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Determination of Reactivities by Molecular Orbital Theory (I)

Theoretical Treatment on the Photochemical Reaction of Benzene and Maleic Anhydride

by

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분자 궤도론에 의한 반응성 계산 (I)

Benzene과 Maleic Anhydride간의 광화학 반응

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ABSTRACT

The MO's of maleic anhydride are calculated using the parameter values, $h_{\dot{O}}=1$, $h_{\ddot{O}}=2$, $k_{C=O}=1$, $k_{C-O}=0.8$, and $\delta\alpha_n=2\times(0.3)^n$. 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.

요 약

Maleic Anhydride의 분자궤도를 다음의 파라미터를 사용하여 계산하였다.

$h_{\dot{O}}=1$, $h_{\ddot{O}}=2$, $k_{C=O}=1$ $k_{C-O}=0.8$ $\delta\alpha_n=2\times(0.3)^n$

얻어진 분자궤도들로부터 Benzene과 Maleic Anhydride(MA)의 광화학반응의 작용 에너지를 구하였다. 작용 에너지에는 상수항이 포함될 수 있으며 이 항이 작용 에너지에 크게 기여함을 보였고 이 반응의 메카니즘은 계산된 작용 에너지로 잘 설명됨을 밝혔다. 또한 MA의 두번 째 첨가반응이 광화학적으로 가능하며 MA-Benzene의 부가 생성물은 잘 알려진 입체 화학적 구조를 가져야함을 증명하였다.

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,

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* Material taken from master thesis of M-H. W. at Seoul National University.

L_p, 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 L_p is less than 3.6.

For alternant hydrocarbons, Dewar's simple approximation method gives satisfactory results(5).

Benzene has a L_p value 4.0, so under usual conditions it does not react with MA to give adduct. But it was found that benzene forms a complex with MA under usual conditions (6), (7).

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 (8), (9).

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 (10).

Recently Salem developed a intermolecular orbital theory of the interaction between conjugated systems (11), (12).

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 2p 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(13). 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:

$h_{\dot{O}}=1$ $h_{C=O}=1$

$h_{\ddot{O}}=2$ $k_{C-O}=0.8$

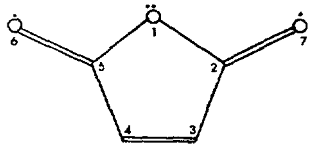
These values are recommended ones for simple MO calculations(14).

And the auxillary inductive parameter was taken from the paper of Goodwin(15).

$$\delta\alpha_n=2\times(0.3)^n$$

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_{2v} and are numbered in the usual manner.



Marsh *et al.* have shown from the X-ray diffraction data that the crystal MA molecule is slightly non-planar (16).

The oxygen atom within the five-membered ring lying 0.03 A 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 desities aand bond-orders calculated from these MO's are shown in Fig. 1.

TABLE 1. Energies and MO's of MA

Energy	C_1	C_2	C_3	C_4	C_5	C_6	C_7
2.97536	0.67971	0.41439	0.23080	0.23080	0.41439	0.20977	0.20977
1.97887	0.00000	−0.47987	−0.17145	0.17145	0.47987	0.49023	−0.49023
1.59119	−0.66280	0.16935	0.41186	0.41186	0.16935	0.28646	0.28646
1.08250	−0.07290	0.04444	−0.45583	−0.45583	0.04444	0.53871	0.53871
0.23657	0.00000	0.37208	0.35216	−0.35216	−0.37208	0.48738	−0.48738
−0.86914	0.30424	−0.54556	0.26624	0.26624	−0.54556	0.21988	0.21988
−1.43544	0.00000	0.36234	−0.58876	0.58876	−0.36234	0.14878	−0.14878

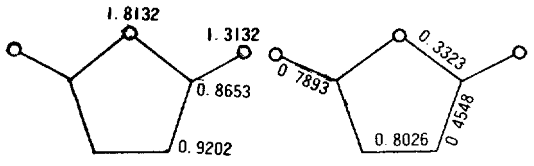


Fig. 1. Charge Densities and Bond-Orders of MA

3. Intermolecular orbital theory.

In Salem's papers (11), (12) the thermal interaction energy is given by the eqation (1).

$$E_{int}=-\sum_{rr'}(q_r+q_{r'}')\gamma_{rr'}'S_{rr'}'-2\sum_{j}^{occ}\sum_{k'}^{unocc}\frac{(\sum_{rr'}c_{jr}c_{k'r'}\gamma_{rr'})^2}{E_{k'}-E_j}-2\sum_{j'}^{occ}\sum_{k}^{unocc}\frac{(\sum_{rr'}c_{kr}c_{j'r'}\gamma_{rr'})^2}{E_k-E_{j'}}\cdots\cdots(1)$$

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

$$\Delta E_{int}^{(j\to k)}=-(|\sum_{rr'}c_{jr}c_{j'r'}\gamma_{rr'}|-|\sum_{rr'}c_{kr}c_{k'r'}\gamma_{rr'}|)+\sum_{rr'}(c_{jr}^2-c_{kr}^2)\gamma_{rr'}S_{rr'}+\sum_{\substack{all\ j'\\(\neq j)}}\frac{(\sum_{rr'}c_{jr}c_{j'r'}\gamma_{rr'})^2}{E_{j'}-E_j}-\sum_{\substack{all\ j'\\(\neq k)}}\frac{(\sum_{rr'}c_{kr}c_{j'r'}\gamma_{rr'})^2}{E_{j'}-E_k}\cdots\cdots(2)$$

Where

$$S_{rr'}=\int\phi_r\phi_{r'}d\tau$$

$$\gamma_{rr'}=\int\phi_r\frac{1}{2}(v+v')\phi_{r'}d\tau$$

v is some effective potential field of the first molecule and v' that of the second molecule. The matrix element $\gamma_{rr'}$ is assumed to be proportional to the overlap integral $S_{rr'}$

$$\gamma_{rr'}/\beta=kS_{rr'}$$

From the theoretical considerations the constant k was taken to be 3 (11), (12). If the two interacting molecules are different, the first term of (2) disappears. However, if there is a near-degeneracy between Ψ_j or Ψ_k and any $\Psi_{j'}$, the equation (2) does not hold true. In such a case, the change in interaction energy must be calculated from the secular equation (3).

$$\begin{vmatrix} E_j-E & H_{jj'}-S_{jj'}E \\ H_{jj'}-S_{jj'}E & E_{j'}-E \end{vmatrix}=0$$

or

$$E^2(1-S_{jj'}^2)-E(E_j+E_{j'}-2S_{jj'}H_{jj'})+E_jE_{j'}-H_{jj'}^2=0\cdots\cdots(3)$$

Let us consider the interacting molecules between singly occupied orbital Ψ_j and the other doubly occupied orbital $\Psi_{j'}$ of different energy as shown in Fig. 2.

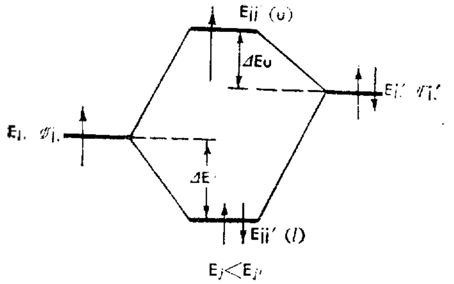


Fig. 2. Interaction Between Singly Occupied Orbital Ψ_j and Doubly Occupied Orbital $\Psi_{j'}$.

The change in interaction energy, $\Delta E_{jj'}^{int}$ is given by the equation (4).

$$\Delta E_{jj'}^{int}=2E_{jj'}(l)+E_{jj'}(u)-(2E_{j'}+E_j)-E_{jj'}^{int}$$
$$=E_j-E_{jj'}(u)\cdots\cdots(4)$$

where

$$E_{jj'}^{int}=2(E_{jj'}(l)+E_{jj'}(u))-2(E_{j'}+E_j)$$

This term is difficult to calculate using (3). Thus Salem assumed that this term is the same as the loss in interaction energy in amount equal to the stabilization energy of Ψ_j with $\Psi_{j'}$ which is tentatively assigned to be noccupied.

That is,

$$\Delta E_{jj'}^{int}=E_j-E_{jj'}(u)=-\frac{(H_{jj'}-S_{jj'}E_j)^2}{E_{j'}-E_j}\cdots\cdots(5)$$

When Ψ_j are not well separated from $\Psi_{j'}$ solving the equation (3), we get the following results.

$$E_{jj'}'(l)=E_j-\Delta E_l$$
$$E_{jj'}(u)=E_j'+\Delta E_u\cdots\cdots(6)$$

where ΔE_l and ΔE_u are functions of $S_{jj'}$ without constant terms.

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

$$\Delta E_{jj'}^{int}=E_j-E_{jj'}(u)$$
$$=(E_j-E_{j'})-\Delta E_u\cdots\cdots(7)$$

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 $\Psi_{j'}$ is higher in energy level than the singly or unoccupied orbital Ψ_j.

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

This contradiction can be overcome by considering that the electrons have a tedency 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, $\Delta E_{int}^{(j\to k)}$, should be modified as follows.

$$\Delta E_{int}^{(j\to k)} = -(|I_{kk'}| + |I_{jj'}|) + (I_{jj'}S_{jj'} - I_{kj'}S_{jj'}) + \sum_{j'}^{unocc} \frac{(H_{jj'}-S_{jj'}E_j)^2}{E_{j'}-E_j} - \sum_{\substack{j' \\ (\neq k')}}^{unocc} \frac{(H_{kj'}-S_{kj'}E_k)^2}{E_{j'}-E_k} + \sum_{\substack{i' \\ (\neq j')}}^{occ} \Delta E_{ji'}^{int} + \sum_{j'}^{occ} \Delta E_{ij'}^{int} \quad \cdots\cdots (8)$$

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 $E_{k'}-E_j$ is less than 0.7β.* The photochemical interaction energies are calculated from the equation (8), and the equation (3) is solved to the second powers of $S_{jj'}$.

In dioxane, the dipole moment of MA is 3.91 D. (18). The calculation gives 1.68D. for the π-moment of MA, and the direction of the diplole 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 (19). MA has a triplet excitation energy of 72 kcal/mole (20). This corresponds to about 1β. From the calculated energies the first $\pi\to\pi^*$ transition energy of MA is 0.84593β. Simple MO method cannot distinguish between singlet and triplet states. But the LCAO method really gives the mean between singlet and triplet states(21), 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. 3.

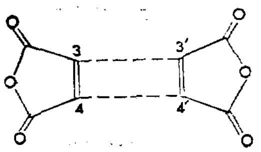


Fig. 3. Configuration of Interaction of two MA Molecules.

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

$$E_{int}/\beta = -1.059(S_{33'}^2 + S_{44'}^2) - 6.273\ S_{33'}S_{44'} \cdots (9)$$

Whatever the respective values of the two overlaps, $S_{33'}$ and $S_{44'}$, 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 Ψ_4 to the lowest antibonding Ψ_5. Using the eq. (8), we obtain a change in interaction energy due to excitation.

$$\Delta E_{int}^{(4\to 5)}/\beta = 0.995(S_{33'} + S_{44'}) + 0.252(S_{33'}^2 + S_{44'}^2) + 0.260\ S_{33'}S_{44'} \cdots\cdots (10)$$

In eq. (10), there appear a large attractive first-order term and a significant attractive second-order cross-term in $S_{33'}S_{44'}$. Eq. (9) and (10) give, for the interaction energy E_{int}^* in the photochemical reaction.

$$E_{int}^*/\beta = 0.995(S_{33'} + S_{44'}) - 0.807(S_{33'}^2 + S_{44'}^2) - 3.103\ S_{33'}S_{44'} \cdots\cdots (11)$$

The over-all stabilization for $S_{33'}=S_{44'}=0.2$ is

$E^*_{int}=0.213\beta=-14.80$ kcal/mole($\beta_{spectroscopic}=3$ eV).

MA itself yields two dimers on irradiation in solution, while only one of them is obtained on irradiation of solid (22).

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.

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* Eq. (1) and (3) give nearly the same results if the energy difference is larger than 0.7β.

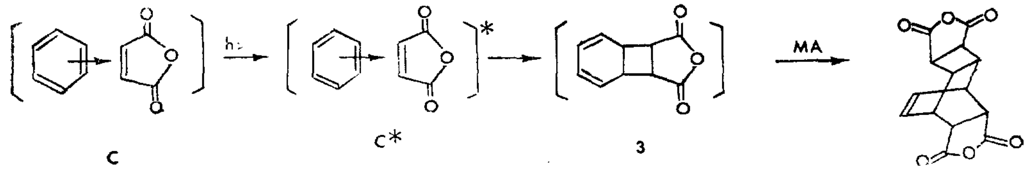
Photochemical reaction of MA with benzene

In the photochemical reaction of MA with benzene, the following mechanisms are proposed [20].

(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.



C C* 3

But it is not known with certainty whether the second MA addition is photochemical or takes place by thermal reaction[22]. 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 [23][24][25]. And also it is not yet clear why MA should undergo 1,2 addition to benzene when the conventional 1,4-addition would give a virtually strainless product[26]. The benzene-MA adduct is formed through both the triplet and the singlet state charge-transfer complex [8][20].

And the complex excitation is much more closely related to the excitation of MA rather than to that of benzene [20]. Thus it is not unreasonable to take the MA-benzene complex in the excited state as the adduct of a ground-state benzene and an excited MA.

1,4-addition of benzene with MA

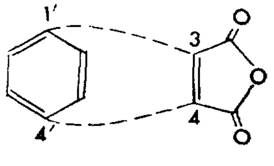


Fig. 4. Configuration of 1,4-Addition of MA and Benzene.

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

From the eq. (1),

$$E_{int}/\beta=-1.572(S_{31'}^2+S_{44'}^2)+3.667\,S_{31'}S_{44'}\cdots(12)$$

The stabilization energy for $S_{31'}=S_{44'}=0.2$ is $E_{int}=0.021\beta=-1.45$ kcal/mole. However this is small, so that no cycloaddition will occur. Using the eq. (8).

$$\Delta E_{int}^{(4-5)}/\beta=0.165+7.563(S_{31'}^2+S_{44'}^2)-16.260\,S_{31'}S_{44'}\cdots\cdots\cdots\cdots(13)$$

Eq. (12) and (13) give, for the interaction energy, E^*_{int}, in the photochemical interaction.

$$E^*_{int}/\beta=0.165+5.991(S_{31'}^2+S_{44'}^2)-12.593\,S_{31'}S_{44'}\cdots\cdots\cdots\cdots(14)$$

The overall stabilization energy for $S_{31'}=S_{44'}=0.2$ is $E^*_{int}=0.141\beta=-9.80$ 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 result [24]. But the photochemical interaction energy does not seem to be enough to occur 1,4-addition.

From the above calculations together with Mulliken's proposals [27], 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 [28], but 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 [29].

1,2-addition of benzene and MA

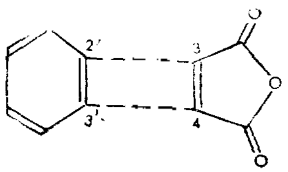


Fig. 5. Configuration of 1,2-Addition of MA and Benzene.

From the eq. (1),

$$E_{int}/\beta=-1.592\,(S_{32'}+S_{43'})-1.616\,S_{32'}S_{44'}\cdots(15)$$

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)

$$\triangle E^{\ddagger}_{int}/\beta=0.165+7.569(S_{32'}^2+S_{43'}^2)+9.230\ S_{32'}S_{43'}\cdots\cdots(16)$$

Eq. (15) and (16) give

$$E^*_{int}/\beta=0.165+5.997\ (S_{32'}^2+S_{43'}^2)+7.614\ S_{32'}S_{44'}\ \cdots\cdots(17)$$

The over-all stabilization energy for $S_{32'}=S_{43'}=0.2$ is

$E^*_{int}=0.945\beta=-65.66$ kcal/mole.

This stabilizaton 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 ⁽²⁶⁾.

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 ⁽²⁴⁾.

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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.

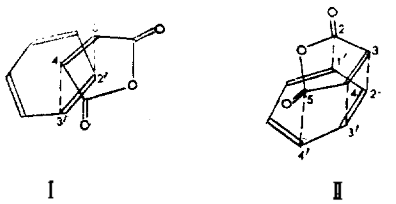

Fig. 6. Configurations of 1, 2-Cycloaddition of MA and Benzene.

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⁾⁽¹³⁾.

Calculations of interaction energy of the configuration II give

$$E_{int}/\beta=-1.592(S_{32'}^2+S_{43'}^2)-1.616\ S_{32'}S_{43}+[-0.926(S_{21'}S_{32'}+S_{43'}S_{54'})+0.577(S_{21'}S_{43'}+S_{32'}S_{54'})+0.658\ S_{21'}S_{54'}-1.469(S_{21'}^2+S_{54'}^2)]\cdots(18)$$

ant

$$E^*_{int}/\beta=0.165+5.977(S_{32'}^2+S_{43'}^2)+7.614\ S_{32'}S_{43'}+[-4.143(S_{21'}S_{32'}+S_{43'}S_{54'})+3.036(S_{21'}S_{43'}+S_{32'}S_{54'})-3.544\ S_{21'}S_{54'}-1.029(S_{21'}^2+S_{54'}{}^2)]\ \cdots(19)$$

The square brackets represent additional interactions due to $S_{21'}$ and $S_{54'}$. From the above equations(18) and (19), it can be seen that the additional interactoins 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 paralell ⁽²⁰⁾. From the structure of MA molecule ⁽¹⁶⁾, it can be assumed that $S_{21'}$ is nearly equal to $S_{32'}$. If $S_{21'}=0.2$ and $S_{43'}=0.2$, the over-all stabilization energy is $E^*_{int}=0.635\beta=-44.12$ 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 canfiguration 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 **1** rather than the formula **2**.

The second addition of MA to benzene

After the first addition step was accomplished, the remaining π-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),

$$E_{int}/\beta=0.193(S_{31'}^2+S_{44'}^2)+6.883\ S_{31'}S_{44'}\ \cdots(20)$$

$$E^*_{int}/\beta=0.372+1.226(S_{31'}^2+S_{44'}^2)+1.650\ S_{31'}S_{44'}\cdots\cdots(21)$$

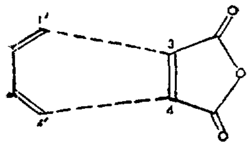

Fig. 7. Configuration of 1,4-Cycloaddition of MA and Butadiene.

For $S_{31'}=S_{44'}=0.2$, the thermal interaction energy is $E_{int}=0.291\beta=-20.22$ kcal/mole and the photochemical interaction energy is $E^*_{int}=0.536\beta=-37.24$ kcal/mole. As shown above, the second addition can be accomplished by the photochemical reaction as well as by the thermal reaction. Furthemore, the theoretical results predict that the former is more favorable than the latter. Even if the second addition step is photochemical, the conclusion reached from the experimental results by Hardham and Hammond (20) that the quantum yield does not depend upon a light intensity and that the quantum yield is increased with increasing the initial concentration of MA are not changed, for the conc-entration of MA in its excited state, which can have the chance to react with the intermediate **3** is expec-ted to be very small, and under their experimental conditions, the excited MA can be formed only thro-ugh the dissociation of the excited MA-benzene com-plex.

In view of our calculations the excited MA is predicted to be more reactive toward benzene than toward the intermediate **3**. Furthermore the dissociation reaction is endothermic, and benzene exists in large amount. Therefore it can be concluded that both the thermal and the photochemical reactions are the second addition steps.

The adduct **1** was also found to be formed by the γ-irradiation (30). It is predicted that the modes of addition reactions are the same as those of the photochemical reactions from the stereochemical structures of the products under γ-irradiation, and that if some suitable assumptions are made as Dougherty does in the mass-spectrometric reactions (31), this reaction can be also treated by the simple MO methods.

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