



Photolysis of mono- through deca-chlorinated biphenyls by ultraviolet irradiation in *n*-hexane and quantitative structure-property relationship analysis

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Abstract

The photolysis of 16 polychlorinated biphenyls (PCBs) (including mono- through deca-chlorinated) in *n*-hexane was investigated under ultraviolet irradiation using a 500-W high-pressure mercury lamp. Photolysis of PCBs follows pseudo-first-order reaction kinetics, with photolysis rate constants ranging between 0.0011 s^{-1} for PCB-52 and 0.0574 s^{-1} for PCB-118. The degradation rates of PCBs by high-pressure mercury lamp irradiation were remarkably independent with respect to the degree of chlorination. Furthermore, partial least squares (PLS) models were developed to provide insight into which aspect of the molecular structure influenced PCB photolysis rate constants. It was found that the photolysis rates of PCBs increased with an increase in the net charge on the carbon atom (q_C), $(E_{\text{LUMO}} - E_{\text{HOMO}})^2$, and the *Y*-axis dipole moment (μ_y) values, or the decrease in the energy of the second highest occupied molecular orbital ($E_{\text{HOMO}-1}$), energy of the lowest unoccupied molecular orbital (E_{LUMO}), $E_{\text{LUMO}} + E_{\text{HOMO}}$, $E_{\text{LUMO}} - E_{\text{HOMO}}$, most positive atomic charge (q^+), and the twist angle of the chlorine atom (TA) values.

Key words: Photolysis; polychlorinated biphenyls; *n*-hexane; partial least squares; quantum chemical descriptors

Introduction

Polychlorinated biphenyls (PCBs), widely used as industrial fluids, dielectric fluids, plasticizers, and heat exchangers in the past (Hutzinger *et al.*, 1974; Wong and Wong, 2006), are highly toxic chemicals that have been released into the environment. On account of their lipophilicity, thermal, and chemical stability (Sedlak and Andren, 1991; Halmann *et al.*, 1996), PCBs have become a group of ubiquitous contaminants that occur in the air, sediments, water, fish, and humans (Risebrough *et al.*, 1968; Muir *et al.*, 1996; Helm and Bidleman, 2003; Mai *et al.*, 2005; Naert *et al.*, 2006; Tetttenhorst *et al.*, 2006). Although application of these chemicals has been banned in industrialized countries since the late 1970s, their continued presence in the environment poses considerable hazards to human health (Guo *et al.*, 1997; Houde *et al.*, 2006). Investigations on their transport and transformation have been extensively carried out in recent years.

Photolysis has been identified as an important process for the degradation of PCBs in the environment. Of late, many studies have been carried out on photolysis of PCBs in various solvents and media (Huang *et al.*, 1996; Lores *et al.*, 2002; Manzano *et al.*, 2004; Chu *et al.*, 2005). The photolysis efficiency of PCBs has been found to be affected

by the specific solvent (Wong and Wong, 2006). On account of its reasonable solubility, transparency, and ability as a hydrogen donor (Bezares-Cruz *et al.*, 2004), *n*-Hexane has been adopted in previous studies on PCBs photolysis. Ruzo *et al.* (1974b) studied the photolysis of 3,3',4,4'-TetraCB (congener 77) in hexane with 300 nm light and reported that 3,4,4'-TriCB (congener 37) and 4,4'-DiCB (congener 15) were produced. Miao *et al.* (1996, 1999) studied photolysis of PCB congeners (congener 5, 31, 52, 77, 87, 126, 138, 169) in hexane under UV irradiation. They found that coplanar and symmetrical PCBs showed that the lower photoreactivities and the reactivities of the chlorine atoms at various positions were in the order of *ortho*- > *meta*- > *para*-position of PCB rings. Chang *et al.* (2003a, 2003b) reported the dechlorination of PCBs in hexane and water under UV irradiation and the relationship between the electric charge distribution on the carbon atom and site of dechlorination occurrence.

Thus far, only limited PCB congeners have been investigated in previous studies; especially for the photolysis of highly chlorinated PCBs such as PCB-209 in hexane. Therefore, the photochemical behaviors of PCB congeners in *n*-hexane are not fully understood. Furthermore, because of the large expenses on money, time, and equipment, it is difficult to measure the photolysis rate constants for all PCB congeners. Thus, quantitative structure-property

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relationships (QSPRs) have been developed relating the photolytic process data to molecular structural descriptors. When significant QSPR models are obtained, they may also provide an insight into the particular aspect of the molecular structure which influences photolysis. Among various molecular structure descriptors used for QSPR models, quantum chemical descriptors can be easily obtained by computation, can clearly describe the defined molecular properties, and are not restricted to closely related compounds. The development of QSPR models in which quantum chemical descriptors are used is of great importance. Previous studies also indicate that QSPR models for PCBs photolysis have been successfully developed using quantum chemical descriptors (Isaura *et al.*, 2005; Niu *et al.*, 2006a).

The aim of this present study was to determine the photolysis of 16 PCBs, including mono- through deca-chlorinated, in *n*-hexane under UV irradiation, by using a 500 W high-pressure mercury lamp, and to examine the photolysis rate constants and photoproducts of these PCB congeners in hexane. In addition, the aim was also to predict the photolysis rate constants of other PCBs and further understand the mechanism of PCB photolysis in hexane. QSPR models for PCB photolysis rate constants in hexane have been developed using quantum chemical descriptors. As partial least squares (PLS) regression can analyze data with strongly collinear, noisy, and numerous *X* variables (Wold *et al.*, 2001), it has been used for model development in this present study.

1 Materials and methods

1.1 Materials

Sixteen standard PCBs (99% purity) including mono- through deca-substituted congeners 2-MonoCB (PCB-1), 2,2'-DiCB (PCB-4), 2,2',5-TriCB (PCB-18), 2,4,4'-TriCB (PCB-28), 2,4',5-TriCB (PCB-31), 2,2',3,5'-TetraCB (PCB-44), 2,2', 5,5'-TetraCB (PCB-52), 2,2', 4,5,5'-PentaCB (PCB-101), 2,3',4,4',5-PentaCB (PCB-118), 2,2',3,4,4',5'-HexaCB (PCB-138), 2,2',3,4',5',6-HexaCB (PCB-149), 2,2',4,4',5,5'-HexaCB (PCB-153), 2,2',3,4,4',5,5'-HeptaCB (PCB-180), 2,2',3,3',4,4',5,5'-OctaCB (PCB-194), 2,2',3,3',4,4',5,6,6'-NonaCB (PCB-207), and 2,2',3,3',4,4',5,5',6,6'-DecaCB (PCB-209), were purchased from Accustandard Co. (New Haven, USA). HPLC grade *n*-hexane was obtained from Fisher Scientific International Inc. (Hampton, USA). The numbering system suggested by IUPAC (International Union of Pure and Applied Chemistry) was used throughout this study.

1.2 Photochemical experiments

Solutions (30 ml) of sixteen PCB congeners (1.0 µg/ml in *n*-hexane individually) were irradiated with a 500-W high-pressure mercury lamp in quartz tubes. The distance between the UV lamp and quartz tubes was 5 cm. The experiments were performed at room temperature (25°C) and were conducted in triplicate. The 1.0 ml solution under UV irradiation was taken at each time point, and

the control sample was taken at the same time. As for the analysis of photoproducts of PCBs, the initial test solution in a quartz tube was changed to 10 ml (10 µg/ml), and a 0.5-ml sample was taken at each time point.

1.3 Analysis methods

The concentrations of PCB congeners and photoproducts were quantified with a gas chromatography (GC) (Agilent 6890 plus GC, Agilent Technologies Co. Ltd., USA) equipped with a micro electron capture detector (µECD), and a HP-5 capillary column (30 m × 0.32 mm i.d., film thickness 0.25 µm, Hewlett-Packard Co., USA). A volume of 1 µl was injected into a splitless mode. Nitrogen was used as the carrier gas with a flow of 1.0 ml/min. Temperatures of injector and electron capture detector were set at 250 and 280°C, respectively. The oven temperature was programmed as follows: 60°C for 1 min; 5°C/min to 150°C; 10°C/min to 280°C, and 280°C for 18 min.

1.4 Quantum chemical descriptors calculation

Quantum chemical descriptors were obtained by semi-empirical PM3 methods contained in MOPAC 2000 (version 1.11), which was implemented in ChemOffice 2004 (CambridgeSoft Corporation, USA). PM3 was a preferred semi-empirical molecular orbital algorithm and less time consuming than *ab initio* methods (Chen *et al.*, 2000). Thus it was used in this present study.

According to the suggestion that a number of descriptors should be included in an adequate model to characterize the compounds (Kaliszan, 1993; Xu *et al.*, 2005), a total 21 MOPAC derived descriptors reflecting the overall and carbon-chlorine character of PCB molecules were calculated in this study. These are molecular weight (M_w), final heat of formation (HOF), total energy (T_E), electronic energy (E_E), core-core repulsion energy (CCR), dipole moment (μ), *X*-axis dipole moment (μ_x), *Y*-axis dipole moment (μ_y), *Z*-axis dipole moment (μ_z), hybrid (H), energy of the second highest occupied molecular orbital (E_{HOMO-1}), energy of the highest occupied molecular orbital (E_{HOMO}), energy of the lowest unoccupied molecular orbital (E_{LUMO}), energy of the second lowest unoccupied molecular orbital (E_{LUMO+1}), most positive atomic charge (q^+), most negative atomic charge (q^-), most positive atomic charge on the chlorine atom (q_{max}^+), least positive atomic charge on the chlorine atom (q_{min}^+), and bond order between carbon atom and chlorine atom (BO), which are potentially reactive. Furthermore, the two following descriptors, net charge on the carbon atom (q_C), and twist angle of the chlorine atom (TA), were determined corresponding to the BO. According to the previous studies on PCBs photolysis (Ruzo *et al.*, 1974a, 1974b; Bunce, 1989; Miao *et al.*, 1999), BO was selected for each PCB congener on the more substituted ring and longer bond length. The introduction of BO and its related descriptors into models would enhance the characterization for reactions on specific positions. In addition to the variables listed earlier, three combinations of frontier molecular orbital energies, $E_{LUMO} - E_{HOMO}$, $E_{LUMO} + E_{HOMO}$, and $(E_{LUMO} -$

$E_{\text{HOMO}})^2$, were also included in the predictor variable set, and they had already been evidenced on the application of these parameters for developing QSPR models (Devillers *et al.*, 2002; Chen *et al.*, 2003; Niu *et al.*, 2006a, 2006b). The $E_{\text{LUMO}}-E_{\text{HOMO}}$ and $E_{\text{LUMO}} + E_{\text{HOMO}}$ were related to absolute hardness and electron negativity, respectively (Chen *et al.*, 2000).

1.5 Statistical analysis

The QSPR models were developed using Partial Least Squares (PLS) analysis, as implemented in the Simca (Simca-S Version 6.0, Umetri AB and Erisoft AB) software. The conditions for the computation were based on the default options of the software. The criterion used to determine the model dimensionality and the number of significant PLS components was cross-validation (CV) (Chen *et al.*, 2001).

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 larger than 0.5. Model adequacy is 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). Besides the standard error of predicted values ($\text{SE}_{\text{pred.}}$) given by the PLS analysis, another standard error (SE) was adopted to assess the predictive power of the regression model. SE was defined as follows in multiple regression analysis,

$$\text{SE} = \sqrt{\frac{\sum_{i=1}^n (\log k_{p\text{-observed}_i} - \log k_{p\text{-predicted}_i})^2}{n - k - 1}} \quad (1)$$

where, $\log k_{p\text{-observed}}$ and $\log k_{p\text{-predicted}}$ are the observed and predicted (over the test set) values of the dependent variable, respectively, and n stands for the number of observations used for model building in the training set.

2 Results and discussion

2.1 Photolysis kinetics of PCBs

The photolysis procedure of all individual PCB congeners is fitted with pseudo-first-order kinetics during irradiation under a high-pressure mercury lamp, in *n*-hexane solution. Thus, the first-order kinetics was applied to explain the photolysis rates of all the 16 PCBs in *n*-hexane. Previous investigations on photolysis of PCBs in different solutions also observed similar results (Moor and Pagni, 1987; Lin *et al.*, 1995; Miao *et al.*, 1996, 1999; Chang *et al.*, 2003a).

The photolysis rate constants of PCB congeners in this study are shown in Table 1. The results in Table 1 show that the maximum photolysis rate constant (for PCB-118) is approximately 52 times larger than the minimum value (for PCB-52). Even though they are dissolved in the same solvent, PCB congeners have degraded faster in this study than those reported by other authors (Miao *et al.*, 1999; Chang *et al.*, 2003a). As the reaction conditions in this study are similar to those in previous studies (Miao *et al.*, 1999; Chang *et al.*, 2003a), the difference in reaction rates can be attributed to the difference in UV intensities, which has been evidenced elsewhere (Bezares-Cruz *et al.*, 2004).

It can be concluded from this study that the rate constants of higher chlorinated species, such as, PCB-180, PCB-194, PCB-207, and PCB-209, are almost comparative, which are modest among the 16 PCB congeners. Moreover, isomers of PCB-18, PCB-28, and PCB-31 have undergone degradation in greatly varied time ranges. Thus, the number of chlorine atoms of PCBs may not be a decisive factor for their photolysis rates. Similar results have also been reported in previous studies (Hutzinger *et al.*, 1974; Sawhney, 1986). Interestingly, the coplanar PCB congener 118 with one *ortho* substituted chlorine atom is photodegraded easily, which is different from other coplanar congeners (congener 77, 127, and 169) of non-*ortho* substitution (Miao *et al.*, 1999). This result

Table 1 Photolysis rate constants k_p (s^{-1}) of 16 PCB congeners (including mono- through deca-chlorinated) upon exposure to UV irradiation in *n*-hexane

No.	IUPAC ^a number of PCB ^b congeners	$\log k_p$		$\text{SE}_{\text{pred}}^{\text{e}}$	Diff. ^f
		Observed ^c	Predicted ^d		
1	PCB-1 (2-)	-1.543	-1.536	±0.137	-0.007
2	PCB-4 (2,2'-)	-1.960	-2.074	±0.165	0.115
3	PCB-18 (2,2',5-)	-2.615	-2.665	±0.127	0.050
4	PCB-28 (2,4,4'-)	-1.504	-1.306	±0.133	-0.199
5	PCB-31 (2,4',5-)	-1.527	-1.596	±0.092	0.069
6	PCB-44 (2,2',3,5'-)	-2.246	-2.325	±0.091	0.079
7	PCB-52 (2,2',5,5'-)	-2.970	-2.543	±0.103	-0.427
8	PCB-101 (2,2',4,5,5'-)	-2.148	-2.211	±0.104	0.063
9	PCB-118 (2,3',4,4',5-)	-1.241	-1.452	±0.101	0.211
10	PCB-138 (2,2',3,4,4',5'-)	-1.451	-1.511	±0.071	0.059
11	PCB-149 (2,2',3,4',5',6-)	-1.938	-1.995	±0.127	0.057
12	PCB-153 (2,2',4,4',5,5'-)	-1.899	-1.871	±0.085	-0.028
13	PCB-180 (2,2',3,4,4',5,5'-)	-1.652	-1.967	±0.101	0.316
14	PCB-194 (2,2',3,3',4,4',5,5'-)	-1.595	-1.464	±0.142	-0.131
15	PCB-207 (2,2',3,3',4,4',5,6,6'-)	-1.625	-1.457	±0.089	-0.168
16	PCB-209 (2,2',3,3',4,4',5,5',6,6'-)	-1.605	-1.544	±0.104	-0.061

^a International Union of Pure and Applied Chemistry; ^b polychlorinated biphenyl; ^c data from this study; ^d $\log k_p$ values; ^e standard errors for the predicted $\log k_p$ values; ^f difference between observed and predicted $\log k_p$ values.

is also not consistent with the explanation that the extended conjugation between two phenyl rings in a planar configuration leads to a lower photolysis rate constant as reported by Miao *et al.* (1999). It can be observed from this study that the photolysis rate constants of symmetrical congeners (congener 4, 153, 194, 209) except PCB-52 range between 0.0110 s^{-1} for PCB-4 and 0.0254 s^{-1} for PCB-194, and as the number of chlorine atoms increases, the effect of *ortho* chlorines involved in a 2, 5 (or 3, 6) substitution pattern is not significant (Bunce *et al.*, 1978). Additionally, a lower chlorinated PCB congener PCB-18 with 2,2' substitution also suffers an extraordinarily lower rate constant compared with its isomers that are substituted with one chlorine atom at the *ortho* position. Thus, it can be concluded from the earlier description that photolysis rate constants of PCB congeners not only relate to the properties of the whole molecular-like LUMO energies (Miao *et al.*, 1999), but also those of the specific position for reaction. To attain more information on the theoretical details, further investigation has been carried out according to the QSPR models with quantum chemical descriptors developed as follows.

2.2 PLS analysis models

Variable importance in the projection (VIP) is a parameter in PLS analysis that shows the importance of a variable in a PLS model. Terms with a large value of VIP, larger than 1, are the most relevant for explaining the dependent variable. PLS analysis models with the photolysis rate constant (see Table 1) as a dependent variable and the 24 quantum chemical descriptors as independent variables have been developed, and have generated many results. The optimal model, which has the largest Q^2_{cum} , was obtained through stepwise culling of the model with the smallest VIP value out. Following the analysis methods described earlier, model (1) was obtained. The fitting results are listed in Table 2. $R^2_{X(\text{adj.})(\text{cum})}$ and $R^2_{Y(\text{adj.})(\text{cum})}$ 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. It can thus be concluded, from Table 2, that the four PLS principal components were selected in model (1), which explained 71.9% variance in the independent variables, and 80.5% variance in the dependent variable.

The plot of the observed and predicted values for model (1) is shown in Fig.1. The compound numbers in Fig.1 correspond to those in Table 1. Seen from Table 2 and Fig.1, the correlation between the observed and predicted $\log k_p$ values of PCBs is significant ($R = 0.926$, $p < 0.001$). The model may be used to make a prediction for other PCBs. Based on model (1), the $\log k_p$ values for PCBs were predicted and the predicted values are listed in Table 1. The predictions may give an initial estimation of PCB photolysis in hexane. The results obtained from this study show that the molecular structural characteristics of PCBs govern the photochemical degradation of these molecules in *n*-hexane.

There are in total nine predictor variables included in

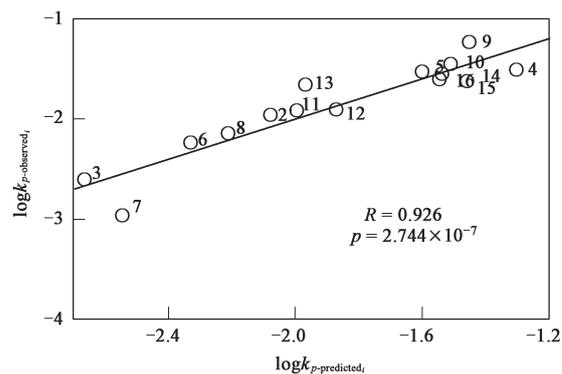


Fig. 1 Plot of observed photolysis rate constants (from Table 1) vs. those predicted by model (1).

model (1). VIP values for the variables are listed in Table 2. Based on the unscaled pseudo-regression coefficients of the independent variables and constants transformed from PLS results, an analytical QSPR equation can be obtained as follows: Model (1):

$$\log k_p = -25.748 - 2.043E_{\text{HOMO-1}} + 14.490q_c - 2.948 \times 10^{-4}\text{TA} - 4.965 \times 10^{-2}(E_{\text{LUMO}} - E_{\text{HOMO}}) + 8.673 \times 10^{-4}(E_{\text{LUMO}} - E_{\text{HOMO}})^2 - 1.424(E_{\text{LUMO}} + E_{\text{HOMO}}) - 8.463 \times 10^{-1}E_{\text{LUMO}} - 59.738q^+ + 2.504 \times 10^{-1}\mu_y$$

$$n = 16, k = 4, Q^2_{\text{cum}} = 0.620, R = 0.926, p = 2.744 \times 10^{-7}, \text{SE} = 0.203$$

(2)

In model (1), four PLS components were selected. According to the PLS weights ($W^*(1)$, $W^*(2)$, $W^*(3)$, and $W^*(4)$) listed in Table 3, it can be seen how much a single variable contributes in each PLS component to the modeling of $\log k_p$. The first PLS component is mainly related to the descriptors TA, E_{LUMO} , $E_{\text{HOMO-1}}$, $E_{\text{LUMO}} - E_{\text{HOMO}}$, and $(E_{\text{LUMO}} - E_{\text{HOMO}})^2$. The absolute values of $W^*(1)$ for these five descriptors are larger than 0.360 and larger than the absolute values of $W^*(1)$ for other descriptors. Among these descriptors, $(E_{\text{LUMO}} - E_{\text{HOMO}})^2$, $E_{\text{LUMO}} - E_{\text{HOMO}}$, and $E_{\text{HOMO}} + E_{\text{LUMO}}$ are significantly inter-correlated with each other (see Table 4). Increasing $(E_{\text{LUMO}} - E_{\text{HOMO}})^2$ values or decreasing $E_{\text{LUMO}} - E_{\text{HOMO}}$ and E_{LUMO} values of PCBs leads to the increasing of $\log k_p$ values. According to Pearson (1986), the absolute hardness can be defined as $1/2(E_{\text{LUMO}} - E_{\text{HOMO}})$, which is regarded

Table 3 Variable importance in the projection (VIPs) and partial least squares (PLS) weights ($W^*(1)$, $W^*(2)$, $W^*(3)$, and $W^*(4)$) for the molecular structural descriptors included in model (1)

Variables	VIP	$W^*(1)$	$W^*(2)$	$W^*(3)$	$W^*(4)$
$E_{\text{HOMO-1}}$	1.1183	-0.360	-0.699	-0.431	-0.399
q_c	1.0734	0.302	0.142	-0.218	0.671
TA	1.0569	0.364	0.347	-0.401	-0.264
$E_{\text{LUMO}} - E_{\text{HOMO}}$	1.0263	-0.399	0.060	-0.021	0.240
$(E_{\text{HOMO}} - E_{\text{LUMO}})^2$	1.0233	-0.394	0.073	-0.002	0.280
$E_{\text{HOMO}} + E_{\text{LUMO}}$	1.0095	-0.318	0.069	-0.524	-0.796
E_{LUMO}	0.9769	-0.376	0.062	-0.286	-0.307
q^+	0.8809	0.160	-0.524	-0.641	-0.662
μ_y	0.7938	0.278	0.477	0.078	-0.018

Table 2 Model fitting results for model (1)

k^a	$R^2_{X(\text{adj.})(\text{cum})}^b$	$R^2_{Y(\text{adj.})(\text{cum})}^c$	Eig^d	$Q^2_{\text{cum}}^e$	SE ^f
1	0.339	0.533	4.064	0.431	0.203
2	0.643	0.627	2.770	0.489	
3	0.719	0.705	0.818	0.549	
4	0.719	0.805	0.317	0.620	

^a the number of the PLS principal components; ^b cumulative variance of all the X 's; ^c cumulative variance of all the Y 's; ^d eigenvalue denoting the importance of the PLS principal components; ^e cumulative cross-validated regression coefficient; ^f standard error.

as a measure of energy stabilization in chemical systems, and chemical structures tend to be more stable at larger values of the $E_{\text{LUMO}}-E_{\text{HOMO}}$ gap (Niu *et al.*, 2005). It can thus be concluded that PCB congeners with bigger absolute hardness values tend to be more stable. The descriptor $E_{\text{HOMO}-1}$ is related to the polarizability, which measures the ability of the electrons in a molecule to move easily as a result of a stimulus. As the electrons in the molecules with large polarizability can move easily (Ehresmann *et al.*, 2003), both excited singlet and triplet states of the molecules of such compounds may not be stable, that is, they may undergo processes such as internal conversion, fluorescence, and so on, resulting in low photolysis rates (Chen *et al.*, 2000). TA describes the twist angle of the chlorine atom at the specific substitution position, and it indicates the p - π conjugation between the carbon atom and the chlorine atom, especially discerning the reaction differences among *ortho*-, *meta*-, and *para*-positions. The result shows that PCBs with higher TA values tend to be more photostable.

The second PLS component is loaded primarily on descriptor $E_{\text{HOMO}-1}$, q^+ , and μ_y , for which the absolute $W^*(2)$ values are larger than 0.470 and remarkably larger than the absolute values of $W^*(2)$ for the other descriptors. μ_y stands for the dipole in Y -axis direction. It is another independent variable characterizing the local structures of PCB molecules besides TA. μ_y is regarded as the specification of μ . The pseudo-regression coefficients of q^+ and μ_y in model (1) show that the increasing q^+ values or decreasing μ_y values of PCBs may lead to the decreasing of $\log k_p$ values of PCBs in *n*-hexane. The third PLS component is loaded primarily on descriptor $E_{\text{HOMO}} + E_{\text{LUMO}}$ and q^+ , for which the absolute values are larger than the absolute values of $W^*(3)$ for the other descriptors. As indicated by the pseudo-regression coefficient for q^+ , increasing q^+ values of PCBs lead to the decreasing of $\log k_p$ values. The fourth PLS component is loaded primarily on descriptors $E_{\text{HOMO}} + E_{\text{LUMO}}$, q_C , and q^+ , for which the absolute

values are larger than the absolute values of $W^*(4)$ for the other descriptors. The results show that the photolysis rate constants of PCBs in *n*-hexane increase with the increasing of q_C values of PCBs. This conclusion is different from the results reported by Chang *et al.* (2003a), who found that the higher the charge distribution for carbon to which chlorine is attached, the easier it is for photodechlorination to occur, that is, the degradation rate constants are higher with smaller q_C values. However, the result in this study is accessible, in that, reductive dechlorination of PCBs under UV irradiation is a radical reaction with homolysis of the C-Cl bond (Bunce *et al.*, 1989; Manzano *et al.*, 2004). As a result, the average distribution of charges between the C atom and the Cl atom may facilitate the reaction.

3 Conclusions

In this study, photolysis of PCBs (including mono-through deca-chlorinated) using high-pressure mercury lamp irradiation in *n*-hexane was investigated. It was found that photolysis of PCB congeners followed pseudo-first-order kinetics. The photolysis rate constants ranged between 0.0011 s^{-1} for PCB-52 and 0.0574 s^{-1} for PCB-118. The results showed that the degradation rates of PCBs in *n*-hexane were remarkably independent of the degree of chlorination. Benzene was detected as the successive photoproduct of biphenyl in addition to the reported photoproducts. Moreover, a QSPR model on the PCB photolysis rate constants was developed. It was found that the photolysis rate constants of PCBs increased with the increase in q_C , $(E_{\text{LUMO}}-E_{\text{HOMO}})^2$ and μ_y values, or the decrease in energy of $E_{\text{HOMO}-1}$, E_{LUMO} , $E_{\text{LUMO}} + E_{\text{HOMO}}$, $E_{\text{LUMO}}-E_{\text{HOMO}}$, q^+ , and TA values.

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Table 4 Correlation coefficients between quantum chemical descriptors of PCBs

	μ_y	$E_{\text{HOMO}-1}$	E_{LUMO}	$E_{\text{LUMO}}-E_{\text{HOMO}}$	$E_{\text{LUMO}}+E_{\text{HOMO}}$	$(E_{\text{LUMO}}-E_{\text{HOMO}})^2$	q^+	q_C	TA
μ_y	1.000								
$E_{\text{HOMO}-1}$	-0.296	1.000							
E_{LUMO}	0.079	-0.130	1.000						
$E_{\text{LUMO}}-E_{\text{HOMO}}$	0.037	0.074	0.956*	1.000					
$E_{\text{LUMO}}+E_{\text{HOMO}}$	0.112	-0.313	0.961*	0.837*	1.000				
$(E_{\text{LUMO}}-E_{\text{HOMO}})^2$	0.037	0.072	0.955*	0.999*	0.836*	1.000			
q^+	-0.166	0.301	-0.873*	-0.816*	-0.856*	-0.819*	1.000		
q_C	0.179	-0.152	-0.221	-0.257	-0.170	-0.252	0.305	1.000	
TA	0.524	-0.512	-0.064	-0.177	0.047	-0.171	0.005	0.652*	1.000

* Correlation is significant at the 0.01 level.

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