PHOTODEGRADATION OF BDE-47 IN VISCOUS ORGANIC SOLVENT UNDER THE IRRADIATION OF ULTRAVIOLET LIGHT

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Introduction

Polybrominated diphenyl ethers (PBDEs) have been extensively used in plastics, electronics and textiles as additive flame retardants[1]. When these BFR containing products or materials were disposed of as waste in incinerators, PBDEs would easily migrate from the waste into the environment. As one of the persistent organic pollutants (POPs), photodegradation seems to be the main transformation process for PBDEs in the environment. Due to their hydrophobic and lipophilic characteristic, PBDEs might be adsorbed to articles released from the incineration. Several of combustion generated aerosols are believed to consist of an elemental carbon core coated by a viscous organic liquid layer[2]. For the purpose of assessing the health impact of PBDEs adsorbed to the combustion aerosol, it's necessary to understand the photodegradation behavior of PBDEs in viscous organic liquid. Although previous literatures have reported the photodegradation of PAHs in viscous diisooctylphthalate (DiOP), so far there's no similar study for the PBDEs. BDE-47 is the most important congener within the penta-product of PBDEs, also the dominant congener found in almost all environmental and biotic samples[3]. In this paper, we report the photodegradation kinetic of BDE-47 in hexane containing viscous DiOP and some aerosol components. Photodegradation products were quantified, and possible reaction process was elucidated.

Materials and Methods

BDE-47 (2,2',4,4'-tetrabromodiphenyl ether) at 50 mg L^{-1} each in isooctane was purchased from AccuStandard Inc., USA. Photodegradation experiments were performed in a Rayonet photochemical reactor (RPR 200, Southern New England Ultraviolet, USA), equipped with two lamps (RPR- 3000Å or RPR-2537Å, with the dominant wavelength of 300 nm or 254 nm). Cylindrical quartz tube containing 30mL hexane solution of 20μg L^{-1} BDE-47 containing DiOP and aerosol components was placed at the centre of reactor chamber. All experiments were performed at room temperature, with corresponding dark control tests conducted. At proper interval, 1 mL of solution was taken from the tube. These samples were treated with sulfuric acid to remove the DiOP for chromatographic analysis. All photodegradation experiments were performed in triplicate and corresponding dark control tests were conducted.

The PBDEs analytical standard solution BDE-AAP-A-15X was purchased from AccuStandard (USA) for quantification, which contains 39 PBDE congeners. Irradiated samples were analyzed using an Agilent 6890 gas chromatography equipped with a micro electron capture detector (μECD). A HP-5 capillary column (30m×0.32mm×0.25μm) was used, with nitrogen as carrier gas. The split-splitless injector was kept at a temperature of 280 ℃ and the oven temperature program was: 80 ℃, hold for 2 min, rate 20℃ min^{-1} to 200 ℃, hold for 2 min, rate 5℃ min^{-1} to a final temperature of 280 ℃, hold for 15 min. Agilent ChemStation software was used for the quantification.

The identification of degradation products was confirmed by GC/MS-NCI analysis on a Trace gas chromatography connected to a Trace DSQ quadrupole mass spectrometry (Thermo Finnigan, USA) with a DB-5 MS capillary column (30m×0.32mm×0.25μm). Helium was used as the carrier gas at a flow rate of 1 ml min^{-1}. The temperature program was: 80℃, hold for 2 min, rate 10℃ min^{-1} to 180℃, hold for 1 min, rate 3℃ min^{-1} to 210℃, rate 2℃ min^{-1} to 260℃, rate 3℃ min^{-1} to 280℃, hold for 15 min, rate 10℃ min^{-1} to a final temperature 300 ℃, hold for 2 min. The injector, ion source and transfer line temperatures were 280, 260 and 260 ℃, respectively. The mass spectrometry was used in the negative chemical ionization mode with methane as reagent gas. The samples were both analyzed in full scan mode (m/z = 50-750) and SIM mode (m/z = 79, 81).

Results and discussion

Effects of DiOP content on the photodegradation of BDE-47

Dark control experiments for BDE-47 showed no disappearance or appearance of degradation products. Photodegradation kinetics of BDE-47 in hexane containing different content of DiOP was shown in Figure 1. High regression coefficients can be obtained for all concentration data series for the linear fitness between $ln(C_0/C)$ and t. Obviously, all photodegradation in different solution under both lengths of ultraviolet light follow the pseudo-first order reaction kinetics, the photodegradation rate constants, half-lives and regression coefficients were shown in Table 1. With the increase of DiOP content, the degradation became slower.

It's interesting that the photodegradation rate of BDE-47 in hexane contains same content of DiOP under the irradiation of 254 nm UV was much slower than that under the irradiation of 300 nm UV. It's reversed from the situation of photodegradation of PBDE-47 in pure hexane. For the elucidation, the UV absorbance spectrum of DiOP and the concentration variation of DiOP during the photodegradation process were further studied. As shown in Figure 2, DiOP has strong absorbance in 254 nm, but no absorbance in 300 nm. It's consistent with the fact that DiOP concentration decreased under the irradiation of 254 nm UV but kept still under the irradiation of 300 nm. Therefore the experiment result can be explained as below: 1) viscous component retarded the transfer of BDE-47 in hexane, which thus slower the photodegradation of BDE-47, especially under the irradiation of 300 nm UV; 2) competitive absorbance of photon become more important than transfer retardance under the irradiation of 254 nm.

Photodegradation products of BDE-47

In order to identify as many of photoproducts in this study as possible, GC retention times and mass spectra of the products were compared to those of standards. The observed photoproducts were mostly less brominated diphenyl ethers. Under the irradiation of both 300 nm and 254 nm, main photodegradation products in different solution are the same along all irradiation time, including BDE-28, BDE-17 and BDE-15. This result indicated that the main decomposition mechanism of BDE-47 would be successive reductive debromination, which was in agreement with the previous report for photolysis of five individual PBDE congeners on solid-phase microextraction fibres[4]. No brominated benzene, PBDE-solvent adducts were detected by GC/MS in our experiment. It seems that cleavage of inter-ring bonds to produce brominated benzenes and replacement reactions to form PBDE-solvent adducts may not be significant mechanisms under our experimental conditions. The decomposition process of BDE-47 in viscous organic solvent here was potentially the same as that in pure hexane reported in our previous study[5].

Effect of aerosol components on the photodegradation

Two aerosol components, 2-methoxyphenol (MP) and vanillin (VA), were added into the hexane solution containing 5% DiOP with the concentration of 0.4, 2.0, or 10.0 mg/L to investigate their effects on the photodegradation. The photodegradation data was shown in Table 2. And the typical kinetics under the addition of 2.0 mg/L was shown in Figure 3. The photodegradation under the irradiation of both 300 nm and 254 nm were found to follow the pseudo first-order kinetics. For both 300 nm and 254 nm, the existence of MP and VA seems to further retard the photodegradation of BDE-47. The effect of MP and VA under 300 nm was even greater than that under 254 nm. This might indicate that aerosol components also contribute to the persistence of BDE-47 in atmospheric environment.

More addition of MP or VA will further slower the photodegradation, but the effect was relatively not so significant. MP and VA are good proton donors for the photodegradation, which might speed up the

photodegradation. However such expected effect was overwhelmed by the competitive absorbance in our experiments because hexane itself can provide enough protons. Products identified by GC/MS analysis were also found to be BDE-28, BDE-17 and BDE-15, and no brominated benzene, PBDE-solvent adducts were detected. It means the existence of MP and VA didn't change the decomposition mechanism of BDE-47.

The results of this study may partly explain the persistence of BDE-47 in the atmospheric environment: The sunlight only contain the weak ultraviolet light with the wavelength of higher than 280 nm, the photodegradation would be slow. As BDE-47 was likely adsorbed in the surface organic layer of aerosols, the viscous component would greatly inhibit the photodegradation of BDE-47. Aerosol components like MP or VA will further slower the photodegradation.

References:
1. Frank R., Katherine H. L., Mark D. S. and John N. L. *The Science of the Total Environment* 2001; 275: 1-17
2. Feilberg A., Nielsen T. *Environ. Sci. Technol.* 2001; 35: 108-113
3. Hites R. A. *Environ. Sci. Technol.* 2004; 38: 945-956
4. Sanchez-Prado L., Llompart M. Lores M., Garcia-Jares C., Cela, R. *J. Chromatogr. A.* 2005; 1071: 85-92
5. Fang L., Huang J., Yu G., Wang L. N. *Chemosphere*. 2008; 71: 258-267

Table 1: Photodegradation rate constants, half-lives and regression coefficients in hexane containing different content of DiOP

DiOP content (%)	irradiation with 300 nm UV			irradiation with 254 nm UV		
	k （h^{-1}）	$t_{1/2}$ （h）	R^2	k （h^{-1}）	$t_{1/2}$ （h）	R^2
0	1.66×10^1	4.23×10^{-2}	0.9994	2.51×10^2	2.22×10^{-3}	0.9987
1	2.37	3.31×10^{-1}	0.9937	1.18	5.48×10^{-1}	0.9746
5	9.06×10^{-1}	9.04×10^{-1}	0.9941	4.13×10^{-1}	1.87	0.9788
10	4.53×10^{-1}	1.61	0.9891	2.06×10^{-1}	3.29	0.9643
20	2.20×10^{-1}	3.38	0.9775	8.31×10^{-2}	8.92	0.9893
30	1.35×10^{-1}	5.29	0.9884	5.37×10^{-2}	1.23×10^1	0.9926

Table 2: Photodegradation rate constants, half-lives and regression coefficients in hexane containing 5% of DiOP and aerosol components

Aerosol Component	irradiation with 300 nm UV			irradiation with 254 nm UV		
	k （h^{-1}）	$t_{1/2}$ （h）	R^2	k （h^{-1}）	$t_{1/2}$ （h）	R^2
MP (0.4 mg/L)	6.69×10^{-1}	1.03	0.9976	3.01×10^{-1}	2.28	0.9947
MP (2.0 mg/L)	6.69×10^{-1}	1.09	0.9986	2.99×10^{-1}	2.30	0.9950
MP (10.0 mg/L)	6.65×10^{-1}	1.08	0.9969	3.07×10^{-1}	2.32	0.9927
VA (0.4 mg/L)	6.91×10^{-1}	1.08	0.9982	3.25×10^{-1}	2.16	0.9949
VA (2.0 mg/L)	6.24×10^{-1}	1.25	0.9764	3.10×10^{-1}	2.26	0.9742
VA (10.0 mg/L)	6.22×10^{-1}	1.30	0.9962	2.92×10^{-1}	2.42	0.9893

Figure 1: Photodegradation kinetics of BDE-47 in hexane containing different content of DiOP
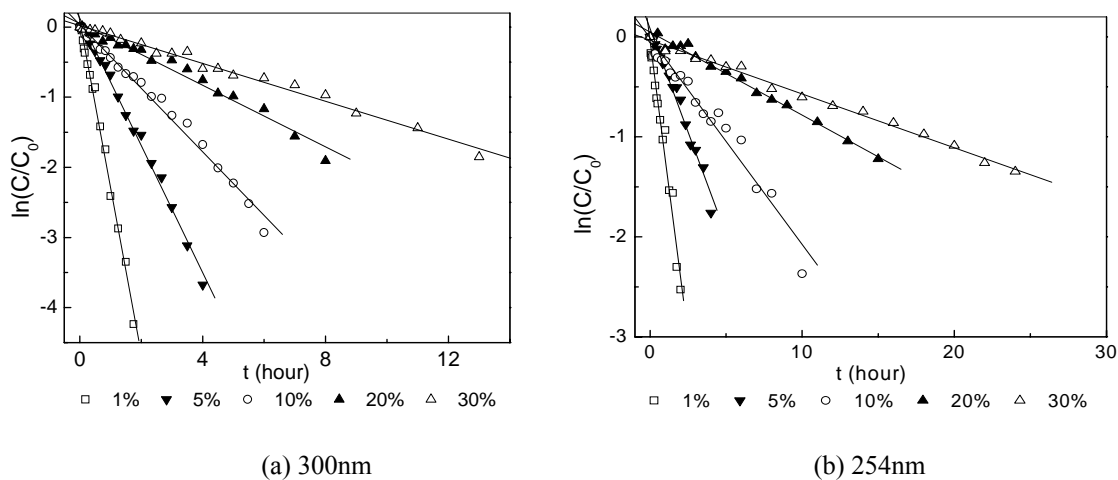

(a) 300nm

(b) 254nm

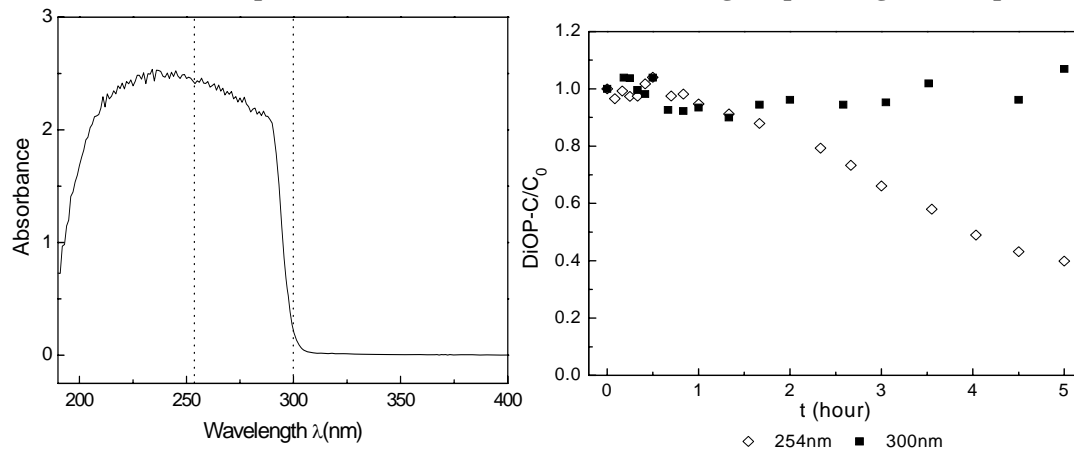**Figure 2: UV absorbance spectrum and the variation of DiOP during the photodegradation process**

Figure 3: Photodegradation kinetics of BDE-47 in hexane containing DiOP and aerosol components

(a) 300nm

(b) 254nm