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Formation of Octa-Chlorinated Dibenzo-p-dioxin and Its Thermal Decomposition Products from Pyrolysis Reaction of Pentachlorophenate

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Usually octa-chlorinated dibenzo-p-dioxin (octa-CDD) exists as impurities in technical penta-chlorophenol and in chlorinated phenoxyacetic acids.¹ In addition, octa-CDD has been found in emission from municipal waste incinerators²⁻⁵ and in several environmental samples including sediment or sea water with relatively higher concentration over other chlorinated dibenzo-p-dioxins.^{6,7} The main polychlorinated dibenzo-p-dioxins (PCDDs) including octa-CDD found in the fly ash are similar to those formed in the pyrolysis of commercial chlorophenols.⁸ Therefore, the burning of chlorophenols is of interest in connection with incineration conditions designed to destroy waste PCDDs.

In this study, octa-CDD and some of PCDDs were produced by microscale pyrolysis of pentachlorophenate (PCP) at relatively high temperature. The mixture of octa-CDD and its thermal decomposition products was separated and identified by high resolution gas chromatography-mass spectrometry (GC-MS). Specifically, potassium pentachlorophenate in the reaction tube containing alumina beads was pyrolyzed at 700 °C, at which most of the incinerators operate. After

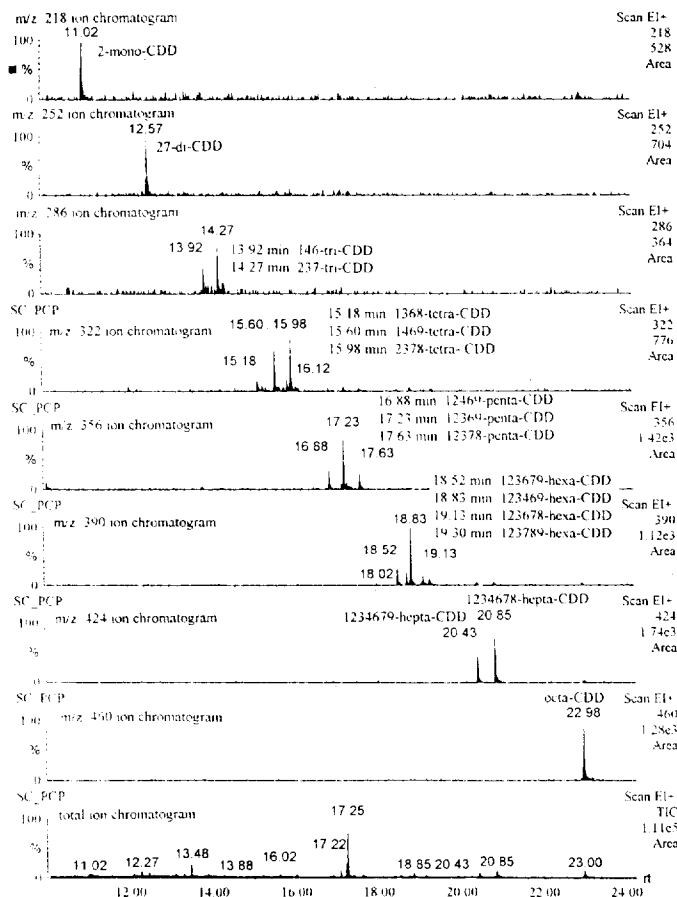
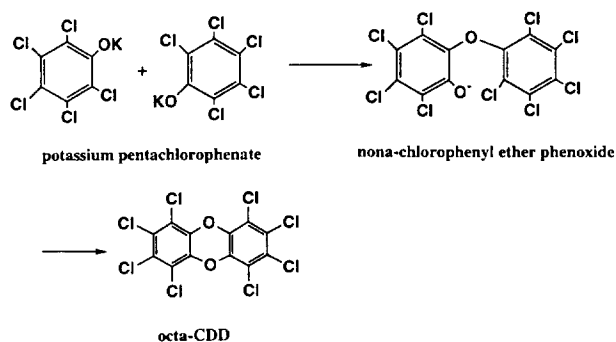


Figure 1. Typical total ion chromatogram and ion chromatograms of pyrolysates obtained from the pyrolysis of pentachlorophenate. Chromatographic conditions as follows: injection temperature 280 °C; splitless mode; column SPB-5 30 m×0.25 mm; oven temperature: initial temperature 100 °C held for 2 min and increased at 20 °C/min to 200 °C and then programmed at 10 °C/min to 300 °C.

pyrolysis, the pyrolysates adsorbed on the surface of alumina beads and glass reaction tube were dissolved in methylene chloride by sonication for 10 min. The dissolved products were placed on an alumina column, eluted with 20 mL of methylene chloride, and then evaporated under a nitrogen stream. The unreacted reagents such as PCP and other polar compounds were readily removed from this column by clean-up procedure. The extracts were analyzed by high resolution capillary column GC-MS (Fisons Inst., Trio-1000, Manchester, UK).

As seen from the total ion chromatogram and ion chromatograms shown in Figure 1, octa-CDD and several PCDDs were detected, but no polychlorinated dibenzofurans (PCDFs) were found.⁹ The formation of octa-CDD can be explained as two-step condensation process through an aromatic substitution reaction *via* nona-chlorodiphenyl ether phenoxide as an intermediate, as indicated in Scheme 1. However, the formation mechanism of the dechlorinated products from octa-CDD is not yet equivocal. It could be explained by two pathways. One pathway is that octa-CDD formed from the condensation of pentachlorophenate can be converted into hepta-, hexa- and lower CDDs by sequential thermal dechloro-



Scheme 1. Formation of octa-CDD from the pyrolysis of pentachlorophenolate.

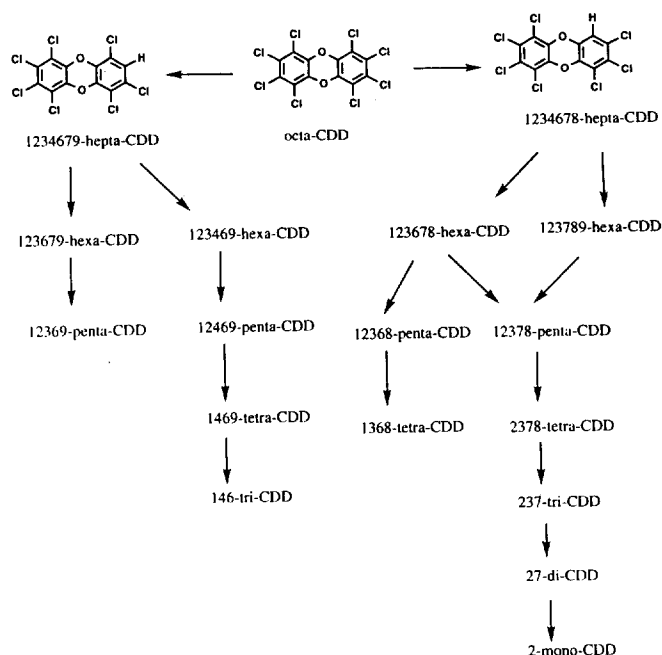
Table 1. Distribution ratios of total PCDDs and toxic congeners produced from the thermal dechlorination of octa-CDD

Compounds	% of total PCDD	toxic 2367-congeners (TEF)	toxic PCDDs (%)
1. octa-CDD	14.2	octa-(0.001)	14.2
2. hepta-CDDs	22.7	1234678-hepta-(0.01)	14.6
3. hexa-CDDs	18.9	123678-hexa-(0.1)	3.0
		123789-hexa-(0.1)	1.0
4. penta-CDDs	18.6	12378-penta-(0.5)	3.7
5. tetra-CDDs	10.0	2378-tetra-(1.0)	5.5
6. tri-CDDs	3.7	—	—
7. di-CDDs	6.0	—	—
8. mono-CDDs	5.9	—	—
Total	100%		42%

TEF: toxicity equivalent factor¹³

mination. The other pathway is that the lower-chlorinated PCDDs may be formed through the condensation of PCP with lower-chlorophenates, which are the decomposition products of PCP. The former pathway is thought to be predominant because the dechlorination of pentachlorophenolate reduces the resonance stability of phenoxide. In other words, it can be explained that the formation of octa-CDD from the pyrolysis of PCP may be energetically more favored than the dechlorination of pentachlorophenolate.

Table 1 presents the weight fractions of various PCDDs and toxic 2378-congeners formed from the pyrolysis reaction. As shown in Table 1, substantial amounts of octa- and hepta-CDDs were formed, and mono- through tri-CDDs were also formed in total amounts of slightly less than 15% of all the PCDDs. It is not surprising to observe that the amount of total toxic PCDD were 42% of all the PCDDs, because octa- and hepta-congeners, the major products, contribute of 28.8% of PCDD. The weight fractions of PCDDs were dependent on the experimental conditions such as temperature and reaction time. The amounts of lower-chlorinated PCDDs increased under the conditions of higher temperature and longer time. Formation of a wide variety of lower chlorinated dibenzo-p-dioxins presumably supports the thermal dechlorination pathways of octa-CDD as shown in Scheme 2. The right-hand side indicates that the chlorine atoms are lost



Scheme 2. Proposed thermal dechlorination pathways of octa-CDD.

mainly in peri (1, 4, 6 and 9) positions to produce toxic 2,3,7, 8-congeners, while the left-hand side displays that the chlorine atoms are lost in both peri- and lateral (2, 3, 7, and 8) positions yielding PCDDs of very low toxicity.

The abundances of hepta-isomers observed in the dechlorination of octa-CDD are presented in the *m/z* 424 ion chromatogram of Figure 1. The amount of 1234678-hepta-CDD at retention time 20.85 min is greater than that of 1234679-hepta-CDD at 20.43 min. Their abundance ratio amounts to 2.5 : 1, which indicates a special decomposition pathway of octa-CDD in thermolysis. In the earlier photolysis studies of octa-CDD, several groups¹⁰⁻¹² reported that the loss of chlorine atom preferentially takes place in the lateral position (2, 3, 7 and 8) during the UV-irradiation on octa-CDD. In contrast, Niessner *et al.*¹³ recently reported that the octa-CDD preferentially loses a chlorine atom in the peri-position under photolytic conditions, which is consistent with our observation. It may be concluded that the conversion of octa-CDD to hepta-CDDs by either thermolysis or photolysis prefers the loss a chlorine atom in the peri-position (1, 4, 6 and 9) next to ether bridge. In addition, the thermal degradation of octa-CDD increased the toxicity because the toxicity equivalents (TEQ) of octa-CDD is one-tenth of that of 1234678-hepta-CDD.¹⁴

As also shown in *m/z* 390 ion chromatogram of Figure 1, several dechlorinated hexa-CDDs from hepta-CDD were observed at retention times 18.83, 19.13 and 19.30 min. Especially, the toxic 123478- and 123678-hexa-CDDs as minor products were detected at the retention times 19.13 and 19.30 min, respectively. The identification of these products was based on the match of retention times and mass spectra with authentic standards. The predominant product among the hexa-CDD isomers at retention time 18.83 min is assigned as 123469-hexa-CDD, which was confirmed by the

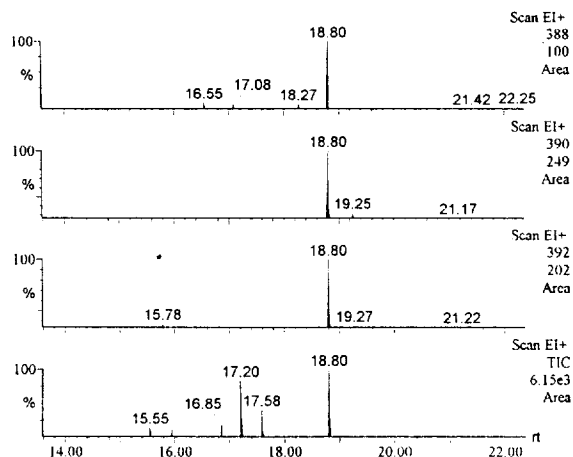


Figure 2. Total ion chromatogram and ion chromatograms of pyrolysates obtained from the pyrolysis of the mixture PCP and 2,3,6-TCP and 300 °C.

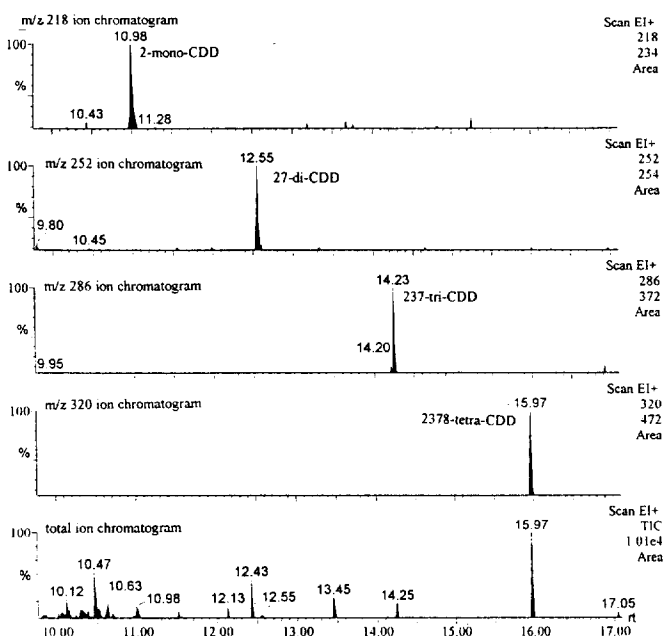


Figure 3. Total ion chromatogram and ion chromatograms of pyrolysates obtained from the pyrolysis of 2,4,5-TCP at 300 °C.

pyrolysis of the mixture of PCP and 236-trichlorophenate at 300 °C. From the result shown in Figure 2, 123469-hexa-CDD as the major product was detected at retention time 18.80 min which is practically identical to the retention time of the predominant hexa-CDD produced from thermal dechlorination of octa-CDD.

The 123469-hexa-CDD may be sequentially dechlorinated to form the 12369-penta-CDD as shown in m/z 356 ion chromatogram of Figure 1. The trace amount of toxic 12378-penta-CDD detected at retention time 17.63 min was produ-

ced by the dechlorination of both toxic hexa-congeners. Two tetra-CDDs together with 2378-tetra-CDD were formed *via* different pathways. An interesting observation is that the most toxic 2378-tetra-CDD was also detected with the amount of 5.5% of the total PCDDs. The 237-tri-, 27-di- and 2-mono-CDDs were produced by the sequential dechlorination of 2378-tetra-CDD. The thermal dechlorination pathway of 2378-tetra-CDD could be confirmed by the analysis of products from the pyrolysis of 245-trichlorophenate. As shown in Figure 3, the most abundant 2378-tetra-CDD was due to the pyrolysis of 245-TCP. The sequentially dechlorinated products of 2378-tetra-CDD were also observed as 237-tri-, 27-di- and 2-mono-CDDs.

Consequently, it is of special interest that the highly toxic 2378-tetra-CDD and 12378-penta-CDD were formed during the burning of pentachlorophenates at 700 °C. Although they were found to be minor constituents, uncontrolled burning of chlorophenols could be an important source to produce hazardous PCDDs. In particular, it is found that the main decomposition pathway is reductive dechlorination and the chlorines in peri positions are preferentially lost. Thus, the toxicity of dechlorinated PCDD was increased because of forming toxic 2378-congeners. From the observation of thermal dechlorination, it is also concluded that the ring of more substituted chlorines in a dioxin molecule will lose first a chlorine in pyrolysis, except for the conversion of 1234679-hepta-CDD into 123469-hexa-CDD.

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