

Photodegradation of Polybrominated Diphenyl Ethers in Organic Solvents and Surfactant Solution

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Introduction

Polybrominated diphenyl ethers (PBDEs) are a group of brominated flame retardants (BFRs) used in large quantities (de Wit 2002). Due to their global distribution, persistence, bioaccumulation and potential toxicity, the major components of commercial penta- and octa-products were recently decided as new POPs added to the Stockholm Convention. Photodegradation is the main transformation process for PBDEs in the environment and previous studies showed that PBDEs underwent photodebromination in various artificial and natural matrixes (Eriksson et al. 2004; Palm et al. 2004; Söderström et al. 2004). The aim of this study was to investigate the photodegradation kinetics of eighteen lower brominated PBDEs (mono- to hepta-) in organic solvents, and attempted to identify the effects of bromination degree and substitution pattern on PBDE photodegradation. Furthermore, photolytic experiments were also performed in nonionic surfactant solutions in regard to eliminating PBDE contamination.

Materials and Methods

All PBDE standard solutions were purchased from AccuStandard Inc. (New Haven, CT, USA). The standard solutions of Polybrominated dibenzofuran (PBDF) were supplied by Cambridge Isotope Laboratories, Inc. (Andover, MA, USA). Hexane and methanol were of HPLC grade and obtained from J.T. Baker Inc. (USA) and Fisher Scientific Inc. (USA), respectively. Nonionic surfactants of Brij 35 (TM) and Brij 58 (TM) were purchased from Amresco (USA) and Sigma (USA), respectively. PBDEs in irradiated samples were quantified using GC-ECD (Agilent 6890 plus), and quantification and qualification of PBDFs were performed by GC-MS (Shimadzu GCMS-QP 2010 Plus, Kyoto, Japan). The analytical methods used have been described in our previous studies (Fang et al. 2008; Li et al. 2010). All photodegradation experiments were carried out in a RPR-200 Rayonet photochemical reactor (Southern New England Ultraviolet, USA) equipped with RPR-3000Å or 2537Å lamps.

Results and Discussion

The photodegradation of eighteen PBDEs under 300 nm irradiation all well followed pseudo-first-order kinetics in hexane ($R^2 = 0.998\sim 1.000$) or methanol ($R^2 = 0.996\sim 1.000$), of which the linear regression models for BDE-8, BDE-33, BDE-47, BDE-119 and BDE-154 (di- to hexa-) were taken for examples (Figure 1). The results of photodegradation rate constants (k) of eighteen PBDEs in hexane and methanol were presented in Figure 2 (a). Except for mono- and di-BDEs, the rate constants of all other PBDEs in hexane were higher than those in methanol, and this phenomenon can be

attributed to the better ability of hexane as a hydrogen donor (Bezares-Cruz et al. 2004; Palm et al. 2004). Moreover, the rate constants of PBDEs were also affected by their bromination degree and substitution pattern. The photodegradation rate constants generally decreased with the decreasing degree of debromination, e.g., the photodegradation rate constants of BDE-153 (hexa-) were $1.11 \times 10^{-2} \text{ s}^{-1}$ in hexane and $7.48 \times 10^{-3} \text{ s}^{-1}$ in methanol, which were 19.9 and 11.4 times the values of BDE-1 (mono-), respectively. This result was in consistent with the photodecomposition of fifteen PBDEs in methanol/water (Eriksson et al. 2004), and the explanation was that the higher brominated congeners absorbed at longer wavelengths (Figure 2 (b)). On the other hand, the lower rate constants of penta-BDEs of BDE-100 and BDE-119 than those of most tetra-BDEs indicated the substitution pattern was also an important factor for PBDE photodegradation.

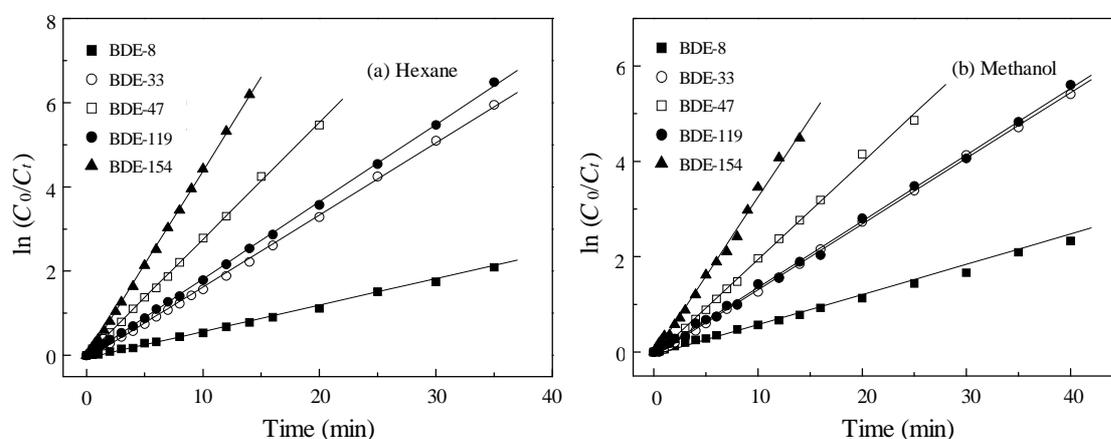


Figure 1. Photodegradation of five PBDEs (di- to hexa-) in hexane (a) and methanol (b).

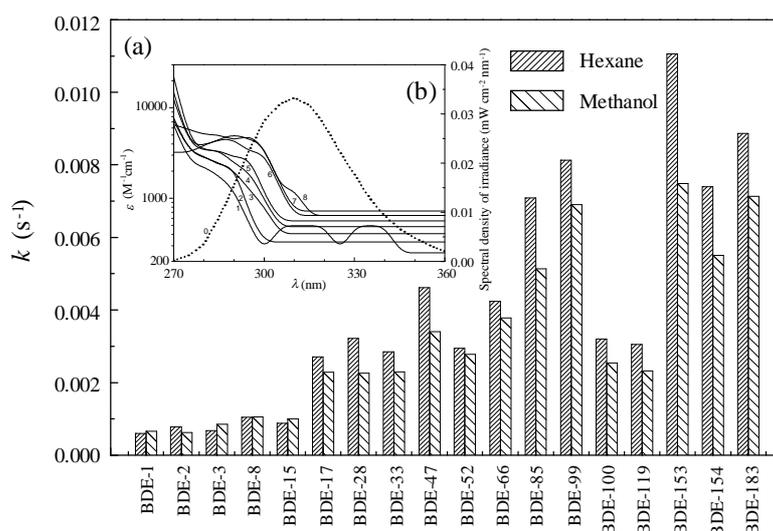


Figure 2. Rate constants (k) of eighteen PBDEs (mono- to hepta-) in hexane and methanol (a), and absorption spectra of seven PBDEs in methanol and the spectral distribution of irradiance density for (b).

300 nm UV lamp (the line numbers were as follows: 0, the UV light source emission; 1, BDE-3; 2, BDE-15; 3, BDE-33; 4, BDE-66; 5, BDE-85; 6, BDE-154; 7, BDE-183; 8, BDE-153) (b).

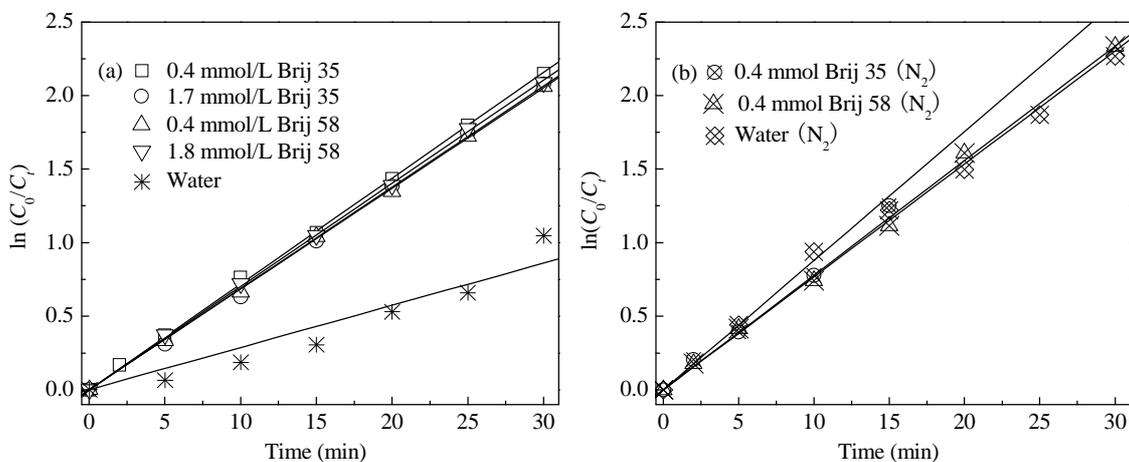


Figure 3. Photodegradation of BDE-99 in Brij 35 and Brij 58 solutions of, and Milli-Q water.

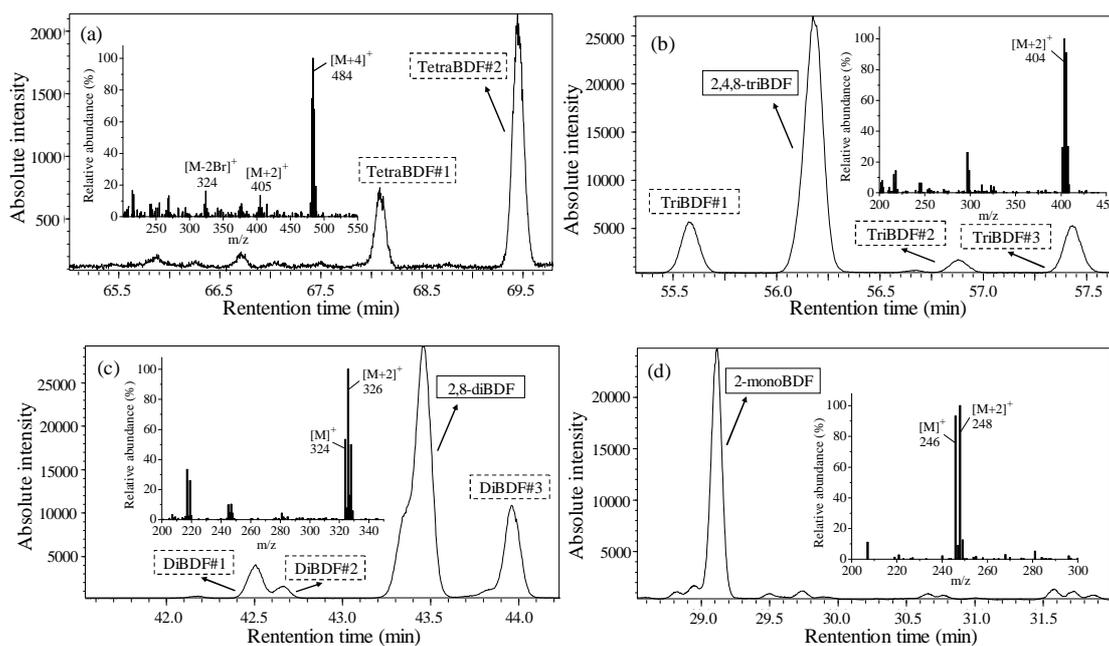


Figure 4. Photoproducts of BDE-99 as mono- to tetra-BDFs in surfactant solutions: (a) tetra-BDFs, (b) tri-BDFs, (c) di-BDFs and (d) mono-BDFs (Congeners in solid closed square were confirmed by standards while in dash closed square were identified by mass spectra obtained in full scan mode).

In addition, photodestruction of BDE-99 was investigated in the solutions of nonionic surfactants of Brij 35 and Brij 58 under 254 nm irradiation. As shown in Figure 3 (a), the photodegradation of BDE-99 followed pseudo-first-order kinetics ($R^2 = 0.977-1.000$) in all solutions. The rate constants

were from $11.4 \times 10^{-4} \text{ s}^{-1}$ to $14.9 \times 10^{-4} \text{ s}^{-1}$ in surfactant solutions and $6.1 \times 10^{-4} \text{ s}^{-1}$ in Milli-Q water, indicating the photodegradation can be efficiently enhanced by the surfactants. The effects of surfactant concentration and structure on BDE-99 photodegradation were not significant (Figure 3 (a)) in this study and the possible explanation was that BDE-99 was retained in the coils of hydrated PEO chains in both surfactants micelles, and thus the reaction conditions were roughly the same in different surfactant solutions.

When dissolved oxygen was driven off by introducing high purity nitrogen into the solutions, the rate constants in surfactant solutions were almost unchanged while the rate constant in Milli-Q water was more than one time increased. This result implied that the quenching effects of DO on BDE-99 photodegradation can be effectively eliminated by Brij 35 and Brij 58, and the accelerating effect of the surfactants on BDE-99 photodegradation was mostly attributed to the elimination of adverse influence of DO. Finally, it was note of worthy that PBDFs were indentified as BDE-99 photoproducts in Brij 35 and Brij 58 solutions (Figure 4) and the pattern of PBDFs was the same with or without the presence of DO. As a result, the formation of PBDFs should be considered when the method was applied for eliminating PBDE contamination.

Acknowledgement

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