Determination of Reactivities by Molecular Orbital Theory (I)

Theoretical Treatment on the Photochemical Reaction of Benzene and Maleic Anhydride

by

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(Received November 27, 1969)

ABSTRACT

The MO's of maleic anhydride are calculated using the parameter values, $h_e=1$, $h_a=2$, $k_{e_a}=1$, $k_{e_0}=0.8$, and $\delta_{e_a}=2 \times (0.3)^*$. With these MO's the interaction energies of the photochemical reaction of maleic anhydride (MA) with benzene are calculated using intermolecular orbital theory. It is shown that there are cases where the interaction energy includes a constant term and this term takes a great role in the photochemical interaction energy, and that with the calculated interaction energies the reaction mechanism is quite well explained. And it is proved that the photochemical reaction is possible for the second addition step of MA to benzene, and that the MA-benzene adduct should have the well-known stereochemical structure.

1. INTRODUCTION

The reactions of aromatic hydrocarbons and MA are typical examples of the Diels-Alder reactions\(^{(1)}\). For the Diels-Alder reactions two types of reaction mechanisms have been proposed—the two-step and one-step mechanisms\(^{(2), (3)}\).

On the basis of one-step mechanism, Brown\(^{(4)}\) suggested the application of para-localization energies,
Lp, as a MO model of the transition state. He has shown that aromatic hydrocarbons apparently give an adduct with MA under usual experimental conditions only if Lp is less than 3.6.

For alternant hydrocarbons, Dewar's simple approximation method gives satisfactory results\(^1\).

Benzene has a Lp value 4.0, so under usual conditions it does not react with MA to give an adduct. But it was found that benzene forms a complex with MA under usual conditions \(^5\), \(^6\).

And it was also discovered that two molecules of MA react with one molecule of benzene under the influence of UV radiation to give a 2:1 adduct by successive 1, 2 and 1, 4-additions \(^6\), \(^7\).

The localization method cannot explain the anomalous behavior of benzene and MA in the photochemical reaction. And even the possibility that MA can form a complex with benzene is not explained by this method.

The localization method has a weakness that it deals only with the diene or only with the dienophile \(^8\).

Recently Salem developed an intermolecular orbital theory of the interaction between conjugated systems \(^9\), \(^10\).

This theory assumes that the molecular interaction in its incipient stages can be treated by second-order perturbation theory and rehybridization occurs in a significant manner only after the incipient intermolecular bonding between C=C orbitals is established. With this theory both the thermal reaction A+B and the photochemical reaction A+B* can be handled with simple MO's.

### 2. Calculation of MO's of MA

Hoffmann and Woodward performed a calculation of MO's of MA by extended Hückel method\(^12\).

Since this is not appropriate in the simple MO calculations, the MO's are calculated by HMO method. The h, k parameters used for oxygen atoms are taken as follows:

\[
\begin{align*}
h_1 &= 1 \\
h_2 &= 2 \\
k_{c-o} &= 0.8
\end{align*}
\]

These values are recommended ones for simple MO calculations\(^13\).

And the auxiliary inductive parameter was taken from the paper of Goodwin\(^19\),

\[
\delta_{n-m} = 2 \times (0.3)^n
\]

Here \(n\) denotes n-th carbon atom from the oxygen atoms.

This value was reported to be satisfactory for benzoic acid. The nuclei of MA belong to the point group \(C_{3v}\) and are numbered in the usual manner.

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**Table 1. Energies and MO's of MA**

<table>
<thead>
<tr>
<th>Energy</th>
<th>(C_1)</th>
<th>(C_2)</th>
<th>(C_3)</th>
<th>(C_4)</th>
<th>(C_5)</th>
<th>(C_6)</th>
<th>(C_7)</th>
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<td>0.67971</td>
<td>0.41439</td>
<td>0.23080</td>
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<td>0.20977</td>
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<td>-0.17145</td>
<td>0.17145</td>
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<td>-0.49023</td>
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<tr>
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<td>0.38876</td>
<td>-0.36234</td>
<td>0.14878</td>
<td>-0.14878</td>
</tr>
</tbody>
</table>

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Marsh et al. have shown from the X-ray diffraction data that the crystal MA molecule is slightly non-planar \(^15\).

The oxygen atom within the five-membered ring lying 0.03 Å from the plane of the other atoms. In the HMO approximation, MA can be assumed to be planar. The calculated results are summarized in Table 1.

Charge densities and bond-orders calculated from these MO's are shown in Fig. 1.
3. Intermolecular orbital theory.

In Salem's papers (11), (15) the thermal interaction energy is given by the equation (1).

\[ E_{int} = -\sum_i (\alpha_i + \alpha_i^* ) \eta_{ij} S_{ij} \]

\[ = -2 \sum_i \sum_j (\alpha_i \alpha_i^* )_{ij} S_{ij} \frac{E_i - E_j}{E_i - E_j} \]

And the change in interaction energy, from the case where both molecules were in their ground-state is given by the equation (2).

\[ \Delta E_{int} = -\left[ \sum_i (\alpha_i + \alpha_i^* )_{ij} \eta_{ij} S_{ij} \frac{E_i - E_j}{E_i - E_j} \right] \]

\[ + \sum_i \sum_j (\alpha_i \alpha_i^* )_{ij} S_{ij} \frac{E_i - E_j}{E_i - E_j} \]

\[ \frac{\sum_j (\alpha_i \alpha_i^* )_{ij} S_{ij}}{E_i - E_j} \]

Where

\[ S_{ij} = \int \phi_i^* \phi_j d\tau \]

\[ \eta_{ij} = \int \phi_i^* \frac{1}{\sqrt{\tau}} (\tau + 1) \phi_j d\tau \]

\( \tau \) is some effective potential field of the first molecule and \( \eta_{ij} \) that of the second molecule. The matrix element \( \eta_{ij} \) is assumed to be proportional to the overlap integral \( S_{ij} \)

\[ \eta_{ij} / \delta = k S_{ij} \]

From the theoretical considerations the constant \( k \) was taken to be 3 (11), (15). If the two interacting molecules are different, the first term of (2) disappears. However, if there is a near-degeneracy between \( \psi_j \) or \( \psi_k \) and any \( \psi_i \), the equation (2) does not hold true. In such a case, the change in interaction energy must be calculated from the secular equation (3).

\[ \begin{pmatrix} E_j - E_{ij} & \psi_j \psi_i \psi_k \\ E_{ij} - S_{ij} E_{ij} & E_{ij} - E_{ij} \end{pmatrix} = 0 \]

or

\[ E^2(1-S_{ij}^2) - E_{ij}^2 + 2E_{ij}^2 - 2E_{ij} E_{ij} = 0 \]

Let us consider the interacting molecules between singly occupied orbital \( \psi_j \) and the other doubly occupied orbital \( \psi_k \) of different energy as shown in Fig. 2.

![Fig. 2. Interaction between Singly Occupied Orbital \( \psi_j \) and Doubly Occupied Orbital \( \psi_k \).

The change in interaction energy, \( \Delta E_{ij} \), is given by the equation (4).

\[ \Delta E_{ij} = 2(E_{ij} - E_{ij}^0 - (2E_j - E_k) - E_{kk}^0) \]

\[ = E_{ij} - E_{ij}^0 \]

where

\[ E_{ij} = 2(E_{ij}^0 + E_{ij}^0) - 2(E_k + E_k) \]

This term is difficult to calculate using (3). Thus Salem assumed that this term is the same as the loss in interaction energy due to the stabilization energy of \( \psi_j \) with \( \psi_k \) which is tentatively assigned to be occupied.

That is,

\[ \Delta E_{ij} = E_j - E_{ij}^0 = \frac{(H_{ij} - S_{ij} E_{ij})^2}{E_{ij} - E_j} \]

When \( \psi_j \) are not well separated from \( \psi_k \), solving the equation (3), we get the following results.

\[ E_{ij}(I) = E_j - \Delta E_i \]

\[ E_{ij}(u) = E_j + \Delta E_i \]

where \( \Delta E_i \) and \( \Delta E_u \) are functions of \( S_{ij} \) without constant terms.

Therefore, in such a case the change in interaction energy is,

\[ \Delta E_{ij} = E_j - E_{ij}^0 \]

\[ = (E_j - E_k) - \Delta E_u \]

As a result, the interaction energy should contain a constant term, which is zeroth-order in the overlap. Generally this term appears when the doubly or half occupied orbital \( \psi_k \) is higher in energy level than the singly or unoccupied orbital \( \psi_j \).

This term has a stabilizing effect in all cases. Since
it is a constant, the over-all interaction energy will have a stabilizing effect, although the overlap is zero. Apparently this is in contradiction with the Salem's assumption that the interaction occurs through the orbital overlapping.

This contradiction can be overcome by considering that the electrons have a tendency to take a lower energy level if available and to be stabilized by the amount of the corresponding energy difference. Also it is fully conceivable that as the reacting molecules come closer, the field produced by them can cause the splitting of their MO's even though the overlap does not take place in practice. As a result the constant term appears.

This is the very case in the photochemical reaction of MA with benzene. Thus, the over-all change in interaction energy, $\Delta E_{\text{int}}$, should be modified as follows.

$$\Delta E_{\text{int}} = -(1/2) \left[ |I_{1}\rangle - |I_{2}\rangle \right] + (1/2) \sum_{ij} \left( S_{ij} - I_{ij} S_{ii} \right) + \sum_{ij} \left( \frac{H_{ij} - S_{ij} E_{i}}{E_{j} - E_{i}} \right) - \sum_{ij} \frac{\Delta E_{ij}}{2} + \sum_{ij} \frac{\Delta E_{ij}^{*}}{2}$$

For different molecules, the first two terms and the restrictions under the summation symbols disappear.

### 4. RESULTS AND DISCUSSION

Thermal interaction energies are calculated from the eq. (1). However, equation (3) is used when the energy difference $E_{i} - E_{j}$ is less than $0.7 \beta$. The photochemical interaction energies are calculated from the equation (8) and the equation (3) is solved to the second powers of $S_{ij}$.

In dioxane, the dipole moment of MA is 3.91 D. The calculation gives 1.68D. For the $\pi$-moment of MA, and the direction of the dipole is perpendicular to the C-C double bond toward the ether oxygen. This is a satisfactory result for a heteroatom compound in a simple MO method. MA has a triplet excitation energy of 72 kcal/mole. This corresponds to about 1.5$\beta$. From the calculated energies the first $\pi-\pi^*$ transition energy of MA is 0.84993.$\beta$. Simple

MO method cannot distinguish between singlet and triplet states. But the LCAO method really gives the mean between singlet and triplet states, and the difference between them is small. Hence the calculated transition energy is considered to be well close to the experimental value.

### Photodimerization of MA

Let us consider the cycloaddition of the two MA molecules as schematized in Fig. 2.

![Configuration of Interaction of two MA Molecules](image)

The dotted lines indicate pairs of interacting atoms. The interaction energy of two ground-state molecules is given by eq. (9).

$$E_{\text{int}}/\beta = -1.069(S_{\text{2S}} - S_{\text{2S}}^*) - 6.273 S_{\text{2S}} S_{\text{2S}}^*$$

Whatever the respective values of the two overlaps, $S_{\text{2S}}$ and $S_{\text{2S}}^*$, the interaction energy is repulsive. Let us now calculate the energy for the photochemical reaction in which one MA molecule is excited, an electron having jumped from the top bonding $\psi_1$ to the lowest antibonding $\psi_3$. Using the eq. (8), we obtain a change in interaction energy due to excitation.

$$\Delta E^{\text{exc}}/\beta = 0.995(S_{\text{2S}} - S_{\text{2S}}^*) + 0.260(S_{\text{2S}}^* - S_{\text{2S}}^*)$$

In eq. (10), there appear a large attractive first-order term and a significant attractive second-order cross-term in $S_{\text{2S}} S_{\text{2S}}^*$. Eq. (9) and (10) give, for the interaction energy $E_{\text{int}}$ in the photochemical reaction.

$$E_{\text{int}}/\beta = 0.995(S_{\text{2S}} - S_{\text{2S}}^*) - 0.807(S_{\text{2S}} - S_{\text{2S}}^*)$$

$$- 3.103 S_{\text{2S}} S_{\text{2S}}^*$$

The over-all stabilization for $S_{\text{2S}} = S_{\text{2S}}^* = 0.2$ is $E_{\text{int}}/\beta = -14.80$ kcal/mole ($\beta = -4$ ev).

MA itself yields two dimers on irradiation in solution, while only one of them is obtained on irradiation of solid. Now that the calculated MO's of MA, as shown above, explain the experimental results satisfactorily, the obtained MO's can be used for further calculations.
Photochemical reaction of MA with benzene

In the photochemical reaction of MA with benzene, the following mechanisms are proposed:

1. Excitation of the MA-benzene complex to its excited state.
2. Collapse of the excited complex to a mono-adduct.
3. Reaction of the first adduct with MA in a thermal reaction.

But it is not known with certainty whether the second MA addition is photochemical or takes place by thermal reaction. And although the structure of the adduct is taken to be 1 as shown, there has been a considerable amount of discussions on this subject.

The overall stabilization energy for \( S_{2v} = S_{4v} = 0.2 \) is \( E_{\text{stab}} = 0.141 \beta = -9.80 \text{ kcal/mole} \). The stabilization energy of the complex is larger in the excited state than in the ground-state by 8.35 kcal/mole. This is in agreement with experimental results.

From the above calculations together with Mulliken’s proposals, it can be understood why absorption of a quantum by a weakly bound complex should be able to lead, not to its dissociation, as has been suggested, to its stabilization. Equation (14) shows that if the overlap decreases the stabilization energy for 1,4-addition complex increases slightly. Thus the formation of the intermediate 3 from the excited MA-benzene complex requires energy to overcome this stabilization and the rate of 1,2-addition will be slightly retarded. This is in agreement with the fact that the formation of the first adduct is rate-determining.

1.4-addition of benzene with MA

![Fig. 4. Configuration of 1,4-Addition of MA and Benzene.](image)

The configuration of this interaction is shown in Fig. 4.

From the eq. (1):

\[
E_{\text{stab}}/\beta = -1.572(S_{2v}^+ + S_{4v}^-) + 3.667 S_{1v} S_{3v} \tag{12}
\]

The stabilization energy for \( S_{2v} = S_{4v} = 0.2 \) is \( E_{\text{stab}} \approx -0.021 \beta = -1.45 \text{ kcal/mole} \). However this is small,

so that no cycloaddition will occur. Using the eq. (8):

\[
J E_{\text{tot}}(1-2)/\beta = 0.165 + 7.585(S_{1v}^- + S_{4v}^-)
\]

\[
-16.260 S_{2v} S_{3v} \tag{13}
\]

Eq. (12) and (13) give, for the interaction energy, 

\[
E_{\text{tot}}(1-2) = 0.165 + 5.991(S_{1v}^- + S_{4v}^-)
\]

\[
-12.598 S_{2v} S_{3v} \tag{14}
\]

The overall stabilization energy for \( S_{2v} = S_{4v} = 0.2 \) is \( E_{\text{stab}} = 0.141 \beta = -9.80 \text{ kcal/mole} \). The stabilization energy of the complex is larger in the excited state than in the ground-state by 8.35 kcal/mole. This is in agreement with experimental results.

From the above calculations together with Mulliken’s proposals, it can be understood why absorption of a quantum by a weakly bound complex should be able to lead, not to its dissociation as has been suggested, to its stabilization. Equation (14) shows that if the overlap decreases the stabilization energy for 1,4-addition complex increases slightly. Thus the formation of the intermediate 3 from the excited MA-benzene complex requires energy to overcome this stabilization and the rate of 1,2-addition will be slightly retarded. This is in agreement with the fact that the formation of the first adduct is rate-determining.

1.2-addition of benzene and MA

![Fig. 5. Configuration of 1,2-Addition of MA and Benzene.](image)

From the eq. (1):

\[
E_{\text{tot}}/\beta = -1.592 (S_{1v}^- + S_{3v}) - 1.616 S_{2v} S_{3v} \tag{15}
\]

At the outset we see that all the second-order effects
are repulsive.

Hence such a thermal 1,2-addition should be energetically unfavorable.

For a photochemical reaction, using the eq. (8)
\[ \Delta E^* = \frac{1}{2} \beta = 0.165 + 7.569(S_{eq}^+ + S_{eq}^-) \]
\[ + 9.230 S_{eq}S_{eq} \] ...........................(16)

Eq. (15) and (16) give
\[ E^*_{ax} = 0.165 + 5.997 (S_{eq}^+ + S_{eq}^-) \]
\[ -7.614 S_{eq}S_{eq} \] ..............................(17)

The overall stabilization energy for \( S_{eq}^- = S_{eq}^+ = 0.2 \) is
\[ E^*_{ax} = 0.945 \text{ kcal/mole}. \]

This stabilization is very large, so that 1,2-cycloaddition will occur. Now it is clear why MA should undergo 1,2-addition rather than 1,4-addition (21).

The MA-benzene adduct is assigned the structural and stereochemical formula 1. While, Angus and Bryce-Smith have suggested the stereochemical structure 2 for the MA-benzene adduct on the basis of the usual stereochemistry of Diels-Alder reactions and in order to account for the UV absorption which they observed. But Grovenstein et al. showed that their results were in error (19).

From the above calculations alone, the formation of adduct 1 or 2 are equally probable. There are two possible configurations of 1,2-cycloaddition, I and II as schematized in Fig. 6.

![Diagram](image)

**Fig. 6. Configurations of 1,2-Cycloaddition of MA and Benzene.**

Configuration I will lead to the adduct 1, and configuration II will lead to the adduct 2. The photochemical interaction energy of configuration II cannot be assumed to be the same as that of configuration I, for it is possible that two additional atom-atom interactions operate (interaction 21' and 54'). And the important secondary interaction vary from one reaction to another (11)(19).

Calculations of interaction energy of the configuration II give
\[ E_{int/\beta} = -1.896(S_{eq}^+ + S_{eq}^-) - 1.816 S_{2p}S_{2p} \]
\[ + ( - 0.996(S_{2p}S_{2p} + S_{2p}S_{2p}) \]
\[ + 0.577(S_{2p}S_{2p} + S_{2p}S_{2p}) \]
\[ - 0.668 S_{2p}S_{2p} - 1.469(S_{2p}^+ + S_{2p}^-) \] ............................(18)

and
\[ E^*_{ax/\beta} = 0.165 + 5.977(S_{eq}^+ + S_{eq}^-) \]
\[ + 7.614 S_{eq}S_{eq} + ( - 4.143(S_{2p}S_{2p} \]
\[ - S_{2p}S_{2p} + 3.026(S_{2p}S_{2p} + S_{2p}S_{2p}) \]
\[ - 3.544 S_{2p}S_{2p} - 1.029(S_{2p}^+ + S_{2p}^-) \] ............................(19)

The square brackets represent additional interactions due to \( S_{eq}^- \) and \( S_{eq}^+ \). From the above equations (18) and (19), it can be seen that the additional interactions destabilize the thermal reaction as well as the photochemical reaction. The molecular planes of the diene and the dienophile of the Diels-Alder reactions are roughly parallel (12). From the structure of MA molecule (16), it can be assumed that \( S_{2p} \) is nearly equal to \( S_{2p} \). If \( S_{2p} = 0.2 \) and \( S_{2p} = 0.2 \), the overall stabilization energy is \( E^*_{ax/\beta} = 0.635 \text{ kcal/mole} \).

The interaction energy is greater in configuration I than in configuration II by 21.54 kcal/mole. That is, the reaction path through configuration I is more favorable than that through configuration II. Thus it is evident that the photochemical 1,2-addition of MA to benzene adduct will be the formula I rather than the formula 2.

**The second addition of MA to benzene**

After the first addition step was accomplished, the remaining z-system of the intermediate 3 may be approximated as that of butadiene. So the second addition step can be treated as the reaction of MA and butadiene.

Using the eq. (1) and (8).
\[ E_{int/\beta} = ( - 0.198(S_{eq}^+ + S_{eq}^-) + 6.883 S_{2p}S_{2p} \] ............................(20)
\[ E^*_{ax/\beta} = 0.372 + 1.226(S_{eq}^+ + S_{eq}^-) \]
\[ - 1.650 S_{2p}S_{2p} \] ..............................(21)
ACKNOWLEDGEMENT

We are grateful to Dr. J. H. Choi of the Atomic Energy Research Institute for providing us with laboratory facilities.

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