



# Effects analysis of substituent characteristics and solvents on the photodegradation of polybrominated diphenyl ethers



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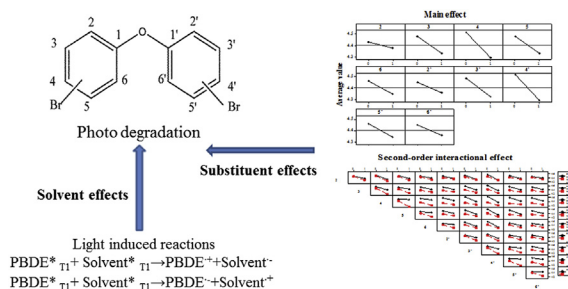
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## HIGHLIGHTS

- Photodegradation tendencies of polybrominated diphenyl ethers (PBDEs) were analysed.
- The effects of each substituent position on photodegradation of PBDEs were studied.
- Full factorial experimental design was used to study substituent characteristics.
- The effect of solvents on the photodegradation of PBDEs was analysed.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The ultraviolet spectra and electron transition information of 209 polybrominated diphenyl ethers (PBDEs) in gas were first calculated via time-dependent density functional theory using Gaussian 09 software. The main and second-order interactional effects of substituent characteristics on the photodegradation of PBDEs were then analysed using a full factorial experimental design. Solvent effects were considered to research the effect and promotion mechanism of solvent molecules on the photodegradation of PBDEs compared with that in gas. The results showed that the introduction of substituents at each position promoted excitation of PBDEs from their ground states to excited states to induce photodegradation. The different positions affected the photodegradation of PBDEs with magnitudes of *para* > *meta* > *ortho*. The congeners with a concentrated distribution of substituents can always be photodegraded more easily than those with separated substituents. From the viewpoint of light-induced reactions, the electron transfer reactions between molecules of PBDE\* T1 and Solvent\* T1 are the main driving force for the enhanced photodegradation of PBDEs in solvents compared with that in gas.

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## 1. Introduction

Polybrominated diphenyl ethers (PBDEs), a typical group of persistent organic pollutants (POPs), contain a total of 209 kinds of

congeners with different numbers of Br atoms and substituent positions (Crosse et al., 2012; Kim et al., 2015). A large amount of literature showed that PBDEs have distributed in various environmental media, and can cause non-negligible harm to humans and other organisms because of their high enrichment, environmental stability and difficult removal (Lyche et al., 2012; Rigét et al., 2013). The degree of difficulty of photodegradation of PBDEs can be used

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to assess their persistence in the environment. That means congeners that are more easily degraded by light or catalysis possess a weaker environmental persistence than those that are more difficult to degrade (Bastos and Eriksson, 2008). Meanwhile, through the analysis of photo degradation products, the environmental risk of PBDEs can be assessed systematically from the viewpoint of secondary pollutants. The fate of PBDEs in the environment provides a theoretical basis to control PBDEs (Daniels, 2011).

Photodegradation is a very important pathway to eliminate PBDEs in gas and water (Raff and Hites, 2006). Photochemical reactions of PBDEs in solvent follow pseudo-first-order kinetics (Eriksson et al., 2004; Fang et al., 2008). Although the molecular structures of the 209 PBDEs are very similar, their degradation abilities after ultraviolet (UV) irradiation are significantly different because they are influenced by the PBDE substitution pattern (Grabda et al., 2007; Oslman et al., 2006). However, previous studies on the influence of substituent characteristics on the photodegradation of PBDEs have not been systematic and universal enough. The interactional effect between different substituent characteristics has not been considered, and there are also some ambiguous conclusions about the effects of substituents on the photodegradation of PBDEs (Christiansson et al., 2009; Fang et al., 2008; Xiong et al., 2015). The photodegradation rates of PBDEs generally decrease with the number of bromine substituents, but there are many exceptions, and their corresponding behaviours have been expounded from different substituent characteristics in previous studies. For example, Fang et al. (2008) reported that brominated phenyl rings with a 2,4,6 substitution pattern make PBDEs more stable and difficult to photodegrade, while Eriksson et al. (2004) stated that the distribution asymmetry was main reason for the variable photodegradation rates of PBDEs. It has been reported that the photodegradation differences between higher brominated PBDEs are small because of their more complicated molecular structures. Thus, it was more important for the bromine substituted pattern to account for the effect on the photodegradation.

Full factorial experimental design, an important statistical method to assess the intensities of the major effects (single factor) and combined effects (interactional effects) on the target detection of each experimental factor, has been validated by the Environmental Protection Agency (Svensgaard and Hertzberg, 1994). Using a full factorial experimental design provides a new approach to explore the essential effects between different substituent positions on the POP properties of PBDEs, and has been successfully used to analyse the effect of substituent characteristics on the typical properties of PBDEs and polychlorinated biphenyls (Jiang and Li, 2015, 2016).

Regarding the first photochemical law, the ability to absorb UV light is necessary for the occurrence of the photochemical reactions of PBDEs under natural light irradiation. The UV spectrum of natural light is distributed in the range of 110–380 nm. Biphenyl substances often display two main UV absorption peaks (Bunce, 1982): the first is located at a wavelength of 202 nm with a molar extinction coefficient  $\epsilon$  of 44000, which is named the main band. The second adsorption peak is located at 242 nm ( $\epsilon$  of 17000), which is named the  $\kappa$  band.

Many studies have revealed that even a slight change of a structural or environmental parameter can result in marked changes of the photodegradation behaviour of PBDEs (Fasnacht and Blough, 2003; Luo et al., 2015; Park et al., 2000). The complex composition or a slight change of the environment medium makes detailed analysis more difficult to carry out via chemical experiments alone. However, quantum chemical calculations provide a micro perspective to analyse imperceptible changes (Gupta et al., 2013; Luo et al., 2015). Meanwhile, organic solvents have been

successfully used to simulate environmental media to explore the photochemical behaviour of organic compounds. For example, methanol and acetone can be used to replace plant epidermal components (Katagi, 2004); acetonitrile can be used to study the photoproduction mechanism of protons in the quenching of excited arenes (Kai et al., 1992); dimethyl sulfoxide (DMSO) can be used in experiments on biological systems (Mallakin et al., 1999). These organic solvents have different optical absorptivity, so they have been used to simulate different environmental media to determine the effects of solvent on the electron transition during photodegradation of PBDEs (Fang et al., 2009; Feilberg and Nielson, 2000; Shao et al., 2013). The aim of this paper is to research the effect of substituent characteristics on the photodegradation behaviour of PBDEs and analyse the mechanism of the effect of solvent on the photodegradation of PBDEs via theoretical calculations.

## 2. Methods and data

### 2.1. Quantum chemical calculation

The optimal structures of 209 PBDEs in the ground state were first calculated at the B3LYP/6-31 + g(d) level of theory via the density functional theory (DFT). Then, the UV spectra of the 209 PBDEs were calculated at the B3LYP/6-311++g(d, p) level using the time-dependent density functional theory (TD-DFT), which gave the first excitation wavelength ( $\lambda$ , nm), first excited state transition energy (eV) and oscillator strength ( $f$ , units). The quantum chemical calculations were constructed in Gauss view 5.0 and then submitted to the Gaussian 09 package for calculation (Frisch et al., 2009).

Previous research on the photodegradation of PBDEs in solvents has mainly used DMSO, tetrahydrofuran (THF), acetonitrile, chloroform, acetone, methanol, ethanol and hexane (Fang et al., 2009; Katagi, 2004; Mallakin et al., 1999). Therefore, we selected these eight organic solvents to analyse the effect of solvent on the photodegradation of PBDEs via theoretical calculations. BDE-15 and BDE-47 were selected as typical PBDEs because of their wide distribution in each medium and environmental refractory (Gregoraszczyk et al., 2016; Qiu et al., 2010; Wang et al., 2015). Theoretical calculations based on a self-consistent reaction field (SCRf) have been proved a reliable approach to understand the influence of solvents on other materials in terms of their microscopic structures (Greco et al., 2001; Xie et al., 2009). The polarisable continuum model (PCM), one of the most widely used SCRf models, has been used to study the effects of solvents on electronic structure and other properties, and the theoretical values calculated by the PCM were very similar to experimental values (Gramatica, 2007; Meng et al., 2007). The UV spectra of BDE-15 and BDE-47 in the eight different organic solvents were calculated via the PCM at the B3LYP/6-311++g(d, p) level of theory to analyse the effects of solvent on the photodegradation of PBDEs.

### 2.2. Full factorial experimental design

Ten substituent positions of PBDEs were used as factors in the full factorial experimental design, and the number of Br atoms at each position was taken as the level. Then, the final full factorial experimental design was established with ten factors (*ortho*-2, A; *meta*-3, B; *para*-4, C; *meta*-5, D; *ortho*-6, E; *ortho*-2', F; *meta*-3', G; *para*-4', H; *meta*-5', J; *ortho*-6', K) and two levels (0, 1) using Minitab software with a resolution of V (Table A.1 in the Supplementary Materials). The number of each position is shown in Fig. 1. Before the effect analysis, the fixed effect model in Minitab software was used to validate the suitability of calculated data to the established full factorial experimental design from views of normality assumption, independence assumption and homogeneity

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