of cyclohexane (to scavenge radicals) at wavelengths of 310 ± 26 nm. A mixture of chlorine in helium was employed as a reference chemical actinometer.

Analysis of Siskiwit Lake Sediment. A 12.5 cm long sediment core was collected from Lake Siskiwit, Isle Royale (N 48º 00' 13", W 88º 47' 40") on September 4, 2005. The top 2.5 cm and the bottom 2.5 cm of the core were separately combined with Na_2SO_4 and Soxhlet extracted with 1:1 (vol/vol) acetone/hexane for 24 hours in the dark. The bottom core segment was analyzed as a field blank and used to establish the background level of PBDEs that may have been introduced during sampling and laboratory work. Samples were cleaned up and analyzed using an Agilent 5973 gas chromatographic mass spectrometer operating in the electron-capture negative-ionization, selected ion-monitoring mode (ECNI-SIM), as described by Zhu and Hites (2005). Normal QC/QA precautions were followed.

Results and Discussion.

A relative rate method was used to measure the gas-phase rate constants of the reaction of OH radicals with diphenyl ether and with several PBDEs (BDE-1, 2, 3, 4, 7, 11, and 15) at ~1 atm between the temperatures of 326–388 K. The Arrhenius expression for each compound was used to extrapolate the OH rate constants at 298 K; these values are shown in Figure 1. The experimentally determined rate constants are in reasonable agreement with those estimated from the structure-activity relationship developed by Zetzsch (1982) and Kwok and Atkinson (1995) although they fall short in predicting the dependence of reactivity on the bromine substitution pattern.

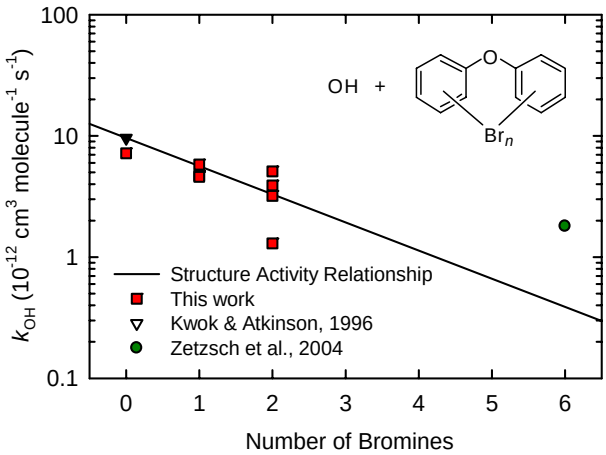

Figure 1. Comparison of OH reaction rate constants (at 298 K) derived from our gas-phase measurements to those measured by others and those calculated by the SAR.

Irradiations of PBDE/He gas mixtures with the output from a Hg(Xe) arc lamp (λ = 310 ± 26 nm) for 6–10 minutes led to loss of PBDEs (Figure 2). The linearity of the data in this semi-log plot of reactant signal versus time shows that the decays follow first order kinetics with the slope equal to the first-order photolysis rate. The photolysis rates are directly correlated to the absorption cross-sections of PBDEs at 310 nm and increase with the degree of bromination. Using chlorine as a chemical actinometer and from measurements of PBDE absorption cross sections in solution, the quantum yield for the photolysis of 2,4-dibromodiphenyl ether (BDE-7) was calculated to be 0.5 ± 0.1 at 325 K.

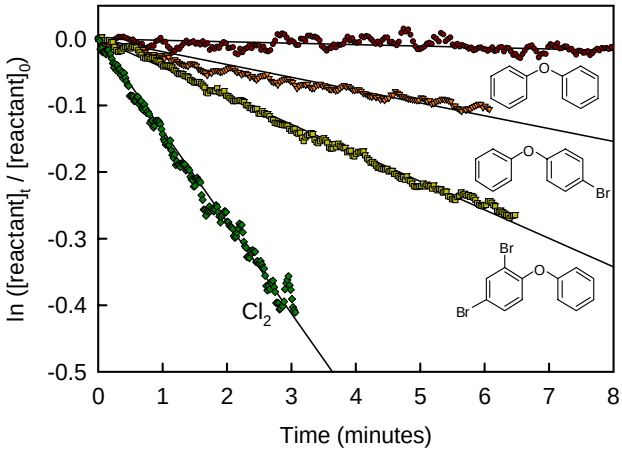

Figure 2. Decay of diphenyl ether, BDE-3, BDE-7, and chlorine in the vapor phase versus time of exposure to 310 nm radiation. Chlorine decays were measured at 298 K; all others were at 325 K.

Atmospheric residence times with respect to OH radical reactions and photolysis were calculated to evaluate the relative importance of each process in removing PBDEs from the atmosphere; see Figure 3. Hydroxyl radical residence times were derived from $\tau_{OH} = \{k_{OH}\,[OH]\}^{-1}$, using OH rate constants predicted from structure activity relationships (Zetzsch 1982; Kwok & Atkinson 1995), and an average global OH concentration of 9.7×10^5 molecules cm^{-3}. Photolysis residence times, τ_{photo} were calculated for 20 PBDE congeners with 1–10 bromines from, $\tau_{photo} = [\int_{\lambda} \sigma(\lambda)F(\lambda)\phi(\lambda)d\lambda]^{-1}$, where $\sigma(\lambda)$, $F(\lambda)$, and $\phi(\lambda)$ are the wavelength-dependent absorption cross-sections, actinic fluxes, and quantum yields, respectively. Absorption cross sections were determined from UV-visible spectra of PBDEs in *iso*-octane solutions and quantum yields of 0.5 were assumed for all congeners, in accordance with the measurements discussed above. The Tropospheric Ultraviolet-Visible (TUV 4.2) software package (Madronich & Flocke 1998) was used to estimate actinic flux.

The comparison of OH and photolysis residence times in Figure 3 suggests that photolysis is the dominant loss process for PBDEs in the atmosphere. However, this is likely only true for those molecules in the gas phase. A number of physical and chemical effects may hinder the photolysis of PBDEs adsorbed to particles (those congeners with 6 or more bromines). These include the shielding of UV light by the particle, photophysical quenching by neighboring molecules in the condensed phase, and enhanced recombination in a 'solvent cage' within the aerosol. The combined OH radical and photolysis residence times that include the effect of the partitioning of PBDEs onto particles are also shown in Figure 3. In this case, it is assumed that the fraction of PBDE molecules in the particle phase do not undergo photolysis. This result implies that congeners predominantly in the gas-phase (e.g., BDE-47) will be removed primarily by photolysis, while those congeners bound mostly to particles (e.g., BDE-209) will be unaffected by sunlight. Air and precipitation sampling data from our laboratory suggest that the most important loss process for BDE-209 and other particle-bound congeners is wet and dry deposition.

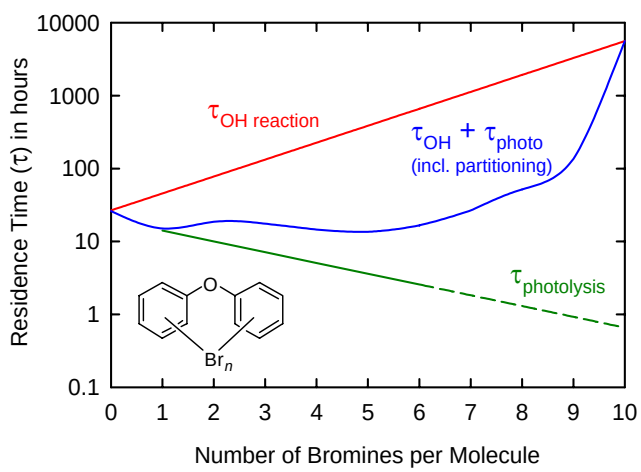

Figure 3. Atmospheric residence times for polybrominated diphenyl ethers as a function of bromination level derived from calculated OH rate constants and photolysis frequencies. Combined OH plus photolysis residence times are shown that include the effect of particle partitioning (i.e., the assumption is made that PBDEs do not undergo photolysis in the particle phase.)

These conclusions may explain the congener pattern of PBDE contamination found in sediments collected from the bottom of Siskiwit Lake, located on Isle Royale in northern Lake Superior; see Figure 4. This remote lake has few human visitors and receives no water from Lake Superior, making atmospheric deposition the only source of anthropogenic chemicals to its waters. The most abundant PBDE congener present in Siskiwit Lake sediment is BDE-209 (95%). A comparison of the PBDE congener profile found in

Siskiwit Lake to that found in air samples (combined vapor and particle phases) obtained from Eagle Harbor, MI, (near the shore of Lake Superior) shows a shift toward increased BDE-209 levels in the sediments. If wet and dry deposition were the only loss processes of PBDEs from the atmosphere above Lake Superior, then profiles from both samples should be comparable. Atmospheric processes, such as photolysis and OH radical reactions are likely intervening during long range atmospheric transport and lead to the depletion of the tetra- and penta-brominated congeners before deposition.

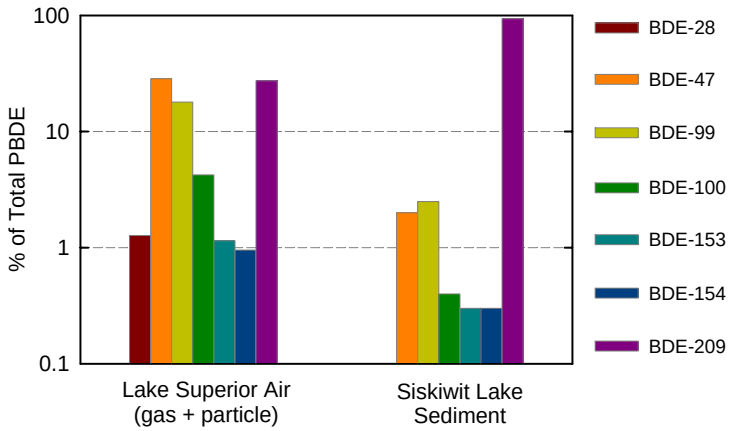

Figure 4. PBDE congener profiles in various environmental samples collected in and around Lake Superior. The air profile is from average particle and vapor phase PBDE concentrations in samples collected by IADN at Eagle Harbor, Michigan, between January and December, 2004. The Siskiwit Lake sediment sample was collected in September 2005 and analyzed in our laboratory.

Acknowledgments

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References.

Kwok ESC, Atkinson R, Arey J. 1995. Environ Sci Technol 29:1591.

Kwok ESC, Atkinson R. 1995. Atmos Environ 29:1685.

Madronich S, Flocke S. 1998. In: Handbook of Environmental Chemistry, Boule P. (ed.), Springer, Heidelberg, pp. 1-26.

Zetzsch C, Palm W-U., Krüger H-U. 2004. Organohal Compds 66:2281.

Zetzsch C. 1982. Predicting the Rate of OH-Addition to Aromatics using σ^+-Electrophilic Substituent Constants for Mono- and Polysubstituted Benzene. Proc. 15th Informal Conference on Photochemistry (Slanger, T.; Golden, D. M., eds.) pp. 29-32, Stanford, CA, USA.

Zhu LY, Hites RA. 2005. Environ Sci Technol 39:3488.