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Metal-mediated chlorinated dibenzo-*p*-dioxin (CDD) and dibenzofuran (CDF) formation from phenols

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Abstract

Heterogeneous formation of chlorinated dibenzo-*p*-dioxins (CDDs) and dibenzofurans (CDFs) on $CuCl_2$ from three phenols without *ortho* chlorine and one phenol with two *ortho* chlorines was studied in a flow reactor over a temperature range of 325–450 °C. Heated nitrogen gas streams containing 8% oxygen, 1.5% benzene vapor, and equal amounts of phenol, 3-chlorophenol, 3,4-dichlorophenol and 2,4,6-trichlorophenol vapor (700 ppmv, each) were passed through a 1 g particle bed of silica and 0.5% (Cu mass) $CuCl_2$. Maximum product yields of greater than 1.4% phenol conversion to CDD and 5.7% phenol conversion to CDF were observed between 400 and 450 °C. CDDs formed with loss of one chlorine atom were favored. While total CDD/F yield varied with temperature, CDD/F homologue and isomer distributions did not vary significantly with temperature. Based on the results of experiments with single phenol precursors, phenol precursors could be assigned to all PCDD/F products. Of the chlorinated phenols without *ortho* chlorine that were studied, 3,4-dichlorophenol was found to have the greatest propensity to form CDFs.

Keywords: Chlorinated dibenzo-*p*-dioxin (CDD); Chlorinated dibenzofuran (CDF); Copper(II) chloride; Chlorinated phenols

1. Introduction

In municipal waste incinerators, chlorinated dibenzo-*p*-dioxin (CDD) and dibenzofuran (CDF) byproducts can be formed by two general pathways: (1) homogeneous, gas-phase reactions, and (2) heterogeneous, metal-mediated reactions. The first route, which is observed in post-combustion gas at temperatures between 500 and 700 °C, occurs via precursors. The second route, which is observed in particle collection devices at temperatures between 250 and 450 °C, may involve precursors of similar structure (e.g. chlorinated phenols, benzenes, and polychlorinated biphenyls) or particulate carbon (de novo synthesis). Municipal waste incinerator data from kiln gas and stack samples suggest that the first route favors the formation of dibenzofuran and less chlorinated CDD/F congeners, whereas the latter route favors the formation of highly chlorinated CDD congeners (Hagenmaier et al., 1987; Yamamoto et al., 1989).

The mechanisms of CDD/F formation 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., 1997), and graphitic carbon (Stieglitz et al., 1989). Nonetheless, there remains much uncertainty

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about the predominant pathway of CDD/F formation in combustion systems, particularly in the heterogeneous environment of particle collection devices.

Research in our laboratory has addressed CDD/F formation from chlorinated phenols, both in the gas phase and on the surface of copper(II) chloride ($CuCl_2$) particles. $CuCl_2$ is known to be one of the most active catalysts in dioxin formation. CDD/F distributions from chlorinated phenols depend on the distribution of phenol precursors and on the relative rates of formation from different phenol pairs. We have addressed this topic by studying three sets of chlorinated phenols those with both *ortho* sites chlorinated, those with one *ortho* site chlorinated, and those with no *ortho* chlorinated.

Phenols that have both *ortho* sites chlorinated produce only CDDs, which are formed by the loss of two chlorine atoms from both phenols. We have shown that CDD isomer distributions produced from these phenols do not vary significantly over a wide range of reaction conditions. Total CDD yield and homologue distribution do vary, however (Mulholland and Ryu, 2001). Moreover, we found that these CDD isomer patterns are consistent with distributions found in samples from municipal waste incinerator.

Chlorinated phenols that contain only one *ortho* chlorine substituent produce both CDDs and CDFs. In gas-phase pyrolysis of 2-chlorophenol (Yang et al., 1998) and 2,3-dichlorophenol (Mulholland et al., 2001), we have shown that yields of CDD products, formed by loss of both *ortho* chlorine atoms in the pair of reacting phenols, are greater than yields of CDF products, which are formed without chlorine loss. In gas-phase oxidative environments, on the other hand, CDFs are the major products (Nakahata and Mulholland, 2000). On particles containing $CuCl_2$, CDD/F formation from chlorinated phenols with only one *ortho* chlorine substituent was found to favor CDD formation with one chlorine loss over CDF formation with no chlorine loss (Ryu and Mulholland, 2002).

One *ortho* chlorine is needed to form CDD, whereas one unchlorinated *ortho* carbon is needed to form CDF. For illustration, possible CDD/F formation pathways from 3,4-dichlorophenol (3,4-DCP) and 2,4,6-trichlorophenol (2,4,6-T_3CP) are shown in Fig. 1. Pathway (1)

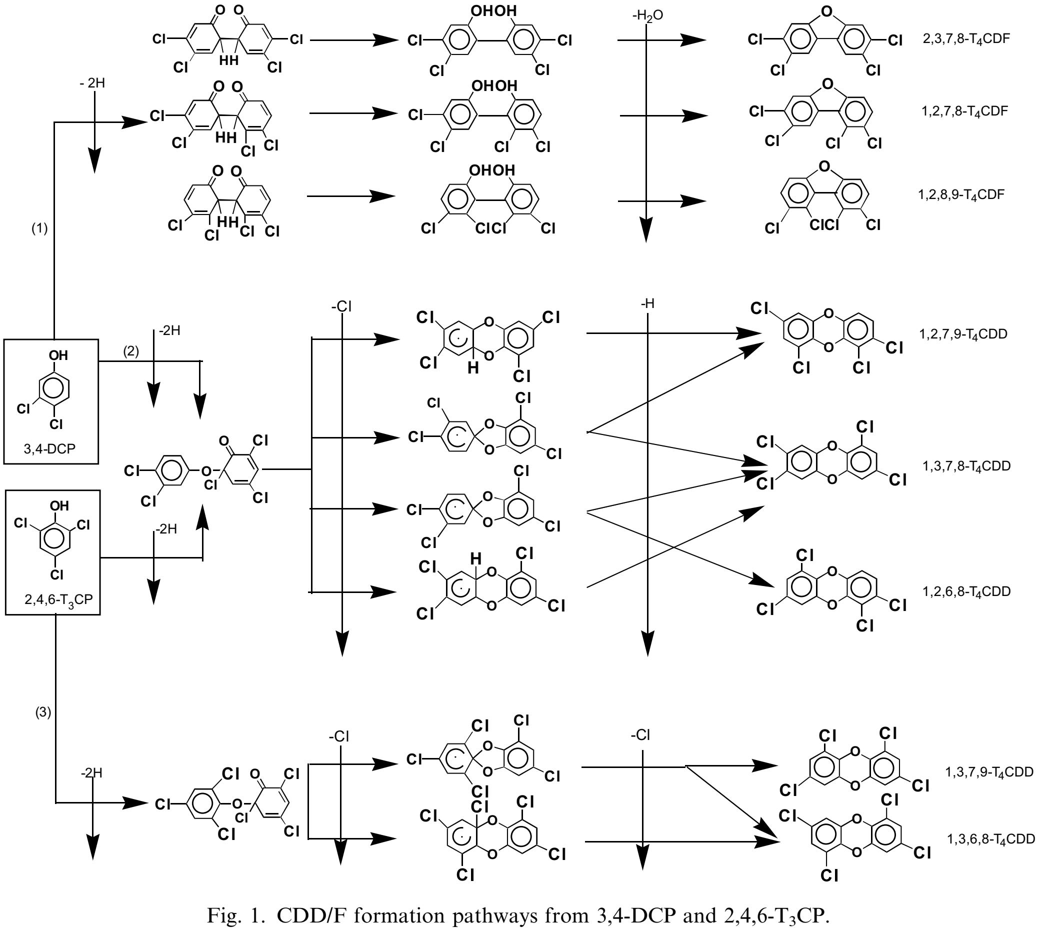

Fig. 1. CDD/F formation pathways from 3,4-DCP and 2,4,6-T_3CP.

in Fig. 1 depicts three 2,3,7,8-, 1,2,7,8-, and 1,2,8,9-tetrachlorodibenzofuran (T_4CDF) isomers being formed without chlorine loss from two 3,4-DCP. Pathway (2) depicts three 1,2,7,9-, 1,3,7,8-, and 1,2,6,8-tetrachlorodibenzo-*p*-dioxin (T_4CDD) being formed with one *ortho* chlorine loss from 3,4-DCP and 2,4,6-T_3CP. Pathway (3) depicts 1,3,6,8- and 1,3,7,9-tetrachlorodibenzo-*p*-dioxin (T_4CDD) being formed with loss of two chlorine atoms from two 2,4,6-T_3CP.

Here we address CDD/F formation on $CuCl_2$ by chlorinated phenols without *ortho* chlorine substituents. Specifically, we address the following questions. Is CDF formation favored in a combination of chlorinated phenols without *ortho* chlorine substituent? Can chlorinated phenols without *ortho* chlorine produce CDD products by reacting with chlorinated phenols with *ortho* chlorine? Which of these phenols have the greatest propensity to form CDD/F products? Finally, do CDD/F isomer distributions provide a fingerprint for CDD/F formation via this channel? This work, together with results already published or CDD/F formation from phenols with one and two *ortho* chorine substituents (Mulholland and Ryu, 2001; Ryu and Mulholland, 2002, respectively), provides a comprehensive experimental investigation of CDD/F formation from phenols on copper(II) chloride. We do not address the detailed formation mechanism on $CuCl_2$, which involves adsorption, reaction, and desorption; other researchers have proposed reaction mechanisms analogous to the Ullmann II reaction (Tuppurainen et al., 1998). Recently, Lomnicki and Dellinger (2003) have shown a detailed surface-mediated PCDD/F formation mechanism on CuO/silica surface.

2. Experimental

2.1. Methods

The experimental apparatus is shown in Fig. 2. Experiments were conducted in an electrically heated quartz tube flow reactor, 40 cm in length and 1.7 cm in diameter. Equal molar amounts of phenol (Ph), 3-chlorophenol (3-CP), 3,4-dichlorophenol (3,4-DCP), and

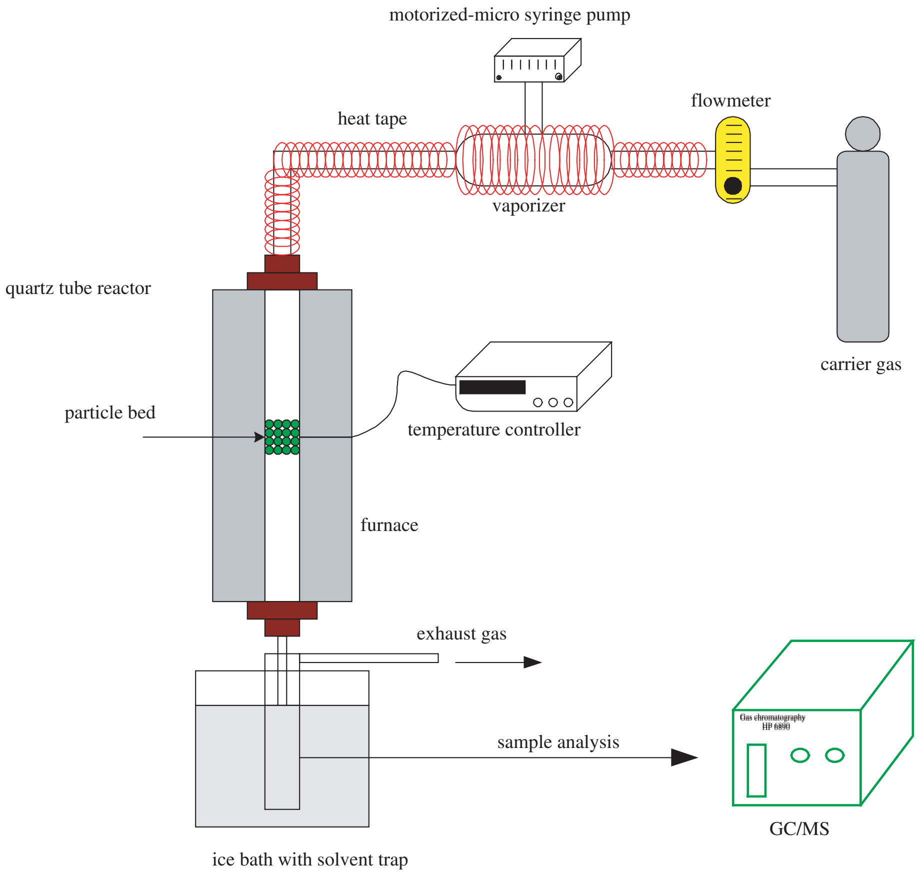

Fig. 2. Apparatus.

2,4,6-trichlorophenol (2,4,6-T_3CP) were dissolved in benzene. The benzene/chlorinated phenol solution was injected into a heated glass vessel by micro-syringe pump (Sage Instruments, model 341B-Boston, MA) at a rate of 10 μl/min. The reactant stream was immediately vaporized in a gas stream of 92% nitrogen and 8% oxygen. The resulting gas stream contained 1.5% benzene vapor and 700 ppmv of each phenol (2800 ppmv total). A 1 g particle bed of 1 cm height, consisting of SiO_2 (99.6% purity, 325 mesh) and 0.5% (by Cu mass) $CuCl_2$ (anhydrous, 99.999+% purity), was located at the center of the reactor. The $SiO_2/CuCl_2$ particle bed was prepared by mechanical mixing. This method has been shown to provide repeatable results (Mulholland and Ryu, 2001; Ryu and Mulholland, 2002). Experiments were carried out over a temperature range of 325–450 °C, in 25 °C increments, at a gas velocity of 2.7 cm/s (0.3 s of contact time). Experiments were run for approximately 20 min to collect enough samples, with the entire product gas stream rapidly quenched and soot and aromatic tar samples collected in an ice-cooled dichloromethane trap.

2.2. Instrumental analysis and identification

Sample solutions were filtered and then analyzed by GC/MS (HP 6890 series gas chromatograph with model 5973 mass selective detector-EI type) with autosampler equipped with a HP-5MS capillary column with length 30 m, i.d. 0.25 mm and phase 0.25 μm film of crosslinked 5% PH ME siloxane (J&W Scientific, CA). A GC was carried out with splitless injection and He as carrier gas. For identification, the mass spectrometer was operated in the scan mode, and for quantification, in selected ion mode (SIM). Preliminary identification of CDD/F products was based on published relative retention times for similar columns (Hale et al., 1985; Ryan et al., 1991). Final identification was based on available standards and gas-phase synthesis experiments from single precursors and precursor pairs. Seventy-four of 75 CDD congeners and 121 of 135 CDF congeners have been synthesized from phenol pairs. All four monochlorodibenzofuran (MCDF) isomers were separated, as were 13 of 16 dichlorodibenzofurans (DCDFs), 25 of 28 trichlorodibenzofurans (T_3CDFs), 34 of 38 tetrachlorodibenzofurans (T_4CDFs), 22 of 28 pentachlorodibenzofurans (P_5CDFs), 12 of 16 hexachlorodibenzofurans (H_6CDFs), 2 of 4 heptachlorodibenzofurans (H_7CDFs), and octachlorodibenzofuran (OCDF). CDD isomer peak separation was as follows: 2 peaks for 2 monochlorodibenzo-*p*-dioxin (MCDD) isomers, 7 peaks for 10 dichlorodibenzo-*p*-dioxin (DCDD) isomers, 10 peaks for 14 trichlorodibenzo-*p*-dioxin (T_3CDD) isomers, 15 peaks for 22 tetrachlorodibenzo-*p*-dioxin (T_4CDD) isomers, 12 peaks for 14 pentachlorodibenzo-*p*-dioxin (P_5CDD) isomers, 7 peaks for 10 hexachlorodibenzo-*p*-dioxin (H_6CDD) isomers, 2 peaks for 2 heptachlorodibenzo-*p*-dioxin (H_7CDD) isomers. A universal response factor was used for CDDs and CDFs based on dibenzo-*p*-dioxin (DD) and dibenzofuran (DF), respectively.

3. Results and discussion

3.1. Overall product distributions

Experiments with the benzene solution containing four phenols (Ph, 3-CP, 3,4-DCP, 2,4,6-T_3CP) were conducted over a temperature range of 325–450 °C. Yields of overall product groups are shown in Table 1. Chlorinated benzene (CBz) yields were observed to peak at 21.7% (percent of phenol input, carbon basis) at 400 °C. By chlorination, a maximum total chlorinated phenol (CP) product yield of 1.7% was observed at 325 °C. A maximum perchloroethylene (PCE) yield of 3.6% was observed at 375 °C. Total chlorinated quinone (CQs) yields were very small, about 0.1% between 325 °C and 375 °C, and decreased with increasing temperature. Optimum formation temperatures for these compounds are consistent with results of similar experiments with chlorinated phenols with one *ortho* chlorine atom described elsewhere (Ryu and Mulholland, 2002). A maximum total CDD yield of 1.4% was observed at 425 °C; a maximum CDF yield of 5.7% was observed at 425 °C. CDF formation was favored over CDD formation.

Table 1
Overall product yields (percent of phenol input, carbon basis, except where noted)

	325 °C	350 °C	375 °C	400 °C	425 °C	450 °C
CDDs	0.061	0.067	0.20	0.55	1.36	0.48
CDFs	0.13	0.36	1.25	2.83	5.72	5.04
CPs	1.67	1.05	0.82	0.95	0.78	0.78
CBz*	0.63	1.95	2.80	3.41	2.92	2.72
PCE	0.82	2.90	3.56	2.59	1.47	0.80
CQs	0.113	0.134	0.125	0.037	0.019	0.008

* CBz yields are based on percent of phenol and benzene input.

3.2. Chlorinated phenol formation

Phenol reactant recovery and chlorinated product yields are shown in Fig. 3. The highest recovery was unreacted 2,4,6-T_3CP; the least recovered was 3,4-DCP. Phenol reactant recovery decreased with increasing temperature. Chlorination product yields were greatest at low temperatures (325–350 °C).

Chlorination products at *ortho* (2, 6) and *para* (4) sites were favored over chlorination at *meta* (3, 5) sites. Chlorination of phenol at 352–452 °C has been found to involve only *ortho* and *para* positions (Born et al., 1993), and this was explained by the electrophilic aromatic substitution mechanism for the *ortho*/*para*-directing OH group of phenol (Luijk et al., 1994).

Phenol chlorination produced 2-, 4-chlorophenols and then 2,4- and 2,6-dichlorophenols. From a pure phenol experiment, more 2-CP was produced than 4-CP. 3-CP chlorination produced 2,3-, 2,5- and 3,4-DCP. From a pure 3-CP experiment, more 2,5-DCP was produced than 2,3-DCP and 3,4-DCP. 3,4-DCP chlorination produced 2,4,5- and 2,3,4-T_3CP, with much more 2,4,5-T_3CP produced than 2,3,4-T_3CP. These results suggest that both steric and electronic factors govern phenol chlorination. Pentachlorophenol (PCP) was also produced in small amounts, showing that chlorination can occur at *meta* (3, 5) sites as well.

3.3. Chlorinated benzene formation

From phenol and benzene experiments on copper(II) chloride, we observed that chlorinated benzenes (CBz) can be formed from chlorinated phenols (CP) either by chlorodehydroxylation or by chlorination of benzene. Phenol chlorodehydroxylation leads to specific benzene products; e.g. 3,4-DCP chlorodehydroxylation produces

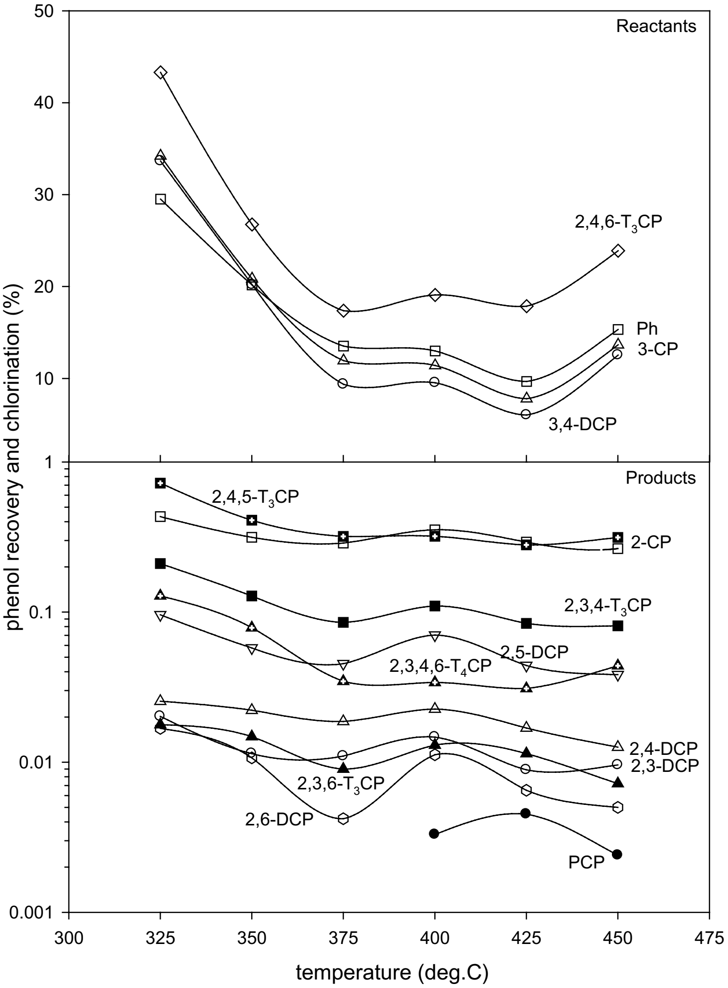

Fig. 3. Phenol reactant recovery and phenol chlorination product yields.

Table 2
Chlorinated benzene yields

	Yield (percent total phenol/benzene conversion)						Isomer fraction	
	325 °C	350 °C	375 °C	400 °C	425 °C	450 °C	Avg	St.dev.
MCBz	0.694	2.14	3.01	3.60	2.98	2.68		
1,3-DCBz	0.009	0.044	0.071	0.133	0.149	0.166	0.254	0.056
1,4-DCBz	0.031	0.070	0.126	0.108	0.098	0.105	0.329	0.155
1,2-DCBz	0.012	0.080	0.133	0.221	0.237	0.262	0.416	0.102
1,3,5-T_3CBz	0.0000	0.0000	0.0003	0.0010	0.0014	0.0020	0.017	0.015
1,2,4-T_3CBz	0.0017	0.0054	0.014	0.0212	0.0294	0.0324	0.470	0.162
1,2,3-T_3CBz	0.0055	0.0124	0.013	0.0174	0.0158	0.0197	0.513	0.176
1,2,3,5-T_4CBz	0.0016	0.0045	0.0084	0.0101	0.0120	0.0100	0.515	0.098
1,2,4,5-T_4CBz	0.0001	0.0006	0.0013	0.0014	0.0013	0.0016	0.067	0.020
1,2,3,4-T_4CBz	0.0028	0.0046	0.0056	0.0068	0.0056	0.0069	0.418	0.116
PCBz	0.0028	0.0080	0.0113	0.0102	0.0065	0.0052		
HCBz	0.0018	0.0037	0.0051	0.0039	0.0027	0.0014		

1,2,4-T_3CBz. Born et al. (1993) also reported that CBz could be produced from chlorinated phenols by chlorodehydroxylation. Chlorination of benzene is favored at sites *ortho* and *para* to other chlorine substituents. Chlorinated benzene yields based on benzene and phenol reactant feeds are shown in Table 2. Monochlorobenzene (MCBz) was the major product, with chlorinated benzenes observed through hexachlorobenzene (HCBz).

Ratios of CBz formed by chlorodehydroxylation and by benzene chlorination are shown in Fig. 4. The ratio of 1,3- and 1,2-CBz was almost constant, and less than 1. This result indicates that formation of 1,2-CBz formed by benzene chlorination was greater than formation of 1,3-CBz formed from 3-CP chlorodehydroxylation. The ratios 1,2,4-/1,2,3-T_3CBz and 1,2,3,5-/1,2,3,4-T_4CBz increased with increasing temperature. At low temperatures, 1,2,3-T_3CBz and 1,2,3,4-T_4CBz produced from benzene chlorination were greater than 1,2,4-T_3CBz and 1,2,3,5-T_4CBz produced from chlorodehydroxylation of 3,4-DCP and 2,4,6-T_3CP reactants. These results show that benzene chlorination is dominant at low temperatures, but phenol chlorodehydroxylation increases with temperature. Weber and Hagenmaier (1999) measured isomer distributions of chlorinated benzenes from municipal solid waste incinerator. They reported the favored formation of 1,2-/1,2,3-/1,2,3,4-CBz, which is similar to benzene chlorination patterns.

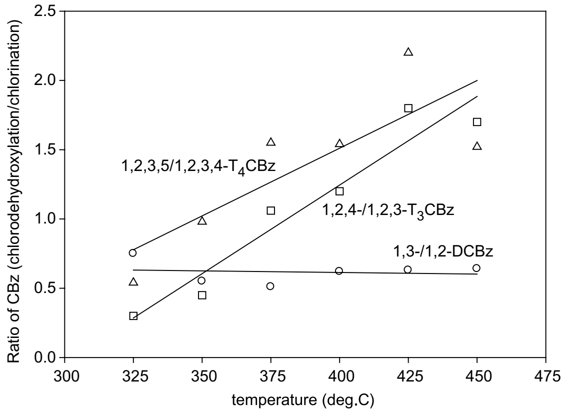

Fig. 4. Ratio of chlorinated benzenes from phenol chlorodehydroxylation and benzene chlorination.

3.4. PCE and CQ formation

The production of PCE from phenols and benzene was already reported (Ryu and Mulholland, 2002). A maximum perchloroethylene (PCE) yield of 3.6% based on chlorinated phenol input was observed at 375 °C. Above 375 °C, yield decreased as shown in Table 1. Born et al. (1993) suggested that PCE very likely results from ring opening oxidative breakdown of chlorinated phenols.

Chlorinated quinone (CQ) products, which included dichlorinated and trichlorinated quinones, were formed in very small amounts, about 0.1% based on chlorinated phenol input between 325 °C and 375 °C. Above these temperatures, CQ yield decreased (Table 1). A mechanism of benzoquinone formation by removal of the chlorine atom during electrochemical incineration of 4-chlorophenol has been proposed by Johnson et al. (1999). Basu and Wei (2000) also proposed that dichlorobenzoquinone compounds were formed from 2,4,6-trichlorophenol in the aqueous phase Fenton's reagent (aqueous solution of hydrogen peroxide and ferrous ion). The two dichlorobenzoquinones were 2,6-dichloro-1,4-benzoquinone and 3,5-dichloro-1,6-benzoquinone; which one occurs depends on which chlorine is removed. Recently, Lomnicki and Dellinger (2003) also have shown a detailed CQ formation mechanism from 2-CP on a CuO/silica surface.

3.5. CDD/F formation

Total yields for CDD/F homologues are shown in Fig. 5. CDF product yields were greater than CDD product yields. DF through P_5CDF products were observed. Peak CDF yields also occurred at 425 °C, but CDF yields remained high above this temperature. DCDF products were greatest at all temperatures. CDF homologue distribution varied little with temperature. CDD products from dibenzo-*p*-dioxin (DD) through penta (P_5CDD) were observed. Highest peak yields of DD through P_5CDDs were observed at 425 °C. The T_4CDD fraction was highest at all temperatures. There was little variation in the CDD homologue distribution with temperature.

To assess which phenol combinations produce the most CDDs and CDFs, isomer distributions were examined. The dependence of the isomer patterns on temperature is examined to assess the potential for using these patterns as fingerprints for the CDD/F formation by the phenol precursor mechanism.

3.6. CDF isomer distributions

Isomer yields for CDF products, shown in order of decreasing yields, are listed in Table 3 as percent of total phenol conversion. CDF isomers that could not be separated are listed in groups. CDF congeners formed based on pathway 1 (Fig. 1) are listed.

All major CDF products are formed from chlorinated phenol reactants that lack *ortho* chlorine. These are 1,2-DCDF, 1,2,7-/2,3,9-T_3CDF, 1-MCDF, 1,7-DCDF, 1,2,7,8-T_4CDF, 3-MCDF, 2,3-DCDF, DF, 2,3,7-T_3CDF, 1,2,9-T_3CDF, 3,7-DCDF, 2,3,7,8-T_4CDF, 1,2,8,9-T_4CDF, and 1,9-DCDF. CDF products in lower yields are also produced from phenol chlorination products.

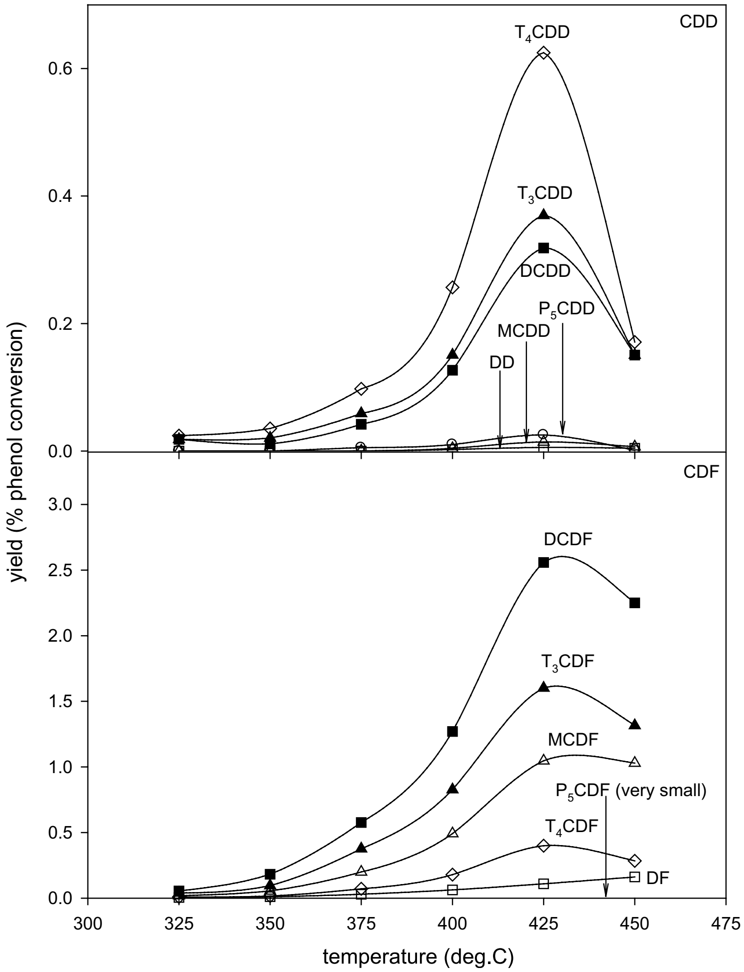

Fig. 5. CDD/F homologue yields.

Table 3
Likely CDF precursors and CDF congener yields

Furan products	Reactants (pathway 1)	Reactant + CP product (pathway 1)	Yield (percent phenol conversion)						Isomer fraction	
			325 °C	350 °C	375 °C	400 °C	425 °C	450 °C	Avg	St.dev.
1,2	ph + 3,4		0.050	0.143	0.450	0.937	1.804	1.533	0.767	0.083
1,2,7/2,3,9	3 + 3,4		0.028	0.084	0.334	0.711	1.334	1.108	0.836	0.064
1	ph + 3		0.019	0.049	0.175	0.415	0.885	0.789	0.871	0.077
1,7	3 + 3		0.0039	0.018	0.082	0.220	0.505	0.410	0.144	0.050
1,2,7,8	3,4 + 3,4		0.0089	0.016	0.065	0.152	0.315	0.243	0.901	0.086
3	ph + 3		0.0000	0.006	0.024	0.077	0.161	0.240	0.129	0.077
2,3	ph + 3,4		0.0007	0.004	0.021	0.061	0.139	0.195	0.043	0.026
DF	ph + ph		0.0051	0.011	0.030	0.063	0.109	0.161		
2,3,7	3 + 3,4		0.0008	0.0012	0.015	0.045	0.106	0.106	0.079	0.098
1,2,9	3 + 3,4		0.0000	0.0002	0.010	0.033	0.087	0.062	0.046	0.026
1,8		3 + 4	0.0000	0.018	0.022	0.025	0.045	0.039	0.032	0.034
3,7	3 + 3		0.0000	0.0000	0.002	0.012	0.029	0.047	0.007	0.008
1,2,8		4 + 3,4	0.0104	0.0101	0.014	0.019	0.039	0.024	0.028	0.023
1,2,4		ph + 2,4,5	0.0000	0.0000	0.0035	0.019	0.036	0.017	0.011	0.010
2,3,7,8	3,4 + 3,4		0.0000	0.0000	0.0028	0.0079	0.028	0.014	0.034	0.028
1,2,8,9	3,4 + 3,4		0.0000	0.0000	0.0005	0.0058	0.020	0.013	0.023	0.023
1,9	3 + 3		0.0000	0.0000	0.0000	0.0059	0.021	0.018	0.003	0.004
1,4		ph + 2,5	0.0000	0.0000	0.0007	0.0086	0.016	0.0084	0.003	0.003
1,2,4,7		3 + 2,4,5	0.0000	0.0000	0.0023	0.0091	0.014	0.0043	0.022	0.021
1,2,6,7		2,3 + 3,4	0.0000	0.0000	0.0000	0.0032	0.0114	0.0083	0.013	0.014
1,2,6,8/1,4,6,7/1,4,7,8		3,4 + 2,4/2,3 + 2,5/3,4 + 2,5	0.0000	0.0000	0.0006	0.0006	0.0097	0.0004	0.006	0.009
1,2,4,6,7		2,3 + 2,4,5	0.0000	0.0000	0.0002	0.0014	0.0021	0.0004	0.813	0.225
2,4,6,7/2,3,4,9/1,4,6,9		2,3 + 2,4/3 + 2,3,4/2,5 + 2,5	0.0000	0.0000	0.0000	0.0000	0.0018	0.0010	0.001	0.002
2,3,4,8,9		3,4 + 2,3,4	0.0000	0.0000	0.0000	0.0006	0.0017	0.0000	0.187	0.225

CDF isomer patterns were largely independent of temperature, even though total CDF yield varied significantly. This is evidenced by the small standard deviation in isomer fractions for the six experiments.

The relative propensity of the chlorinated phenol reactants studied to form CDFs was ascertained by identifying the phenol precursors for each product. The results, shown in Fig. 6, indicate the following ranking of CDF formation potential for the three chlorinated phenol reactants: 3,4-DCP > 3-CP > phenol. Thus, 3,4-DCP is most likely to form CDF products, whereas it was found to be least likely to form CDD products. In gas phase oxidative environments at higher temperatures, on the other hand, phenol had the highest propensity to form CDF products (Nakahata, 2001).

The ranking of CDF formation potential from phenol combinations for the three chlorinated phenol reactants is as follows: phenol + 3,4-DCP > 3-CP + 3,4-DCP > phenol + 3-CP > 3-CP + 3-CP > 3,4-DCP + 3,4-DCP > phenol + phenol.

3.7. CDD isomer distributions

Product yields for CDD congeners, with isomer fractions, shown in order of decreasing yields, are listed in Table 4 as a percent of total phenol conversion. CDD isomers that could not be separated are listed in groups. CDD congeners formed based on the pathways 2 (one chlorine loss) and 3 (two chlorine loss) of Fig. 1 are listed.

As shown in Table 4, CDD products formed from chlorinated phenol reactants were favored over CDD products that were formed from chlorinated phenol reactant and product, with the exception of 1,2,7,9-T_4CDD. The most abundant CDD products were 1,3,6-T_3CDD, 1,3-DCDD, 1,3,6,8-, 1,3,7,8-, 1,3,7,9-T_4CDD, 1,3,9-T_3CDD, 1,2,6,8-, and 1,2,7,9-T_4CDD.

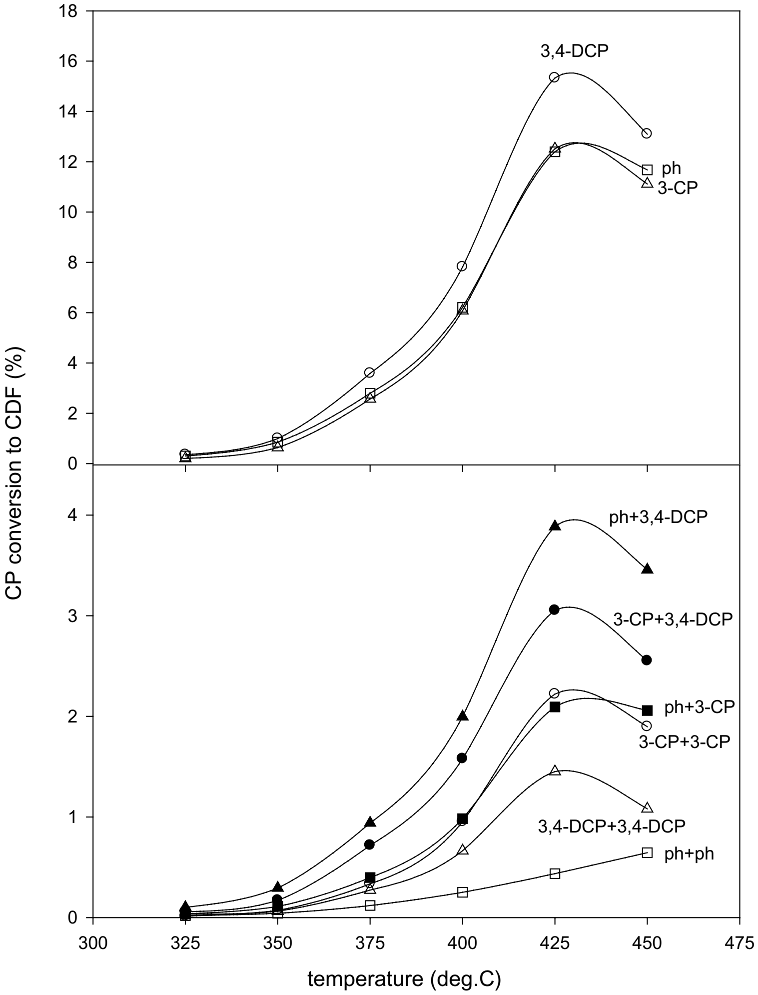

Fig. 6. CDF formation propensity of phenol, 3-CP, and 3,4-DCP.

Table 4
Likely CDD precursors and CDD congener yields

Dioxin products	Reactants (pathway 2 or 3)	Reactant + CP product (pathway 2)	Yield (percent phenol conversion)						Isomer fraction	
			325 °C	350 °C	375 °C	400 °C	425 °C	450 °C	Avg	St.dev.
1,3,6	3 + 2,4,6		0.018	0.019	0.051	0.131	0.312	0.135	0.867	0.023
1,3	ph + 2,4,6		0.018	0.011	0.041	0.120	0.284	0.142	0.939	0.036
1,3,6,8	Two 2,4,6		0.0056	0.012	0.033	0.090	0.243	0.058	0.354	0.024
1,3,7,8	3,4 + 2,4,6		0.015	0.016	0.039	0.088	0.172	0.061	0.343	0.052
1,3,7,9	Two 2,4,6		0.0032	0.0065	0.024	0.063	0.161	0.041	0.246	0.0080
1,3,9	3 + 2,4,6		0.0006	0.0016	0.0044	0.013	0.029	0.012	0.079	0.0053
1,2,6,8	3,4 + 2,4,6		0.0004	0.0004	0.0015	0.0085	0.025	0.0054	0.030	0.011
2,3		2 + 3,4	0.0008	0.0000	0.0009	0.0063	0.024	0.0083	0.050	0.022
1,2,7,9	3,4 + 2,4,6		0.0003	0.0005	0.0005	0.0045	0.017	0.0047	0.019	0.010
1,2,4,6,8/1,2,4,7,9		2,4,5 + 2,4,6	0.0000	0.0000	0.0034	0.0060	0.012	0.0009	0.650	0.176
2		2 + 3	0.0000	0.0000	0.0003	0.0042	0.011	0.0051	0.885	0.133
1,2,6		3 + 2,3,4	0.0000	0.0000	0.0035	0.0022	0.0087	0.0014	0.027	0.022
2,3,7		3 + 2,4,5	0.0000	0.0000	0.0004	0.0028	0.0119	0.0020	0.018	0.011
1,2,3		ph + 2,3,4,6	0.0000	0.0000	0.0000	0.0023	0.0087	0.0004	0.010	0.011
DD		ph + 2	0.0000	0.0000	0.0000	0.0023	0.0056	0.0043		
1,2,3,6,8		2,3,4 + 2,4,6	0.0000	0.0000	0.0017	0.0020	0.0071	0.0001	0.235	0.095
1,2		2 + 3,4	0.0000	0.0000	0.0000	0.0008	0.0057	0.0000	0.0060	0.0084
1,2,3,7,9		2,3,4 + 2,4,6	0.0000	0.0000	0.0000	0.0013	0.0048	0.0000	0.080	0.096
2,7/2,8		3 + 2,5	0.0000	0.0000	0.0000	0.0000	0.0047	0.0007	0.0049	0.0070
1,2,3,7/1,2,3,8		2,5 + 2,3,4	0.0000	0.0000	0.0000	0.0014	0.0032	0.0005	0.0033	0.0025
1		2 + 3	0.0000	0.0000	0.0000	0.0000	0.0032	0.0016	0.115	0.133
1,2,7,8		3,4 + 2,4,5	0.0000	0.0000	0.0000	0.0007	0.0022	0.0005	0.0023	0.0016
2,3,7,8		3,4 + 2,4,5	0.0000	0.0000	0.0000	0.0002	0.0023	0.0000	0.0011	0.0017
1,3,6,9		2,5 + 2,4,6	0.0000	0.0000	0.0000	0.0004	0.0007	0.0000	0.0007	0.0008
1,2,4,7,8		3,4 + 2,3,4,6	0.0000	0.0000	0.0000	0.0007	0.0018	0.0000	0.035	0.041

These CDD products can be formed by pathway 2 (one chlorine loss) or pathway 3 (two chlorine loss). 3-CP and 2,4,6-T_3CP can form 1,3,6-, 1,3,9-, 1,3,7-, 1,3,8-T_3CDD, but 1,3,7-, 1,3,8-T_3CDD was not detected. The 1,3,6,8- and 1,3,7,9-T_4CDD pair is formed by two chlorine loss that occurs in the reaction of two 2,4,6-T_3CP precursors. The 1,3,7,8-, 1,2,6,8-, and 1,2,7,9-T_4CDD pair is formed by the loss of one chlorine in the combination of 3,4-DCP and 2,4,6-T_3CP precursors. These results demonstrate that CDD products are formed by the loss of one chlorine from combination of chlorinated phenol precursors without *ortho* chlorine (phenol, 3-CP, 3,4-DCP) and with two *ortho* chlorine (2,4,6-T_3CP). The 2,4,6-T_3CP is known as most reactive precursor to form CDD products between chlorinated phenols with two *ortho* chlorine (Mulholland and Ryu, 2001). Results shown here indicate 2,4,6-T_3CP also readily forms CDD products by combination with phenols without *ortho* chlorine, such as phenol, 3-CP and 3,4-DCP. Chlorinated phenol products are likely responsible for some CDD products formed in low yields.

Little variation in the CDD isomer distributions with temperature was observed, even though the total CDD yield did vary significantly. This is also evidenced by the small standard deviation in isomer fractions for the six experiments.

Chlorinated phenol precursor pairs were assigned to each major CDD product. To assess the relative CDD formation propensities of the chlorinated phenol reactants studied. The result, shown in Fig. 7, indicates the ranking of CDD formation potential for the four chlorinated phenol reactants is as follows: 2,4,6-$T_3CP \gg$ 3-CP > phenol > 3,4-DCP.

The bottom panel of Fig. 7 indicates the reactivity of phenol, 3-CP and 3,4-DCP to produce CDD products by combination with 2,4,6-T_3CP. The CDD formation

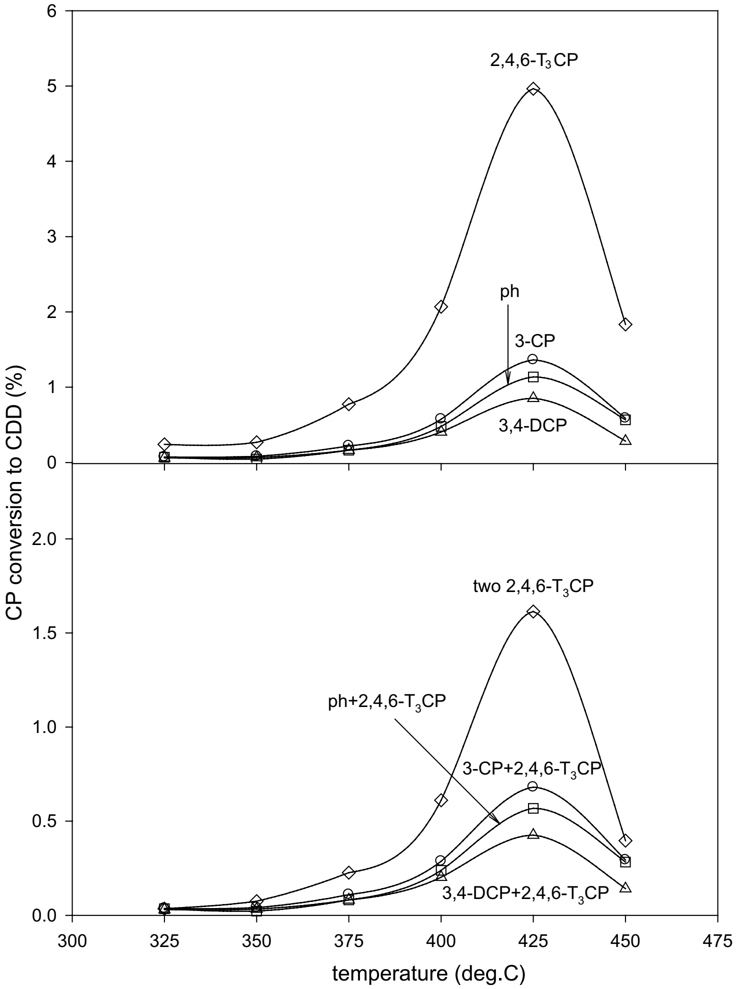

Fig. 7. CDD formation propensity of phenol, 3-CP, 3,4-DCP, and 2,4,6-T_3CP.

potential of phenol, 3-CP, and 3,4-DCP was much less than that of two 2,4,6-T_3CP. Thus, CDD formation by one chlorine loss occurs at much lower rate than CDD formation by two chlorine loss from chlorinated phenols that have two *ortho* chlorines.

4. Conclusion

The formation of CDD and CDF products on copper(II) chloride ($CuCl_2$) from phenol, 3-CP, 3,4-DCP, and 2,4,6-T_3CP was observed. CDF formation is favored over CDD formation. CDD products are formed by loss of one chlorine from chlorinated phenols without *ortho* chlorine with chlorinated phenols with two *ortho* chlorine. CDD/F isomer patterns are largely independent of temperature; therefore, the isomer patterns may provide a fingerprint for CDD/F formation by this mechanism. Phenol chlorination by $CuCl_2$ is also controlled by steric and electronic factors and plays an important role in higher chlorinated CDD/F formation and in much broader CDD/F isomer formation.

Results reported here and two previous publications (Mulholland and Ryu, 2001; Ryu and Mulholland, 2002) provide a complete experimental investigation of CDD/F formation by phenol condensation on particles containing copper(II) chloride.

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