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Mechanism of PCBs formation from the pyrolysis of chlorobenzenes

Peng-Yan Liu, Ming-Hui Zheng *, Bing Zhang, Xiao-Bai Xu

Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, P.O. Box 2871, Beijing 100085, People's Republic of China

Abstract

Polychlorinated biphenyls (PCBs) were formed by pyrolysis of chlorobenzenes in a HCl atmosphere. Varieties of substituted chlorobenzenes were used as model compounds to optimize the condensation reaction. Lower chlorinated benzenes produce more PCBs than that of higher ones. Up to 0.7 μg PCBs/mg 1,2,3-trichlorobenzene was produced through the condensation reaction. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Polychlorinated biphenyls; Chlorobenzenes; Formation; Condensation; Mechanism

1. Introduction

Formation of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in combustion processes of chlorine containing organic materials has been frequently studied. The most important precursors for PCDD/Fs are aromatic structures like chlorobenzenes and chlorophenols (Buser, 1979; Sommeling et al., 1994; Born et al., 1993). A better understanding of the mechanism of PCDD/Fs formation provides a better guidance for devising technical control measures and improving the performance of practical combustion equipment to reduce PCDD/Fs emissions. However, few studies on the formation of polychlorinated biphenyls (PCBs) from pyrolysis or combustion processes of chlorine containing organic materials have been published. Buser, 1979 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. Dorrepaal and Louw (1978) and Sommeling et al. (1993) proved that formation of PCBs from the gas-phase oxychlorination of chlorobenzenes, but few systematic experiments on formation of PCBs have been reported.

Bao et al. (1993) reported findings of PCBs in the waste from reaction stills of a chemical factory in China. The factory produces trichlorobenzenes by pyrolysis of hexachlorocyclohexane. Since HCl atmosphere exits in the reaction still, this made us think HCl may play a role in formation of PCBs. At this study, pyrolysis of chlorobenzenes takes place in a HCl atmosphere.

2. Materials and methods

The experiments were carried out in glass tubes. HCl was prepared by adding about 5 μl sulfuric acid and 15 mg anhydrous cupric chloride in a one-end sealed capillary tubing (1.5 mm i.d.) and then inserted the capillary tubing into another tube (50 × 4.2 mm^2 i.d.) that contained 4 mg of different kinds of chlorinated benzenes. The glass tube was sealed under atmospheric pressure, and heated in an oven. When the tube was removed from the oven, it cooled at room temperature. 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

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* Correspondence author. Fax: +86-10-6292-3563.

E-mail address: zhengmh@mail.rcees.ac.cn (M.-H. Zheng).

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alumina column (250 × 10 mm^2 i.d., with basic alumina, which is activated at temperature of 660°C for 6 h). We first elute with 50 ml *n*-hexane, and then 80 ml 2% (v/v) methylene chloride in *n*-hexane. The last elute was evaporated to 0.5 ml for GC/ECD or GC/MS analysis of PCBs.

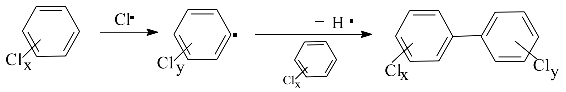
Three equipments were used in this study. Hitachi 663-50 GC equipped with ECD and DB-5 capillary column (30 m × 0.25 mm i.d., J&W). VG-Trio 2000 GC/MS equipped with an EI source and HT-8 capillary column (30 m × 0.25 mm i.d.,SGE). Hewlett–Packard 6890 GC equipped with 5973 MSD and HP-5 capillary column (30 m × 0.25 mm i.d.).

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. Congener was identified by comparison to published Arcolor mixtures chromatograms (Capel et al., 1985).

The quantification of PCBs was performed by comparison of the response of all peaks in the sample with those in Aroclor mixtures.

3. Results and discussion

Dorrepaal and Louw, 1978 and Sommeling et al. (1993) reported the thermally initiated free-radical chain chlorination of a variety of substituted benzenes in the gas phase. They suggested a pathway of formation of PCBs from chlorobenzenes as shown in Scheme 1.



Scheme 1. Formation of PCBs from the pyrolysis of chlorobenzenes.

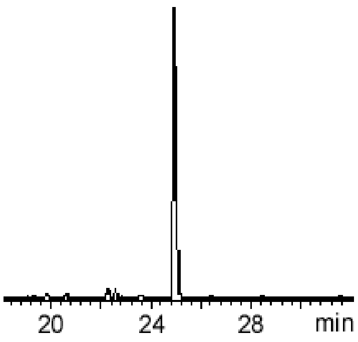


Fig. 1. Mass fragmentogram of 2,2′,3,3′,4,4′,5,5′-octachlorobiphenyl from the condensation reaction of 1,2,3,4-tetrachlorobenzene (HP GC/MS).

If HCl is present in a combustion system, various equilibrium reactions may occur to provide chlorination agents. These reactions can be catalyzed by $CuCl_2$. Free-radical chlorine can be produced as following equations:

$$2HCl + 1/2\ O_2 \rightarrow H_2O + Cl_2$$

$$Cl_2(+M) \rightarrow 2Cl^{\cdot} + M$$

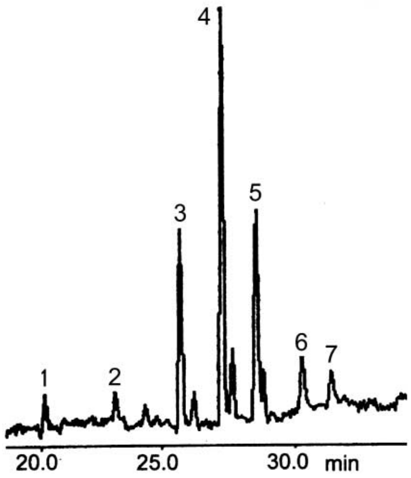


Fig. 2. Mass fragmentogram of PCBs from the condensation reaction of 1,2,3-trichlorobenzene at 280°C (VG GC/MS); peak assignment: 1, 2 = penta-, 3 = 2,2′,3,3′,4,4′-hexa-, 4 = hexa- 5 = 2,2′,3,3′,4,4′,5-hepta-, 6 = hepta-, 7 = 2,2′,3,3′4,4′,5,5′-octachlorobiphenyl.

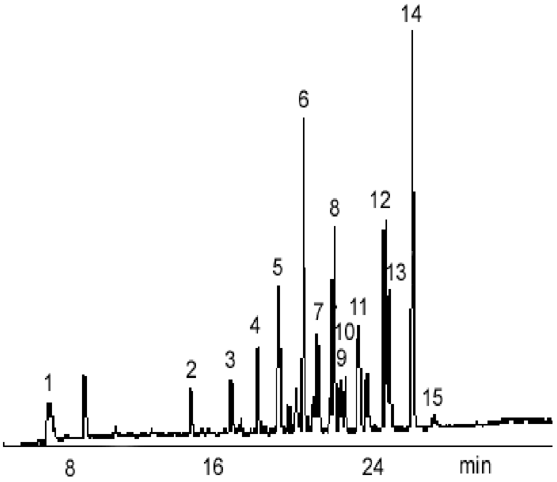


Fig. 3. TIC chromatogram of PCBs from the condensation reaction of 1,2,3-trichlorobenzene at 450°C (HP GC/MS); peak assignment: 1 = hexachlorobenzene, 2,3 = penta-, 4,5,6 = hexa-, 7,8,11 = hepta-, 9,10,12,13 = octa-, 14 = nona-, 15 = decachlorobiphenyl.

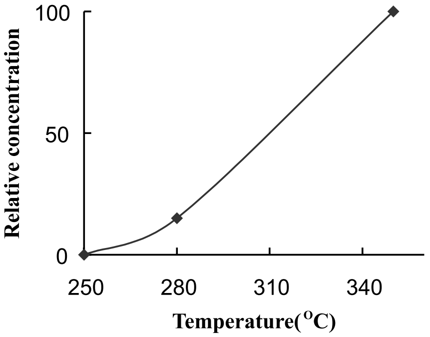


Fig. 4. Effect of temperature on the yield of PCBs.

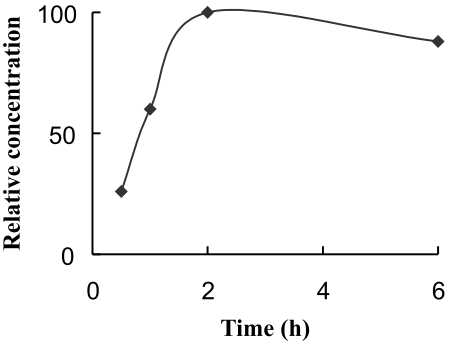


Fig. 5. Effect of reaction time on the yield of PCBs.

1,3-dichlorobenzene, 1,2,3-trichlorobenzene 1,2,4,5-tetrachloro-benzene, 1,2,3,4-tetra-chlorobenzene and pentachlorobenzene were used as model compounds to optimize the condensation reaction. Lower chlorinated benzenes produce more PCBs than that of higher ones. Up to 0.7 μg PCBs/mg 1,2,3-trichlorobenzene was produced through the condensation reaction.

We use 1,2,3,4-tetrachlorobenzene as starting compound, while it was heated at 280°C for 2 h, the main product of the reaction is octachlorobiphenyl. This can be see from Figs. 1–3 show the mass fragmentogram and total ion current (TIC) chromatogram of PCBs from condensation of 1,2,3-trichlorobenzene at different temperature, respectively.

Factors effecting the PCBs formation such as $CuCl_2$, temperature and reaction time were studied. NaCl was used instead of $CuCl_2$ as chlorine source. It was observed that less PCBs were produced in the presence of NaCl than that of $CuCl_2$. This indicates that $CuCl_2$ plays the catalyzing role in converting HCl into Cl_2. It was found that the total yield of PCBs increased with increasing temperature (Fig. 4). As can be seen from Fig. 5, no significant variances in amount of PCBs were observed when reaction time was longer than 2 h.

Acknowledgements

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