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Formation of Polychlorinated Dibenzo-p-Dioxins and Their Thermal Decomposition Products from Pyrolysis Reactions of Chlorophenates

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Abstract : Polychlorodibenzo-p-dioxins(PCDDs) have been prepared by microsacale pyrolysis of trichlorophenates. During the pyrolysis reaction, dechlorinated dibenzo-p-dioxins were also formed by the thermolysis of PCDDs. The dechlorination pathways of PCDDs were suggested in this reaction. The identification of these products was performed using capillary column gas chromatography-mass spectrometry.

Keywords : Chlorophenates, Pyrolysis, Formation of polychlorinated dibenzo-p-dioxin, Dechlorination Pathways, GC/MS analysis

1. Introduction

Polychlorinated dibenzo-p-dioxins (PCDDs) usually exist as impurities in technical chlorophenols and in other chloro compounds.[1,2] In adition, PCDDs are also found in emitted gases from municipal waste incinerators and in several environmemtal samples like fly ash, sludge, sediment and soil.[3-5]

Several types of chlorinated dibenzo-p-dioxins are produced when chlorophenates are pyrolyzed for a few seconds at 400°C - 600°C.[6-8] Therefore, the burning of chlorophenols which are widely conducted in industry is of interest in connection with incineration condition designed to destroy waste chlorinated dibenzo-p-dioxins.

PCDDs were produced by microscale pyrolysis of chlorophenates at relatively higher temperature. Although PCDDs are known as highly stable compounds, these compounds are converted into lower chlorinated products under high temperature condition. Therefore, a mixture of lower chlorinated dibenzo-p-dioxins was produced by the thermal dechlorination during the pyrolysis reactions. Several groups[9-14] have investigated for the

dechlorination products of dibezondioxins and dibenzofurans under photolytic condition.

In this study, PCDD and some of dechlorinated products were produced by microscale pyrolysis of chlorophenate at relatively high temperature. Identification of the PCDDs including lower chlorinated dioxins was performed by capillary column gas chromatography - mass spectrometry. This paper reports on investigation of the dechlorination mechanism of PCDD formed by the pyrolysis of chlorophenates.

2. EXPERIMENTAL

The various PCDDs were prepared by microscale pyrolysis of different chlorophenates. The potassium salts of these chlorophenols were prepared by combining 10 mg of chlorophenol and 3 ml of 1M potassium hydroxide in methanol solution, and then flash evaporated with a rotatory evaporator. The dried residue was placed into a vacuum oven at 60^{o}C for overnight to remove the trace amount of water.

The reaction tubes 5-6 cm were prepared by sealing the ends of disposable borosilicate glass pasteur pipets. About 0.5 mg of chlorophenate was inserted into the ampule, and glass wool and alumina were placed in both ends of the reaction tube. The tip of the reaction tube was then flame sealed and inserted into a muffle furnace with introgen gas flowing at a rate 100ml/min. The furnace temperature was initially 100^{o}C held for 10 min and then increased to 400^{o}C at a rate 100^{o}C/min 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 100ml of methylene chloride. In some cases unreacted chlorophenates were removed by subject the pyrolysate to chromatographic separation on a mini column of acidic alumina by eluting the chlorinated dioxins with 20 ml of methylene chloride.

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 utilized. A fused-silica capillary column coated with SPB-5 cross linked 5% phenyl methylsilicone (30m x 0.25mm I.D., 0.25um film thickness) was used. The column led directly into the ion source. The GC temperature program was as follows: initial temperature was 100^{o}C, held for 4 min, increased by 20^{o}C/min to 200^{o}C, and then increased by 10^{o}C/min to 300^{o}C held for 5 min. Samples were injected the splitless mode. The carrier gas was helium (99.999%) at 0.9ml/min. Injector temperature was 280^{o}C, interface temperature was 280^{o}C and ion source temperature was 200^{o}C. The mass spectrometer was operated at 70eV in the electron impact (EI) mode using scan and selected ion monitoring (SIM). The selected ions used in SIM mode were m/z 320 and 322 for tetrachlorodibenzo-p-dioxins (CDDs) between 14 and 16.5 min, m/z 286 and 288 for tri-CDDs between 14 and 15 min, m/z 252 and 254 for di-CDDs between 11.8 and 13.5 min and m/z 218 and 220 for mono-CDDs between 10.8 and 11.5 min.

3. Results and Discussion

In many cases the pyrolysis of potassium-trichlorophenates produces a mixture of tetra-CDDs and lower chlorinated dibenzodioxins. The formation of tetra-CDDs from the pyrolysis of potassium-trichlorophenates can be explained by two-step condensation process through aromatic substitution reaction via penta-chlorodiphenyl ether phenoxide as an intermediate. However, the

formation mechanism of the dechlorinated products from the tetra-CDD is not yet equivocal. It could be explained by two pathways. One pathway is that tetra-CDD 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 lower-chlorinated CDDs may be formed through the condensation of trichlorophenate with lower-chlorophenates, which are the decomposition products of the trichlorophenates. The former pathway is thought to be predominant because the dechlorination of trichlorophenate reduces the resonance stability of phenoxide.

As a typical example of this process, the self-condensation of the 2,3,6-trichlorophenate(TCP) yields the tetra-CDD congeners and their dechlorination products like tri-, di and mono-chloro dibenzodioxins. The formation of the four tetra-CDDs from the condensation of 236-TCP can be explained by the direct-condensation and Smiles rearrangement.[15,16] The 1469-, 1269- and 1267-tetra-CDD were formed by direct condensation and 1289-tetra-CDD was formed by the Smiles rearrangement, as shown in Figure 1. The ratios of the four tetra-CDD isomers was found to be 14.6:70.2:12.7:2.5 on the basis of m/z 320 ion chromatogram of GC/MS analysis. The most abundant peak in the m/z 320 ion chromatogram was found to be 1269-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 1469- and 1267-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 the 1,4,8- (14.05 min), 1,4,6- (14.12 min), 127- (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 Figure 1, mono- and di-CDDs were also detected by sequential dechlorination of tri-CDDs. From the observation of thermal dechlorination, it is concluded that the ring of more substituted chlorines in a dioxin molecule will be lost first a chlorine in pyrolysis reaction. The another dechlorination pathway is that a chlorine atom in vicinal chlrorines is more easily loses than non-vicinal chlorines. Mazer[17] reported that the tetra-CDFs preferentially loses a chlorine atom in vicinal chlorines under photolytic condition, which is consistent with our observation.

As seen from the total ion chromatogram and ion chromatograms shown in Figure 2, octa-CDD and several PCDDs were detected from the pyrolysis of pentachlorophenate, but no polychlorinated dibenzofurans (PCDFs) were found.[18] The abundances of hepta-isomers observed in the dechlorination of octa-CDD is presented in the m/z 424 ion chromatogram of Figure 2. 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 groups[11,12]

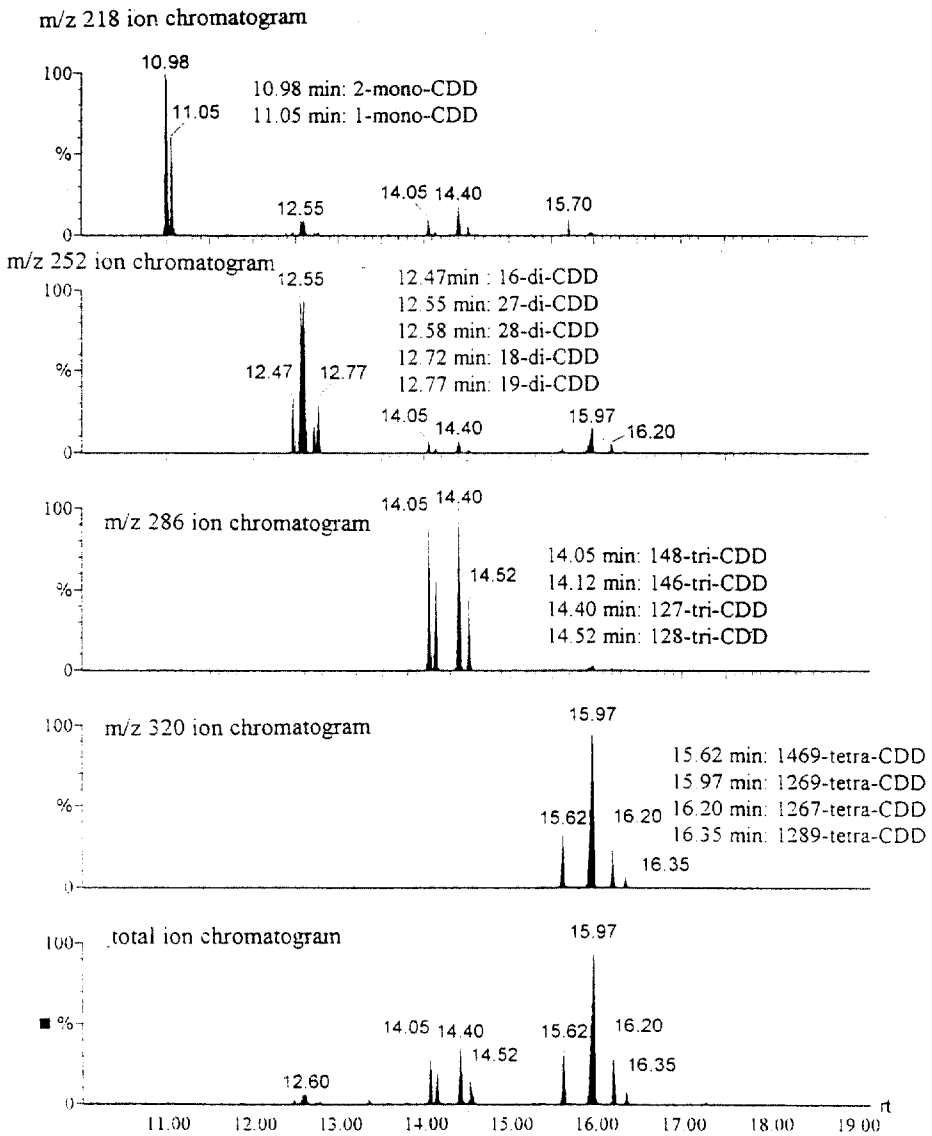

Figure 1. Total ion chromatogram and extracted ion chromatograms of pyrolysate obtained from the pyrolysis of 236-trichlorophenate at 400°C.

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 preferrs 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 of1234678-hepta-CDD.[19]

As also shown in m/z 390 ion chromatogram of Figure 2, 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 pyrolysis of the mixture of PCP and 236-trichlorophenate at 300^{o}C.

The 123469-hexa-CDD may be sequentially dechlorinated to form the 12369-penta-CDD as shown in m/z 356 ion chromatogram of Figure 2. The trace amount of toxic 12378-penta-CDD detected at retention time 17.63 min was produced 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.

From the thermal dechlorination, it is concluded that the ring of bservation more substituted chlorines in a dioxin molecule will be lost first a chlorine in pyrolysis reaction. The another dechlorination pathway is that a chlorine atom in vicinal chlrorines is more easily loses than non-vicinal chlorines. 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^{o}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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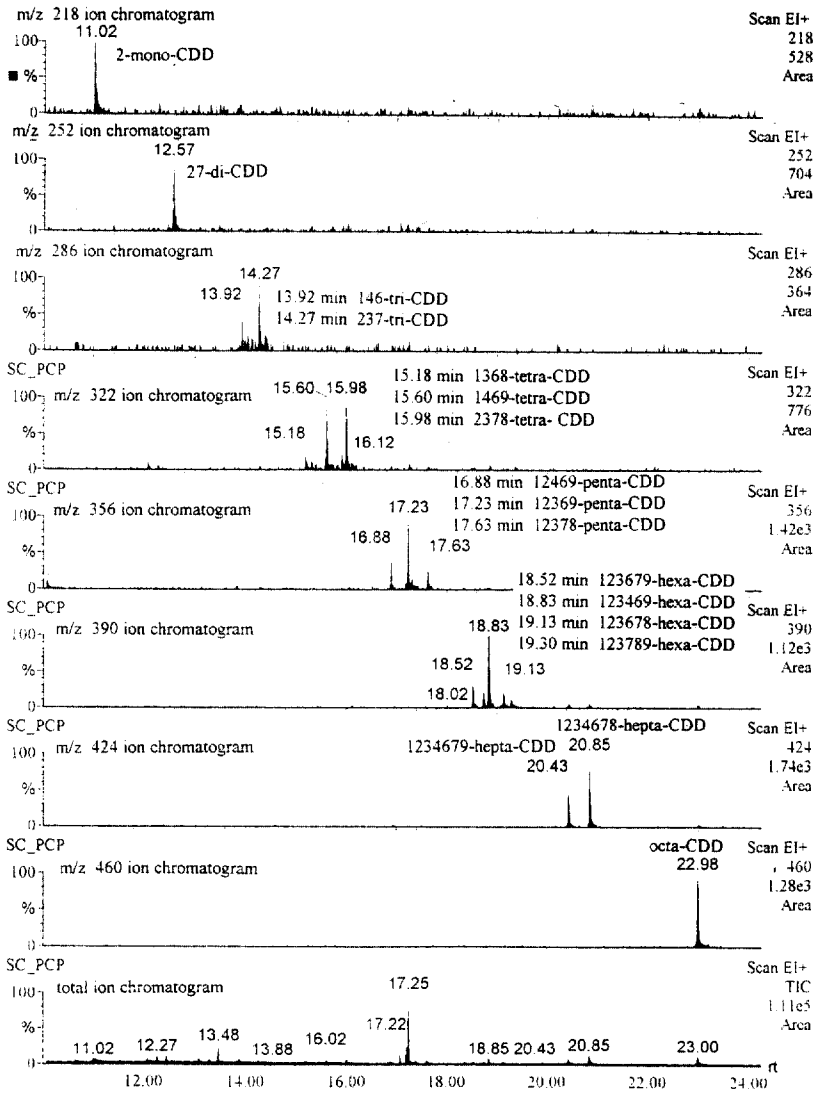

Figure **2**. Typical total ion chromatogram and ion chromatograms of pyrolyzates obtained from the pyrolysation of pentachrophenate. Chromatographic conditions are as follows: injection temperature 280°C; splitless mode; column SPB-5 25m x 0.25mm; oven temperature: initial temperature at 100°C held for 2min and increased 20°C/min to 280°C and then programmed at 10°C/min to 300°C.

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