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Photolytic debromination pathway of polybrominated diphenyl ethers in hexane by sunlight

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ABSTRACT

The objective of this work is to identify the photolytic debromination pathways of polybrominated diphenyl ethers (PBDEs). Thirteen PBDEs (BDEs 209, 208, 207, 206, 196, 183, 154, 153, 100, 99, 85, 47 and 28) in hexane were individually exposed to sunlight for up to 64 h. A total of 180 PBDEs were screened and 74 BDE debromination products were detected. The disappearance rate constant increased exponentially with increasing number of bromines. While no evident difference in debromination preference among *ortho*, *meta* and *para* bromines was found for heavier congeners, the vulnerability rank order was *meta* $\geq$ *ortho* $>$ *para* for the lighter congeners ($\leq$8 Br). The total molar mass of PBDEs continuously decreased during sunlight exposure, indicating PBDEs were transformed to non-PBDE compounds. A stochastic least squares debromination pathway model was developed to simulate the reactions and determine the yields to extend the results beyond the experimental observations.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) are subject to photolytic debromination, producing potentially more toxic and environmentally-persistent compounds. PBDE photolysis experiments have been carried out under either artificial UV light or natural sunlight on a wide variety of solid matrices, including sediment (Söderström et al., 2004; Ahn et al., 2006), house dust (Stapleton and Dodder, 2008), silica gel, soil, sand (Söderström et al., 2004), plastics (Kajiwara et al., 2008), sodium sulfate, automobile dust (Lagalante et al., 2011), quartz glass, silica particles, and humic acid-coated silica particles (Hua et al., 2003), clay minerals, and metal oxides (Ahn et al., 2006), and in solvents such as hexane (Watanabe and Tatsukawa, 1987; Bezares-Cruz et al., 2004; Fang et al., 2008), toluene (Hagberg et al., 2006; Davis and Stapleton, 2009), isooctane (Zeng et al., 2010), tetrahydrofuran (Davis and Stapleton, 2009), methanol (Christiansson et al., 2009; Davis and Stapleton, 2009), water (Sánchez-Prado et al., 2006), water–organic solvent mixtures (Eriksson et al., 2004; Mas et al., 2008; Christiansson et al., 2009) and nonionic surfactant solutions (Li et al., 2008). During photolysis, stepwise debromination typically follows first order kinetics, and the reaction rate depends strongly on the bromination level of the reactant PBDE congener and the properties of the matrices.

By comparing their findings with those in previous studies, Ahn et al. (2006) concluded that the sorbent matrix had little to no effect on the debromination products. Davis and Stapleton (2009) observed that the photodegradation pathways of nonaBDEs were consistent among the different solvent matrices tested. The similarity in product formation may be extended beyond photolysis to other reactions of PBDEs. For example, the same set of brominated congeners were produced from both photolytic and anaerobic microbial debromination of octaBDEs (Zeng et al., 2010).

Debromination pathway is defined here as the bromine substitution patterns of the products which are most likely to form during a sequential debromination of a PBDE congener. As debromination reactions involve the breakage of a C–Br bond, the molecular stability is ultimately determined by the weakest C–Br bond. The observed similarity in debromination pathways has led to modeling efforts aimed at describing the pathway using quantum structural descriptors (Zeng et al., 2008, 2010). However, experimental data are still limited, hindering model development and validation, as well as a deeper understanding of reaction mechanisms and quantification of uncertainty. Stochastic models have proven to be powerful tools in the identification and prediction of reaction pathways. Bzdusek et al. (2006) developed

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and applied a least squares model for the dechlorination of polychlorinated biphenyls (PCBs). To our knowledge, such approaches have yet to be adopted to elucidate the debromination pathways of PBDEs.

In this study, photolytic debromination of 13 PBDE congeners in hexane was investigated. The primary goal was to determine the debromination pathway and identify the bromine substitution characteristics which are related to debromination stability. Using our previously published retention time database of 180 PBDE chemical standards (Wei et al., 2010a), substantially more PBDE products were confidently identified in this study than in previously published studies. Data analysis was conducted utilizing an approach based on homolog dominance of reactant (mother) and product (daughter) congeners and the variation with time of the molar fractions of bromines at *ortho*, *meta* and *para* positions. A debromination pathway model was developed based on least squares principles to simulate debromination and to extend more broadly the results of the experimental findings.

2. Materials and methods

2.1. Materials

A total of 180 neat PBDE congeners were provided by AccuStandard (New Haven, CT). For the sunlight exposure experiments, 13 individual PBDE congeners were purchased from Cambridge Isotope Laboratories (Andover, MA), including BDEs 209, 208, 207, 206, 196, 183, 154, 153, 100, 99, 85, 47 and 28. The purities of all PBDE standards were higher than 98%. A mixture of 39 PBDEs (EO5113), decabromobiphenyl (BB209) and ^{13}C-labeled decachlorobiphenyl (CB209L) were also purchased from Cambridge Isotope Laboratories. The bromine substitutions of all PBDEs involved in this paper are summarized in Supplementary Data Table S1.

2.2. Experimental

The sunlight irradiation experiments were performed on selected days of clear skies in August and September of 2008 on the roof of the School of Public Health West building at University of Illinois at Chicago (41.8685, −87.6788), approximately 4 km from a weather monitoring station in Chicago, where hourly solar radiation data were available (Table S2). BDEs 209, 208, 207, 206, 196, 183, 154, 153, 100, 99, 85, 47 and 28 were reacted individually with the following initial concentrations: 60 ng/mL for BDE209, 20 ng/mL for nona-BDEs, 10 ng/mL for BDE196, and 9 ng/mL for lower brominated congeners. For each mother congener, a series of 1 mL solutions were placed into 2 mL screw-capped clear Pyrex® glass vials and exposed to sunlight (Table S2). At pre-selected time intervals (10, 20, 30 min, and 1, 2, 4, 8, 16, 32, 64 h), one of the vials for each congener was removed from sunlight, and CB209L and BB209 were added as internal standards.

Analyses of PBDEs were performed on an Agilent 6890 gas chromatograph (GC) coupled with 5973 electron capture negative chemical ionization mass spectrometer (ECNI-MS) detector. An Rtx-1614 capillary column (30 m × 0.25 mm i.d., 0.1 μm film thickness; Restek Corporation) was used with helium as the carrier gas. Each sample was introduced into GC/MS through a programmable temperature vaporization (PTV) large volume injection port. A total of 60 μL was injected in each run, with three injections of 20 μL each at 10 s intervals. The temperature program for the PTV inlet was from 40 °C holding for 1.5 min, followed by a ramp to 300 °C at 600 °C/min. The vent flow was 100 mL/min until 1.4 min. The purge flow was 50 mL/min from 2.75 min until 10 min. The initial oven temperature was 90 °C for 3 min, and then increased to 200 °C at 10 °C/min and further to 300 °C at 2 °C/min. The final temperature was kept for 15 min until the run was completed. The MS ion source, quadrupole and interface temperatures were 200, 106, and 280 °C, respectively. Methane was used as moderating gas. The MS was operated in selected ion monitoring (SIM) mode with *m/z* 486.6 and 488.6 for BDE209, 79 and 81 for PBDEs and BB209, and 510 and 512 for PCB209L. GC/MS parameters with PTV large volume injection were optimized for PBDEs in our previous study (Wei et al., 2010b).

The identification of PBDE debromination products was based on matching of retention times, and assisted with our previously developed relative retention times of 180 PBDE congeners (Wei et al., 2010a). The retention time shifts of individual congeners were within ±0.05 min. Instrumental blanks of hexane were injected to ensure that the analytical system was free of PBDEs. Each PBDE standard solution was stored in a frigerator at 4 °C in darkness before sunlight exposure. Duplicate analyses were made for samples of BDEs 99, 100, 153, 154, and 183 at 64 h exposure time. The mean relative percent difference (RPD) was 15% and the median was 9% ($N = 84$).

2.3. Debromination pathway model

A PBDE debromination pathway model was developed based on the same idea of the dechlorination model for PCBs (Bzdusek et al., 2006) to examine whether model predicted sequences of reactions could explain the observed PBDE congener profiles. Unlike the model of Zeng et al. (2008) which predicts rate constants from estimated enthalpy of formation, the debromination pathway model is not a kinetic model. No *a priori* knowledge of the thermodynamic or kinetic properties of the reaction is needed to elucidate the reaction pathway. The model uses a stochastic chain algorithm to find the best fitted target profile. A hypothetical debromination scheme, which is the totality of all possible one-step debromination reactions, was set up and imported into the model. From a statistical point of view, this debromination scheme provides a space of all possible events. Starting from the bromine substitution pattern of the input profile (mother profile), the model follows the scheme to generate an altered profile (daughter profile). The objective is to minimize S, the sum of squares of differences between the experimentally obtained target profile x_j and an altered profile $\hat{x}_j$:

$$S = \sum_{j=1}^{m} \left(\hat{x}_j - x_j\right)^2 \tag{1}$$

where x_j or $\hat{x}_j$ are the molar concentrations of congener j, and m is the total number of congeners considered. A total of 1000 random sequences of relevant debromination reactions were evaluated. This number of sequences was sufficiently high to make the results independent of the reaction sequence. In a given sequence of reactions, the first debromination reaction was repeated until a minimum of S was achieved, then subsequent debromination reactions were evaluated in the same way, until all reactions had taken place. Each reaction sequence was repeated five times to assure that all possible congeners were present and that S was minimized. The average yield is then determined, which is the number of repeats for each debromination reaction, and the average congener profile $\hat{x}_j$ was then generated based on the 1000 sequences.

3. Results and discussion

3.1. Disappearance kinetics of mother congeners

The concentrations of all mother PBDE congeners decreased exponentially over time. The first order rate constant of mother congener disappearance was obtained from the slopes of the plots of ln (C/C_0) versus exposure time (Fig. S1), where C is the concentration at a given exposure time, and C_0 is the initial concentration. The reaction rate constants presented in Fig. 1 should be taken with caution because they are dependent of incident solar irradiation, temperature, and possibly other factors that were not controllable during this experiment.

As expected, the congeners with a higher degree of bromination generally had higher first order removal rates, in agreement with the findings of other studies (Bezares-Cruz et al., 2004; Eriksson et al., 2004; Mas et al., 2008). In addition, the rate constant increased in an exponential manner with the

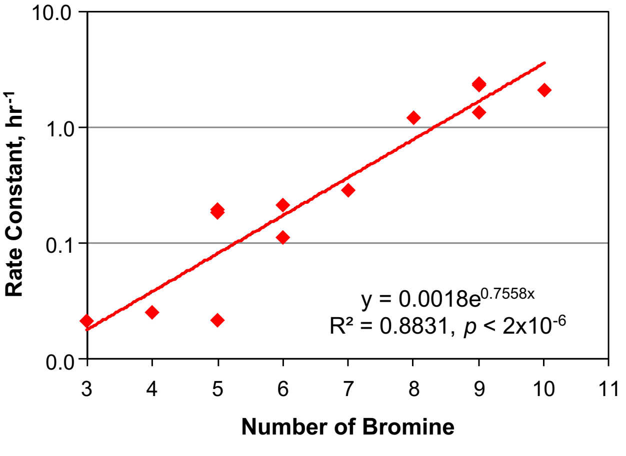

Fig. 1. Dependence of debromination rate constant on the number of bromines in the PBDE molecule.