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Mechanism of Formation of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans in the Catalyzed Combustion of Carbon

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Combustion experiments of an activated carbon (Norit RX Extra), catalyzed by $CuCl_2$, were conducted in triplicate in a flow of moist air containing 5 vol % HCl at 300 °C to reveal the mechanism of formation of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). The catalyst concentration was varied from 0, 0.1, 0.5, 1.0, to 5.0 wt %. After partial combustion (1 h), the samples were analyzed on the presence of PCDDs and PCDFs. The total yield of these compounds amounted to 19 (0.1 wt % $CuCl_2$) and 2 (5.0 wt % $CuCl_2$) $\mu g/g$ of carbon. The PCDD/PCDF ratio showed a decrease from 33 to 0.2. At low copper concentrations, predominantly PCDDs are formed with an isomer pattern that can be explained completely as a product of chlorophenol condensation reactions. At high copper concentrations, the PCDD/PCDF isomer distribution pattern shifts toward a characteristic waste incineration fly ash pattern. A proposal for the mechanism of formation of PCDDs and PCDFs in the catalyzed combustion of carbon will be presented. Condensation reactions of 2,4,6-trichlorophenol on carbon (0 wt % $CuCl_2$) resulted in the formation of predominantly PCDDs with an identical isomer distribution pattern as observed in the catalyzed combustion of carbon. Active carbon was shown to catalyze the condensation reaction of 2,4,6-trichlorophenol into PCDDs.

Introduction

Recent developments in the research area on the mechanism of formation of polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) in municipal waste incineration (MWI) processes clearly indicate a correlation between the oxidation of the fly ash residual carbon and the formation of polychlorinated aromatic compounds including PCDDs and PCDFs (1-4). Copper complexes are considered to be the catalytic active species. Copper(II) chloride is a well-known (oxy)chlorination catalyst (5) and is able to oxidize active carbon at relatively low temperatures found in electrostatic precipitaton (ESP) conditions (1, 6, 7). Gullett et al. have shown the activity of Cu(II) complexes in the formation of PCDDs and PCDFs by (i) the metal-catalyzed production of Cl_2 from HCl and O_2 (Deacon process), (ii) the chlorination of aromatic structures by Cl_2, and (iii) the metal-catalyzed formation of dual-ring structures (8, 9). In an earlier study (10), we developed a fly ash model system consisting of active carbon, copper(II) chloride, and hydrogen chloride and studied the formation of PCDDs and PCDFs under

conditions that are found in ESP of fly ash particles in incineration processes. The formation of PCDDs and PCDFs was shown to occur during the catalyzed combustion of carbon in the presence of a chlorine source.

This study on the mechanism of formation of PCDDs and PCDFs was performed in a model fly ash system under ESP conditions. The influence of the catalyst concentration on the formation characteristics of PCDDs and PCDFs from active carbon in the low temperature combustion in the presence of HCl was investigated.

Because initial results of the formation of PCDDs and PCDFs in the catalyzed combustion of carbon showed a PCDD congener pattern that could be explained entirely as the result of condensation reactions of a limited set of chlorophenol precursor compounds, 2,4,6-trichlorophenol was passed over a carbon surface under ESP conditions (300 °C, moist air). The PCDD congener distributions were compared with those obtained in the catalyzed combustion of carbon. Gas-phase condensation reactions of 2,4,6-trichlorophenol at 300 and 600 °C were used as a comparison to study the influence of active carbon. Finally, the results of both studies are summarized in a proposed mechanism of formation of PCDDs and PCDFs in the catalyzed combustion of carbon.

To our knowledge, no direct correlation between the release of chlorophenols from a macromolecular carbon structure and the formation of PCDDs in a heterogeneous system has been shown before. The presence of chlorophenols with 2,4,6-trichloro-, 2,3,4,6-tetra-, and pentachlorophenol as the most abundant (and the thermodynamically most stable) chlorophenols in MWI effluents (11, 12) has been used by Ballschmiter et al. (12) and Born (13) to explain the observed PCDD congener patterns in fly ash. However, these authors base their data upon a gas-phase source of chlorophenols.

Experimental Section

Materials. These materials were used: ^{13}C-labeled PCDD and PCDF standards (CIL, Woburn, MA); SiO_2–Al_2O_3, LA-300-10P, 420 m^2/g, d_p = 106-150 μm (AKZO Chemie Nederland B.V., Amsterdam, The Netherlands); Norit RX Extra, an acid-washed, steam-activated peat char, 1100 m^2/g, d_p = 100-325 μm; Aktiv Kohle, DARCO 6060, 100-325 mesh powder (Aldrich Chemie, Sternheim, Germany); fly ash (municipal waste incinerator, Zaandam, The Netherlands); HCl (4.0) (UCAR Specialty Gases, Nieuw-Vennep, The Netherlands); N_2 (4.0), O_2 (4.0), and technical air (Hoekloos, Schiedam, The Netherlands); $CuCl_2$ (Janssen Chimica, Tilburg, The Netherlands); 2,4,6-trichlorophenol (98%) (Merck Schuchardt, München, Germany).

Catalyzed Combustion of Carbon. Combustion experiments of activated carbon (Norit RX Extra), loaded

Table 1. Elemental Analysis of Active Carbon (Mean Deviation of Duplo Experiment in Parentheses)

	Cu (μg/g)	Fe (μg/g)	Al (μg/g)	Cl (μg/g)
Norit RX Extra	9 (0)	235 (15)	380 (2)	1150
DARCO Aktiv Kohle	27 (6)	1560 (340)	587 (8)	2590 (71)
detection limit	1	5	8	

with 0, 0.1, 0.5, 1.0, and 5.0 wt % $CuCl_2$ by pore volume impregnation, were conducted in triplicate in a flow of moist air containing 5 vol % HCl at 300 °C. The sample size was 0.5 g, the reaction time was 1 h, and the gas-flow rate was 100 mL min^{-1}. Before pore volume impregnation, the carbon was heated in a nitrogen atmosphere (6 h, 500 °C) to remove volatile organic species. Two additional experiments were conducted with carbon samples (Norit RX Extra; 0 and 0.5 wt % $CuCl_2$) under the same conditions but without HCl in the gas flow, as a blank and a reference test, respectively. A second type of activated carbon (Aktiv Kohle, DARCO without $CuCl_2$) was tested for comparison. Table 1 presents the elemental analysis of both types of active carbon. Copper, iron, and aluminium were measured with ICP-AES. Chlorine was measured with ion chromatography. A second series of combustion experiments was conducted in triplicate with a physical mixture of activated carbon (Norit RX Extra, 0.5 wt % $CuCl_2$) and SiO_2-Al_2O_3 in the ratio of 1:1 by weight. The experimental conditions were identical to those described above. The combustion experiments were performed in a horizontal Pyrex tube reactor. After preheating the reactor, an inlet tube with a cylindrical sample basket was introduced into the center of the reactor. The gas flow through the fixed bed was controlled by mass flow controllers. A chamber containing ceramic pellets was used to mix the nitrogen and oxygen flows before entering a washing bottle filled with water (20 °C). The moist (5 vol % H_2O) N_2/O_2 and HCl (5 vol %) gas flows were separately connected to the inlet tube. A cold trap (hexane, 0 °C) was used to collect possibly evaporated species. After the experiments were done, the samples were weighed to determine the combustion loss. Other apparatus, Soxhlet extraction procedure with toluene and clean-up method including a RP-HPLC fractionation, have been described previously (14–16).

Condensation Reactions of Chlorophenols. The condensation reactions of 2,4,6-trichlorophenol were performed in duplicate. The chlorophenols entered the reactor by means of a diffusion cell as described by Miguel and Natush (17). A flow of nitrogen, technical air, or moist technical air (20 mL/min) was passed through the diffusion cell (100 °C, 30 min) containing 2,4,6-trichlorophenol. The vapor concentration amounted to approximately 0.021 μmol/mL or 0.42 μmol/min and entered two types of reactors for gas-phase and surface-catalyzed condensation reactions. In the gas-phase reactions in air at 300 and 600 °C, the vapor was passed through a coiled quartz tube reactor (volume 10 mL; total length 40 cm; inner diameter 6.35 mm; 19 coils; coil diameter 17 mm). The mean residence time was 30 s. In the surface-catalyzed reactions in nitrogen and in (moist) air at 300 °C, the vapor was passed through a fixed bed of carbon (Norit RX Extra; 1.0 g; volume 0.94 mL). The mean residence time was 2.8 s.

Before being used, the 2,4,6-trichlorophenol was purified by washing an alkaline solution of this compound with *n*-hexane to remove PCDDs, PCDFs, and other nonpolar contaminants.
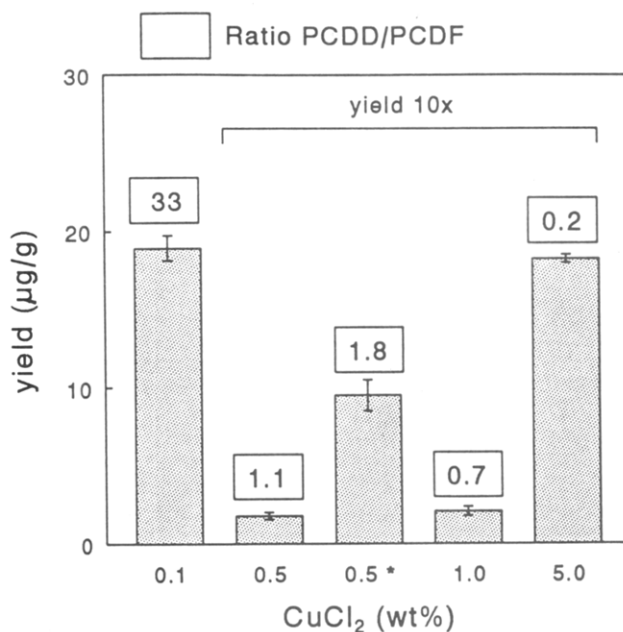
Figure 1. Total yield of PCDDs and PCDFs and PCDD/PCDF ratio in the catalyzed combustion of carbon for different $CuCl_2$ loadings. (*) mixed with silica–alumina (1:1).

Analysis. The formation of PCDDs and PCDFs in incineration processes shows a typical isomer distribution pattern including almost all 210 possible congeners (18). This study only deals with tetra- to octachlorinated PCDDs and PCDFs. The results are given as the sum of different PCDD and PCDF isomer groups: tetrachlorinated (ΣCl_4-DD and ΣCl_4DF), pentachlorinated (ΣCl_5DD and ΣCl_5-DF), etc. The HRGC-LRMS analyses were performed on a Hewlett-Packard GC-MSD operated in electron impact selected-ion-monitoring mode, using a 60-m SP-2331 fused-silica column (0.32 mm i.d., d_f = 0.2 μm, Supelco).

Full-scan analysis of carbon extracts from the combustion experiments was performed to analyze possible precursor compounds in the *de novo* synthesis. The conversion of chlorophenols over carbon at 300 °C resulted in a series of condensation products, which were observed in the RP-HPLC fractionation and could not be assigned as PCDDs. These condensation products were analyzed in the full-scan mode, using a 30-m DB-5 fused-silica column [0.32 mm i.d., 0.25 μm d_f, J&W, cold on-column injection, T-program (70 °C (40 °C/min) → 320 °C)].

Results and Discussion

Catalyzed Combustion of Carbon. In the presence of HCl in the combustion gas, no sample weight loss was observed. The blank experiment of carbon (Norit RX Extra, 0 wt % $CuCl_2$, 0 vol % HCl) did not result in the formation of PCDDs and PCDFs. The PCDDs and PCDFs that were formed in the other combustion experiments remained adsorbed on the carbon surface. Less than 0.5% was found in the cold trap under chosen conditions (0.5 g of C, 1 h, 300 °C). Figure 1 shows the total yield of PCDDs and PCDFs and the PCDD/PCDF ratio as a function of the catalyst concentration. First, a dramatic decrease from 19 to 0.2 ppm is observed going from 0.1 to 0.5 wt % $CuCl_2$. Then a slight increase to a level of 2 ppm is observed going to 5.0 wt % $CuCl_2$. The addition of an acidic silica–alumina support to Norit RX Extra (0.5 wt % $CuCl_2$), in a ratio of 1:1 by weight, results in an increase in the yield by a factor of 5.

Table 2. Relative Percentages of Products within PCDD/F Isomer Groups (in %)

		combustion							condensation	
	fly ash	carbon	carbon	carbon	carbon	carbon	carbon	Si–Al	C13φOH	
									carbon	gas phase
CuCl₂ (wt %)		0.5	0	0.1	0.5	1.0	5.0	0.5	0	0
HCl (mL/min)		0	5	5	5	5	5	5	0	0
T (°C)		300	300	300	300	300	300	300	300	600
T4CDD										
1,3,6,8	9.75	9.71	69.31	72.70	61.56	64.69	8.02	67.13	54.24	56.46
1,3,7,9	19.71	6.26	26.03	24.19	23.46	22.37	5.10	21.41	44.52	43.06
1,3,7,8	13.14	11.50	0.86	0.49	2.08	3.53	0.00	1.61	0.14	0.24
1,3,6,9 / 1,2,4,7 / 1,2,4,8	6.24	18.08	0.74	0.28	3.59	4.70	0.00	2.11	0.08	0.09
1,2,6,8	2.94	4.73	0.49	0.32	0.70	2.34	0.00	0.68	0.02	0.08
1,4,7,8	0.58	1.02	0.00	0.00	0.00	0.00	0.00	0.23	0.00	0.00
2,3,7,8	8.00	3.25	0.00	0.00	1.05	0.00	0.00	0.06	0.00	0.00
1,2,3,4 / 1,2,3,7 / 1,2,3,8 / 1,2,4,6 / 1,2,4,9	16.50	23.62	0.99	0.73	4.57	1.29	0.00	4.51	0.00	0.04
1,2,3,6 / 1,2,7,9	8.75	6.46	0.71	0.43	1.24	0.66	0.00	1.01	0.00	0.02
1,2,7,8 / 1,4,6,9	6.33	8.06	0.00	0.12	0.52	0.00	9.98	0.19	0.00	0.00
1,2,3,9	2.77	2.32	0.18	0.32	0.00	0.41	0.00	0.18	0.00	0.00
1,2,6,9	1.19	2.09	0.28	0.00	0.72	0.00	0.00	0.20	0.00	0.00
1,2,6,7	2.47	1.98	0.40	0.45	0.52	0.00	76.89	0.68	0.00	0.00
1,2,8,9	1.65	0.90	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
T4CDF										
1,3,6,8	1.63	0.00	0.00	0.00	0.00	0.00	0.00	0.00	44.81	42.57
1,3,7,8 / 1,3,7,9	5.24	1.57	3.48	4.75	2.34	2.50	3.07	2.49	0.00	6.20
1,3,4,7	0.91	0.78	1.27	2.80	2.65	4.73	4.80	4.20	0.00	0.16
1,4,6,8	1.38	1.64	6.76	5.83	6.37	4.45	2.57	6.65	0.00	2.06
1,2,4,7	1.12	3.94	13.60	13.21	11.38	11.22	6.10	9.23	0.00	0.67
1,3,6,7	1.30	0.00	1.46	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1,3,4,8	0.99	1.85	1.40	3.95	3.14	3.23	3.04	4.20	0.00	0.11
1,3,4,6 / 1,2,4,8	2.06	4.18	6.92	7.82	7.15	7.02	6.47	6.88	0.00	0.00
1,2,4,6	3.47	9.91	6.96	5.02	6.42	6.49	3.55	4.54	0.00	1.17
1,2,6,8 / 1,2,3,7 / 1,4,7,8	4.39	0.00	1.42	4.35	3.71	5.19	12.51	6.31	0.00	0.46
1,3,6,9	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2,3,4,9 / 1,2,3,4	2.58	9.53	26.33	18.15	17.75	16.91	3.72	12.14	55.19	35.11
1,2,3,8 / 1,4,6,7 / 2,4,6,8 / 1,2,3,6	6.11	7.02	4.53	9.82	8.59	9.11	8.99	7.44	0.00	0.00
1,3,4,9	0.48	1.07	0.15	0.51	0.94	0.86	0.00	0.58	0.00	0.00
1,2,7,8	6.48	4.20	0.20	0.85	1.94	2.78	15.18	4.47	0.00	0.00
1,2,6,7	2.96	3.89	1.25	1.41	2.20	2.67	6.90	2.95	0.00	0.27
1,2,7,9 / 1,4,6,9	0.15	0.00	0.00	1.59	0.06	0.11	0.91	0.16	0.00	0.00
1,2,4,9	3.77	6.23	3.50	1.73	4.52	2.79	0.65	3.94	0.00	5.86
2,3,6,8	0.00	0.00	0.00	0.00	0.00	0.15	0.38	0.00	0.00	0.00
2,4,6,7	6.81	5.41	4.87	4.53	4.35	3.20	0.82	3.03	0.00	4.61
1,2,3,9 / 2,3,4,7	6.26	10.32	9.36	6.67	7.45	7.52	3.47	8.15	0.00	0.19
1,2,6,9	0.84	0.39	0.00	0.00	0.33	1.58	3.09	0.31	0.00	0.08
2,3,7,8	6.98	10.07	1.53	2.05	3.76	3.01	4.92	2.01	0.00	0.15
2,3,4,8	2.30	0.00	2.32	2.02	0.32	1.00	0.00	5.00	0.00	0.20
2,3,4,6	8.22	6.33	2.60	2.19	2.29	2.35	0.85	1.72	0.00	0.08
2,3,6,7	9.63	4.95	0.08	0.24	0.76	1.13	3.83	1.70	0.00	0.12
3,4,6,7	13.11	5.12	0.00	0.48	0.84	0.00	2.47	0.47	0.00	0.00
1,2,8,9	0.82	0.59	0.00	0.04	0.65	0.00	1.71	1.42	0.00	0.00
P5CDD										
1,2,4,7,9 / 1,2,4,6,8	15.99	19.09	37.37	35.90	39.60	39.37	19.58	40.44	42.34	36.55
1,2,3,6,8	10.92	11.53	34.88	35.60	32.45	31.61	12.17	31.98	27.91	31.30
1,2,4,7,8	3.97	9.42	0.07	0.06	0.38	1.28	3.47	0.69	0.00	0.00
1,2,3,7,9	29.75	7.03	27.04	27.35	23.70	20.40	7.45	21.14	28.98	32.15
1,2,4,6,9 / 1,2,3,4,7	4.73	18.36	0.02	0.32	1.15	2.08	1.05	2.35	0.77	0.00
1,2,3,7,8	19.25	10.50	0.15	0.06	0.00	5.26	27.17	2.11	0.00	0.00
1,2,3,6,9	1.42	2.10	0.03	0.04	0.00	0.00	0.00	0.00	0.00	0.00
1,2,4,8,9 / 1,2,4,6,7	4.93	9.55	0.03	0.11	0.00	0.00	22.26	0.00	0.00	0.00
1,2,3,4,6	1.21	8.91	0.07	0.29	2.72	0.00	6.18	0.83	0.00	0.00
1,2,3,6,7	0.00	0.00	0.00	0.25	0.00	0.00	0.00	0.21	0.00	0.00
1,2,3,8,9	7.83	3.52	0.34	0.03	0.00	0.00	0.67	0.24	0.00	0.00

Table 2 (Continued)

		combustion								condensation
	fly ash	carbon	carbon	carbon	carbon	carbon	carbon	Si–Al		C13φOH
					P5CDF					
1,3,4,6,8	2.99	2.84	7.12	6.65	8.09	8.61	2.29	6.09		12.86
1,2,4,6,8	3.11	3.89	12.42	10.62	10.29	11.95	3.94	9.54		17.42
2,3,4,7,9	3.05	3.16	18.63	14.70	15.14	13.34	2.93	13.19		3.58
1,3,4,7,9	0.62	0.51	0.27	0.44	0.32	0.67	0.27	0.63		2.22
{ 1,3,4,7,8 / 1,2,3,6,8	9.30	6.22	2.22	5.62	5.32	6.39	8.87	5.72		16.00
1,2,4,7,8	0.53	4.76	1.42	4.27	4.37	5.66	0.00	5.36		0.99
{ 1,3,4,6,7 / 1,2,4,7,9	4.48	4.22	1.54	3.19	3.55	4.02	6.66	3.31		2.23
1,2,4,6,7	3.10	3.69	1.16	2.43	3.27	2.66	3.79	2.83		0.70
{ 1,2,3,4,7 / 2,3,4,6,9	4.54	8.79	20.07	17.62	15.47	16.28	13.86	16.21		0.19
1,3,4,6,9	0.69	1.16	0.34	1.14	0.43	0.60	0.58	0.47		0.37
{ 1,2,3,4,8 / 1,2,3,7,8	11.42	7.71	8.72	10.13	7.84	7.73	21.64	13.50		1.47
1,2,3,4,6	2.08	4.69	5.44	5.43	3.85	3.62	0.00	0.70		0.24
1,2,3,7,9	1.15	0.00	0.00	0.00	0.80	0.96	0.00	0.71		0.49
1,2,3,6,7	3.43	3.71	1.04	0.93	0.92	1.19	6.08	2.23		0.23
{ 1,2,4,6,9 / 2,3,4,8,9	4.72	6.99	2.81	3.03	4.41	4.70	10.25	4.69		0.36
1,3,4,8,9	1.31	1.20	0.00	0.00	0.15	0.41	0.31	0.46		0.00
1,2,3,6,9	0.61	0.44	0.00	0.00	0.00	0.23	0.52	0.00		0.00
2,3,4,6,8	5.50	10.07	9.56	10.68	5.49	4.51	1.29	3.39		39.10
1,2,3,4,9	0.64	1.68	1.43	1.09	0.90	0.66	0.55	1.18		0.00
1,2,4,8,9	0.85	0.96	0.00	0.00	0.12	0.65	2.47	1.07		0.00
2,3,4,7,8	7.48	11.54	2.71	0.73	4.62	2.12	5.16	4.81		0.69
1,2,3,8,9	1.30	0.12	1.20	0.00	0.88	0.00	1.58	1.63		0.00
2,3,4,6,7	27.10	11.66	1.92	1.32	3.76	3.04	5.96	2.29		0.86
					H6CDD					
{ 1,2,4,6,7,9 / 1,2,4,6,8,9 / 1,2,3,4,6,8	27.81	36.77	77.41	78.94	68.79	67.38	38.39	61.72	79.19	
{ 1,2,3,6,7,9 / 1,2,3,6,8,9	28.00	25.69	16.02	15.09	24.97	28.87	26.59	26.75	7.34	
1,2,3,4,7,8	5.39	10.23	0.13	0.00	0.15	0.52	7.86	2.99	0.00	
1,2,3,6,7,8	10.50	6.51	3.79	3.54	4.94	3.23	12.51	4.35	5.76	
1,2,3,4,6,9	0.83	2.93	0.12	0.09	0.00	0.00	0.16	0.00	0.00	
1,2,3,7,8,9	21.58	4.02	2.24	2.08	1.15	0.00	8.50	3.18	7.12	
1,2,3,4,6,7	5.89	13.84	0.29	0.26	0.00	0.00	5.99	1.01	0.00	
					H6CDF					
1,2,3,4,6,8	6.68	7.11	20.47	21.92	16.15	22.17	4.55	14.77		34.90
{ 1,3,4,6,7,8 / 1,3,4,6,7,9	15.06	11.75	12.17	13.72	16.30	13.24	13.60	15.10		14.03
1,2,4,6,7,8	13.91	12.81	14.14	16.67	16.11	18.47	11.44	14.86		11.16
1,2,4,6,7,9	1.78	1.39	1.24	1.98	2.23	1.42	2.94	3.76		0.00
{ 1,2,3,4,7,8 / 1,2,3,4,7,9	12.59	9.58	33.14	18.06	21.64	18.02	15.2	26.98		13.56
1,2,3,6,7,8	15.62	12.68	2.96	16.61	11.80	13.74	15.93	9.50		11.60
1,2,4,6,8,9	0.37	11.44	0.74	0.00	0.63	0.00	0.00	2.24		0.00
1,2,3,4,6,7	10.26	11.44	5.18	8.44	9.06	10.11	17.38	9.52		8.66
1,2,3,6,7,9	2.40	0.00	0.00	0.00	0.00	0.00	1.86	0.67		0.00
{ 1,2,3,4,6,9 / 1,2,3,6,8,9	2.79	2.50	2.30	0.69	2.24	2.12	5.51	2.61		0.00
1,2,3,7,8,9	2.20	0.00	0.00	0.00	0.00	0.00	1.60	0.00		0.00
1,2,3,4,8,9	1.56	3.13	2.03	0.00	0.59	0.00	5.04	0.00		0.00
2,3,4,6,7,8	14.78	16.17	5.64	1.90	3.24	0.70	4.88	0.00		6.10
					H7CDD					
1,2,3,4,6,7,9	32.37	56.22	38.63	69.96	43.17	52.16	44.08	45.76	0	
1,2,3,4,6,7,8	67.63	43.78	61.37	30.04	56.83	47.84	55.92	54.24	100	
					H7CDF					
1,2,3,4,6,7,8	81.98	91.84	79.57	100	86.84	94.14	62.86	87.99		
1,2,3,4,6,7,9	8.28	0.00	8.28	0	4.47	5.86	11.78	12.01		
1,2,3,4,6,8,9	4.22	8.16	9.41	0	8.69	0.00	15.52	0.00		
1,2,3,4,7,8,9	5.52	0.00	2.73	0	0.00	0.00	9.84	0.00		

In the range of 0.1–5.0 wt % CuCl$_2$, the PCDD/PCDF ratio decreases from 33 to 0.2. The addition of silica–alumina increases the PCDD/PCDF ratio by a factor of 1.6.

The experiments without CuCl$_2$ showed rather large deviations with total yields of PCDDs and PCDFs ranging from 2.5 to 60 ppm (PCDD/PCDF ratio ≈20). At higher catalyst loadings, the results of the combustion experiments were more reproducible. The reference active carbon (DARCO) yields lower amounts of PCDDs and PCDFs than Norit RX Extra, which may be related to the surface area and structure of both types of carbon.

Figure 2, panels a (top) and b (bottom), shows the contributions of tetra- to octachlorinated isomer groups to the sum of PCDDs and PCDFs, respectively. In general, the higher the CuCl$_2$ catalyst loading, the higher the degree of chlorination. For PCDDs a maximum is found within the tetra- and pentachlorinated isomers (0.1 wt % CuCl$_2$), penta- and hexachlorinated isomers (0.5–1.0 wt % CuCl$_2$), or hepta- and octachlorinated isomers (5.0 wt % CuCl$_2$).
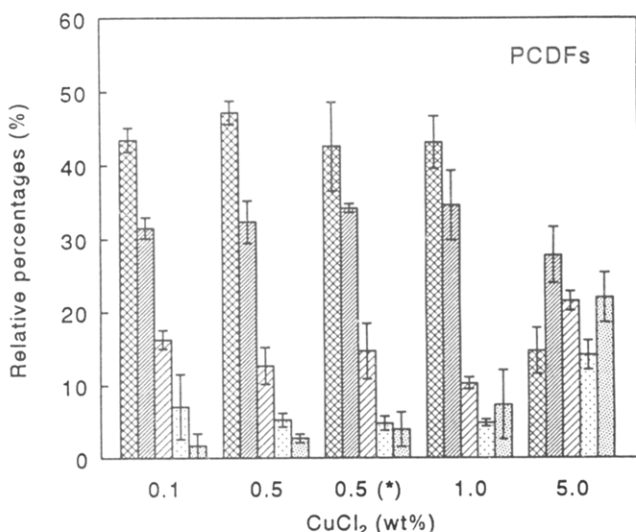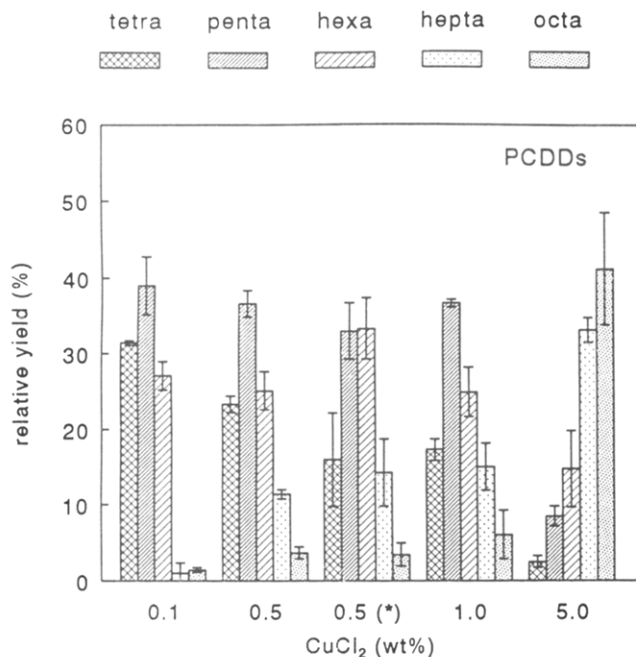
Figure 2. Relative yield of PCDDs and PCDFs in the catalyzed combustion of activated carbon for different CuCl₂ loadings. (*) mixed with silica–alumina (1:1).
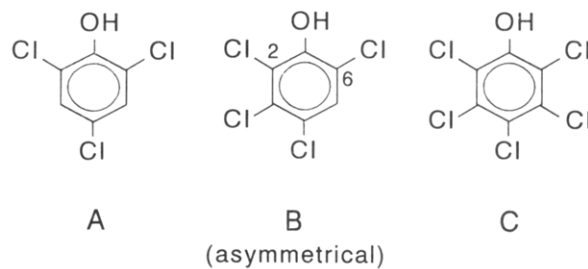

Figure 3. Set of relevant chlorophenols in incineration processes.

Table 3. Major Products from 2,4,6-Trichlorophenol on Carbon (Moist Air, 300 °C)

isomer	combination	isomer	combination
1,3,6,8	A-A	1,2,3,4,6,8	A-C or C-A (SR)
1,3,7,9	A-A (SR)[a]	1,2,3,6,8,9	B_6-B_2
1,2,4,7,9	A-B_2	1,2,3,6,7,9	B_6-B_2 (SR)
1,2,4,6,8	A-B_2 (SR)	1,2,3,6,7,8	B_6-B_6
1,2,3,6,8	A-B_6	1,2,3,7,8,9	B_6-B_6 (SR)
1,2,3,7,9	A-B_6 (SR)		

[a] SR = Smiles rearrangement.

For PCDFs a maximum is found within the tetra- and pentachlorinated isomers (0.1–1.0 wt % CuCl₂). No clear maximum is observed for 5 wt % CuCl₂, but a high degree of chlorination can be perceived. The addition of silica–alumina causes a slight shift toward a higher degree of chlorination within the PCDDs. These results are in good agreement with earlier experiments [0.5 wt % CuCl₂/C, 2 h (10)]. However, the 1-h experiments resulted in lower yields and in a lower maximum in the degree of chlorination of PCDDs and PCDFs.

The yield of PCDDs and PCDFs in the reference experiment (0.5 wt % CuCl₂ without HCl) was 0.6 ppm. The PCDD/PCDF ratio was 1.7. The chlorine source in the reference experiment may originate from active carbon itself (see Table 1) or may be delivered by the addition of (inorganic) CuCl₂. Remarkably, the yield of PCDDs and PCDFs (0.5 wt % CuCl₂) without HCl was about three times higher than in the presence of HCl.

The CuCl₂ concentration on active carbon has a large influence not only on the total yield of PCDDs and PCDFs and on the PCDD/PCDF ratio described above but also on the isomer distribution pattern of PCDDs and PCDFs. The isomer distribution pattern within the tetra- to heptachlorinated PCDDs and PCDFs is shown in Table 2 for all types of experiments performed in this study. In the catalyzed combustion of activated carbon in the presence of HCl, a PCDD isomer distribution pattern is observed that can be explained completely by condensation reactions of a limited set of chlorophenol precursors. If CuCl₂ is present at trace levels up to 0.1 wt %, predominantly PCDDs are formed. The observed PCDD isomer distribution pattern is very selective toward metasubstituted compounds as described by Ballschmiter et al. (12). When the CuCl₂ concentration further increases to a level of 5 wt %, the PCDD/F isomer distribution pattern shows a shift toward a characteristic fly ash pattern.

The major PCDD constituents in the catalyzed combustion of carbon shown in Table 2 are 1,3,6,8- and 1,3,7,9-T₄CDD; 1,2,4,7,9-, 1,2,4,6,8-, 1,2,3,6,8-, and 1,2,3,7,9-P₅CDD; and a limited set of H₆CDD isomers. Together, they account for over 90% of the total yield of PCDDs and PCDFs. This selective formation of PCDD congeners is considered to be the result of condensation reactions of chlorophenol precursors. In Figure 3, the structures of pentachlorophenol and the thermodynamically stable 2,4,6-trichloro- and 2,3,4,6-tetrachlorophenol are shown. The PCDD congeners mentioned above can be described as condensation products of these three chlorophenols. The combination of chlorophenol precursors, the occurrence of a Smiles rearrangement, and the position of the chlorine substituent where coupling occurs are presented in Table 3.

The selectivity toward metasubstituted PCDDs cannot be explained from the chlorination of the parent molecule dibenzo-p-dioxin. The copper-catalyzed chlorination of DD in a model fly ash system shows a selectivity toward the 2,3,7,8-positions (19) and resembles an electrophilic aromatic substitution pattern. However, the mechanism of chlorination may still be an electrophilic aromatic substitution for the ortho/para-directing OH group in phenol results in 2,4,6-substitution.

In going from 0.1 to 5.0 wt % CuCl₂, a dramatic decrease of the total yield of PCDDs and PCDFs is observed first and then a slight increase. In this range, a shift toward a fly ash pattern is also found. The initial decrease in the

Table 4. Formation Characteristics of PCDDs and PCDFs in Catalyzed Combustion of Carbon; [HCl] 5 mL/min, [CuCl₂] 0.5 wt %

conditions	HCl	CuCl₂	HCl/CuCl₂	HCl/CuCl₂/ SiO₂–Al₂O₃
PCDD pattern	chlorophenol	fly ash	chlorophenol	chlorophenol
yield PCDD/F (ppm)	2.5–60	0.6	0.2	1.0
ratio PCDD/PCDF	20	1.7	1.1	1.8

total yield of PCDDs and PCDFs indicates the occurrence of oxidative degradation of PCDDs and PCDFs by CuCl₂. PCDFs are formed in much lower yields than PCDDs at low copper concentrations, but dominate at higher copper concentrations. An explanation for this phenomenom may be given by (i) differences in the mechanism of formation, *i.e.*, in the case of PCDDs the intermediate formation of chlorophenols is rather important whereas the presence of structural units such as furans or biphenyls in carbon may lead to the formation of PCDFs. For example, furan units are present in the structure of coal (Norit RX Extra is a steam-activated peat char) which has been proposed by Shinn (*20*), and confirmed by Bruinsma (*21*) in the emission of benzofurans and dibenzofurans during coal combustion. (ii) The fact that PCDFs are less prone to oxidative degradation than PCDDs. According to Schwarz (*6*), the breakdown of PCDDs and PCDFs under similar conditions on fly ash is correlated with the presence of ether bridges and not with dechlorination processes. Therefore, PCDFs are more stable in (model) fly ash systems. In addition, compounds without oxygen such as chlorobenzenes remain unaffected when passing a (model) fly ash surface, and biphenyl is less prone to (oxy)-chlorination than diphenyl ether (*13, 22, 23*). Therefore, it is assumed that (di)benzofuran units within the carbon structure are partially chlorinated and released when the surrounding polyaromatic carbon structure is burnt off by CuCl₂.

The results of the formation characteristics of PCDDs and PCDFs from HCl, 0.5 wt % CuCl₂, 0.5 wt % CuCl₂ + HCl, and 0.5 wt % CuCl₂ + HCl + SiO₂–Al₂O₃ are summarized in Table 4.

In the presence of only HCl, a chlorophenol pattern is observed within the PCDDs. PCDFs are hardly formed, while the PCDD/PCDF ratio is approximately 20. The PCDDs are condensation products of a limited set of chlorophenols. In our opinion, the coupling reaction of chlorophenols is catalyzed by active carbon. This will be discussed in the next section.

Applying only CuCl₂, a PCDD/PCDF isomer distribution is observed that resembles that of municipal waste incinerator fly ash. Relatively more PCDFs are formed (PCDD/PCDF ratio of 1.7) than in the experiments with HCl as the chlorinating agent. The total yield of PCDDs and PCDFs is much lower (0.6 ppm versus 2.5–60 ppm for HCl). No direct correlation with chlorophenols as precursors for PCDDs can be made, and a different mechanism of formation has to be taken into consideration when only CuCl₂ is present. Differences within the isomer distribution patterns of PCDDs and PCDFs clearly suggest a different mechanism of formation. We assume that the nature of the chlorine source plays an important role in the mechanism of formation of PCDDs and PCDFs. The *de novo* synthesis of PCDDs and PCDFs from particulate organic carbon present in fly ash and from inorganic alkali chloride by a process that is strongly activated by copper ions (*4*) displays a fly ash pattern. In the catalyzed combustion of carbon, which is closely related to the *de novo* synthesis, a dependency on the nature of the copper complex and on the presence of inorganic salts is observed (*6, 7*). This may be reflected in the mechanism of formation of PCDDs and PCDFs by the *de novo* synthesis. Therefore, we suggest that CuCl₂ can act both as a catalyst and as a reactant.

A combination of HCl and CuCl₂ results in a lower total yield of PCDDs and PCDFs and a lower PCDD/PCDF ratio as compared to reactions with HCl or CuCl₂. If both CuCl₂ and HCl are present, two processes interfere: (i) Increasing the CuCl₂ concentration causes an oxidative breakdown of PCDDs and PCDFs. PCDFs are less prone to oxidation, and a shift in the PCDD/PCDF ratio is observed. (ii) Chlorination of the macromolecular carbon structure by HCl stabilizes carbon against burn-off and causes a decrease in the delivery of low molecular weight aromatic fragments (*5, 10, 24*). The relative importance of chlorination (HCl in a metal-catalyzed process) and oxidation (CuCl₂) influences the total yield of PCDDs and PCDFs, their relative ratios, and their isomer distribution pattern.

Addition of silica–alumina causes an increase in the total yield of PCDDs and PCDFs and in the PCDD/PCDF ratio. This is explained as a matrix dilution effect, causing a decrease in the oxidative breakdown and introducing a material that has been shown to promote chlorination (*10*) instead of dechlorination as was observed in the case of carbon (*25*).

At higher CuCl₂ loadings, the chlorophenol pathway is suppressed. Relatively more inorganic chlorine is available for chlorination resulting in conditions resembling those of the blank experiment with 0.5 wt % CuCl₂. In Table 2, a shift toward a fly ash pattern is observed. This is explained by the oxidative breakdown of PCDDs as well as that of chlorophenol precursors by CuCl₂. The possibility that CuCl₂ is a reactant (chlorine source) and implications for the mechanism of formation of PCDDs and PCDFs are discussed earlier.

In addition to PCDDs and PCDFs, several organic compounds such as chlorobenzenes, hexachlorobutadiene, hexachlorobenzofuran, and phthalate esters have been detected by full-scan GC-MS analysis of the carbon surface and the cold trap. Chlorophenols have been identified only in trace concentrations in the cold trap. The absence of these compounds on the carbon surface (also in the experiments without CuCl₂) confirms the assumption that chlorophenols are very reactive on model fly ash surfaces. The presence of hexachlorobenzofuran supports the possibility of the presence of furan structures in (active) carbon.

Based upon the results of this study, the following mechanism of formation of PCDDs and PCDFs in the catalyzed combustion of active carbon under ESP conditions is suggested:

(1) The carbon structure is partially chlorinated by CuCl₂ and HCl.

(2) The carbon structure is partially oxidized by Cu(II) complexes.

(3) Carbon is stabilized against burn-off by the presence of organic chlorine.

(4) A relatively small burn-off of the chlorinated carbon surface gives rise to the production of chlorinated compounds such as

Table 5. Conversion of 2,4,6-Trichlorophenol into Tetra- to Octachlorinated PCDDs and PCDFs

T (°C) atm conversion	carbon					gas phase			
	300 nitrogen (%)	(SD)	300 air (%)[a]	300 moist air (%)	(SD)	300 air (%)	(SD)	600 air (%)	(SD)
T4CDD	2.8	(0.7)	4.8	4.3	(1.3)	1.4×10^{-2}	(2.1×10^{-3})	1.2×10^{-1}	(8.2×10^{-2})
P5CDD	1.5×10^{-2}	(4.6×10^{-3})	4.5×10^{-2}	4.1×10^{-2}	(8.1×10^{-3})	4.3×10^{-5}	(4.6×10^{-6})	2.9×10^{-4}	(1.8×10^{-4})
H6CDD	6.6×10^{-4}	(3.2×10^{-4})	4.4×10^{-3}	7.2×10^{-3}	(5.4×10^{-3})	5.6×10^{-5}	(5.6×10^{-5})		
H7CDD				1.2×10^{-3}	(5.2×10^{-4})	5.1×10^{-5}	(3.4×10^{-5})	1.4×10^{-5}	(1.4×10^{-5})
O8CDD						1.2×10^{-4}	(6.0×10^{-5})	1.3×10^{-5}	(1.3×10^{-5})
T4CDF	2.2×10^{-4}	(3.3×10^{-5})	5.4×10^{-4}	6.8×10^{-4}	(4.4×10^{-6})	2.4×10^{-4}	(1.9×10^{-4})	1.3×10^{-2}	(2.2×10^{-3})
P5CDF						2.9×10^{-4}	(1.9×10^{-4})	2.1×10^{-3}	(1.4×10^{-3})
H6CDF						3.7×10^{-4}	(2.6×10^{-4})	9.1×10^{-5}	(5.5×10^{-5})
H7CDF						4.1×10^{-4}	(2.5×10^{-4})	3.4×10^{-5}	(3.4×10^{-5})
O8CDF									
PCDD/PCDF ratio	13×10^{3}		9×10^{3}	6×10^{3}		11		8	

[a] Single experiment.

chlorobenzenes, hexachlorobutadiene, hexachlorobenzofuran, and chlorophenols.

(5) The isolation of low molecular weight products from carbon delivers precursors in the formation of PCDDs and PCDFs. In particular, chlorophenols are very reactive precursors in the formation of PCDDs from carbon. The dibenzofuran structure may be isolated directly from the carbon structure.

(6) PCDDs and PCDFs are oxidized by $CuCl_2$. PCDFs are less prone to oxidative breakdown than PCDDs. Copper plays a dual role because it is necessary for the de novo synthesis of PCDDs and PCDFs, but it also catalyzes their oxidative destruction.

Condensation Reactions of Chlorophenols. Table 5 presents the conversion of 2,4,6-trichlorophenol into tetra- to octachlorinated PCDDs and PCDFs. The high PCDD/PCDF ratios in the gas–solid-phase reaction of 2,4,6-trichlorophenol on carbon indicate a high selectivity toward the formation of PCDDs. Only very small amounts of tetrachlorinated dibenzofurans were observed. The relatively low conversion of approximately 4% may be due to partial condensation on cold spots in the interface between difussion cell and reactor. The main condensation products are 1,3,6,8-tetrachlorodibenzo-p-dioxin and 1,3,7,9-tetrachlorodibenzo-p-dioxin (Smiles rearrangement product) (see also Table 2). Small amounts of higher chlorinated PCDDs were detected. The yield of PCDDs is hardly influenced by the presence of oxygen and/or water.

A comparison of the conversion of 2,4,6-trichlorophenol into PCDDs on carbon at 300 °C with the gas-phase reactions at 300 °C clearly shows a catalytic activity of activated carbon for the condensation reaction. The overall conversion of 2,4,6-trichlorophenol into PCDDs and PCDFs in the gas phase is a factor of 100 lower than in the presence of carbon, and the PCDD/PCDF ratio is a factor of 1000 lower. This can be explained either by the presence of copper in activated carbon at a ppm level (see Table 1) or by a catalytic activity of activated carbon. The latter is supposed to offer a realistic explanation for the enhanced reactivity of 2,4,6-trichlorophenol toward condensation reactions. The planarity of the polyaromatic surface structure (graphene layers) of activated carbon has a concentration-enhancing effect on the condensation reaction of chlorophenols. The catalytic activity of activated carbon has also been mentioned by Dickson et al. (25).

Scheme 1. Penta- and Hexachlorinated PCDDs Originating from Chlorination of 2,4,6-Trichlorophenol or from Chlorination of 1,3,6,8-Tetrachlorodibenzo-p-dioxin
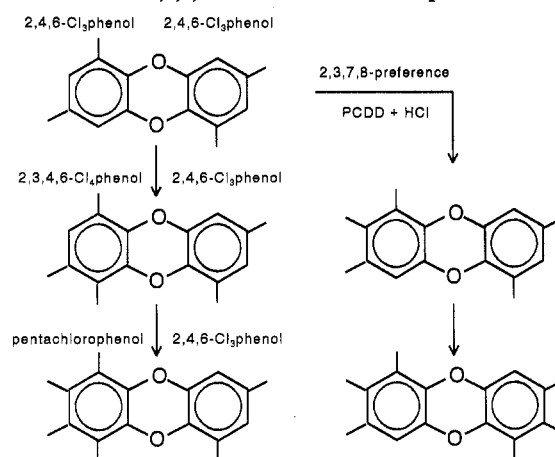
The PCDD isomer distribution is identical to that obtained in the catalyzed combustion of activated carbon in the presence of HCl (see Table 2). These results confirm the mechanism of formation of PCDDs that has been suggested in the previous section: In the catalyzed combustion of a carbon with trace concentrations of copper, PCDDs are formed from a limited set of chlorophenol intermediates. Apparently, the (oxy)chlorination of carbon initiates the isolation of chlorinated phenol structures. Their chlorination pattern is determined by the presence of the ortho/para-directing and -activating OH group.

Surprisingly, the condensation reactions of one precursor, 2,4,6-trichlorophenol, yield an identical PCDD isomer distribution pattern as was observed in the catalyzed combustion of carbon. This observation led to the question of how higher chlorinated compounds can be formed from 2,4,6-trichlorophenol on carbon. The coeluting hexachlorodibenzo-p-dioxins (1,2,4,6,7,9/1,2,4,6,8,9/1,2,3,4,6,8) on SP-2331 (see Table 2), were separated on a DB-5 column (26) and could be assigned as predominantly 1,2,3,4,6,8-H_6CDD (95%). Based upon the observed isomer pattern within the penta- and hexachlorinated PCDDs, it is concluded that 2,4,6-trichlorophenol is further chlorinated into 2,3,4,6-tetrachlorophenol and pentachlorophenol. Scheme 1 presents the expected PCDD isomer patterns from further chlorination of the precursor compound 2,4,6-trichlorophenol versus further chlorination of 1,3,6,8-T_4CDD, i.e., a primary condensation product of 2,4,6-trichlorophenol. The formation of higher chlorinated PCDDs is possible by the release of 2 equiv HCl in the
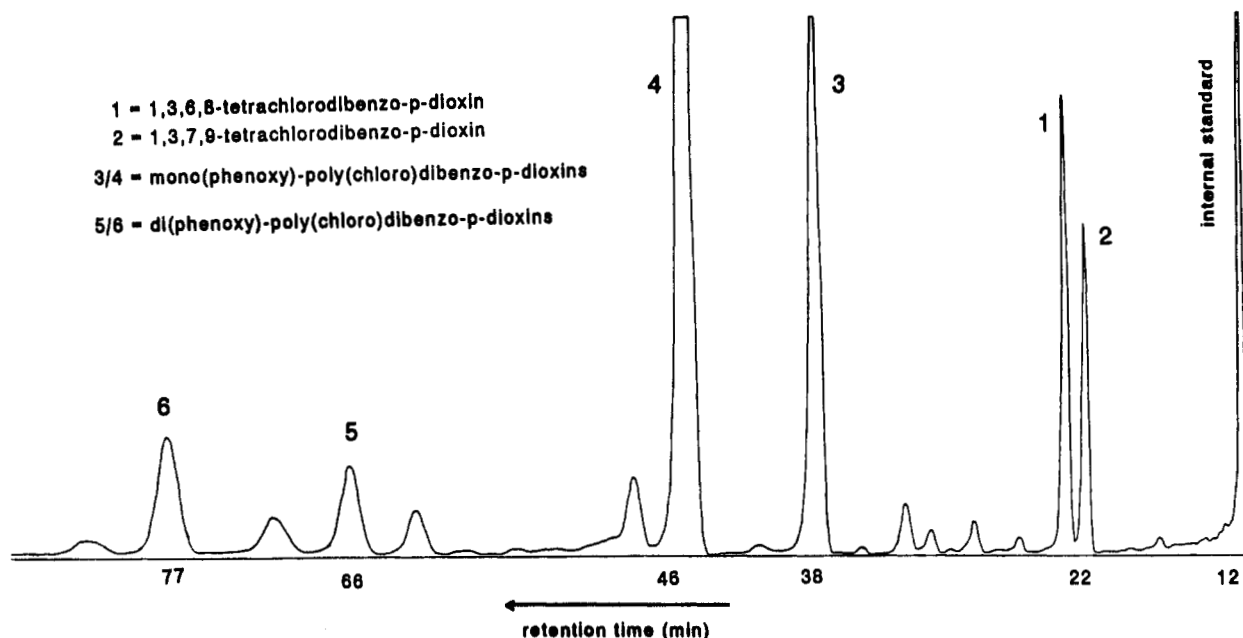
1 = 1,3,6,8-tetrachlorodibenzo-p-dioxin
2 = 1,3,7,9-tetrachlorodibenzo-p-dioxin
3/4 = mono(phenoxy)-poly(chloro)dibenzo-p-dioxins
5/6 = di(phenoxy)-poly(chloro)dibenzo-p-dioxins

retention time (min)

Figure 4. HPLC chromatogram of condensation products of 2,4,6-trichlorophenol on carbon at 300 °C.

condensation reaction of two chlorophenols. In this respect, it is concluded from the isomeric PCDD composition that the chlorination of phenols occurs at much faster than that of the PCDD products.
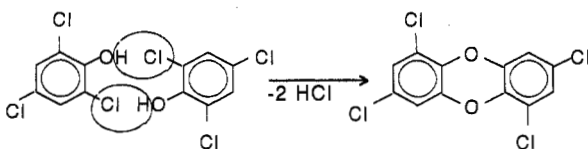
The conversion of 2,4,6-trichlorophenol into PCDDs and PCDFs in the gas phase at 600 °C is higher than at 300 °C. In the gas-phase reaction, relatively more PCDFs are formed than in the gas–solid-phase reaction on the carbon surface because the PCDD/PCDF ratio is a factor of 1000 lower. Within the PCDDs, a typical chlorophenol condensation pattern is again observed, while the PCDFs display a broader spectrum. The PCDD isomer distribution pattern is similar to those observed in the catalyzed combustion of carbon and in the gas–solid-phase condensation reactions of 2,4,6-trichlorophenol on a carbon surface at 300 °C (see Table 2). However, the PCDF isomer distribution pattern differs from the fly ash pattern as well as from the PCDF pattern obtained in the catalyzed combustion of carbon. It shows a preference for 1,3- and 1,2,4- (1,3,4-) substition patterns that can be explained by a mechanism of formation of dibenzofuran from two phenoxy radicals that has been described by Born (13). A similar PCDF pattern is also observed in the gas–solid-phase condensation reaction of 2,4,6-trichlorophenol on a carbon surface at 300 °C (where only very small amounts of tetrachlorodibenzofurans could be detected with a PCDD/PCDF ratio of 10^4). Consequently, the distinctive PCDF pattern in the catalyzed combustion of carbon may involve other routes of formation and other precursors such as chlorobenzenes, biphenyls, benzofurans, or diphenyl ethers.

The relative rates of formation of PCDDs from the reaction of 2,4,6-trichlorophenol on carbon (0 wt % CuCl$_2$; 1.0 g of C; 0.42 μmol of 2,4,6-trichlorophenol/min; 300 °C; 0.5 h) and from the catalyzed combustion of carbon (0 wt % CuCl$_2$; 5 mL/min HCl; 0.5 g of C; 300 °C; 1 h) under similar conditions can be estimated roughly as follows:

The conversion of 2,4,6-trichlorophenol into PCDDs is approximately 4% (see Table 5). The highest yield of PCDDs in the catalyzed combustion of carbon is 60 μg/g of C (PCDD/PCDF ratio ≈20). Applying the assumptions that $M_w^{PCDD} \approx 350$ and $M_w^{active\ carbon} \approx 144$ (C$_{12}$ units), the conversion of active carbon into PCDDs is $1.2 \times 10^{-3}\%$. The relative rate of 2,4,6-trichlorophenol versus carbon is then approximately 3000. This is in the same order of magnitude as the relative rates of 510–46.000 reported by Dickson et al. (25) or somewhat higher than the relative rate of 100 reported by Altwicker et al. (27).

Phenoxy-Substituted PCDDs. Another explanation for the low conversion of 2,4,6-trichlorophenol into PCDDs on carbon at 300 °C was given by the RP-HPLC analysis. RP-HPLC is included in the PCDD/PCDF cleanup procedure (16). Figure 4 shows the RP-HPLC chromatogram of the products obtained from the reactions of 2,4,6-trichlorophenol on carbon (300 °C, air).

The main peaks could be assigned to phenoxy-substituted PCDDs by full-scan GC/MS. It is evident that the reactivity of chlorophenols toward condensation is so high that a series of (poly)phenoxy-substituted PCDDs is formed. Figure 5 shows the total ion current of the full-scan GC/MS analysis with corresponding mass spectra. Phenoxy-substituted PCDDs have also been found in stack gases of municipal waste incinerators (28) and in fly ash effluents in laboratory experiments (29, 30). The presence of these coupling products in the catalyzed combustion of carbon and in fly ash is under further investigation.

Relevance for Incineration and Combustion Processes. The competition between several processes described in this study is assumed to take place on fly ash as well. Copper may play a dual role in the formation and destruction of PCDDs and PCDFs. Based upon the results of this study, CuCl$_2$ levels in the ppm range as observed in fly ash may offer optimum conditions for the formation of PCDDs and PCDFs from residual carbon and HCl.

The contribution of gas-phase processes of formation of 2,4,6-substituted chlorophenol precursor compounds in the boiler section of an MWI to the formation of PCDDs in the cooler ESP section must be considered (see also ref 13). A reduction in the formation of PCDDs and PCDFs may be achieved by a quick cooling of flue gases to
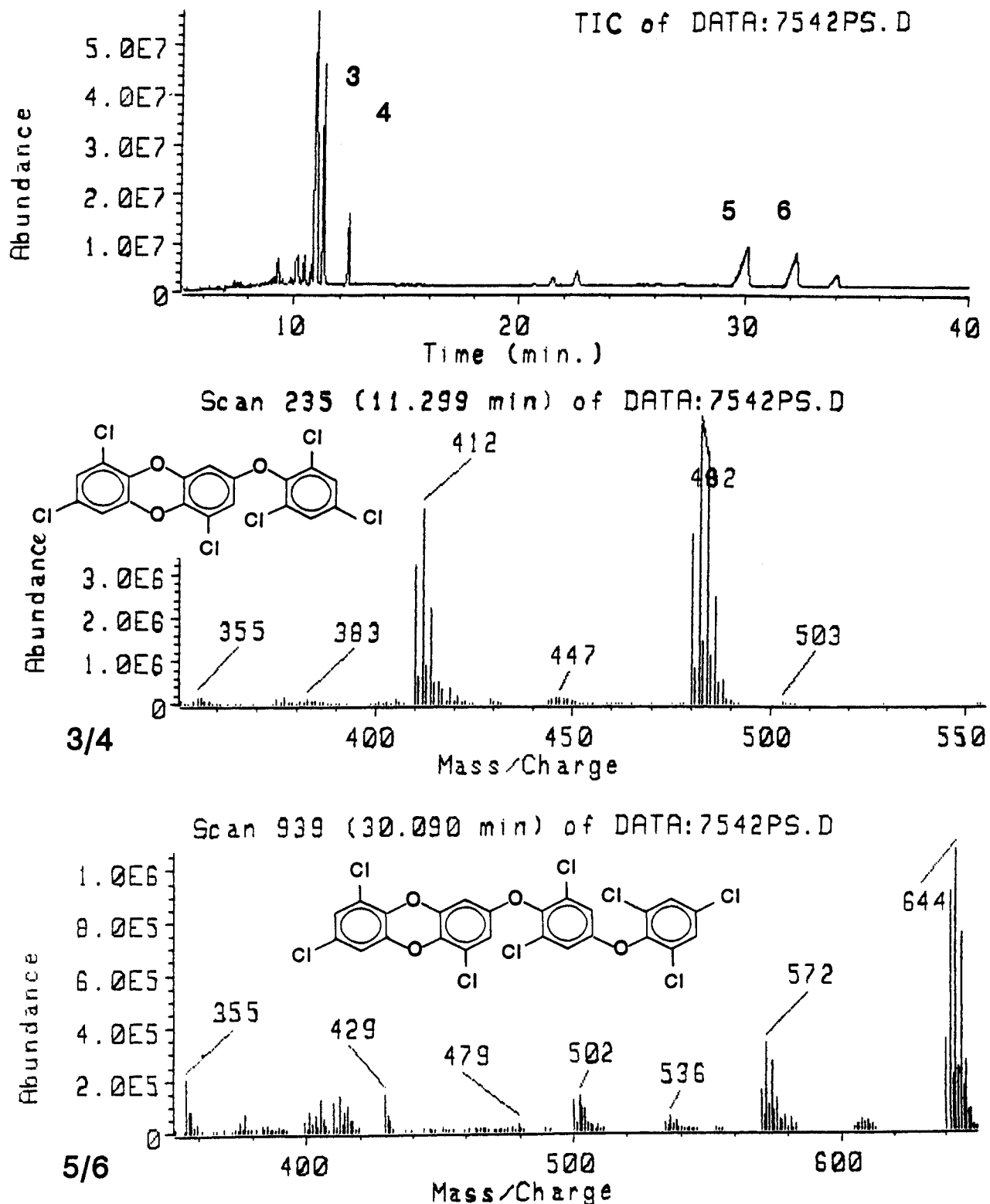
Figure 5. GC/MS TIC and mass spectra of mono(phenoxy)-/poly(chloro)dibenzo-*p*-dioxins and di(phenoxy)-/poly(chloro)dibenzo-*p*-dioxins.

temperatures below 250 °C.

HCl seems to be an important chlorination agent for PCDDs and PCDFs as well as for their precursors (see also ref 31). Inhibition of PCDD and PCDF formation may be achieved by trapping HCl in a very early stage of the flue gas cleaning. Hot gas cleaning of the flue gases to reduce the amount of chlorine seems to be one important way to reduce the emissions of chlorinated hydrocarbons (see also ref 32). However, in practice this may be complicated due to the high temperatures involved.

The recently introduced application of carbon filters to clean the flue gases behind the ESP section in MWIs is suspicious, because condensation reactions of chlorophenols which survive the ESP section may lead to the formation of PCDDs and PCDFs on the carbon surface, even at lower temperatures. Although the emission of PCDDs and PCDFs will be reduced, the filter itself may be highly contaminated.

Conclusions

PCDDs and PCDFs are formed in the catalyzed combustion of carbon under ESP conditions in the presence of HCl and/or CuCl$_2$. Depending on the nature of the

chlorinating agent, a chlorophenol pattern (HCl) or a shift toward a fly ash pattern (CuCl$_2$ as inorganic chlorine source) is observed. In the combustion of carbon with trace concentrations of copper, PCDDs are formed at a much higher rate than PCDFs. The PCDDs arise directly from the macromolecular carbon structure by the isolation of chlorophenol intermediate structures.

Variation of the CuCl$_2$ concentration at a fixed HCl concentration of 5 vol% in the gas flow has dramatic influences on the total yield of PCDDs and PCDFs, on the PCDD/PCDF ratio, and on their isomer distribution pattern. If both chlorinating agents are present, a competition between several processes such as chlorination, formation, and destruction determines the PCDD/PCDF formation characteristics.

The condensation reaction of 2,4,6-trichlorophenol on carbon under ESP conditions reveals a similar PCDD pattern as observed in the catalyzed combustion of carbon in the presence of HCl. The condensation reactions of chlorinated phenols are catalyzed by active carbon. Chlorination reactions of 2,4,6-trichlorophenol to higher chlorinated phenols occur much faster than chlorination reactions of the PCDDs formed by condensation reactions. Besides PCDDs also (poly)phenoxy-substituted PCDDs are formed by additional condensation reactions of chlorophenols and PCDDs.

Formation of PCDDs by the coupling of chlorophenols on carbon occurs approximately 3000 times faster than the de novo synthesis from active carbon.

Literature Cited

(1) Schwarz, G.; Stieglitz, L. Chemosphere 1992, 25, 277–282.
(2) Milligan, M. S.; Altwicker, E. R. Environ. Sci. Technol. 1993, 27, 1595–1601.
(3) Stieglitz, L.; Eichberger, M.; Schleihauf, J.; Beck, J.; Zwick, G.; Will, R. Organohalogen Compd. 1992, 8, 285–288.
(4) Stieglitz, L.; Zwick, G.; Beck, J.; Bautz, H.; Roth, W. Chemosphere 1989, 19, 283–290.
(5) Allen, J. A.; Clark, A. J. Rev. Pure Appl. Chem. 1971, 21, 145–166.
(6) Singoredjo. L. Ph.D. Thesis, University of Amsterdam, 1992.
(7) Schwarz, G. Thesis, University Heidelberg, 1991.
(8) Gullett, B. K.; Bruce, K. R.; Beach, L. O.; Drago, A. M. Chemosphere 1992, 25, 1387–1392.
(9) Gullett, B. K.; Bruce, K. R.; Beach, L. O. Chemosphere, 1990, 20, 1945–1952.
(10) Luijk, R.; Dorland, C.; Kapteijn, F.; Govers, H. A. J. Fuel 1993, 72, 343–347.
(11) Aittola, J. P.; Vänni, P. Organohalogen Compd. 1992, 8, 213–216.
(12) Ballschmiter, K.; Swerev, M. Fresenius Z. Anal. Chem. 1987, 328, 125–127.
(13) Born, J. G. P. Thesis, University of Leiden, 1992.
(14) Van Berkel, O. M.; Olie, K.; van den Berg, M. Int. J. Environ. Anal. Chem. 1989, 34, 51–67.
(15) Addink, R.; Drijver, D. J.; Olie, K. Chemosphere 1991, 23, 1205–1211.
(16) Olie, K.; Slot, P. C.; Wever, H. Chemosphere 1989, 19, 103–108.
(17) Miguel, A. H.; Natusch, D. F. S. Anal. Chem. 1975, 47, 1705.
(18) Yasuhara, A.; Hiroyasu, I.; Morita, M. Environ. Sci. Technol. 1987, 21, 971–979.
(19) Luijk, R.; Dorland, C.; Smit, P., Jansen, J.; Govers, H. A. J. Chemosphere, in press.
(20) Shinn, J. H. Fuel 1984, 63, 1187.
(21) Bruinsma, O. S. L. Thesis, University of Amsterdam, 1988.
(22) Born, J. P. G.; Louw, R.; Mulder, P. CCE Special Report Series 89-07; Leiden University: Leiden, 1989 (in Dutch).
(23) Hoffman, R. V.; Eiceman, G. A.; Long, Y. T.; Margaret C. C.; Lu, M. Q. Environ. Sci. Technol. 1990, 24, 1635–1641.
(24) Hall, C. R.; Holmes, R. J. Carbon 1992, 30, 173–176.
(25) Dickson, L. C.; Lenoir, D.; Hutzinger, O. Environ. Sci. Technol. 1992, 36, 1822–1828.
(26) Ryan, J. J.; Conacher, H. B. S.; Panopio, L. G.; Lau, P. P. Y.; Hardy, J. A.; Masuda, Y. J. Chromatogr. 1991, 541, 131–183.
(27) Altwicker, E. R.; Milligan, M. S. Chemosphere 1993, 27, 301–307.
(28) Janssens, J. J.; Schepens, P. J. C. Biomed. Environ. Mass Spectrom. 1988, 16, 179–182.
(29) Schwarz, G.; Stieglitz, L.; Roth, W. Organohalogen Compd. 1990, 3, 169–172.
(30) Naikwadi, K. P.; Hom, K. P.; Karasek, F. W. Chemosphere 1989, 19, 579–584.
(31) de Leer, E. W. B.; Lexmond, R. J.; de Zeeuw, M. A. Chemosphere 1989, 19, 1141–1152.
(32) Strömberg, B. Organohalogen Compd. 1992, 9, 275–278.