Bull. Environ. Contam. Toxicol. (1997) 59:83-89

Bulletin of Environmental Contamination and Toxicology

Formation of Polychlorinated Biphenyls from the Pyrolysis of Hexachlorocyclohexane in the Presence of Fe_2O_3

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Received: 21 January 1997/Accepted: 5 March 1997

Industrial manufacture of polychlorinated biphenyls(PCBs) was based on the chlorination of biphenyl by anhydrous chlorine on heating in the presence of suitable catalysts (Dobson et al. 1993). Mullin et al. (1984) synthesized all 209 PCB congeners by diazo coupling of chloroanilines and chlorobenzenes. Other than the commercial production or laboratory synthesis of PCBs as mentioned above, there were few additional reports on the formation of PCBs. Buser (1979) observed the formation of small quantities of higher chlorinated biphenyls from the pyrolysis of chlorobenzenes at 62O°C, but the mechanism of the formation of PCBs had not been investigated. Zinburg et al.(l981) reported the formation of chlorobenzenes and chlorophenols by heating hexachlorocyclohexane (HCH) in the presence of H_2SO_4 or H_2O_2 in water, but pyrolysis of HCH in the presence of iron (III) oxide (Fe_2O_3) had not been reported.

Bao et al. (1993) reported findings about 10% of PCBs in the waste from reaction stills affiliated to a large chemical factory in northern of China for production of trichlorobenzenes by pyrolysis of non-gamma HCH. To investigate the mechanism of the formation of PCBs, a series of experiments was performed. We discovered that hydrogen chloride can catalyze the condensation reaction of chlorobenzenes with chlorophenols into PCBs. The results provided a mechanism of formation of PCBs from the pyrolysis of HCH in the chemical factory.

MATERIALS AND METHODS

Thirty milligrams of non-gamma isomers of HCH(98%, Dagu Chemical Factory, China) and 0.3-40 mg of Fe_2O_3 (99.5%, Beijing Chemical Works, China) were sealed in a glass tube (50 x 4.2 mm i.d.) and heated to 250- 4OO°C for 0.5-8 hr. After cooling, the tube was crushed and the reaction products were extracted with 25 ml 5% (v/v) toluene in n-hexane

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under ultrasonication. Fifty milliliters of the extract was cleaned up on an alumina column(250 X 10 mm i. d., basic alumina, activated at temperature of 660°C for 6 hr). The column was washed with 50 ml hexane, then eluted with 50 ml 2% (v/v) methylene chloride in hexane. This fraction was evaporated to 0.5 ml for GC/ECD or GC/MS analysis of PCBs. For the analysis of chlorobenzenes, 5 ml of the extracted solution was cleaned up on the alumina column as stated above. Chlorobenzenes are eluted with 80 ml 2% methylene chloride in hexane for GC/ECD analysis. Chlorophenols in 1 ml of the extract is derivatized by reaction with pentafluorobenzoyl chloride as previously described (Bao et al. 1990) before GC analysis.

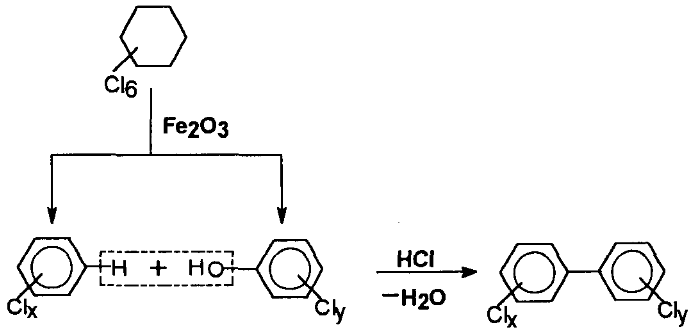
Hydrogen chloride was prepared by adding O-4 -µl sulfuric acid and 10 mg sodium chloride in a one end sealed capillary tubing and then insert the capillary tubing into a glass tube (50X4.2 mm i.d.) containing 2 mg 1,2,3-trichlorobenzene and 2 mg 2,4,6-trichlorphenol. The glass tube was sealed under atmospheric pressure, and heated at 280°C for 2 hr. Extraction and the clean up procedure were the same as mentioned above.

Hitachi 663-50 gas chromatograph equipped with electron capture detection (ECD), and DB-5 fused silica capillary column(30m X 0.25 mm i.d., J&W) was used. Carrier gas was nitrogen at 20 ml/min. Identification of PCBs was carried out with VG-7070E-HF GUMS instrument equipped with an El source (70 ev, 300°C).

The quantification of PCBs was performed by comparison of the response of all peaks in the sample with those in Aroclor mixtures. Congener was identified by comparison to published Arcolor mixtures chromatograms (Capel et al. 1985) and relative retention time of PCB congeners (Mullin et al.1984). Identification of the compounds was based on the selected-ion monitoring (SIM) mode of the GC/MS using two most abundant ions of the molecular ion clusters.

RESULTS AND DISCUSSION

Pyrolysis of HCH at 280°C without Fe_2O_3 showed the formation of ca. 0.15 mg chlorobenzenes/mg HCH (approximately 55% of 1,2,4-tri-, 40% of 1,2,3-tri-, 2% of 1,2,4,5- tetra- and 3% of 1,2,3,4-tetrachlorobenzene) and only about 0.1 µg chlorophenols/mg HCH (2,4-di-, 2,4,6-tri- and 2,3,4,6-tetrachlorophenol), but PCBs were not detected. However, with the presence of 20 mg Fe_2O_3 at 280°C, 0.18 mg chloro-benzenes/mg HCH (approximately 66% of 1,2,4-tri-, 25% of 1,2,3- tri-, 5% of 1,2,4,5-tetra- and 3% of 1,2,3,4-tetrachlorobenzene), 14 µg chloro-



Scheme I Formation of PCBs from the pyrolysis of HCH.

phenols/mg HCH (approximately 13% of 2-, 26% of 2,4-di-, 31% of 2,4,6-tri-, 26% of 2,3,4,6-tetra, 3% of pentachlorophenols) and 0.55 µg PCBs/mg HCH were formed. The experiment revealed that the quantity of chlorbenzenes did not increase any more with increasing quantity of Fe_2O_3 from 0.3 to 40 mg. The total yield of chlorophenols increased with increasing quantity of Fe_2O_3 till the quantity of Fe_2O_3 reaches 20 mg. Chromatograms of chlorobenzenes and chlorophenols formed by the pyrolysis of HCH in the presence of Fe_2O_3 at temperature of 280°C were shown in Fig. 1 and Fig. 2, respectively. The formation of PCBs is shown in Scheme I.

1,2,3-trichlorobenzene and 2,4,6-trichlorophenol were used as model compounds to optimize the condensation reaction. Chlorobenzenes did not react with chlorophenols without HCl. The total yield of PCBs increased with increasing concentration of HCl by increasing of H_2SO_4 from 0 to 4 µl. A combination of HCl and Fe_2O_3 resulted in lower yield of PCBs as compared to the reaction with HCl. Fig. 3 showed the mass fragmentogram of 2,3,4,2',4',6'-hexachlorbiphenyl formed from the condensation reaction of 1,2,3-trichlorbenzene with 2,4,6-trichlorophenol in the presence of Fe_2O_s (28O°C, 2 hr).

Factors effecting the PCBs formation such as the level of Fe_2O_3, temperature and reaction time were systematically studied. It had been found that the total yield of PCBs increased with increasing quantity of Fe_2O_3, followed by a decrease. The later decrease in the total yield of PCBs seemed to indicate the occurrence of oxidative degradation of PCBs by Fe_2O_3 This hinted that Fe_2O_3 played a dual role because it was necessary for the formation of chlorophenols and synthesis of PCBs, but it also catalyzed the oxidative destruction of PCBs. Fig. 4 showed the total yield of PCBs as a function of Fe_2O_s level (4A; 280°C, 2 hr), temperature (4B; 20 mg Fe_2O_3, 2 hr) and reaction time (4C; 20 mg Fe_2O_3, 28O°C).

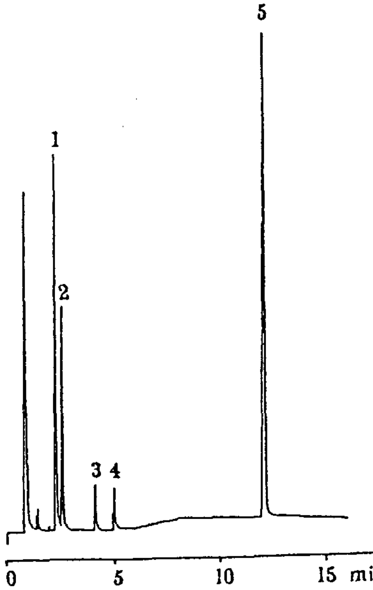


Figure 1 Chromatogram of chlorobenzenes formed by the pyrolysis of HCH in the presence of Fe_2O_3. Temperature program: 120°C 5 min, 4°C /min, 190°C 10 min. 0.2 μl injection. Peak assignment: 1=1,2,4-trichlorobenzene,2=1,2,3-trichlorobenzene,3=1,2,4,5-tetrachlorobenzene, 4=1,2,3,4-tetrachlorobenzene,S=HCH.

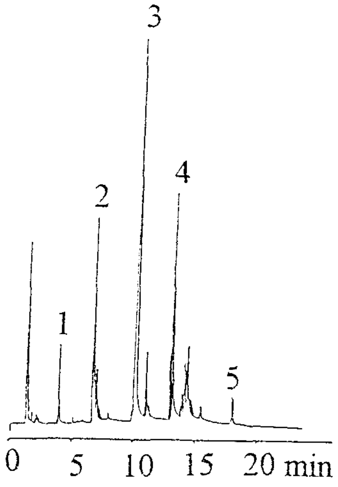


Figure 2 Chromatogram of chlorophenols formed by pyrolysis of HCH in the presence of Fe_2O_3. Temperature program: 160°C 5 min, 4°C/min, 240°C 10 min. 2 μl injection. Peak assignment: 1=2-chlorophenol,2=2,4-dichlorophenol, 3=2,4,6-trichlorophenol, 4=2,3,4,6-tetrachlorophenol, 5= pentachlorophenol.

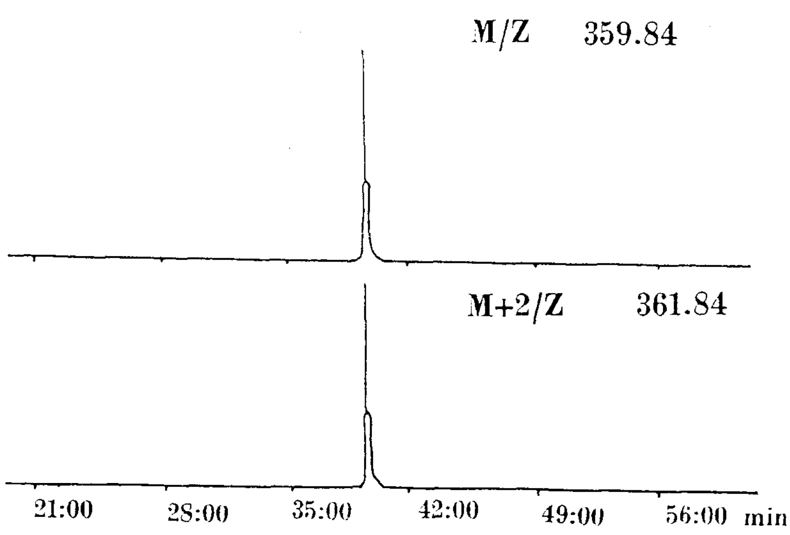


Figure 3 Mass fragmentogram of 2,3,4,2',4',6'-hexachlorobiphenyl from the condensation reaction of 1,2,3-trichlorobenzene and 2,4,6-trichlorophenol in the presence of HCl. Capillary fused silica column: 50 m X 0.32 mm i.d. BP-5 (SGE). 2 µl splitless injection. Temperature program: 50°C,20°C/min, 180°C, 4°C/min, 290°C 30 min.

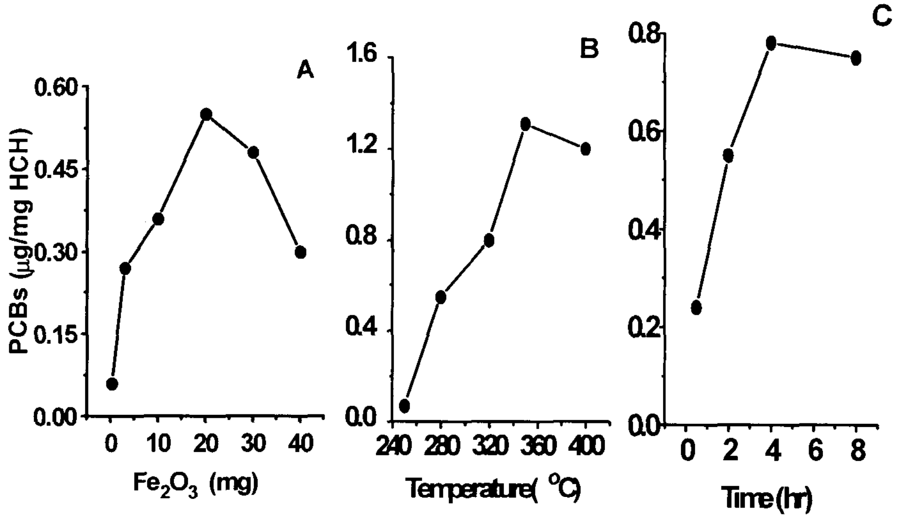


Figure. 4 Effect of (A) quantity of Fe_2O_3, (B) temperature and (C) reaction time on total yield of PCBs.

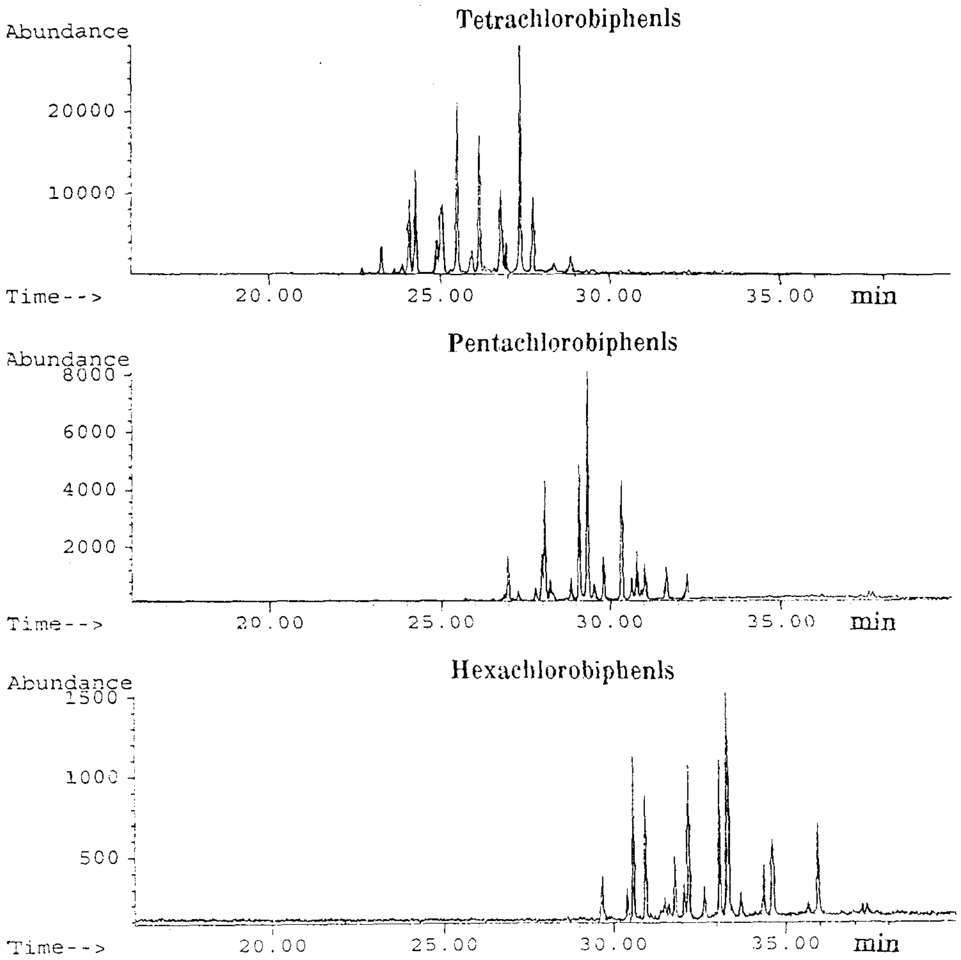


Figure. 5 Mass fragmentogram showing elution of PCBs as transformation products of HCH on heating 280% in the presence of Fe_2O_3. Capillary fused silica column: 30 m X 0.25 mm i.d. HP-5 (HP). 0.2 µl splitless injection. Temperature program: 90°C 2 min, l0°C/min, 120°C, 4°C /min, 280°C 20 min.

Fig.5 shows PCBs formed from the pyrolysis of HCH at 280°C in the presence of Fe_2O_3. The main products of PCBs were tetra- and pentachlorobiphenyl congeners. The total quantity of hexachlorobiphenyl isomers was one order of magnitude lower than that of tetrachlorinated isomers. Heptachlorobiphenyl isomers were relatively minor components. Octa- to decachlorobiphenyl congeners were not detected. The pattern of PCBs distribution suggested that mono- and dichlorophenols reacted with trichlorobenzenes more readily than the tri-, tetra- and pentachlorophenol.

Acknowledgments. Financial support from National Natural Science

Foundation of China is gratefully acknowledged. Additional thanks to Dr. Chu Shaogang for discussion.

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