

MECHANISMS FOR PCDF AND PCB FORMATION FROM FIRES: PATHWAYS FROM OXIDATION OF CHLOROBENZENES

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ABSTRACT

Fires provide optimum conditions to produce polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/F) as well as polychlorinated biphenyls (PCB). In this study, we deploy the density functional theory (DFT) to simulate the production of PCB, and polychlorinated dibenzofurans (PCDF), which are formed in fires from the precursor chlorobenzene in preference to polychlorinated dibenzo-*p*-dioxins (PCDD). We demonstrate that, combinations of chlorobenzene with chlorophenyl radicals generate PCB compounds through an exothermic reaction of 18.7 kcal/mol. H on the pivot bond could be self-expulsed through an energy barrier of 21.7 kcal/mol to produce 2,2'-dichlorobiphenyl. Combinations of chlorobenzene and chlorophenoxy radicals, formed in early stages of the oxidation of chlorobenzene, afford 16 different precursors for PCDFs. All these reactions are endothermic, between 18.3 to 38.8 kcal/mol at 298 K, with activation enthalpies higher by 3-10 kcal/mol than the reaction enthalpies.

KEYWORDS: Fire chemistry, Formation of dioxins in fires, Density Functional Theory (DFT)

INTRODUCTION

Unenclosed burning of various materials in the ambient environment produces greater emissions of pollutants than that involving controlled combustion systems in industry.^{1,2} These systems incorporate adequate mixing of fuel and air at high temperatures and select appropriate gas-phase residence times to achieve high degree of combustion completeness, where fuel is converted into water and carbon dioxide. Open burning as a non-ideal combustion process produces carbon monoxide, methane, volatile organic pollutants (VOP) such as benzene, semi-volatile organic pollutants (SVOP) such as polycyclic aromatic hydrocarbons (PAH) in addition to soot and particulate matter (PM).¹

Among various pollutants, open burning of a wide range of fuels also leads to formation of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (often denotes as dioxins). Dioxins are persistent, bioaccumulative and toxic (PBT)³, formed almost inevitably in all thermal systems when chlorine and carbon sources are presents. For these reasons, dioxins are a major public concern. Although emissions of dioxins from industrial sources have been decreasing¹ over the last decade, as a consequence of operational improvements and deployment of cleaning equipment, contribution of open burning to the global inventory of dioxins has witnessed a dramatic increase. For example, burning of household wastes is one of the largest airborne sources of dioxins in the United States.⁴

Under fires conditions, PCDD/F species are emitted near the ground level allowing their deposition directly in the urban areas unlike the case of industrial combustion processes, where tall stack distribute the pollutants in the environment.¹ This means that dioxin emissions from fire sources are most likely to have local impact in the vicinity of the emission source. Unfortunately, measurements of dioxin emissions from fires are only available in the literature for a limited number of fire types, with the existing data summarised in Table 1. Forest fires constitute a significant source of dioxins on a global scale, contributing appreciably to dioxin inventories in some countries, such as Australia.⁵

TABLE 1. Emissions of dioxins from different fires types

Source	Emissions (mg/kg)	Ref
Forest fires	$1.5 \times 10^{-4} - 6.7 \times 10^{-3}$	6
Burning of agricultural crops	5.4×10^{-4}	7
Burning of pools of liquid fuels	4.3×10^{-4}	7
Barrels burning of household wastes	26×10^{-3}	8
Burning of automobile shredder residue	4.45	9
Pesticide bags	2.2×10^{-4}	10
Treated wood	2.7×10^{-1}	11

Lemieux *et al.*¹ have defined what they called the worst-case scenario for dioxins formation in open fires. This includes poor gas-phase mixing, low temperature of combustion, insufficient oxygen content, the presence of particulate matter (PM) bound to copper species and the presence of hydrochloric acid or molecular chlorine. A number of formation mechanisms for PCDD/F has been proposed. Two temperature windows promote the formation of PCDD/F.¹² The first, between 500 and 800 °C facilitates the generation of PCDD/F from precursors, such as chlorobenzenes (PCBz) and chlorophenols (PCP). In this temperature window, the rate determining steps involve the cyclisation of polychlorobiphenyls and polychlorodiphenyl ethers, with pathways based on radical reaction (open shell pathways) dominating those involving enolisation/tautomerisation (closed shell pathways), both under oxidative and non-oxidative conditions.¹³ The second route, operating between 200 and 400 °C, involves the formation of PCDD/F from precursors in catalytic processes with metals and metal oxides, from the burrnof of carbon matrix or from the so-called *de novo* process. In the open burning of household wastes in barrels, a strong correlation exists between emissions of PCDD/F and concentration of hydrochloric acid and copper.¹² Deacon reaction is responsible for converting HCl into Cl₂, which then chlorinate the gaseous precursors.

In our previous study,¹³ we investigated the formation of PCDD/F from 2-chlorophenol using the density functional theory (DFT), with the results of the computations compared with available experimental results. We found that the formation of chlorinated bis keto dimers, which results from cross coupling of 2-chlorophenoxy at the *ortho* carbon bearing hydrogen (a known direct route for PCDF formation), passes through a tight transition structure with a barrier of 9.4 kcal/mol (0 K). Three routes for the formation of the most abundant PCDD/PCDF species (*viz.*, 4,6-dichlorodibenzofuran, 4,6-DCDF, and 1-monochlorodibenzo-*p*-dioxin, 1-MCDD) in oxidation and pyrolysis of 2-chlorophenol were discussed. In the case of 4,6-DCDF, formation through H or $\text{HO} + \text{keto-keto} \rightleftharpoons \text{H}_2$ or $\text{H}_2\text{O} + \text{keto-keto} \rightleftharpoons \text{H}_2$ or $\text{H}_2\text{O} + \text{enol-keto} \rightleftharpoons \text{H}_2$ or $\text{H}_2\text{O} + 4,6\text{-DCDF} + \text{HO}$, was shown to be the preferred route. The other two routes proceed via closed shell processes ($\text{keto-keto} \rightleftharpoons \text{enol-keto} \rightleftharpoons \text{enol-enol} \rightleftharpoons \text{H}_2\text{O} + 4,6\text{-DCDF}$) and ($\text{keto-keto} \rightleftharpoons \text{enol-keto} \rightleftharpoons (\text{H}\cdot, \text{OH}\cdot) 4,6\text{-DCDF} \rightleftharpoons \text{H}_2\text{O} + 4,6\text{-DCDF}$).

In this study, we apply the same approach to investigate the formation of PCDD/F from the gas phase reactions of chlorobenzenes (PCBz). Table 2 summarises typical emissions of PCBz from fires, along with the emissions of polychlorinated phenols (PCP) and benzenes. Note that for PCBz, the literature reports very few measurements for fires. PCBz in fires result either from burning the material itself or from chlorination of the abundant benzene, with chlorine formed through conversion of HCl into Cl₂ by means of the Deacon reaction. For combustion processes occurring in municipal solid waste incinerators, the concentration of chlorobenzenes was found to correlate well with that of HCl¹³, which indicates that chlorobenzene is most likely produced through chlorination of benzene ring rather than from evaporation of PCBz from the combusted material. Furthermore, a good correlation was established between the emissions of PCDD/F congeners and PCBz, with the emission of both species exhibiting similar dependence on temperature and residence time.¹⁵

TABLE 2. Emissions of benzene, chlorophenols and PCBz (in mg/kg) from different fires categories

Fire type	Benzene	Chlorophenols	Chlorobenzenes	Ref
Forest fires	230	---	---	16
Agriculture crop	208	52	---	17
Land cleaning debris	305	---	---	18
Fuel liquid	1022	---	---	7
Household waste	980	1.2	0.37	19
Scrap tires	2180.6	---	---	20
Pesticide bags	50	---	---	10
Fibreglass	---	---	25	21
Shredder residue	9584	---	---	9

The complexities of a fire environment prevent one from studying in detail the kinetics of a single chemical reaction; a large number of reacting species existing at the same instant, metal catalysts obscure the kinetics of gas reactions, and temperature and radical fields are poorly defined. However, these complexities can be avoided by employing an *ab initio* approach (*i.e.*, numerical solution of the Schrödinger equation) to study the kinetics and thermodynamics of a reaction of interest, or a group of reactions. Although time-consuming and intricate in their own right, *ab initio* calculations provide detailed insights at the atomic scale of the reacting species. This is the approach adopted in the present work. The result of this study will serve to build a detailed kinetic mechanism, supplying thermokinetic parameters for the formation of PCDD/F (mainly PCDF) from PCBz. We also investigate other parallel reactions, such as self-decomposition of chlorophenoxy radicals and the formation of polychlorinated biphenyls (PCB). For simplicity, we have chosen to study the monochlorinated benzene (C_6H_5Cl), though the results should be applicable to other PCBz congeners. Our aim in this study is to recap all possible reactions that could take place in the oxidation of chlorobenzene and lead to the formation of PCDD/F and PCBs in fires.

COMPUTATIONAL DETAILS

All calculations were performed with the Gaussian 03 suite of programs.²² Optimised geometries and harmonic vibrational frequencies of all reactants, products and transition structures on the reaction potential-energy surface have been calculated using the hybrid density functional theory (DFT) of B3LYP which employs the three parameter Becke exchange functional, B3²³, with the Lee-Yang-Parr nonlocal correctional functional LYP²⁴ along with the polarised basis set of 6-31G(d).²⁵ Stationary points on reaction potential energy surfaces (PES) were characterised either as minima or transition structures (TS) through the analysis of their vibrational frequencies, where transition structures contain one and only one imaginary frequency along the reaction coordinate. Where appropriate, intrinsic reaction coordinates (IRC) calculations have been used to link the reactant and product with their transition structures along the reaction pathway. Where the main discussion is based on enthalpies at 298 K, Gibbs free energies ($\Delta_r G$) are introduced when they differ significantly from the enthalpy values.

RESULTS AND DISCUSSION

Polychlorobenzenes (PCBz) in the presence of oxygen at temperatures above 300 °C produce substantial amounts of PCDF and polychlorinated biphenyls (PCB).²⁶ Without oxygen, chlorination reactions dominate and form higher chlorinated congeners. While a mixture of chlorinated phenols and chlorinated phenoxy radicals produces comparable amounts of PCDD and PCDF, as is the case of municipal solid waste incinerators, homologue profiles from oxidation of PCBz are largely dominated by PCDF congeners, where the sum of PCDD corresponds to less than 10%²⁶ of the total PCDD/F. Thus, it is clear that PCDF generated from oxidation of PCBz could not be formed via the same

mechanism as PCDD/F produced from chlorophenols/chlorophenoxy; *i.e.*, from cross-coupling of two chlorinated phenoxy radicals, at carbon sites bearing the hydrogen atoms.

In the presence of no interaction between the triplet dioxygen molecule and monochlorobenzene (MCP), the initial decomposition step corresponds to a direct ejection of either H or Cl from the benzene ring. Cl more readily abstracts H than Cl from MCP. If sufficient oxygen is present in the system, it competes with chlorine in attacking the available radical site that resulted from H abstraction by Cl from MCP. This process leads to the formation of three chlorophenylperoxy radicals. At moderate temperature, the main exit channel for the chlorophenylperoxy radicals constitutes the expulsion of the terminal oxygen atoms of the peroxy group to form three chlorophenoxy radicals. Fig. 1 illustrates these reactions.

Table 3 reports the reaction energies ($\Delta_r E^o_0$), enthalpies ($\Delta_r H^o_{298}$) and Gibbs free energies ($\Delta_r G^o_{298}$). Being less endothermic by 22 kcal/mol than the 112 kcal/mol aromatic C-H bond, C-Cl bond fission initiates the decomposition process. Cl readily abstracts H to form three chlorophenyl radicals at the *meta*, *para* and *ortho* carbons. H abstraction from *meta* carbon to form HCl and 3-chlorophenyl radical is slightly preferred over abstractions from the other two sites. The triplet dioxygen (${}^3\Sigma_g^- \text{O}_2$) adds to the three phenyl radicals without barriers, with $\Delta_r G^o_{298}$ of these reactions corresponding to 32.6, 33.5 and 34.6 kcal/mol; this process forms 2-, 3- and 4-chlorophenylperoxy radicals, respectively. The addition of the triplet oxygen produces no distinct transition structure. Thus, the variational reaction rate of this process depends on temperature. As it is the case for the non-chlorinated phenyl peroxy radical,²⁷ the adduct undergoes several isomerisation reactions, at low to intermediate temperatures ($T \leq 600$ K). At high temperatures, the main exit channel corresponds to the fission of the O-O peroxy bond to form O and the phenoxy radicals.

The energies for oxygen addition and O departure from the phenoxy peroxy are only slightly different from that of a non-chlorinated phenyl,²⁷ indicating that chlorination (at least mono chlorination) of the benzene ring does not change the oxidation mechanism. This will be examined further in the next section. The formation of 2-chlorophenoxy radical is non-spontaneous by 29.9 kcal/mol and it is slightly less endergonic than the formation of the other two chlorophenoxy radicals. Hence, the formation of the three chlorophenoxy radicals proceeds at similar rates. However, for the sake of simplicity, we will focus our subsequent discussion on 2-chlorophenoxy radical as the most stable congener.

TABLE 3. Energetics for the formation of chlorophenoxy radicals from the oxidation of chlorobenzene.

	$\Delta_r E^o_0$	$\Delta_r H^o_{298}$	$\Delta_r G^o_{298}$
chlorobenzene \rightarrow Cl + phenyl	90.3	91.1	81.5
chlorobenzene + Cl \rightarrow HCl + 2-chlorophenyl	15.1	15.6	13.3
chlorobenzene + Cl \rightarrow HCl + 3-chlorophenyl	13.7	14.2	11.9
chlorobenzene + Cl \rightarrow HCl + 4-chlorophenyl	14.4	15.0	12.6
2-chlorophenyl + O ₂ \rightarrow 2-chlorophenylperoxy	-43.0	-43.8	-32.6
3-chlorophenyl + O ₂ \rightarrow 3-chlorophenylperoxy	-44.1	-44.9	-33.5
4-chlorophenyl + O ₂ \rightarrow 4-chlorophenylperoxy	-45.1	-45.9	-34.6
2-chlorophenylperoxy \rightarrow 2-chlorophenoxy + O	38.2	39.0	29.9
3-chlorophenylperoxy \rightarrow 3-chlorophenoxy + O	38.5	39.3	30.2
4-chlorophenylperoxy \rightarrow 4-chlorophenoxy + O	40.0	40.8	31.7

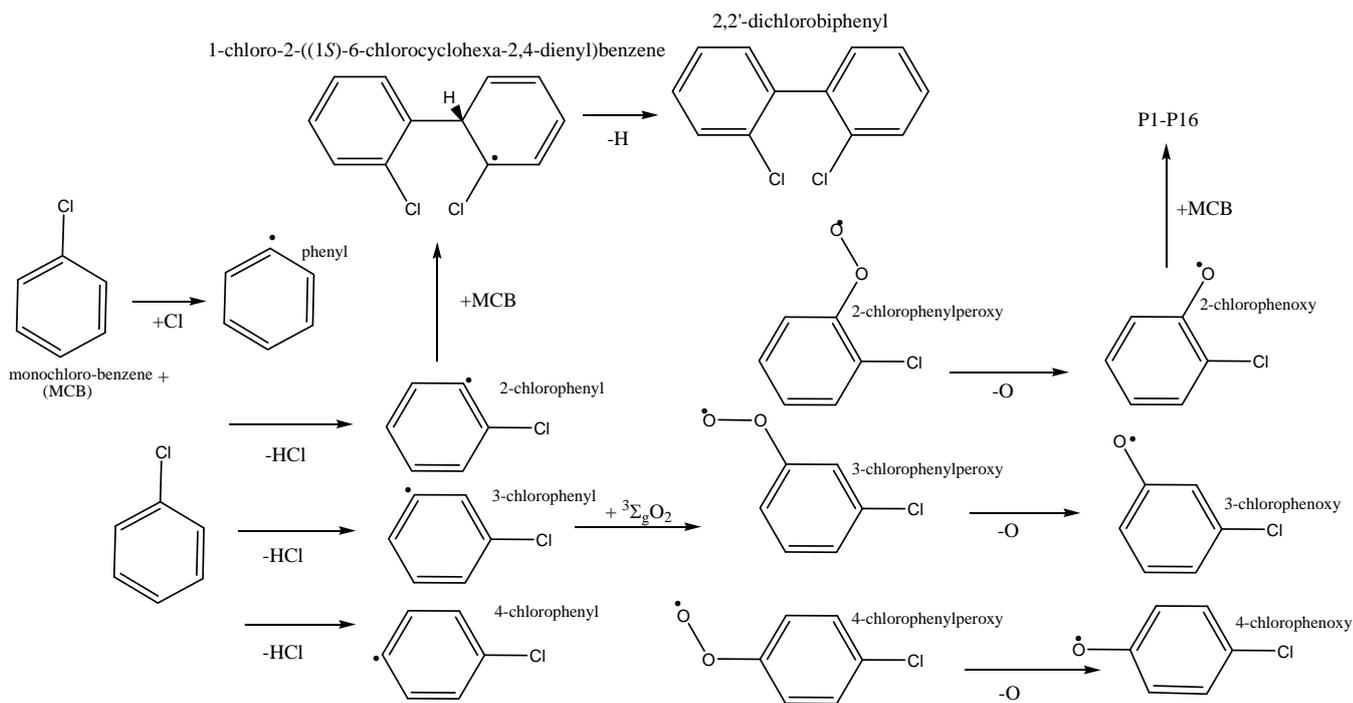


FIGURE 1. Schematic diagram of the reaction pathways for the formation of PCDFs from the oxidation of chlorobenzene

Formation of PCB

Among the 209 possible PCB congeners, twelve possess analogous toxicity to PCDD/F, especially 2,3,7,8-substituted PCDD/F.²⁸ As PCB consist of two phenyl rings joined by a pivot bond, there exists a stereochemical similarity to PCDD/F congeners. PCB compounds have been found to induce hormone-related cancer, adversely affecting human health. From the analysis of experimental results, the literature suggests the formation of PCB from reacting chlorobenzenes with chlorophenyls.²⁸⁻³⁰ However, to the best of our knowledge, the relevant reaction pathways have not yet been studied theoretically by means of DFT.

As shown in Fig. 1, 2-chlorophenyl reacts with mono-chlorobenzene (MCB) at the *ortho* site to produce 1-chloro-2-((1S)-6-chlorocyclohexa-2,4-dienyl)benzene without a detectable barrier. The exothermicity of the reaction amounts to 18.7 kcal/mol, and exergonicity to only 5.9 kcal/mol, with respect to the separated reactants; the latter owing to the entropic penalty associated with such bimolecular reactions. The length of the C-H bond at the sp^3 -hybridised carbon atom on the edge of the pivot bridge exceeds that of the aromatic C-H bond by only 0.02 Å. Nevertheless, this has a substantial impact on reducing the endothermicity of H expulsion to only 21.7 kcal/mol. With respect to standard Gibbs free energy change of the reaction, an excess of 13.3 kcal/mol indicates the spontaneous nature of the reaction and the facile transformation into the non-coplanar PCB, 2,2'-dichlorobiphenyl. A discrete transition structure was found for H expulsion, located 27.8 kcal/mol above the reactant. The calculated bond length of the C_{sp^2} - C_{sp^2} pivot bridge corresponds to 1.493 Å, in excellent agreement with the experimental value of also 1.493 Å, as derived from X-ray diffraction measurements.²⁷

Self-decomposition of 2-Chlorophenoxy

As the production of PCDF from the oxidation of chlorobenzene involves the bimolecular reaction between chlorobenzene and chlorophenoxy, it is essential to investigate another exit channel for 2-chlorophenoxy, *i.e.*, the self-decomposition of 2-chlorophenoxy. The yield of PCDF from the oxidation of chlorobenzenes depends on the balance or the superposition between unimolecular decomposition and bimolecular reaction with chlorobenzenes. Electron density calculations³¹ for phenoxy radical have revealed that 41.3 and 39.1% of the unpaired spin density are located on the phenyl oxygen (O) and the *para*-carbon (*p*-CH) respectively in the keto resonance structure (mesomer) of the phenoxy radical. Taking into account the large stability of the phenoxy and chlorophenoxy radicals³¹, owing to their resonance stabilisation energy, chlorophenoxy radicals could build up in appreciable concentrations to enable self condensation to occur to produce PCDD/F.

Fig. 2 presents the potential energy surface for the unimolecular decomposition of 2-chlorophenoxy. The reaction mechanism displayed here is the same as that proposed and well established for the non-chlorinated phenoxy radical. The unimolecular decomposition proceeds through a cyclisation of 2-chlorophenoxy to form 1-chlorobicyclo [3.1.0]hex-2-en-6-one (1). The reaction is non-spontaneous by 49.6 kcal/mol. The formation of the fused three-member ring in (1) occurs through the tight transition state (TS1), which resides 52.5 kcal/mol above 2-chlorophenoxy. A ring opening of (1) gives 2-chlorocyclopenta-2,4-dienecaldehyde (2) residing 38.5 kcal/mol above 2-chlorophenoxy. The transition structure (TS2) exhibits the largest barrier of 59.8 kcal/mol (relative to 2-chlorophenoxy) along the decomposition pathways making this step the rate determining one. Subsequently, carbon monoxide (CO) departs (2) to produce 1-chlorocyclopenta-1,3-diene (3) through a trivial free energy barrier of 3.2 kcal/mol. The initial decomposition products (3) and CO lie 15.9 kcal/mol above 2-chlorophenoxy. In the view of the high energy barriers and the endoergic nature of the decomposition pathway in Fig. 2, chlorophenoxy is expected to accumulate in appreciable amount enabling both self-condensation to form PCDD/F and reaction with chlorobenzene to form PCDF.

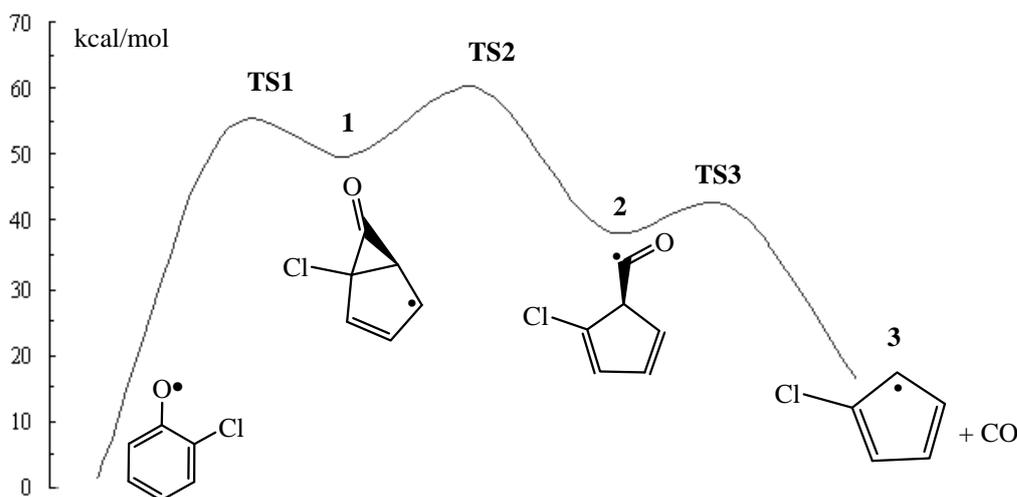


FIGURE 2. Relative free energy (at 298 K) for the thermal decomposition of 2-chlorophenoxy computed at the B3LYP/6-31G(d) level of theory

Reactions of 2-Chlorophenoxy and Chlorobenzene

Oxidation of chlorobenzene, under conditions corresponding to those of open burning, produces a mixture of chlorophenoxy/monochlorobenzene. In a mixture of chlorophenoxy/chlorophenol, there are 9 radical-radical, 2 molecule-molecule and 3 radical-molecule possible reactions.¹³ In the case of

chlorobenzene/2-chlorophenol mixture, there are 16 possible reactions resulting in the formation of 16 different structures. The possible products are:

- 1-chloro-2-phenoxybenzene (P1)
- 1-chloro-2-((1S)-6-chlorocyclohexa-2,4-dienyloxy)benzene (P2)
- (R)-1-chloro-2-(5-chlorocyclohexa-2,4-dienyloxy)benzene (P3)
- (R)-1-chloro-2-(4-chlorocyclohexa-2,4-dienyloxy)benzene (P4)
- (1R,1'S)-2',3-dichloro-1,1'-bi(cyclohexa-3,5-dien)-2-one (P5)
- (R)-2-chloro-6-phenylcyclohexa-2,4-dienone (P6)
- (1R,1'S)-3,3'-dichloro-1,1'-bi(cyclohexa-3,5-dien)-2-one (P7)
- (1R,1'S)-3,4'-dichloro-1,1'-bi(cyclohexa-3,5-dien)-2-one (P8)
- (1S,1'S)-1,5'-dichloro-1,1'-bi(cyclohexa-3,5-dien)-2-one (P9)
- (S)-6-chloro-6-phenylcyclohexa-2,4-dienone (P10)
- (1S,1'S)-1,6'-dichloro-1,1'-bi(cyclohexa-3,5-dien)-2-one (P11)
- (1S,1'S)-1,4'-dichloro-1,1'-bi(cyclohexa-3,5-dien)-2-one (P12)
- (S)-2-chloro-4-((R)-1-chlorocyclohexa-2,4-dienyl)cyclohexa-2,5-dienone (P13)
- (S)-3-chloro-4-((R)-1-chlorocyclohexa-2,4-dienyl)cyclohexa-2,5-dienone (P14)
- (S)-2-chloro-4-((R)-2-chlorocyclohexa-2,4-dienyl)cyclohexa-2,5-dienone (P15)
- (R)-2-chloro-4-((S)-4-chlorocyclohexa-2,4-dienyl)cyclohexa-2,5-dienone (P16)

Structures for P1-P16 are displayed in Fig. 3 and their corresponding transition structures are presented in Fig. 4 where the most important optimum atomic distance between chlorobenzene and 2-chlorophenoxy are shown. Reaction enthalpies and activation enthalpies along with other energetics are calculated and tabulated in Table 4.

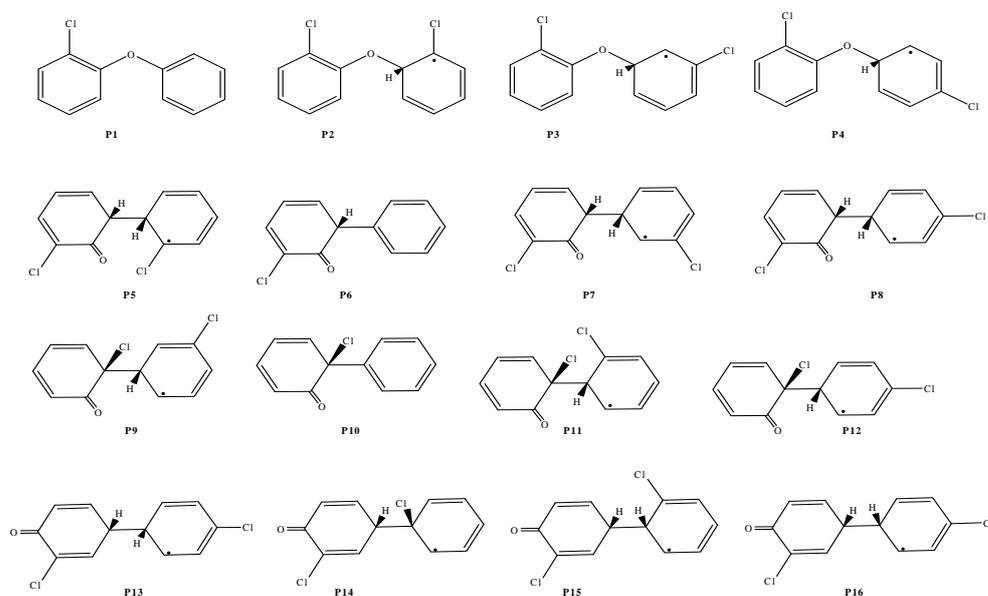


FIGURE 3. Possible products the reactions between chlorobenzene and 2-chlorophenoxy

All intermediates, P1-P16, form in endothermic processes, with $\Delta_r H_{298}^\circ$ ranging from 18.3 for P1 to 37.2 kcal/mol for P11, respectively. The entropic penalties increase the corresponding $\Delta_r G_{298}^\circ$ values to 21.9 and 49.6 kcal/mol, respectively. The activation enthalpies vary from 21.1 for TS_P4 to 38.8 kcal/mol for TS_P10, respectively, and the corresponding free energies of activations are 33.7 and 54.6 kcal/mol. As the phenolic oxygen of the 2-chlorophenoxy contains the largest portion of the spin density, P1-P4 constitute the most stable intermediates. Species P5-P16 display non-coplanar conformation around the $C_{sp^3}-C_{sp^3}$ pivot bond. Strong steric repulsion removes Cl atoms from the pivot bridge in P1, P6 and P10. The pivot bond length is between 1.585 and 1.614 Å indicating no substantial overlapping of the electron cloud of π -electrons across this bond.

Formation of PCDF

Cl and H substituents attached to the pivot bridge on the P5-P16 intermediates are loosely held to C atoms. Cl-C bond (1.845 Å) on C atoms of the pivot bridge is longer by 0.1 Å than the equilibrium aromatic Cl-C bond. The H-C bond is 0.015 Å longer than the equilibrium H-C aromatic bond. The substituents are expected to depart the intermediates either by self-ejection or through reactions with radicals drawn from the radical pool in the fire environment. The species 2-phenylcyclohexa-2,4-dienone (P10') in Fig. 5 results from the expulsion of Cl from the pivot bridge. The phenolic oxygen then cyclises on the neighbouring *ortho* carbon as shown in Fig. 5 in an endergonic step of 16.1 kcal/mol. H expulsion from C-O bridge affords dibenzofuran through a free energy barrier of 14.2 kcal/mol, with the separated products residing 2.3 kcal/mol above P10'.

For the intermediates P1-P4, the *ortho* carbon to the C atom bonded to the ether O could attack on one of the *ortho* sites on the other phenyl ring. Considering P1 as the most stable intermediate, carbon bonded to Cl atom is found to approach one of the *ortho* C atom and make dibenzofuran while Cl atom combines with H atom attached to the *ortho* C and make HCl. The reaction is exothermic by 14.8 kcal/mol, with an entropy gain of 0.027 kcal/(mol K), and exergonicity of 22.7 kcal/mol at 298.15 K. However this process incurs a substantial energy barrier of 75.1 kcal/mol. In a nutshell, all the intermediates P1-P16 could be regarded as precursors to PCDF. The formation of PCDDs must result from reactions involving a mixture of chlorophenoxy radicals and chlorophenols where the self-condensation of phenoxy dominates over either self-condensation of chlorophenols or coupling reactions of chlorophenols and chlorophenoxy radicals.

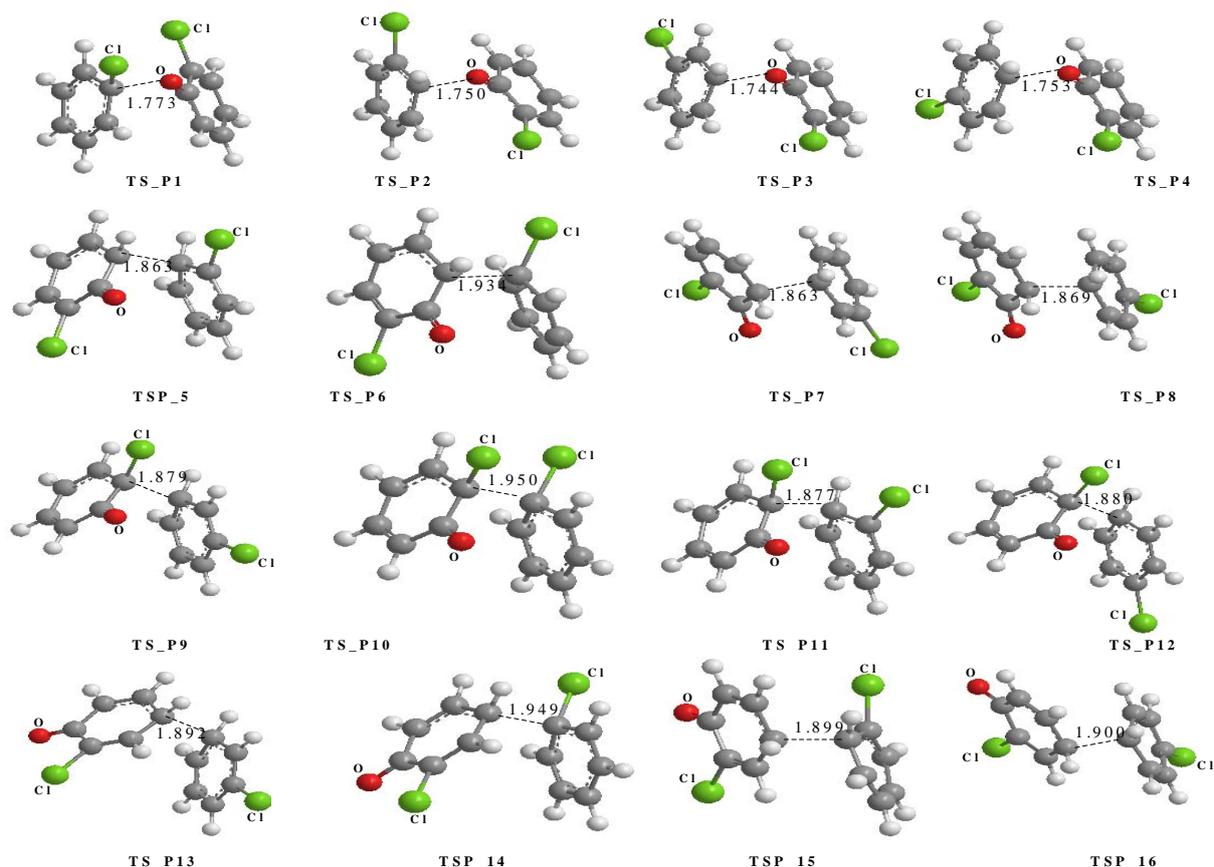


FIGURE 4. Transition structures appearing along the reaction pathways, which produce the intermediates P1-P16 from the reactions between chlorobenzene and 2-chlorophenoxy. Cl and O symbols denote chlorine and oxygen atoms respectively.

TABLE 4. Reaction energies ($\Delta_r E^{\circ}_0$), enthalpies ($\Delta_r H^{\circ}_{298}$) and Gibbs free energies ($\Delta_r G^{\circ}_{298}$) for the formation of the intermediates P1-P16 from the reactions between monochlorobenzene (MCP) and 2-chlorophenoxy (Clp). The corresponding values for the activation (the height of the transition structure in terms of E , H and G , respectively) are listed below each product (denoted with TS_P1-16).

	$\Delta_r E^{\circ}_0$	$\Delta_r H^{\circ}_{298}$	$\Delta_r G^{\circ}_{298}$
MCP + Clp	0.0	0.0	0.0
TS_P1	25.3	25.3	37.7
P1+Cl	17.9	18.3	21.9
TS_P2	21.7	21.6	34.0
P2	18.8	18.8	30.9
TS_P3	22.6	22.5	34.8
P3	19.6	19.6	31.6
TS_P4	21.6	21.5	33.7
P4	18.7	18.7	30.5
TS_P5	30.7	30.7	43.4
P5	30.7	30.9	42.9
TS_P6	35.6	35.7	48.5
P6+Cl	19.6	20.1	30.6
TS_P7	32.5	32.4	45.0
P7	30.7	30.9	42.9
TS_P8	31.4	31.3	43.9
P8	29.8	30.0	42.0
TS_P9	36.0	36.0	48.9
P9	33.4	36.0	48.9
TS_P10	41.2	41.2	54.6
P10+Cl	27.4	27.5	40.0
TS_P11	38.8	38.8	51.8
P11	37.0	37.2	49.6
TS_P12	34.6	34.6	47.5
P12	32.4	32.6	44.8
TS_P13	32.3	32.4	44.6
P13	29.0	29.2	41.1
TS_P14	35.6	35.7	48.2
P14	19.5	20.0	30.8
TS_P15	32.6	32.6	45.1
P15	27.5	27.6	39.6
TS_P16	31.6	31.7	43.8
P16	28.4	28.5	40.4

CONCLUSIONS

Oxidation of chlorobenzene in fires to produce PCDF and PCB has been investigated theoretically by means of the density functional theory (DFT). The initial step constitutes the expulsion of Cl to form phenyl radical. Free Cl radicals readily convert chlorobenzene into chlorophenyl through H abstraction to form HCl in a non-spontaneous reaction, with $\Delta_r G^{\circ}_{298}$ of 11.9 – 13.3 kcal/mol. Chlorophenoxy radicals result from dioxygen addition to the radical site of chlorophenoxy peroxy radicals. Peroxy bond fission to produce phenoxy radicals is the dominant exit channel at moderate to high reaction temperatures. Owing to their great relative stability, the phenoxy radicals combine with chlorobenzene to form direct precursors for PCDF. Spin density in phenoxy radicals is mainly concentrated on the phenolic oxygen, thus pathways corresponding to the combination of chlorobenzene (at its four distinguishable sites) with chlorophenoxy at the phenolic oxygen are the most accessible, based on the calculated reaction and activation enthalpies.

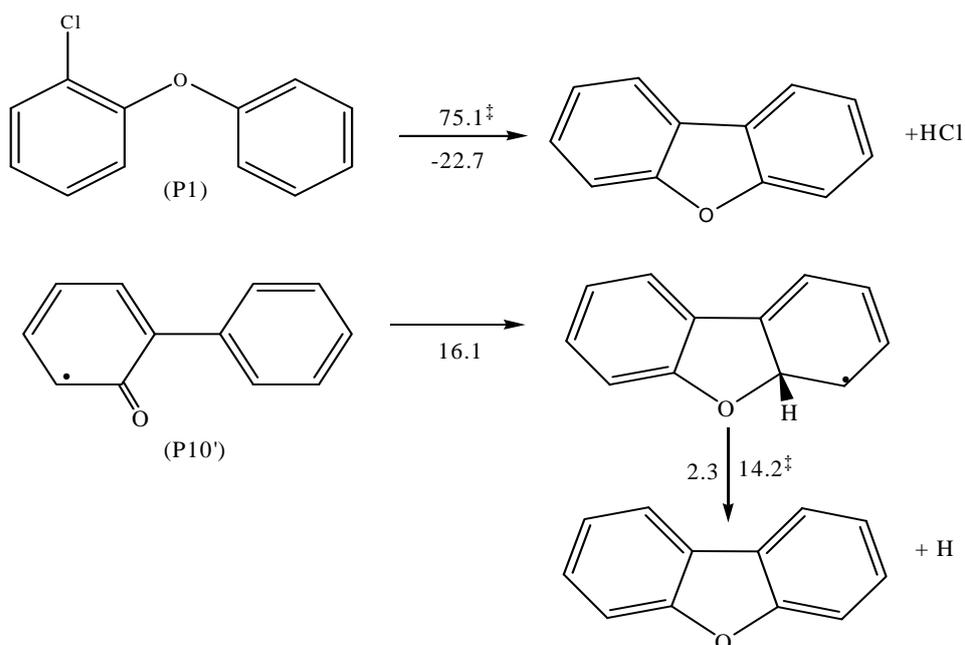


FIGURE 5. Two pathways for the formation of dibenzofuran from P1 and P10' calculated at the B3LYP/6-31G(d) level of theory. Values are Gibbs free energies ($\Delta_r G_{298}^o$), other values (‡) are the relative free energies of activation ($\Delta_r G^\ddagger$).

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