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[illegible] OF POLYCHLORINATED DIBENZOFURANS, PCDF, FROM
[illegible] OF [illegible] PCB ISOMERS

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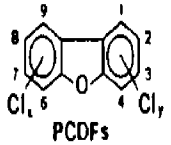
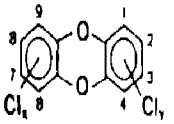
Introduction

The polychlorinated dibenzofurans (PCDFs, structure see below) are a series of tricyclic aromatic compounds, of chemical, biological and toxicological interest, similar to the polychlorinated dibenzo-p-dioxins (PCDDs, see below).



PCDFs



PCDDs

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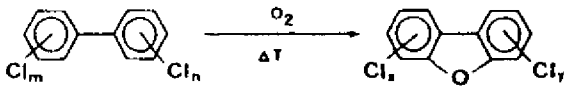
The PCDFs have been identified as undesired trace contaminants in chlorophenols[6] their derivatives like phenoxy acid,[7] and in polychlorinated biphenyls (PCBs).[8] Most recently, PCDFs have been identified in fly ash and flue gases of municipal incinerators and industrial heating facilities.[9,10] They might be ubiquitous products of combustion processes.[11,12]

PCBs are industrial chemicals of wide use and they are now known to be widely distributed in the environment. Although the thermal conversion of PCBs into PCDFs under pyrolytic conditions could be expected, experimental evidence to our knowledge was not reported prior to our previous publication.[13,13]

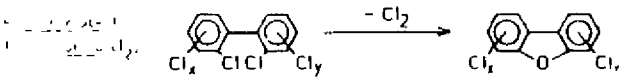


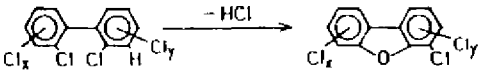
PCBs **PCDFs** $x+y \leq m+n$

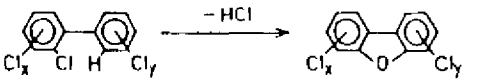
However increased levels of PCDFs (ppm-range) were observed in a PCB heated to 300°C for a week in the presence of air and in a PCB used in a heat exchange system for extended periods of time.[14,15]

In our previous papers we have reported on the formation of PCDFs from the pyrolysis of commercial PCBs.[10,13] These pyrolyses were carried out in sealed quartz mini-ampoules in the presence of air at temperatures of 500-700°C. The yields of the PCDFs were in the ppm range. In addition to PCDFs unreacted PCBs, chlorinated benzenes, naphthalenes, and other chlorinated compounds were also observed, which were found as possible intermediate products.

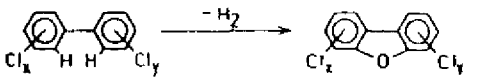
Using high resolution gas chromatography/mass spectrometry we have further shown that most of the major PCDF isomers found in the pyrolyses are the same as those formed in the pyrolyses of individual PCB isomers. These findings strongly suggest that these PCDFs originate from the uncontrolled burning of PCBs. Furthermore, individual PCB isomers we have found that undergo cyclization processes in the pyrolyses are molecular models, predestined to yield different PCDF isomers from the same







In this paper now the occurrence of these reaction routes in the pyrolysis of individual PCBs is further documented. The formation of PCDFs was investigated in pyrolysis experiments using 3 tetra-, 5 penta-, 7 hexa-, 2 hepta- and 1 octachlorobiphenyl. Our experiments show the generality of the above reactions and these can be used to predict the formation of specific PCDFs. A fourth, additional reaction route was found to occur with some PCB isomers.



Experimental

Polychlorinated biphenyls used for pyrolysis:

Eighteen PCB isomers were obtained from various sources as neat solids. All isomers were checked for isomeric purity and absence of recalcitrant impurities as described. Single peaks were obtained and only in general [illegible] of the PCBs contained detectable impurities. PCBs were prepared in concentrations [illegible] per vial.

Micropyrolysis of PCBs

[illegible] PCB isomers [illegible] were pyrolyzed at 500°C in [illegible] The pyrolysis tubes were [illegible] and sealed [illegible] under [illegible] vacuum [illegible]

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Table 1 List and sources of PCB isomers investigated

Compound	Source	Compound	Source
2,3,3',5-tetrachlorobiphenyl	a	2,4,5,2',4',5'-hexachlorobiphenyl	b
2,3,5,6-	a	2,4,6,2',4',6'-	b
2,6, 6	b	2,4,5,2',4',6'-	c
		2,3,4,2',3',5'-	a
		2,3,5,2',3',5'-	a
		2,3,6,2',3',6'-	a
2,3,3',5,6-pentachlorobiphenyl	a	3,4,5,3',4',5'-	a
2,4,5,2',5	a	2,3,4,5,2',3',4'-Heptachlorobiphenyl	e
2,4,5,3',4'	c	2,3,4,5,2',4',5'-	e
2,4,6,2',4'-	c		
2,3,5,2',5	a	2,3,4,5,2',3',4',5'-octachlorobiphenyl	c

a = Dr J McKinney, National Institute of Environmental Health Sciences, Research Triangle Park, NC, USA

b = Dr R Andersson, University of Umeå, Umeå, Sweden

c = AFR Corp., Hope, MI, USA, courtesy of Dr J McKinney

d = Dr C A Wachtmeister, Institute of Stockholm, Stockholm, Sweden

e = Dr Y Masuda, Daiichi College of Pharmaceutical Sciences, Fukuoka, Japan

GC-MS analysis

A Finnigan 4000 quadrupole GC-MS instrument with EI source and coupled to a 50 m x 0.36 mm ID SE-54 glass capillary column was used. The column was interfaced to the MS via a platinum capillary jet. The operating conditions were as previously described [10] however the column was used somewhat higher elution temperatures for PCDFs (same order of elution) than a 25 m SE-54 column interfaced via a glass lined stainless steel tube.

In a first phase complete mass spectra were recorded using the data system. In a second phase, the samples were analyzed with optimal isomer separation using mass specific detection (mass fragmentography) of PCDFs by monitoring molecular ions at m/e 220, 304, 338, 372, 406 and 440 for the tri- to octachloro compounds.

Standard and reference PCDFs

The PCDF standard compounds, for the present investigation were kindly supplied by Dr Masuda, Fukuoka, Japan and Poland, as listed in Figure 1 and by Mr Lindahl. In Figure 1 we have used fragment peaks of a GC-MS separable mixture of 4 isomeric tetrachlorodibenzofurans and hexachlorodibenzofurans (see Table 2).

Additional established the elution order of the 4 tetra-CDFs 1,3,6,8-, 2,3,7,8-, 1,3,7,9- and 2,4,6,8-, all separated on SE-54 [illegible]

Table 2 Standard and reference PCDFs used in the present study

Compound	Peak number (see Fig 1)	Source and remarks
2,3,8-tri-CDF	-	a
1,3,6,8-tetra-CDF	1	a,b
1,3,7,9-	2	b
2,4,6,8-	3	b,c
1,3,6,-	4	a
1,2,4,6	5	a
2,3,6,8-	6	a,d
2,3,7,8-	7	e
3,4,6,7-	8	a
1,2,4,6,8-penta CDF	9	c,f
1,3,4,7,8-	10	b (contains also 1,3,4,8,9-penta CDF)
1,2,4,7,8-	11	d,b (contains also 1,2,4,8,9-penta-CDF)
1,3,4,7,9-	12	b
1,2,3,7,8-	13	g
2,3,4,6,8-	14	c,f
1,2,3,4,8-	15	f
1,2,3,6,7-	16	d
2,3,4,8,9-	17	d
2,3,4,7,8-	18	e
1,3,4,8,9-	19	b (contains also 1,3,4,7,8-penta CDF)
2,3,4,6,7-	20	d
1,2,4,8,9-	21	b (contains also 1,2,4,7,8-penta-CD
1,2,3,4,6,8-hexa CDF	22	c,f
1,2,4,6,7,8-	23	c,f
1,2,4,6,8,9-	24	c
1,2,3,4,7,8-	25	d
1,2,3,6,7,8-	26	d
3,4,6,7,8-	27	c,f (contains also 1,2,3,4,6,7,8-hepta-CDF)
1,2,3,4,6,7,8-hepta CDF	-	c,f (contains also 2,3,4,6,7,8-hepta-CDF)

a = Dr M Morita, Tokyo Metropolitan Research Laboratory of Public Health, Tokyo, Japan

b = Mr R Lindahl, University of Umeå, Sweden, prepared through the acetal cyclization of polychlorinated diphenylether [16]

c = Mr A Garå, University of Umeå, Sweden, prepared from 3,7-dichlorodibenzofuran by acetylation, chlorination and reduction [17]

d = Dr Y Masuda, Daiichi College of Pharmaceutical Sciences, Fukuoka, Japan

e = Dr J McKinney, National Institute of Environmental Health Sciences, Research Triangle Park, NC, USA

f = Mr A Garå, University of Umeå, Sweden, prepared through the acetal cyclization of polychlorinated diphenylether [16]

g = Dr A Poland, McArdle Laboratory, Madison, Wisc., USA

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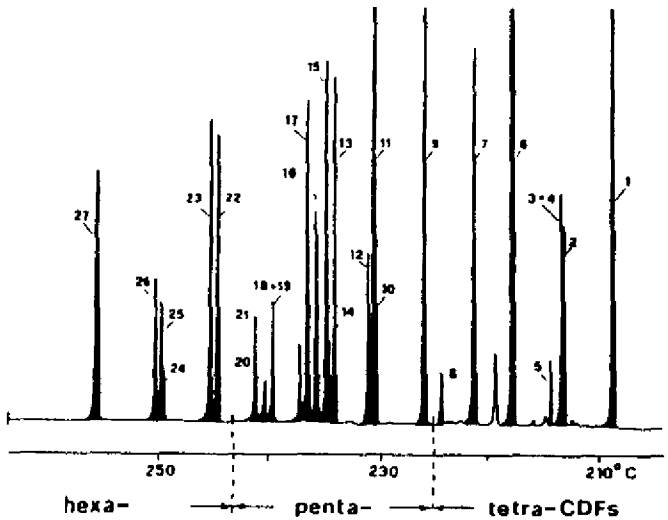


[illegible] mass fragmentograms [illegible] and [illegible] of a composite sample of [illegible] and hexa CDFs [illegible] mass capillary col[illegible]

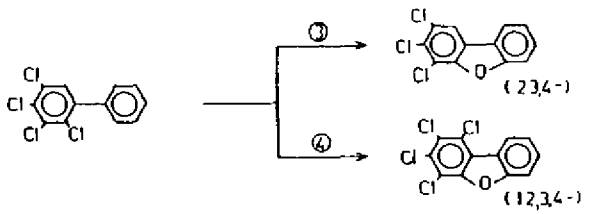
[illegible] discussion

Pyrolysis of tetrachlorobiphenyl

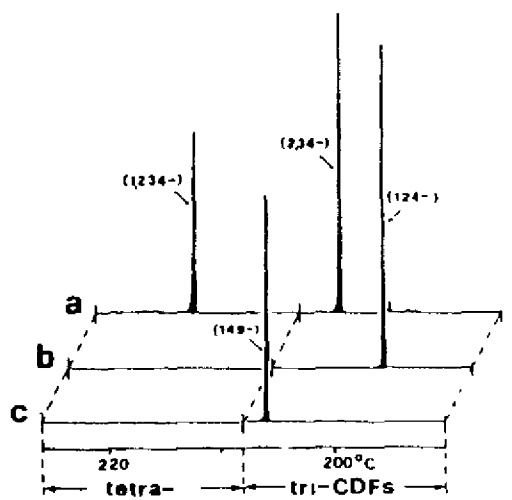
[illegible] pyrolysis of [illegible] see [illegible] Mass [illegible] the elution of [illegible] CDFs

[illegible] pyrolysis of 2 [illegible] of [illegible] tri- and [illegible] see Figure [illegible] expected [illegible] route [illegible] formation of a tetra CDF from this PCB [illegible]

and in fact only very minor amounts of additional isomers were observed



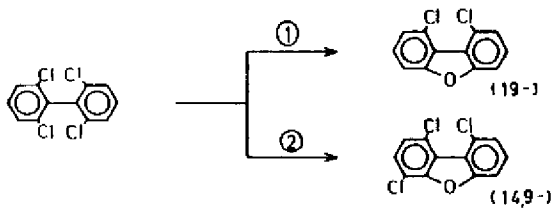
As shown in Figure 2b, the pyrolysis of 2,3,5,6-tetrachlorobiphenyl lead to the formation of a tri-CDF. The product expected is 1,2,4 tri-CDF formed via reaction route 3. The formation of di-, tri- and tetra CDFs from this PCB via reaction routes 1, 2 and 4 is not possible and in fact no additional PCDFs were observed.



[illegible] mass fragment[illegible]

MONS 213510

As previously reported,[16] the pyrolysis of 2,6,2',6'-tetrachlorobiphenyl formed a di- and a tri-CDF (e.u.t. on of [illegible] show in Figure 2c). The expected di-CDF is the 1,9-substituted isomer formed via reaction route 1. The formation of a tri-CDF from this tetrachlorobiphenyl has to involve a rearrangement reaction, the isomer expected is 1,4,9-tri-CDF (reaction route 2). This PCB cannot form tri- and tetra-CDFs via reaction routes 3 and 4, and again no additional PCDFs were observed.

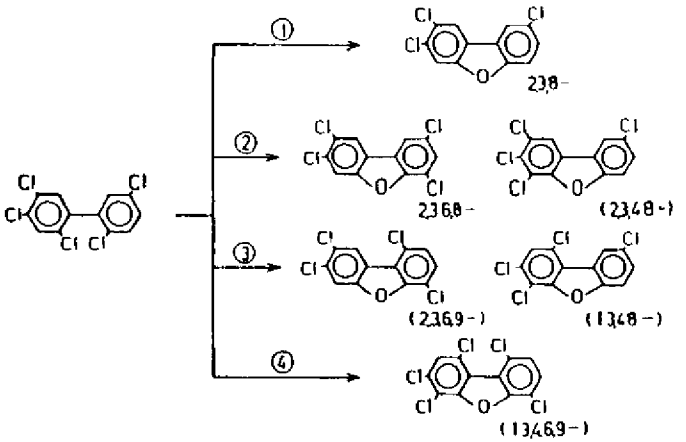


Pyrolysis of pentachlorobiphenyls

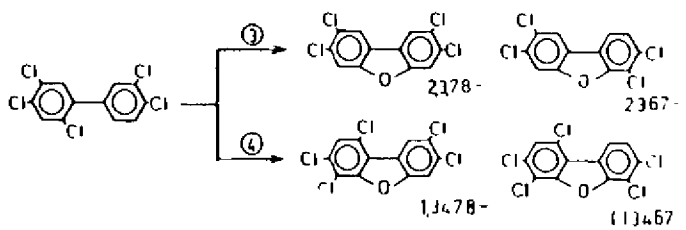
The pyrolysis of five pentachlorobiphenyls was investigated (see Table 1). Mass fragmentograms showing the [illegible] of tri-, tetra- and penta-CDFs are given in Figure 3.

The pyrolysis of 2,3,4,5,6-pentachlorobiphenyl lead to the formation of a tetra-CDF as the major product and smaller amounts of four tri-CDFs (see Figure 3a). The tetra-CDF expected is the 1,2,3,4-substituted isomer formed via reaction route 3, the same isomer was also observed from the pyrolysis of 2,3,4,5-tetrachlorobiphenyl. The formation of PCDFs via reaction routes [illegible] is not possible from this PCB. The finding of small amounts of tri-CDFs could mean that these PCDFs are formed in a non-specific dechlorination process of 1,2,3,4-tetra-CDF or of pentachlorobiphenyl prior to cyclization. In either case, the expected PCDFs contain Cl-substituents exclusively in one of the two carbon rings of the dibenzofuran nucleus (4 possible isomers). Two of these tri-CDFs were tentatively identified [illegible] pyrolysis products of 2,3,[illegible] and 2,3,6-tetrachlorobiphenyl (see Figure 2a and b).

As shown in Figure 3b, 2,[illegible]-pentachlorobiphenyl formed a major tri-CDF and smaller amounts of 4 tetra-CDF and a penta-CDF. This number of PCDFs can be expected from the pyrolysis of this PCB via reaction routes 1, 2, 3 and 4 (see Scheme below). PCDFs identified by co-chromatography with reference compounds (see Table 2) were 2,3,8-tri- and 2,3,8-tetra-CDF [illegible] reaction routes 1 and 2, respectively. So far [illegible] has been made [illegible] remaining tetra-CDFs. A small amount of [illegible] was observed [illegible]



The pyrolysis of 2,4,5,3',4'-pentachlorobiphenyl lead to the formation of two tetra- and a penta-CDF (see Figure 3c). No tri-CDFs can be expected from this PCB via reaction route 1. The two tetra-CDFs were identified by co-chromatography with reference compounds (see Table 2) as the 2,3,7,8- and 2,3,6,7-substituted isomers formed via reaction route 3. This PCB cannot form tetra-CDFs via reaction route 2 and in fact no additional tetra-CDFs were observed. Pyrolysis of this PCB is expected to form two penta-CDFs via reaction route 4, namely 1,3,4,7,8- and 1,3,4,6,7-penta-CDF (see Scheme below). However, only the formation of 1,3,4,7,8-penta-CDF could be confirmed.



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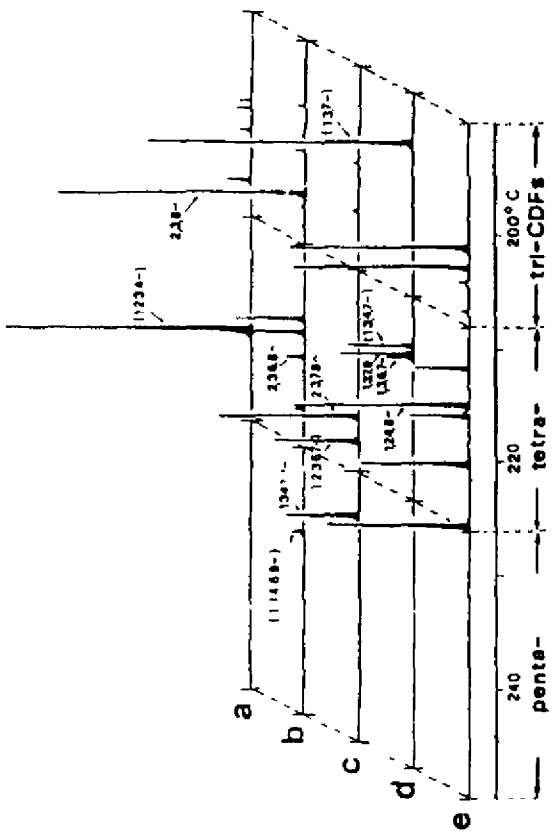
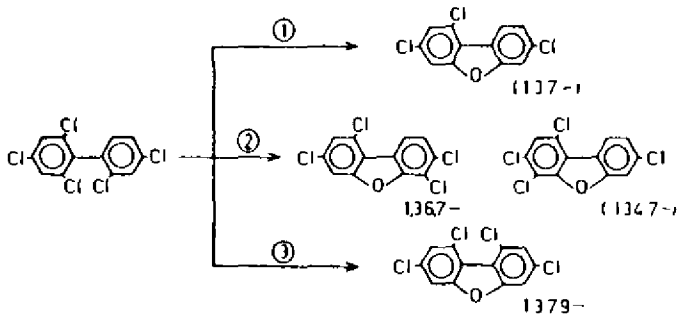
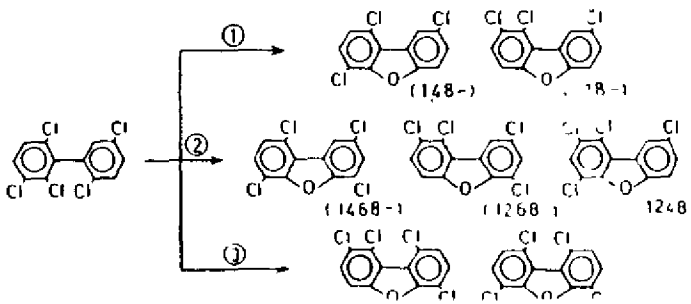


Mass fragmentograms (m/e 270, 304 and 338) of pyrolyzed pentachlorobiphenyls showing elution of tri-, tetra- and penta-CDFs from (a) / 3,4,5,6- (b) / 2,4,5,2'- (c) 2,4,5,3',4'-, (d) 2,4,6,2',4'- and (e) 2,3,5,2',5'-pentachlo- [illegible] Original column conditions as in Figure 1

Pyrolysis of 2,4,6,2',4'-pentachlorobiphenyl gave a tri- and three tetra-CDFs as shown in Figure 3d. This number of isomers can be expected from this PCB via reaction routes 1 and 3 (see Scheme below). The formation of a penta-CDF via reaction route 2 is not possible and in fact no penta-CDF was observed. The tri-CDF expected is the 1,3,7- substituted isomer. Two of the tetra-CDFs were confirmed as 1,3,6,7- and 1,3,7,9-tetra-CDF formed via reaction routes 2 and 3 respectively, the third tetra-CDF (first eluting) is expected to be 1,3,4,7-tetra-CDF, an additional isomer formed via reaction route 2.



The pyrolysis of 2,3,6,2',5'-pentachlorobiphenyl lead to the formation of two tri- and five tetra-CDFs (see Figure 3e) as expected from this PCB via reaction routes 1 and 3 (see Scheme below). Again the formation of a penta-CDF via reaction route 2 is not possible and in fact no penta-CDF was observed.



MONS 213512

One of the main products was tentatively identified as 1,2,4,8-tetra-CDF, a pyrolysis product of 2,4,5,4'-tetrachlorodiphenylether.[18] Two of the tetra-CDFs (1,2,6,9- and 1,4,6,9-) are also expected pyrolysis products of 2,3,6,2',3',6'-hexachlorobiphenyl (see later).

Pyrolysis of hexachlorobiphenyls

The pyrolysis of seven hexachlorobiphenyls was investigated (see Table 1). Mass fragmentograms of pyrolyzed samples are given in figure 4. They show the elution of tetra-, penta- and hexa-CDFs.

The results of the pyrolysis of 2,4,5,2',4',5'- and 2,4,5,2',4',6'-hexachlorobiphenyl were previously reported.[10,13] However, the identity of some of the resulting PCDFs was tentative and could not be confirmed at that time for lack of reference compounds. Additional standards available now made it possible to confirm these tentative identifications. In case of 2,4,5,2',4',5'-hexachlorobiphenyl, the formation of a tetra- and two penta-CDFs was observed (see Figure 4a). These PCDFs were identified as 2,3,7,8-tetra-, 2,3,4,7,8- and 1,3,4,7,8-penta-CDF formed via reaction routes 1, 2 and 3, respectively. In case of 2,4,5,2',4',6'-hexachlorobiphenyl, a tetra- and a penta-CDF were found (see Figure 4b) and identified as 1,3,7,9-tetra- and 1,3,4,7,9-penta-CDF formed via reaction routes 1 and 2. The formation of a penta-CDF via reaction route 3 is not possible with this PCB and in fact no additional penta-CDF was observed. None of the two hexachlorobiphenyls showed the formation of significant amounts of hexa-CDFs.

From the pyrolysis of 2,4,5,2',4',5'-hexachlorobiphenyl, the formation of a major tetra- and some minor penta-CDFs was observed (see Figure 4c). The tetra-CDF expected is the 1,3,7,8-substituted isomer formed via reaction route 1. The expected penta-CDFs are 2,3,4,7,9- and 1,3,4,7,8-penta-CDF (reaction route 2), and 1,3,4,7,9-penta-CDF (reaction route 3). However, only the formation of 1,3,4,7,8- and 1,3,4,7,9-penta-CDF could be confirmed. The formation of 1,3,4,7,9-penta-CDF remained unclear.

The pyrolysis of 2,3,4,2',3',4'-hexachlorobiphenyl lead to the formation of a tetra- and a penta-CDF (see Figure 4d). They were identified as 3,4,6,7-tetra- and 1,2,4,6,7-penta-CDF, the isomers expected from the pyrolysis of this PCB via reaction routes 1 and 1 respectively. The [illegible] via reaction route 2 is not possible with this hexachlorobiphenyl. The formation of a hexa-CDF could not be confirmed.

The pyrolysis of 2,3,6,2',3',6'-hexachlorobiphenyl gave a major and a minor tetra-CDF and a major penta-CDF (see Figure 4e). The major PCDFs were identified as 2,3,7,8-tetra- and 1,2,4,6,8-penta-CDF. The expected products from the pyrolysis of this PCB via reaction routes 1 and 1 respectively. Again, the formation of a penta-CDF via reaction route 3 is not possible [illegible] observed [illegible] identity and source [illegible] penta-CDF remained unclear.

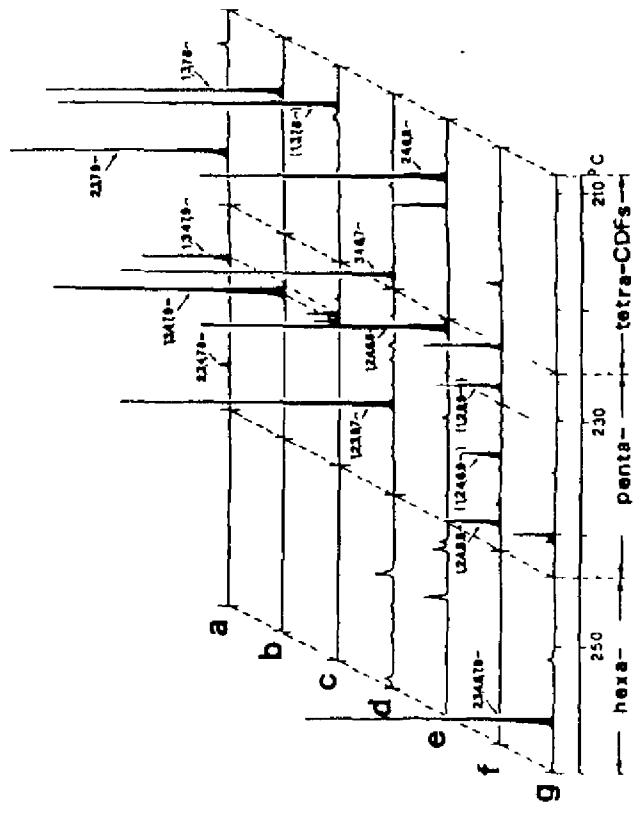


Figure 4. Mass fragmentograms (m/c 304, 338 and 372) of pyrolyzed hexachlorobiphenyls showing elution of tetra-, penta- and hexa-CDF from (a) 2,4,5,2',4',5'-, (b) 2,4,5,2',4',6'-, (c) 2,4,5,2',4',5'-, (d) 2,3,4,2',3',4'-, (e) 2,3,5,2',3',6'-, (f) [illegible] and (g) 3,4,5,3',4',5'-hexachlorobiphenyl. Column conditions as in Figure 1.

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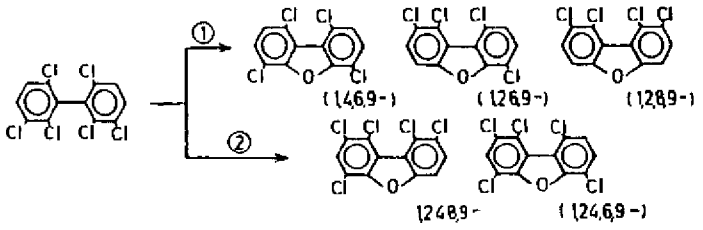
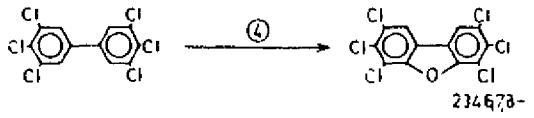
Pyrolysis of 2,3,6,2',3',6'-hexachlorobiphenyl yielded three tetra- and two penta-CDFs (see Figure 4f); the number of isomers expected via reaction routes 1 and (reaction route 3 and 4 not possible for this PCB). In case of the tetra-CDFs, the expected isomers are 1,4,6,9- and 1,2,6,9-tetra-CDF. The first two eluting isomers were also observed from the pyrolysis of 2,3,6,2',3',6'-pentachlorobiphenyl (see earlier); therefore the last eluting tetra-CDF was tentatively identified as the 1,2,3,9-substituted isomer. In case of the penta CDFs, the expected isomers are 1,2,3,8,9- and 1,2,4,6,9-penta-CDF. A confirmation of 1,2,4,6,9-penta CDF could be confirmed by co-chromatography with a reference sample (see Table 2); the identification of 1,2,4,6,9-penta-CDF as the first eluting isomer remains tentative.



The major pyrolysis product of 2,3,6,2',3',6'-hexachlorobiphenyl was identified as 2,3,4,6,7,8-hexa-CDF (see Figure 4g). This PCDF is formed via reaction route 4. The formation of tetra- and penta-CDFs via reaction routes 1, 2 and 3 is not possible for this PCB isomer. Nevertheless, small amounts of penta-CDFs were observed, but the identity and source of these CDFs remained unclear.

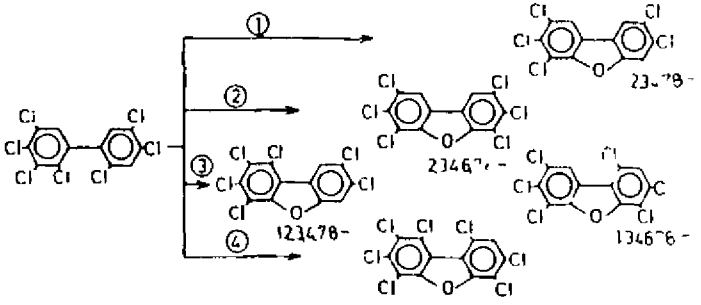


Pyrolysis of hepta- and octachlorobiphenyls

The pyrolysis of two hepta- and one octachlorobiphenyl was investigated (see Table 1). All three isomers are main components of higher chlorinated commercial PCBs. Mass fragmentograms of pyrolyzed samples are given in Figure 5.

The pyrolysis of 2,3,4,5,2',3',4'-heptachlorobiphenyl lead to the formation of penta-, hexa- and hepta-CDFs (see Figure 5a). A single penta-CDF is formed, it was confirmed as 2,3,4,6,7-penta-CDF, the expected product from the pyrolysis of this PCB via reaction route 1. In case of the hexa-CDFs the formation of two isomers was observed (not completely separated from each other). The expected isomers are 1,2,3,4,6,7- and 1,2,3,6,7,8-hexa-CDF (reaction route 3). The formation of the latter was confirmed by comparison to a reference sample (see Table 2). In addition, Figure 5a shows the elution of three hepta-CDFs. The main isomer was confirmed as 1,2,3,4,6,7,8-hepta-CDF, the product expected via reaction route 4. However significant amounts of 1,2,3,4,6,7,9- and 1,2,3,4,6,7,9-hepta CDF were also found. The formation of these isomers is unexpected but was so far not further investigated.

The pyrolysis of 2,3,4,5,2',4',5'-heptachlorobiphenyl again lead to the formation of penta-, hexa- and hepta-CDFs (see Figure 5b). The penta-CDF was confirmed as the 2,3,4,7,8- substituted isomer formed via reaction route 1. In case of the hexa-CDFs the formation of two major and a minor isomer was observed. One of the major isomers confirmed as 1,2,3,4,7,8-hexa-CDF, the minor as 2,3,4,6,7,8-hexa-CDF, they are probably formed via reaction routes 3 and 2, respectively (see Scheme below). The other major hexa-CDF is expected to be 1,2,4,6,7,8-hexa CDF. Another product expected via reaction route 3. The mass fragmentogram also shows the elution of hepta CDFs. The major isomer was confirmed as 1,2,3,4,6,7,9-hepta CDF, the expected product from this PCB via reaction route 4. However smaller amounts of additional hepta CDFs were also observed.



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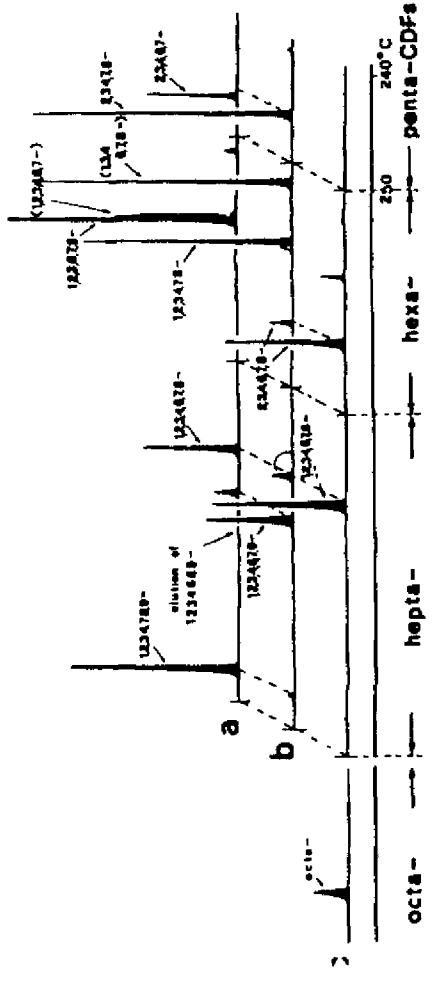
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Reference

1 C Rappe, H R Buser and H-P Bosshardt, Ann New York Acad Sci , in press

2 A Poland, E Glover and J R Smith, Bull Environ Contam Toxicol , 251, 4936 (1976)

3 J A Moore, E E McConnell, D A Dalgard and M K Harris, Ann New York Acad Sci , in press

4 H Kuroki and I Masuda, Chemosphere 7, 471 (1978)

5 H R Buser, C Rappe and M Gara, Chemosphere 7, 439 (1978)

6 C Rappe, M Gara and H R Buser, Chemosphere, In press

7 C Rappe, H R Buser and H-P Bosshardt, Chemosphere, 7, 431 (1978)

8 J G Vos, J H Koeman, H L van der Maas, M C ten Noever de Brauw and R H de Vos, Food Cosmet Toxicol , 8 25 (1970)

9 K Olie, P L Jermeulen and O Hutzinger, Chemosphere 6, 455 (1977)

10 H R Buser, H-P Bosshardt, C Rappe and R Lindahl Chemosphere 7 419 (1978)

11 Dow Chemical Company The Grace Chemistree of Fire, Report, November, 1976

12 R J Smith, Science, 202, 1180 (1978)

13 H R Buser, H-P Bosshardt and C Rappe, Chemosphere 7, 109 (1973)

14 M Morita, J Takagaki, [illegible] and H Ishida, Bull Environ Contam Toxicol , 18, 67 (1977)

15 M Morita, J Takagaki, [illegible] Bull Environ Contam Toxicol , 17 (1976)

16 A Norstrom, K Andersson and C Rappe, Chemosphere 5 319 (1976)

17 A S Wende, J J Wade, [illegible] D Ridge and A Poland, 167th National Meeting of the American Chemical Society, Los Angeles 1974

H R Buser, [illegible] Laboratory [illegible] Sweden 1975

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