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Reactions of Dibenzofuran and 1,2,3,4,7,8-Hexachlorodibenzo-*p*-dioxin on Municipal Waste Incinerator Fly Ash

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Dibenzofuran (DF) on fly ash can be converted to polychlorinated dibenzofurans (PCDF) in a N₂/O₂/HCl atmosphere, yielding especially 2,3,7,8-substituted congeners. This is consistent with an electrophilic aromatic substitution mechanism. 1,2,3,4,7,8-Hexachlorodibenzo-*p*-dioxin (1,2,3,4,7,8-H₆CDD) on fly ash can be chlorinated by HCl both in N₂ and O₂ atmospheres. Dechlorination and decomposition reactions are not important under these conditions, and isomerization reactions do not take place either. 1,2,3,4,7,8-H₆CDD dechlorinates or decomposes on fly ash when no HCl is present. Only a limited number of dechlorination products are formed. Chlorination and dechlorination are separate processes, not occurring simultaneously.

Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) were detected in emissions of municipal waste incinerators in 1977 (1). Formation occurs in the post-combustion zone of the incinerator ($T < 600$ °C), rather than in the oven during the actual incineration process (2). These formation reactions are catalyzed by residue particles (fly ash) that are carried into the post-combustion zone together with the off-gas of the incineration process. Metal ions present in fly ash (Cu and Fe) convert macromolecular carbon to PCDD/PCDF (de novo synthesis) (3). The carbon content of fly ash can be up to ca. 7% (4). Other pathways yielding these toxic compounds include formation from chlorophenols (5) and propene (6), both on fly ash. Such small volatile organic molecules (precursors) can be adsorbed on the fly ash surface from the gas phase and are subsequently converted to PCDD/PCDF. Both NaCl (7) and HCl (8) act as a chlorine source during the formation reactions of PCDD/PCDF.

Chlorination reactions of DF on Al₂O₃-SiO₂ with HCl at 300 °C yield mainly 2,3,7,8-substituted congeners; the route

of chlorination is 2 → 8 → 3 → 7 → 1 → 4 → 6 → 9 (9). This order of chlorination is consistent with an electrophilic aromatic substitution mechanism. Born investigated chlorination of DF on fly ash, but found only formation of mono- and dichloro congeners (5). We wanted to know whether the electrophilic mechanism also holds for the fly ash surface and therefore carried out experiments with DF in a N₂/O₂/HCl atmosphere.

OCDD formed from pentachlorophenol starts to dechlorinate on fly ash after 5 min at 300 °C, indicating that formation and destruction/dechlorination reactions are parallel pathways occurring simultaneously (10). To learn more about these processes, we chose to study chlorination and dechlorination of 1,2,3,4,7,8-H₆CDD. With a hexachlorodibenzodioxin, simultaneous chlorination (resulting in H₇CDD-OCDD) and dechlorination (resulting in lower chlorinated congeners) can be measured.

Experimental Section

Materials. The chemicals used in our cleanup have been described before (11). Only the chemicals used in our experiments are reported here: dibenzofuran (98%, Aldrich Chemie, Steinheim, FRG); 1,2,3,4,7,8-hexachlorodibenzo-*p*-dioxin (99%, Amchro, Sulzbach/ Taunus, FRG); fly ash from the municipal waste incinerator in Zaandam, The Netherlands; hydrogen chloride (gas, 4.0 grade, UCAR, Nieuw-Vennep, The Netherlands); nitrogen (5.0 grade, Hoekloos, Schiedam, The Netherlands); oxygen (4.5 grade, Hoekloos).

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 either DF or 1,2,3,4,7,8-H₆CDD as a solution in hexane. After evaporation of the solvent, 1.0–2.0 g of the mixture was placed in a cylindrical sample basket and coupled with a glass inlet tube for introduction of a gas flow through the fly ash bed. The 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 0–50 min, preceded by 10–20 min of heating under a gas flow (identical with the reaction gas) in order for the sample basket, inlet tube, and reactor to reach the set point temperature (218–348 °C, accuracy ±7 °C). A gas stream (N₂/O₂/HCl; N₂/HCl; O₂/HCl; N₂) 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 flow meter. N₂ and O₂ were mixed in a mixing chamber ($V = 800$ mL) containing ceramic pellets. HCl was introduced into the gas stream after the mixing chamber. 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. Fly ash fractions and cold traps were generally combined after the experiment and analyzed for PCDD/F together. However, sometimes cold traps were analyzed separately to provide information on the amount of PCDD/F that evaporated from the fly ash surface during the experiment.

Cleanup and Analysis. These have been described before (11). Only the T₄CDD-OCDD and T₄CDF-OCDF

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TABLE 1

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

experiment no.	reactant	atmosphere	ΣPCDD	ΣPCDF
1 ^b	DF	N ₂ , O ₂ , HCl	0.09 ± 0.02	0.98 ± 0.03
2 ^c	1,2,3,4,7,8-H ₆ CDD	N ₂ , HCl	2.37 ± 0.66	0.01 ± 0.01
3 ^d	1,2,3,4,7,8-H ₆ CDD	O ₂ , HCl	3.02 ± 0.03	0.003

^a All experiments in duplicate, mean value ± range is given. ^b 2.0 g of fly ash with 33 nmol/g DF; $T = 348 \pm 7^\circ\text{C}$; 50-min reaction; flow: N₂ 112 ± 2 mL/min, O₂ 12 mL/min, HCl 6.5 ± 2.2 mL/min. ^c 1.0–1.1 g of fly ash with 3.19 ($s = 0.37$) nmol/g 1,2,3,4,7,8-H₆CDD; $T = 248 \pm 7^\circ\text{C}$; 15-min reaction; flow: N₂ 59 ± 1 mL/min, HCl 5.5 mL/min. ^d Same as under footnote c, but with flow of O₂ 57 ± 1 mL/min, HCl 5.5 mL/min.

congeners were analyzed. 1,2,3,4,7,8-H₆CDD was checked for contamination. A purity of 103% was found, which is not significantly different from the 99% guaranteed by the manufacturer. Heating a sample of carbon-free fly ash at 350 °C in a N₂/O₂/HCl mixture resulted in 0.05 nmol/g PCDD and 0.11 nmol/g PCDF. The cleanup procedure, the fly ash, and the DF were all checked for background PCDD/F. Results were in-between 0.011 and 0.023 nmol/g ΣPCDD/PCDF. These contributions are negligible when compared with the amount of PCDD/F formed during our experiments.

Results and Discussion

In Table 1, the results of experiments with DF and 1,2,3,4,7,8-H₆CDD are reported.

Chlorination of DF. We chose to perform the experiment with DF under similar conditions as in the post-combustion chamber in an incinerator, i.e., at 348 °C, and in a N₂/O₂/HCl mixture. To make a comparison with de novo synthesis experiments possible, we performed the experiment at typical de novo synthesis reaction times: 50 min.

Ca. 3% of the DF is converted to T₄CDF–OCDF congeners (experiment 1), which is somewhat higher than the 0.3–1.0% found by Luijk for chlorination of DF on Al₂O₃–SiO₂ at 250–300 °C (12). The higher temperature during experiment 1 (348 °C) might explain the difference. Some PCDD is formed in experiment 1, 0.09 nmol/g. As described under Cleanup and Analysis, some background formation of PCDD from organics left on the fly ash will occur, and the 0.09 nmol/g may stem partially from that source. It does not constitute proof of the transformation of DF to DD.

When setting ΣT₄CDF–OCDF = 100%, ca. 70% of the PCDF formed is OCDF. Under the reaction conditions used, where HCl is present as a chlorinating agent, dechlorination of PCDF formed is obviously not a predominant pathway.

The isomer distributions within the various PCDF homologues show a distinct trend toward 2,3,7,8-substitution. The order of chlorination 2,3,7,8 (ca. 25%) → 1,2,3,7,8 (ca. 34%) → 1,2,3,4,7,8 (ca. 53%) → 1,2,3,4,6,7,8 (ca. 91%) is clearly observed. The relative contribution of these isomers within their homologues is given in parentheses. The increase from 25% for 2,3,7,8-T₄CDF to 91% for 1,2,3,4,6,7,8-H₇CDF can be explained by the conversion of structurally related isomers. Within the T₄CDF group, isomers other than 2,3,7,8, e.g., 1,2,3,7 and 1,2,7,8, which can also be converted to 1,2,3,7,8, are present at percentages of ca. 10%. Thus, the 1,2,3,7,8-P₅CDF isomer is formed at higher percentages than 2,3,7,8-T₄CDF, because it can be formed from more than one T₄ isomer. The electrophilic

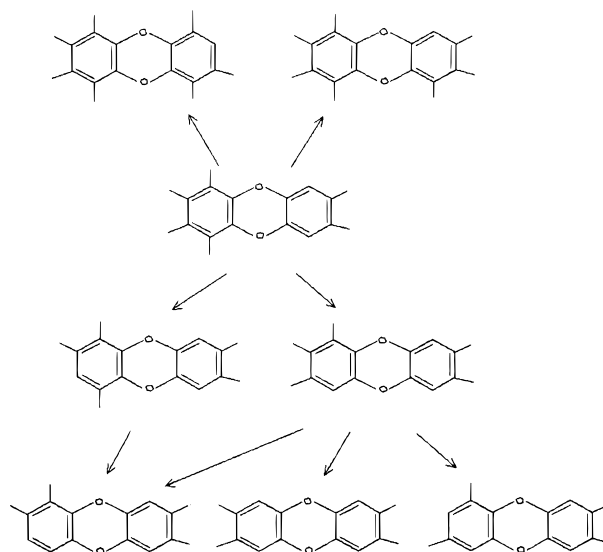


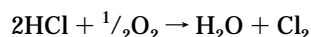
FIGURE 1. Route of chlorination and dechlorination for 1,2,3,4,7,8-H₆CDD (Cl atoms are not shown).

chlorination mechanism for DF holds on fly ash too and can explain part of the PCDF formed.

The preferred formation of 2,3,7,8 congeners from DF differs from the isomer distribution that is found in de novo synthesis experiments under similar conditions. Typically, at 348 °C in a N₂/O₂/HCl mixture with carbon as a reactant on fly ash, no preference for 2,3,7,8-substitution occurs (11), indicating that DF is not an intermediate in de novo synthesis of PCDF from carbon.

Chlorination of 1,2,3,4,7,8-H₆CDD. Chlorination experiments with 1,2,3,4,7,8-H₆CDD were carried out at 248 °C (experiments 2 and 3, Table 1). We chose this temperature to compare the results of these experiments with those described below (studying dechlorination and decomposition). We used mixtures of N₂/HCl (experiment 2) and O₂/HCl (experiment 3). This makes a comparison possible of the influence of these gases, which are both present in incinerator flue gas, on chlorination processes. We chose a short reaction time (15 min) to avoid that the chlorination process would proceed toward an almost 100% formation of OCDD, which would eliminate useful information regarding the chlorination pathway at the heptachlorodibenzodioxin level.

In N₂, a great variance was seen between duplicate experiments, resulting in a mass balance of between 54 and 95%. With O₂, we obtained a mass balance of 94–96%. We calculated this mass balance by (ΣT₄CDD–OCDD/1,2,3,4,7,8-H₆CDD before experiment) × 100%. No significant amounts of PCDF were detected, and the transformation PCDD → PCDF does not occur. Our results show that chlorination takes place in both atmospheres. Griffin (13) has suggested that HCl passed over fly ash is converted to Cl₂ (Deacon reaction) according to:



Since in experiment 2 with N₂ no O₂ was present, this pathway should not be operative. Therefore other chlorination routes must exist. The Deacon reaction may be partially responsible for the chlorination of 1,2,3,4,7,8-H₆CDD in experiment 3.

Cold traps were not analyzed separately, and the amount of 1,2,3,4,7,8-H₆CDD evaporating from the fly ash surface

TABLE 2

Yields of PCDD Homologues during Dechlorination/Decomposition of 1,2,3,4,7,8- H₆CDD (in nmol/g of fly ash)^a

	exp 4, 0 min	exp 5, 6 min	T = 218 °C exp 6, 12 min	exp 7, 18 min	exp 8, 24 min	exp 9, 30 min
T ₄ CDD	0.01 (0)	0.03 (0.03)	0.06 (0.03)	0.07 (0.01)	0.05 (0.04)	0.08 (0.02)
P ₅ CDD	0.18 (0.02)	0.31 (0.14)	0.43 (0.04)	0.42 (0.02)	0.34 (0.05)	0.47 (0.05)
H ₆ CDD	2.65 (0.20)	1.87 (0.44)	1.24 (0.26)	1.12 (0.04)	1.25 (0.53)	1.04 (0.07)
H ₇ CDD	0.02 (0)	0.02 (0.01)	0.01 (0.01)	0.02 (0)	0.02 (0.01)	0.02 (0)
OCDD	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)
total	2.86 (0.23)	2.23 (0.29)	1.75 (0.28)	1.63 (0.04)	1.66 (0.47)	1.60 (0.09)

	exp 10, 0 min	exp 11, 6 min	T = 248 °C exp 12, 12 min	exp 13, 18 min	exp 14, 24 min	exp 15, 30 min
T ₄ CDD	0.04 (0.01)	0.05 (0.01)	0.11 (0.04)	0.15 (0.08)	0.07 (0.01)	0.10 (0.02)
P ₅ CDD	0.28 (0.02)	0.31 (0.05)	0.53 (0.16)	0.56 (0.06)	0.39 (0.06)	0.47 (0.02)
H ₆ CDD	0.82 (0.20)	0.90 (0.30)	0.81 (0.03)	0.80 (0.14)	0.71 (0.15)	0.45 (0.02)
H ₇ CDD	0.02 (0)	0.02 (0.01)	0.02 (0)	0.01 (0)	0.02 (0)	0.01 (0)
OCDD	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)
total	1.16 (0.23)	1.27 (0.23)	1.46 (0.18)	1.52 (0.21)	1.20 (0.16)	1.03 (0.04)

^a All experiments carried out three times; mean concentration is shown (s) in parentheses; conditions: 1.0 g of fly ash mixed with 3.19 (s = 0.37) nmol/g 1,2,3,4,7,8-H₆CDD; T = 218 or 248 °C; reaction time: 20 min warming up + 0–30 min reaction; N₂ = 59 ± 3 mL/min.

is not known. In any case, our results show that chlorination of the starting compound and possibly desorption is favored under these conditions rather than dechlorination and decomposition. Especially in O₂ these latter two reactions are almost negligible. This is corroborated by the homologue distributions found. With ΣT₄CDD–OCDD = 100%, in N₂ 86 ± 2% and in O₂ 94 ± 1% of the starting 1,2,3,4,7,8-H₆CDD is recovered. The amount of H₇CDD + OCDD is 13 ± 3% in N₂ and 5 ± 1% in O₂. T₄CDD and P₅CDD congeners are present at <1%.

The isomer distribution found for the H₆CDD homologue shows that isomerization of the starting compound is limited. With ΣH₆CDD = 100%, the amount of the other isomers is <1%. Results of the two H₇CDD congeners—1,2,3,4,6,7,9 and 1,2,3,4,6,7,8—show that some dechlorination may play a role in experiment 2 with N₂. In O₂ the 1,2,3,4,6,7,9 isomer is formed at ca. 2%, compared to ca. 98% for 1,2,3,4,6,7,8. The route of formation is depicted in Figure 1. Only the latter isomer can be formed directly from 1,2,3,4,7,8-H₆CDD. In N₂ the percentage of 1,2,3,4,6,7,9 is higher, ca. 21% and ca. 79% for 1,2,3,4,6,7,8. Isomerization of 1,2,3,4,7,8-H₆CDD, followed by chlorination, might explain the formation of 1,2,3,4,6,7,9 but is unlikely since extensive isomerization of the starting compound is not observed. Dechlorination of OCDD to 1,2,3,4,6,7,9 is a plausible alternative.

Due to the variance between duplicate experiments with N₂, it is difficult to draw conclusions regarding differences in mass balance between N₂ and O₂. Homologue distributions show that in N₂ more chlorination occurs than in O₂ and some dechlorination from OCDD to 1,2,3,4,6,7,9-H₇CDD takes place in N₂. This dechlorination is not followed by a H₇CDD → H₆CDD step. O₂ may adsorb better on the fly ash surface than the inert N₂, thus blocking active sites of the fly ash for reactions. Hence, a higher percentage of 1,2,3,4,7,8-H₆CDD remains intact.

Dechlorination and Decomposition of 1,2,3,4,7,8-H₆CDD. Experiments to study the dechlorination and decomposition were carried out at 218 and 248 °C. These lower temperatures were chosen to avoid desorption of the starting compound from the fly ash surface, which is

essential for the study of dechlorination/decomposition kinetics and applying first-order kinetics to this process. In all experiments the desorption of the starting material was <7%. However, the scatter in the data does not allow for the calculation of rate constants. Since dechlorination reactions of OCDD and OCDF proceed quickly in an inert atmosphere and on a short time scale, (14), we chose N₂ as a carrier gas and reaction times of 0–30 min.

Results of our experiments (4–15) are shown in Table 2. Both at 218 and 248 °C dechlorination/decomposition of the starting compounds occurs. As only the T₄CDD–OCDD homologues were measured, the mono-trichlorodibenzodioxins escape detection. The 1,2,3,4,7,8-H₆CDD lacking in the mass balance can either be present as DD and mono-trichlorodibenzodioxin or be decomposed. These processes also take place during the 20 min needed for the sample basket to reach the set point temperature, and therefore the mass balance [calculated by (ΣT₄CDD–OCDD/1,2,3,4,7,8-H₆CDD before experiment) × 100%] is <100% at t = 0 min. At 218 °C the mass balance decreases from ca. 90% at t = 0 min to ca. 50% at t = 30 min. At 248 °C there is no significant decrease, due to the variance between the triplicate experiments, and the mass balance fluctuates between 30 and 50%.

Dechlorination of the starting compound to T₄CDD–P₅CDD congeners occurs readily, and after 30 min at 218 °C (with ΣT₄CDD–OCDD = 100%), ca. 65% is 1,2,3,4,7,8-H₆CDD, ca. 29% is P₅CDD, and ca. 5% is T₄CDD. Chlorination hardly takes place, and H₇CDD is only 1%. No PCDF were detected in any of these experiments. At 248 °C after 30 min, ca. 55% of ΣT₄CDD–OCDD is present as T₄CDD or P₅CDD.

In Figure 1, the dechlorination route of 1,2,3,4,7,8-H₆CDD is shown. Again no isomerization of the starting compound is observed. Both the 1,2,4,7,8 (loss of Cl at the 3-position) and the 1,2,3,7,8 isomer (loss of Cl at the 4-position) are formed in a ratio of 30–40% and 60–70%, indicating that loss of Cl at the 4-position is preferred. Other isomers formed have a negligible contribution. The isomer patterns do not depend on the reaction time and temperature. Of the T₄CDD isomers, only the 1,3,7,8, 2,3,7,8, and

1,2,7,8 are formed in a ratio of 25–35%:35–65%:0–20%. These percentages do change with reaction time or temperature, but without clear trend. Van Berkel et al. found that 2,3,7,8-substituted congeners are the most stable on fly ash under dechlorination and destruction conditions (15). This is also seen in our experiments as the 2,3,7,8 and 1,2,3,7,8 isomers are the most important within the T₄CDD and P₅CDD homologues, respectively. Furthermore, the three T₄CDD isomers formed all have two Cl atoms in each ring rather than [3+1] or [4+0]. Similar results were found by Hagenmaier and co-workers for the dechlorination of OCDD on copper-powder: Cl loss occurs in the most substituted ring, yielding congeners with equal numbers of Cl atoms in each ring (16).

Conclusions

Chlorination of DF on fly ash yields all possible PCDF congeners. However, there is a tendency for the formation of 2,3,7,8-substituted congeners. The chlorination reaction follows an electrophilic aromatic substitution mechanism. DF appears not to be an intermediate in PCDF formation from carbon.

With HCl, the chlorination of 1,2,3,4,7,8-H₆CDD takes place both in N₂ and O₂. This shows that the Deacon reaction cannot be the exclusive chlorination pathway on fly ash, since this reaction requires the presence of oxygen. In fact, in O₂, less chlorination is observed than in N₂, which can be explained by assuming a better adsorption of O₂ on the fly ash surface, thus reducing the number of active sites available for reactions. Dechlorination and decomposition are minor pathways. The 1,2,3,4,6,7,8 isomer is formed directly from the starting compound. No isomerization of the starting compound takes place.

Without the presence of HCl, 1,2,3,4,7,8-H₆CDD readily dechlorinates or decomposes. Only a limited set of T₄CDD and P₅CDD isomers is formed through stepwise dechlorination. No chlorination occurs under these circumstances.

Our experiments show that chlorination and dechlorination are separate processes. PCDD present on fly ash will dechlorinate or decompose if no strong gaseous chlorinating agent is present. The fly ash itself is not capable of chlorinating PCDD. On the other hand, if such an agent is present, dechlorination should make a negligible contribution.

Other groups have reported on PCDD formation from unchlorinated starting material on fly ash without HCl, e.g., from carbon (4). The chlorination of the DD structure must in these cases occur at an early stage of the reaction, likewise before oxidative breakdown of the carbon macromolecule.

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