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Formation of chlorinated phenols, dibenzo-*p*-dioxins, dibenzofurans, benzenes, benzoquinnones and perchloroethylenes from phenols in oxidative and copper (II) chloride-catalyzed thermal process

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Abstract

Formation of polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and chlorinated phenols on $CuCl_2$ from unsubstituted phenol and three monochlorophenols was studied in a flow reactor over a temperature range of 100–425 °C. Heated nitrogen gas streams containing 8.0% oxygen were used as carrier gas. The 0.00024 mol of unsubstituted phenol and 0.00039 mol of each monochlorophenol were passed through a 1 g and 1 cm SiO_2 particle containing 0.5% (Cu by mass) $CuCl_2$. Chlorination preferentially occurred on *ortho*-(2, 6) and *para*-(4) positions. Chlorination increased up to 200 °C, and thereafter decreased as temperature increased. Chlorination of phenols plays an important role in the formation of the more chlorinated PCDD/Fs. Chlorinated benzenes are formed possibly from both chlorination of benzene and chlorodehydroxylation of phenols. Chlorinated phenols with ortho chlorine formed PCDD products, and major PCDD products were produced via loss of one chlorine. For PCDF formation, at least one unchlorinated ortho carbon was required.

Keywords: Phenol condensation pathways; Chlorophenols; $CuCl_2$-catalyzed formation; Chlorination; PCDD/F formation mechanism; Thermal process

1. Introduction

Copper chloride ($CuCl_2$) can lead to aromatic condensation reactions as well as chlorination reactions of aromatics at temperatures between 250 and 450 °C. (Stieglitz et al., 1989; Vogg and Stieglitz, 1989). Condensation reactions can take place via precursors such as chlorinated phenols or benzenes. Chlorination also occurs via precursors or PCDD/Fs (Addink and Olie, 1995; Addink and Altwicker, 1998).

Two chlorination mechanisms based on copper chloride have been proposed. First, the Deacon reaction leads to molecular chlorine formation. In the Deacon reaction, $CuCl_2$ is a catalyst. The aromatic molecules are chlorinated by Cl_2 (or $Cl\cdots Cl$) as following.

$$4HCl + O_2 \rightarrow 2Cl_2 + 2H_2O \qquad (1)$$

$$ArH + Cl \cdots Cl \rightarrow ArCl + HCl \qquad (2)$$

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

$$ArH + CuCl_2 \rightarrow ArHCl^{\cdot} + CuCl \qquad (3)$$

$$ArHCl^{\cdot} + CuCl_2 \rightarrow ArCl + CuCl + HCl \qquad (4)$$

Born et al. (1993) found that $CuCl_2$ chlorination preferably occurs on the ortho and para positions of phenol. The hydroxyl group (OH) is pivotal for adsorption/chemisorption at the particle surface to enable chlorination.

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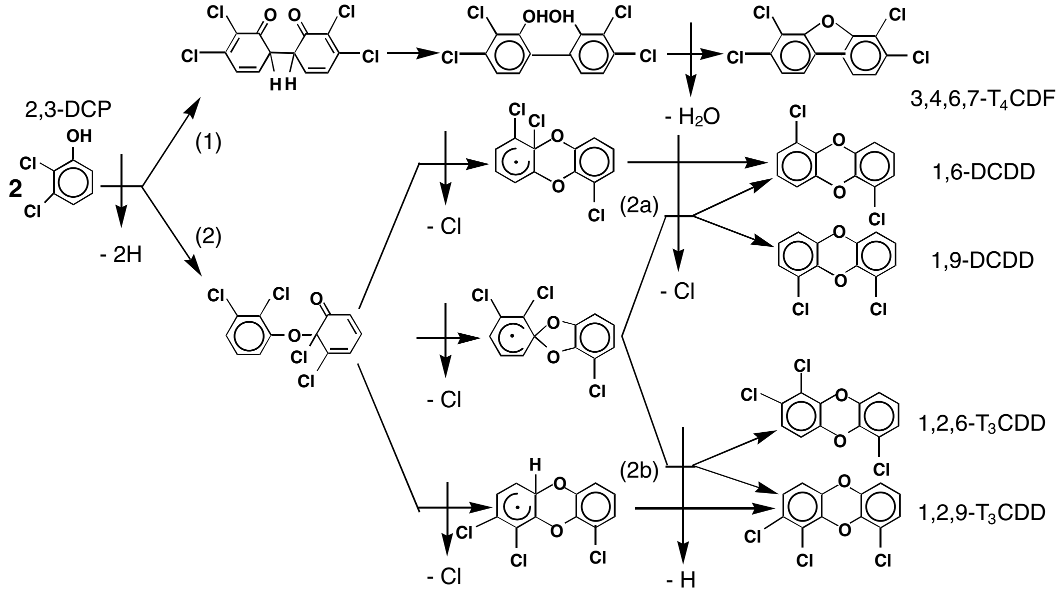

Fig. 1. PCDD/F formation pathways from 2,3-dichlorophenol (DCP).

A chlorinated phenol molecule after chemisorption on the fly ash can undergo various reactions, such as isomerization, oxidative breakdown, chlorination and/or condensation, before distinct products (CO_2, CBz, PCDDs) are released.

To illustrate the PCDD/F formation mechanism, gas-phase pathways from 2,3-DCP are shown in Fig. 1. PCDF formation most likely occurs by carbon–carbon coupling of phenoxyl radicals at ortho positions (pathway 1). Such coupling requires at least one unsubstituted ortho carbon in each reactant and leads to the keto-tautomer of the *o*,*o*′-dihydroxybiphenyl (DOHB) intermediate. Subsequent enolizations restore aromaticity to the molecule, producing the more stable DOHB intermediate. Loss of H_2O from DOHB yields 3,4,6,7-T_4CDF with no loss of chlorine.

The formation of PCDD, on the other hand, results via the coupling of a phenolic oxygen to a chlorinated ortho carbon of a second phenoxy radical, producing the keto-tautomer of *o*-phenoxyphenol (POP) (pathway 2). Subsequent loss of a chlorine atom produces a resonance-stabilized phenoxy–phenoxy radical, which can undergo a five-member ring closure similar to a Smiles rearrangement. Ring expansion with elimination of a second chlorine atom results in the formation of a pair of 1,6- and 1,9-DCDD isomers (pathway 2a). Also, ring expansion with elimination of the hydrogen atom results in the formation of a pair of 1,2,6- and 1,2,9-T_3CDD isomers (pathway 2b). A six-member ring closure with elimination of the chlorine or hydrogen atom leads only to 1,6-DCDD and 1,2,9-T_3CDD congeners.

In this paper, results are presented on direct chlorination and condensation of unsubstituted phenol and the three monochlorophenols. Questions addressed are as follows.

(1) At what temperatures does chlorination occur?
(2) To what extent does chlorination occur? Is pentachlorophenol (PCP) formed? What is the pattern of chlorination?
(3) At what temperatures does phenol condensation occur to form PCDD/Fs?
(4) What is the effect of chlorine substitution at phenol, ortho, meta, or para sites on PCDD/F formation?

2. Experimental methods

Experiments were conducted in an electrically heated, quartz tube flow reactor, 40 cm in length and 1.7 cm in diameter. A nominal residence time in the quartz tube reactor was 15 s. Separate experiments were performed with unsubstituted phenol (Ph), 2-chlorophenol (2-CP), 3-chlorophenol (3-CP), and 4-chlorophenol (4-CP). The phenol reactants were placed in a heated glass vessel and vaporized in a gas stream consisting of 92% nitrogen and 8% oxygen. The amounts of reactants used were about 0.00024 mols for unsubstituted phenol and about 0.00039 mols for each monochlorophenol. A 1 g particle bed of 1 cm height, consisting of SiO_2 (99.6% purity, 325 mesh) and 0.5% (mass) $CuCl_2$ (anhydrous, 99.999+% purity), was located at the center of the reactor. Experiments were carried out in 25 °C increments at a gas velocity of 2.7 cm/s over a temperature range from 100 °C to 425 °C for phenol and from 300 °C to 425 °C for each monochlorophenol. Gas flow rate was changed to keep a constant residence time. The duration of each experiment was approximately 10 min for unsubstituted phenol and 20 min for three monochlorophenols.

The entire product gas stream was rapidly quenched and aromatic tar samples were collected in an ice-cooled dichloromethane trap. Sample and rinse solutions were combined and filtered, 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/PCDF 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 as well as gas-phase synthesis experiments from single precursors and precursor pairs. Seventy-four of 75 PCDD congeners and 121 of 135 PCDF congeners have been synthesized. A universal response factor was used for PCDDs and PCDFs based on dibenzo-*p*-dioxin (DD) and dibenzofuran (DF), respectively.

3. Results and discussion

3.1. Overall products

Experiments with pure unsubstituted phenol and monochlorophenols were conducted over a temperature range of 100 °C–425 °C for phenol and from 300 °C to 425 °C for monochlorophenols. Reactant recoveries of phenol and three monochlorophenols and all other product yields are shown in Fig. 2. At low temperature, much higher reactant recoveries were obtained. The recoveries of phenol reactants decreased with increasing temperature. The major products were chlorinated phenols (CP), perchloroethylene (PCE), chlorinated benzenes (CBz), chlorinated benzoquinnones (CQ), chlorinated dibenzofuran (PCDF), and chlorinated dibenzo-*p*-dioxin (PCDD).

At 100 °C, the unsubstituted phenol recovery was 98% and about 1% of the chlorinated phenols and 0.1% of the chlorinated benzenes were formed. The yield of chlorinated phenols increased with temperatures up to 200 °C. A maximum 6.3% yield of chlorinated phenols was obtained at 200 °C, and then decreased as temperature increased. PCE was detected at 250 °C, and had a maximum yield of 0.7% between 350 °C and 425 °C. Chlorinated benzenes increased with temperature, with a maximum yield of about 0.15% at 425 °C. Dibenzofuran (DF) was formed from condensation of unsubstituted phenol pairs. The yield of DF increased with temperature, with a maximum 0.06% of yield at 425 °C. Dibenzo-*p*-dioxin (DD) was formed in small amounts, with a maximum 0.002% yield at 425 °C.

Monochlorophenol reactant recovery at 300 °C was 73.3%, 71.9%, and 63.4% for each monochlorophenol. The recovery of monochlorophenol reactants also decreased with increasing temperature. PCE was produced in abundant amounts over all the temperature range for each of the three monochlorophenols. The yield of PCE increased up to 375 °C, and thereafter decreased as temperature increased. A maximum yield of PCE was about 8%, 11%, and 7.6% for 2-CP, 3-CP and 4-CP, respectively at

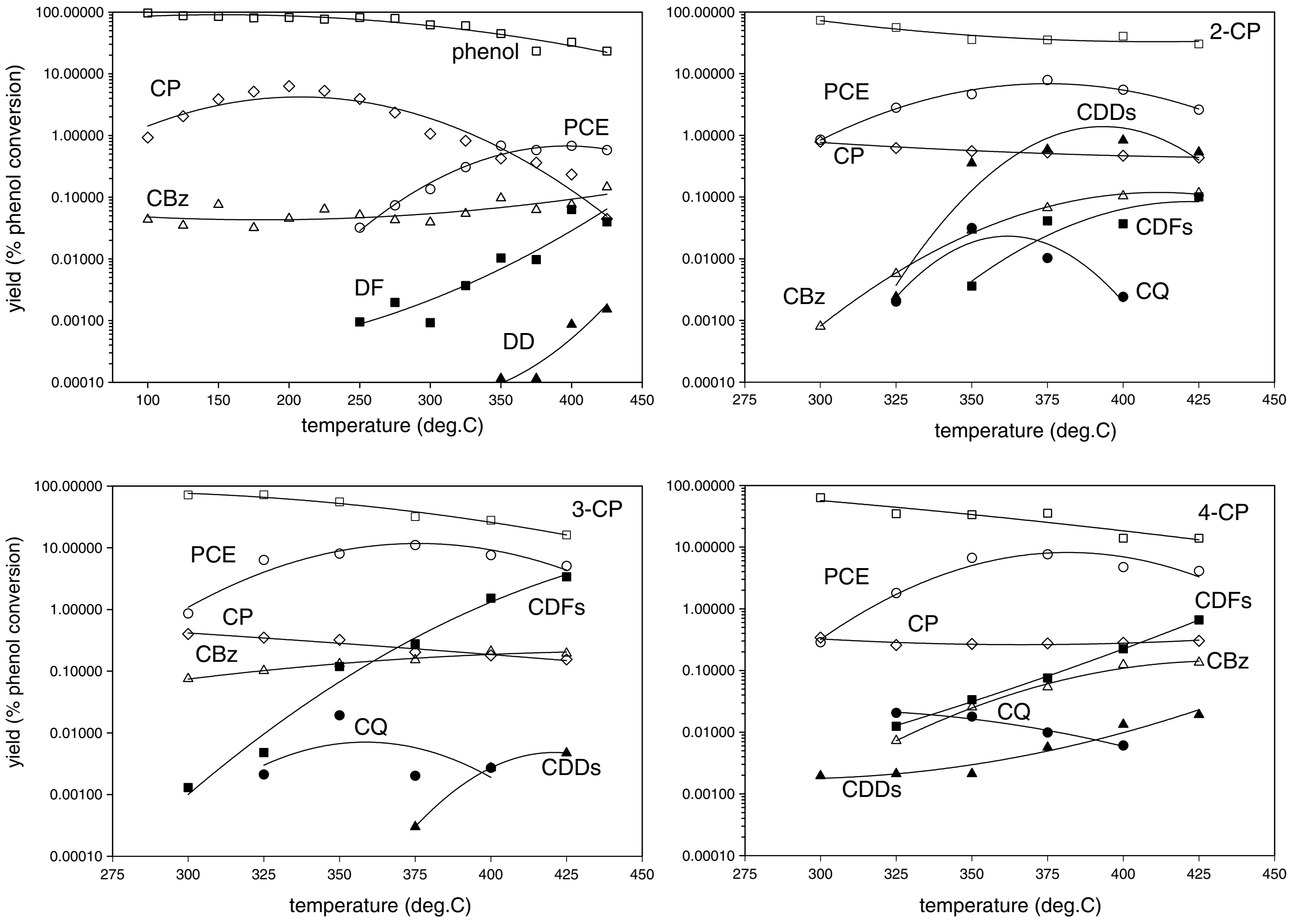

Fig. 2. Phenol reactant recoveries and other product yields.

375 °C. A higher amount of PCE was formed but only 0.7% of PCE yield was obtained from unsubstituted phenol experiment.

Chlorinated phenol products were formed at 300 °C and thereafter decreased with increasing temperature. Maximum yields of chlorinated phenols were 0.77%, 0.40%, and 0.34%, respectively at 300 °C. In unsubstituted phenol experiments over a temperature range from 100 °C to 425 °C, the total yield of chlorinated phenol products was observed to peak at 200 °C. This is consistent with the results shown in Fig. 2 in which chlorinated phenol yields decrease with temperatures above 300 °C.

Chlorinated benzene products also started to form at 300 °C and increased with increasing temperature. Maximum yields of chlorinated benzenes were about 0.11%, 0.20%, and 0.13% for 2-CP, 3-CP, and 4-CP, respectively, at 400–425 °C.

For PCDD/F formation, 2-CP produced 0.83% yields of PCDDs and 0.10% yields of PCDFs at 400 °C and 425 °C. 3-CP produced 0.005% yields of PCDDs and 3.4% yields of PCDFs at 425 °C; 4-CP reactant formed 0.02% yields of PCDDs and 0.66% yields of PCDFs at 425 °C. Also, chlorinated benzoquinones (CQ) were detected between 325 °C and 400 °C, which is a little lower than that of a maximum PCDD/F formation. This compound was not produced from unsubstituted phenol. A maximum yield of CQ was 0.03% at 350 °C from 2-CP. 3-CP produced 0.02% yield at 350 °C. 4-CP produced 0.02% of a maximum yield at 325 °C. A possible explanation of the mechanism of CQ formation will be discussed later.

3.2. Phenol chlorination

Chlorinated phenol product distributions are shown in Table 1. Chlorination products at ortho (2, 6) and para (4) sites were observed for unsubstituted and three monochlorophenols. This result is consistent with previous research by others. Chlorination of phenol has been found to involve only ortho and para positions (Born et al., 1993).

However, the temperature at which maximum chlorination occurred was different. Born et al. (1993) found chlorination was favored at a temperatures range of 350–450 °C. Different chlorination mechanisms, such as the Deacon reaction and direct chlorination, may explain the divergent findings. The direct chlorination reaction by $CuCl_2$ was found to occur at a much lower temperature (150 °C) than Deacon controlled (400 °C) chlorination (Taylor et al., 1998). Gullett et al. (1990) found that the chlorination of phenols in the gas phase takes place most effectively in the temperature region of 300–400 °C.

Phenol produced 2-, 4-, 2,4-, 2,6-, 2,4,6- chlorinated phenols. The maximum yield of 2-CP and 4-CP was 4.76% and 1.15%, respectively at 200 °C. The chlorination product 2,4-DCP was preferred over 2,6-DCP. The chlorination pattern is as follows:

$$\text{Phenol} \rightarrow 2-\text{CP} > 4-\text{CP} \rightarrow 2,4-\text{DCP} > 2,6-\text{DCP} \\ \rightarrow 2,4,6-T_3\text{CP}$$

In 2-CP experiments, only three chlorinated phenols (2,4-DCP, 2,6-DCP, 2,4,6-T_3CP) were produced. Maximum yields were observed at 300 °C. 2,4-DCP was favored over 2,6-DCP at all temperatures except 425 °C.

In 3-CP experiments over temperature range of 300–425 °C, 2,3-, 2,5-, and 3,4-DCP were derived from ortho/para chlorination, with 2,5-$\gg$2,3-$>$3,4-DCP. This result might be explained by a statistical factor.

3-CP has two ortho sites (2, 6) and one para (4) site to be chlorinated. Chlorination of ortho sites is favored over chlorination at the para site, with 2,3- and 2,5-DCP

Table 1
Yields of chlorinated phenol products (percent phenol conversion)

Reactant	Products	Temperature (°C)													
		100	125	150	175	200	225	250	275	300	325	350	375	400	425
Phenol	2-CP	0.769	1.639	3.083	4.040	4.761	3.892	3.030	1.841	0.960	0.758	0.413	0.356	0.230	0.041
	4-CP	0.154	0.394	0.694	0.887	1.149	0.998	0.646	0.338	0.066	0.047	0.010	0.008	0.004	0.002
	2,4-DCP	0.006	0.018	0.085	0.201	0.393	0.394	0.223	0.174	0.036	0.016	0.002	0.000	0.000	0.000
	2,6-DCP	0.000	0.000	0.000	0.000	0.004	0.008	0.004	0.003	0.000	0.000	0.000	0.000	0.000	0.000
	2,4,6-T_3CP	0.000	0.000	0.000	0.000	0.000	0.006	0.006	0.005	0.001	0.000	0.000	0.000	0.000	0.000
2-CP	2,4-DCP									0.379	0.312	0.282	0.280	0.238	0.204
	2,6-DCP									0.282	0.257	0.229	0.226	0.219	0.216
	2,4,6-T_3CP									0.128	0.053	0.044	0.024	0.012	0.015
3-CP	2,5-DCP									0.262	0.228	0.227	0.139	0.128	0.110
	2,3-DCP									0.061	0.055	0.051	0.032	0.030	0.024
	3,4-DCP									0.044	0.042	0.027	0.019	0.013	0.014
	2,4,5-T_3CP									0.021	0.013	0.011	0.007	0.006	0.004
	2,3,4-T_3CP									0.005	0.004	0.002	0.001	0.001	0.001
	2,3,6-T_3CP									0.006	0.006	0.002	0.002	0.002	0.001
	2,3,4,6-T_4CP									0.002	0.004	0.002	0.002	0.001	0.000
4-CP	2,4-DCP									0.305	0.238	0.262	0.264	0.266	0.294
	2,4,6-T_3CP									0.037	0.020	0.007	0.011	0.015	0.009

produced preferentially over 3,4-DCP. In 4-CP experiments, only two chlorinated phenols were formed, showing that chlorination is favored at ortho sites.

The ratio of ortho/para chlorinated phenol product yields was calculated at temperatures between 100 and 425 °C for unsubstituted phenol, and between 300 and 425 °C for monochlorophenols. Results are shown in Fig. 3. Chlorination at ortho site(s) increases with increasing temperature. Chlorination at ortho sites is favored over chlorination at the para site for unsubstituted phenol and 3-CP. Ratios of ortho/para chlorinated phenols (2-/4-CP) from phenol chlorination are between 4 and 64, and between 5 and 10 (2,5-/3,4-DCP) and 1.3 and 2.7 (2,3-/3,4-DCP) from 3-CP chlorination. But ratios ranged only from 0.7 to 1.1 (2,6-/2,4-DCP) from 2-CP chlorination.

In chlorination, the ortho/para directing OH group of phenol is explained by the electrophilic aromatic substitution mechanism (Luijk et al., 1994). Electron densities at each carbon of the phenols were calculated using the semi-empirical molecular orbital method (PM3) with optimal conformation. Results are shown in Table 2. The bold figures in Table 2 represent the highest electron density at each atom that can be chlorinated. Chlorination is favored at carbons with high electron density. For example, phenol has three carbons with high electron density: the two ortho (2, 6) carbons and one para (4) carbon. Moreover, 2- and 6-carbons have the same electron density, which is higher than the density of the 4-carbon. This is consistent with results in the phenol experiment in which 2-CP produced more than 4-CP.

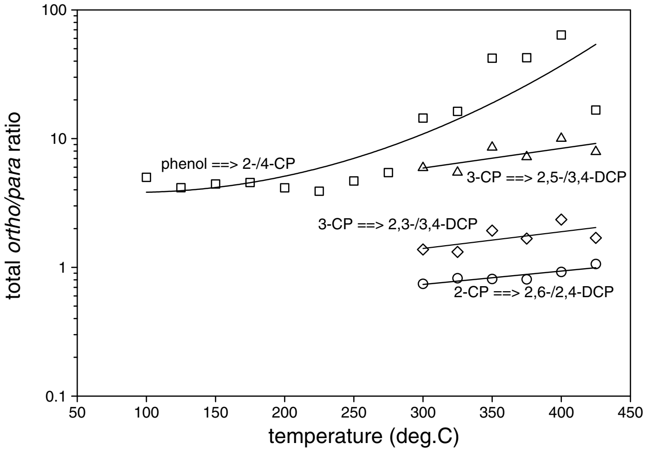

Fig. 3. Ortho/para ratios of chlorinated phenol products.

Table 2
Electron densities of chlorinated phenol carbon atoms

PM3	C-1	C-2	C-3	C-4	C-5	C-6
Phenol	3.9013	**4.1702**	4.0611	4.1444	4.0611	**4.1702**
2-CP	3.8988	4.1725	4.0683	4.1314	4.0596	**4.1858**
3-CP	3.8875	4.1480	4.0863	4.1471	4.0450	**4.1988**
4-CP	3.9002	**4.1585**	4.0613	4.1657	4.0613	**4.1585**

Calculated by PM-3 method.

Thus, the major factors controlling the phenol chlorination pattern appear to be electronic (electron density) and statistical (number of equivalent chlorination sites due to molecular symmetry).

Weber and Hagenmaier (1999a) reported that the most abundant chlorophenols are ortho and para chlorinated phenols such as 2,4-DCP, 2,4,6-T_3CP, 2,3,4,6-T_4CP, and PCP. This distribution could be explained from ortho/para chlorination of unsubstituted phenol. The concentration of unsubstituted phenol in the gas effluent of MWI (municipal waste incinerators) is more than 100 times higher than that of chlorinated phenols (Weber and Hagenmaier, 1999b). Therefore, phenol chlorination is a possible source of abundant chlorinated phenols.

Yamamoto and Inoue (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: namely, 2,4,6-T_3CP, 2,3,4,6-T_4CP and PCP.

3.3. PCDD/Fs formation

Results, shown in Table 3, indicate total PCDD/F yield and isomer distribution from phenol reactants over all temperature ranges. The primary CDD/F products are DF (phenol), DD/1-MCDD/4,6-DCDF (2-CP), 1,7/3,7/1,9-DCDF (3-CP), 2,8-DCDF (4-CP), respectively. The gas-phase PCDD/F formation pathway is shown in Fig. 4.

Small amounts of secondary PCDD/F products were produced from chlorinated phenol products. 1,3/1,7/1,8-DCDD isomers are formed from 2-CP and 2,4-DCP, and 1,6/1,9-DCDD isomers are formed from 2-CP and 2,6-DCP by the loss of one chlorine (Ryu and Mulholland, 2002) or two 2,6-DCP by the loss of two chlorine (Mulholland and Ryu, 2001). Condensation of 2-CP and 2,4,6-T_3CP by the loss of one chlorine or 2,6-DCP and 2,4,6-T_3CP by the loss of two chlorine produced 1,3,6-T_3CDD isomer. 3-CP also produced secondary PCDD/F products, 2,7/2,8/1,7/1,8-DCDD isomers from 3-CP and 2,5-DCP by one chlorine loss, only 1,2,7/2,3,9-T_3CDF from 3-CP and 3,4-DCP that can form 1,2,7/2,3,9/2,3,7/1,29-T_3CDF isomers. Secondary PCDD/F, 2,7/2,8-DCDD, 1,3,7/1,3,8-T_3CDD and 2,4,8-T_3CDF were produced from reactant 4-CP and 2,4-DCP or two 2,4-DCP formed from chlorination.

Three monochlorophenols have different chlorine substitution patterns called ortho, meta, and para. Each of the three different chlorine substitution patterns shows a different propensity for PCDD/F formation. A maximum yield of PCDD/F from 2-CP reactant was 1.53% phenol conversion on PCDD at 400 °C and 0.1% phenol conversion at 425 °C. 3-CP produced a maximum yield of 0.005% phenol conversion on PCDD, and 3.38% phenol conversion on PCDF at 425 °C. 4-CP produced a maximum 0.019% PCDD yield of phenol conversion, and 0.66% of phenol conversion on PCDF at 425 °C. 2-CP has the greatest propensity to form PCDD, but is likely the least inclined to form PCDF products. 3-CP has the greatest propensity to form PCDF, but is the least to form PCDD products.

Table 3
PCDD/F yield (percent phenol conversion) and isomer distributions from phenols

Reactants	CDD/F products	Temperature (°C)								Isomer avg	Fraction st. dev.
		250	275	300	325	350	375	400	425		
Phenol	DF	0.0010	0.0020	0.0009	0.0037	0.0104	0.0097	0.0631	0.0399		
	DD	0.0000	0.0000	0.0000	0.0000	0.0001	0.0001	0.0009	0.0015		
	DD/DF	0.0000	0.0000	0.0000	0.0000	0.0110	0.0117	0.0137	0.0383		
2-CP	DD			0.0000	0.0000	0.0672	0.6217	0.6915	0.2863		
	2-MCDD			0.0000	0.0000	0.0152	0.0317	0.0411	0.0318	0.0482	0.0258
	1-MCDD			0.0000	0.0024	0.3293	0.5349	0.7511	0.4778	0.9518	0.0258
	13-DCDD			0.0000	0.0000	0.0045	0.0157	0.0327	0.0191	0.7327	0.1324
	46-DCDF			0.0000	0.0000	0.0036	0.0412	0.0369	0.1006		
	16/17/18-DCDD			0.0000	0.0000	0.0042	0.0061	0.0077	0.0050	0.2644	0.1264
	19-DCDD			0.0000	0.0000	0.0001	0.0000	0.0000	0.0000	0.0029	0.0064
	136-T3CDD			0.0000	0.0000	0.0000	0.0006	0.0014	0.0004		
	total CDD			0.0000	0.0024	0.4206	1.2106	1.5254	0.8204		
	total CDF			0.0000	0.0000	0.0036	0.0412	0.0369	0.1006		
	CDD/CDF					115.54	29.41	41.35	8.15		
3-CP	17-DCDF			0.0013	0.0048	0.1150	0.2629	1.3967	2.9331	0.9297	0.0529
	37-DCDF			0.0000	0.0000	0.0027	0.0104	0.0913	0.3679	0.0576	0.0470
	19-DCDF			0.0000	0.0000	0.0007	0.0041	0.0355	0.0698	0.0128	0.0088
	27/28-DCDD			0.0000	0.0000	0.0000	0.0003	0.0023	0.0036	0.9012	0.1188
	17/18-DCDD			0.0000	0.0000	0.0000	0.0000	0.0004	0.0011	0.0988	0.1188
	127/239-T3CDF			0.0000	0.0000	0.0008	0.0014	0.0028	0.0062		
	Total CDD			0.0000	0.0000	0.0000	0.0003	0.0027	0.0047		
	Total CDF			0.0013	0.0048	0.1193	0.2788	1.5262	3.3771		
	CDD/CDF			0.0000	0.0000	0.0000	0.0010	0.0018	0.0014		
4-CP	28-DCDF			0.0000	0.0125	0.0337	0.0758	0.2256	0.6606		
	27/28-DCDD			0.0020	0.0021	0.0021	0.0057	0.0125	0.0185		
	248-T3CDF			0.0000	0.0000	0.0000	0.0000	0.0000	0.0001		
	137/138-T3CDD			0.0000	0.0000	0.0000	0.0000	0.0008	0.0007		
	Total CDD			0.0020	0.0021	0.0021	0.0057	0.0133	0.0192		
	Total CDF			0.0000	0.0125	0.0337	0.0758	0.2256	0.6607		
	CDD/CDF				0.1690	0.0629	0.0748	0.0589	0.0291		

Only phenols with chlorine in the ortho position are capable of forming PCDD. But ortho chlorine is not available in either 3- or 4-CP, and these have a higher probability of forming PCDF products. In Table 3, the ratio of total PCDD/F product shows that 4-CP has a much higher propensity to form PCDD products compared to 3-CP. The PCDD/F ratio decreased as temperatures increased.

This result is consistent with the gas-phase experiment. Weber and Hagenmaier (1999a), reported that ortho/para chlorinated phenols are very reactive to form POP (phenoxyphenol), intermediate for PCDD and meta chlorinated phenols favored the formation of DOHB (dehydroxybiphenyls), intermediate for PCDF. This finding is also consistent with previous gas-phase results (Nakahata and Mulholland, 2000), which suggested that chlorine substitution at phenol meta carbons (3 and 5) favors PCDF formation over chlorine substitution at the para carbon (4).

3.4. *(Chloro-) benzenes formation*

In this section, chlorinated benzene homologue and isomer distributions are addressed to identify the mechanism of chlorinated benzenes. Average homologue and isomer fractions of chlorinated benzenes with standard deviation are shown Table 4. Bold figures represent the most abundant homologue and isomer groups.

Phenol produced monochlorobenzene (MCBz) in the most abundant amount, showing 95% of chlorobenzene homologue group. Dichlorobenzene (DCBz) was the most abundant homologue group, about a 70% fraction, of all chlorinated benzenes, from three monochlorophenols and the most abundant DCBz isomers were different depending on the substitution pattern. 1,2-DCBz isomer was about 97% from 2-CP, and 1,3-DCBz isomer was about 99% from 3-CP, and 1,4-DCBz was about 99% from 4CP. Thus, MCBz, 1,2-, 1,3-, and 1,4-DCBz were likely produced by chlorodehydroxylation of phenol, 2-CP, 3-CP, and 4-CP, respectively. Born et al. (1993) also reported polychlorinated benzenes are formed by chlorodehydroxylation of chlorinated phenols.

In a previous study (Ryu, Ph.D, Dissertation, 2002), the formation of chlorinated benzenes shows the following patterns: MCBz, 1,2-DCBz, 1,2,3-T_3CBz, 1,2,3,4-T_4CBz. Chlorinated benzenes could be formed from either chlorination of major DCBz isomers or from chlorodehydroxylation of chlorinated phenol products.

For the 2-CP experiment, the isomer fraction of 1,2,4-T_4CBz and 1,2,3-T_3CBz is 0.62 and 0.38. 1,2,4-T_3CBz

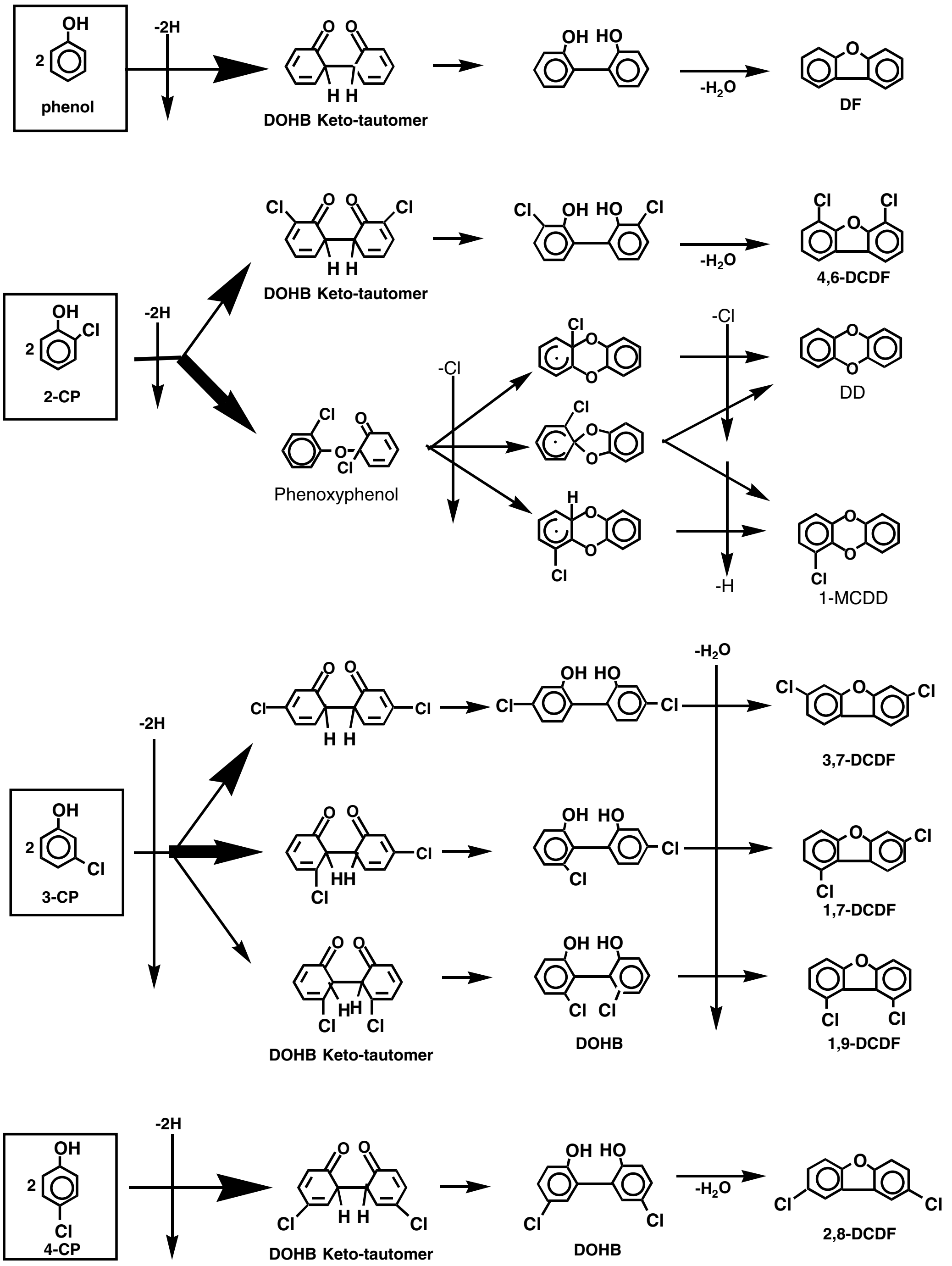

Fig. 4. Pathways of PCDD/F formation from phenols.

could formed from chlorinated phenol products, 2,4-DCP and 1,2,3-T$_3$CBz from 2,6-DCP, by chlorodehydroxylation, and 1,2,3-T$_3$CBz also could be from chlorination of 1,2-DBz. 1,2,3,5-T$_4$CBz is formed from 2,4,6-T$_3$CP, and 1,2,3,4-T$_4$CBz is produced from chlorination of either 1,2,4-T$_3$CBz or 1,2,3-T$_3$CBz (2,3,6-T$_3$CP is not available for 1,2,3,4-T$_4$CBz formation by chlorodehydroxylation).

3-CP produced about 70% of 1,2,4-T$_3$CBz and 30% of 1,2,3-T$_3$CBz. 1,2,4-T$_3$CBz is formed from 2,5- and 3,4-DCP. 1,2,3-T$_3$CBz is formed from either 2,3-DCP or chlorination of 1,3-DCBz already formed. 1,2,4,5-T$_4$CBz is formed from 2,4,5-T$_3$CP. 1,2,3,4-T$_4$CBz is formed from 2,3,4- and 2,3,6-T$_3$CP or chlorination of 1,2,3-T$_3$CBz.

4-CP produced 1,2,4-T$_3$CBz that is possibly formed from 2,4-DCP. 1,2,3,5-T$_4$CBz is formed from 2,4,6-T$_3$CP and 1,2,3,4-T$_4$CBz is formed from chlorination of 1,2,4-T$_3$CBz. Isomer distributions of chlorinated benzene from phenol are very similar to that of the chlorinated benzene formed from benzene only chlorination discussed in a previous study (Ryu, Ph.D. Dissertation, 2002). But here, 1,2-

Table 4
Chlorinated benzene average homologue and congeners distributions

Homologues	Phenol		2-CP		3-CP		4-CP	
	Avg.	St. dev.	Avg.	St. dev.	Avg.	St. dev.	Avg.	St. dev.
MCBz	**0.9506**	0.0693	0.0467	0.0761	0.0288	0.0465	0.0466	0.0578
DCBz	0.0331	0.0512	**0.7066**	0.0654	**0.7474**	0.0976	**0.7578**	0.0289
T$_3$CBz	0.0149	0.0228	0.1514	0.0872	0.1469	0.0741	0.1282	0.0445
T$_4$CBz	0.0005	0.0010	0.0501	0.0326	0.0465	0.0236	0.0475	0.0334
P$_5$CBz	0.0004	0.0009	0.0191	0.0205	0.0238	0.0206	0.0173	0.0171
H$_6$CBz	0.0006	0.0020	0.0261	0.0342	0.0066	0.0070	0.0025	0.0031
Isomers								
1,3-DCBz	0.0189	0.0302	0.0239	0.0324	**0.9961**	0.0070	0.0015	0.0030
1,4-DCBz	0.0630	0.1176	nd	nd	0.0024	0.0041	**0.9985**	0.0030
1,2-DCBz	**0.9180**	0.1112	**0.9761**	0.0324	0.0014	0.0030	nd	nd
1,3,5-T$_3$CBz	nd	nd	0.0004	0.0012	0.0002	0.0007	nd	nd
1,2,4-T$_3$CBz	nd	nd	**0.6181**	0.0873	**0.6992**	0.1181	**1.0000**	0.0000
1,2,3-T$_3$CBz	**1.0000**	0.0000	0.3815	0.0872	0.3006	0.1181	nd	nd
1,2,3,5-T$_4$CBz	nd	nd	**0.8199**	0.0939	0.1226	0.0682	**0.8694**	0.1050
1,2,4,5-T$_4$CBz	nd	nd	nd	nd	0.4010	0.1474	0.0011	0.0031
1,2,3,4-T$_4$CBz	**1.0000**	0.0000	0.1801	0.0939	**0.4764**	0.0957	0.1295	0.1047

DCBz is 92% of total DCBz, while it was only 55% in benzene chlorination. This high formation of 1,2-DCBz is attributed to higher formation of 2-CP than 4-CP. 1,2-DCBz is formed from 2-CP and 1,4-DCBz is produced from 4-CP by chlorodehydroxylation.

3.5. Perchloroethylene (PCE) formation

The yield of PCE from phenols was higher from three monochlorophenols than from phenol (Fig. 2). Born et al. (1993) also reported comparable quantities of PCE are formed at 427 °C. They mentioned that the PCE product very likely results from ring opening oxidative breakdown of chlorinated phenols. Furthermore, they suggested that PCE should be monitored in municipal waste incinerator effluent gases as a possible indicator of PCDD/F emissions. Other researchers also have mentioned PCE formation in fly ash catalyzed reactions (Jay and Stieglitz, 1991; De Leer et al., 1989). Little research has been done on the mechanism of PCE formation and more study is needed.

3.6. Chlorinated benzoquinones formation

Chlorinated benzoquinone compounds were detected in very small amounts over the temperature range 325–400 °C in the 2-CP, 3-CP and 4-CP experiments (Fig. 5). Unsubstituted phenol produced no chlorinated benzoquinone compounds. Each monochlorophenol produced a dichlorinated benzoquinone (e.g. 2,6-dichloro-1,4-benzoquinone). In addition, 3-CP produced a small amount of another trichlorobenzoquinone. Possible molecular structures of chlorinated quinone products are shown in Fig. 6.

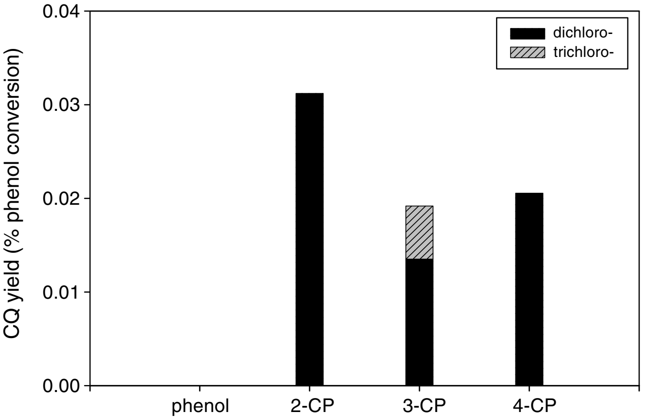

Fig. 5. Yields of chlorinated quinones from monochlorophenols at 350 °C.

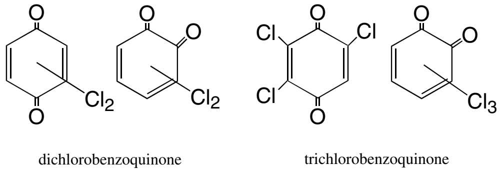

Fig. 6. Molecular structures of chlorinated quinone compounds.

Quinone compounds were produced from chlorinated phenols in another study (Johnson et al., 1999). The researchers proposed that the pathway to benzoquinone formation occurred by removal of the chlorine atom during electrochemical incineration of 4-chlorophenol, as shown in Fig. 7.

Basu and Wei (2000) 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 2,4-dichloro-1,6-benzoquinone and 3,5-dichloro-1,6-benzoquinone; which one occurs depends on which chlorine is removed. It was impossible

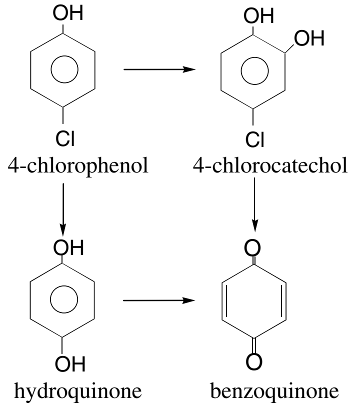

Fig. 7. Proposed pathway of benzoquinone formation from 4-CP (Johnson et al., 1999).

to distinguish between these two in the mass spectra because of their similar structure and identical molecular weights.

If the same formation mechanism is applied to the formation of chlorinated benzoquinones in this study, unchlorinated quinone should be formed from 2-CP and 4-CP by removal of chlorine. However, unchlorinated quinone was not observed. According to the Basu mechanism, 3-CP cannot produce quinone. However, in this study 3-CP formed di- and trichlorinated benzoquinone compounds. Only 3-CP produced a tetrachlorophenol (2,3,4,6-T_4CP) and a trichlorobenzoquinone. Therefore, chlorinated benzoquinones could be produced via the Basu mechanism from chlorinated phenol products formed from phenol reactant (2-, 3-, 4-CP) chlorination.

If CQ is formed from chlorinated phenols by replacing a Cl atom at an ortho or para site, why was no unchlorinated quinone formed from 2-CP or 4-CP, and no monochlorinated quinone formed from 2,4-DCP and 2,6-DCP? Perhaps these less chlorinated quinines do not desorb from the particle surface. The two oxygen substituents on quinone make it more likely to adsorb to the surface than other observed products. Therefore, a trichlorophenol is required to produce a dichlorobenzoquinone that does desorb. This explanation is consistent with the yields of the more chlorinated phenol products at 325–400 °C in this experiment.

On the other hand, the formation mechanism of chlorinated benzoquinone compounds on $CuCl_2/SiO_2$ might be different because of the very complex surface chemistry. More study is needed to identify the formation mechanism by which chlorinated benzoquinone compounds are formed.

4. Conclusions

The chlorination reaction and formation of PCDDs, PCDFs, and CP on $CuCl_2$ from unsubstituted phenol and three monochlorophenols was observed. Chlorination was favored on ortho and para carbon (2,4,6-) of phenols. At 200 °C, a maximum yield of chlorinated phenols was observed, yielding about 6.3% conversion. Controlling factors for chlorination appear to be electronic and statistical. Chlorinated benzenes are formed by chlorodehydroxylation of chlorinated phenols. Perchloroethylene and chlorinated benzoquinones are also formed from chlorinated phenols. A maximum yield of PCDD and PCDF formation was obtained at temperatures between 400 and 425 °C. Ortho and para chlorinated phenols have a greater propensity to form PCDD products and meta chlorinated phenols have a greater propensity to form PCDFs.

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