

## MECHANISM OF FORMATION OF POLYCHLORINATED BIPHENYLS FROM THE PYROLYSIS OF CHLOROBENZENES

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### Introduction

Formation of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in combustion processes of chlorine containing organic materials has been frequently studied. Precursors for PCDD/Fs are aromatic structures like chlorobenzenes and chlorophenols[1]. However, few studies on the formation of polychlorinated biphenyls(PCBs) from pyrolysis of chlorine containing organic materials have been published. Buser observed the formation of small quantities of higher chlorinated biphenyls from the pyrolysis of chlorobenzenes at 620°C, but the mechanism of the formation of PCBs had not been investigated[2]. Sommeling suggested a hypothesis pathway of formation of PCBs from the gas-phase oxychlorination of chlorobenzenes[1], but few experiments supported the hypothesis have been reported.

We have previously studied the mechanism of formation of PCBs from the pyrolysis of hexachlorocyclohexane(HCH) in the presence of iron (III) oxide[3]. Chlorobenzenes, chlorophenols, hydrogen chloride, and about 0.55 µg PCBs/mg HCH were formed during the process. At this study, chlorobenzenes are used instead of HCH as starting compounds, formation of PCBs takes place at hydrogen chloride atmosphere.

### Material and Methods

The experiments were carried out in a glass tube. Hydrogen chloride was prepared by adding about 5 µl sulfuric acid and 15 mg cupric chloride anhydrous in a one end sealed capillary tubing and then inserted the capillary tubing into a glass tube (50×4.2 mm i.d.) that contained 4 mg different kinds of chlorobenzenes. The glass tube was sealed under atmospheric pressure, and heated at 280°C for 2 h. After cooling, the tube was crushed and the reaction products were extracted with 25 ml 5%(v/v) toluene in n-hexane under ultrasonication. The extract was cleaned up on an alumina column(250×10 mm i. d., basic alumina, activated at temperature of 660°C for 6 h) that contained 8 g basic alumina. The column was washed with 50 ml hexane, then eluted with 50 ml 2% (v/v) methylene chloride in hexane. The last fraction was evaporated to 0.5 ml for GC/ECD or GC/MS analysis of PCBs.

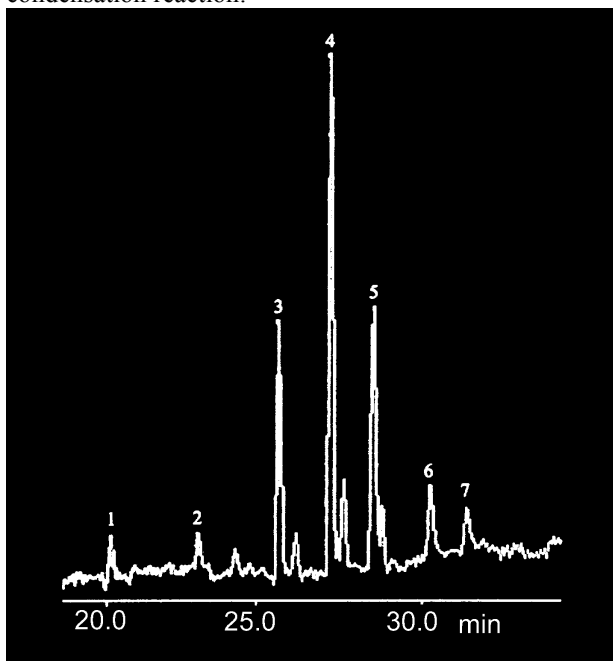
Hitachi 663-50 gas chromatograph equipped with electron capture detection (ECD), and DB-5 fused silica capillary column(30 m×0.25 mm i.d., J&W) was used. Carrier gas was nitrogen at 20 ml/min. Identification of PCBs was carried out with VG-Trio 2000 GC/MS instrument equipped with an EI source (70 ev). Capillary fused silica column: 30 m×0.25 mm i.d., HT-8 (SGE). Temperature program: 160°C 2min, 5°C /min, 300°C 30 min.

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[4]. Identification of the compounds was based on the selected-ion monitoring (SIM) mode of the GC/MS using two most abundant ions of PCBs molecular ion clusters.

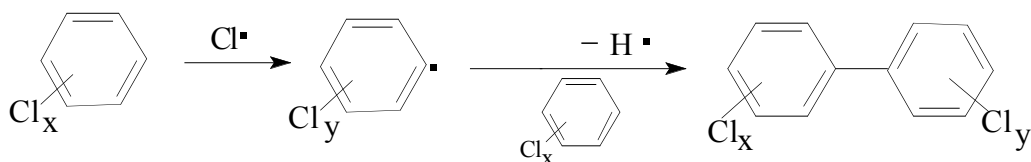
## Results and Discussion

Figure 1 shows PCBs formed from the pyrolysis of 1,2,3-trichlorobenzene at 280°C in the presence of HCl. Up to 0.7 µg PCBs/mg 1,2,3-trichlorobenzene was produced through the condensation reaction.



**Figure 1** Mass fragmentogram of PCBs from the condensation reaction of 1,2,3-trichlorobenzene

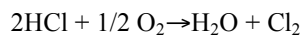
Peak assignment: 1, 2=pentachlorobiphenyl, 3=2,2',3,3',4,4'-hexachlorobiphenyl, 4=hexachlorobiphenyl, 5=2,2',3,3',4,4',5'-heptachlorobiphenyl, 6=heptachlorobiphenyl, 7=2,2',3,3',4,4',5,5'-octachlorobiphenyl.



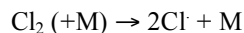
**Scheme I** Formation of PCBs from the pyrolysis of chlorobenzenes.

Sommeling suggested a hypothesis pathway of formation of PCBs from the gas-phase oxychlorination of chlorobenzenes as scheme 1[1]. Our experiments show that this pathway of

formation of PCBs can be really occurred. Free chlorine can be formed according to following equation



This reaction can be catalyzed by  $\text{CuCl}_2$ . Free-radical chlorine can be produced as following equation



1,3-dichlorobenzene, 1,2,3-trichlorobenzene, 1,2,4,5-tetrachlorobenzene, 1,2,3,4-tetrachlorobenzene and pentachlorobenzene were used as model compounds to optimize the condensation reaction. Lower chlorinated benzenes produce more PCBs than that of higher ones.

Factors effecting the PCBs formation such as  $\text{CuCl}_2$ , temperature and reaction time were studied.  $\text{NaCl}$  was used instead of  $\text{CuCl}_2$  as chlorine source. It was observed that less PCBs were produced in the presence of  $\text{NaCl}$  than that of  $\text{CuCl}_2$ . This indicates that  $\text{CuCl}_2$  plays the catalyzing role in converting  $\text{HCl}$  into  $\text{Cl}_2$ . It was found that the total yield of PCBs increased with increasing temperature. At  $350^\circ\text{C}$ , about 5 times more PCBs produced than that of at  $280^\circ\text{C}$ . No significant variances in amount of PCBs were observed when reaction time was longer than 2 h.

### Acknowledgments

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