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FORMATION OF POLYCHLORINATED DIBENZO-P-DIOXINS/DIBENZOFURANS ON FLY ASH FROM PRECURSORS AND CARBON MODEL COMPOUNDS

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Abstract—In this article the formation of polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) on waste incinerator fly ash is described. Model experiments were performed by heating organic-C-free fly ash with organic model compounds. Both chlorobenzenes and phenol form PCDD and PCDF via condensation reactions. Phenol is 10–540 times as reactive as the chlorobenzenes. A second (and separate) formation pathway is from oxidative breakdown of macromolecular carbon. This route was studied with hexane, toluene and three anthraquinone derivatives as carbon model compounds. Aliphatic, monocyclic aromatic and functionalized quinone parts of carbon may all contribute to PCDD and PCDF formation, but the latter pathway appears to be the most important. Functional groups play an important role in the potential of these various carbon parts to form PCDD and PCDF.

Key Words—Carbon model compounds, fly ash, functional groups, polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzofurans, precursors.

1. INTRODUCTION

Polychlorinated dibenzo-*p*-dioxins (PCDD) and dibenzofurans (PCDF) are toxic compounds present in emissions from, among others, the paper industry[1], steel production[2] and waste incineration[3]. The structure and nomenclature of these compounds is given in Fig. 1. Formation in waste incineration facilities takes place in the post combustion zone at temperatures ranging from 200 to 600°C[4]. Residue particles (fly ash) are carried together with the off-gas into this low-temperature area of the incinerator, in which the gases are cooled down and passed through an air pollution control device before being emitted from the stack. Fly ash

contains macromolecular carbon (called residual carbon)[5], various small organic compounds[6], chlorine atoms and metal ions[7], which are the basic ingredients for formation reactions. PCDD/PCDF formation proceeds through a heterogeneous catalyzed mechanism taking place on the fly ash surface[8].

In the literature two separate pathways have been postulated for fly ash catalyzed PCDD/PCDF formation: (i) small organic compounds (precursors) yield PCDD/PCDF and (ii) oxidative breakdown of residual carbon generates PCDD/PCDF.

The precursors from mechanism (i) can be either already present on the fly ash surface or are adsorbed from the gas phase. An example of this category is condensation of chlorophenols to give almost exclusively PCDD[9]. Propene is another reactant in this category, which recently has been identified as being capable of formation of both PCDD and PCDF on fly ash[10]. Obviously a more complex set of reactions than with chlorophenols is involved, e.g. C–C bond formation, aromatization and chlorination.

Mechanism (ii) for PCDD/PCDF formation on fly ash is called “*de novo* synthesis” and involves macromolecular residual carbon structures. The percentage of residual carbon present on fly ash can be up to around 7%[5]. Oxidative breakdown of this carbon results in a great variety of compounds, including PCDD/PCDF, and chlorination precedes fragmentation of the residual carbon structure[11]. These reactions are catalyzed by Cu and Fe ions[12]. Some experiments suggest that the basic DD and DF structures already exist within the residual carbon and are released upon oxidative breakdown[13]. The chemical structure of the residual carbon naturally

Fig. 1. Structure of polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF). 2,3,7,8-*T*₄CDD=tetrachloroDD with Cl atoms at 2,3,7 and 8 positions; P₅CDD=pentachloroDD; H₆CDD=hexachloroDD; H₇CDD=heptachloroDD; O₈CDD=octachloroDD; T₄CDF=tetrachloroDF, etc.

present on fly ash is not known, but when removed from the fly ash and replaced by activated carbon, PCDD/PCDF formation readily occurs[14]. This suggests that the residual carbon on fly ash may have some properties in common with activated carbon. Soot contains almost equal amounts of carbon atoms in linear and in aromatic parts[15]. Carbonyl- and carboxyl-groups are present in other forms of carbon, like carbon black[16]. Residual carbon on fly ash may contain both aliphatic and aromatic fractions and also functional groups like CO, COOH and OH.

Whether these two formation routes are separate pathways in real incinerators depends on the degradation products formed from oxidative breakdown of residual carbon on fly ash. Oxidation of residual carbon generates, among others, chlorophenols [5]. If these compounds are formed at sufficiently high concentrations to give condensation reactions yielding PCDD, the route residual carbon $\rightarrow$ chlorophenol $\rightarrow$ PCDD exists. This seems indeed to be true for PCDD formation from activated carbon alone (i.e. without fly ash)[9]. Residual carbon could then yield PCDD/PCDF partially through direct release from the residual carbon structure and partially via intermediates. This would make the distinction of formation from precursors and from residual carbon artificial.

We carried out a series of experiments with nine different compounds to learn more about these two different pathways and the relation between them.

Chlorobenzenes and chlorophenols are both present in the flue gas of waste incineration plants[17] and structurally related to PCDD/PCDF, i.e. they are possibly good precursors. Previous research has shown that gas phase reactions of chlorinated benzenes in air yield PCDD/PCDF[18], but chlorobenzene[7] and 1,4-dichlorobenzene[13] did not give any PCDD/PCDF formation on fly ash. Because of this inconclusive evidence, chlorobenzene (containing one chlorine atom) and 1,2,4,5-tetrachlorobenzene and pentachlorobenzene (which need less chlorination to yield PCDD/PCDF) were tested for their ability to form PCDD/PCDF on fly ash. Phenol was chosen as a model compound for chlorophenols and studied under the same reaction conditions as the chlorobenzenes, to make a comparison of the reactivity of both compound classes possible. With this information we can also establish whether chlorobenzenes and chlorophenols are intermediates in *de novo* synthesis, i.e. to what extent mechanisms (i) and (ii) are related.

To model the second mechanism of *de novo* synthesis from residual carbon, we chose hexane as representing the aliphatic part of residual carbon and toluene to model the aromatic parts with an aliphatic (in this case methyl-) substituent. The influence of functional groups was studied through experiments with anthraquinone, 2-anthraquinone-carboxylic acid (hereafter: 2-aca) and 2,6-dihydroxy-anthraquinone (hereafter: 2,6-diOH). With the outcome of these experiments, we can determine what parts of the residual carbon structure are responsible

for PCDD/PCDF formation and what is the role of the various functional groups (carbonyl, carboxyl and hydroxy).

Preliminary results of our investigation have been published elsewhere[19].

2. EXPERIMENTAL

2.1 Materials

The following materials were used: aluminum oxide 90 active, basic (activity stage I, 70–230 mesh, Merck, Darmstadt, Germany); anthraquinone (97%, Aldrich Chemie, Steinheim, Germany); 2-anthraquinone-carboxylic acid (98%, Aldrich Chemie, Steinheim, Germany); carbon tetrachloride (distilled, Merck, Darmstadt, Germany); chlorobenzene (glass distilled grade, Aldrich Chemical, Milwaukee, Wisconsin, USA); copper(II)chloride (Janssen Chimica, Beerse, Belgium); dichloromethane (glass distilled grade, Rathburn, Walkerburn, Scotland); 2,6-dihydroxy-anthraquinone (97%, Aldrich Chemie, Steinheim, Germany); fly ash from the Municipal Waste Incinerator, Zaanstad, The Netherlands; hexane (glass distilled grade, Rathburn, Walkerburn, Scotland); hydrogen chloride (solution, 37%, Merck, Darmstadt, Germany); hydrogen chloride (gas, 4.0 grade, UCAR, Nieuw-Vennep, The Netherlands); methanol (glass distilled grade, Rathburn, Walkerburn, Scotland); nitrogen (5.0 grade, Hoekloos, Schiedam, The Netherlands); nonane (98%, Aldrich Chemie, Steinheim, Germany); oxygen (4.5 grade, Hoekloos, Schiedam, The Netherlands); pentachlorobenzene (98%, Aldrich Chemie, Steinheim, Germany); phenol (p.a., Merck, Darmstadt, Germany); silica gel 60 (70–230 mesh, Merck, Darmstadt, Germany); silver nitrate (p.a., Merck, Darmstadt, Germany); sodium hydrogencarbonate (p.a., Merck, Darmstadt, Germany); sodium hydroxide (p.a., Baker Chemicals, Deventer, The Netherlands); sulphuric acid (95–97%, Merck, Darmstadt, Germany); 1,2,4,5-tetrachlorobenzene (98%, Aldrich Chemie, Steinheim, Germany); toluene (glass distilled grade, Rathburn, Walkerburn, Scotland).

2.2 Experimental apparatus

Experiments are reported in Table 1, in which the following abbreviations are used: 2-aca is 2-anthraquinone-carboxylic acid, 2,6-diOH is 2,6-dihydroxy-anthraquinone.

2.2.1 Description of experiments 2a, 2b, 4, 7, 8 and 9. From the incinerator fly ash all organic material was removed by heating at 550°C for 90 minutes under a stream of air saturated with water. Reaction mixtures contained 88.9–99.8% fly ash, 1.9–2.0% CuCl₂ (not present in experiments 2b and 4) and 0.2–9.1% reactant. These ingredients were mixed by shaking. A little of the mixture (1.0–2.1g) 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. A sample basket and inlet

Table 1. Yields of PCDD/PCDF in nanomole/g fly ash

Exp. no.	Reactant (i)	Σ PCDD	Σ PCDF	[PCDD]:[PCDF](ii)	Conversion (iii)
1	Chlorobenzene	9.0 $\pm$ 4.0	9.8 $\pm$ 4.8	[0.89–0.98]	2.5 $\pm$ 1.2 $\times 10^{-4}$ %
2a	1,2,4,5-Tetrachlorobenzene	2.5 $\pm$ 2.3	1.1 $\pm$ 0.9	[1.0–2.4]	8.4 $\pm$ 7.7 $\times 10^{-4}$ %
2b	1,2,4,5-Tetrachlorobenzene	1.3 $\pm$ 1.1	0.46 $\pm$ 0.01	[0.5–5.2]	1.6 $\pm$ 1.0 $\times 10^{-3}$ %
3	Pentachlorobenzene	0.07 $\pm$ 0.02	0.08 $\pm$ 0.01	[0.6–1.3]	< 4.4 $\times 10^{-5}$ %
4	Phenol	3.6 $\pm$ 0.8	3.3 $\pm$ 0.6	[1.06–1.12]	3.2 $\pm$ 0.6 $\times 10^{-3}$ %
5	Hexane	2.3 $\pm$ 1.1	11.0 $\pm$ 8.2	[0.18–0.42]	2.1 $\pm$ 1.5 $\times 10^{-4}$ %
6	Toluene	2.0 $\pm$ 1.6	6.8 $\pm$ 1.6	[0.07–0.43]	6.8 $\pm$ 2.5 $\times 10^{-4}$ %
7	Anthraquinone	0.06	0.20 $\pm$ 0.01	[0.29–0.32]	< 1.1 $\times 10^{-4}$ %
8	2-aca (iv)	9.99 $\pm$ 0.37	9.29 $\pm$ 0.04	[1.03–1.12]	9.6 $\pm$ 0.2 $\times 10^{-3}$ %
9	2,6-diOH (v)	> 136	6.76 $\pm$ 0.44	> 20.6	> 1.3%

All experiments were carried out at $348 \pm 7^\circ\text{C}$ for 50–60 minutes and performed in duplicate, mean value $\pm$ range is given; gas flow: N_2 104 ± 7 ml/min, O_2 11 ± 1 ml/min and HCl 5.5 ± 0.9 ml/min. (i): Amounts of reactant used in mmol: chlorobenzene 14.9; 1,2,4,5-tetrachlorobenzene 0.22–0.42; pentachlorobenzene 0.82; phenol 0.044; hexane 12.6; toluene 2.6; anthraquinone 0.48; 2-aca 0.4; 2,6-diOH 0.022. (ii): The ratio lies within the interval given. (iii): Calculated by $(\Sigma\text{T}_4\text{CDD}-\text{OCDD} + \Sigma\text{T}_4\text{CDF}-\text{OCDF})/n$ mole reactant $\times 100\%$. (iv): 2-aca: 2-anthraquinone-carboxylic acid. (v): 2,6-diOH: 2,6-dihydroxy-anthraquinone.

tube were fit into a horizontal pyrex glass reactor and put into a furnace (Lenton CSC 1100 Split Tube Furnace with PID 808 temperature controller, Leicestershire, UK). A gas stream (N_2 , O_2 , HCl) was then introduced. The flow was controlled by Series 840 Side=Trak® mass flow controllers (Sierra Instruments, Monterey, CA, USA). The flow was checked before and after the experiment with a flow meter. The gases were mixed in a mixing chamber ($V=800$ mL) containing ceramic pellets. Experiments lasted for 50–60 minutes, preceded by 10 minutes of heating in order for the sample basket, inlet tube and reactor to reach the setpoint temperature (348°C , accuracy $\pm 7^\circ\text{C}$). During these 10 minutes the gas stream was already passing through the fly ash bed. Products evaporating from the fly ash surface were collected using a cold trap (60 ml 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.

2.2.2 Experiment 3. A mixture of 98.0% fly ash and 2.0% CuCl_2 (2.0 g) was placed in a glass tube between two plugs of glasswool. A glass basket containing the reactant was placed at the beginning of the glass tube. The glass tube was heated in 10 minutes to the desired temperature. The rest of the experiment was carried out as described above.

2.2.3 Experiments 1, 5 and 6. Pure fly ash or a mixture of 98.0% fly ash/2.0% CuCl_2 (2.0–2.1 g) was placed in the cylindrical sample basket. The liquid reactants were vaporized into the gas stream by means of a motor-driven syringe (Braun Medical, Utrecht, The Netherlands) at a rate of 0.33–0.66 ml/h; the gas stream with the reactant passed the fly ash bed subsequently. This technique provides a constant stream of reactant onto the fly ash. The rest of the experiment was carried out as described above.

2.3 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 ^{13}C -labeled PCDD/F in nonane as internal standard, the sample was soxhlet extracted with 400 ml toluene for 24 hours. The extract was concentrated to a few milliliters and brought onto a column, filled from top to bottom with 22% H_2SO_4 on silica, 44% H_2SO_4 on silica, silica and 33% NaOH on silica. The column was eluted with 50 ml hexane. The eluent was concentrated to a few milliliters. This extract was brought onto two consecutive columns filled with AgNO_3 on silica and Al_2O_3 . The columns were eluted with 80 ml hexane, 20 ml 10% CCl_4 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, and PCDD/F were then transferred into 50 μl methanol and injected into a HPLC for subsequent clean up. (Pump: Beckman, model 110A; liquid flow: 2.3 ml min^{-1} of methanol; injection port: Altex 210 with 100 μl sample loop; detection: Beckman, 160 absorbance detector; wave length: 254 nm; pre column: Chrompack, 6cm $\times$ 3.8 mm ID; column: Zorbax ODS, C18, 5 μm , 25 cm $\times$ 9.4 mm ID; 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% NaHCO_3 in water and PCDD/F were isolated by shaking with 3×2 ml hexane. This extract was concentrated to a few μl and analyzed with GC-MSD.

2.4 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 ($T=110^\circ\text{C}$); $T_{\text{det}}=250^\circ\text{C}$; inlet pressure: 12 psi He; temperature program SP-2331: initial $T=140^\circ\text{C}$ (20 seconds), rate $30^\circ\text{C}/\text{min}$ to $T=200^\circ\text{C}$ (0 seconds), rate $3^\circ\text{C}/\text{min}$, final $T=250^\circ\text{C}$ (44 minutes); temperature program DB-5: initial $T=140^\circ\text{C}$ (0 seconds), rate $40^\circ\text{C}/\text{min}$, final $T=300^\circ\text{C}$ (12 minutes). The T_4CDD , P_5CDD ,

H₆CDD, H₇CDD and OCDD and T₄CDF, P₅CDF, H₆CDF, H₇CDF and OCDF congeners were determined by single ion monitoring measuring M+, M+2, M+4 and M+6 masses, detection limit 0.01 ng/g. Quantification: the following ¹³C-labeled congeners (Cambridge Isotope Laboratories, Woburn, MA, USA) 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; OCDF.

Blanks were taken from all reactants, fly ash and CuCl₂ and analyzed for PCDD/PCDF. Concentrations were between 0.001 and 0.33 nanomole/g fly ash (Σ PCDD/PCDF). Carbon-free fly ash (treated at 550°C for 90 minutes) is no longer capable of PCDD/PCDF formation. This was determined by carrying out an experiment with 2.0 g of fly ash under the reaction conditions used. Results were 0.16 nanomole/g fly ash (Σ PCDD/PCDF).

3. RESULTS AND DISCUSSION

In Table 1 results of the compounds tested are reported. These include chlorobenzene, 1,2,4,5-tetrachlorobenzene, pentachlorobenzene and phenol as precursors. Hexane, toluene, anthraquinone, 2-anthraquinone-carboxylic acid (2-aca) and 2,6-dihydroxy-anthraquinone (2,6-diOH) were tested as carbon model compounds. In Fig. 2 the structure of the three anthraquinones is given.

3.1 [PCDD]:[PCDF] ratios with precursors

Use of the [PCDD]:[PCDF] ratios will provide information about the reaction mechanisms involved in the formation of these compounds.

Chlorobenzene (experiment 1) and 1,2,4,5-tetrachlorobenzene (Experiments 2a and 2b) form both PCDD and PCDF, as does phenol. Ratios of

[PCDD]:[PCDF] vary between 0.5 and 5.2 for the two chlorobenzenes, with a phenol value of around 1.1 being found. Experiment 3 with pentachlorobenzene yielded no more PCDD/PCDF than found in blanks.

As reported in the introduction, other authors found no PCDD/PCDF formation from chlorobenzenes on fly ash [7,13]. We used HCl as a chlorinating agent, which provides a chlorine source in addition to the chloride naturally present in fly ash. HCl was not used by these other authors. This might explain the opposite results found.

Formation of PCDD from chlorobenzenes can be explained by assuming oxidation to chlorophenols, followed by a condensation reaction as depicted in Fig. 3. 1,3,6,8-T₄CDD is formed in Fig. 3 through direct condensation of 2,4,6-trichlorophenol and 2,4,6-trichlorophenolate. Formation of 1,3,7,9-T₄CDD through the Smiles rearrangement [20] is also shown. PCDF formation from chlorobenzenes proceeds through the reaction given in Fig. 4. In the second step of this condensation reaction, H₂ or Cl₂ may be eliminated too, depending on the chlorination pattern of the intermediate chlorodiphenylether [21]. Both mechanisms may be similar to the Ullmann condensation in which Cu(I) catalyzes the condensation of halogenated benzenes and phenolates to yield diphenylethers [22]. In that case the condensation reaction in Fig. 4 would be between a chlorobenzene and chlorophenolate.

Chlorophenols can be formed from phenol by chlorination. PCDD formation from phenol (Experiment 4) can then be explained by the condensation reaction in Fig. 3. However, other authors found little or no PCDF formation from phenol [23]. The reaction phenol→chlorobenzenes has been observed on fly ash [7], which can form PCDF subsequently via the reaction in Fig. 4.

3.2 [PCDD]:[PCDF] ratios with carbon model compounds

With hexane a [PCDD]:[PCDF] ratio of 0.18–0.42 is found. Formation of both compounds from hexane requires a complicated reaction sequence, probably involving (oxy)chlorination, ring closure and aromatization. Aromatization of hexane is possible on Zn [24]. Our results show that a simple aliphatic molecule, which even lacks a double bond, can be converted to PCDD/PCDF.

Experiment 6 with toluene gives a [PCDD]:[PCDF] ratio of 0.07–0.43. PCDD/PCDF formation from toluene on fly ash has been established before by De Leer *et al.*, but was not quantified [25]. Isomer distributions found with toluene (see Section 3.7) suggest chlorophenols as intermediates in PCDD formation from toluene. However, the [PCDD]:[PCDF] ratio measured with toluene is lower than that found with phenol, i.e. the route via chlorophenols is probably not predominant.

Of the three anthraquinone derivatives, the parent structure itself is not active in PCDD/PCDF forma-

2,6-Dihydroxy-anthraquinone (2,6-diOH)

Fig. 2. Structure of the anthraquinone derivatives.

Fig. 3. Formation route of PCDD from 2,4,6-trichlorophenols.

Fig. 4. Formation route of PCDF from chlorobenzenes and chlorophenols.

tion (Experiment 7): yields were not higher than found in anthraquinone itself. Experiment 8 shows that 2-aca forms PCDD and PCDF in a ratio equal to phenol (around 1.1) but 2,6-diOH (Experiment 9) has a ratio of at least 20. OCDD formation from this compound could not be quantified, hence the minimum value given here.

2,6-diOH has two OH-groups and condensation of two molecules leads to a DD structure in the middle of the condensation product, which could subsequently be released, explaining the strong ten-

dency to form PCDD. Dissociation of 2,6-diOH could lead to two molecules of phenol and two molecules of CO. Phenol produces equal amounts of PCDD and PCDF, implying that this reaction is not predominant.

3.3 Conversion factors with precursors

In the last column of Table 1 conversion factors are reported for the nine reactants studied. The conversion was calculated by $(\Sigma T_4CDD-OCDD + \Sigma T_4CDF-OCDF/n \text{ mole of reactant}) \times 100\%$. Care

has to be taken when comparing the various conversion factors: the reaction conditions were identical for all experiments (348°C, reaction time 50–60 minutes, $\text{N}_2/\text{O}_2/\text{HCl}$), but reactants were administered in different ways. Solid compounds were mixed with the fly ash before the experiment to provide optimum contact. Pentachlorobenzene, however, was placed in a basket at the beginning of the reactor and evaporated onto the fly ash, as the mixing of this compound with the fly ash presented some problems. Liquids were evaporated into the gas stream before the fly ash bed during the whole experiment by means of a volumetric pump. Mixing of the fly ash with a reactant probably results in a more effective contact between reactant and matrix than when the reactant is supplied to the fly ash via the gas stream. Furthermore, different amounts of reactant were used in the experiments and conversion factors are probably concentration dependent. Also, CuCl_2 was added as a catalyst in Experiments 1, 2a, 3 and 7–9 to stimulate PCDD/F formation.

Chlorobenzene has a conversion factor of $2.5 \pm 1.2 \times 10^{-4}\%$. The four experiments with 1,2,4,5-tetrachlorobenzene showed a great variance in reactivity and it can only be said that this compound is at least as reactive as chlorobenzene. Pentachlorobenzene does not form significant amounts of PCDD/PCDF. This suggests that only chlorobenzenes with 1–4 chlorine atoms do form PCDD/PCDF. Buser[18] pyrolyzed tri-, tetra- and pentachlorobenzenes at 620°C and showed that the lowest formation of PCDD/PCDF occurred with pentachlorobenzene. Phenol is between 10–540 times more reactive in PCDD/PCDF formation than the chlorobenzenes. This greater reactivity underlines the importance of the OH-group, probably through better adsorption/chemisorption on the fly ash and the possibility of condensation of two molecules to form PCDD as depicted in Fig. 3.

At 300°C the ratio [chlorobenzenes]:[chlorophenols]:[PCDD+PCDF] formed from residual carbon on fly ash is around 14:1.4:1 [5]. Taking for chlorobenzenes $10^{-3}\%$ as a conversion factor and for phenol $10^{-2}\%$, implies that the formation of PCDD and PCDF during *de novo* synthesis via chlorobenzenes and chlorophenols as intermediates is $\ll 1\%$. Thus, there is no direct link between PCDD/PCDF formation mechanisms from chlorobenzenes and chlorophenols and formation mechanisms from carbon on fly ash.

This link may exist in experiments with activated carbon alone as reported by Luijk *et al.* [9]. However, these authors noted that the specific PCDD formation from carbon via chlorophenols disappeared when 0.5% CuCl_2 was added. The CuCl_2 is assumed to destroy the PCDD formed to a great extent, leading to similar [PCDD]:[PCDF] ratios as measured for *de novo* synthesis from (residual) carbon on fly ash. The presence of Cu ions on fly ash ($\sim 0.2\%$) [7] explains why such a mechanism is not operative on fly ash.

3.4 Conversion factors with carbon model compounds

Hexane has a conversion factor that is within the same order of magnitude as chlorobenzene. Hexane is more volatile than chlorobenzene, probably leading to less adsorption, but also to a higher migration across the fly ash surface and increased potential to reach active catalytic sites. Toluene is not significantly more reactive than hexane in PCDD/PCDF formation.

Anthraquinone does not form PCDD/PCDF and its conversion is $< 1.1 \times 10^{-4}\%$. Experiments with its derivatives (2-aca and 2,6-diOH) show that the anthraquinone structure itself may be resistant to a fly ash catalyzed reaction, but that functional groups like OH and COOH greatly enhance its reactivity: more than 1.3% of 2,6-diOH is converted to PCDD/PCDF. Obviously the two carbonyl groups in the anthraquinone structure do not impede PCDD/PCDF formation.

When considering hexane, toluene and the three anthraquinone derivatives as model compounds for the various parts of activated (and residual) carbon, our results show that aliphatic chains, monocyclic aromatic rings with aliphatic side chains and quinone-like structures with functional groups all have the potential to build PCDD/PCDF.

It is interesting to compare the conversion factors of the carbon model compounds with that of carbon. In experiments performed with carbon under identical conditions, around 10 nanomole/g of PCDD/PCDF was formed from 22 mg carbon/g. With a molar weight for carbon of 144 ($12 \times {}^{12}\text{C}$ -units) the conversion factor is $6.5 \times 10^{-3}\%$. This is higher than the values found for hexane and toluene and lower than the conversions found for 2-aca and 2,6-diOH. This suggests that the linear and monocyclic aromatic parts of the macromolecular carbon structure contribute less to PCDD/PCDF formation than the quinone structures. However, the [PCDD]:[PCDF] ratios found with 2-aca and 2,6-diOH are both > 1 , whereas the ratio in our experiments with carbon is approximately 0.3. If the quinone structures are indeed the most important source of PCDD/PCDF formation from carbon, a ratio > 1 (as found with 2-aca and 2,6-diOH) would be expected. Additional research will be needed to clarify this issue.

3.5 Degree of chlorination

For all compounds tested the average degree of chlorination of the PCDD and PCDF formed was calculated (Table 2). Values for chlorobenzene are lower than for 1,2,4,5-tetrachlorobenzene. The degree of chlorination of both PCDD and PCDF is higher with phenol as reactant than with chlorobenzene, but the values found with phenol do not differ from 1,2,4,5-tetrachlorobenzene. Hence, the amount of chlorine in the starting compound does not influence the degree of chlorination of the resulting PCDD/PCDF, i.e. the availability of chlorine is not a limiting factor.

The same observation can be made for the carbon

Table 2. Average degree of chlorination of PCDD and PCDF for all reactants

Exp. no.	Reactant	PCDD	PCDF
1	Chlorobenzene	6.23 ± 0.05	5.35 ± 0.03
2a	1,2,4,5-Tetrachlorobenzene	7.18 ± 0.16	6.68 ± 0.65
2b	1,2,4,5-Tetrachlorobenzene	7.17 ± 0.47	6.02 ± 0.00
3	Pentachlorobenzene	(i)	(i)
4	Phenol	7.61 ± 0.02	6.91 ± 0.01
5	Hexane	6.36 ± 0.25	5.67 ± 0.14
6	Toluene	7.20 ± 0.32	5.77 ± 0.09
7	Anthraquinone	(i)	(i)
8	2-aca (ii)	7.50 ± 0.02	6.58 ± 0.06
9	2,6-diOH (iii)	(iv)	7.21 ± 0.05

Calculated by setting $\Sigma T_4CDD-OCDD$ or $\Sigma T_4CDF-OCDF$ 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. (i): No PCDD/PCDF formed. (ii): 2-aca: 2-anthraquinone-carboxylic acid. (iii): 2,6-diOH: 2,6-dihydroxy-anthraquinone. (iv): Not calculated because the amount of OCDD could not be quantified.

model compounds in Experiments 5–9 and in general there is no clear relationship between the degree of chlorination and the structure of the starting compound. In all experiments the number of chlorine atoms in PCDD is higher than in PCDF, suggesting greater stability of PCDD against degradation/dechlorination reactions than PCDF.

3.6 Isomer distributions with precursors

The isomer distributions found in our experiments can be used to describe some mechanisms operative on fly ash. These distributions are obtained by setting e.g. $\Sigma T_4CDD=100\%$, followed by calculating the individual contribution of each isomer within the homologue.

With chlorobenzene and phenol, high percentages (between 5 and 85%) of 2,3,7,8- T_4CDD , 1,2,3,7,8- P_5CDD , 1,2,3,4,7,8- H_6CDD and 1,2,3,4,6,7,8- H_7CDD are formed. This can be explained by assuming DD as an intermediate. Chlorination of DD follows an electrophilic mechanism, the order of chlorination being $2 \rightarrow 8 \rightarrow 3 \rightarrow 7 \rightarrow 1 \rightarrow 4 \rightarrow 6 \rightarrow 9$ [26]. DD can be formed by condensation of phenol (eliminating two molecules of H_2) or *o*-chlorophenol via the mechanism in Fig. 3. This establishes the conversion of chlorobenzene to (chloro)phenols. With 1,2,4,5-tetrachlorobenzene as reactant, PCDD isomer distributions showed a great variance and no conclusions can be drawn.

Part of the PCDD isomer distribution of phenol may be explained by condensation of chlorophenols as depicted in Fig. 3 too. Formation of 1,3,6,8- and 1,3,7,9- T_4CDD is possible from coupling of 2,4,6-trichlorophenol. In a similar way 1,2,4,7,9; 1,2,4,6,8; 1,2,3,6,8 and 1,2,3,7,9- P_5CDD can be formed by condensation of 2,4,6-trichlorophenol and 2,3,4,6-tetrachlorophenol. 1,2,3,4,6,8- H_6CDD is formed from 2,4,6-tetrachlorophenol and pentachlorophenol. These three chlorophenols are the most important in incinerator flue gas [17] and are likely to be formed from chlorination of phenol on fly ash.

Table 3 shows results of PCDD isomer distribu-

tions within homologues. The isomers that can be formed from these three chlorophenols are shown. Note that some isomers cannot be separated and only the sum is given. For the two T_4CDD and four P_5CDD isomers listed, the percentages formed with phenol are higher than with carbon.* As described above, chlorophenols are not intermediates in PCDD formation from carbon on fly ash. Within the H_6CDD homologue the sum of 1,2,4,6,7,9 + 1,2,4,6,8,9 + 1,2,3,4,6,8 is higher with phenol than with carbon. This is likely due to additional formation of 1,2,3,4,6,8 from 2,4,6-trichlorophenol and pentachlorophenol.

PCDF isomer distributions (not shown) suggest that with chlorobenzene and 1,2,4,5-tetrachlorobenzene, some congeners are formed out of each other by chlorination. These congeners are identical for both chlorobenzenes, i.e. the chlorination pattern of 1,2,4,5-tetrachlorobenzene is not retained in the PCDFs formed. PCDF congeners formed from phenol have a tendency for 2,3,4,7, and 2,4,6,8-substitution (not shown).

3.7 Isomer distributions with carbon model compounds

With hexane, toluene and 2-aca as reactant, chlorophenols are intermediates in PCDD formation too. This can be seen in Table 3—the percentages of the PCDD isomers which can be formed from the three chlorophenols are higher with these reactants than with carbon. However, with 2,6-diOH the 'chlorophenol' pattern is lacking in the PCDD isomer distribution. In fact, this distribution is quite similar to the one found with carbon.

For formation of chlorophenols from toluene side-

*The percentages of T_4CDD and P_5CDD isomers reported in Table 3 are from experiments carried out under the same reaction conditions as used in Experiments 1–9; however, NaCl was used as a chlorine source. Experiments with HCl resulted in too low concentrations of these two isomer groups to calculate reliable isomer distributions. However, values given for the H_6CDD isomers in Table 3 are from experiments with HCl.

Table 3. PCDD isomer distributions of phenol, hexane, toluene, 2-anthraquinone-carboxylic acid and carbon

Isomer	Phenol	Hexane	Toluene	2-aca (i)	Carbon
1,3,6,8	33 ± 5%	24 ± 2%	75 ± 1%	54%	3%
1,3,7,9	15 ± 2%	16 ± 2%	25 ± 1%	35 ± 1%	3%
1,2,4,7,9 +	22 ± 5%	29 ± 5%	49 ± 7%	32%	9%
1,2,4,6,8 (ii)					
1,2,3,6,8	26 ± 2%	22 ± 2%	37 ± 5%	32 ± 1%	6%
1,2,3,7,9	12%	18%	14 ± 1%	20 ± 1%	6%
1,2,4,6,7,9 +	47 ± 1%	39 ± 6%	48 ± 18%	45%	9%
1,2,4,6,8,9 +					
1,2,3,4,6,8 (ii)					

Obtained by setting, e.g., $\sigma\text{T}_4\text{CDD} = 100\%$, followed by calculating the percentage of each isomer within the group. (i): 2-aca: 2-anthraquinone-carboxylic acid. (ii): Peaks not separated during GC/MSD analysis; the sum is given.

chain oxidation is necessary, possibly by conversion to benzaldehyde and loss of CO. The results with 2-aca show that part of this compound is converted to chlorophenols too, i.e. the anthraquinone structure dissociates, perhaps via benzoic acid as intermediate.

With hexane, the PCDF isomer distribution has a tendency for formation of 1,4,7,8- and 2,3,7,8-substituted congeners. PCDF formed from toluene has a preference for, among others, 2,3,7,8 and 2,3,4,7 substituted congeners, with 2-aca for, among others, 1,2,4,6 substituted congeners. 2,6-diOH generates some PCDF congeners through dechlorination. In general, the PCDF isomer distribution shows a greater variance between the compounds than the PCDD distribution. Part of the important peaks can be explained by assuming chlorination or dechlorination of PCDF congeners after formation.

The carbon model compounds form PCDD via chlorophenols, with the exception of 2,6-diOH. With real carbon as reactant this route is negligible; 2,6-diOH is at least 130 times as reactive in PCDD/PCDF formation as 2-aca and at least 1400 times as reactive as hexane and toluene. There are obviously great differences in reactivity between the various carbon parts and the PCDD/PCDF isomer distribution formed from carbon might almost entirely be determined by structures resembling 2,6-diOH. We calculated the degree of correlation between isomer distributions found with a reactant and with carbon.[†] Results are: hexane $r = 0.84$, toluene $r = 0.52$, 2-aca $r = 0.70$, 2,6-diOH $r = 0.81$. Clearly hexane (despite the fact that part of the PCDD is formed from chlorophenols) and 2,6-diOH have an isomer distribution that most resembles the one found with carbon. However, the reactivity of hexane (and aliphatic carbon parts) is probably too low to give an important contribution during PCDD/PCDF formation from carbon.

4. CONCLUSIONS

Both chlorobenzenes and chlorophenols yield PCDD and PCDF on incinerator fly ash and contribute to formation of these toxic compounds during the process of waste incineration. The formation mechanism of both PCDD and PCDF involves condensation reactions of chlorobenzenes and chlorophenols.

Experiments with carbon model compounds suggest that aliphatic, monocyclic aromatic and functionalized quinone structures in carbon can form PCDD/PCDF. However, the reactivity of the quinones is so high that they could be responsible for almost all PCDD and PCDF formed from carbon, even if their relative concentration within the carbon structure is <1%. However, certainty about this question can only be obtained with knowledge of the quinone concentration in the carbon residue in incinerator fly ash, which is lacking at the moment. OH- and COOH-groups are important in increasing the potential for PCDD/PCDF formation. These groups might provide better adsorption of the reactant to the fly ash surface. Furthermore, the presence of OH-groups gives the possibility of condensation reactions, which is absent with the COOH-group. Other effects—e.g. the activating and o/p directing properties of the OH-group in electrophilic aromatic substitution—might play a role too. Such a substitution might lead to side-reactions, eventually perhaps also generating PCDD and PCDF.

With the conversion factors measured, calculations show that neither chlorobenzenes nor chlorophenols is an important intermediate in PCDD/PCDF formation from carbon, i.e. mechanisms (i) and (ii) are separate pathways indeed. Their relative importance determines whether PCDD/PCDF formed in the post combustion zone stem from precursors or from *de novo* synthesis. Our experiments lasted for 50–60 minutes and simulate only PCDD/PCDF formation on collected fly ash particles (e.g. in an electrostatic precipitator used to remove fly ash particles from the flue gas stream). Uncollected fly ash will have a short (seconds) residence time in the post combustion zone before being

[†]Calculated by linear regression. Isomer percentages found with the reactant (102 values) and with carbon (also 102 values) were used as x and y values respectively; r then represents the degree of similarity between the two isomer distributions.

emitted from the stack. *De novo* synthesis has a long time scale (minutes to hours) and will make a negligible contribution to uncollected fly ash. The ratio between PCDD/PCDF originating from precursors and from carbon will therefore be different for these two categories of fly ash particles.

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