PHOTOCHEMICAL REACTIONS OF BROMINATED DIPHENYLETHERS IN ORGANIC SOVENTS AND ADSORBED ON SILICON DIOXIDE IN AQUEOUS SUSPENSION

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Introduction

Polybrominated diphenylethers (BDEs) are in use as flame retardants worldwide and are found as xenobiotics in environmental samples[1-4]. Photolysis by sunlight, one of the potential abiotic degradation pathways, is found to be rapid in laboratory experiments, especially for deca-BDE, the most prominent BDE[5-7] as compared to commercial penta- and octa-BDEs. Due to the extremely low water solubility of BDEs, these experiments were mostly performed in organic solvents so far, and a few in environmental matrices (sand and soil)[6] and on dry[4] and hydrated[8] quartz glass. However, detailed UV absorption spectra of deca-BDE and debrominated BDEs in the relevant wavelength range above 300 nm have become available only recently[8], besides the UV maxima[9] of a number of synthesized congeners at shorter wavelengths and an exploratory study from our laboratory[10]. Other important parameters to assess the abiotic degradation in the environment, such as OH-rate constants and photolytic quantum yields of BDEs are not available. Furthermore, analysis of BDEs was mostly performed by GC-MS, and the capability of HPLC with a diode array detector (DAD) has not yet been exploited.

This study presents kinetic results on the photolysis of BDEs in tetrahydrofuran (THF) with detailed photolytic pathways for a tetra-BDE (2,2'4,4'-BDE), a hexa-BDE (2,2'4,4',5,5'-BDE) and deca-BDE. Employing HPLC with a diode array detector (DAD) as analytical tool, quantum yields of BDEs with N_{Br} = 1-10 are determined. Furthermore, the formation of brominated dibenzofurans (BDFs) was investigated. Since the environmental relevance of photolysis experiments in organic solvents is questionable, first results on photolysis of deca-BDE adsorbed on silicon dioxide particles, suspended in water, are presented.

Methods and Materials

UV spectra were determined by a double beam spectrometer with pre monochromator (Lambda 45, Perkin Elmer) with a resolution of 2 nm in 1 nm steps using quartz cuvettes with d=1 cm and d=5 cm at ambient temperature against the corresponding solvent as reference. A photolysis apparatus on an optical bench[11] (Amko, Tornesch, Germany) with a Xe lamp XBO 1000 (500-1000 W, Osram, Germany) was used for the photolysis. Light was focused by mirrors through a water filter (equipped with quartz windows) and an optical glass filter into a stoppered quartz cuvette (d=1 cm, irradiated area $A = 2\ cm^2$, volume $V = 3$ ml) with the corresponding solution. Xe lamp, mirrors and the water filter were cooled by tap water, cooling of the cuvette ($T = 295 \pm 1$ K) was accomplished by a thermostat. After a given irradiation time the cuvette was removed and the solution was analyzed by HPLC. Actinometric measurements were performed with iron oxalate. Details of the quantum yield measurements using a polychromatic light source can be found elsewhere[11-13].

Analysis of all compounds was performed by HPLC (Agilent 1100, quaternary pump, autosampler and DAD detector) with the following parameters: detection wavelength 230 nm; injection volume 5 µl; Eclipse column XDB C8, 5 µm (Agilent); isocratic eluent using 80% acetonitrile and 20% water; 1 ml/min flow.

Selected fractions, separated by HPLC, were analyzed by GC-MS. The eluent (acetonitrile/water=80/20) from the fraction of interest was collected at the outlet of the DAD for a given time (1-3- minutes) in a separate vial (1-3 ml). The solvent was evaporated under a flow of nitrogen at about 50 °C, and the compounds were dissolved again in pure acetonitrile and transferred to a GC vial. Fractions were investigated by GC-MS (Thermo Finnigan Trace GC) with the following parameters: column: Restek RTX5MS, injection volume: 2 µl, inlet temperature: 220 °C, transfer-line temperature: 250 °C, ion-source temperature: 200 °C, oven-temperature gradient: hold 2 min at 40 °C – increase temperature to 300 °C with 10 °C/min – hold 10 min.

Different concentrations of BDE (between 7 – 700 mg/l) and all other reference compounds and the mixtures Bromkal 70-5 DE und DE79 were prepared in glass flasks using THF as solvent and stored in the dark in the refrigerator. Deca-BDE was found to be stable in the dark at least for a period of 2 months. For photolysis experiments usually 3 ml of the corresponding BDE-solution was photolysed and analysed by HPLC directly without clean up or enrichment.

Experiments to investigate the photolysis of deca-BDE adsorbed on carrier materials in water were performed using silicon dioxide (Aerosil 380, Degussa, specific area 380 m^2/g Aerosil) as carrier material. 20-200 mg of deca-BDE were dissolved in THF and 1000 mg of Aerosil 380 added (theoretical coatings 2-17%), and the material was mixed using a high-speed stirrer (Ultra Turrax T25, Ika-Werk Germany) at 11000 rpm for 5 minutes. After removing the solvent by a rotary evaporator the coated Aerosil 380 was vacuum dried over night using an oil pump ($p = 0.05$ mbar).

For the photolysis actual coatings of deca-BDE, obtained by HPLC, in the range of 4-13 % were used. Suspensions of deca-BDE adsorbed in Aerosil 380 were prepared by weighting 50 mg of the coated Aerosil 380 in a round-bottomed flask, adding 100 ml of deionized water and dispersing by the high-speed stirrer at 11000 rpm for 5 minutes. Suspensions were always aged over night (12 hours) to remove the bigger particles by sedimentation. For the photolysis a cuvette (d=1cm) was filled with 3 ml of the always freshly prepared, aged suspension. Experiments were performed with stirred and unstirred suspensions. At a given photolysis time 100 µl of the suspension was transferred to a HPLC vial, 400 µl of THF was added, the carrier material was removed by a centrifuge (2 minutes, 2400 rpm) and the solution was analysed by HPLC. It should be noted, that the removal of Aerosil 380 particles from THF by the centrifuge is by far more efficient than from water.

Congeners and commercial mixtures of BDEs and BDFs and solvents were used as received from Aldrich, Promochem, Albemarle and Great Lakes. Silicon dioxide (Aerosil 380, specific area 380 m^2/g) was obtained from Degussa, Germany. A water purification system (Membra Pure, Germany) delivered deionized water with a resistivity of 18.4 M Ω cm.

Results and Discussion

The assignment of congeners and at least BDEs with a defined number of bromine atoms, N_{Br}, was performed from available reference compounds, from published compositions of commercial BDEs, i.e. from the mixtures Bromkal 70-5 DE and DE-79[1,14] and from the kinetic behaviour of the products in the photolysis of 2,2',4,4'-BDE, 2,2',4,4',5,5'-BDE and deca-BDE. UV-spectra observed by the DAD were normalized to the UV-spectra obtained from the UV-spectrometer using a linear regression of a corresponding set of spectra for available reference compounds. Integrals with different boundaries (220 – 340 nm) were calculated from plots of the molar absorption coefficients of the available reference compounds (diphenylether, 4-BDE, 4,4'-BDE, 2,2',4,4'-BDE, 2,2',4,4',5,5'-BDE and deca-BDE) versus wavenumber (in cm^{-1}). The best linear correlation of these integrals versus the number of bromine atoms ($\int \varepsilon d\nu \pm 2\sigma = (5 \pm 10)\cdot 10^5 + (1.1 \pm 0.2)\cdot 10^6 \cdot N_{Br}$, R=0.996) was found for the boundaries 280 – 340 nm and used as normalization factor for UV-spectra of BDEs from the DAD not available as reference compounds. UV absorption spectra, lamp intensities and a typical sunlight spectrum are shown in Figure 1.

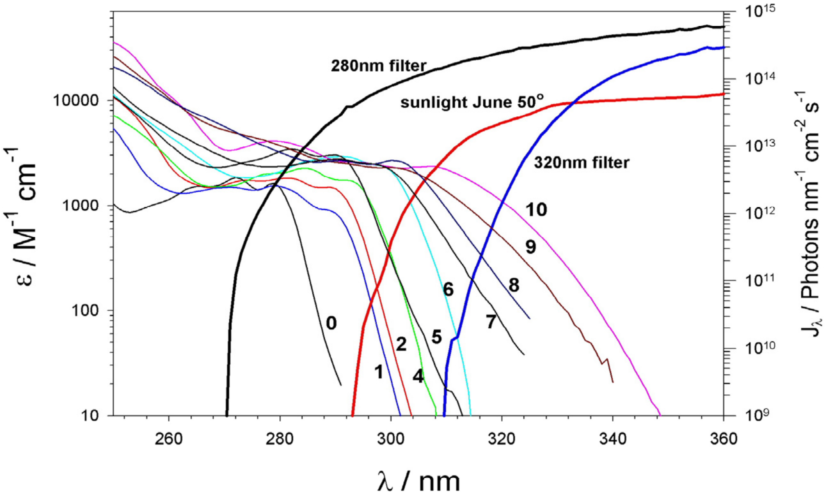

Figure 1: UV spectra of diphenyl ether and BDEs with *1, 2, 4, 6* and *10* Br atoms, as determined by UV spectroscopy. UV spectra from HPLC chromatograms are determined by DAD for *5* and *7-9* and interpolated. The labels denote N_{Br}, the number of Br atoms. *1:* 4-BDE, *2:* 4,4'-BDE, *4:* 2,2',4,4'-BDE, *5:* probably 2,2',4,4',6-BDE , *6:* 2,2',4,4',5,5'-BDE, *7, 8, 9:* most abundant hepta-BDE, octa-BDE and nona-BDE occurring during photolysis of *10:* deca-BDE. Absolute light intensities for two optical filters and sunlight intensities for Europe (June, 50° N) are also included[15].

From the investigation of the kinetics of the photolysis of 2,2',4,4'-BDE, 2,2',4,4',5,5'-BDE and deca-BDE a consecutive loss of bromine atoms was found down to the parent molecule diphenyl ether. Complex kinetic schemes were required to model the observed concentration profiles. The time dependent concentration profiles of 2,2',4,4'-BDE shown in Figure 2 are a fairly transparent example. Quantum yields are found to be high (Φ=0.2-0.6 in THF) and in accord with the only available value for 4-BDE (Φ=0.38, in acetonitril/water)[16] and almost independent of the number of bromine atoms.

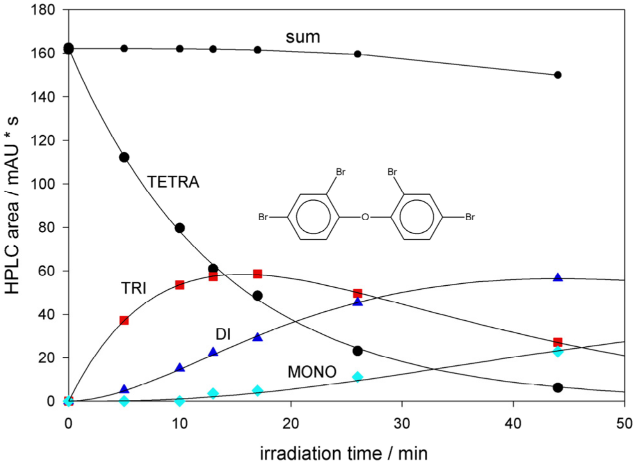

Figure 2: Photolysis of 2,2',4,4'-BDE (THF, c=21.8 mg/l) using the polychromatic light source (□>280 nm). The photolysis proceeds by debromination via mainly 2,4,4'-BDE, 4,4'-BDE and 4-BDE to diphenylether. Lines are results of a model for a simple reaction scheme of consecutive debromination, confirmed by the mass balance of the diphenyl ethers.

Very recently, another study[17] reported UV spectra of deca-BDE, 2,2',3,3',4,4',5-BDE, 2,3,3',4,4',5,6-BDE, 2,2',3,4,4',5-BDE, 2,2',4,4',6,6'-BDE, 2,2',3,4,4'-BDE, 3,3',4,4'-BDE and 2,2',4,4'-BDE in THF and a UV spectrum of 2,2',4,4'-BDE in methanol for comparison (showing a blue-shift by less than 1 nm). Photolytic quantum yields in methanol/water (80:20) were reported to be significantly lower than the values of our study in THF. This solvent effect on quantum yield causes a systematic increase of photolytic rate constants going from methanol/water (80:20) via pure methanol to THF observed for selected BDEs (by more than a factor of two) and a decrease of the photolytic rate constant for deca-BDE in water (by about two orders of magnitude), observed in the same study[17]. A marked decrease of photolytic rate constants to 1/3 has also been reported for 4,4'-BDE from methanol via acetonitrile to acetonitrile/water (50:50)[18].

It thus appears that the ability of the solvent to act as a hydrogen donor is decisive for the high quantum yields found in THF. Hence, the photolysis of BDE is typical of a halogenated aromatic compound[19,20]. The photochemistry in organic solvents can be assumed to start with the radical cleavage of the carbon-bromine bond, as usual for halogenated aromatics[21] and as desired for a flame retardant in case of fire. The half-life due to photolysis of BDEs in THF by sunlight (June, 50°) is short for deca-BDE (about 10 minutes) and increases to more than one year for 4-BDE. . Half-lives of all other BDEs are between these limits. One should note that these half-lives increase drastically for the lower sunlight intensities of the winter season or for BDEs in soil or water.

Brominated dibenzofurans (BDFs) were identified as intermediates from the photolysis of deca-BDE by their characteristic UV spectra and confirmed by analysing fractions of the HPLC eluent by GC-MS, where at least four different BDFs were found with N(Br) = 1,2,3,4 (in agreement with the recent study in methanol/water[7,17], where up to pentaBDFs were reported). The BDFs absorb UV above 300 nm and are photolysed with high quantum yield[22,23]. Higher brominated BDFs were not found, and any higher brominated BDFs would be superimposed in the HPLC by the corresponding BDE, formed at much higher yield. These results are in accordance with the early study of Watanabe and Tatsukawa[5] who detected BDFs up to hexaBDF in the initial phase of the photolysis.

Up to now photolysis of deca-BDE was mainly investigated in organic solvents. Obviously such experiments are not good models for the behaviour of BDEs in the environment. We have performed for the first time photolysis experiments with deca-BDE adsorbed on pyrogenic silicon dioxide as carrier material in aqueous suspension (Figure 3).

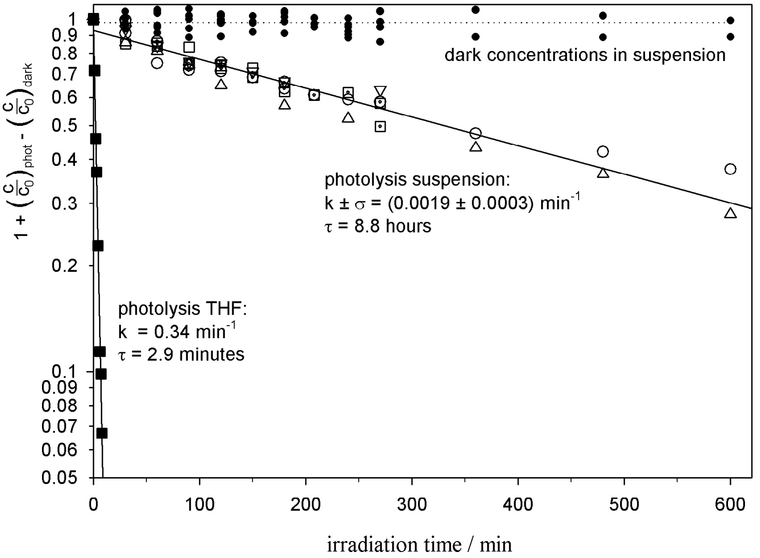

Figure 3: Photolysis of deca-BDE in THF (131 mg/l) and adsorbed on silicon dioxide in an aqueous suspension (coating 4%-13%, 500 mg/l Aerosil 380). Six experiments performed in stirred and unstirred suspensions are shown. Concentrations found in suspensions were corrected by the corresponding dark concentrations.

Again, adsorbed deca-BDE was found to be degradable by UV light, but with a much lower rate constant than in THF solution. It appears, that the adsorption of the non-planar deca-BDE molecule[24] on the SiO_2 at sub-monolayer coverage lowers the photolytic quantum yield markedly, in agreement with the enhanced photostability of decaBDE adsorbed on quartz glass[8,25] by more than an order of magnitude. However, this contrasts with a recent observation that adsorption of decaBDE on silicagel had no retarding effect on photolytic rate constants[26]. Brominated BDFs are confirmed as short-lived trace intermediates in our study on SiO_2 and in the majority of the other heterogeneous photolytic studies.

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