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Correlation between Relative Sensitivities for Electron Capture Detector and Chemical Structure of Aromatic Halogeno and Nitro Compounds

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Relative sensitivities of an electron capture detector (ECD, ^{63}Ni) for aromatic halogeno and nitro compounds were measured at detector temperatures of 230, 290, and 320 °C. The effects of various substituents on the sensitivity of ECD were determined. A good correlation was recognized between the relative sensitivities of ECD and the positions of substituents for aromatic chloro, bromo, and nitro compounds. The plotted logarithm values of ECD sensitivities for aromatic chloro and bromo compounds *vs.* Hammett's σ values of various substituents are not linear, but the plots for aromatic nitro compounds follow a straight line. Modified σ values (σ_H) were determined on the basis of the relative sensitivities of aromatic chloro compounds. Plots of aromatic chloro, bromo, and nitro compounds *vs.* σ_H values gave straight lines. The temperature dependence of electron capture coefficients for these compounds was determined using D.C. mode. The electron capture spectra obtained are similar to those using pulsed mode.

Various organic compounds containing a halogen, oxygen, and sulfur atom exhibit electron capture sensitivities. Many reports of ECD sensitivities for these compounds have been published.[1-5] Lovelock and others reported the electron absorption coefficients for polychlorinated benzenes using a ^{3}H detector (pulsed mode).[1] The correlation between the sensitivity of various pesticides and their molecular structure was examined by Zielinski and others[2-4] using a ^{3}H detector. But in these studies the complete rule of the correlation could not be established and the temperature dependence of the sensitivity was not considered.

Wentworth *et al.*[6-12] have studied the thermal electron attachment to various compounds using the pulse-sampling technique. In their reports, the temperature dependence of electron capture coefficients (K values) was elucidated. Activation energies for electron capture reactions and the electron affinities of these compounds were also calculated.

Vessman *et al.*[13] investigated the correlation of the temperature dependence of sensitivities with the molecular structure for benzophenone derivatives by using a ^{3}H detector (D.C. mode).

Recently, Kojima and Satouchi *et al.*[14-19] investigated minutely the temperature dependenc of K values by using a ^{63}Ni detector which could operate at a higher detector temperature than the ^{3}H detector used by Wentworth *et al.* They pointed out that electron capture reactions for aromatic halogeno compounds were similar to bimolecular nucleophlic substitution.

In this work, sensitivities of ECD for aromatic halogeno and nitro compounds at three different detector temperatures were determined by using a ^{63}Ni detector. Moreover, the temperature dependence of electron capture coefficients was investigated. The relationships between ECD response and the molecular structure of these compounds were studied with D.C. mode. We intend to use this relationship for prediction of ECD sensitivity and for identification of unknown samples.

Experimental

Apparatus and Materials. A Varian aerograph 2100 type gas chromatograph with an electron capture detector (^{63}Ni, 8.5 mCi) was used in this experiment. Applied voltage was supplied with D. C. mode. The glass column (2 mm$\phi \times$ 1.5 m) was packed with Gaschrom Q (100—120 mesh) coated with 5% Bentone 34 and 5% Silicone DC-200. Nitrogen gas was used as a carrier gas; the flow rate was 30 ml/min. The temperature of the sample injection part was kept at 200 °C. The column temperature was set ordinarily at 100 °C. The temperature of the detector cell (foil temperature) was changed from 150 (130) to 350 °C (290 °C). The reagents used were all commercially available (special and guaranteed grade from Tokyo Chemical Co.). All reagents were checked by gas chromatography and distilled before use if necessary.

Procedure. The relative sensitivity (hereafter abbreviated to *R.S.*) was obtained by calculating the relative peak area per mole of the compound, using *p*-dichlorobenzene as a standard. The sample size was so chosen as to keep the peak area within a linear range on the calibration curve. The area under the chromatographic peak was obtained by multiplying the peak height by the width at half point of peak height. The relative retention time (hereafter abbreviated to *R.R.T.*) was also obtained by using *p*-dichlorobenzene as a standard, ordinarily at a column temperature of 100 °C. The electron capture coefficient (K value) was calculated from the following equation 1 derived by Wentworth:

$$K = (F/S \cdot N)\int (I_b - I_e)/I_e \cdot dx, \qquad (1)$$

where F is the carrier gas flow rate (l/min), S is the chart speed (cm/min), N is the amount of sample injected (mol), and I_b and I_e are the detector current without and with capturing species in the detector, respectively. Since the detector signal is proportional to $(I_b - I_e)$, we can convert the term of $(I_b - I_e)/I_e$ to $(I_b - I_{ep})/I_{ep}$. $(I_b - I_{ep})$ is the recorder response corresponding to the maximum peak height; I_{ep} can be obtained by subtracting $(I_b - I_{ep})$ from I_b. So Eq. 1 can be converted to

$$K = (F/S \cdot N)\{(I_b - I_{ep})/I_{ep}\} \cdot W. \qquad (2)$$

The integral in the Eq. 1 corresponds to the peak area on the chromatogram in Eq. 2, where W is the width at the half peak height.

TABLE 1. RELATIVE SENSITIVITY FOR ECD AND RELATIVE RETENTION TIME OF AROMATIC CHLORO COMPOUNDS

Compound	Relative sens. (230 °C)	Relative sens. (290 °C)	Relative sens. (320 °C)	Relative retention time
Chlorobenzene	0.0013	0.00170	0.00140	0.526
p-Dichlorobenzene	1.00	1.00	1.00	1.00
m-Dichlorobenzene	2.18	2.16	1.91	1.31
o-Dichlorobenzene	1.76	1.57	1.88	2.21
1,2,3-Trichlorobenzene	27.2	21.6	21.6	7.21
1,2,4-Trichlorobenzene	11.0	12.6	12.4	3.07
1,3,5-Trichlorobenzene	22.3	19.1	18.2	1.88
1,2,3,4-Tetrachlorobenzene	82.1	42.6	63.6	9.79a)
1,2,3,5-Tetrachlorobenzene	84.0	44.4	51.8	5.41a)
1,2,4,5-Tetrachlorobenzene	36.2	24.5	28.9	5.75a)
Pentachlorobenzene	642.0	109.7	232.4	11.6b)
Hexachlorobenzene	498.9	102.2	217.6	25.5b)

a) Determined at a column temperature of 120 °C.
b) Determined at a column temperature of 140 °C.

Results and Discussion

Relative Sensitivity for ECD and Relative Retention Time. *R.S.* for ECD and *R.R.T.* of polychlorinated benzenes are tabulated in Table 1. *R.S.* of ECD becomes larger as the number of chlorine atoms increases, except that the result of *R.S.* for pentachlorobenzene (PCB) is larger than that of hexachlorobenzene (HCB). This tendency is similar to that of the electron absorption coefficient determined with a ^3H detector by Lovelock *et al.*1) Shimokawa *et al.*20) measured the relative electron capture efficiencies of halobenzenes, compared with biphenyl as a reference material, in glassy 2-methyltetrahydrofuran at 77 K by absorption spectrometry. They defined the relative electron capture efficiency (K_s/K_{ϕ_2}) as follows:

$$OD^\circ/OD = 1 + (K_s/K_{\phi_2})\cdot([s]/[\phi_2]),$$

where OD° and OD represent the optical densities of biphenyl anion (410 nm) in the absence and presence of solute, K_s and K_{ϕ_2} are the electron capture coefficients of the given solute and of biphenyl, and [s] and $[\phi_2]$ are the concentrations of given solute and of biphenyl. OD° and OD correspond to I_b and I_e, respectively, in our report. Their report also shows that the relative electron capture efficiency becomes larger with increasing the number of chlorine atoms. The relative electron capture efficiency of PCB is also larger than that of HCB. They attributed this fact to the shielding effect of the π-orbital system by the substituent chlorine atom on the benzene ring. The same effect was observed in the electron capture reaction of polychlorinated benzenes in our gas chromatographic study.

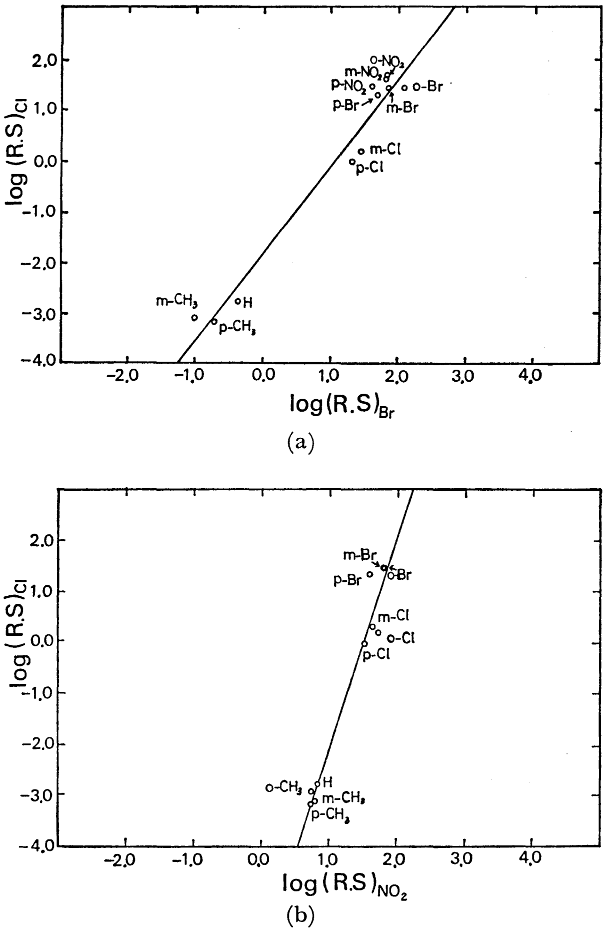
R.R.T. values of polychlorinated benzenes ordinarily become larger as the number of chlorine atoms increases.

TABLE 2. RELATIVE SENSITIVITY FOR ECD AND RELATIVE RETENTION TIME OF AROMATIC CHLORO, BROMO, AND NITRO COMPOUNDS

Compound	Relative sens. (230 °C)	Relative sens. (290 °C)	Relative sens. (320 °C)	Relative retention time
p-Chlorotoluene	0.00116	0.00068	0.00135	0.90
m-Chlorotoluene	0.00117	0.00081	0.00105	0.89
o-Chlorotoluene	0.00134	0.00120	0.00160	0.87
p-Bromochlorobenzene	31.6	21.6	18.9	1.76
m-Bromochlorobenzene	46.7	28.9	26.2	2.48
o-Bromochlorobenzene	47.1	29.1	27.1	3.04
p-Chloronitrobenzene	63.6	31.4	26.2	9.55
m-Chloronitrobenzene	89.1	42.3	43.9	13.03
o-Chloronitrobenzene	102.7	53.8	43.7	28.44
Bromobenzene	0.540	0.430	0.444	0.97
p-Dibromobenzene	88.9	50.0	31.4	2.99
m-Dibromobenzene	141.8	69.8	45.0	3.79
o-Dibromobenzene	219.3	117.6	56.6	6.00
p-Bromotoluene	0.293	0.193	0.220	1.60
m-Bromotoluene	0.108	0.0980	0.0997	1.60
p-Bromonitrobenzene	80.4	38.7	20.6	16.4
m-Bromonitrobenzene	144.8	65.5	44.6	23.9
o-Bromonitrobenzene	148.2	68.2	46.4	—
Nitrobenzene	15.8	7.36	3.48	6.32
p-Nitrotoluene	18.8	5.64	2.61	15.50
m-Nitrotoluene	15.0	6.52	3.29	11.76
o-Nitrotoluene	25.4	5.49	2.49	8.91

R.S. for ECD and *R.R.T.* of aromatic chloro, bromo, and nitro compounds with diverse substituents are summarized in Table 2. *R.S.* of monosubstituted benzenes are in the order of NO_2>Br>Cl. *R.S.* of nitrobenzene becomes higher with decreasing detector temperature. *R.S.* of disubstituted benzenes are in the order of Br(dibromobenzene)>Cl(dichlorobenzene). This order is in accordance with that of the ECD reactivity of disubstituted benzenes which was investigated with plasma chromatography by Karasec *et al.*21) *R.S.* for ECD of these compounds varies greatly with the kind of substituents. The effects on *R.S.* of ECD with changing substituents for disubstituted compounds are clearly recognizable in Table 2. *R.S.* for ECD of a methyl-substituted compound which was derived from a monosubstituted one becomes lower than that of the original one. For example, *R.S.* for ECD of bromotoluene is smaller than that of bromobenzene. The same result was obtained for chlorotoluene. An exceptional result was observed for nitrotoluene only at a detector temperature of 230 °C. *R.S.* for ECD of the compound which was derived from an electron donative substituent such as a methyl group becomes smaller than the original one. On the other hand, if a chloro, bromo, or nitro group which is an electron attractive substituent is introduced into the monosubstituted compound, *R.S.* for ECD of the compound becomes higher than that of the original. *R.S.* for ECD of the compound into which a nitro substituent was introduced becomes larger as the detector temperature decreases.

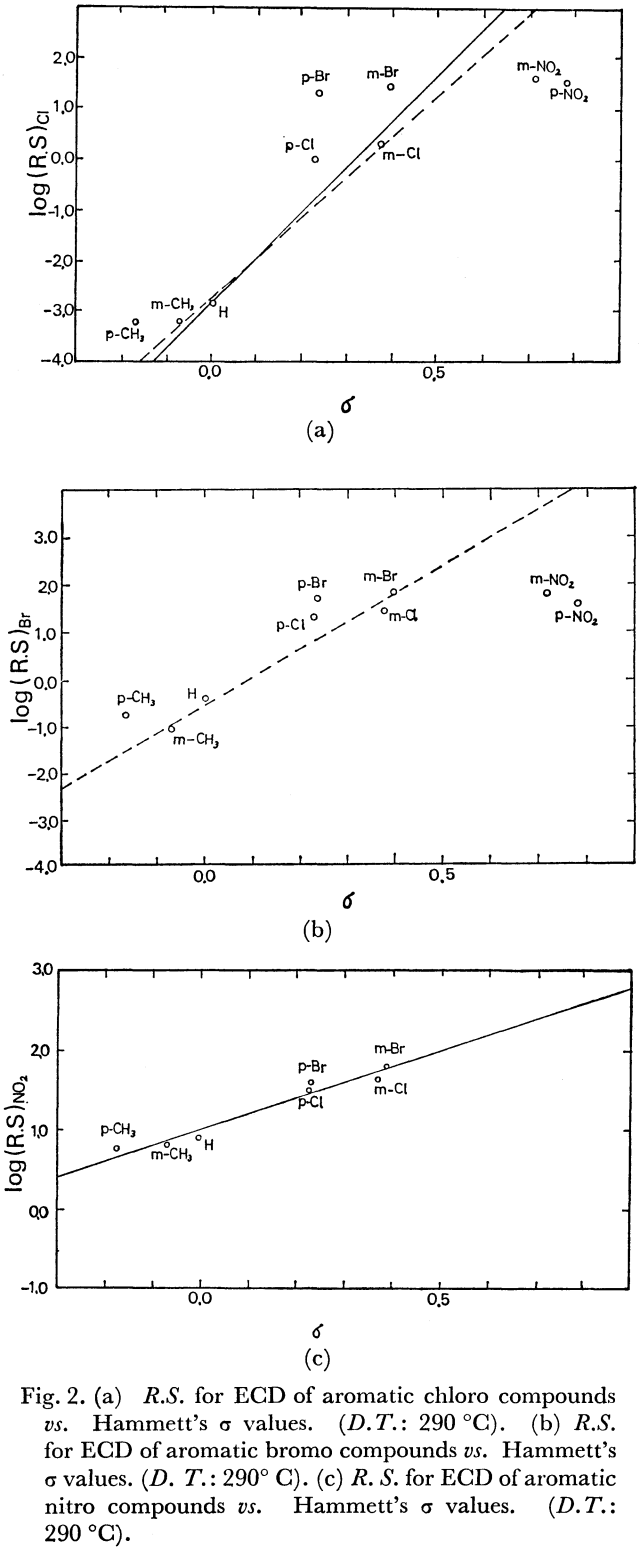
In order to investigate the effect of substituents on the ECD sensitivity in more detail, logarithm values of *R.S.* for these compounds were plotted against varying isomeric (*o*-, *m*-, and *p*-) positions and various kinds of substituents. The correlation between *R.S.* for ECD of aromatic chloro compounds ($Cl-C_6H_4-X$, X: substituent) and bromo compounds ($Br-C_6H_4-X$, X: substituent) is shown in Fig. 1 (a). The line was drawn by the least squares procedure. The correlation coefficient was 0.9813. Good correlation was obtained. The correlation between *R.S.* of aromatic chloro compounds ($Cl-C_6H_4-X$) and nitro compounds ($O_2N-C_6H_4-X$) is shown in Fig. 1 (b). Excellent correlation was given between chloro and nitro compounds. At detector temperatures of both 230 and 320 °C excellent correlations were observed. From these facts, the substituted effect for the electron capture reaction can be deduced. Logarithm values of *R.S.* for disubstituted compounds *vs.* Hammett's σ values were also plotted (Figs. 2 (a), (b), (c)). In Figs. 2 (a) and (b), most of plots deviate from the straight lines which were drawn using the average method. But the plots for the original compounds (chlorobenzene and bromobenzene) and the *meta*-substituted compounds are found to be linear, except for *m*-Br and *m*-NO_2 in Fig. 2(a) and *m*-NO_2 in



(a)

(b)

Fig. 1. (a) Correlation between *R.S.* for ECD of aromatic chloro compounds ($Cl-C_6H_4-X$) and bromo compounds ($Br-C_6H_4-X$) with varying substituents X. (*D.T.*: 290 °C). (b) Correlation between *R.S.* for ECD of aromatic chloro compounds and nitro compounds ($O_2N-C_6H_4-X$) with varying substituents X. (*D.T.*: 290 °C).



(a)

(b)

(c)

Fig. 2. (a) *R.S.* for ECD of aromatic chloro compounds *vs.* Hammett's σ values. (*D.T.*: 290 °C). (b) *R.S.* for ECD of aromatic bromo compounds *vs.* Hammett's σ values. (*D. T.*: 290° C). (c) *R. S.* for ECD of aromatic nitro compounds *vs.* Hammett's σ values. (*D.T.*: 290 °C).

Fig. 2(b). The plot of *m*-Br lies above the dotted straight line in Fig. 2(a), because the reactivity of bromo substituent is greater than that of the chloro substituent. The plots of *para*-substituted compounds are also above the dotted line. These facts suggest, as noted by Satouchi *et al.*,[17,18] that the electron capture reaction of these compounds seems to be the radical reaction. The plot of Hammett's σ values *vs.* *R.S.* of aromatic nitro compounds are shown in Fig. 2(c). Each plot was found to be almost linear by calculating with the least-squares procedure. The electron capture reactions of aromatic nitro compounds seem to obey Hammett's law and thus seem to take place in a different way from other aromatic halogeno compounds. Generally, the reactions of aromatic nitro compounds in an electron capture detector are described as taking place by the non-dissociative mechanism. Since those reactions obey Hammett's law, it is considered that a polar effect by substituents has a direct effect on the first stage of reaction, namely, on the stage of electron attachment. The modified σ values (σ_H) which are suitable for *R.S.* of these aromatic chloro and bromo compounds were determined at a detector temperature of 290 °C. These values were calculated from the line in Fig. 2(a) which was drawn by the average method as $\sigma_H=0$ for the hydrogen atom. The σ_H values are listed in Table 3.

TABLE 3. SIGMA σ_H VALUES[a)]

Substituent	σ_H value	Substituent	σ_H value
p-CH_3	−0.044	*p*-Br	+0.454
m-CH_3	−0.035	*m*-Br	+0.469
o-CH_3	−0.017	*o*-Br	+0.469
p-Cl	+0.307	*p*-NO_2	+0.473
m-Cl	+0.343	*m*-NO_2	+0.487
o-Cl	+0.329	*o*-NO_2	+0.499

a) σ_H values were determined at a detector temperature of 290 °C.

The plots of σ_H values *vs.* the logarithm values of *R.S.* of aromatic bromo compounds are shown in Fig. 3 (a) Every plot gives a straight line. The plots of σ_H values *vs.* the logarithm values of *R.S.* of aromatic nitro compounds are shown in Fig. 3(b). Each plot also gives a straight line. At detector temperatures of 230 and 320 °C, the plots of σ_H values *vs.* the logarithm values of *R.S.* of these compounds also give straight lines. Even for *ortho*-substituted compounds, the plots fit a straight line, too. It seems that the steric effect does not take part in the electron capture reaction at least for *ortho*-substituted compounds. Then, if *R.S.* for ECD of a few compounds are known, *R.S.* of other compounds can be predicted from σ_H values. The plots of σ_H value *vs.* sigma values which were determined for ESR nitrogen coupling constants[22)] of *para*-substituted derivatives of nitrobenzene are shown in Fig. 4. Except for NO_2 substituent, good correlation is shown. This fact suggests that the σ_H values are parameters related to the stability of anion radicals for these compounds. The plot of the activation energy E^*(kcal/mol) in electron capture reactions reported by Satouchi *et al.* *vs.* the values of $\rho^*\sigma_H$ are shown in Fig. 5. The values of $\rho^*\sigma_H$ are directly proportional to the E^* values. The ρ^* value represents the slope of the plot of the logarithm values of *R.S.* *vs.* σ_H. Thus $\rho^*\sigma_H$ values represent log *R.S.*

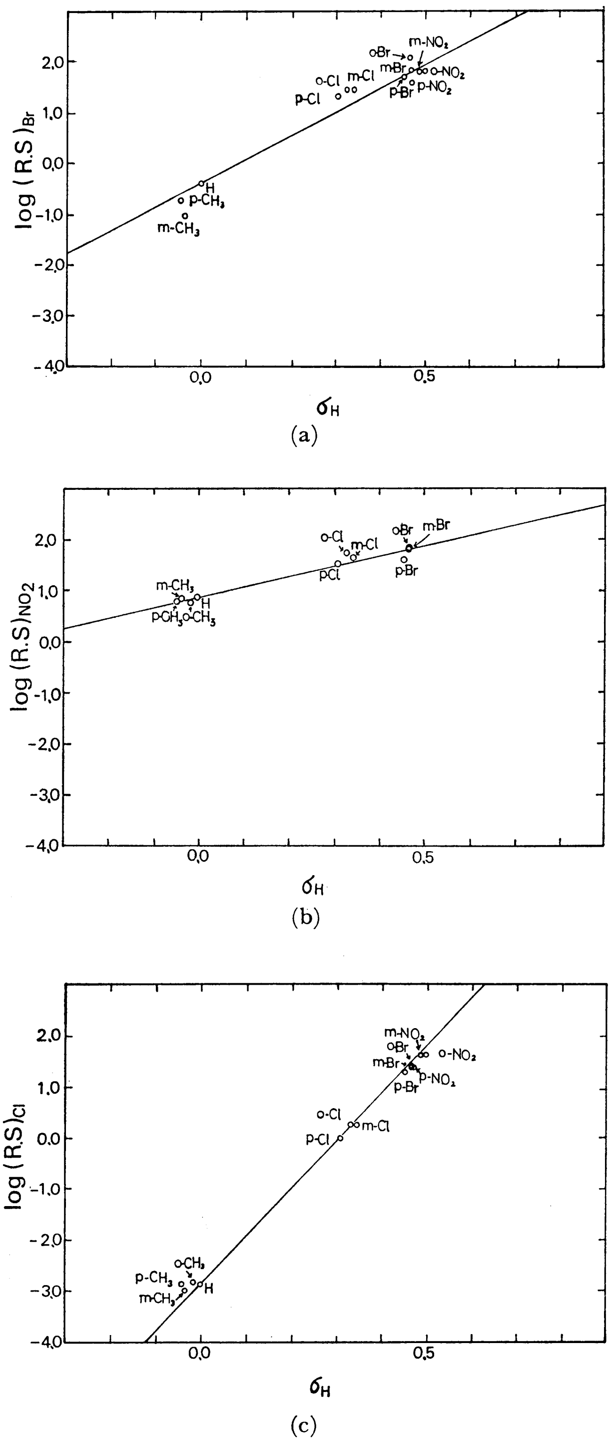


Fig. 3.(a) *R.S.* for ECD of aromatic bromo compounds *vs.* modified σ value (σ_H). (*D.T.*: 290 °C). (b) *R.S.* for ECD of aromatic nitro compounds *vs.* σ_H value. (*D.T.*: 290 °C). (c) *R.S.* for ECD of aromatic chloro compounds *vs.* σ_H value. (*D.T.*: 320 °C).

Temperature Dependence of Electron Capture Coefficients. The temperature dependence of electron capture coefficients (*K* values) was examined to investigate more

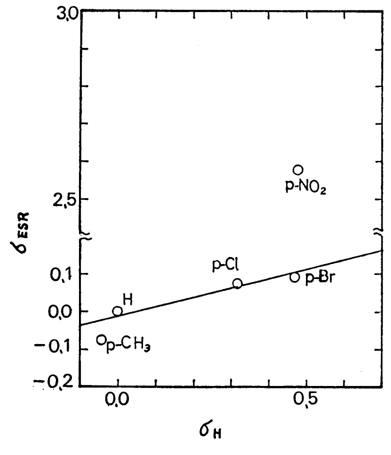


Fig. 4. σ_H values *vs.* Sigma constants determined from ESR nitrogen coupling constant of aromatic nitro compounds.

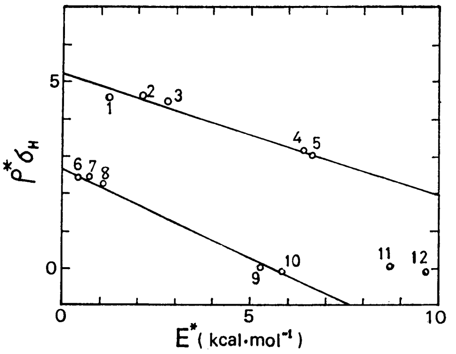


Fig. 5. $\rho^*\sigma_H$ (*D.T.*: 290 °C) *vs.* the activation energies reported by Satouchi *et al.*[17]
1: *m*-Chloronitrobenzene, 2: *o*-chloronitrobenzene, 3: *p*-chloronitrobenzene, 4: *m*-dichlorobenzene, 5: *o*-dichlorobenzene, 6: *m*-bromonitrobenzene, 7: *o*-bromonitrobenzene, 8: *p*-bromonitrobenzene, 9: bromobenzene, 10: *o*-bromotoluene, 11: chlorobenzene, 12: *o*-chlorotoluene.

minutely the mechanism of electron capture reaction by D.C. mode. The temperature dependences of *K* values for aromatic chloro, bromo, and nitro compounds are shown in Figs. 6(a) and (b). They were measured at a column temperature of 100 °C. The temperature dependences of *K* values which were measured at a column temperature of 140 °C are shown in Fig. 6(c). The temperature dependences of mono, di, tri, and tetrachlorobenzene have negative slopes. The magnitude of the negative slope becomes smaller with increasing numbers of chlorine atoms. For PCB and HCB, the temperature dependences of *K* values have positive slopes. The slope of PCB is larger than that of HCB. The temperature dependences of these chlorobenzenes show inflection points which are not observed in pulsed mode. For aromatic nitro compounds, the temperature dependences of *K* values show the positive slopes at the higher detector temperatures. Wentworth *et al.*[10] suggested that information on electron capture reaction mechanisms can be obtained from the temperature dependence of *K* values by not only pulsed mode but also D.C. mode. They gave the formula for $\{(b-[e^-])/[e^-]\}$ by assuming only either a non-dissociative reaction or a dissociative reaction. They expected that the magnitude of the slope given by D.C. mode would be smaller than that of pulsed mode. The values of apparent activation energies E^* and electron affinities EA' are tabulated in Table 4. They were calculated from the magnitude of slopes.

The patterns of temperature dependence of *K* values were classified into the following three types (Fig. 7).

A) Chlorobenzene type (chlorobenzene and chlorotoluene isomers)

The temperature dependence of *K* value shows a negative slope at the higher temperature and zero or a small

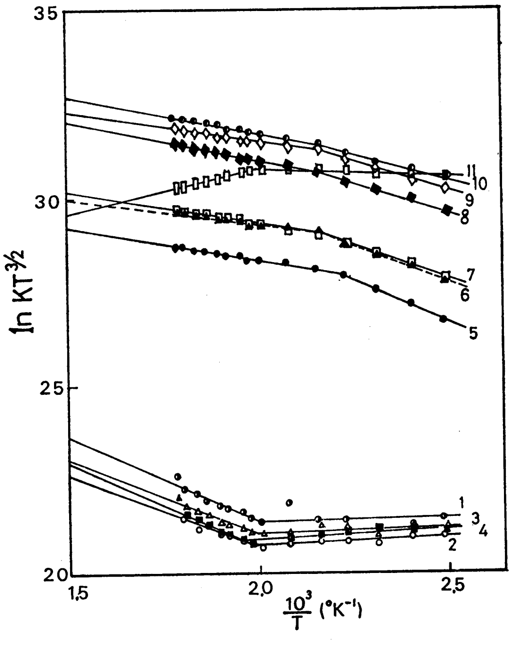


Fig. 6 (a).

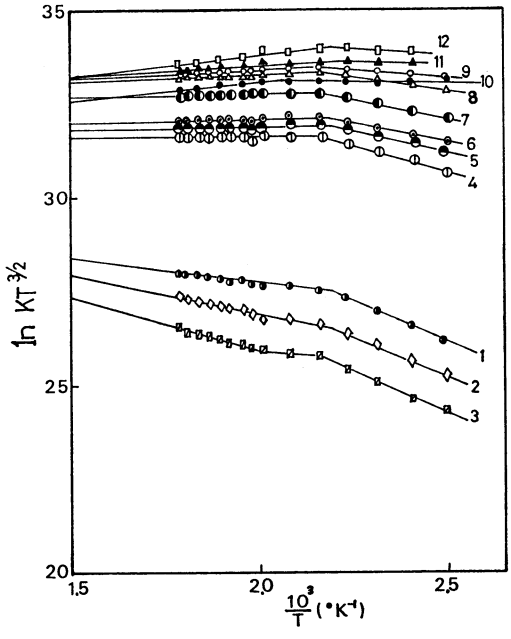


Fig. 6 (b).

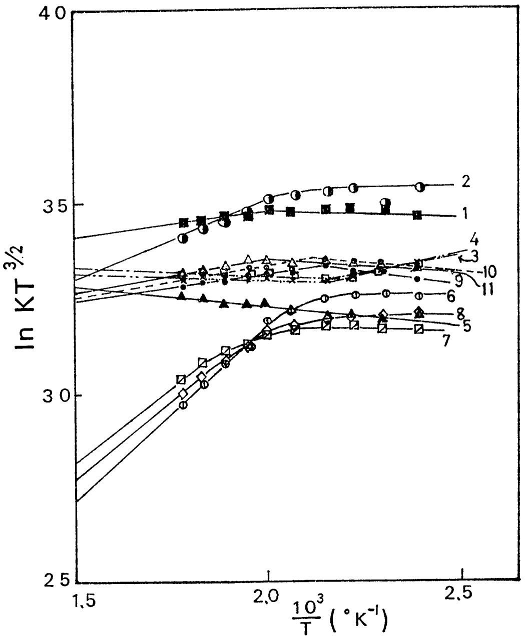


Fig. 6 (c)

Fig. 6 (a). Temperature dependence of electron capture coefficients (K values) measured at a column temperature of 100 °C.
1: Chlorobenzene, 2: *p*-chlorotoluene, 3: *m*-chlorotoluene, 4: *o*-chlorotoluene, 5: *p*-dichlorobenzene, 6: *m*-dichlorobenzene, 7: *o*-dichlorobenzene, 8: 1,2,4-trichlorobenzene, 9: 1,3,5-trichlorobenzene, 10: 1,2,3-trichlorobenzene, 11: nitrobenzene.

(b). Temperature dependence of K values measured at a column temperature of 100 °C. (*compounds were measured at 140 °C)
1: Bromobenzene, 2: *p*-bromotoluene, 3: *m*-bromotoluene, 4: *p*-bromochlorobenzene, 5: *m*-bromochlorobenzene, 6: *o*-bromochlorobenzene, 7: *p*-dichlorobenzene, 8: *m*-dibromobenzene, 9: *o*-dibromobenzene, 10*: *p*-bromonitrobenzene, 11*: *o*-bromonitrobenzene, 12*: *m*-bromonitrobenzene.

(c). Temperature dependence of K values measured at a column temperature of 140 °C.
1: Hexachlorobenzene, 2: pentachlorobenzene, 3: 1,2,3,4-tetrachlorobenzene, 4: 1,2,3,5-tetrachlorobenzene, 5: 1,2,4,5-tetrachlorobenzene, 6: *o*-nitrotoluene, 7: *m*-nitrotoluene, 8: *p*-nitrotoluene, 9: *p*-chloronitrobenzene, 10: *o*-chloronitrobenzene, 11: *m*-chloronitrobenzene.

Table 4. Apparent electron affinities (EA') and activation energies (E^*) for aromatic chloro, bromo, and nitro compounds in D.C. mode

Compound	EA' (kcal/mol)	−Slope $\times R^{a)}$ (kcal/mol)	$E^{*\,b)}$ (kcal/mol)
Chlorobenzene		9.17	5.96
p-Dichlorobenzene		3.60	1.33
m-Dichlorobenzene		2.84	1.15
o-Dichlorobenzene		3.43	1.61
1,2,3-Trichlorobenzene		3.97	2.48
1,2,4-Trichlorobenzene		3.97	2.70
1,3,5-Trichlorobenzene		3.06	2.31
1,2,3,4-Tetrachlorobenzene		0.84	
1,2,3,5-Tetrachlorobenzene		0.71	
1,2,4,5-Tetrachlorobenzene		2.01	0.41
Pentachlorobenzene	7.54		
Hexachlorobenzene	2.55		
p-Chlorotoluene		7.29	6.30
m-Chlorotoluene		9.09	6.19
o-Chlorotoluene		8.17	6.22
m-Chloronitrobenzene	2.61		
o-Chloronitrobenzene	2.31		
Bromobenzene		2.55	1.06
p-Bromotoluene		3.97	2.75
m-Bromotoluene		5.74	4.84
p-Bromonitrobenzene	1.99		
m-Bromonitrobenzene	2.26		
o-Bromonitrobenzene	1.14		
Nitrobenzene	4.81		
p-Nitrotoluene	15.79		
m-Nitrotoluene	14.90		
o-Nitrotoluene	18.06		

a) Calculated from $\ln KT^{2/3}$ *vs.* $1/T$ in kcal/mol.
b) Calculated from $\ln K$ *vs.* $1/T$.

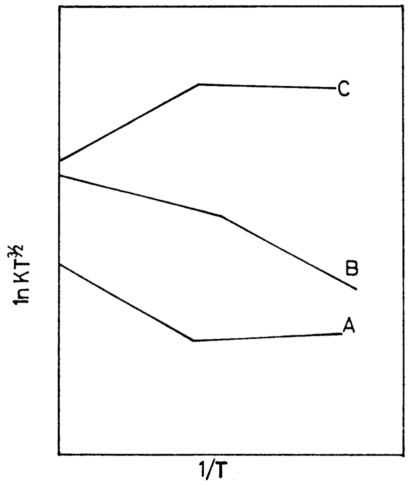


Fig. 7. Types of temperature dependence of K values. A: Chlorobenzene type, B: dichlorobenzene type, C: nitrobenzene type.

positive slope at the lower detector temperature. This type of compound appears to undergo mainly dissociative electron attachment at the higher detector temperature. The magnitude of the negative slope in D.C. mode is smaller than in pulsed mode.

B) Dichlorobenzene type (dichlorobenzene, trichlorobenzene, bromobenzene, and bromotoluene isomers) The temperature dependence of K value shows a negative slope which has an inflection point. The magnitude of the negative slope at the lower detector temperature is smaller than at the higher temperature. The reaction of this type may proceed chiefly according to dissociative electron attachment. The E^* values calculated from the magnitude of slopes at the higher detector temperature with D.C. mode are smaller than those with pulsed mode. The inflection points, whose physical meaning is not obvious, could be used for identification of unknown samples.

C) Nitrobenzene type (nitrobenzene, nitrotoluene isomers, PCB, HCB, and other nitro compounds) The temperature dependence of K value gives a positive slope at the higher temperature and a negative or zero slope at the lower temperature. In pulsed mode, this type of compound undergoes non-dissociative electron capture reaction. Similarly they seem to undergo non-dissociative electron attachment in D.C. mode. But for bromonitrobenzene and chloronitrobenzene isomers the magnitude of the positive slope is smaller than that in pulsed mode at the higher temperature. At the lower detector temperature, a negative slope is observed. Therefore, it is considered that these compounds undergo both dissociative and non-dissociative electron capture reactions. Since plots of both σ_H values and of Hammett's σ values *vs.* *R.S.* of aromatic nitro compounds give straight lines, the stage of electron attachment and elimination of the halogen atom may be important in the electron capture reaction of nitro compounds such as chloronitrobenzene isomers.

As mentioned above, the temperature dependence of K value in D.C. mode was similar to that in pulsed mode. Ordinarily, the magnitude of the slope, which corresponds to the calculated value of apparent activation energy (E^*) or electron affinity (EA'), was smaller than in pulsed mode. For example, the E^* value of chlorobenzene was found to be 5.96 kcal/mol in D.C. mode and 8.6 kcal/mol in pulsed mode by Satouchi *et al.*[17] As pointed out by Wentworth *et al.*,[10] this result may be attributed to the fact that electrons in the detector of D.C. mode have an additional energy given by the applied voltage. With this applied voltage in D.C. mode, the negatively charged ion of a sample molecule moves to the anode and discharges an electron. This effect is also observed in the case of disubstituted compounds containing electron attractive substituents. As regards this effect, an interesting phenomenon was observed. At the tailing part of the peak, some shape deformation (negative dip) was observed, as shown in Fig. 8. This phenomenon was not caused by detector contamination. This deformation could not be observed at higher temperatures. The reason for the appearance of the negative dip is not obvious, but the following experimental results were obtained. This negative dip can be observed in electron capture response of dissociative type compounds such as chlorobenzene, but is not observed or is less observed in non-dissociative type compounds such as nitrobenzene and other nitro compounds. The depth of negative dip for *meta*-substituted compounds is larger than for *para*- and *ortho*-substituted compounds.

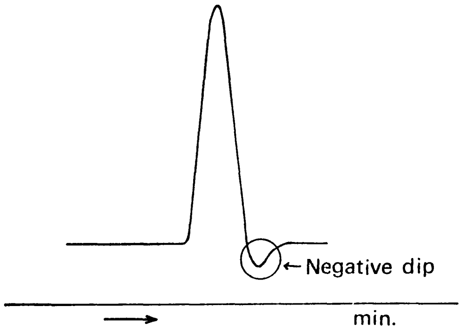


Fig. 8. Negative dip in the peak of gaschromatogram.

Summary

The mechanism in electron capture reaction can be determined by measuring the temperature dependence of K value in D.C. mode as well as in pulsed mode. We have used chromatographic data such as shape, slope, and inflection point in the curve of the temperature dependence of K value along with the data of retention time for identification of unknown substances.

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