

ROLE OF ALIPHATIC PRECURSORS IN THE FORMATION MECHANISM OF PCDD/F, PCB AND PCN

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The environmental and health hazards of chlorinated compounds are well documented. However, it was the discovery of their presence in the effluent of municipal waste incinerators and the realization that broad segments of the population are exposed to these chemicals that raised the most concern. Subsequent research has shown that combustion or thermal processes that contain a source of chlorine emit measurable quantities of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/F), polychlorinated biphenyls (PCB), polychlorinated naphthalenes (PCN) and polychlorinated biphenylenes (PCBN). Consequently, the US-EPA has launched a Combustion Strategy designed to reduce the emissions of dioxins and "dioxin-like" compounds from combustion sources.

In this paper, the formation mechanism of all dioxin and "dioxin-like" compounds is discussed using PCDD/F as an example. This is a valid assumption as all these chlorinated compounds have shown similar behavior in various zones of an incinerator. For example, concentration of all these compounds decreases sharply in the after-burner and then again increases in incinerator cool zone. Also, principal component analysis conducted by Fangmark et al. shows that PCDD/F, PCB, and PCN are closely related.[1]

Several origins of PCDD/F emissions from combustion sources have been proposed. They include: 1) native PCDD/F present in the combustor's fuel or waste feed, 2) formation via homogeneous gas-phase reactions from chlorinated hydrocarbon (CHC) precursors, 3) surface catalyzed synthesis from CHC precursors, and 4) so-called *de novo* synthesis in which elemental or graphitic carbon contained in fly-ash or soot is converted to PCDD/F. Although many studies have been conducted to determine the yields of PCDD/F under various conditions, very little progress has been made in determining a mechanism of formation. The mechanistic situation is complicated even more by the tendency of researchers to discuss each of these pathways as if they were totally independent. Most laboratory studies of various proposed pathways have been unable to achieve the rates of PCDD/F formation and PCDD to PCDF ratios observed in these field studies. However, three recent studies have demonstrated that appreciable yield of PCDD/F can be formed on time scales of 1.0 - 60 s with PCDD to PCDF ratios of $\ll 1.0$ which is in rough agreement with field results.[1-3] These studies have four commonalities: 1) a temperature window of 250 to 450 °C that favors rapid formation; 2) formation at rates and reaction times equivalent to that experienced by entrained particles in cool zones of combustors; 3) the presence of a largely silica-based surface; and most importantly 4) the need for an upstream source of combustion generated species.

Although these studies provide strong evidence of a new pathway to formation of PCDD/F, the mechanism has not been established. We hypothesize that it is the presence of a combustion effluent that distinguishes these studies from earlier studies of PCDD/F formation.

The combustion-generated hydrocarbons (radicals/molecular species) under post-combustion conditions are either themselves a carbon source for PCDD/F formation or they activate fly-ash bound carbon. Also, the nature and rate of reactions of chlorine on fly-ash surfaces is of considerable importance as chlorine may be involved in the liberation of solid carbon in the *de novo* process. If chlorination is sufficiently fast on surfaces, it may also mean that combustion-generated hydrocarbons adsorbed on surfaces may be chlorinated or somehow activate surface-bound carbon to form PCDD/F. Either of these latter pathways may be the mechanism for the fast *de novo* process.

In the pathways depicted in figure 1, we propose that the initial step is the formation of small chlorinated hydrocarbons directly by radical recombination in the gas phase or from surface bound carbon. It is established that some soot is formed in even well-controlled flames through molecular growth mechanisms involving small, stable but reactive hydrocarbon species. This soot is formed in the transition between the visible flame and the surrounding high-temperature thermal zone of combustors. Even if the quantities of soot that are formed are small, the amount of carbon that is tied up as soot or char in fly-ash is far in excess of that needed to form the observed stack concentrations of PCDD/F. However, for soot to form PCDD/F there must be a suitable pathway for liberating the carbon to participate in further reactions. The physical and chemical nature of the soot may affect the composition and yield of the PCDD/F precursors. The possible *de novo* formation of PCDD/F or precursors from soot and carbonaceous fly-ash particles has been discussed by several researchers. Simply heating fly-ash samples at temperatures from 250-600 C in the presence of air has apparently resulted in PCDD/F formation, although the rate of formation, 0.2-20 ng PCDD/F per gram of fly-ash per second, is too slow to account for yields in full-scale combustors. We hypothesize that this so-called "rapid *de novo*" formation is initiated by reactive radicals that attack the carbon network of the soot or fly-ash to form small-molecule precursors to PCDD/F.

In our mechanism, the solid carbon structure is attacked at its periphery, resulting in a degradation of the overall network. Other researchers have proposed that larger species may be formed directly from the solid carbon reagent. Release of (substituted) benzenes, anthracene, phenols, and even PCDD/Fs have been proposed to result from electrophilic attack of the graphitic carbon perpendicular to the graphitic plane. However, recent study by Schoonenboom and Olie has shown that PCDD/F during anthracene combustion (large species from soot) was formed not directly but by recombination of anthracene degradation products.[4] This result is consistent with our hypothesis that carbon in fly ash/soot will most probably be liberated in form of small aliphatic hydrocarbon.

To further verify our hypothesis, we selected acetylene, a common combustor effluent, as an example of small aliphatic hydrocarbon that may be liberated from fly ash/soot or a product of radical recombination. We then investigated acetylene chlorination and condensation reactions on different types of copper salt impregnated surfaces under typical post-combustion incineration conditions.[5] This project was a collaborative effort between the University of Dayton and GSF-Munich. Experiments were conducted with acetylene or acetylene/HCl-mixtures in a quartz reactor filled with copper salts impregnated on Borosilicate foam of known pore size at temperatures between 150 to 500 °C. Reactions of acetylene in a very fuel lean atmosphere (fuel-air equivalence ratio ~0.06) on CuCl₂ impregnated Borosilicate foams produced a variety of chlorinated organic compounds. This system was able to chlorinate acetylene to form chlorinated C₂ compounds. Besides these, condensed products up to C₈ chloroorganics were analyzed in the gas phase; PCDD/F and other higher molecular weight compounds were adsorbed on the

Borosilicate surface. The most striking feature in the distribution of reaction products was the high degree of chlorination of the organic moiety. A majority of products were perchlorinated. An interesting observation was the lack of unchlorinated acetylene polymerization products. Furthermore, cracking products and compounds with an odd number of carbon atoms were not detected under these reaction conditions. The main reaction products formed in the acetylene-CuCl₂/BS system were as follows: Tetrachloroethylene (C₂Cl₄) > hexachlorobutadiene (C₄Cl₆) > trichloroethylene (C₂HCl₃) > pentachlorobutadiene (C₄HCl₅) > tetrachlorovinylacetylene (C₄Cl₄) > hexachlorobenzene (C₆Cl₆) > tetrachloroethane > C₆Cl₈ (two different isomers) > pentachlorobenzene (C₆HCl₅) > C₆Cl₆ (isomer of hexachlorobenzene) > C₆Cl₄ > C₈Cl₉H. The same behavior was found for CuO impregnated Borosilicate in the presence of HCl. However, temperatures above 300 °C were required for this catalytic system. Based on our results, we propose that acetylene is chlorinated by CuCl₂ in a ligand transfer oxidation mechanism to mono- and dichloroacetylene and other less unsaturated chlorinated C₂ compounds. Chlorinated acetylenes can then form oligomers in a surface-catalyzed reaction. It was shown by Stahl et al. that reactive dichloroacetylene is stabilized in metal complexes.[6] These metal-dichloroacetylene complexes react with additional dichloroacetylene to form chlorinated metallacylopentadienes, which can be intermediates in dichloroacetylene condensation reactions. According to the Glaser and Cadiot-Chodikiewicz reaction, Cu⁺ complexes are possible catalysts. Chlorinated metallacylopentadiene can form chlorinated butadienes in oxidative chlorination reaction with CuCl₂, or react with dichloroacetylene in an insertion or Diels-Alder type reaction to form chlorinated benzenes. In the 300 °C experiments, the ratio of chlorinated benzenes to PCDD/F was 112 which is consistent with incinerator data. However, chlorophenol concentration was two orders of magnitude lower than PCDD/F. This is not consistent with incinerator data where chlorophenol concentration is three to five orders of magnitude higher than PCDD/F. This is because phenols under these reaction conditions are rapidly oxidized on reactive surfaces.

Similar results were obtained by Mulder and Jarmohamed during oxychlorination and combustion of propene on fly-ash.[7] They observed that at mild conditions polychlorinated C₁, C₂, and C₃ species were formed but at higher temperature (470 to 550 °C) substantial amounts of polychlorinated benzenes, dibenzodioxins and mono- and dibenzofurans were formed. Chlorinated phenols were not observed in this study. Based on the results of oxychlorination of acetylene and propene, we can conclude that small aliphatic hydrocarbons from soot or from radical recombinations are first chlorinated and then subjected to condensation reactions that lead to formation of chlorinated cyclic precursors like polychlorinated benzenes (PCBz), polychlorinated phenols (PCPh), and polychlorinated cyclohexanes (PCHx). Our conclusion that hydrocarbons chlorinate and then condense was further validated by the results of the Imagawa and Miyazaki study.[8] In this study, they found that it is not chlorinating reactions of benzene and naphthalene that are dominant in the formation of PCBz and PCNs, but condensation reactions of chlorinated C₁ and C₂ species.

It is likely that under post-combustion conditions, all of the above mentioned cyclic precursors will be in a state of equilibrium, converting back and forth depending on slight changes in reaction conditions. As shown in figure 2, these cyclic precursors can then react to form PCDD/F, PCBs, PCNs and PCBNs. The formation pathways shown in figure 2 have been validated

by numerous laboratory and field studies. Our mechanism shows that formation of all of these chlorinated pollutants is closely related.

References

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Figure 1 – A chlorination and condensation pathway in combustion/thermal sources.

Figure 2 – Formation pathways for PCDD/F, PCB, PCN and PCBN.

