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Formation of Chlorinated Dibenzo-*p*-dioxins and Dibenzofurans (CDD/F) and Their Precursors in Oxidation of 4-Chlorobiphenyl

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ABSTRACT

This study investigates the gas-phase thermal oxidation of 4-chlorobiphenyl (4-CB) over a temperature range of 300 to 700 °C, under conditions similar to those occurring in fires and open burning of waste. The experiments deployed an isothermal flow reactor made of high purity quartz and equipped with a sample collection system to adsorb volatile and semi-volatile organic compounds (VOC/SVOC), the latter included chlorinated dibenzo-*p*-dioxins and dibenzofurans (CDD/F). The analysis was performed by gas chromatography-quadrupole mass spectrometry (GC-QMS) and GC-ion trap MS/MS (GC-ITMS/MS), for VOC and SVOC, respectively. Under oxidative conditions, the thermal degradation of 4-CB produced VOC species; mainly, naphathelene, styrene, and benzaldehyde. Selected ion monitoring (SIM), performed on the GC-QMS instrument, confirmed the formation of minor species, such as chlorophenols (CP) and chlorobenzenes (CBz), first observed to form in experiments conducted around 500 °C. The trace analysis by GC-ITMS/MS identified mono and dichlorinated isomers of CDD/F (dioxins), with monochlorodibenzofurans (MCDF) as the dominant homologue group. We observed the formation of 3-chlorodibenzofuran at temperature as low as 300 °C, possibly by direct oxidation of 4-CB by singlet oxygen ($^1\Delta_g$) generated on the walls of the quartz reactor, or by catalytic oxidation of 4-CB by the transition metals remaining in the high purity quarts at sub-ppm levels. Other CDD/F form in gas-phase reactions at temperature in excess of 600 °C.

KEYWORDS: Chemical fires, trace pollutants in fires, polychlorinated dibenzo-*p*-dioxins and dibenzofurans, PCDD/F

INTRODUCTION

Polychlorobiphenyls (PCB) constitute a class of important persistent organic pollutants (POP), first identified as environmental contaminants in 1966 [1]. Prior to their phase-out in late 1970s [2], they served as coolants and insulating fluids in transformers and capacitors. In spite of PCB production concluding in the late 1970s, these compounds continue to be detected in every part of the world, in water, soil, as well as in tissues of bird and fish [3], although PCB abundance in the environment has been decreasing gradually since 1995. Long term intake of PCB-contaminated food may cause cancers [4]. For this reason, in recent years, more attention has been devoted to the fate of monochlorobiphenyls (MCB) in the environment, as a consequence of their role as food contaminants. For example, MCB have been included in food monitoring programs of the European Scientific Committee for Food (SCF, Brussels, Belgium) [5].

In the past 20 years, investigations have focused mainly on the removal and destruction of PCB from contaminated soil, water and industrial waste. Thermal decomposition, photodegradation, supercritical water, and indeed a range of other techniques have been studied as means to decompose PCB [6-8]. As several PCB fires occurred in the late of 1980s and the early of 1990s [9], a number of previous studies also investigated the formation of PCDD/F in PCB fires [10, 11]. The oxidation of PCB produces CO_2, CO, H_2O and HCl, and, as a side reaction, also

CDD/F. Earlier research recognised the formation of CDD/F precursors (CP – chlorinated phenols and CBz – chlorinated benzenes) in PCB fires [12-14]. The yield of PCDD/F usually amounts to around 0.01-1 %, but it may also be as high as 6 % [15, 16]. Most of the previous studies involved a lower temperature range (around 300 °C) with reactant enclosed in gas ampoules, with little attention devoted to distinguishing the contributions of surface and gas-phase reactions to the total yield of CDD/F, with limited concurrent measurements of CP and CBz. This situation has prompted us to re-examine the formation of CDD/F from monochlorinated biphenyls. Similarly to our work, more recent investigations of gas-phase reactions employed reactors built of high purity quartz, to minimise the effect of surface reactions and also decouple the effects of surface and gas-phase reactions [17-19]. For the same purpose, there are also reports in literature of applying boric acid to coat the reactor walls to minimise their catalytic activity [20,21].

In this study, we investigate the formation of CDD/F and their precursors in oxidation of 4-chlorobiphenyl (4-CB). Lack of data on the yields of CDD/F formation by homogeneous and catalytic pathways makes it difficult to estimate the combined formation of CDD/F in actual fires of chlorinated biphenyls. A study on the thermal decomposition of 4-CB in gas-phase reactions would be of assistance in revealing the yield of toxic products by this pathway, as a first step in gaining a fundamental understanding of CDD/F formation in fires.

We hypothesise that, a small fraction of the ground state (triplet) oxygen converts on the reactor walls into an excited species of oxygen, the so-called singlet oxygen ($^1\Delta_g$ O_2). By performing experiments using the high purity quartz reactor, we gain understanding of the contribution of surface-generated singlet oxygen into the formation of organic pollutants in fires. Our study demonstrates that even surfaces that show no chlorination and condensation effects may still synthesise specific congeners of CDD/F. This occurs in pathways that involve no prior formation of CDD/F precursors, such as CP and CBz, but require the appearance of singlet oxygen. Only at temperatures above 600 °C, we observed emissions of the classical chlorinated monaromatic precursors of CDD/F, which react among themselves to form several mono and dichlorinated isomers of CDD/F.

EXPERIMENTAL

Reactor system

We have assembled a bench-scale apparatus as illustrated in Fig. 1, to perform gas-phase oxidation experiments of 4-CB. With the details of a similar apparatus described elsewhere [22], here, we will only provide a brief description. The experimental apparatus generated vapours of 4-CB in flowing nitrogen, with the mixture of nitrogen and 4-CB then supplemented with a controlled amount of oxygen (99.999 % purity) and the resulting gases directed into a heated high purity quartz tube (99.995%, Table 1), where the actual thermal decomposition of 4-CB takes place. A plug of pre-cleaned glass wool, inserted into the flow, ensured uniform mixing of inlet gases prior to entering the reactor. A micro gas chromatograph (Varian, Australia), equipped with a molecular sieve 5 Å column, monitored the concentration of N_2 and O_2 in the inlet gases entering the reactor.

VOC and CDD/F were captured in separate experiments, by an adsorbent cartridge packed with 200 mg of XAD-2 resin (Sigma, Australia). After each experiment, we washed the quartz reactor tube with hexane, with the solution collected and analysed for the products condensed on the inside surface of the tube. We cleaned the tube further with acetone and then baked it out at 200 °C in the furnace to remove trace contaminants that could have affected the results of subsequent experiments. Finally, the exhaust gases bubbled through a dichloromethane (Merck, Australia)

solvent trap, just in case pollutants generated in the experiments happened to overload the XAD-2 cartridges. The products exiting the reactor were quenched to room temperature. The experiments designed to capture VOC and CDD/F products lasted 3 and 6 h, respectively.

Table 1. Main impurities in alumina and quartz materials of the reactors' walls [18].

Impurities (ppm)	[b]Al	[b]Si	B	Ca	[a]Cu	[a]Fe	K	Li	Mg	[a]Mn	Na	Ni	P	[a,b]Ti	[a]Zr	OH-	[a]Zn
Quartz	14		<0.2	0.4	<0.05	0.2	0.6	0.6	0.1	<0.05	0.7	<0.1	<0.2	1.1	0.8	<5	-
Alumina	-	<3000	-	-	200	<3000	-	-	100	100	-	-	-	300	-	-	600

[a]: typical transition metals [23]
[b]: oxides often applied as catalyst supports

For each thermal oxidation experiment, around 30 mg of 4-CB (98.8%, Apollo, UK), a white solid powder at room temperature, was loaded onto a tray in a polytetrafluoroethylene (PTFE) tube of 8 mm in inner diameter (i.d.) installed vertically inside a vaporiser, made of an old GC oven (Shimadzu, Japan), as illustrated in Fig. 1. The 4-CB contained two impurities 0.9 % biphenyl and 0.3 % 4,4'-dichlorobiphenyl. To vaporise the 4-CB at low mass rates (approximately 0.05 mg/min), we maintained the oven at 75 °C. At this evaporation rate, the fuel equivalence ratio in the experiments corresponded to 0.07.
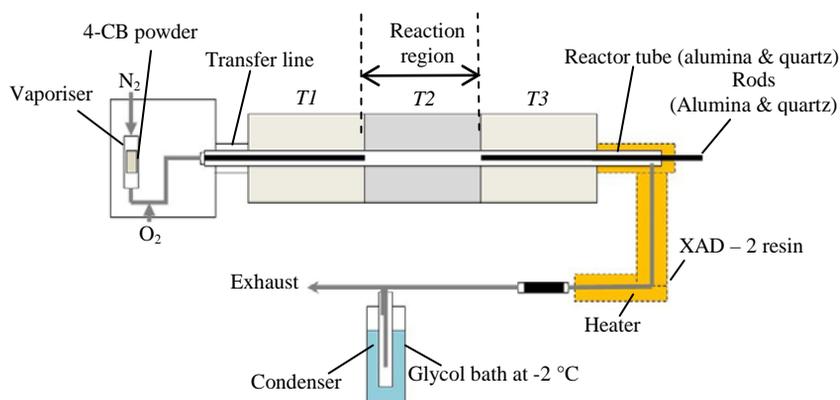

Figure 1. A sketch of experimental apparatus.

The oxidation of 4-CB occurred in the central (reaction) zone of the quartz tube (Fig. 1) maintained at isothermal conditions by a three-zone electrically heated furnace, operated over the temperature range of between 300 and 700 °C. A transfer line, heated to 175 °C, coupled the vaporiser to the reactor to avoid condensation of 4-CB in the reactor's inlet stream. Two quartz rods were inserted into both ends of the quartz tube to adjust the reactor volume, to maintain constant residence time (5 s) in all experiments.

Product analysis

We followed the general procedure of NIOSH Method 1003 to analyse VOC products with some modification as necessary for our system. Although the National Institute for Occupational Safety and Health (NIOSH) recommended carbon disulfide (CS_2), we found that *n*-hexane provided more effective desorption of the product VOC from the resin than CS_2. The *n*-hexane extract from XAD-2 resin was filtered and injected (1 μL), at 1:10 split, into the Varian CP3800

GC, with the injector temperature set to 260 °C. The gas chromatograph equipped with a 30 m Varian VF-5ms capillary column, 0.25 mm i.d. and 0.25 μm in film thickness, operated at a constant flow of helium carrier gas of 1 mL/min. The GC was coupled to a Varian 1200 quadrupole MS to identify and quantitate the VOC products. The temperature program of the GC commenced from 35 °C, held for 5 min, followed by a temperature ramp of 10 °C/min up to 245 °C, kept for 10 min. The MS ionisation electron impact voltage employed corresponded to 70 eV while both the source and the transfer line were maintained at 250 °C. Together the NIST library and genuine standards afforded the identification of the VOC products.

After 6 hours of sampling, the XAD-2 resin were transferred into a thimble and extracted with toluene for 12 h in an automated Soxhlet unit (Buchi). The XAD-2 resin extract and the sample from washing the reactor and PTFE connection tubes were concentrated and analysed separately. Both samples were cleaned up to remove their matrix using glass chromatography columns loaded with basic and acidic silica gel, followed by more cleaning columns containing basic and acidic alumina. The rotary evaporator served to concentrate the solutions prior to 1 μL splitless injections into Varian 3800 GC coupled to Saturn 2000 ITMS/MS for the CDD/F analysis, with the injector kept at 280 °C. The gas chromatography used a VF-5ms capillary column (60 m length, 0.25 mm i.d., 0.25 μm film thickness), and operated with constant flow of helium of 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.

RESULTS AND DISCUSSION

VOC analysis

We explored the effect of temperature on the formation of VOC from the thermal decomposition of 4-CB, and analysed products on the GC-QMS, in full scan mode, detecting nine VOC products. The chlorine containing compounds, such as 1-chloro-ethynylbenzene, commenced to be observed from 600 °C, in the total ion count (TIC) analysis. Figure 2 shows an example of a chromatograph from an experiment conducted at 600 °C, indicating the elution order of the product species. The International Agency for Research on Cancer (IARC) identifies some of these products, including styrene, benzofuran, naphthalene and 1,2,3-trichlorobenzene, as possible carcinogens. By applying the selected ion monitoring (SIM) on GC-QMS, we also identified trace concentrations of dioxin precursors, such as chlorobenzenes and chlorophenols, as illustrated in Figs. 3 and 4.

All CDD/F precursors started to form at temperatures in excess of 500 °C. 4-chlorophenol (4-CP) represents the dominant precursor, with its yield increasing gradually from 500 to 650 °C, and then rising up dramatically at temperature higher than 650 °C. Monochlorobenzene as the second dominant precursors, gives the same trend as with 4-CP. We found minor amounts of the three dichlorobenzene (DCBz) isomers once the temperature reached 600 °C. The yields of DCBz corresponded to less than 5 μmol/mol 4-CB, declining to below the limit of detection when the temperature exceeded 675 °C. The yield of phenol increased greatly with rising temperature starting from 500 °C, and reached a maximum at 600 °C. The yield of 2-CP remained much lower than that of phenol, increasing gently between 450 and 550 °C, and then rising more rapidly to peak at around 625 °C, then dropping at higher temperatures.

The dissociation energy of the C-H bond in benzene is around 102 kcal/mol [24], lower than that of C-H bond in 4-CB of 110 kcal/mol. The typical dioxin precursors, such as MCBz and 2-CP, have been studied to gain insights into the mechanism of PCDD/F formation in fires [25-27]. In
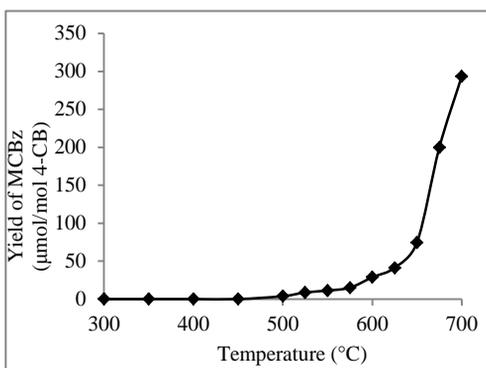
fires of MCBz, the initiation step corresponds to the expulsion of Cl to form phenyl radical, necessitating overcoming the activation enthalpy ($\Delta_r H°_{298}$) as high as 91.1 kcal/mol [25]. With H abstraction, the CBz convert to chlorophenyl radicals in a non-spontaneous reaction. This affords oxygen to add to the radical site of the chlorophenyl radicals forming a chlorophenylperoxy radical. The activation enthalpy needed for this process to proceed can be as high as 40.8 kcal/mol, requiring elevated reaction temperatures [25]. The phenoxy radicals combine with MCBz to form direct precursors for CDD/F.
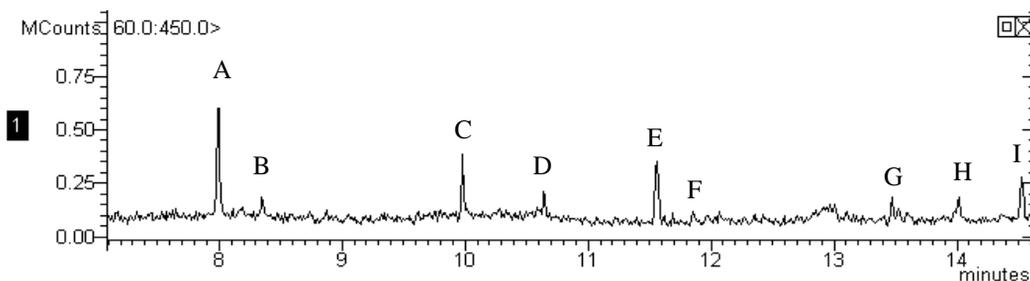
Figure 2. Chromatograph of VOC analysis in experiment conducted at 600 °C: A-phenylethyne; B-styrene; C-benzaldehyde; D-benzofuran; E-acetophenone; F-1-chloro-4-ethynylbenzene; G-naphthalene; H-1,2-naphthalenedione; I-3-phenylfuran.
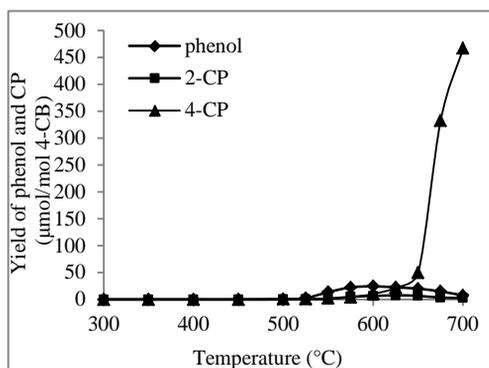
Figure 3. The yield of phenol and 2-CP   **Figure 4.** The yield of MCBz

In our system, minor amounts of dioxin precursors start to form around 500 °C, increasing with rising temperature, consistently with kinetic studies. Evidently, the rates of the oxidation and dechlorination reactions are not significant at these low temperatures. We detected 3-MCDF even at 400 °C in our system, indicating the appearance of a catalytic wall-induced process in the experiments. It was reported that uranium catalysts induce the formation of CDD/F at temperature even less than 400 °C, in combustion of monochlorobenzene [28]. Catalytic combustion can efficiently remove even very dilute pollutants, with abundance of less than 1%). Typical transition metal catalysts include Cr, Cu, U, Co, Ti, Mn and Zn [23]. Table 1 illustrates that these metals are also present in the high purity quartz, typically at sub-ppm concentrations. We suspect that these impurities may induce catalytic wall effects, oxidising our reactant at low temperatures. An alternative explanation for the formation of CDD/F involves singlet oxygen ($^1\Delta_g$), an excited state of oxygen. Singlet oxygen may form from triplet oxygen via surface reactions at catalytic sites on walls of the quartz tube. Particularly, surfaces of Cu, Fe were reported to produce singlet oxygen, even at room temperature [29]. This means that a minor

amount of singlet oxygen can feasibly form on reactor's walls, governing the formation of CDD/F at temperatures of less than 400 °C [18,19].

CDD/F analysis

We identified all of the four congeners of monochlorodibenzofurans (MCDF), as illustrated in Fig. 5(a); 2-MCDF and 4-MCDF by injecting the authentic standards on GC-ITMS/MS, and 1-MCDF and 3-MCDF by the published elution order for DB-5 columns [30]. Out of the isomers of MCDF, 3-MCDF starts to form at 400 °C, with all of the four MCDF congeners found at 500 °C and with 3-MCDF as the dominant congener. The other three MCDF congeners also increased significantly in abundance with the rising temperature. The yield of MCDF at 300 °C of 0.02 ng/g of 4-CB corresponds to the concentration of MCDF in procedural blanks. Thus, all CDD/F remain under the limit of detection at this temperature (Fig. 6).

Only 2-monochlorodibenzo-*p*-dioxin (2-MCDD) formed at temperatures below 600 °C, and a very minor amount of 1-MCDD, in comparison with 2-MCDD, appeared at temperatures above 650°C. Compared with the formation of CDF, the yield of CDD is much lower, indicating preference of the thermal decomposition of 4-CB to form furans rather than dioxins.

Out of three isomers of dichlorodibenzofurans (DCDF), we identified 2,3-DCDF by injecting a genuine standard. The yield of DCDF increased dramatically in the experiments conducted at temperatures above 600 °C. Nakano and Weber have studied the DCDF congeners separation on different columns including DB-5 column [30-32], allowing us to propose a tentative identification of the remaining isomers, from the elution order, as 3,7-DCDF and 4,6-DCDF (Fig. 5(b)). 3,7-DCDF is always the most abundant DCDF isomer, forming directly from the 4-CB impurity of 4,4'-dichlorobiphenyl. In further studies, we plan to confirm this identification by obtaining and injecting genuine standards, and by modifying the temperature program of the GC.
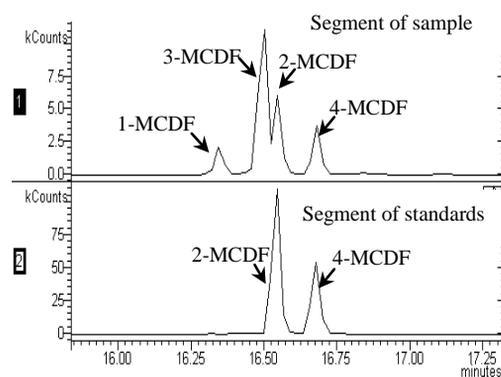
Figure 5(a). Identification of MCDF congeners
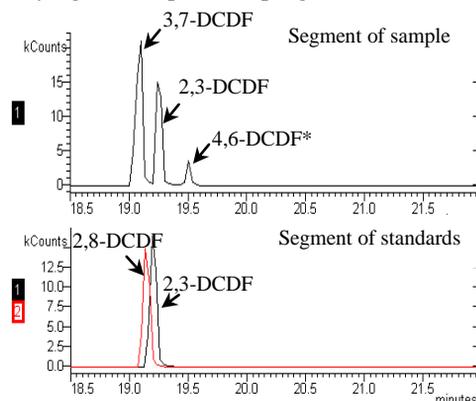
Figure 5(b). Identification of DCDF congeners

Mechanism of CDD/F Formation

As there are no CDD/F precursors detected below 500 °C, at 400 °C, 3-MCDF must have formed directly from 4. Summoogum et al. [19] studied the oxidation of biphenyl reacting with singlet oxygen through an overall barrier of 31 kcal/mol, which is sufficiently low to afford the formation of 3-MCDF even at 400 °C, as observed in our experiments. It is also possible that, 3-MCDF formed as a consequence of surface oxidation of adsorbed 4-CB, in a catalytic process facilitated by the residual transition metals present in the high purity quartz (Table 1). With temperature increasing, gas phase reactions commenced to dominate the distribution of CDD/F

products, resulting in formation of the remaining congeners of MCDF. Above 600 °C, 3-MCDF may also form in reactions of triplet (ground state) oxygen with 4-CB.
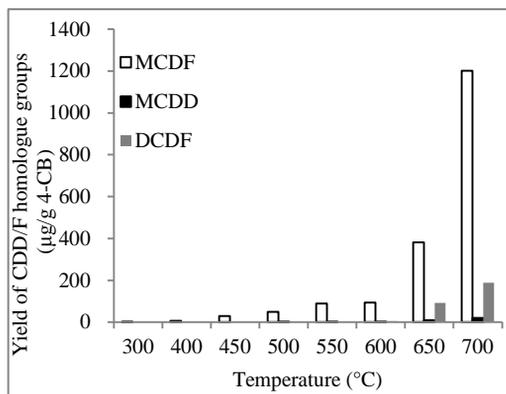

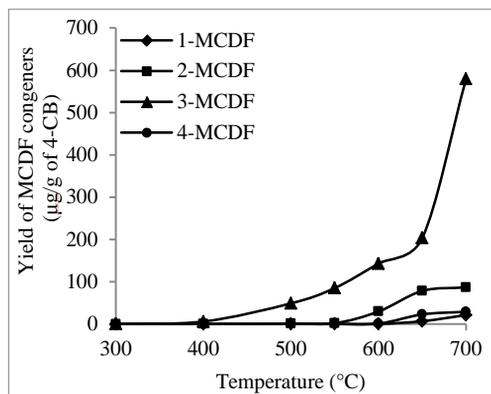**Figure 6.** Yield of all homologue groups

Figure 7. Yield of MCDF congeners

Figure 8(b) shows the distribution of DCDF congeners. There are three DCDF congeners found in the oxidation of 4-CB. At low temperature, the distribution of these three congeners seems uniform (always around 20 ~ 40%), however with temperature increasing, especially above 600 °C, the yield of 3,7-DCDF increased dramatically and became the dominant congener. Scheme 1 illustrates the formation of 4,6-DCDF from 2-CP in gas phase [33]. Both 4,6-DCDF and 2-CP are minor products. 2-CP happens to be the most widely studied precursor for CDD/F. The decomposition of 2-CP can in principle be initiated by loss of the phenoxyl hydrogen by unimolecular, bimolecular, or possibly other low energy pathways (including heterogeneous reactions). The most favourable pathways for generating chlorophenoxy radicals involve hydrogen abstraction by H• or Cl•, the addition of O_2, followed by O-O scission and emission of O•. It is also possible that, the peroxide isomerises forming hydroperoxide, which then loses the •OH group.

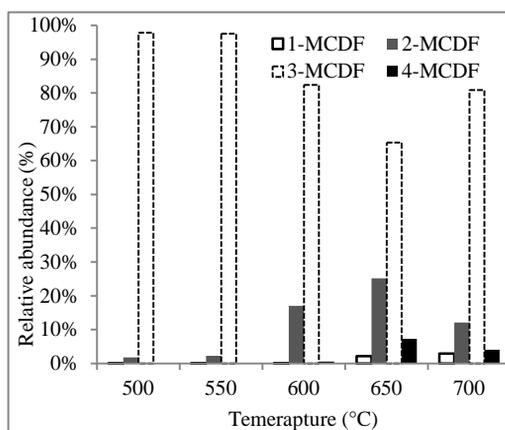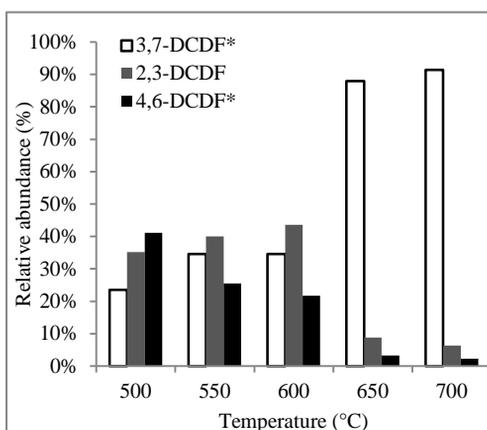**Figure 8(a).** Distribution of MCDF congeners

**Figure 8(b).** Distribution of DCDF congeners

With respect to Scheme 1, after generating the 2-chlorophenoxyl radicals, the two carbon-hydrogen centred radical mesomers react to form a diketo-dimer intermediate. Following the

abstraction of hydrogen, the dimer rearranges, giving off an •OH radical and forming 4,6-DCDF. Altarawneh et al. have performed the density-functional-theory calculations to confirm the reaction pathway from 2-CP to 4,6-DCDF. These authors also reported the formation of 1-MCDD from oxidation of 2-CP [27,34]. MCBz, as the most abundance precursor in our experiments, also participates in the formation of PCDD/F [35]. The fission of the weakest bond (C-Cl) in MCBz results in the release of Cl radicals which then preferentially abstract H from the parent MCBz, affording the three isomers of the monochlorophenyl radicals. The monochlorophenyl radicals react with oxygen molecule and eventually yield chlorophenoxy radicals. The chlorophenoxy radicals combine with MCBz molecular to produce distinct intermediates. Many of these intermediates are considered to be direct precursors for the formation of CDF congeners [27].
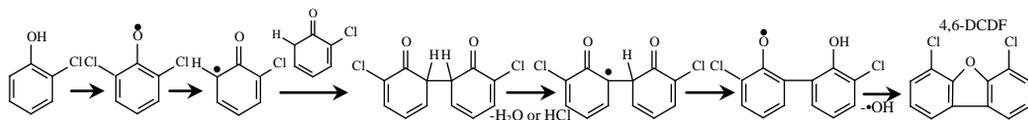

Scheme 1. Postulated pathways for the formation of 4,6-DCDF from 2-chlorophenol [30]

The 2-chlorophenoxy radicals can also form 4-MCDF. Scheme 2 depicts the radical-molecule pathway to 4-MCDF from 2-CP. In this reactions, the initial step is the displacement of •OH by by a phenoxy radical. The resulting compound can then extrude HCl to form 4-MCDF directly.
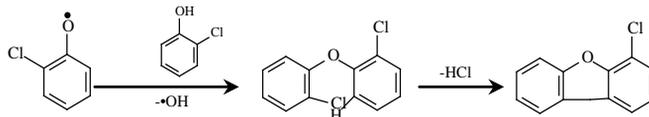
Scheme 2. Radical-molecule pathway to from 4-MCDF from 2-CP

At temperature below 600 °C, the formation of MCDF could be explained by the singlet oxygen pathway (Scheme 3). Our preliminary quantum chemical calculations for the non-chlorinated biphenyl confirm the viability of this new mechanism of formation of CDD/F [19]. The conversion of 3-MCDF into 2-MCDF could be rationalised in view of the reported tendency of chlorine atoms to abstract and replace hydrogen atoms [34]. Thus, 2-MCDF could in principle be sourced from 3-MCDF via bimolecular reactions consisting of chlorine abstraction by H atoms from C_3 followed by chlorination at C_2 as shown in Scheme 3.
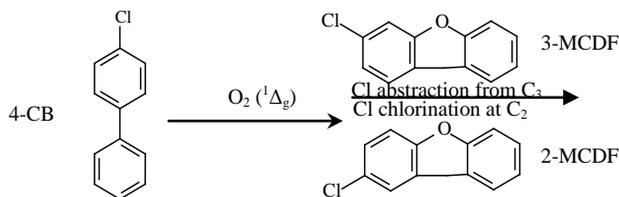
Scheme 3. Proposed singlet oxygen pathway for the formation of MCDF

CONCLUSIONS

In this contribution, we have studied the thermal decomposition of 4-CB in a high purity quartz reactor, using a sampling train to capture a wide range of toxic species. The products included nine species of VOC, nine congeners of CDD/F and three CDD/F precursors. GC-QMS and GC-ITMS/MS served to indentify and quantitate the product species. 3-MCDF forms at temperatures

as low as 400 °C, in spite of no precursors being detected at this temperature. We explain this phenomenon by formation of O_2 ($^1\Delta_g$) on the reactor's walls, as a consequence of the presence of transition metals at concentration level of less than 1 ppm. We expect 4,6-DCDF, 4-MCDF and 1-MCDD to arise due to the condensation reactions involving 2-CP and 2-chlorophenoxy radicals, at temperature in excess of 600 °C. Phenol, 2-CP and MCBz exist in the same temperature window as 4,6-DCDF, 4-MCDF and 1-MCDD. 3,7-DCDF forms from the impurity 4,4'-dichlorobiphenyl present in 4-CB. The present measurements indicate that in fires of 4-CB, the formation of pollutants by precursor pathways will be dominated by surface reactions between 400 and 600 °C and by gas-phase kinetics above 600 °C.

ACKNOWLEDGEMENT

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