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FORMATION OF POLYCHLORINATED DIBENZO-p-DIOXINS
(PCDDs) AND DIBENZOFURANS (PCDFs) BY BURNING OR
HEATING CHLOROPHENATES

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Introduction

Thousands of tons of chlorophenols are annually produced for use as wood preservatives (fungicides), as slimicides in paper mills, bactericides in cutting fluids and industrial oils, as herbicides and as starting materials for a series of other products like the chlorinated phenoxy acids 2,4-D and 2,4,5-T.

Chlorophenols contain a variety of contaminants and byproducts. In addition to other chlorophenols, they may contain up to several percent of polychlorinated phenoxyphenols (predioxins). Polychlorinated dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs) and diphenyl ethers often are present in the range of tens to hundreds of ppm.¹

PCDDs and PCDFs are two groups of compounds whose presence in chlorophenols as well as in other products give rise to much concern. In case of the

PCDDs, 75 different isomers exist ranging from the mono- to the octachloro compound; the corresponding number for the PCDFs is 135. Some of these isomers have extreme toxicological properties, the most toxic and biologically active isomers are 2,3,7,8-tetra-CDD, 1,2,3,7,8-penta-CDD, 1,2,3,6,7,8- and 1,2,3,7,8,9-hexa-CDDs. Moreover, the acute toxicity, biological activity and enzyme induction has been found to vary greatly for closely related isomers.²⁻⁴

PCDDs can be formed by dimerization of chlorophenates during pyrolysis. Higginbotham *et al.*⁵ first reported on the formation of various PCDDs in 1968, but no quantifications were made and the authors did not discuss the possibility of positional isomers. The pyrolysis of 2,3,4,6-tetrachlorophenate was studied by Aniline.⁶ The product contained two isomeric hexa-CDDs but no attempts were made to isolate the individual isomers or to perform a structural determination. Buser synthesized a large number of tetra-, penta- and hexa-CDDs using micropyrolysis of different chlorophenates.⁷⁻⁹ The compounds were characterized by high-resolution gas chromatography and mass spectrometry without actual isolation.

Large quantities of chlorophenols are used as fungicides in the wood industry. Prior to the final use, the top layers with the applied chlorophenate are removed and the wood shavings burned for heating purpose or used in the plywood production. During this burning, PCDDs could conceivably be formed.

In the present investigation we have identified and quantified PCDDs formed during the uncontrolled open burning of leaves and wood wool impregnated with commercial and purified chlorophenates. The analytical technique used has allowed the identification of individual isomers of PCDDs. No attempts were made to find the optimal conditions in burning for the formation of PCDDs and PCDFs. For comparison we have also studied the micropyrolysis of a few chlorophenates at 280°C.

Experimental

Compounds

The chlorophenate formulations used without further purification in

the burning experiments were Servarex teknisk (Gullviks Fabriks AB, Malmö, Sweden; lot Npnr 524) and Kymmene KY-5 (Kymmene OY, Kuusankoski, Finland; lot 132/16). These formulations contain approximately 5 % of 2,4,6-tri-, 50 % of 2,3,4,6-tetra- and 10 % of pentachlorophenol as their sodium salts. The levels of polychlorinated phenoxyphenols (predioxins) are about 0.2 to 0.5 % of the penta- to octachloro compounds.¹⁰ The amounts of PCDDs and PCDFs were determined according to known methods¹¹ and found to be 20 and 150 ppm, respectively (see Table 1 and Results and Discussion).

2,4,6-Tri- and pentachlorophenol of an isomeric purity of > 99 % were prepared by multiple recrystallisations. No predioxins were detected (< 1 ppm). The levels of PCDDs are reported in Table 2. Both compounds were used in the burning experiments as their sodium salts.

Burning and sampling procedures

The chlorophenates (1.0 g) were dissolved in 20 ml of water and sprayed over 30 g birch leaves or wood wool. After spraying, the materials were dried overnight at room temperature. For burning, they were placed on a metal screen in a glass bowl, this allowed an air stream from the sides. The materials were ignited and burned spontaneously in open fires. The smoke gases were drawn through a glass funnel into a glass filter using a vacuum pump (capacity: 100 l/min). Pumping was started before ignition and was terminated 15 min after burning ceased. The filter contained 15 g of charcoal (Norit PK, 0.5-1 mm) or Amberlite XAD-2 (20-50 mesh), both purified by Soxhlet extraction (methylene chloride, 24 hours). After burning, the glass equipment was washed with 150 ml of methylene chloride; the adsorbant was Soxhlet extracted for 10 hours using this washing solution.

Sample purification

Aliquots (25 %) of the burning extracts were concentrated and purified on silica gel micro-columns (0.5 g silica gel, 70-230 mesh, Merck, in 150 x 5 mm disposable Pasteur pipette) using 6 ml of n-hexane as eluant. Further purification was carried out on alumina micro-columns (1.0 g basic alumina, Woelm, in Pasteur pipette) by elution with 10 ml each of 2 % and 50 % methylene chloride in n-hexane.¹² The 50 %-fractions containing the PCDDs and PCDFs were

concentrated and the residues redissolved in 500 μ l of n-tetradecane. Aliquots of 2 μ l were used for analysis.

Micropyrolysis

Samples of 10 mg of chlorophenates were subjected to micropyrolyses at 280° C for 30 minutes. The exact experimental conditions and the clean-up procedure used have been previously described.⁷

GC-MS Analysis

A Finnigan 4000 quadrupole GC-MS instrument equipped with EI source (70 eV, 250° C) and a Finnigan 6111 data system was used. An OV-17 glass capillary column (50 m, 0.36 mm ID) was coupled via a platinum capillary interface leading directly into the ion-source. Sample aliquots of 2 μ l were injected splitlessly (vaporizer temperature 270° C) and the column programmed from 200 to 240° C with 2° C/min. The helium carrier gas pressure was 1.40 at.

The samples were analyzed for the presence of PCDDs and PCDFs using mass specific detection (mass fragmentography) by continuously monitoring molecular ions at m/e 320, 354, 388, 422 and 456 for the tetra- to octa-CDDs and at m/e 304, 338, 372, 406 and 440 for the tetra- to octa-CDFs. Two runs for a sample were required. The detection limits for the tetra- to octachloro compounds in the present case ranged from 0.01 to 0.20 μ g/g chlorophenate. Some of the samples were reanalyzed by recording complete mass spectra (m/e 35-460, 1.4 sec/scan) using the data system.

Results and Discussion

In our burning experiments we selected two of the most commonly used chlorophenol formulations on the Scandinavian market. They both consist of a mixture of 2,4,6-tri-, 2,3,4,6-tetra- and pentachlorophenate. The levels of PCDDs found in the two formulations are similar (see Table 1) and this is also the case for the PCDFs (see below).

Wood wool and birch leaves were impregnated with these formulations, ignited and burned. The burning of the leaves proceed slower and at a lower temperature with formation of more smoke and steam than the burning of the

wood wool. Several individual burnings were carried out and the smoke gases were analyzed for PCDDs and PCDFs after adsorption on a charcoal or Amberlite XAD-2 filter. These two adsorbants were selected to study the efficiency for the adsorption of these compounds.¹³

Amounts of PCDDs formed in the burnings

In Table 1 we report the amounts of PCDDs found after the burning of impregnated wood wool and birch leaves. It can be seen that the amounts of PCDDs increased and that PCDDs of all degrees of chlorination are formed.

Table 1. Amounts of PCDDs found in burning experiments of commercial chlorophenates

	(µg PCDDs / g chlorophenate)						
	S E R V A R E X						K Y - 5
	original sample	birch leaves			wood wool		original sample
		charcoal	ash	XAD-2	charcoal	XAD-2	birch leaves charcoal
Tetra-CDDs	0.7	35	17	26	96	210	0.4 30
Penta-CDDs	5.2	90	58	59	120	357	3.5 84
Hexa-CDDs	9.5	80	74	57	110	347	5.3 82
Hepta-CDDs	5.6	8	18	8	65	29	2.1 8.2
Octa-CDD	0.7	0.3	6.4	0.2	1.2	1.2	0.3 0.4

The burning of impregnated birch leaves did yield very similar amounts of PCDDs for both formulations when trapping on charcoal was used. Somewhat lower values were found when using Amberlite XAD-2, but this is not considered to be significant.

The burning of birch leaves did yield considerable amounts of ash. Analysis of ash from a Servarex burning indicates a similar amount of PCDDs as in the smoke gases with some preference of the higher chlorinated and somewhat smaller amounts of the lower chlorinated dioxins.

The burning of Servarex was also carried out using wood wool and the smoke gases were trapped on charcoal or XAD-2. The amounts of PCDDs formed in these experiments were higher with both adsorbants than in the burning of birch leaves. The higher amount of PCDDs found in the XAD-2 filter as compared to the charcoal filter could be due to some variations in the burning conditions. In addition to the PCDDs reported in Table 1, we have also found some tri-CDDs, which however were not identified or quantified.

The results from the burning of purified 2,4,6-tri- and pentachlorophenates are given in Table 2. In these experiments we used only birch leaves and trapping of the smoke gases on charcoal filters. The levels of PCDDs dramatically increased during these burnings. In the case of the 2,4,6-trichlorophenate, the dominating PCDDs are tetra-CDDs. In the case of the pentachlorophenate the highest level was found for the octa-CDD, but the amounts of hexa- and hepta-CDDs were found to exceed 50 µg/g pentachlorophenate.

Table 2. Amounts of PCDDs found in burning experiments of purified chlorophenates

	(µg PCDDs / g chlorophenate)			
	2,4,6-Trichlorophenate		Pentachlorophenate	
	original sample	<u>birch leaves</u> charcoal	original sample	<u>birch leaves</u> charcoal
Tetra-CDDs	< 0.02	2100	< 0.02	5.2
Penta-CDDs	< 0.03	5.0	< 0.03	14
Hexa-CDDs	< 0.03	1.0	< 0.03	56
Hepta-CDDs	< 0.1	3.0	0.3	172
Octa-CDD	< 0.1	6.0	0.9	710

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Table 3. Identification of PCDDs in burning extracts (see Figure 1)

Peak	PCDD isomer	Peak	PCDD isomer
1	1,3,6,7-tetra-CDD	13	1,2,3,7,8-penta-CDD
2	1,3,7,9- "-	14	1,2,4,6,7,9-hexa-CDD ^{b)}
3	2,3,7,8- "-	15	1,2,3,4,6,8- "-
4	1,2,3,8- "- a)	16	1,2,3,6,8,9- "- c)
5	1,2,6,9- "-	17	1,2,3,4,6,9- "-
6	1,2,6,7- "-	18	1,2,3,4,7,8- "-
7	1,2,8,9- "-	19	1,2,3,6,7,8- "-
8	penta-CDDs from pyro- lysis of 2,4,6- tri- and 2,3,4,6-tetrachlorophenate	20	1,2,3,7,8,9- "-
9		21	1,2,3,4,6,7- "-
10		22	1,2,3,4,6,7,9-hepta-CDD
11	1,2,4,7,8-penta-CDD	23	1,2,3,4,6,7,8- "-
12	1,2,3,4,7- "-	24	octa-CDD

a) or the Smiles product 1,2,3,7-tetra-CDD

b) or the Smiles product 1,2,4,6,8,9-hexa-CDD

c) or the Smiles product 1,2,3,6,7,9-hexa-CDD

Identification of PCDDs formed in the burnings

The analytical technique used allowed the identification of individual isomers of PCDDs. A typical run from the burning of Servarex on birch leaves is given in Figure 1 a.

In the case of the major isomers, more information concerning discrete PCDDs and PCDFs could be obtained by running complete EI mass spectra. These showed intense molecular ions with the expected ion clustering due to the chlorine isotopes and the known characteristic fragmentation.¹²

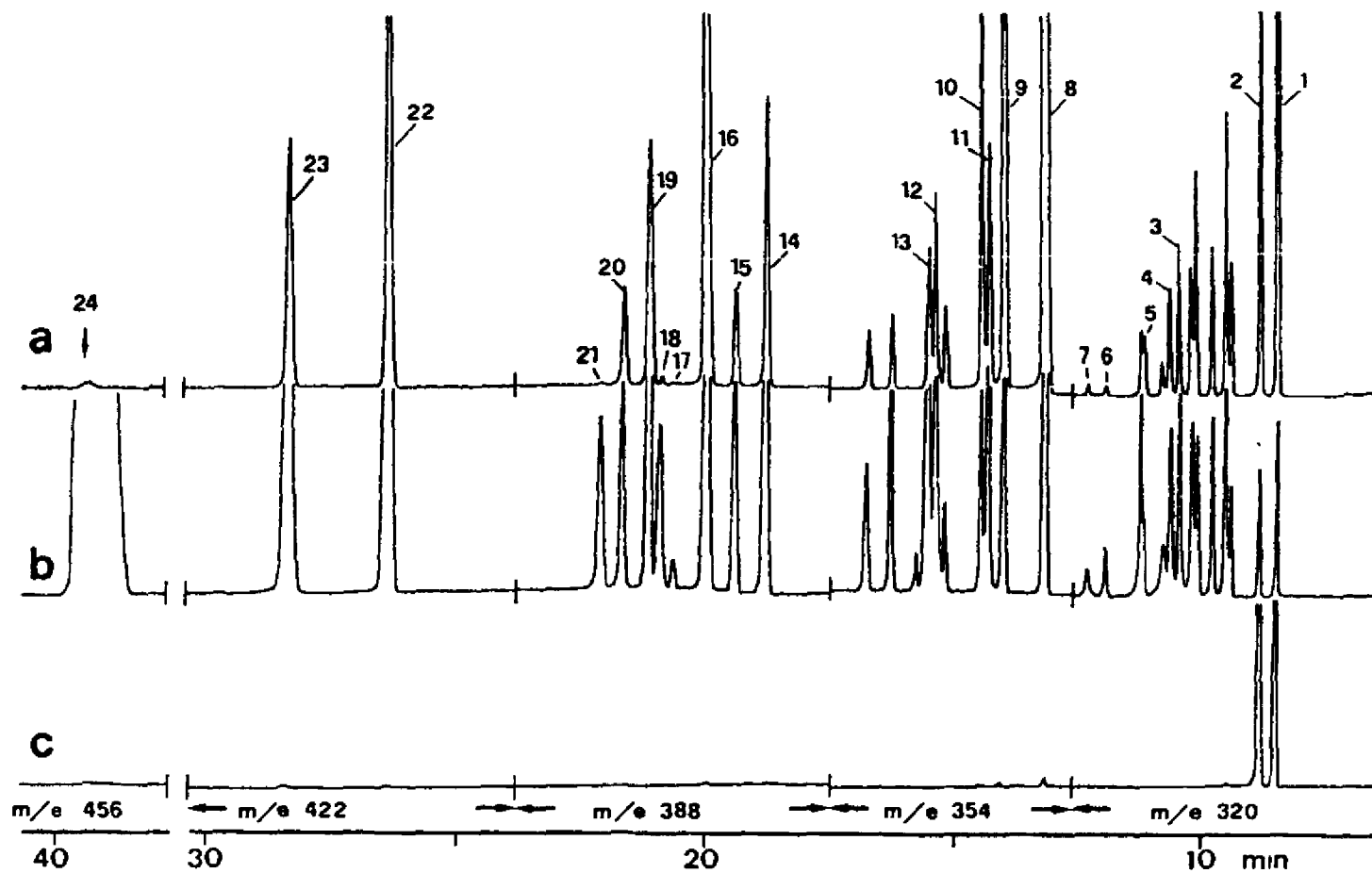


Figure 1 Mass fragmentograms (50 m OV-17 glass capillary column, 200-240° C) showing elution of PCDDs from the burnings on birch leaves of a) Servarex, b) purified pentachlorophenolate and c) purified 2,4,6-trichlorophenolate; m/e 320, 354 etc. for the tetra- to octa-CDDs. Peak identification see Table 3.

A comparison of retention times of PCDDs in the burning extracts with synthetic PCDD standards made it possible to identify the major constituents. In addition, the substitution patterns were checked by studying ions in the low mass range as recently described.⁹ This technique gave additional support for the assignment of the various PCDDs given in Fig.1 and Table 3. The substitution pattern was defined as the number of chlorine atoms in each carbon ring of a dioxin molecule.

Among the tetra-CDDs in Fig.1 a, we can see up to 14 of the theoretically possible 22 isomers. The major components were found to have a 2:2 substitution pattern (two chlorine atoms in each carbon ring). The main isomers are the 1,3,6,8- and 1,3,7,9-tetra-CDD, both of which are found comparably little biologically active.²⁻⁴ These two isomers are the normal dimerization⁷⁻⁹ and the Smiles rearrangement^{14,15} products from 2,4,6-trichlorophenolate. A minor peak has the same retention time as the highly toxic 2,3,7,8-tetra-CDD; in addition this peak also showed the 2:2 chlorine substitution pattern (peak 3).

Among the penta-CDDs, we can see up to 9 of the theoretically possible 14 isomers. With one exception, all of them had a 3:2 chlorine substitution pattern. However, there are few penta-CDD standards available; one peak has the same retention time as the highly toxic 1,2,3,7,8-penta-CDD (peak 13).

Among the hexa-CDDs (10 theoretically possible isomers), we see 5 isomers in medium to higher concentrations (3 additional isomers are present in minute quantities as well). The major hexa-CDD is the 1,2,3,6,8,9-substituted isomer; the others are 1,2,4,6,7,9-, 1,2,3,4,6,8-, 1,2,3,6,7,8- and 1,2,3,7,8,9-hexa-CDD. 1,2,3,4,6,8-Hexa-CDD is a condensation product of 2,4,6-tri- and pentachlorophenolate with a 4:2 chlorine substitution pattern,⁹ the other isomers have 3:3 substitutions and are dimerization products of 2,3,4,6-tetrachlorophenolate. The most toxic of these isomers are considered to be 1,2,3,6,7,8- (peak 19) and 1,2,3,7,8,9-hexa-CDD (peak 20).² Both the hepta-CDDs and octa-CDD were also present.

Typical runs from the burning of the purified chlorophenates are given in Fig. 1 b and 1 c. In the case of the 2,4,6-trichlorophenolate (Fig. 1 c) the only tetra-CDDs were the 1,3,6,8- and 1,3,7,9-isomers. In the case of the

pentachlorophenate (Fig. 1 b), the octa-CDD was the main product. In addition to the octa-CDD we found both hepta-CDDs, eight hexa-CDDs and several penta- and tetra-CDDs. In the formation of the lower chlorinated PCDDs a nonspecific dechlorination process must be involved.

A comparison of the chromatograms in Fig. 1 reveals that the distribution of the individual isomers is different in the burning of technical products (Fig. 1 a) as compared to the purified samples (Fig. 1 b and c). The obvious dimerization products (peaks 1, 2 and 24) dominate to a higher degree in the case of the purified samples.

It is worth noticing that very similar chromatograms were obtained in burning experiments of Servarex and in micropyrolyses of the same formulation. Most of these PCDD isomers are also found in fly ash samples.^{8,9}

PCDFs in starting materials and burning extracts

Using the same technique as described for the PCDDs above, we have quantified the PCDFs found in the starting materials and burning extracts. Due to the lack of suitable PCDF standards, no identification of the discrete isomers was possible. In both formulations 40-50 individual isomers were present, while the burning extracts contained less than 10, but in part some of these were newly formed.

The main PCDFs in the starting materials are the hexa- and hepta-CDFs present at levels of 60-70 µg/g each, and the amounts found for the tetra-, penta- and octa-CDF were about 10 µg/g. The same levels and the same isomers were found in the two formulations studied.

After burning, the levels of most PCDFs were generally much decreased (as opposed to PCDDs) but the level of a few individual PCDFs nevertheless increased, e.g. the major tetra-CDF (unknown isomer) increased during burning more than 100-fold (from 0.04 to 5 µg/g). Two of these isomers were not at all found in the starting materials. 2,3,7,8-Tetra-CDF, which is considered to be the most toxic of all PCDFs,¹⁶ was only a minor component in all these samples. In the starting material less than 0.1 % of the total tetra-CDFs.

The same PCDFs were formed in the micropyrolysis of Servarex as in the burning experiments, but from the burning and the micropyrolyses of the

purified chlorophenates no PCDFs could be found. Consequently, the newly formed PCDFs are formed from impurities in the technical products, probably in reactions with higher absolute yields than those leading to PCDDs.

Conclusions

From a mechanistic point of view the PCDDs found in the burning extracts can be formed in three different ways:

- A. by dimerization of chlorophenates,
- B. by dechlorination of higher chlorinated PCDDs and
- C. by cyclization of predioxins.

The fact that the purified tri- and pentachlorophenates also yield large amounts of PCDDs strongly suggests a dimerization reaction. The fact that hepta-CDDs and lower chlorinated PCDDs are formed from pure pentachlorophenate suggests that a dechlorination reaction is also involved. The thermal cyclization of predioxins has been reported previously.¹⁷ It seems quite plausible that the three reactions A, B and C yield various and different PCDD isomers.

An examination of the kinetic situation reveals that reaction A, which is a dimerization should be a bimolecular reaction, while dechlorination (B) and cyclization (C) are monomolecular. Consequently, the ratio of the isomers formed in burning reactions should be dependent on the chlorophenate concentration. The dimerization reaction (A) gives lower yields in more diluted systems. The concentrations used in the burnings here are quite high, and further work is needed to verify that hypothesis. However, it is worth noticing that within an evaporating droplet the concentration of nonvolatile components gradually increases resulting in spotwise high concentrations. Consequently, the local concentration is not as low as indicated by the mean concentration found.

Other variables in the burnings are temperature and flow rate of air. Both are difficult to control during open burning. However, as mentioned previously, no attempts were made to find the optimal conditions for the formation of PCDDs and PCDFs.

Of special interest is the observation of PCDD isomers with the same retention time and chlorination pattern as the highly toxic 2,3,7,8-tetra-CDD and 1,2,3,7,8-penta-CDD. Although they are found to be only minor constituents, in individual burnings both have been found at levels exceeding 10 µg/g chlorophenate. It can also be pointed out that these two isomers cannot be formed in the expected dimerization reactions (A), consequently they are formed in dechlorination reactions (B) or cyclizations of predioxins (C), present as impurities in the commercial formulation. No 2,4,5-trichlorophenol could be detected in the commercial formulations.

It is also of interest to compare the formation of PCDDs reported on here with the potential formation of 2,3,7,8-tetra-CDD from various 2,4,5-T precursors, a question associated with some controversy in the past. Previously, we reported that no 2,3,7,8-tetra-CDD could be found by burning various samples of vegetation, sprayed or spiked with 2,4,5-T ester or salts.¹⁸ The combustion gases, soot particles and ashes were analyzed by the same technique as used here, and the detection limit was 4 µg 2,3,7,8-tetra-CDD/g 2,4,5-T burned. Our results are supported by the recent publications of Stehl *et al.*¹⁹ on burning vegetation sprayed with purified 2,4,5-T esters and salts, and by Ahling *et al.* on burning a 2,4,5-T ester formulation.²⁰

The burning of chlorophenates or material like wood shavings, plywood or waste oil containing chlorophenates seems to be a more important source to environmental pollution by PCDDs including 2,3,7,8-tetra-CDD than the accidental burning of 2,4,5-T derivatives or vegetation treated with 2,4,5-T derivatives.

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