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Electron Scavenging by Benzene Derivatives in Alcohol Glasses

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Electron scavenging efficiencies by benzene derivatives in alcohol glasses were studied by employing gamma radiolysis at 77 K. Scavenging efficiencies, $1/[S]_{1/2}$, were quasi-linear with the adiabatic electron affinities (EA) of the acceptors and they increased as the solvation time of the trapped electron became long. Electron scavenging was explained as a tunneleing of the unsolvated electron; the pre-exponential factor in the tunneling rate was calculated by employing the Morse function developed by Wentworth *et al.* in the gas phase, which gave an EA dependence in accordance with the experimental results.

A variety of molecules can capture a low energy electron in the gas phase to form molecular anions or dissociate into fragment radicals and anions. In the condensed matrices, also. the electron capture process has been studied extensively by using polar and non-polar solvents. But few reports have been published which discuss the relation between mechanisms of electron scavenging in the gas and the condensed matrices. This paper is a first step to explain the mechanism of electron scavenging in the glass in terms of reactions in the gas phase.

It has been widely admitted that, in the glass, the trapped or solvated electrons (e_t^- or e_s^-) react withsolutes and their parent positive ions through tunneling. The simple expressions of the tunneling theory were given by Miller[1)] and he succeeded in estimating the tunneling distances between e_s^- and solute molecules and also the decay of e_s^- over a very wide range of time.[1,2)] However, there are some discrepancies between the estimated values and the experimental results, especially in polar matrices. For example, the experimental tunneling distance of e_s^- in a benzene solution of ethanol was much smaller (≤ 17 Å) than the estimated value.[1)] The observed decay of e_s^- was much slower than the calculated curve for the case of NO_3^- in the alkaline water glass.[2)] These discrepancies may result from an oversimplification in his theory, in which the nature of the acceptor molecule is not taken into consideration and in which the tunneling occurs only from the solvated state. The electronic level of the anion of the acceptor molecule must resonate with that of the trapped electron. The transition from the neutral state to the anionic state occurs without changing the nuclear configurations before and after accepting the electron (Franck-Condon principle). In this paper, the Franck-Condon restriction is taken into consideration in the pre-exponential factor of the tunneling rate along with the treatment developed in the gas phase studies.[3,4)]

In polar matrices, the electron is stabilized in pre-existing shallow traps.[5)] The depth of these potential wells changes with time upon solvation. Miller suggested that the extremely restricted tunneling to benzene in ethanol occurs within 1 μ sec when the traps are shallow.[1)] Steen also suggested the importance of tunneling of the pre-solvated electrons.[6)] The reactivity of e_t^- in shallow traps in ethanol at 4K was noticably larger than that of e_s^- at 77K, which can be attributed to a more efficient tunneling from shallow traps than from the solvated state.[7)]

Halogenated benzene derivatives have been studied as regards the attachment of a low energy electron in the gas phase by both the electron beam experiments[8,9)] and the thermal electron attachment experiments.[3,4)] Wentworth *et al.*, obtained the formulation for the electron attachment rate using the simple Morse function and succeeded in explaining qualitatively both experimental results.[4)] They estimated the adiabatic electron affinities for some halogenated benzenes, which play the most important role in the electron capture process.[4)] In this report, Steelhammer and Wentworth's method is extended to the electron attachment through tunneling in condensed media.

Experimental

Reagent grade methanol, ethanol, *n*- and *iso*-propanol were used as solvents without further purification. Reagent grade of benzene derivatives were added aerobically without purification.

The solutions were quenched to glasses by the usual rapid cooling technique in suprasil cells of 0.2 cm thickness. The glasses were irradiated at 77 K by ^{60}Co gamma ray with a dose rate of 1.88×10^{20} eV/g·hr for 3 min in the case of MeOH (5 mol% H_2O) and EtOH glasses and for 5 min in the cases of *n*-PrOH and *iso*-PrOH glasses. The optical density (O.D.) at the peak in the absorption spectrum of e_s^- was measured at 77 K within 1 min after the irradiation.

Dissociative electron attachments to chloro-, bromo-, and iodobenzene do not produce any free radicals, except the solvent radical in the alcohol at 77 K. The anions of benzene, alkylated benzene, and fluorobenzene are protonated, and converted to the hexadienyl type radicals which show an absorption spectrum in the near UV region.[10)] Therefore, the O.D. at the peak of e_s^- in the visible region could be obtained accurately for all benzene derivatives.

Results and Discussion

Experimental Results. Figure 1 shows the plots of log O.D. *vs.* the concentrations of the added scavengers in ethanol at 77K. Good linearlity was also obtained for other solvents and solutes. The concentrations, $[S]_{1/2}$, which reduce the e_s^- yield to a half of those in pure solvents, were determined from these semilogarithmic plots and are shown in Table 1.

Experimental tunneling distances, a, as defined by Miller,[1)] were obtained by the formula:

$$a = \left(\frac{10^3}{8.0\pi}\frac{\ln 2}{[S]_{1/2}}\frac{M}{d}\right)^{1/3} \text{(Å)} \qquad (1)$$

TABLE 1. $[S]_{1/2}$ IN mol %; EXPERIMENTAL TUNNELING DISTANCE a AND SIMULATED TUNNELING DISTANCE a' IN Å

Formula	MeOH			EtOH			n-PrOH			iso-PrOH		
	$[S]_{1/2}$	a	a'[a)]	$[S]_{1/2}$	a	a'	$[S]_{1/2}$	a	a'	$[S]_{1/2}$	a	a'
1,3,5-$C_6H_3(CH_3)_3$				0.77	12.7							
p-$C_6H_4(CH_3)_2$				0.64	13.5							
$C_6H_5CH_3$	0.85	11.0		0.67	13.4		0.265	19.9		0.25	20.4	
C_6H_6	0.88	10.9		0.68	13.3		0.24	20.5		0.24	20.7	
C_6H_5F	0.75	11.4		0.40	15.9		0.17	23.0		0.145	24.4	
o-$C_6H_4CH_3Cl$	0.64	12.1	6.4[b)]	0.35	16.6	10.2	0.165	23.3	12.7	0.10	27.7	14.0
C_6H_5Cl	0.62	12.2	12.4	0.265	18.2	20.3	0.14	24.6	22.7	0.095	28.2	24.1
o-$C_6H_4CH_3Br$	0.52	12.9	10.7	0.25	18.5	18.5	0.145	24.3	21.0	0.09	28.6	22.3
C_6H_5Br	0.49	13.2	13.1	0.23	19.1	21.0	0.125	25.5	23.4	0.08	29.8	24.8
C_6H_5I	0.49	13.2	14.9	0.20	20.0	22.8	0.12	25.9	25.3	0.07	31.2	26.6
o-$C_6H_4Cl_2$	0.465	13.4	15.5	0.18	20.7	23.4	0.11	26.6	25.9	0.065	31.9	27.2
p-$C_6H_4Cl_2$				0.15	22.0							
1,3,5-$C_6H_3Cl_3$				0.11	24.3							

a) τ was assumed to be 10 ns. The same values as in other solvents were inserted for the other parameters.
b) Only this value was estimated from Eq. (7′).

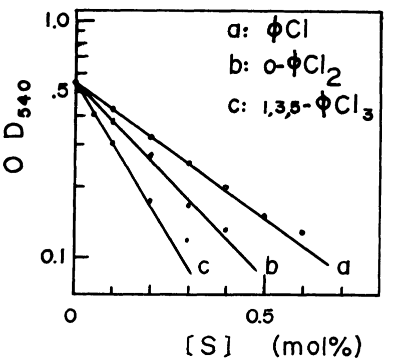

Fig. 1. Semilogarithmic plots of the yields of e_s^- (O.D. at 540 nm) $vs.$ scavenger concentrations in ethanol at 77 K.

where M and d are the molecular weight and the density of the solvent and $[S]_{1/2}$ is in mol %. The values of a are tabulated for each solvent in the second column of Table 1.

In Fig. 2 the scavenging efficiencies, the reciprocals of $[S]_{1/2}$, were plotted against the *adiabatic electron affinity*, EA,[4)] for o-$C_6H_4CH_3Cl$, C_6H_5Cl, o-$C_6H_4CH_3Br$, C_6H_5Br, and o-$C_6H_4Cl_2$. The scavenging efficiency is nearly linear with the electron affinities of the solutes in all the different alcohols. The deviation from linearity is especially small in ethanol. Because the EA's of C_6H_6, C_6H_5F, and C_6H_5I are unknown, these EA's are estimated by putting their scavenging efficiencies on the best fit line in ethanol. They are −0.75, −0.52, and 0.0 eV, respectively. For these three additional points (a, b, and c in Fig. 2), the linearity is still as good as for other three solvents.

From Fig. 2 and Table 1 we can find two main results.

(1) For various benzene derivatives in each solvent, the scavenging efficiency, $1/[S]_{1/2}$, and the experimental tunneling distance, a, become large as EA increases. $1/[S]_{1/2}$ $vs.$ EA is roughly linear.

(2) $1/[S]_{1/2}$ and a are strongly dependent upon the nature of the matrix. The order of increase is MeOH, EtOH, n-PrOH, and iso-PrOH.

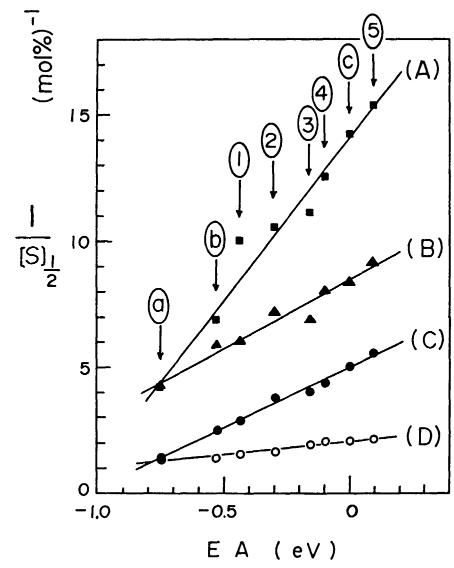

Fig. 2. Plots of $[S]_{1/2}^{-1}$ $vs.$ EA. The solvents are iso-PrOH (A) ■, n-PrOH (B) ▲, EtOH (C) ● and MeOH (D) ○.
EA of o-$C_6H_4CH_3Cl$ ①, C_6H_5Cl ②, o-$C_6H_4CH_3Br$ ③, C_6H_5Br ④, and o-$C_6H_4Cl_2$ ⑤ are from Ref. 4, while EA of C_6H_6 ⓐ, C_6H_5F ⓑ and C_6H_5I ⓒ were determined from the line (C).

Simple Model for Acceptor. The exponential dependence of the yield of e_s^- on the scavenger concentration in Fig. 1 shows that the scavenging is due to the epithermal electron capture or to the tunneling of the trapped electron. If we take the former process, it is difficult to explain the strong dependence of scavenging efficiency on the matrix because the degradation spectrum of the epithermal electron must not differ so much among these alcohol solvents.

Result (1) of the preceeding section implies clearly that the contribution from EA of the acceptor should not be ignored in the tunneling model. Result (2) suggests that tunneling occurs mainly when the potential well of the trapped electron is shallow. The times for the trapped electron to reach the stable spectra at 77K are <3, ~7, ~40, and ~100 μs for MeOH, EtOH, n-PrOH, and *iso*-PrOH, respectively.[11] This order is the same as that in result (2).

In order to simplify the ploblem, we make the following assumptions. The secondary electron is stabilized in the pre-solvated state, and it tunnels to the acceptor molecules or it becomes solvated after surviving for a life time of τ. There is only one kind of shallow trap with a depth of V. Once the electron is solvated, it cannot tunnel to the acceptor.

The usual tunneling procedure refers to the final state of the electron in the free continuum. In our case, however, the final state is the electron in a molecular orbital of the anion. Therefore, the expression of the tunneling rate, k_{tun},[12] must be modified by introducing F into the pre-exponential factor as

$$k_{\text{tun}} = \nu \mathrm{F} \exp\left\{-\frac{2a}{\hbar}\sqrt{2m(V-E)}\right\}, \tag{2}$$

where ν is the impinging frequency of e_t^- in the potential well, a is the tunneling distance or the barrier width, $\hbar$ is Planck's constant divided by 2π, m is the electron mass, V is the depth of the well measured from the bottom of the conduction band, and E is the energy of e_t^- measured from the bottom of the well. F has a meaning close to the Franck-Condon factor and it must be written as a function of the EA of the acceptor. The resonance electron transfer from e_t^- to the acceptor is so fast that the nuclear configuration of the acceptor cannot change during the electron tunneling. Therefore, it can be written as the vertical transition between the two adiabatic potential energy curves of the neutral state and the negative-ion state. For the calculation of F we follow Steelhammer and Wentworth's treatment, which explained successfully the vertical electron attachment process in the gas.[3,4]

When the incident electron has the energy E_{v}, the vertical transition requires the following energy relation:

$$\begin{aligned} E_{\text{v}} = {} & -2kD^{\circ}_{\text{AB}}\mathrm{e}^{-\beta(r-r_{\circ})} + D^{\circ}_{\text{AB}}\mathrm{e}^{-2\beta(r-r_{\circ})} \\ & -EA_{\text{A or B}} + D_{\text{AB}} \end{aligned} \tag{3}$$

where the parameters are the same as those in Ref. 4: namely, k is the parameter to determine the potential energy curve of the acceptor anion, D°_{AB} is the bond dissociation energy referenced to the minimum of the function, r_0 is the equilibrium internuclear separation for the C–X bond (X=halogen), $\beta=\nu_0(2\pi^2\mu/D^{\circ}_{\text{AB}})^{1/2}$, ν_0 is the fundamental vibrational frequency for the C–X stretching mode, μ is the reduced mass, EA_{A} is the electron affinity of the aromatic radical in the case of the formation of the molecular negative ion and EA_{B} is that of the halogen atom in the case of a dissociative negative-ion, and D_{AB} is the bond dissociation energy measured from the zero-point energy level.

In condensed media, the energy of e_t^- is $(V-E)$ under the quasi-free electron level. Because the latter is V_0 above the vacuum level, the trapped electron state is expressed as $V_0-(V-E)$ referenced to the vacuum level. When the electron is captured by the neutral molecule, the molecular negative ion is stabilized by the medium electronic polarization energy of P_-. Therefore, the electron energy to be given to the acceptor has the following equation:

$$E_{\text{v}} = V_{\text{o}}-(V-E)-P_-. \tag{4}$$

Upon tunneling, the internuclear separation of the neutral molecule, r, must satisfy Eqs. (3) and (4). The probability density, $p(E_{\text{v}})$, of finding the nuclear configulation at r in the zero vibrational state of the neutral molecule is[4]

$$p(E_{\text{v}})\mathrm{d}E_{\text{v}} = \frac{\sqrt{\alpha/\pi}\,\mathrm{e}^{-\alpha(r-r_{\circ})^2}}{2\beta D^{\circ}_{\text{AB}}(\mathrm{e}^{-2\beta(r-r_{\circ})}-k\mathrm{e}^{-\beta(r-r_{\circ})})}\mathrm{d}E_{\text{v}}, \tag{5}$$

where $\alpha=\sqrt{\mu f/\hbar^2}$ and f is the force constant for the C–X bond.

If we assume that the density of the resonance state of the trapped electron is unity within the small range of ΔE_{v} around E_{v} and vanishes in the other region, F is expressed as

$$F = p(E_{\text{v}})\Delta E_{\text{v}}. \tag{6}$$

Under the condition of $\nu \mathrm{F}\tau \geqq 10$,[13] the tunneling distance a' is

$$a' \cong 5.0 + \frac{1}{\sqrt{V-E}}\ln(\nu p(E_{\text{v}})\Delta E_{\text{v}}\tau) \ (\text{Å}), \tag{7}$$

where 5.0 is added as the correction term from the radii of both the trapped electron cavity and the acceptor, and $(V-E)$ is in eV. When $\nu \mathrm{F}\tau < 10$,[13] a' is

$$a' \cong 5.0 + \frac{1}{\sqrt{V-E}}(6\nu p(E_{\text{v}})\Delta E_{\text{v}}\tau)^{1/3} \ (\text{Å}). \tag{7'}$$

Miller estimated 10^{15}/s for ν as the case of the one dimensional problem.[1] But if we take into consideration the attenuation from the fractional solid angle into which the electron enters,[14] ν must be reduced by a factor of about 10^2 for the tunneling distances in our results. ΔE_{v} is the width of the resonant vibrational levels. Though we have no exact knowledge about this width, ΔE_{v} is assumed to be the order of several spans of the lattice vibration of the matrix around the trapped electrons and less than the vibrational spacings of the acceptor molecule. Tentatively we take $\Delta E_{\text{v}}=10^{-2}$ eV for all solutes and solvents. The absorption band of the pre-solvated electron in ethanol at 4 K shows a threshold at about 0.5 eV. Since the absorption of the pre-solvated electron is a bound-free transition,[15] we take $(V-E)=$ 0.5 eV. In the case of the other solvents, photo-ionization thresholds of the pre-solvated electron have not been determined, and therefore we assume the same value for the other solvents. There is no direct information for V_0 and P_- given by experiment. Fueki *et al.*[16] calculated successfully the energy of the trapped electron in ethanol for the case of $V_0 \geq 0$. Allen *et al.*[17] claimed the polarization energy of SF_6^- in the non-polar liquid as about -0.65 eV. Therefore, we have assumed that (V_0-P_-) is roughly 1.0 eV, leading to $E_{\text{v}}=0.5$ eV.

$p(E_{\text{v}})$'s of different halobenzene molecules were calculated to explain the line shapes of the electron attachment cross-sections but were given in arbitrary units.[4] In this paper, we recalculated $p(E_{\text{v}})$ absolutely for various E_{v} using the same values of parameters in Morse functions as in Ref. 4. Molecular negative-ion potential energy curves were taken for o-$\mathrm{C_6H_4CH_3Cl}$, $\mathrm{C_6H_5Cl}$, o-$\mathrm{C_6H_4CH_3Br}$, $\mathrm{C_6H_5Br}$, and o-$\mathrm{C_6H_4Cl_2}$ and the dissociative negative-ion potential energy curve for $\mathrm{C_6H_5I}$ as in the case of Steelhammer and Wentworth.[4] These

TABLE 2. $p(E_v)$ IN $(\mathrm{eV})^{-1}$

	o-$C_6H_4CH_3Cl$	C_6H_5Cl	o-$C_6H_4CH_3Br$	C_6H_5Br	C_6H_5I	o-$C_6H_4Cl_2$
$p(E_v)$	0.157×10^{-3}	0.174	0.524×10^{-1}	0.282	1.04	1.57

imply that the trapped electron tunnels to the π^* orbital for the five Cl or Br substituted benzenes and to the σ^* orbital of the C–X bond for C_6H_5I. The values of $p(E_v)$ at $E_v=0.5$ eV are listed in Table 2.

The halflife of the pre-solvated electron, τ, in ethanol at 77K was measured to be about 2.5 μs at 1260 nm.[18] The τ's in n- and *iso*-PrOH at 77K were not obtained, but the absorption spectra of the trapped electron in these matrices and in the EtOH matrix became stable at 40 and 100 μs and at 7 μs after the pulse respectively.[11] The half-lives in n- or *iso*-PrOH were then assumed as $2.5/7\times40$ or $2.5/7\times100$ μs respectively by normalizing the above times, which were required for reaching the stable spectra in EtOH. The tunneling distances, a', obtained from Eq. (7) are shown in Table 1. Similar calculations were carried out on MeOH, assuming that τ in this matrix is 10 ns.

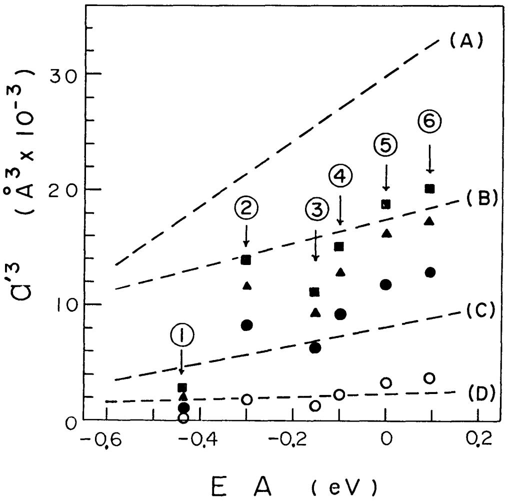

Fig. 3. Plots of a'^3 *vs.* EA. The dotted lines are experimental one; (A) *iso*-PrOH, (B) n-PrOH, (C) EtOH, and (D) MeOH. Other notations are same as those in Fig. 2 with exceptions of C_6H_5I ⑤ and o-$C_6H_4Cl_2$ ⑥.

Discussion of the Model Calculation. The simulated values of a'^3 are compared to the experimental values of a^3 in Fig. 3. $EA=0.0$ eV for C_6H_5I was tentatively assumed from Fig. 2 for convenience in comparison, though the present model states that the electron tunneling occurs directly to the dissociative state of the orbital for a C–I bond. The simulated values in EtOH and n-PrOH are consistent with the experimental ones, not only in the tendency with EA but also in their absolute values. In *iso*-PrOH the deviation is serious. This deviation comes partly from the uncertainty of the numerical values in each parameter. Especially τ in *iso*-PrOH may be underestimated, since the absorption spectrum observed by a pulse experiment extended far into the infrared region even at 100 μs after a pulse.[11]

In MeOH, the trapped electron prior to solvation was observed neither by the pulse radiolysis at 77 K[11] nor by the gamma ray radiolysis at 4 K.[5] The spectra obtained in those experiments show that the electron has already been solvated. Therefore, it is reasonable to consider that the solvation time in MeOH is very short. In this paper, a solvation time of 10 ns gives the best fitting in the scavenging curves, as is shown in Fig. 3.

The linear relationship between a'^3 and EA can not be proved directly from Eq. (8) *via* Eq. (5). In Eq. (5), k in the case of the molecular negative ion state contains EA of the acceptor as

$$k^2=\frac{EA+(D^\circ_{\mathrm{AB}}-EA_{\mathrm{A}})-\frac{1}{2}h\nu_{0\mathrm{AB}}+\frac{1}{2}h\nu_{0\mathrm{AB}^-}}{D^\circ_{\mathrm{AB}}},\qquad(8)$$

where $h\nu_{0\mathrm{AB}}$ and $h\nu_{0\mathrm{AB}}{}^-$ are the vibrational energies of the C–X streching mode in the neutral and ionic states.[4] In Fig. 3, o-$C_6H_4CH_3Cl$ and o-$C_6H_4CH_3Br$ deviate seriously. These deviations are partly removed if we take E_v larger than 0.5 eV, though $p(E_v)$ of o-$C_6H_4Cl_2$ decreases in this energy region since the peak in $p(E_v)$ exists at an energy lower than 0.5 eV. But the present simple model cannot explain the linearity of a^3 *vs.* EA obtained experimentally.

We checked the possibility of the electron tunneling to the molecular negative-ion state for the case of C_6H_5I. The tentatively assumed value the $EA=0.0$ eV from Fig. 2 is inserted into Eq. (8), neglecting the zero vibrational energy, and gives $k=0.321$. Using this value, we can get $p(E_v)=0.332\times10^{-2}$/eV at $E_v=0.5$ eV. But this value gives a very small tunneling distance for C_6H_5I. This fact suggests that tunneling to the π^* orbital is not involved for C_6H_5I as much as the electron attachment in the gas phase.[3,4] Bond dissociation occurs rather dominantly at C–I rather than C–Br in p-C_6H_4BrI, while both bond dissociations occured at C–Br and C–Cl in p-C_6H_4ClBr.[10] These facts support the contention that the dissociative electron tunneling goes through via a molecular negative-ion state for Cl or Br substituted benzenes, but proceeds by a direct dissociation process for I substituted benzenes.

For an appropriately improved model to explain especially the linear relationship between a'^3 and EA, the following features should be taken into consideration. (1) The dynamical process of the solvation by the trapped electrons is more complicated. Though how exactly make the solvation proceed is unclear, it is more realistic to deepen the well continuously rather than discretely. Then, k_{tun} must be a function of time through $(V-E)$. (2) The pre-solvated electrons exist in traps with different potential depths.[15] There may exist more shallowly trapped electrons than 0.5 eV in quicker periods. The distribution of the potential depths must be taken into consideration for k_{tun} in the improved model. This effect may be important especially for small EA acceptors.

The condition that $E_v>-EA$, is necessary for the tunneling of the trapped electron. Since EA is -0.75 or -0.52 eV for C_6H_6 or C_6H_5F as estimated above, this condition is violated for these solutes if E_V is 0.5 eV. But tunneling can occur to C_6H_5F or C_6H_6 experimentally. This difficulty may be partly removed by considering the above situations.

Electron Affinity. There remain remarkable discrepancies among the reported EA values of C_6H_6 and C_6H_5F.[19] EA's in the abscissa in Fig. 2 for the five Cl or Br substituted benzenes were determined through Eq. (8) and, following Eq. (9),[4]

$$k = 1 - \frac{E_V^p + EA_A + \frac{1}{2}h\nu_0}{2D_{AB}^\circ}. \qquad (9)$$

This may be also applicable to C_6H_6 or C_6H_5F if we take D_{AB}° of the C–H bond in C_6H_6 and of the C–F bond for C_6H_5F. We tried to test the validity of EA of C_6H_6 or C_6H_5F estimated from Fig. 2 using these relations. The D_{AB}° of the C–H or C–F bond in benzene is 102 or 115 kcal/mol. Neglecting the zero vibrational energy, we obtained $E_V^p = 1.5$ eV for C_6H_6 or $E_V^p = 1.1$ eV for C_6H_5F by using our estimated values of $EA = -0.75$ or -0.52 eV, respectively. These E_V^p values should be compared to the peak energies in the energy loss resonance, which were interpreted to be a temporary negative ion resonance.[9,20] Compton *et al.*[20] reported that these peak energies were 1.55 eV for C_6H_6 and 1.35 eV for C_6H_5F; here agreement between the estimated E_V^p values and the measured values is good, suggesting that the estimation of the adiabatic electron affinities of benzene derivatives can be determined reasonably well by using the lines in Fig. 2.

Table 3. EA in eV

Formula	EA (eV)
1,3,5-$C_6H_3(CH_3)_3$	-0.78 ± 0.10
1,4-$C_6H_4(CH_3)_2$	-0.72 ± 0.10
$C_6H_5CH_3$	-0.73 ± 0.10
C_6H_6	-0.75 ± 0.10
C_6H_5F	-0.52 ± 0.10
p-$C_6H_4Cl_2$	0.35 ± 0.15
1,3,5-$C_6H_3Cl_3$	0.85 ± 0.20

In Table 3 we tabulated the EA values so determined from the line of EtOH for methylated benzenes and chlorinated or fluorinated benzenes. Large changes in EA are recognized by halogen atom substitution. Addition of one Cl atom to the ring increases EA by about 0.4—0.5 eV, suggesting that additivity in EA is also valid for Cl as well as for F.[21] On the other hand, no large change in EA is seen in C_6H_6 or other methylated benzenes, implying that the effect of the CH_3 group on EA is small compared to the case of a halogen.

The anion of C_6H_6 is known to exist stably in the condensed media,[22] though the EA of C_6H_6 is negative. The condition that the anion can be stable in the condensed medium is

$$V_0 - P_- + EA > 0. \qquad (10)$$

Due to the factor of $V_0 - P_-$, stable existence of the benzene anion does not imply necessarily that $EA > 0$. In this sense, the recent conclusion that $EA > 0$[19a] for C_6H_6 is questionable.

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