It is of much interest to inquire whether the structure of the benzene-iodine complex belongs to the symmetry of $G_{2V}$ or $G_{6V}$. Here the former is called the $R$ (resting) model and the latter the $A$ (axial) model. Some recent experiments on the infra-red spectra of this complex and the observation of the crystalline state of the benzene-bromine complex support the $A$ model of $C_{6v}$ symmetry. In this article the author concludes from a theoretical consideration that the $A$ model is most probable for the structure of the benzene-iodine complex. In the $A$ model, the charge-transfer takes place from $\phi_0$, the MO (molecular orbital) of benzene to $\phi(\sigma_u, 5p)$, the MO of iodine. The energy loss of the charge-transfer state which is involved in adopting the $A$ model instead of the $R$ model, is supplied by the "disscreening effect" and the interaction energy between the no-bond state and the charge-transfer state. This interaction energy is far larger in the $A$ model than in the $R$ model.

The stabilization energy, the dipole moment, the charge-transfer spectrum and the oscillator strength are calculated, and we have obtained fairly good agreement with the observations.

§ 1. Introduction

Many interesting observations about the benzene-iodine complex have been reported. This complex shows an intense characteristic absorption near $\lambda = 2900$ A which does not appear in case benzene and iodine exist independently. Mulliken has explained this absorption theoretically as the charge-transfer spectrum, and estimated the oscillator strength of this spectrum at 0.30 from the experimental value obtained by Green and Ress. This complex has the dipole moment 0.72 D, which is an evidence of the existence of the charge-transfer state. The stabilization energy has been measured by Bower as 1.72 kcal/mol.

To a certain extent Mulliken has succeeded in a semi-empirical explanation of the above mentioned observations in view of the charge-transfer mechanism, by means of the $R$ model (Fig. 1). However, Ferguson has recently concluded from the observation of infra-red spectra of this complex that the $A$ model having the $C_{6v}$ symmetry (Fig. 2) is suitable to this complex. Hassel has observed that the benzene-bromine complex has the axial structure in the crystalline state, in which the distance between the carbon and the next bromine atom is 3.70 A. We are

* The previous paper published in Prog. Theor. Phys. 20, 133 (1958) is called "I" of the present series.
now much interested in a theoretical explanation of the benzene-iodine complex having the $C_{6v}$ symmetry.

Fig. 1

The solid line represents the MO of iodine, $\phi (\sigma_w, 5p)$. The dotted line represents the MO's of benzene, $\phi_{-1}$ in Fig.1 and $\phi_0$ in Fig. 2.

The reasons why Mulliken has given up the $A$ model and adopted the $R$ model are summarized as follows.

The vacant MO of iodine to which an electron of benzene may transfer is

$$\phi (\sigma_w, 5p) = 2(1-S_A)^{-1/2}(z_A - z_A'),$$

which is a strongly antibonding MO, spreading along the direction of bond. Here $z_A$ and $z_A'$ are $5p$ atomic orbitals of iodine, and $S_A$ is the overlap integral

$$S_A = \int z_A z_A'\, dv. \tag{2}$$

The occupied orbitals of benzene are written as

$$\phi_0 = 6^{-1/2}(z_1 + z_1 + z_2 + z_2 + z_3 + z_4), \tag{3}$$

$$\phi_{-1} = 12^{-1/2}(2z_1 + z_1 - z_2 - 2z_2 - z_3 + z_4), \tag{4}$$

$$\phi_{-1} = 4^{-1/2}(z_1 + z_2 - z_3 - z_4). \tag{5}$$

where $z_1 \sim z_4$ are $2p^2$ atomic orbitals of corresponding carbon atoms. In the case of the $R$ model, the charge-transfer takes place from (5) to (1), which is easily verified from symmetry consideration. On the other hand, if we adopt the $A$ model, we cannot but consider the charge-transfer from (3) to (1). This process is energetically more difficult to arise at first glance, because $\phi_0$ is lower in energy than $\phi_{-1}$.

Next, in the calculation of the energy of the charge-transfer state, the electrostatic attraction between the charged molecules must be taken into account. The mean separation distance between the charged centers of the benzene cation and the iodine anion is greater in the $A$ model than in the $R$ model, and therefore the stabilization in the energy of the charge-transfer state arising from the electro-static attraction favours the $R$ model. In order to explain theoretically that the $A$ model is suitable to this complex, we must overcome the above mentioned points.

§ 2. Theory with numerical calculation

The ground state wave function of this complex $BA$ ($B$ and $A$ refer to benzene
and iodine respectively) is written as

$$\mathcal{F}_N = a\mathcal{F}_0 + b\mathcal{F}_1,$$

(6)

where $\mathcal{F}_0$ is no-bond wave function

$$\mathcal{F}_0 = \mathcal{F}(BA) = \mathfrak{A} \mathcal{F}_B \mathcal{F}_A,$$

(7)

and $\mathfrak{A}$ is the antisymmetrizer. Further

$$\mathcal{F}_B \mathcal{F}_A = \phi_B (1) \phi_A (2) [B][A],$$

(8)

in which $[B]$ and $[A]$ denote the configuration of electrons in the occupied MO's of $B$ except $\phi_B$, and that of electrons in the occupied MO's of $A$, respectively. In (8)

$$\phi_B = \phi_{-1},$$

for the $R$ model,

$$\phi_B = \phi_0,$$

for the $A$ model.

$\mathcal{F}_1$ is the wave function describing the charge-transfer state

$$\mathcal{F}_1 = \mathcal{F}(B^+ A^-),$$

(9)

which is written in detail as

$$\mathcal{F}_1 = (2 + 2S_{BA})^{-1/2} (\mathcal{F}_1 + \mathcal{F}_1)$$

(10)

$$\mathcal{F}_1 \mathcal{F}_1 = \mathfrak{A} \phi_B (1) \phi_A (2) [B][A]$$

(11)

$$\mathcal{F}_1 \mathcal{F}_1 = \mathfrak{A} \phi_B (1) \phi_A (2) [B][A],$$

(12)

$S_{BA} = \int \mathcal{F}_0 \mathcal{F}_1 dv.$

The coefficients of (6) have the relation

$$a^2 + 2abS + b^2 = 1,$$

(13)

$$S = \int \mathcal{F}_0 \mathcal{F}_1 dv = \{2/(1 + S_{BA})\}^{1/2} S_{BA}.$$

(14)

As $[B]$ and $[A]$ are regarded as fixed in the calculation, the effect of these electrons may be treated as a part of the effective Hamiltonian. In (6) the mixing of $\mathcal{F}_1$ into $\mathcal{F}_0$ seems to be very small ($a \gg b$), so the second order perturbation theory is an adequate approximation in this case. The ground state energy of this complex is

$$W_N \equiv W_0 + \frac{(H_{01} - S W_0)^2}{W_1 - W_0} \approx W_0 - \frac{H_{01}^2}{W_1 - W_0},$$

(15)

where

$$W_0 = \int \mathcal{F}_0 \mathcal{H} \mathcal{F}_0 dv, \quad W_1 = \int \mathcal{F}_1 \mathcal{H} \mathcal{F}_1 dv, \quad H_{01} = \int \mathcal{F}_0 \mathcal{H} \mathcal{F}_1 dv.$$

(16)

The stabilization energy is

$$\Delta W = H_{01}^2 / (W_1 - W_0).$$

(17)
It must be determined from the estimation of the stabilization energy whether the R model or the A model should be suitable to the benzene-iodine complex. In estimating (17) the denominator \((W' - W)\) takes a smaller value in the R model than in the A model as mentioned in §1. Here we are led to use the following approximation for \(H_{01}\), otherwise it must be treated as a semi-empirical parameter.

\[
H_{01}' = \beta S / S_p,
\]

where \(S_p\) is the overlap integral between \(2\rho\pi\) orbitals of adjacent carbon atoms in benzene, and \(\beta\) is the resonance integral of the corresponding orbitals, of the magnitude \(-40\) kcal/mol.

\[
S_p = \int \chi_i \chi_{ii} \, dv = 0.26.
\]

The width of the benzene ring \(2.41\) Å is nearly equal to the interatomic distance of the iodine molecule \(2.66\) Å. Therefore, in the R model, the \(2\rho\pi\) carbon atomic orbital is almost orthogonal to the \(5\rho\) iodine atomic orbital, and the overlap integral between them becomes nearly zero.

In the case of the A model, we may easily understand from the orientations of atomic orbitals that the value of \(S_p\) becomes largest. Here we ought to use (3) as \(\phi_n\) and the polarized form of (1) for \(\phi_A\), which is written as

\[
\phi_A = N^{-1/2} (\chi_A - i \chi_{A'}). \tag{19}
\]

In order to estimate the parameter \(\lambda\), we may adopt the following consideration as a reasonable one. The positive charge of benzene in the charge-transfer state is assumed to be at the center of the benzene ring, and the negative charge density about \(A\) or \(A'\) atom of iodine is thought to be inversely proportional to the distance between the positive charge of benzene and the \(A\) or the \(A'\) atom of iodine respectively. Then we obtain \(\lambda = 0.82\).

Thus the overlap integral \(S\) is calculated at

\[
S = 0.0058 \quad \text{for the R model},
\]

\[
S = 0.11 \quad \text{for the A model},
\]

where the Slater orbitals are used for the carbon and the iodine atomic orbitals and the Mulligan approximation\(^5\) is used for the heteropolar integral. (20) suggest very small interaction energy for the R model, therefore we may conclude that the R model is not adequate to this complex. In the following our discussion shall be directed to the A model and let us examine how to overcome what Mulliken has pointed out.

The interaction energy \(H_{01}'\) is estimated by substituting (18) with (20), and we obtain

\[
H_{01}' = -0.72 \text{ eV}. \tag{21}
\]

The energy of the no-bond state is
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\[ W_0 = \int \phi_0 \mathcal{H} \phi_0 \, d\nu \]
\[ = \int \phi_0 \alpha(1) \phi_0 \beta(2) (H_n + H_A) \phi_0 \alpha(1) \phi_0 \beta(2) \, d\nu \]
\[ \approx 2 \int \phi_n H_n \phi_n \, d\nu \]
\[ \approx -2I_n \]
\[ \approx -2(9.2 + 1.7) \text{eV}. \]  

(22)

Here the electronic Hamiltonian is the sum of the self-consistent one-electron Hamiltonian and they are considered to be constructed by two parts, part B and part A. \( I_n \) is the second ionization potential of benzene and is estimated to be the sum of the first ionization potential 9.2 eV and \(-\beta = 1.7 \text{eV}\).

On the other hand, the charge-transfer state, as has been written in (11), has the positive hole in part B. In the evaluation of the energy of this state we must take account of the effect of this positive hole in the electronic Hamiltonian, that is to say, the Hamiltonian referred to B is to be \( H_B \), then

\[ W_1 = \int \phi_1 \mathcal{H} \phi_1 \, d\nu \]
\[ = \int \phi_1 \alpha(1) \phi_1 \beta(2) (H_n + H_A) \phi_1 \alpha(1) \phi_1 \beta(2) \, d\nu \]
\[ \approx \int \phi_n H_n \phi_n \, d\nu + \int \phi_A H_n \phi_A \, d\nu + \int \phi_A H_A \phi_A \, d\nu, \]  

(23)

where

\[ \int \phi_A H_A \phi_A \, d\nu = -E_A \approx -1.8 \text{eV} \]  

(24)

in which \( E_A \) is the electron affinity of the iodine molecule and has been reported at the magnitude of larger than 1.8 eV\(^9\)

\[ \int \phi_A H_n \phi_A \, d\nu = -1/r_* = -3.3 \text{eV} \]  

(25)

seems to be a good approximation as the inter-molecular distance is very large, where \( r_* \) is the distance between the positive charge of benzene and the mean charge distribution of the iodine molecule. Next,

\[ \int \phi_n H_n \phi_n \, d\nu = \int \phi_n H_n \phi_n \, d\nu + \mathcal{A} \]
\[ = -I_n + \mathcal{A}. \]  

(26)

Here \( \mathcal{A} \) is the effect arisen from that the Hamiltonian has changed from \( H \) to \( H^+ \), and called the “dis-screening effect” hereafter. It is estimated approximately as the difference of the Coulomb interactions between above two states,
Here $r_i$ is the mean distance between the $2p\pi$ electron and the positive charge at the center of the benzene ring, and $\tilde{\delta}$ and $\tilde{\delta}^+$ are the orbital exponents of the neutral $2p\pi$ carbon atom and that of the positive carbon ion respectively. $r_i$ is easily estimated at 1.65 $\text{Å}$ (3.12 a.u.), then

$$D \approx (1.625 - 1.80)/3.12$$

$$=-0.056 \text{ a.u.} = -1.52 \text{ eV.}$$

In (26), $D$ is in appearance the stabilization energy for the electron left in $\phi_n$, but the above estimation of $D$ in (27) contains all stabilization energies for the electrons not only in $\phi_n$ but also in $\phi_{+1}$ and $\phi_{-1}$ of benzene. And this treatment is fortunately valid in this problem.*

From the foregoing results we obtain

$$W_1 - W_0 = I_B - E_A - 1/r_e + D$$

$$= 4.3 \text{ eV.} \quad (28)$$

Now we calculate the stabilization energy, using (28) and (21) combined with (17),

$$dW = 0.12 \text{ eV} = 2.8 \text{ kcal/mol.}$$

The coefficients $a$ and $b$ in (6) are evaluated by using

$$b/a = -H_{0'}/(W_1 - W_0) \quad (29)$$

and the normalization condition (13), at

$$a = 0.97, \quad b = 0.16. \quad (30)$$

The dipole moment of the ground state

$$\mu_N = -e \int \Psi_N \sum_i r_i \Psi_N \, dv \quad (31)$$

is calculated in quite the same way as Mulliken \cite{31} has used, at

$$\mu_N = 0.94 \text{ D.}$$

In order to calculate the charge-transfer spectrum and the oscillator strength associated with it, the excited state shall be considered.

$$\Psi_N = a^* \Psi_1 - b^* \Psi_0$$

$$a^{*2} - 2a^* b^* S + b^{*2} = 1. \quad (32)$$

The energy of the excited state is given as

* For this discussion the author is very much obliged to Prof. S. Nagakura.
The frequency of the charge-transfer spectrum is given as

\[ \nu = W_x - W_N = W_1 - W_0 + \frac{2H_{01}}{(W_1 - W_0)} \]

and we obtain

\[ \nu = 36,500 \text{ cm}^{-1}. \]

The coefficients \( a^* \) and \( b^* \) are estimated at

\[ a^* = 1.00, \quad b^* = 0.27. \]

The oscillator strength

\[ f = (4.704 \times 10^{-7}) \nu \mu_{EN}^2, \]

where \( \mu_{EN} \) is the transition dipole, is calculated by the similar procedure to that of calculating the ground state dipole moment, and then we obtain

\[ f = 0.34. \]

§ 3. Discussion and conclusion

The calculated results are tabulated in Table 1, where we can see fairly good agreement between the calculated results and the observed values. The charge-transfer spectrum 36,500 cm\(^{-1}\) in the observed values of Table 1 is the value which is obtained by adding 2,000 cm\(^{-1}\) to the actual observed value as a solvent effect.

<table>
<thead>
<tr>
<th></th>
<th>calc.</th>
<th>obs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>stabilization energy (kcal/mol)</td>
<td>2.8</td>
<td>1.72(^{2)})</td>
</tr>
<tr>
<td>dipole moment (Debye unit)</td>
<td>0.94</td>
<td>0.72(^{2)})</td>
</tr>
<tr>
<td>charge-transfer spectrum (cm(^{-1}))</td>
<td>36,500</td>
<td>36,500(^{1)})</td>
</tr>
<tr>
<td>oscillator strength</td>
<td>0.34</td>
<td>0.30(^{2)})</td>
</tr>
</tbody>
</table>

From the preceding calculations we can conclude as follows: The geometrical structure of the benzene-iodine complex is not the \( R \) model having the symmetry of \( C_{2v} \) which has been postulated by Mulliken, but the \( A \) model having the symmetry of \( C_{6v} \) which is supported by the recent experiments. We have concluded that the \( R \) model is not suitable to this complex by the estimation of the interaction energy between the no-bond state and the charge-transfer state of this complex. Mulliken has not exactly calculated the overlap integral between these two states, but has simply assumed for it the value of 0.1, which is, however, obtained when we adopt the \( A \) model. The estimation of the overlap integral is essentially im-
portant, so long as it is assumed that the interaction energy is proportional to the value of the overlap integral, as has been done in (18). Though the Slater orbital of high quantum number, say the $5\rho$ atomic orbital of iodine, does not seem to be adopted as a fully accurate one, the semi-quantitative treatment may be possible under the approximations assumed in this article. Also we may note that Mulliken has used 1.2 eV for the electron affinity of the iodine molecule (the observed value is larger than 1.8 eV.)

The charge-transfer does not always take place from the highest occupied orbital of the charge-donating molecule to the lowest vacant orbital of the charge-accepting molecule. In other words, we should not expect the simple relation between the first ionization potentials of the charge-donating molecules and the charge-transfer spectra of the complexes. In this problem we cannot but consider the charge-transfer from $\phi_0$ of benzene to $\phi(\sigma_w, 5\rho)$ of iodine, where the former is not the highest occupied orbital of benzene. The energy loss caused by adopting the A model is compensated by the introduction of the “disscreening effect” which is the stabilization energy for the electrons left in the MO’s of the charge-donating molecules. This effect is originated from the change of the orbital exponents of the atomic orbitals of the charge-donating molecule, corresponding to the change from the neutral state to the positively charged state of the molecule.

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