

Chemical Decomposition of Toxic Organic Chlorine Compounds

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1. Introduction

Polychlorinated biphenyls (PCBs) have been used widely as a heat medium, electrical insulating oil, etc., due to its high chemical stability and ability to insulate electricity. However, as it was revealed that PCBs, when discharged to the environment, accumulated in vivo and caused liver disorder, in Japan, the production and use of PCBs was banned in 1972. The cumulative amount of PCBs produced in the world was about 1 million tons up to 1970 and that in Japan amounted to about 60 thousand tons by 1972. Electrical equipment involving the use of PCBs such as capacitor, transformer, etc., is currently being used in large quantities and the custody of one becoming obsolete is obligated. As the result of custody of such equipment over a long period of time, the containers become more and more time worn with increased danger of PCB leakage. On the other hand, according to the survey of custodial circumstance of PCB waste conducted in 1993, approximately 7% of the equipment were lost. These are reasons why prompt establishment of a technique that can make PCB waste non-toxic is desired.

The base catalyzed decomposition process (BCD process) is a chemical process of decomposing PCBs developed by the United States Environmental Protection Agency (US-EPA). The decomposing reaction in BCD process is explained as follows:

Hydrogen radical is generated from paraffin oil by catalytic dehydrogenation reaction and chlorine atoms of PCBs are substituted thereby biphenyl is formed as a product. In this reaction, chlorine is neutralized with sodium hydroxide into sodium chloride. The produced biphenyl is considered to be readily combustible together with paraffin oil without generating toxic substances.

Since the early literature contained few quantitative reports of PCB congeners generated and/or degraded in BCD process, the present authors examined them and obtained the time-course of PCB decomposition. We also examined whether toxic substances like dioxins would

be generated in this process or not.

2. Experimental

2.1 Apparatus

The structure of the apparatus used for the experiment is shown in Fig. 1. The apparatus consists of a 300-ml three neck flask, a condenser, a mantle heater and a stirrer and stirring was carried out at 400 rpm. In the trap receiver is condensed water formed by the reaction.

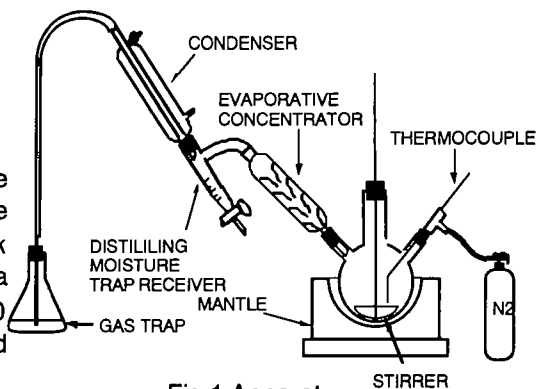


Fig.1 Apparatus

2.2 Methods

Kanechlor KC-300 (equivalent to Aroclor 1242) was used as PCBs and paraffin oil having a function of a hydrogen donor and fuel oil which largely contained components with a high boiling point and which was cheap and readily available were used.

Pre-determined amounts of PCBs, sodium hydroxide and carbonaceous catalyst were added to 150 ml of fuel oil and the mixture was heated in nitrogenous atmosphere at around 300 to 350 °C for several hours and the PCBs concentration was measured before, during and after the reaction.

The analytical instrument used was GC/MS (HP5890 Series II/5971) with a column of HP-5MS (30m × 0.25mm, 0.25 μm film-thickness).

Experiment 1: Kanechlor with a PCB concentration of 24000 ppm was subjected to decomposition treatment under the conditions described above and the concentration of each of the PCB congeners was measured to obtain the time-course of PCB decomposition (minimum detectable concentration: 1 μg/g).

Experiment 2: Kanechlor of 37000 ppm was subjected to decomposition treatment under the conditions described above and the concentration of each of the PCB congeners was measured to obtain the time-course of PCB decomposition. The sample was cleaned up with alumina column, silica gel column, etc. to improve analytical precision (minimum detectable concentration: 0.2 μg/g).

Experiment 3: Kanechlor of 37000 ppm was subjected to decomposition treatment under the conditions described above and formation of toxic by-products such as dioxins was examined.

3. Results and Discussion

3.1 Experiment 1

Fig. 2 shows the time-course of PCB decomposition and that of the temperature in the flask. In thirty minutes after the start of the experiment, the temperature reached to 300 °C and about 70 % of PCBs were decomposed after one hour. After two hours, the PCBs concentration was reduced to 1 ppm or less.

AGC/MS chromatogram of the sample before heating is shown in Fig. 3. unknown compounds

contained in fuel oil were observed within the retention time of 8.6 - 10.6 minutes, di-chloro biphenyl within that of 11.7 - 13.3 minutes, tri-chloro biphenyl within 13.3 - 16.0 minutes, tetra-chloro biphenyl within 16.0 - 19.1 minutes and penta- within 18.8 - 22.9 minutes. Mono-chloro biphenyls as well as higher chlorinated biphenyls were not observed in this sample.

Fig. 4 shows the chromatogram one hour after the start of the experiment. A peak of biphenyl at the retention time of 9.0 minutes and three peaks of mono-chloro biphenyl at 10.1, 10.9 and 11.1 minutes, respectively, were newly observed. The peaks of di-chloro biphenyl increased, those of tri-chloro biphenyl decreased and tetra- and higher chloro compounds were not observed any more. As Fig. 5 shows the chromatogram two hours after the beginning of the experiment, the peak of biphenyl is prominent and the presence of PCBs is not observed. It was ascertained that the small peaks within 9.1 - 10.6 minutes were those of unknown compounds contained in fuel oil.

3.2 Experiment 2

The periodical change of the concentration of each

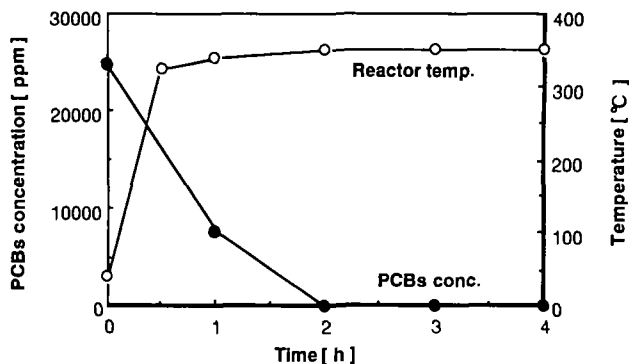


Fig.2 Time-course of PCB decomposition and temperature

Table.1 Decomposition of PCBs by BCD process (Experiment 2)

PCB	Reaction time (min)				
	0	30	60	120	180
Mono-	<2	610	6400	12	ND
Di-	3400	20000	3300	ND	ND
Tri-	22000	16000	140	ND	ND
Tetra-	11000	1800	1.8	ND	ND
Penta-	490	1.2	ND	ND	ND
Hexa-	32	ND	ND	ND	ND
Hepta-	5.1	ND	ND	ND	ND
Octa-	ND	ND	ND	ND	ND
Nona-	ND	ND	ND	ND	ND
Deca-	ND	ND	ND	ND	ND
Total PCBs	37000	38000	9800	12	ND

Unit: $\mu\text{g/g}$, ND: $<0.2\mu\text{g/g}$

Table.2 Decomposition of dioxins/furans (Experiment 3)

	KC-300	After 2 hours
Dibenzo-p-dioxin		
Total PCDDs	0	0
Dibenzofuran		
2,3,7,8-T4CDF	0.20	ND
T4CDFs	4.00	ND
1,2,3,7,8-P5CDF	0.09	ND
2,3,4,7,8-P5CDF	0.08	ND
P5CDFs	1.10	ND
2,3,7,8-substituted H6CDFs	0.08	ND
H6CDFs	0.27	ND
2,3,7,8-substituted H7CDFs	0.03	ND
H7CDFs	0.05	ND
O8CDF	0.01	ND
Total PCDFs	5.40	0
Total PCDDs+ Total PCDFs	5.40	0

unit: $\mu\text{g/g}$

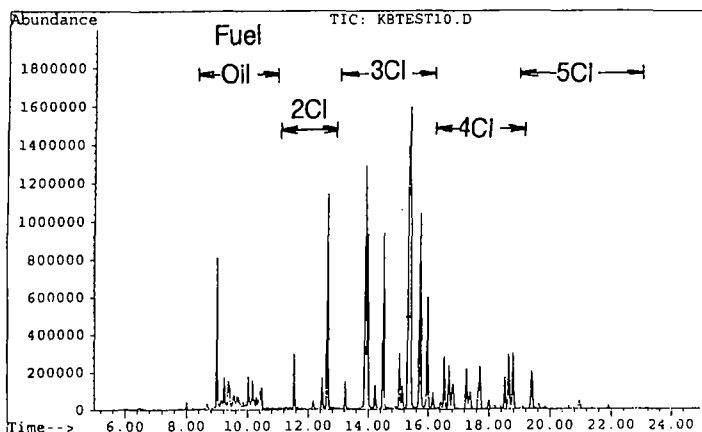


Fig.3 GC/MS chromatogram of PCBs before treatment (Experiment 1)

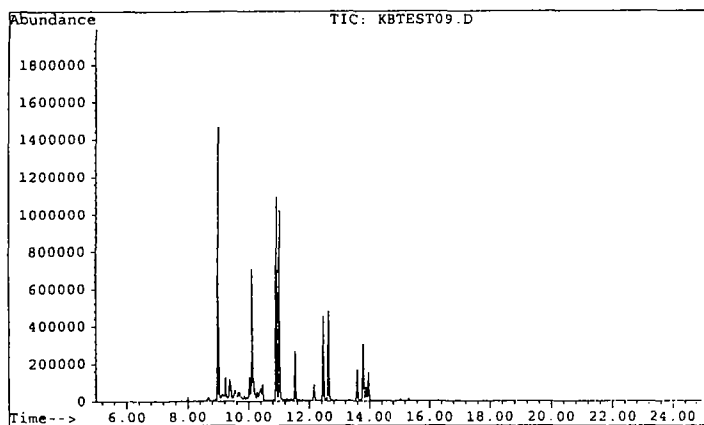


Fig.4 GC/MS chromatogram after 1 hour (Experiment 1)

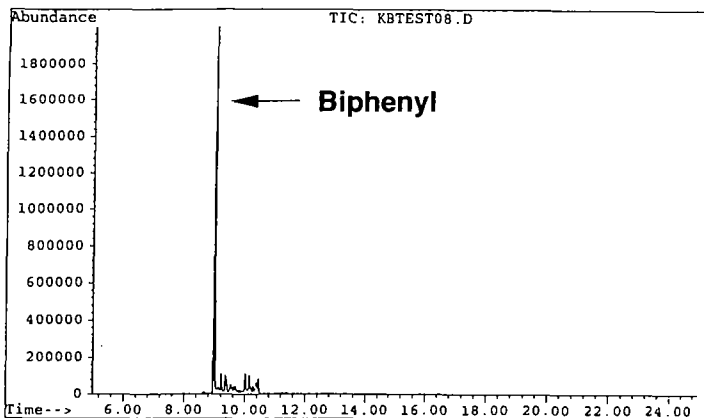


Fig.5 GC/MS chromatogram after 2 hours (Experiment 1)

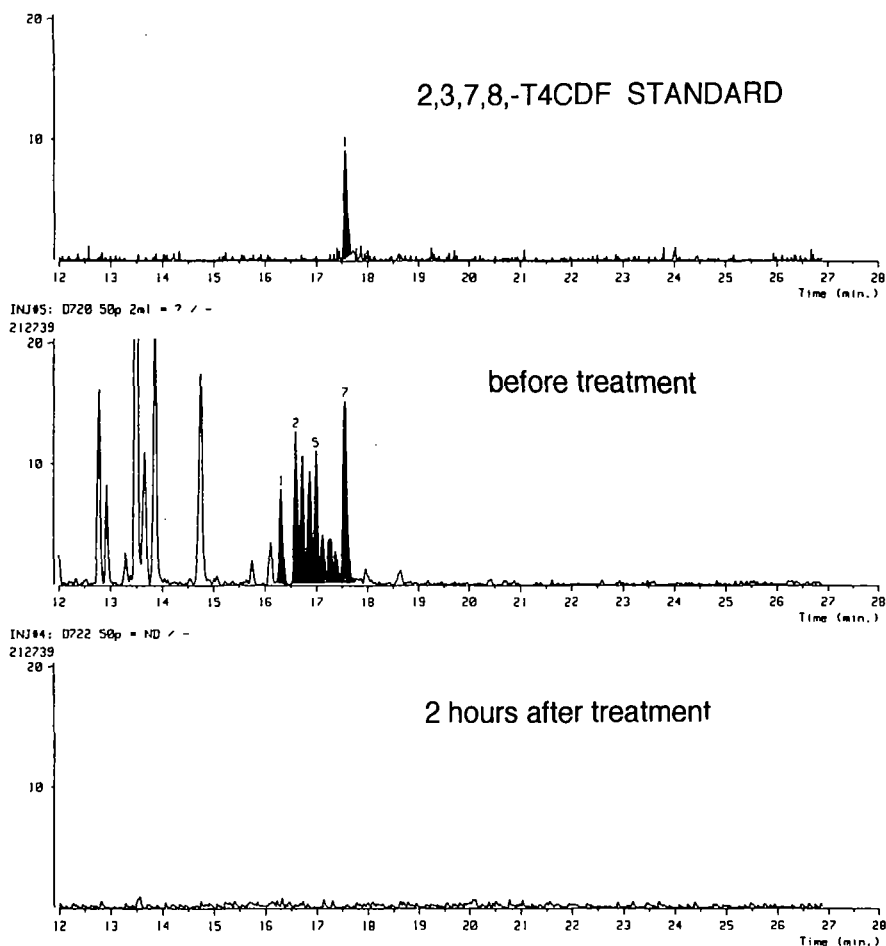


Fig.6 Decomposition of T4CDF shown by GC/MS chromatograms

congener of PCBs is shown in Table 1. The sample before treatment contained the largest amount of tri-chloro biphenyl which was $22000 \mu\text{g/g}$ followed by $11000 \mu\text{g/g}$ of tetra-chloro biphenyl and $3400 \mu\text{g/g}$ of di-chloro biphenyl and the presence of up to hepta-chloro biphenyl with minimum detectable concentration being $0.2 \mu\text{g/g}$ was observed. After 30 minutes of experiment, dechlorination reaction proceeded to some extent and di-chloro biphenyl was largest in quantity increasing to $20000 \mu\text{g/g}$ while tri-chloro biphenyl decreased and hexa- and higher chlorine compounds were not detected. After 60 minutes, the peak shifted to mono-chloro biphenyl which increased to $6400 \mu\text{g/g}$ while di-, tri- and tetra-chloro biphenyl decreased and penta- and higher chlorine compounds were not detected. Further, after 120 minutes, only $12 \mu\text{g/g}$ of mono-chloro biphenyl remained and di- and higher chlorine compounds were no more detected. Decomposition of PCBs was further effected to less than $0.2 \mu\text{g/g}$ as total PCBs after 180 minutes. The decomposition of PCBs is greater than 99.999%

Table.3 GC/MS Conditions

GC Conditions		MS: JEOL SX-102A	
Items	Conditions	Items	Conditions
Instrument	GC: HP5890 SERIES-II	MS: JEOL SX-102A	
Column	DB-5 60m(Length)×0.25mm(I.D.) 0.25 μm(Film Thickness)	Ion Source	EI
Column Temp.	150(1 min hold) 15°C/min 250°C(0 min hold) 6°C/min 290°C	Ion Source Temp.	270 °C
Injection Method	Splitless (1 min)	Ionization Energy	70 eV
Injection Temp.	300°C	Ionization Current	600 μA
Carrier Gas	He ml/min	Accel. Voltage	10 kV
Injection Volume	1 μl	Resolution	10000

complete in the time studied.

3.3 Experiment 3

The KC-300 was analyzed and found to contain 5.4 ppm of dioxins. Three kinds of GC/MS chromatograms, that is, those of standard sample of 2,3,7,8-T4CDF and of the sample before the experiment and 2 hours after treatment are shown in Fig. 6. While the peaks of PCBs are present within 12.0 - 16.2 minutes and those of T4CDF within 16.3 - 17.6 minutes before start of the experiment, they are decomposed and all the peaks disappeared after 2 hours (the minimum detectable concentration being 0.2 ng/g). The concentration of dioxins is shown in Table. 2. Thus, it can be understood that the BCD process is remarkably effective also for the decomposition of dioxins and is free from the formation of dioxins.

The condition of GC/MS is shown in Table.3.

4. Conclusion

The BCD process was tested in connection with chemical decomposition of PCBs using an apparatus consisting of a small reactor and a condenser. The results obtained are as follows:

- 1) Higher chlorinated biphenyls are converted to lower chlorinated compounds via stepwise dechlorination and the chlorine free biphenyl is produced.
- 2) It requires 2 to 3 hours for the PCBs concentration to reach to less than 1 ppm.
- 3) Decomposition rate of 99.999% (less than 0.2 μg/g) is readily achieved.
- 4) The BCD process is effective also for the decomposition of dibenzofurans contained in PCBs and no dioxins are produced during the reaction.
- 5) The reaction occurred in the liquid phase with little gas generation; PCBs, PCDF and PCDD could not be detected in exhaust gas.

5. References

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- 3) Tiernan T.O., D.J. Wagel, G.F. VanNess, J.H. Garrett, J.G. Solch, M.S. Hanes, C.J. Rogers, and A. Kornel (1993): Treatment of Complex Chemical Wastes with the Base Catalyzed Decomposition (BCD) Process. DIOXIN' 93, 289-292.