Role of C-Cl Bonds in the Formation of Polychlorinated Dibenzo-p-dioxins/Dibenzofurans from Soot

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Introduction

An important aspect of the formation of polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF) is the role of carbon-chlorine bonds. In the de novo formation of PCDD/F from carbon, such bonds could exist prior to the release of these compounds from the carbon structure. Experimental evidence of increase of carbon-chlorine bonds in carbon during thermal treatment was presented by Stieglitz et al. (1). These authors proposed that chlorination preceded oxidation of the carbon. A carbon that is rich in carbon-chlorine bonds could perhaps produce PCDD/F without the presence of metal catalysts and/or inorganic chloride. In this paper we present results of PCDD/F formation experiments that were carried out with soots from the combustion of benzene and o-dichlorobenzene (=ODB-soot).

Material and Methods

Soot was prepared from the combustion of benzene or o-dichlorobenzene by a procedure modified somewhat from the one described in (2). The equivalence ratio was 1.7. After preparation, the benzene soot was extracted with hexane and the ODB-soot with hexane and toluene for 24 h. After the extraction, the soots were dried overnight under reduced pressure.

The benzene soot was chlorinated prior to PCDD/F formation experiments by heating for 60 min in our flow system (see below) at 200-400 °C in N_2 (ca. 70 mL/min) with dichloromethane by passing N_2 through an impinger containing CH_2Cl_2. Ca. 10 g/h of CH_2Cl_2 was used. After the chlorination reaction, the soot was heated for another 60 min in N_2 to remove any residue of dichloromethane.

For the actual PCDD/F formation experiment, 0.01 g of benzene soot or ODB-soot was mixed with 0.50 g silica. In some experiments, 0.015-0.02 g of Cu (powder), $CuCl_2$ or Cu_2O was added. These mixtures were then diluted further with 0.47-0.49 g glass beads. Total sample weight was 1 g. The mixture was placed in a pyrex glass or quartz tube against a glass frit with a plug of glasswool at the upstream end of the bed. The tube was heated in a furnace for 60 min to the desired temperature under a stream of N_2. Once the mixture had reached the reaction temperature (277-450 °C), a mixture of

10% O_2 in N_2 was passed through the bed for 60 min at a rate of 90-92 mL/min. Any PCDD/F desorbing from the bed was collected in an ice-cooled trap filled with toluene.

Sample clean up and analysis have been described elsewhere (3). Only the T_4CDD-OCDD and T_4CDF-OCDF were quantified.

The amount of C-Cl bonds in the soots was determined by heating a soot/silica mixture in our flow system for 90 min at 700 °C in 10% O_2/N_2; this assured complete combustion, with the chlorine evolving as HCl, which was collected in a cold trap filled with de-ionized water. The Cl^- was titrated with a 0.02 M $AgNO_3$ solution (standardized against KCl).

Results and Discussion

The use of soot from benzene and o-dichlorobenzene made it possible to compare PCDD/F formation from reactants without and with pre-existing C-Cl bonds. Benzene soot results are shown in Figure 1. The benzene soot contained no PCDD/F after preparation. In addition, no C-Cl bonds could be detected in this soot. These results were, of course, not surprising, given the absence of chlorine sources in the benzene soot preparation. The soot was extracted with hexane to remove any potential PCDD/F precursors. A de novo run with this soot at 299 °C yielded no PCDD/F (labeled 'None' in Figure 1).

Chlorination of the benzene soot for 60 min in N_2 at 200 °C with CH_2Cl_2 yielded no detectable amount of C-Cl bonds in that soot, suggesting this temperature was too low. The subsequent PCDD/F formation experiment at 299 °C (Figure 1, 'CH_2Cl_2, 200 °C') produced only 6 ng/g of PCDD/F.

The pre-chlorination of the benzene soot was repeated at 400 °C with CH_2Cl_2; this yielded 2.2 mg C-Cl bonds per gram of silica. When this soot was used in a formation experiment, 510 ng/g of PCDD/F was formed, ca. 85% being OCDF (3rd bar in Figure 1, ' CH_2Cl_2, 400 °C'). However, the possibility existed that precursors had been formed during the treatment of the benzene soot with CH_2Cl_2 at 400 °C. Therefore, the treatment of the benzene soot with CH_2Cl_2 at 400 °C was repeated, followed by extraction of the soot with toluene. This toluene extract contained no PCDD/F, proving that no PCDD/F formation took place during the treatment with CH_2Cl_2. The toluene-extracted, CH_2Cl_2-treated (at 400 oC) benzene soot, contained only 600 μg/g C-Cl bonds. When compared to the 2.2 mg/g present before toluene extraction, this showed that the major part of C-Cl bonds (1.6 mg/g) formed in the CH_2Cl_2 treatment at 400 °C was extractable, i.e. only 600 μg/g C-Cl bonds were formed in the benzene soot. In a PCDD/F formation run at 299 °C, the toluene-extracted soot produced no PCDD/F (Figure 1, 'CH_2Cl_2, 400 °C, tol'). We concluded that precursors formed during the treatment of benzene soot with CH_2Cl_2 at 400°C were responsible for the subsequent PCDD/F formation shown in Figure 1 (3rd bar). When removed, the benzene soot, although containing ca. 600 μg/g C-Cl bonds, gave no PCDD/F.

To test the PCDD/F formation potential of the benzene soot, 2% Cu^{++} as $CuCl_2$ was added to the soot/silica mixture (last bar in Figure 1, '2% Cu^{++}'), but no CH_2Cl_2 treatment was applied. This experiment yielded ca. 3700 ng/g PCDD/F. The[PCDD]:[PCDF] ratio was ca. 0.1, with ca. 50% of the PCDF formed as OCDF. Stieglitz et al. reported on formation of PCDD/F from soot from a domestic oil burner,

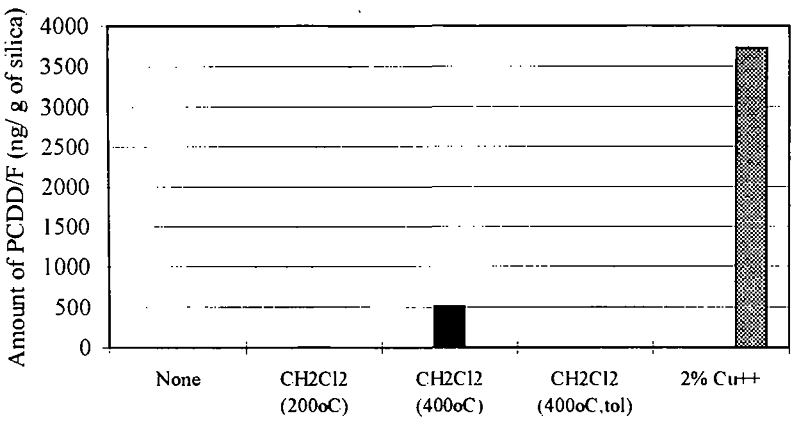

Figure 1. PCDD/F formation from benzene soot at 299 °C.
Conditions: 0.01 g benzene soot, 0.50 g silica, 0.47-0.49 g glass beads; 60 min; T=299 °C; flow: 10% O_2/N_2 92 mL/min. None: no-pre-chlorination; CH_2Cl_2: soot treated with CH_2Cl_2 at 200 or 400 °C before PCDD/F run; 2% Cu^{++}: 2% copper (II) as $CuCl_2$.

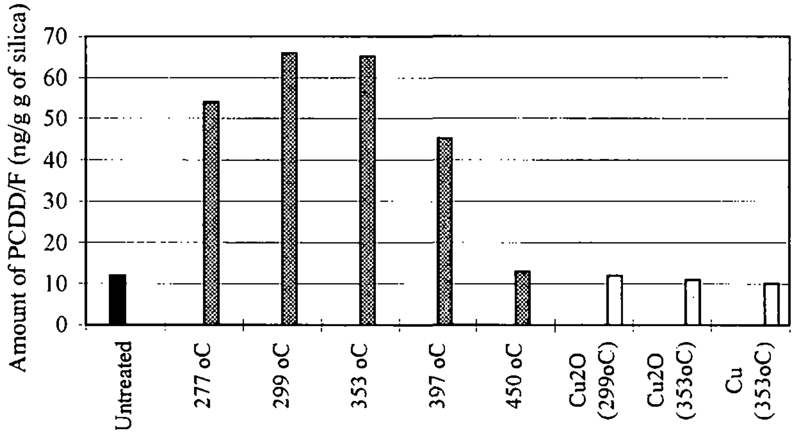

Figure 2. PCDD/F formation from o-dichlorobenzene soot.
Conditions: 0.01 g o-dichlorobenzene soot, 0.50 g silica, 0.47-0.49 g glass beads; 60 min; T=277-450 °C; flow: 10% O_2/N_2 90 mL/min. Untreated: PCDD/F in soot before run; 2nd series of bars (5): temperature varied, no metals added; 3rd series of bars (3): 2-3% Cu_2O or Cu(s) added to soot/silica mixture.

also at 300 °C, with copper (II) and KCl on Mg-Al-silicate (4). These authors also observed this low [PCDD]:[PCDF] ratio (ca. 0.03). Lee et al. reported that the presence of copper was required to generate any PCDD/F from a soot deposit (from fuel oil)/HCl mixture (5).

Figure 2 shows the results of experiments with ODB-soot. This soot was extracted with hexane and toluene after preparation to remove any potential PCDD/F precursors. After this treatment, the ODB-soot contained 300 μg/g C-Cl bonds. We decided to use the ODB-soot with this C-Cl bond content and not to attempt any further chlorination prior to PCDD/F formation experiments. The first black bar in Figure 2 shows the amount of PCDD/F (ca. 12 ng/g) still present after the hexane and toluene extraction. The second series of 5 bars show the amount of PCDD/F formed when the ODB-soot was heated for 60 min in 10% O_2/N_2 between 277-450 °C. Although there is some increase in PCDD/F compared to the starting soot, no significant amounts were formed in this temperature range. Since the ODB-soot already contained C-Cl bonds, unchlorinated copper compounds should increase oxidation rates needed for the release of PCDD/F from the soot structure, if the mechanism was solely one of copper catalysis. However, addition of either Cu_2O (299°C and 353°C) or Cu (as powder, 353 °C) only decreased formation of PCDD/F compared to the other runs, perhaps through copper catalyzed dechlorination/decomposition (last series of 3 bars in Figure 2).

Conclusions

Experiments with benzene soot (with 600 μg/g C-Cl bonds) or ODB-soot (with 300 μg/g C-Cl bonds) yielded no or only small amounts of PCDD/F. This suggested that although C-Cl bonds were already present in the reactant, metal ions were needed for oxidation of the soot. However, addition of unchlorinated copper powder or Cu_2O to ODB-soot had no effect. Only addition of $CuCl_2$ to unchlorinated benzene soot produced ca. 3.7 μg/g PCDD/F. $CuCl_2$ could be unique in providing both the chloride needed for PCDD/F and enhancing oxidation rates of carbon. Future work at higher (> 600 μg/g) C-Cl bond concentrations in soots could show whether PCDD/F formation is possible without additives.

Acknowledgments

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