

POLYCHLORINATED NAPHTHALENE (PCN) AND DIBENZOFURAN (PCDF) CONGENER PATTERNS FROM PHENOL PRECURSORS IN THERMAL PROCESS: [I] A PRIORI HYPOTHESIS OF PCN AND PCDF FORMATION PATHWAYS FROM MONOCHLOROPHENOLS

Jae-Yong Ryu^{†,1}, Do Hyong Kim², Kum-Chan Choi³ and Jeong-Min Suh⁴

¹Environmental Research Team, Daegu-Gyeongbuk Development Institute, Daegu, Korea

²Environmental Engineering, Georgia Institute of Technology, Atlanta, GA, USA

³Department of Environmental Engineering, Dong-A University, Pusan, Korea

⁴Department of Regional Environmental System Engineering, Pusan National University, Miyeon, Korea

Abstract : The gas-phase formation of polychlorinated naphthalenes (PCNs) and dibenzofurans (PCDFs) was experimentally investigated by slow combustion of the three chlorophenols (CPs): 2-chlorophenol (2-CP), 3-chlorophenol (3-CP) and 4-chlorophenol (4-CP), in a laminar flow reactor over the range of 550 to 750°C under oxidative condition. Contrary to the a priori hypothesis, different distributions of PCN isomers were produced from each CP. To explain the distributions of polychlorinated dibenzofuran (PCDF) and PCN congeners, a pathway is proposed that builds on published mechanisms of PCDF formation from chlorinated phenols and naphthalene formation from dihydrofulvalene. This pathway involves phenoxy radical coupling at unsubstituted ortho-carbon sites followed by CO elimination to produce dichloro-9, 10-dihydrofulvalene intermediates. Naphthalene products are formed by loss of H and/or Cl atoms and rearrangement. The degree of chlorination of naphthalene and dibenzofuran products decreased as temperature increased, and, on average, the naphthalene congeners were less chlorinated than the dibenzofuran congeners. PCDF isomers were found to be weakly dependent to temperature, suggesting that phenoxy radical coupling is a low activation energy process. Different PCN isomers, on the other hand, are formed by alternative fusion routes from the same phenoxy radical coupling intermediate. PCN isomer distributions were found to be more temperature sensitive, with selectivity to particular isomers decreasing with increasing temperature.

Key Words : Municipal waste incinerator, Thermal process, Combustion, Polychlorinated Naphthalenes, Polychlorinated Dibenzofurans, Chlorophenol

INTRODUCTION

It has been known for some time that polychlorinated naphthalenes (PCNs) are formed from combustion processes along with polych-

lorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs).¹⁻²⁾ There are 75 PCN congeners containing one to eight chlorine atoms. Although data on the toxicity of individual PCNs are very limited, some PCNs are known to strongly bioaccumulate and to exhibit dioxin-like toxicity.³⁻⁶⁾ While substantial improvements in the understanding of thermal PCDD/PCDF formation

[†] Corresponding author

E-mail: jyryu@dgi.re.kr

Tel: +053-770-5112 , Fax: +053-770-5069

processes have resulted from extensive laboratory study, much less fundamental study of PCN formation has been conducted.

In 1975, Cypres and Bettens⁷⁾ first reported on naphthalene formation from phenol. Chlorinated phenols are known PCDD and PCDF precursors, as first reported in the late 1980s.⁸⁾ Since that time, many researchers have noted the simultaneous formation PCNs and PCDDs/PCDFs. In previous studies in this laboratory, formation of PCNs with PCDDs/PCDFs from chlorinated phenols was observed in gas-phase pyrolysis⁹⁾ and oxidation¹⁰⁾; however, no attempt was made to elucidate the detailed mechanism of PCN formation.

One possible mechanism of PCN formation from chlorinated phenols is based on reactions known to occur in the counterpart system without chlorine. Phenoxy radical decomposes via CO loss to produce the cyclopentadienyl (CPDyl) radical, and CPDyl radicals combine and rearrange to form naphthalene.¹¹⁻¹⁷⁾ The CPDyl radical is resonance-stabilized over all of its five carbon atoms. It has been shown to contribute to polycyclic aromatic hydrocarbon growth in flames. A detailed mechanism of naphthalene formation from CPDyl radicals was proposed by Melius *et al.*¹⁸⁾ using quantum chemical modeling methods. This mechanism has been extended to indene and other aromatic species containing external five-member rings.¹⁹⁾ Melius *et al.*¹⁸⁾ proposed dimerization of CPDyl radicals to form 9,10-dihydrofulvalene followed by conversion of five-member rings to six-member rings via radical rearrangements involving three-member ring closing and opening. Due to resonance, there are several alternative routes for the radical rearrangements shown. In the unchlorinated system, all of these routes lead to the same product - naphthalene. When chlorine is present, however, the alternative routes give rise to the formation of several PCN products from a single 9,10-dihydrofulvalene. This will be discussed later.

In a methane/air diffusion flame containing benzene, toluene, and styrene, McEnally and Pfeifferle²⁰⁾ concluded that naphthalene formed from CPDyl self-reaction was not significant

compared to naphthalene formed from propargyl addition to benzyl radical and from the H-abstraction/carbon-addition mechanism. In post-combustion gas, however, under conditions in which PCDDs and PCDFs are formed from chlorinated phenols, PCNs may be formed from chlorinated CPDyl radicals produced by chlorinated phenoxy radical decomposition.

Recently, Cieplik *et al.*²¹⁾ proposed reaction pathways for the formation of naphthalene in the thermal hydrogenolysis of dibenzo-*p*-dioxin and dibenzofuran. These reaction schemes involve radical intermediates similar in structure to the dihydroxybiphenyls and phenoxyphenols which are known to be intermediates in dibenzofuran and dibenzo-*p*-dioxin formation, respectively, from phenols. Therefore, an alternative hypothesis for the mechanism of PCN formation from phenols would be that phenoxy radical combination leads to intermediates of PCNs as well as PCDDs/Fs. Unlike the CPDyl radical in which all five carbon atoms are reactive, resonance in the phenoxy radical results in only three of its six carbon atoms (the *ortho*- and *para*- sites) as reactive sites. Thus, this alternative mechanism results in more isomer selectivity in the product distribution.

To test the first hypothesis that PCNs can be formed from chlorinated phenols via cyclopentadienyl radicals in post-combustion gas, the slow combustion of three chlorophenols (CPs) was studied in a flow reactor. This paper describes the experimental methods and approach, presents a *priori* predictions of PCN formation from CPs, shows the experimental results of congener-specific PCN and dioxin (PCDD and PCDF) measurements, and proposes a modified mechanism of PCN formation from phenols to account for differences between the *a priori* hypotheses and the experimental results. In addition, the effect of temperature on gas-phase PCN and PCDF formation from CPs was also investigated to gain further mechanistic insight on these processes.

MATERIALS AND METHODS

Experimental and Analytical Methods

Experimental setup is shown in Figure 1. A laminar flow, isothermal quartz tube reactor (40 cm in length and 1.7 cm in diameter) was used to study PCN formation from three chlorophenols (CPs). Two of the chlorophenols, 2-CP and 3-CP, were heated to liquid form and fed by syringe pump into a heated glass vessel where the reactant was vaporized and mixed with a nitrogen/oxygen gas stream. The third chlorophenol, 4-CP, formed a melt that was too viscous to be fed by syringe. This reactant was heated directly in the glass vessel and vaporized at the same rate as the syringe-fed liquid reactants were fed. The gas stream entering the reactor consisted of nitrogen with 8% oxygen and 0.3% CP vapor. The three CP reactants were obtained from Aldrich, Inc. (Milwaukee, WI) with specified chemical purities of greater than 98%. From chemical analysis, the major impurities were found to be phenol (0.2-0.3% by weight) and other chlorophenols and dichlorophenols (0.03-0.08% by weight). Experiments were conducted in triplicate at 600°C, the temperature at which total PCN yield was greatest; duplicate experiments for 2-CP were conducted at 700, 725 and 750°C. A reactor residence time of 10 seconds was maintained. The entire product stream was immediately quenched at the outlet of the reactor and collected in a dual ice-cooled dichloromethane trap. Samples were filtered to remove soot.

Identification and quantification of PCN, PCDD, and PCDF congeners was accomplished with a Hewlett-Packard 6890 series gas chromatography with HP-5MS column (30 m, 0.25 mm i.d., 0.25 μm film thickness) coupled to a Hewlett-Packard 5973 mass spectrometer. The column oven temperature was programmed from 38 to 80°C at a rate of 3°C/min, 180 to 250°C at a rate of 5°C/min, 250 to 280°C at a rate of 6°C/min, and a final hold time of 3 min. For quantification, the mass spectrometer was operated in selective ion mode at the two most intensive and characteristic ion masses. Elution time was used to identify isomers. Naphthalene, dibenzo-p-dioxin, and dibenzofuran products are formed from two phenol reactants. Therefore, expected products in these

experiments were congeners containing up to two chlorine atoms.

PCN isomers were identified based on the elution order of PCNs in Halowax 1001, 1014, and 1051 standards.²²⁻²⁴⁾ Both monochloronaphthalene (MCN) isomers, 1- and 2-MCN, were separated, and seven peaks were separated for the ten dichloronaphthalene (DCN) isomers. DCN isomers co-eluting were as follows: 1,5-/1,6-/1,7-DCN and 2,6-/2,7-DCN. Naphthalene was used as a universal response factor to estimate PCN product yields.

PCDD and PCDF products were also measured. Procedures for identifying these products have been published previously.²⁵⁾ Both monochlorodibenzo-p-dioxin (MCDD) isomers and all four monochlorodibenzofuran (MCDF) isomers were separated. Seven peaks were obtained for the ten dichlorodibenzo-p-dioxin (DCDD) isomers; two of these peaks contain co-eluting isomers (1,6-/1,7-/1,8-DCDD and 2,7-/2,8-DCDD). It is interesting to note that the DCDD isomers that co-elute in our system are structurally analogous to the DCN isomers that co-elute. (Due to their identical symmetry, the number of DCN and DCDD isomers is the same. The numbering system is different, however, with the unfused portion of the PCN second ring composed of the 5, 6, 7, and 8 carbon atoms whereas these are 6, 7, 8, and 9 in the PCDD numbering system.) In the case of

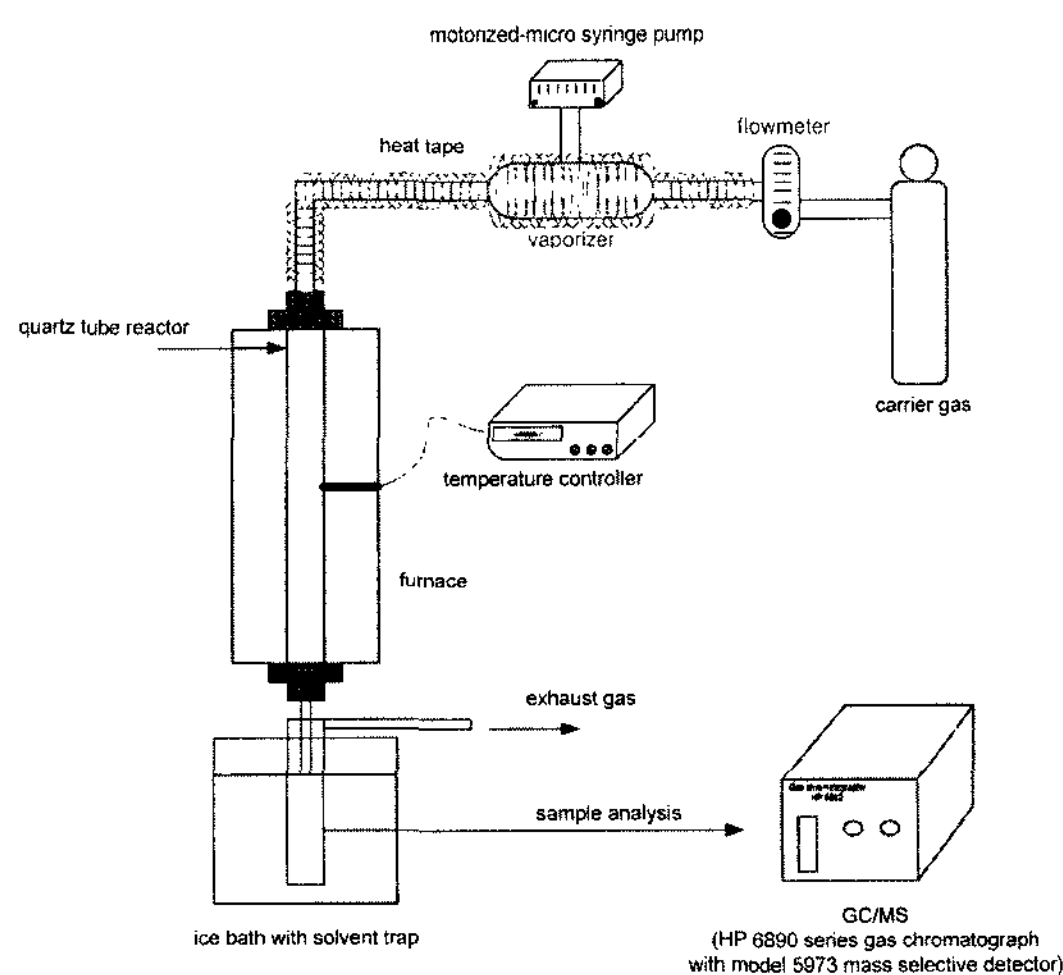


Figure 1. Experimental apparatus

dichlorodibenzofuran (DCDF) isomers, 15 peaks were obtained for the 16 DCDF isomers; only the 2,7-/1,2-DCDF isomers co-elute. In addition, CO measurements in the exhaust gas were performed with a Hewlett-Packard 5890 II series gas chromatography coupled to thermal conductivity detector (TCD) with HP-MOLSIV column (15 m, 0.53 mm i.d., 0.25 μm film thickness).

A Priori Hypotheses

Before performing experiments, PCN isomer products from the three CPs were predicted based on the *a priori* hypothesis that phenoxy radicals decompose to CPDyl radicals, which combine and rearrange to form naphthalenes via the mechanism proposed by Melius *et al.*¹⁸⁾ The three CPs form the same chloro-CPDyl radical (Figure 2). To predict which PCN products will be formed, we consider all possible combinations of the chloro-CPDyl radical at unsubstituted carbon atoms. The presence of chlorine inhibits carbon-carbon coupling at substituted sites. Three dichlorodihydrofulvalenes can be formed (Figure 2). These dihydrofulvalenes are then converted to naphthalenes via the mechanism shown in Figure 3. In translating the dihydrofulvalene-to-naphthalene mechanism to a chlorinated system, we include an alternative radical formation step involving carbon-chlorine bonds, which are much weaker than carbon-hydrogen bonds. If hydrogen migrates to a chlorinated site in the conversion of 9,10-dihydrofulvalene to 1,10-dihydrofulvalene (first reaction in Figure 3), loss of that chlorine can occur (replacing the second and third reactions shown in Figure 3).

The fused bond in naphthalene, between the 9 and 10 carbon atoms, is formed by any of the following five carbon pairs in dihydrofulvalene: 9,10; 9,5; 9,8; 10,1; and 10,4. Via each of these routes, a pair of PCN products is formed. Thus, ten PCN products could be formed from each 9,10-dihydrofulvalene. Due to symmetry, not all of the products are unique. For example, from the 2,6-dichloro-9,10-dihydrofulvalene shown in the leftmost pathway of Figure 2, fusion across the 9,10 carbon atoms, 9,8 carbon atoms, and

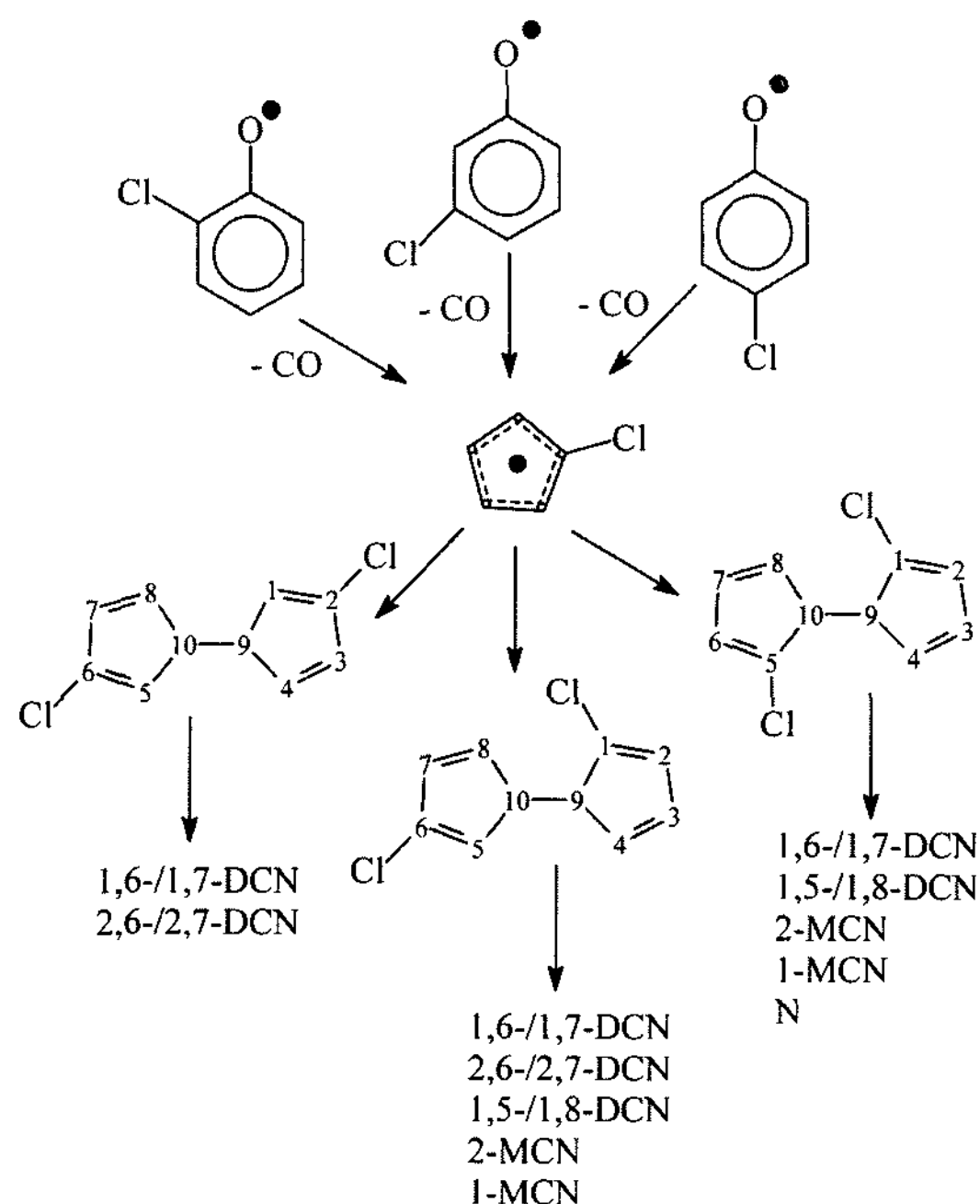


Figure 2. *A priori* hypothesis of PCN formation from chlorophenols

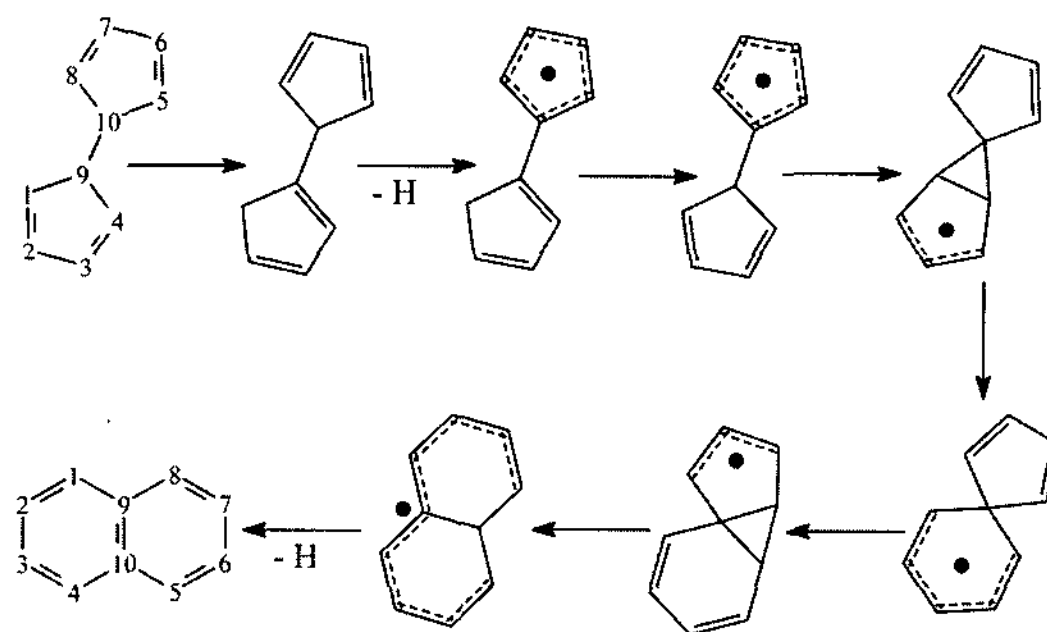


Figure 3. Reaction mechanism proposed by Melius *et al.* (1996) for the conversion of 9,10-dihydrofulvalene to naphthalene.

10,4 carbon atoms yields the 2,6-/2,7-DCN pair. Fusion across the 9,5 carbon atoms and 10,1 carbon atoms yields the 1,6-/1,7-DCN pair. In the case of the 1,6-dichloro-9,10-dihydrofulvalene shown in the center pathway of Figure 2, eight different PCN products can be formed: 1,6-, 1,7-, 2,6-, 2,7-, 1,5- and 1,8-DCN and 2- and 1-MCN. The third CPDyl combination produces 1,5-dichloro-9,10-dihydrofulvalene (rightmost pathway in Figure 2), which leads to seven naphthalene products: 1,6-, 1,7-, 1,5- and 1,8-DCN, 1- and 2-MCN, and naphthalene.

RESULTS AND DISCUSSION

Preliminary Results on PCN and PCDF Formation from CPs at 600°C

To test a priori hypotheses, PCN and PCDF products from CP reactants at 600°C were investigated, and CP reactant recovery and yields of phenol, total naphthalene, total dibenzofuran and total dibenzo-p-dioxin products from the individual CP reactant experiments are summarized in Table 1. The amount of unreacted CP recovered at 600°C and 10 seconds ranged from 21% for 3-CP to 33% for 2-CP, indicating that 3-CP is most easily destroyed thermally, whereas 2-CP is least easily destroyed. Phenol yield ranged from 0.16% to 0.29% of CP reactant. Phenol, an impurity in the CP reactant, may result from incomplete reaction or may be produced by CP hydrodechlorination. Phenol yields increased with temperature over the range of 450 to 750°C (not shown). Thus, CP hydrodechlorination appears to be the major source of phenol in these experiments. Phenol yield was greatest from 2-CP. The formation of phenol can lead to other, less chlorinated naphthalene and dioxin products, as will be discussed.

As expected, naphthalene and dioxin products were observed. Total yields of naphthalenes ranged from 0.0073% from 4-CP to 0.013% from 3-CP; total yields of dibenzofurans ranged from 0.0075% from 2-CP to 3.4% from 3-CP. Dibenzop-dioxin was observed from 2-CP, with a yield of 0.0014%.

Much of the CP reactants undergo decomposition and oxidation to form low molecular weight products. Since the oxidation pathways were not the subject of this investigation, these products were not measured. Based on the low yield of benzene (not shown) and lack of toluene and styrene products, we conclude that naphthalene

formation via addition of two- or three-carbon species was negligible.

Total yields of naphthalene (N) and chlorinated naphthalenes (MCN and DCN), and dibenzofuran (DF) and chlorinated dibenzofurans (MCDF and DCDF) are shown in Figure 4 on a percent CP molar conversion basis. The PCN homologue distribution produced by 2-CP is very different than those produced by 3- and 4-CP. Only a trace amount (less than 0.0001%) of DCN was detected from 2-CP. From 3-CP, 0.0017% DCN yield was observed. From 3- and 4-CP, MCN yields were highest; from 2-CP, naphthalene yield was greatest. These results suggest that the major route of PCN formation from chlorinated phenols is via loss of at least one chlorine atom. The high yields of DF and MCDF as well as N and MCN suggest that phenol contributed significantly to the formation of dibenzofuran and naphthalene products.

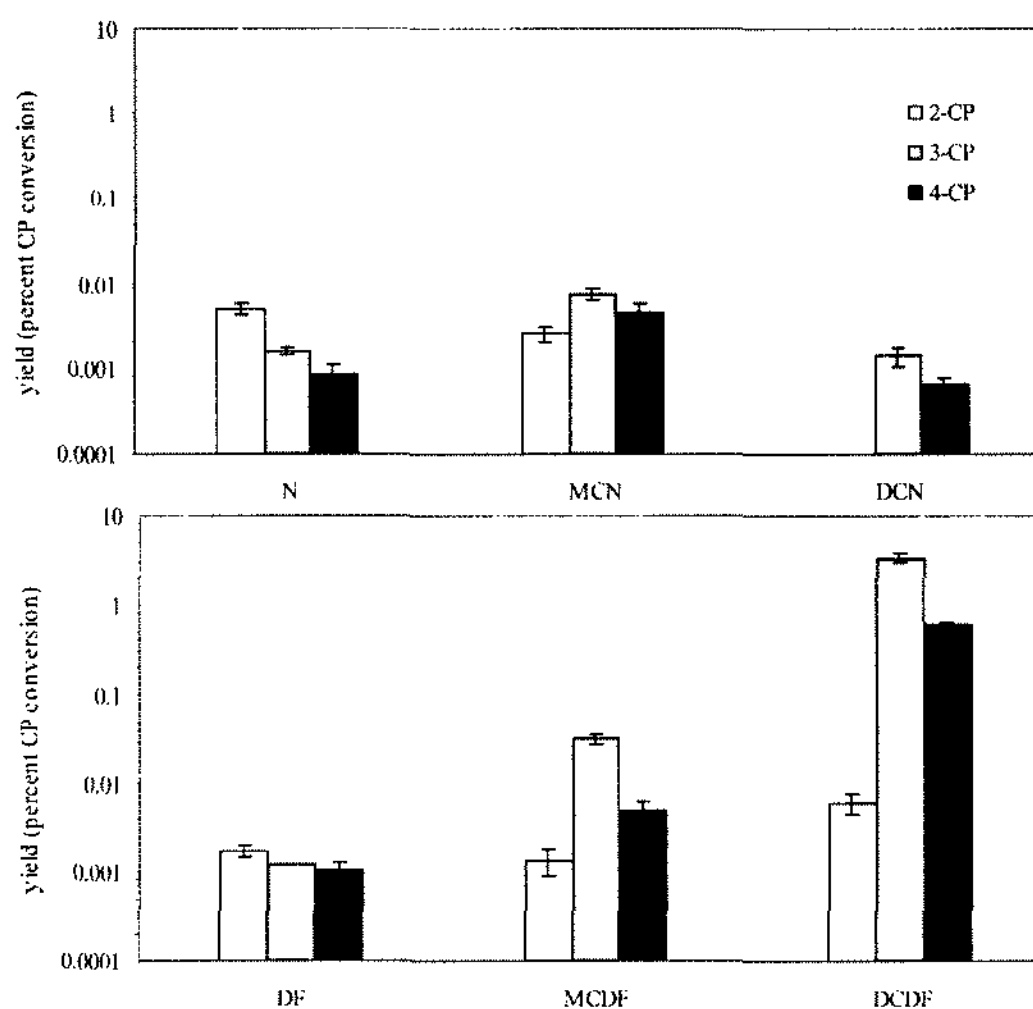


Figure 4. Naphthalene (top) and dibenzofuran (bottom) homologue distributions

Within each homologue, the total naphthalene and dibenzofuran yields from the different CP

Table 1. CP recovery and product yields (% phenol conversion) at 600°C

	CP recovery		phenol		PCN		PCDF		PCDD	
2-CP	32.6846	(2.2905)*	0.2882	(0.0365)	0.0027	(0.0006)	0.0075	(0.0020)	0.0014	(0.0003)
3-CP	21.2494	(2.2296)	0.2076	(0.0292)	0.0090	(0.0015)	3.4042	(0.4183)		
4-CP	26.1117	(0.6825)	0.1606	(0.0224)	0.0052	(0.0013)	0.6101	(0.0175)		

* standard deviation

reactants have a similar pattern. That is, 2-CP produced the highest N and DF yields and 4-CP produced the lowest N and DF yields. In the case of the monochlorinated and dichlorinated products, 3-CP produced the highest yields. Thus, there appears to be a strong, positive correlation between naphthalene formation and dibenzofuran formation from CPs, rather than an inverse relationship. This contradicts to a priori hypothesis.

In Figure 5, all but one of the expected PCN congeners were, however, detected and quantified. That is, 1-MCN, 2-MCN and 1,5-/1,6-/1,7-DCN, and 2,6-/2,7-DCN were observed; we were not able to detect 1,8-DCN. None of the other DCN congeners were detected, which implies that MCN and DCN products could be formed from the chlorinated dihydrofulvalenes. It is also noted that 2-CP produced only a trace amount of DCN (1,5-/1,6-/1,7-DCN peak).

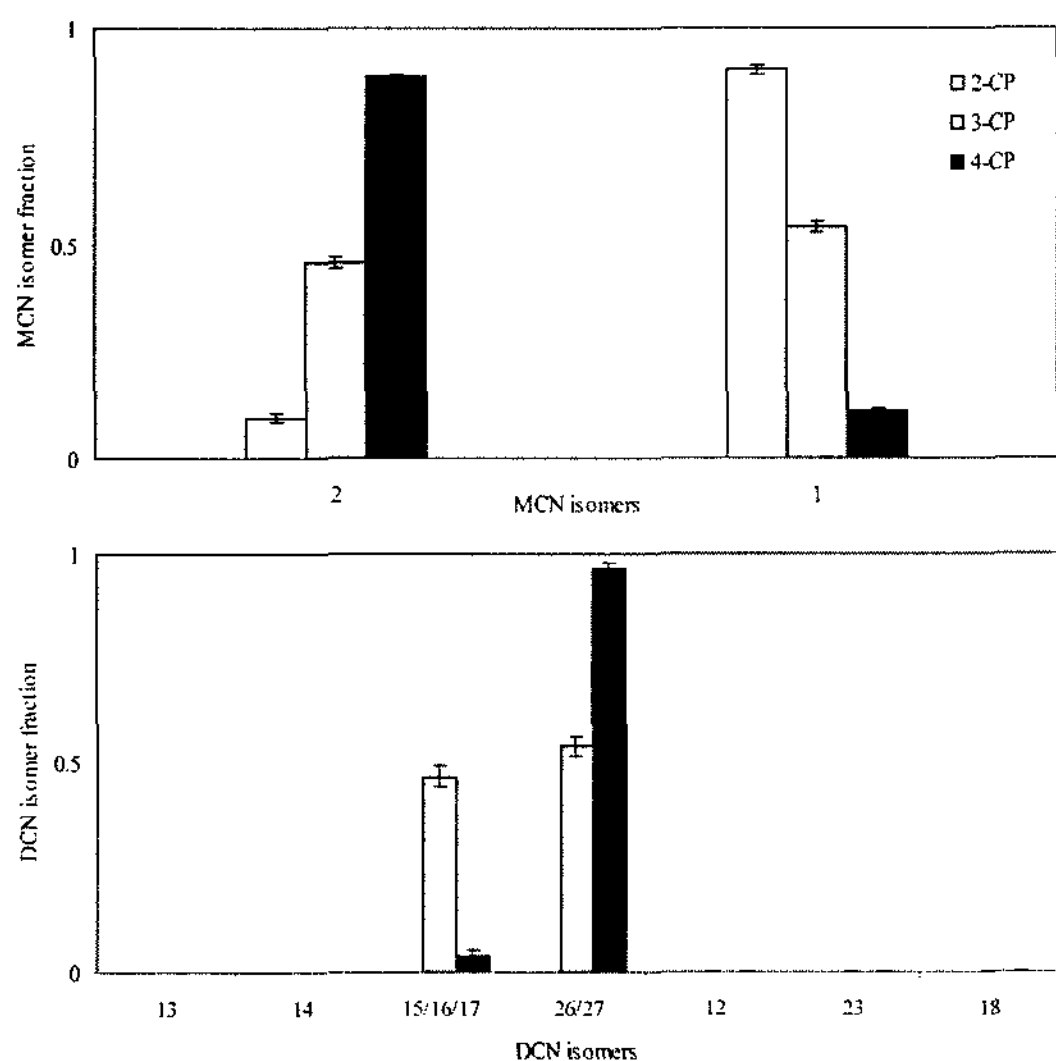


Figure 5. MCN (top) and DCN (bottom) isomer distributions. Isomers are listed in order of elution

The MCN isomer patterns from the three CPs are completely different. 2-CP produced mostly 1-MCN, 3-CP produced nearly equal amounts of 1- and 2-MCN, and 4-CP produced mostly 2-MCN. The DCN isomer patterns from 3-CP and 4-CP are also different. 3-CP produced nearly equal amount of the 1,5-/1,6-/1,7-DCN and 2,6-/

2,7-DCN peaks, whereas 4-CP produced 2,6-/2,7-DCN almost exclusively. Thus, we reject a priori hypothesis that the PCN isomer patterns would be the same from the three CP reactants due to a common radical precursor chloro-CPDyl.

PCDF isomer distributions are shown in Figure 6. All expected isomers were observed: 4,6-DCDF from 2-CP; 1,7-, 3,7-, and 1,9-DCDF from 3-CP; 4,6-DCDF from 2-CP. In addition, DF and MCDF isomers were detected. From 2-CP and phenol, 4-MCDF is formed. From 3-CP and phenol, 1- and 3-MCDF are formed. From 4-CP and phenol, 2-MCDF is formed. DF is produced from two phenols. The relative yields of phenol, DF, and N from the three CP reactants are consistent. That is, 2-CP produced the most phenol, N, and DF, and 4-CP produced the least phenol, N, and DF. Thus, the CP hydrodechlorination to form phenol leads to the formation of less chlorinated naphthalene and dibenzofuran products than those produced from the parent CP alone.

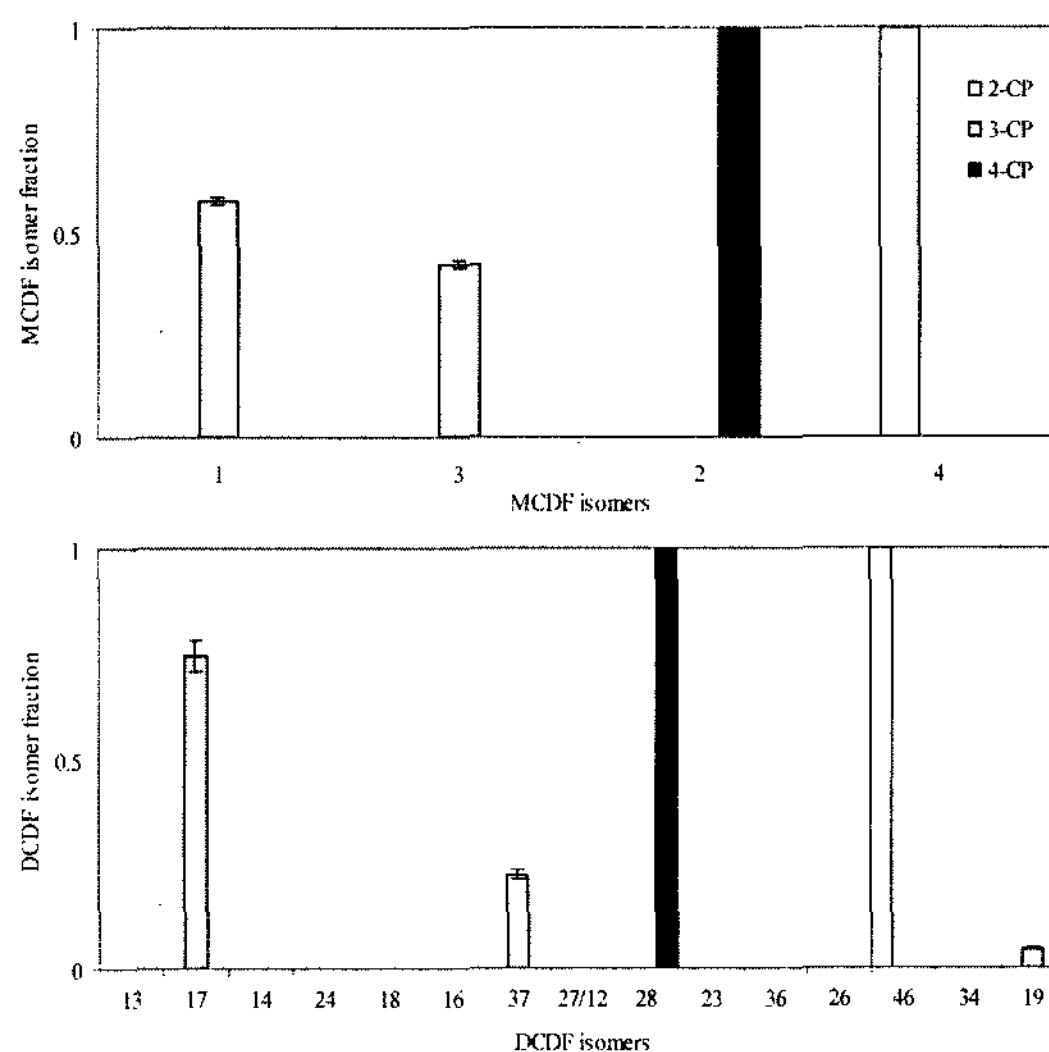


Figure 6. MCDF (top) and DCDF (bottom) isomer distributions. Isomers are listed in order of elution

To account for the differences in PCN isomer distributions, and to explain the apparent correlation of PCN and PCDF yields, an alternative formation mechanism is needed. The dependence of PCN isomer distributions on CP reactant chlorination

pattern suggests that coupling must involve a reactant derivative other than the chloro-CPDyl radical. Moreover, the correlation of PCN and PCDF product formation suggests that they might be formed from a common intermediate, the formation of which is rate limiting. These observations lead us to modify our proposed scheme for PCN formation from CPs.

Proposed Pathway of PCN Formation from CPs

Based on the observed simultaneous formation of PCNs and PCDFs from CPs, PCN formation pathways from CPs are proposed that build on the dihydrofulvalene-to-naphthalene mechanism of Melius *et al.*¹⁸⁾ The proposed overall reaction pathway for PCDF and PCN formation from chlorophenols is depicted in Figure 7; the detailed reaction schemes from each CP are presented in Figure 8-10.

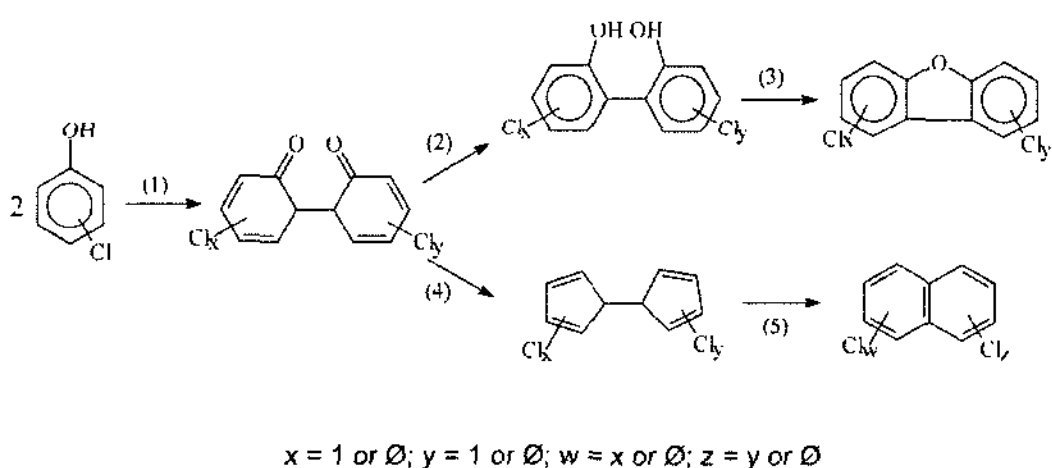


Figure 7. Overall PCDF and PCN formation pathways from chlorophenols

Chlorophenols can lose hydrogen or chlorine to produce chlorophenoxy or phenoxy (with hydrogen migration) radicals. These resonance-stabilized radicals can couple at unchlorinated ortho carbon sites to produce the diketo tautomer of DOHB (step 1 in Figure 7). In PCDF formation, this intermediate undergoes keto-enol tautomerization to form DOHB (step 2); subsequent elimination of H₂O yields the PCDF product (step 3). Alternatively, dihydrofulvalene is formed by CO elimination from the diketo-dimer intermediate (step 4). Elimination of CO from both stable and radical systems of phenol has been studied.²⁶⁻²⁸⁾ Subsequent fusion of dihydrofulvalene to form naphthalene products is depicted by step 5. Unlike

PCDF formation, PCN formation from the diketo-dimer intermediate may involve chlorine loss.

Experimental evidence of the preferred translation of the 9,10 carbon atoms of 9,10-dihydrofulvalene to the 9,10 carbon atoms of naphthalene is that 4-CP produced a large 2,6-/2,7-DCN peak and a small 1,5-/1,6-/1,7-DCN peak (Figure 5). Translation of the 9,10 carbon atoms of 9,10-dihydrofulvalene to the 9,10 carbon atoms of naphthalene produces 2,6- and 2,7-DCNs whereas translation of the 9,5 or 10,4 carbon atoms of 9,10-dihydrofulvalene to the 9,10 carbon atoms of naphthalene produces 1,6- and 1,7-DCNs.

Experimental evidence of the preferred hydrogen migration to a chlorinated site in the conversion of 9,10-dihydrofulvalene to 1,10-dihydrofulvalene, followed by loss of that chlorine atom, is that

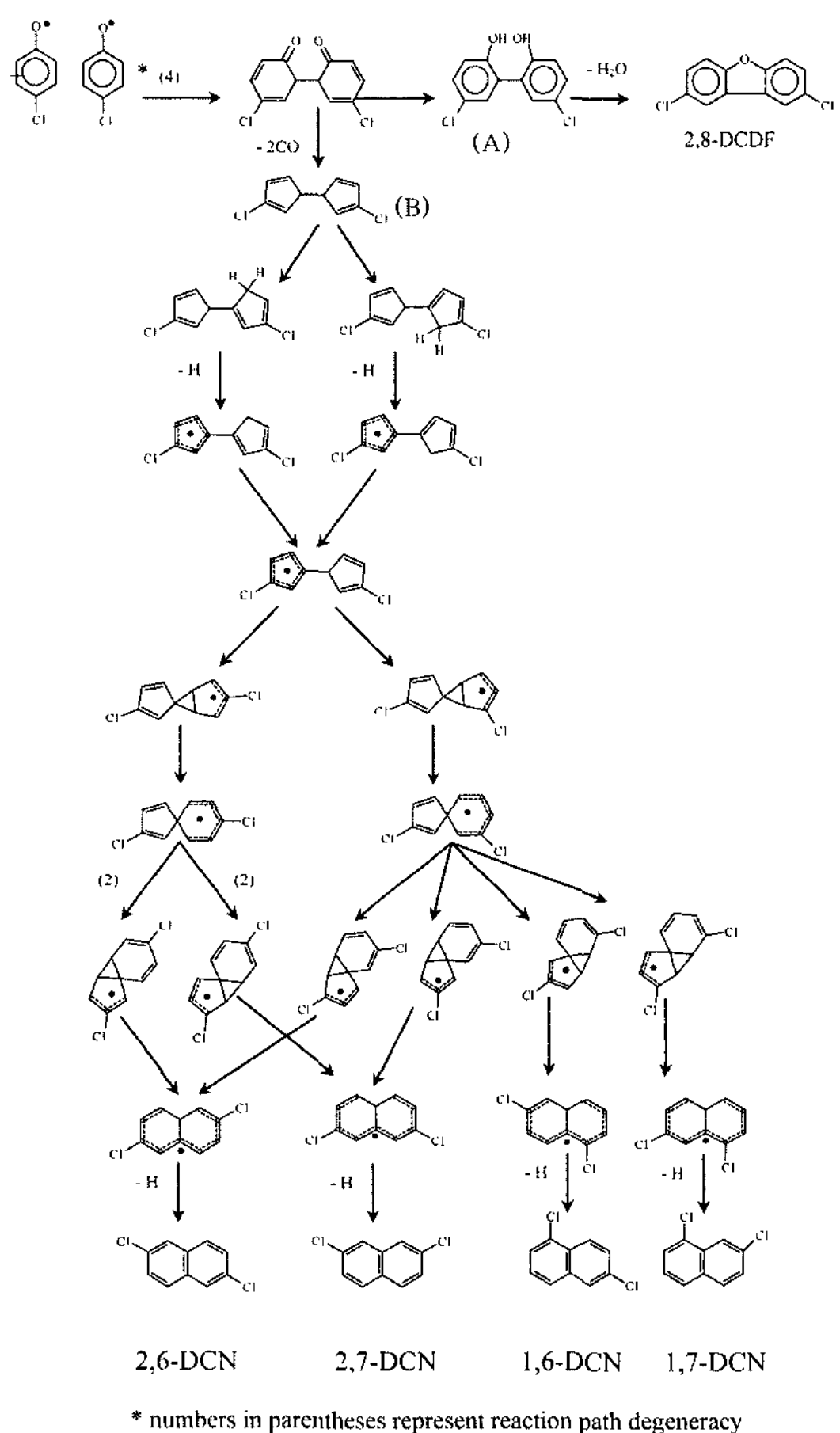


Figure 8. PCDF and PCN formation pathways from 4-CP

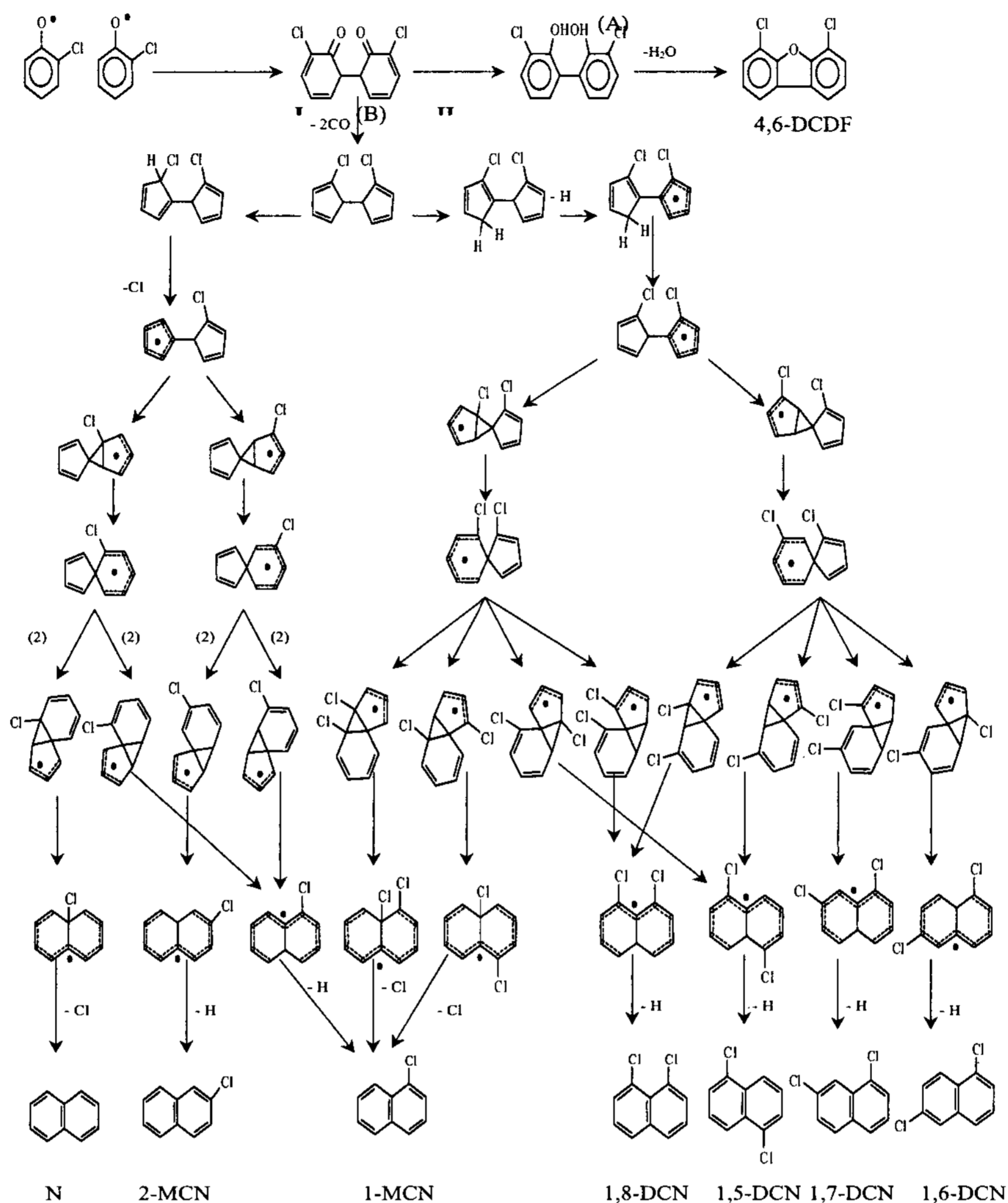


Figure 9. PCDF and PCN formation pathways from 2-CP

2-CP produced very little DCNs (Figure 4). Formation of much more 1-MCN than 2-MCN from 2-CP (Figure 5) is consistent with translation of the 9,10 carbon atoms of 9,10-dihydrofulvalene to the 9,10 carbon atoms of naphthalene.

In the case of 3-CP, three ortho-ortho couplings are possible, leading to the formation of three dichloro-*o,o*-dihydroxybiphenyls and three dichloro-9,10-dihydrofulvalenes. In Table 2, predicted PCDF and PCN products from 3-CP are listed, as well as those from 4-CP and 2-CP. In addition, predicted PCDF and PCN products formed via these pathways from combinations involving phenol are listed. Predictions based on the proposed reaction scheme are consistent with the observed PCN and PCDF isomer distributions, shown in

Figures 5 and 6, respectively.

Overall, PCN products were less chlorinated than PCDF products (Figure 4). For example, DCDF yields were a factor of 100 greater than DCN yields, whereas naphthalene and dibenzofuran yields were similar. This may be due to loss of chlorine in PCN formation and not in PCDF formation. Although phenol concentrations were much lower than CP reactant concentrations in these experiments, phenol appears to have played an important role in both PCN and PCDF formation. In previous work¹⁰, it was observed that PCDF formation from the less chlorinated phenol congeners was greater than that from more chlorinated phenol congeners. The experimental results presented here indicate that chlorine sup-

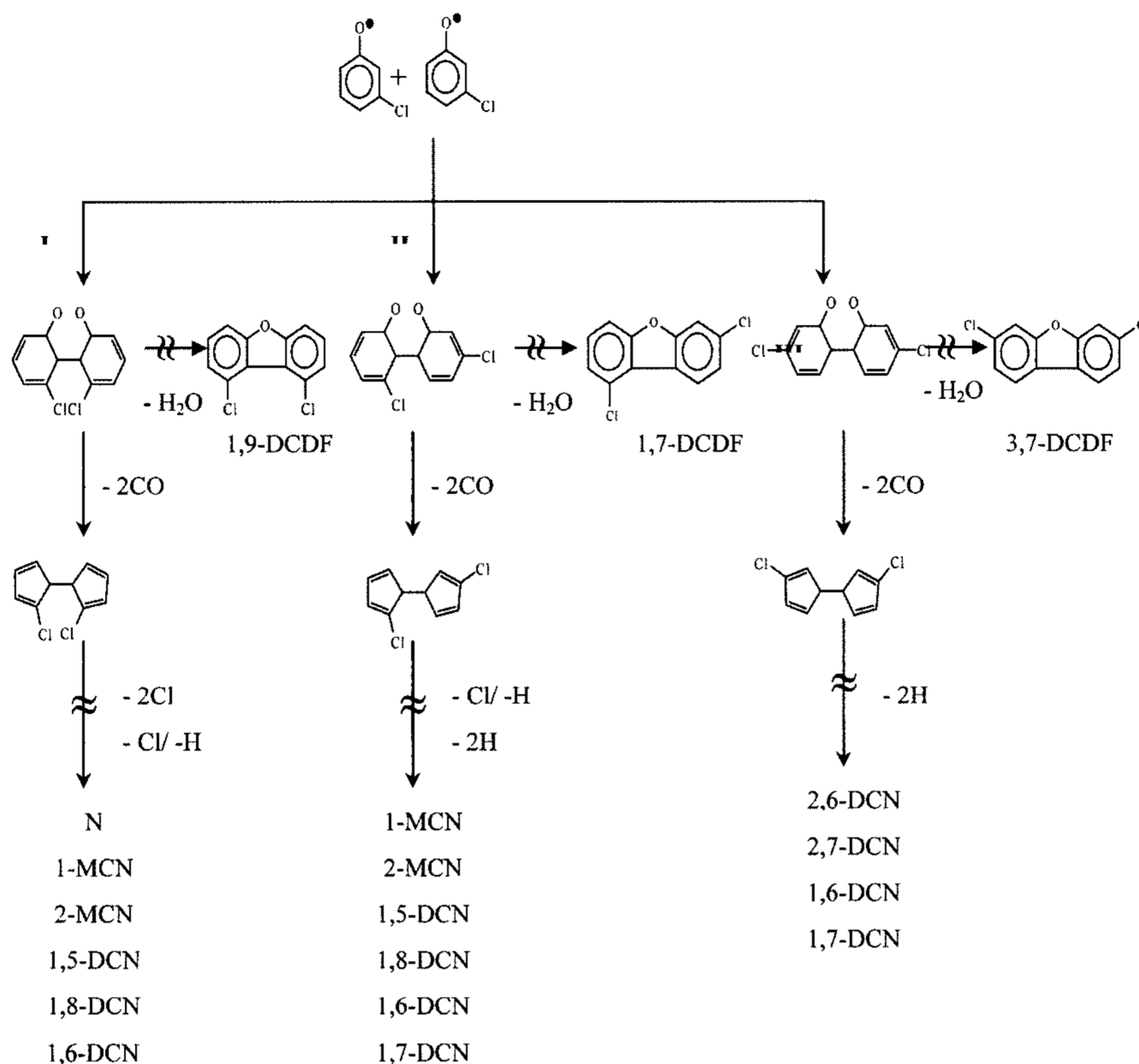


Figure 10. PCDF and PCN formation pathways from 3-CP

presses PCN formation as well. One explanation is that the withdrawal of electron density by chlorine substituents from the ring systems suppresses CO elimination and PCN formation.

Other reaction schemes might also be consistent with the experimental observations. For example, radical-molecule routes involving either CPDyl or phenoxy radical adding to CP reactant would

Table 2. Predicted PCN and PCDF products from chlorophenols

Chlorophenol reactant	Naphthalene products	Dibenzofuran and dibenzo-p-dioxin products
 2-CP	 1,5-, 1,6-, 1,7-, 1,8-DCNs 1-, 2-MCNs N	 4,6-DCDF DD
3-CP	1,5-, 1,6-, 1,7-, 1,8-, 2,6-, 2,7-DCNs 1-, 2-MCNs N	1,7-, 3,7-, 1,9-DCDFs
4-CP	1,6-, 1,7-, 2,6-, 2,7-DCNs	2,8-DCDF

result in isomer specificity in PCN products. The correlation of PCDF and PCN product distributions suggests to us that the rate-determining step is likely the same, however. That is, if PCDF formation from phenols involves only phenoxy radical coupling, then PCN formation likely does as well since the rate of CO elimination to form CPDyl radical is likely to be different from the three CPs. We further investigated the effect of temperature on gas-phase PCN and PCDF formation from chlorophenols to gain more mechanistic insight on these processes, which the experimental results are shown in next section.

Temperature-dependent Formation of PCNs and PCDFs from CPs

CP Recovery and Overall Product Distribution

Chlorophenol reactant recovery and yields of products are shown in Table 3 as percent yields of carbon feed. Unreacted CP was 51%, 36%, and 35.5% for 2-CP, 3-CP and 4-CP, respectively, at 550°C and less than 1% at 750°C. Unsubstituted phenol was one of major products from all three chlorophenols; its yield was a maximum at 675°C, with yields of 1.7% from 2-CP, 0.5% from 3-CP and 2% from 4-CP. The results demonstrate that hydrodechlorination is greatest for ortho and para chlorine in the parent phenol. The formation of phenol leads to other, less chlorinated naphthalene and furan products, as will be discussed.

Yields of CO from the decomposition and oxidation of chlorophenol were a maximum at 700°C, with peak yields of 63% for 2-CP, 43% for 3-CP, and 60% for 4-CP. At higher temperatures CO oxidation to CO₂ occurs.²⁹⁾

The total yields of dibenzofuran products peaked between 625°C and 675°C, with maximum yields of 0.21%, 2.2% and 1.3% for 2-CP, 3-CP and 4-CP, respectively. Dibenzo-p-dioxin (DD) was observed only from 2-CP, with a peak yield of 0.05% observed at 650°C. These results confirm that dibenzofuran formation is favored by meta substitution in the parent chlorophenol¹⁰⁾, and that ortho chlorine is necessary for dibenzo-p-dioxin formation.¹⁹⁾

Maximum yields of naphthalene products were observed between 675°C and 725°C, with yields of 0.91%, 0.39% and 0.94% from 2-CP, 3-CP and 4-CP, respectively. Thus, ortho and para substitution on the parent phenol favored naphthalene product formation. Based on the low yield of benzene (not shown) and styrene (not detected), naphthalene formation via phenol decomposition to two- or three-carbon species and subsequent growth by HACA pathways was not significant under our experimental conditions.

The ratio of naphthalene to dibenzofuran products was greatest for 2-CP and least for 3-CP (Figure 11). As temperature increased, this ratio increased for each of the CP reactants. These results suggest that CO elimination (step 4 in Figure 7) that leads to naphthalene formation becomes increasingly favored relative to tautomerization (step 2 in Figure 7) that leads to dibenzofuran formation as temperature increases.

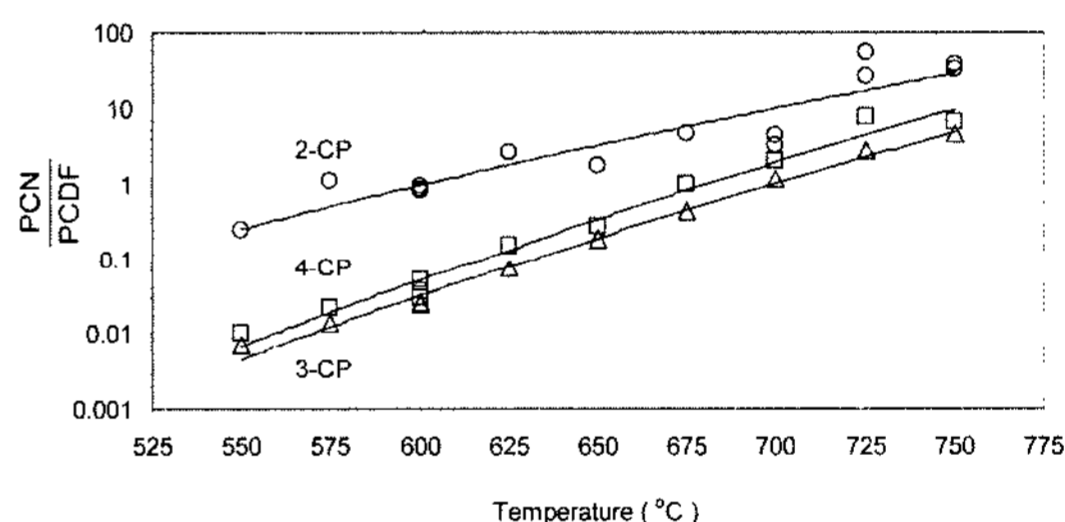


Figure 11. Ratio of total naphthalene to total dibenzofuran product yields from CPs

PCDF and PCN Congener Yields Over Temperature

In Table 3, DCDF products are favored at lower temperatures. As temperature increases, the total yields of MCDF and DF become bigger fractions of the total dibenzofuran product yield. At 750°C, DF was the major dibenzofuran product. The PCN product distributions show a similar trend with temperature as the PCDF product distributions, with the unchlorinated congener becoming increasingly the dominant product at high temperatures. Unlike the PCDF product distributions, however, the total yields of monochlorinated and unchlorinated congeners were greatest in the

Table 3. Percent yields (carbon basis) of product yields from chlorophenols

		Temperature (°C)								
Product		550	575	600 ^a	625	650	675	700	725	750
2-CP	2-CP	51.7745	42.5040	32.6846	37.3295	33.8293	15.4041	3.2119	0.0105	0.0310
	CO	0.6108	1.2217	4.4455	10.3842	19.5467	44.7945	63.5268	13.4384	7.6354
	phenol	0.3792	0.3356	0.2882	0.9342	1.7175	1.8600	0.9875	0.0050	0.0187
	naphthalene	0.0041	0.0139	0.0128	0.1127	0.2120	0.8033	0.5840	0.0618	0.0616
	2-MCN	0.0002	0.0010	0.0011	0.0121	0.0186	0.0503	0.0214	0.0004	0.0003
	1-MCN	0.0039	0.0154	0.0084	0.0627	0.0612	0.1045	0.0377	0.0023	0.0014
	15-/16-/17-DCN	0.0001	0.0003	0.0002	0.0012	0.0013	0.0021	0.0005	n.d.	n.d.
	26-/27-DCN	n.d. ^b	trace ^c	0.0000	0.0002	0.0003	0.0009	0.0002	n.d.	n.d.
	DF	0.0006	0.0031	0.0056	0.0316	0.0997	0.1627	0.1754	0.0024	0.0017
	4-MCDF	0.0028	0.0038	0.0040	0.0138	0.0309	0.0318	0.0182	0.0001	trace
3-CP	46-DCDF	0.0310	0.0208	0.0170	0.0274	0.0402	0.0159	0.0059	trace	trace
	DD	0.0152	0.0191	0.0014	0.0386	0.0546	0.0266	0.0098	0.0002	0.0002
	3-CP	35.4738	33.8259	21.2494	21.4742	9.0654	2.3811	0.5642	0.0041	0.0072
	CO	0.9163	3.0542	3.7329	15.4745	20.7684	36.0392	42.7584	7.3300	3.0542
	phenol	0.3923	0.3949	0.2076	0.4364	0.4808	0.6293	0.2850	0.1326	0.0316
	naphthalene	0.0041	0.0047	0.0073	0.0518	0.1929	0.2828	0.3430	0.1372	0.2125
	2-MCN	0.0017	0.0062	0.0100	0.0528	0.0874	0.0986	0.0423	0.0100	0.0077
	1-MCN	0.0019	0.0072	0.0112	0.0550	0.0913	0.0916	0.0438	0.0114	0.0091
	15/16/17-DCN	0.0007	0.0020	0.0029	0.0120	0.0156	0.0109	0.0024	0.0004	0.0002
	26/27-DCN	0.0007	0.0025	0.0039	0.0156	0.0187	0.0152	0.0030	0.0006	0.0003
4-CP	DF	0.0002	0.0016	0.0021	0.0112	0.0176	0.0561	0.0317	0.0166	0.0165
	1-MCDF	0.0048	0.0384	0.0355	0.1076	0.0759	0.1434	0.0522	0.0106	0.0080
	3-MCDF	0.0022	0.0245	0.0291	0.0940	0.0674	0.1430	0.0534	0.0096	0.0094
	17-DCDF	0.9264	1.0626	0.9280	1.5502	1.4342	0.5707	0.1774	0.0157	0.0119
	37-DCDF	0.2635	0.3773	0.3401	0.5963	0.4298	0.2083	0.0547	0.0036	0.0032
	19-DCDF	0.0823	0.1041	0.0928	0.1600	0.1459	0.0493	0.0130	0.0008	0.0006
4-CP	4-CP	35.9636	26.4475	26.1117	23.9358	19.5361	11.7435	2.6042	0.1873	0.0032
	CO	0.6108	1.8325	2.3415	4.2758	10.9950	26.2659	61.0834	6.7192	4.2758
	phenol	0.2129	0.3507	0.1606	1.0277	2.0037	2.1807	1.3604	0.2246	0.0728
	naphthalene	0.0009	0.0013	0.0037	0.0330	0.1880	0.4896	0.6548	0.8569	0.5470
	2-MCN	0.0009	0.0032	0.0066	0.0420	0.1130	0.1688	0.1200	0.0807	0.0262
	1-MCN	0.0001	0.0004	0.0010	0.0073	0.0229	0.0390	0.0394	0.0277	0.0164
	15/16/17-DCN	n.d.	n.d.	0.0000	0.0003	0.0007	0.0008	0.0012	0.0004	0.0001
	26/27-DCN	0.0004	0.0014	0.0015	0.0090	0.0205	0.0226	0.0118	0.0047	0.0010
	DF	0.0002	0.0006	0.0018	0.0071	0.0353	0.0674	0.0817	0.0512	0.0514
	2-MCDF	0.0011	0.0038	0.0108	0.0393	0.1219	0.1181	0.0890	0.0319	0.0172
28-DCDF	0.2320	0.2816	0.3138	0.5514	1.1362	0.5473	0.2331	0.0459	0.0203	

^aaverage value of triplicate at 600°C; ^b n.d. = not detected; ^c trace = yield < 0.0001%

case of naphthalene formation even at the lowest temperature studied (550°C).

For all three CPs, the high yields of DCDF and DCN products at low temperatures, relative to DCDF and DCN yields at high temperatures,

are consistent with ortho-ortho carbon coupling of two chlorophenoxy radicals. As temperature increases, organic chlorine decreases. Increases in MCDFs and DF relative to DCDFs and MCNs and N relative to DCNs suggest coupling of

chlorophenoxy radical with phenoxy radical. The identification of DCDF and DCN isomers, discussed in the next section, confirms this conclusion.

Another inference can be drawn from examination of the PCN and PCDF homologue distributions. PCN products from all three chlorophenols were less chlorinated than PCDF products. DCDF yields were a couple of orders of magnitude higher than DCN yields, MCDF yields were similar to MCN yields, and dibenzofuran yields were an order of magnitude lower than naphthalene yields. The presence of chlorine may suppress CO elimination in the ring systems by withdrawing electron density, leading to higher DCDF yields than DCN yields.

All expected PCDF and PCN isomers produced by the coupling of two chlorophenoxy radicals (Table 2) were observed (Table 3), except for 1,8-DCN. Trace amounts of 1,8-DCN were observed from 2-CP, with yields of less than 0.0001%. In addition, several unexpected PCDF and PCN peaks were observed, consistent with the coupling of chlorophenoxy radical with phenoxy radical and the coupling of two phenoxy radicals. For example, 2-CP produced 4-MCDF and DF in addition to the expected 4,6-DCDF. 4-CP produced 2-MCDF and DF in addition to the expected 2,8-DCDF, as well as 1- and 2-MCNs and N in addition to the expected 1,6-, 1,7-, 2,6- and 2,7-DCN products.

In Figure 12, ratios of MCDF and DCDF isomers produced from 3-CP are shown as a function of temperature. The results show that the MCDF and DCDF isomer distributions are only weak functions of temperature. In Figure 13, ratios of MCN and DCN isomer peaks produced from each of the chlorophenols are shown as a function of temperature. The results show that the MCN and DCN isomer distributions from 2-CP and 4-CP are strong functions of temperature, whereas the MCN and DCN isomer distributions from 3-CP are not. The selectivity to particular PCN isomers decreased as temperature increased; that is, the ratios tended to go toward one.

Different ortho-ortho phenoxy radical couplings, which are only possible in the case of 3-CP,

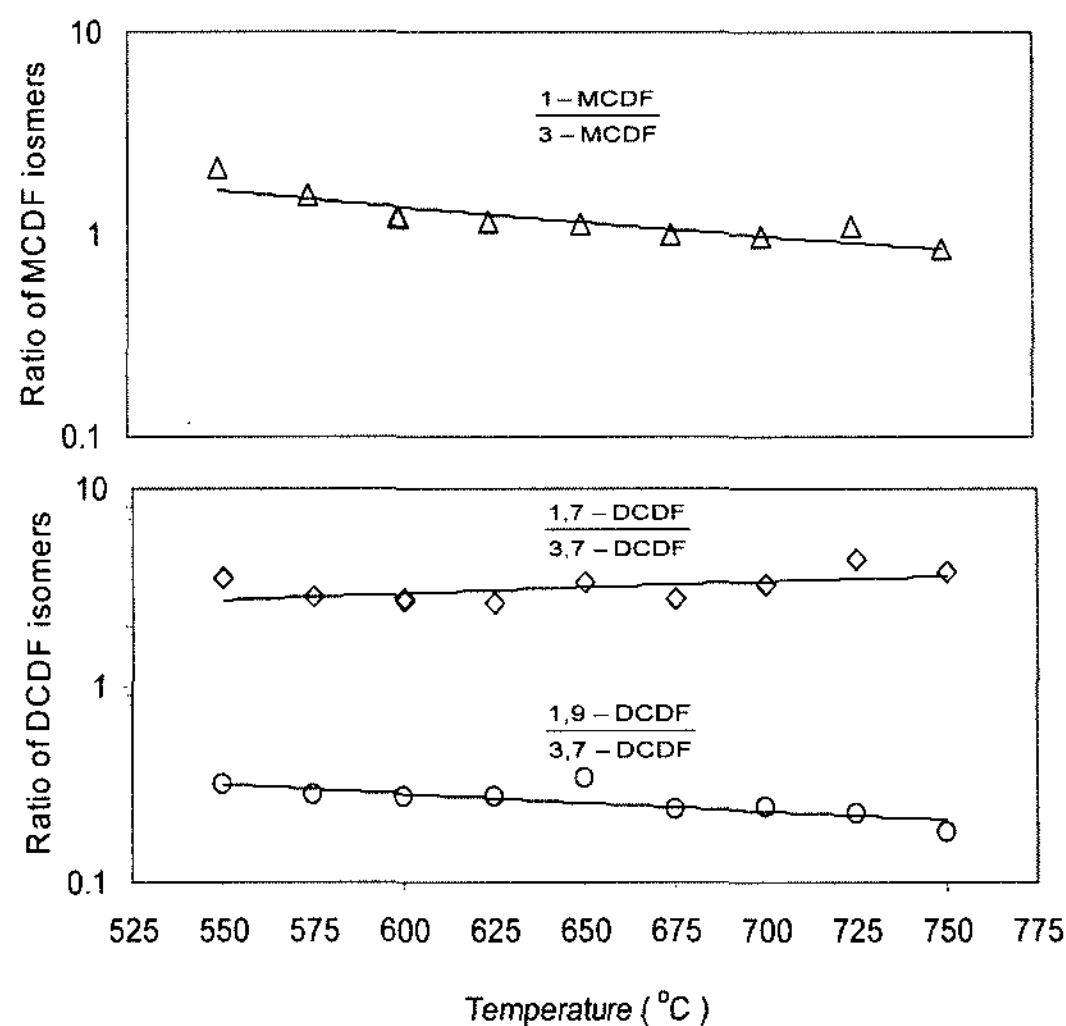


Figure 12. Ratios of MCDF and DCDF isomers from 3-CP

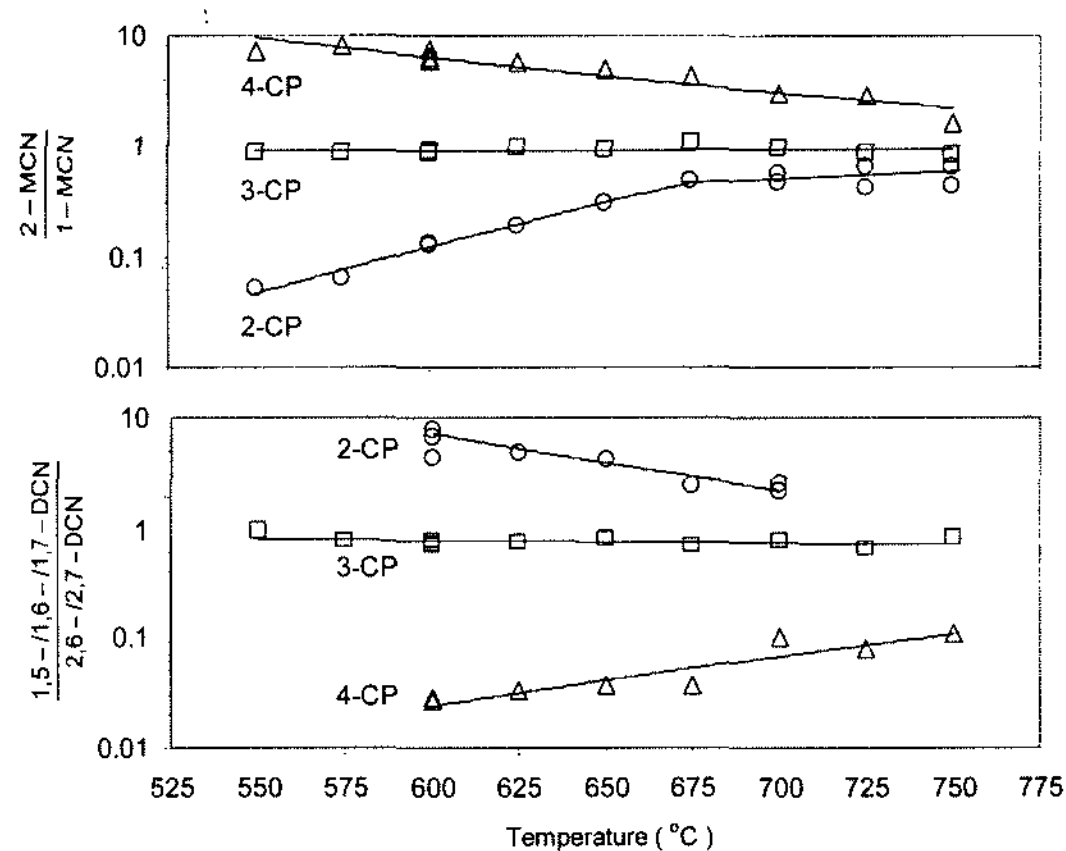


Figure 13. Ratios of MCN and DCN isomers from chlorophenols

result in the formation of different PCDF isomers and different sets of PCN isomers. The distributions of these isomers were found to be weakly dependent on temperature, consistent with a low activation energy process for phenoxy radical recombination. The distributions of different PCN isomers formed from 2- and 4-CP, on the other hand, were found to be much more sensitive to temperature, suggesting that the alternative fusion routes from the same dihydrofulvalene intermediate have different activation energies. These fusion routes involve three-member ring closure by intramolecular radical addition to π -bond.

Alternative routes of PCN formation are possible.

A detailed computational study was performed on the keto-enol tautomerization of phenol and 2,4-cyclohexadienone, with CO elimination from the keto tautomer (2,4-cyclohexadienone) to form cyclopentadiene via an acyclic intermediate.²⁸⁾ A heat of reaction of 20 kcal/mol for the formation of naphthalene from the 2-chlorophenol radicals via the recombination of cyclopentadiene radicals has been reported.³⁰⁻³¹⁾ Another possible reaction sequence that may affect PCN formation from CPs is chlorine migration. Intramolecular rearrangement of chlorine by 1,5-sigmatropic shift in the cyclopentadiene ring has a similar energy barrier as that of hydrogen³²⁻³³⁾, suggesting that chlorine can move as easily as hydrogen. Such chlorine migration would lead to the formation of additional PCN isomers.

CONCLUSIONS

In summary, this work addresses the formation of PCNs and PCDFs from chlorophenols in post-combustion gas streams. The experimental results presented here support the hypothesis that PCNs and PCDFs are formed from a common intermediate produced by ortho-ortho carbon coupling of phenoxy radicals. The distributions of PCN and PCDF products indicate that phenoxy radical couplings containing fewer chlorine substituents tend to form naphthalenes rather than dibenzofurans. PCN isomer distributions were found to be temperature sensitive, with selectivity to particular isomers decreasing with increasing temperature. These experimental results provide information that can be used to develop and test detailed mechanisms for the formation of PCNs from phenols in combustion exhaust gas.

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