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# Theoretical investigations on direct photolysis mechanisms of polychlorinated diphenyl ethers

Se Wang [a], Ce Hao [a,*], Zhanxian Gao [a], Jingwen Chen [b], Jieshan Qiu [a]

[a] State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116024, China
[b] Key Laboratory of Industrial Ecology and Environmental Engineering (MOE), School of Environmental Science and Technology, Dalian University of Technology, Dalian 116024, China

## HIGHLIGHTS

- PCDEs photodechlorination rate is predicted to be the highest among all the pathways.
- The $MBDE_{C-Cl}$ of PCDEs decreases with increasing chlorination degree.
- The $MBDE_{C-O}$ of PCDEs decreases with increasing chlorination degree.
- Photolysis products (CDE1, CDE3, chlorobenzene, and 2-CDF) were predicted for CDE8.

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## ABSTRACT

Polychlorinated diphenyl ethers (PCDEs) are a focus of current environmental concern as a group of ubiquitous potential persistent organic pollutants. There are still significant gaps in our knowledge concerning the photolysis mechanisms of PCDEs. In this study, the direct photolysis mechanisms of PCDEs were investigated by density functional theory. The direct photolysis of PCDEs has three potential reaction pathways including photodechlorination, C—O bond photodissociation, and PCDFs formation. Taking a representative PCDE (i.e., CDE8) for example, we found that C—Cl bond dissociation is the rate-determining step for the photodechlorination. Chlorobenzene is predicted to be photoproduct of CDE8 through the photodissociation of the C—O bond. Furthermore, the calculated mean bond dissociation energies of both C—Cl and C—O bonds of 20 PCDEs decrease with the increased degree of chlorination. It is also found that the photoactivity of PCDEs increases with an increase of chlorination degree by evaluating the average charge of Cl atoms and mean bond dissociation energies of C—Cl and C—O bonds from reaction thermodynamics. Our findings provided a new insight into the mechanisms of direct photolysis of PCDEs, which may be useful in the future in utilizing quantum chemistry calculation in investigating the behavior and fate of organic pollutants in the environment.

## 1. Introduction

Polychlorinated diphenyl ethers (PCDEs), a group of halogenated aromatic compounds, are mainly produced as unwanted byproducts from technical chlorophenols and chlorinated phenoxyacetic acids as well as by incomplete combustion (Domingo, 2006). PCDEs have been frequently detected in environmental samples including water (Koistinen et al., 2010), soils (Persson et al., 2007), sediments (Sormunen et al., 2008), humans adipose tissue (Domingo, 2006), and fish (Martí-Cid et al., 2007). Moreover, PCDEs can enter into human body via the food intake, which causes negative effects on human health (Martí-Cid et al., 2008). Due to their persistence, bioaccumulation and toxicity (Rosiak et al., 1997; Lyytikäinen et al., 2003), recently a lot of attention has been drawn to the studies on the behavior and fate of PCDEs in the environment (Chen et al., 2007; Zeng et al., 2007; Liu et al., 2011).

Many studies have been carried out on the photolysis of organic pollutants (Norström et al., 1976; Mamantov, 1985; Sabljic and Peijnenburg, 2001; Sanchez-Prado et al., 2006; Izadifard et al., 2008; Fernandez-Alvarez et al., 2009; Langford et al., 2011; Holt et al., 2012). Photolysis of PCDEs in organic solvents may be relevant for specific soil remediation processes where organic solvents are used to extract PCDEs or other persistent organic pollutants sorbed to solid matrixes. Choudhry et al. (1977) observed that the main photoproducts of PCDEs are dechlorinated PCDEs, and the minor photoproducts are polychlorinated dibenzofurans (PCDFs). PCDFs are frequently detected in the organisms (Corsolini

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* Corresponding author. Tel./fax: +86 411 84986335.
*E-mail address:* haoce@dlut.edu.cn (C. Hao).

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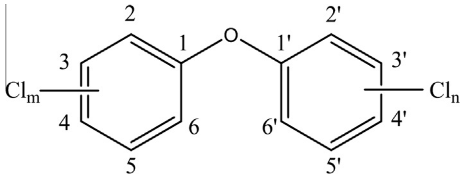

**Fig. 1.** A structural formula of PCDEs and numbering scheme for atomic positions.

et al., 2002) and the environment (McLachlan and Sellström, 2009), and identified as extremely toxic pollutants (Hung et al., 2013). Moreover, the structures of PCDEs are similar to those of polybrominated diphenyl ethers (PBDEs). The potential photoproducts of PBDEs not only include lower brominated PBDEs and PBDFs (Eriksson et al., 2004; Bendig and Vetter, 2010), but also bromophenols and bromobenzenes via the dissociation of C—O bond (Bendig and Vetter, 2013). Thus, chlorophenols and chlorobenzenes might also be the potential photoproducts of PCDEs through the dissociation of C—O bond. However, there are no reports that the photolysis of PCDEs forms such the two photoproducts, namely chlorophenols and chlorobenzenes, both of which are extremely toxic to human and hazardous to the environment (Yan et al., 2008; Feltens et al., 2010; Ma et al., 2011; Giesen et al., 2012). Moreover, chlorophenols are considered to be precursors for the formation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) (Qu et al., 2009). In addition, previous studies demonstrated that bromination degree had a great impact on the photoactivity of PBDEs (Fang et al., 2008, 2009; Wang et al., 2012). Due to the fact that PCDEs (Fig. 1) and PBDEs both have 1–10 Cl and Br halogens on the two benzene rings, respectively, chlorination degree can be also a crucial factor impacting the photoactivity of PCDEs. However, experimental data on the direct photolysis of PCDEs are scarce (Choudhry et al., 1977) and the mechanisms of photochemical reactions are still being clarified.

Recently, there has been a growing interest to explore various computational approaches to better understand and predict the behavior and fate of persistent organic pollutants in the environment (Sabljic, 2001; Yamada et al., 2008; Zhao et al., 2008; Kovacevic and Sabljic, 2013a,b; Wang et al., 2014). For example, we have also predicted that the photoactivity of PBDEs increased with the increased degree of bromination by the calculation of Br atoms charge and electronic excitation energies of PBDEs (Wang et al., 2012). In addition, the density functional theory (DFT) calculations of bond dissociation energy of C—Cl bond were employed to predict the photodechlorination pathway of hexachlorobenzene (Yamada et al., 2008) and polychlorinated biphenyls (Wang et al., 2014).

In the present study, we employed theoretical chemistry calculations to investigate the direct photolysis mechanisms of PCDEs in photodechlorination, photolysis through the dissociation of C—O bonds, and photolysis forming PCDFs. We have also predicted the main photoproducts of PCDEs and compared this theoretical investigation with previous experimental findings. In addition, the possible effects of chlorination degree on the photoactivity of PCDEs were investigated by evaluating the average Cl atom charge ($q_{Cl}$), the C—Cl bond dissociation energies ($BDE_{C-Cl}$), and the C—O bond dissociation energies ($BDE_{C-O}$).

## 2. Computational methods

As depicted in Fig. S1 (Supplementary data), 20 PCDEs (including 1–10 chlorine substituted congeners) were selected as model compounds in the present study. The geometry optimizations of the PCDEs in gas phase were carried out using DFT (Kohn et al., 1996; Zhao and Han, 2012). Becke's three-parameter hybrid exchange function with Lee–Yang–Parr gradient-corrected correlation functional (Becke, 1993) with 6-311+G(d,p) basis set was utilized. The vibrational frequencies were also calculated at the same level in order to characterize the nature of the obtained stationary points. Geometries (minimum point) were characterized with no imaginary vibrational frequency. The atomic charges were examined by the natural bond orbital (NBO) scheme at B3LYP/6-311++G(d,p) level of theory.

A homolytic cleavage reaction in gas phase is as follows:

$$RA{-}BR'\ (g) \rightarrow RA^{\cdot}(g) + R'B^{\cdot}(g) \qquad (1)$$

where RA—BR' is reactant, and $RA^{\cdot}$ and $R'B^{\cdot}$ are product radicals. R and R′ are substituent groups linked to atom A and atom B, respectively. The bond dissociation energy (*BDE*) can be described as follows:

$$BDE = E_{RA^{\cdot}} + E_{R'B^{\cdot}} - E_{RA-BR'}$$

where $E_{RA-BR'}$ is the single-point energy of RA—BR′, and $E_{RA^{\cdot}}$ and $E_{R'B^{\cdot}}$ are the single-point energy for radicals $RA^{\cdot}$ and $R'B^{\cdot}$, respectively. Zero-point energy correction has been considered in estimating the bond dissociation energy. Thus, the $BDE_{C-Cl}$ and $BDE_{C-O}$ for each PCDEs congener can be obtained based on above-mentioned formulae.

Because of its well-defined structure, CDE8 was chosen as a representative one to investigate the direct photolysis mechanisms of PCDEs. The photolysis pathways of CDE8 in gas phase in the lowest excited triplet state were calculated employing DFT method at B3LYP/6-311+G(d,p) level of theory, as the lowest excited triplet state was found to be long-lived photochemical reaction precursors for many compounds (Wei et al., 2013). The geometries in the lowest triplet state were calculated with a spin multiplicity of 3 (Wei et al., 2013). Transition states were characterized with one imaginary vibrational frequency. Intrinsic reaction coordinate (IRC) calculations were performed to confirm that transition states connect with the corresponding reactants and products. Zero-point energy correction has been considered in estimating the reaction activation energy. All calculations were carried out using the Gaussian 09 software package (Frisch et al., 2009).

## 3. Results and discussion

### 3.1. Geometries of PCDEs

The geometry optimization of 20 PCDEs in the ground state were carried out at the B3LYP/6-311+G(d,p) level of theory, and the conformations and structural parameters of 20 PCDEs are shown in Fig. S1 and Tables S1 and S2 (Supplementary data). The optimized values of the structural parameters of CDE138 (Table S1 in Supplementary data) are in good agreement with the X-ray experimental values of Nevalainen and Rissanen (1994). Moreover, as can be seen from Table S2 (Supplementary data), the geometries of 20 PCDEs differ in the C1—O bond length ranging from 1.367 Å to 1.380 Å and the O—C1′ bond length ranging from 1.370 Å to 1.386 Å. The mean value of the C1—O bonds lengths is 1.373 Å, and the C1′—O bonds lengths 1.378 Å. The largest difference between the two C—O bonds lengths within a PBDE congener is about 0.016 Å (CDE119), implying that the difference is governed by the chlorine substitution pattern on the two benzene rings. In addition, for each PCDEs congener, the length of the C—O bond of the benzene ring with more Cl substituents is shorter than that with less Cl substituents (Table S2 in Supplementary data). The angle C1—O—C1′ of CDE155, 201, 207, 208, and 209 (about 125°) is larger than that of the remaining 15 PCDEs (about 120°). This may be caused by a high steric effect induced by four *ortho* chlorines of CDE155, 201, 207, 208, and 209.