Formation of mixed halogenated dibenzo-*p*-dioxins and dibenzofurans (PXDD/Fs)

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HIGHLIGHTS

- We investigated mechanistic and kinetic parameters for PXDD/F generation.
- The keto-ether adducts act as direct intermediate to form dioxin species.
- The di-keto structures initiate the production of furan compounds.
- PXDD/F formation mechanism is only sensitive to halogen substituent at *ortho* site.

GRAPHICAL ABSTRACT
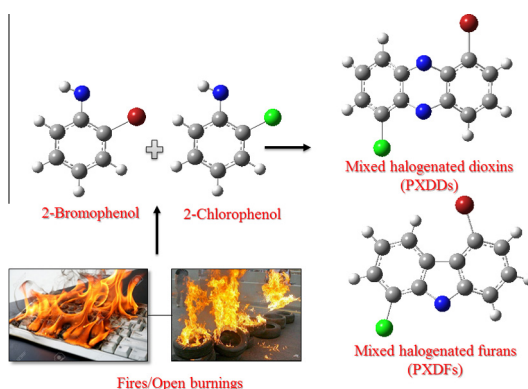
ABSTRACT

This contribution investigates mechanistic and kinetic parameters pertinent to formation of mixed dibenzo-*p*-dioxins and dibenzofurans (PXDD/Fs) from the condensation reactions involving 2-chlorophenoxy (2-CPxy) and 2-bromophenoxy (2-BPxy) radicals. Keto-ether structures act as direct intermediates for the formation of DD, 1-MCDD, 1-MBDD, 1-B,6-CDD and 1-B,9-CDD molecules. Likewise, diketo adducts initiate the formation of 4-MCDF, 4-MBDF and 4-B,6-CDF compounds through interconversion and rearrangement reactions. As formation mechanisms of halogenated dibenzo-*p*-dioxins and dibenzofurans from precursors of brominated and chlorinated phenols are insensitive to substitution at *meta* and *para* sites, our mechanistic and kinetic analysis of reactions involving 2-BPxy and 2-CPxy should also apply to higher halogenated phenoxy radicals.

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1. Introduction

Brominated flame retardants (BFRs) signify a group of brominated hydrocarbons added frequently to polymeric materials to delay ignition and to improve the fire resistance traits of treated materials. Based on their combustion chemistry, these compounds display tendency to transform into incomplete combustion products (ICPs), most notably, polybrominated dibenzo-*p*-dioxins and dibenzofurans (PBDD/Fs) (Ebert and Bahadir, 2003; Weber and Kuch, 2003; Birnbaum and Staskal, 2004). PBDD/Fs along with their chlorinated counterparts, polychlorinated dibenzo-*p*-dioxins and dibenzofuran (PCDD/Fs) discharge into the environment from nearly all thermal processes, including uncontrolled fires, recycling facilities, municipal waste incinerators, smouldering and other

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combustion systems (Tame et al., 2003, 2007; Wang et al., 2010; Wanga et al., 2010; Duan and Li, 2011).

Both gas-phase homogeneous and surface-mediated routes operate in the formation of PCDD/Fs and PBDD/Fs. Heterogeneous pathways, especially, via the so-called de novo synthesis, appear to bear more importance than pure gas-phase corridors in the formation of PCDD/Fs and PBDD/Fs alike (Tuppurainen et al., 2003; Ortuno et al., 2014). However, the presence of potent gas phase precursors greatly enhances the contribution of the gaseous corridor (Dickson et al., 1992; Altarawneh et al., 2009; Yu et al., 2011). Chlorophenols (CPs) (Karasek and Dickson, 1987; Dickson et al., 1992; Kari et al., 2000) and bromophenols (BPs) (Dumler et al., 1989; Evans and Dellinger, 2003a, 2005b) comprise the most-discussed precursors for the formation of PCDD/Fs and PBDD/Fs, respectively. In addition, CPs and BPs function commonly as feed stocks and intermediates in manufacturing of halogenated flame retardant chemicals.

Along the same line of enquiry, the co-combustion of bromine and chlorine-bearing materials, as in fire involving BFRs and polyvinyl chloride (PVC), leads the formation of mixed halogenated dibenzo-p-dioxins and dibenzofurans (PXDD/Fs) (Weber and Kuch, 2003; Hayakawa et al., 2004; Schuler and Jager, 2004). Stieglitz et al. (1989) reported the formation of PXDD/Fs from carbonaceous particulate matter and inorganic chloride in the presence of bromine. Söderström and Marklund (2002) observed the generation of complex mixture of PXDD/Fs from incineration of artificial municipal wastes containing both chlorine and bromine input sources. Open burning of municipal waste and the thermal recycling of discarded electrical and electronic equipment constitute major sources for emission of PXDD/Fs (Buser, 1987; Vehlow et al., 2000; Lemieux et al., 2002; Weber and Kuch, 2003; Xiezhi et al., 2008). Once emitted into air and water bodies, these pollutants can easily undergo long-range transport to remote areas.

Isomers of PXDD/Fs have been detected in various environmental matrices such as sewage sludge (Hagenmaier et al., 1992), air and bulk deposition (Hayakawa et al., 2004), soil and sediments (Kannan et al., 1998; Myers et al., 2012), fly ash (Schafer and Ballschmiter, 1986; Harless and Lewis, 1989; Schwind et al., 1998; Nakao et al., 2002), and industrial emissions (Du et al., 2010). In total, there exist 4600 distinct congeners of PXDD/Fs (Brigden and Labunska, 2009). The toxicity of each congener depends on the degree, position and type of halogenated substituents on the aromatic ring. Therefore, close to one thousand congeners of PXDD/Fs are reported to induce toxic effects as a consequence of halogenation at the lateral 2, 3, 7 and 8 positions (Mason et al., 1987; Behnish et al., 2001; Brigden and Labunska, 2009).

Quantum chemical and experimental studies have revealed detailed reaction mechanisms and kinetic parameters for the formation of PCDD/Fs and PBDD/Fs, whereas the available literature on the reaction pathways controlling emission of PXDD/Fs remains rather scarce. Dillinger's group examined experimentally the potential of a mixture of 2-CP and 2-BP to produce congeners of PXDD/Fs in inert and oxidising environments (Evans and Dellinger, 2005a, 2006). Few studies addressed the effect of temperature and residence time on the degree of halogenation of PXDD/Fs (Söderström and Marklund, 2000, 2004). These authors demonstrated that, formation of PXDD/Fs follows the same operating mechanism as that for PCDD/Fs and PBDD/Fs. However, distinct halogenation patterns appear for PXDD/Fs, in reference to those of PCDD/Fs and PBDD/Fs. Reduction in temperature and longer residence time increase the chlorine to bromine ratio in PXDD/Fs. Yields of PXDD/Fs and their homologue distributions depend on bromine and chlorine content in input feed stream (Funcke et al., 1997; Kawamoto and Ishikawa, 2005).

Based on an analogy to the controlling mechanisms that underpin the production of PCDD/Fs and PBDD/Fs in the combustion systems, PXDD/Fs arise in mixtures of CPs and BPs through condensation modes incorporating molecule/molecule, molecule/radical and radical/radical reactions followed by intermolecular rearrangements of initially formed intermediates. Among these condensation modes, radical/radical dimerisation reactions represent the most accessible corridors in the formation of PCDD/Fs and PBDD/Fs, in comparison to molecule/molecule coupling reactions that demand high activation barriers (Altarawneh et al., 2007; Yu et al., 2011). Halogenated phenoxy radicals form either via direct fission of their hydroxyl OH bonds or through bimolecular reactions with OH, H, Br and Cl (Altarawneh et al., 2008; Xu et al., 2010; Gao et al., 2013). Furthermore, enzyme-catalysed reactions readily degrade CPs into smaller, yet toxic constituents (Öberg et al., 1990; Li et al., 2015).

To this end, the current study elucidates gas phase mechanistic pathways leading to the formation of PXDD/Fs from bimolecular reactions of 2-CP and 2-BP molecules and their derived phenoxy radicals. The objective is twofold, firstly to assess the energy requirements for all routes participating in the formation of PXDD/Fs, and secondly to deduce reaction rate constants of key elementary unimolecular and bimolecular reactions. The article investigates thoroughly the relative importance of the competing pathways, providing the first mechanistic interpretation for the experimental trends reported in literature.

2. Computational details

The Gaussian09 (Frisch et al., 2009) programme executes all structure optimisations and energy calculations. All calculations have been performed at the meta hybrid density theory functional (DFT) level of M062X (Zhao and Truhlar, 2008), together with the polarised basis set of 6-311+G(d,p) (Montgomery et al., 1994). The M062X hybrid *meta* exchange correlation functional was designed to predict accurate thermochemical and kinetic parameters for general applications in organic reactions. Single-point energy calculations, with the extended basis set of 6-311+G(3df,2p) for selected reaction, have modified the computed reaction (in kJ) and activation enthalpies (in kJ mol^{-1}) only marginally, in the range of 0.2–1.5 units. This finding agrees with our analogous result from recent studies on formation of PCDD/Fs and PBDD/Fs from chlorinated and brominated diphenyl ethers, respectively (Altarawneh and Dlugogorski, 2013, 2014). We have shown that deploying higher basis sets alters marginally the energies calculated by M05 and M06 functionals. Intrinsic reaction coordinate (IRC) (Fukui, 1981; Hrant et al., 2005) calculations serve to link the transition states with their reactants and products. The kinetic and statistical-thermodynamic (KiSThelP) program (Canneaux et al., 2004) computes all reaction rate constants based on the conventional transition state theory (TST). A one-dimensional Eckart functional accounts for the plausible contributions from quantum tunnelling effects (Eckart, 1930). We fit reaction rate constants to the Arrhenius formula, $k(T) = Ae^{-(Ea/RT)}$, over the temperature range of 300–1200 K.

3. Results and discussions

3.1. Formation of 2-chlorophenoxy and 2-bromophenoxy radicals

Self-dimerisation reactions of chlorophenoxy (Evans and Dellinger, 2003b; Tuppurainen et al., 2003) and bromophenoxy (Evans and Dellinger, 2003a, 2005b; Yu et al., 2011) radicals