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Influence of HCl and Cl₂ on the Formation of Polychlorinated Dibenzo-*p*-dioxins/Dibenzofurans in a Carbon/Fly Ash Mixture

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Formation of polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) from carbon on incinerator fly ash was investigated using HCl and Cl₂ as a chlorinating agent. The formation proceeds roughly at an equal rate with both gases. These results do not support the theory that chlorination reactions on the fly ash surface take place through free Cl₂ generated by the Deacon reaction. Once formed, PCDD/F remain adsorbed on the fly ash surface until ca. 350 °C; at ca. 400 °C, the major part of these compounds has evaporated from the fly ash to the gas phase.

Introduction

De novo synthesis of polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) from macromolecular carbon has been identified as one of the major sources of formation of these toxic compounds on municipal waste incinerator fly ash (1, 2).

For chlorination of the aromatic DD/DF ring structures, different mechanisms have been proposed. Both Hagenmaier et al. (3) and Vogt et al. (4) advanced the Deacon reaction to explain chlorination reactions on fly ash:

In this reaction, free Cl₂ is involved. Schwarz suggested an alternative mechanism in which the macromolecular carbon structure is chlorinated by a surface-bound metal chloride and afterwards broken down by gaseous O₂ into small organic molecules among other PCDD/F. No free Cl₂ is involved in this chlorination reaction (5). We investigated PCDD/F formation from carbon on fly ash with both HCl and Cl₂ to test the Deacon hypothesis and to learn more about the homologue and isomer distributions of PCDD/F formed.

During the experiments with Cl₂, separate analyses were made of the fly ash surface and the cold trap (in which

evaporated PCDD/F are collected). This provides more information about the fly ash/gas-phase partition of PCDD/F in the temperature range 300–400 °C. It is important to know the extent to which PCDD/F is bound to fly ash at these temperatures, which are typical in the post-combustion zone of an incinerator. Preliminary results of our investigation have been published before (6).

Experimental Section

Materials. The following materials were used: activated carbon (Darco G-60, 100–325 mesh, Aldrich Chemie, Steinheim, FRG); aluminum oxide 90 active, basic (activity stage I, 70–230 mesh, Merck, Darmstadt, FRG); carbon tetrachloride (distilled, Merck); chlorine gas (electronic grade, UCAR, Nieuw-Vennep, The Netherlands); dichloromethane (glass distilled grade, Rathburn, Walkersburn, Scotland); fly ash from the municipal waste incinerator, Zaanstad, The Netherlands; hexane (glass distilled grade, Rathburn); hydrogen chloride (gas, 4.0 grade, UCAR); hydrogen chloride (solution, 37%, Merck); methanol (glass distilled grade, Rathburn); nitrogen (5.0 grade, Hoekloos, Schiedam, The Netherlands); nonane (98%, Aldrich Chemie); oxygen (4.5 grade, Hoekloos); silica gel 60 (70–230 mesh, Merck); silver nitrate (p.a., Merck); sodium hydrogen carbonate (p.a., Merck); sodium hydroxide (p.a., Baker Chemicals, Deventer, The Netherlands); sulfuric acid (95–97%, Merck); toluene (glass distilled grade, Rathburn).

Experimental Apparatus. From the fly ash, all organic material was removed by heating at 550 °C for 90 min under a stream of air saturated with water. The fly ash was mixed with 2% carbon by shaking the mixture of the two solids. A total of 2.0 g of the mixture was placed in a cylindrical sample basket and coupled with a glass inlet tube for introduction of a glass flow through the fly ash bed. Sample basket and inlet tube were fit into a horizontal Pyrex glass reactor and put in a furnace (Lenton CSC 1100 split tube furnace with PID 808 temperature controller, Leicestershire, U.K.). Experiments lasted for 60 min, preceded by 30 min of heating without a gas flow in order for the sample basket, inlet tube, and reactor to reach the set point temperature (298–398 °C, accuracy ±7 °C). A gas stream (N₂, O₂, and HCl or Cl₂) was introduced. The flow was controlled by Series 840 Side=Trak mass flow controllers (Sierra Instruments, Monterey, CA). The flow was checked before and after experiments with a flowmeter. The various gases were mixed in a mixing chamber (V = 800 mL) containing ceramic pellets. Products evaporating from the fly ash surface were collected using a cold trap (60 mL of toluene cooled with ice). After the experiment, the fly ash bed was taken out of the furnace immediately and cooled to room temperature. Cold traps were either analyzed separately or combined with the toluene used for Soxhlet extraction before the beginning of this extraction.

Cleanup. The fly ash samples were extracted with 50 mL of a 3% HCl solution and dried overnight at room temperature. After adding 200–400 µL of a solution of ¹³C-labeled PCDD/F in nonane as internal standard, the sample was Soxhlet extracted with 400 mL of toluene for 24 h. The extract was concentrated to a few milliliters and brought onto a column, filled from top to bottom with 22% H₂SO₄ on silica, 44% H₂SO₄ on silica, silica, and 33% NaOH on

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TABLE 1

Yields of PCDD/F (in nmol/g of Fly Ash)^a

exp no.	temp (°C)	ΣPCDD	ΣPCDF	[PCDD]:[PCDF] ^b
1 ^c	20–348	0.05 (0.03)	1.63 (0.46)	0.03 ± 0.01
2 ^d	298	0.16 ± 0.04	0.74 ± 0.05	0.21 ± 0.07
3 ^d	323	1.03 ± 0.02	2.86 ± 0.74	0.39 ± 0.11
4 ^d	348	2.71 ± 1.27	7.84 ± 0.92	0.33 ± 0.12
5 ^d	373	3.11 ± 0.34	15.06 ± 0.22	0.21 ± 0.02
6 ^d	398	3.05 ± 0.25	12.91 ± 0.18	0.24 ± 0.01
7 ^e	298	0.15 ± 0.06	1.50 ± 0.18	0.09 ± 0.03
8 ^e	323	0.99 ± 0.23	8.22 ± 1.38	0.12 ± 0.01
9 ^e	348	0.83 ± 0.06	18.91 ± 9.00	0.06 ± 0.03
10 ^e	373	0.50 ± 0.21	19.94 ± 3.97	0.025
11 ^e	398	0.77 ± 0.69	27.99 ± 4.42	0.022 ± 0.019

^a Experiment 1 was performed three times, s between brackets, rest performed in duplo, mean value ± range is given. ^b The mean value ± range is given. ^c 2.0 g of 98.0% fly ash and 2.0% carbon; no gas flow; sample heated from 20 to 348 °C during 30 min; mean of three experiments. ^d 2.0 g of 97.8% fly ash and 2.2% carbon; gas flow N₂ 99 ± 1 mL/min, O₂ 12 ± 0.3 mL/min, HCl 5.0 ± 0.2 mL/min; reaction time 60 min; mean of two experiments. ^e 2.0 g of 97.8% fly ash and 2.2% carbon; gas flow N₂ 99 ± 2 mL/min, O₂ 12 ± 0.3 mL/min, Cl₂ 4.8 ± 0.2 mL/min; reaction time 60 min; mean of two experiments.

silica. The column was eluted with 50 mL of hexane. The eluent was concentrated to a few milliliters. This extract was brought onto two consecutive columns filled with AgNO₃ on silica and Al₂O₃. The columns were eluted with 80 mL of hexane, 20 mL of 10% CCl₄ in hexane, and 30 mL of dichloromethane. The dichloromethane fraction was concentrated to a few milliliters and filtered on a HPLC filter. This extract was evaporated to dryness, PCDD/F were then transferred into 50 µL of methanol and injected into a HPLC (pump, Beckman Model 110A; liquid flow, 2.3 mL min⁻¹ methanol; injection port, Altex 210 with 100-µL sample loop; detection, Beckman, 160 absorbance detector; wave length, 254 nm; precolumn, Chrompack, 6 cm × 3.8 mm i.d.; column, Zorbax ODS, C18, 5 µm, 25 cm × 9.4 mm i.d.; column temperature, 30 °C). PCDD/F were separated in two fractions. Fraction 1 contained all PCDD/F congeners except OCDF; fraction 2 contained OCDF. The fractions were mixed with 2% NaHCO₃ in water, and PCDD/F were isolated by shaking with 3 × 2 mL of hexane. This extract was concentrated to a few microliters and analyzed with GC/MSD.

Analysis. GC/MSD, Hewlett-Packard 5970 mass selective detector coupled with Hewlett Packard 5890 GC; column, Supelco SP 2331 (60 m), for all PCDD/F except OCDF, J&W DB-5 (30 m) for OCDF; injection, cold on-column injection (*T* = 110 °C); *T*_{det} = 250 °C; inlet pressure, 12 psi He; temperature program SP-2331, initial *T* = 140 °C (20 s), rate 30 °C/min to *T* = 200 °C (0 s), rate 3 °C/min, final *T* = 250 °C (44 min); temperature program DB-5, initial *T* = 140 °C (0 s), rate 40 °C/min, final *T* = 300 °C (12 min). T₄CDD-OCDD and T₄CDF-OCDF were determined by single ion monitoring measuring M⁺, M + 2, M + 4, and M + 6 masses. Quantification: The following ¹³C-labeled congeners (Cambridge Isotope Laboratories, Woburn, MA) were added for quantification, assuming equal response for all isomers within an isomer group (solution in nonane, concentrations 23–49 ng/mL): 2,3,7,8-T₄CDD, 2,3,7,8-T₄CDF, 1,2,3,7,8-P₅CDD, 2,3,4,7,8-P₅CDF, 1,2,3,6,7,8-H₆CDD, 1,2,3,4,7,8-H₆CDF, 1,2,3,4,6,7,8-H₇CDD, 1,2,3,4,6,7,8-H₇CDF, OCDD, and OCDF.

Three blanks included one sample of carbon/fly ash and two experiments under reaction conditions c and d (see Table 1) at room temperature. These were analyzed for

PCDD/F; results were PCDD 0.001 nmol/g fly ash and PCDF 0.002–0.14 nmol/g fly ash.

Results and Discussion

Results of our experiments are reported in Table 1.

Formation without Gas Flow. All the experiments described in this paper were preceded by 30 min of heating the fly ash/carbon mixture in the sample basket to the temperature required. No gas stream was applied during this period, and the sample basket was in open connection with the air outside the reactor. In order to test whether PCDD/F formation takes place under these circumstances, experiment 1 (Table 1) was carried out in threefold. The fly ash/carbon mixture was heated from room temperature to 348 °C for 30 min and afterwards analyzed for PCDD/F formed. Formation indeed occurs under these conditions, 0.05 nmol/g PCDD and 1.63 nmol/g PCDF is formed. When the sample is heated under an overpressure of N₂ (but still without a gas flow), no significant PCDD/F formation is observed. Consequently, the formation of PCDD/F from carbon in experiment 1 can only be explained by assuming diffusion of O₂ into the fly ash bed. Such diffusion is not possible when the whole experimental apparatus is sealed off from the outside air, and indeed under such circumstances no PCDD/F formation takes place. A more detailed study of PCDD/F formation under these conditions will be published elsewhere (7).

Comparison of HCl and Cl₂. In experiments 2–6 and 7–11, the formation of PCDD/F has been studied between 298 and 398 °C, using HCl and Cl₂ as chlorinating agents (Table 1). With HCl, the optimum temperature for formation lies around 373 °C (based on ΣPCDD/F); with Cl₂ the optimum temperature is at 348 °C or higher (also based on ΣPCDD/F). Somewhat lower optimum temperatures were found by Milligan et al. (8): between 300 and 330 °C for various carbon/fly ash mixtures. These authors used similar percentages of O₂ and flow rates but shorter reaction times (30 min). Furthermore, no HCl or Cl₂ was added to the gas stream in their experiments. These results show that the optimum formation temperature probably depends on the reaction conditions used. As these conditions will also be different for various incinerators, there is no single optimum temperature for de novo synthesis of PCDD/F during the process of waste incineration. A broad temperature zone between 300 and 400 °C appears to be the most effective for PCDD/F formation from carbon.

In HCl, the [PCDD]:[PCDF] ratio varies between 0.14 and 0.50 and in Cl₂ it is between 0.003 and 0.13, implying that PCDF formation is favored in the presence of Cl₂ compared to HCl. This is especially seen at temperatures of 348 °C or higher, whereas the ratio in HCl does not depend on the reaction temperature. The difference between the [PCDD]:[PCDF] ratios in HCl and Cl₂ strongly suggests that different routes of PCDD/F formation exist for both chlorinating agents. Various authors have suggested that chlorination of the carbon macromolecule and of DD/F related structures in it occurs before these compounds are released as such (5, 9). HCl and Cl₂ may then have a different potential to chlorinate carbon.

Figures 1 and 2 show the percentages of H₇CDD + OCDD and H₇CDF + OCDF formed in HCl and Cl₂ (ΣT₄CDD-OCDD and ΣT₄CDF-OCDF = 100%). Formation of these higher chlorinated homologues is predominant in both gases; the effect in Cl₂ is stronger than in HCl. In HCl, there is a clear

FIGURE 1. Percentage of H₇CDD + OCDD as function of the temperature.

FIGURE 2. Percentage of H₇CDF + OCDF as function of the temperature.

increase of the hepta- and octa-CDD/CDF with the rise of the temperature; no such effect is observed in Cl₂.

We can use a comparison of the amounts of PCDD/F formed with HCl and with Cl₂ to establish the role of the Deacon reaction. If the Deacon reaction is an important chlorination pathway in the experiments with HCl, Cl₂ should be the major chlorinating agent. In the two series of experiments, the concentrations of HCl and Cl₂ used were nearly equal, ca. 5 mL/min. A direct comparison of the amount of Cl incorporated into PCDD/F in both the HCl and Cl₂ atmosphere is possible. This amount is calculated for each experiment by multiplying the concentration of T₄CDD/DF/g with 4, P₅CDD/DF/g with 5, etc. and adding the various concentrations of nanomole of Cl for the 10 homologues. The ratio [nanomole of Cl in HCl]:[nanomole of Cl in Cl₂] varies from 0.3–0.5 at 298 °C to 0.4–0.6 at 398 °C, so no significant change is observed. Note that in the experiments with Cl₂ (containing two Cl atoms compared to one in HCl) the amount of Cl present in the atmosphere is twice as high as in the experiments with HCl. Correcting for this fact means multiplying the ratio calculated with a factor 2, i.e., the ratio varies between 0.6 and 1.2.

In a HCl atmosphere Cl₂ can be generated by the Deacon reaction, which has a conversion of 0.1%–1.3% on fly ash (10, 11). Thus, the concentration of Cl₂ in experiments 2–6 is at least 100 times less than in experiments 7–11, but still about the same amount of Cl is incorporated in PCDD/F in both series of experiments. This suggests that in HCl chlorination pathways other than via Cl₂ alone are operative. For a precise answer to this question, additional research is required as the amount of Cl₂ generated in HCl is already more than is incorporated in PCDD/F. Increasing the amount of Cl₂ with a factor of 100–1000 (which is done in

experiments 7–11) may have no effect if a zero-order dependence in [Cl₂] exists.

The distributions on the individual isomers within the homologues tend to be fairly temperature independent for the experiments in HCl. There is some change within H₆-CDD for the 1,2,4,6,7,9, 1,2,4,6,8,9, 1,2,3,4,6,8, 1,2,3,6,7,9, 1,2,3,6,8,9, and 1,2,3,4,7,8 isomers. The other isomers within this group remain constant. For the two H₇CDD isomers, the ratio of ca. 40%:60% (1,2,3,4,6,7,9, 1,2,3,4,6,7,8) at 298 °C, which is also characteristic for our original fly ash, changes to ca. 10%:90% at 373 °C. Within the H₇CDF group, the 1,2,3,4,6,7,8 isomer rises from ca. 60% at 298 °C to ca. 80% at 398 °C.

For the experiments in Cl₂, concentrations of all the tetra–hepta homologues formed are too low to draw reliable conclusions regarding the isomer distributions except for H₇CDF. Within this group, an almost exclusive formation of the 1,2,3,4,6,7,8 isomer is observed, up to 98% at 323 and 398 °C. In original fly ash, this percentage is ca. 75%.

Fly Ash/Vapor-Phase Partition. In experiments 7–11, fly ash and cold trap were analyzed separately, thus enabling us to study the partition between the solid phase and the gas phase during our experiments. Vogt et al. (12) studied the phase distribution of PCDD/F: at 300 °C, all PCDD/F were present on fly ash (>99.9%), whereas at 400 °C this is only ca. 25%. As our experiments were carried out at various temperatures between 300 and 400 °C, we could determine the temperature at which the evaporation sets in more precisely.

In our investigation, we found that 94–100% of all PCDD/F remain adsorbed on the fly ash surface up till 348 °C. Desorption sets in between 348 and 373 °C and becomes the predominant process between 373 and 398 °C. At 398 °C, 75–98% of all PCDD and 47–92% of all PCDF are found in the gas phase. Hence, desorption of the majority of the PCDD and PCDF takes place between 350 and 400 °C.

These temperatures are higher than those reported by Altwicker et al. (13), who found that evaporation of PCDD/F from the fly ash takes place between 285 and 350 °C. At 300 °C, 37% of the PCDD/F had evaporated; at 350 °C, this was 94%. A difference in flow rate does not explain these observations, as the flow rate used by Vogt et al. (670 mL/min) is comparable to the one used by Altwicker et al. (800–1000 mL/min). The same holds for the reaction time: although Vogt et al. used 120-min experiments, at 300 °C no PCDD/F has evaporated from the fly ash, whereas in Altwicker's experiments 37% has evaporated in only 60 min. The different fly ashes used may have various adsorption properties and hence give PCDD/F desorption at different temperatures.

Conclusions

Experiments described in this paper show an optimum temperature for PCDD/F formation from carbon, which is higher than found by other authors. The optimum temperature zone for de novo synthesis appears to be, when combining results from different investigations, in between 300 and 400 °C. Consequently, de novo synthesis may also play a role upstream of the electrostatic precipitator where temperatures can be higher than 300 °C.

The difference in the [PCDD]:[PCDF] ratio found with HCl and with Cl₂ as a chlorinating agent suggests that chlorination does not follow the same route with these compounds. Amounts of PCDD and PCDF formed with either HCl or Cl₂ are fairly equal. These two observations

do not support the occurrence of the Deacon reaction in de novo synthesis. If the Deacon reaction takes place at the fly ash surface, it only plays a minor role. Hence, the crucial role of HCl in PCDD/F formation in incinerators can only be explained with other theories, perhaps via direct chlorination from the HCl molecule. Apart from HCl, also salts like NaCl will play a role as a chlorinating agent.

Desorption of PCDD/F from the fly ash surface starts above ca. 350 °C in our experiments. However, results found by other groups show that desorption can take place at lower temperatures (285–350 °C) too. Parameters like reaction time or flow rate do not offer a straight-forward explanation for this observation. Adsorption properties and surface area of the various fly ashes probably play a role. As carbon generally has good adsorption properties, the carbon content of the fly ash used might be important too. In any case, removal of fly ash particles from the flue gas in an incineration plant should be carried out at temperatures as low as possible to keep the fraction of gaseous PCDD/F to the minimum.

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