

PHOTOLYSIS OF 2, 2', 4, 4'-TETRABROMODIPHENYL ETHER IN MICELLAR SOLUTIONS OF NONIONIC SURFACTANTS

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Introduction

High level of polybrominated diphenyl ethers (PBDEs) contamination caused by illegal and unsafe recycling operation of electronic wastes (e-wastes) in China has aroused great concern in recent years¹⁻⁴. As an extensively used flame retardant applied in electrical and electric products, PBDEs are physically added rather than covalently bound to the materials⁵, and thus readily released into the environment through the crude disposal activities. Up to 3570 ng/g,dw of PBDEs has been found in soil samples collected from contaminated sites at Guiyu of China, which was 950 times higher than the concentration of local control sample³ and 8 times higher than the level in soil sample from electronic industrial site in other country⁶. Surfactants remediation technology has been suggested to be promising for the remediation of hydrophobic organic compounds contaminated soils^{7,8}, and destructive process as photolysis of arylhalide contaminants in surfactant solutions has proved to be fast and effective, as well as facilitating the reuse of the washing solution⁹⁻¹¹. In this paper, photodegradation of 2, 2', 4, 4'-tetraBDE (BDE-47), one of the most frequently found PBDE congeners in contaminated soil, in micellar solutions of three nonionic surfactants were investigated.

Materials and methods

Different concentrations of 2, 2', 4, 4'-tetraBDE ranging from 4.1 to 40 $\mu\text{g L}^{-1}$ were prepared in de-ionized water (pretreated by a 0.22 μm Millipak membrane fitted in a Milli-Q water purification system, France), hexane (Dima, USA), and 2 g L^{-1} surfactant solution of Brij 35 (Amresco, USA), Brij 58 (Sigma, USA) and Tween 80 (Beijing Yili Fine Chemical Co., Ltd., China). All the surfactants were used without further purification, and the physical and chemical characteristics of those surfactants were listed in Table 1. 50 mL of each solution were introduced into a quartz tube (32 mm \times 15 cm) outfitted with a ground stopper, and then irradiated by a RPR-2537 \AA lamp (254nm dominate) in a RPR-200 Rayonet photochemical reactor (Southern New England Ultraviolet, USA). An aliquot was removed from the solution at specified times. 2, 2', 4, 4'-tetraBDE and its photoproducts in hexane were analyzed directly; while for samples containing surfactants, 1 mL of solution were drawn exactly with a graduated pipette, then extracted with 6 mL hexane, and finally concentrated to 1 mL under a gentle stream of high purity nitrogen in a water bath at 40 $^{\circ}\text{C}$. PBDE congeners were separated on a 30 m \times 0.32 mm \times 0.25 μm HP-5 column installed on GC-ECD (Agilent 6890 plus), and further identified and quantified by comparing retention times and peak areas with PBDE standards (AccuStandard EO-5099); the temperature program was: 60 $^{\circ}\text{C}$, hold 2 min, rate 25 $^{\circ}\text{C min}^{-1}$ to 110 $^{\circ}\text{C}$, hold 2 min, rate 8 $^{\circ}\text{C min}^{-1}$ to 140 $^{\circ}\text{C}$, hold 4 min, rate 2 $^{\circ}\text{C min}^{-1}$ to 180 $^{\circ}\text{C}$, hold 1 min, rate 2 $^{\circ}\text{C min}^{-1}$ to temperature of 240 $^{\circ}\text{C}$, hold 5 min, and rate 2 $^{\circ}\text{C min}^{-1}$ to a final temperature of 280 $^{\circ}\text{C}$, hold 15min. 2 μL splitless injections were performed when the inlet temperature was 280 $^{\circ}\text{C}$. The temperature of detector was 280 $^{\circ}\text{C}$. Moreover, as being concentrated to the volume of approximate 100 μL , samples underwent further analysis for products confirmation by GC-MS (Thermo Finnigan TRACE DSQ) using a 30 m \times 0.25 mm \times 0.25 μm DB-5 MS column. The injector parameters and oven program were the same as above except for the inject volume of 5 μL . The temperatures of ion source and transfer line were 250 and 280 $^{\circ}\text{C}$, respectively. The EI mass spectra were recorded in full scan mode with the m/z ranging from 60 to 500, and SIM mode by measuring molecular fragment ions. The possible PBDEs photolysis products in samples were tentatively identified with the mass spectra reported in a previous study¹⁴. UV absorption spectra of 2g/L surfactant solutions were obtained on DR 5000 (Hach, USA), ranging from the wavelength of 200 to 300 nm (1 nm step size) at ambient temperature.

Results and discussions

Photodegradation of 2,2',4,4'-tetraBDE with time under UV irradiation in individual solutions was presented in

Figure 1 (a). The photodecay of 2,2',4,4'-tetraBDE within three nonionic surfactants, de-ionized water, and hexane all well followed pseudo-first-order kinetics (r^2 ranging from 0.968 to 0.999). The photolysis rates increased from $2.92 \times 10^{-2} \text{ min}^{-1}$ in pure water without surfactants to 4.44×10^{-2} and $4.93 \times 10^{-2} \text{ min}^{-1}$ in the presence of Brij 58 and Brij 35. Such enhancement in the presence of Brij 35 and Brij 58 might be explained as the micelles provided by the surfactants can both supply nonaqueous conditions and act as the hydrogen sources for the photodebromination reaction. As no typical hydrogen sources were added, the possible hydrogen sources attributing to the acceleration of photolysis reaction were supposed to be the surfactants themselves, which was consistent with the previous results obtained from the photodechlorination of polychlorobenzene congeners and DDT irradiated at 253.7 nm in Brij 58 and Brij 35^{9, 15}. According to the surfactant concentration in the experiment, 2,2',4,4'-tetraBDE were all virtually solubilized in the micelles; in addition, photodecay of 2,2',4,4'-tetraBDE in organic solvent of hexane was similar to that in Brij 35 as presented in **Figure 2**, suggesting the comparable hydrophobic conditions provided by the micelles. On the other hand, photodebromination of 2,2',4,4'-tetraBDE has been significantly hindered in the presence of Tween 80, which was probably due to the strong absorption of the surfactant solution to the light source at 253.7 nm as shown in **Figure 3**, therefore reducing the incident light intensity.

A representative decay of 2,2',4,4'-tetraBDE along with the variation of its photodecomposition products, in micellar solution of 2 g L^{-1} of Brij 35, was shown in **Figure 4**. Main photolysis products of 2,2',4,4'-tetraBDE were found to be mono- to tri-BDEs, which indicated that the main overall reaction occurring in surfactant solutions was photoreduction, specifically resulting in a consecutive loss of bromine atoms. 2,2',4-BDE and 2,4,4'-triBDE were obtained as tri-BDE photoproducts, in which 2,4,4'-triBDE was absolutely dominant over the other. 4,4'-diBDE was identified as the main di-BDE photoproducts, followed by 2,4'-diBDE; a third di-BDE product was also observed, and might be either 2,2'-diBDE or 2,4-diBDE due to the co-eluting of the two congeners. After 70 min of irradiation, 4-BDE was predominant in the solution as the debrominated product, with trace amounts of 2-BDE. As a result, the photolysis products profile in the experiment indicated that photodebromination of 2,2',4,4'-tetraBDE and its products in Brij 35, Brij 58 and Tween 80 was readily occurred on the *ortho* position, that is the bromine atoms at the *ortho* position of the PBDE congeners showed relatively higher reactivity than those at *para* positions, which was in agreement with a recent study on the photolysis of 2,4,4'-BDE and 2,2',4,4'-BDE in hexane irradiated by a 500 W mercury lamp¹⁶.

The mole balance has been calculated for the photodegradation of 2,2',4,4'-BDE in Brij 35, and the total PBDEs obtained in the solution after a 10 min irradiation was more than ninety percent of the initial 2,2',4,4'-BDE. However, the sum of PBDEs decreased to be around sixty and thirty percent of the initial 2,2',4,4'-BDE in the 60 min and 90 min irradiated solutions, respectively. This fact gave evidence of the existence of other minor pathways during the photolysis. Actually besides the debrominated products, tri-BDF and di-BDF were also found after 20 min irradiation, and mono-BDF was further found after 60 min irradiation in both Brij 35 and Brij 58. The possible photolysis pathways of 2,2',4,4'-BDE was demonstrated in **Figure 5**.

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Table 1 Physical and chemical characteristics of Brij 35, Brij 58, and Tween 80

Name	Chemical formula and/or name	Formula weight ^a	CMC ^b (mg L ⁻¹)	N _{aggr} ^c
Brij 35	C ₁₂ H ₂₅ (OCH ₂ CH ₂) ₂₃ OH, polyoxyethylene (23) lauryl ether	1198	51.51 ^d 190.48 ^e	40 ^d
Brij 58	C ₁₆ H ₃₃ (OCH ₂ CH ₂) ₂₃ OH, polyoxyethylene (20) cetyl ether	1124	89.92 ^a	70 ^e
Tween 80	polyoxyethylene (20) sorbitan monooleate	1310	12.97 ^d ; 65.65 ^f	58 ^f

^a Provided by the supplier; ^b CMC: critical micellar concentration; ^c N_{aggr}, aggregation number, i.e., average number of surfactant molecules per micelle; ^d reference 9; ^e reference 12; ^f reference 13.

Fig. 1 Photodebromination of 2,2',4,4'-tetraBDE in de-ionized water, hexane, and solutions containing 2g/L surfactants (a); first order decay of 2,2',4,4'-tetraBDE in all solutions irradiated at 253.7 nm (b).

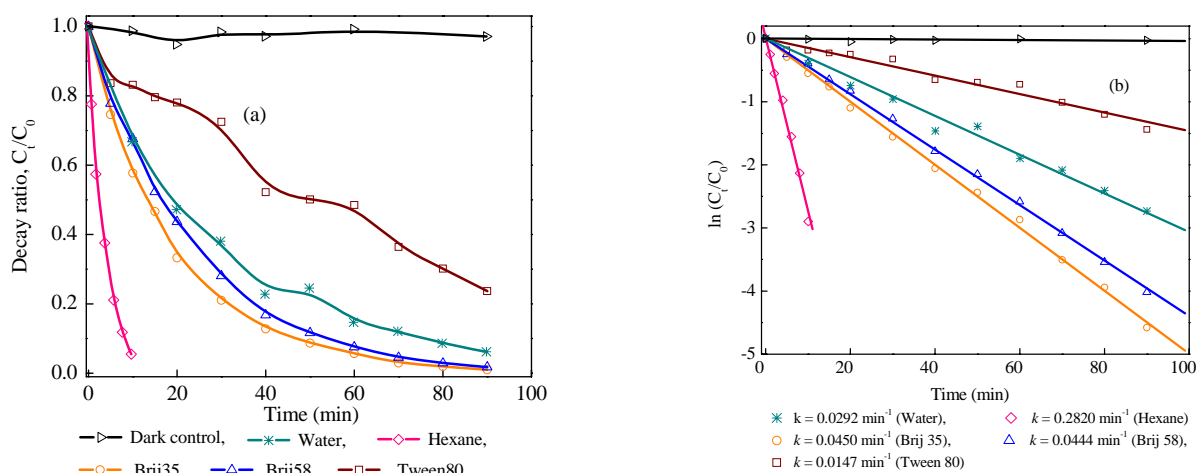


Fig.2 Photodebromination of BDE-47 and its photodegradation products TriBDE in solution containing Brij 35 (solid symbol, solid line), and hexane (open symbol, dash dot line).

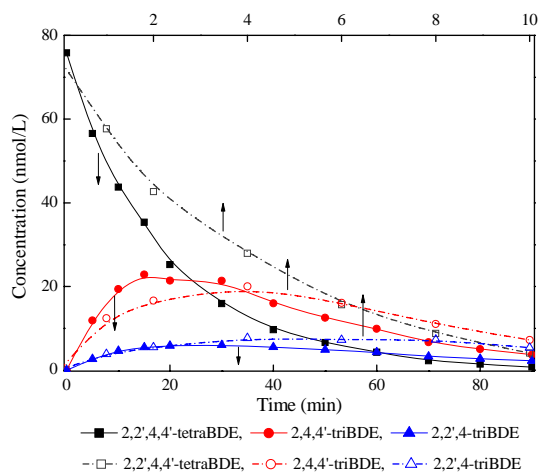


Fig.3 UV absorption spectra of various surfactant solutions at the concentration of 2g/L.

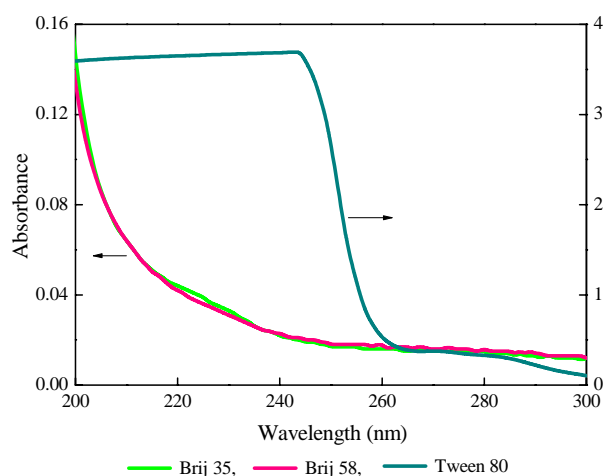


Fig.4 Photodebromination of BDE-47 and its photodegradation homologues (mono- to tri-BDEs) in micellar solutions of 2g/L nonionic surfactant Brij 35 (Lines only indicate trends in the data).

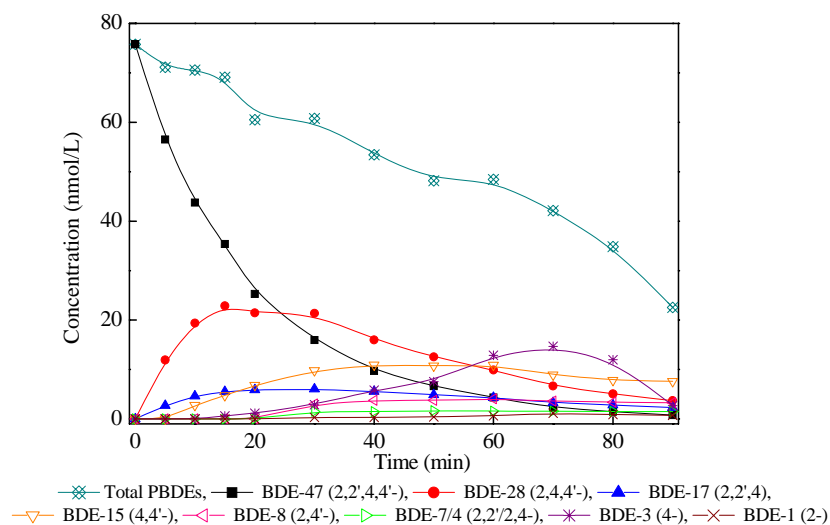


Fig.5 Proposed photodegradation pathways of 2,2',4,4'-BDE in Brij 35 (→ major photolysis products, → minor photolysis products, possible photolysis products).

