© The Chemical Society of Japan NOTES *Bull. Chem. Soc. Jpn.*, **53**, 1435—1436 (1980)

Correlation between Electron Capture Detector Response and Chemical Structure for 1,2,3,4,5,6-Hexachlorocyclohexane

Yukikazu HATTORI,* Yoshio KUGE, and Shingo ASADA

Environmental Pollution Control Center of Osaka Prefecture, 1-3-62, Nakamichi, Higashinari-ku, Osaka-shi, Osaka 537

(Received May 2, 1979)

Synopsis. The relative sensitivities of an electron capture detector for four 1,2,3,4,5,6-hexachlorocyclohexane isomers were measured at different detector temperatures. The temperature dependence of the electron capture coefficients (K) for these compounds was determined. The K values of these compounds increased with a decrease in the detector temperature. These results show that the electron capture reactions of these compounds 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 widely used for environmental and other various analyses. Many reports about ECD sensitivities for various compounds have been published,[1–4] but the temperature dependence of the sensitivity was not 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, thus elucidating the temperature dependence of the electron capture coefficients (K) for various compounds. They reported a correlation between the ECD response and the chemical structure for many compounds.

The present authors have previously studied[12–14] the ECD response and the temperature dependence for various aromatic halogeno and nitro compounds and for phthalate esters with the d.c. mode.

In this work, we have determined the ECD sensitivities and the temperature dependence for 1,2,3,4,5,6-hexachlorocyclohexane(BHC) isomers and studied the correlation between the ECD response and the chemical structure for these compounds. We intend to use these results for the identification and prediction of unknown compounds.

Experimental

Apparatus and Materials. A Varian aerograph 2100 type gas chromatography with an ECD (^{63}Ni, 8.5 mCi) was used in this experiment. Applied voltage was supplied with the d.c. mode. The glass column (2 mmϕ × 1.5 m) was packed with Gaschrom Q (100—120 mesh) coated with 2% Silicone OV-17. Extra pure nitrogen gas (Teikoku Sanso Co., Ltd.) was used as the carrier gas; it was purified by passage through two tubes packed with Molecular Sieve 5A and through an Oxy-trap tube (Alltech Associates Co., Ltd.), at the flow rate of 30 cm^3/min. The column temperature was set at 170 °C. The injector temperature was kept at 200 °C. The detector temperature was varied from 190 °C to 320 °C. BHC isomers (pesticides, analytical grade) and hexachlorobenzene (HCB)(special grade) were obtained from Wako Pure Chemical Co., Ltd. All the reagents were checked by gas chromatography.

Procedure. The relative sensitivity (RS) was obtained by calculating the relative peak area per mole of the compound, using HCB as a standard. The sample size was so chosen as to keep the peak area within a linear range on the calibration curve. The K values, the electron affinities (EA'), and the RS values were calculated by the method reported in a previous paper.[12]

Results and Discussion

Relative Sensitivities of ECD for BHC Isomers. The RSs of ECD for BHC isomers at three different detector temperatures are tabulated in Table 1. The RSs of the four isomers were in the order of $\alpha > \gamma > \delta \gg \beta$. Especially, the RS for β-BHC was less than those of the other isomers by a factor of about two or three. The RS's of BHC isomers are much larger than that of HCB, which has an equal number of chlorine atoms to BHC. These results may be attributed to the difference in the molecular skeleton and in the coformations of the C–Cl bonds in BHC and HCB.

TABLE 1. RELATIVE SENSITIVITIES FOR ECD OF BHC ISOMERS AND HEXACHLOROBENZENE

Compound	Relative sens. (230 °C)	Relative sens. (290 °C)	Relative sens. (320 °C)
α-BHC	7.68	4.74	6.21
β-BHC	2.46	1.99	2.74
γ-BHC	6.81	4.67	6.06
δ-BHC	6.27	3.99	4.99
Hexachlorobenzene	1.00	1.00	1.00

The Temperature Dependence of the ECD Response for BHC Isomers. Gas chromatograms of BHC isomers at three different detector temperatures are shown in Fig. 1. As the detector temperature is lowered, the peak heights showing ECD sensitivity become higher. Then the temperature dependences of ECD response were studied. Figure 2 shows the temperature dependence of the K values of four kinds of BHC isomer and HCB. It was found that the temperature dependence of the K values for these compounds showed positive slopes, but that of β-isomer showed an almost zero slope. If the plots of ln $KT^{3/2}$ against $1/T$ show a positive slope, the electron capture reaction of the compound proceeds non-dissociatively.[6] Therefore, the electron capture reaction for BHC isomers appears to proceed non-dissociatively. These compounds were then supposed to capture an electron and to form stable negative ions. Aue *et al.*[15] studied the products of

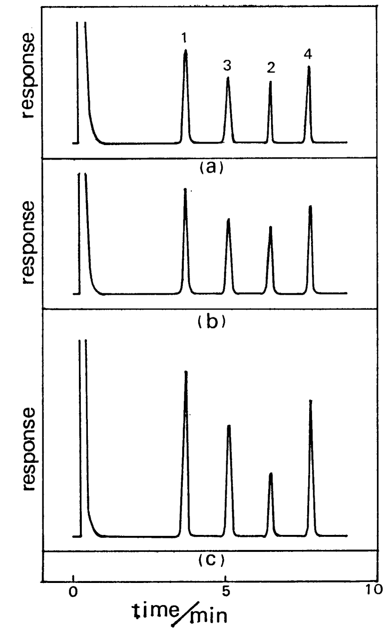

Fig. 1. Gas chromatograms of BHC isomers at different detector temperatures.
(a): 320 °C, (b): 290 °C, (c): 230 °C, 1: α-BHC, 2: β-BHC, 3: γ-BHC, 4: δ-BHC.

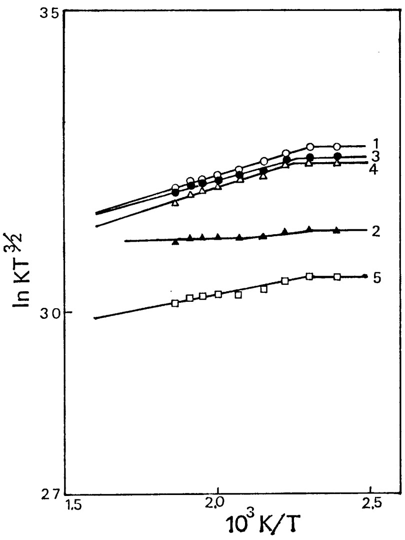

Fig. 2. Temperature dependence of K values.
1: α-BHC, 2: β-BHC, 3: γ-BHC, 4: δ-BHC, 5: hexachlorobenzene.

three BHC isomers and various polychlorobenzenes in an ECD. They suggested that BHC isomers were largely preserved in contrast to those of other polychlorobenzenes. This fact may support the idea that the electron capture reaction for BHC isomers proceeds non-dissociatively.

In Table 2, the values of the electron affinities (EA') calculated from the magnitude of the positive slopes plotted ln $KT^{3/2}$ *vs.* $1/T$ and the conformations[16] of the C–Cl bonds in the molecule of BHC are listed. The EA' values of α,γ, and δ isomers were about 13 kJ/mol, while that of HCB was about 8 kJ/mol. The magnitude of the EA' values were in the order of

Table 2. Apparent electron affinities(EA') and conformations of BHC isomers and hexachlorobenzene

Compound	EA' / kJ mol^{-1}	Conformation of chlorine atoms[a)]
		b) c)
α-BHC	12.68	aaeeee
β-BHC	5.06	eeeeee
γ-BHC	12.01	aaaeee
δ-BHC	13.85	aeeeee
Hexachlorobenzene	8.12	—

a) From Ref. 16. b) a: Axial bond. c) e: Equatorial bond.

δ>α>γ>HCB>β. Among the four kinds of BHC isomer, the temperature dependence of the K values, the ECD sensitivity, and the EA' value of β-isomer were very different from those of other isomers. Generally, cyclohexane derivatives adopt the most energetically favarable conformation, in which most substituents are equatorial.[17] All the chlorine substituents of β-isomer are equatorial and so β-isomer has the more stable structure compared with the other BHC isomers. Our experimental results concerning β-isomer may be related to the difference in the conformation. In this way, the electron capture reaction for BHC isomers is affected by the molecular conformations.

References

1) J. E. Lovelock, "Gas Chromatography," ed by N. Brenner, Academic Press, New York (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. Gas Chromatogr.*, **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, *Bunseki Kagaku*, **22**, 1428 (1973).
10) M. Satouchi and T. Kojima, *Bunseki Kagaku*, **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*, **8**, 1102 (1978).
14) Y. Kuge, Y. Hattori, S. Asada, and S. Yamada, *Chem. Lett.*, **1979**, 208.
15) S. Kapita and W. A. Aue, *J. Chromatogr.*, **148**, 343 (1978).
16) R. D. Obrien, "Insecticides," Academic Press, New York (1967), p. 183.
17) S. Umezawa, "Yuki Kagaku," Maruzen (1962), pp. 6—14.