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Formation of Tetra-Chlorinated Dibenzo-p-dioxins and Their Thermal Decomposition Products from Pyrolysis Reactions of Tri-Chlorophenates

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Tetra-chlorodibenzo-p-dioxins (tetra-CDDs) were prepared by microscale pyrolysis of trichlorophenates. During the pyrolysis reaction, tri-, di-, and mono-CDDs were also formed by the thermolysis of tetra-CDDs. The dechlorination pathways of tetra-CDDs were suggested for this reaction. The identification of these products was performed with capillary column gas chromatography-mass spectrometry.

Introduction

Chlorophenols can be precursors in the formation of polychlorinated dibenzo-p-dioxins (PCDDs) during the industrial production processes. Tetra-chlorinated dibenzo-p-dioxins (tetra-CDDs) usually exist as impurities in technical chlorophenols and in other chloro compounds.[1,2] In particular, 2,3,7,8-tetra-CDD is formed as a byproduct[3] during the high temperature hydrolysis of tetrachlorobenzene to 2,4,5-trichlorophenoxy acid. In addition, tetra-CDDs are also found in emit-

ted gases from municipal waste incinerators and in fly ash, sludge, sediment and soil.[4~6]

Several types of chlorinated dibenzo-p-dioxins are produced when chlorophenates are pyrolyzed for a few seconds at 300 ℃-400 ℃.[7~9] The main polychlorinated dibenzo-p-dioxins found in the fly ash are similar to those formed in the pyrolysis of commercial chlorophenols.[10] Therefore, understanding the pyrolysis mechanism of chlorophenols is important to optimize incineration condition for minimizing the producing waste chlorinated dibenzo-p-dioxins.

Tetra-CDDs were produced by microscale pyrolysis of trichlorophenates (TCPs) at relatively high temperature. Although tetra-CDDs are known as highly stable compounds, these compounds are converted into less chlorinated products under high temperature condition. Therefore, a mixture of less chlorinated dibenzo-p-dioxins might be produced by the thermal dechlorination during the pyrolysis reactions. Several groups[11~16] have investigated the dechlorinated products of dibenzodioxins and dibenzofurans under photolytic condition. However, the chemical natures of thermally dechlorinated products, less chlorinated dibenzo-p-dioxins, remains still unknown as well as the mechanism of their formation.

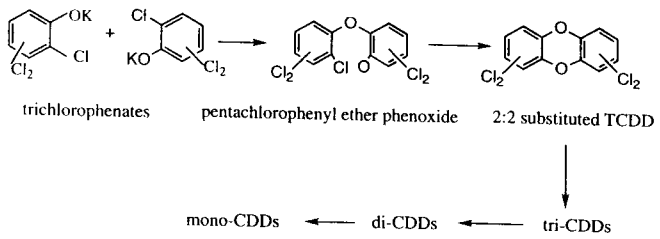
In this study, tetra-CDD and some of dechlorinated products were prepared using microscale pyrolysis of TCP at relatively high temperature. Identification of the tetra-CDDs and less chlorinated dioxins was performed by capillary column gas chromatography-mass spectrometry. And also the dechlorination mechanism of tetra-CDDs including 2,3,7,8-tetra-CDD is also investigated under the high temperature condition.

Experimental

Chemicals. Chlorophenols purchased from Aldrich (Milwaukee, WI, USA) were of 99% purity. Potassium hydroxide and solvents were obtained from J.T. Baker (Phillisburg, NJ, USA). All solvents used in this study were of pesticide residue analysis grade. Alumina used as clean-up column was purchased from Supelco (Bellfonta, PA, USA). The chlorinated dibenzo-p-dioxin standard compounds including the mixture of 2,3,7,8-substituted isomers were obtained from Cambridge Isotope Laboratories (Woburn, MA, USA) and Chemsyn Science Laboratories (Lenexa, KS, USA).

Preparation of Tetra-CDDs. Potassium salts of various chlorophenols were prepared in a 50 mL round flask by mixing 10 mg of chlorophenol and 3 mL of 1 M potassium hydroxide in methanol, and then evaporated using a rotatory evaporator. The residue was further dried under vacuum oven at 60 ℃ for overnight.

Reaction tubes (5-6 cm) were prepared by sealing one end of disposable borosilicate glass pasteur pipets. About 0.5 mg of chlorophenate was added into the tube,whose both ends were packed with glass wool and alumina. The tip of the reaction tube was flame sealed and then placed into a muffle furnace when nitrogen gas was allowed to flow at a rate of 100 mL/min. The furnace temperature was initially 100 ℃, held for 10 min and then increased to 400 ℃ at a rate of 100 ℃/min, and held for 1 hr. The reaction tube was removed from the furnace and allowed to cool to ambient temperature. It was opened and the contents were thoroughly rinsed out with 100 mL of methylene chloride. In some cases unreacted chlorophenates were removed from the pyrolysate by chromatographic separation on a mini column of acidic alumina using methylene chloride (20 mL) as the eluent for the chlorinated dioxins.



Scheme 1. Formation of tetra-CDD and their thermal dechlorination products from the pyrolysis of trichlorophenates.

Gas Chromatography/Mass Spectrometry (GC/MS). A Fisons GC-MS system consisted of a model 8000 series gas chromatograph and a model Trio-1000 quadrupole mass spectrometer (Fisons Inst., Manchester, U.K.) was used. A SPB-5 cross linked 5% phenyl methylsilicone fused-silica capillary column (30 m×0.25 mm I.D., 0.25 um film thickness) was used. The column was directly interfaced to the ion source. The oven temperature was initially 100 ℃ (held for 4 min), increased at 20 ℃/min to 200 ℃, and then at 10 ℃/min to 300 ℃ (held for 5 min). Samples were injected in the splitless mode. The carrier gas was helium (99.999%) at 0.9 mL/min and column head pressure at 6 psi. The injector temperature, interface temperature and ion source temperatures were 280, 280 and 200 ℃, respectively. The electron impact source was operated at 70 eV in scanning and selected ion monitoring (SIM) modes. The selected ions used in SIM mode were at m/z 320 and 322 for tetra-CDDs between 14 and 16.5 min, at m/z 286 and 288 for tri-CDDs between 14 and 15 min, at m/z 252 and 254 for di-CDDs between 11.8 and 13.5 min and at m/z 218 and 220 for mono-CDDs between 10.8 and 11.5 min. The dwell time for each ion in SIM mode was set at 45 ms.

Results and Discussion

In many cases the pyrolysis of potassium-trichlorophenates produces a mixture of tetra-CDDs and less chlorinated dibenzodioxins. The formation of tetra-CDDs can be explained by two-step condensation process through aromatic substitution reaction via penta-chlorodiphenyl ether phenoxide as an intermediate, as indicated in Scheme 1. However, the formation mechanism of the dechlorinated products from tetra-CDDs is not yet clear. It could be explained by two pathways. One pathway is that tetra-CDDs formed from the condensation of trichorophenate can be converted into tri-, di- and mono-CDDs by sequential thermal dechlorination. The other pathway is that the less-chlorinated CDDs may be formed through the condensation of trichlorophenate with less-chlorophenates, which are the decomposition products of the trichlorophenates. The former pathway is thought to be predominant because the dechlorination of tri-chlorophenate reduces the resonance stability of phenoxide. In other words, it can be explained that the formation of less-chlorinated products from the sequential dechlorination of tetra-CDDs

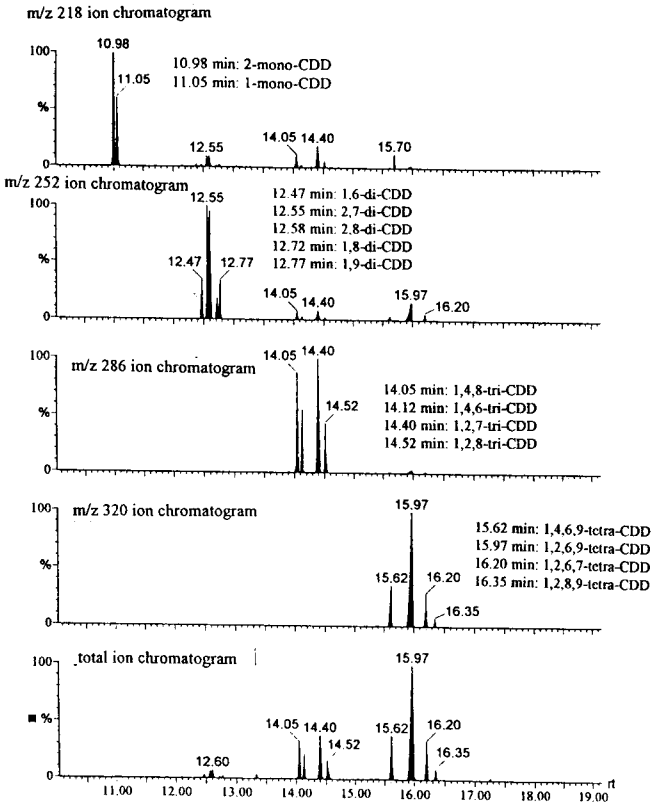


Figure 1. Total ion chromatogram and extracted ion chromatograms of pyrolysate obtained from the pyrolysis of 236-trichlorophenate at 400 ℃.

may be energetically more favored than the dechlorination of trichlorophenate. Thus, most of the less-chlorinated products in this reaction were presumably formed by the thermolysis of tetra-CDDs.

As a typical example of this process, the self-condensation of 2,3,6-trichlorophenate (TCP) yields tetra-CDD congeners and their dechlorination products like tri-, di and mono-chloro dibenzodioxins. The chromatogram obtained from the thermal condensation of 2,3,6-TCP is shown in Figure 1. Figure 1 shows a total ion chromatogram and the ion chromatograms for the ions at m/z 218 for mono-CDDs, at m/z 252 for di-CDDs, at m/z 286 for tri-CDDs and at m/z 320 for tetra-CDDs. These chromatograms reveal the formation of four tetra-CDD isomers and their thermal dechlorination products such as four tri-, five di- and two mono-CDD. As shown in Table 1, the amount ratios of di-, tri- and tetra-CDDs to total amount of chlorinated dibenzo-p-dioxins were about 5, 29 and 66%, respectively. The most abundant isomer among the dioxins formed was found to be tetra-CDD isomers. Although mono-CDDs were also formed in this reaction, their amount was insignificant. The amount of lower chlorinated dibenzo-p-dioxins was increased when the reaction was done at higher temperature and for longer time. The higher chlorinated CDDs such as penta- and hexa-CDDs were not formed and no polychlorinated dibenzofurans were found under these reaction conditions.

The formation of tetra-CDDs from the condensation of 2,3,6-TCP can be explained by either direct-condensation and

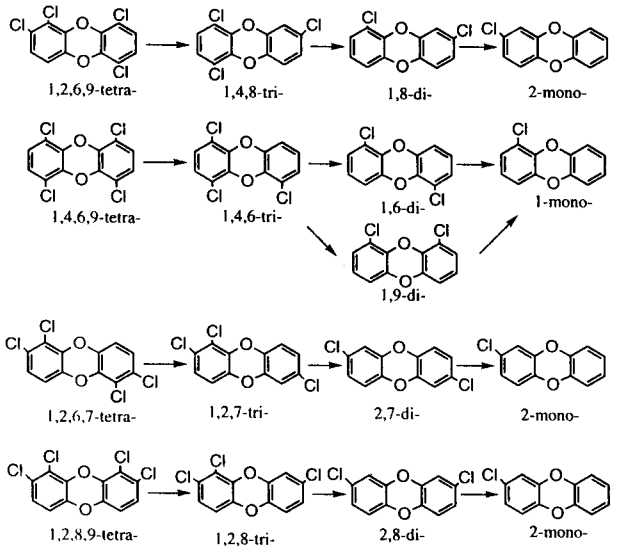
Table 1. Distribution ratios of total dioxins and dechlorinated products produced from pyrolysis of 236-trichlorophenate

Compounds	% of total CDDs	isomer	% of isomer
1. tetra-CDDs	66.2	1,4,6,9-tetra-CDD	14.9
		1,2,6,9-tetra-CDD	70.6
		1,2,6,7-tetra-CDD	12.7
		1,2,8,9-tetra-CDD	2.8
2. tri-CDDs	28.6	1,4,8-tri-CDD	27.7
		1,4,6-tri-CDD	15.3
		1,2,7-tri-CDD	42.8
		1,2,8-tri-CDD	14.2
3. di-CDDs	4.9	1,6-di-CDD	15.5
		2,7-di-CDD	27.9
		2,8-di-CDD	41.9
		1,8-di-CDD	4.9
		1,9-di-CDD	9.8
4. mono-CDDs	0.3	2-mono-CDD	66.9
		1-mono-CDD	33.1

the Smiles rearrangement.[17,18] As shown in Figure 1, 1,4,6,9-, 1,2,6,9- and 1,2,6,7-tetra-CDDs were formed by direct condensation and 1289-tetra-CDD was formed by the Smiles rearrangement. The ratios of the four tetra-CDD isomers was found to be 14.9 : 70.6 : 12.7 : 2.8 on the basis of m/z 320 ion chromatogram of Figure 1. The most abundant peak in the m/z 320 ion chromatogram was found to be 1,2,6,9-tetra-CDD at retention time 15.97 min. The 1289-tetra-CDD formed by the Smiles rearrangement was observed as the least abundant peak at retention time 16.35 min. The peaks observed at retention times at 15.69 and 16.20 min could be identified as 1,4,6,9- and 1,2,6,7-TCDDs, respectively.

During the pyrolysation of tri-chlorophenates, mono-, di- and tri-CDDs can be formed from the dechlorination of tetra-CDD isomers. Mono-CDDs have two isomers and their retention times were 11.00 (2-mono-CDD) and 11.07 min (1-mono-CDD). The di-CDD isomers were eluted between 11.8 and 13 min, and tri-CDD isomers were eluted between 13.5 and 14.8 min under the chromatographic condition. The four tri-CDDs could be assigned as 1,4,8- (14.05 min), 1,4,6- (14.12 min), 1,2,7- (14.40 min) and 1,2,8-tri-CDD (14.52 min), which may be made from the dechlorination of 1,2,6,9-, 1,4,6,9-, 1,2,6,7- and 1,2,8,9-tetra CDDs, respectively. As shown in Scheme 2, mono- and di-CDDs were mainly formed by sequential dechlorination of tri-CDDs. From the observation of thermal dechlorination for tetra- and octa-CDD[19] which is previously reported, it is concluded that the ring of more substituted chlorines in a dioxin molecule will lose first a chlorine in pyrolysis reaction. Another dechlorination pathway is that a chlorine atom in vicinal chlrorines is more easily lost than non-vicinal chlorines. Mazer[20] reported that the tetra-chlorinated dibenzofurans preferentially lose a chlorine atom in vicinal chlorines under photolytic condition, which is consistent with our observation.

Another interesting work is the preparation of 2,3,7,8-tetra-CDD by the pyrolysis of 2,4,5-TCP. As shown in Figure 2, the predominantly 2,3,7,8-tetra-CDD was formed by the pyrolysis of 2,4,5-TCP, but the amounts of dechlorinated products



Scheme 2. Proposed thermal dechlorination pathways of tetra-CDDs produced from the pyrolysis of 236-trichlorophenate.

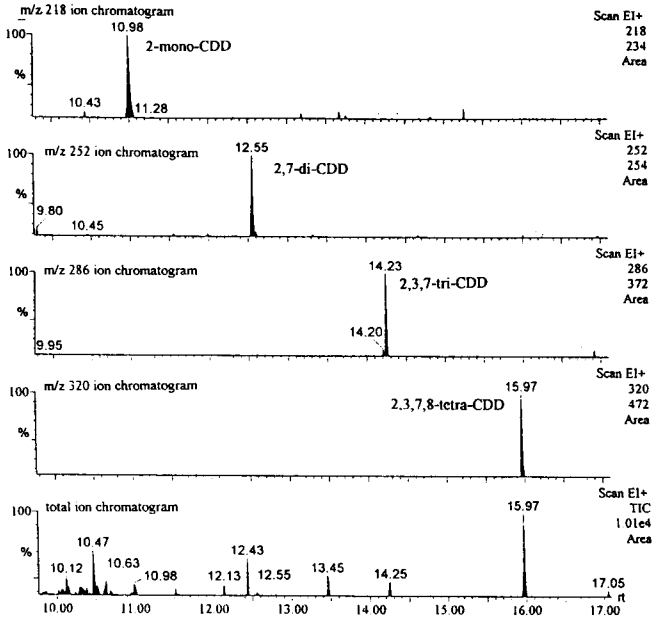
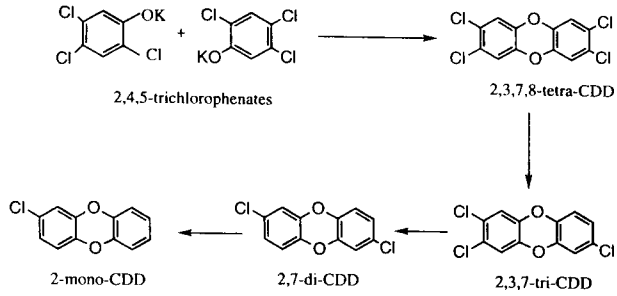


Figure 2. Total ion chromatogram and extracted ion chromatograms of pyrolysate obtained from the pyrolysis of 245-trichlorophenate.

were found to be very small. As shown in Figure 2, the 2,3,7,8-tetra-CDD was obtained as a single tetra-CDD product by the pyrolysis reaction unlike other reactions, and its thermal dechlorination products were also a single-CDD. Scheme 3 represents the thermal dechlorination pathway of 2,3,7,8-tetra-CDD. As shown in Scheme 3, 2,3,7-tri-, 2,7-di- and 2-mono-CDDs were formed from the sequential dechlorination of 2,3,7,8-tetra-CDD. This data will be useful for verifying the dechlorination mechanism of toxic-2,3,7,8-substituted-CDDs.

In fact, the lock of authentic standards for the correct identification of the thermal dechlorination products could lead



Scheme 3. Formation of 2378-tetra-CDD and its thermal dechlorinated products from the pyrolysis of 245-trichlorophenate.

to misinterpretation of results obtained. Therefore, confirmation of thermal dechlorination products needs to be carried out by comparison with standards that should be prepared by pyrolysis of less chlorinated phenates. In this study, the identification of tetra-CDDs and less chlorinated products was also performed by the pyrolysation of various chlorophenates. Each peak could be identified with the chlorine position of tetra-CDDs by comparing with authentic standards which are commercially available and are prepared by pyrolysis of less chlorinated phenates, and with the elution order on a less polar column, which was previously investigated by Buser and Rappe.[21~23] According to the Buser and Rappe's study, the elution order of polychlorinated dibenzo-p-dioxin (PCDD) is associated with the presence and number of vicinal hydrogen and chlorine. The more the number of vicinal hydrogen and chlorine in a dioxin molecule, the longer the elution time in a chromatogram. Therefore, this elution trend can be helpful to identify the chlorinated dioxins formed from the pyrolysation.

Conclusion

The pyrolysis of TCP led to the formation of tetra-CDDs and less chlorinated compounds. Tetra-CDDs preferently lost a chlorine atom from peri-position and tri-CDDs lose chlorine from the more substituted ring. These dechlorination pathways seem to be helpful for the identification of dechlorinated products of higher chlorinated dibenzo-p-dioxins. No polychlorinated dibenzofurans were observed from the pyrolysates of chlorophenates.

The yields of tetra-CDDs and less chlorinated products were dependent on the pyrolysis temperature and reaction time. The amounts of less chlorinated products increased under the condition of higher temperature and longer reaction time. Peak assignment of pyrolysate products was made based on the match of chromatographic retention times and mass spectra of authentic standards. Particularly, the chromatographic retention times provide important information on the identity of PCDD isomers. The comparison of the retention times of PCDDs formed from pyrolyssis with authentic standards which are commercially available could be used to assign the position of chlorine in PCDD with the help of the elution order of PCDDs on a less polar column.

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Atomic Absorption Spectrophotometric Determination of Trace Cadmium after Preconcentration by Extracting Its 8-Hydroxyquinoline Complex into Molten Benzophenone

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A sensitive method for the determination of trace cadmium after the preconcentration by extracting its 8-hydroxyquinoline complex into a molten benzophenone was developed. Several experimental conditions such as the pH of solution, the amounts of 8-hydroxyquinoline and benzophenone, stirring time, and standing time were optimized. Trace cadmium in 100 mL water sample was chelated with 2.5 mL of 0.001 M 8-hydroxyquinoline at pH 8.0. After 0.07 g benzophenone was added, the solution was heated to about 70 ℃ and stirred vigorously for 1 minute to dissolve the complex quantitatively in a molten benzophenone, and stood for 30 minutes to reproduce the microcrystalline benzophenone. The benzophenone containing Cd-8-hydroxyquinoline complex was filtered and dissolved in acetone. Cadmium was determined by a flame atomic absorption spectrophotometry. The interfering effects of diverse concomitant ions were investigated and eliminated. This method could be applied to natural water samples and the recovery of more than 90% was obtained in the real samples.

Introduction

The determination of trace cadmium in a natural water is of importance in connection with water pollution. Cadmium is present in river or stream at the level of μg/mL or less. So, cadmium should be separated and concentrated from the bulk matrix prior to an actual determination. Several preconcentration methods such as coprecipitation,[1] liquid-liquid extraction,[2,3] flotation,[4] non-boiling evaporation,[5] ion-exchange resin sorption,[6] adsorption by active carbon[7] and electrolytic deposition[8] have been used for the determination of cadmium.

In this work, the solid-liquid extraction which is based on a solid-liquid separation following a liquid-liquid extraction has been used on the separation and preconcentration of cadmium. The solid-liquid extraction has got several advantages over the liquid-liquid extraction.[9] It is less tedious because the distribution of the nonpolar complex between an aqueous phase and a molten nonpolar organic phase is attained in equilibrium within a few minutes owing to a high temperature. And the concentration factor, that is, the sensitivity can be enhanced by the complete extraction of metal ions in a 100 mL aqueous solution with only small amount of the solid solvent (~0.07 g). Usually, common organic sol-