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Schoonenboom, M.H.; Olie, K.

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Formation of PCDDs and PCDFs from Anthracene and Chloroanthracene in a Model Fly Ash System

MIRJAM H. SCHOONENBOOM* AND KEES OLIE

Department of Environmental and Toxicological Chemistry, University of Amsterdam, Amsterdam Research Institute of Substances in Ecosystems, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

Anthracene and 2-chloroanthracene have been investigated as model compounds for carbon in the formation of PCDDs and PCDFs. The formation of PCDDs and PCDFs from anthracene reaches a maximum around 300 °C. Many chlorinated products beside PCDDs and PCDFs are identified after formation from 2-chloroanthracene, including chlorinated anthracenes, naphthalenes, and benzylnaphthalenes. This suggests that part of the PCDDs and PCDFs formed from anthracene probably comes from recombination of its degradation products.

Introduction

After the discovery of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in fly ash and flue gas of municipal waste incinerators in 1977 (1), much research has been undertaken in order to elucidate the formation mechanism of these compounds. PCDDs and PCDFs appeared to be formed in a fly ash catalyzed reaction in the temperature range of 200–400 °C (2–7). There are two main routes postulated for the formation of PCDDs and PCDFs during the incineration of municipal waste. The first route is formation from particulate organic carbon via the so-called *de novo* synthesis. The PCDDs and PCDFs are formed when the carbon is catalytically oxidized with copper as the main catalyst (8–11). The second formation route is formation from (gas-phase) precursor compounds, like (chloro)benzenes and -phenols (11–14). Those precursors are formed as products of incomplete combustion and couple in a heterogeneous reaction on the fly ash surface to PCDDs and PCDFs.

It is not known yet which route is predominant in the formation of PCDDs and PCDFs in a municipal waste incinerator. In order to elucidate part of the formation mechanism that will occur in a municipal waste incinerator, we have studied the formation of PCDDs and PCDFs from anthracene and chloroanthracene. The temperature dependence of formation of PCDDs and PCDFs from anthracene is studied to compare those results with the temperature dependence of formation of these compounds from carbon.

The molecular structure of carbon consists of layers of aromatic rings of the type existing in graphite (15). This ordered structure can be disturbed by oxygen and hydrogen atoms (16). Part of the layer can also contain aliphatic chains. Graphite, which consists of pure carbon, does not react to form PCDDs and PCDFs in *de novo* synthesis (8). Thus, it is necessary for the formation of PCDDs and PCDFs that the structure of the graphite is disturbed (e.g., with hydrogen or oxygen). Anthracene was chosen as a model compound for carbon because it consists of three aromatic rings that are more or less comparable with the aromatic rings in carbon.

There are two reaction pathways for the formation of PCDDs and PCDFs from carbon. The first is a two-stage mechanism that was first reported by Heinbuch and Stieglitz for brominated compounds (17). The first step is side-by-side chlorination of the edges of the macromolecular carbon structure. The second step is oxidative breakdown of the carbon. This yields PCDDs and PCDFs with chlorine atoms substituted in the ortho-position to each other. The second reaction pathway is degradation of the carbon to smaller molecules, after which coupling to PCDDs and PCDFs can occur. Those reaction pathways can also occur from anthracene. When one or two carbon atoms of the anthracene molecule are replaced by oxygen, PCDDs and PCDFs are formed without the need for ring coupling. Anthracene can however also degrade to smaller molecules, after which coupling to PCDDs and PCDFs can occur. When using 2-chloroanthracene as a model compound for carbon, the first chlorination step is already performed making further chlorination easier. When PCDDs and PCDFs are directly formed from chloroanthracene by oxidation, higher amounts of 2,3,7,8-substituted congeners can be expected in comparison with formation from anthracene.

As fly ash is a poorly defined, inhomogeneous support, we used alumina impregnated with copper chloride and potassium chloride as a model system. Aluminium is one of the major compounds of fly ash (18), probably present as oxide (19). Copper is identified as one of the most important compounds of fly ash in the formation of PCDDs and PCDFs (4, 8, 20, 21). Alumina impregnated with copper chloride and potassium chloride appeared to be a good model system in earlier experiments with activated carbon as carbon source (22). We also will vary the acidity of the alumina support to obtain optimum reaction conditions for the formation of PCDDs and PCDFs from anthracene.

Experimental Section

Alkaline or acidic alumina was impregnated with a solution of KCl and CuCl₂ in methanol. The methanol was evaporated under a nitrogen stream at 50 °C. This led to a concentration of 0.23% Cu and 3.2% Cl on alkaline alumina and of 1.6% and 6.4%, respectively, on acidic alumina. Except for the 6.4% Cu on acidic alumina, this is in agreement with the concentrations of those compounds on fly ash (0.02–0.5% Cu and 1.75–31.87% Cl (18, 20)).

A sample of 105 mg anthracene or 2-chloroanthracene was placed in front of a spiralized glass tube, followed by 7.8 g of the impregnated alumina. The glass tube was placed in a GC-oven (modified Varian Model 3700 gas chromatograph) under a flow of 8 mL/min technical air. The air

* Corresponding author fax: + 31-20-4210710.

TABLE 1

Experimental Conditions for Formation of PCDD/Fs from Carbon Model Compounds.

no.	support	model compd	temp (°C)	N ^a
1	alkaline alumina ^b	anthracene	300	1
2	acidic alumina ^a		300	1
3	acidic alumina ^c	anthracene	250	2
4	acidic alumina ^c	anthracene	300	3
5	acidic alumina ^c	anthracene	350	3
6	acidic alumina ^c	anthracene	400	3
7	acidic alumina ^c	2-chloroanthracene	300	2

^a Number of samples. ^b Impregnated with 0.8% CuCl₂ and 5.6% KCl. ^c Impregnated with 5.6% CuCl₂ and 5.2% KCl.

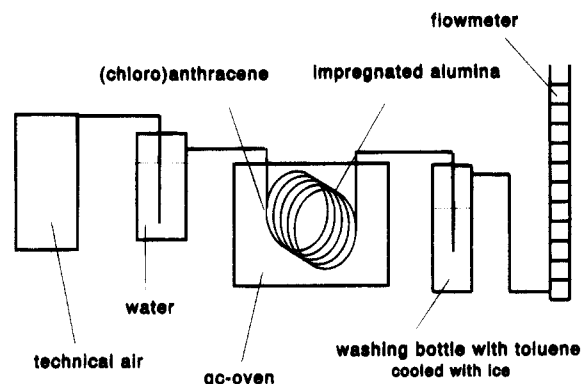


FIGURE 1. Apparatus.

flowed through a washing bottle filled with water and subsequently passed the anthracene/2-chloroanthracene. In this way, the reactant was evaporated onto the matrix.

The oven was heated for 2 h at different temperatures, as can be seen in Table 1. All volatile organic substances were collected in a washing bottle filled with toluene and cooled with ice, placed after the flow tube. During the 2 h of heating, all (chloro)anthracene was evaporated onto the alumina support. Part of the anthracene might remain in the washing bottle or on the alumina, but we have not quantified this. A schematic drawing of the apparatus is shown in Figure 1.

Extraction, Cleanup, and GC/MS Analysis. This has been described in earlier experiments (22).

Materials. Aluminium oxide 90 active, basic (activity stage I) (70–230 mesh) was from Merck, Darmstadt, Germany. Aluminium oxide 90 active, acidic (activity stage I) (70–230 mesh) was from Merck, Darmstadt, Germany. Anthracene was from J. T. Baker Chemical Corporation, Philipsburg, NJ. 2-Chloroanthracene, 95%, was from Aldrich Chemical Corporation, Milwaukee, WI. Copper(II) chloride hydrate was from Janssen Chimica, Beerse, Belgium. Technical air was from Hoekloos, Schiedam, The Netherlands. Potassium chloride, p.a., was from Merck, Darmstadt, Germany.

Results and Discussion

In two blank extractions (extraction and cleanup of ¹³C labeled PCDDs and PCDFs), only trace amounts of PCDDs and PCDFs were found (<1 ng). In the blank experiment (exp no. 2), some PCDD and PCDF congeners were found in very low amounts [normally <0.6 ng, with the exception of 2 ng for 1,2,3,4,7,8-H₆CDD (a low level contamination due to carry over of high 1,2,3,4,7,8-H₆CDD amounts in earlier experiments)].

TABLE 2

Amount of PCDD/F Formed at Different Temperatures from Anthracene on Acidic Alumina Support (ng)^a

	exp no.			
	3 at 250 °C	4 at 300 °C	5 at 350 °C	6 at 400 °C
T ₄ CDD	7 (2)	5 (6)	nd ^c	nd
P ₅ CDD	18 (9)	26 (25)	nd	nd
H ₆ CDD	34 (6)	46 (32)	nd	nd
H ₇ CDD	31 (14)	50 (24)	nd	nd
O ₈ CDD	8.5 (0.1)	36 (10)	nd	nd
PCDD	122 (27)	154 (94)		
T ₄ CDF	16 (2)	139 (123)	1.2 (1.0)	nd
P ₅ CDF	4.9 (1.6)	447 (189)	nd	nd
H ₆ CDF	5.6 (1.0)	740 (323)	1.0 (0.3)	2.0 (0.7)
H ₇ CDF	2.4 (0.4)	434 (273)	0.8 (0.3)	2.5 (0.4)
O ₈ CDF	2.6 (0.3)	38 (16) ^b	nd	2.0 (0.8)
PCDF	31 (5)	1784 (749)	2.7 (1.3)	6.5 (0.5)
PCDD/PCDF	3.8 (0.2)	0.08 (0.04)		

^a All experiments are in triplicate (standard deviation is given in parentheses), except for experiment no. 3, which is in duplicate (range is given in parentheses). The range is calculated by subtracting the values of the two experiments and dividing this by 2. ^b Range of two experiments. ^c nd not detected; detection limit varies between 0.08 and 1.8 ng.

On alkaline alumina/0.8% CuCl₂, only small amounts of PCDD/Fs were found (exp no. 1). When using acidic alumina/5.6% CuCl₂, large quantities of PCDD/Fs were found (exp no. 4). This difference due to the effect of the acidity of the alumina support and the copper chloride concentration was also found in the literature for the formation of PCDDs and PCDFs from carbon (8, 22, 23).

In earlier experiments (22), we found 94 ng of PCDDs and PCDFs formed from carbon under the same conditions (alkaline alumina/0.8% CuCl₂) where we did not find PCDD/Fs formed from anthracene. This suggests that PCDD/F formation from anthracene is less efficient than the formation from carbon. Due to the higher volatility of anthracene with respect to carbon, we cannot exclude that the lower formation from anthracene is caused by a lesser availability.

In Table 2, the amount of PCDD/F formed on acidic alumina/5.6% CuCl₂ at different temperatures is given. At 350 and 400 °C, only small amounts of PCDDs and PCDFs were found. At 250 and 300 °C, high amounts of PCDDs and PCDFs were found, primarily at 300 °C. This optimum temperature was also found for the formation from carbon (24). The increase of PCDD/F formation between 250 and 300 °C is completely due to higher amounts of PCDFs. This results in a sharp decrease of the [PCDD]:[PCDF] ratio. The ratio of 3.8 found at 250 °C is remarkable high compared to the ratios normally found for formation from carbon at 300 °C, which are usually below 1. Original fly ash itself however can have PCDD/F ratios > 1 (22, 25). Addink *et al.* (26) also found a very high [PCDD]:[PCDF] ratio at 250 °C for formation from carbon. The ratio they found decreased sharply between 250 and 300 °C as well. This suggests that the PCDD/F formation from anthracene and carbon might have the same rate-determining step. Another possible explanation for the similar behavior of anthracene and carbon in the PCDD/F formation could be that the difference in [PCDD]:[PCDF] ratio is due to a different effect of the temperature on the destruction of PCDDs in comparison with the destruction of PCDFs. Van Berkel *et al.* (27) have studied the influence of temperature

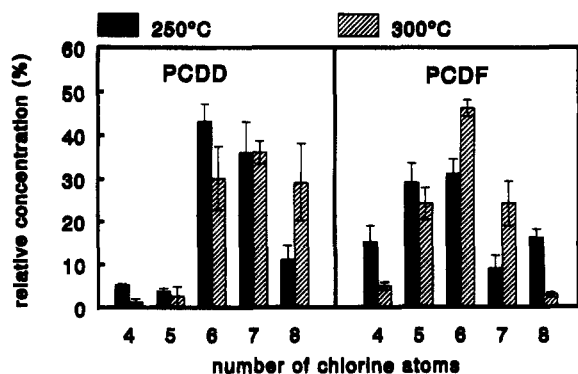


FIGURE 2. PCDDs and PCDFs formed from anthracene at 250 and 300 °C.

on the destruction of OCDD and OCDF on fly ash. At 250 °C, they found a slightly higher dechlorination rate for OCDD in comparison with OCDF. At 300 °C, however, they found a higher dechlorination rate for OCDF in comparison with OCDD. When we assume PCDDs have the same behavior as OCDD and that PCDFs have the same behavior as OCDF, this difference in dechlorination rate found by van Berkel *et al.* would give a higher [PCDD]:[PCDF] ratio at 300 °C than at 250 °C. This is in conflict with our finding.

We can now make the conclusion that the difference in [PCDD]:[PCDF] between 250 and 300 °C is not caused by a difference in destruction rate but by a difference in formation rate. So the conclusion that PCDD/F formation from anthracene and carbon might have the same rate-determining step is supported by this finding. Further research on the mechanism of formation from both anthracene and carbon is necessary.

In Figure 2, the homologue distribution at 250 and 300 °C is given. Within one homologue group, not all isomers could be quantified because of interferences. Assuming a zero concentration for these isomers would underestimate the real amount of a homologue group. In order to make a fair comparison between different experiments, we have only taken into account the isomers that could be quantified in every experiment, leading to a distribution that can differ from the values in Table 2. At 300 °C, there were more higher chlorinated congeners than at 250 °C, as was also found in the PCDD/F formation from carbon (28). This is probably due to a better chlorination at higher temperatures. It could also be due to a high dechlorination rate at 300 °C for the lower chlorinated congeners. Because of the lack of dechlorination studies, we cannot verify this hypothesis.

When chloroanthracene was used as starting material, the amount of PCDD/F formed varies widely between duplo experiments, so formation rates cannot be compared with anthracene. The homologue distribution of anthracene and chloroanthracene differed greatly only for OCDF as can be seen in Figure 3. More higher chlorinated congeners seem to be formed from chloroanthracene. This can be expected because one chlorine atom is already present in the reactant giving rise to easier further chlorination.

The isomer distribution yields for anthracene and chloroanthracene differed only slightly, as can be seen for H₆CDD, H₇CDD, P₅CDF, and H₆CDF in Figure 4. This indicates that the isomer pattern is not determined by the chlorination of anthracene. It can be the result of the dechlorination of higher chlorinated congeners to lower

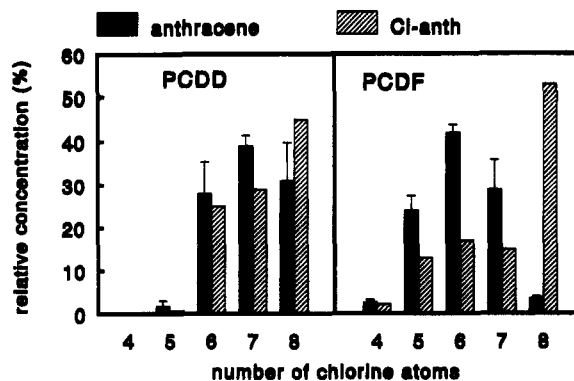


FIGURE 3. PCDDs and PCDFs formed from anthracene and 2-chloroanthracene at 300 °C.

chlorinated ones. Another explanation could be the destruction of the (chlorinated) anthracene to smaller molecules, after which PCDDs and PCDFs are formed.

The isomer distribution at 250 and at 300 °C differed especially for the furans (Figure 4). Isomers with three or more places substituted at the 3,4,6,7-positions were formed more at 300 °C in comparison with 250 °C. For P₅CDF, this results in higher amounts of the 2,3,4,6,8-, 2,3,4,6,7-, and 2,3,4,7,8-chlorinated isomers. For H₆CDF, this results in higher amounts of the 1,3,4,6,7,8-, 1,3,4,6,7,9-, 1,2,3,4,6,7-, and 2,3,4,6,7,8-chlorinated isomers. PCDF isomers substituted at the 3,4,6,7-positions were also formed predominantly from carbon, especially at 350 °C (with respect to 300 °C), which was reported in earlier experiments (28). The reported two-stage mechanism there, however, cannot explain side-by-side chlorination in anthracene because anthracene has no fixed polymer structure and can be chlorinated on all sides of the molecule.

In one of the duplo experiments with 2-chloroanthracene (exp no. 7), some crystals were found in the eluents after the alumina column, so we have looked for other chlorinated products beside PCDDs and PCDFs. Some of the extract after the alumina column was sampled, of which mass spectra were scanned from 100 to 600 AMU. We could identify many chlorinated products, which are reported in Table 3. This, however, is only a part of the chlorinated products formed because a lot of chlorinated products could be lost during the previous cleanup steps.

From the products found, we can construct a reaction mechanism for the formation of these compounds. (Chloro)anthracene is chlorinated to (higher) chlorinated anthracenes. Those chloroanthracenes are destroyed to chloronaphthalenes and chlorobenzenes. We could not find chlorobenzenes because they are discarded during the cleanup on the alumina column. The chloroanthracenes, chloronaphthalenes, and chlorobenzenes can couple giving chlorobenzylanthracenes, chlorobinaphthalenes, and some other products that are reported in Table 3. Due to the many destroying and coupling products we found, we suppose that the PCDDs and PCDFs are likely to be formed by decomposition of the (chloro)anthracene and by coupling of the smaller fragments to PCDDs and PCDFs. Direct formation of PCDD/Fs via chlorination and oxidation of the anthracene itself, however, cannot be excluded by this experiment.

Conclusions

PCDDs and PCDFs are formed from anthracene and chloroanthracene on an acidic alumina support. The

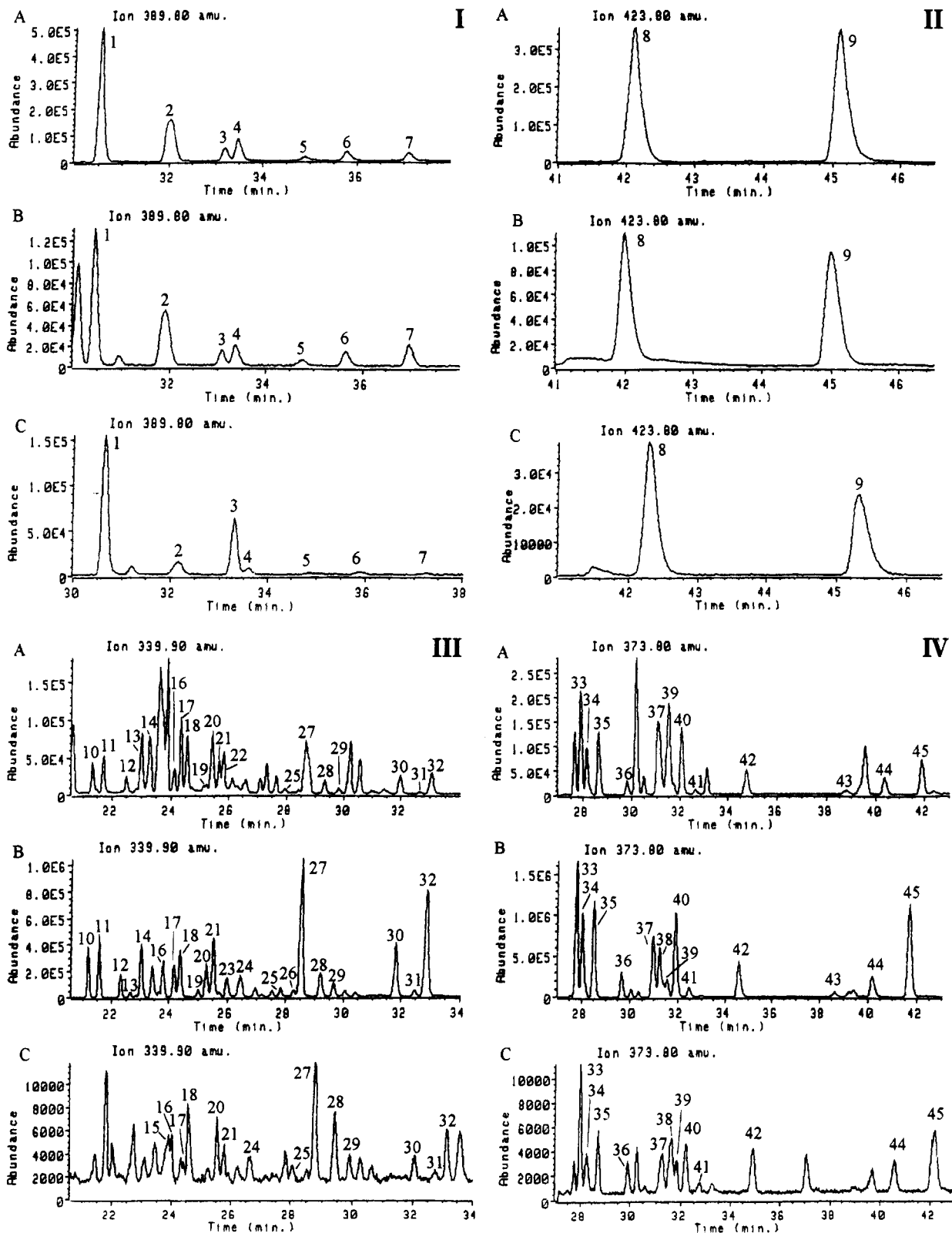
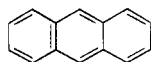
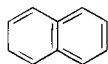
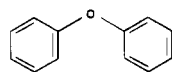
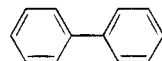
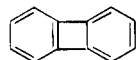
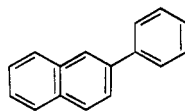
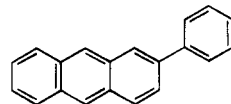
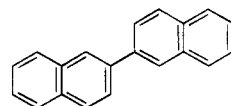


FIGURE 4. MSD chromatogram for H₄CDD (I), H₇CDD (II), P₅CDF (III), and H₆CDF (IV) isomers: (A) chloroanthracene, 300 °C; (B) anthracene, 300 °C; (C) anthracene, 250 °C. Explanation of numbers in the figure: H₄CDD—1, 1,2,4,6,7,9-, 1,2,4,6,8,9-, 1,2,3,4,6,8-, 2, 1,2,3,6,7,9-, 1,2,3,6,8,9-, 3, 1,2,3,4,7,8-, 4, 1,2,3,6,7,8-, 5, 1,2,3,4,6,9-, 6, 1,2,3,7,8,9-, 7, 1,2,3,4,6,7-. H₇CDD—8, 1,2,3,4,6,7,9-, 9, 1,2,3,4,6,7,8-. P₅CDF—10, 1,3,4,6,8-, 11, 1,2,4,6,8-, 12, 2,3,4,7,9-, 13, 1,3,4,7,9-, 14, 1,3,4,7,8-, 1,2,3,6,8-, 15, 1,2,4,7,8-, 16, 1,3,4,6,7-, 1,2,4,7,9-, 17, 1,2,4,6,7-, 18, 1,2,3,4,7-, 2,3,4,6,9-, 19, 1,3,4,6,9-, 20, 1,2,3,4,8-, 1,2,3,7,8-, 21, 1,2,3,4,6-, 22, 1,2,3,7,9-, 23, 1,2,3,6,7-, 24, 1,2,4,6,9-, 2,3,4,8,9-, 25, 1,3,4,8,9-, 26, 1,2,3,6,9-, 27, 2,3,4,6,8-, 28, 1,2,3,4,9-, 29, 1,2,4,8,9-, 30, 2,3,4,7,8-, 31, 1,2,3,8,9-, 32, 2,3,4,6,7-. H₆CDF—33, 1,2,3,4,6,8-, 34, 1,3,4,6,7,8-, 1,3,4,6,7,9-, 35, 1,2,4,6,7,8-, 36, 1,2,4,6,7,9-, 37, 1,2,3,4,7,8-, 1,2,3,4,7,9-, 38, 1,2,3,6,7,8-, 39, 1,2,4,6,8,9-, 40, 1,2,3,4,6,7-, 41, 1,2,3,6,7,9-, 42, 1,2,3,4,6,9-, 1,2,3,6,8,9-, 43, 1,2,3,7,8,9-, 44, 1,2,3,4,8,9-, 45, 2,3,4,6,7,8-

formation of these products from anthracene is most effectively around 300 °C. The same optimum temperature is found for the formation from carbon. The [PCDD]:[PCDF]

ratio decreases sharp from 3.8 to 0.08 going from 250 to 300 °C, which is also true for the formation from carbon. This suggests that the PCDD/F formation from anthracene and

TABLE 3

Chlorinated Products Formed from Chloroanthracene^aAnthracene
tri, tetra and hexa chlorinatedNaphthalene
tri to octa chlorinateddiphenylether
hepta to deca chlorinatedbiphenyl
nona chlorinatedbiphenylene
penta chlorinatedbenzylanthracene^{*}
octa and nona chlorinatedbenzylanthracene
penta to nona chlorinated or[†]binaphthalene
penta to nona chlorinated

^a The asterisk (*) indicates the phenyl group can be coupled at both the α - and β -positions of the naphthalene molecule. Only the latter is depicted. The exclamation point (!) indicates that we cannot make a distinction between the two molecules. The phenyl molecule can be coupled at different places of the anthracene molecule; the two naphthalene molecules can both be coupled at the α - and β -positions.

carbon is performed via the same rate-determining step.

The isomer distributions of PCDD/Fs after formation from anthracene and chloroanthracene differ only slightly. This suggests that this pattern is the result of the dechlorination of higher chlorinated congeners to lower chlorinated ones or (chlorinated) anthracene is degraded to smaller molecules, which are recombined to PCDDs and PCDFs.

We could find destruction products from chloroanthracene and also coupling products of these molecules. This suggests that part of the PCDDs and PCDFs formed from anthracene probably comes from recombination of its degradation products. We cannot give a conclusion about the direct formation of PCDDs and PCDFs from (chloro)anthracene.

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