

# Photodebromination Of Opaque Slurries Using Titania-Coated Mercury Electrodeless Discharge Lamps

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**Abstract**—Degradation of decabromodiphenyl ether (BDE209) dissolved in n-hexane and in the mixture of n-hexane with water and microglass beads using microwave assisted photoreaction was examined. A novel electrodeless discharge lamp coated with titania oxide (anatase) and placed in a microwave field directly in a bulk of suspension was used to generate UV/Vis radiation. This method enhances penetration of UV/Vis light. Positive microwave effects (probably only heat effects) compensate relatively low irradiance intensity of UV/Vis generated in a microwave field.

The rate of BDE209 congener debromination was high and reaction efficiency after 240 minutes of BDE209 dehalogenation exceeded 99% even with high concentrations of 10 000 ng/mL. Similarly, the pathway of PBDE photodebromination by successive losses of bromine atoms was confirmed as the main initial pathway, in some cases also influenced by PBDE substitution patterns. Lower brominated congeners, including tri - brominated congener BDE28, were determined.

In spite of the use of titania oxide coated electrode emitting UV-vis irradiation and at the presence of water, the prevailing mechanism of photodegradation of PBDEs was probably photolysis. Oxidation products of photodegradation of PBDEs were not observed likely due to the low intensity of UV irradiance.

**Keywords**— *Electrodeless discharge lamp; Polybrominated diphenyl ethers; Slurries; Microwaves; Photolysis; Photocatalysis*

## I. INTRODUCTION

Polybrominated diphenyl ethers (PBDEs) are nowadays recognized as globally distributed pollutants, and can be detected in most environmental and biological samples. Moreover, their amount has been increasing lately.<sup>1</sup> Although PBDEs are almost insoluble in water, these compounds are found in water and/or sediments at concentrations harmful to health. The major concern associated with these compounds is that they can later migrate out from finished products and be released into the environment. Decabromodiphenyl ether (deca-BDE, BDE209) accounts for more than 80% of the PBDEs used worldwide and is apparently less toxic than other

lower-brominated congeners PBDE. However, recent research demonstrates that deca-BDE can be absorbed and metabolized by humans and other animals and other biota to more toxic tetra-BDE (BDE47, BDE49), penta-BDE (BDE99), hexa-BDE (BDE154), hepta- and octa-BDE.<sup>2,3</sup>

Based on available evidence, mainly polyhalogenated compounds such as PCBs (particularly PBDEs) undergo photolytic decomposition under certain conditions. Photolysis is expected to be the dominant transformation process for these compounds when the substance is exposed to the light significantly. However, the hydrophobicity of polyhalogenated compounds implies that in an aquatic environment, they will tend to partition into benthic sediments, where light exposure is negligible.

To enhance the reaction rate of sequential debromination of hydrophobic pollutants dispersed in aquatic sediments it is advantageous to first concentrate the PBDEs from the aqueous environment containing sediments by their extraction into organic solvents. The hydrophobicity of polyhalogenated compounds implies that in an aquatic environment they tend to partition into benthic sediments, where light exposure is insignificant. Such extracts are mostly muddy and turbid and the penetration of UV light into the bulk of the liquid from the outside is considerably suppressed. In such a case, the method of exciting the UV radiation by microwaves in electrodeless discharge lamp which is placed directly into the bulk of the liquid seems the best solution.

Photo induced degradation of BDE209 dissolved in n-hexane samples under the simultaneous influence of microwaves and UV light source generated by a novel electrodeless discharge lamp EDL was therefore studied and the results are submitted in this contribution.

Recent papers have demonstrated an improvement of degradative efficiency by coupling of microwave radiation with electrodeless discharge lamps EDL (in the combination TiO<sub>2</sub> (slurry) + EDL + MW field) to the photocatalytic degradation of various substrates.<sup>4,5</sup>

An original photochemical reactor consisting of an electrodeless discharge lamp was introduced by Klan.<sup>6</sup> It was reported to be a prospective tool for

photochemistry with good efficiency, simplicity and inexpensiveness by simultaneous application of UV and MW irradiation.<sup>7-15</sup>

Photodegradation kinetics of several PBDEs, particularly BDE209, have been reported in various matrixes, demonstrating that it photodegrades primarily via debromination.<sup>16-21</sup> When exposed to ultraviolet light in the environment, deca-BDE debrominates into lower, obviously more dangerous congeners. The rate of the debromination can vary from a few minutes to hours and days depending on whether the deca-BDE is dissolved in organic solvents or water, or is adsorbed on sediments and soils.<sup>22-24</sup> It has been reported that advanced oxidation catalytic processes using UV radiation could potentially, through sequential debromination, remove bromine from the PBDEs almost completely, and therefore they could be used as a promising technology for the treatment of contaminated wastewater.<sup>25</sup>

Sewage sludge is a dominant source of PBDE. In sludge from some Czech waste water treatment plants, BDE209 was detected as the prevailing congener in concentrations up to 1403 ng/g<sup>26</sup> and the total amount of 10 lower PBDEs (BDE 28, 47, 49, 66, 85, 99, 100, 153, 154, 183) were up to 605 ng/g. A possible technological procedure enabling a significant reduction of degradation time lies in extracting PBDE by suitable organic solvents. After the mechanical separation of the solid phase from the extraction agent and the subsequent heat separation and solvent recycling, reasonable amounts of residual solvents with high concentration of PBDE can be obtained. Such residual solvents usually contain even a certain amount of imperfectly separated sediment and original moisture.

The aim of this contribution is to verify the possibilities of debromination initiated by UV/Vis light emitted via electrodeless discharge lamp coated with an anatase film with the participation of microwave radiation in a non-transparent three-phase system. It consisted of solid microparticles (glass microparticles imitating sediment particles) and two immiscible liquids (hexane and water). BDE209 was dissolved in hexane at high concentration of about 15 000 ng/mL. Glass was chosen as inert material to eliminate any catalytic participation of sediment particles in photodebromination. Regarding the simultaneous presence of water and a possible catalytic impact of anatase, it could be theoretically assumed that even though photolysis has the major impact, photocatalysis might also participate. Therefore, the further aim was to specify to what extent the processes of photolysis and photocatalysis influence the kinetics of debromination within such an arrangement. This template, modified in MS Word 2007 and saved as a "Word 97-2003 Document" for the PC, provides authors with most of the formatting specifications needed for preparing electronic versions of their papers. All standard paper components have been specified for three reasons: (1) ease of use when formatting individual papers, (2) automatic compliance to electronic requirements that facilitate the concurrent

or later production of electronic products, and (3) conformity of style throughout a conference proceedings. Margins, column widths, line spacing, and type styles are built-in; examples of the type styles are provided throughout this document and are identified in italic type, within parentheses, following the example. Some components, such as multi-levelled equations, graphics, and tables are not prescribed, although the various table text styles are provided. The formatter will need to create these components, incorporating the applicable criteria that follow.

## II. EXPERIMENTAL

### A. Chemical materials

n-Hexane (99+%, Sigma Aldrich), titanium tetraisopropoxide (97%, Sigma Aldrich), decabromodiphenyl ether (98%, Sigma Aldrich, deca-BDE, BDE209). Microglass beads 3-10  $\mu\text{m}$ , Corpuscular C-PGL-6 (simulating sandy-loam soil with higher content of clay, size fraction below 0.01 mm), First, confirm that you have the correct template for your paper size. This template has been tailored for output on the A4 paper size. If you are using US letter-sized paper, please close this file and download the file "MSW\_USltr\_format".

### B. EDL

The system pattern for EDLs preparation was described previously by Cirkva.<sup>4,27,28</sup> 2.5  $\mu\text{g}$  Hg and stainless steel wire were placed to an EDL blank (Pyrex glass) and the system was sealed less than 20 Torr vacuum. The dimensions of cylindrical lamp were 20 mm (diameter) x 50mm.

Light intensity in  $\mu\text{Wcm}^{-2}$  measurements was carried out on a USB2000 spectrometer with a fiber optic probe and an operating software package OOIrad-C (Ocean Optics, USA). When the microwave field was switched on, it generated a UV/Vis discharge in the lamp (light intensity 5.56  $\mu\text{W/cm}^2$ , light wavelength 313-579 nm, 2 layers of TiO<sub>2</sub>). The TiO<sub>2</sub> sol was prepared by hydrolysis of titanium tetraisopropoxide. The TiO<sub>2</sub> film was prepared by dip-coating of pretreated support into TiO<sub>2</sub> sol and the film was finalized by a thermal treatment at 673 K. The thickness of the film was 130 nm. The crystal phase of titanium dioxide was analyzed by XRD. The observed structure phases revealed anatase with a certain amorphous fraction. The average density of TiO<sub>2</sub> was approximately 0.8 mg/cm<sup>2</sup> and the area of the electrode surface was about 15.4 cm<sup>2</sup>. The wavelengths emitted by the lamp are depicted in the following Figure:

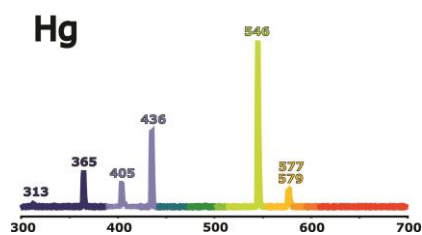


Fig. 1. The wavelengths emitted by the lamp

### C. Reactions under UV/Vis radiation

To exclude any potential influencing of chemical reaction by PBDE adsorption or catalytic influence of solid phase,<sup>22</sup> microglass beads were used as the solid phase, since such influences are generally not expected with them. Microglass beads and hexane containing BDE209 were placed into a glass boiling flask of 150 mL content. Most experiments were performed with a heterogeneous suspension containing 88g of n-hexane, 8g of water and 4g of microglass beads. This reaction suspension simulates the possible real suspension consisting of dried extraction sludge contaminated by BDE209 and hexane as residual water from concentrated sewage sludge. A glass boiling flask was placed into the cavity of a microwave oven. A mercury electrodeless discharge lamp was submerged into the treated suspension. The electrode was kept approximately 2 cm below the suspension surface while mixing of the suspension was caused by boiling of the liquid. The flask was placed into the cavity of a microwave oven (Panasonic NN-GD 566M, 600 W - 900 Watt) with the water condenser protruding from the oven's top through the sealed opening. Different times of microwave field application ranging from 0 to 240 minutes were tested. Microwave radiation was initiated at the power of 600 W. The temperature of the reaction environment was close to the boiling point of n-hexane.

Initial concentrations of BDE209 in n-hexane were 14.125 ng/mL, where the bulk of liquid contained n-hexane together with 4 wt.% of solid particles and 8 % of water. This system simulated the appearance of real three-phase slurries after the extraction of organics from contaminated muddy sediments with n-hexane. Physically, this system could be considered as a three phase system due to the water-in-oil phase.

The mercury electrodeless discharge lamp with a thin nanoporous film of TiO<sub>2</sub> was submerged into the treated suspension. The flask was placed into the cavity of the microwave oven (Panasonic NN-GD 566M, 600 W - 900 Watt) with the water condenser protruding from the oven's top through a sealed opening.<sup>29</sup> Different times of the microwave field application ranging from 0 to 240 minutes were tested. Microwave radiation was initiated at the power of 600 W. The temperature of the reaction environment was close to the boiling point of n-hexane. Independent control measurements of the influence of the presence of solid particles on the decrease in UV radiation intensity generated by the mercury discharge tube through the constantly stirred emulsion of 50mm layer thickness and containing the above-mentioned composition of hexane and water without the particles but with the presence of solid particles showed the decrease in radiation intensity by 55-57%.

### D. Analysis

Samples of n-hexane with dissolved BDE209 before and after the reaction were analyzed. The particles were separated by centrifugation, dried at 105°C, washed via iso-octane and the washing solution was analyzed independently. BDE209

contents in the samples of microglass beads after the treatment were undetectable.

Samples of n-hexane were diluted by iso-octane and analyzed in the Institute of Chemistry and Food Analysis, Prague Institute of Chemical Technology, by GC/MS in the mode of negative chemical ionization (NCI) with methane as reagent gas. Identification and quantification was accomplished by the method of calibration using selected congeners PBDE (provider Cambridge Isotope Laboratory, U.S.A.) The samples were analyzed by using Shimadzu 2010 gas chromatography equipped with a micro-electron capture detector. A HP-5 capillary column (30m x 0.32mm i.d., 0.25 μm film thickness, Agilent Technologies) was used with nitrogen carrier gas. The split-splitless injector was kept at the temperature of 280°C for 2 min, increased to 200°C at the rate of 20°C min<sup>-1</sup> and held so for 2 min, then it was increased to 280°C at the rate of 5°C min<sup>-1</sup> and held at 280°C. The identification of degradation products was confirmed by GC-MS-NCI analysis connected to a Trace DSQ quadrupole mass spectrometry (Thermo Finnigan) with a DB-5 MS capillary column. Helium was used as the carrier gas at the flow rate of 1 mL min<sup>-1</sup>.

### E. BDE209 adsorption on TiO<sub>2</sub> layer

The aim was to prove the potential influence of photocatalysis on the degradation mechanism of bromine atoms. It is assumed that primary BDE209 adsorption on TiO<sub>2</sub> layer on the electrode is an important condition related to the predominate process of photocatalysis. Adsorption conditions are showed in Table 1.

TABLE I. ADSORPTION CONDITIONS

Sample	Conditions
0	Basic specimen, 15 000 ng/mL, 25°C
1	Adsorption in the cold state, 2hr, stirred, 25°C
2	Adsorption in the cold state, 4 hr, stirred, 25°C
3	Adsorption during boiling, 4 hr, 68-70°C

## III. RESULTS

### A. Debromination of BDE 209

Table 2 demonstrates the results of debromination of BDE209 in-hexane where the bulk of liquid contained n-hexane together with 4 % of solid particles and 8% of water simulating appearance of a real three-phase extract after the extraction of organics from muddy sediments contaminated with n-hexane. Microwave radiation was initiated at 600 W; intensity of UV radiation was 5.56 μW/cm<sup>2</sup>. As evident from Table 2, debromination by successive losses of bromine atoms was confirmed as the main initial degradation photodegradation pathway of PBDEs.

TABLE II. RATE OF DEBROMINATION OF BDE209 UNDER SIMULTANEOUS INFLUENCE OF MICROWAVES AND UV LIGHT; CONCENTRATIONS AT FOUR REACTION TIMES ARE IN NG/ML

Congener	0 min	60 min	120 min	240 min
BDE 28	< 0.05	< 0.05	1.1	11.7
BDE 47	0.3	5.5	13.9	69.9
BDE 49	< 0.05	< 0.05	8.5	72.1
BDE 66	< 0.05	0.4	9.1	54.8
BDE 85	< 0.05	0.9	12.4	37.4
BDE 99	< 0.05	< 0.05	86.1	173
BDE 100	1.4	130	124	159
BDE 153	1.5	28.3	173	215
BDE 154	0.5	16.1	138	142
BDE 183	10.4	285	324	355
BDE 196	< 0.05	968	1390	558
BDE 197	< 0.05	496	446	288
BDE 203	< 0.05	2012	2167	1285
BDE 206	366	1644	532	150
BDE 207	218	1830	544	142
BDE 209	14125	3421	298	115

Degradation of bromine atoms from BDE209 molecule was similar for both samples containing 4% or 8% microspheres. It was proved that the degradation rate of BDE209 congener depended on the solid phase content only little. BDE209 concentration reached within 240 minutes of reaction was chosen as the speed rate debromination indicator. Debromination was fastest with the relatively most transparent sample, which might, however, be expected considering the theory of UV radiation emission.

TABLE III. BDE209 CONCENTRATION (NG/ML) AFTER 240 MIN OF REACTION WITH VARIOUS CONTENTS OF SOLID PARTICLES. REACTION CONDITIONS ARE IDENTICAL WITH TABLE II.

Sample	0%	4%	6%	8%
BDE209, ng/mL	40 +-10	115+-8	176+-8	295+-6

Reproducibility was investigated by using samples in triplicates. They indicated good reproducibility, and 90% of all chromatographic peaks in n-hexane vary less than 25% among the replicates.

#### B. BDE209 Adsorption on TiO<sub>2</sub> layer

To prove the potential influence of photocatalysis on the degradation mechanism of bromine atoms, BDE209 adsorption on TiO<sub>2</sub> layer was tested as an important condition related to the predominate process of photocatalysis. The results are demonstrated in Table 4. For adsorption conditions see Table I.

TABLE IV. CONCENTRATIONS OF CONGENERS OF PBDE IN HEXANE SAMPLES AFTER ADSORPTION EXPERIMENTS, NG/ML.

Congener	Sample 0	Sample 1	Sample 2	Sample 3
BDE 28	<	<	<	<
BDE 47	<	<	<	<

BDE 48	<	<	<	<
BDE 49	<	<	<	<
BDE 66	<	<	<	<
BDE 85	<	<	<	<
BDE 99	<	<	<	<
BDE 100	<	<	<	<
BDE 153	<	<	<	<
BDE 154	<	<	<	<
BDE 183	<	<	<	<
BDE 196	<	<	<	<
BDE 197	12.2	16.2	15.5	17.2
BDE 203	<	<	<	<
BDE 206	320	369	405	509
BDE 207	438	588	617	702
BDE 209	15 241	14 975	14 008	14 701

The analyses show that the adsorption of BDE on TiO<sub>2</sub> layer is negligible.

#### IV. DISCUSSION

All potential intermediates in reductive debromination of DBE209 led to lower brominated congeners as had been formerly indicated in solar irradiated samples.<sup>3</sup> The photochemical PBDEs reaction rates decrease with the decreasing number of bromine substituents in the molecule, and in some cases they were influenced by the PBDE substitution pattern.<sup>30</sup> The rate of debromination under the condition of generation of UV light in a microwave field is more rapid in comparison with solar irradiation, but slower with regard to the condition when high irradiation intensity mercury UV-lamps were applied and the irradiation intensity was obviously three orders higher. Debromination of BDE209 preferentially started only in one ring, in positions 6' and 5'. In spite of the relatively lower intensity of UV irradiation in these experiments, the rate of debromination of BDE209 was very high and after 240 minutes of reaction, the efficiency of dehalogenation of BDE209 was 99.2%. Lower brominated congeners, including (2, 4, 4')-tri-brominated congener were safely determined. Currently, little is known about the fate of PBDEs under the conditions when microwaves not only excite the UV radiation in the lamp (which is covered by nanoporous TiO<sub>2</sub> in the special film arrangement) but may also affect reaction mechanisms and the reaction rate. The degradation pathways with only small variations basically follow the sequential process and do not differ from those already published data<sup>3,19,22,23</sup> obtained by means of using classic UV lamps or solar radiation. Deviations are obvious especially in connection to the time of degradation beginnings. Certain congeners were not detected at all during the EDL application (e.g. BDE18, BDE101, BDE52); this might, nevertheless, be associated with various initial conditions. Previous studies (Bezares-Cruz<sup>3</sup>, Söderström<sup>24</sup>) showed that reductive debromination was the main photodegradation mechanism for BDE-209. Contrary to the photolysis of PCBs in hexane<sup>22</sup>, no brominated benzene, as well as oxidation products like bromodioxines, was detected in this study in concordance with Fang.<sup>11</sup> Additionally, PBDE-solvent adducts were also not detected by GC-MS in our experiments.

The speed of BDE209 degradation using EDL was comparable with conventional UV lamps although the light intensity was considerably lower with EDL. This could probably be attributed to high reaction temperatures during working with EDL since its microwaves generate a significant heat and the reaction was, therefore, conducted at the boiling point of the liquid. Regarding similar reaction pathways of degradation during photolysis, either with or without the presence of microwaves, it could be assumed that the influence of microwaves on the reaction kinetics lies mainly in the fast heating of reaction liquid. The advantage of using an EDL lamp is the possibility to work with little transparent liquids.

The probable pathway of individual selected PBDE congeners suggested on the basis of our results:

66

(↑)

209 → 207 → 197                      154 → 99 → 47 → (28)

207 → 196 → 183 → 154 → 100 → 47 → (28)

→ 206 → 203 → 153 → 99 → 47 → (28)

The mechanism of degradation of bromine atoms from congeners with a low content of bromine atoms proceeded much slower due to the lack of available relevant analytical data in this field.

A necessary condition for photocatalysis, i.e. the adsorption of treated substance on the catalytic layer, was not met. Therefore, it can be assumed that the process of BDE debromination may, under these conditions, be considered as photolysis, and the catalytic TiO<sub>2</sub> activity is not expected.

## V. CONCLUSIONS

Application of UV light evoked in the microwave field by electrodeless discharge lamp containing nanosize porous TiO<sub>2</sub> and located in the bulk of contaminated environment is, in general, a feasible option for debromination of polybrominated diphenyl ethers present in the three phase (water-organic solvent-particles) almost non transparent systems. The frequency of UV light of 365 nm and the intensity of UV irradiation of about 5 -10 μW/cm<sup>2</sup>, which are typical parameters related to this technique, are suitable for initiating efficient oxidation processes of complex organic compounds. The initial rate of debromination of deca-brominated diphenyl ether in n-hexane under such conditions of non-transparent media was apparently identical with the initial reaction rates obtained in experiments with direct UV irradiation of fully transparent systems (BDE209 dissolved in pure n-hexane) by a customary medium pressure Hg lamp. The positive microwave induced thermal effects sometimes probably compensate the relatively low irradiance intensity of UV generated in microwave field. EDLs can be placed in the bulk of slurries up to the distance accessible for microwaves. For decontamination of contaminated turbid solutions and/or slurries, the use of electrodeless lamps emitting

MW radiation seems to be the best solution. Oxidation products of PBDEs photodegradation was not observed probably due to the low intensity of UV irradiance emitted by EDL. The influence of photocatalysis on the debromination seems negligible.

## ACKNOWLEDGMENT

The financial support of the Technology Agency of the Czech Republic No. TA04020700 is gratefully acknowledged.

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