PHOTOCHEMISTRY OF 2,2',4,4',5,5'-HEXABDE (BDE-153) IN THF AND ADSORBED ON SiO2: FIRST OBSERVATION OF OH REACTIVITY OF BDEs ON AEROSOL

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Introduction

BDE-153 (2,2',4,4',5,5'-hexabromo diphenylether) is a component of the flame retardant mixtures penta- and octaBDE and a trace constituent of decaBDE[1-3]. Furthermore, it may occur as a minor intermediate in the photolysis of decaBDE. We have previously studied the UV spectrum and quantum yield for the photolysis of BDE-153 in tetrahydrofuran (THF) solution[3], and we now present a comparison of the photolytic degradation pathways of this symmetrical molecule in solution and adsorbed at sub-monlayer thickness on aerosol particles, made of fused silica (Aerosil 380), in an aerosol smog chamber facility[4]. Furthermore, the aerosol smog chamber technique allows us to expose aerosol-borne compounds to OH radicals, which are known to clean the atmosphere efficiently from air pollutants. Atmospheric residence times of air pollutants can then be assessed from the rate constants for the reaction with OH radicals[5], and a first, preliminary result on BDE-153 + OH will be presented.

Methods and Materials

Irradiations of BDE-153 (Albemarle) in THF were performed at room temperature, employing a filtered Xe lamp (Osram XBO, 1000 W) and irradiating 1 cm quartz cuvettes on an optical bench at a distance of 70 cm from the lamp housing[6], or by an array of 8 fluorescent lamps (Philips TL-12, 40 W) irradiating the quartz cuvette at a distance of 1.5 m. The emission spectrum of the Xe lamp was filtered to wavelengths greater than 280 nm, the TL-12 lamps have a cut-off around 270 nm. The larger UV intensity of these light sources (as compared to sunlight, > 300nm) enables us to achieve photolysis of hexaBDE down to almost complete debromination within about an hour. Irradiations of the coated aerosol particles and their exposure to OH radicals were performed in an aerosol smog chamber facility, described elsewhere in detail[4,7], that has been modified as follows[8]: The height of the glass cylinder (inner diameter 1 m) has been reduced to 2 m, and it is situated in a thermostated styrofoam box, where it is cooled to 7 °C. It is irradiated by the 8 Philips TL-12 lamps from the top, using Teflon film (FEP 200A) as window material. A sub-monolayer coating of BDE-153 on fused silica particles is prepared by mixing 1 g of Aerosil 380 (7 nm primary particle diameter, specific surface: 380 m^2/g according to DEGUSSA company) with a solution of 10 mg of

BDE-153 in toluene and removing the solvent in a rotary evaporator. A portion of 80 mg of this powder is mixed by an Ultra-Turrax stirrer with 80 ml of distilled water to produce a suspension.

An aerosol chamber experiment starts by feeding 40 ml of this suspension by a motor driven syringe to a nozzle, where it is atomized by preheated air to produce an aerosol in order to fill the smog chamber. The droplets dry out to particle aggregates of about 0.3 µm average diameter in a Liebig cooler and enter the chamber, where mass densities around 1 mg/m^3 can be reached at relative humidities around 50% at the temperature of 7 °C. Aerosol samples ranging from 30 to 160 liters are taken on Teflon filters (Sartorius SM11807) before and during the experiment at approximately hourly intervals at a sampling flow rate of 7 l/min (replenishing the chamber continuously by purified air). The mass of every second aerosol sample is determined on a microbalance (Sartorius SC2) after neutralizing excess charge of the filters by a beta radiation source (^{85}Kr). Exposure of the coated aerosol particles to OH radicals is performed in darkness by injecting ozone (6 ppm) that reacts with hydrazine from a flow of air (300 ml/min), saturated at 5 °C, to form OH. The OH radicals are monitored by their reaction with hydrocarbon traces (benzene, n-hexane and 2,2-dimethylbutane), employing perfluorohexane as inert standard, where samples of 20 ml are preconcentrated at hourly or half-hourly intervals in a glass-lined steel capillary at ~100 K and analyzed by GC on an Al$_2$O$_3$ PLOT column (Chrompack)[9]. Analysis of the products from the Xe lamp irradiation was performed by HPLC-DAD and detecting at 230 nm, analysis of the TL-12 irradiations and aerosol smog chamber runs was performed by GC (8 m CP Sil 5 CB, Chrompack) and ECD detection. The aerosol samples, taken on Teflon filters, are extracted by 1 ml of toluene in sample vials in an ultrasonic bath and, after sedimentation of the particles by a centrifuge, likewise analyzed by on-column injection of 5 µl of the extracts each.

Results and Discussion

Time profiles of BDEs during photolysis of 2,2',4,4',5,5'-hexaBDE in THF by the Xe light source (λ >280 nm) are shown in fig. 1. The photolysis proceeds by progressive loss of bromine atoms from the single hexaBDE congener to a mono-brominated congener. The assignment of the various brominated BDEs was performed using the kinetic behaviour and the HPLC retention times listed in fig. 1, which decrease systematically with the loss of Br substituents. The mass balance of the BDEs appears to be poorer than for similar photolysis experiments on 2,2',4,4'-tetraBDE[3]. The slightly increasing mass balance for the initial phase may be caused by errors in molar absorption coefficients (which had been estimated by an interpolation of band strengths between the available 4-monoBDE, 4,4'-diBDE, 2,2',4,4'-tetraBDE, BDE-153 and decaBDE)[3], and this might be the influence of the absorption cross sections of the pentaBDEs, which appear to have higher absorption coefficients than the average. No brominated dibenzofurans were detected in the photolysis of BDE-153 in THF. The assignment of the pentaBDEs, tetraBDEs, triBDEs, diBDEs and monoBDEs is much less certain (only two of the expected three pentaBDEs are separated by HPLC) than with the photolysis of 2,2',4,4'-tetraBDE, and the final mass balance can be expected to be influenced by a lack of detection of the many minor tetra-, tri- and diBDEs expected.
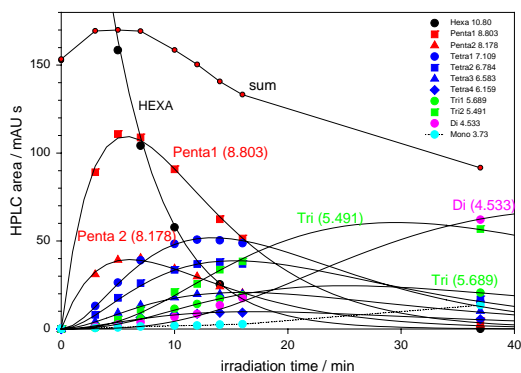
Fig. 1: HPLC areas of products found in the photolysis of 2,2',4,4',5,5'-hexaBDE (THF, c = 27.8 mg/l) using a Xe light source (λ>280 nm). Lines shown are results from a model calculation[3]. Values in parentheses are the corresponding retention times of the products. The areas found for the monoBDE (dotted line) were too low to be used in the model. For clarity, the first three data points for hexaBDE (where an exponential decrease occurs as well) are not shown.

Chromatograms observed in an analysis of the products by GC from a similar photolysis in THF are displayed in figure 2, where the three pentaBDEs can be assigned to fairly equal yields of BDE-101 (2,2',4,5,5'-pentaBDE) and BDE-118 (2,3',4,4'5-penta BDE) and a slightly larger yield of BDE-99 (2,2',4,4',5-pentaBDE). This pattern looks different from environemental monitoring studies, where BDE-18 is not among the major entaBDEs. The assignment of these BDEs has recently been confirmed from their expected retention times[10]; those of the lower BDEs are uncertain because of the insufficient resolution and large number of possible congeners, where BDE-47 (2,2',4,4'-tetraBDE) may be among the products from the degradation of BDE-99. A quite different product distribution is observed for photolysis of a monolayer of BDE-153 on fused silica aerosol (1% BDE-153 by weight of Aerosil 380), where chromatograms of extracts from aerosol samples (30 – 160 l, increasing with time of the experiment in order to account for the deposition of particles, that occurred at a decay rate of 0.147 h^{-1} in this run) are displayed in figure 3.

Although the distribution of the three pentaBDEs looks quite similar to those of figure 2, the distribution of the peaks with shorter retention time is completely different, and no assignment should be attempted from the retention times alone without any other identification methods or authentic calibration standards. In the heterogeneous system the combined yield of the three pentaBDEs is about 10% of the initial hexaBDE only. Surprisingly, no typical tetraBDEs are identified as intermediates from the photolysis of the pentaBDEs (the large peak in the region of the tetraBDEs is mirex, that is present as a standard on the aerosol), except a single, stable compound at 17 min retention time. The same compound (though at much lower yield) was observed in THF solution.
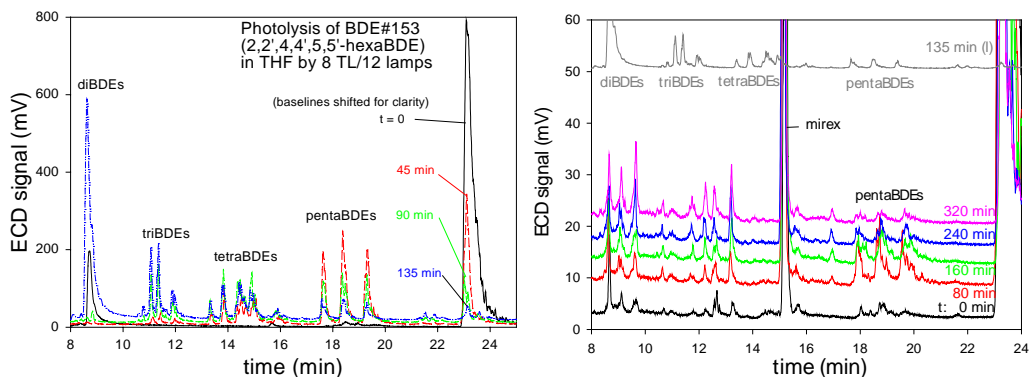
Fig. 2 (left): Gas chromatograms from a homogeneous-phase photolysis of BDE-153, dissolved in THF (0.88 mg/l), by fluorescent lamps (Philips TL-12). All three possible pentaBDEs are formed as intermediates, and more tetra- and triBDEs can be distinguished by GC analysis than by HPLC as well. The diBDE appears to be a different congener than the impurity of the BDE-153 sample.
Fig. 3 (right): A comparison of BDEs derived from photolysis of aerosol-borne 2,2',4,4',5,5'-hexaBDE (coated in sub-monolayer thickness on SiO_2 particles, Aerosil 380) by 8 TL-12 lamps at irradiation times ranging from 80 to 320 min in comparison with photolysis of a solution of the same substance in THF by the same lamps for 135 min. It is quite clear from these chromatograms that the product distribution from photolysis in heterogeneous systems differs from homogeneous systems.

It should be noted that the occurrence of OH radicals (which might be produced by the irradiation) was checked in these aerosol chamber experiments and was found to be below 2×10^6 cm^{-3} and that a significant production of hydroxylated or oxygenated compounds by OH radicals is unlikely under these conditions.

Time profiles of aerosol-borne BDE-153 in various heterogeneous systems, in darkness (as blank), under UV irradiation (including the lumped pentaBDEs from the irradiation) and in the presence of OH radicals are shown in fig. 4 in comparison to those in the homogeneous system. Remarkable is the much larger yield of penta-, tetra- and triBDEs (which are even not corrected for the approximately linear increase of the ECD response with the number of bromine substituents) and the more rapid photolysis (by a factor of three) in the homogeneous system. This retardation of the photolysis and lower yield of debromination products in heterogeneous systems is in accord with similar observations on decaBDE[3, 11-13].

Finally, we investigated the degradation of aerosol-borne 2,2',4,4',5,5'-hexaBDE by OH radicals in a dark experiment, producing OH from the reaction of hydrazine with ozone. A considerable and definitely significant consumption of the hexaBDE was observed during exposure to OH levels of 1.8×10^7 cm^{-3}, causing a decrease of hexaBDE to 50% of the initial value within 6 h. Figure 4 includes the time profile of the hexaBDE of this first OH exposure in comparison with a blank run in the absence of OH (that was derived from an experiment on the adherence of the commercial octaBDE mixture DE-79, containing BDE-153).

Although a variation of the OH level in such experiments is required to demonstrate a linear dependence of the decay rates on OH level and to perform a determination with a reasonable precision, a preliminary value of $k_{OH}=1.8 \times 10^{-12}$ cm^3 s^{-1} can be obtained for the rate constant from this single run (with an uncertainty of about ±50%). Another important point is that a detection of degradation products, such as hydroxylated compounds, is required for a proof of the reaction with OH, and that no products (which are expected to be phenolic) were traceable by our non-polar column in the chromatograms. Another trace constituent of the samples (possibly a hexaBDE) at shorter retention time turned out to be less reactive, another one at longer retention time (possibly a heptaBDE) was even more reactive than BDE-153.
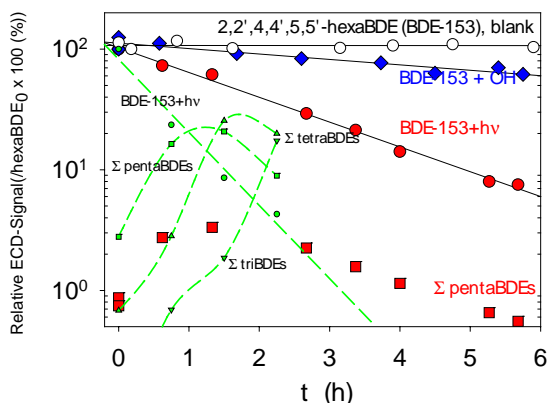

Fig. 4: Comparison of time profiles of BDE-153 and yields of the lumped pentaBDEs (squares) from aerosol chamber experiments (large symbols) and in THF solution (small symbols, dashed lines). Note the poor mass balance < 10 % pentaBDEs of the aerosol experiment and the more rapid photolysis and much larger yield of penta-, tetra- and triBDEs in THF solution. Also included is a blank experiment in darkness and an experiment in the presence of OH radicals, causing a significant consumption of BDE-153 (diamonds).

On the other hand, this preliminary value of the OH reactivity of 2,2',4,4',5,5'-hexaBDE would be almost an order of magnitude larger than an estimated value of $k_{OH}= 0.2317 \times 10^{-12}$ cm^3 s^{-1}, that is obtained from current structure/reactivity relations employing the Hammett-equation[14-16] and the electrophilic substituent constants of Brown and Okamoto[16]. Assuming an annual average atmospheric level of OH of 10^6 cm^{-3} as global seasonal mean value, the half-life of BDE-153 is estimated to be less than 5 days (in contrast to a value of the half-life exceeding one month, derived from the estimated value). It thus appears that structure/reactivity relations need to be developed for brominated aromatics. One might discuss an influence of the adsorption on reactivity (as seen here on photolysis), and it should be mentioned that reactions of OH radicals with aromatics in solution are generally faster than in the gas phase.

Photolysis of BDE-153 may be fairly efficient: comparing the overlaps of its UV absorption spectrum in THF with the intensity of natural sunlight and with the intensity of the Xe light source delivers a half-life of a few hours (assuming that the quantum yield is independent of wavelength

and medium). A similar consideration for the aerosol-borne photolysis then yields a half-life of less than 1 day for BDE-153 on UV-transparent atmospheric particles (dependent on season and latitude, given here for June at 50° latitude).

In summary, photolysis can be a major abiotic degradation pathway of BDE-153, if accessible to sunlight. The photolysis of BDE-153 in THF leads to successive debromination. Photolysis of BDE-153 as coating on fused silica particles delivers different degradation products, and removal of particle-borne BDE-153 by OH radicals appears to be surprisingly efficient.

Acknowledgements

References
1 WHO (1994) Brominated diphenyl ethers, Environmental Health Criteria Series EHC 162, World Health Organization, Geneva.
2 Sjödin A., Jakobsson, E., Kierkegaard, A., Marsh G., Sellström, U. (1998) J. Chrom. A 822, 83.
3 Palm , W.-U., Kopetzky, R., Sossinka, W., Krüger, H.-U., Liu, Q., Barcellos da Rosa, M., Thomas, S., Zetzsch C. (2003) UV spectra, photolysis and photochemistry of poly-brominated diphenyl ethers in organic solvents and adsorbed on particles. Final report to BSEF, Fraunhofer-Institute ITEM, Hannover.
4 Behnke, W., Holländer, W., Koch, W., Nolting, F., Zetzsch, C. (1988) Atmos. Environ. 22, 1113.
5 Kwok, E.S.C., Atkinson, R., Arey, J. (1995) Environ. Sci. Technol. 29, 1591.
6 Palm, W.-U., Kopetzky, R., Ruck, W. (2003) J. Photochem. Photobiol. A 156, 105.
7 Palm, W.-U., Elend, M., Krüger, H.-U., Zetzsch, C. (1997) Environ. Sci. Technol. 31, 3389.
8 Krüger, H.-U., Zetzsch, C. (2003) Exploratory study of the adherence, photolysis and OH reactivity of aerosol-borne decaBDE and lower BDEs, final report to BSEF, University of Bayreuth.
9 Nolting, F., Behnke, W., Zetzsch, C. (1988) J. Atmos. Chem. 6, 47.
10 Rayne, S., Ikonomou, M.G. (2003) J. Chromatogr. A 1016, 235.
11 Söderström, G., Sellström, U., de Wit, C., Tysklind, M. (2004) Environ. Sci. Technol. 38, 127.
12 Watanabe, I. (2002) Proc. 11 th Conf. of Environ. Chemistry, Japan Soc. of Environ. Chem., Tokyo, pp. 121-2, see: Watanabe, I., Sakai, S. (2003) Environ. Internat. 29, 665.
13 Hua, I., Kang, N., Jafvert, C. T. and Fabrega-Duque, J. R. (2003). Environ. Toxicol. Chem. 22, 798; Jafvert, C., and Hua, I. (2001). Photochemical reactions of

decabromodiphenyl oxide and 2,2',4,4'-tetrabromodiphenyl oxide. Final report to BFRIP, Purdue University, West Lafayette, IN, USA.

14 Kwok, E.S.C., Atkinson, R.   (1995) Atmos. Environ. 29, 1685; Atmospheric Oxidation Program, Syracuse Research Corp., http://www.syrres.com/esc/aop.htm.

15 Zetzsch, C. (1982) Proc. XVth Informal Conf. on Photochemistry (T. Slanger, D.M. Golden, eds.), pp. 29-32, Stanford, CA, USA.

16 Brown, H.C., Okamoto, Y. (1958) J. Am. Chem. Soc. 80, 4979.