QUANTITATIVE STRUCTURE-PROPERTY RELATIONSHIPS FOR DIRECT PHOTODEGRADATION OF POLYBROMINATED DIPHENYL ETHERS

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Abstract

The direct photodegradation of 16 individual polybrominated diphenyl ethers (PBDEs) substituted with 1-7 bromine atoms was investigated in *n*-hexane using a Rayonet photochemical reactor equipped with two lamps (λ_{max}=300nm). The results indicate that photodegradation of PBDEs follows pseudo-first-order reaction kinetics, with photodegradation rate constants ranging between 6.72×10^{-4} s^{-1} for BDE3 and 1.11×10^{-2} s^{-1} for BDE153. Based on the determined photodegradation rate constants, quantitative structure-property relationships (QSPR) models were developed by partial least squares (PLS) method and 15 fundamental quantum chemical descriptors computed by PM3 Hamiltonian. The QSPR model suggests that the photodegradation rates of PBDEs increase with the increase of molecular weight (M_W), largest positive atomic charge on a bromine atom (Q_{Br+}), most positive net atomic charge on a hydrogen atom (Q_{H+}), largest negative atomic charge on a carbon atom (Q_{C-}) and largest negative atomic charge on a oxygen atom (Q_{O-}) values, or the decrease of total energy (*TE*) and energy of the second highest occupied molecular orbital (E_{HOMO-1}) values.

Introduction

Polybrominated diphenyl ethers (PBDEs) have been extensively used in a range of applications including plastics, electronics and textiles as flame retardants. Recently, concern about the risks of PBDEs has increased due to their global distribution, toxicity, persistence and potential for bioaccumulation[1-3]. However, very limited information is available regarding their environmental transformation and degradation. Direct photolysis appears to be an important transformation process for PBDEs[4]. Several studies on the photodegradation of PBDEs have been reported using different light sources, matrices and PBDE congeners[5-9]. Previous studies mostly focused on decaBDE[6-8], which indicate that reductive debromination is the dominant photolysis mechanism[5-7]. Different matrices affect the photolysis rate of PBDEs strongly but have little effect on the products[6].

Photolysis rate is a key parameter characterizing the kinetic properties of photochemical reaction. However, direct photolysis rate constant data for PBDEs are rather scarce, especially for lower brominated congeners, because of large expenditures of money, time and equipments. As the alternative approach, quantitative structure-property relationship (QSPR) model can be developed for photolysis rate constants of PBDEs from their molecular structural descriptors, which may generate predicted photolysis process data efficiently[10-11]. The objective of this study is to determine photolysis rate constants of 16 representative PBDE congeners in hexane under UV irradiation (λ_{max}=300nm), then develop QSPR predictive model by partial least squares (PLS) regression and find dominant factors of photodegradation of PBDEs in hexane.

Materials and Methods

Sixteen individual PBDE congeners substituted with 1-7 bromine atoms at 50 mg/L each in isooctane were 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). Emission wavelength of the lamp ranged from about 250 to 350 nm, with a maximum intensity at 300 nm. Cylindrical quartz vessel containing 30mL hexane solution of 20μg/L individual PBDE congener was placed at the centre of reactor chamber. All experiments were performed at room temperature, with corresponding dark control tests conducted.

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 as follows: initial temperature hold at 80 ℃ for 2 min, increased to 200 ℃ at a rate of 20 ℃/min and hold for 2 min, then increased to 280 ℃ at a rate of 5 ℃/min, and hold for 15 min. Agilent ChemStation software was used for the quantification.

Quantum chemical descriptors were obtained by PM3 Hamiltonian contained in MOPAC 2000, which was implemented in Chem3D Ultra (Ver.9.0, CambridgeSoft). In this study, a total of 15 MOPAC derived descriptors were used in this study, reflecting the overall characters of the PBDE molecules (Table 1). Additionally, three combinations of frontier molecular orbital energies, E_{LuMO}-E_{HOMO}, $(E_{\mathrm{LuMO}}\text{-}\mathrm{E}_{\mathrm{HOMO}})^2$ and E_{LuMO}+E_{HOMO}, which were proven to be significant in previous photolysis QSPR studies of recalcitrant organic pollutants[10-12], were selected as independent variables.

Simca software (Simca-S Version 6.0, Umetri AB and Erisoft AB) was used to develop QSPR model by PLS analysis. The criterion used to determine the model dimensionality is cross validation (CV). The obtained QSPR model is considered to have a good predictive ability when the cumulative cross-validated regression coefficient (Q^2) for the extracted components, Q^2_{cum}, is higher than 0.5. Model adequacy was mainly measured as the number of PLS principal components (k), Q^2_{cum}, the correlation coefficient between observed values and fitted values (R), and the significance level (p).

Table 1 List of molecular structural descriptors

Symbols	Description
M_{W}	Molecular weight
ΔH_{f}	Standard heat of formation
TE	Total energy
EE	Electronic energy
CCR	Core-core repulsion energy
E_{HOMO}	The energy of the highest occupied molecular orbital
$E_{\mathrm{HOMO-1}}$	The energy of the second highest occupied molecular orbital
E_{LUMO}	The energy of the lowest unoccupied molecular orbital
$E_{\mathrm{LUMO+1}}$	The energy of the second lowest unoccupied molecular orbital
Q_{Br}^{+}	The largest positive atomic charge on a bromine atom
Q_{H}^{+}	The most positive net atomic charges on a hydrogen atom
Q_{C}^{-}	The largest negative atomic charge on a carbon atom
Q_{O}^{-}	The largest negative atomic charge on a oxygen atom
μ	Dipole moment
α	Average molecular polarizability

Results and Discussion

Photodegradation rates. Direct photodegradation of all 16 individual PBDE congeners in hexane under 300 nm UV lamps is fitted for pseudo first-order kinetics, which is in agreement with the photolysis of PBDE congeners in methanol/water (8:2) mixtures and pure methanol[5]. The photodegradation rate constants of PBDE congeners in the present study were shown in Fig.1. The observed rate difference is up to 16 fold between the slowest photolysis PBDE congener (BDE 3) and the fastest one (BDE 153) in this study. Generally, higher brominated diphenyl ethers degraded faster than the lower brominated congeners, which is similar to the results of previous study[5]. The number of bromine atoms in PBDE congener seems to be an important factor for their photodegradation rates. However, this trend seems not suitable for some congeners like BDE 52, BDE 100 and

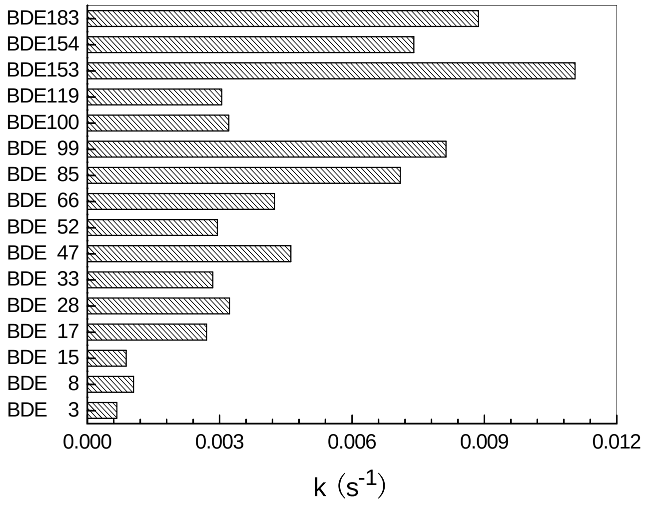

Fig.1 Photodegradation rate constants (s^{-1}) of 16 PBDE congeners in hexane (λ_{max}=300 nm)

BDE 119. Possible explanation is that BDE 52 has a symmetrical bromine substitute structure, while BDE 100 and BDE 119 both have one specific brominated phenyl ring with 2,4,6 substitution pattern. Hence, the photoreactivity of PBDE congeners is also affected by the positions of substituted bromine.

QSPR models. Variable importance in the projection (*VIP*) is a parameter in PLS analysis that shows the importance of a variable in a PLS model. Based on some fundamental quantum chemical descriptors computed by PM3 Hamiltonian, QSPR model for photodegradation rate constants of PBDEs in hexane under 300nm UV lamps was developed by PLS regression. Previous studies found that not all predictor variables were necessary for PLS modeling[10-12]. The optimal model, selected by the statistics Q^2_{cum}, R and p, was obtained through stepwise culling the variable with the smallest *VIP* value out. Following the analysis methods described above, model (1) was obtained as the primary model, while model (2) was obtained as the final model. The fitting results are listed in Table 2. $R^2_{\text{X(adj)(cum)}}$ and $R^2_{\text{Y(adj)(cum)}}$ stand for cumulative variance of all the *X*'s and *Y*'s, respectively, explained by all extracted components, *Eig* stands for the eigenvalue which denotes the importance of the PLS principal components. Plots of observed and predicted values for the two models are shown in Fig.2-3.

Model (1):

$$\log k_p\left(hexane\right)=$$

$$-6.2646+2.126\times10^{-4}M_W+3.928\times10^{-4}\Delta H_f-4.96\times10^{-5}TE-8.63\times10^{-6}EE+1.04\times10^{-5}CCR-8.641\times10^{-2}E_{HOMO}$$

$$-0.200E_{HOMO-1}-0.105E_{LOMO}-0.108E_{LOMO+1}+1.055Q_{Br+}+3.784Q_{H+}+1.066Q_{C-}+1.443Q_{O-}-7.398\times10^{-3}\mu$$

$$+1.426\times10^{-3}\alpha-6.228\times10^{-2}(E_{LOMO}-E_{HOMO})-3.562\times10^{-3}(E_{LOMO}-E_{HOMO})^2-5.393\times10^{-2}(E_{LOMO}+E_{HOMO})$$

Model (2):

$$\log k_p\left(hexane\right)=$$

$$-9.2275+5.667\times10^{-4}M_W-1.323\times10^{-4}TE-0.533E_{HOMO-1}+2.8126Q_{Br+}+10.091Q_{H+}+2.8432Q_{C-}+3.8465Q_{O-}$$

Table 2 Model fitting results for model (1) and (2)

Model	k	$R^2_{\text{X(cum)}}$	$R^2_{\text{X(adj)(cum)}}$	$R^2_{\text{Y(cum)}}$	$R^2_{\text{Y(adj)(cum)}}$	Eig	Q^2_{cum}	*R*	*p*	*SE*
(1)	1	0.657	0.611	0.833	0.822	10.520	0.796	0.913	8.052×10^{-7}	0.152
(2)	1	0.631	0.539	0.895	0.887	4.418	0.879	0.946	3.172×10^{-8}	0.121

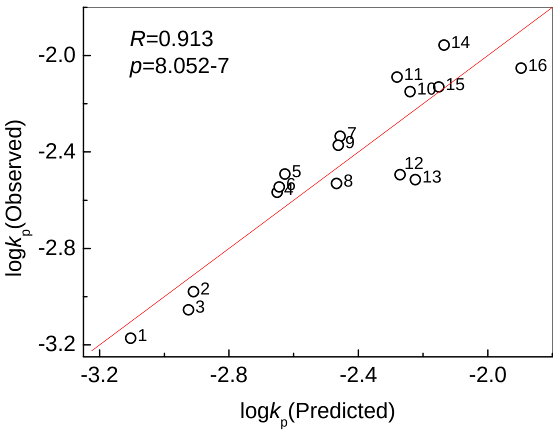

Fig.2 Plots of observed vs. predicted logk_{p} values in model (1)

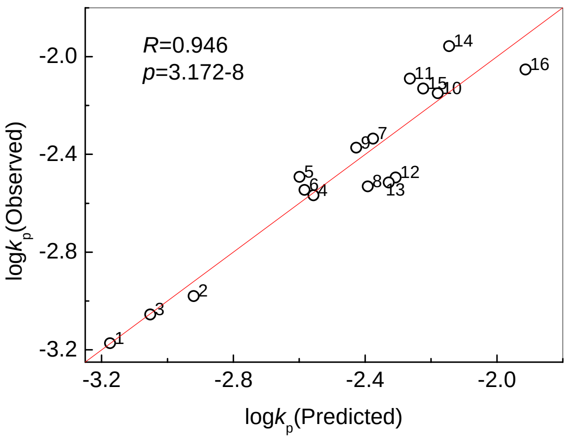

Fig.3 Plots of observed vs. predicted logk_{p} values in model (2)

By comparison of statistics parameters, model (2) is much better than model (1) and other intermediate models. Thus, model (2) is adopted as the optimal QSPR model for photodegradation rate constants of PBDEs in hexane. As shown in Table 2 and Fig. 3, the correlation between observed and predicted $\log k_p$ values of PBDEs in model (2) is significant. As the cross-validated Q^2_{cum} value is remarkably above 0.50, the model (2) is surely stable and has good predictive ability. The results indicated that direct photolysis of PBDEs in hexane is dominant by their molecular structural characteristics.

Table 3 Correlation coefficients between some quantum chemical descriptors of PBDEs in Fig. 1 ($p<0.01$)

	M_w	TE	EE	E_{HOMO-1}	E_{LUMO+1}	Q_{Br+}	Q_{H+}	Q_{C-}	Q_{O-}	α
M_w	1									
TE	-1	1								
EE	-0.997	0.997	1							
E_{HOMO-1}	-0.435	0.435	0.379	1						
E_{LUMO+1}	-0.964	0.964	0.952	0.546	1					
Q_{Br+}	0.870	-0.870	-0.864	-0.418	-0.877	1				
Q_{H+}	0.829	-0.829	-0.812	-0.365	-0.871	0.793	1			
Q_{C-}	0.332	-0.332	-0.356	0.274	-0.301	0.264	0.276	1		
Q_{O-}	0.615	-0.615	-0.606	-0.138	-0.539	0.763	0.612	0.108	1	
α	0.989	-0.989	-0.976	-0.548	-0.963	0.853	0.812	0.223	0.598	1

There are totally seven predictor variables included in model (2). As indicated by the pseudo-regression coefficients, the degradation rate constants of PBDEs increase with the increase of M_W, Q_{Br}^+, Q_H^+, Q_C^- and Q_O^- values , or the decrease of *TE* and E_{HOMO-1} values. The descriptor M_W correlates with *TE* negatively at the 0.01 level, as shown in Table 3. Thus, increasing M_W values of PBDEs leads the increase of $\log k_p$ values. As all the PBDE congeners have the same parent diphenyl ether, it can be concluded that the photodegradation rates increase with the increasing of bromine atoms in the parent molecule. The descriptors E_{HOMO-1} is related to the polarizability, which measures the ability of the electrons in a molecule to move easily as a result of a stimulus[10]. The descriptors, Q_{Br}^+, Q_H^+, Q_C^- and Q_O^-, which are related with the bromine substitution positions of PBDEs, account for the reactive centers of PBDE molecules[11]. Therefore, the results from the QSPR model also reflect that direct photodegradation rate of PBDEs is dependent on both the degree of bromination and the substitution pattern.

Acknowledgements

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