

PATHWAYS FOR THE DEGRADATION OF PCBs BY THE SODIUM DISPERSION METHOD

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Summary

Nine PCB congeners were individually degraded by the sodium dispersion method (S.D.) and the major dechlorination pathways were proposed. The pathways and the reactivity of the chlorines were quite different from photochemical dechlorination (P.C.D.) or catalytic hydro-dechlorination over palladium/carbon catalyst (C.H.D). The dechlorination pathways by S.D. seemed to be dependent on the numbers of chlorine atom and on the positions of the substituted chlorine atom.

Introduction

In Japan, a special measures law on promotion of waste PCBs management requiring that waste PCBs be treated within 15 years was enacted on June 15 2001, because wastes containing PCB have been remained untreated for a long time. The PCBs degradation technologies by chemical dechlorination have been developed and some methods are about to be started. Although PCBs can be degraded by these methods, the degradation mechanisms have not been well studied. Therefore, it is important to study the intermediates, final products, and degradation pathways of any proposed decomposition process. We have already reported dechlorination pathways of nine PCB congeners by P.C.D. and C.H.D.^{1,2} In this study, the same congeners have been degraded by S.D and the differences of the pathways and the reactivity of the chlorines among the three methods were discussed.

Materials and Methods

Nine individual congeners (IUPAC No., #1, #2, #3, #21, #52, #118, #126, #153 and #209) for starting materials of reaction were purchased from AccuStandard Co. All reactions by S.D. were carried out in the 500mL glass flask. 600g of hexadecane and 60mg of PCB congeners were stirred and heated to 60 °C in N₂ atmosphere. And then 10% dispersed sodium (<10µm) was added in the flask and the reactions were started. The aliquots (40mL) of the liquid phase were periodically sampled during the decompositions. The samples were analyzed by GC/MS, Auto Spec-Ultima at a resolution of 10,000 with HT-8 capillary column (0.22mm x 50m x 0.25µm).

Results and Discussion

1. Degradation of monochlorobiphenyls (#1, #2, #3)

Degradation of monochlorobiphenyl mainly produced biphenyl, phenylcyclohexadiene, phenylcyclohexane, and phenylcyclohexane, similar to Ariizumi's report³. We compared three monochlorobiphenyls (M₁CBs) to determine the relative reactivity of the ortho, meta, and para chlorine atoms. The concentration of each of the three congeners was 330 µmol/L at the beginning of the run. Figure 2 shows the concentrations of the M₁CBs at

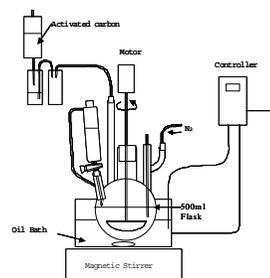


Figure 1 Experimental apparatus

different reaction times. The dechlorination of #3 was a little faster than that of #1 or #2. Therefore, the reactivity of the chlorines is thought to decrease in the order para > meta, ortho. Meanwhile, the chlorine at the ortho position was easily dechlorinated by P.C.D.^{1,4,5} and lost slowest by C.H.D.^{1,2}.

2. Degradation of #21, #52, #118, #126, #153, and #209

Figure 3 shows the major pathways of #21, #52, #118, #126, #153, and #209 on the basis of the analytical results.

2-1. Degradation of 2,3,4-trichlorobiphenyl (#21)

Congener #21, which has three adjacent chlorine substituents, suffers from steric congestion. After 5 min of reaction, the concentration of #7, the meta-dechlorination product, was about twice as high as the concentrations of #5 and #12, the ortho- and para-dechlorination products. We considered that chlorine atom situated between two other chlorines showed high reactivity, because of the steric congestion. The major product of didechlorination was #3, which was produced mainly by ortho dechlorination of #7. In the case of C.H.D., the dechlorination was easy at the para position⁶, while the degradation of #21 was easy at the ortho position by P.C.D.

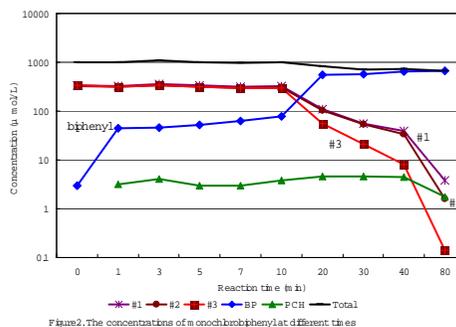


Figure 2. The concentrations of monochlorobiphenyls at different times

2-2. Degradation of 2,2',5,5'-tetrachlorobiphenyl (#52)

Congener #52, the major congener of commercial PCBs, is a symmetrical biphenyl with chlorine substituents in the ortho and meta positions of biphenylring. After 5 min of reaction, the concentration of #26, the ortho-dechlorination product, was about four times that of the meta-dechlorination product. The dechlorination mainly occurred at the ortho position and produced #26 and #11, similar to P.C.D., while the degradation was easy at the meta position by C.H.D.

2-3. Degradation of 2,3',4,4',5-pentachlorobiphenyl (#118)

Congener #118, a monoortho PCB, has a different number of chlorine atoms on each of the biphenylring. The concentrations of the para-dechlorination products, #67 and #70, were about three times as high as the concentration of the ortho-dechlorination product, #77, and about twelve times as high as the concentrations of the meta-dechlorination products, #66. The amount of #67, the product of para dechlorination of the less-substituted phenyl ring, was less than that of #70, #77, and #66, the dechlorination product of the less-substituted ring. In the unsymmetrical PCBs, dechlorination tended to occur on the more-substituted ring, similar to P.C.D. The reactivity of the chlorine substituents is thought to decrease in the order para > ortho > meta. The major didechlorination products were #33, #35 and #29. In the reaction of C.H.D., the dechlorination was easy at the para position, similar to S.D., while at the ortho position by P.C.D.

2-4. Degradation of 3,3',4,4',5-pentachlorobiphenyl (#126)

Congener #126, a non-ortho-chlorinated PCB, has three consecutive chlorine substituents on one of the biphenylring. After 5 min of reaction, the #79:#78:#77:#81 molar ratio was 40:12:12:1. The amount of #79, the product of para dechlorination of the more-substituted phenyl ring, was more than that of #78, the product of para dechlorination of the less-substituted phenyl ring. The didechlorination produced almost equal amounts of #35, #36 and #38. In the case of P.C.D. and C.H.D., the dechlorination was easy at the para position, similar to S.D.

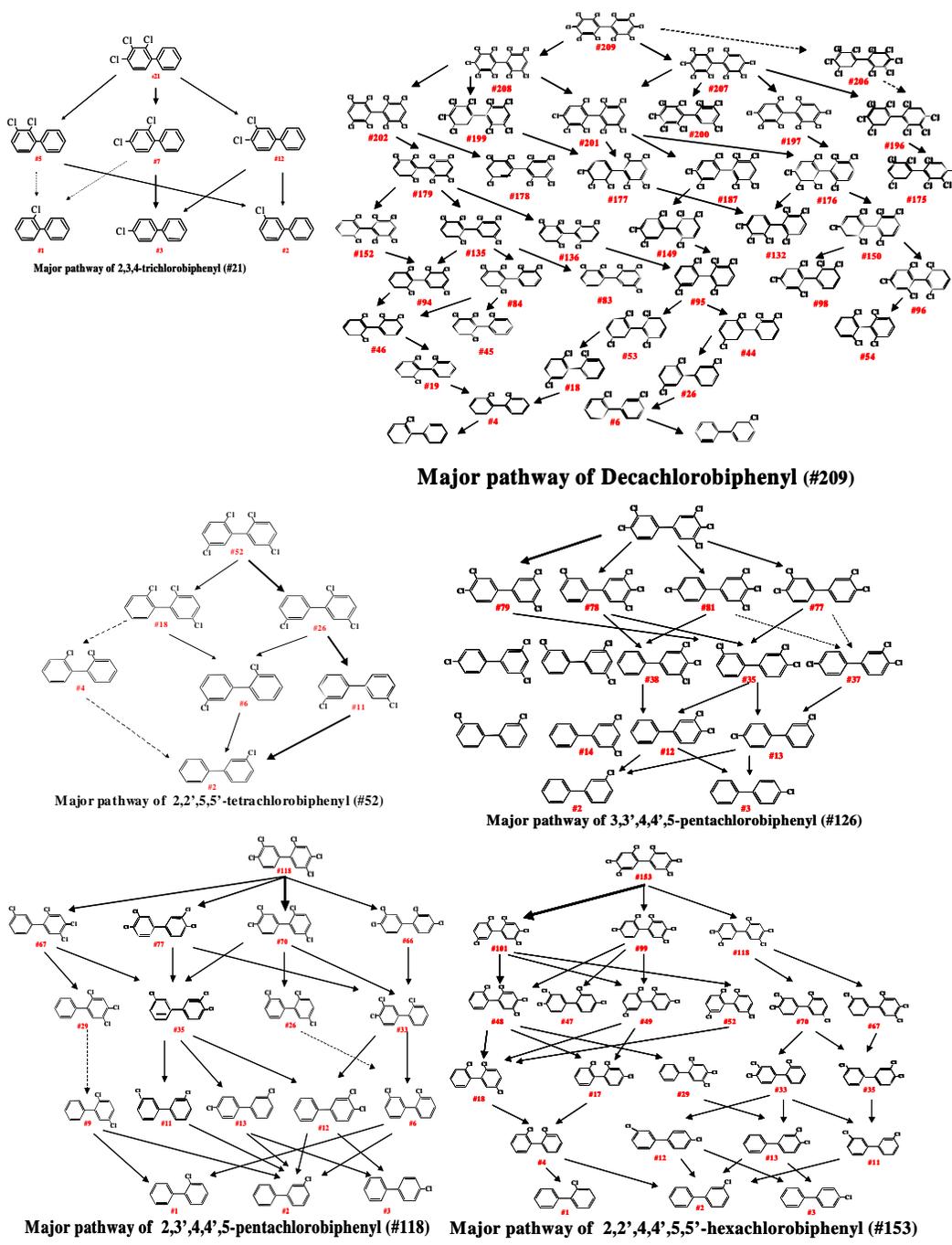


Figure 3 Major pathways of #21, #52, #118, #126, #153, and #209

2-5. Degradation of 2,2',4,4',5,5'-hexachlorobiphenyl (#153)

Congener #153 is a symmetrical biphenyl with chlorine substituents in the ortho, meta, and para positions of both rings. After 5 min of reaction, the #101:#118:#99 ratio was 10:1.6:1. The reactivity of the chlorine substituents decreased in the order para > ortho > meta, similar to C.H.D., while in the order para > ortho > meta by P.C.D.

2-6. Degradation of decachlorobiphenyl (#209)

Dechlorination of congener #209 produced #208, #207, and #206, as the ratio of 8:5.6:1. The reactivity of the chlorine substituents is thought to decrease in the order para > meta > ortho. The following dechlorination produced a small quantity of and many kinds of isomers, and the pathways spread widely. In the case of P.C.D. and C.H.D., dechlorination of congener #209 produced almost equal amounts of #207 and #208, and #206 was not observed.

3. Effect of substituents on the degradation rate

We calculated the kinetic constants of the nine congeners in the beginning ten-min-reaction (Table 1). The effects on the degradation rate of the position of the chlorine substituent (ortho, meta, or para), the total number of chlorine atoms, and the nature of the atoms next to the chlorine substituent will be discussed in this section.

Table 1 Degradation constants in the beginning ten-min-reaction

Congener	#1	#2	#3	#21	#52	#118	#126	#153	#209
Total chlorines	1	1	1	3	4	5	5	6	8
Kinetic constants (min ⁻¹)	0.0107	0.0184	0.0243	0.342	0.363	0.668	0.416	0.565	0.746

The chlorine at the para position was easily dechlorinated except for #21. In the case of #21, chlorine atoms situated between two other chlorines showed high reactivity, and similar results were observed in the dechlorination of congener #126 to produce #79. Total number of chlorine atoms influenced the decomposition rate, because the congener was degraded more quickly in proportion to total chlorines of PCBs. The different number of chlorine atoms on each of the biphenylring seemed to influence the dechlorination rate, and the reactions occurred on the more-substituted ring.

Conclusions

Nine PCB congeners were degraded by the sodium dispersion method and the major dechlorination pathways were proposed. The chlorine at the para position was easily dechlorinated. The chlorine situated between two other chlorines showed high reactivity and the dechlorination usually occurred on the more-substituted ring. The kinetic constants were in the order according to the total number of chlorine atoms. The rates and pathways of the S.D. dechlorination seemed to be related to the electronic and steric effects.

Acknowledgements

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

References

1. Y. Noma, T. Muramatsu, K. Nishizawa, M. Ohno, S. Sakai, (2002) *Organohalogen Compounds*, 56, 413
2. Y. Noma, M. Ohno, S. Sakai (2003) *Fresenius Environ. Bull.*, 12, 1, in press
3. A. Ariizumi, T. Otsuka, M. Kamiyama, M. Hosomi, (1997) *J. Environ. Chem.*, 7, 793
4. Xiu-Sheng Miao, Shao-Gang Chu, and Xiao-Bai Xu, (1999) *Chemosphere*, 39, 1639
5. T. Nishiwaki, M. Usui, K. Anda, M. Tobita, (1979) *Nippon Kagaku Kaishi*, 10, 1343
6. F. Murena and E. Schioppa, (2000) *Applied Catalysis B: Environmental*, 27, 257