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Stable carbon isotope analysis ($\delta^{13}C$ values) of polybrominated diphenyl ethers and their UV-transformation products

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ABSTRACT

Polybrominated diphenyl ethers (PBDEs) are frequently detected in food and environmental samples. We used compound specific isotope analysis to determine the $\delta^{13}C$ values of individual PBDEs in two technical mixtures. Within the same technical product (DE-71 or DE-79), BDE congeners were the more depleted in ^{13}C the higher brominated they were. In contrast, the products of light-induced hydrodebromination of BDE 47 and technical DE-79 were more enriched in ^{13}C because of more stable bonds between ^{13}C and bromine. As a result, the $\delta^{13}C$ values of the irradiated solution progressed diametrically compared to those of the technical synthesis. The ratio of the $\delta^{13}C$ values of BDE 47 to BDE 99 and of BDE 99 to BDE 153 are thus suggested as indicators to distinguish native technical products from transformation products. Ratios <1 are typical for native congeners (e.g. in DE-71) while the reversed ratio (>1) is typical of transformation products.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) have been heavily used as additive flame retardants in fire prevention for decades. Major applications include plastics, furniture, cars and electronics (de Boer et al., 2000; WHO, 1994). PBDE products were sold as three different technical mixtures based on their average bromine content, i.e. technical pentaBDE (TPBDE; 50–60% pentaBDE congeners; typical product: DE-71, U.S.A.), technical octaBDE (TOBDE; 31–35% octaBDE congeners, typical product: DE-79, U.S.A.) and technical decaBDE (TDBDE; ~97% decaBDE, typical product: DE-83, U.S.A.). Theoretically, there are 209 different PBDE congeners, but technical BDE products each contain only about 10 congeners (La Guardia et al., 2006). The highest demand for technical mixtures in the global market existed for TDBDE (54,800 t or >80% of the PBDE production in 1999), followed by TOBDE and TPBDE (de Wit, 2002). While industrial useful, PBDEs were found to be detrimental to the environment. Additive flame retardants such as PBDEs can leach out from the products as verified by their detection in different environmental compartments (de Wit, 2002), and thus TPBDE and TOBDE were classified as persistent organic pollutants (POPs). As a result of these environmental concerns, TPBDE and TOBDE were banned in the European Union in 2003 (Cox and Efthymiou, 2003). Since 2006, these products were also prohibited in several states in the U.S. (U.S. Environmental protection agency website, 2006).

The most frequently detected PBDE congeners in the environment are tri- to hexabrominated, which are the constituents of TPBDE and, to a lesser degree, of TOBDE (de Wit, 2002). This observation is surprising, as one would expect to more frequently detect constituents of TDBDE based on the volumes of industrial consumption. Hence, it was argued that significant amounts of the lower brominated PBDE congeners in the environment may have been formed from higher-brominated congeners by biotic or abiotic hydrodebromination (Christiansson et al., 2009). Research confirmed that transformation of TOBDE and TDBDE by UV light and bacteria can lead to BDE 47, BDE 99, and BDE 100, the predominant congeners found in TPBDE (Christiansson et al., 2009; Gaul et al., 2006). Understanding the environmental fate of PBDEs requires the experimental verification of the origins of these compounds. In the case of PBDEs, it must be distinguished whether a specific PBDE congener in a sample is (i) an accumulated contaminant or (ii) the product of the hydrodebromination of higher-brominated congeners. Such issues can be studied by compound specific isotope analysis (CSIA) using gas chromatography in combination with isotope ratio mass spectrometry (GC-IRMS) (Merritt et al., 1995; Schmidt et al., 2004). Stable carbon isotope analysis is based on the determination of the $^{13}C/^{12}C$ ratio of

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the CO_2 obtained from the sample relative to the CO_2 obtained from a reference standard. The result of the measurement is expressed in δ values in per mil. Due to the higher binding energies and/or lower mobility of heavier isotopes (here ^{13}C) different physical, chemical, and biochemical reactions may lead to a minute, yet measurable discrimination of the heavy isotope (Mook, 2000). Since the reference standard, a standardized carbonate (V_{PDB}), is among the substances with the highest $^{13}C/^{12}C$ ratio, the $\delta^{13}C$ values of virtually all polyhalogenated POPs are negative and typically in the range −20 to −30‰ (Vetter, 2011). However, individual compounds and congeners of a particular compound class may be composed of slightly different $\delta^{13}C$ (Melander and Saunders, 1980; Mook, 2000; Vetter et al., 2006).

CSIA is a powerful complement to conventional concentration analysis in fate studies (Reddy et al., 2000; Holmstrand et al., 2010). To date, only scattered data on $\delta^{13}C$ values for POPs are available, e.g. for polychlorinated biphenyls (PCBs) (Drenzek et al., 2001; Horii et al., 2005), polychlorinated naphthalenes (PCNs) (Horii et al., 2005), chlorinated solvents (Ertl et al., 1996; Beneteau et al., 1999), DDT (Reddy et al., 2002), toxaphene (Vetter et al., 2005), hexachlorocyclohexanes (HCHs) (Badea et al., 2009), polychlorinated dibenzo-*p*-dioxins (Horii et al., 2008; Liu et al., 2010), and PBDEs (Vetter et al., 2008). Occasionally, these studies pointed out changes in the carbon isotope composition during transformation reaction as for example degradation or enzymatic chlorination (Drenzek et al., 2001). Thus far, CSIA studies on PBDEs were only performed with standard reference compounds (Vetter et al., 2008), and $\delta^{13}C$ values of PBDEs in degraded samples were not available.

In this study, we first determined the $\delta^{13}C$ values of synthesized pure PBDE standards and technical mixtures. Then, we determined the $\delta^{13}C$ values of PBDE congeners in solutions treated by simulated sunlight that initiated hydrodebromination. We then studied the $\delta^{13}C$ values of the PBDE congeners in the irradiation products in order to find indications for changes in the $\delta^{13}C$ values during photochemical transformation and possibly further environmental degradation processes.

2. Materials and methods

2.1. Chemicals and standards

Analyses of technical pentabromodiphenyl ether (DE-71) and technical octa bromodiphenyl ether (DE-79), both from Great Lakes Chemical Corporation (Indianapolis, IN), were carried out using solutions of 0.52 g/L and 1.09 g/L in *iso*-octane, respectively. Solutions of irradiated DE-79 were produced according to Bendig and Vetter (2010). BDE 47 was synthesized in our lab according to published procedures (Vetter and Jun, 2003) while BDE 15 was purchased from Alfa Aesar (Karlsruhe, Germany). Methanol (HPLC grade) was from Fisher Scientific (Leicestershire, Great Britain) and *iso*-octane (SupraSolv, for gas chromatography) was from Merck (Darmstadt, Germany). The internal standard 2,3-dibromopropyl-2,4,6-tribromophenyl ether (DPTE) was synthesized as described elsewhere (von der Recke and Vetter, 2007).

2.2. Gas chromatography coupled with isotope ratio mass spectrometry (GC-IRMS)

CSIA measurements by GC-IRMS were based on the method described in detail elsewhere (Vetter et al., 2008). The following changes were made: the oxidation reactor temperature was set to 1000 °C. A 30 m × 0.25 mm i.d. column coated with 0.25 d_f Rxi-5Sil MS (Restek, Germany) was installed in the GC oven. The GC oven was programmed as follows: 70 °C (hold time 1.5 min), at 10 °C/min to 210 °C, at 5 °C/min to 300 °C (hold time 2 min for BDE 47 and DE-71 or 35 min for DE-79). Injector temperatures were set to 250 °C for BDE 47 irradiation solutions and to 300 °C for technical mixtures of PBDEs. Thorough reoxidation was performed after every sequence (minimum once a day) by oxygen backflush for 2 h. Short reoxidation was operated after every single run for 2–5 min. To ensure the stability of the instrument, the analytes were usually dissolved in a solution of the internal standard DPTE (0.106 g/L in *iso*-octane). The first run after thorough reoxidation was discarded. We paid attention to that the areas of the analytes between different samples and analytes were as comparable as possible. For this reason, diluted and/or concentrated samples were reanalyzed. The internal standard DPTE was used in the first and last run of a sequence in order to verify constant instrumental conditions. $\delta^{13}C$ values were expressed in per mil (‰) relative to international reference standards distributed by the International Atomic Energy Agency (IAEA, Vienna, Austria). The $\delta^{13}C$ value is defined as:

$$\delta^{13}C = \left(\left(R_{\text{sample}}/R_{\text{reference}}\right) - 1\right) \times 1000(‰) \tag{1}$$

where R_{sample} and $R_{\text{reference}}$ are the $^{13}C/^{12}C$ ratios of the sample and an international reference standard material, respectively. Samples with negative $\delta^{13}C$ values are depleted in ^{13}C compared to the international reference standard.

The observed isotope fractionation due to the preferential cleavage of bonds involving the lighter carbon isotope can be derived by means of the Rayleigh equation (Mariotti et al., 1981; Hirschorn et al., 2007):

$$R/R_0 = f^{(\alpha-1)} \tag{2}$$

where α is the fractionation factor, f is the fraction of compound remaining, R_0 is the initial isotopic ratio and R is the isotopic ratio of the compound after transformation process.

Plotting ln(f) vs. ln(R/R_0) results in straight lines and the slope (m) of the linear regression enables to determine the fractionation factor α experimentally with $m = (\alpha - 1)$ (see below). The isotopic enrichment factor ε is defined as follows:

$$\varepsilon = 1000(\alpha - 1)[‰] \tag{3}$$

The uncertainty of ε was based on the 95% confidence interval derived from isotope measurements at different points in time. For the final calculations the mean of the individual uncertainties were used. Apparent kinetic isotope effects (AKIE) were calculated according to Elsner et al. (2005):

$$\text{AKIE}_E = \frac{1}{1 + z \times \frac{n}{x} \times \varepsilon_{\text{bulk}}/1000} \tag{4}$$

where n is the number of the atoms of the element considered of which x are located at the reactive site and z the number of chemically equivalent reactive positions that compete for reaction (Elsner et al., 2005; VanStone et al., 2008). The AKIE value was calculated for the remaining BDE 47 in the UV-irradiated solution and therefore $n = 12$, $x = 1$ and $z = 2$.

The isotope balance ($\delta^{13}C_{\text{total}}$) (Eq. (5)) of the total PBDEs during dehalogenation reaction was calculated according to Stelzer et al. (2009):

$$\delta^{13}C_{\text{total}} = \frac{\sum\left(C_i \times \delta^{13}C_i\right)}{C_{\text{total}}} \tag{5}$$

with C_i being the molar fraction of each compound and the respective carbon isotope signature ($\delta^{13}C_i$). The uncertainty ($\Delta_{\text{tot}}\delta^{13}C_{\text{total}}$) (Eq. (6)) of the isotope balance was calculated by means of equation (6) (Stelzer et al., 2009). The calculation incorporates the standard deviation of the isotope measurements ($\Delta\delta^{13}C_i$) and a correction of the accuracy for the concentration analysis of 10% ($\Delta C_i = 0.1 \times C_i$).

$$\Delta_{\text{tot}}\delta^{13}C_{\text{total}} = \frac{\sqrt{\sum\left(C_i \times \Delta\delta^{13}C_i\right)^2 + \sum\left(\left[\delta^{13}C_i - \delta^{13}C_{\text{total}}\right] \times \Delta C_i\right)^2}}{C_{\text{total}}} \tag{6}$$

Optimum sample amounts in current CSIA systems have been described to be 30–70 ng carbon per compound (Vetter et al., 2008). Taken into account the different degree of bromination of the PBDEs studied (di- to octaBDE), we attempted to inject ∼70–100 ng of individual PBDE congener for appropriate CSIA measurements. All samples were analyzed, if possible, in quintuplicates. Nalimov outliers were eliminated (level of significance 5%).

2.3. Gas chromatography coupled with electron ionization mass spectrometry (GC/EI-MS)

Analyses were performed with a CP-3800/1200 GC–MS System (Varian, Darmstadt, Germany) operated in EI-full scan mode (m/z 30–800). The injector and transfer line temperature was set to 250 °C and 280 °C, respectively. Ion source conditions were 200 °C and 70 eV. A 30 m × 0.25 mm i.d. column coated with 0.25 d_f HP-5ms (J&W Scientific, Agilent, Waldbronn, Germany) was installed in the GC oven. The oven program was the same as used for GC-IRMS analyses.

2.4. UV-irradiation experiments

Irradiation experiments were performed in methanol according to Bendig and Vetter (2010). BDE standard solutions (1 mL) were filled into quartz glass cuvettes (0.5 cm path length, Zeiss, Jena, Germany) which were then placed in cylindrical quartz beakers (60 mm high, 30 mm diameter) capped with a Teflon stopper. The beakers were surrounded by flowing water of 20 °C (Bendig and Vetter, 2010). The solutions were irradiated with a sunlight simulator (SOL 500, 400 W, Hönle,