

THE DEGRADATION PRODUCTS OF PCBs BY THE SODIUM DISPERSION METHOD

Yukio Noma¹, Yoshito Mitsuhashi², Kiyoshi Matsuyama², Shin-ichi Sakai³

¹ National Institute for Environmental Studies, 16-2, Onogawa, Tsukuba, Ibaraki 305-8506, Japan

² Toyota Motor Corporation, 1, Toyota-cho, Toyota, Aichi 471-8571, Japan

³ Kyoto University, Environment Preservation Center, Yoshida-Honmachi, Sakyo-ku, Kyoto 606-8501, Japan

Introduction

In Japan, PCBs treatment has been really working, since a special measures law on promotion of waste PCBs management was enacted on June 15 2001. This law is required that waste PCBs be treated within 15 years because wastes containing PCBs have been remained untreated for a long time. The PCBs destruction technologies by chemical dechlorination have been developed and the sodium dispersion method (SD) is now operated in two cities by national program. An actually applicable technique for decomposition of PCBs should be required to be the safe and stable destruction methods. Therefore it is important to study the intermediate substances, the final substances, and by-products through the decomposition process. We have already reported dechlorination pathways of nine PCBs congeners by SD¹. The main reaction by SD is thought to be the dechlorination at low temperature and the polymerization at high temperature². In this study, we investigated the structures of the final degradation products of PCBs by SD, especially polymerized products, and that all organic chlorinated compounds would disappear finally or not.

Materials and Methods

4-chlorobiphenyl for starting materials of reaction was purchased from AccuStandard Co. Quarterphenyls (QPs), *o*-QP, *m*-QP, *p*-QP, *o,p*-QP, *o,m*-QP, and *m,p*-QP, were gifts from a scientist in Hiroshima Prefectural Health and Environment Center, Japan³. 2,2',5,5'-tetrachloro-*p,p*-quaterphenyl was purchased from Ultra Scientific Co. All reactions by SD were carried out in the 500mL glass flask. 500g of hexadecane and 750mg of PCB congeners were stirred and heated to 160 °C in N₂ atmosphere (Table1). And then 25.6% dispersed sodium (<10µm) was added in the flask and the reactions were started. The samples after a reaction for 60 minutes were analyzed mainly by HRGC/HRMS (HP6890/ Autospec Ultima) using with electron ionization (EI), chemical ionization (CI), direct-insertion (DI), selected ion monitoring (SIM), and negative CI (NCI) methods. The samples were also measured by total organic halogen (TOX) analysis using a Mitsubishi Chemistry TOX analyzer, TOX-10.

Table 1 Experimental Conditions

| PCB IUPAC No. | 4-Chlorobiphenyl #3 | Insulation oil Blank (non-PCB) |
|------------------|------------------------|-----------------------------------|
| PCB (mg) | 750 | 0 |
| Hexadecane(g) | 500 | 500 |
| PCB (mg/kg) | 1500 | 0 |
| Cl (mol) | 0.00398 | — |
| SD(g) | 25.6%SD, 46.4g | 25.6%SD, 46.4g |
| Na (mol) | 0.517 | 0.517 |
| Na/Cl (mol/mol) | 130 | — |
| Temp (°C) | 160 | 160 |
| Na diameter (µm) | <10 µm | <10 µm |

Results and Discussion

(1) Final degradation products

The dechlorinated products of 4-chlorobiphenyl were mainly biphenyl, phenylcyclohexadiene, phenylcyclohexene, and phenylcyclohexane, while dicyclohexyl was not detected in these experimental conditions (Figure 1).

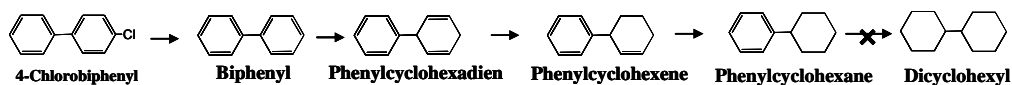


Figure 1 Dechlorinated products of 4-chlorobiphenyl

The polymerized products of 4-chlorobiphenyl were analyzed by some methods. QPs and polychlorinated Quarterphenyls (PCQs) were analyzed because they might be generated by the dechlorination and dimerization reaction of 4-chlorobiphenyl. QPs have six types of isomers involving the bonding positions of phenyl, *o*-QP, *m*-QP, *p*-QP, *o,p*-QP, *o,m*-QP, and *m,p*-QP. PCQs were the remarkable compounds as dimers of PCBs, which were detected in causal rice oil and patient blood of Yusho⁴. PCQs have six skeletal isomers and more than 100,000 chlorine-bonding isomers theoretically. Mono- through tetra-chlorinated QPs were analyzed because tetra-chlorinated QPs were considered to be maximally substituted with chlorines derived from 4-chlorobiphenyl. Therefore the compounds whose mass numbers were 306 (quarterphenyls), 340 (mono-chloroquarterphenyls, MoCQs), 374 (di-chloroquarterphenyls, DiCQs), 408 (tri-chloroquarterphenyls, TrCQs), and 442 (tetra-chloroquarterphenyls, TeCQs) were searched by HRMS-SIM method. When QPs were measured by HRMS-SIM, *p*-QP and *m,p*-QP were detected in sub-ppm level (Figure 2). When PCQs were

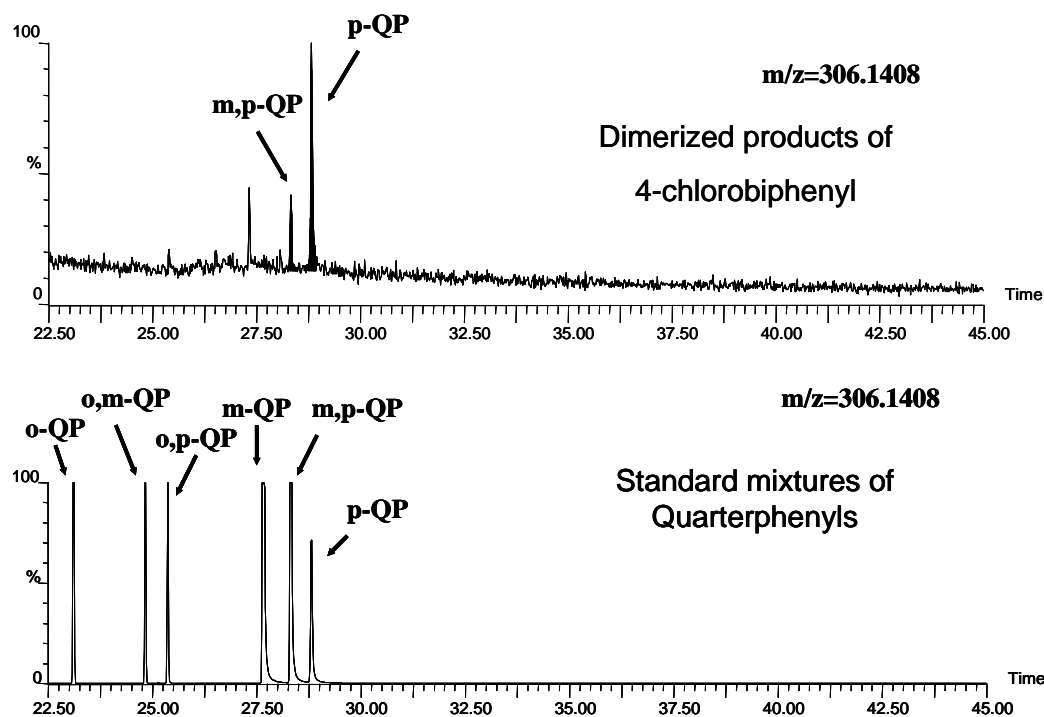


Figure 2 Dimerized products of 4-chlorobiphenyl (HRMS-SIM)

measured by HRMS-SIM, MoCQs, DiCQs, TrCQs, and TeCQs were not detected (Figure 3). By HRMS analysis with DI, m/z 534.4183 and 758.6713 were detected. The mass number of 534.4183 was consistent with 534.4225 as the theoretical precision mass number of $C_{40}H_{54}$ (Figure 4). The mass number of 758.6713 was consistent with 758.6730 as the theoretical precision number of $C_{56}H_{86}$. Therefore they were considered to have $C_{40}H_{54}$ or $C_{56}H_{86}$ as composition formula.

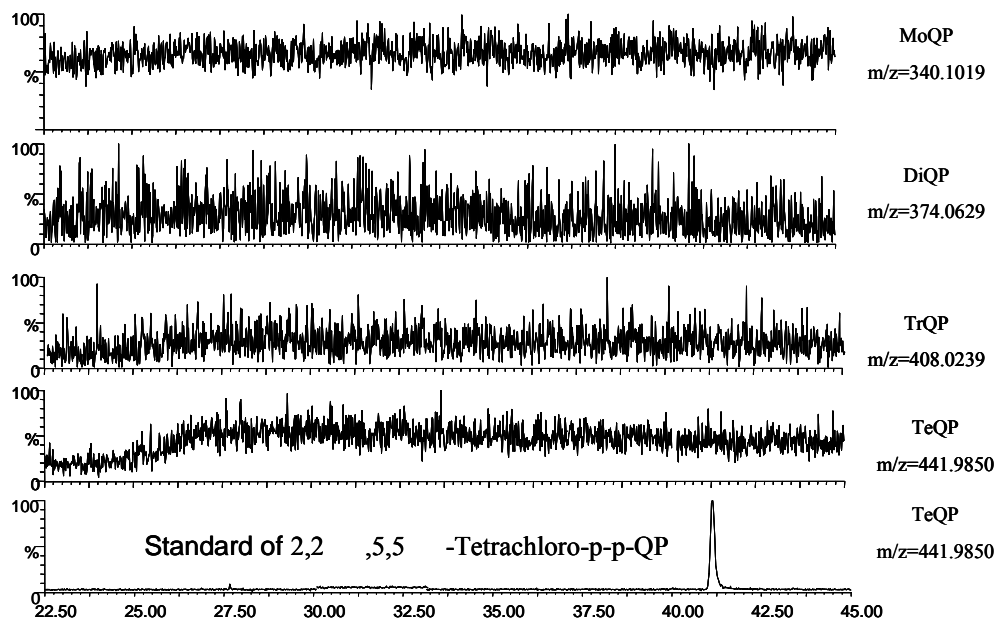


Figure 3 Degradation products of 4-chlorobiphenyl and tetrachloro quaterphenyl (HRMS-SIM)

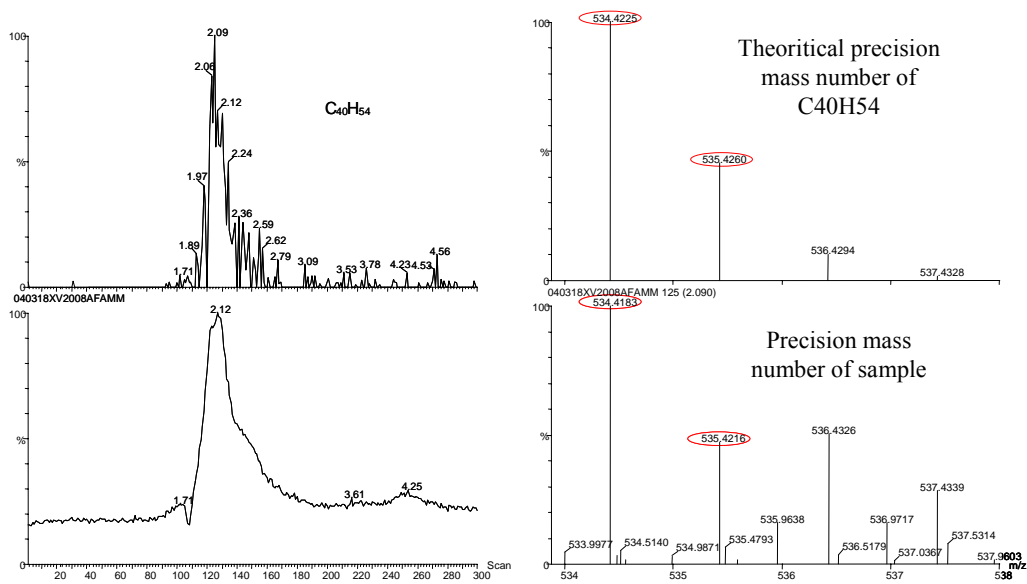


Figure 4 Masschromatogram by DI method (HRMS-EI)

The compound which had $C_{40}H_{54}$ [$C_{24}H_{17} + C_{16}H_{33} + H_4$] was presumed to be the polymerized product which hexadecane added to two phenylcyclohexadiens (Figure 5). The compound which had $C_{56}H_{86}$ [$C_{24}H_{16} + 2(C_{16}H_{33}) + H_4$] was presumed to be the polymerized product which two hexadecanes added to two phenylcyclohexadiens. It was presumed that hexadecane was the source of hydrogen because there was no compound to be a hydrogen source in the reaction system except for hexadecane as the solvent.

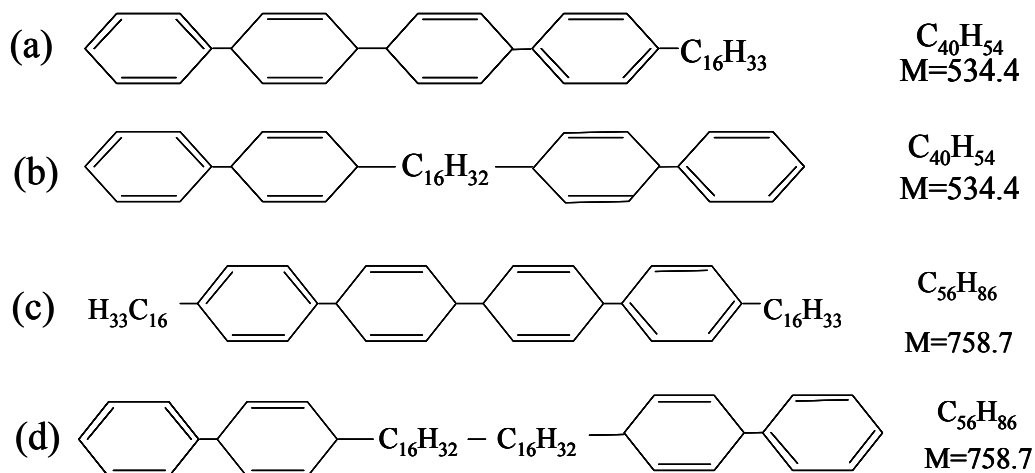


Figure 5 Possible structure of polymerized products of 4-chlorobiphenyl

(2) To check the remaining organic chlorinated compounds

Total organic halogenated compounds in the final products were measured by TOX analysis instrument. These concentrations were below 1 mg/L.

The organic chlorinated compounds were searched by MS analysis because they usually have characteristic mass spectrums by chlorine isotopic ions as the molecular or fragment ions. Major compounds detected were hydrocarbons and no peaks originated from organic chlorinated compound were observed from the results of some MS methods. Moreover, when $m/z=35$ and $m/z=37$ as ^{35}Cl and ^{37}Cl were measured by NCI in order to investigate dechlorination fragment, large peaks with the relative isotope abundance of 3:1 from chlorines were not observed. Thus it was checked that organic chlorinated compounds had not remained finally in a sub-ppm level.

As the results, it was thought the dechlorination and the polymerization were main reactions in the degradation of PCBs by SD, and hexadecane was much concerned in the reactions as the hydrogen source.

Acknowledgements

This study was financially supported by Waste Management Research Grants from the Ministry of the Environment of Japan.

References

1. Noma Y, Mitsuhara Y, Matsuyama K, Sakai S. *Organohalogen Comp*2003;63:280.
2. Ariizumi A, Otsuka T, Kamiyama M, M. Hosomi M. *J. Environ. Chem.*1997;7:793.
3. Mochiike A, Sakamoto I, Hoshita N. *Chem. Pharm. Bull.*1983;3994.
4. Miyata H, Kashimoto T, Kunita N. *J. Food Hyg. Soc. Jpn.*1978;364.