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Theoretical study on the formation mechanism of pre-intermediates for PXDD/Fs from 2-Bromophenol and 2-Chlorophenol precursors *via* radical/molecule reactions☆

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ABSTRACT

This study investigates reaction pathways for the formation of pre-PXDD/F intermediates *via* a radical/molecule mechanism. Thermodynamic and kinetic parameters for the combination reactions of 2-bromophenol (2-BP) and 2-chlorophenol (2-CP) precursors with key radical species including the phenoxy radicals, the phenyl radicals and the phenoxyl diradicals were calculated in detail. The couplings of phenoxy radicals with 2-B(C)P tend to produce pre-PXDD intermediates of halogenated *o*-phenoxyphenol. The combinations of phenyl and phenoxyl diradicals with 2-B(C)P produce two types of structures, i.e., dihydroxybiphenyl and *o*-phenoxyphenyl, which exclusively act as prestructures of PXDFs. These condensation reactions, especially those involving the phenyl C atom sites in phenyl and phenoxyl diradicals, are proven to be both thermodynamically and kinetically favorable and are nearly comparable with the corresponding steps involved in the radical/radical reactions. Most importantly, reactions of phenyl and phenoxyl diradicals with halogenated phenols solely lead to the formation of PXDFs, which to some extent provides a plausible explanation for the high PXDF-to-PXDD ratios in the real environment. Therefore, our study reveals the pivotal role of the radical/molecule mechanism in homogeneous gas-phase PXDD/F formation, especially in PXDF formation. The present results fill in a knowledge gap that has hitherto existed regarding dioxin formation and improve our understanding of PXDD/F formation characteristics in the environment.

1. Introduction

Polychlorinated dibenzo-p-dioxins/dibenzofurans (PCDD/Fs) are well-known environmental pollutants that are strongly linked to extremely high toxicity, carcinogenicity, and bioaccumulation potential. Polybrominated dibenzo-p-dioxins/dibenzofurans (PBDD/Fs) and mixed polybrominated/chlorinated dibenzo-p-dioxins/dibenzofurans (PXDD/Fs) are PCDD/F analogues in which the chlorine atoms in PCDD/Fs are totally and partially substituted by bromine atoms, respectively. Due to the structural similarity, PBDD/Fs and PXDD/Fs possess eco-toxicological and toxicological properties quite similar to their chlorinated counterparts; thus, both chemical categories pose a severe threat to human health and the environmental safety (Samara et al., 2009; Olsman et al., 2007). All these chemicals have never been intentionally synthesized in industrial processes (Du et al., 2010; Söderström and Marklund, 2002). While a deep insight into the formation mechanism of PXDD/Fs is of importance, as it can serve as a basis for minimizing or even eliminating dioxin emissions.

Two general pathways including *de novo* synthesis and precursor route were proposed to account for the formation of PXDD/Fs (Altarawneh et al., 2009b; Weber and Kuch, 2003). The former one refers to the combination reactions origining from elemental carbon, oxygen, hydrogen, and chlorine catalyzed by typical transition metals in the temperature region of 200–400 °C (Stieglitz, 1998). While the latter involves reactions of numbers of precursors such as chlorinated phenols, chlorobenzenes and several large molecular pesticides occurring both on the transition metal-contained fly ash

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surfaces in lower temperature windows of 200–400 °C and in the gas-phase at higher temperatures (>600 °C) (Altarawneh et al., 2008; Altarawneh et al., 2009a). A general trend with PXDFs as dominant emission products has been observed in waste incinerators and some industrial processes such as secondary copper production and iron ore sintering etc (Du et al., 2010; Duan et al., 2011; Li et al., 2015; Wang et al., 2015; Xiao et al., 2016). Earlier studies indicated that *de novo* synthesis generates more PXDFs than PXDDs (Ryan and Altwicker, 2004). The studies performed by Luijk et al. (1994) and Ryan and Altwicker. (2004) proposed that PCDDs with more oxygen atoms (ether bridges) are more prone to oxidation degradation than PCDFs which may result in higher PCDF to PCDD ratios in the *de novo* synthesis process. Although the *de novo* synthesis was generally taken as a common interpretation that in the incinerator systems where PXDFs are major polyhalogenated dioxin products (Ortuno et al., 2014), in fact, apart from the *de novo* corridors, precursor routes also yield more PXDFs than PXDDs. For instance, Ryu et al. (2005) investigated the homologue patterns of PCDD/Fs from chlorophenol condensation reactions, and the results suggest that the PCDF-to-PCDD molar ratio was approximately 200 and 3 in the gas-phase and particle-mediated experiments, respectively. More PCDFs were attributed to the homogenous reactions (Ryu et al., 2005). Moreover, the precursor pathway was reported to be approximately 10^2–10^5 times faster than the *de novo* synthesis (Altwicker and Milligan, 1993; Dickson et al., 1992). Accordingly, the precursor route, especially the gaseous reactions, may contribute greatly to the high PXDF-to-PXDD ratios in environmental samples.

Chlorophenols (CPs) and bromophenols (BPs), potent and direct precursors of PXDD/Fs, are among the most abundant aromatic compounds in the incinerator gas emissions (Evans and Dellinger, 2005; 2006). Two reaction patterns including radical/radical and radical/molecule combinations were proposed to account for the homogeneous gas-phase formation of PXDD/Fs from CPs and BPs. Consensus of opinion in the literature indicates that the radical/radical mechanism bears more importance than the radical/molecule mechanism, and the contribution of the latter has long been overlooked (Louw and Ahonkhai, 2002; Sidhu and Edwards, 2002). For the formation of PCDD/Fs, the radicals involved include chlorophenoxy radicals, chloro- and hydroxyl-substituted phenyl radicals, and chlorinated phenoxyl diradicals (also called chlorinated α-ketocarbene), which are important intermediates (Lomnicki et al., 2008; Pan et al., 2013; Zhang et al., 2014). Similarly, bromophenoxy radicals play an important role in the formation of PBDD/Fs and PXDD/Fs (Saeed et al., 2015; Shi et al., 2015). As far as we know, there is no research available pertinent to bromo- and hydroxyl-substituted phenyl radicals or brominated phenoxyl diradicals. However, by analogy to the chlorinated systems, it is reasonable to assume that the brominated phenyl radicals and phenoxyl diradicals follow similar pathways to form PBDD/Fs and PXDD/Fs.

The most discussed radical/radical mechanism is composed of self-/cross-combinations of these above-mentioned radical species. However, previous research on the gas-phase formation mechanism indicates that dioxins rather than furans are the favored products in the radical/radical combination reactions (Yasuharu and Mutsumi, 1999; Zhang et al., 2008), which is in stark contrast to the experimental observations that furans are the main products. In other words, the existing radical/radical mechanism cannot make a full explanation on the known fact that PXDFs are predominant products in gas-phase reactions. As stated, this significant discrepancy has implications for the possible involvement of other routes under high temperature conditions, for instance, the radical/molecule mechanism. A careful examination of the literature shows that previous radical/molecule mechanism studies exclusively considered the reactions of BP/CP molecules with the halogenated phenoxy radicals. Early studies suggested that the reactions might be hindered due to the energetically unfavorable halogen or hydroxyl displacement steps in the initial reactions between BP/CPs and halogenated phenoxy radicals (Louw and Ahonkhai, 2002). For this reason, the contribution of the radical/molecule mechanism has long been overlooked to total PXDD/F emissions. As far as we know, however, so far, there are no available studies on the possible combination reactions of BP/CPs with substituted phenyl and phenoxyl diradicals. We therefore turn our attention to the above-mentioned condensation reactions for the following reasons. First, phenyl and phenoxyl diradicals have great potential to form dioxins (Pan et al., 2013; Zhang et al., 2014). Second, both the phenyl and phenoxyl diradicals have a typical σ-type radical center that possesses high reactivity and therefore are likely to react with CP and BP molecules readily. Third, exclusive PCDF formation by chlorinated benzenes may be strongly correlated with the reactions of phenyl carbon radicals that afford high PXDF-to-PXDD ratios (Nganai et al., 2011; 2014).

In this work, using 2-bromophenol (2-BP) and 2-chlorophenol (2-CP) as model compounds, we investigated the initial pathways for the gas phase formation of PXDD/Fs through the condensation reactions of 2-BP/2-CP with substituted phenyl radical 2-hydroxylphenyl (**PR2**), 2-hydroxyl-3-bromo-phenyl (**BPR2**) and 2-hydroxyl-3-chloro-phenyl (**CPR2**), phenoxyl diradical (**PR3**), substituted phenoxyl diradicals 3-bromo-2-oxocyclohexa-2,5-dienylidene (**BPR3**) and 3-chloro-2-oxocyclohexa-2,5-dienylidene (**CPR3**) (shown in Fig. 1). The objective of this work is to explore new mechanisms for the formation of PXDD/Fs and determine the effect of these two types of radicals on the resulting PXDF-to-PXDD ratio. The optimized structures of the molecules and radicals involved in this work are depicted in Fig. 1.

2. Computational methods

All of the electronic structure calculations were conducted using the Gaussian 09 program suite (Frisch et al., 2010). Fully geometrical optimizations for the reactants, intermediates, and products involved in this work were conducted using the BB1K functional with the standard 6-311G(d,p) basis set. The vibrational frequencies were calculated at the same level of theory to determine the nature of minima and first-order saddle points and to provide the zero-point vibrational enthalpy (ZPH). Single point energy calculations were refined at the BB1K/6-311+G (3df,2p) level. The BB1K functional performs well on saddle point geometry and barrier height calculations and has been successfully used in previous dioxin formation studies (Pan et al., 2013; Zhao et al., 2004). Calculations of the intrinsic reaction coordinate (IRC) were performed to confirm that each transition state (TS) is connected to the two desired minima. Furthermore, as will be seen in the following section, the geometries of the intermediates and transition state structures involved in the reactions of 2-B(C)P molecule with H radical were optimized at the BB1K and M06-2X functional combined with the standard 6-311G(d,p), def-TZVP, and aug-cc-pVDZ basis sets, and the corresponding activation and reaction enthalpies were also calculated in order to indentify the reliability and accuracy of the method adopted in this work.

The kinetic calculations were carried out using the kinetic and statistical thermodynamic (KiSThelP) program (Canneaux et al., 2014). The reaction rate constants for all the radical/molecule combination reactions were calculated based on the conventional transition state theory (TST) over the temperature range of 600–1200 K. The effect of quantum tunneling on rate constants was considered based on the one-dimensional Wigner's formalism as implemented in the KiSThelP program (Wigner, 1937). Pressure-dependent reaction rate constants for several unimolecular