

POLYCHLORINATED NAPHTHALENE (PCN) AND DIBENZOFURAN (PCDF) CONGENER PATTERNS FROM PHENOL PRECURSORS IN THERMAL PROCESS: [II] EXPERIMENTAL RESULTS FROM DICHLOROPHENOLS (DCPs)

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Abstract : Polychlorinated naphthalenes (PCNs) formed along with dibenzo-p-dioxin and dibenzofuran products in the slow combustion of dichlorophenols (DCPs) at 600°C were identified. Each DCP reactant produced a unique set of PCN products. Major PCN congeners observed in the experiments were consistent with products predicted from a mechanism involving an intermediate formed by ortho-ortho carbon coupling of phenoxy radicals; polychlorinated dibenzofurans (PCDFs) are formed from the same intermediate. Tautomerization of the intermediate and H₂O elimination produces PCDFs; alternatively, CO elimination to form dihydrofulvalene and fusion produces naphthalenes. Only trace amounts of tetrachloronaphthalene congeners were formed, suggesting that the preferred PCN formation pathways from chlorinated phenols involve loss of chlorine. 3,4-DCP produced the largest yields of PCDF and PCN products with two or more chlorine substituents. 2,6-DCP did not produce tri- or tetra-chlorinated PCDF or PCN congeners. It did produce 1,8-DCN, however, which could not be explained.

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

INTRODUCTION

Formation of polychlorinated naphthalenes (PCNs) along with other halogenated aromatic compounds, such as polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), has been observed to occur in combustion exhaust gas.¹⁻³⁾ Recent studies showed a strong correlation between several

PCN and PCDF congeners in municipal waste incinerator (MWI) fly ash, suggesting that the formation pathways might be similar.⁴⁻⁵⁾ It has also been reported that the amount of PCNs formed from a pilot-scale solid waste incinerator was the same order of magnitude as PCDD/F yields.⁶⁾ While the mechanism of PCN formation in incinerators is not well understood, concern about the presence of PCNs in environment has risen.

Formation of naphthalene at high temperatures in flames has largely been attributed to the hydrogen-abstraction/acetylene-addition (HACA) me-

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chanism.⁷⁻⁹⁾ In post-combustion gas, however, under conditions in which PCDDs and PCDFs are formed from chlorinated phenols, PCNs may be formed directly from coupling of chlorinated phenoxy radicals. In previous studies in this laboratory, formation of PCNs with PCDDs/PCDFs was observed in gas-phase pyrolysis¹⁰⁾ and oxidation¹¹⁾ of chlorinated phenols. No attempt was made to elucidate the detailed mechanism of PCN formation as many of the PCN congeners were unidentified.

Some studies suggest that naphthalene formation from phenol in flames can occur by combination of cyclopentadienyl (CPDyl) radicals, produced from the decomposition of phenoxy radical via loss of CO.¹²⁻¹⁵⁾ Melius and coworkers¹⁶⁾ performed quantum chemical modeling on naphthalene formation from dihydrofulvalene, proposing that the recombination of CPDyl radicals produces dihydrofulvalene which then undergoes intramolecular rearrangements via resonance-stabilized radicals. Three-member ring closure and opening results in fusion of the bi-cyclic dihydrofulvalene intermediate to form naphthalene.

Recently, we studied the slow oxidation of monochlorophenols (MCPs) and proposed PCN formation pathways that build on the published mechanisms of PCDF formation from chlorinated phenols and naphthalene formation from dihydrofulvalene.¹⁷⁾ Major dibenzo-p-dioxin, dibenzofuran and naphthalene products in each homologue class from each of the three MCPs are listed in Table 1. Overall pathways to major products from 2-MCP are depicted in Figure 1; a more detailed reaction scheme is shown in our previous publication.

In combustion exhaust gas at temperatures between 550 and 750°C, chlorophenols form resonance-stabilized radicals either by loss of the phenolic hydrogen or loss of a chlorine substituent and migration of the phenolic hydrogen to form the stable radical. Chlorophenoxy radical coupling between an oxygen and an ortho carbon with chlorine substituent (pathway I, figure 1) leads to the formation of dibenzo-p-dioxin products via a five-member ring intermediate and loss of two chlorine atoms.¹⁸⁾ Carbon-carbon coupling at unchlorinated ortho sites of pairs of chlorophenoxy

Table 1. Major naphthalene, dibenzofuran and dibenzo-p-dioxin products from MCPs.

reactant	naphthalenes	dibenzofurans and dibenzo-p-dioxins
2-MCP	1,5-DCN	4,6-DCDF
	1-MCN	4-MCDF
	N	DF
		DD
3-MCP	2,6-, 2,7-, 1,6-, 1,7-DCNs	1,7-, 3,7-, 1,9-DCDFs
	1-,2-MCNs	1-,3-MCDFs
	N	DF
4-MCP	2,6-, 2,7-DCNs	2,8-DCDF
	2-MCN	2-MCDF
	N	DF

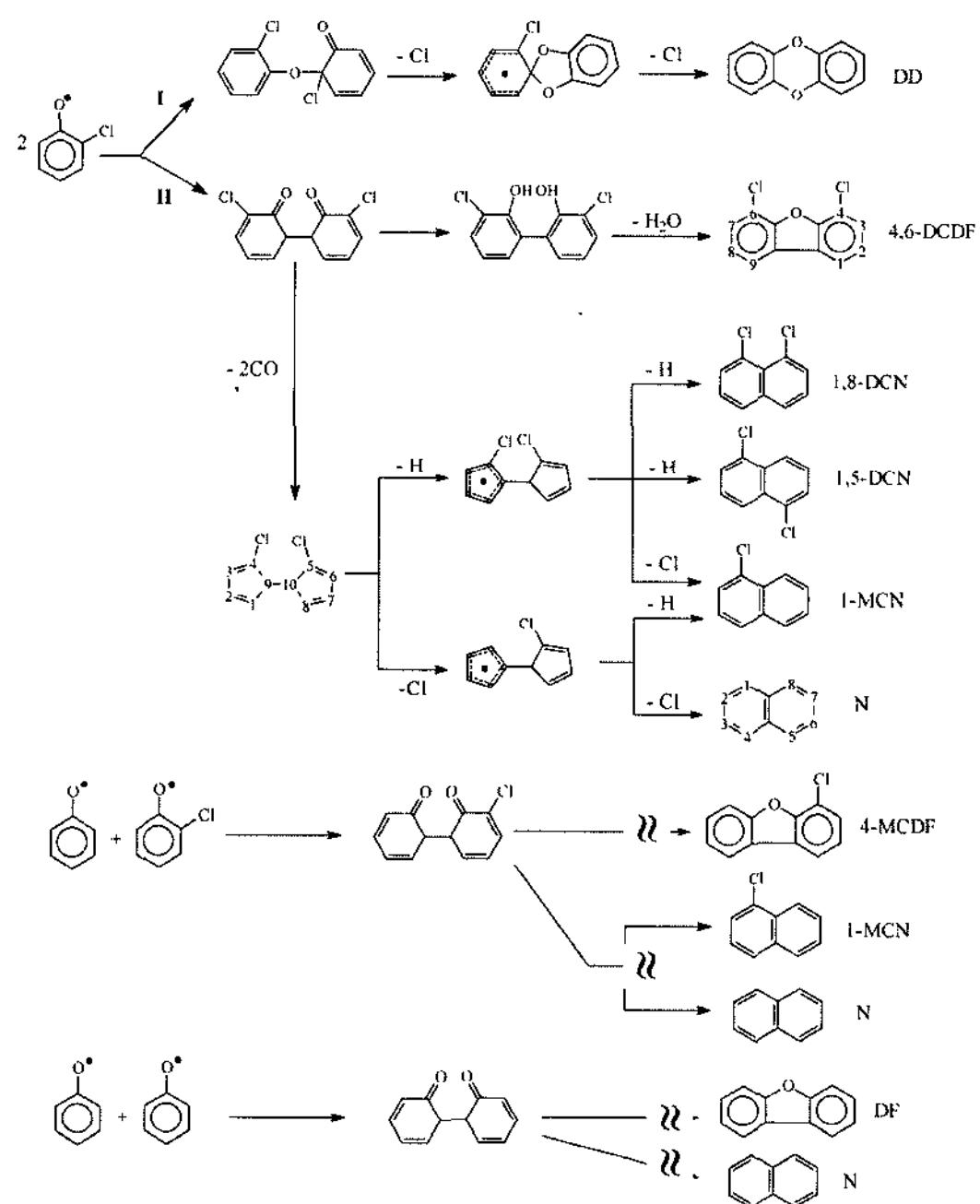


Fig. 1. Major dibenzo-p-dioxin, dibenzofuran, and naphthalene products from 2-MCP.

and/or phenoxy radicals (pathway II, figure 1) results in the formation of both dibenzofuran products without chlorine loss and naphthalene products with loss of zero to two chlorine atoms. In the formation of dibenzofuran products, tautomerization produces the dihydroxybiphenyl (DOHB) intermediate, followed by loss of H₂O to yield dibenzofuran.^{5,19,20)} Alternatively, elimination of CO from each ring system yields a dihydrofulvalene intermediate, followed by naphthalene formation via pathways analogous to the mechanism proposed

by Melius *et al.*¹⁶⁾ The predominant naphthalene products observed in the MCP experiments were isomers formed by fusion across the 9-10 dihydrofulvalene bond. From each of the three MCPs, dichloronaphthalene yields were much lower than monochlorinated and unchlorinated congeners.

In this article, we present dibenzo-*p*-dioxin, dibenzofuran and naphthalene product yields from the slow combustion of the six dichlorophenols (DCPs). Predicted products, based on reaction pathways developed from the previous MCP experimental results²¹⁾, are compared with experimental observations. Possible correlations between PCN and PCDF yields are assessed.

METHODS

Experimental and Analytical Methods

A laminar flow, isothermal quartz tube reactor (40 cm in length and 1.7 cm in diameter; 10 second residence time) was used to study PCN formation from each of the six DCPs. DCP reactant was dissolved in benzene (1:2 molar ratio) and fed by syringe pump into a glass vessel, located upstream of reactor inlet. The glass vessel was heated to vaporize the reactant stream. Nitrogen with 8% oxygen and 0.1% DCP vapor was injected into the reactor. Experiments were conducted at 600°C, the temperature at which PCN yields were greatest under our experimental condition.²²⁾ The entire product stream was immediately quenched at the outlet of the reactor and collected in an ice-cooled dichloromethane double trap system. Gas and rinse solutions were filtered to remove soot.

Benzene was used to get the DCP reactant into solution. Experiments with benzene only (i.e. without DCP reactant) demonstrated that phenol was almost entirely derived from hydroxylation of benzene and not dechlorination of DCP. Otherwise, benzene was not reactive under these conditions.

Analysis of PCDD, PCDF and PCN congeners was accomplished with a Hewlett-Packard 6,890 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 as follows: 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.

Procedures for identifying PCDF and PCDD products have been published previously.^{11,22)} PCN congeners were identified based on the published relative retention time and elution order of PCNs in Halowax 1001, 1014, and 1051.²³⁻²⁵⁾ Unchlorinated dibenzo-*p*-dioxin, dibenzofuran and naphthalene were used as universal response factors to estimate yields of PCDD, PCDF and PCN products, respectively.

Predicted Dibenzo-*p*-dioxin, Dibenzofuran and Naphthalene Products from DCPs

To test our proposed reaction scheme, we developed a priori hypotheses for the major dibenzo-*p*-dioxin, dibenzofuran and naphthalene products from DCPs; these are listed in Table 2. Based on the MCP experimental results, we predicted major isomer products in each homologue by considering the following reaction schemes: coupling of two dichlorophenoxy radicals to yield dichlorodibenzo-*p*-dioxin (DCDD), tetrachlorodibenzofuran (T₄CDF), tetrachloronaphthalene (T₄CN), trichloronaphthalene (T₃CN) and dichloronaphthalene (DCN) products; coupling of dichlorophenoxy radical with the monochlorophenoxy radical formed by loss of ortho chlorine to form monochlorodibenzo-*p*-dioxin (MCDD), trichlorodibenzofuran (T₃CDF), T₃CN, DCN and monochloronaphthalene (MCN) products; coupling of dichlorophenoxy radical with a phenoxy radical formed via hydroxylation of benzene to form dichlorodibenzofuran (DCDF), DCN and MCN products and naphthalene (N); coupling of monochlorophenoxy radical with phenoxy radical to produce MCDF products. As an example, pathways to major isomer products in each dibenzo-*p*-dioxin, dibenzofuran and naphthalene homologue are depicted for 2,4-DCP in Figure 2.

Table 2. Predicted major chlorinated naphthalene, dibenzofuran and dibenzo-p-dioxin products from DCPs.

reactant	naphthalenes	dibenzofurans and dibenzo-p-dioxins
2,4-DCP	1,3,5,7-, 1,3,6,8-T ₄ CNs	2,4,6,8-T ₄ CDF
	1,3,6-, 1,3,7-T ₃ CNs	2,4,8-T ₃ CDF
	1,3-, 2,6-, 2,7-DCNs	2,4-DCDF
	2-MCN	2-, 4-MCDFs
2,5-DCP	1,4,5,8-T ₄ CN	2,7-, 2,8-DCDDs
	1,4,5-, 1,4,6-, 1,4,7-, 1,4,8-T ₃ CNs	1,4,6,9-T ₄ CDF
	1,4-, 1,5-, 1,6-, 1,7-, 1,8-DCNs	1,4,7-, 1,4,9-T ₃ CDFs
	1-, 2-MCN	1,4-DCDF
		1-, 3-, 4-MCDFs
3,5-DCP	1,3,5,7-, 1,3,6,8-T ₄ CNs	2,7-, 2,8-DCDDs
	1,3,6-, 1,3,7-T ₃ CNs	1,3,7,9-T ₄ CDF
	1,3-, 2,6-, 2,7-DCNs	1,3,7-, 1,3,9-T ₃ CDFs
	2-MCN	1,3-DCDF
2,3-DCP	1,2,5,6-, 1,2,7,8-T ₄ CNs	1-, 3-MCDFs
	1,2,5-, 1,2,6-, 1,2,7-, 1,2,8-T ₃ CNs	1,3,7,9-T ₄ CDF
	1,2-, 1,5-, 1,6-, 1,7-, 1,8-DCNs	3,4,7-, 3,4,9-T ₃ CDFs
	1-, 2-MCN	3,4-DCDF
		1-, 3-, 4-MCDFs
3,4-DCP	1,2,6,7-, 2,3,6,7-, 1,2,7,8-T ₄ CNs	1,6-, 1,9-DCDDs
	1,2,5-, 1,2,6-, 1,2,7-, 1,2,8-, 2,3,5-, 2,3,6-T ₃ CNs	1,3,7,8-, 1,3,8,9-, 2,3,7,8-T ₄ CDFs
	1,2-, 2,3-, 1,5-, 1,6-, 1,7-, 1,8-DCNs	1,2,7-, 1,2,8-, 1,2,9-, 2,3,7-, 2,3,8-, 2,3,9-T ₃ CDFs
	1-, 2-MCN	1,2-, 2,3-DCDFs
		1-, 2-, 3-MCDFs
		4,6-DCDF
2,6-DCP	1,5-, 1,8-DCNs	4-MCDF
	1-MCN	1,6-, 1,9-DCDDs
		1-MCDD

RESULTS AND DISCUSSION

DCP Recovery and Overall Product Distributions

DCP reactant recovery and yields of phenol, total MCP, total naphthalene, total dibenzofuran, and total dibenzo-p-dioxin products for each DCP reactant are shown in Figure 3, expressed as a percent DCP conversion (carbon basis). The amount of unreacted DCP recovered ranged from 4% for 3,4-DCP to 13% for 2,4- and 2,6-DCPs. MCP yields from dechlorination of DCP reactants were greatest for 2,4- and 2,6-DCPs, indicating that the ortho and para sites are preferentially

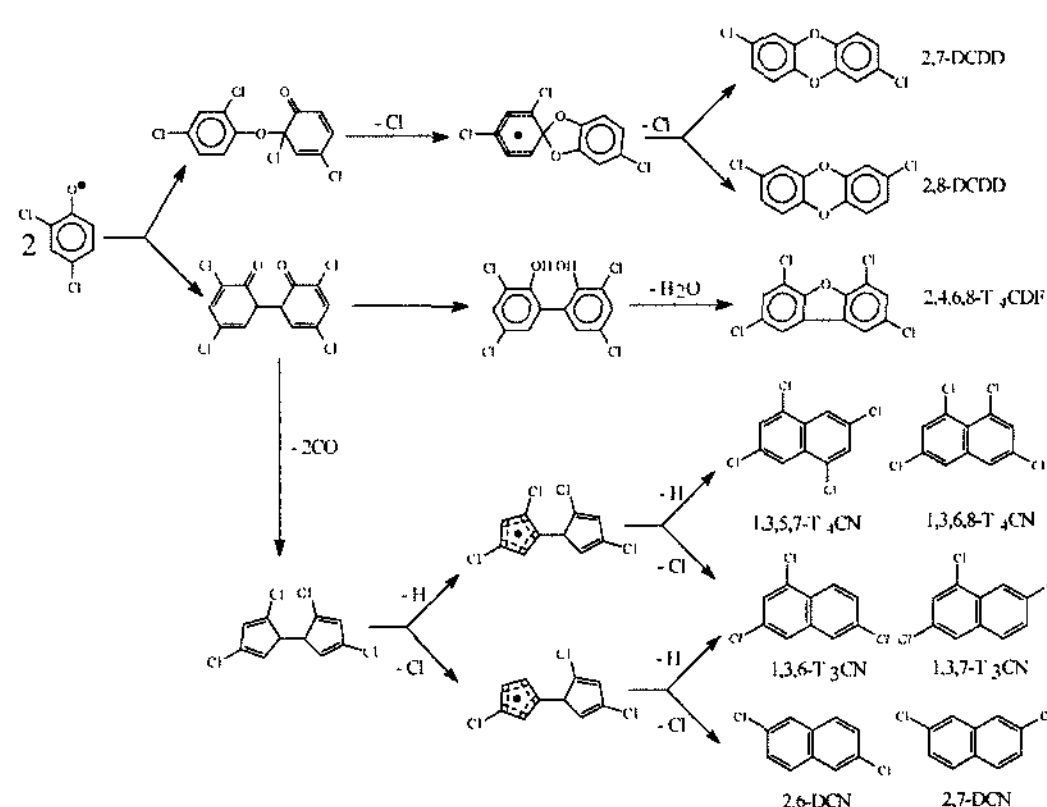


Fig. 2. Predicted dibenzo-p-dioxin, dibenzofuran, and naphthalene products from 2,4-DCP.

Additional dibenzofuran and naphthalene products expected from the following couplings:

- 2,4-dichlorophenoxy + 4-chlorophenoxy → 2,4,8-T₃CDF
- 2,4-dichlorophenoxy + phenoxy → 2,4-DCDF, 1,3-DCN, 2-MCN
- 4-chlorophenoxy + phenoxy → 2-MCDF
- 2-chlorophenoxy + phenoxy → 4-MCDF
- phenoxy + phenoxy → DF, N

dechlorinated. In the case of 2,4-DCP, 4-MCP was the major dechlorination product indicating that dechlorination at the ortho site is greater than dechlorination at the para site. Unchlorinated phenol yields were greater than MCP yields, by more than an order of magnitude for 2,5-, 3,5-, 2,3- and 3,4-DCPs; yields ranged from 0.8% to 2.4% of total DCP feed. Only in the cases of 2,4- and 2,6-DCPs, which had the highest MCP yields, might dechlorination have been a significant source of phenol. Total yields of naphthalene products ranged from 0.004% for 3,5-DCP to 0.009% for 2,3-DCP. Dibenzofuran product yields were higher, ranging from 0.007% for 2,5-DCP to 0.3% for 3,4-DCP. Dibenzo-p-dioxin products were observed only from 2,4- and 2,6-DCPs, with yields of 0.001% and 0.003%, respectively. Although not measured in these experiments, it is known from the MCP experiments that CO yields are high under these conditions, with significant decomposition of the DCP to low molecular weight products.

These results do not suggest a correlation between naphthalene and dibenzofuran product yields. For example, 2,3-DCP produced the greatest

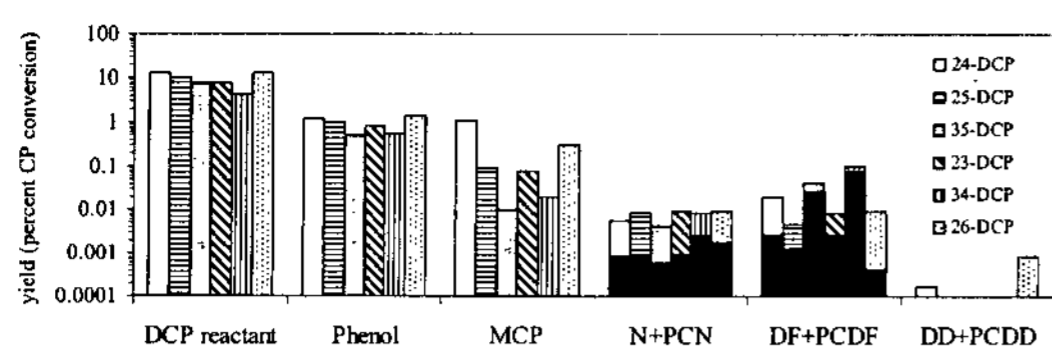


Fig. 3. DCP recovery and phenol, naphthalene, dibenzofuran and dibenzo-p-dioxin product yields (black bars indicate PCN and PCDF yields only from DCPs).

naphthalene product yield but the second to lowest dibenzofuran product yield. The results show that the presence of ortho chlorine on the DCP reactant inhibits dibenzofuran product formation, promotes dibenzo-p-dioxin product formation, and does not appear to have a significant effect on total naphthalene product formation. It will be shown, however, that ortho chlorine does reduce the formation T_3CN and T_4CN products.

PCN and PCDF Homologue Distributions

Total naphthalene homologue and dibenzofuran homologue yields are shown in Figure 4. T_4CN s were detected only in trace amounts, and only from 3,4-DCP. This suggests that the major route of PCN formation from chlorinated phenols is by loss of at least one chlorine atom. The total T_4CDF yields, on the other hand, were similar in magnitude to the yields of other homologues. In particular, the two DCPs without ortho chlorine (i.e. 3,5- and 3,4-DCPs) had high T_4CDF yields. Yields of N, MCNs and DCNs were of similar order of magnitude. The PCN homologue with greatest yield was unchlorinated naphthalene from

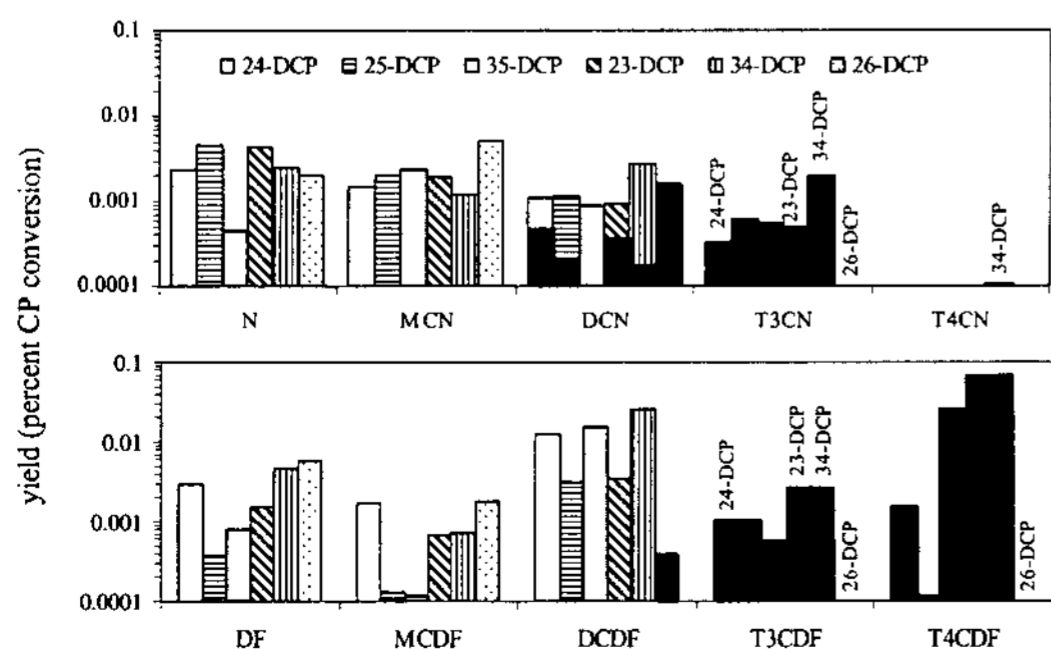


Fig. 4. PCN (top) and PCDF (bottom) homologue yields from DCPs (black bars indicate PCN and PCDF congeners only from DCPs).

2,3-, 2,4- and 2,5-DCPs, MCN from 3,5- and 2,6-DCPs, and DCN from 3,4-DCP. 3,4-DCP produced the greatest T_3CN yield.

Regarding PCDF formation, 3,4- and 3,5-DCPs produced more T_4CDF products than other homologues. For each of the six DCPs, DCDF product yield exceeded T_3CDF product yield, and DF product yield exceeded MCDF product yield. These results are consistent the major PCDF precursors being DCP reactant and phenol from hydroxylation of benzene. PCDFs are formed without loss of chlorine; therefore, two DCPs produce T_4CDF s, DCP and phenol produce DCDFs, and two phenols produce DF. MCDF and T_3CDF products are formed from DCP and MCP formed by DCP dechlorination. MCP yields were significantly lower than phenol yields (Figure 3).

2,6-DCP produced no T_3CDF or T_4CDF products and no T_3CN or T_4CN products, consistent with mechanism predictions (Table 2). Less chlorinated naphthalene and dibenzofuran products were formed, as expected. 3,4-DCP, on the other hand, produced the greatest DCDF, T_3CDF and T_4CDF product yields, as well as the greatest DCN, T_3CN and T_4CN product yields. Thus, ortho chlorine on phenol appears to inhibit the formation of PCN congeners without chlorine loss, consistent with previous observations on PCN formation from MCPs¹⁷⁾.

PCN and PCDF Isomer Distributions

PCN and PCDF isomer fractions are shown in Figures 5 and 6, respectively. The different patterns of PCN isomers for each DCP supports the finding from the previous MCP study that the primary pathway of PCN formation is not a recombination of chlorinated CPDyl radicals as originally hypothesized¹⁷⁾; otherwise, only two different PCN product patterns are expected from the six DCPs because only two types of chlorinated CPDyl radicals are formed via CO elimination from dichlorophenoxy radicals. PCDF isomers also bear the signature of the phenol reactants, as expected. Not only did 3,4-DCP produce the largest yields of di-, tri- and tetra -chlorinated dibenzofurans and naphthalenes (Figure 4), but this

DCP produced the broadest distribution of PCDF and PCN products (Figures 5 and 6). This is consistent 3,4-DCP having both ortho sites unchlorinated (unlike 2,3-, 2,4-, 2,5- and 2,6-DCPs) and lacking symmetry (unlike 3,5-DCP).

To more easily compare observed naphthalene,

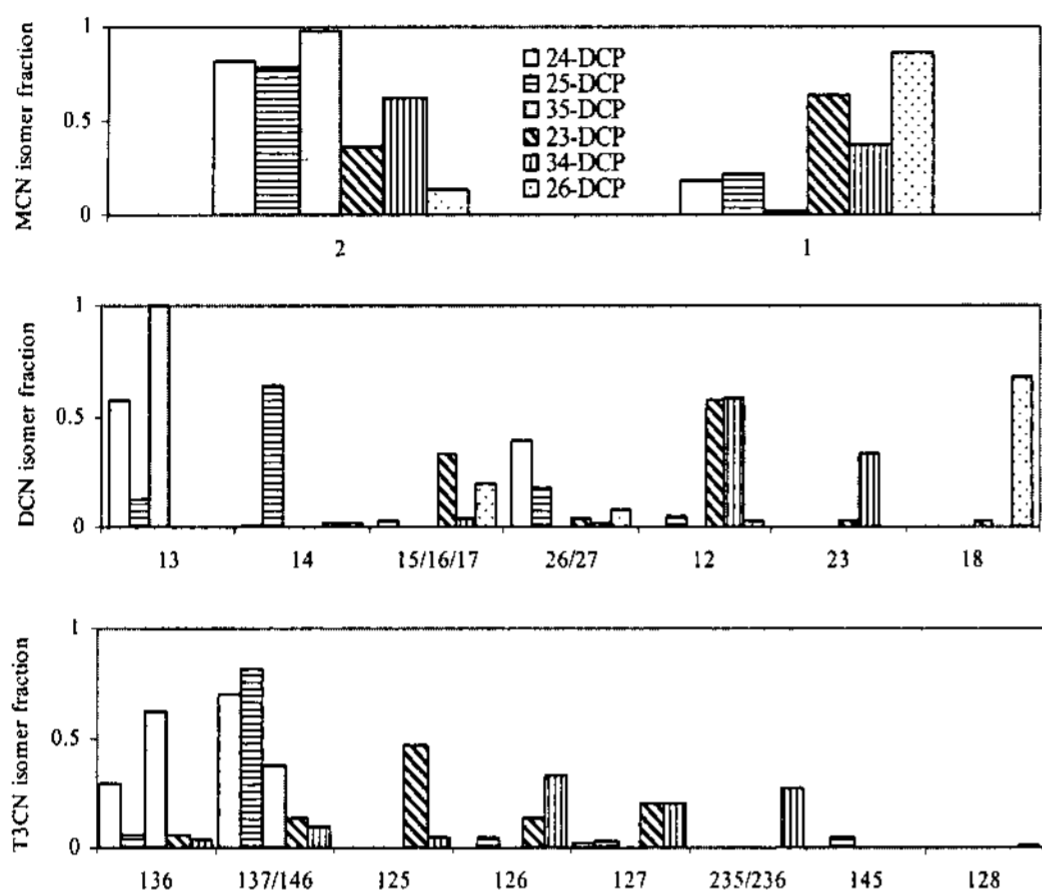


Fig. 5. PCN isomer fractions from DCPs. Only observed PCN isomers (yield >0.00001%) are listed, in order of elution in our analytic system.

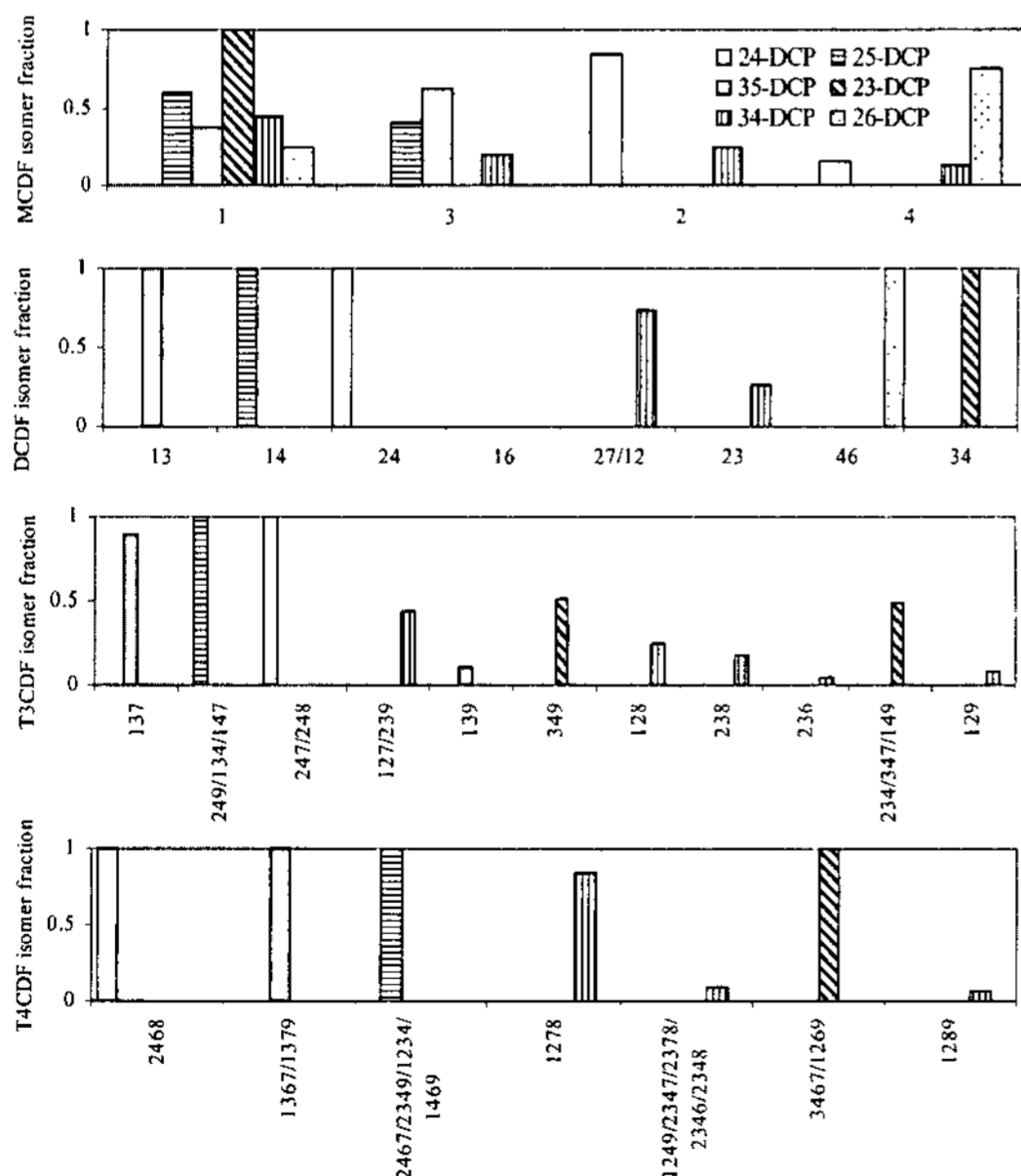


Fig. 6. PCDF isomer fractions from DCPs. Only observed PCDF isomers (yield >0.00001%) are listed, in order of elution in our analytic system.

dibenzofuran and dibenzo-p-dioxin products with those predicted (Table 2), major product peaks in each homologue are listed in Table 3, with predicted products indicated in bold. The observed major peaks agree well with those predicted. All predicted PCDF products were detected, and the less chlorinated congeners (MCDF products and DF) are consistent with those predicted from

Table 3. Observed major naphthalene, dibenzofuran and dibenzo-p-dioxin products from DCPs.*

reactant	observed naphthalene peaks	observed dibenzofuran and dibenzo-p-dioxin peaks
2,4-DCP	<u>1,3,7</u> -/1,4,6-, <u>1,3,6</u> -T ₃ CNs <u>1,3</u> -, <u>2,6</u> -/2,7-DCNs <u>2</u> -MCN N	<u>2,4,6,8</u> -T ₄ CDF 2,4,7-/2,4,8-T ₃ CDF <u>2,4</u> -DCDF <u>2</u> -, <u>4</u> -MCDF DF <u>2,7</u> -, <u>2,8</u> -DCDDs
2,5-DCP	<u>1,3,7</u> -/1,4,6-T ₃ CN <u>1,4</u> -DCN <u>2</u> -MCN N	2,4,6,7-/2,3,4,9-/1,2,3,4 -/1,4,6,9-T ₄ CDF 2,4,9-/1,3,4-/1,4,7-T ₃ C DF <u>1,4</u> -DCDF <u>1</u> -, <u>3</u> -MCDF DF
3,5-DCP	<u>1,3,6</u> -, <u>1,3,7</u> -/1,4,6-T ₃ CNs <u>1,3</u> -DCN <u>2</u> -MCN N	1,3,6,7-/1,3,7,9-T ₄ CDF <u>1,3,7</u> -T ₃ CDF <u>1,3</u> -DCDF <u>3</u> -, <u>1</u> -MCDF DF
2,3-DCP	<u>1,2,5</u> -, <u>1,2,7</u> -, <u>1,2,6</u> -T ₃ CNs <u>1,2</u> -, <u>1,5</u> -/1,6-/1,7-DCNs <u>1</u> -, <u>2</u> -MCN N	<u>3,4,6,7</u> -/1,2,6,9-T ₄ CDF <u>3,4,9</u> -, 2,3,4-/3,4,7-/1,4,9-T ₃ C DF <u>3,4</u> -DCDF <u>1</u> -MCDF DF
3,4-DCP	<u>1,2,6,7</u> -T ₄ CN <u>1,2,6</u> -, <u>2,3,5</u> -/2,3,6-, <u>1,2,7</u> -T ₃ CNs <u>1,2</u> -, <u>2,3</u> -DCNs <u>2</u> -, <u>1</u> -MCN N	<u>1,2,7,8</u> -, <u>2,3,7,8</u> -/..., <u>1,2,8,9</u> -T ₄ CDFs <u>1,2,7</u> -/2,3,9-, <u>1,2,8</u> -, <u>2,3,8</u> -, <u>1,2,9</u> -T ₃ CDFs 2,7-/1,2-, <u>2,3</u> -DCDF <u>1</u> -, <u>2</u> -, <u>3</u> -, 4-MCDF DF
2,6-DCP	<u>1,8</u> -DCN <u>1</u> -MCN N	<u>4,6</u> -DCDF <u>4</u> -, 1-MCDF DF <u>1,6</u> -, <u>1,9</u> -DCDDs <u>1</u> -MCDD

*Largest peaks are listed first. Predicted products from Table 2 are bold and underlined.

reactions between MCP and phenol and two phenols. Predicted dibenzo-p-dioxin products were formed in very small amounts relative to dibenzofuran products, except for 2,6-DCP. Observed major PCN peaks agree with those predicted.

Three further observations can be made from the information in Table 3. First, the lack of detectable T4CN products from all DCPs except 3,4-DCP indicates that PCN formation is favored with one chlorine atom loss, particularly when chlorine is at an ortho position. Second, predicted PCN congeners with 1,8 chlorine substituents were not found, except in the case of 2,6-DCP, suggesting that formation of these congeners with greater steric hindrance is not favored. Third, in all cases except 2,6-DCP, the major DCN peak was that produced from DCP and phenol without chlorine atom loss, not that from two DCPs with loss of two chlorine atoms or that from DCP and MCP with loss of one chlorine atom.

The only major PCN peak that is not consistent with our prediction of major products is the formation of 1,8-DCN from 2,6-DCP. While 2,6-DCP dechlorination yields 2-MCP and 2-MCP is expected to produce both 1,5- and 1,8-DCNs, our 2-MCP experimental results indicate that 1,5-DCN, not 1,8-DCN, is the predominant isomer formed from 2-MCP. The 1,8- isomer was the major DCN peak from 2,6-DCP. As stated above, PCN congeners with 1,8 chlorine substitution are otherwise not observed. One possible explanation is that the 1,8-DCN was formed via the dibenzo-p-dioxin intermediate (oxygen-carbon coupling) rather than the dibenzofuran intermediate²⁶. Since 2,6-DCP does not have an unchlorinated ortho site, only oxygen-carbon coupling occurs without chlorine loss. An alternative pathway of PCN formation from a phenol with both ortho sites chlorinated might lead to other PCN products. Since these phenols are the most abundant congeners in combustion exhaust (e.g. 2,4,6-trichlorophenol, 2,3,4,6-tetrachlorophenol and pentachlorophenol), more experimental study and computational study are needed to develop a reaction scheme consistent with congener-specific PCN formation from 2,6 chlorinated phenols.

CONCLUSIONS

Identification of chlorinated dibenzofuran, dibenzo-p-dioxin and naphthalene congeners from slow combustion of each of the six DCPs supports a proposed mechanism of PCN formation that involves the same phenoxy couple intermediate as that for PCDF formation. This link between PCN and PCDF formation may explain observed correlations of PCN and PCDF yields in combustion systems. These results also provide data that can be used to computationally study congener-specific mechanisms of PCN formation from chlorinated phenols. PCN formation from phenols with 2,6 chlorine substituents requires further study.

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