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Electron-Capture Reaction of Halogenated Benzenes in MTHF Glass at 77 K

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The relative electron-capture efficiency of a number of halogenated benzenes was determined by means of competition with biphenyl as a reference material in glassy MTHF at 77 K. It was observed that the efficiency increased as the number of chlorine-atom substitutions on the benzene ring increased. Similar results were obtained for brominated benzenes. An excellent linear correlation is found between the logarithm of the efficiency and the polarographic reduction potential of a series of chlorinated benzenes. Moreover, a semilog plot of the efficiency *vs.* electron affinity of monohalogenated benzenes is apparently linear. The mechanisms of the electron-capture reaction are also discussed.

The study of the radiolysis of organic halogen compounds has advanced greatly in the last decade. These compounds have often been used as electron scavengers, because there is an effective way for examining ionic reactions in irradiated glass. Knowledge of the reactivity of organic halogen compounds with electrons is necessary for understanding and formulating the kinetics of the reaction process.

In spite of the many investigations on electron-capture reactions, the effect of halogen atom substitution in benzene is not fully understood.

In the present work, the relative efficiencies of electron capture by halogenated benzenes were determined in terms of the decrease in OD at 410 nm for biphenyl anions in glassy MTHF at 77 K.

Experimental

Reagents of special and guaranteed grade from Tokyo Kasei Co., Ltd. were used as received, except for 2-methyltetrahydrofuran (MTHF). The MTHF was purified by passage through a column of activated alumina. An MTHF solution of about 0.04 M biphenyl containing various halogenated benzenes was placed into a spectrosil vessel (10× 10 mm) and dissolved oxygen was purged by bubbling nitrogen gas prior to irradiation. The sample was immersed in liquid nitrogen during the irradiation with ^{60}Co γ-ray. Measurement of the optical absorption was carried out at 77 K with a Cary 14R spectrophotometer.

The dose rate was determined by the Fricke dosimetry method to be 2.0×10^{18} eV/g h and the irradiation dose was about 5.0×10^{17} eV/g for all samples.

Results and Discussion

It is well known that biphenyl is an appropriate scavenger for the electrons generated by irradiation in organic glasses at 77 K, because its reactivity with electrons is very fast, $k=4\times10^9\ \mathrm{M^{-1}\,s^{-1}}$, and moreover, the biphenyl anion is identifiable in an absorption spectrum by a high absorption coefficient in the near-UV region. Hamill and his coworkers have used biphenyl as a reference material for determining the reactivity of some solutes with electrons in glassy media.[1] The competitive reaction of biphenyl with the solute for electrons is, in general, as follows:

$$e^- + C_{12}H_{10} \longrightarrow C_{12}H_{10}^-$$

$$e^- + \text{Solute} \longrightarrow \text{Product}$$

Assuming that the electron capture reaction is a simple competitive process, the biphenyl-anion optical density in various solute concentration is given by the following expression:

$$\frac{\mathrm{OD}^\circ}{\mathrm{OD}} = 1 + \frac{K_s}{K_{\phi_2}}\frac{[\mathrm{s}]}{[\phi_2]} \tag{1}$$

where OD° and OD represent the optical densities of the biphenyl anion (410 nm) in the absence and in the presence of the solute, respectively, K_s and K_{ϕ_2} are the electron-capture coefficients of a given solute and of biphenyl, respectively, [s] and $[\phi_2]$ are the concentrations of a given solute and of biphenyl, respectively. The OD at 410 nm decreased with an increase in the concentration of chlorinated benzenes.

Arai *et al.* have shown recently by the low-temperature pulse radiolysis of halogenated compounds in ethanol glass that a strong absorption based on product negative ions appears in the visible to UV region.[2] In 1,2,3-trichlorobenzene, for example, there is no absorption for $\lambda>380$ nm, but below *ca.* 360 nm a strong absorption is observed ($\lambda_{\max}\approx320$ nm). If the absorption of negative ions of the halogenated benzenes used in our experiments affects that of biphenyl (especially at $\lambda_{\max}=410$ nm), then Eq. 1 is not suitable.

Then, competitive experiments were carried out after confirming that no absorption of solute anions was observed in the region around 410 nm.

The plot of OD°/OD for constant biphenyl concentration (0.04 M) should be a straight line as a function of the solute concentration. Figure 1 shows a plot of OD°/OD *vs.* $[\mathrm{s}]/[\phi_2]$ obtained in an MTHF solution of monochlorobenzene, 1,2-dichlorobenzene, and 1,2,4-trichlorobenzene at 77 K. The slope of the line in Fig. 1 corresponds to the relative electron-

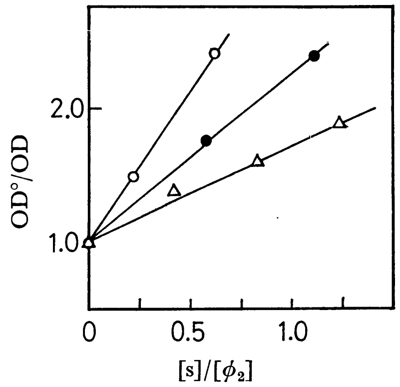


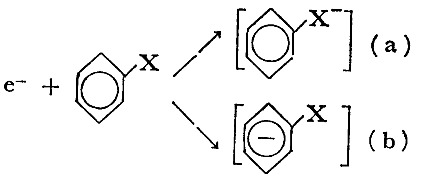
Fig. 1. Plot of OD°/OD *vs.* $[\mathrm{s}]/[\phi_2]$ in irradiated MTHF glass at 77 K.
-○-: 1,2,4-$C_6H_3Cl_3$, -●-: 1,3-$C_6H_4Cl_2$, -△-: C_6H_5Cl.

Table 1. THE RELATIVE ELECTRON CAPTURE EFFICIENCIES OF HALOGENATED BENZENES, γ-BHC, AND HEXACHLOROETHANE

No.	Material	K_s/K_{ϕ_2}
1	C_6H_5Cl	0.49
2	$1,2\text{-}C_6H_4Cl_2$	1.12
3	$1,3\text{-}C_6H_4Cl_2$	1.09
4	$1,4\text{-}C_6H_4Cl_2$	1.03
5	$1,2,4\text{-}C_6H_3Cl_3$	1.88
6	$1,2,3\text{-}C_6H_3Cl_3$	2.02
7	$1,3,5\text{-}C_6H_3Cl_3$	2.55
8	$1,2,3,4\text{-}C_6H_2Cl_4$	3.42
9	$1,2,3,5\text{-}C_6H_2Cl_4$	2.90
10	$1,2,4,5\text{-}C_6H_2Cl_4$	3.62
11	C_6HCl_5	6.60
12	C_6Cl_6	4.42
13	C_6H_5Br	0.84
14	$1,4\text{-}C_6H_4Br_2$	1.30
15	$1,3,5\text{-}C_6H_3Br_3$	2.78
16	C_6H_5F	0.05
17	C_6H_5I	0.88
18	γ-BHC	3.39
19	C_2Cl_6	4.04

capture efficiency (K_s/K_{ϕ_2}). Such competitive experiments were carried out for a number of chlorinated and brominated benzenes, as well as fluorobenzene and iodobenzene. The results are tabulated in Table 1. As can be seen in Table 1, the electron-capture coefficient (K_s) increases generally with an incraese in the number of chlorine or bromine atoms substituted on the benzene ring. While, no difference in the efficiency of the di-, tri-, and tetrachlorobenzene isomers was observed, the order of the reactivity for monohalogenated benzene is fluoro≪chloro<bromo<iodobenzene, which is the same as that for hydrated electrons in aqueous solutions.[3]

The electron-capture reaction for an aromatic compound is shown in the following scheme as formulated for monohalogenated benzene.[4]



The initial addition of an electron to the aromatic compound appears to occur predominantly by reaction process (b).[5] Therefore, the initial process for chlorinated benzenes is preferably the interaction of the π-orbital system of the benzene ring with the electron. Studier and Hart have suggested that the reaction of benzene with the electron is similar to reaction process (b).[6] However, the direct interaction for the substituent halogen atom on the benzene ring, which corresponds to reaction process (a), may be possible. In the case of monohalogenated benzene, the order of the relative electron-capture efficiencies may be explained by the effect of net electron-withdrawing, which is estimated from Hammett's parameters, σ_I and σ_R, of substituent halogen atoms on the benzene ring. σ_I and σ_R represent Hammett's parameters for inductive and resonant (mesomeric) effects, respectively.[7]

The decrease in the relative electron-capture efficiency for hexachlorobenzene in comparison with pentachlorobenzene would be attributed to a great extent to shielding of the π-orbital system by substituent chlorine atoms on the benzene ring. The value of the efficiency for hexachlorobenzene is similar to that of aliphatic hexachloro-compounds, such as hexachloroethane and γ-BHC. This fact indicates that the π-orbital system of hexachlorobenzene provides a lower contribution to electron capture than that of other chlorinated benzenes.

Christodouleas and Hamill have found that the relative electron-capture efficiency of aromatic hydrocarbons, such as phenanthrene, is correlated to the polarographic reduction potential.[8] It was found that the relative electron-capture efficiencies in the present results can also be roughly correlated with the reduction potential of the various monohalogenated benzene derivatives, which have been determined in aprotic solvents by Sease *et al.*[9] Recently, Tsuji has determined the reduction potential of a series of chlorinated benzenes by the differential pulse polarographic method and shown that the value increased proportionally with the number of substituted chlorine atoms on the benzene ring from mono- to hexachlorobenzene.[10] And also no difference in the reduction potential for isomers of polychlorinated benzenes was observed.[11] The results of the relative electron-capture efficiencies for isomers are in accord with the trend of the polarographic reduction potential.

Figure 2 shows a semilogarithmic plot of the relative electron-capture efficiency *vs.* the reduction potential of chlorinated benzenes. Interestingly, the plot, as shown in Fig. 2, is very linearly from mono- to pentachlorobenzene, except for hexachlorobenzene.

The relationship between the logarithm of the electron-capture efficiency and the reduction potential from mono- to pentachlorobenzene can be expressed by

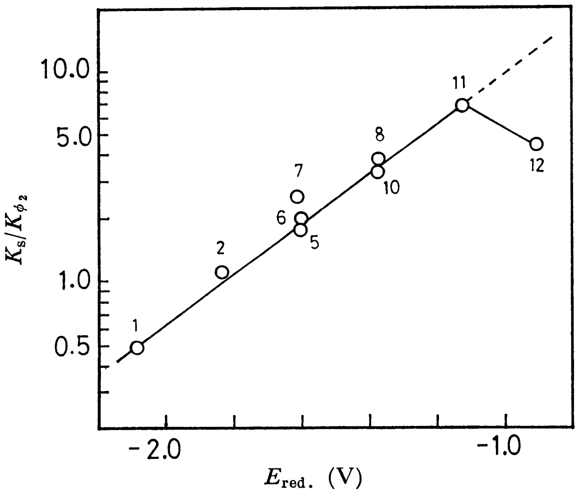


Fig. 2. Plot of $\log K_s/K_{\phi_2}$ *vs.* reduction potential ($E_{red.}$) of a series of chlorinated benzenes. The values of reduction potential for penta- and monochlorobenzene estimated from the secondary peak of hexachlorobenzene and 1,2-dichlorobenzene measurements, respectively. Key is shown in Table 1.

following equation, which is plotted in Fig. 2:

$$\log K_s/K_{\phi_2} = a\,E_{\text{red.}} + b \qquad (2)$$

where $E_{\text{red.}}$ is the reduction potential, and a and b are constants. Nenner and Schulz have accurately measured the electron affinity using electron transmission spectroscopy.[12)] They indicated that a good correlation between the polarographic reversible electrode potential and the electron affinity was observed. The reversible electrode potential for halogenated benzenes cannot be obtained from the usual polarographic measurement, because dissociation preferentially occurs prior to the reversible reaction. However, it is clear that the reversible electrode potential is related to the reduction potential of halogenated compounds.[12)] Thus, the logarithm of the relative electron-capture efficiency may be linear as a function of the quasi-electron affinity which is estimated from the polarographic reduction potential. Therefore, a similar relation to that shown in Fig. 2 can be expected for accurate electron affinities. A semilog plot of the relative electron capture efficiency *vs.* the electron affinity[12)] of monohalogenated benzenes is shown in Fig. 3. Figure 3 shows that the relative electron-capture efficiencies for halogenated benzenes are given as a function of the electron affinity as has been mentioned for the reactivity of many compounds with hydrated electrons by Anbar and Hart.[13)]

Wentworth and his coworkers have proposed that the relation between the electron-capture coefficient and the electron affinity in gas phase can be shown to be[14)]

$$\log KT^{3/2} = \log A + \log k_L/k_M + EA/RT \qquad (3)$$

where A is composed fundamental constants, including the mass of the electron, k_L and k_M are the rate constant for neutralization of negative ions and electrons, respectively and EA is the electron affinity. Thus, the relative electron-capture efficiency would be given by following expression:

$$\log K_s/K_{\phi_2} = \log(k_L)_s - \log(k_L)_{\phi_2} + (EA)_s/RT - (EA)_{\phi_2}/RT \qquad (4)$$

where the subscripts ϕ_2 and s refer to biphenyl and solute, respectively. Assuming that the rate of neutralization is very slow at a low temperature of 77 K, Eq. 4 can be rewritten as follows:

$$\log K_s/K_{\phi_2} = (EA)_s/RT - (EA)_{\phi_2}/RT, \qquad (5)$$

where $(EA)_{\phi_2}/RT$ is constant at 77 K. Equation 5 indicates that a linear relationship between $\log K_s/K_{\phi_2}$ and $(EA)_s$, and that the slope is dependent on the temperature. The semilog-linearity in Fig. 3 can apparently be explained by Eq. 5. According to Eq. 5, the slope is given by $1/RT$, which has a value of 150. However, the slope of the line in Fig. 3 is about 3.5. Since such a great difference between the observed slope (Fig. 3) and the slope calculated from Eq. 5 is observed, a treatment similar to that in the gas phase may not be applicable at low temperatures.

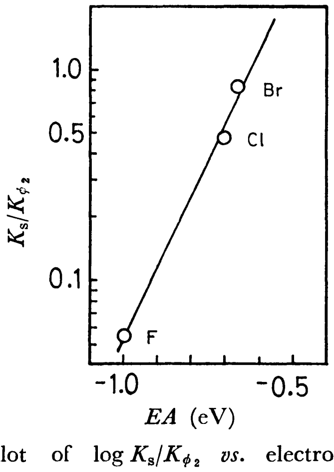


Fig. 3. Plot of $\log K_s/K_{\phi_2}$ *vs.* electron affinity of monohalogenated benzenes.

On the other hand, Miller has emphasized that the tunneling mechanism for the electron-capture reaction is of importance in glassy media and has suggested that the electron affinity is a predominant factor in determining whether or not the tunneling reaction can occur.[15)] Namiki *et al.* have pointed out that the scavenging efficincy is linear as a function of the adiabatic electron affinity of the acceptor in alcoholic glasses.[16)] They discussed the electron-capture process on the basis of the tunneling model. This consideration is interesting, but until recently only limited data had been available on accurate electron affinities of a series of halogenated benzenes in order to conform the relationship between the relative electron-capture efficiency and the electron affinity. For a more detailed explanation on this relationship, measurements of the efficiencies for many kinds of substituted benzenes will be necessary.

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