Gas-phase Polychlorinated Naphthalene Formation from Chlorophenols

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Introduction

Formation of polychlorinated naphthalenes (PCNs) in combustion processes was observed along with other halogenated aromatic compounds such as polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs)[1,2]. Recent studies indicated the strong correlation between several PCN and PCDF isomers in municipal waste incinerator (MWI) fly ash, suggesting that the reaction pathways for the formation of PCN and PCDF might be very similar[3,4]. Sakai and co-workers also reported that the amount of PCNs formed from the pilot-scale solid wastes incinerator was of the same order of magnitude as PCDD/Fs[4]. In previous studies in this laboratory, formations of PCNs with PCDDs/PCDFs from chlorinated phenols were observed in gas-phase pyrolysis and oxidation[5,6].

Recently, we proposed PCN formation pathways from monochlorophenols[7] based on reactions known to be formation of naphthalene from the recombination of cyclopentadienyl (CPDyl) radical combining with phenoxy radical coupling[8,9.] Proposed PCN formation pathways are further extended to explain the isomer distribution of PCN congeners produced during slow combustion of each of the six dichlorophenols (DCPs). In this paper, the congener-specific PCN measurements from DCPs are presented, and PCDD and PCDF measurements are also presented to investigate the correlation between PCN and PCDDs/Fs formation in combustion.

Methods and Materials

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 six dichlorophenols (DCPs). Dichlorophenol reactant was dissolved in benzene and fed by syringe pump into the reactor. Nitrogen with 8% oxygen and 0.3% reactant vapor was injected into the reactor. Experiments were conducted at 600 ^{o}C, the temperature at which PCN yields were greatest. The entire product stream was collected in an ice-cooled dichloromethane (DCM) dual trap. Identification and quantification of individual PCN, PCDD and PCDF congeners was accomplished with Hewlett-Packard 6890 series gas chromatography with HP-5MS column (30m, 0.25mm i.d., 0.25μm film thickness) coupled to Hewlett-Packard 5973 mass spectrometer. Individual PCN isomer was identified based

on the retention time and elution order of PCNs in Halowax 1001, 1014, and 1051 standards compared to those of published reports[10-12]. Procedures for identifying PCDD and PCDF products have been published previously[6,13]. More detailed descriptions of experimental and analytical conditions are presented in elsewhere[5-7].

Results and Discussion

DCP recovery and overall product distribution: DCP reactant recovery and yield of phenol, monochlorophenol (MCP), total naphthalene, total dibenzofurans and total dibenzo-p-dioxin products from the individual DCP reactant experiments at 600 ^{o}C are shown in Figure 1, expressed in percent chlorinated phenol (CP) conversion. The amount of unreacted DCP recovered ranged from 4% for 3,4-DCP to 13% for 2,4- and 2,6-DCPs. The yields of MCP from dechlorination of DCP reactants were measured based on conversion of DCP reactant: 3% for 2,4-DCP, 1% for 2,6-DCP, and 0.3% for 3,5-DCP, suggesting the preferential dechlorination sites as ortho- and para-position. Unchlorinated phenol was observed in larger amounts, with yields ranging from 0.8% to 2.4% of total DCP feed. Control experiments without DCP reactant demonstrate that phenol was derived from hydroxylation of benzene and not further dechlorination of DCP.

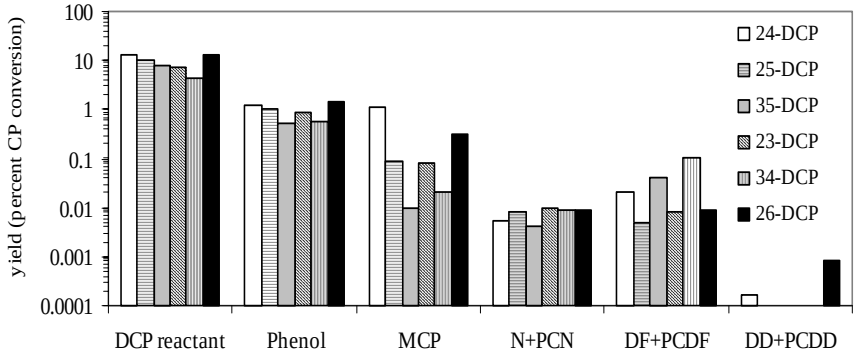

Figure 1. DCP recovery and phenol product yield.

The formation of phenol and MCP can lead to the formation of lower chlorinated naphthalenes and dioxin products though the concentrations of phenol and MCP are much lower than DCP reactant concentrations. Total yields of unchlorinated and chlorinated naphthalene (N and PCN), ranged from 0.004 to 0.009%. Total dibenzofuran (DF and PCDF) yields were slightly higher; yield of 0.3% from 3,4-DCP was greatest and least from 2,5-DCP with a yield of 0.007%. Total dibenzo-*p*-dioxin (DD and PCDD) yields were much lower and observed only from 2,4- and 2,6-DCPs with yields of 0.001% and 0.003%, respectively.

PCN and PCDF homologue distributions: Total yields of naphthalene (N) and chlorinated naphthalenes (mono = MCN, di = DCN, tri = T_3CN and tetra = T_4CN), and dibenzofuran (DF) and chlorinated dibenzofurans (MCDF, DCDF, T_3CDF and T_4CDF) are shown in Figure 2. The predominant PCN homologue was unchlorinated naphthalene from 2,3-, 2,4- and 2,5-DCPs, MCN from 3,5- and 2,6-DCP and DCN from 3,4-DCP. Yields of T_4CN were much lower, with trace

amounts observed only from 3,4-DCP. This suggests that the major route of PCN formation from chlorinated phenols is via loss of at least of one chlorine atom. Experiments with 1-MCN and 1,4-DCN as reactants indicated that dechlorination and Cl-atom migration on aromatic ring do not occur at 600 ^{o}C.

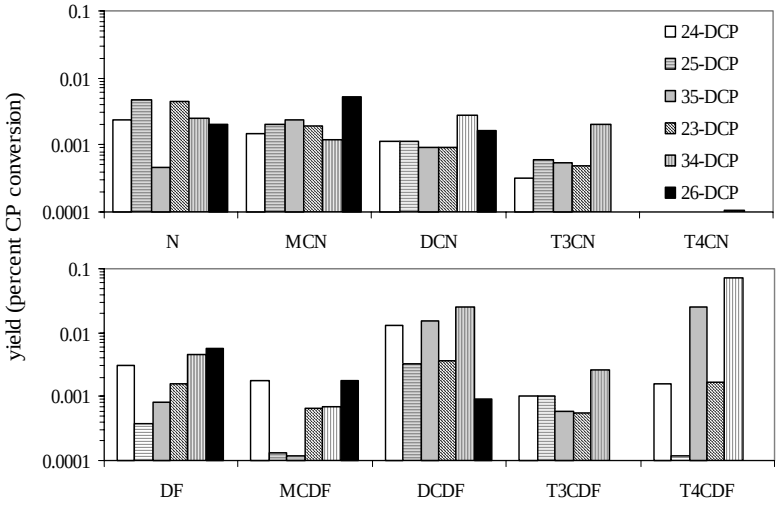

Figure 2. PCN (top) and PCDF (bottom) homologue distributions from DCPs.

Regarding PCDF formation, 3,4- and 3,5-DCPs produced T_4CDF products the most and 2,4-, 2,5- and 2,3-DCPs produced mostly DCDF products. Unchlorinated dibenzofuran (DF) was produced the most from 2,6-DCP. Consistent with previous observations on PCN formation from MCPs, ortho chlorine on phenol appears to inhibit both PCDF and PCN formation[7]. Here, 2,6-DCP, with two ortho chlorines, produced the least tri- and tetrachlorinated PCDF and PCN products. On the other hand, 3,4-DCP, with no ortho chlorines, produced the most tri- and tetrachlorinated PCDF and PCN products.As already mentioned, phenol is formed from the hydroxylation of benzene. The high yields of DF and N suggest that phenol is very reactive in the formation of naphthalenes and dibenzofurans. Much of the DCP reactants undergo decomposition and oxidation to form low molecular weight products.

PCN and PCDF isomer distributions: PCN and PCDF isomer patterns in Figure 3 illustrate the dependence of their formation on DCP reactants. The different PCN isomer patterns from DCPs suggested that the primary pathway of PCN formation from DCPs was not a recombination of chlorinated CPDyl radicals; otherwise, only two different PCN isomer patterns are expected from six DCPs because only two types of chlorinated CPDyl radicals can be formed via decomposition of DCPs. This result is consistent with that found previously in a study of PCN formation from MCPs[7].

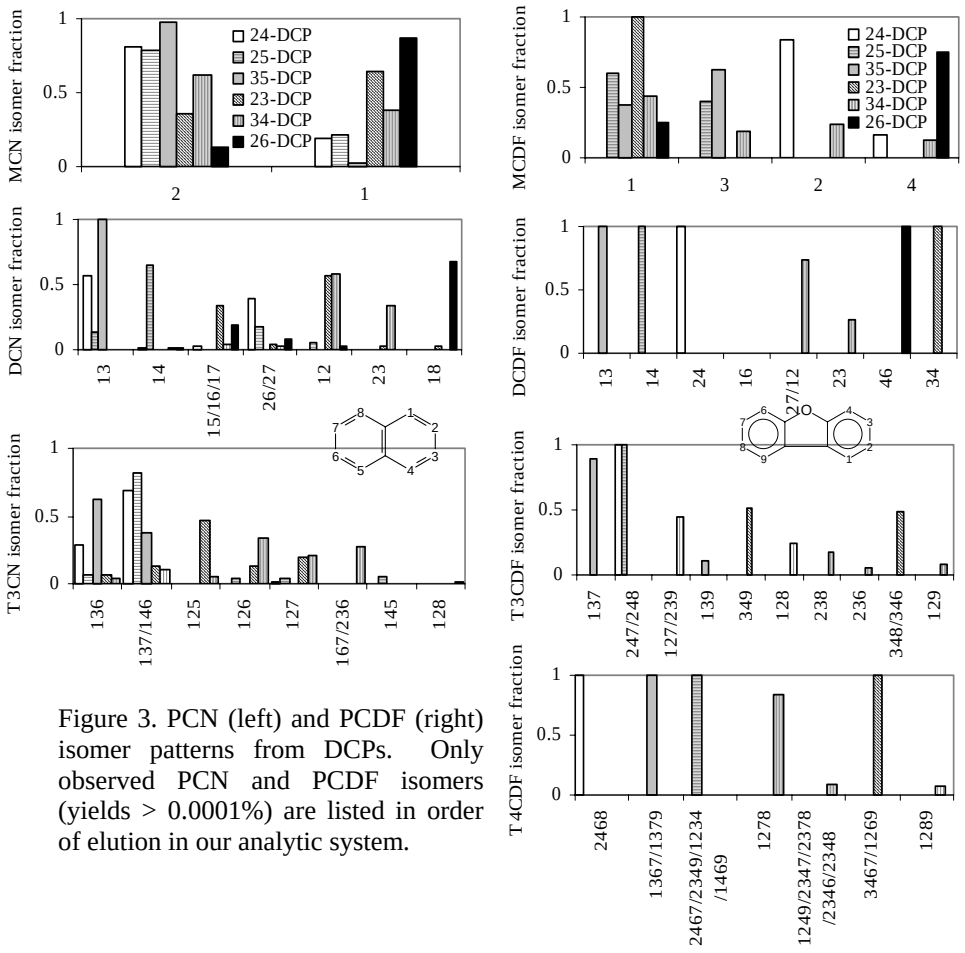

Figure 3. PCN (left) and PCDF (right) isomer patterns from DCPs. Only observed PCN and PCDF isomers (yields > 0.0001%) are listed in order of elution in our analytic system.

In the case of PCDF formation, carbon-carbon coupling of phenoxy radicals at unchlorinated ortho sites, followed by tautomerization to form a dihydroxybiphenyl (DOHB) intermediate, and then H_2O elimination to produce PCDF. All expected PCDF isomers were detected and the observed less chlorinated dibenzofurans (MCDF, DCDF and T_3CDF) are formed from reactions between the dechlorinated DCP reactants and MCP and phenol products.

Proposed mechanism of T_3CN formation from DCPs: Previously reported PCN and PCDF formation pathways from MCPs were further extended to explain the observed PCN and PCDF products from DCPs[7]. The proposed mechanism was based on the known PCDF formation pathways by phenol condensation, phenoxy radicals couple to form the *o,o'*-dihydroxybyphenyl (DOHB) intermediate[9,14]. Here, CO elimination produces the 9,10-dihydrofulvalene intermediate leading to PCN formation competes with tautomerization that produces the DOHB intermediate leading to PCDF formation. The 9,10-dihydrofulvalene compounds from each DCP reactants are

not the same, and lead to different sets of PCN products following conversion of dihydrofulvalene to naphthalene via three-member ring closure and opening whereas in the unchlorinated system, all of alternative routes for the radical rearrangement in the dihydrofulvalene-to-naphthalene mechanism lead to the same product – naphthalene[8]. Given the distributions of PCN products observed, the preferred PCN formation pathway from chlorinated dihydrofulvalene appears to be involving a loss of chlorine atom when it located at 1,4,5,8 sites (the numbering of dihydrofulvalene is shown in Figure 4). Experimental evidence of loss of Cl atoms in PCN formation is the high yield of T_3CN and DCN products and the lack of T_4CN products from all DCPs. To explain the observed PCN and PCDF products, the formation pathways of PCN and PCDF products from 3,4-DCP are proposed in Figure 4. Using same pathways, PCN products from each DCP are predicted and compared with the observed PCN products, which are summarized in Table 1. Major T_3CN products observed are well matched with the predictions.

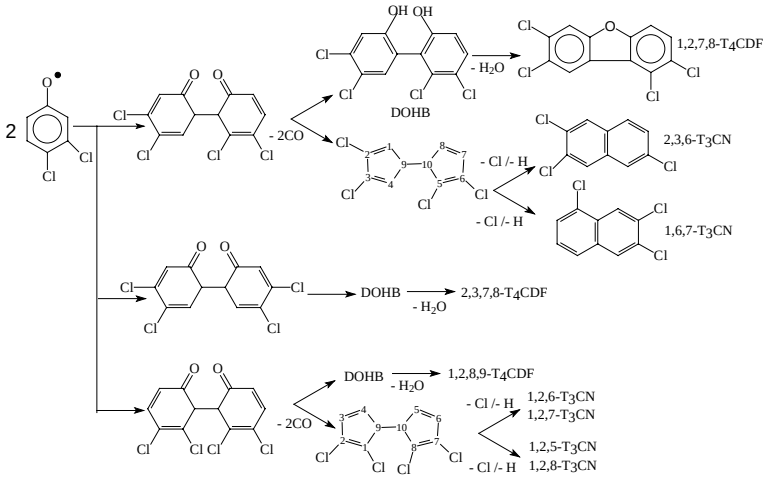

Figure 4. Major PCDF and PCN product pathways and minor products from 3,4-DCP.

Table 1. Comparison of predicted and observed PCN isomers from DCPs.

CP reactant	Predicted T_3CN isomers	Observed T_3CN isomers*
2,4-DCP	1,3,6-, 1,3,7-	1,3,7-/1,4,6-, 1,3,6-
2,5-DCP	1,4,5-, 1,4,6-	1,3,7-/1,4,6-, 1,3,6-, 1,4,5-, 1,2,6-, 1,2,7-
3,5-DCP	1,3,6-, 1,3,7-	1,3,6-, 1,3,7-/1,4,6-
2,3-DCP	1,2,5-, 1,2,6-, 1,2,7-, 1,2,8-	1,2,5-, 1,2,7-, 1,2,6-, 1,3,7-/1,4,6-, 1,3,6-
3,4-DCP	1,2,5-, 1,2,6-, 1,2,7-, 1,2,8-, 1,6,7-, 2,3,6-	1,2,6-, 1,6,7-/2,3,6-, 1,2,7-, 1,3,7-/1,4,6-, 1,2,5-, 1,3,6-, 1,2,8-
2,6-DCP	none	trace

*isomers are listed in order of yield.

Formation of MCN and DCN products: Less chlorinated PCN and PCDF products observed could be explained by the same mechanism involving unchlorinated phenol and MCP products in addition to DCP reactants. The high yield of DCDF indicated that these products were formed from a reaction of phenol and DCP reactants, which the predictions of DCDF products via phenol condensation pathway are consistent with the observations. Hence, less chlorinated PCN may also

be formed from the same coupling as that produced less chlorinated PCDF. For an example, the carbon-carbon coupling of phenol and 3,4-DCP is expected to produce 1,2- and 2,3-DCDF, which the same phenoxy coupling could also lead to 1,2- and 2,3-DCN in accordance with the proposed PCN mechanism. In previous work, it was observed that gas-phase PCDF formation from phenols is favored from lower chlorinated phenols[6-7]. The presence of chlorine in the ring system favors tautomerization and PCDF formation over CO elimination and PCN formation. One explanation is that the withdrawal of electron density by Cl-atoms from the ring systems suppresses CO elimination and PCN formation to a greater extent than it suppresses tautomerization and PCDF formation.

The proposed PCN formation pathways, however, do not explain all of our results. The isomer pattern of DCN products suggests that the most abundant DCN isomers are produced by coupling of phenol and DCP without a loss of chlorine atom rather than with loss of one chlorine. Another result that is not explained by the proposed pathways is that of 1,8-DCN formed from 2,6-DCP. 1,8-DCN appears to be formed from reaction of 2-MCP and 2,6-DCP, not from 2-MCP only (previous experimental results showed that 2-MCP did not produce 1,8-DCN)[7]. These results suggest that PCN products can be formed from different phenoxy coupling rather than ortho-ortho coupling. To elucidate the mechanism, further experimental and/or computational studies are needed. In addition, Cl-atom migration on CPD ring[15] would lead to the formation of additional PCN isomers. In this work, however, no evidence of Cl-atom migration was observed. There are other possible pathways for PCN formation in combustion processes such as *de no* synthesis, other precursors, surface catalyzed reactions and thermal hydrogenolysis of dibenzo-*p*-dioxin and dibenzofuran. Here, we address on the PCN isomer patterns produced from chlorinated phenols in the gas-phase.

Acknowledgments
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