

# Formation of Toxic Species in Oxidation of 4-Chlorobiphenyl

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## Abstract

In this study, 4-chlorobiphenyl (4-CB) was investigated in a laboratory-scale apparatus to determine the products of its thermal decomposition, under conditions similar to those that occur in fires and waste combustion. The apparatus consisted of a laminar flow reactor equipped with a sampling system for intercepting the volatile and condensable products. A XAD-2 cartridge was used to trap the volatile organic compounds (VOC) and polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/F). The analysis of VOC involved high resolution gas chromatography (HRGC) – quadrupole mass spectrometry (QMS) while HRGC – ion trap (IT) MS/MS quantitated the PCDD/F produced. The VOC analysis revealed the formation of chlorophenols and chlorobenzenes, which are important precursors for the formation of PCDD/F. Other detected products included benzaldehyde, naphthalene, 3-ethylbenzaldehyde, 1-chloro-4-ethynylbenzene and benzofuran. The results indicative the formation of mono to octa PCDF, as well as mono, di and hexa to octa chlorinated DD, with monochlorodibenzofuran (MCDF) being the most abundant CDD/F formed. This contribution reports the yields of all PCDD/F homologue groups together with the equivalence of the toxic congeners from the oxidation of 4-CB at 600 °C.

*Keywords:* Oxidation, 4-CB, VOC, PCDD/F.

## 1. Introduction

PCB constitute a group of persistent organic pollutants, widely applied as coolants and insulating fluids (transformer oil) in transformers and capacitors in industrial processes from the 1930s until the late 1970s [1, 2]. They exhibit environmental toxicity and display tendency to accumulate in the environment. In spite of the PCB production concluding in the late 1970s, these compounds remain being detected in water, sediments, as well as bird and fish tissue of species in every part of the world [3]. In recent years, more attention has been devoted to the fate of monochlorobiphenyls (MCB) in the environment and to its role as a food contaminant. For example, MCB have been included in food monitoring programs of the European Scientific Committee for Food (SCF, Brussels, Belgium). From this perspective, we selected to study 4-CB as an example of MCB.

In the past 20 years, investigations focused on the removal and destruction of PCB from contaminated soil, water and industrial waste. Photodegradation, supercritical water, and some other techniques have been studied as means to decompose PCB [5, 6]. In particular, insights have been gained into the formation of PCDD/F under oxidative, catalytic and pyrolytic conditions of PCB mixtures [7, 8]. The yield of PCDD/F under oxidation conditions usually amounts to around 0.01-1 %, but it may also be as high as 6 % [9, 10].

The present understanding of the products in the combustion of MCB is quite limited, especially in comparison to other PCDD/F precursors such as chlorobenzenes and chlorophenols [10, 11]. Although some of VOC were detected under a hydrothermal decomposition of 4-CB around 300 °C [12], lack of data regarding the concentration of PCDD/F as products of PCB decomposition makes it a challenging task to

evaluate their risk. A study on the thermal decomposition of 4-CB would be of assistance in revealing the toxic products and should be useful in advancing the understanding of the impact of PCB oxidation on the environment. In this study, we concentrate on the thermal decomposition of 4-CB at 600 °C in oxygen containing atmosphere to determine the formation of VOC. Further experiments to obtain the yields of PCDD/F are conducted at 300 and 600 °C.

## 2. Experimental Setup

### 2.1 Experimental Apparatus

The experimental setup consists of three sections: a reactant vaporiser, an alumina tubular-flow reactor and a product collection system. Figure 1 illustrates the experiment apparatus in detail.

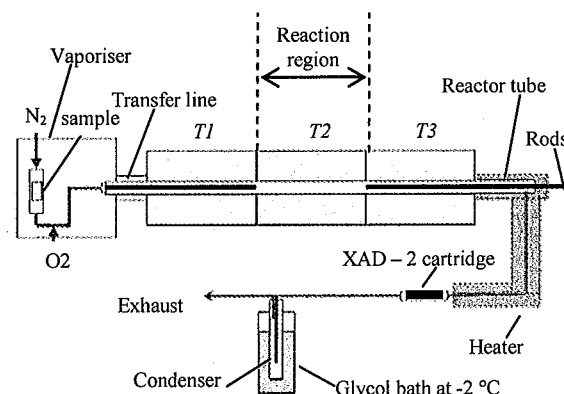


Fig 1. A sketch of experimental apparatus

**Reactant vaporiser:** 4-CB (98.8%, Apollo, UK), a white solid powder at room temperature, was placed in a polytetrafluoroethylene (PTFE) tube of 8 mm in inner diameter (i.d.), installed in an oven (Shimadzu, Japan).

The oven, maintained at 75 °C, induced evaporation of 4-CB at a rate of approximately 0.02 mg/min. For the studies of low oxygen combustion, the vapour was diluted in nitrogen flow and mixed with a controlled amount of oxygen prior to entering the reactor. The concentration of O<sub>2</sub> was monitored by a Varian CP 2003 micro gas chromatograph ( $\mu$ GC) to ensure the ratio O<sub>2</sub>/N<sub>2</sub> to remain constant at 6.0  $\pm$  0.5 %, resulting in the fuel equivalence ratio of 0.07.

**Reactor:** The reactor section comprised an alumina tube (99.8%) with i.d. of 5 mm, installed along the centreline of a three-zone furnace (Labtek, Australia) equipped with a temperature controller (Eurotherm 3216, Australia). The furnace has been calibrated up to 800 °C with a thermocouple placed along the tube to define the location of a uniform temperature zone (about 26 cm in length). Two alumina rods (4 mm o.d.) were inserted into the alumina tube to define the reactor volume and to force the reactants and products to flow in the annular space. The latter ensured the vapours to reach the reaction zone rapidly, minimising their decomposition in lower temperature regions. This set-up permitted to maintain the same residence time at different temperatures, by adjusting the inserted length of one of the rods. To prevent the 4-CB vapour from condensing prior to entering the reactor, a temperature of the transfer line was set to 175 °C with a coiled tubular heater (Helios, Australia), positioned between the reactor and the vaporiser. The end of the reactor tube was attached to a product collection system.

**Product collection system:** VOC and PCDD/F were collected from two separate experiments. The sampling time was set at six and two hours for PCDD/F and VOC measurements, respectively. In both experiments, 200 mg of XAD-2 resin (Supelpak-2, Sigma-Aldrich, Australia) was loaded into the glass cartridge. The connection tube, made of PTFE, was heated up to 140 °C to ensure the complete trapping of all VOC reaction products by the resin. For PCDD/F products, we did not heat the connection tube to transfer all PCDD/F to the XAD-2 cartridge, as the condensation of higher chlorinated PCDD/F on the alumina tube was difficult to avoid. Rather, we washed the tubes with dichloromethane/acetone/hexane, to remove the adsorbed products.

## 2.2 Analysis

**HRGC-QMS analysis of VOC:** We modified the general procedures of the NIOSH Method 1003 as necessary for our system. The XAD-2 resin was not desorbed by CS<sub>2</sub> as stipulated in Method 1003. We selected *n*-hexane instead of CS<sub>2</sub>, as *n*-hexane provided more effective desorption of VOC from the XAD-2 resin. The *n*-hexane extract was filtered and injected (1  $\mu$ L) (split 1:10) into the HRGC-QMS, equipped with the VF-5ms column (30 m length, 0.25 mm i.d., 0.25  $\mu$ m film thickness). Helium was used as the carrier gas at a constant flow rate of 1.0 mL/min. The injector operated at 260 °C, and the temperature program started from 35 °C, held for 5 min, and then increased with a temperature

ramp of 10 °C/min up to 245 °C, held for 10 min. MS ionisation electron impact voltage was set at 70 eV. Both the source and the transfer line were maintained at 250 °C. The eluted peaks were identified by matching their mass spectra with those from the NIST library, and from genuine standards.

**GC-(IT)MS/MS analysis of PCDD/F:** The United States Environmental Protection Agency (USEPA) Standard Method 1613 was modified to include the determination of mono to tri chlorinated congeners. After 6 hours of sampling, the XAD-2 resin was Soxhlet (Buchi Extraction System-B-811) extracted in a hot mode in toluene for 12 hours. The XAD-2 resin extract and samples from washing the alumina reactor and PTFE connection tube were concentrated and analysed separately. All samples were cleaned up to remove their matrix using glass chromatography columns loaded with basic and acidic silica gel, followed by more cleaning using columns containing basic and acidic alumina. The solutions were concentrated prior to HRGC-(IT) MS/MS analysis. The sample (1  $\mu$ L) was introduced into an injector (280 °C) operated in a splitless mode. Chromatographic separation was achieved with a VF-5ms capillary column (60 m length, 0.25 mm i.d., 0.25  $\mu$ m film thickness) with helium as the carrier gas (1 mL/min). The oven temperature program induced 80 °C (held for one min), and then a rise to 235 °C (held for 10 min) at 10 °C/min, subsequent increase to 275 °C (held for 9 min) at 5 °C/min and then to 310 °C (held for 6 min) at 10 °C/min. We maintained the transfer line, ion trap, and manifold temperatures at 270 °C, 200 °C and 80 °C, respectively. The detection limits of HRGC-(IT) MS/MS for PCDD/F correspond to between 0.3 and 3.0 pg/ $\mu$ L (except 6.0 pg/ $\mu$ L for octachlorinated dibenzofuran).

## 3. Results and Discussions

### 3.1 VOC analysis

We explored the effect of temperature on the formation of VOC from the thermal decomposition of 4-CB, with the results, from the experiment performed at 600 °C, presented in Figure 2 and Table 1. In total, we identified 12 major products. Very small concentrations of benzaldehyde and ethyl benzaldehyde isomers were observed at 300 °C. Their abundance increased with the reaction temperature. Phenylethyne, styrene and acetophenone were produced at 500 °C and their yield increased slightly with temperature. The chlorine containing product, 1-chloro-4-ethynylbenzene, was first identified at 550 °C. Its yield increased rapidly between 550 and 600 °C. Other species such as 1,2,3-trichlorobenzene, benzofuran, 1,2-naphthalenedione, 3-phenylfuran were only found in the products from the experiment conducted at 600 °C. Styrene and benzaldehyde were confirmed by injecting authentic standards, because of the incomplete match with the NIST database. All of the 12 major products, including styrene, benzofuran, naphthalene and 1,2,3-

trichlorobenzene are classified by the International Agency for Research on Cancer (IARC) as possible carcinogens.

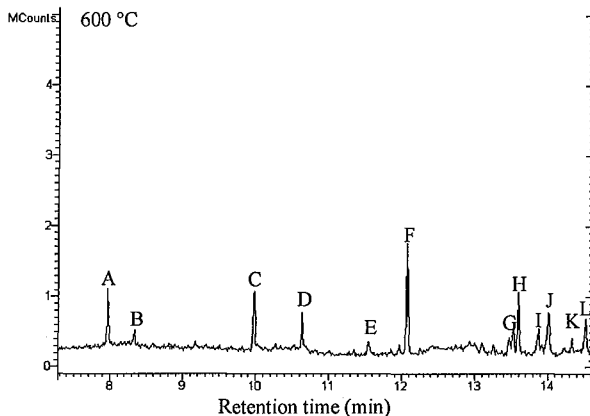


Fig 2. Chromatogram of a VOC analysis, for an experiment performed at 600 °C

Table 1. Identified products generated by oxidation decomposition of 4-CB at 600 °C

Peak	Product	Structure	R.T. (min)
A	phenylethyne	<chem>C#Cc1ccccc1</chem>	8.0
B	styrene	<chem>C=Cc1ccccc1</chem>	8.4
C	benzaldehyde	<chem>O=Cc1ccccc1</chem>	10.1
D	benzofuran	<chem>c1ccc2c(c1)occc2</chem>	10.7
E	acetophenone	<chem>CC(=O)c1ccccc1</chem>	12.0
F	1-chloro-4-ethynylbenzene	<chem>C#Cc1ccc(Cl)cc1</chem>	12.1
G	naphthalene	<chem>c1ccc2ccccc2c1</chem>	13.5
H	3-ethyl-benzaldehyde	<chem>CCc1cccc(C=O)c1</chem>	13.6
I	4-ethyl-benzaldehyde	<chem>CCc1ccc(C=O)cc1</chem>	13.9
J	1,2-naphthalenedione	<chem>O=C1C=CC(=O)C=C2C=CC=CC12</chem>	14.1
K	1,2,3-trichlorobenzene	<chem>ClC1=CC(Cl)=CC(Cl)=C1</chem>	14.3
L	3-phenylfuran	<chem>c1ccc2c(c1)occc2</chem>	14.5

As a number of studies have suggested chlorobenzenes and chlorophenols as precursors for the formation of PCDD/F under oxidative conditions [e.g., 13, 14], we have performed the selective ion monitoring (SIM) on ions (i.e.,  $m/z$ ) identifying these species. We have detected and quantitated 12 precursors, namely chlorobenzene, *o*-, *m*- and *p*-dichlorobenzene, 1,2,3- and 1,2,4-trichlorobenzene, phenol, 2-chlorophenol, 2,4- and 2,6-dichlorophenol, as well as 2,4,6- and 2,4,5-trichlorophenol. Congeners of chlorobenzenes yielded higher abundances than those of chlorophenols, with chlorobenzene as the dominant precursor.

### 3.2 PCDD/F analysis

As indicated by the measurements reported in Table 2, the oxidation 4-CB favours the formation of PCDF over PCDD, possibly owing to the role of benzaldehyde as a PCDF precursor [14]. Note that PCDD/F tend to condense on the walls of the reactor tube and the connection tube prior to reaching the XAD-2 resin. A number of PCDD congeners remained undetected (i.e., below the limit of detection). The yield of monochlorodibenzofuran (MCDF) was 85 % of the total yield of PCDF, followed by dichlorodibenzofuran (DCDF) with the yield of 12.7 %. The formation of precursors appears to peak around 600 °C, resulting in a parallel maximum in the appearance of PCDD/F. The present results offer an improved understanding of oxidative decomposition of 4-CB, affording the calculations of the yield of toxic products. Note however that, bench-scale experiments cannot replicate all aspects of real fires, and hence their results represent an approximation to the measurements expected in large-scale fire conditions.

Table 2. Quantification of detected PCDD/F at 600 °C; the measurements are reported in  $\mu\text{g/g}$  of 4-CB

Congeners	Reactor tube	PTFE tube	XAD-2	Subtotal
MCDF	85.0	4.21	0.584	89.8
MCDD	0.0655	0.0079	0.0066	0.0799
DCDF	12.6	0.558	0.390	13.5
DCDD	0.0114	n.d.	n.d.	0.0114
TriCDF	1.15	0.0397	n.d.	1.19
TriCDD	n.d.	n.d.	n.d.	n.d.
TCDF	0.695	n.d.	n.d.	0.695
TCDD	n.d.	n.d.	n.d.	n.d.
PeCDF	0.295	n.d.	n.d.	0.295
PeCDD	n.d.	n.d.	n.d.	n.d.
HxCDF	0.249	n.d.	n.d.	0.249
HxCDD	0.0419	n.d.	n.d.	0.0419
HpCDF	0.109	n.d.	n.d.	0.109
HpCDD	0.0965	n.d.	n.d.	0.0965
OCDF	0.0135	n.d.	n.d.	0.0135
OCDD	0.0424	n.d.	n.d.	0.0424
Sum				106

Table 3. Quantification of detected PCDD/F at 300 °C ( $\mu\text{g/g}$  of 4-CB)

Congeners	Reactor tube	PTFE tube	XAD-2	Subtotal
MCDF	0.590	n.d.	n.d.	0.590

n.d. – not detected or below the detection limit  
MCDD/F, DCDD/F, TriCDF, TCDD/F, PeCDD/F, HxCDD/F, HpCDD/F, OCDD/F denote mono, di, tri, tetra, penta, hexa, hepta and octa chlorinated dibenzo-p-dioxins and dibenzofurans

The identification of PCDD/F congeners within the homologue groups was based on the injection of genuine standards, and comparisons with the literature measurements of the retention order on the same capillary column (VF-5ms) [13, 15]. Figures 3 and 4 show the identification of MCDF and MCDD, respectively. 3-MCDF represents the most abundant congener among MCDF, followed by 2-MCDF and 4-MCDF, while 1-MCDF remained below the limit of detection. We detected only 1-MCDD of the two possible isomers of MCDD. Figure 5 illustrates a chromatogram of HxCDF with identification of detected HxCDF congeners. As seen in Table 3, we detected 10

out of 17 toxic PCDD/F congeners and calculated the toxic equivalence (TEQ) to correspond to 38.5 ng TEQ-WHO<sub>2005</sub>/(g 4-CB).

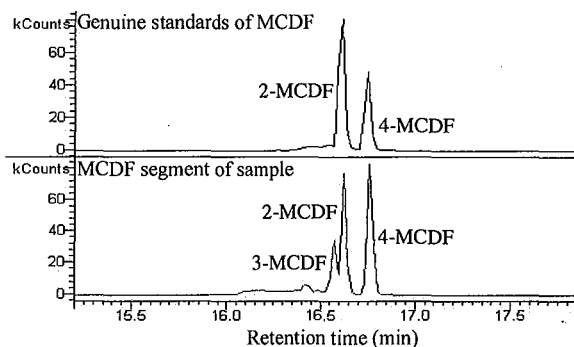


Fig. 3 Comparison of GC-MS/MS chromatograms of the MCDF in an experimental sample and in a genuine standard

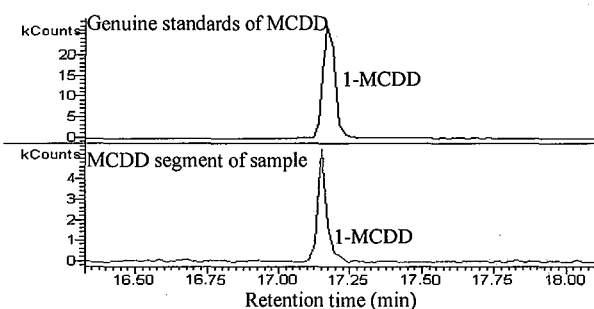


Fig. 4 Comparison of GC-MS/MS chromatograms of the MCDD in an experimental sample and in a genuine standard

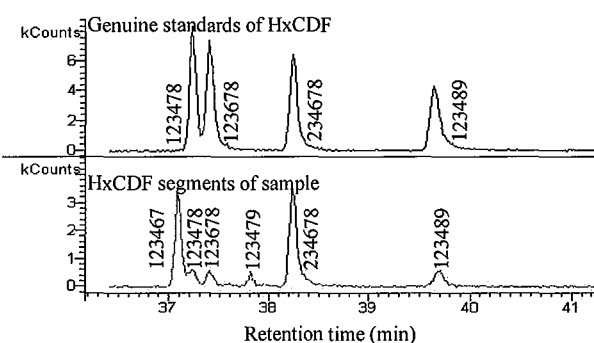


Fig. 5. Comparison of GC-MS/MS chromatograms of the HxCDF in an experiment sample and in genuine standards.

#### 4. Conclusion

This study has deployed a laboratory scale apparatus to trap a wide range of products of the thermal decomposition of 4-chlorobiphenyl. The VOC analysis revealed a number of species, including benzaldehyde, benzofuran, and 1-chloro-4-ethynylbenzene as major products, and chlorophenols and chlorobenzenes as precursors for PCDD/F. In particular, we have identified the dominant PCDD/F congeners by injecting authentic standards and published retention orders. The oxidation of 4-CB favours the formation of PCDF compared to PCDD. The quantitation of the PCDD/F yields, obtained in this study, contributes an improved understanding of

the oxidation of 4-CB, permitting an evaluation of potential hazards and quantification of risks, related to this chemical, to the public health and the surrounding environment.

Table 3. TEQ-WHO<sub>2005</sub>/(g 4-CB) at 600 °C

Congeners	ng TEQ-WHO <sub>2005</sub> /g 4-CB
2,3,7,8-TCDD	n.d.
2,3,7,8-TCDF	2.3
1,2,3,7,8-PCDD	n.d.
1,2,3,7,8-PCDF	0.5
2,3,4,7,8-PCDF	18.1
1,2,3,4,7,8-HxCDD	n.d.
1,2,3,6,7,8-HxCDD	n.d.
1,2,3,7,8,9-HxCDD	n.d.
1,2,3,4,7,8-HxCDF	3.4
1,2,3,6,7,8-HxCDF	1.4
1,2,3,7,8,9-HxCDF	9.6
2,3,4,6,7,8-HxCDF	2.2
1,2,3,4,6,7,8-HpCDD	n.d.
1,2,3,4,6,7,8-HpCDF	0.8
1,2,3,4,7,8,9-HpCDF	0.1
OctaCDF	n.d.
OctaCDD	0.1
Sum	38.5

#### 5. Acknowledgments

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## B. Enthalpies of Formation of Monochlorinated and Dichlorinated Phenols Involving $^{35}\text{Cl}$ and $^{37}\text{Cl}$ Isotopes

Tables 5, 6, and 7 show the estimated heats of formation of different chlorophenols' isotopologues. Since there are no experimental data for the enthalpy of formation of chlorinated benzenes with  $^{37}\text{Cl}$ , the enthalpies of formation of chlorinated phenols with chlorine were calculated by adjusting the heat of formation of the light isotopomer. This adjustment procedure was done by determining the difference in enthalpy calculated by quantum chemistry and adding it to the value estimated by the isodesmic reaction for the light isotopomer.

It should be noted that  $^{37}\text{Cl}$  isotope has a negligible effect on the heat of formation which, generally, tends towards stabilisation. However, the differences are very small and any subsequent difference in reactivity due to this difference would be very difficult to verify experimentally. Somewhat intriguingly, substitution of  $^{37}\text{Cl}$  leads to destabilisation in some compounds.

Table 5: Heats of formation of chlorophenol containing  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$ . (kJ/mol).

	CBS-QB3		G4-MP2	
	35	37	35	37
2	-132.97	-133.01	-132.18	-132.22
3	-126.51	-126.45	-126.11	-126.15
4	-124.65	-124.69	-123.99	-124.03
5	-126.19	-126.23	-126.09	-126.13
6	-119.95	-119.99	-119.06	-119.11

Table 6: Heats of formation of Dichlorophenol containing  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$  as estimated using CBS-QB3 (kJ/mol).

Dichlorophenol	35,35	37,35	35,37	37,37
2,3	-154.39	-154.43	-154.43	-154.33
2,4	-157.06	-157.11	-157.11	-157.15
2,5	-153.85	-153.90	-153.90	-153.94
2,6	-152.84	-152.88	-152.88	-152.92
3,4	-145.59	-145.63	-145.63	-145.68
3,5	-151.57	-151.61	-151.61	-151.66
3,6	-140.96	-141.00	-141.00	-141.05
4,5	-145.35	-145.36	-145.36	-145.40
4,6	-144.17	-144.22	-144.22	-144.26
5,6	-140.75	-140.77	-140.77	-140.81

The two methods employed in this study gave very consistent results in terms of isotopic effect on the heat of formation. In most cases, as calculated by the both

methods, the position of the isotope substitution had no significant effect.

Table 7: Heats of formation of Dichlorophenol containing  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$  as estimated using G4-MP2 (kJ/mol).

Dichlorophenol	35,35	37,35	35,37	37,37
2,3	-154.09	-153.86	-154.13	-153.89
2,4	-155.89	-155.93	-155.93	-155.98
2,5	-153.49	-153.53	-153.53	-153.57
2,6	-151.25	-151.29	-151.29	-151.33
3,4	-145.52	-145.57	-145.57	-145.61
3,5	-151.29	-151.33	-151.41	-151.37
3,6	-140.47	-140.53	-140.53	-140.58
4,5	-145.35	-145.39	-145.39	-145.44
4,6	-142.70	-142.75	-142.75	-142.79
5,6	-140.59	-140.40	-140.40	-140.44

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