

CARBON CHLORINATION IN DE NOVO FORMATION MECHANISM

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Introduction

The de novo mechanism is considered a major pathway for the formation of PCDD/F since it was first proposed by Vogg and Stiezigz¹ in 1986. Numerous studies have been conducted to elucidate different aspects of de novo mechanism and determine different variables that control PCDD/F formation via the de novo mechanism. It is now accepted that the PCDD/F formation via de novo occurs in two steps².

- 1) The transfer of chlorine to carbonaceous particulate material with the formation of carbon-chlorine bond and
- 2) The oxidation degradation of the macromolecular structure to carbon dioxide along with the release of chloroaromatics like dioxins and furans.

It has been demonstrated that in the presence of metal chlorides like CuCl₂, the chlorination of carbon occurs rapidly in pyrolytic conditions (absence of oxygen) through the following reaction.



Although this reaction explains the results observed in laboratory studies with synthetic fly ash (with CuCl₂), the presence of CuCl₂ at high temperatures (500-850°C) is highly unlikely. At high temperatures, CuCl₂ dissociates to give CuCl and Cl₂ and in the presence of oxygen formation copper oxides are also observed. However, at lower temperatures CuCl₂ can be regenerated by reactions of HCl with CuCl or CuO. In any case, the concentration of CuCl₂ in fly ash is very low. Some authors have also suggested that the particulate carbon could be directly chlorinated by Cl₂. Although Cl₂ concentration in incinerator exhaust gas is extremely low, Cl₂ can be generated 'in situ' from HCl via the Deacons reaction. The hypothesis of the direct chlorination of carbon with Cl₂ was validated by the results of a recent study by Gonzalez et al. where they investigated chlorination of carbonaceous material with Cl₂ to improve the properties of carbonaceous material as adsorbent³. Gonzalez et al. observed an increase in weight (~7% during thermogravimetric analysis) when Cl₂ was added to the flow under pyrolytic conditions. This increase in the weight of carbonaceous material was attributed to the formation of the chlorine-carbon bond. From the above discussion, it is clear that carbon can be chlorinated by metal chlorides or directly by Cl₂, however, the exact mechanism of chlorine and its impact on PCDD/F is not known. In this work, the chlorination of carbon was investigated with the objective of elucidating the chlorination mechanism and its impact on organic pollutant formation.

Methods and Materials

In this study, Printex-U (a flame soot supplied by Degussa AG) was used as a carbon source. The reason for choosing Printex-U as a carbon source is because of the extensive data available in the literature for Printex-U⁴. As-received Printex-U (soot) had a significant quantity (around 0.5%) of aromatic and polyaromatic hydrocarbons (PAHs) adsorbed on it. These PAHs were adsorbed during the soot collection process after it was generated in a flame reactor.

All experiments were conducted in a fixed bed flow reactor system that has been described in detail elsewhere⁵. A schematic of the reactor system used in the present study is shown in Figure 1. The experiments were conducted at reactor temperatures of 300, 400 and 500°C. For all experiments, the fixed bed reactor was made of 0.2 g soot and the total reaction time was 60 minutes. A part of the effluent (1/25 of total flow) from the reactor chamber was trapped at -60°C on the head of a DB-5 column. Quantification of these semivolatile products was based on the response of anthracene-D8 as an internal standard. The internal standard was added in a auxiliary flow (5 mil/min) after the reactor but before the split flow. Reactor gas was helium for desorption experiments and air for combustion experiments. For chlorination experiments, 8.3 µl/s (0.5 ml/h) of Cl₂ was injected in the gas reactor flow.

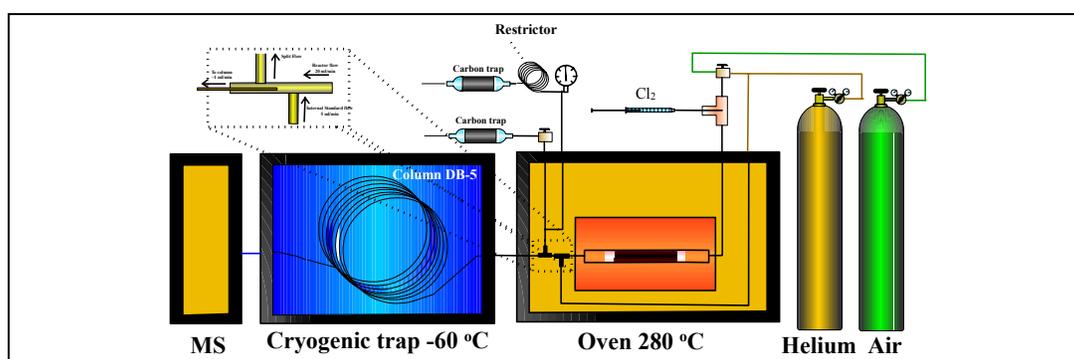


Figure 1. Schematic drawing of University of Dayton flow reactor system.

Results and Discussion

Experiments were performed in three steps: desorption (1 hr), chlorination (1 hr) and combustion (1 hr). The first step, desorption, removes all organic compounds present on the original soot. In the second step, pure Cl₂ was introduced to chlorinate the desorbed soot. In the last step, combustion was conducted to thermally oxidize the soot and release any chlorinated organics that might be formed during chlorination steps. Table 1 shows temperatures at every step for each of the five experiments conducted in this set.

Table 1. Temperatures of different steps in the experiments.

| Experiment | Desorption (°C) | Chlorination (°C) | Combustion (°C) |
|------------|-----------------|-------------------|-----------------|
| 1 | 300 | 300 | 300 |
| 2 | 300 | 300 | 400 |
| 3 | 400 | 400 | 400 |
| 4 | 500 | 500 | 400 |
| 5 | 500 | 500 | 500 |

Table 2 shows the concentrations of aromatic and chlorinated compounds observed from the experiments listed in Table 1. The major chlorinated compounds identified were monochloroanthracene and monochloropyrene and in lower concentration dichloroanthracene and dichloropyrene.

Table 2. Yield of PAH and Chlorinated PAH (mg/kg soot)

| Experiment | Chlorination | | | | Combustion | | | |
|------------|--------------|------|-----|--------|------------|------|-----|--------|
| | Bz | ClBz | PAH | Cl-PAH | Bz | ClBz | PAH | Cl-PAH |
| 1 | 0.2 | 2.2 | 65 | 4 | 0.2 | 5.9 | 48 | 7 |
| 2 | 0.5 | 1.6 | 55 | 11 | 1.0 | 2.7 | 130 | 10 |
| 3 | nd | nd | 14 | 0.9 | 0.5 | 3.5 | 7.2 | 1.0 |
| 4 | nd | 0.1 | nd | nd | 0.01 | 0.2 | nd | nd |
| 5 | nd | nd | nd | nd | nd | nd | nd | nd |

nd → Not detected (<0.1 mg/kg soot)

Examination of Table 2 shows that the yields of chlorinated compounds (both benzene and PAHs) decrease with increases in the desorption temperature. At the highest desorption temperature (500°C), only a very small amount of chlorinated benzenes were observed. This suggests that Cl₂ is able to chlorinate the semivolatile or soluble organic fraction (carbon fraction that can be thermally desorbed at T ≤ 350°C) but not the elemental fraction (graphitic carbon that requires temperatures higher than 350°C) of the soot. However, the results of Gonzalez et al. suggest that Cl₂ continues to chlorinate carbon black by forming a C-Cl bond until almost 800°C. The only explanation that is consistent with the results obtained in our laboratory and by Gonzalez et al. is that it is possible to chlorinate elemental carbon by forming C-Cl bonds, but this chlorinated elemental carbon does not release of chlorinated aromatics during combustion. On the other hand, the yield of chloropyrene and chloranthracene suggest that direct chlorination of high molecular weight semivolatile compounds is possible. To better understand the role of oxygen in carbon chlorination mechanism, experiments 1,3 and 5 were repeated by changing Cl₂ introduction from pyrolytic to combustion phase. The results of these experiments show that there is a decrease in the chlorination efficiency of Cl₂ in the presence of oxygen. The overall yield of chlorinated products was much smaller in these modified 1,3 and 5 experiments when compared to the original 1,3 and 5 experiments.

The results of this study contradict the de novo mechanism theory which states that oxidation of chlorinated carbonaceous material produces aromatic compounds (chlorinated and nonchlorinated compounds) whereas our results suggest that chlorinated compounds produced are probably from chlorination of adsorbed PAHs (soluble organic fraction) usually present in the carbonaceous materials. This is not the first work to show that chlorinated carbonaceous material does not yield chlorinated aromatic. During their investigation of combustion of chlorobenzene soot, Addink and Altwicker⁶ found that combustion of soot with C-Cl bonds does not lead to the formation of large quantities of PCDD/F. Addink and Altwicker⁶ conclude that CuCl₂ is needed to form significant quantities of PCDD/F.

The results of this study clearly suggest that yields of chlorinated products are dependent on soluble and elemental carbon content of the fly ash particle. However, the role of the metal in chlorination is still not clear. To understand the role of metal in chlorination, we conducted a set of combustion experiments with CuCl₂ (2 wt% by Cu) at 400°C (see Table 3).

Table 3. Product Yields from CuCl₂ Experiments

| Products | Soot Without Desorption | Soot Desorbed at 500°C |
|-----------------|-------------------------|------------------------|
| PAH | 3600 | nd |
| Chlorinated PAH | 450 | nd |
| Chlorobenzenes | 67 | 18 |

nd → Not detected (<0.1 mg/kg soot)

The results of CuCl_2 experiments also show that the yield of chlorinated products is directly related to the soluble organic fraction of the carbon. However, in the presence of CuCl_2 , a small amount of chlorobenzenes are formed from elemental carbon. This is due to the formation of metal-oxy-chloro complexes on soot surface that lead to formation of chlorobenzenes. Also, the presence of metals changes the role of oxygen in the chlorination process. In the presence of metals, oxygen enhances the rate of chlorination by converting HCl to Cl_2 via Deacon reactions and by forming metal hypochlorites (Cu_2OCl_2) with a higher chlorinating efficiency than metal chlorides.

Since the soluble organic fraction of carbon determines the yield of chlorinated pollutant, we wanted to see how different solvent and thermal extraction techniques change the soluble organic fraction. To achieve this objective, we extracted soot with toluene and dichloromethane for 24 hours. After extraction, the solvent was removed at 80°C in low-pressure conditions for 8 hours. These extracted soot samples were then desorbed in helium for 1 hour at 300°C and after analysis of compounds the soot was desorbed for one more hour at 500°C .

Table 4 shows the concentration of PAH and solvent from desorption of extracted soot at 300°C and 500°C . It is interesting to note that a considerable quantity of PAH (~ 40 mg/kg) is present in the extracted soot even after it was desorbed for one hour at 300°C .

Table 4. Yields of organic compounds obtained from desorption of extracted soot.

| Solvent | Desorption at 300°C | | Desorption at 500°C (after desorption at 300°C) | |
|-----------------|-----------------------------------|------|---|-----|
| | Residual solvent | PAH | Residual solvent | PAH |
| Dichloromethane | 260 | 143 | nd | 40 |
| Toluene | 660 | 1050 | 3 | 98 |

nd \rightarrow Not detected (<0.1 mg/kg soot)

Conclusions

The results of this study suggest that Cl_2 can directly chlorinate the semivolatile fraction of soot. If all the soluble organic fraction of soot is removed by desorbing it at 500°C , no PAH will be formed from this soot sample during combustion. Elemental carbon will form chlorobenzenes only in the presence of metal chloride and oxygen. These results suggest that the yield of chlorinated or non-chlorinated PAH from carbon studies is directly related to carbon sample's soluble organic fraction. Care should be taken to prepare (extraction, desorption) carbon samples for experiments, as it had significant impact on experimental results. The results of this study showed that chlorinated elemental carbon structures do not release chlorinated aromatics on combustion.

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