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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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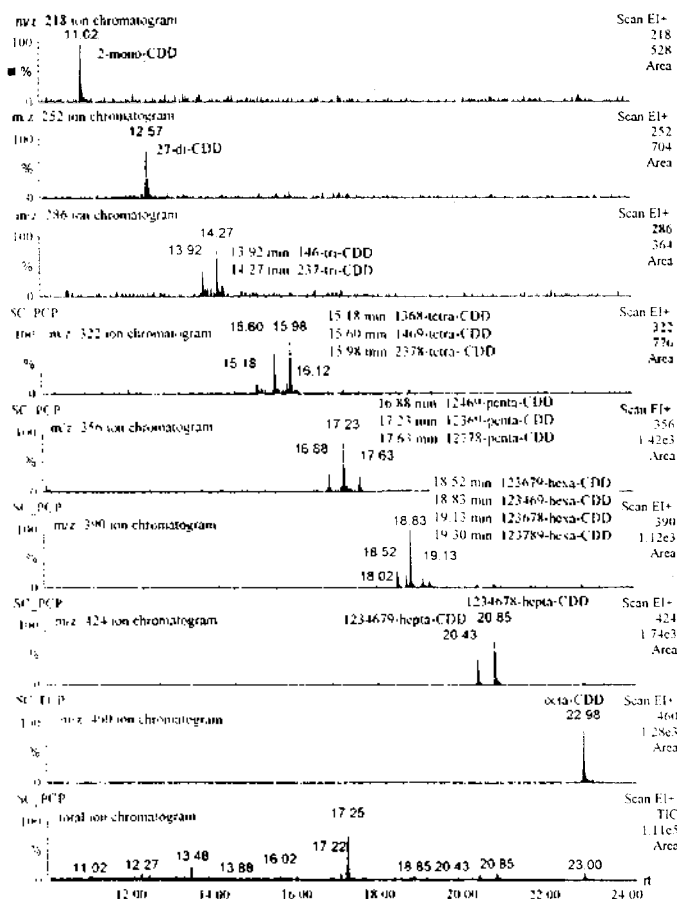
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Usually octa-chlorinated dibenzo-p-dioxin (octa-CDD) exists as impurities in technical penta-chlorophenol and in chlorinated phenoxyacetic acids.<sup>1</sup> In addition, octa-CDD has been found in emission from municipal waste incinerators<sup>2-5</sup> and in several environmental samples including sediment or sea water with relatively higher concentration over other chlorinated dibenzo-p-dioxins.<sup>6,7</sup> 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.<sup>8</sup> 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

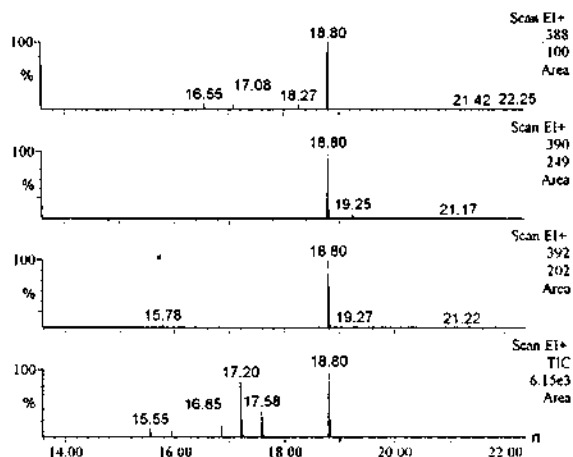


**Figure 1.** Typical total ion chromatogram and ion chromatograms of pyrolysates obtained from the pyrolysis of pentachlorophenate. Chromatographic conditions as follows: injection temperature 280 °C; splitless mode; column SPB-5 30 m×0.25 mm; oven temperature: initial temperature 100 °C held for 2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

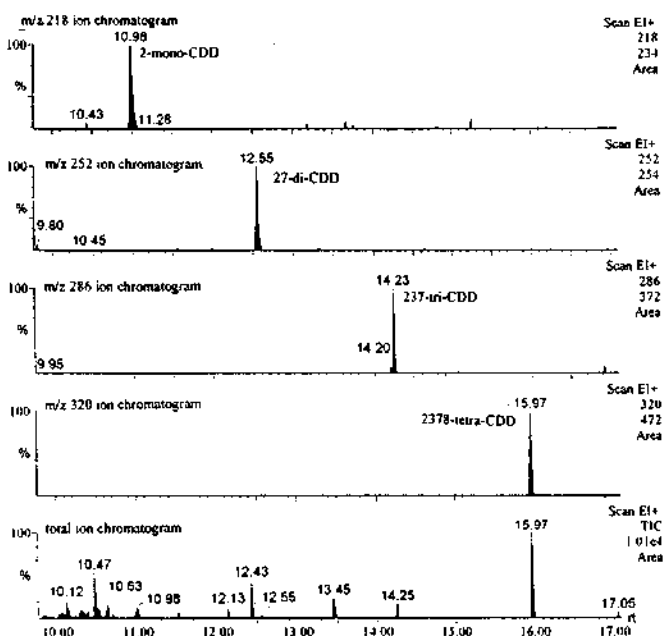
pyrolysis, the pyrolysates adsorbed on the surface of alumina beads and glass reaction tube were dissolved in methylene chloride by sonication for 10 min. The dissolved products were placed on an alumina column, eluted with 20 mL of methylene chloride, and then evaporated under a nitrogen stream. The unreacted reagents such as PCP and other polar compounds were readily removed from this column by cleanup 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.<sup>9</sup> 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-





**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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