Summary of EMPACT Project Activities and Deliverables
James A. Mulholland, Environmental Engineering, Georgia Tech

In this project, our goal was to extend our previous work on PCDD/F formation, supported by NSF, to complex mixtures of chlorinated phenol precursors. Doctoral student Duane Nakahata studied gas-phase, homogeneous pathways under RFHEE support, and doctoral student Jae-Yong Ryu studied CuCl2-catalyzed, heterogeneous pathways under EPA support.

In gas-phase experiments, effects of the location of chlorine substitution and the number of chlorine substituents on phenol precursors were studied for two mixtures: 23-, 24- and 25-dichlorophenols (1) and 2-, 23-, 234- and 2345- chlorinated phenols (2). Formation of dibenzofuran from phenol was found to be the dominant gas-phase pathway. Therefore, a computational study was undertaken to study this reaction (3).

In the CuCl2 experiments, PCDDs were the major products, and 2,4,6 chlorinated phenols were the most important precursors (4). Since dibenzofuran and, to a lesser extent, dibenzo-p-dioxin were major products in the gas phase, chlorination of these compounds on CuCl2 was also studied (5). Finally, PCDD/F isomer patterns from incinerators were compared with those produced by phenol condensation pathways, chlorination pathways, and dechlorination pathways (6). This last research product, which represents a synthesis of our findings, will be of value in the interpretation of jet-REMPI measurements of PCDD/F emissions.

RFHEE, Marcie Francis, Chlorine Chemical Council, $25,000, 1/99 - 1/00:

EPA, Brian Gullett, EPA, $25,000, 5/99 – 9/01:
5. Ryu, J.-Y., and Mulholland, J.A., Chlorination of Dibenzofuran and Dibenzop-dioxin Vapor by Copper (II) Chloride. To be submitted - Chemosphere, 8/01.
7. Feb. 21, 2001, presentation at EPA
EFFECT OF DICHLOROPHENOL SUBSTITUTION PATTERN ON FURAN AND DIOXIN FORMATION

DUANE T. NAKAHATA AND JAMES A. MULHOLLAND
Environmental Engineering
Georgia Institute of Technology
Atlanta, GA 30332-0312, USA

The gas-phase formation of tetrachlorodibenzofurans (T₄CDFs) and dichlorodibenzo-p-dioxins (DCDDs), and trichlorodibenzofuranols (T₃CDF-ols) from combinations of 2,3-, 2,4-, and 2,5-dichlorophenols (DCPs), each of which have one ortho site chlorinated, was studied to assess the effect of chlorine substitution pattern on reactivity. Benzene containing DCP, dissolved individually and in mixtures of equal amounts, was vaporized when combined with a heated gas stream (1% total organic vapor, 8% oxygen) and passed through a 10s flow reactor. Maximum gas phase formation of furan and dioxin occurs at temperatures between 500 and 700 °C. Results confirm that chlorine substitution at ortho sites is necessary for dioxin formation via carbon-oxygen coupling, whereas formation of both dibenzofurans and dibenzofuranols occurs via carbon-carbon coupling at unsubstituted ortho sites. Effects of the second chlorine substituent were complex. In single DCP precursor experiments, 2,3-DCP strongly favored T₄CDF formation, whereas the greatest DCDD yield was from 2,4-DCP. T₃CDF-ol was produced only from 2,5-DCP, consistent with a reaction mechanism that requires a chlorine meta substituent adjacent to an unsubstituted ortho site in the phenol precursor. In DCP mixture experiments, T₄CDF yields were greatest from 2,3- and 2,5-DCP, two 2,3-DCP, and 2,3- and 2,4-DCP, consistent with these combinations of phenoxy radicals having at least steric hindrance in carbon-carbon coupling. DCDD yields were greater from combinations of 2,3- and 2,4-DCP than from combinations of two 2,3-DCP, two 2,4-DCP, and two 2,5-DCP. In all cases, homogeneous gas-phase formation of furan was favored over dioxin from DCP containing one ortho chlorine substituent. Moreover, secondary furan products, but not dioxin products, were formed by reactions involving phenol, produced from benzene, and monochlorophenols, produced from DCP. This work contributes to a better understanding of factors that control the distribution of furan and dioxin products formed in the gas phase of combustion exhaust streams.

Introduction

In incinerators, polychlorinated dibenzop-dioxins (PCDD) and dibenzofurans (PCDF) are formed from chlorinated phenols by homogeneous, gas-phase reactions at high temperatures in the post-combustion zone, as well as through low-temperature, heterogeneous, fly ash-mediated pathways in particle collection devices. In spite of considerable research over the past 25 years, a detailed understanding of the chemical mechanisms of PCDD/F formation is still incomplete. For example, little is known about factors that govern the distribution of PCDD/F congeners produced from multiple precursors. Chlorinated phenols and phenol are the most direct PCDD/F precursors [1] and among the most abundant aromatic compounds found in incinerator gas emissions [2]. However, effects of the degree (number of chlorine atoms) or pattern of substitution of chlorinated phenol precursors on PCDD/F formation are not well understood.

Chlorinated phenols and phenol readily form neutral phenoxy radicals capable of reacting at the oxygen site as well as at the ortho and para carbon sites [3]. PCDD can be formed by phenolic oxygen coupling to a chlorinated ortho carbon site of a second phenoxy radical to form the keto-tautomer of o-phenoxyphenol (POP) [4]. This radical-radical route is likely favored over a radical-molecule route due to the abundance of phenoxy radicals and the large energy barrier (more than 20 kcal/mol) for phenoxy radical addition to phenol [5]. The electron-withdrawing Cl-atom substituent facilitates oxygen-carbon coupling. Subsequent loss of a Cl atom results in the formation of a resonance-stabilized phenoxyphenoxophenol radical, which can undergo five-membered ring closure similar to Smiles' rearrangement [6]. Ring expansion with elimination of a second Cl atom results in the formation of a pair of PCDD isomers [7].

PCDF formation, on the other hand, most likely occurs by carbon-carbon coupling of phenoxy radicals at ortho sites, which leads to the o,o'-dihydroxybiphenyl (DOHB) intermediate [8] via its keto-tautomer. Coupling occurs at less crowded (unsubstituted) ortho sites. Phenoxy radicals preferentially approach each other in a sandwich-like
2702 INCINERATION, COMBUSTION OF SOLID WASTES AND METALS

![Reaction pathways for conversion of 2-CP to 4,6-DCDF (1) and DD (2) and conversion of 3-CP to 1,7-DCDF (1) and 7-MCDF-1-ol (3).](image)

FIG. 1. Reaction pathways for conversion of 2-CP to 4,6-DCDF (1) and DD (2) and conversion of 3-CP to 1,7-DCDF (1) and 7-MCDF-1-ol (3).

gy with overlap of the aromatic π systems; coupling occurs at sites of highest spin density and for geometries of least steric hindrance [9]. Loss of H₂O from DOHB yields PCDF with no loss of chlorine.

The routes to PCDF and PCDD described above are depicted by paths (1) and (2), respectively, in Fig. 1 for the combination of two 2-chlorophenoxy radicals. In a paper presented at the previous combustion symposium [10], we showed results of 2-chlorophenol (2-CP) pyrolysis indicating that path (2) to dibenzo[p]dioxin (DD) is favored over path (1) to 4,6-dichlorodibenzofuran (4,6-DCDF) in the absence of oxygen. Under oxidative conditions, however, path (1) to 4,6-DCDF is favored. These results are consistent with thermodynamic estimates of the following overall reactions.

2 2-CP → DD + 2 HCl
\[ \Delta H = +1 \text{ kcal/mol} \]  
(1)

2 2-CP → 4,6-DCDF + H₂ + H₂O
\[ \Delta H = +12 \text{ kcal/mol} \]  
(2)

2 2-CP + 0.5 O₂ → 4,6-DCDF + 2 H₂O
\[ \Delta H = -46 \text{ kcal/mol} \]  
(3)

Under pyrolytic conditions, DD formation (reaction 1), which is nearly thermoneutral, is thermodynamically favored over 4,6-DCDF formation (reaction 2), which is endothermic. Under oxidative conditions, 4,6-DCDF formation (reaction 3), which is highly exothermic, is thermodynamically favored.

A third pathway was identified in our previous work as well—the formation of dibenzo furanol from a phenol with an unsubstituted ortho site adjacent to a Cl-substituted meta site. This is depicted by path (3) in Fig. 1 for one combination of 3-chlorophenoxy radicals. The DOHB intermediate can either eliminate H₂O to produce 1,7-dichlorodibenzofuran (1,7-DCDF), as shown by path (1), or eliminate HCl to produce 7-chlorodibenzofuran-1-ol (7-MCDF-1-ol), as shown by path (3).

In this paper, effects of the chlorination pattern of three dichlorophenol (DCP) isomers on the distribution of furan and dioxin products are discussed. 2,3-DCP, 2,4-DCP, and 2,5-DCP were studied because each contains one Cl-substituted and one unsubstituted ortho carbon site; therefore, both PCDD and PCDF products can be formed. Dibenzo furanol products can be produced from 2,5-DCP. Isomer-specific products of paths (1), (2) and (3) shown in Fig. 1 are listed in Table 1.

**Experimental**

Experiments were conducted in an electrically heated, quartz tube flow reactor, 40 cm in length and 1.9 cm in diameter, at temperatures ranging from 500 to 700 °C in 25 °C increments. Benzene solutions containing single and multiple DCP reactants
FURAN AND DIOXIN FORMATION FROM DICHLOROPHENOLS

TABLE 1

Expected dioxin and furan products from combinations of dichlorophenols

<table>
<thead>
<tr>
<th>DCP combination</th>
<th>23-/23-</th>
<th>24-/24-</th>
<th>25-/25-</th>
<th>23-/24-</th>
<th>23-/25-</th>
<th>24-/25-</th>
</tr>
</thead>
<tbody>
<tr>
<td>T₄CDF</td>
<td>3467-</td>
<td>2468-</td>
<td>1469-</td>
<td>2467-</td>
<td>1467-</td>
<td>1468-</td>
</tr>
<tr>
<td>DCDD</td>
<td>16/-19-</td>
<td>27/-28-</td>
<td>27/-28-</td>
<td>17/-18-</td>
<td>17/-18-</td>
<td>27/-28-</td>
</tr>
<tr>
<td>T₃CDF-1-ol</td>
<td></td>
<td>269-</td>
<td>267-</td>
<td>268-</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(150 mg each per 1 mL benzene) were prepared. A syringe pump injected reactant solution continuously into a heated (170 °C) gas stream of 92% nitrogen and 8% oxygen. The resulting gas stream contained approximately 1% benzene vapor and 0.1% DCP vapor (each). A nominal residence time in the reaction zone of 10 s was maintained. Aromatic products and soot were collected using a dual icedichloromethane (DCM) trap. Sample solutions were filtered (0.2 μm pore), with soot yields (DCM-insoluble fractions) determined gravimetrically.

Filtered sample solutions were analyzed by gas chromatography-mass spectrometry (GC-MS) with a DB-5 ms GC column. The elution order of PCDF on DB-5 columns is known [11]. The six tetrachlorodibenzofuran (T₄CDF) isomer products listed in Table 1 were separated and identified, as were four of the six dichlorodibenz-α,α'-dioxin (DCDD) isomer products. The 1,7- and 1,8-DCDD isomers and the 2,7- and 2,8-DCDD isomers coelute. Two trichlorodibenzofuranol (T₃CDF-ol) peaks were observed, easily differentiated from trichlorodibenzo-p-dioxin isomers by elution time. In addition to these furan and dioxin products from DCP pairs, secondary products arising from combinations involving phenol and chlorophenols were identified. These include three dichlorodibenzofuran (DCDF) isomers, all four monochlorodibenzofurans (MCDF), and unchlorinated dibenzofuran (DF). Six small trichlorodibenzofuran (T₃CDF) peaks and one small monochlorodibenzo-furanol (MCDF-ol) peak were also detected. Standards used to determine response factors included all detected phenols and benzenes and unchlorinated DF and DD.

Results and Discussion

Overall Product Distributions at 600 °C

Product yields from individual DCP experiments and DCP mixture experiments at 600 °C are listed in Table 2 on a percentage of carbon feed basis. The amount of unreacted DCP recovered at 600 °C ranged from 3% to 4.5% of the total carbon feed, or 45% to 60% of the DCP feed. Total aromatic product yields ranged from 1.8% to 2.8%. Soot yields were higher in DCP mixture experiments than in single DCP experiments, likely due to the higher total DCP concentrations in the mixture experiments. While the total carbon feed rate remained the same, the fraction of total DCP, which is more reactive than benzene, was greater in the mixture experiments.

In all cases, the major aromatic product was unchlorinated phenol, with yields at 600 °C ranging from 1.2% to 1.8%. DCP dechlorination products were also observed, with total chlorophenol (CP) yields ranging from 0.1% to 0.25%. Given the low CP yields, it is clear that phenol was derived from benzene and not CP dechlorination. Dichlorobenzences were also derived from DCP. No chlorination products were observed. Relative rates of DCP dechlorination at different sites can be deduced from CP isomer yields. 2,3- and 2,5-DCP produced 2.6 and 3.1 times as much 3-CP as 2-CP, whereas 2,4-DCP produced only 1.3 times as much 4-CP as 2-CP. Therefore, dechlorination of phenols appears to be favored at ortho and, to a lesser extent, para sites. An implication of this result is that dechlorination of phenol precursors in the gas phase favors furan formation since ortho chlorine substituents are required for dioxin formation.
An examination of the yields of furan and dioxin product homologues listed in Table 2 provides information on the relative reactivity of DCP to form T₄CDF, DCDD, and T₃CDF-ol. In all cases, T₄CDF yields exceed DCDD yields, particularly from 2,3-DCP alone, where the ratio of T₄CDF to DCDD yields is 19. DCDD yields are greatest when 2,4-DCP is a reactant. As expected, T₃CDF-ol is formed only when 2,5-DCP is present. From 2,5-DCP alone, T₃CDF-ol yield is greater than yields of T₄CDF and DCDD.

In addition to these furan and dioxin products from DCP combinations, large amounts of DCDF products and DF were found, as well as smaller amounts of T₃CDF and MCDF products. When 2,5-DCP was a reactant, one MCDF-ol product was observed. These products can be explained by reactions involving the phenol and CP products cited above. DCDF and DF can be formed from combinations of phenol and DCP and two phenols, respectively. The T₄CDF and MCDF products can be derived from combinations of DCP and CP and phenol and CP, respectively. MCDF-ol can be derived from phenol and 2,5-DCP. Evidence supporting these claims is provided by identification of product isomers, as well as by comparison of the temperature dependence of product and precursor yields. These results are presented next for 2,3-/2,4-DCP and 2,3-/2,5-DCP mixture experiments.

2,3-/2,4-DCP Mixture Results

Reactant and product yields from slow combustion of the mixture of 2,3- and 2,4-DCP in benzene, over the temperature range of 500 to 700 °C, are shown in Fig. 2. At 500 °C, virtually all of the DCP reactants were recovered. At 700 °C, 90% of the DCP had reacted. Peak T₄CDF and DCDD yields of 0.3% and 0.04% (carbon feed basis), respectively, occurred between 575 and 600 °C. These yields represent 2.3% and 0.3% DCP conversion, respectively.
FURAN AND DIOXIN FORMATION FROM DICHLOROPHENOLS

Above 625 °C, yields of DCDF, MCDF, and DF products became dominant. As temperature increased, the PCDF distribution shifted to less-chlorinated homologues. At 700 °C, yields of DF were greatest, followed by MCDF, DCDF, T₄CDF, and T₃CDF.

Yields of T₄CDF and DCDF isomers and DCDD isomer pairs are shown in Fig. 3. The T₄CDF isomer with the highest yield is 1,4,6,7-T₄CDF, which is derived from combination of two 2,3-DCP, isomer with the highest yield 2,4,6,7-T₄CDF, which is produced by combination of 2,4-DCP and 2,3-DCP, is produced in smallest amount. Yields of all three T₄CDF isomers peak at 575 °C. The two DCDF isomers observed are 3,4-DCDF and 2,4-DCDF. The former is formed by combination of 2,3-DCP and phenol. The latter is formed by combination of 2,4-DCP and phenol. Yields of both DCDF isomers peak at 650 °C; phenol yields peak between 650 and 675 °C.

Yields of DCDD isomer pairs are shown in the bottom panel of Fig. 3. The isomer pair with highest yield is 1,7-/1,8-DCDD, which results from combination of 2,3- and 2,4-DCP. DCDD isomer pairs, which results from combination of two 2,3-DCP, is produced in smallest yield. One possible explanation is that PCDD formation, unlike PCDF formation, involves coupling of phenoxy radicals at different sites. Preferred oxygen-carbon coupling may involve one phenoxy radical with a reactive oxygen and one with a reactive ortho carbon.

2,3-/2,5-DCP Mixture Results

Reactant and product yields from slow combustion of the mixture of 2,3- and 2,5-DCP in benzene, over the temperature range of 525 to 700 °C, are shown in Fig. 4. These results are very similar to the 2,3-/2,4-DCP mixture results shown in Fig. 2. Yields of T₄CDF and DCDF isomers, DCDD isomer pairs, and dibenzofuranol products are shown in Fig. 5. The T₄CDF with the highest yield is the 1,4,6,7 isomer, which is derived from combination of 2,3- and 2,5-DCP. Next is 3,4,6,7-T₄CDF, formed by combination of two 2,3-DCP. In least abundance is 1,4,6,9-T₄CDF, formed from two 2,5-DCP. As discussed in the following section, these results are consistent with considerations of steric hindrance associated with the carbon-carbon coupling of phenoxy radicals. Yields of the three T₄CDF isomers peak at 625 °C. Two DCDF isomers are observed: 1,4-DCDF and 3,4-DCDF. The former is formed by the
Yields of both DCDF isomer pairs peak at 650 °C, the temperature at which the T₄CDF and DCDD products peak. 2-MCDF-1-ol can be formed from combination of 2,5-DCP and phenol. Yields of this product peak at 650 °C, the same temperature at which the DCDF products peak.

Carbon-Carbon Coupling of Phenoxy Radicals

Recently, we proposed that the favored formation of 1,7-DCDF from 3-chlorophenol over 3,7- and 1,9-DCDF might be due to differences in steric hindrance associated with sandwich-type approach geometries of 3-chlorophenoxy radicals during carbon-carbon coupling [12]. We tested this hypothesis by examining geometries of 2,3-, 2,4-, and 2,5-dichlorophenoxy radical coupling (Fig. 6). Interactions of aligned chlorine and oxygen atoms are noted. The 2,3-/2,3-DCP and 2,3-/2,4-DCP combinations each have one Cl-Cl interaction. The 2,3-/2,5-DCP combination has one Cl-O interaction. The 2,4-/2,4-DCP combination has two Cl-Cl interactions and the 2,5-/2,5-DCP combination has two Cl-O interactions. Based on the number of interactions, combinations of 2,3-/2,3-DCP, 2,3-/2,4-DCP, and 2,3-/2,5-DCP, which produce 3,4,6,7-, 2,4,6,7-, and 1,4,6,7-T₄CDF, respectively, should be favored over combinations of 2,4-/2,4-DCP and 2,5-/2,5-DCP, which produce 2,4,6,8- and 1,4,6,9-T₄CDF, respectively. The experimental results are consistent with these observations.

Conclusion

Experimental results reported here provide new information on effects of substitution pattern of dichlorophenols containing one ortho chlorine substituent on the distribution of dibenzofuran, dibenzo-p-dioxin and dibenzofuranol products formed in the gas phase. The overall goal of this work is to develop a predictive understanding of factors controlling these distributions from phenol precursors.

Acknowledgment

Support from the Research Foundation for Health and Environmental Effects and the Environmental Protection

FIG. 5. Yields of PCDF, PCDD, and PCDF-ol isomers from 2,3- and 2,5-DCP in benzene.

FIG. 6. Sandwich-type approach geometries for carbon-carbon coupling of dichlorophenoxyl radicals.
Agency (QT-OH-99-000537) and from the National Science Foundation (CTS-9457028) is gratefully acknowledged.

REFERENCES

Gas-phase PCDD/F Formation from 2-, 23-, 234- and 2345-Chlorinated Phenols

Duane T. Nakahata and James A. Mulholland

Introduction

In incinerators, polychlorinated dibenzo-\(p\)-dioxins (PCDD) and dibenzofurans (PCDF) are formed from chlorinated phenols by homogeneous, gas-phase reactions at high temperatures in the post-combustion zone, as well as through low-temperature, heterogeneous, fly ash-mediated pathways in particle collection devices. In spite of considerable research over the past 25 years, a detailed understanding of the chemical mechanisms of PCDD/F formation is still incomplete. For example, little is known about factors that govern the distribution of PCDD/F congeners produced from multiple precursors. (Although much of the laboratory research since the early 1980s has addressed the latter pathway [1], detailed understanding of how PCDD/F are formed via either pathway is still incomplete.) Chlorinated phenols and phenol are the most direct PCDD/F precursors [2] and among the most abundant aromatic compounds found in incinerator gas emissions [3]. However, effects of the degree (number of chlorine atoms) or pattern of substitution of chlorinated phenol precursors on PCDD/F formation are not well understood.

Chlorinated phenols and phenol readily form neutral, ambident phenoxy radicals capable of reacting at the oxygen site as well as at the ortho and para carbon sites [4]. PCDD can be formed by phenolic oxygen coupling to a chlorinated ortho carbon site of a second phenoxy radical to form the keto-tautomer of o-phenoxyphenol (POP) [5]. This radical-radical route is likely favored over a radical-molecule route due to the abundance of phenoxy radicals and the large energy barrier (more than 20 kcal/mol) for phenoxy radical addition to phenol [4,6]. The electron-withdrawing Cl-atom substituent facilitates oxygen-carbon coupling. Subsequent loss of Cl-atom results in the formation of a resonance-stabilized phenoxyphenoxy radical, which can undergo five-member ring closure similar to Smiles rearrangement [7]. Ring expansion and elimination of a second Cl-atom result in the formation of a pair of PCDD isomers [8].

PCDF formation, on the other hand, most likely occurs by carbon-carbon coupling of phenoxy radicals at ortho sites, which leads to the \(o,o\)-dihydroxybiphenyl (DOBP) intermediate [9] via its keto-tautomer. Coupling occurs at less crowded (unsubstituted) ortho carbon sites. Phenoxy radicals preferentially approach each other in a "sandwich-like" geometry with overlap of the aromatic \(\pi\) systems; coupling occurs at sites of highest spin density and for geometries of least steric hindrance [10]. Loss of \(\text{H}_2\text{O}\) from DOPB yields PCDF with no loss of chlorine. The routes to PCDF and PCDD described above are depicted by paths (1) and (2), respectively, in Fig. 1 for the combination of two 2-chlorophenoxy radicals.

FIG. 1

In this paper, effects of the degree of chlorination of four phenols on dioxin and formation are discussed. A mixture of 2-chlorophenol (2-CP), 2,3-dichlorophenol (2,3-DCP),
2,3,4-trichlorophenol (2,3,4-T<sub>3</sub>CP) and 2,3,4,5-tetrachlorophenol (2,3,4,5-T<sub>4</sub>CP) was studied since each contains one Cl-substituted and one unsubstituted ortho carbon site; therefore both PCDD and PCDF products can be formed. In addition, since each combination of the different reactants yields a unique product, the relative tendencies of each reactant to form PCDD/F can be compared. Isomer-specific products of paths (1) and (2) shown in Fig. 1 are listed in Table 1.

**TABLE 1**

**Experimental**

Experiments were conducted in an electrically heated, isothermal quartz tube flow reactor, 40 cm in length and 1.9 cm in diameter, at temperatures ranging from 500 to 700°C in 25°C increments. An equimolar benzene solution of all of the chlorinated phenol reactants (0.25 mMol each per 1.0 ml benzene) was prepared. A syringe pump injected the reactant solution at a rate of 10 μl/min continuously into a heated (170°C) gas stream of 92% nitrogen and 8% oxygen. The resulting gas stream contained approximately 2.5% benzene vapor and 0.2% reactant (total) vapor. The flow rate of the carrier gas was controlled to provide a nominal residence time in the reaction zone of 10 s. Aromatic products and soot were collected using a dual ice-cooled dichloromethane (DCM) trap. Sample solutions were filtered (0.2-μm pore) and soot yields (the DCM-insoluble fraction) were determined gravimetrically.

The filtered sample solutions were analyzed by GC/MS using a HP-5ms GC column. The elution order of PCDF on HP-5ms columns is known [11]. All four monochlorodibenzofurans (MCDF) were identified, as were unchlorinated dibenzofuran (DF), four isomers of dichlorodibenzofuran (DCDF), three isomers of T<sub>3</sub>CDF, and three T<sub>4</sub>CDF isomers. Small amounts of P<sub>3</sub>CDF (two isomers), H<sub>6</sub>CDF (two isomers), and H<sub>7</sub>CDF (one isomer) were detected. A trace amount of unchlorinated dibenzo-p-dioxin (DD) was detected. Identification of these isomers was based on the results of previous single precursor experiments, elution order and relative retention times. In addition, naphthalene and several of its chlorinated congeners were identified. Standards used to determine response factors in this study include phenol, 2-CP, 2,3-DCP, 2,3,4-T<sub>3</sub>CP, 2,3,4,5-T<sub>4</sub>CP, DF, DD and naphthalene. Response factors of PCDF product isomers were assumed equal.

**Results and Discussion**

**Overall Product Distribution**

Product yields from the mixture of chlorinated phenols at 500, 550, 600, 650 and 700°C are listed in Table 2 on a carbon feed basis. At 500°C recovery of each of the unreacted phenols ranged from 1.0 to 1.4% of the total carbon feed, or 50 to 70% of each reactant. The amount of unreacted feed decreased with increasing reactor temperature, but at each temperature the residual amount of 2-CP was highest. Above 500°C, the phenols decreased in abundance as the number of chlorine atoms increased; the yield of 2,3,4,5-T<sub>4</sub>CP was lowest. At 650°C, more than 95% of the phenols had reacted.

**TABLE 2**
The yield of unextractable soot was highest at 650°C (0.14% of carbon feed), as was the total yield of aromatic products (6.73%). For this study, aromatic products include chlorinated benzenes, naphthalenes, and dibenzofurans, as well as unchlorinated phenol, naphthalene and DF. Within these groups, the PCDFs in general, exhibited maximum yields between 550 and 600°C. The benzenes, naphthalenes and unchlorinated dibenzofuran had maxima near 650°C. Above 550°C, the major aromatic product was unchlorinated phenol, which had a maximum yield of 5.80% at 650°C.

The large yield of phenol, as noted in previous work, is attributed to the reaction of oxygen with benzene (used as the solvent for the feed in these reactions), and not as a result of the dechlorination (by H-atom substitution) of 2-CP. However, 3-CP and 3,4-DCP, which are likely dechlorination products of 2,3-DCP and 2,3,4-T₃CP, respectively, were observed. No chlorination products were observed, however. The yields of these products provide insight on the relative reactivity of the reactants with respect to dechlorination at the ortho position. Since twice as much 3-CP is produced as 3,4-DCP, 2,3-DCP seems to be more susceptible to dechlorination than 2,3,4-T₃CP. In contrast, it appears that the reactant 2,3,4,5-T₄CP does not favor the loss of ortho-Cl, since 3,4,5-T₃CP was not detected. It was also previously observed that the ortho site appears to be the location most favored for dechlorination of phenols, the para position is less favored, and the meta site is least favored. The current results support this hypothesis since 2,4-DCP, which would result from dechlorination of 2,3,4-T₃CP at the meta position, was not detected.

An examination of the yields of furan and dioxin products listed in Table 2 and shown in Figure 2 provides information on the relative reactivity of the phenols to form these products. While a variety of PCDFs and DF were formed, no PCDDs and only a small amount of DD were detected. T₄CDF, DCDF and DF products predominate. The formation of specific furan products can be explained by reactions of the phenol and chlorinated phenols discussed above. For example, DF can be formed by a combination of two phenols, whereas DCDF can be produced from a DCP and a phenol, or from two CPs. T₄CDF may be formed in three ways: T₄CP and phenol, T₃CP and CP, or two DCPs. Below 550°C, most of the feed was unreacted, which corresponds to the rather low yields of the products. As reactor temperature increases, the PCDF distribution shifts from higher to less chlorinated homologues. This shift may be explained by comparing the average concentration of chlorinated phenols in the reactor (highest at low temperatures), to the unchlorinated phenol concentration (peaks at high temperature, at about 675°C). As the reactor temperature is increases, the ratio of phenol to chlorinated phenols also increases. Since the reactants are less chlorinated at higher reactor temperatures, the resulting products are therefore less chlorinated.

Fig. 2

The chlorinated phenols also appear to undergo H-atom substitution of the hydroxyl group. This would explain the formation of benzenes having chlorine atoms at adjacent sites. For example, while chlorobenzene (resulting from 2-CP), 1,2-dichlorobenzene (from 2,3-DCP) and 1,2,3-trichlorobenzene (from 2,3,4-T₃CP) were observed, neither 1,3- nor 1,4-dichlorobenzene was detected. Interestingly, 2,3,4,5-T₄CP, which does not favor dechlorination, also resists loss of OH, since the expected product (1,2,3,4-tetrachlorobenzene) was not detected.
Although not the subject of this paper, the formation of naphthalene and its chlorinated homologues may be explained by another pathway—condensation and rearrangement of two cyclopentadienyl fragments produced from (chlorinated) benzene or phenol.

**PCDF Isomer Yields**

Product isomer yields from the slow combustion of the mixture of chlorinated phenols, over a temperature range from 500 to 700°C, are depicted in Fig. 3 (MCDF through T3CDF) and Fig. 4 (T4CDF through H6CDF). The yield of 4-MCDF, which is produced from 2-CP and phenol, is largest of the MCDFs and peaks near 600°C at 0.04% (carbon feed basis). 1- and 3-MCDF, which are formed from 3-CP and phenol, reach a maximum yield of 0.01% (total) near 650°C, which corresponds to the temperature at which 3-CP peaks. A small amount of 2-MCDF (produced from 4-CP and phenol) was detected at 600 and 650°C.

For DCDFs, the greatest yield is obtained from 3,4-DCDF between 575 and 600°C (0.07%). This isomer is produced from 2,3-DCP and phenol. Next highest are 1,2- and 2,3-DCDF, which result from 3,4-DCP and phenol, and which peak near 600°C (0.006%) and 650°C (0.004%), respectively. (Peak 3,4-DCP yield occurs between 600 and 625°C.) Lowest is 4,6-DCDF, formed from two 2-CPS, which reaches maximum between 550 and 575°C (0.003%).

The most abundant T3CDF isomer is 2,3,4-T3CDF, which is a product of 2,3,4-T3CP and phenol. Its maximum yield of 0.04% occurs near 575°C. Next is 3,4,6-T3CDF, which is formed from 2,3-DCP and 2-CP, and which peaks between 550 and 575°C (0.011%). The least abundant isomers are 1,2,7- and 2,3,9-T3CDF, which co-elute. These products result from 3,4-DCP and 3-CP. Their maximum occurs near 600°C (0.003%).

For T4CDFs, the yield of 1,2,3,4-T4CDF is the greatest at 0.08%. This isomer is formed from a combination of 2,3,4,5-T4CP and phenol. 3,4,6,7-T4CDF, which is a product of two 2,3-DCPs, is much lower in abundance, with a maximum yield of only 0.006%. Lower still is 2,3,4,6-T4CDF, which results from 2,3,4-T3CP and 2-CP. Its peak yield is 0.004%. Yields of all three isomers peak between 550 and 575°C.

Two isomers of P5CDF were identified, 1,2,3,4,6- and 2,3,4,6,7-P5CDF. The former is the product of 2,3,4,5-T4CP and 2-CP, while the latter results from the coupling of 2,3,4-T3CP and 2,3-DCP. Although 1,2,3,4,6-P5CDF is twice as abundant as 2,3,4,6,7-P5CDF, both products reach their maximum yield near 550°C (0.012% and 0.005%, respectively).

Of the H6CDF isomers, only 1,2,3,4,6,7-H6CDF could be quantified. A product of 2,3,4,5-T4CP and 2,3-DCP, its maximum yield was 0.015% at 550°C. Trace amounts were detected of 2,3,4,6,7,8-H6CDF, which is formed by the coupling of two 2,3,4-T3CPs.

The most highly chlorinated PCDF congener detected was 1,2,3,4,6,7,8-H7CDF, which forms from 2,3,4,5-T4CP and 2,3,4-T3CP. Its maximum yield was 0.0015%, occurring at 550°C.
PCDF Formation Potential of Phenols

Observing the yields of DF and various PCDF congeners from the slow combustion of the phenol mixture, it is evident that some reactant pairings form furan products more readily than others do. In previous studies we proposed a hypothesis that the formation of PCDF is affected by differences in steric hindrance associated with “sandwich-type” approach geometries of the phenoxy radicals during carbon-carbon coupling. Fewer interactions of aligned chlorine and oxygen substituents lead to greater product yield. Using 3-CP in one study and a mixture of DCP isomers in another, experimental results were found to be consistent with this hypothesis. Relative product yields in the current work will be examined for evidence consistent with this hypothesis.

In the analysis of the PCDF isomer yields, above, it was noted that the most abundant isomer in each of the mono- through tetrachlorinated homologue groups was formed from phenol and a chlorinated phenol. With these pairings, only the 2,3,4,5-T4CP + phenol combination has a Cl-O interaction in its approach geometry. The other combinations have no interactions between Cl or O atoms at all. It is evident that once phenol is formed from benzene, it reacts as well as the chlorinated phenols that were present in the original reactant mixture. To compare the reactivity of all the phenols, it is useful to examine the product yields at 550 to 575°C since in this range, the concentration of phenol in the reactor is similar to that of the chlorinated reactants. Table 3 lists the furan products in order of their abundance, their respective precursors and the number of chlorine or oxygen approach interactions.

| TABLE 3 |

In general, it can be seen that the phenol pairings that result in fewest Cl-O and Cl-Cl approach interactions result in the highest furan yield. However, the very low yield of 4,6-DCDF, which results from the coupling of two 2-CPs, and which has no steric interactions, is anomalous. Even among the five reactant pairs involving unchlorinated phenol, there is a distinct difference between the yield of greater than 0.07% at 575°C (for DF, 1,2,3,4-T4CDF or 3,4-DCDF) and the less than 0.05% yield of 2,3,4-T3CDF or 4-MCDF. It is apparent that other factors in addition to steric hindrance are important in furan formation from phenols.

Examination of the yields in Table 3 for pairings of phenol + X, or for 2-CP + X (where X can be any of the reactants), results in an interesting observation. When X is either 2-CP or 2,3,4-T3CP, the product yield is much lower than if X is phenol, 2,3-DCP or 2,3,4,5-T4CP. This pattern suggests that chlorine substitution in the meta position enhances, whereas ortho or para substitution reduces furan formation.

Conclusions

The results presented here are the first that directly compare furan formation among several phenol precursors that differ only in the degree of chlorination. These results show that several effects are important in the gas-phase formation of dibenzofuran and chlorinated dibenzofurans from such mixtures. First, the product yields are consistent with a reaction mechanism that involves orienting the reactants in a parallel, “sandwich” geometry prior to coupling at unsubstituted ortho carbon sites. In this geometry, fewer steric interactions of
substituent chlorine and oxygen atoms will result in higher product yield. Therefore coupling of two highly chlorinated (>2 Cl) precursors is much less favored than if one or both reactants is less chlorinated (≤2 Cl).

Second, the location of the chlorine substituent produces a noticeable effect on the product yield when other factors are about equal. Chlorine in the meta position favors furan formation, whereas ortho and para substitution reduces it. This effect, for the present, is a qualitative one.

Since real mixtures are much more complex, a quantitative understanding of the factors that affect PCDD/F formation is necessary to be able to develop a predictive model. Continued study of the reactivity of the precursors and of the details of the reaction mechanisms are therefore needed.

**Acknowledgment**

Support of the Research Foundation for Health and Environmental Effects and the Environmental Protection Agency (QT-OH-99-000537) is gratefully acknowledged.
References

<table>
<thead>
<tr>
<th>Dioxins</th>
<th>2-CP</th>
<th>2,3-DCP</th>
<th>2,3,4-T&lt;sub&gt;3&lt;/sub&gt;CP</th>
<th>2,3,4,5-T&lt;sub&gt;4&lt;/sub&gt;CP</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-CP</td>
<td>dibenzodioxin</td>
<td>1-MCDD</td>
<td>1,2-DCDD</td>
<td>1,2,3-T&lt;sub&gt;3&lt;/sub&gt;CDD</td>
</tr>
<tr>
<td>2,3-DCP</td>
<td>1,6-/1,9-DCDD</td>
<td>1,2,6-/1,2,9-T&lt;sub&gt;3&lt;/sub&gt;CDD</td>
<td>1,2,3,6-/1,2,3,9-T&lt;sub&gt;4&lt;/sub&gt;CDD</td>
<td></td>
</tr>
<tr>
<td>2,3,4-T&lt;sub&gt;3&lt;/sub&gt;CP</td>
<td>1,2,6,7-/1,2,8,9-T&lt;sub&gt;4&lt;/sub&gt;CDD</td>
<td>1,2,3,6,7-/1,2,3,8,9-T&lt;sub&gt;4&lt;/sub&gt;CDD</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,3,4,5-T&lt;sub&gt;4&lt;/sub&gt;CP</td>
<td></td>
<td></td>
<td>1,2,3,6,7,8-/1,2,3,7,8,9-H&lt;sub&gt;6&lt;/sub&gt;CDD</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Furans</th>
<th>phenol</th>
<th>2-CP</th>
<th>2,3-DCP</th>
<th>2,3,4-T&lt;sub&gt;3&lt;/sub&gt;CP</th>
<th>2,3,4,5-T&lt;sub&gt;4&lt;/sub&gt;CP</th>
</tr>
</thead>
<tbody>
<tr>
<td>phenol</td>
<td>dibenzofuran</td>
<td>4-MCDF</td>
<td>3,4-DCDF</td>
<td>2,3,4-T&lt;sub&gt;3&lt;/sub&gt;CDF</td>
<td>1,2,3,4-T&lt;sub&gt;4&lt;/sub&gt;CDF</td>
</tr>
<tr>
<td>2-CP</td>
<td>4,6-DCDF</td>
<td>3,4,6-T&lt;sub&gt;3&lt;/sub&gt;CDF</td>
<td>2,3,4,6-T&lt;sub&gt;4&lt;/sub&gt;CDF</td>
<td>1,2,3,4,6-P&lt;sub&gt;5&lt;/sub&gt;CDF</td>
<td></td>
</tr>
<tr>
<td>2,3-DCP</td>
<td>3,4,6,7-T&lt;sub&gt;4&lt;/sub&gt;CDF</td>
<td>2,3,4,6,7-P&lt;sub&gt;5&lt;/sub&gt;CDF</td>
<td>1,2,3,4,6,7-H&lt;sub&gt;6&lt;/sub&gt;CDF</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,3,4-T&lt;sub&gt;3&lt;/sub&gt;CP</td>
<td>2,3,4,6,7,8-H&lt;sub&gt;6&lt;/sub&gt;CDF</td>
<td>1,2,3,4,6,7,8-H&lt;sub&gt;7&lt;/sub&gt;CDF</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,3,4,5-T&lt;sub&gt;4&lt;/sub&gt;CP</td>
<td></td>
<td>OCDF</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
TABLE 2.
Product yields (percent carbon feed basis) from a mixture of chlorinated phenols in benzene.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>500</th>
<th>550</th>
<th>600</th>
<th>650</th>
<th>700</th>
</tr>
</thead>
<tbody>
<tr>
<td>unreacted phenols:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-CP</td>
<td>1.392</td>
<td>1.214</td>
<td>0.776</td>
<td>0.266</td>
<td>0.011</td>
</tr>
<tr>
<td>2,3-DCP</td>
<td>1.036</td>
<td>0.832</td>
<td>0.509</td>
<td>0.092</td>
<td>nd</td>
</tr>
<tr>
<td>2,3,4-T3CP</td>
<td>1.011</td>
<td>0.660</td>
<td>0.257</td>
<td>0.013</td>
<td>nd</td>
</tr>
<tr>
<td>2,3,4,5-T4CP</td>
<td>1.044</td>
<td>0.500</td>
<td>0.089</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>Total unreacted phenols</td>
<td>4.483</td>
<td>3.206</td>
<td>1.631</td>
<td>0.371</td>
<td>0.011</td>
</tr>
<tr>
<td>unextractable product (soot)</td>
<td>0.000</td>
<td>0.270</td>
<td>0.082</td>
<td>0.144</td>
<td>0.000</td>
</tr>
<tr>
<td>Total aromatic products</td>
<td>0.230</td>
<td>1.400</td>
<td>3.769</td>
<td>6.730</td>
<td>0.772</td>
</tr>
<tr>
<td>phenol</td>
<td>0.190</td>
<td>1.126</td>
<td>3.203</td>
<td>5.800</td>
<td>0.503</td>
</tr>
<tr>
<td>3-CP</td>
<td>nd</td>
<td>nd</td>
<td>0.015</td>
<td>0.019</td>
<td>nd</td>
</tr>
<tr>
<td>3,4-DCP</td>
<td>nd</td>
<td>0.003</td>
<td>0.008</td>
<td>0.007</td>
<td>nd</td>
</tr>
<tr>
<td>chlorobenzene</td>
<td>nd</td>
<td>nd</td>
<td>0.015</td>
<td>0.063</td>
<td>0.051</td>
</tr>
<tr>
<td>1,2-dichlorobenzene</td>
<td>nd</td>
<td>nd</td>
<td>0.016</td>
<td>0.044</td>
<td>0.016</td>
</tr>
<tr>
<td>1,2,3-trichlorobenzene</td>
<td>nd</td>
<td>nd</td>
<td>0.014</td>
<td>0.024</td>
<td>0.004</td>
</tr>
<tr>
<td>Total chlorinated benzenes</td>
<td>nd</td>
<td>nd</td>
<td>0.045</td>
<td>0.131</td>
<td>0.071</td>
</tr>
<tr>
<td>naphthalene</td>
<td>nd</td>
<td>nd</td>
<td>0.024</td>
<td>0.212</td>
<td>0.117</td>
</tr>
<tr>
<td>chloronaphthalenes</td>
<td>nd</td>
<td>nd</td>
<td>0.006</td>
<td>0.012</td>
<td>nd</td>
</tr>
<tr>
<td>dichloronaphthalenes</td>
<td>nd</td>
<td>nd</td>
<td>0.005</td>
<td>0.008</td>
<td>nd</td>
</tr>
<tr>
<td>trichloronaphthalenes</td>
<td>nd</td>
<td>0.001</td>
<td>0.008</td>
<td>0.017</td>
<td>nd</td>
</tr>
<tr>
<td>Total naphthalenes</td>
<td>nd</td>
<td>0.001</td>
<td>0.043</td>
<td>0.248</td>
<td>0.117</td>
</tr>
<tr>
<td>dibenzofurans:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DF</td>
<td>nd</td>
<td>0.026</td>
<td>0.159</td>
<td>0.314</td>
<td>0.069</td>
</tr>
<tr>
<td>MCDFs</td>
<td>0.002</td>
<td>0.024</td>
<td>0.047</td>
<td>0.033</td>
<td>nd</td>
</tr>
<tr>
<td>DCDFs</td>
<td>0.003</td>
<td>0.051</td>
<td>0.079</td>
<td>0.045</td>
<td>nd</td>
</tr>
<tr>
<td>T3CDFs</td>
<td>0.006</td>
<td>0.041</td>
<td>0.052</td>
<td>0.032</td>
<td>nd</td>
</tr>
<tr>
<td>T4CDFs</td>
<td>0.015</td>
<td>0.095</td>
<td>0.072</td>
<td>0.030</td>
<td>nd</td>
</tr>
<tr>
<td>P5CDFs</td>
<td>0.007</td>
<td>0.017</td>
<td>0.009</td>
<td>0.006</td>
<td>nd</td>
</tr>
<tr>
<td>H2CDFs</td>
<td>0.006</td>
<td>0.014</td>
<td>0.006</td>
<td>0.003</td>
<td>nd</td>
</tr>
<tr>
<td>H3CDFs</td>
<td>nd</td>
<td>0.001</td>
<td>0.001</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>OCDF</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>Total PCDFs</td>
<td>0.040</td>
<td>0.244</td>
<td>0.265</td>
<td>0.148</td>
<td>nd</td>
</tr>
<tr>
<td>Total DF + PCDFs</td>
<td>0.040</td>
<td>0.270</td>
<td>0.424</td>
<td>0.462</td>
<td>0.069</td>
</tr>
<tr>
<td>dibenzodioxin</td>
<td>nd</td>
<td>trace</td>
<td>trace</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>PCDDs</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>Product ratios:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenol / DF</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chlorinated phenols / PCDFs</td>
<td>112.1</td>
<td>13.2</td>
<td>6.2</td>
<td>2.7</td>
<td></td>
</tr>
<tr>
<td>Phenol / chlorinated phenols</td>
<td>0.04</td>
<td>0.35</td>
<td>1.9</td>
<td>14.6</td>
<td>45.7</td>
</tr>
<tr>
<td>DF / PCDFs</td>
<td>0.0</td>
<td>0.11</td>
<td>0.60</td>
<td>2.1</td>
<td></td>
</tr>
</tbody>
</table>

*not detected
TABLE 3.  
Characteristics of DF/PCDF products from a mixture of chlorinated phenols in benzene.  
(listed in order of yield at 575°C)

<table>
<thead>
<tr>
<th>Product</th>
<th>Reactants</th>
<th>Yield (% carbon feed)</th>
<th>Approach</th>
<th>Interactions*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>550°C</td>
<td>575°C</td>
<td></td>
</tr>
<tr>
<td>DF</td>
<td>Phenol+phenol</td>
<td>0.026</td>
<td>0.077</td>
<td>None</td>
</tr>
<tr>
<td>1,2,3,4-T₄CDF</td>
<td>Phenol+2,3,4,5-T₄CP</td>
<td>0.085</td>
<td>0.074</td>
<td>1 Cl-O</td>
</tr>
<tr>
<td>3,4-DCDF</td>
<td>Phenol+2,3-DCP</td>
<td>0.047</td>
<td>0.070</td>
<td>None</td>
</tr>
<tr>
<td>2,3,4-T₃CDF</td>
<td>Phenol+2,3,4-T₃CP</td>
<td>0.030</td>
<td>0.041</td>
<td>None</td>
</tr>
<tr>
<td>4-MCDF</td>
<td>Phenol+2-CP</td>
<td>0.024</td>
<td>0.038</td>
<td>None</td>
</tr>
<tr>
<td>3,4,6-T₃CDF</td>
<td>2-CP+2,3-DCP</td>
<td>0.011</td>
<td>0.011</td>
<td>None</td>
</tr>
<tr>
<td>1,2,3,4,6,7-H₆CDF</td>
<td>2,3-DCP+2,3,4,5-T₄CP</td>
<td>0.014</td>
<td>0.009</td>
<td>1 Cl-O, 2 Cl-Cl</td>
</tr>
<tr>
<td>1,2,3,4,6-P₅CDF</td>
<td>2-CP+2,3,4,5-T₄CP</td>
<td>0.012</td>
<td>0.008</td>
<td>1 Cl-O, 1 Cl-Cl</td>
</tr>
<tr>
<td>3,4,6,7-T₄CDF</td>
<td>2,3-DCP+2,3-DCP</td>
<td>0.006</td>
<td>0.005</td>
<td>1 Cl-Cl</td>
</tr>
<tr>
<td>2,3,4,6,7-P₅CDF</td>
<td>2,3-DCP+2,3,4-T₃CP</td>
<td>0.005</td>
<td>0.005</td>
<td>2 Cl-Cl</td>
</tr>
<tr>
<td>2,3,4,6-T₄CDF</td>
<td>2-CP+2,3,4-T₃CP</td>
<td>0.004</td>
<td>0.003</td>
<td>1 Cl-Cl</td>
</tr>
<tr>
<td>4,6-DCDF</td>
<td>2-CP+2-CP</td>
<td>0.003</td>
<td>0.003</td>
<td>None</td>
</tr>
<tr>
<td>1,2,3,4,6,7,8-H₇CDF</td>
<td>2,3,4-T₃CP+2,3,4,5-T₄CP</td>
<td>0.001</td>
<td>0.001</td>
<td>1 Cl-O, 3 Cl-Cl</td>
</tr>
<tr>
<td>2,3,4,6,7,8-H₈CDF</td>
<td>2,3,4-T₃CP+2,3,4-T₃CP</td>
<td>trace</td>
<td>trace</td>
<td>3 Cl-Cl</td>
</tr>
</tbody>
</table>

*For the geometry resulting in the least number of interactions.
FIG. 1. Reaction pathways for conversion of 2-CP to 4,6-DCDF (1) and DD (2)
FIG. 2. Reactant and product yields from a mixture of chlorinated phenols in benzene.
FIG. 3. MCDF, DCDF and T₃CDF yields from a mixture of chlorinated phenols in benzene.
FIG. 4. T₄CDF, P₅CDF and H₆CDF yields from a mixture of chlorinated phenols in benzene.
Captions

TABLE 1. Expected dioxin and furan products from combinations of chlorinated phenols.

TABLE 2. Product yields (percent carbon feed basis) from a mixture of chlorinated phenols in benzene.

TABLE 3. Characteristics of DF/PCDF products from a mixture of chlorinated phenols in benzene.

Fig. 1. Reaction pathways for conversion of 2-CP to 4,6-DCDF (1) and DD (2)

Fig. 2. Reactant and product yields from a mixture of chlorinated phenols in benzene.

Fig. 3. MCDF, DCDF and T₃CDF yields from a mixture of chlorinated phenols in benzene.

Fig. 4. T₄CDF, P₅CDF and H₆CDF yields from a mixture of chlorinated phenols in benzene.
Abstract for poster presentation at The Seventh Congress on Toxic Combustion By-products

Ab Initio Modeling of Dibenzofuran Formation from Phenol Condensation

D.T. Nakahata and J.A. Mulholland
Georgia Institute of Technology, School of Civil and Environmental Engineering

The gas-phase formation of dibenzofuran (DF) and chlorinated dibenzofurans (CDFs) from phenol and chlorinated phenol precursors has been observed in the exhaust stream of combustion processes and has been studied in the laboratory. Experimental results indicate that DF and CDF formation occurs via carbon-carbon coupling of phenoxy radicals at unsubstituted *ortho* sites; hence only those precursors with at least one unchlorinated *ortho* site will form DF/CDF. Each unique DF/CDF congener originates from a specific pair of phenolic precursors. Experiments also show that the number and pattern of additional chlorine substituents affect the yield of DF/CDF significantly, but in a complex manner. One proposed formation mechanism suggests that both electronic and steric effects due to chlorine substitution are important in the formation of the reacting phenoxy radicals and in development of the transition state and first intermediate product in the reaction pathway. However these effects cannot easily be measured nor predicted.

The current study analyzes the steric and electronic effects of DF/CDF formation from phenolic precursors by using computational chemistry to model the species in the proposed formation mechanism. *Ab initio* quantum mechanical methods are employed to determine the optimized structures and to calculate the energies of the reactants, products, intermediates and transition states formed in the reaction pathway. The B3LYP hybrid density functional method and the 6-31G* polarized valence double-zeta basis set are used in this analysis. Transition state theory is used to compare the computational results with the experimental data. The overall goal of this work is to develop a predictive understanding of factors controlling the relative rates of formation of DF/CDF congeners from chlorinated phenols. The results will lead to a predictive model of CDF isomer patterns that provide a fingerprint of the gas-phase phenol condensation mechanism.
Ab Initio Modeling of Dibenzofuran Formation from Phenol Condensation

Duane T. Nakahata and James A. Mulholland, Georgia Institute of Technology
Keiji Morokuma, Emory University

Background

Hypothesis / Objective

Computational Results

Methodology

Summary

Conclusions

Follow-on Work

The support of the following is gratefully acknowledged: EPA, NSF and DOE.
Introduction

In incinerators, dibenzofuran (DF) and chlorinated dibenzofurans (CDF) are formed from phenol and chlorinated phenols by homogeneous, gas-phase reactions at high temperatures in the post-combustion zone. In spite of considerable research over the past 25 years, a detailed understanding of the chemical mechanisms of DF/CDF formation is still incomplete. For example, little is known about factors that govern the distribution of DF/CDF congeners produced from a mixture of precursors.

Chlorinated phenols and phenol are the most direct DF/CDF precursors [1] and among the most abundant aromatic compounds found in incinerator gas emissions [2]. However, effects of the degree (number of chlorine atoms) or pattern of substitution of chlorinated phenol precursors on DF/CDF formation are not well understood.

This project investigates in detail the first step in the reaction pathway of DF formation (from phenoxy radical) using computational chemistry. (The DF formation mechanism is summarized below.) Current ab initio computational methods allow calculation of many properties of the species of interest. Such calculations can provide information on the most stable geometry of the molecule (or radical) as well as parameters such as energy and vibrational frequencies.

Background

Chlorinated phenols and phenol readily form neutral, ambident phenoxy radicals capable of reacting at the oxygen site as well as at the ortho and para carbon sites [3]. DF/CDF formation most likely occurs by carbon-carbon coupling of phenoxy radicals at ortho sites, which leads to the o,o'-dihydroxy biphenyl (DOHB) intermediate [4] via its keto-tautomer. Coupling occurs at less crowded (unsubstituted) ortho carbon sites. Phenoxy radicals preferentially approach each other in a "sandwich-like" geometry with overlap of the aromatic π systems; coupling occurs at sites of highest spin density and for geometries of least steric hindrance [5]. Enolization of the keto-tautomer and loss of H₂O from DOHB yields
DF/CDF. The route to dichlorodibenzofuran (DCDF) described above is depicted by path (1) in Figure 1 for the combination of two 2-chlorophenoxy radicals.

In laboratory experiments mixtures of phenol (P) and three chlorophenol (CP) isomers and mixtures of three dichlorophenol (DCP) isomers were studied to assess the effects of the chlorination pattern on CDF formation. Although some patterns emerged—chlorine in the meta position enhances CDF formation—without other tools it is still not possible to quantitatively predict the yield of a unique CDF product from its reactants.

![Reaction pathways for conversion of 2-CP to 4,6-DCDF (1) and DD (2)](image)

**FIG. 1.** Reaction pathways for conversion of 2-CP to 4,6-DCDF (1) and DD (2)

**Computational Methodology**

The following species were analyzed using the Gaussian 98 program [6]: phenoxy radical (C₆H₅O) as well as the product of the first reaction step, the keto-tautomer of DOHB. In addition, the transition state between the reactants and product was investigated. The geometry of each species was optimized using the 6-31G* polarized valence double-zeta basis set and the B3LYP hybrid density functional method, which couples the three-parameter Becke exchange functional with the correlation functional of Lee, Yang and Parr.

For each species, the input (guess) geometry was specified in z-matrix form, using nominal bond lengths and angles, and was converted by the program into redundant internal coordinates. For an optimization to a minimum, the Hessian matrix was estimated on the first step and subsequently updated. In all cases the Berny optimization method was used. The optimization was converged when criteria for the maximum force component, the root-mean-square force, the maximum step component and the root-mean-square step were satisfied [7]. Following geometry optimization, the nature of each stationary point was verified to be a
minimum using a frequency calculation with the same method and basis set. The DOHB (keto-tautomer) product is shown in Figure 2.

![Diagram of keto-tautomer of dihydroxybiphenyl]

**FIG. 2.** The product of the coupling of two phenoxy radicals: keto-tautomer of dihydroxybiphenyl.

**Locating the Transition State**

It was unclear if a transition state (TS) existed between the reactants and product. Since the shape of the potential energy surface (PES) was unknown, a scan of the PES along the reaction coordinate was required. The likely reaction coordinate was the ortho-ortho carbon bond distance, since it is the only bond being formed in the reaction step, while other bonds are maintained between reactants and product.

Several partial optimizations were performed, in which the ortho C-C bond distance was fixed but all other parameters were variables. Since the calculated C-C bond distance in the product is 1.546 Å, fixed distances of 1.65, 1.75, 2.00, 2.25 and 2.50 Å were chosen for these optimizations. The calculated energies were compared to those of the reactants and product. (These data are provided in Computational Results, below.) Along this coordinate, all the energy values were between reactants and product. However, the energy at 2.25 Å appeared to be near a local maximum; the geometry at this C-C distance was selected as the guess in the search for the TS.

In the TS optimization, the Gaussian program was directed to calculate the Hessian matrix analytically to determine the local curvature of the PES. This enabled the search for the first-order saddle point to proceed in the correct direction. In the optimized TS geometry,
the C-C bond distances was calculated to be 2.216 Å. Following the optimization, the nature of this stationary point was verified to be a saddle point using a frequency calculation. The TS structure is shown in Figure 3.

![Figure 3](image)

**FIG. 3.** The transition state in the formation of the keto-tautomer of dihydroxybiphenyl.

**Finding another Local Minimum**

At C-C bond lengths greater than that of the TS, the calculated energies of partially optimized structures decrease. Since the energy of two completely separated reactants is higher than the TS energy, it was evident that energy passes through a minimum between the two states. This local minimum was identified using an optimization calculation using one of the partially optimized structures as the initial guess. The optimized geometry is a van der Waals complex (pi-complex) and is shown in Figure 4. It consists of two parallel, but offset phenoxy moieties.

![Figure 4](image)

**FIG. 4.** The pi-complex leading to the formation of the TS.
Computational Results

The calculated energies (with respect to completely separated reactants) as a function of the C-C bonding distance are shown in Table 1 and Figure 5. Also computed are the angle $\theta$ between the planes containing the phenoxy moieties and the angle $\phi$ that depicts the twist of the two rings relative to each other around the new C-C bond. (Formally the angle $\phi$ is the dihedral angle formed by the meta and ortho carbons of one ring and the ortho and ipso carbons of the other ring.) These angles are depicted in Figure 6.

<table>
<thead>
<tr>
<th>Species</th>
<th>$E(UB+HF-LYP)$ or $E(RB+HF-LYP)$ (B3LYP/6-31G*)</th>
<th>$\Delta E$ kcal/mol</th>
<th>$R$(Å)</th>
<th>$\theta$</th>
<th>$\phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>phenoxy radical (C6H5O)</td>
<td>U -305.827641570</td>
<td>0.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 x phenoxy radical</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pi-complex</td>
<td>R -613.661152717</td>
<td>-3.68</td>
<td>2.763</td>
<td>0.00</td>
<td>57.29</td>
</tr>
<tr>
<td>partial opt 1d</td>
<td>R -613.650183216</td>
<td>-3.07</td>
<td>2.500</td>
<td>7.97</td>
<td>59.14</td>
</tr>
<tr>
<td>partial opt 1c</td>
<td>R -613.658463877</td>
<td>-2.00</td>
<td>2.250</td>
<td>15.90</td>
<td>61.32</td>
</tr>
<tr>
<td>Transition State</td>
<td>R -613.658416824</td>
<td>-1.97</td>
<td>2.216</td>
<td>17.10</td>
<td>61.97</td>
</tr>
<tr>
<td>partial opt 1b</td>
<td>R -613.661428805</td>
<td>-3.86</td>
<td>2.000</td>
<td>26.50</td>
<td>63.03</td>
</tr>
<tr>
<td>partial opt 1a</td>
<td>R -613.671272450</td>
<td>-10.03</td>
<td>1.750</td>
<td>41.00</td>
<td>61.94</td>
</tr>
<tr>
<td>partial opt 1</td>
<td>R -613.674579743</td>
<td>-12.11</td>
<td>1.650</td>
<td>51.58</td>
<td>60.32</td>
</tr>
<tr>
<td>DOHB (keto tautomer)</td>
<td>R -613.677479386</td>
<td>-13.93</td>
<td>1.546</td>
<td>89.65</td>
<td>69.07</td>
</tr>
</tbody>
</table>

Table 1. Calculated Energies and Angles.

2 Ph-O- $\rightarrow$ dihydroxybiphenyl (keto tautomer)

![Diagram showing calculated energies vs. C-C distance](image)

FIG 5. Calculated Energies vs. C-C Distance.
Conclusions

This project has investigated the first reaction step in the formation of dibenzofuran from phenoxy radicals. The optimized structures and energies of the phenoxy reactants, the dihydroxybiphenyl (keto-tautomer) product, the intervening transition state and intermediates along the reaction coordinate have been calculated using B3LYP method and 6-31G* basis set. In addition the existence of a van der Waals complex has been predicted.

The use of ab initio computational methods to analyze reactants and products can provide insights into differences in reactivity. However reaction rates and reactivity are still dependent on the transition states encountered and the energy needed to overcome the activation barrier. Therefore these differences must be investigated by further detailed study of the relevant transition states.
References


Formation of Polychlorinated Dibenzo-p-dioxins by CuCl₂-Catalyzed Condensation of 2,6 Chlorinated Phenols

James A. Mulholland* and Jae-Yong Ryu
Environmental Engineering, Georgia Institute of Technology, Atlanta GA 30332-0512

* corresponding author’s e-mail address: james.mulholland@ce.gatech.edu

ABSTRACT

CuCl₂-catalyzed formation of polychlorinated dibenzo-p-dioxins (PCDDs) from four 2,6 chlorinated phenols was studied in an isothermal flow reactor. Heated gas streams containing oxygen (8%, mole) and 2,6-dichlorophenol, 2,4,6-trichlorophenol, 2,3,4,6-tetrachlorophenol and pentachlorophenol vapor (0.03%, each) were passed through 1 cm particle beds containing CuCl₂. Two gas velocities, 2.7 and 0.5 cm/s, were studied, with phenol-to-CuCl₂ molar ratios varied by varying the duration of experiments. PCDD yields were greatest between 300 and 450°C, with 60% phenol conversion to PCDDs observed at low gas velocity and high to phenol-to-CuCl₂ ratios. Homologue distributions were shifted to highly chlorinated congeners at low temperature, high gas velocity, and low phenol-to-CuCl₂ ratio, conditions under which total PCDD yields were low. Isomer distributions did not vary significantly, however. The major PCDD product was 1,2,3,4,6,8-H₆CDD, formed from 2,4,6-trichlorophenol and pentachlorophenol. This congener, and other PCDDs formed from the three 2,4,6 chlorinated phenols, are major constituents of incinerator PCDD distributions.

keywords: dibenzo-p-dioxin, PCDD, chlorinated phenols, copper (II) chloride
INTRODUCTION

In municipal waste incinerators, polychlorinated dibenzo-p-dioxin (PCDD) and dibenzofuran (PCDF) byproducts are formed by two general pathways: (1) homogeneous, gas-phase reactions, and (2) heterogeneous, catalytic reactions. The former route, which is observed in post-combustion gas at temperatures between 500 and 700°C, occurs via precursors and strongly favors the formation of dibenzofuran and less chlorinated PCDD/F congeners. The latter route, which is observed in particle collection devices at temperatures between 250 and 400°C, may involve precursors of similar structure or particulate carbon. This pathway favors the formation of highly chlorinated PCDD/F congeners (Hagenmaier et al., 1989; Yamamoto et al., 1989).

PCDD/F formation mechanisms have been studied extensively, including gas-phase condensation of phenoxy radicals (Born et al., 1989) and flyash-mediated, metal-catalyzed formation from phenols (Born et al., 1993), polycyclic aromatic hydrocarbons (Hell et al., 2000) and graphitic carbon (Stieglitz et al., 1989). PCDD formation rates from precursors that are similar in structure, such as chlorinated phenols, have been found to be significantly faster than rates from particulate carbon, or de novo synthesis, under typical incinerator conditions (Dickson et al., 1992; Altwicker and Milligan, 1993). Nonetheless, there remains much uncertainty about the predominant pathway(s) of PCDD/F formation in combustion systems.

PCDD/F isomer patterns may provide fingerprints of formation mechanism (Wehrmeier et al., 1998). For example, PCDD/F isomer patterns produced from polycyclic aromatic hydrocarbons on flyash have been compared to emissions from a fluidized bed incinerator (Weber et al., 1999). In addition to the mechanisms described above, chlorination of less chlorinated congeners produced in the gas phase (Wikstrom and Marklund, 1999) and dechlorination of highly chlorinated congeners produced by de novo synthesis (Iino et al., 2000)
have been proposed as factors that might control PCDD/F isomer distributions. Chlorination on catalytic surfaces has been found to occur predominantly at the 2,3,7,8 positions (Luijk et al., 1994). On the other hand, dechlorination was found to be favored at the 2,3,7,8 positions, resulting in PCDD/F isomer distributions very different than those produced by chlorination (Iino et al., 2000 and 2001). PCDD/F distributions produced from chlorinated phenols are not well known, however. While distributions produced from individual precursor combinations have been studied, little is known about distributions from chlorinated phenol mixtures typical of incinerator exhaust gas.

PCDD/F distributions from chlorinated phenols depend on the distribution of chlorinated phenols and the relative rates of formation from different phenol pairs. This paper addresses the latter. Regarding the former, Ballschmiter et al. (1987 and 1988) and Yamamoto et al. (1989 and 1990) reported that the major chlorinated phenols found in municipal waste incinerators are the congeners with ortho and para sites (2,4,6 carbons) chlorinated. There are three of these: 2,4,6-trichlorophenol (2,4,6-T3CP), 2,3,4,6-tetrachlorophenol (2,3,4,6-T4CP) and pentachlorophenol (PCP). Combination of phenols with both ortho positions chlorinated produces only PCDD products, with loss two Cl atoms, one from each phenol.

To illustrate the PCDD formation mechanism from 2,6 chlorinated phenols, pathways for gas-phase condensation of two 2,6-dichlorophenols (2,6-DCPs) are shown in Figure 1. The resonance-stabilized phenoxy radical is reactive at multiple sites (ambident). With both ortho sites chlorinated, oxygen-carbon coupling produces o-phenoxy ketone (A). Both radical-radical and radical-molecule mechanisms may occur (Wiater-Protas and Louw, 2001). In either case, four combinations are possible for phenols containing 2,6 chlorine substituents. In the example of 2,6-DCP, however, only one combination is unique due to symmetry. Loss of Cl atom
produces the phenoxyphenoxy radical, which can undergo either five-membered ring closure (Sidhu et al., 1995) or six-membered ring closure (Born et al., 1993), as illustrated in Fig. 1. Expansion of the five-membered ring intermediate with elimination of a second Cl atom yields either 1,6- or 1,9-dichlorodibenzo-p-dioxin (DCDD). For 2,6 chlorinated phenols, there are four possible five-membered ring expansion steps, two to each of two carbon atoms. In general, this can result in the formation of two 16/19 isomer pairs. For 2,6-DCP, only one 16/19 isomer pair is produced due to symmetry. On the other hand, there are only two possible six-membered ring closure steps; in the case 2,6-DCP, the only product formed by this route is 1,6-DCDD.

Figure 1

We have studied DCDD formation from 2,6-DCP in the gas phase and on particles containing copper (II) chloride (CuCl₂) (Mulholland et al., 2001a). In each set of experiments, the same DCDDs were formed - the 1,6 and 1,9 isomers. Maximum conversion of 2,6-DCP to DCDD products was greater by CuCl₂-catalyzed condensation (3%) than by gas-phase condensation (1%), and occurred at a lower temperature (350°C vs. 550°C). While total DCDD yields varied by over three orders of magnitude, the distribution of 1,6- and 1,9-DCDD isomers remained nearly constant. The 1,6-DCDD yield accounted for 65% (± 2%) of the total in the CuCl₂-catalysis experiments, and 55% (± 2%) in the gas-phase experiments.

In this paper, we address the relative rates of CuCl₂-catalyzed PCDD formation from 2,6-DCP and the three 2,4,6 chlorinated phenols: 2,4,6-T₃CP, 2,3,4,6-T₄CP and PCP. Expected PCDD products are shown by equations (1) through (10), with 16/19 isomers listed in pairs. Sensitivities of PCDD product distributions to temperature, gas velocity and phenol-to-CuCl₂ ratio are examined to assess how these distributions might be used as a fingerprint of PCDD formation by CuCl₂-catalyzed condensation of 2,6 chlorinated phenols.
EXPERIMENTAL METHODS

Experiments were conducted in an electrically heated, quartz tube flow reactor, 40 cm in length and 1.7 cm in diameter. 2,6-DCP, 2,4,6-T₃CP, 2,3,4,6-T₄CP and PCP were dissolved in benzene in a molar ratio of 1:100 (each). The solution was injected by micro-syringe pump into a heated glass vessel, where it was immediately vaporized in a gas stream of 92% nitrogen and 8% oxygen. The resulting gas stream contained 3% organic vapor. At the center of the reactor, a 1 g particle bed of 1 cm height, consisting of 0.5% (mass) CuCl₂ in silicon dioxide (SiO₂), was located. The nominal gas velocity was 2.7 cm/s, corresponding to a gas-particle contact time of 0.3 s. Experiments were carried out over the temperature range 200 to 500°C in 50°C increments. Experiments were run for approximately 20 minutes, corresponding to a total phenol-to-CuCl₂ molar ratio of 2.9. At 300°C, additional experiments were performed to assess effects of experiment duration (1 to 300 min) and gas velocity (0.5 and 2.7 cm/s).
The entire product gas stream was rapidly quenched. Soot and aromatic tar samples were collected in an ice-cooled dichloromethane trap. Sample solutions were filtered and then analyzed by GC/MS (HP 6890 series gas chromatograph with model 5973 mass selective detector) equipped with a HP-5MS capillary column. Preliminary identification of PCDD products was based on published relative retention times for similar columns (Ryan et al., 1991). Final identification was based on available standards and gas-phase synthesis experiments from single precursors and precursor pairs. All 75 PCDD congeners have been synthesized. A universal response factor was used for PCDDs based on dibenzo-p-dioxin.

Not all PCDD isomers could be separated. Of the ten expected product pairs (see equations 1 through 10), four could not be separated using our analytical methods. These are 1,2,4,6-/1,2,4,9-

\( \text{T}_4 \text{CDD} \) from combination of 2,6-DCP and 2,3,4,6-\( \text{T}_4 \text{CP} \), 1,2,4,6,8-/1,2,4,7,9-\( \text{P}_5 \text{CDD} \) from combination of 2,4,6-\( \text{T}_3 \text{CP} \) and 2,3,4,6-\( \text{T}_4 \text{CP} \), and the 1,2,4,6,7,9-/1,2,4,6,8,9- and 1,2,3,6,7,9-/1,2,3,6,8,9-\( \text{H}_6 \text{CDD} \) pairs from two 2,3,4,6-\( \text{T}_4 \text{CP} \) precursors. All other products were separated.

RESULTS

Total PCDD Yield and PCDD Homologue Distribution

The yields of total PCDD products and PCDD homologues are shown in Figure 2 as a percent conversion of total phenol reactants. Experiments were conducted in triplicate at 300°C; error bars represent standard deviations of these measurements. As expected, no PCDF products were formed from 2,6 chlorinated phenols. PCDD products were observed at temperatures ranging from 250 to 450°C. In the absence of CuCl\(_2\), no PCDD products were formed at these temperatures. A maximum total PCDD yield of 10.8% phenol conversion was observed at 400°C. Peak H\(_6\)CDD, P\(_5\)CDD, T\(_4\)CDD and T\(_3\)CDD yields of 4.6%, 2.5%, 1.3% and 0.3%, respectively, were observed at 400°C. Maximum H\(_7\)CDD and OCDD yields of 1.4% and 1.9%
occurred at 350°C and 300°C, respectively. No DCDD products were detected, even though the 1,6 and 1,9 isomers were expected by combination of 2,6-DCP. Since these products were observed in previous experiments with high concentrations of only the 2,6-DCP precursor, we conclude that 2,6-DCP has a lower propensity to form PCDDs than the other three chlorinated phenols studied.

Figure 2

Normalized homologue distributions are shown as a function of temperature in Figure 3. Total H₆CDD yield was greatest at all temperatures, accounting for 38 to 47% of the total PCDD yield. The T₃CDD, T₄CDD and P₅CDD fractions increased with increasing temperature, and the H₇CDD and OCDD fractions decreased. To assess which phenol combinations have the greatest propensity for PCDD formation, and which PCDD congeners are produced in greatest amount from phenol pairs, product isomer distributions are examined.

Figure 3

PCDD Isomer Distributions

Fractions of T₃CDD through H₇CDD isomers produced at 300, 350, 400 and 450°C are shown in Figure 4. All of the PCDD products listed in equations (2) through (10), based on the mechanism depicted in Figure 1, were found; moreover, no other PCDD products were observed. This result indicates that CuCl₂-catalyzed PCDD formation from 2,6 chlorinated phenols follows a pathway similar to gas-phase condensation, allowing for formation of both 16 and 19 isomers.

Figure 4

While the homologue distributions change significantly with temperature (Figure 3), the isomer distributions do not (Figure 4). At all temperatures, more 1,3,6-T₃CDD was produced than 1,3,9-T₃CDD. These are products of the combination of 2,6-DCP and 2,4,6-T₃CP. Major
T₄CDD products are the 1,3,6,8 and 1,3,7,9 isomers, formed from two 2,4,6-T₃CP precursors. The four other T₄CDD isomers were formed from 2,6-DCP and 2,3,4,6-T₄CP in much lower yields. Four P₃CDD peaks were observed. Yields of the 1,2,3,6,8/1,2,3,7,9 pair in total are slightly greater than yields of the 1,2,4,6,8/1,2,4,7,9 pair, which co-elute; both pairs are produced from combination of 2,4,6-T₃CP and 2,3,4,6-T₄CDD. The five H₆CDD peaks observed represent seven products. The major PCDD product at all temperatures was 1,2,3,4,6,8-H₆CDD; this congener is produced from combination of 2,4,6-T₃CP and PCP. Of the three pairs of H₆CDD products formed from two 2,3,4,6-T₄CP precursors, the 1,2,3,6,7,9/1,2,3,6,8,9 pair is favored. Of the two H₇CDD products from combination of 2,3,4,6-T₄CP and PCP, more of the 1,2,3,4,6,7,8 isomer was produced than the 1,2,3,4,6,7,9 isomer.

As discussed later in this paper, ratios of select isomer products derived from these experiments provide insight on factors controlling the isomer distributions. Moreover, these results may provide a fingerprint of PCDD formation by CuCl₂-catalyzed condensation of 2,6 chlorinated phenols. But first, results are presented to assess the dependence of PCDD product distributions on gas velocity and duration of experiment.

Effects of Gas Velocity and Duration of Experiment

Effects of gas velocity over the stationary particle bed and duration of experiment were assessed at 300°C. At a nominal gas velocity of 2.7 cm/s, which corresponds to a 0.3 second gas-particle contact time, experiments of 10, 20, 40, 60, 90 and 120 minute duration were conducted. This corresponds to phenol-to-CuCl₂ molar ratios ranging from 1.4 to 17.2. By reducing the total gas flow rate by a factor of five, a gas velocity of 0.54 cm/s was studied, which corresponds to a 1.5 second gas-particle contact time. At this gas velocity, experiments of 1 to 300 minute duration were conducted, corresponding to phenol-to-CuCl₂ molar ratios of 0.05 to 14.3.
Yields of phenol reactants increased as experiment duration increased (Figure 5). Approximately 90% recovery of 2,4,6-T₃CP and PCP was obtained for the 2.7 cm/s gas velocity experiment at a phenol-to-CuCl₂ ratio of 17.2 (top panel); approximately 30% recovery of these reactants was obtained for the 0.54 cm/s experiment at a phenol-to-CuCl₂ ratio of 14.3. Yields of 2,6-DCP and 2,3,4,6-T₄CP were lower. This result, which is likely due to phenol chlorination preferentially at ortho/para sites, may explain the higher yields of PCDDs produced from 2,4,6-T₃CP and PCP. For experiments of short duration, low yields of phenol reactants were obtained. For example, for the 0.54 cm/s experiments, only small amounts of phenol reactants were recovered for phenol-to-CuCl₂ ratios of less than 1, corresponding to experimental duration of less than 20 minutes. With no PCDDs or other products detected under these conditions, this result appears to be evidence that phenol reactants are efficiently scavenged by CuCl₂ particles and remain sorbed until nearly all sites are occupied. Vigorous rinsing with dichloromethane solvent failed to extract phenols from particle surfaces, suggesting chemical sorption.

Figure 5

Total PCDD product yields are shown for the two sets of experiments in Figure 6. For phenol-to-CuCl₂ ratios of less than 2, phenol conversion to PCDDs was small. For high phenol-to-CuCl₂ ratios (long experimental duration), total conversions were steady at about 25% for the 2.7 cm/s gas velocity experiments and 60% for the 0.54 cm/s experiments. Summing PCDD products and reactant recovery, total carbon collection for the steady conditions was greater than 80%. These results suggest that, once all CuCl₂ particle sites are occupied, PCDD formation is efficient. Moreover, the lower yield of PCDDs and higher yield of phenol reactants for the 2.7 cm/s experiments compared to the 0.54 experiments is evidence of a kinetic limitation in PCDD formation. That is, the time required for the gas to pass through the particle bed in the high gas
velocity experiments (0.3 seconds) appears to limit the conversion of phenols to PCDD products relative to the low gas velocity experiments with longer gas-particle contact time (1.5 seconds).

Figure 6

Normalized PCDD homologue distributions are shown in Figure 7 for the high (top panel) and low (bottom panel) gas velocity experiments of varied duration. For high phenol-to-CuCl₂ ratios, corresponding to long experimental duration, the homologue distributions appear to be steady. In these experiments, small amounts of 1,6- and 1,9-DCDD were detected with the other PCDD products. From most abundant to least, the order of total homologue yield was as follows in both sets of experiments: \( H_6 \text{CDD} > P_5 \text{CDD} > H_7 \text{CDD} > T_4 \text{CDD} > OCDD > T_3 \text{CDD} > \text{DCDD} \). This homologue distribution obtained at 300°C is similar to that produced for the nominal case (2.7 cm/s gas velocity and 2.9 phenol-to-CuCl₂ ratio) at 400°C (see Figure 3) where PCDD formation was greatest. Thus, once the experiment is of sufficient duration such that a steady condition is reached, there is little dependence of the homologue distribution on gas velocity, even though the total dioxin yield did vary. Similarly, the product isomer distributions did not vary significantly with gas velocity for experiments of sufficient duration, as will be shown in the following section.

Figure 7

These results indicate that steady-state distributions of PCDDs produced by CuCl₂-catalyzed condensation of 2,6 chlorinated phenols are not strongly dependent on temperature and gas velocity, parameters that have a significant effect on total PCDD yield. Thus, PCDD product ratios may provide a fingerprint for this mechanism of formation.
DISCUSSION

PCDD product ratios are examined to further ascertain the dependence of homologue and isomer distributions on temperature, gas velocity, and duration of experiment. In Table I, ratios of isomers produced from the same pair of chlorinated phenols are listed for conditions with yields large enough to quantify. In the first five columns of data, the fraction of the 1,6 product (A) in the 16/19 isomers produced in pairs are shown. Ten such pairs are expected from the 2,6 chlorinated phenols studied (see equations 1 through 10). Four of these pairs co-elute, and a fifth, the 1,6-/1,9-DCDD pair from 2,6-DCP, was produced in amounts too small to quantify. In previous results with only the 2,6-DCP reactant in high concentrations, the 1,6 isomer was favored over the 1,9 isomer. In the current experiments, preferential formation of each of the 1,6 isomers over their 1,9 isomer partners was observed for all conditions studied. When the phenol-to-CuCl₂ ratio was sufficiently large such that significant PCDD formation occurred, there was very little variation in the 16/19 isomer distributions. That is, all of the 1,6 isomer fractions were approximately 0.60 (± 0.05).

Table I

In the second set of isomer ratio data in Table I (last five columns), yields of isomers formed by loss of different ortho Cl atoms in 2,3,4,6-T₄CP are compared; i.e., PCDD products formed by Cl loss from the 2 carbon versus the 6 carbon. In combinations of 2,3,4,6-T₄CP with 2,6-DCP, 2,4,6-T₃CP and PCP, in which the 2 and 6 carbons are equivalent by symmetry, PCDD products A are those derived from Cl loss from the 2 carbon, and PCDD products B are those derived from Cl loss from the 6 carbon. In combination of two 2,3,4,6-T₄CPs, PCDD products A are those derived from Cl loss at one 2 carbon and one 6 carbon, B are those derived from Cl loss at both 2 carbons, and C are those derived from Cl loss at both 6 carbons. These isomer ratios also
do not vary significantly with temperature and gas velocity. At low phenol-to-CuCl₂ ratios, loss of Cl atom at the 2 carbon of 2,3,4,6-T₃CP appears to be slightly favored in combination with 2,6-DCP, 2,4,6-T₃CP and PCP. For two 2,3,4,6-T₃CPs, loss of one Cl atom from a 2 carbon and the other Cl atom from a 6 carbon is favored. At high phenol-to-CuCl₂ ratios, these PCDD isomer products are very nearly statistically distributed.

Since the distribution of PCDD products from the same pair of chlorinated phenol precursors is constant over a range of exhaust gas conditions, the ratios shown in Table I may be invariant features of PCDD distributions produced by the CuCl₂-catalyzed phenol condensation mechanism. Ratios of PCDD products from different phenol pairs, listed in Table II, will depend on the distribution of chlorinated phenol precursors, however. By comparing measured PCDD product ratios with statistical values based on an equal molar mixture of chlorinated phenol precursors, the relative propensity of the phenol pairs to produce PCDDs is assessed. In the first three columns of data in Table II, ratios of isomers produced from different phenol pairs are shown. Total T₄CDD product yields from 2,6-DCP and 2,3,4,6-T₄CP were much less than that from two 2,4,6-T₃CPs, even though twice as many combinations of 2,6-DCP and 2,3,4,6-T₄CP than combinations of two 2,4,6-T₃CPs would occur statistically. Similarly, P₅CDD product yields from 2,6-DCP and PCP were much less than those from 2,4,6-T₃CP and 2,3,4,6-T₄CP, whereas statistically there is an equal likelihood of combinations of these phenol pairs. The results suggest that PCDD formation from 2,6-DCP is less than the three 2,4,6 chlorinated phenols, particularly for the low gas velocity experiments. H₆CDD product yields were greater than statistically expected from 2,4,6-T₃CP and PCP than from two 2,3,4,6-T₄CPs, suggesting that 2,4,6-T₃CP and PCP have the greatest propensity for PCDD formation. Chlorination of the phenol reactants resulted in lower yields of 2,6-DCP and 2,3,4,6-T₄CP than 2,4,6-T₃CP and PCP.
(see Figure 5), which might contribute to lower PCDD product yields from 2,6-DCP and 2,3,4,6-
T₄CP. The differences in reactant yields, however, do not appear to be sufficient to explain the
differences in PCDD product yields.

Table II

In the last six columns of Table II, ratios of DCDD through H₇CDD products from selected
phenol pairs to OCDD, which is produced from two PCPs, are shown. DCDD product yields
from two 2,6-DCPs were much lower than statistically predicted, as were products from 2,6-DCP
and 2,4,6-T₃CP and from 2,6-DCP and PCP. As before, PCDD product yields from 2,6-DCP
relative to those from 2,4,6-T₃CP and PCP were even lower at the low gas velocity.

The distribution of PCDD products from different phenol pairs (Table II) vary more with
temperature and gas velocity than the distribution of PCDD products from the same phenol pair
(Table I). Nevertheless, the variation in PCDD distributions, particularly the isomer distributions,
is small compared to the variation in total PCDD yields. Major PCDD products of CuCl₂-
catalyzed condensation of 2,6 chlorinated phenols are as follows: 1,2,3,4,6,8-H₆CDD, 1,2,4,6,8,-
1,2,4,7,9-, 1,2,3,6,8- and 1,2,3,7,9-P₅CDDs, and 1,3,6,8- and 1,3,7,9-T₄CDDs. These same
congeners have been identified as major PCDD products at several municipal waste incinerators
where full PCDD distributions have been measured (Ballschmiter and Swerev, 1987; Yamamoto
and Inoue, 1990; Weber and Hagenmaier, 1999). In work to be published elsewhere (Mulholland
et al., 2001b), major PCDD products derived from experiments using a typical distribution of the
ten most abundant chlorinated phenols found in municipal waste incinerator emissions are shown
to consist largely of those derived from the three 2,4,6 chlorinated phenols. Thus, 2,4,6
chlorinated phenols are the major source of PCDDs produced by CuCl₂-catalyzed phenol
condensation, and likely a major source of PCDDs in municipal waste incinerators.
CONCLUSION

The most abundant chlorinated phenols found in incinerator emissions are those with chlorine substituents at ortho and para sites, namely 2,4,6-T₃CP, 2,3,4,6-T₄CP and PCP. When a gas stream containing these phenols is contacted with particles containing CuCl₂ at temperatures between 300 to 450°C, PCDDs are produced, including those congeners that are most abundant in typical incinerator emissions. While total PCDD yield strongly depends exhaust gas conditions such as temperature and gas velocity, there is only a weak dependence of PCDD homologue and isomer distributions on these parameters when the duration of the experiment is sufficiently long. The same PCDD products in the gas phase at higher temperatures are produced by heterogeneous CuCl₂-catalyzed reaction pathway, but the homologue distribution produced heterogeneously favors highly chlorinated congeners whereas gas-phase formation favors less chlorinated congeners. Results from short duration experiments suggest that the chlorinated phenol reactants are sorbed to particle surface until the phenol-to-CuCl₂ molar ratio exceeds one, at which point PCDD products begin to be formed and released. The major PCDD product is 1,2,3,4,6,8-H₆CDD, formed by combination of 2,4,6-T₃CP and PCP. 2,6-DCP exhibits less of a propensity to form PCDDs than the other three phenols studied. In general, pairs of PCDD isomers, one the 1,6 positions chlorinated and the other with the 1,9 positions chlorinated, are formed from condensation of 2,6 chlorinated phenols. For five pairs for which these isomers could be measured individually, the 1,6 isomer accounted for 60% (±5%) of the total, independent of yield. Other PCDD product ratios are computed that suggest a fingerprint of PCDD formation by CuCl₂-catalyzed combination of 2,6 chlorinated phenols.
Acknowledgments

Support for this research was provided by the National Science Foundation (CTS-9457028), the Research Foundation for Health and Environmental Effects, and the Environmental Protection Agency (QT-OH-99-000537).

REFERENCES


Table I. PCDD isomer fractions from the same phenol precursors.

<table>
<thead>
<tr>
<th>phenol pair:</th>
<th>26+246</th>
<th>246x2</th>
<th>26+2346</th>
<th>246+2346</th>
<th>2346x2</th>
<th>2346+26</th>
<th>2346+246</th>
<th>2346x2</th>
<th>2346+PCP</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCDD product(s) A:</td>
<td>136</td>
<td>1368</td>
<td>1236</td>
<td>12368</td>
<td>123678</td>
<td>12461249</td>
<td>1246812479</td>
<td>123679123689</td>
<td>1234679</td>
</tr>
<tr>
<td>PCDD product(s) B:</td>
<td>139</td>
<td>1379</td>
<td>1239</td>
<td>12379</td>
<td>123789</td>
<td>123612399</td>
<td>12368123799</td>
<td>1234679124689</td>
<td>1234678</td>
</tr>
<tr>
<td>PCDD product(s) C:</td>
<td>123679</td>
<td>123689</td>
<td>123679</td>
<td>1236799</td>
<td>1236799</td>
<td>1236799</td>
<td>1236799</td>
<td>1236799</td>
<td>1236799</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>statistical fraction:</th>
<th>16 isomer (A) fraction of 16/19 pair (A and B)</th>
<th>A/total</th>
<th>A/total</th>
<th>A/total</th>
<th>B/total</th>
<th>A/total</th>
</tr>
</thead>
<tbody>
<tr>
<td>ph/Cu=2.9 T = 300°C</td>
<td>0.68</td>
<td>0.64</td>
<td>0.64</td>
<td>0.64</td>
<td>0.64</td>
<td>0.64</td>
</tr>
<tr>
<td>u=2.7cm/s</td>
<td>0.60</td>
<td>0.60</td>
<td>0.60</td>
<td>0.60</td>
<td>0.60</td>
<td>0.60</td>
</tr>
<tr>
<td>350°C</td>
<td>0.62</td>
<td>0.62</td>
<td>0.62</td>
<td>0.62</td>
<td>0.62</td>
<td>0.62</td>
</tr>
<tr>
<td>400°C</td>
<td>0.59</td>
<td>0.59</td>
<td>0.59</td>
<td>0.59</td>
<td>0.59</td>
<td>0.59</td>
</tr>
<tr>
<td>450°C</td>
<td>0.57</td>
<td>0.57</td>
<td>0.57</td>
<td>0.57</td>
<td>0.57</td>
<td>0.57</td>
</tr>
<tr>
<td>T = 300°C ph/Cu=2.9</td>
<td>0.68</td>
<td>0.64</td>
<td>0.64</td>
<td>0.64</td>
<td>0.64</td>
<td>0.64</td>
</tr>
<tr>
<td>u=2.7cm/s</td>
<td>0.60</td>
<td>0.60</td>
<td>0.60</td>
<td>0.60</td>
<td>0.60</td>
<td>0.60</td>
</tr>
<tr>
<td>350°C</td>
<td>0.62</td>
<td>0.62</td>
<td>0.62</td>
<td>0.62</td>
<td>0.62</td>
<td>0.62</td>
</tr>
<tr>
<td>400°C</td>
<td>0.59</td>
<td>0.59</td>
<td>0.59</td>
<td>0.59</td>
<td>0.59</td>
<td>0.59</td>
</tr>
<tr>
<td>450°C</td>
<td>0.57</td>
<td>0.57</td>
<td>0.57</td>
<td>0.57</td>
<td>0.57</td>
<td>0.57</td>
</tr>
</tbody>
</table>

Table II. PCDD product ratios from different phenol precursors.

<table>
<thead>
<tr>
<th>phenol pair A: 26+2346 26+PCP 246+PCP</th>
<th>A products / B products</th>
<th>A products / B product (OCDD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T = 300°C ph/Cu=2.9 u=2.7cm/s</td>
<td>26x2 26+246 246x2 246+2346 2346+PCP</td>
<td>123679123689 1234679</td>
</tr>
<tr>
<td>350°C</td>
<td>0.12 0.12 0.21 0.21 13.9</td>
<td>0.000 0.04 0.22 0.10 1.8 0.78</td>
</tr>
<tr>
<td>400°C</td>
<td>0.11 0.11 0.24 0.24 8.4</td>
<td>0.000 0.07 0.28 0.15 1.6 0.86</td>
</tr>
<tr>
<td>450°C</td>
<td>0.19 0.19 0.44 0.44 19.5</td>
<td>0.000 0.36 1.56 0.63 5.6 1.80</td>
</tr>
<tr>
<td>A products / B products</td>
<td>26x2 26+246 246x2 246+2346 2346+PCP</td>
<td>123679123689 1234679</td>
</tr>
<tr>
<td>T = 300°C ph/Cu=2.9 u=2.7cm/s</td>
<td>0.12 0.12 0.21 0.21 13.9</td>
<td>0.000 0.04 0.22 0.10 1.8 0.78</td>
</tr>
<tr>
<td>350°C</td>
<td>0.09 0.09 0.24 0.24 11.1</td>
<td>0.000 0.18 0.78 0.36 3.5 1.56</td>
</tr>
<tr>
<td>400°C</td>
<td>0.21 0.21 0.42 0.42 5.4</td>
<td>0.000 0.43 1.28 0.50 3.5 1.95</td>
</tr>
<tr>
<td>450°C</td>
<td>0.28 0.28 0.57 0.57 4.9</td>
<td>0.000 0.47 1.57 0.69 4.1 2.19</td>
</tr>
<tr>
<td>123679123689 1234679</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A products / B product (OCDD)</td>
<td>123679123689 1234679</td>
<td></td>
</tr>
<tr>
<td>T = 300°C ph/Cu=2.9 u=0.5cm/s</td>
<td>0.03 0.03 0.08 0.08 10.6</td>
<td>0.000 0.05 0.68 0.12 3.5 1.47</td>
</tr>
<tr>
<td>4.3</td>
<td>0.11 0.11 0.12 0.12 5.2</td>
<td>0.000 0.07 0.62 0.14 2.0 1.40</td>
</tr>
<tr>
<td>5.7</td>
<td>0.09 0.09 0.12 0.12 5.5</td>
<td>0.001 0.15 1.04 0.22 3.1 1.77</td>
</tr>
<tr>
<td>7.1</td>
<td>0.11 0.11 0.13 0.13 5.0</td>
<td>0.002 0.20 1.10 0.24 3.2 1.93</td>
</tr>
<tr>
<td>8.6</td>
<td>0.11 0.11 0.12 0.12 5.0</td>
<td>0.002 0.20 1.23 0.26 3.5 2.03</td>
</tr>
<tr>
<td>10.0</td>
<td>0.09 0.09 0.12 0.12 5.2</td>
<td>0.001 0.15 1.22 0.25 3.4 1.97</td>
</tr>
<tr>
<td>11.4</td>
<td>0.14 0.14 0.12 0.12 4.4</td>
<td>0.005 0.27 1.50 0.30 3.8 2.17</td>
</tr>
<tr>
<td>12.9</td>
<td>0.11 0.11 0.12 0.12 4.9</td>
<td>0.002 0.25 1.78 0.35 4.6 2.44</td>
</tr>
<tr>
<td>14.3</td>
<td>0.12 0.12 0.13 0.13 4.8</td>
<td>0.002 0.29 1.77 0.37 4.6 2.47</td>
</tr>
<tr>
<td>17</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure Captions

Figure 1. Reaction pathways for gas-phase formation of 1,6- and 1,9-DCDD from 2,6-DCP.

Figure 2. Yields of total PCDDs and PCDD product homologues.

Figure 3. Distribution of PCDD homologues.

Figure 4. Distribution of T\textsubscript{3}CDD, T\textsubscript{4}CDD, P\textsubscript{5}CDD, H\textsubscript{6}CDD and H\textsubscript{7}CDD isomers.

Figure 5. Yields of phenol reactants at 300°C for two gas velocities (u = 2.7 and 0.5 cm/s) shown as a function of duration of experiment, corresponding to phenol/Cu molar ratios ranging from 0.05 to 17.

Figure 6. Total PCDD yields at 300°C for two gas velocities (u = 2.7 and 0.5 cm/s) shown as a function of duration of experiment, corresponding to phenol/Cu molar ratios ranging from 0.05 to 17.

Figure 7. Distribution of PCDD homologues at 300°C for two gas velocities (u = 2.7 and 0.5 cm/s) shown as a function of duration of experiment, corresponding to phenol/Cu molar ratios ranging from 0.05 to 17.
Figure 1. Reaction pathways for gas-phase formation of 1,6- and 1,9-DCDD from 2,6-DCP.
Figure 2. Yields of total PCDDs and PCDD product homologues.
Figure 3. Distribution of PCDD homologues.
Figure 4. Distribution of $T_3$CDD, $T_4$CDD, $P_5$CDD, $H_6$CDD and $H_7$CDD isomers.
Figure 5. Yields of phenol reactants at 300°C for two gas velocities (u = 2.7 and 0.5 cm/s) shown as a function of duration of experiment, corresponding to phenol/Cu molar ratios ranging from 0.05 to 17.
Figure 6. Total PCDD yields at 300°C for two gas velocities (u = 2.7 and 0.5 cm/s) shown as a function of duration of experiment, corresponding to phenol/Cu molar ratios ranging from 0.05 to 17.
Figure 7. Distribution of PCDD homologues at 300°C for two gas velocities (u = 2.7 and 0.5 cm/s) shown as a function of duration of experiment, corresponding to phenol/Cu molar ratios ranging from 0.05 to 17.
Chlorination of Dibenzofuran and Dibenzo-\(p\)-dioxin Vapor by Copper (II) Chloride

Jaeg-Yong Ryu and James A. Mulholland
Environmental Engineering, Georgia Institute of Technology, Atlanta GA 30332-0512

ABSTRACT

The chlorination pattern of dibenzofuran (DF) and dibenzo-\(p\)-dioxin (DD) vapor when passed over a particle bed of 0.5\% (mass) copper (II) chloride (CuCl\(_2\)) mixed with silicon dioxide (SiO\(_2\)) was studied. Gas streams consisting of 92\% (molar) N\(_2\), 8\% O\(_2\) and 0.1\% DF and/or DD vapor were introduced to an isothermal flow reactor containing the CuCl\(_2\)/SiO\(_2\) particle bed. The nominal gas-particle contact time was 0.3 seconds. DF experiments were conducted over the temperature range 200 to 500°C. DF chlorination experiments at 300°C were conducted with 2.5 and 4.4 second gas-particle contact times. One experiment with an equimolar mixture of DF and DD was performed at 250°C. In the 0.3 second experiments, maximum conversion of DF to chlorinated dibenzofuran of 11\% (molar) occurred at 225°C, with mono through hexa congeners observed. Chlorination was favored at the four lateral sites, i.e. the 2,3,7,8 positions, on the least substituted ring system, resulting in a balanced distribution of chlorine substituents. Monochlorodibenzo-furans (MCDFs) were the major products. At maximum yield the distribution of MCDF isomers was as follows: 45\% 2-MCDF, 46\% 3-MCDF, 8\% 1-MCDF and 1\% 4-MCDF. At higher temperatures (e.g. 450°C), where total DF conversion was less than 1\%, this distribution of MCDF isomers was quite different: 55\% 4-MCDF, 20\% 2-MCDF, 15\% 3-MCDF and 10\% 1-MCDF. With longer gas-particle contact time, the degree of DF chlorination increased. At 2.5 second and 300°C, a much broader distribution of PCDF products was observed, including octachlorodibenzo-furan (OCDF); MCDFs were still the major products. At 4.4 second and 300°C, however, OCDF was the major product. The total DF conversion to OCDF was low, less than 1\%.

Chlorination of DD was also favored at the four lateral sites (2,3,7,8-positions) on the least substituted ring system. At 250°C, the total chlorination of DD and DF was approximately the same as the chlorination of DF alone; however, chlorination of DD was twice as great as chlorination of DF in the DF/DD mixture experiment. These results further support the pattern observed by others of 2,3,7,8 chlorination of DF and DD in a heterogeneous environment, and provide new information on the relative rates of DF and DD chlorination as well as the temperature dependence of isomer products. While chlorination to the perchlorocongeners is possible, the specificity of the chlorination pathway does not appear to be consistent with the broader isomer distributions found in field data beyond the mono- and di-chloro homologues. Nonetheless, chlorination may contribute to the production of individual products, such as the 2,3,7,8 congeners.

keywords: dibenzofuran, dibenzo-\(p\)-dioxin, PCDF, PCDD, chlorination, copper (II) chloride
INTRODUCTION

In municipal waste incinerators, polychlorinated dibenzo-p-dioxin (PCDD) and dibenzofuran (PCDF) by-products are formed both in post-combustion gas at high temperatures (between 600 and 800°C) and in particle collection equipment at low temperatures (between 200 and 400°C). The former condition strongly favors PCDF formation, whereas the latter condition can result in large amounts of highly chlorinated PCDD and PCDF congeners (Hagenmaier et al., 1989; Yamamoto et al., 1989). PCDD/F formation has been studied extensively, including formation by metal catalyzed de novo synthesis from graphitic carbon (Stieglitz et al., 1989) and polycyclic aromatic hydrocarbons (PAHs) on flyash (Hell et al., 1997), by condensation of precursors such as chlorinated phenols (Born et al., 1989) and benzenes (Ballschmiter et al., 1988), and by acetylene growth schemes (Huang and Buekens, 1998).

The distribution of PCDD/F congeners in combustion emissions may provide evidence of the predominance of a formation mechanism (Wehrmeier et al., 1998). Alternatively, a quantitative understanding of the relative rates of formation of PCDD/F congeners may allow for extrapolation from limited measurements to a more complete assessment of toxic PCDD/F emissions (Oser et al., 1997; Gullett and Wikstrom, 2000). Chlorination and dechlorination reactions may affect the distribution of PCDD/F congeners. A number of researchers have shown that chlorination of dibenzo-p-dioxin (DD) occurs predominantly at the 2,3,7,8 positions (Eiceman and Rghei, 1982; Rghei and Eiceman, 1983; Munslow et al., 1987; Luijk et al., 1992; Luijk et al., 1994; Addink et al., 1996; Wehrmeier et al., 1998). Less information is available on dibenzofuran (DF) chlorination pattern. Luijk et al. (1994) indicated that DF chlorination was also favored at the 2,3,7,8 positions. Dechlorination leads to very different isomer patterns. The predominant PCDF produced by de novo synthesis from graphitic carbon was observed to be octachlorodibenzofuran (Iino, 1998), with less chlorinated isomer distributions explained by dechlorination reactions that favor PCDF congeners with the 4,6 positions still chlorinated (Iino et al., 2001).

Chlorination of DF may be a significant source of PCDFs found in municipal waste incinerators due to the high concentration of unsubstituted phenol in the flue gas (Wikstrom and Marklund, 2000). At high temperature (600 to 800°C), condensation of unsubstituted phenol readily produces DF. Wikstrom and Marklund found the concentration of DF in incinerator effluent greater than total PCDF concentration by a factor of 100 to 1000, and speculated that the source of PCDFs was the chlorination of DF at low temperatures. Chlorination can occur by metal catalysis, and, in particular, by copper (II) chloride (CuCl₂). The Deacon process can convert HCl to Cl₂, which then can lead to gas-phase DF chlorination. The overall Deacon reaction is as follows.

\[
4 \text{HCl} + \text{O}_2 \rightarrow 2 \text{Cl}_2 + 2 \text{H}_2\text{O} \quad (1)
\]

Alternatively, direct chlorination of an aromatic molecule such as DF by CuCl₂ can occur by the following transfer mechanism (Stieglitz et al., 1990; Hoffman et al., 1990).

\[
\text{ArH} + \text{CuCl}_2 \rightarrow \text{ArHCl}^* + \text{CuCl} \quad (2)
\]

\[
\text{ArHCl}^* + \text{CuCl}_2 \rightarrow \text{ArCl} + \text{CuCl} + \text{HCl} \quad (3)
\]
Recently, Gullett and Wikstrom (2000) suggested that the less chlorinated PCDF emissions might be used as an indicator of PCDD/F toxic equivalency. Emission of less chlorinated PCDF congeners can be more easily assessed by newly developed on-line instruments for measuring gas-phase concentrations than can tetra through octachlorinated congeners which partition to the solid phase. In this paper, we examine the chlorination of DF by copper (II) chloride. The limited work on DF chlorination (Luijk et al., 1994) was focused on the distribution of tetra through octa congeners. We also investigate the temperature dependence of chlorination pattern. Finally, we address the relative rates of chlorination of DF and DD.

**EXPERIMENTAL METHODS**

The experimental apparatus is shown in Fig. 1. Experiments were conducted in an electrically heated, quartz tube flow reactor, 40 cm in length and 1.7 cm in diameter. A small amount (40 mg) of high purity DF was placed in a glass vessel and heated. Reactant vapor was transported to the reactor by a 92% nitrogen, 8% oxygen gas stream. The resulting gas stream, containing 0.1% (nominal) DF vapor, was introduced to the isothermal reactor with a total residence time of 15 s. A 1 g particle bed consisting of 0.5% (mass) copper (II) chloride (CuCl$_2$) in silicon dioxide (SiO$_2$) was located at the center of the reactor. The nominal gas-particle contact time was 0.3 s, corresponding to a gas velocity of 2.7 cm/s. Experiments at 300°C for gas-particle contact times of 2.5 and 4.4 s, corresponding to gas velocities of 0.32 and 0.18 cm/s, were also conducted. Experiments were carried out over the temperature range 200 to 500°C in 25°C increments. One experiment was carried out at 250°C with DF and DD vapor in equal amounts (molar).

Experiments were run for approximately 30 minutes to collect sufficient samples, with the entire product gas stream rapidly quenched and soot and aromatic tar samples collected in an ice-cooled dichloromethane trap. Tests confirmed that there was no effect of experiment duration on the distribution of products for experiments lasting up to 30 minutes. Sample solutions were filtered and then analyzed by GC/MS (HP 6890 series gas chromatograph with model 5973 mass selective detector) equipped with a HP-5MS capillary column. Preliminary identification of PCDF products was based on published relative retention times for similar columns (Hale et al., 1985). Final identification was based on available standards and gas-phase synthesis experiments from single precursors and precursor pairs. Many, but not all, of the 135 PCDF congeners have been synthesized. All four monochlorodibenzofuran (MCDF) isomers were separated, as were thirteen of sixteen dichlorodibenzofurans (DCDFs), 25 of 28 trichlorodibenzofurans ($T_3$CDFs), and 34 of 38 tetrachlorodibenzofurans ($T_4$CDFs). GC/MS response factors were assumed to be equal for all PCDF congeners, based on the DF response factor.
RESULTS AND DISCUSSION

Dibenzofuran Chlorination Pattern

Unreacted DF and yields of PCDF homologues are shown in Fig. 2. Between 200 and 300°C, DF conversion to PCDF ranged from 5 to 11%, with MCDF through H6CDF (hexachlorinated dibenzofuran) congeners detected. Maximum conversion was observed at 225°C. Maximum MCDF and DCDF yields of 7% (DF conversion) and 3.4%, respectively, occurred at 225°C. For T3CDF, a maximum yield of 0.84% was found at 250°C. Maximum T4CDF, P5CDF and H6CDF yields of 0.22%, 0.08% and 0.04%, respectively, were observed at 300°C. Under these conditions, carbon recovery was high. At 350°C and above, less than 1% of the DF was converted to PCDF, and only MCDF congeners were detected.

Fig. 2

The temperature dependence of the peak homologue yields is consistent with the findings of Luijk et al. (1992 and 1994) in that more thermal input is needed to generate the more chlorinated congeners. Eiceman and Rghei (1982) reported that chlorination of PCDDs becomes increasingly endothermic with increasingly chlorinated congeners. Our results differ, however, in that Luijk et al. found much higher degrees of chlorination. Possible reasons for this difference are differences in HCl concentration, DF-to-CuCl2 molar ratio, and gas-particle contact time. In these experiments, chlorination likely occurred by direct transfer from CuCl2 due to the lack of HCl initially in the system. HCl is needed for the Deacon process (equation 1). As shown in equations (2) and (3), two moles of CuCl2 are needed for each chlorine addition. With higher CuCl2 concentration and longer gas-particle contact times, the degree of DF chlorination is expected to increase. The latter was found to be true, as will be described in the next section.

Isomer yields are shown in Fig. 3. These results show clearly that DF chlorination is favored at lateral (2,3,7,8) positions in a balanced manner (i.e. first on one carbon ring, then on the other). The 2- and 3-MCDF yields were similar, with much lower yields of 1- and 4-MCDF. The second Cl atom was preferentially added to the 7 or 8 position. 3,7-DCDF, which is formed by chlorination of 3-MCDF, was the major DCDF isomer produced, with 2,7-DCDF, which is formed by chlorination of either 2- or 3-MCDF, in next highest yield. Yields of 2,8-DCDF, formed from 2-MCDF, and 2,3-DCDF, formed from 2- or 3-MCDF, were of similar magnitude, and 1,7-DCDF yields were slightly greater than 1,8-DCDF yields. These results suggest that chlorination at the 3 (or 7) position is favored over chlorination at the 2 (or 8) positions. The presence of 1,7- and 1,8-DCDFs and lack of 2,6- and 3,6-DCDFs is somewhat surprising given that 4-MCDF yields generally exceeded 1-MCDF yields. Perhaps chlorination at the 4 position suppresses further chlorination more than chlorination at the 1 position. The major T3CDF product was the 2,3,7 isomer, with 2,3,8-T3CDF found in next highest yield. Small amounts of 1,2,7-/2,3,9- (co-elute), 1,2,8- and 1,3,7-T3CDF were also detected. Again, no products with the 4 or 6 positions chlorinated were found. Only two T4CDF peaks were observed, with yields of the 2,3,7,8 isomer much greater than yields of 1,2,7,8-T4CDF. The only other products detected were 1,2,3,7,8-P5CDF and 1,2,3,7,8,9-H6CDF.

Fig. 3
As far as we know, the finding that the 3 and 7 positions in DF are more likely to be chlorinated than the 2 and 8 positions has not been reported. Preferential chlorination of DD at the 2 and 8 positions has been reported (Munslow et al., 1987; Rghei and Eiceman, 1985). The formation of 4-MCDF but not higher chlorinated PCDF with 4 or 6 chlorine atom substituents suggests that 4-MCDF is very stable; that is, 4-MCDF is not easily chlorinated. This finding is further supported by examining the MCDF isomer distribution as a function of temperature (Fig. 4). At temperatures of 375°C and above, the major MCDF product is 4-MCDF. Total MCDF yields at these temperatures are less than 1% (DF conversion), however, compared with a peak MCDF yield of 7% at 225°C. The 1-MCDF isomer fraction also increases with increasing temperature, while the 2- and 3-MCDF isomer fractions decrease. These results suggest that PCDF congeners with 1,4,6,9 substituents might be less easily chlorinated than PCDF congeners with 2,3,7,8 substituents. Hagenmaier et al. (1989) reported that both formation and destruction can be catalyzed by metals in flyash. Wehrmeier et al. (1998) reported that PCDDs chlorinated at the 1,4,6,9 positions are destroyed more slowly than PCDDs chlorinated at the 2,3,7,8 positions due to differences in the frontier orbital (HOMO-LUMO) energy gaps.

Fig. 4

Effect of Gas Velocity / Gas-Particle Contact Time

Results at 300°C for two reduced gas velocities demonstrate DF chlorination patterns for highly chlorinated PCDF homologues. Fig. 5 shows a dramatic shift in the homologue distribution at low gas velocity. The homologue distributions for gas velocities of 2.7 and 0.32 cm/s, corresponding to gas-particle contact times of 0.3 and 2.5 s, were similar, although the total PCDF yield was higher for the latter and chlorination all the way to OCDF was observed. The major products were MCDFs, accounting for approximately 60% of the total PCDF yield. The major product at the low gas velocity of 0.18 cm/s (gas-particle contact time of 4.4 s), however, was OCDF. We speculate that this result is due to the following. First, PCDF stay sorbed to the particle surface longer for lower gas velocities, resulting in further chlorination. Second, the longer the gas-particle contact time at the lower gas velocities results in destruction of PCDF, preferentially the less chlorinated congeners.

Fig. 5

Isomer distributions for a gas-particle contact time of 2.5 s are shown in Fig. 6a. Compounds shown in parentheses are tentatively identified based on synthesis of some isomers and published elution order. A much broader distribution of PCDF congeners was observed than in the case of the 0.3 s results. The MCDF results show that 4-MCDF was favored at 2.5 s rather than the 2- and 3-MCDF isomers which were favored at 300°C for the 0.3 s contact time. Thus, the effect of lower gas velocity on the MCDF distribution is similar to the effect of higher temperature. We speculate that subsequent chlorination and/or destruction preferentially occurs to 2- and 3-MCDF. The major T\textsubscript{4}CDF, P\textsubscript{3}CDF and H\textsubscript{6}CDF products were the 2,3,7,8-, 1,2,3,7,8- and 1,2,3,6,7,8- congeners. This was also the case for a gas-particle contact time of 4.4 s (Fig. 6b).
Comparison with Incinerator Data

In Table 1, the distribution of major MCDF, DCDF, T₃CDF and T₄CDF products from our DF chlorination experiments are compared to three recently published sets of incinerator data: fluidized bed incinerator (FBI) data (Weber and Hagemaier, 1999), laboratory fluidized bed reactor (FBR) data using municipal solid waste (Wikstrom, 1999), and municipal waste incinerator (MWI) data (Iino et al., 1999). The distribution of MCDF isomers from the FBI was similar to our distribution at 225°C, the temperature of maximum yield for the 0.3 s gas-particle contact time experiments. The FBR results are more similar to our MCDF isomer distribution for the 300°C, 2.5 s gas-particle contact time experiment. The distributions of DCDF isomers from the FBI and FBR were similar to our DCDF isomer distribution for the 300°C, 2.5 s gas-particle contact time experiment; 2,7-, 2,8-, 3,7- and 2,3-DCDF yields represented 44% of our total DCDF yield compared to 50% and 43% for the FBI and FBR, respectively. The distributions of T₃CDF and T₄CDF isomers measured in our experiments were more extreme than the FBI and FBR results. In our 2.5 s experiment, which was less extreme than our 0.3 s experiments, the 2,3,7 and 2,3,8 isomers represented 37% of the total T₃CDF yield, and the 2,3,7,8 isomer represented 50% of the total T₄CDF yield. In the FBI, the 2,3,7 and 2,3,8 isomers represented less than 10% of the total T₃CDF yield, and the 2,3,7,8 isomer represented only 0.5% of the total T₄CDF yield.

Table 1

Chlorination of Dibenzo-p-dioxin and Dibenzofuran

An experiment at 250°C was carried out with an equimolar mixture of DD and DF to assess their relative rate of chlorination. Congener yields are listed in Table 2, and homologue profiles are shown in Fig. 8. The results show that both the total conversion of DD and the degree of chlorination of PCDD products are greater than the total conversion of DF and the degree of chlorination of PCDF products. The total chlorination of DD and DF in this experiment was similar to the total chlorination of DF at 250°C, but, in the case of the DD/DF mixture, chlorination of DD was about twice as great as chlorination of DF. This suggests that there is a competition for chlorination sites, with DD chlorination favored.

Table 2; Fig. 7

DD and DF chlorination pathways leading to the 2,3,7,8-T₄CDD/F congeners are shown in Fig. 9. The predominant pathways observed at 300°C and below are shown by the heavy arrows. At higher temperatures, where total yields were much smaller, the product distributions were more uniform.

Fig. 8
CONCLUSION

The distribution of mono through octa PCDF and PCDD congeners produced from DF and DD chlorination by CuCl₂ has been measured as a function of temperature for a gas-particle contact time of 0.3 seconds. Maximum conversion of DF to PCDF of 11% (molar) occurred at 225°C, with mono through hexa congeners observed. Chlorination was favored at the four lateral positions (2,3,7,8) and on the less substituted ring system. At maximum yield, the distribution of MCDF isomers was as follows: 45% 2-MCDF, 46% 3-MCDF, 8% 1-MCDF and 2% 4-MCDF. At higher temperatures (e.g. 450°C), where total DF conversion was less than 1%, this distribution of MCDF isomers was quite different: 55% 4-MCDF, 20% 2-MCDF, 15% 3-MCDF and 10% 1-MCDF.

Longer gas-particle times were also studied by decreasing the gas velocity. The degree of DF chlorination increased as gas-particle time increased. At 2.5 second and 300°C, a much broader distribution of PCDF products was observed, including octachlorodibenzo-furan (OCDF); MCDFs were still the major products. At 4.4 second and 300°C, however, OCDF was the major product. The total DF conversion to OCDF was low, less than 1%. Comparison of the more highly chlorinated PCDF isomer distributions with field data demonstrates significant differences in the pattern of chlorination.

Chlorination of DD was also favored at the four lateral sites (2,3,7,8-positions) on the least substituted ring system. At 250°C, the total chlorination of DD and DF was approximately the same as the chlorination of DF alone; however, chlorination of DD was twice as great as chlorination of DF in the DF/DD mixture experiment. These results further support the pattern observed by others of 2,3,7,8 chlorination of DF and DD in a heterogeneous environment, and provide new information on the relative rates of DF and DD chlorination as well as the temperature dependence of isomer products. While chlorination to the perchlorocongeners is possible, the specificity of the chlorination pathway does not appear to be consistent with the broader isomer distributions found in field data beyond the mono- and di-chloro homologues. Nonetheless, chlorination may contribute to the production of individual products, such as the 2,3,7,8 congeners.

Acknowledgments

Support by the National Science Foundation (CTS-9457028), the Research Foundation for Health and Environmental Effects, and the Environmental Protection Agency (QT-OH-99-000537) is gratefully acknowledged.
REFERENCES


Table 1. Comparison of yields of select MCDF, DCDF, T$_3$CDF and T$_4$CDF isomers.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>MCDF 1/2/3/4</td>
<td>10%/49%/40%/1%</td>
<td>14%/33%/29%/24%</td>
<td></td>
<td>8%/45%/46%/1% (225°C, 0.3 s)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>13%/31%/23%/33% (300°C, 2.5 s)</td>
</tr>
<tr>
<td>DCDF 27+28+37+23</td>
<td>50%</td>
<td>43%</td>
<td></td>
<td>90% (225°C, 0.3 s)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>44% (300°C, 2.5 s)</td>
</tr>
<tr>
<td>T$_3$CDF 237+238</td>
<td>10%</td>
<td>22% (incl. 234-)</td>
<td></td>
<td>84% (225°C, 0.3 s)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>37% (300°C, 2.5 s)</td>
</tr>
<tr>
<td>T$_4$CDF 2378</td>
<td>0.5%</td>
<td>&lt;5%</td>
<td>1-4%</td>
<td>87% (225°C, 0.3 s)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>50% (300°C, 2.5 s)</td>
</tr>
</tbody>
</table>
Table 2. Results of DD/DF mixture experiment at 250°C.

<table>
<thead>
<tr>
<th>unreacted DD</th>
<th>87.7% of DD feed</th>
<th>unreacted DF</th>
<th>84.9% of DF feed</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCDD 2-</td>
<td>1.642% DD conversion</td>
<td>MCDF 2-</td>
<td>0.980% DF conversion</td>
</tr>
<tr>
<td>1-</td>
<td>0.077%</td>
<td>3-</td>
<td>0.725%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1-</td>
<td>0.112%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4-</td>
<td>0.052%</td>
</tr>
<tr>
<td>DCDD 2,7-/2,8-</td>
<td>0.752%</td>
<td>DCDF 3,7-</td>
<td>0.142%</td>
</tr>
<tr>
<td>2,3-</td>
<td>0.130%</td>
<td>2,7-</td>
<td>0.136%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2,8-</td>
<td>0.047%</td>
</tr>
<tr>
<td>T₃CDD 2,3,7-</td>
<td>0.638%</td>
<td>T₃CDF 2,3,7-</td>
<td>0.030%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2,3,8-</td>
<td>0.014%</td>
</tr>
<tr>
<td>T₄CDD 2,3,7,8-</td>
<td>0.121%</td>
<td>T₄CDF 2,3,7,8-</td>
<td>0.006%</td>
</tr>
</tbody>
</table>

Total Cl = 0.118 moles Cl / mole DD feed

Total Cl = 0.058 moles Cl / mole DF feed
Figure Captions

Fig. 1. Experimental apparatus.

Fig. 2. Unreacted DF and yields of PCDF homologues.

Fig. 3. Yields of PCDF congeners.

Fig. 4. MCDF isomer distribution.

Fig. 5. Unreacted dibenzofuran yield and PCDF homologue distributions from DF chlorination experiments at 300°C for three gas-particle contact times.

Fig. 6a. PCDF isomer distributions from DF chlorination experiments at 300°C for gas-particle contact time of 2.5 seconds.

Fig. 6b. PCDF isomer distributions from DF chlorination experiments at 300°C for gas-particle contact time of 4.4 seconds.

Fig. 7. Yields of PCDF and PCDD homologues from chlorination of an equimolar mixture of DF and DD at 250°C.

Fig. 8. Pathways for DD and DF chlorination.
Fig. 1. Experimental apparatus.
Fig. 2. Unreacted DF and yields of PCDF homologues.
Fig. 3. Yields of PCDF congeners.
Fig. 4. MCDF isomer distribution.
Fig. 5. Unreacted dibenzofuran yield and PCDF homologue distributions from DF chlorination experiments at 300°C for three gas-particle contact times.
Fig. 6a. PCDF isomer distributions from DF chlorination experiments at 300°C for gas-particle contact time of 2.5 seconds.
Fig. 6b. PCDF isomer distributions from DF chlorination experiments at 300°C for gas-particle contact time of 4.4 seconds.
Fig. 7. Yields of PCDF and PCDD homologues from chlorination of an equimolar mixture of DF and DD at 250°C.
Fig. 8. Pathways for DD and DF chlorination.
PCDD/F Isomer Patterns from Combustion: Fingerprints for Source Identification

J.A. Mulholland¹, J.-Y. Ryu¹, D.T. Nakahata¹, B.K. Gullett², F. Iino²*, and E. Wikstrom²*

¹Georgia Institute of Technology, School of Civil and Environmental Engineering
²U.S. Environmental Protection Agency, National Risk Management Research Laboratory
*Joint Program with Oak Ridge Institute for Science and Education

Abstract

Polychlorinated dibenzo-p-dioxin (PCDD) and dibenzofuran (PCDF) isomer distributions from combustion systems can be used for formation pathway identification. While total PCDD/F emissions and, to a lesser extent, homologue distributions from incinerators have been found to vary widely depending on combustion conditions, isomer distributions do not. Various kinetic and thermodynamic hypotheses have been proposed to explain this. Proposed mechanisms can be grouped in two general categories: condensation of precursors, such as chlorinated phenols, and formation from particulate carbon, termed de novo synthesis. In addition to these pathways, isomer patterns may be affected by chlorination and dechlorination reactions. Here, isomer patterns of all PCDD/F homologues produced by chlorinated phenol condensation both in the gas phase and on copper (II) chloride (CuCl₂), chlorination of dibenzo-p-dioxin (DD) and dibenzofuran (DF), and dechlorination of octachlorodibenzo-p-dioxin (OCDD) and octachlorodibenzofuran (OCDF) are presented. Thermodynamic distributions from molecular modeling are also shown. These are compared to distributions found in municipal waste incinerator samples.

PCDD/F isomer patterns produced by different formation pathways in controlled experiments are distinct and robust, largely unaffected by combustion conditions. Gas-phase phenol condensation favors PCDF formation, with peak yields between 550 and 650°C. Phenol, produced from benzene at these temperatures, exhibits the highest reactivity; hence, DF is a major product. Under CuCl₂-catalyzed conditions, PCDDs are favored, with peak yields between 300 and 400°C. Due to the high concentrations of ortho/para substituted phenols (e.g., 2,4,6-trichlorophenol), major product pairs include 1,3,6,8-/1,3,7,9-T₄CDD and 1,2,4,6,8-/1,2,4,7,9-P₅CDD. CuCl₂-catalyzed DD/DF chlorination occurs at 200-250°C, with 2,3,7,8 congeners favored. On the other hand, dechlorination of OCDD/OCDF favors congeners that retain chlorine substituents in ortho positions to oxygen (i.e., 1,4,6,9 PCDDs and 4,6 PCDFs).

PCDD isomer patterns from municipal waste incinerators are most similar to those produced by CuCl₂-catalyzed phenol condensation. The heptachlorodibenzofuran isomer pattern is most similar to that produced by dechlorination, whereas the monochlorodibenzofuran distribution is similar to a chlorination pattern. One explanation is that a bimodal PCDF distribution is produced by formation of DF via gas-phase phenol condensation, followed by chlorination, and by de novo synthesis of OCDF, followed by dechlorination. Contributions by multiple pathways appear likely for intermediate PCDF homologues.
Introduction

Polychlorinated dibenzo-p-dioxin (PCDD) and dibenzofuran (PCDF) byproducts are formed by two general pathways in combustion: (1) homogeneous, gas-phase reactions, and (2) heterogeneous, catalytic reactions. The former route, which is observed in post-combustion gas at temperatures between 500 and 700°C, occurs via precursors and strongly favors the formation of dibenzofuran and less chlorinated PCDF congeners. The latter route, which is observed in particle collection devices at temperatures between 250 and 400°C, may involve precursors of similar structure or particulate carbon. This pathway favors the formation of highly chlorinated PCDD/F congeners (Hagenmaier et al., 1987; Yamamoto et al., 1989). PCDD/F formation mechanisms have been studied extensively, including gas-phase reactions involving phenoxy radicals (Born et al., 1989) and flyash-mediated, metal-catalyzed formation from phenols (Born et al., 1993), polycyclic aromatic hydrocarbons (Hell et al., 2000) and graphitic carbon (Stieglitz et al., 1989). PCDD formation rates from precursors that are similar in structure, such as chlorinated phenols, have been found to be significantly faster than rates from particulate carbon, or de novo synthesis, under typical incinerator conditions (Dickson et al., 1992; Altwicker and Milligan, 1993). Nonetheless, there remains much uncertainty about the predominant pathway(s) of PCDD/F formation in combustion systems.

PCDD/F isomer patterns may provide fingerprints of formation mechanism (Wehrmeier et al., 1998). For example, PCDD/F isomer patterns produced from polycyclic aromatic hydrocarbons on flyash have been compared to emissions from a fluidized bed incinerator (Weber et al., 1999). In addition to the mechanisms described above, chlorination of less chlorinated congeners produced in the gas phase (Wikstrom and Marklund, 1999) and dechlorination of highly chlorinated congeners produced by de novo synthesis (Iino et al., 2000) have been proposed as factors that might control PCDD/F isomer distributions. Chlorination on catalytic surfaces has been found to occur predominantly at the 2,3,7,8 positions (Luijk et al., 1994; Addink et al., 1996). Surface-mediated dechlorination has also been studied (Hagenmaier et al., 1987; Wiesmuller, 1990). PCDD/F distributions produced from mixtures of chlorinated phenols have been studied by a number of researchers (Weber and Hagenmaier, 1999; Wiater-Protas and Louw, 2001).

In this paper, we evaluate the hypothesis that distributions of PCDD/F isomers from combustion of municipal solid waste can be used for source attribution. That is, formation pathways can be deduced from these fingerprints. To be used in this way, distributions must be similar over a wide range of conditions, yet dissimilar for different formation pathways. We start by demonstrating that PCDD/F distributions produced by three mechanisms that have recently been studied in our laboratories are robust and unique. Previously unpublished results of gas-phase, homogeneous and CuCl$_2$-catalyzed, heterogeneous PCDD/F formation from a typical distribution of chlorinated phenols are presented, as well as recently published results of dibenzo-p-dioxin (DD) and dibenzofuran (DF) chlorination (Ryu and Mulholland, 2001) and octachlorinated congener (OCDD and OCDF) dechlorination (Iino et al., 2001). We then compare isomer patterns obtained from eight municipal waste incinerators with those produced by municipal solid waste combustion in the laboratory as well as thermodynamic distributions. Finally, we compare the incinerator data with the isomer patterns by three formation pathways and draw conclusions about the mechanism of formation.
PCDD/F Isomer Distributions: Sources and Description

Data used in this analysis of PCDD/F isomer distributions produced by different mechanisms in combustion processes were derived from a number of sources, as described below.

**MWI Field Data.** Field data were obtained for fly ash samples from eight municipal waste incinerators in Japan, as described elsewhere (lino et al., 1999). Four of these were fluidized bed incinerators, and four were stoker-type incinerators. PCDD/F isomer distributions were remarkably similar (lino et al., 2000; lino et al., 2001).

**MSW Combustion Laboratory Experiments.** Municipal solid waste combustion experiments were performed in a laboratory scale fluidized bed reactor, as described by Wikstrom et al. (1998). Eleven experiments were performed under different combustion conditions. Flue gas samples were taken before and after the convective section. Total PCDD/F yield and homologue patterns varied significantly, but PCDD/F isomer patterns did not (Wikstrom and Marklund, 2000).

**Thermodynamic Calculations.** Thermodynamic PCDD/F isomer distributions were derived from Gibbs free energy values calculated at 300°C using the semi-empirical molecular modeling method PM3. Thermodynamic distributions derived using the AM1 and MNDO methods are similar to those derived using the PM3 method (Mulholland et al., 2001). Over the temperature range of interest (200-700°C), differences in the isomer distributions were small relative to differences between thermodynamic distributions and the field and laboratory measured distributions.

**Phenol Condensation Experiments.** Gas-phase, homogeneous formation and CuCl₂-catalyzed, heterogeneous formation of PCDDs/Fs have been studied in an electrically heated, quartz tube flow reactor, as described elsewhere (Nakahata and Mulholland, 2000; Mulholland and Ryu, 2001). In this paper, we present previously unpublished results of two experiments performed using a mixture of ten chlorinated phenols based on a distribution reported by Ballschmiter et al. (1988). For these experiments, the input vapor phase concentrations of the chlorinated phenols, benzene, oxygen and nitrogen are listed in Table 1. The most abundant chlorinated phenols found in incinerator flue gas are the 2,4,6 congeners, namely 2,4,6-trichlorophenol, 2,3,4,6-tetrachlorophenol, and pentachlorophenol. Results are presented for a gas-phase experiment performed at 600°C and 10 second residence time. While total PCDD/F yields and homologue distributions vary significantly with temperature and residence time, PCDD/F isomer distributions do not. Results are also presented for a heterogeneous experiment in which the gas stream was passed through a bed of silicon dioxide and copper (II) chloride (0.5%, mass) particles. The gas-particle contact time was 0.3 second and the temperature was 400°C. As with the gas-phase experiments, PCDD/F isomer distributions were relatively insensitive to temperature and time.

| Table 1 |
Observed pathways of chlorinated phenol condensation to form PCDD/F congeners are summarized in Fig. 1 for 2,3-dichlorophenol. Carbon-carbon coupling at unchlorinated ortho positions results in the formation of a PCDF with no chlorine loss; in this case, 3,4,6,7-tetrachlorodibenzofuran is formed. Oxygen-carbon coupling at the chlorinated ortho position followed by five-member ring closure results in the formation of two sets of isomer pairs – one pair with loss of two Cl atoms and the other pair with loss of one Cl atom. These PCDD/F formation pathways are observed both in the gas phase as well as in surface-catalyzed reactions. There are significant differences in the distribution of PCDD/F products formed, however. In the gas phase, PCDF products are mostly produced. In addition, dechlorination of the chlorinated phenols occurs, primarily at the 2,4,6 positions. This results in further PCDF formation. In the CuCl₂-catalysis experiments, on the other hand, PCDD products are favored. In addition, chlorination of the phenols occurs, primarily at the 2,4,6 positions. This results in further PCDD formation. In this paper, PCDD/F distributions from both gas-phase and CuCl₂-catalysis experiments are presented.

**Fig. 1**

**DD/DF Chlorination Model.** Experiments were performed in our laboratory on the chlorination of dibenzo-p-dioxin (DD) and dibenzofuran (DF) on CuCl₂ particles. Results are being published elsewhere (Ryu and Mulholland, 2001). At temperatures between 200 and 300°C, 92% nitrogen, 8% oxygen gas streams containing 0.1% DD and DF vapor were passed through a silicon dioxide particle bed containing 0.5% (mass) CuCl₂. Complete chlorination to the octachlorinated congeners was observed for gas-particle contact times of 2.5 seconds and greater. Total DD/DF conversion and the degree of chlorination varied significantly for the different experimental conditions. Variation in the PCDD/F isomer patterns was much less, however. Chlorination was favored at the 2,3,7,8 positions for both DD and DF. This result is consistent with the findings of others (Luijk et al., 1994; Addink et al., 1996).

Using the experimental data, simple models of DD/DF chlorination were developed (Fig. 2), analogous to the OCDD/F dechlorination models of lino and co-workers (2000 and 2001). The first-order model uses the monochlorinated isomer distribution to predict subsequent chlorination based on statistical factors and partitioning between chlorination products. The model accurately predicts the observed order of isomers in all distributions, with the exception of 1,9 chlorinated PCDF products whose formation is slightly over-predicted by the first-order model. It is likely that it is more difficult to add the second Cl atom to the PCDF bay region than the first.

**Fig. 2**

**OCDD/F Dechlorination Model.** lino and co-workers have developed first-order models for PCDD/F dechlorination based on the dechlorination of octachlorinated congeners (OCDD/F) to form heptachlorinated congeners (lino et al., 2000; lino et al., 2001). Model parameters are shown in Fig. 3. Dechlorination of OCDD is favored at lateral sites (2,3,7,8). Dechlorination of OCF is favored at bay sites (1,9) and lateral sites (2,3,7,8), resulting in favored formation of PCDF isomers with 4,6 Cl substituents. Recent experimental results of OCF dechlorination on CuO particles agrees well with the dechlorination model predictions, except for PCDF products
with both 1,9 Cl substituents removed which appear to be over-predicted by the model. It is likely that it is easier to remove the first Cl atom from the PCDF bay region than the second.

Fig. 3

**PCDD/F Isomer Distributions: Comparison**

*PCDDs.* Tetra-, penta- and hexachlorinated dibenzo-\(p\)-dioxin (T\(4\)CDD, P\(5\)CDD and H\(6\)CDD) isomer distributions from MWI field samples, MSW combustion laboratory samples, phenol condensation experiments, DD chlorination model, OCDD dechlorination model, and PM3 thermodynamic calculations are shown in Figs. 4-6. The PCDD product groupings are necessary due to combinations of co-eluting isomers from researchers using different analytical methods. In the field and laboratory distributions, standard deviations of all measurements are given. In all three isomer sets, the field and laboratory distributions (top two panels) are remarkably similar. Moreover, they are significantly different than the thermodynamic distributions (bottom panel). Isomer distributions from MWI field samples appear to most resemble the CuCl\(_2\)-catalyzed phenol condensation distributions for all three homologues shown.

Figs. 4-6

The most abundant T\(4\)CDD isomers produced in municipal waste combustion in the field and laboratory are the 1,3,6,8 and 1,3,7,9 isomers. This is the isomer pair produced by condensation of two 2,4,6-trichlorophenols. In both the gas phase and CuCl\(_2\)-catalyzed phenol condensation experiments, this isomer pair was also produced in greatest abundance. Chlorination favors the formation of 2,3,7,8-T\(4\)CDD, whereas dechlorination yields a more uniform distribution of isomers.

The most abundant P\(5\)CDD isomers produced in municipal waste combustion in the field and laboratory are as follows: 1,2,4,6,8- and 1,2,4,7,9- (co-elute), 1,2,3,6,8- and 1,2,3,7,9-P\(5\)CDDs. These are the two isomer pairs produced by condensation of 2,4,6-trichlorophenol and 2,3,4,6-tetrachlorophenol, and were the major P\(5\)CDD products from the phenol condensation experiments. Chlorination strongly favors the formation of 1,2,3,7,8-P\(5\)CDD, whereas dechlorination yields a more uniform distribution of isomers.

In the case of the H\(6\)CDD isomer distribution, the two largest peaks are the 1,2,4,6,7,9- and 1,2,4,6,8,9- H\(6\)CDD peak and the 1,2,3,4,7,9- and 1,2,3,6,8,9-H\(6\)CDD peak. These peaks include two isomer pairs produced by condensation of two 2,3,4,6-tetrachlorophenols, and the 1,2,3,4,6,8 isomer is produced by condensation of 2,4,6-trichlorophenol and pentachlorophenol. In the phenol condensation experiments, these were also the largest peaks, although the 1,2,3,4,7,9- and 1,2,3,6,8,9-H\(6\)CDD peak was larger unlike the municipal waste combustion field and laboratory results. One explanation is that the phenol distribution used for the phenol condensation experiments, based on the data of Ballschmiter et al. (1988), contained more 2,3,4,6-tetrachlorophenol than either 2,4,6-trichlorophenol or pentachlorophenol, whose PCDD product is part of the first peak. As in the cases of the T\(4\)CDD and P\(5\)CDD isomer distributions, chlorination and dechlorination produced a H\(6\)CDD isomer distribution significantly different than that observed by municipal waste combustion.
PCDFs. Tetra-, penta- and hexachlorinated dibenzofuran (T\textsubscript{4}CDF, P\textsubscript{5}CDF and H\textsubscript{6}CDF) isomer distributions from MWI field samples, MSW combustion laboratory samples, phenol condensation experiments, DF chlorination model, OCDF dechlorination model, and PM3 thermodynamic calculations are shown in Figs. 7-9. The PCDF product groupings are necessary due to combinations of co-eluting isomers from researchers using different analytical methods. In the field and laboratory distributions, standard deviations of all measurements are given. In all three isomer sets, the field and laboratory distributions (top two panels) are similar. Moreover, they are significantly different than the thermodynamic distributions (bottom panel). Isomer distributions from the MWI field samples most resemble the dechlorination patterns.

Figs. 7 – 9

The largest single T\textsubscript{4}CDF peak in the MWI field samples and the laboratory MSW combustion flue gas is the 2,4,6,7 isomer. Another T\textsubscript{4}CDF isomer found in significantly greater abundance in the field samples than thermodynamically expected is the 3,4,6,7 isomer. These two T\textsubscript{4}CDF isomers contain 4,6 Cl substituents. These isomers are favored by the dechlorination pathway, but not the chlorination or phenol condensation routes of PCDF formation. Examination of the P\textsubscript{5}CDF and H\textsubscript{6}CDF isomer patterns reveals a similar result. Two of the largest P\textsubscript{5}CDF peaks in the field samples are the 1,2,4,8,9/2,3,4,6,7-P\textsubscript{5}CDF peak and the 2,3,4,6,8-P\textsubscript{5}CDF peak. Dechlorination favors the isomers containing 4,6 Cl substituents. Similarly, 1,2,3,4,6,8-, 1,2,4,6,7,8-, 1,2,3,4,6,7- and 2,3,4,6,7,8-H\textsubscript{6}CDF isomers, all of which contain 4,6 Cl substituents, were the largest single isomer peaks in the field samples. These isomers are favored by dechlorination, but not chlorination or phenol condensation.

Correlation Analysis. A correlation analysis was performed to provide a quantitative assessment of the similarities between PCDD/F isomer distributions. Results, shown in Table 2, confirm that, based on isomer patterns, CuCl\textsubscript{2}-catalyzed phenol condensation is the most likely source of PCDDs in municipal waste incineration, and dechlorination pathways are most likely responsible for the T\textsubscript{4}CDF, P\textsubscript{5}CDF and H\textsubscript{6}CDF isomer distributions. The correlation analysis results suggest that chlorination and gas-phase phenol condensation pathways may be responsible for less chlorinated PCDF isomer formation, as suggested by the increasing R-value for these patterns with decreasing chlorine. This result is consistent with laboratory results that indicate that gas-phase phenol condensation favors PCDFs over PCDDs, and less chlorinated PCDF congeners over more chlorinated PCDF congeners.

Table 2

Before closing, we point out that there may be other mechanisms of PCDD/F formation that affect isomer distributions. For example, fast de novo reactions or formation from precursors other than phenols may contribute directly to the formation of PCDD/F isomers. In addition, multiple mechanisms may contribute similarly to the formation of some PCDD/F isomer distributions. The results presented in this paper provide a means for testing these hypotheses on PCDD/F formation mechanisms in combustion systems.
Conclusion

PCDD/F isomer patterns found municipal waste incinerator samples and in laboratory experiments in which municipal solid waste is combusted are robust, largely unaffected by combustion conditions, and different than thermodynamic distributions. Likewise, PCDD/F isomer patterns from controlled laboratory experiments in which different formation mechanisms are studied are distinct and robust. Gas-phase phenol condensation favors PCDF formation, with peak yields between 550 and 650°C. Phenol, produced from benzene at these temperatures, exhibits the highest reactivity; hence, DF is a major product. Under CuCl$_2$-catalyzed conditions, PCDDs are favored, with peak yields between 300 and 400°C. Due to the high concentrations of ortho/para substituted phenols (e.g., 2,4,6-trichlorophenol), major product pairs include 1,3,6,8-/1,3,7,9-T$_4$CDD and 1,2,4,6,8-/1,2,4,7,9-P$_5$CDD. CuCl$_2$-catalyzed DD/DF chlorination occurs at 200-250°C, with 2,3,7,8 congeners favored. On the other hand, dechlorination of OCDD/OCDF favors congeners that retain chlorine substituents in ortho positions to oxygen (i.e., 1,4,6,9 PCDDs and 4,6 PCDFs).

PCDD isomer patterns from municipal waste incinerators are most similar to those produced by CuCl$_2$-catalyzed phenol condensation. On the other hand, PCDF isomer patterns are most like those from dechlorination, particularly for the highly chlorinated homologues. For less chlorinated homologues, the PCDF isomer distributions may be most similar to those from chlorination. One explanation is that a bimodal PCDF distribution is produced by formation of DF via gas-phase phenol condensation, followed by chlorination, and by de novo synthesis of OCDF, followed by dechlorination.

Acknowledgment

Support for this research was provided by the National Science Foundation (CTS-9457028), the Research Foundation for Health and Environmental Effects, and the Environmental Protection Agency (QT-OH-99-000537).
References


Table 1. Input gas stream composition for phenol condensation experiments.

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>nitrogen</td>
<td>90.5</td>
</tr>
<tr>
<td>oxygen</td>
<td>7.9</td>
</tr>
<tr>
<td>benzene</td>
<td>1.1</td>
</tr>
<tr>
<td>chlorinated phenols:</td>
<td></td>
</tr>
<tr>
<td>2,5-dichlorophenol</td>
<td>0.026</td>
</tr>
<tr>
<td>2,6-dichlorophenol</td>
<td>0.025</td>
</tr>
<tr>
<td>3,4-dichlorophenol</td>
<td>0.024</td>
</tr>
<tr>
<td>2,3,4-trichlorophenol</td>
<td>0.012</td>
</tr>
<tr>
<td>2,3,6-trichlorophenol</td>
<td>0.006</td>
</tr>
<tr>
<td>2,4,6-trichlorophenol</td>
<td>0.149</td>
</tr>
<tr>
<td>2,3,4,5-tetrachlorophenol</td>
<td>0.013</td>
</tr>
<tr>
<td>2,3,4,6-tetrachlorophenol</td>
<td>0.175</td>
</tr>
<tr>
<td>2,3,5,6-tetrachlorophenol</td>
<td>0.004</td>
</tr>
<tr>
<td>pentachlorophenol</td>
<td>0.047</td>
</tr>
</tbody>
</table>
Table 2. Correlation R values for PCDD/F isomer distributions with field data.

<table>
<thead>
<tr>
<th></th>
<th>T$_4$CDD</th>
<th>P$_3$CDD</th>
<th>H$_6$CDD</th>
<th>T$_4$CDF</th>
<th>P$_3$CDF</th>
<th>H$_6$CDF</th>
</tr>
</thead>
<tbody>
<tr>
<td>field data</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>laboratory data</td>
<td>0.931</td>
<td>0.869</td>
<td>0.991</td>
<td>0.881</td>
<td>0.927</td>
<td>0.770</td>
</tr>
<tr>
<td>thermodynamic</td>
<td>0.130</td>
<td>0.599</td>
<td>0.623</td>
<td>0.293</td>
<td>0.435</td>
<td>0.506</td>
</tr>
<tr>
<td>phenol condensation:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>gas phase</td>
<td>0.950</td>
<td>0.945</td>
<td>0.388</td>
<td>0.411</td>
<td>0.273</td>
<td>0.206</td>
</tr>
<tr>
<td>CuCl$_2$-catalyzed</td>
<td>0.986</td>
<td>0.990</td>
<td>0.763</td>
<td>0.054</td>
<td>0.109</td>
<td>-0.012</td>
</tr>
<tr>
<td>chlorination</td>
<td>-0.177</td>
<td>-0.127</td>
<td>-0.375</td>
<td>0.668</td>
<td>0.477</td>
<td>0.410</td>
</tr>
<tr>
<td>dechlorination</td>
<td>-0.045</td>
<td>0.232</td>
<td>0.760</td>
<td>0.805</td>
<td>0.886</td>
<td>0.890</td>
</tr>
</tbody>
</table>
Figure Captions

Fig. 1. 2,3-Dichlorophenol condensation pathways.

Fig. 2. DD/DF chlorination pathway model.

Fig. 3. OCDD/OCDF dechlorination pathway model.

Fig. 4. T₄CDD isomer distributions.

Fig. 5. P₃CDD isomer distributions.

Fig. 6. H₆CDD isomer distributions.

Fig. 7. T₄CDF isomer distributions.

Fig. 8. P₃CDF isomer distributions.

Fig. 9. H₆CDF isomer distributions.
Fig. 1. 2,3-Dichlorophenol (2,3-DCP) condensation pathways.
Fig. 2. DD/DF chlorination pathway model.

\[ F_{\text{isomer}} \propto S \ a^j \ b^k \]

- \( S = \) statistical factor
- \( j = \) CI atoms added at 1
- \( k = \) CI atoms added at 2
- \( l = \) CI atoms added at 3
- \( m = \) CI atoms added at 4
Fig. 3. OCDD/OCDF dechlorination pathway model.
Fig. 4. T₄CDD isomer distributions.
Fig. 5. P₅CDD isomer distributions.
Fig. 6. $H_6CDD$ isomer distributions.
Fig. 7. T₄CDF isomer distributions.
Fig. 8. P₅CDF isomer distributions.
Fig. 9. H₆CDF isomer distributions.