# Analysis of Octabrominated Diphenylether DE-79 by 1HNMR, UV Spectra and photolytic transformation

Alfred Preiß<sup>1</sup>, Manfred Elend<sup>1</sup>, Ana-Maria Geller<sup>2</sup>, Qing Liu<sup>3</sup>, Heinz-Ulrich Krüger<sup>2</sup>, Cornelius Zetzsch<sup>2</sup>

<sup>1</sup>Fraunhofer-Institute for Toxicology and Experimental Medicine

<sup>2</sup>University of Bayreuth

<sup>3</sup>Beijing Center for Physical and Chemical Analysis

## Introduction

The overlap of the UV spectra of the brominated diphenylethers (BDEs) with sunlight is known to increase with the degree of bromination<sup>1</sup>. Accordingly, photolysis can be an important environmental transformation process and may occur even indoors at the surface of flame retarded materials. Quantum yields of debromination are large in organic solvents (close to 0.5), and it appears that the quantum yields decrease with increasing polarity of the solvent<sup>1-2</sup>. In heterogeneous systems, where decaBDE (BDE209) and various components of the technical octaBDE mixture DE-79 (Great Lakes Chem. Corp.) are adsorbed on surfaces (such as quartz glass), the quantum yields of decaBDE become extremely low<sup>2</sup>. On the other hand, brominated furans are found among the debromination products in solvents and in heterogeneous systems<sup>1-3</sup>. Preliminary results from a photolyis study of commercial mixtures are presented, taking technical octaBDE DE-79 in THF as a first example.

The <sup>1</sup>H NMR shifts in technical brominated diphenylether (BDE) mixtures obtained by Sondack et al. (see table 1)<sup>4</sup>, and progress in sensitivity of the instrumentation enable us to assign additional components in DE-79, providing shifts for the protons in 2,2',3,3',4,4',6-heptaBDE171 and 2,2',3,4,4',5,5'-heptaBDE180 and thus a quantitative analysis down to the trace level. This will enable us to obtain detailed information about the photolytic transformation pathways.

## Materials and Methods

*Chemicals:* Chloroform-d1 99.96% was from Deutero GmbH, The technical octabromodiphenyl ether mixture DE-79 was obtained from Great Lakes Chemical Corporation (ref. 80191634), a sample of 2,2',4,4'-tetraBDE47 (lot. 8996-3) was provided by Albemarle Corporation, and 2,4,6-trinitrotoluene 99.8% wasa special gift from WASAG Corporation.

## Instruments and Quantification:

A sample of 8.8 mg DE-79, dissolved in 300  $\mu$ l of CDCl<sub>3</sub>, was investigated with a Bruker DRX 600 NMR spectrometer, using 2,4,6-trinitrotoluene (0.775 mM) as external standard for calibration of CHCl<sub>3</sub> and employing the zg30 pulse program with an acquisition time of 2.1 s and a delay of 30 s. A spectrum of 2,2',4,4'-tetraBDE47 (3.23 mg, dissolved in 300  $\mu$ l CDCl<sub>3</sub>) was measured for comparison.

The photolysis of DE-79 was carried out by a Xe lamp (Osram XOP-7, 500W, filtered by 5 mm Duran glass) in a merry-go-round apparatus (Dema, Bornheim), irradiating up to 10 quartz cuvettes (1 cm) with the solutions simultaneously. HPLC analysis was performed by an Agilent 1100 system, injecting 5  $\mu$ l into a Zorbax Eclipse XDB-C8 RP column (4.6x150mm, 5 $\mu$ m), employing acetonitrile/water 80/20 or 72/28 as eluent and taking spectra at 2 nm resolution by the diode array.

## **Results and Discussion**

The <sup>1</sup>H NMR spectrum of DE-79 is displayed in fig. 1, and table 1 summarises and discusses the analysis. The table specifies the protons, their chemical shifts and averaged integral intensities as well as the concentration and mass

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fraction of individual BDEs. Quantitative data were obtained from the CHCl<sub>3</sub> content of 6.55 mM in the solvent, delivering proton integrals of 1.99 in the presence of DE-79 and 0.151 in the presence of tetraBDE47. The sample of tetraBDE47 was confirmed to have a purity of 98% - in reasonable agreement with an analysis by HPLC-DAD, which indicated well-resolved impurities of 0.5% each of two other BDEs. The sum of the identified components in DE-79 amounts to 95.2% of the total mass, and longer acquisition times may allow us to identify more trace components, some of which can be expected as synthesis byproducts and are known from earlier work on gas chromatograms of the penta mixtures DE-71 and Bromkal 70-5 DE



Fig. 1: <sup>1</sup>H NMR spectrum of the BDEs of DE-79, including the reference, CHCl<sub>3</sub> at 7.260 ppm.

The HPLC analysis by Palm et al. (2003)<sup>2</sup> determined an additional amount of 1.6 % w/w of decaBDE in the sample of DE-79 and portions of 14 and 1% for the two nonaBDEs (BDE207 and 206), 22, 8 and 7% for the three resolved octaBDEs (197, 196 and 203), 35, 2.2 and 1.5% for two of the heptaBDEs (possibly 183, 180, 173) and 7.3% for the sum of hexaBDE153 and hexaBDE154 (where the latter is a known hexaBDE peak in GC analysis with a contribution of about 1%, close to the detection limit of our NMR analysis). Chromatograms of the HPLC analysis of DE-79 closely resemble those obtained by Sondack et al.<sup>4</sup> for the commercial octa mixture from Bromine Compounds, Ltd., Beer Sheva, Israel, where the retention of BDEs on a RP column has been described to increase in the series tetraBDE47, pentaBDE99, hexaBDE153, heptaBDE183, octaBDE203, octaBDE196, octaBDE197, nonaBDE206, nonaBDE207 and decaBDE209, employing a standard of hexaBDE153 and additional samples of technical pentaBDE and high-melting octaBDE products from the same manufacturer.

Various gas chromatograms of DE-79 are now available in the literature, from companies and from our laboratory, confirming the three major octaBDEs and the two heptaBDEs 180 and 171 (where the NMR shifts are presented for the first time) by commercial standards and that the present NMR analysis comprises all major trace components, except for 2,2',4,4',5,6'-hexaBDE154, where an integral of 0.33 at 7.79 ppm shift (close to the expected 3,3'-protons) may tentatively be converted to a content of 1.2% w/w in DE-79, thus improving the mass balance to 96.4%.

Table. 1: Quantitative analysis and assignment of BDEs in samples of 2,2',4,4'-tetraBDE47 and the commercial octaBDE mixture Great Lakes DE-79, using literature values of chemical shifts observed by Sondack et al.<sup>4</sup> and a shift of 7.260 ppm for  $CHCl_3$ .

BDE	H pos.	Shift (ppm)	Shift (ppm)	Integral/	mg/300µl	% w/w
		This work	Literature	Proton		
2,2',4,4'-	3,3'	7.79	7.79	0.5	10.54	98%
TetraBDE47	5,5'	7.38	7.37			
	6,6'	6.71	6.71			
2,2',3,4,4',5',6- HeptaBDE183	5	7.98	7.98	4.4	3.14	36
	3'	7.89	7.90			
	6'	6.59	6.58			
2,2',3,3',4,4',6,6'- OctaBDE197	5,5'	7.84	7.85	2.07	1.64	19
2,2',3,3',4,4',5,6,6'-	5'	7.83	7.81	1.34	1.16	13.1 <sup>a)</sup>
NonaBDE207 <sup>a)</sup>						
2,2',3,3',4,4',5,6'- OctaBDE196	5	7.99	8.00	1.02	0.80	9.1
	6'	6.61	6.60			
2,2',4,4',5,5'- HexaBDE153	3,3'	7.91	7.90	1.01	0.64	7.3
	6,6'	7.09	7.08			
2,2',3,4,4',5,5',6- OctaBDE203 <sup>b)</sup>	3'	7.90	7.88	0.70	0.55	6.2 <sup>b)</sup>
	6'	6.57	6.62			
2,2',3,4,4',5,5'-	6	7.05	-	0.265	0.19	2.2 <sup>c)</sup>
HeptaBDE180 <sup>09</sup>	3'	7.92	-			
	6'	7.13	-			
2,2',3,3',4,4',6-	5	7.97	-	0.198	0.14	1.6 <sup>d)</sup>
HeptaBDE171 <sup>d)</sup>	5'	7.45	-			
	6'	6.23	-			
2,2',3,3',4,4',5,5',6- NonaBDE206	6'	6.62	6.63	0.07	0.06	0.7

#### a) preliminary assignment; no COSY/COSYIr coupling

#### b)preliminary assignment

c)preliminary assignment, based on the observation that the o-proton is shifted by approx. 0.4 ppm to higher field strength if the other ring carries two Br substituents in o-position, compare 2,2',4,4',5,5'-hexaBDE153 and 2,2',3,4,4',5',6-heptaBDE183, where the protons 3' and 6' cause a COSYIr p-coupling.

d)preliminary assignment, shift similar to 2,2',3,3',4,4',5,6'-octaBDE196; shift of the o-proton to higher field by >0.2ppm by the absence of o-Br; COSY o-coupling observed.

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One may use the mole fractions of DE-79 of the present study of 0.40 (BDE183), 0.19 (BDE197), 0.12 (BDE 207), 0.09 (BDE196), 0.09 (BDE153), 0.06 (BDE203), 0.024 (BDE180), 0.017 (BDE171), 0.012 (BDE154) and 0.006 (BDE206) and the UV spectra of our HPLC analysis in order to set up a library UV spectra. The UV spectra of individual chromatographic peaks of the DAD can either be placed on an absolute basis by fitting log-normal functions to the peaks. Such a behaviour is implied by the double logarithmic plot of the chromatograms, shown in fig. 2, where the relative width of the peaks is found to be remarkably independent of retention time. Minor overlapping traces can easily be recognised in DE-79, which need to be confirmed by GC and NMR. Using simply the peak height, a raw evaluation of the data by the peak height delivers the relative UV spectra of fig. 2, which can be compared with absolute data from available pure standards. Photolysis of DE-79 by a Xe lamp ( $\lambda$  > 300nm) for a period of 1 h delivers the dashed chromatogram in fig. 2, where a rapid decrease of decaBDE and nonaBDE207 and a concomitant formation of several peaks with a well-structured UV spectrum attributed to brominated dibenzofurans is observed. Photolysis of 2,2',4,4',5,5'-hexaBDE153 in THF has been investigated separately (the peak consisting mainly of BDE153 is marked in fig. 2). Because of symmetry, it delivers three pentaBDEs (equal yields of 2,2',4,5,5'-pentaBDE101 and 2,3',4,4',5-pentaBDE118 and twice as much 2,2',4,4',5-pentaBDE99)<sup>5</sup> and then debrominates further -where no furans were observed as debromination products, which are known to be extremely photolabile<sup>6</sup>.



Fig. 2: UV spectra of the components of DE-79, separated by HPLC (*left*) and chromatograms of DE-79 (2.5 mg/ml THF) and its photolysis products (*right*). DecaBDE, the rightmost peak, is known to debrominate most rapidly to form all three nonaBDEs, only two of which are separated. Brominated furans (F) can be clearly identified among the photolysis products from their characteristic UV spectra.

In view of the widespread applications of brominated diphenylethers<sup>3</sup> it appears to be desirable to further quantify the constituents of commercial BDEs and to clarify the conditions (indoors and outdoors) under which furans may be formed from the commercial penta and octa mixtures, including decaBDE and to identify the BDE congeners responsible for the furans.

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