

IDENTIFICATION OF POLYBROMINATED DIBENZOFURANS FROM PHOTOLYSIS OF DECA-BROMODIPHENYLETHER BY UV SPECTROSCOPY

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Introduction

Brominated flame retardants are a group of substances which have, in recent years, attracted considerable attention due to their potentially negative effects on man and the environment. Most intensely discussed today are polybrominated diphenylethers (BDEs), because of their persistence and hydrophobic properties, that makes them amenable to bioaccumulation and biomagnification.¹ An important environmental transformation process of decaBDE (BDE209) may be photolysis²⁻⁹, that occurs even indoors³ or possibly at the surface or in the surface layer of flame retarded materials. Photolysis can be catalysed by photosensitizers (such as humic substances) or can be inhibited by shading or by energy transfer to solids upon adsorption to surfaces.⁴⁻⁶

Watanabe and Tatsukawa² were the first to find that decaBDE, dissolved in n-hexane, debrominates rapidly under solar irradiation with a half-life of less than 0.5h, resulting in a large variety of lower brominated BDEs (nona- to tetraBDEs) and brominated dibenzofurans (hexa- to monoBDFs). A photolytic half-life of decaBDE below 2 days has been observed even indoors in standard solutions in white glass³. Eriksson et al.⁷ performed photodecomposition experiments by a solar simulator with BDE congeners of different bromination degree in methanol, tetrahydrofuran (THF) and methanol/water (80:20). They observed that di- to pentaBDFs were formed from decaBDE, whereas Ohta et al.⁸ did not report a formation of BDFs in their study of the photolysis of decaBDE in toluene by various light sources, including a tungsten lamp and sunlight, in spite of well resolved chromatograms with many debromination products. A thorough investigation of the pathways leading to BDFs is desirable, since the World Health Organization (WHO) concluded that BDFs are similar in their persistence and toxicity to the chlorinated analogues; high toxicity or biological activity was found for 2,3,7,8-tetraBDF¹⁰ and has recently been demonstrated by Olsman et al. from bioassays for the photodebromination products of decaBDE¹¹. Although a significant human exposure to BDEs is likely¹², an analysis of the atmosphere surrounding television sets in a test chamber did not detect any emission of BDFs from the flame-retarded rear portion of the cabinet¹³.

The present study investigates the products formed from photolysis of a saturated solution of decaBDE in THF, identifies BDFs from characteristic UV spectra and attempts to assign the degree of bromination and the substitution pattern of individual congeners.

Materials and Methods

Chemicals: DecaBDE209 (98%) was obtained from Aldrich (lot 08203HQ), technical octabromo- and pentabromodiphenylethers (DE-79 and DE-71) from Great Lakes Chem. Corp., dibenzofuran (99%) from Aldrich, and a standard of the 2,3,7,8-substituted tetra- to heptaBDFs and dibenzodioxins from Cambridge Isotope Laboratories (EDF 2046). THF (99.9%, stabilised) was from Riedel de Haen and was distilled using a 75 cm Vigreux column, and acetonitrile (HPLC grade, 99.8%) was from VWR/Prolabo. The water was deionised to 18.4 MΩ cm resistivity (Membra Pure, Germany).

Instruments and Quantification: A saturated solution of decaBDE209 (10 g/l) containing an additional sediment of solid decaBDE209 was prepared in 3ml of THF in a quartz cuvette (d=1cm). The photolysis was performed by 4 lamps (Philips TL29D16, 16W each) at a distance of 20 cm between light source and cuvette for a time

period of up to 48 h. The saturated solution was treated for 7 min in an ultrasonic bath before taking samples of 100 µl of the irradiated solution, which were transferred to vials containing 1.5 ml of THF. HPLC analysis was performed by an Agilent 1100 system with quaternary pump, autosampler and DAD detector employing the following parameters: detection wavelength 230 nm, width 8 nm, injection volume 5 µl, flow 1 ml/min, a Zorbax Eclipse XDBC8RP column (4.6×150mm, 5 µm - Agilent), isocratic eluent using 80% acetonitrile and 20% water at 20°C. Furthermore, the samples were analysed by a quadrupole GC-MS instrument (5890 Series II and MSD 5970, Hewlett Packard) using electron impact ionisation (70eV) and an autosampler (7673A, Hewlett Packard) with the following parameters: a 15 m column (DB-5HT, Chrompack), 0.25 mm inner diameter, 0.1 µm film thickness, 1 µl injection volume, 300°C injector temperature, 340°C transfer line temperature, 1 ml/min He as carrier gas, temperature program (described by Rayne and Ikononou)¹⁴: hold at 100°C for 1 min, 2°C/min to 140°C, 4°C/min to 220°C, 8°C/min to 330°C and hold for 1.2 min.

Results and Discussion

Figure 1 shows a double logarithmic diagram of a HPLC chromatogram of the saturated solution of decaBDE, photolysed for 48h. Several debrominated BDEs (183, 203, 196, 197, 206 and 207) can be identified from their UV spectra and retention times by comparison with the components of technical octabromodiphenylether, DE-79. Unresolved components are contained in the peaks of BDE 196 and 183.

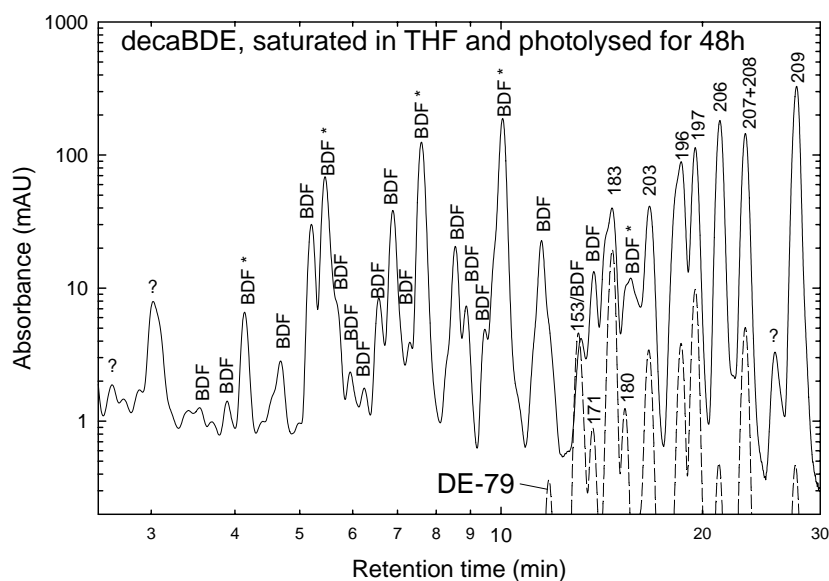


Figure 1: HPLC chromatogram of the photolysed solution in comparison with a solution of technical octabromodiphenylether, DE-79. Several BDEs occur in both samples but most if not all the other peaks are BDFs. UV spectra of the peaks marked as BDF* are displayed in fig. 2.

On the other hand, the UV spectra of the peaks with the retention times of the BDEs 153, 171 and 180 show structured bands, which differ largely from the smooth bands of the pure BDE components of DE-79. In fact, they closely resemble the spectrum of dibenzofuran, that has a sharp band at 250 nm and a stronger, triangular band at 280 nm. All peaks with retention times between 3.5 and 12 min show such spectra and are thus identified as BDFs. The spectra of the two peaks with question marks below 3.5 min are neither BDE- nor BDF-like. The spectrum of the peak between decaBDE (209) and BDE 207/208 with a question mark looks BDE-like, although octaBDF would be expected in that range of retention times. Figure 2 shows the UV spectra of selected BDF peaks, marked with an asterisk in Figure 1, in comparison with the spectra of dibenzofuran and 2,3,7,8-tetraBDF. Although an assignment of the BDFs from their retention times and UV spectra alone without a genuine standard is not possible, one can see that the bathochromic shift of the bands increases systematically with the retention times of the HPLC (i.e., most probably with the degree of bromination). Furthermore, a spectrum of 2,3,7,8-

tetraBDF has a much stronger bathochromic shift of the triangular band (maximum at 305 nm) than the BDFs from photolysis of decaBDE with maxima below 300 nm. UV spectra of all other 2,3,7,8-substituted pentaBDFs, hexaBDFs and heptaBDFs were studied and found to have maxima of the triangular band between 305 and 307 nm. This excludes the 2,3,7,8-substituted BDFs as major products from the photolysis of decaBDE. The large bathochromic shift of the 2,3,7,8-BDFs causes a large overlap with sunlight and is a main reason for their photolability, in accord with the short lifetime of 0.7 min in sunlight observed for 2,3,7,8-tetraBDF in *i*-octane by Buser¹⁵ and with the large photolytic quantum yields determined by Lenoir et al. in *n*-hexane.¹⁶

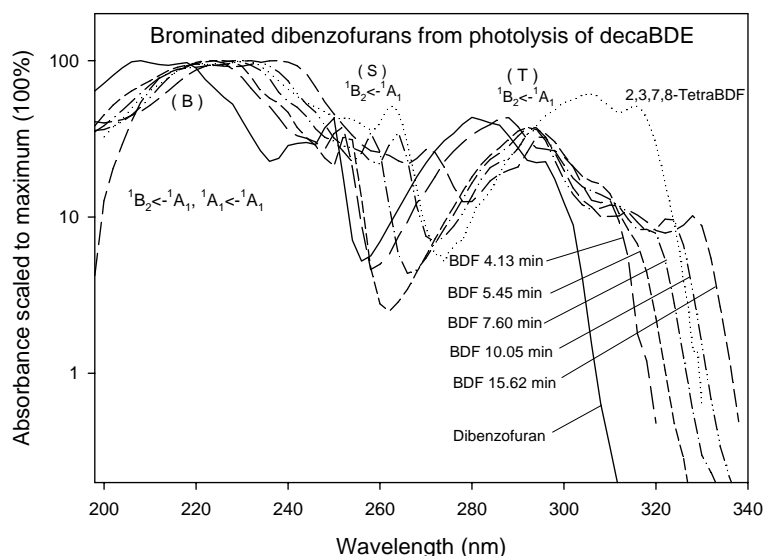


Figure 2: Normalised UV spectra of dibenzofuran and the HPLC peaks at retention times of 4.13, 5.45, 7.60, 10.05 and 15.62 min, marked BDF* in Fig. 1. Their band shape, which largely differs from the smooth, benzenoid bands of the BDEs, identifies them clearly as polybrominated dibenzofurans. Three band regions can be distinguished, a broad, bell-shaped band (B), a very characteristic, sharp peak (S) with a concomitant shoulder at shorter wavelengths and a triangular band (T) with additional vibronic transitions, mainly at longer wavelengths. The transitions have been characterised by Bree et al (1973).¹⁸

An analysis by GC-MS is shown in Figure 3. Several BDEs formed photolytically from decaBDE can be identified by comparison of the retention times and mass spectra with the components of the technical octabromo- and pentabromodiphenylethers DE-79 and DE-71: nonaBDE206, 207 and the missing third nonaBDE208 (that is known to co-elute with nonaBDE207 in HPLC) and octaBDEs 196, 203, 197, 201 and another octaBDE isomer, heptaBDE183 and mainly a single other heptaBDE isomer. Surprisingly, there are no hexaBDEs (such as BDE153 and 154), pentaBDEs (such as BDE85, 99 and 100) nor any lower BDEs. The BDFs can clearly be distinguished from the BDEs by their stronger M^+ peaks (2 amu lower than the BDEs), and there are various tri- and tetraBDFs, two pentaBDFs and a hexaBDF. No octaBDF and no heptaBDF were detected at the expected retention times. The retention times of the observed BDFs were in the expected range, and the isotope pattern of the M^+ peaks confirmed the degree of bromination of the BDFs derived from HPLC retention times and UV spectra. The presence of tri- and tetraBDFs has been explained by stating that the formation of the furan ring is possible for BDEs of any level of bromination as long as one ortho position is nonbrominated. Watanabe and Tatsukawa⁷ observed higher brominated dibenzofurans (up to hexaBDFs) in the initial phase of the photolysis experiments and lower BDFs in the final phase. Possibly debromination rather than cyclization occurred in higher BDEs. Photolysis of a thin film of solid decaBDE in a quartz tube by sunlight was found to be much slower than in solution, forming hexa- to nonaBDEs and a large number of tetra- to octaBDFs but no BDEs with less than 6 Br atoms.¹⁷

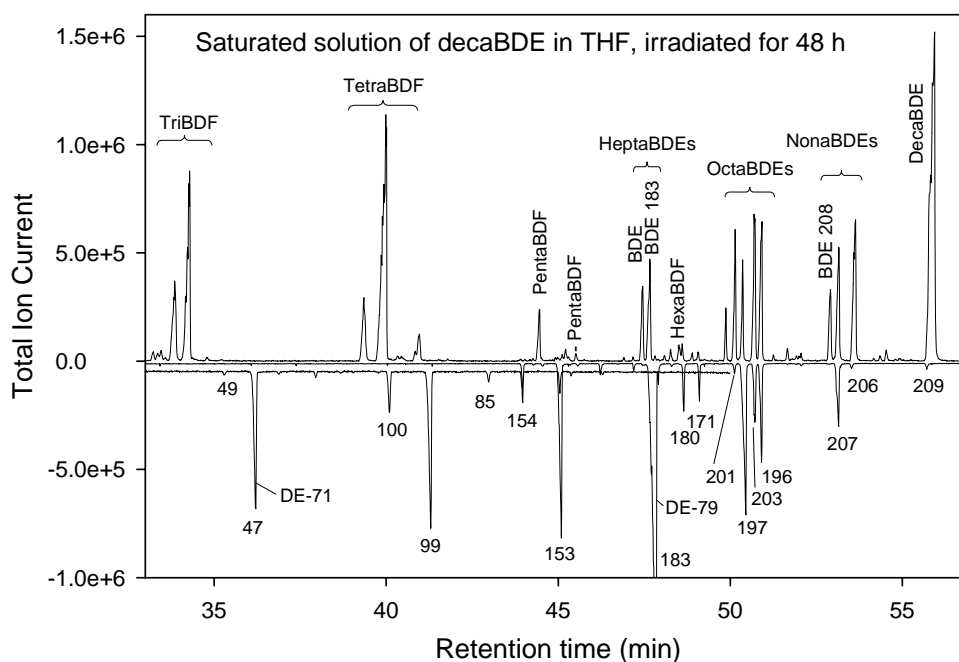


Figure 3: Total ion chromatogram ($m/z > 390$) of the photolysed solution of decaBDE in comparison with technical octaBDE DE-79 and pentaBDE DE-71. The BDFs are identified from their isotope pattern and from their relatively large M^+ peak.

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