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Influence of water on the homogeneous gas-phase formation mechanism of polyhalogenated dioxins/furans from chlorinated/brominated phenols as precursors

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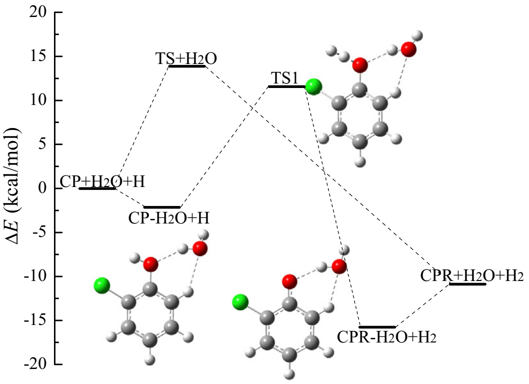
HIGHLIGHTS

- Influences of water on gas-phase formations of PHDD/Fs were revealed for the first time by lowering barriers.
- Water plays a catalytic effect on the formation of HPRs and the H-shift step.
- New lower-energy pathways were found in the H abstraction reactions of HPs.
- The energy profile in the presence/absence of water was constructed and compared.

GRAPHICAL ABSTRACT



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ABSTRACT

Water is of great chemical importance due to its ability to form hydrogen bond. Polyhalogenated dibenzo-*p*-dioxin/benzofurans (PHDD/Fs) are notorious due to their persistence, bioaccumulation and extremely high toxicity. Water is ubiquitous, and a deep knowledge of its influence on the formation mechanism of PHDD/Fs is necessary. This work investigated the influence of water on the homogeneous gas-phase formation of PHDD/Fs from halogenated phenols (HPs) as precursors by using quantum chemical calculations with the aid of the MPWB1K theoretical approach in connection with the 6-31+G(d,p) and 6-311+G(3df,2p) basis sets. The schematic energy profile in the presence of water was constructed and compared with the situation without water. This study reveals for the first time that the introduction of water promotes the formation of halogenated phenoxy radicals (HPRs) from the H abstraction reactions of HPs with atomic H and OH radicals by lowering the reaction energy barriers and opening new low-energy pathways. Another intriguing finding of this work is that the inclusion of a water molecule produces a catalytic effect on the H-shift step involved in the formation of PHDFs and thus their formation potential is enhanced.

1. Introduction

Polychlorinated dibenzo-*p*-dioxin/benzofurans (PCDD/Fs) are subjected to the international Stockholm Convention on persistent

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organic pollutants (POPs) and as such listed under the European Directive 850/2004 due to their extreme toxicity, bioaccumulation and persistency in the environment (Schecter, 1994; Wang et al., 2006; Choudhry et al., 1983). They can be unintentionally produced from various industrial operations such as metal smelting, pulp bleaching, organochlorine chemical manufacturing, and solid waste incineration (Yasuhara et al., 2001; Addink et al., 1998; Olie et al., 1977). Moreover, polybrominated dibenzo-*p*-dioxin/benzofurans (PBDD/Fs) have been also concerned due to the structure similarity to PCDD/Fs (Wang et al., 2008; Evans and Dellinger, 2006; Haglund, 2010; Samara et al., 2009, 2010). Electrical and electronic products commonly contain a wide range of brominated flame retardants (BFRs), and thus the electronic waste recycling has been identified as a main source of PBDD/Fs (Ma et al., 2009; Li et al., 2007). Analysis of persistent organic pollutants (POPs) in human samples has revealed that PBDD/Fs contribute to 15% of the total dioxin TEQ (Ericson Jogsten et al., 2010). However, PBDD/Fs have not currently covered by the convention despite their very similar physicochemical properties, toxicity and geochemical behaviors with their chlorinated congeners in the environment.

PCDD/Fs are formed via two general pathways, *de novo* synthesis and precursor pathways. The latter is 10^2–10^5 times faster than the former (Addink and Olie, 1995; Tuppurainen et al., 1998). The relative yields produced from precursors are 72 to 99,000 times higher than those formed via the *de novo* synthesis (Addink and Olie, 1995; Tuppurainen et al., 1998). Chlorophenols (CPs) are generally considered as the predominant precursors of PCDD/Fs and implicated as key intermediates in the *de novo* synthesis (Karasek and Dickson, 1987; Shaub and Tsang, 1983; Altwicker, 1996). PCDD/Fs are formed from CPs via two general mechanisms: homogeneous gas-phase mechanism and heterogeneous metal-mediated mechanism. The homogeneous gas-phase mechanism can make a significant contribution to the PCDD/F formations (Luijk et al., 1994; Dickson et al., 1992). Excellent linear correlation between the PCDD/F and PBDD/F concentrations revealed that they had a similar formation mechanism (Wang et al., 2010; Wang and Chang-Chien, 2007). Bromophenols (BPs) were found to be the most direct precursors of PBDD/Fs (Evans and Dellinger, 2005a,b,c).

Water has long been considered a subject of chemical interest due to its abundance and unique properties, especially its ability to form hydrogen bonds. Water introduces many unusual features into kinetics and energetics of chemical and biological reaction systems. For example, the water molecule can form hydrogen bonded complexes with many atmospheric species such as $OH{\cdot}H_2O$, $HO_2{\cdot}H_2O$, $O_3{\cdot}H_2O$, $HNO_3{\cdot}H_2O$, $OClO{\cdot}H_2O$ and $H_2SO_4{\cdot}H_2O$, modifying their stability and photochemical features (Mauldin et al., 2012; Vöhringer-Martinez et al., 2010). In addition, it can participate actively the gas-phase reaction of SO_3 with H_2O to produce H_2SO_4 (Morokuma and Muguruma, 1994) and the unimolecular decomposition of CF_3OH (Schneider and Wallington, 1996). Water vapor is always amply present in industrial operations. In some plants, flue gases are quenched with water before their cleaning. Therefore, the influence of water on the formation of halogenated dioxins/furans must be clarified. Several experimental studies have been carried out to explore the effect of water on the PCDD/F formations by *de novo* synthesis and the heterogeneous precursor routes, but no consensus has been obtained. Stieglitz found that water enhances the yield of PCDD/Fs in oxidized fly ash (Stieglitz et al., 1990). However, Jay and Briois reported a decrease in the total amount of PCDD/Fs formed in the presence of water (Jay and Stieglitz, 1991; Briois et al., 2007).

In the previously published papers, we have investigated the homogeneous gas-phase formation of PCDD/Fs from CPs as precursors as well as the homogeneous gas-phase formation of PBDD/Fs from BPs as precursors (Zhang et al., 2008, 2010, 2009; Yu et al., 2011; Xu et al., 2010; Gao et al., 2013). Based on these studies, the present work focuses on the influence of water on the homogeneous gas-phase formation mechanism of polyhalogenated dibenzo-*p*-dioxin/benzofurans (PHDD/Fs, including PCDD/Fs and PBDD/Fs) from halogenated phenols (HPs, including CPs and BPs) with the aid of quantum chemical calculations.

2. Computational methods

All the electronic structure calculations were carried out by using density functional theory (DFT) with the aid of Gaussian 09 programs (Frisch et al., 2009). Based on the modified Perdew and Wang exchange functional (MPW) and Becke's 1995 correlation functional (B95), MPWB1K is an excellent method for thermochemistry, thermochemical kinetics, hydrogen bonding and weak interactions (Zhao and Truhlar, 2004). The geometrical parameters of the reactants, transition states, intermediates, and products were optimized at the MPWB1K level with a standard 6-31+G(d,p) basis set. For all stationary points, the vibrational frequency analysis was also performed at the same level to verify whether they are minima with all positive frequencies or transition states with one and only one imaginary frequency. Each transition state was verified to connect the designated reactants and products by performing an intrinsic reaction coordinate (IRC) analysis. To yield more reliable energy values, a more flexible basis set, 6-311+G(3df,2p), was used for single-point energy calculations. The reliability of the MPWB1K level for the geometrical parameters and energies was tested in our previous studies on the formation of PCDD/Fs from 2-CP as precursor as well as the formation of PBDD/Fs from 2-BP, 2,4-DBP and 2,4,6-TBP as precursors (Zhang et al., 2008; Yu et al., 2011). All the relative energies quoted and discussed in this work include zero-point energy (ZPE) correction with unscaled frequencies obtained at the MPWB1K/6-31+G(d,p) level.

3. Results and discussion

3.1. Formation of halogenated phenoxy radicals

The homogeneous gas-phase formation of PHDD/Fs from CPs and BPs as precursors was proposed to involve halogenated phenoxy radical–radical coupling, and radical–molecule recombination of halogenated phenoxy radicals (HPRs) and halogenated phenol (HP) molecules. The radical–molecule recombination requires the displacement of halogen and hydroxyl as the first step, which is not energetically favored (Altarawneh et al., 2007; Evans and Dellinger, 2005a,b,c). Therefore, the radical–molecule recombination is not competitive with the radical–radical coupling. The dimerization of halogenated phenoxy radicals (HPRs) is the major pathway for the formation of PHDD/Fs (Altarawneh et al., 2007; Evans and Dellinger, 2005a,b,c). The formation of HPRs is the initial and key elementary step involved in the formation of PHDD/Fs. HPRs can be formed through the loss of the phenoxyl-hydrogen via unimolecular, bimolecular, or possibly other low-energy pathways (including heterogenous reactions). The unimolecular reaction includes the decomposition of CPs and BPs with the cleavage of the O–H bond. The bimolecular reactions include the phenolic-hydrogen abstraction from HPs by the active radicals such as H, OH, O (^{3}P), Cl, et al. These active radicals may exist in the industrial processes and combustion environment. The reaction kinetic model of the PHDD/F formations indicated that PHDD/F yields are most sensitive to the reaction of phenoxyl-hydrogen abstraction from halogenated phenols by H and OH radicals (Khachatryan et al., 2003). The reactions of CPs and BPs with H and OH radicals are the dominant propagation pathways for the formation of HPRs. Therefore, this work firstly