

REACTIONS OF 2-CHLOROPHENOL AND 2-BROMOPHENOL: MECHANISMS OF FORMATION OF MIXED HALOGENATED DIOXINS AND FURANS (PXDD/Fs)

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Introduction

Polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs) and polybrominated dibenzo-*p*-dioxins and furans (PBDD/Fs) form invariably as unwanted byproducts, in the presence of trace sources of halogens, in thermal systems including smouldering, municipal waste incineration, fires as well as combustion stoves and burn barrels.¹⁻⁴ PCDD/Fs and PBDD/Fs arise both in homogenous and heterogeneous processes, the former involving precursor species reacting in the gas phase, and the latter comprising the so-called precursor and de novo catalytic pathways. Gaseous chlorophenols (CPs) and bromophenols (BPs) act as potent precursors.⁵⁻⁷ The co-existence of brominated flame retardants (BFRs) and polyvinyl chlorides (PVC) in house fires and in thermal treatment and recycling of electrical and electronic wastes establishes a unique environment for the formation of mixed chlorinated and brominated dibenzo-*p*-dioxins and furans (PXDD/Fs).⁸⁻¹⁰ The toxicity of PXDD/Fs strongly depends on position and number of chlorine and bromine substituents.¹¹⁻¹² Overall, there are 4600 distinct PXDD/Fs congeners, with around one thousand of them exhibiting toxic nature as a consequence of their halogenation at positions 2, 3, 7 and 8 on the aromatic rings.

While great deal of research on PCDD/Fs and PBDD/Fs has revealed in detail their formation mechanisms, the reaction pathways controlling emission of PXDD/Fs have received less attention. Dellinger's group reported that, oxidation and pyrolysis of mixtures containing 2-chlorophenol (2-CP) and 2-bromophenol (2-BP) leads to the production of several congeners of PXDDs¹³⁻¹⁴, in addition to the appearance of PCDD/Fs and PBDD/Fs. Based on demonstrated mechanisms of the formation of PCDD/Fs and PBDD/Fs, the principal steps overriding the formation of PXDDs from chlorinated and brominated phenols involve condensation reactions, intermolecular rearrangements of intermediates as well as halogenation and hydrogenation reactions. Nevertheless, a comprehensive understanding of the mechanism governing the formation of PXDDs necessities addressing all plausible chemical reactions on a precise atomic basis.

To this end, this theoretical contribution investigates gas-phase bimolecular reactions involving 2-CP and 2-BP molecules (and their derived phenoxy radicals), as an initial corridor for the formation of PXDD/Fs. Our aim is twofold, firstly to survey energetic requirements for the formation of initial pre-PXDDs intermediates and secondly to assess the selectivity of prominent reaction steps depending on the presence of H, Cl or Br at the *ortho* site on the phenol molecule. Recently, we have reported the thermochemical and kinetic parameters, for reactions pathways operating in the formation of PCDD/Fs¹⁵ and PBDD/Fs¹⁶ from correspondingly chlorinated and brominated diphenyl ethers, to remain largely insensitive to degree and pattern of halogenation at *meta*-, and *para*-substituted sites. Thus, the results presented herein for 2-CP and 2-BP should also be applicable to more completely halogenated congeners of phenols.

Methodology

Structural optimisation and energy calculations are performed with the Gaussian09 suite¹⁷ of programs at a meta hybrid density theory functional (DFT) level of M062X, together with the basis set of 6-311+G(d,p). Computations of the intrinsic reaction coordinates (IRC) link transition structures with their reactants and products. KiSTheP package¹⁸ serves to compute reaction rate constants. We fit the reaction rate constants to the simple Arrhenius formula, $k(T) = A e^{-E_a/RT}$, in the temperature range of 300 K to 1200 K.

Results and Discussion

In an analogy to the well-established mechanism for the formation of PCDDs and PBDDs, PXDD/Fs arise in bimolecular reactions involving radical/radical, molecule/molecule, and molecule/radical combinations followed by cyclisation of the initially formed intermediates. As 2-CP and 2-BP molecules exhibit very similar O-H bond dissociation enthalpy (359.4 kJ mol⁻¹ and 361.2 kJ mol⁻¹), it is anticipated that 2-chlorophenoxy (2-CPxy) and 2-bromophenoxy (2-BPxy) radicals form in the same temperature window, either via unimolecular or bimolecular reactions. It follows that, 2-CPxy and 2-BPxy co-exist in the combustion media. Figure 1 depicts all plausible

products from bimolecular reactions of one 2-chlorophenoxy (2-CPxy) radical with one 2-bromophenoxy (2-BPxy) radical. As there exist four radical sites in 2-CPxy and 2-BPxy, and O–O coupling remains unstable, there are 15 isomeric structures (D1-D15) that result from the combination of radicals on the phenolic oxygen, on H, Cl, and Br-substituted *ortho* carbons and on H-bearing *para* carbons in CPxy and BPxy molecules. As the two phenyl rings could easily rotate about C–C/C–O linkages, energies in Figure 1 correspond to the most stable conformers of each structure.

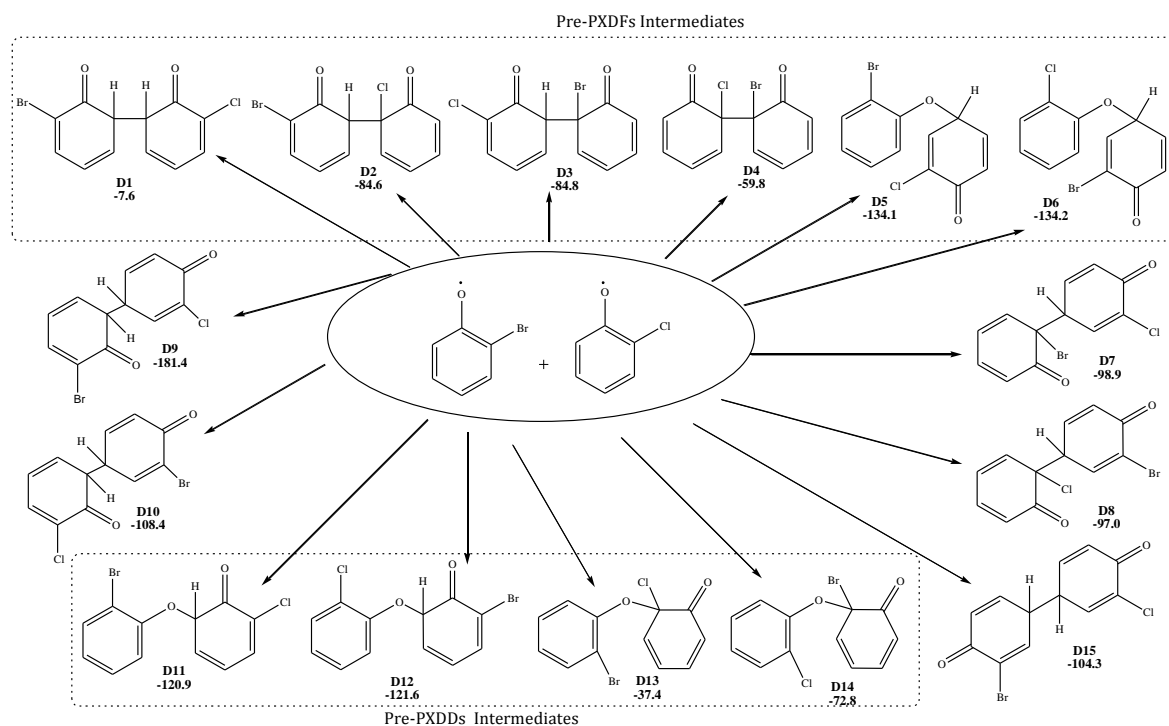


Figure 1: Formation of stable structures from the reaction of 2-bromophenoxy and 2-chlorophenoxy radicals. Reaction enthalpies at 298.15 K (kJ mol⁻¹) are set in bold font.

Two phenoxy radicals each with one available *ortho*-substituted halogen atom may combine to form keto-ether species that act as prerequisites for the generation of PXDD congener's, whereas, two phenols each with one available *ortho*-substituted hydrogen may react to form diketo species that transform into PXDFs. The coupling of 2-CPxy and 2-BPxy at *ortho-ortho* carbon sites bearing a hydrogen or a halogen atom and *para-para* carbon sites bearing a hydrogen atom lead to the formation of D1-D4 and D15 isomers, respectively. Structures of D11-D12 and D13-D14 evolve from the attachment of the phenolic oxygen to an *ortho* carbon (H) or an *ortho* carbon (halogen) site, correspondingly, whereas D7 and D8 arise through coupling of *ortho* carbon bearing halogen with *para* carbon (H). Intermediates of D9 and D10 result from coupling of an *ortho*-substituted carbon site to a *para*-substituted carbon site. Structures of D1-D6 act as pre-PXDFs intermediates and D11-D14 as pre-PXDDs intermediates (see Fig 1). Among all structures, the formation of the D9 intermediate constitutes the most exothermic initial corridor. As all intermediates evolve without encountering an intrinsic reaction barrier, the thermodynamics control the abundances of these moieties. Besides serving as building blocks for the formation of PXDD/Fs, unimolecular decomposition of some of these intermediates leads to formation of other mixed halogenated compounds, most notably benzofurans, naphthalenes and biphenyl ethers.

Closed shell pathways encountered in the molecule/molecule reactions usually require overcoming very high activation barriers (evoked by HBr, HCl and H₂ elimination reactions). For this reason, we have excluded these pathways from our analysis to focus on the two more accessible radical/molecule reactions; i.e., between 2-CP and 2-BPxy, and between 2-BP and 2-CPxy. Figures 2a and 2b illustrate the products of these radical/molecule coupling modes for 2-CP/2-BPxy and 2-BP/2-CPxy, respectively. Products from these bimolecular reactions represent important pre intermediates (pre-PXDD and pre-PXDF) in the formation of PXDD/Fs. Figure 2 embeds the values of reaction enthalpy and activation enthalpy, for the six reaction pathways (R1-R6).

Overall, the reaction of 2-CP/2-BPxy and 2-BP/2-CPxy exhibit similar mechanistic and kinetic characteristics. For example, similar activation energies accompany the attachments of the phenoxy O in the two systems at *ortho*-substituted hydrogen (R1 and R5) and halogen (R2 and R4) bearing sites. The latter group of reactions results in a subsequent eviction of the halogen atom. It is evident from Figure 2 that, pathways leading to elimination of atomic chlorine (R2) and bromine (R4) incur significantly lower activation energies than the corresponding reactions involving the elimination of HCl (R6) and HBr (R3). This elimination occurs as a consequence of the attack of the hydroxyl group of 2-CP and 2-BP molecules on the *ortho*-bonded Cl and Br atoms in 2-CPxy and 2-BPxy moieties, respectively. Owing to a weaker aromatic C-Br bond ($349.3 \text{ kJ mol}^{-1}$) in reference to an aromatic C-Cl bond ($399.6 \text{ kJ mol}^{-1}$), the elimination of HBr (R3) requires lower activation enthalpy, by 15.1 kJ mol^{-1} , in comparison to the elimination of HCl (R6).

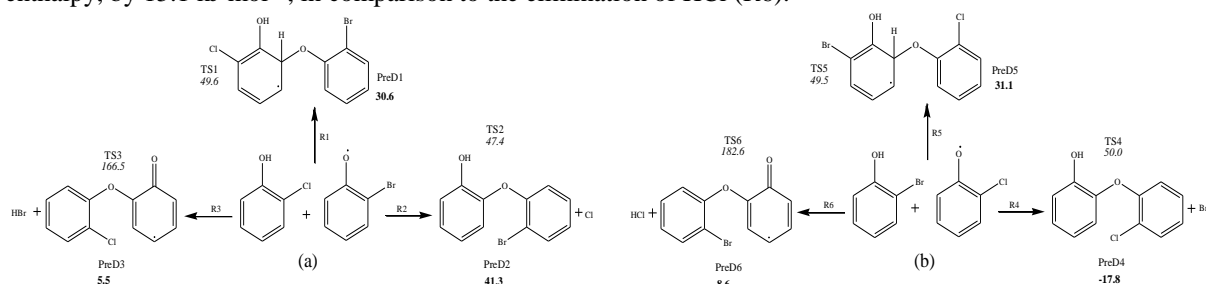


Figure 2: Pathways to predioxin structures from the combination of 2-chlorophenol molecule and 2-bromophenoxy radical (a) and 2-bromophenol molecule and 2-chlorophenoxy radical (b). Values in bold and italic denote reaction and activation enthalpies; respectively. All values are in kJ mol^{-1} calculated at 298.15 K.

Next, we turn our attention to investigate the effect of halogenation type on prominent reaction steps involved in the formation of PXDDs. Final ring-closure reactions often constitute a rate-determining step in the formation mechanism of PCDDs and PBDDs. In Figure 3, we consider two cases of ring-closure reactions, an open-shell route (Figure 3a) and a closed-shell route (Figure 3b). Herein, the Gibbs free energy changes of reactions (ΔG_r) computed with ChemRate program are introduced to assess the nature of the reactions. Substitution of both *ortho* sites on one phenyl ring with chlorine and bromine (see structures of preD7 and preD8) enables us to assess the effect of the halogenation type on kinetics of the final ring-closure step.

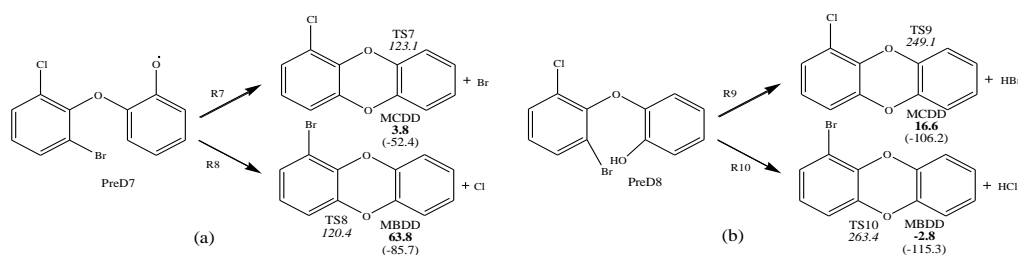


Figure 3: Ring-closure reactions for open (a) and closed (b) shell categories. Values in bold and italic denote reaction and activation enthalpies, respectively at 298.15 K. Values in bracket represent Gibbs free energy change of reaction at 900 K. All values are in kJ mol^{-1} .

As depicted in Figure 3a, attachment of the phenoxy radical site in preD7, on one phenyl ring, to the bromine- and chlorine- substituted *ortho* positions (R7 and R8, respectively), on the other phenyl ring, occurs simultaneously with the departure of these two halogen atoms and results in the formation of MCDD and MBDD molecules, respectively. Reactions R7 and R8 demand similar activation enthalpies. To demonstrate the thermodynamic feasibility of the reactions described in Figure 3, we also quote the Gibbs free energy change of reaction (ΔG_r), as calculated at 900 K. Based on ΔG_r values, we predict reactions R7-R10 to be vastly spontaneous. The intra-annular displacement of HBr requires a lower activation barrier than that of HCl ($249.1 \text{ kJ mol}^{-1}$ versus $263.4 \text{ kJ mol}^{-1}$), distinguishing the effect of *ortho*-substituted halogenation type on these condensation reactions, as shown in Figure 3b. Table 1 lists the reaction rate parameters for pathways shown in Figures 2 and 3. At a temperature relevant to the homogenous formation of dioxins, i.e., 900 K, we found that, the rate of ring-closure reaction R7 (bromine *ortho*-substituted site) closely matches that of R8 (chlorine *ortho*-

substituted site). At the same temperature, ring-closure reaction R9 (bromine *ortho*-substituted site) rate exceeds that of R10 (chlorine *ortho*-substituted site) by almost seven times. Reaction R2 proceeds at a rate of $6.2 \times 10^{-19} \text{ cm}^3 \text{ s}^{-1} \text{ molecule}^{-1}$ that is slightly higher than that of corresponding R1 ($5.2 \times 10^{-19} \text{ cm}^3 \text{ s}^{-1} \text{ molecule}^{-1}$). We predict that, the reaction rate constant for the elementary reaction R5 to surpass, by a factor of three, the parallel competing reaction of R4. The resulting rate constant values for reactions R7 and R8 remain in reasonable agreement with the recent theoretically predicted values for the analogues systems of PCDD/Fs and PBDD/Fs.¹⁹⁻²⁰

Table 1: Arrhenius rate parameters for bimolecular/unimolecular reactions fitted in the temperature range of 300 K-1200 K. Values of arrhenius parameter (A) are in ($\text{cm}^3 \text{ s}^{-1} \text{ molecule}^{-1}$) and values of activation enthalpies (E_a) are in kJ mole^{-1} units.

Reaction	A	E_a	Reaction	A	E_a
2-CP + 2-BPxy \rightarrow preD1	2.0×10^{-15}	61.8	2-BP+ 2-CPxy \rightarrow preD6	1.1×10^{-14}	196.7
2-CP + 2-BPxy \rightarrow preD2	1.4×10^{-15}	58.0	PreD7 \rightarrow MCDD	1.3×10^{11}	116.5
2-CP + 2-BPxy \rightarrow preD3	9.8×10^{-15}	180.1	PreD7 \rightarrow MBDD	2.2×10^{11}	118.3
2-BP+ 2-CPxy \rightarrow preD4	8.5×10^{-16}	59.8	PreD8 \rightarrow MCCD	1.5×10^{12}	250.1
2-BP+ 2-CPxy \rightarrow preD5	2.8×10^{-15}	61.8	PreD8 \rightarrow MBDD	1.5×10^{12}	264.8

In conclusion, this thermochemical and kinetic investigation studied the formation of PXDD/Fs from combinations of 2-chlorophenol and 2-bromophenols, in a radical/radical and radical/molecule coupling modes. The last proceeds preferentially, via elimination of a halogen atom rather than through the displacement of HCl and HBr. The coupling of radicals afford 15 distinct isomers in which six could serve as direct building blocks for the formation of mixed halogenated furans and four for the generation of brominated (D12), chlorinated (D11) dehalogenated (D13-D14) dioxins. It is inferred that, open-shell ring-closure reactions are insensitive to the type of halogenation on the neighbouring phenyl ring. However, the analogous closed-shell ring-closure pathways clearly favour the departure of HBr over that of HCl.

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