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FORMATION OF POLYCHLORINATED DIBENZOFURANS (PCDFs) AND DIBENZO-p-DIOXINS
(PCDDs) FROM THE PYROLYSIS OF CHLOROBENZENES

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Hans Rudolf Buser
Swiss Federal Research Station
CH - 8820 Wädenswil, Switzerland

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INTRODUCTION

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Polychlorinated dibenzofurans (PCDFs) and dibenzo-p-dioxins (PCDDs) are two series of tricyclic aromatic compounds with similar chemical, physical and toxicological properties (for structures see below). In all, there are 75 PCDD and 135 PCDF isomers ranging from the mono- to the octachloro compounds. Some of these compounds have extraordinary toxic properties. Toxicity seems to depend highly on the number and position of the chlorine substituents; 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-tetra-CDD) and the corresponding dibenzofuran analogue (2,3,7,8-tetra-CDF) appear to be the most toxic isomers.

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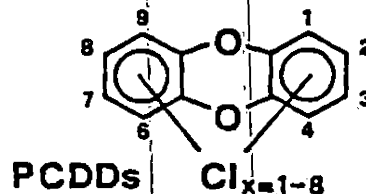
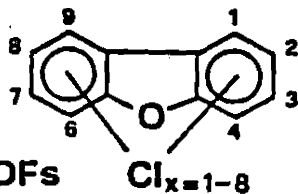
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PCDFs and PCDDs were involved in several accidents and have caused severe intoxications like Yusho in south-west Japan in 1968, and environmental contaminations like that of Seveso, Italy in 1976. Until recently, they were mainly regarded as undesired

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trace contaminants of certain industrial chemicals such as chlorophenols and their derivatives (phenoxy acids) and polychlorinated biphenyls (PCBs). However, they can also be formed in substantial amounts from these industrial chemicals through pyrolytic reactions.^{1,2} Furthermore, PCDFs and PCDDs have been identified in fly ash and flue gases of municipal and industrial incinerators,^{3,4} and recently it was reported that they are possibly ubiquitous products of combustion processes.⁵

In this paper, we wish to report on the formation of PCDFs and PCDDs through pyrolytic reactions from chlorobenzenes. In model experiments using sealed quartz mini-ampoules, we show that tetra- to octa-CDF and also tetra- to octa-CDD are formed from the pyrolysis of tri-, tetra- and pentachlorobenzenes in the presence of air. In addition to PCDFs and PCDDs, chlorophenols and a series of other chlorinated compounds were formed in these pyrolyses. Since chlorobenzenes are used in fairly large quantities as solvents and as starting materials in a variety of chemical processes, this formation of PCDFs and PCDDs may be of some importance and the disposal of chlorobenzenes through incineration or burning of wastes and residues from such processes should be strictly controlled in order to prevent environmental and occupational exposures from the hazardous PCDFs and PCDDs.

EXPERIMENTAL

Compounds

The following chlorobenzenes were obtained from Fluka, Buchs, Switzerland in purum or technical quality: 1,2,3-, 1,2,4- and 1,3,5-tri-, 1,2,3,4-, 1,2,3,5- and 1,2,4,5-tetra-, and pentachlorobenzene. None of these chemicals contained detectable quantities of PCDFs, PCDDs, PCBs, chlorophenols, polychlorinated diphenyl ethers (PCDPEs), naphthalenes (PCNs) or styrenes (PCSSs). Standard solutions of chlorobenzenes were prepared at concentrations of 10 mg/ml in n-hexane.

Micropyrolysis of chlorobenzenes

Samples (200 µg) of tri-, tetra- and pentachlorobenzene were pyrolyzed at 620°C in separate, sealed quartz mini-ampoules (volume 0.3 ml) in the presence of air. The exact pyrolysis conditions were as previously described.² In case of the tri- and tetrachlorobenzenes, the pyrolysis was carried out on mixtures containing equal amounts of each isomer. In addition, a combined chlorobenzene sample (500 µg) containing equal amounts of each tri-, tetra- and pentachlorobenzene (7 compounds) was pyrolyzed. After pyrolysis, 100 µl of benzene was added to each sample and a 2-µl aliquot used for analysis.

GC-MS Analysis

A Finnigan 4000 quadrupole GC-MS instrument coupled to a 50 m Silar 10c glass capillary column (0.36 mm ID) was used. The column was interfaced to the MS via a platinum capillary.

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The column conditions were as follows: 100°, 2 min isothermal, 10°/min to 140°, 5°/min to 240°C.

The pyrolyzed samples were analyzed for neutral compounds by recording complete EI mass spectra (70 eV, m/e 35-500, 2 sec/scan) using a Finnigan 6111 data system. The acquired mass spectra were searched for specific compounds by running appropriate mass chromatograms and recalling mass spectra if required. Semi-quantifications were made for PCDFs and PCDDs using mass chromatograms at M^+ , $M^+ + 2$ or $M^+ + 4$ after calibration with known quantities of reference compounds. The limits of detection using this mode of operation ranged from 0.03-0.1 ng/injection for the tetra- to octachloro compounds. Some of the samples were reanalyzed for phenolic compounds after methylation with diazomethane in ether.

The combined chlorobenzene pyrolyzate was reanalyzed for best PCDF and PCDD isomer separation using mass specific detection (mass fragmentography) and a slower (2°/min) column temperature programming rate. The ions monitored were $M^+ + 2$ or $M^+ + 4$ at m/e 306 (tetra-), 340 (penta-), 374 (hexa-), 410 (hepta-) and 444 (octa-) for the PCDFs minimizing interference from PCNs (PCDPEs that would interfere at these m/e values were not present), and M^+ , $M^+ + 2$ or $M^+ + 4$ at m/e 320 (tetra-), 354 (penta-), 388 (hexa-), 424 (hepta-) and 460 (octa-) for the PCDDs.

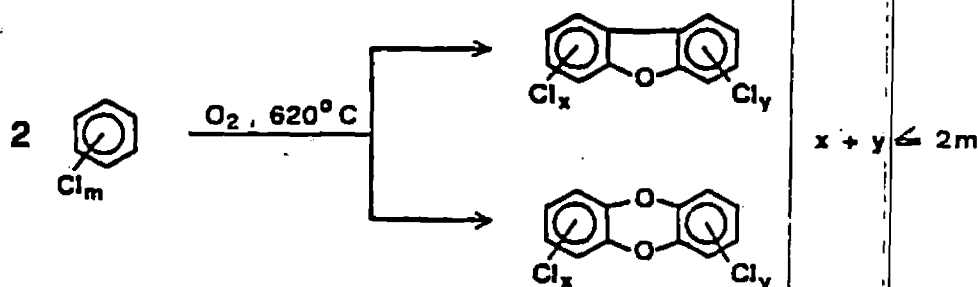
RESULTS AND DISCUSSION

The pyrolyses of tri-, tetra- and pentachlorobenzenes were carried out in sealed quartz mini-ampoules at 620°C in the presence of air. The temperature used was in the range where we previously observed the formation of PCDFs from PCBs.² The amounts of chlorobenzenes (200-500 µg) pyrolyzed were larger than the amounts of PCBs pyrolyzed in that previous study. The pyrolyzates of chlorobenzenes were analyzed directly; no clean-up was required and no interference in the determination of PCDFs and PCDDs was observed from the presence of large quantities of undecomposed chlorobenzenes.

In the pyrolyzed samples, chlorobenzenes were still the major components present. The decomposition was higher for the lower chlorinated species and was > 95% for the trichlorobenzenes, ~ 90% for the tetrachlorobenzenes and ~ 50% for pentachlorobenzene in the combined chlorobenzene pyrolyzate. Chlorobenzenes with a higher degree of chlorination than the compounds used for pyrolysis were observed in all pyrolyzates, e.g. tetra- and penta- from trichlorobenzenes, penta- and hexa- from tetrachlorobenzenes, and hexa- from pentachlorobenzene; these higher chlorinated benzenes must have been formed in a chlorination process from lower chlorinated congeners. The formation of chlorobenzenes with a lower degree of chlorination than the compounds used for pyrolysis was not observed. In addition to chlorobenzenes, mass spectral analyses of the pyrolyzates revealed the presence of a

series of other chlorinated compounds including PCDFs, PCDDs, chlorophenols and in some cases PCNs, PCSs and PCBs; PCDFs and polychlorinated biphenyls were not observed.

Significant quantities of PCDFs and PCDDs were found in most of the pyrolyzed samples (see Tables 1 and 2). The formation of these tricyclic aromatic compounds is bimolecular; the likelihood of this formation is highly dependent on the concentration of chlorobenzenes in the reaction system. In these experiments, rather high concentrations were used; the yields are expected to be substantially smaller if lower concentrations were used.



As seen in Table 1, significant quantities of PCDFs were formed from the tri- and tetrachlorobenzenes and from the combined chlorobenzene sample. Tetra-, penta- and hexa-CDFs were formed from trichlorobenzenes, and hexa-, hepta- and octa-CDFs from tetrachlorobenzenes. Pentachlorobenzene gave only a small amount of hepta- and octa-CDF. The combined sample formed PCDFs ranging from the tetra- to the octachloro compounds. In general, the PCDFs formed had chlorine numbers of $2m-2$, $2m-1$ and $2m$, where m is the chlorine number of the chlorobenzene employed. In case of the trichlorobenzenes, some higher chlorinated dibenzofurans (hepta-CDF) were also observed; presumably, they are formed from higher chlorinated benzenes produced during pyrolysis.

In Figure 1, mass fragmentograms of the combined chlorobenzene pyrolyzate show the elution of tetra-, penta-, hexa-, hepta- and octa-CDF on the 50m Silar 10c glass capillary column. A complex isomeric mixture is observed; it includes octa-CDF, all 4 hepta-CDFs, 13 of a total of 16 hexa-CDFs, around 20 of a total of 28 penta-CDFs, and up to 20 tetra-CDFs. Many of these isomers were identified by co-chromatography with reference compounds; these peak identifications are given in Table 3. The complex isomeric mixture observed suggests the formation of these PCDFs via several reaction routes. The known toxic isomers (2,3,7,8-tetra-, 1,2,3,7,8- and 2,3,4,7,8-penta-CDF) are present but not as main components.

In case of the PCDDs (see Table 2), the amounts formed in these pyrolyses were smaller than the amounts of PCDFs observed. However, substantial amounts of PCDDs (hexa-, hepta- and some octa-CDD) were still observed from the tetrachlorobenzenes and from the combined chlorobenzene sample (tetra- to hepta-CDDs). Smaller amounts of tetra- and penta-CDD were

Table 1 : For

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Table 1 : Formation of PCDFs from the pyrolysis of chlorobenzenes

Compounds	PCDFs formed (ng/sample)				
	tetra-	penta-	hexa-	hepta-	octa-
Trichlorobenzenes ^a	400	1100	550	50	< 5
Tetrachlorobenzenes ^b	< 2	5	160	450	200
Pentachlorobenzene ^c	< 2	< 5	< 5	5	30
Combined chlorobenzenes ^d	80	600	1100	600	60

a: 200 µg total with equal amounts of 1,2,3-, 1,2,4- and 1,3,5-trichlorobenzene

b: 200 µg total with equal amounts of 1,2,3,4-, 1,2,3,5- and 1,2,4,5-tetrachlorobenzene

c: 200 µg pentachlorobenzene

d: 500 µg total with equal amounts of all tri-, tetra- and pentachlorobenzenes (7 compounds)

Table 2 : Formation of PCDDs from the pyrolysis of chlorobenzenes

Compounds	PCDDs formed (ng/sample)				
	tetra-	penta-	hexa-	hepta-	octa-
Trichlorobenzenes ^a	30	20	< 5	< 5	< 5
Tetrachlorobenzenes ^b	< 2	5	140	160	30
Pentachlorobenzene ^c	< 2	< 2	< 5	< 5	5
Combined chlorobenzenes ^d	50	220	220	70	5

a,b,c,d : explanations see Table 1

obtained from the trichlorobenzenes; pentachlorobenzene gave only an insignificant amount of octa-CDD. In Figure 2, mass fragmentograms of the combined chlorobenzene pyrolyzate show the elution of tetra-, penta-, hexa-, hepta- and octa-CDD. Isomer assignments are given in Table 3. The known toxic isomers (2,3,7,8-tetra-, 1,2,3,7,8-penta-, 1,2,3,6,7,8- and 1,2,3,7,8,9-hexa-CDD) were present but again not as main components.

In addition to PCDFs and PCDDs, other chlorinated compounds were also observed from these pyrolyses. All pyrolyzed samples showed the presence of chlorophenols. The degree of chlorination of these phenols was the same and higher than the degree of chlorination of the chlorobenzenes used: tri-, tetra- and pentachlorophenol were observed from trichlorobenzenes, tetra- and pentachlorophenol from tetrachlorobenzenes, and pentachlorophenol also from pentachlorobenzene. These chlorophenols could possibly serve as reaction

Table 3 : Identification of PCDF and PCDD isomers in the combined chlorobenzene pyrolyzate (Figures 1 and 2)

Peak No. (see Figure 1)	PCDF isomer	Peak No. (see Figure 2)	PCDD isomer
1	1,3,6,8-tetra-CDF	1	1,3,6,8-tetra-CDD
2	1,3,7,9-	2	1,3,7,9-
3	1,3,6,7-	3	1,3,7,8-
4	1,2,4,6-	4	1,3,6,7-
5	2,4,6,8-	5	2,3,7,8-
6	2,3,6,8-	6	1,3,8,9-
7	2,3,7,8-	7	1,2,7,8-
8	1,2,4,6,8-penta-CDF	8	1,2,4,6,8- (or 1,2,4,7,9-)penta-CDD
9	1,3,4,7,9-	9	1,2,3,6,8-
10	1,3,4,7,8-	10	1,2,4,7,8-
11	1,2,4,7,8-	11	1,2,3,7,9-
12	1,2,4,7,9-	12	1,2,3,7,8-
13	1,2,3,7,8-+1,2,3,4,8-	13	1,2,3,6,7-
14	1,2,3,6,7-	14	1,2,3,8,9-
15	1,2,6,7,8-		
16	1,3,4,8,9-		
17	2,3,4,6,8-		
18	1,2,4,8,9-		
19	2,3,4,7,8-		
20	2,3,4,6,7-		
21	1,2,3,4,6,8-hexa-CDF	15	1,2,4,6,7,9- (or 1,2,4,6,8,9-)hexa-
22	1,3,4,6,7,8-	16	1,2,3,4,6,8- CDD
23	1,2,4,6,7,8-	17	1,2,3,6,8,9- (or 1,2,3,6,7,9-)
24	1,2,3,4,7,8-	18	1,2,3,4,7,8-
25	1,2,3,6,7,8-	19	1,2,3,6,7,8-
26	1,2,4,6,8,9-+1,2,3,4,6,7-	20	1,2,3,7,8,9-
27	1,2,3,6,8,9-	21	1,2,3,4,6,7-
28	2,3,4,6,7,8-		
29	1,2,3,4,6,7,8-hepta-CDF	22	1,2,3,4,6,7,9-hepta-CDD
30	1,2,3,4,6,7,9-	23	1,2,3,4,6,7,8-
31	1,2,3,4,6,8,9-		
32	1,2,3,4,7,8,9-		
33	octa-CDF	24	octa-CDD

intermediates in the formation of PCDFs and PCDDs from chlorobenzenes. A reaction of chlorophenol with unreacted chlorobenzene could lead to PCDPes (route A, below), which are known to form PCDFs (and to a lesser degree PCDDs) upon pyrolysis.⁶ However, PCDPes were not actually observed in the samples analyzed here. Dimerization of chlorophenols is a further route to PCDDs (route B, below). The former condensation (route A) via PCDPes may be preferred in these pyrolyses due to the initially much higher concentration of chlorobenzenes present, but for a substantiation of these presumptions and to obtain a more detailed picture of the reactions involved, further work will be required.

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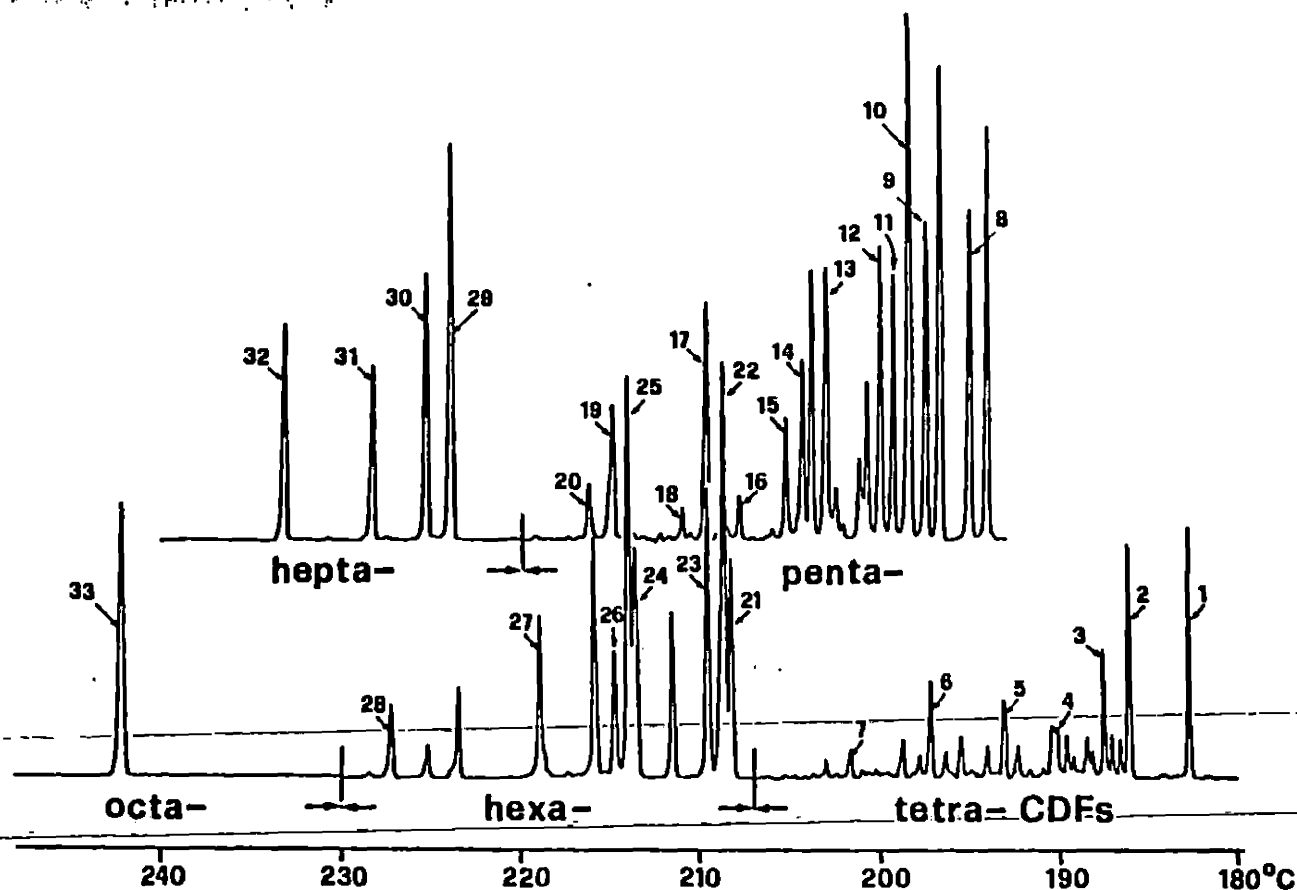


Figure 1: Mass fragmentograms (50 m Silar 10c glass capillary column, m/e 306, 340, 374, 410 and 444) showing elution of tetra-, penta-, hexa-, hepta- and octa-CD in a combined chlorobenzene pyrolyzate. Peak identifications are given in Table 3; experimental conditions see text.

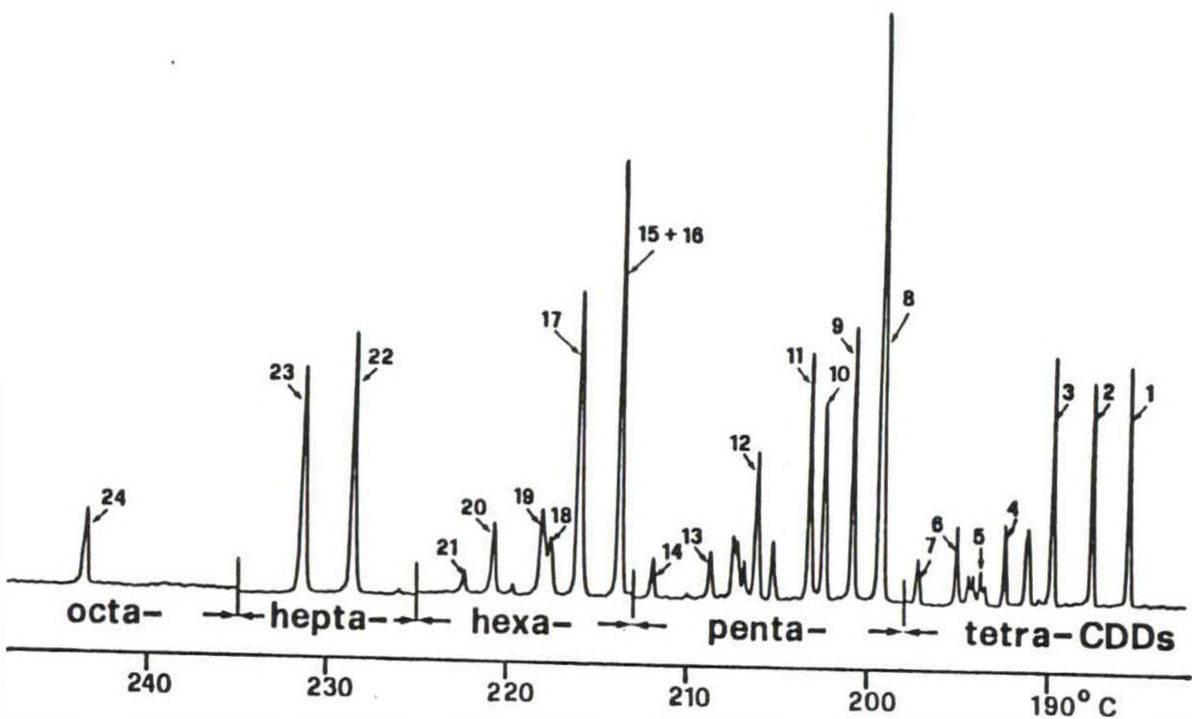
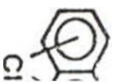


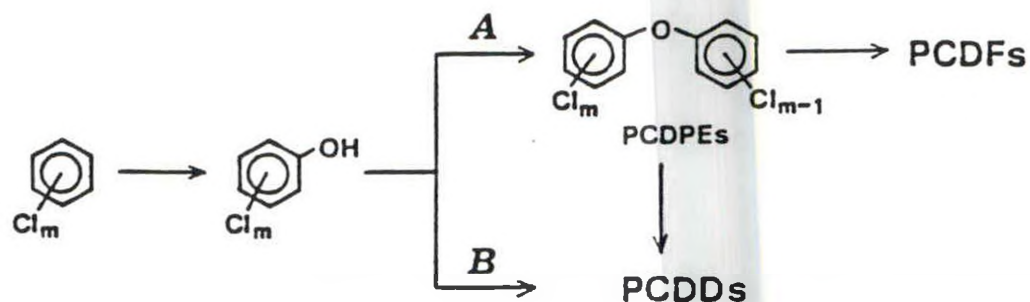
Figure 2 : Mass fragmentograms (50 m Silar 10c glass capillary column, m/e 320, 354, 388, 424 and 460) showing elution of tetra-, penta-, hexa-, hepta- and octa-CDD in a combined chlorobenzene pyrolyzate. Peak identifications are given in Table 3; experimental conditions are the same as in Figure 1.



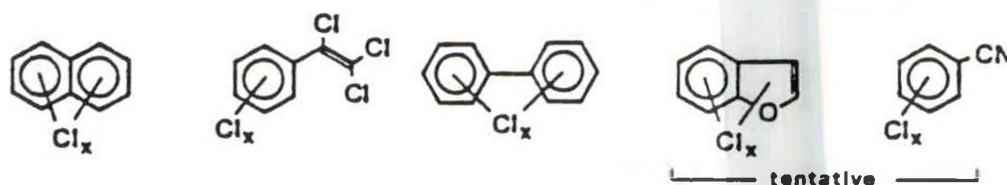
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Additional chlorinated compounds observed in these pyrolyses were PCNs (mainly hepta- and octachloronaphthalenes) and PCSs (hepta- and octachlorostyrenes) from tetra- and penta-chlorobenzenes. Smaller quantities of higher chlorinated biphenyls (PCBs) were also observed. Other chlorinated compounds were present, some of which were tentatively identified as chlorinated benzofurans ($M^+=288$, Cl_5 ; $M^+=322$, Cl_6 ; major fragments M^+-CO and M^+-COCl) and benzonitriles ($M^+=273$, Cl_5 ; $M^+=239$, Cl_4).



CONCLUSIONS

In this paper, we report on the formation of hazardous PCDFs and PCDDs from the pyrolysis of chlorobenzenes. In our model experiments, gas phase pyrolyses of chlorobenzenes were carried out at rather high concentrations corresponding to about 1 g/l of air. At lower concentrations, smaller yields of PCDFs and PCDDs are expected due to the bimolecular character of this formation.

Chlorinated benzenes have been observed in emissions from municipal and industrial incinerators.^{3,4,7} The source of these compounds in these emissions is not completely clear. Chlorobenzenes can be formed from other chlorinated organic compounds including PVC⁸ and possibly even from inorganic chloride and organic materials under pyrolytic conditions,⁹ but the amounts of chlorobenzenes obtained and the concentrations reached via these routes are probably too low to represent a risk for the formation of PCDFs and PCDDs. The situation, however, may be different if attempts are made to dispose of

technical quantities of chlorobenzenes (such as wastes and residues of industrial processes) by incineration. In such a case, the concentration of chlorobenzenes may well reach a range where the formation of PCDFs and PCDDs is probable. Therefore, incineration or burning of chlorobenzenes should be strictly controlled in order to ensure safe disposal and to prevent environmental and occupational exposures not only to chlorobenzenes but also to the hazardous PCDFs and PCDDs.

ACKNOWLEDGEMENTS

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