



The OH-initiated atmospheric chemical reactions of polyfluorinated dibenzofurans and polychlorinated dibenzofurans: A comparative theoretical study



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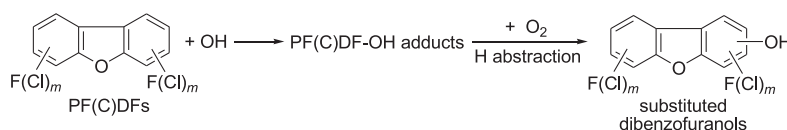
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HIGHLIGHTS

- Atmospheric oxidation reactions of PFDFs and PCDFs were studied theoretically.
- The OH addition reactions of PFDFs are comparable with those for PCDFs.
- The OH additions of PF(C)DFs become slower with higher fluorination or chlorination.
- The O₂ addition reactions of PF(C)DF-OH adducts take place hardly.
- The main oxidation products for PFDFs and PCDFs are substituted dibenzofuranols.

GRAPHICAL ABSTRACT



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ABSTRACT

The atmospheric chemical reactions of some polyfluorinated dibenzofurans (PFDFs) and polychlorinated dibenzofurans (PCDFs), initiated by OH radical, were investigated by performing theoretical calculations using density functional theory (DFT) and B3LYP/6-311++G(2df,p) method. The obtained results indicate that OH addition reactions of PFDFs and PCDFs occurring at C₁₋₄ and C_A sites are thermodynamic spontaneous changes and the branching ratio of the PF(C)DF-OH adducts is decided primarily by kinetic factor. The OH addition reactions of PFDFs taking place at fluorinated C₁₋₄ positions are kinetically comparable with those occurring at nonfluorinated C₁₋₄ positions, while OH addition reactions of PCDFs occurring at chlorinated C₁₋₄ sites are negligible. The total rate constants of the addition reactions of PFDFs or PCDFs become smaller with consecutive fluorination or chlorination, and substituting at C₁ position has more adverse effects than substitution at other sites. The subsequent O₂ addition reactions of PF(C)DF-OH adducts are thermodynamic nonspontaneous processes under the atmospheric conditions, and have high Gibbs free energies of activation ($\Delta_r G^\ddagger$). The substituted dibenzofuranols are the primary oxidation products for PCDFs under the atmospheric conditions. However, other oxidative products may also be available for PFDFs besides substituted dibenzofuranols.

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1. Introduction

Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) are well-known persistent organic

pollutants (POPs) and have caused significant concern from scientists. Meanwhile, scientists have also paid wide attention to polyfluorinated dibenzo-*p*-dioxins and polyfluorinated dibenzofurans (PFDD/Fs) because they are similar to PCDD/Fs in structure. PFDD/Fs were found in the process of the combustion of material containing organofluorine compounds (Weber et al., 1995) and waste incineration (Sakai et al., 1995). Several PFDD compounds were synthesized by Haffer et al. (Haffer et al., 1993, 1994, 1995) and their GC-MS behavior were then investigated (Haffer et al., 1996). The distribution of 2,3,7,8-tetrafluorodibenzo-*p*-dioxin in tissues of rats was researched by Conrad et al. (1996). Some PFDD and PFDF compounds were synthesized and analyzed by Weber et al. (1997; 1999) and their toxicology and metabolic degradation behaviors were studied. The kinetics and distribution of several PFDD/F compounds in organs of rats (liver, thymus and adipose tissue) were studied by Herzke et al. (2002), and the results showed that these PFDD/Fs have remarkably lower toxicity in Wistar rats than the corresponding PCDD/F isomers. The fluorination of dibenzofuran was investigated by Iskra et al. (2008) using caesium fluoroxy sulfate and other fluorinating reagents. In the recent time, the gaseous thermodynamic properties of 75 PFDD (Yang et al., 2010) and 135 PFDF (Shi et al., 2011) congeners at 298.15 K and 101.325 kPa were calculated using density functional theory (DFT) method.

Atmospheric chemical reaction with OH radical is usually considered to be the major pathway in removing POPs such as PCDD/Fs during their transport through the atmosphere (Kwok et al., 1994; Addink and Olie, 1995). Since the experimental determination of active intermediates and reaction paths is difficult in general, computational investigation on the atmospheric oxidation mechanism of POPs become more significant recently. Lee et al. (2004) researched the addition of the OH radical to dibenzo-*p*-dioxin (DD), 2,3,7,8-tetrachlorinated dibenzo-*p*-dioxin (2,3,7,8-TCDD) and octachlorinated dibenzo-*p*-dioxin (OCDD) mechanistically using DFT method. By using DFT calculations, Altarawneh et al. (2008) demonstrated that the atmospheric degradation mechanism of dibenzofuran (DF) initiated by OH addition is different from that of DD. Subsequently, numerous theoretical calculations on the atmospheric chemical reactions of POPs such as PCDDs (Zhang et al., 2011; Wang and Tang, 2011, 2012), Polychlorinated biphenyls (PCBs) (Sun et al., 2015; Dang et al., 2015a; Yang et al., 2016), polycyclic aromatic hydrocarbons (PAHs) (Zhang et al., 2014; Dang et al., 2014, 2015b), polybrominated diphenyl ethers (PBDEs) (Cao et al., 2011, 2012; Zhou et al., 2011, 2013), and chlorinated polycyclic aromatic hydrocarbons (CIPAHs) (Dang et al., 2015c) initiated by OH radical were performed. Using DFT calculation, Zhang and Sun (2014) studied the atmospheric chemical reaction of 2,3,7,8-tetrafluorinated dibenzo-*p*-dioxin (2,3,7,8-TFDD) initiated by OH radical, O₃ and NO₃ radical. More recently, we (2016) conducted a systematic computational investigation on the atmospheric oxidation mechanism of 18 PFDDs with C_{2v} or C_{2h} symmetry, and the results indicated that the substituted phenoxy radicals are the principal oxidation products for PFDDs under the atmospheric conditions.

Up to now, theoretical exploration on the atmospheric chemical reactions of PF(C)DFs is scarce in comparison with PF(C)DDs. Sun et al. (2012) investigated the mechanism and kinetics of atmospheric chemical reactions of 2,3,7,8-tetrachlorinated dibenzofuran (2,3,7,8-TCDF) initiated by an OH radical. In the present work, we carried out a comprehensive theoretical study on the atmospheric chemical reactions of four di-FDFs (DFDFs), six tetra-FDFs (TFDFs), four hexa-FDFs (HFDFs), and octa-FDF (OFDF) with C_{2v} symmetry. For comparison, 15 corresponding PCDFs are also involved in this study. The present studies aim primarily at obtaining a more thorough comprehension on the atmospheric reaction mechanism

of PFDFs and PCDFs and discover the most advantageous path when O₂ exists. Moreover, the influence of successive fluorination or chlorination on the OH addition reactions was explored, and the difference between PFDFs and PCDFs in the OH addition was analyzed.

2. Computational methods

The Gaussian 03 program (Frisch et al., 2003) was used throughout the DFT calculations involved in this study, and the B3LYP hybrid and correlation functional (Becke, 1993; Lee et al., 1988) was applied. The 6-311++G(2df,p) basis set was employed to optimize the geometries of reactants, intermediate complexes, transition states, and products. The vibrational frequencies of all stationary points were also calculated to decide their characteristics and to obtain their thermodynamic properties. Rate constants were computed employing the traditional transition state theory (TST) as (Pilling and Seakins, 1999):

$$k_b = (k_B T/h) \cdot \exp(-\Delta_r G_{298.15K}^\ddagger/RT) \cdot (RT/p^\theta) \cdot (10^6/N_A) \quad (1)$$

for the rate constant of bimolecular reactions (k_b , in cm³ molecule⁻¹ s⁻¹) and

$$k_u = (k_B T/h) \cdot \exp(-\Delta_r G_{298.15K}^\ddagger/RT) \quad (2)$$

for the high-pressure-limit rate constant of unimolecular reactions (k_u , in s⁻¹), where k_B , T , h , $\Delta_r G_{298.15K}^\ddagger$, R , p^θ , and N_A are Boltzmann's constant, thermodynamic temperature, Planck's constant, the Gibbs free energies of activation at 298.15 K with zero-point energy correction, gaseous constant, the standard pressure (101.325 kPa), and Avogadro's constant, respectively. Previous researches on the atmospheric oxidation reactions of polychlorinated dibenzo-*p*-dioxins (PCDDs) (Wang and Tang, 2011, 2012) and polyfluorinated dibenzo-*p*-dioxins (PFDDs) (Zeng et al., 2016) have indicated that B3LYP/6-311++G(2df,p) method in conjunction with TST is applicable to study on the atmospheric oxidation mechanism of POPs.

3. Results and discussion

3.1. Initial addition reactions of PFDFs and PCDFs with OH radical

OH, NO₃ radicals and O₃ all can initiate atmospheric chemical reactions of gaseous compounds. However, both experimental observation (Kwok et al., 1994) and theoretical calculation (Zhang and Sun, 2014) have shown that OH radical is more significant in initiating atmospheric oxidation of POPs than NO₃ radical or O₃. Thus in the present study, only the OH-initiated atmospheric chemical reactions of PFDFs and PCDFs are involved. In addition, former researches have displayed that direct H abstraction from 2,3,7,8-TCDF or 2,3,7,8-TFDD by OH takes place hardly and can be ignorable (Sun et al., 2012; Zhang and Sun, 2014). Therefore, in this section only OH addition reactions of PFDFs and PCDFs were considered.

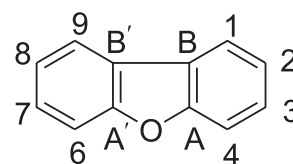


Fig. 1. Structure and atomic numbering of dibenzofuran (DF).

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