

Mechanism of Formation of PCDD/Fs from Production of Trichlorobenzenes

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Introduction

Bao et al. reported findings about 10% of polychlorinated dibenzo-dioxins(PCDDs) and dibenzofurans(PCDFs) in the waste from reaction still affiliated to a large chemical factory in northern of China for production of trichlorobenzenes by pyrolysis of non-gamma isomers hexachlorocyclohexane(HCH)(1). Cheng reported of 118 workers in the factory department 44 had clinical signs of chloracne of many years' duration(2). To investigate the mechanism of the formation of PCDD/Fs, a series of experiments were performed.

Sievers et al. noticed the soil contamination of PCDD/Fs from a company residues at several waste disposal sites in Hamburg(3). The production scheme adopted by the company was much like that of the factory in China mentioned above, The mechanisms of formation of PCDD/Fs from pyrolysis of HCH in chemical processes for production of trichlorobenzenes have not been reported.

Material and Methods

30 mg of non-gamma isomers of HCH(98%) with anhydrous ferric chloride was heated in a sealed glass tube(70×3.9 mm i.d.). Parameters of the present investigation to be varied were FeCl_3 from 10-60 mg, the temperature from 250-400°C, reaction time from 0.5-8 h. The reaction products were extracted with 25 ml 5%(v/v) toluene in hexane under ultrasonication.

15 ml of the extract was cleaned up on an alumina column(250×10 mm i.d. with basic alumina, which was activated at temperature of 660°C for 6 h). The column was washed with 80 ml 2%(v/v) methylene chloride in hexane(LC1), and then eluted with 40 ml 50%(v/v) methylene chloride in hexane(LC2). The chlorobenzenes fraction(LC1) was used for direct GC/ECD analysis. The PCDD/Fs fraction(LC2) was concentrated to 1 ml and was used for GC/MS analysis. Chlorophenols in 1 ml aliquot extract was reacted with pentafluorobenzoyl chloride before GC analysis.

Hitachi 663-50 gas chromatograph equipped with electron capture detection(ECD). DB-5 fused silica capillary column(30×0.25 mm i.d., J&W) was used for analyses of chlorobenzenes and chlorophenols. Analyses for PCDD/Fs were carried out with VG-7070E-HF GC/MS instrument equipped with EI source (70 ev, 300°C). Capillary fused silica column. 60 m×0.32 mm i.d. SP 2331(Supelco).

Results and Discussion

Pyrolysis of HCH at 280°C without FeCl₃ showed that about 0.15 mg chloro-benzenes/mg HCH and only about 0.1 µg chlorophenols/mg HCH were formed, but PCDD/Fs were not detected. However in the presence of 20 mg FeCl₃ at temperature of 280 °C, 0.3 mg chlorobenzenes/mg HCH and 2 µg chlorophenols/mg HCH) and 0.3 µg PCDD/Fs /mg HCH were formed. Chromatograms of chlorobenzenes and chlorophenols formed by the pyrolysis of of HCH in the presence of 20 mg FeCl₃ at temperature of 280°C are shown in Fig.1 and Fig.2 respectively.

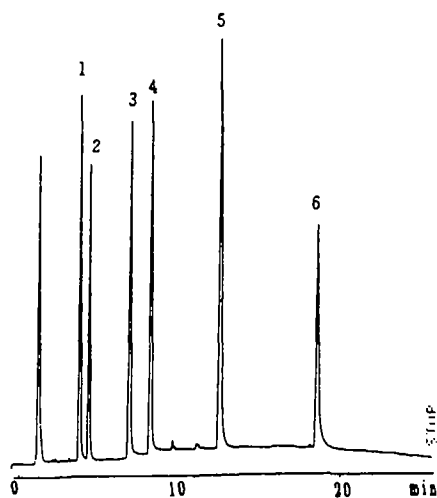


Fig. 1 GC chromatogram of chlorobenzenes formed by the pyrolysis of HCH in the presence of FeCl₃

1=1,2,4-trichlorobenzene, 2=1,2,3-trichlorobenzene, 3=1,2,4,5 -tetrachlorobenzene, 4=1,2,3, 4-tetrachlorobenzene, 5=pentachlorobenzene, 6= α -HCH

Table 1 shows the pattern of PCDD/Fs from products of the laboratory experiments and waste of the chemical factory.

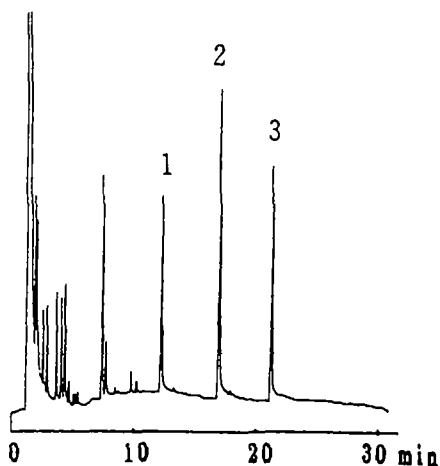


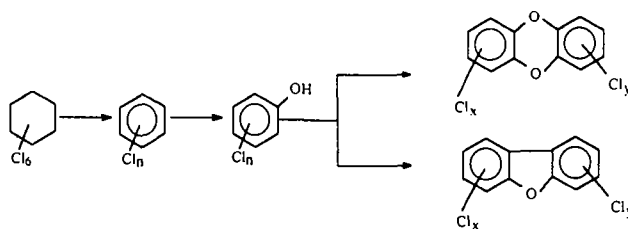
Fig. 2 GC chromatogram of pentafluorobenzoylated chlorophenols formed by the pyrolysis of HCH in the presence of FeCl_3

1=2,4-dichlorophenol, 2=2,4,6-trichlorophenol, 3=pentachlorophenol

A comparison of the PCDD/F isomer distributions shows, (1) hexa- to octachlorodibenzo-dioxins and dibenzofurans are dominated, especially for octachlorodibenzo-dioxin; (2) among tetra- to hexa- substitutes the quantities of PCDFs surpass PCDDs, and among hepta- and octachloro- substitutes PCDDs surpass PCDFs.

It can be seen that FeCl_3 plays an important part in formation of PCDD/Fs from pyrolysis of HCH. FeCl_3 can be originated from the corrosion of reaction still. In fact, 1-4% of Fe^{3+} was detected in the waste from the chemical factory.

The formation of PCDD/Fs requires basically a reaction pathway as depicted in scheme 1.



Scheme 1. Formation of PCDD/Fs from the pyrolysis of HCH

Table 1 PCDD/Fs from the products of the laboratory experiments and waste of the chemical factory ($\mu\text{g/g}$)

| -PCDD/Fs | Products of lab. Experiments | Chemical factory waste |
|--------------------|------------------------------|------------------------|
| T ₄ CDD | 0.3 | 1.3 |
| P ₅ CDD | ND | 6.5 |
| H ₆ CDD | 14.2 | 498 |
| H ₇ CDD | 9.5 | 36377 |
| OCDD | 227.0 | 55959 |
| PCDDs | 251.0 | 92841 |
| T ₄ CDF | 10.8 | 23.1 |
| P ₅ CDF | 22.1 | 360 |
| H ₆ CDF | 19.0 | 1478 |
| H ₇ CDF | 1.6 | 1754 |
| OCDF | 7.5 | 983 |
| PCDFs | 61 | 9598 |

Acknowledgments

Financial support from National Natural Science Foundation of China (grant no. 29707003) is gratefully acknowledged.

References

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