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# Role of Oxygen in Formation of Polychlorinated Dibenzo-*p*-dioxins/Dibenzofurans from Carbon on Fly Ash

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Under an oxygen-deficient flow, no PCDD/F is formed from a carbon/fly ash mixture, but with a mixture of 1% O<sub>2</sub> in N<sub>2</sub> de novo synthesis of PCDD/F sets in. The O<sub>2</sub> concentration was varied 0–10%, formation was highest at 5–10% O<sub>2</sub>. The [PCDD]:[PCDF] ratio rises with increasing [O<sub>2</sub>], but the average degree of chlorination of PCDD and PCDF does not depend on the O<sub>2</sub> concentration. Especially 3,4,6,7-substituted PCDD/F congeners are formed. Without a gas flow, carbon/fly ash mixtures can give PCDD/F formation too: the O<sub>2</sub> now enters the mixture by diffusion. This formation process can continue for several hours. Isomer distributions do not change with increased reaction times. Formation rates under conditions without a gas flow are higher than with a gas flow present, suggesting that O<sub>2</sub> diffusion into the fly ash bed is more efficient than the supply of O<sub>2</sub> through a gas flow.

## Introduction

Research over the past few years has identified carbon as one of the sources of formation of polychlorinated dibenzo-*p*-dioxins (PCDD) and dibenzofurans (PCDF) during incineration of municipal solid waste (1, 2). PCDD/F formation from carbon has been named de novo synthesis. Formation occurs in the post-combustion zone of the incinerator at temperatures between 200 and 500 °C and is catalyzed by fly ash particles. This process can last for several hours and therefore takes place especially in those parts of the post-combustion zone where the fly ash has a long residence time, e.g., an electrostatic precipitator (ESP), which is often part of the air pollution control device of an incinerator (3). The carbon is present on the surface of the fly ash, and Milligan et al. have shown that the carbon content of fly ash can be up to 7% (4). CuCl<sub>2</sub> and FeCl<sub>3</sub>, which are both present in fly ash, are capable of catalyzing the chlorination and oxidative breakdown of the macromolecular carbon structure, resulting in the formation of various small organic molecules, a.o. PCDD/F (5, 6). Oxidation of carbon on fly ash is linked with PCDD/F formation as optimum temperatures for both processes coincide (7). Carbon species capable of PCDD/F formation include activated carbon (8), charcoal (2), residual carbon (i.e., inextractable carbon naturally present on fly ash) (4), and soot (5).

Opposed to this macromolecular pathway is PCDD/F formation from organic molecules (precursors) like benzaldehyde, benzoic acid, phenol, and toluene (9, 10). Some of these compounds may be present in incinerator flue gas due to incomplete combustion and form PCDD/F through fly ash catalysis. Recently, Luijk et al. have suggested that PCDD formation from carbon proceeds via chlorophenol intermediates, implying that the de novo synthesis and precursor pathways may in fact be related (11). However, Dickson et al. found that the formation of PCDD/F from charcoal and of [<sup>13</sup>C<sub>12</sub>]PCDD from <sup>13</sup>C-labeled pentachlorophenol in one experimental system proceeds via separate pathways (1).

Original fly ash contains both macromolecular residual carbon, volatile precursors capable of PCDD/F formation, and PCDD/F formed during the incineration process. When heated under oxygen-deficient conditions, a decrease of the PCDD/F content is observed (12). Without O<sub>2</sub>, the carbon present on the fly ash surface does not act as a source of PCDD/F: O<sub>2</sub> is essential for de novo synthesis. No such prerequisite exists for PCDD formation through the condensation of chlorophenols, which also occurs in N<sub>2</sub> (13).

Vogg et al. varied the amount of O<sub>2</sub> in the gas flow between 0 and 10% when heating original fly ash at 300 °C for 2 h (12). PCDD/F formation already occurs at an O<sub>2</sub> concentration as low as 1%. However, with original fly ash there are other possible reactants apart from carbon, making a precise assessment of the influence of [O<sub>2</sub>] on de novo synthesis difficult. Therefore, we decided to carry out a series of experiments with a mixture of activated carbon

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and fly ash in which the carbon was the sole reactant. The O<sub>2</sub> concentration was chosen at 0, 1, 2, 5, and 10%. The purpose is to study the influence of [O<sub>2</sub>] on the amount of PCDD/F formed, the [PCDD]:[PCDF] ratio, and homologue and isomer distributions.

In a previous paper, we reported on PCDD/F formation from a carbon/fly ash mixture that was heated without a gas flow through the bed (8). It was not clear whether the O<sub>2</sub> required for PCDD/F formation entered the bed by diffusion, was already present between the fly ash particles in the loosely packed bed, or perhaps adsorbed on the fly ash surface. We wanted to test these several possibilities and also look into PCDD/F formation from carbon under these conditions, because these results suggested that small amounts of O<sub>2</sub> were already sufficient for PCDD/F formation. Therefore, we studied de novo synthesis without gas flow at various reaction times and also compared the amounts of PCDD/F formed with and without flow. Preliminary results of this research have been published elsewhere (14).

## 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, Darmstadt, FRG); dichloromethane (glass-distilled grade, Rathburn, Walkerburn, Scotland); fly ash from the municipal waste incinerator, Zaanstad; hexane (glass-distilled grade, Rathburn, Walkerburn, Scotland); hydrogen chloride (solution, 37%, Merck, Darmstadt, FRG); methanol (glass-distilled grade, Rathburn, Walkerburn, Scotland); nitrogen (5.0 grade, Hoekloos, Schiedam, The Netherlands); nonane (98%, Aldrich Chemie, Steinheim, FRG); oxygen (4.5 grade, Hoekloos, Schiedam, The Netherlands); silica gel 60 (70–230 mesh, Merck, Darmstadt, FRG); silver nitrate (p.a., Merck, Darmstadt, FRG); sodium hydrogencarbonate (p.a., Merck, Darmstadt, FRG); sodium hydroxide (p.a., Baker Chemicals, Deventer, The Netherlands); sodium chloride (99%, Aldrich-Chemie, Steinheim, FRG); sulfuric acid (95–97%, Merck, Darmstadt, FRG); toluene (glass-distilled grade, Rathburn, Walkerburn, Scotland).

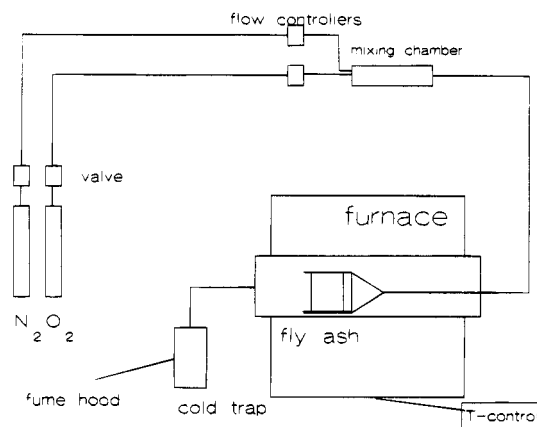
**Experimental Apparatus.** Experiments are reported in Table 1; the experimental apparatus is shown in Figure 1. Description of the experiments 1–5 and 9: From the fly ash, all organic material was removed by heating at 550 °C for 90 min under a stream of air saturated with water. Note that this pretreatment of the fly ash may have changed its composition (e.g., through evaporation of volatile metal chlorides), making it perhaps less suitable to represent actual incinerator fly ash. The fly ash was mixed with 1.5–2.0% carbon (and 2.1% NaCl for experiments 1–5), by shaking. 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. 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.). A gas stream (N<sub>2</sub>, O<sub>2</sub>) was then 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 gases were mixed in a mixing chamber (V = 800 mL) containing ceramic pellets. Experiments lasted for 30–50

**TABLE 1**

**Yields of PCDD/F (in nmol/g of Fly Ash)<sup>a</sup>**

exp no.	[N <sub>2</sub> ]:[O <sub>2</sub> ] (%)	reaction time (min)	ΣPCDD	ΣPCDF	[PCDD]:[PCDF] <sup>b</sup>
1 <sup>c</sup>	100:0	50	0.000	0.003 ± 0.001	[0–0.33]
2 <sup>c</sup>	99:1	50	0.023 ± 0.004	0.76 ± 0.12	0.03
3 <sup>c</sup>	98:2	50	0.046 ± 0.004	1.12 ± 0.01	0.04
4 <sup>c</sup>	95:5	50	0.10 ± 0.05	1.36 ± 0.44	[0.05–0.08]
5 <sup>c</sup>	90:10	50	0.22 ± 0.07	2.16 ± 0.41	[0.09–0.11]
6 <sup>d</sup>	no flow	50	0.32 ± 0.09	2.99 ± 0.07	[0.08–0.14]
7 <sup>d</sup>	no flow	110	0.54 ± 0.17	3.81 ± 0.25	[0.11–0.18]
8 <sup>d</sup>	no flow	230	1.15 ± 0.13	7.28 ± 0.77	0.16
9 <sup>e</sup>	89:11	30	0.08 ± 0.01	1.00 ± 0.11	0.08
10 <sup>f</sup>	no flow	30	0.56 ± 0.32	2.43 ± 0.15	[0.09–0.38]

<sup>a</sup> All experiments were performed in duplicate, mean value ± range is given. <sup>b</sup> The ratio lies within the interval given. <sup>c</sup> 2.0 g of 96.4% fly ash, 1.5% carbon, and 2.1% NaCl; T, 348 ± 7 °C; reaction time, 50 min; N<sub>2</sub>, 200–207 mL/min, O<sub>2</sub>, 0–20 mL/min. <sup>d</sup> 2.0 g of 98.0% fly ash and 2.0% carbon; T, 348 ± 7 °C; reaction time, 50–230 min; no gas flow through the fly ash bed. <sup>e</sup> 2.0 g of 98.0% fly ash and 2.0% carbon; T, 348 ± 7 °C; reaction time, 30 min; N<sub>2</sub>, 114 mL/min, O<sub>2</sub>, 13 ± 2 mL/min. <sup>f</sup> 2.0 g of 98.0% fly ash and 2.0% carbon; T, 348 ± 7 °C; reaction time, 30 min; no gas flow through the fly ash bed.



**FIGURE 1. Experimental apparatus.**

min, preceded by 10 min of heating in order for the sample basket, inlet tube, and reactor to reach the setpoint temperature (348 °C, accuracy ±7 °C). During these 10 min, the gas stream was already passing through the fly ash bed. Products evaporating from the fly ash surface were collected using a cold trap (80 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. The cold trap fractions were combined with the toluene used for Soxhlet extraction before the beginning of this extraction.

Experiments 6–8 and 10: These were carried out as described above but without a gas flow through the fly ash bed. Sample basket, gas inlet tube, and glass reactor were heated during 10 min to the desired temperature, followed by the actual experiment (30–230 min of heating at 348 °C). A cold trap was placed behind the oven for collecting PCDD/F evaporating from the fly ash surface. The other side of the sample basket and glass inlet tube were in open connection with the surrounding air, making diffusion of O<sub>2</sub> into the fly ash bed possible.

**Clean Up.** The fly ash samples were extracted with 50 mL of a 3% HCl solution and dried overnight. After adding 100 μL of a solution of <sup>13</sup>C-labeled PCDD/F in nonane as an 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% H<sub>2</sub>SO<sub>4</sub> on silica, 44% H<sub>2</sub>SO<sub>4</sub> on silica, and silica and 33% NaOH on 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 AgNO<sub>3</sub> on silica and Al<sub>2</sub>O<sub>3</sub>. The columns were eluted with 80 mL of hexane, 20 mL of 10% CCl<sub>4</sub> in hexane and 30 mL dichloromethane. The dichloromethane fraction was concentrated to a few milliliters and filtered on a HPLC filter. This extract was evaporated to dryness, PCDD/F was then transferred into 50 μL of methanol and injected into a HPLC for subsequent cleanup (pump, Beckman Model 110A; liquid flow, 2.3 mL min<sup>-1</sup> of 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 was separated in two fractions. Fraction 1 contained all PCDD/F congeners except OCDF, fraction 2 contained OCDF. The fractions were mixed with 2% NaHCO<sub>3</sub> in water, and PCDD/F was isolated by shaking with 3 × 2 mL of hexane. This extract was concentrated to a few microliters and analyzed with GC/MSD.

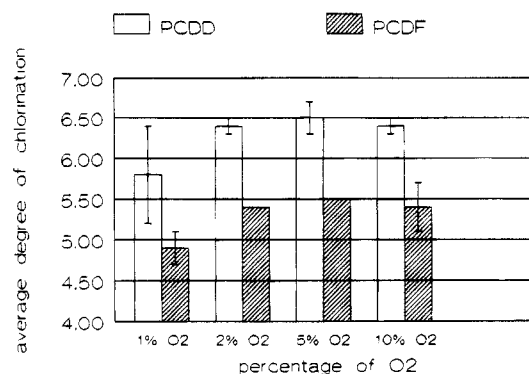
**Analysis.** GCMSD, Hewlett-Packard 5970 mass selective detector coupled with Hewlett Packard 5890 GC; column, Supelco SP 2331 (60 m), for all PCDD/F except OCDF, J&W DB-5 (30 m) for OCDF; injection, cold on column injection (*T* = 110 °C); *T*<sub>det</sub> = 250 °C; inlet pressure, 12 psi He; temperature 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). T<sub>4</sub>CDD-OCDD and T<sub>4</sub>CDF-OCDF were determined by single ion monitoring measuring *M*, *M* + 2, *M* + 4, and *M* + 6 masses. Quantification, the following <sup>13</sup>C-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-T<sub>4</sub>CDD; 2,3,7,8-T<sub>4</sub>CDF; 1,2,3,7,8-P<sub>5</sub>CDD; 2,3,4,7,8-P<sub>5</sub>CDF; 1,2,3,6,7,8-H<sub>6</sub>CDD; 1,2,3,4,7,8-H<sub>6</sub>CDF; 1,2,3,4,6,7,8-H<sub>7</sub>CDD; 1,2,3,4,6,7,8-H<sub>7</sub>CDF; OCDD; OCDF.

Four blanks were taken from the various carbon/fly ash and carbon/NaCl/fly ash mixtures used in experiments 1–10 and analyzed for PCDD/F. ΣPCDD/F was in between 0.001 and 0.017 nmol/g of fly ash.

## Results and Discussion

**Formation with a Gas Flow.** First, a series of experiments (1–5) was carried out with a mixture of activated carbon, NaCl, and fly ash at O<sub>2</sub> concentrations between 0 and 10% (Table 1). The oxygen was mixed with nitrogen.

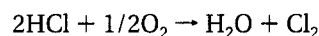
As expected, in experiment 1 (pure N<sub>2</sub>), only trace amounts of PCDD/F were formed. Already at 1% O<sub>2</sub>, 0.023 ± 0.004 nmol/g of PCDD and 0.76 ± 0.12 nmol/g of PCDF were formed. As the O<sub>2</sub> concentration increases, the formation of PCDD/F also rises. Amounts formed at 5 and 10% O<sub>2</sub> overlap due to the variance between duplicate experiments. However, at 10% O<sub>2</sub>, clearly more PCDD/F is formed than at 2%. When setting the amounts of PCDD and PCDF at 1% O<sub>2</sub> at 1, amounts formed at 10% O<sub>2</sub> are PCDD in between 5.5 and 15.3 and PCDF in between 2.0 and 4.0. Thus, for PCDD the rise in formation may be more or less proportional to [O<sub>2</sub>], but with PCDF the increase in



**FIGURE 2.** Average degree of chlorination of PCDD/F as function of [O<sub>2</sub>].

formation is less than proportional. This fact is reflected in the [PCDD]:[PCDF] ratio which increases as [O<sub>2</sub>] increases. Obviously the formation of PCDD from carbon, which contains two oxygen atoms, is stimulated by the presence of O<sub>2</sub>, compared with PCDF which has only one oxygen atom.

Apart from its influence on the amount of PCDD/F formed from carbon, O<sub>2</sub> can influence the homologue distribution in two different ways. Griffin (15) has advanced the Deacon reaction to explain the formation of PCDD/F on fly ash according to



Although HCl is not present in the gas passing the fly ash bed, it could perhaps be produced by the fly ash itself. The increase of [O<sub>2</sub>] would then result in a higher concentration of Cl<sub>2</sub> and consequently in a shift toward higher chlorinated homologues. Schwarz has proposed a mechanism in which carbon is chlorinated by surface-bound metal chlorides and afterward is broken down into PCDD/F. In this chlorine–ligand transfer, the metal ions (e.g., Cu<sup>2+</sup>) are reduced by the transfer and subsequently oxidized by gaseous O<sub>2</sub> (7). The presence of more O<sub>2</sub> could increase the rate of chlorination and hence the amount of higher chlorinated homologues.

In Figure 2, the average degree of chlorination of PCDD and PCDF as function of the O<sub>2</sub> concentration is shown. This degree was found by setting ΣT<sub>4</sub>CDD-OCDD or ΣT<sub>4</sub>CDF-OCDF to 100% for each experiment, calculating the percentage of each DD or DF homologue, multiplying this percentage by the number of chlorine atoms of that homologue, adding these numbers for the five homologues, and finally dividing by 100. No significant change is seen within the homologue distributions of PCDD and PCDF, and the influence of [O<sub>2</sub>] on the degree of chlorination is obviously limited.

Born et al. varied the O<sub>2</sub> concentration during fly ash-catalyzed chlorination of phenol at 250 °C and found a clear increase of the ratio [di- and trichlorophenols]: [monochlorophenols] with higher [O<sub>2</sub>], suggesting that the effect of O<sub>2</sub> on chlorination may exist for phenols but not for PCDD/F formation from carbon (16).

Within homologues there is a tendency for the formation of 3,4,6,7-substituted congeners. This is seen within the T<sub>4</sub>CDF group in which the 3,4,6,7-isomer formed at 30 ± 13% at 1% O<sub>2</sub> (ΣT<sub>4</sub>CDF = 100%) reaches a maximum at 2% O<sub>2</sub>: 68 ± 2%, followed by a decrease to 46 ± 5% at 5% O<sub>2</sub>, and finally an increase to 56 ± 1% at 10% O<sub>2</sub>. The same trend is observed for 2,3,4,6,7-P<sub>5</sub>CDF (maximum of 56 ±

2% at 2% O<sub>2</sub>), 1,2,3,4,6,7-H<sub>6</sub>CDF (maximum of 25 ± 1% at 2% O<sub>2</sub>), and 1,2,3,4,6,7-H<sub>6</sub>CDD (maximum of 41 ± 2% at 2% O<sub>2</sub>).

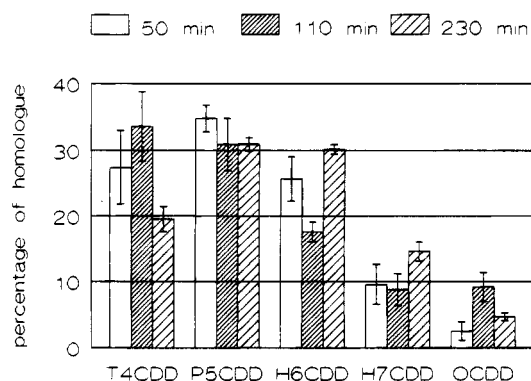
**Formation without a Gas Flow.** Initial experiments with a mixture of carbon and fly ash heated without a gas flow for 30 min at 348 °C resulted in the formation of ca. 0.05 nmol/g of PCDD and ca. 1.6 nmol/g of PCDF, amounts comparable with those formed in experiments 2–5. In experiment 1 (gas stream with only N<sub>2</sub>), no significant amounts of PCDD/F are formed. This implies that, whatever the source of O<sub>2</sub> might be in the experiments without flow, this source is not accessible during experiments with a flow. Two possible explanations are as follows: (i) O<sub>2</sub> is present between the fly ash particles of the bed or adsorbed on their surfaces and capable of participating in PCDD/F formation reactions; however, when a flow is applied, this O<sub>2</sub> is swept away by the gas stream in the initial minutes of the experiment, and no PCDD/F formation takes place (except of course when the gas stream contains O<sub>2</sub>); (ii) O<sub>2</sub> enters the fly ash bed by diffusion during the experiment without flow and participates in PCDD/F formation; when a flow without O<sub>2</sub> is present, the overpressure within the experimental set up excludes the possibility of O<sub>2</sub> diffusion, and no formation is observed.

Hypothesis i was tested by conducting experiments at 348 °C with a carbon/fly ash mixture. This was heated for 4 h under a stream of N<sub>2</sub> (ca. 100 mL/min) and afterward heated without a gas flow for 60 min. Formation still occurs, up to 2.64 nmol/g of PCDD + PCDF. If hypothesis i is correct, O<sub>2</sub> would have been removed from the fly ash bed during the first 4 h (no PCDD/F formation took place during these 4 h, as was checked by analyzing the fly ash) and heating afterward should not result in PCDD/F formation.

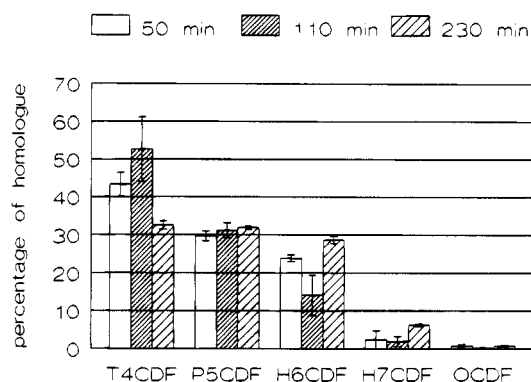
Subsequently, hypothesis ii was tested. Similar experiments, in which the period of heating without a gas flow took place with the experimental system sealed under an overpressure of N<sub>2</sub>, yielded no PCDD/F. O<sub>2</sub> diffusion could not take place under these circumstances and proved to be essential for PCDD/F formation.

Therefore, we concluded that O<sub>2</sub> diffusion into the fly ash bed rather than O<sub>2</sub> already present in the fly ash bed explains the formation observed during the experiments without a flow.

We assumed that the oxygen entering the fly ash bed through diffusion would only be present at the outer edges of the bed rather than in the heart of it. Molecules start penetrating the bed there and will be slowed down by the fly ash particles when traversing the bed. If this is true, less carbon is available for the reaction with O<sub>2</sub> than during an experiment with a gas flow. If the carbon in the zones of the fly ash bed accessible for O<sub>2</sub> is depleted, the formation of PCDD/F stops and a net destruction occurs. To verify this hypothesis, we studied the influence of the reaction time on the formation/destruction process. During experiments 6–8, the reaction time was varied between 50 and 230 min (Table 1). No decrease of the amount of both PCDD and PCDF is observed, and after 230 min 1.15 ± 0.13 nmol/g of PCDD and 7.28 ± 0.77 nmol/g of PCDF have been formed. Obviously the amount of carbon accessible for reaction with O<sub>2</sub> under these conditions is still enough for PCDD/F formation to continue for several hours. With these long reaction times (4 h), O<sub>2</sub> may still be able to diffuse through the whole bed.



**FIGURE 3.** Homologue distribution of PCDD as function of the reaction time for experiments 6–8.



**FIGURE 4.** Homologue distribution of PCDF as function of the reaction time for experiments 6–8.

No significant change is observed in the [PCDD]:[PCDF] ratio during the increase of the reaction time. The ratio in experiments 6–8 is close to the ratio found in experiment 5 with 10% O<sub>2</sub>.

In Figures 3 and 4, the homologue distribution of PCDD and PCDF as a function of the reaction time is shown ( $\Sigma T_4CDD-OCDD = 100\%$ ,  $\Sigma T_4CDF-OCDF = 100\%$ ). There is some change in both homologue distributions when increasing the reaction time from 50 to 110 min and from 110 to 230 min but without a clear trend. Formation of tetra–hexa homologues is favored under these conditions, both for PCDD and PCDF, and these three homologues contribute to ca. 80–95% of the PCDD/F formed.

No change is observed in the isomer distribution within homologues while the reaction time increases from 50 to 230 min. When heating carbon/fly ash for 0.5–6 h at 300 °C under a stream of air, the same isomer distributions of PCDD/F are found, irrespective of the reaction time (17). Obviously, under conditions of net PCDD/F formation, time is not a parameter influencing the isomer distribution.

#### Comparison of Experiments with and without Flow.

To make a proper comparison of the effect of reaction conditions with and without a gas flow, experiments 9 and 10 were carried out (Table 1). Both experiments lasted for 30 min at 348 °C and differed only in that 13 mL/min O<sub>2</sub> and 114 mL/min N<sub>2</sub> passed the fly ash bed during experiment 9, whereas no flow was present during experiment 10. Amounts of PCDD/F formed without a flow are higher than with a flow. The ratio [PCDD with flow]:[PCDD without flow] varies between 0.08 and 0.38, [PCDF with flow]:[PCDF without flow] is between 0.35 and 0.49.

In experiment 9 (with flow) more hepta–octa–CDD/F is formed than in experiment 10 (without flow). When setting  $\Sigma T_4CDD-OCDD = 100\%$  and  $\Sigma T_4CDF-OCDF = 100\%$ ,

results are as follows:  $\Sigma H_7CDD-OCDD = 44.1 \pm 0.4\%$  in experiment 9,  $\Sigma H_7CDD-OCDD = 16.6 \pm 8.2\%$  in experiment 10;  $\Sigma H_7CDF-OCDF = 16.5 \pm 0.7\%$  in experiment 9,  $\Sigma H_7CDF-OCDF = 6.0 \pm 0.2\%$  in experiment 10. This observation is difficult to explain, as the major difference in reaction conditions between experiments 9 and 10 (different  $[O_2]$ ) was shown to have no influence on the degree of chlorination of PCDD/F during experiments 1–5.

In experiment 10, the 3,4,6,7-substituted congeners dominate the various isomer distributions within homologues. Within  $T_4CDF$ , the 3,4,6,7-isomer is ca. 49% ( $T_4CDF = 100\%$ ), within  $P_5CDF$  the 2,3,4,6,7-isomer is ca. 46%, within  $H_6CDF$  the 1,2,3,4,6,7-isomer is ca. 20%, and within  $H_6CDD$  the 1,2,3,4,6,7-isomer is ca. 41%. These percentages are significantly lower in experiment 9. However, within the  $H_7CDD$  and  $H_7CDF$  homologues the isomer distributions are nearly identical in both experiments.

The fact that more PCDD/F is formed in an experiment without gas flow than with a gas flow is certainly surprising; the mass transfer of  $O_2$  to the fly ash particles can be expected to be more effective when supplied by a gas stream under overpressure than through diffusion. However, the opposite appears to be true. Further study will be needed to clarify this issue.

## Conclusions

Oxygen participates in formation reactions of PCDD/F from carbon on fly ash. When the  $O_2$  concentration is varied between 1 and 10% (in  $N_2$ ), the rate of formation increases, and a maximum formation was found at  $\geq 5\%$ . Our results show that PCDD/F formation depends on  $[O_2]$ . A good control of the  $O_2$  concentration during the incineration process is therefore important.

No gas flow is required for PCDD/F formation from carbon/fly ash. Oxygen can enter the fly ash bed through diffusion and initiate oxidative breakdown of the carbon, leading to PCDD/F. This process continues for several hours, the same time scale observed with de novo synthesis experiments under a gas flow. When formation rates with and without flow are compared, the latter process gives the largest amount of PCDD/F. This suggests that the supply of  $O_2$  into the fly ash bed through diffusion is more efficient than supply through a gas stream.

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