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Perspectives on the Formation of Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans during Municipal Solid Waste (MSW) Incineration and Other Combustion Processes

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ABSTRACT
The pathways by which polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) are formed and the interactions between their aromatic precursors, in particular chlorophenols (ClPhs), and transition metal catalysts are discussed. A literature survey and data from pilot-scale combustion experiments allow conclusions to be drawn on the relations between ClPhs and PCDD/Fs in municipal waste incineration and other combustion processes. The results suggest that the ClPh pathway is among the most important for the formation of PCDD/Fs.

Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) are structurally simple, almost planar molecules with 1 or 2 oxygen atoms and 1−8 chlorine atoms attached to the molecular backbone (Figure 1). PCDD/Fs are undoubtedly one of the most toxic molecular families known, having a great diversity of injurious biological effects at the parts-per-million to parts-per-billion level.[1] Interestingly, they may also form naturally,[2] mainly from chlorophenols (ClPhs),[3] although the combustion of organic matter in the presence of chlorine and metals is widely recognized as a major source, alongside other anthropogenic sources such as chemical manufacturing, paper and steel mills, and accidental landfill fires.[4] We review here the pathways by which PCDD/Fs are formed in municipal solid waste (MSW) incineration and other combustion processes. Special emphasis will be placed on ClPhs as precursors of PCDD/Fs, as it seems reasonable to suggest that they play a key role. Ultimately this may lead to a unifying perspective on the PCDD/F formation problem.

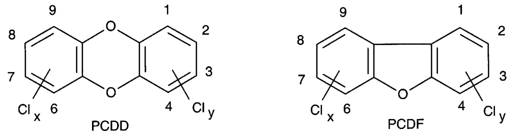

FIGURE 1. Structure and numbering of PCDD/Fs.

PCDD/Fs in Incineration Processes. The presence of PCDD/Fs in the flue gases of municipal waste incinerators was first observed in 1977.[5] Initially it was thought that PCDD/Fs present in the fuel (waste) could survive the incineration process, but later it was demonstrated that these compounds are completely destroyed at the temperatures present in the combustion chamber,[6] so that this cannot be the source of the high concentrations (i.e., ng/Nm^3 in this context) present in the flue gases. Instead, as the gases leave the primary combustion chamber, compounds formed in pyrolytic and pyrosynthetic reactions cool from 1000 °C and subsequently condense, and it is during this process, accompanied by molecular rearrangements, that PCDD/Fs are formed, commonly in the temperature range between 650 and 250 °C. Recent evaluation of data in the literature[7] reveals that the optimum temperature for PCDD/F formation is probably around 350−400 °C.

Intensive research has given some elucidation on how PCDD/Fs may form in combustion processes, although there are still many open questions. The most important trends and results have been summarized in recent reviews.[8−11] Three main pathways have been presented for their formation during combustion: (i) pyrosynthesis, i.e., formation in the gas phase at high temperatures,[12−14] (ii) de novo formation from macromolecular carbon and chlorine at low temperatures,[15] and (iii) formation from various precursors, such as ClPhs or polychlorinated

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diphenyl ethers (“predioxins”), which may be formed in the gas phase during incomplete combustion and combine heterogeneously and catalytically with the fly ash.[16,17] The relative importance of these formation pathways has been subject of much debate, and is still controversial. The following order is considered to be most likely: i < ii < iii.

Although all these pathways have been known for a number of years, few detailed reaction mechanisms, in the strictest sense of the word, can yet be offered for PCDD/F formation. This is due in particular to the extreme complexity of the fly ash matrix, which effectively obscures the identity of the active catalytic sites and the overall processes. In addition, a plethora of organic molecules are capable of forming PCDD/Fs.[9,10]

Our view is that the PCDD/F formation problem is complicated even more by the tendency of many researches to discuss each of the formation pathways as if they were totally independent, although some findings suggest a certain commonality. PCDD/F “signatures”, i.e., patterns describing congener distribution under different combustion conditions, are similar, showing only small variation according to the process involved (municipal waste incineration, medical waste incineration, hazardous waste incineration, biomass fire boilers, etc.).[18] This suggests that the formation pathways may be closely related in all combustion processes. However, the mechanistic details of the pathways are still largely unknown, apart from the condensation of chlorophenols. The role of ClPhs as PCDD/F precursors has been well established in both gas-phase reactions and heterogeneous surface reactions, but it is not certain in the case of de novo pathways. The purpose of this account is to explore whether the ClPh pathway could provide a connective perspective on the PCDD/F formation problem.

Chlorophenol Pathways of PCDD/F Formation

Heterogeneous Reactions. The conversion of ClPhs to PCDDs on fly ash has been thoroughly demonstrated in the literature.[19−30] For example, when penta-ClPh was passed through copper powder at 300 °C, a diverse set of condensation and dechlorination reactions took place, indicating that this is probably an important precursor.[19] The condensation reactions are postulated to include Smiles rearrangements, with a dioxaspiro-type compound as an intermediate.[22−24] This proposition is supported by the finding that the predominant PCDDs formed from 2,4,6-ClPh in heterogeneous reactions are two tetra (1,3,6,8- and 1,3,7,9-TCDD) and four penta (1,2,4,6,8-, 1,2,4,7,9-, 1,2,3,6,8-, and 1,2,3,7,9-PeCDD) isomers.[27,28] Interestingly, the same isomers are the most abundant found among tetra- and penta isomers in the municipal waste incineration effluents,[13] providing further evidence of the commonality in the formation pathways. ClPhs have been found to be highly adsorptive on fly ash, and yields of PCDDs were observed to increase with increasing ClPh concentrations.[25,26] It has been shown that formation from penta-ClPh is 10^2−10^5 times faster than de novo synthesis,[21] indicating that precursor formation may dominate in real incineration situations, although converse claims have also been presented on the basis of the results of kinetic modeling.[31]

Gas-Phase Reactions. It was suggested initially, using a simplified kinetic model in which the key step involves the dimerization of a phenol molecule and a phenoxyl radical, that gas phase formation of PCDDs at high temperatures (pyrosynthesis) is unlikely to occur,[32] although attention has been drawn recently to the fact that predictions of the outcome of this pathway have been several orders of magnitude lower than actual measured dioxin formation.[33] Huang and Buekens[34] suggested after reevaluating the model that the reason for the discrepancy probably lies in additional unknown PCDD formation reactions not included in the model, so that the potential contribution of gas phase reactions to PCDD formation may have been underestimated so far. Indeed, it has been shown that radical/molecule reactions are actually an insignificant pathway for PCDD/F formation in incinerators, compared with the condensation of two (chloro)-phenoxyl radicals.[35] In particular, the formation of dibenzofuran (DF) in the gas phase has been described in terms of the coupling of neutral, resonance-stabilized phenoxyl radicals followed by enolization.[36] In addition, Weber and Hagenmaier[37] have discussed the condensation reactions of ClPhs by pyrolysis as a possible pathway in the formation of PCDD/Fs. In a real incineration situation, unsubstituted phenol is usually much more abundant that ClPhs.[38,39] This implies that dibenzofuran (DF) and lower chlorinated PCDFs (rather than PCDDs) should be expected to result from the primary combustion. Interestingly, this is exactly what has been observed experimentally.[40,41]

De Novo Pathways. The use of the term de novo synthesis has been somewhat halting; i.e., it is often loosely considered to refer to the combustion of dissimilar starting materials such as elemental carbon and sources of oxygen, chlorine, and hydrogen. A more accurate definition would be breakdown reactions in the carbon matrix, as recently pointed out by Iino et al.[42] Fly ash matrix is a complex structure, and it has been found that its carbon morphology can have a marked influence on de novo synthesis, in that degenerated graphitic structures (such as activated carbon, charcoal, carbon black and soot) are oxidized to PCDD/Fs, whereas amorphous carbon and graphite sheets do not serve as a major source for the formation of chlorinated aromatic compounds.[42−44]

Once de novo formation has started, the condensation reactions may take place either via precursors or from structurally distant molecules, so that anthraquinones, polyaromatic hydrocarbons, and even aliphatic or monocyclic aromatic hydrocarbons, for example, are potential carbon sources for the formation of PCDD/Fs.[24,42,43,45,46] Interestingly, it has been proposed that PCDD formation from macromolecular carbon proceeds partly via ClPh intermediates, implying that the de novo and precursor pathways may be closely related.[47,48] On the other hand, it has been found that the formation of PCDD from charcoal and ^{13}C-labeled penta-ClPh proceeds via separate pathways, at least in this particular experimental system.[21]

The condensation of ClPhs is of minor importance in the formation of PCDFs in the de novo processes.[47,48] This experimental finding may be explained with predominance of thermodynamically most stable ClPh isomers, in particular, 2,4,6-, 2,3,4,6-, and penta-ClPh. These isomers have no *ortho*-hydrogen atoms, which are essential for the formation of PCDFs via condensation reactions, as will be discussed below. In contrast, it is possible that PCDFs may be released from biphenyl structures preformed in the carbon matrix; i.e., the overall process can be viewed as a combination between the de novo and the precursor pathways.[47] Thus, it seems that ClPhs do not give PCDFs via de novo reactions, contrasting sharply with heterogeneous surface reactions[27−30] and gas-phase reactions[35,36] in this respect. In any case, the differences between de novo and precursor pathways should not be overemphasized, as they may have many common features in terms of basic chemistry.

In general, de novo pathways lead preferentially to the formation of PCDFs, in contrast to most of the known precursor routes, which generate PCDDs. In addition, de novo pathways produce PCDD/Fs with congener compositions similar to those found in cases of incineration. Thus under practical conditions where the PCDD/F signatures contain large amounts of PCDFs, de novo pathways may be important. It has been observed in laboratory-scale experiments, however, that rates and yields of de novo synthesis are low, as the maximum formation rate did not exceed 200 ng/min (g of fly ash), while the reported yield of precursor synthesis (at 150 μg/m^3 of ClPh) was 3300 ng/m^3, being in accordance with the formation rate in real incinerators.[45,49] However, it is possible to offer an alternative explanation for the abundance of PCDFs over PCDDs (see below).

Influence of the Catalyst. The role of noncatalytic surface reactions in the PCDD/F formation is not well established yet, although it has been proposed that the fly ash surface acts primarily as an adsorption site for PCDD/F precursors.[50] However, the surface-catalyzed formation is generally believed to be the major contribution to PCDD/F emissions in combustion processes. In particular, post-furnace formation of PCDD/Fs seems to take place at detectable rates only under the influence of metal catalysts. The fly ash is enriched with various transition metals and their water-insoluble salts, all of which are well-known catalysts in organic reactions. The formation of active catalytic sites on fly ash depends on the size of the particles condensed from the gas phase, in that a small particle size is more favorable.[51]

The catalytic effect of copper in the de novo pathway has been proven by many authors, e.g., Stieglitz et al.[15,52] have been active in this area. Other metal chlorides have also been tested in this respect, and $FeCl_3$ has been found to catalyze PCDD/F formation efficiently.[53]

We have identified copper as a strong catalyst but have also found $FeCl_3$ to promote PCDD/F formation to a marked extent.[54] It should be emphasized, however, that in our study iron and copper nitrates and chlorides (hydrates) were co-fired with aliphatic fuel or injected directly into the flame. The results suggest that copper and iron do catalyze not only the de novo pathway, but also the formation of aromatic rings, with subsequent chlorination and condensation reactions. Also some metal oxides (Ni, Fe, and Zn) have been proven to catalyze the PCDD/F formation from ClPh precursors.[55]

The presence of catalysts is essential in the precursor pathways, as they reduce the activation energies of condensation reactions thus making the PCDD/F formation possible. More specifically, it seems reasonable to suggest that the role of a catalyst in the heterogeneous formation of PCDDs is at least 3-fold: it facilitates (i) the coupling of two ClPh moieties, (ii) the stabilization of the dioxaspiro intermediate, and (iii) the release of chlorine from an emerging PCDD/F structure, perhaps accompanied by an increase in the oxidation state (from Me^+ to Me^{2+}, i.e., from CuCl to $CuCl_2$, for example). Furthermore, catalysts may participate in metallacyclization reactions of aliphatic hydrocarbons at early stages of the reaction chains,[56] as well as act effective (oxy)chlorination agents throughout the processes. It should be emphasized, however, that many details of the catalytic pathways are still highly speculative.

Kinetic versus Thermodynamic Control. It is primarily the kinetics, not the thermodynamics, that are responsible for the formation of PCDD/Fs in combustion processes. It has been repeatedly suggested, particularly in the case of de novo formation, that the isomer distribution for each PCDD/F homologue may be thermodynamically controlled. However, Addink et al. have performed thermodynamic calculations for the formation of PCDD/Fs by minimizing the Gibbs free energy of system against chemical composition at given temperature and pressure (subject to the constraints of constant abundances of elements).[57] The results indicate that the predicted isomer distribution does not correspond to that found in the experiments. This provides evidence that the distribution of PCDD/Fs does not attain its equilibrium value, suggesting that it is kinetically rather than thermodynamically controlled. Further, the predominance of PCDFs over PCDDs, although the Gibbs energy of formation of the latter is more favorable, provides indirect evidence for the kinetic control.

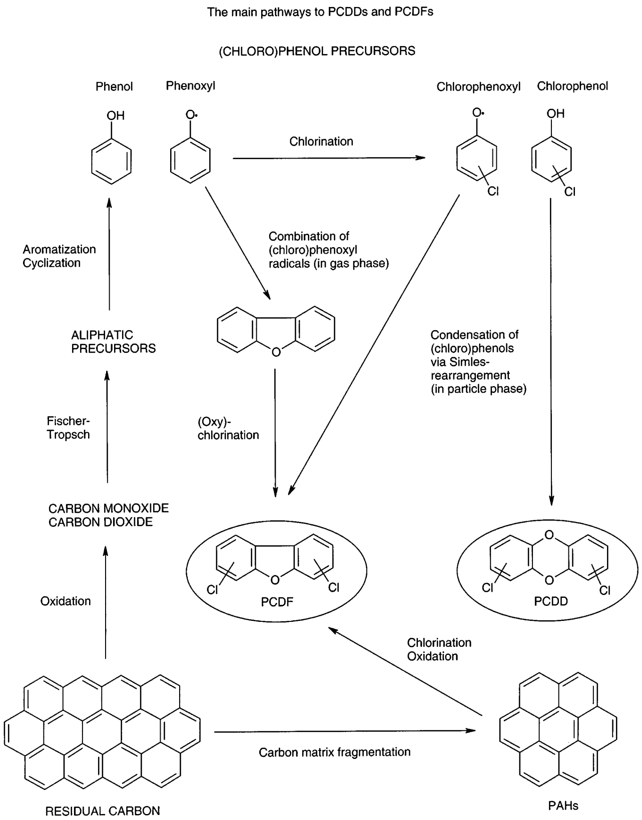
Using laboratory experiments, rate constants have been derived for PCDD/F formation from macromolecular carbon[58,59] and precursors,[21,45] but large differences have been reported by various groups. As a consequence, only wide boundaries of PCDD/F formation and destruction rates in real combustion processes can be evaluated. In fact, the lack of accurate kinetic parameters is a major theoretical bottleneck in this area. However, Altwicker et al. have shown that it is possible to develop a kinetic model for PCDD/F formation from ClPhs based on laboratory rates.[50,60,61] With this model, PCDD emissions found in real incinerators can be explained using the rates of PCDD formation found in the laboratory, indicating that it is possible to link laboratory-scale experiments to real combustion processes, at least in principle.

Pilot-Scale Expriments

It has been our view that pilot-scale experiments represent a reasonable compromise between laboratory tests and full-scale incineration plants, providing an effective means of elucidating PCDD/F formation and inhibition under simplified but 'real' combustion conditions.[51,54,62−67] To this end, we performed a comprehensive series of pilot-scale experiments to determine whether injecting inhibitors directly into flue gases or fuel would significantly reduce PCDD/F formation.[64−66] Simultaneously, the work led to the collection of a comprehensive data set (68 samples up to now), which is also suitable for exploring ClPh-PCDD/F relations.[67] The gas and particle phases were analyzed separately. The most abundant ClPh isomers found throughout the tests were 2-, 4-, 2,4- (+ coeluted 2,5-), 2,4,6-, 2,3,4,5-, and penta-ClPh, i.e., the ortho-para directing effect of the OH group can be seen very clearly. The isomeric distribution of PCDD/Fs was similar to that found in MSW incinerators;[4] i.e., the congener pattern was dominated by hexa- and heptachlorinated furans and highly chlorinated dioxins, and the PCDF to PCDD ratio was typically greater than one throughout the tests. The results were rationalized employing correlation analysis and partial least-squares regression (PLS).

PLS Results. The results indicate that almost all the ClPh isomers correlate either fairly (with PCDDs) or closely (with PCDFs) in the gas phase, but only certain isomers, particularly 2,3,4,6-, and penta-ClPh, are of importance in the particle phase. It appeared that the relationship of TEQ-related PCDD/Fs (i.e., congeners that have a nonzero TEF due to toxicity-enhancing 2-, 3-, 7-, and 8-substitution pattern, commonly known as "the toxic 17") to ClPhs was so close that even a predictive PLS model was feasible employing ClPh concentrations as independent variables. ($\text{TEQ} = \text{toxic equivalence quantity} = \Sigma_i \text{concentration}_i \cdot \text{TEF}_i$, where TEF is a toxic equivalence factor for each congener *i*.) Due to the absorption−desorption of PCDD/Fs and ClPhs between the phases, the gas-phase and particle-phase concentrations were fitted into the same PLS model simultaneously. The predictive ability of the model was good for the hexa- and heptachlorinated congeners (leave-one-out cross-validated correlation coefficients Q^2 of the model varied in the range 0.5−0.9 and conventional correlation coefficients R^2 in the range 0.7−0.9), but only fair or even poor for the other congeners, suggesting that the coupling of 2,3,4,6-, and penta-ClPh is an important route for the formation of PCDD/Fs. Interestingly, introduction of the operation parameters (temperatures at three points in the pilot-scale incinerator, O_2, CO, CO_2, particles, amount of inhibitor, water/gas ratio, residence time) into the PLS model did not lead to an improvement in performance. In contrast, it has been found that in full-scale plants PCDD/F concentrations are strongly dependent on the temperature of the electrostatic precipitatior (ESP) so that high temperatures enhance de novo formation of PCDD/Fs considerably.[68]

Scheme 1. The Main Pathways to PCDDs and PCDFs



This important finding is a caveat that laboratory- and pilot-scale results should not be generalized to full-scale plant too straightforwardly.

ClPhs as Surrogates of PCDD/Fs. Routine measurement of PCDD/Fs is difficult and expensive. As a consequence, there is a growing tendency to find surrogates of PCDD/Fs, e.g., for on-line estimation of PCDD/F emissions; in particular chlorobenzenes have attracted much attention.[69,70] Our results suggest that measurement of ClPhs in waste incineration flue gases, combined with multivariate statistics, could be used as a surrogate for assessment of PCDD/F emissions. Further investigations will be required, however, to evaluate the generalizability of the present results to full-scale plants.

Connective Theory of the Formation of PCDD/Fs

Summing up the above considerations, it is possible to present a scheme for the formation of both PCDFs and PCDDs that start with phenol (Scheme 1). First, primary combustion mainly produces a large amount of nonchlorinated DF via the coupling of two PhO radicals. Also with ClPhs, PCDFs predominate over PCDDs, as long as at least one ortho hydrogen is available. At later stages, dibenzofuran and lower-chlorinated PCDFs are subject to (oxy)chlorination. These routes are probably the main pathways leading to PCDFs. In contrast, only small amounts of dibenzo-*p*-dioxin (DD) and PCDDs are formed during primary combustion. The formation of PCDDs necessarily requires that an ortho chlorine is available, and if all ortho positions of ClPh moieties are chlorinated, PCDDs become the major (if not the only) product; this situation is not representative for real combustion conditions, however. The main pathway leading to PCDDs is different, in that kinetically and/or thermodynamically most stable ClPhs, surviving the primary combustion, react rapidly and with a considerable yield to form PCDDs, when they come into contact with fly ash. This scenario, proposed recently by Louw and co-workers,[35,36,71−74] would neatly explain the overall formation of PCDD/Fs during combustion processes, at least under conditions where the possibility of de novo synthesis is minimum; i.e., the amount of residual carbon is negligible.[75] It has been shown experimentally that PCDDs and PCDFs may well be formed in separate regions of an incinerator,[76,77] at different rates and temperatures, and that this in turn would be consistent with precursor synthesis, but probably not with de novo mechanism. A mechanism of the latter kind would certainly make some contribution, of course, under conditions where a considerable amount of residual carbon is present, but as discussed above, the basic chemistry involved may be not very different from that in the ClPh/precursor pathway.

Concluding Remarks and Future Perspectives

There has been a common but unfortunate practice in previous experimental works in this area of research of restrict attention almost solely to the TEQ-related congeners, i.e., ignoring all lower chlorinated congeners (with 0−3 chlorine atoms) and also most of the higher chlorinated ones. This is probably due to two factors: (i) it is well-known that the biological effects of PCDD/Fs are extremely sensitive to the chlorination pattern, in that the laterally substituted congeners (i.e., those with chlorine atoms in positions 2, 3, 7, and 8) are most toxic, and thus the restriction to the “toxic 17” congeners is understandable, and (ii) the large number of possible congeners, together with limited analytical resources and the lack of suitable model compounds, has often pre-empted a complete analysis. In any case, the resultant picture of the formation pathways is a seriously biased one, as correctly pointed out by Bacher et al. for a decade ago.[78] Fortunately, there is a growing tendency in the recent literature to quantify all highly chlorinated congeners with 4−8 chlorine atoms, and it would be of utmost importance now to quantify all lower-chlorinated congeners as well, in particular, the non-chlorinated parent compounds DD and DF, in every combustion experiment that concerns the formation of PCDD/Fs. This approach would be likely to provide valuable information on formation pathways.

So far, little progress has been made concerning the detailed mechanisms, even for the surface-catalyzed reactions. Most of the studies have been performed using highly chlorinated phenols, in particular 2,4,6-TCP, since they are the most abundant isomers found in waste incineration effluents. However, due to the high degree of chlorination, together with complex dechlorination reactions, they form multiple PCDD/F congeners, pre-empting the mechanistic interpretation. Instead, monochlorinated phenols, with and without ortho chlorines, should be used as a surrogate for more complex phenols in forthcoming experiments.

From a methodological point of view, it seems likely that laboratory- and pilot-scale experiments, rather that theoretical calculations, will allow the elucidation of the formation pathways in sufficient detail. However, as discussed above, the generalization of the results to full-scale plant should always be done with due precaution. In contrast, it can be anticipated that quantum chemical calculations will act only the supporting role, for two reasons: (i) in order to take full advantage of computational methods, the reaction mechanisms should actually be known in advance, and (ii) to obtain reliable results for chlorinated heteroaromatic molecules such as PCDD/Fs, the level of calculations should be very high; this is particularly demanding if heterogeneous processes and catalysts are to be taken into account.

In the future, as our knowledge of the exact reaction mechanisms and their activation energies increases, more detailed kinetic models should be developed in order to characterize PCDD/F emissions from combustion processes. Even today, the best chemical models, such as the scenario sketched briefly above, seem to be on the threshold of providing a framework for understanding the most important mechanistic details, facilitating the development of effective inhibition techniques as a primary goal.

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