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The Correlation between the Electron-capture Detector Response and the Chemical Structure for Polychlorinated Biphenyls†

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The relative sensitivities of an electron-capture detector for various polychlorinated biphenyls were measured at different temperatures. Generally, the sensitivities of these compounds become larger as the number of the chloro substituent increases. The temperature dependence of the electron-capture coefficients(K) for these compounds was also determined. These results show that the electron-capture reactions of polychlorinated biphenyls containing less than four chlorine atoms proceed dissociatively, while for four chlorine atoms the reactions proceed either dissociatively or non-dissociatively. For more than five chlorine atoms, the reactions almost always proceed non-dissociatively.

The electron-capture detector (ECD) which exhibits a highly sensitive response to various organic compounds containing halogen, oxygen, and sulfur atoms is used for the analyses of environmental pollutants. Many reports about ECD sensitivities for various compounds have been published,[1-4] but the temperature dependence of the sensitivity has not been considered in these studies.

Wentworth *et al.*[5-7] and Kojima *et al.*[8-11] studied the electron-capture phenomena by using the pulse-sampling technique. From the temperature dependence of the electron-capture coefficient (K) for various compounds, the activation energies and electron affinities were calculated. The present authors[12-15] have also previously studied the ECD sensitivities and the temperature dependence for various environmental pollutants using the D.C. mode.

In this work, the ECD sensitivities and the temperature dependence for various polychlorinated biphenyl (PCB) isomers were determined. The correlation between the ECD response and the chemical structure for these compounds was also studied.

Experimental

Apparatus and Materials. A Varian aerograph, 2100-type gas chromatograph with an ECD (^{63}Ni, 8.5 mCi) was used in this experiment. The applied voltage was supplied using the D.C. mode. A glass column (2 mmϕ × 1.8 m) was packed with Gaschrom Q (100—120 mesh) coated with 2% Silicone OV-1. The extra pure nitrogen gas (Teikoku Sanso Co., Ltd.) used as a carrier gas was purified by passing it through two tubes (20 cm) packed with Molecular Sieve 5A and an Oxy-trap tube (Alltech Associate Co., Ltd., 4002 type); the flow rate was 30 cm^3/min. The injector temperature was kept at 200 °C. The column temperature was set at 150 °C (1—3 chlorinated biphenyls) and at 180 °C (4—6 chlorinated biphenyls). The detector temperature was varied from 210 °C to 340 °C.

The PCB isomers (Analytical Standard, Analab Co., Ltd.), hexachlorobenzene (HCB) (special grade from Wako Pure Chemical Co., Ltd.) and pentachlorobenzene (PTCB) (guranteed grade from Tokyo Chemical Co., Ltd.) were used without further purification. All the substances were used as hexane (pesticide analytical grade from Wako Pure Chemical Co., Ltd.) solutions and were checked by gas chromatography.

Procedure. The relative sensitivity (*R.S.*) was calculated from the relative peak area per mole of the compound, using HCB as a standard. The relative retention time (*R.R.T.*) was obtained at a column temperature of 150 or 180 °C by using HCB as a standard. The sample size was chosen so as to keep the peak area within a linear range on the calibration curve. The K values, the electron affinities (EA'), and the *R.S.* values were calculated by the method reported in a previous paper.[12] The temperature dependence of the K values was shown by plotting the logarithm values of K or $KT^{3/2}$ against $1/T$, where T was the absolute temperature of the detector cell, which had been predetermined by inserting a Fe-Constantan thermocouple into a vacant ECD cell.

Results and Discussion

Relative Sensitivities of ECD and Relative Retention Times for PCBs. For various PCBs containing 1—6 chlorine atoms, the *R.S.*s of ECD at the detector temperatures of 230 °C, 290 °C and 320 °C and the *R.R.T.*s are tabulated in Table 1. The *R.S.*s of PCBs ordinarily become larger as the number of chloro substituents increases. These results agreed with the reports by Zitko *et al.*[16] and Gregory *et al.*[17] The *R.S.* of PCBs containing the same number of chlorine atoms are not equal, but they depend upon the position of the chlorine substituents. The *R.S.*s of monochlorinated biphenyls (Cl-PCB) were in the order of: 2-chlorobiphenyl>4-chlorobiphenyl>3-chlorobiphenyl; the *R.S.* of 3-chlorobiphenyl was especially small. The *R.S.*s of dichlorinated biphenyls (2Cl-PCB) were in the order of: 4,4′-dichlorobiphenyl> 3,3′-dichlorobiphenyl > 2,2′-dichlorobiphenyl. These orders of the *R.S.*s for mono- and dichlorobiphenyls are in accordance with the report by Gregory *et al.*[17] The *R.S.*s of tri- and tetrachlorobiphenyl were increased by one order of magnitude over those of dichlorobiphenyls. Among the pentachlorobiphenyls, the ECD sensitivity of 2,3,4,5,6-pentachlorobiphenyl was the highest. This compound has five chloro substituents and one phenyl substituent on a benzene ring. The *R.S.* of the compound was on the same level as that of pentachlorobenzene. The *R.S.* value of 2,2′3,5′6-pentachlorobiphenyl, which has three chloro substituents on the 2- or 6- position, was the

† This report constitutes part IV of "The Correlation between Electron-capture Detector Response and the Chemical Structure."

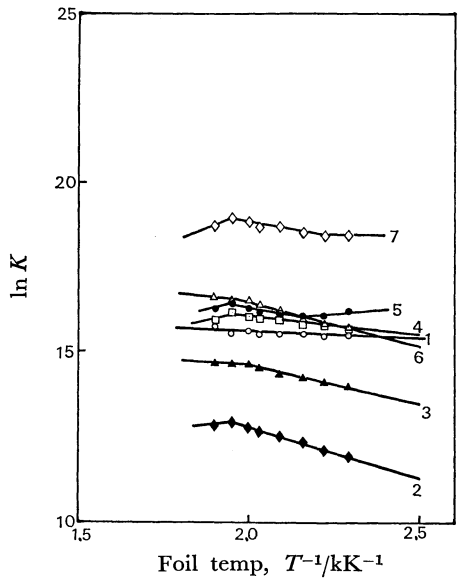

Fig. 1. Temperature dependence of K values measured at a column temperature of 150 °C.
1; 2-Chlorobiphenyl, 2; 3-chlorobiphenyl, 3; 4-chlorobiphnyl, 4; 2,2′-dichlorobiphenyl, 5; 3,3′-dichlorobiphenyl, 6; 4,4′-dichlorobiphenyl, 7; 2,3′,5-trichlorobiphenyl.

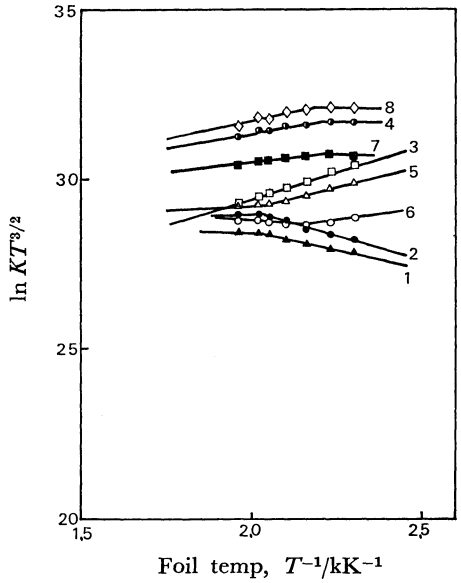

Fig. 2(a). Temperature dependence of K values measured at a column temperature of 180 °C.
1; 2,2′,4,5′-tetrachlorobiphenyl, 2; 2,2′,3,3′-tetrachlorobiphenyl, 3; 2,3′,4′,5-tetrachlorobiphenyl, 4; 2,3,4,5,6-pentachlorobiphenyl, 5; 2,2′,3′,4,5-pentachlorobiphenyl, 6; 2,2′,3,5′,6-pentachlorobiphenyl, 7; 2,2′,3,4,4′,5′-hexachlorobiphenyl, 8; hexachlorobenzene.

smallest.

As the number of chloro substituents increases, the *R.R.T.* value of PCB become larger, much as with the *R.S.* values of PCB. As to the PCB containing the same number of chlorine atoms, when the compound has fewer chlorine atoms on the 2- or 6- position, the value of *R.R.T.* is larger than those of the other compounds.

The Temperature Dependence of the ECD Response for PCBs. The temperature dependence of the K values of PCBs was examined in order to obtain some information about the electron-capture reactions of PCBs. Figures 1, 2(a), and 2(b) show the temperature dependence of the K values of the PCB isomers. The values of electron affinities (EA') and/or the activation energies (E^*) were calculated; they are tabulated in Table 2. The K values of the PCBs which contain fewer chloro substituents, such as mono-, di-, and trichlorinated biphenyls, become larger as the detector temperature increases. Therefore, the reaction of these PCBs appears proceeds dissociatively. The E^* values of Cl–PCBs were in the order of: 3-chlorobiphenyl > 4-chlorobiphenyl > 2-chlorobiphenyl. This order seems to be consistent with the degree of difficulty in eliminating chloro substituents. On the other hand, the *R.S.*s of Cl–PCB were in the order of: 2-chlorobiphenyl > 4-chlorobiphenyl > 3-chlorobiphenyl; this order agrees with that of the ease of eliminating chloro substituents. However, the order of the E^* values of 2Cl-PCBs was 4,4′-dichlorobiphenyl > 3,3′-dichlorobiphenyl > 2,2′-dichlorobiphenyl, the same as that of the *R.S.*s.

The temperature dependence of the K values of tetra-, penta-, and hexachlorinated biphenyl are shown in Figs. 2(a) and (b). The K values of 2,2′,3,3′-, 2,2′,4,5′-, and 2,2′,3,5′-tetrachlorobiphenyl become

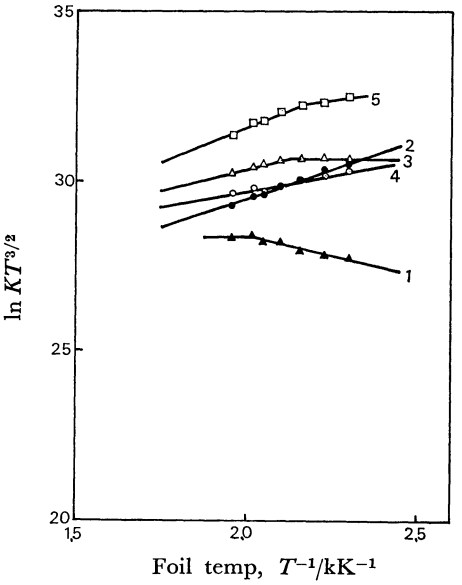

Fig. 2(b). Temperature dependence of K values measured at a column temperature of 180 °C.
1; 2,2′,3,5′-tetrachlorobiphenyl, 2; 2,2′,4,5,5′-pentachlorobiphenyl, 3; 2,2′,3,3′,4,4′-hexachlorobiphenyl, 4; 2,2′,3,4,5′-pentachlorobiphenyl, 5; pentachlorobenzene.

larger as the detector temperature increases; therefore, the EC reactions of these tetrachlorinated biphenyls seem to proceed dissociatively. On the contrary, the K value of 2,3′,4′,5-tetrachlorobiphenyl become smaller as the detector temperature increases, so the EC reaction of this PCB isomer seems to proceed non-dissociatively. From Fig. 1, the EC reaction of 2,3′,5-trichlorobiphenyl seems to proceed dissociatively. The

Table 1. Relative sensitivities for relative retention times of polychlorinated biphenyls

Compound	Relative sens (320 °C)	Relative sens (290 °C)	Relative sens (230 °C)	Relative retention time
2-Chlorobiphenyl[a)]	1.00×10^{-3}	1.30×10^{-3}	9.47×10^{-4}	0.42
3-Chlorobiphenyl[a)]	1.03×10^{-4}	7.78×10^{-5}	3.44×10^{-5}	0.55
4-Chlorobiphenyl[a)]	5.31×10^{-4}	4.73×10^{-4}	2.49×10^{-4}	0.57
2,2′-Dichlorobiphenyl[a)]	2.43×10^{-3}	2.02×10^{-3}	1.25×10^{-3}	0.67
3,3′-Dichlorobiphenyl[a)]	3.22×10^{-3}	2.52×10^{-3}	1.75×10^{-3}	1.22
4,4′-Dichlorobiphenyl[a)]	3.68×10^{-3}	3.02×10^{-3}	1.41×10^{-3}	1.32
2,3′,5-Trichlorobiphenyl[a)]	4.16×10^{-2}	3.24×10^{-2}	1.46×10^{-2}	1.77
2,2′,3,3′-Trichlorobiphenyl[b)]	7.50×10^{-2}	5.47×10^{-2}	2.42×10^{-2}	2.70
2,2′,3,5′-Tetrachlorobiphenyl[b)]	4.21×10^{-2}	2.91×10^{-2}	1.44×10^{-2}	2.37
2,2′,4,5′-Tetrachlorobiphenyl[b)]	4.59×10^{-2}	3.46×10^{-2}	1.57×10^{-2}	2.15
2,3′,4′,5-Tetrachlorobiphenyl[b)]	1.03×10^{-1}	1.03×10^{-1}	1.36×10^{-1}	3.13
2,2′,3,5′,6-Pentachlorobiphenyl[b)]	6.53×10^{-2}	4.86×10^{-2}	3.39×10^{-2}	3.23
2,2′,3′,4,5-Pentachlorobiphenyl[b)]	1.03×10^{-1}	8.71×10^{-2}	8.95×10^{-2}	4.41
2,3,4,5,6-Pentachlorobiphenyl[b)]	7.64×10^{-1}	7.05×10^{-1}	6.50×10^{-1}	4.57
2,2′,3,4,5′-Pentachlorobiphenyl[b)]	1.52×10^{-1}	1.24×10^{-1}	1.30×10^{-1}	4.54
2,2′,3,3′,4,4′-Hexachlorobiphenyl[b)]	2.85×10^{-1}	2.74×10^{-1}	2.40×10^{-1}	9.93
2,2′,3,4,4′,5′-Hexachlorobiphenyl[b)]	3.10×10^{-1}	2.91×10^{-1}	2.52×10^{-1}	8.43
Pentachlorobenzene[b)]	7.69×10^{-1}	9.14×10^{-1}	1.16	7.29
Hexachlorobenzene[a),b)]	1.00	1.00	1.00	1.00

a) The values of the relative sens. and the relative retention time for the compounds marked a) were measured at a column temperature of 150 °C. b) The values of the relative sens. and the relative retention time for the compounds marked b) were measured at a column temperature of 180 °C.

Table 2. Apparent electron affinities (EA') and activation energies (E^*) for polychlorinated biphenyls

Compound	E^* / kJ mol^{-1}	EA' / kJ mol^{-1}
2-Chlorobiphenyl	3.9 (526—436)	
3-Chlorobiphenyl	25.2 (512—436)	
4-Chlorobiphenyl	16.0 (496—436)	
2,2′-Dichlorobiphenyl	10.2 (512—436)	
3,3′-Dichlorobiphenyl	14.1 (512—464)	
4,4′-Dichlorobiphenyl	21.4 (512—436)	
2,3′,5-Trichlorobiphenyl	12.2 (499—450)	
2,2′,3,3′-Tetrachlorobiphenyl	17.9 (496—435)	
2,2′,3,5′-Tetrachlorobiphenyl	13.7 (510—435)	
2,2′,4,5′-Tetrachlorobiphenyl	12.4 (496—435)	
2,3′,4′,5-Tetrachlorobiphenyl		27.1 (510—435)
2,2′,3,5′,6-Pentachlorobiphenyl	1.7 (510—463)	16.6 (463—435)
2,2′,3′4,5-Pentachlorobiphenyl	6.5 (510—489)	
	22.6 (489—435)	
2,2′,4,5,5′-Pentachlorobiphenyl		31.5 (510—435)
2,3,4,5,6-Pentachlorobiphenyl		12.2 (510—436)
2,2′,3,4,5′-Pentachlorobiphenyl		15.7 (510—435)
2,2′,3,3′,4,4′-Hexachlorobiphenyl		17.5 (510—476)
2,2′,3,4,4′,5′-Hexachlorobiphenyl		8.2 (510—449)
Pentachlorobenzene		30.5 (510—463)
Hexachlorobenzene		13.0 (510—463)

The values of E^* and EA' for the compounds were determined at the ranges of detector temperatures(K) which are shown in parentheses.

EC reaction of 2,2′,3,5′-tetrachlorobiphenyl(2,2′3′,5-tetrachlorobiphenyl), with one more chloro substituent added on the 2′-position to 2,3′,5-trichlorobiphenyl, is of the dissociative-reaction type, but 2,3′,4′,5-tetrachlorobiphenyl, with one more chloro substituent added on the 4′-position to 2,3′,5-trichlorobiphenyl, is of the non-dissociative-reaction type.

These phenomena can be explained in the following way. The latter compound is able to form a stable negative ion by catching an electron, and so the EC reaction proceeds non-dissociatively, but it is difficult for the former compound, containing more chloro substituents on the 2- or 2′-position, to form a stable negative molecular ion because of steric hindrance. The EC reactions of penta- and hexachlorinated biphenyls seem to proceed non-dissociatively. These are of the same reaction type as the PTCB, HCB, and BHC isomers which contain five six chloro substituents. These compounds seems to be able to form stable negative ions by catching electrons.

Karasek[18] studied the EC reaction of PCB compounds by means of plasma chromatography. He reported that the peaks corresponding to PCB-ion complexes appeared in negative plasmagrams for tetra- to decachlorobiphenyl compounds. On the other hand, as to mono- and dichlorobiphenyl compounds, no peak corresponding to the negative PCB-ion complex was observed in negative plasmagram; only positive-ion peaks corresponding to the PCB molecule with an added water molecule introduced into the carrier gas were observed. These phenomena are considered to show that these higher-chlorinated biphenyl compounds form stable negative ions, while lower-chlorinated biphenyl compounds do not. This supports our experimental results. Therefore, it is considered that the EC reactions of lower-chlorinated biphenyls proceed dissociatively, while those of higher-chlorinated biphenyls proceed non-dissociatively.

References

1) J. E. Lovelock, "Gas Chromatography," ed by N. Brenner, Academic Press, New York and London (1962), p. 219.
2) W. L. Zielinski, Jr., and L. Fishbein, *J. Chromatogr.*, **28**, 293 (1967).
3) W. L. Zielinski, Jr., L. Fishbein, and R. O. Thomas, *J. Chromatogr.*, **30**, 77 (1967).
4) W. L. Zielinski, Jr., L. Fishbein, and L. Martin, Jr., *J. Gas Chromatogr.*, **5**, 552 (1967).
5) W. E. Wentworth, E. Chen, and J. E. Lovelock, *J. Phys. Chem.*, **70**, 445 (1966).
6) W. E. Wentworth and E. Chen, *J. Gaschromatogr.*, **5**, 170 (1967).
7) W. E. Wentworth, L. W. Kao, and R. S. Becker, *J. Phys. Chem.*, **79**, 1161 (1975).
8) M. Satouchi and T. Kojima, *Anal. Lett.*, **5**, 931 (1972).
9) T. Kojima and M. Satouchi, *Bunsekikagaku*, **22**, 1428 (1973).
10) M. Satouchi and T. Kojima, *Bunsekikagaku*, **25**, 764 (1976).
11) T. Kojima, Y. Tanaka, and M. Satouchi, *Anal. Chem.*, **48**, 1760 (1976).
12) Y. Hattori, Y. Kuge, and S. Nakagawa, *Bull. Chem. Soc. Jpn.*, **51**, 2249 (1978).
13) Y. Hattori, Y. Kuge, and S. Asada, *Nippon Kagaku Kaishi*, **1978**, 1102.
14) Y. Kuge, Y. Hattori, A. Asada, and S. Yamada, *Chem. Lett.*, **1979**, 208.
15) Y. Hattori, Y. Kuge, and S. Asada, *Bull. Chem. Soc. Jpn.*, **53**, 1435 (1980).
16) V. Zitko, O. Hutzinger, and S. Safe, *Bull. Environ. Contam. Toxicol.*, **6**, 160 (1971).
17) N. L. Gregory, *J. Chem. Soc., B*, **1968**, 295.
18) F. W. Karasek, *Anal. Chem.*, **43**, 1982 (1971).