Effect of Decabromodiphenyl Ether on Free Radicals in the Degradation of P-nitrophenol under Ultraviolet Light

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Abstract. Polybrominated diphenyl ether as an additive bromine flame retardant is widely used in industrial products, due to its strong fat-soluble and biological accumulating, it is a new type of ecological risk of environmental organic pollutants, and thus, resulted in more and more serious and widespread pollution. In view of the increasingly severe environmental conditions, this paper selected decabromodiphenyl ether (Deca-BDE) as the research object, based on the limited research data, taking its flame retardant mechanism as the starting point, and preliminarily discussed how the photodegradation of organic pollutants when Deca-BDE coexisted with other organic pollutants was affected by Deca-BDE. The experimental results show that, when ten Deca-BDE coexist with organic pollutants, the signal strength of organic pollutants photodegradation produce free radicals decreases, the preliminary judgment is Deca-BDE have a shielding effect on free radical signal, or Deca-BDE curbed the photodegradation of organic pollutants, lead to degradation of intermediate reduction, to detect the radical signal intensity weaken. Of course, there are still many areas for improvement and improvement in this study, which need to be proved by further research methods. This study is expected to provide guidance for the scientific classification and treatment of organic pollutants.

1. Introduction
Since the 1970s, polybrominated diphenyl ether (PBDEs) as an additive flame retardant has been widely used in plastics, textiles and commercial purposes [1], such as bubble which has strong biological chemicals, toxicity and environmental stability. PBDEs has a certain volatility, can be dissipated into the air, with long distance migration of the atmosphere [2]. At the same time, PBDEs has strong lipophilicity and stable chemical properties, which can be enriched and amplified along with the organisms in the food chain [3]. Recent studies have confirmed that this toxic bromide can interfere with thyroid hormones and interfere with the normal development of the brain and central nervous system in humans and animals [4].

Although the potential harm of PBDEs has been recognized, only a few countries have banned or restricted the use of brominated flame retardants so far due to the good performance of brominated flame retardants [5] and the difficulty in finding substitutes. Most of the newly developed organic flame retardants at home and abroad are still based on bromide [6], the amount of which has been very large [7]. It is estimated that the world demand for PBDES reached 67,400 tons in 2001 [8]. Under this premise, brominated flame retardants will not only be used for a long time in the world, especially in
developing countries, but also maintain a considerable growth rate [9]. According to the relevant monitoring data, the distribution range of PBDEs is almost all over the world, and the subsequent use and treatment of products containing these compounds have caused extensive environmental pollution, and the concentration in the environment shows a growing trend [10], which brings a series of environmental problems. PBDEs was first detected in barracuda, eel and sea trout in Sweden in 1981, and then detected in Marine fish, mussels and sediment [11]. Since then, PBDEs has been continuously reported to be detected in air, water and human body [12]. At present, PBDEs has been regarded as a ubiquitous [13] environmental pollutant [14], and the research on its environmental problems has become a hotspot in current environmental science.

In this paper, the degradation rate of organic pollutants and the changes of free radicals generated during the degradation process were studied when PBDEs coexisted with other organic pollutants. P-Nitrophenol (PNP) was selected as the organic pollutant in the experiment. This study is expected to provide guidance for the scientific classification and treatment of organic pollutants.

2. Materials and methods

2.1. Materials used
Silica powder (1.5 micron, 99.9%, USA), p-nitrophenol (PNP, analytical pure, Shanghai Aladdin Biochemical Technology Co., LTD.), Decabromo diphenyl (Deca-BDE, 98%, Shanghai Aladdin Biochemical Technology Co., LTD.).

2.2. Experimental instruments used
Electron paramagnetic resonance spectrometer (BRUKER A300, Germany), high performance liquid chromatograph (Agilent Technologies 1200 Series, America), high-intensity long-wave ultraviolet lamp (Labino MPXL UV), ultraviolet spectrophotometer (SHIMADZU CORPORATION uv-2600, Japan).

2.3. Experimental procedures
The experimental equipments are shown in the figure 1. For the first group of samples: 25mg, 50mg and 100mg of PNP and 100mg of silica powder were respectively weighed and mixed in the mortar. PNP was loaded onto silica powder particles through grinding. The second group of samples: the concentration was the same as that of the first group, except that 100mg Deca-BDE was added to each sample before loading, and then the mixture of PNP and Deca-BDE was loaded onto silica powder particles through grinding.

The samples were placed in a glass culture dish with a diameter of 9cm to ensure that the samples were spread out as thinly as possible and evenly distributed in the culture dish. Then the petri dish was placed on the circular rotating base, as shown in the figure. The UV lamp was placed 20cm above the circular base, and the rotating switch of the base was opened to ensure even illumination. The dark control group was placed in the same petri dish in the dark. After a certain period of illumination, appropriate samples were taken for analysis.
2.4. Analytical methods

P-nitrophenol and its degradation intermediates were determined by Agilent Technologies 1200 Series HPLC. Operating conditions: Luna 5μ C18 chromatographic column, 4.6mm X 250mm, mobile phase V (methanol) /V (water) =40/60, flow rate 1.0ml/min, injection volume 20μl [15]. The ultraviolet absorption spectra of PNP were obtained by using the ultraviolet spectrophotometer, as shown in figure 2, and the maximum ultraviolet absorption wavelength of PNP is 318nm [16]. The free radical signal intensity of the sample after illumination was measured by EPR [17], and then the mass standardization was carried out to obtain the final free radical signal intensity [18, 19].

3. Result and discussion

The variation trend of signal intensity of free radicals

In the petri dish illumination system, the samples were divided into two groups. One group was silicon dioxide particles loaded with PNP, and the other group was silicon dioxide particles loaded with Deca-BDE and PNP mixture. There were three concentrations of PNP in each group.

Figure 2. Ultraviolet absorption spectra of PNP

Figure 3. Trend of signal intensity in petri dish. In the figure, the hollow legends represent the sample without Deca-BDE added, while the solid legends represent the sample with Deca-BDE added. In the first group, PNP/SiO2 are 25/100, 50/100 and 100/100, respectively. In the second group, PNP/SiO2/Deca-BDE are 25/100/100, 50/100/100 and 100/100/100.
Samples were taken at 0h, 5h, 10h and 22h, respectively, with the duration of illumination. The variation trend of free radical signal strength of the measured samples was shown in the figure after quality standardization. No free radical signal was detected by silica particles or Deca-BDE under UV illumination or without UV illumination. It can be seen from the figure3 that when Deca-BDE was added to the reaction system, the intensity of free radical signal decreased as a whole compared with the other group of samples. Among the samples with the highest concentration of PNP3, the intensity of free radical signal decreased by 45% after Deca-BDE was added. At the same time, dark reactions were performed under the same conditions, and no EPR signals were detected. Thus, it can be concluded that PNP can only generate free radical signals under light conditions.

It can also be seen from the figure3 that the signal intensity of free radicals in all samples increases with the extension of light time. Thus, it can be speculated that PNP is degraded under ultraviolet light [20], with the progress of PNP photodegradation, a large number of degradation intermediates are continuously produced, and free radical signals are also generated along with this process. As for which kind of intermediate produces free radical signals, further analysis of PNP degradation products is required.

Figure 4. EPR spectra of each sample were obtained after 22h exposure to ultraviolet light. a, b and c represent the first group of samples, and d, e and f represent the second group of samples.
4. Conclusion

PNP is degraded under ultraviolet light after loading onto silica particles, and it can generate EPR signal. With the increase of illumination time, the signal strength increases gradually. It can be inferred that the detected free radical signal originates from the degradation intermediate of PNP.

When Deca-BDE was added to the system, the signal intensity of free radicals was decreased. There are two reasons for this phenomenon. One is that Deca-BDE has a certain shielding effect on the free radical signal generated by PNP. Second, Deca-BDE has an inhibitory effect on the photodegradation of PNP, which leads to the reduction of the degradation intermediates of PNP, so the signal strength of free radicals generated is weakened.

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