

# Debromination of PBDEs in DE-83™ Technical Mix by electrolysis

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## Introduction

BDE-209 is the major component in DecaBDE. There is concern that degradation (through photolysis or metabolism) may produce lower brominated BDE congeners that are more toxic to environmental species and to human health.

Photolysis of BDE-209 affords lower brominated diphenyl ethers by either direct homolysis of the C-Br bond or by photoinduced electron transfer [1-4].

Identified products from the metabolic transformation of BDEs include lower brominated diphenyl ethers, as well as methoxy and hydroxy derivatives. Debromination of BDE-209 has been reported in rainbow trout [5], carp [6], rats [7], cows [8] and humans [9], with preferential loss of bromines meta- and para- to the ether linkage. Metabolic debromination of BDEs may also occur through an electron transfer mechanism [10,11].

Electrochemical reduction is by nature an electron transfer process. Hence the objective of this work was to compare the electrochemical debromination of commercial DecaBDE (DE-83™) in the presence of water with the analogous photochemical and metabolic processes.

## Experimental

### Electrolysis Experiments

Electrolyses were performed in an undivided cell with fixed platinum black electrodes. DE-83™ (Great Lakes) was dissolved in freshly distilled THF (Aldrich) (ca. 1 mg/mL) containing tetraethylammonium perchlorate (Fluka), as supporting electrolyte (30 mmol/L), and water (HPLC Grade; Caledon) or D<sub>2</sub>O (CDN Isotopes). A current of 20 mA was applied to the stirred solution resulting in a voltage of 20-26 V. Samples (50 µL) were withdrawn at the chosen time intervals, diluted with 3 mL hexane/10%DCM, and eluted through a short silica plug to remove the supporting electrolyte.

In order to quantitatively determine the BDEs using isotopic dilution, the samples were spiked with MBDE-MXE (<sup>13</sup>C<sub>12</sub>-BDE surrogate mixture) before elution through the silica column. BDE-CVS-EISS (<sup>13</sup>C<sub>12</sub>-BDE-138 injection standard) was added after the eluent volume was reduced and prior to injection on the HRGC/HRMS system. The BDEs were quantitated using a 5-point (BDE-CVS-E) calibration curve

### High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS)

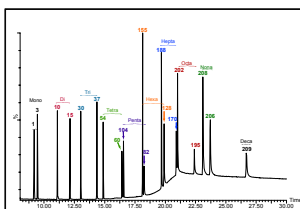
The analyses were conducted on a HP6890 HRGC with a J&W 30 m DB-5HT column (0.25 mm ID, 0.1 µm film), coupled to a Waters Autopsc Ultima HRMS. The injections were done in splitless mode (injector temperature 280°C, constant He flow rate 1.25 mL/min). The temperature program was 100°C (3 min hold), 12°C/min to 280°C, 20°C/min to 325°C (10 min hold).

The mass spectrometer was operated in selected ion monitoring (SIM) mode (EI+) with resolution >10,000 in each of five acquisition functions. The transfer line and source were maintained at 280°C. Perfluorokerosene-H was used as calibration standard.

## Results & Discussions

Technical DecaBDE has higher solubility than pure BDE-209 in organic solvents such as THF due to the presence of impurities. Quantitation of the debrominated products after electrolysis was aided by setting the retention time ranges for each congener group using Wellington Laboratories' window defining mixture BDE-WD (Figure 1), and was corrected for the lower BDE congeners initially present in the DE83 mixture. This assisted in assigning the peaks to the proper congener groups thus allowing the quantification of products with a higher degree of confidence.

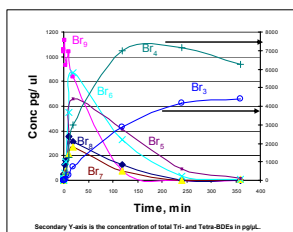
Figure 1. Window Defining Mixture BDE-WD.



Electrolysis of DE-83™ in THF in the presence of water resulted in the formation of a complex mixture, containing di-through nona-bromodiphenyl ethers.

The recoveries for most congeners were near 100%, except for the mono-BDEs (6-10%) and the Di-BDEs (75-85%), whose low recoveries were due to volatilization during solvent evaporation. Sampling times were chosen to allow us to examine both early and late stages of electrolysis (Figure 2). Congener groups nona- to tri-BDEs were quantitated, with the nona congener group corrected for the amount initially present in the technical mixture.

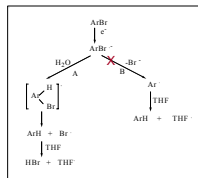
Figure 2. Products of DE-83™ Electrolysis.



The data suggest a rapid, sequential debromination under our conditions, with the most heavily brominated congeners undergoing the fastest debromination. Electron transfer is facilitated the greater the number of electronegative bromine atoms. The tetra- and tri-BDEs were much less reactive under our conditions.

Experiments in the presence of D<sub>2</sub>O were used to probe the mechanism of electrolytic debromination (Figure 3). Following electron transfer, the radical anion can either accept a proton from water (Path 3A) or undergo expulsion of a bromide ion to give an aryl radical that can abstract a hydrogen atom from THF (Path B).

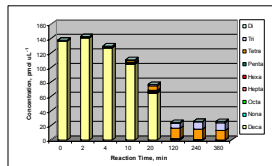
Figure 3. Mechanism of Debromination



When the electrolysis experiments were conducted in the presence of D<sub>2</sub>O, bromine was replaced exclusively by deuterium to give the lower brominated BDE congeners. This demonstrates that proton transfer involves exclusively water (Path A in Figure 3) and rules out the possibility of a hydrogen abstraction by Ar•. Attempts to measure reduction potentials of the individual BDEs in aqueous THF were unsuccessful due to competing reduction of water at the potentials needed to reduce the BDEs.

The sequential reduction of BDE 209 was accompanied by a progressive loss of material balance (Figure 4), possibly due to other pathways (arylation ?) that involve radical intermediates.

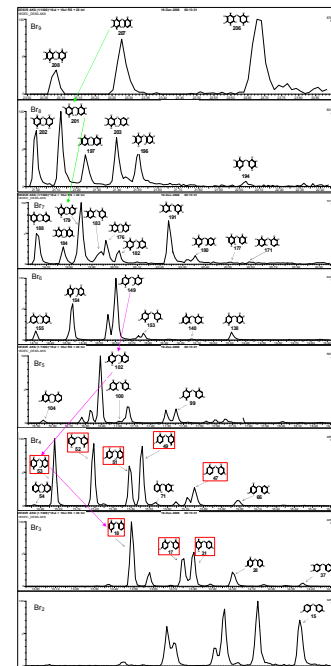
Figure 4. Material balance of BDEs During Electrolysis of Great Lakes DE-83™ Mix



The debrominated BDE products obtained by electrolysis seem to be formed by a limited number of reproducible mechanistic pathways (Figure 5), and are similar to those seen in the debromination of BDE 209 in rainbow trout[5] (although more products were identified in our experiments).

We note a definite preference for debromination at the positions meta and para to the ether linkages. Accordingly, the major products within the congener groups are likely to form through a single debromination of higher major congeners (see the colored arrows in Figure 5).

Figure 5. HRGC/HRMS analysis of the reaction mixture obtained from DE-83™ after 20 minutes of electrolysis.



Structures in red squares were determined by <sup>13</sup>C NMR analysis.

## Conclusions

Electrochemical debromination of BDE-209 involves sequential loss of bromines, to give lower brominated congeners. Debromination is most facile for the most heavily brominated congeners. The reaction takes place by an initial electron transfer, followed by protonation in the partly aqueous medium, followed by loss of a bromine atom. Significantly, the environmentally relevant congeners BDE-47, BDE-99, and BDE-154 do not appear to be major products of debromination of BDE-209 by the electron transfer mechanism.

## References

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