

FORMATION EXPERIMENTS OF POLYCHLORINATED DIBENZO-P-DIOXINS/DIBENZOFURANS WITH Na^{37}Cl

Ruud Addink and Elmar R. Altwicker

Department of Chemical Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180, USA

Introduction

The use of labeled compounds (e.g., ^{13}C , ^{37}Cl , ^{18}O) has great potential for the elucidation of formation pathways of polychlorinated dibenzo-p-dioxins and dibenzofurans. Several authors have studied competition between ^{12}C and ^{13}C carbon compounds, such as native carbon on fly ash, activated carbon, toluene, and pentachlorophenol (1,2,3). Results suggested that PCDF formation could be explained by direct release of the complete DF structure from the carbon. However, the DD structure was partly formed through condensation of chlorophenols (formed from the carbon) and partly also via direct release from the carbon. In another study it was shown that both ^{16}O (from native carbon on fly ash) and ^{18}O (from the gas phase) were incorporated in PCDD/F (4). Use of, e.g., inorganic ^{37}Cl , combined with organic chlorine with the natural ^{35}Cl : ^{37}Cl distribution, would enable us to distinguish between these two sources in the resulting PCDD/F. One important question is to what extent C-Cl bonds that are already present in carbon, are included in PCDD/F in de novo formation. In this paper, we report on results of experiments that were carried out with two soots, using Na^{37}Cl as a chloride source.

Material and Methods

Soot was prepared from the combustion of benzene (runs 1-2) or o-dichlorobenzene (=ODB-soot for runs 3-7) by a procedure modified somewhat from the one described in (5). After preparation the benzene soot was extracted with hexane and the ODB-soot with toluene for 24 h. After extraction the soots were dried overnight.

Sample preparation: Runs 1-2: 0.41-0.44 g silica, 0.01 g benzene soot, 0.025-0.03 g Na^{37}Cl , 0.02-0.025 g $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 0.49-0.54 g glass beads. Runs 3-7: 0.45-0.49 g silica, 0.01 g ODB-soot, 0.0035-0.03 g Na^{37}Cl , 0.003-0.025 g $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 0.48-0.50 g glass beads. In all runs Na^{37}Cl and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ were exchanged in water, followed by evaporation, and mixing with the soot, silica, and beads.

The mixtures were 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 (299-353 °C), a mixture of 10% O_2 in N_2 was passed through the bed for 10-60 min at a rate of 93 ± 6 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 (6). In samples with the natural ^{35}Cl : ^{37}Cl ratio (75.5%:24.5%) the M^+ , $\text{M}+2$, $\text{M}+4$ and $\text{M}+6$ masses of the PCDD/F are usually measured, being those with the highest abundance. In our experiments, we also measured the $\text{M}+8$ - $\text{M}+16$ peaks, since incorporation of ^{37}Cl resulted in PCDD/F with increased masses. From the abundances of these higher masses, relative to the lower ones, the ^{35}Cl : ^{37}Cl ratio in the PCDD/F

formed (deviating from the natural ratio) could be calculated (not shown). Results reported here are for T₄CDD-OCDD and T₄CDF-OCDF.

Results and Discussion

Figure 1 shows results of a comparison of PCDD/F formation from benzene soot and ODB-soot. The benzene soot contained no measurable amount of carbon-chlorine bonds before the experiments, whereas the ODB-soot contained 15 mg chlorine per gram of soot (7). This meant that per 0.01 g of ODB-soot (the amount used in runs # 3-7) 115 µg of ³⁵Cl and 35 µg of ³⁷Cl were present. In all runs Na³⁷Cl was exchanged with CuSO₄·5H₂O in water, and the water evaporated subsequently, which led to partitioning of the ³⁷Cl⁻ ions over Na³⁷Cl and Cu³⁷Cl₂. Hence, the NaCl and CuCl₂ formed in the aqueous exchange step contained 95% ³⁷Cl⁻ and only 5% ³⁵Cl⁻ (the percentage of isotopic impurity in Na³⁷Cl). The Na₂SO₄ and CuSO₄ also formed in the exchange step should have no significant effect. CuSO₄ as a catalyst was found to be inert in PCDD/F formation (8).

Duplicate runs # 1 and 2 (Figure 1) with benzene soot produced both PCDD/F with an average of 6.6 % ³⁵Cl atoms and 93.4 % ³⁷Cl atoms. Since benzene soot contained no C-Cl bonds before the experiment, all chlorine incorporated into PCDD/F stemmed from the inorganic part (NaCl and CuCl₂ formed in the exchange step). The 6.6 % ³⁵Cl was quite close to the 5% ³⁵Cl⁻ present in the exchanged NaCl and CuCl₂. This 6.6% could be seen as a baseline value, found when only inorganic chlorine was available for inclusion in PCDD/F.

Next ODB-soot - with 115 µg ³⁵Cl and 35 µg ³⁷Cl per 0.01 g - was used in runs # 3-7. Results of runs # 3-5 are shown in Figure 1. If chlorine from the ODB-soot (i.e., present before the start of the experiment) was somehow incorporated in PCDD/F formed, the percentage of ³⁵Cl found in the PCDD/F should be higher than found in runs # 1-2. This appeared indeed to be the case. For these three runs an average of ca. 9.5% of ³⁵Cl was found in the PCDD/F formed. The error bars shown in Figure 1 represent the standard deviations found when calculating the average percentage of ³⁵Cl over all congeners for each run. The standard deviations were small and essentially all congeners, both PCDD and PCDF, irrespective of degree of chlorination or substitution pattern, appeared to have the same percentage of ³⁵Cl. Hence, these three runs suggested that chlorine from the ODB-soot did find its way into PCDD/F formed.

Note that varying the reaction time (60 min for # 4, 10 min for # 3) made no difference. Chlorine from ODB-soot, present before the run, and therefore high in ³⁵Cl, could exchange with CuCl₂ (high in ³⁷Cl⁻) after its incorporation in PCDD/F. With a short reaction time (run # 3, 10 min) this exchange could be less and, hence, PCDD/F would have a higher percentage of ³⁵Cl. However, such an effect was not observed. Run # 5, in nitrogen, produced the same percentage of ³⁵Cl in PCDD/F as runs # 3-4. Rates of chlorination and dechlorination in nitrogen could be different from those in oxygen (runs # 3-4) and, hence, lead to a different percentage of ³⁵Cl in PCDD/F. This effect was not observed.

Figure 2 provides further proof of the incorporation of chlorine from ODB-soot into PCDD/F. Runs # 6 and 7 had less exchanged NaCl and CuCl₂ than run # 4, and an increasing percentage of ³⁵Cl in PCDD/F formed. With less inorganic ³⁷Cl⁻ available, the relative importance of organic ³⁵Cl (and organic ³⁷Cl) increased. Assuming that CuCl₂ after exchange (in water) was a better chloride source than NaCl, we calculated [³⁵Cl in ODB-soot + ³⁵Cl⁻ in CuCl₂]/[(³⁵Cl + ³⁷Cl) in ODB-soot + (³⁵Cl⁻ + ³⁷Cl⁻) in CuCl₂] for runs # 4, 6 and 7. Results were respectively 7% (#4), 14% (#6), and 21% (#7), close to the values measured. In this calculation chlorine in ODB-soot and in CuCl₂ were treated equally, and the results were close to the values measured. This suggested that the ratio of ³⁵Cl: ³⁷Cl in ODB-soot and CuCl₂ combined controlled the percentage of ³⁵Cl and ³⁷Cl in PCDD/F formed.

C-Cl bonds from the ODB-soot could either be inserted intact in PCDD/F, or the chlorine could perhaps exchange with chloride ions in CuCl_2 , and then end up in the PCDD/F formed. A fast (min) exchange of chlorine in the ODB-soot with the CuCl_2 could explain the fact that no difference was seen between runs # 3 (10 min) and # 4 (60 min). Such a rapid exchange could take place at the beginning of the experiment, say, in the first 10 min. After this initial period, both ODB-soot and CuCl_2 would have the same ratio of ^{35}Cl and ^{37}Cl . This would also explain why, e.g., T_4CDF had the same percentage of ^{35}Cl as OCDF. If C-Cl bonds from ODB-soot remained intact, T_4CDF , with, e.g., one $\text{C}-^{35}\text{Cl}$ (from the soot) and three ^{37}Cl (from CuCl_2), would have a higher percentage of ^{35}Cl than OCDF with one intact $\text{C}-^{35}\text{Cl}$ bond and seven ^{37}Cl .

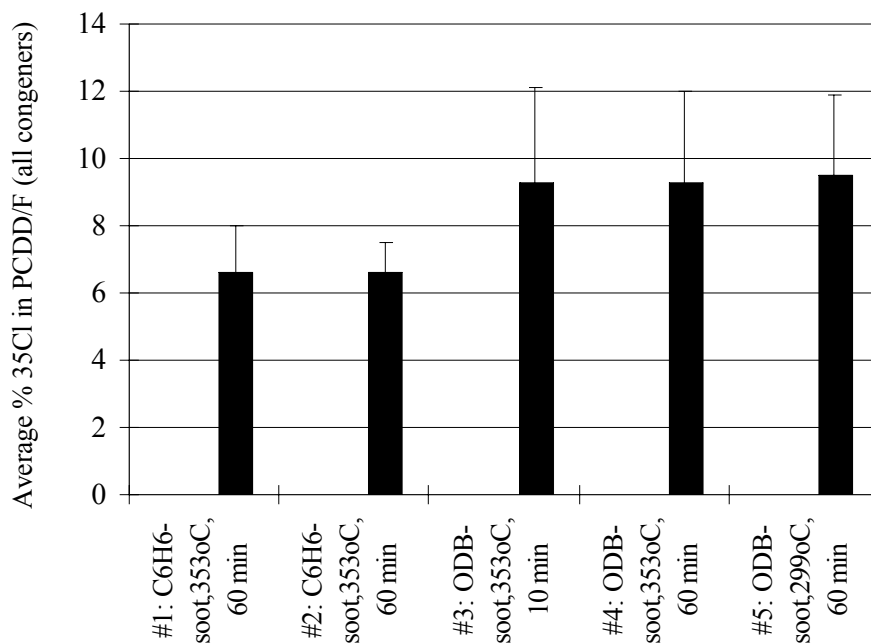


Figure 1. Comparison of C_6H_6 - and ODB-soot w.r.t. percentage of ^{35}Cl found in PCDD/F formed.

Conditions: 0.41-0.46g SiO_2 , 0.01 g C_6H_6 -soot or ODB-soot, 0.025-0.03 g Na^{37}Cl , 0.02-0.025 g $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 0.48-0.54 g beads; 10-60 min; $T=299\text{-}353$ °C; flow: runs #1-4: 10% O_2/N_2 93±6 or run #5: N_2 82 mL/min.

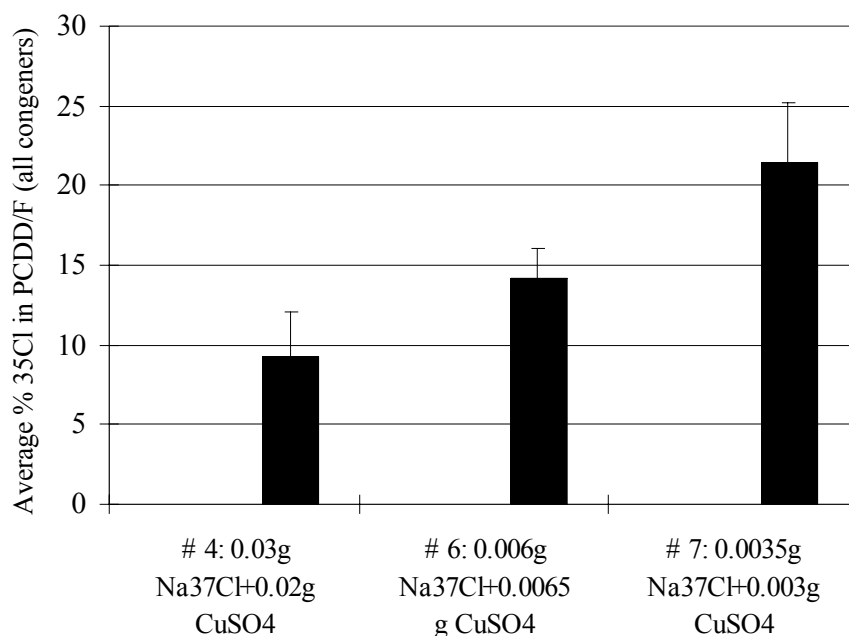


Figure 2. Influence of [Na³⁷Cl] and [CuSO₄.5H₂O] on percentage of ³⁵Cl found in PCDD/F formed from ODB-soot.

Conditions: 0.45-0.49 g SiO₂, 0.01 g ODB-soot, 0.0035-0.03 g Na³⁷Cl, 0.003-0.02 g CuSO₄.5H₂O, 0.49-0.50 g beads; 60 min; T= 353 °C; 10%O₂/N₂ 93±6 mL/min.

Therefore, our results suggested participation of chlorine, existing in C-Cl bonds in soot before an experiment, in PCDD/F formation through rapid exchange with CuCl₂.

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