A Theoretical Treatment of Molecular Complexes. I. Silver-Aromatic Hydrocarbon Complexes

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Theoretical researches of molecular complexes have become active since Mulliken combined the old concepts of molecular compound and established a new theory[1]. Prior to this research many qualitative discussions on molecular complexes had been presented. These are the covalent bond theory by Bennett and Willis[2], the polarization aggregate theory by Briegleb[3], the ionic complex theory by

1) R. S .Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952).

2) G. M. Bennett and G. H. Willis, *J. Chem. Soc.*, **1929**, 256.

3) G. Briegleb, *Z. physik. Chem.*, **B16**, 249 (1932).

Weiss[4], and the complex resonance by Brackmann[5]. Weiss had pointed out that molecular complexes have an ionic structure B^+A^-, so that the lower the ionization potential for an electron donor is, and the higher the electron affinity for an electron accceptor is, the more easily the molecular complex is formed. Brackmann regarded the structure of complex as a resonance hybrid to which no-bond and dative structures contribute.

$$D:A \leftrightarrow D^+:A^-$$

Based upon these concepts, Mulliken presented a quantum mechanical theory on the charge transfer spectra of molecular complex[1]. Further, Mulliken predicted the configuration of benzene-iodine complex, benzene-silver complex and BF_3–$N(CH_3)_3$ complex, and his assumption was proved to be correct except in the case of benzene-iodine complex. With regard to benzene-iodine complex, Aono discussed Mulliken's model and presented a corrected one[6]. It may be true that in spite of these successes, Mulliken's procedure is not very useful to discuss the relative ease of complex formation among different molecules. There are often found some trials of discussing this problem by comparing the magnitude of ionization potentials of electron donors. For example, with respect to the silver-aromatic molecular complex, a correlation between the magnitude of ionization potential of methyl derivatives of 1,2-benzanthracene and their equilibrium constants in complex formation was pointed out by Nakajima[7]. However, this treatment has only a limited application since the ionization potential is not the sole factor relating to the ease of complex formation, and is hence not suitable in discussing the configuration of complex.

In the present paper we make use of the delocalization method in order to approach the conformation of molecular compound, finding a clear correlation between the equilibrium constant and the calculated value of the delocalization energy for silver-aromatic hydrocarbon complexes.

Model and Formulation

In this paper the delocalization method was applied to silver-aromatic hydrocarbon complexes. Since it has been confirmed by X-ray diffraction that in silver-benzene complex silver cation is located above the middle of a carbon-carbon bond of benzene plane[8], we assume that silver cation approaches from above the molecular plane to the middle of a carbon-carbon bond of a benzene ring in aromatic hydrocarbons to form the molecular complex. The π electronic stabilization energy due to delocalization from the occupied orbitals of the aromatic hydrocarbon to the lowest vacant orbital of the silver cation is calculated by the perturbation theory. This procedure is quite similar to the one which has been used in the frontier electron theory presented by some of the present authors[9]. When the aromatic molecule is confined to alternant hydrocarbons and their derivatives, and the silver cation is combined with the rth and the sth carbon atoms of the aromatic hydrocarbon by a weak bond, the secular equation of the π part of the total system which includes the silver cation and the aromatic molecule is written in the simple LCAO MO treatment (overlap neglected) as follows:

$$D(\lambda) = \begin{vmatrix} h-\lambda & 0 & 0 \cdots\cdots 0 & \gamma & \gamma & 0 \cdots\cdots 0 \\ 0 & a_{11}-\lambda & a_{12} \cdots\cdots & a_{rr} & a_{1s} & \cdots\cdots a_{1n} \\ 0 & a_{21} & a_{22}-\lambda \cdots & a_{2r} & a_{2s} & \cdots\cdots a_{2n} \\ \vdots & & & & & \\ 0 & & & & & \\ \gamma & a_{r1} & a_{r2} \cdots\cdots & a_{rr}-\lambda & a_{rs} & \cdots\cdots a_{rn} \\ \gamma & a_{s1} & a_{s2} \cdots\cdots & a_{sr} & a_{ss}-\lambda & \cdots\cdots a_{sn} \\ 0 & & & & & \\ \vdots & & & & & \\ 0 & a_{n1} & a_{n2} \cdots\cdots & a_{nr} & a_{ns} & \cdots a_{nn}-\lambda \end{vmatrix}$$

$$= (h-\lambda)\Delta(\lambda) - \gamma^2\{\Delta_{rr}(\lambda) + \Delta_{ss}(\lambda) - 2\Delta_{rs}(\lambda)\} \quad (1)$$

where

$$\Delta(\lambda) = \begin{vmatrix} a_{11}-\lambda & a_{12} & \cdots\cdots & a_{1n} \\ a_{21} & a_{22}-\lambda & \cdots\cdots & a_{2n} \\ \vdots & \vdots & & \vdots \\ a_{n1} & a_{n2} & \cdots\cdots & a_{nn}-\lambda \end{vmatrix} \quad (2)$$

is the secular determinant for the isolated aromatic molecule, and $\Delta_{rr}(\lambda)$, $\Delta_{ss}(\lambda)$, and $\Delta_{rs}(\lambda)$ are the minors of $\Delta(\lambda)$ corresponding to (rr), (ss) and (rs) elements, respectively; a_{ii} and $a_{ij}(i \neq j)$ are the Coulomb and the resonance integrals, respectively; and h and γ are the Coulomb integral of the silver cation and the resonance integral between the silver cation and the rth and the sth atoms of the aromatic molecule at which the delocalization of π electron takes place, respectively. In presenting the value of energies, we make the zero point equal to the Coulomb integral of

4) J. Weiss, *J. Chem. Soc.*, **1942**, 245; **1943**, 462.
5) W. Brackmann, *Rec. trav. chim.*, **68**, 147 (1949).
6) S. Aono, *Progr. Theoret. Phys. Japan*, **22**, 313 (1959).
7) T. Nakajima, *The Science Reports of the Tôhoku Univ. Ser. I*, **41**, 171 (1957).
8) R. E. Rundle and J. H. Goring, *J. Am. Chem. Soc.*, **72**, 5337 (1950).
9) K. Fukui, T. Yonezawa and C. Nagata, This Bulletin, **27**, 423 (1954).

benzene carbon and express them in units of $(-\beta)$ which is the resonance integral of the benzene C–C bond. If we designate the roots of $\Delta(\lambda)=0$ and $D(\lambda)=0$ as

$$\lambda_1, \lambda_2, \cdots\cdots \lambda_n\ ;\ \lambda^{(1)}, \lambda^{(2)}\cdots\cdots^{(n)}, \lambda^{(h)}$$
$$(\lambda_1 > \lambda_2 > \cdots\cdots > \lambda_n)$$

respectively, among which $\lambda^{(h)}$ will be very close to the value of h and $\lambda^{(j)}$ to λ_j $(j=1,2\cdots\cdots n)$ since γ is small. Namely $\lambda^{(j)}$ and $\lambda^{(h)}$ can be written as $\lambda^{(j)}=\lambda_j+\delta_j$, $\lambda^{(h)}=h+\delta_h$ in which $|\delta_j|$ and $|\delta_h|$ are small. For simplicity, we exclusively treat the following two cases in which $\Delta(\lambda)$ has no multiple root.

Case 1: When h is not equal to any λ_j, we can obtain δ_j as

$$\left.\begin{aligned}\delta_j &= 2\left\{\frac{\Delta_{rr}(\lambda_j)}{(h-\lambda_j)\Delta'(\lambda_j)}+\frac{\Delta_{ss}(\lambda_j)}{(h-\lambda_j)\Delta'(\lambda_j)}-\frac{2\Delta_{rs}(\lambda_j)}{(h-\lambda_j)\Delta'(\lambda_j)}\right\}\gamma^2+[\gamma^4] \\ &\qquad (j=1,2\cdots\cdots n) \\ \delta_h &= -\sum_{j=1}^{n}\left\{\frac{\Delta_{rr}(\lambda_j)}{(h-\lambda_j)\Delta'(\lambda_j)}+\frac{\Delta_{ss}(\lambda_j)}{(h-\lambda_j)\Delta'(\lambda_j)}-\frac{2\Delta_{rs}(\lambda_j)}{(h-\lambda_j)\Delta'(\lambda_j)}\right\}\gamma^2 \\ &\quad +[\gamma^4]\end{aligned}\right\} \quad (3)$$

where $[\gamma^4]$ denotes the higher terms. The delocalization energy, ΔE, is defined as follows:

$$\Delta E = 2\sum_{j=1}^{m}(\lambda^{(j)}-\lambda_j) \quad (4)$$

$$= 2\sum_{j=1}^{m}\left\{\frac{\Delta_{rr}(\lambda_j)+\Delta_{ss}(\lambda_j)-2\Delta_{rs}(\lambda_j)}{(h-\lambda_j)\Delta'(\lambda_j)}\right\}\gamma^2+[\gamma^4]$$

$$= -2\sum_{j=1}^{m}\frac{(C_r^j+C_s^j)^2}{h-\lambda_j}\gamma^2+[\gamma^4] \quad (5)$$

where $j=1,2\cdots\cdots m$ denote the occupied orbitals, and the rth and the sth carbon atoms are adjacent to each other. And C_r^j is the coefficient of the rth atomic orbital in the jth molecular orbital of the isolated aromatic molecule. When h is equal to zero, then the total delocalization energy becomes

$$\Delta E = \{S_r^{(E)}+S_s^{(E)}+2S_{rs}^{(E)}\}\gamma^2+[\gamma^4] \quad (6)$$

where $S_r^{(E)}$, $S_s^{(E)}$ are superdelocalizabilities at the rth and the sth carbon atoms for the electrophilic reaction[9], and $S_{rs}^{(E)}$ is given in Eq. 7 and may be named bond-delocalizability of the bond rs.

$$S_{rs}=\sum_{j=1}^{n}\frac{(\nu_j-\nu)C_r^jC_s^j}{\lambda_j} \quad (7)$$

where ν_j is the number of π electrons in the jth molecular orbital and ν is the number of π electrons in the approaching orbital to or from which the delocalization of electrons occurs. $S_{rs}^{(E)}$ designates S_{rs} in which $\nu=0$.

The formula obtained by Eq. 5 indicates that the magnitude of delocalization energy depends sensitively upon the local symmetry of the molecular orbital; that is to say, when C_r^j and C_s^j have same signs, the magnitude of delocalization energy is large, while it is small in case of different signs. It may be stressed that a conclusion similar to that of Mulliken has thus been derived by the present treatment.

Case 2: When h is equal to the energy of the highest occupied orbital of the isolated aromatic molecule λ_f,

$$\left.\begin{aligned}\delta_j &= 2\left\{\frac{\Delta_{rr}(\lambda_j)}{(h-\lambda_j)\Delta'(\lambda_j)}+\frac{\Delta_{ss}(\lambda_j)}{(h-\lambda_j)\Delta'(\lambda_j)}-\frac{2\Delta_{rs}(\lambda_j)}{(h-\lambda_j)\Delta'(\lambda_j)}\right\}\gamma^2+[\gamma^4] \\ &\qquad (j=1,2,\cdots\cdots n) \\ \left.\begin{matrix}\delta_h\\ \delta_f\end{matrix}\right\} &= \pm\sqrt{-\frac{\Delta_{rr}(h)+\Delta_{ss}(h)-2\Delta_{rs}(h)}{\Delta'(h)}} \\ &\quad \times\gamma+[\gamma^2]\end{aligned}\right\} \quad (8)$$

and the delocalization energy depends dominantly upon the term of first order. Hence, we obtain

$$\Delta E = 2\sqrt{-\frac{\Delta_{rr}(h)+\Delta_{ss}(h)-2\Delta_{rs}(h)}{\Delta'(h)}}\gamma+[\gamma^2]$$
$$= 2|C_r^f+C_s^f|\gamma+[\gamma^2] \quad (9)$$

It may be remarked that in case 2, the magnitude of ΔE depends upon the local symmetry of the highest occupied orbital, the frontier orbital at the bond to be attacked.

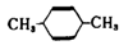
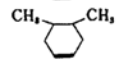
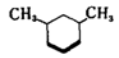
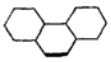
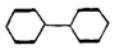
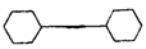
Then the following conclusion can be derived. When h is not equal to any λ_j, the larger the value of $-\sum_j\frac{(C_r^j+C_s^j)^2}{h-\lambda_j}$ is, the easier the molecular complex formation is, and when h is equal to λ_f, the reactivity is proportional to $|C_r^f+C_s^f|$.

Results and Discussion

The easiness of the molecular complex formation depends upon many factors such as delocalization energy, dispersion energy, exchange repulsion energy and electrostatic energy. Therefore, the reactivity should be discussed under consideration of all these factors. In discussing the relative easiness of complex formation of a series of similar compounds, however, it is expected that the energies, other than delocalization energy, contributing to the activation energy, may be approximately constant or negligible. In such a case, the delocalization energy is considered to play a dominant role.

In the present paper, an attempt is made to

TABLE I. THE VALUES OF THE INDEX FOR COMPLEX FORMATION AND THE EQUILIBRIUM CONSTANT FOR THE COMPLEX BETWEEN SILVER CATION AND AROMATIC COMPOUNDS

Aromatic compound	K_1 (mol./l.)$^{-1}$	$S_r^{(E)}+S_s^{(E)}+2S_{rs}^{(E)}$	Energy of the highest occupied orbital
	2.41	1.333	−1.000
	2.63	1.402	−0.669
	2.89	1.553	−0.707
	2.95	1.418	−0.823
	3.03	1.466	−0.763
	3.08	1.600	−0.618
	3.67	1.798	−0.605
	3.94	1.370	−0.705
	6.3	2.139	−0.504
	18.2	2.089	−0.662

Thick lines in the figure of aromatic compounds indicate the bonds with maximum value of the index, which are assumed to be the positions of attack by silver cations.

With regard to toluene and xylene, and carbon-carbon bond adjacent to the methyl group is not taken into account for the sake of steric circumstances.

K_1 is the equilibrium constant for the following reaction

$$Ag^+ + Ar = AgAr^+ \qquad K_1 = (AgAr^+)/(Ag^+)(Ar)$$

explain the reactivity of complex formation of a series of similar compounds by the consideration of the delocalization energy only. The delocalization energies calculated by the formulas stated above are tabulated in Table I together with the equilibrium constants of the first step of the molecular complex formation between silver cation and aromatic compound[10]. A clear parallelism is seen between the index and the equilibrium constant. The parameters used in calculation for methyl group are as follows.

α_{CH_3} (Coulomb integral for methyl group in Eq. 1) = 3

$\beta_{C\text{-}CH_3}$ (resonance integral for CH_3-C bond in Eq. 1) = 1

The energies of the highest occupied levels thus obtained are compared with the observed ionization potentials in Table II. At a glance at this table, a good parallelism is observed between the ionization potential and the energy of the highest occupied level. This implies that the adopted parameters should be appropriate.

TABLE II. RELATION BETWEEN THE IONIZATION POTENTIAL AND THE HIGHEST OCCUPIED LEVEL IN AROMATIC COMPOUNDS

Aromatic compound	Ionization potential eV.	Highest occupied level
Benzene	9.24[a]	−1.000
Toluene	8.82[b]	−0.823
m-Xylene	8.58[a]	−0.763
o-Xylene	8.58[a]	−0.707
p-Xylene	8.48[a]	−0.669
Naphthalene	8.12[a]	−0.618

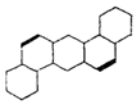
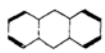
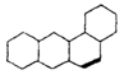
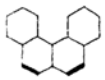
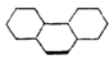
a; From F. H. Field and J. L. Franklin, "Electron Impact Phenomena", Academic Press, Inc., New York (1957).

b; K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957).

The value of index for *o*-xylene seems too large. This discrepancy may partly be ascribed to the neglect of the effect of the steric hindrance between two methyl groups. With regard to biphenyl, the calculation is carried out with

10) L. J. Andrews and R. R. M. Keefer, *J. Am. Chem. Soc.*, 71, 3644 (1949); 72, 5034 (1950).

TABLE III. THE VALUES OF THE INDEX FOR COMPLEX FORMATION AND THE EQUILIBRIUM CONSTANT FOR THE COMPLEX BETWEEN SILVER CATION AND POLYCONDENSED AROMATIC HYDROCARBONS

Aromatic compound	K_1	$S_r^{(E)}+S_s^{(E)}+2S_{rs}^{(E)}$	Energy of the highest occupied orbital
	1.65	1.864	−0.474
	1.35	1.747	−0.414
	1.33	1.900	−0.452
	1.30	1.737	−0.568
	1.09	1.798	−0.605

Thick lines in the figure of aromatic compounds indicate the bonds with maximum value of the index, which are assumed to be the positions of attack by silver cations.

K_1 is the equilibrium constant for the following reaction.

$$Ag^+ + Ar = AgAr^+ \qquad K_1 = (AgAr^+)/(Ag^+)(Ar)$$

the assumption that this compound has a plane structure. Experimental data show that this compound is not planar. If two benzene nuclei are but little conjugated with each other, the value of the equilibrium constant for this compound may reasonably be expected to be approximately twice as large as that of benzene as was pointed out by Andrews et al.[10] On the other hand, the index is scarcely affected by the degree of conjugation between two benzene nuclei. On the occasion of comparison with the value of the index, therefore, the observed value of equilibrium constant must be divided by a factor which is larger than unity and smaller than two. This is the reason why the observed value of the equilibrium constant seems too large in comparison with the magnitude of the index calculated.

It seems that also the value of energy of the highest occupied orbital can be a good measure for complex formation. This fact shows that the ionization potential is also useful as a rough index to discuss the easiness of complex formation, though it is impossible to predict the position of attack as stated above.

Furthermore, the complex formation in polycondensed aromatic hydrocarbons is treated in a similar manner and the results are shown in Table III. In this series the parallelism between the value of index and equilibrium constant[11] is not so good. In these polycondensed aromatic hydrocarbons their molecular size is not uniform. The coordination with silver cations may take place at more than one positions in a molecule which has more than one positions of equal or nearly equal reactivity. One silver cation which has already added to a position in a hydrocarbon molecule will not exert a substantial influence upon the later addition of another silver cation to another position in the same molecule, provided these two positions are sufficiently apart from each other. In such a case, in order to be compared with the calculated value of the theoretical index, the observed value of the equilibrium constant must be modified by considering the number of sites in one molecule as is stated above in the case of biphenyl.

Another factor influencing the easiness of the complex formation is the polarizability which may be different in various cases. This means that ion-induced dipole interactions are not uniform from molecule to molecule, and it is indispensable for the prediction of reactivity to take the ion-dipole interaction into account. This point will be discussed in future.

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11) R. E. Kofahl and H. J. Lucas, *J. Am. Chem. Soc.*, 76, 3931 (1954).