Correlation Diagrams and the Mechanism and Stereochemistry of the Photochemical Diels-Alder Reaction

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The Woodward-Hoffmann rules[1] dictate that [4s + 2s] concerted photocycloadditions are symmetry-forbidden reactions. According to such a formulation, the photocycloaddition of a diene and an olefin is expected to proceed *via* the symmetry-allowed least-motion [2s + 2s] pathway or the non-least-motion symmetry-allowed [4s + 2a] or [4a + 2s] pathway. The Woodward-Hoffmann analysis was carried out on the basis of nonpolar models and we recently proposed that there is a dichotomy between the stereoselectivities of nonpolar and polar photocycloadditions owing to the different types of orbital interactions obtaining in these two general classes of photoreactions.[2] Correlation diagrams can be used fruitfully to analyze the stereoselectivity and mechanism of nonpolar and polar photocycloadditions. In this note, we confine our attention to the case of the photochemical [4 + 2] (Diels-Alder) cycloaddition.

In a photocycloaddition reaction, one can define the donor (D) and the acceptor (A) cycloaddend by reference to their ground-state properties. There are two general photocycloaddition mechanisms.[3] Mechanism 1 constitutes an example of an adiabatic transformation and mechanism 2 an example of a diabatic transformation.[4] Mechanism 2 is the one most often encountered in photochemical reactions, in general. Now, we can distinguish between nonpolar and polar [2 + 2] cycloadditions and between semipolar and polar [4 + 2] cycloadditions.[5] A typical semipolar [4 + 2] cycloaddition is that of butadiene and ethylene. The correlation diagram for the photochemical cycloaddition of butadiene and ethylene is shown in Figure 1. It is assumed that one photoexcited cycloaddend attacks the other one in its ground state. The correlation diagram shows that the lowest excited state of the complex does not correlate with either the lowest excited state of the product or directly with the ground state of the product. Hence, [4s + 2s] photocycloaddition is forbidden to occur *via* mechanisms 1 or 2.

$$\begin{matrix} D^* + A \\ \text{or} \\ D + A^* \end{matrix} \longrightarrow [\text{complex}]^* \longrightarrow P^* \longrightarrow P \qquad (1)$$

$$\begin{matrix} D^* + A \\ \text{or} \\ D + A^* \end{matrix} \longrightarrow [\text{complex}]^* \longrightarrow P \qquad (2)$$

A typical polar [4 + 2] cycloaddition involves a butadiene substituted by electron donor groups and an ethylene substituted by electron acceptor groups. Electron donating groups raise the energy of both the HOMO and the LUMO of butadiene, the former more than the latter, and electron accepting groups act principally by lowering the energy of the ethylene LUMO while leaving the energy of the ethylene HOMO relatively unchanged. As a result, in polar [4 + 2] cycloadditions, the HOMO of the diene has higher energy than the HOMO of the dienophile, a situation similar to the one which obtains in semipolar cycloadditions. On the other hand, *the LUMO of the diene has also higher energy than the LUMO of the dienophile, a situation which is opposite to the one which obtains in semipolar cycloadditions.* The correlation diagram for polar [4 + 2] photocycloaddition is shown in Figure 2 and a major difference between semipolar and polar [4 + 2] photocycloadditions is revealed. Specifically, *the lowest excited state of the reaction complex is a locally excited complex in the former case but an excited charge-transfer complex in the latter case.* Furthermore, the correlation diagram shows that the excited charge-transfer complex does not correlate with the lowest excited state of the product but *it does correlate with the ground state of the product.* This implies that [4s

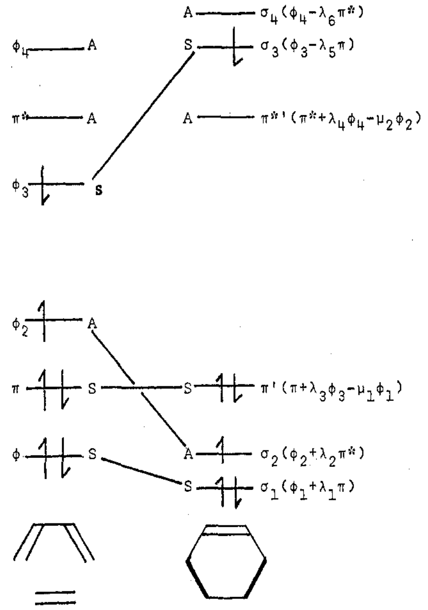

Figure 1. Correlation diagram for a semipolar [4s + 2s] photocycloaddition in which the reaction complex correlates only with a higher excited state $\sigma_1{}^2\sigma_2{}^1\pi'^2\sigma_3{}^1$, of the product as indicated on the diagram. The butadiene MO's are designated ϕ_1, ϕ_2, ϕ_3, and ϕ_4 and the ethylene MO's are π and π^*.

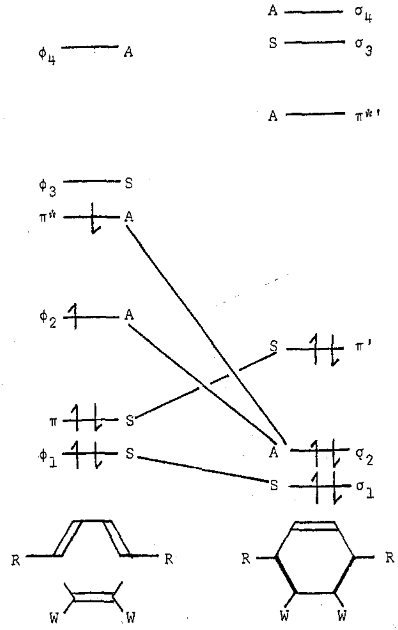

Figure 2. Correlation diagram for a polar [4s + 2s] photocycloaddition. The reaction complex correlates either with a higher excited state of the product, $\sigma_1{}^2\sigma_2{}^1\pi'^2\pi^{*\prime 1}$, or the ground state of the product, $\sigma_1{}^2\sigma_2{}^2\pi'^2$. The latter correlation is shown on the diagram. R = electron-releasing group, W = electron-withdrawing group. Only the butadienic and olefinic MO's are shown and the MO correlations are *intended* correlations.

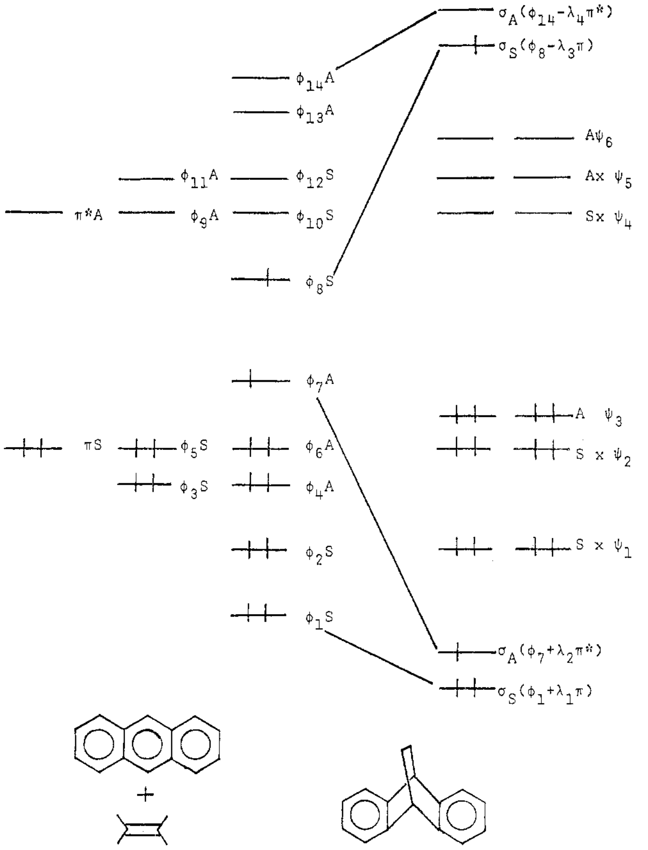

Figure 3. Correlation diagram for the [4s + 2s] photocycloaddition of anthracene and ethylene. The reaction complex correlates with a higher excited state of the product as shown in the diagram. The MO correlations are *intended* correlations.

+ 2s] cycloaddition is photochemically allowed to occur *via* mechanism 2. Similar conclusions are reached when butadiene is substituted by electron acceptor groups and ethyl-

$$\begin{matrix} D^* + A \\ \text{or} \\ D \ + A^* \end{matrix} \longrightarrow [D^+A^-]^* \longrightarrow P$$

ene by electron donor groups. Direct spectroscopic observations[6] indicate that the conversion of D* and A or D and A* to the excited charge-transfer complex is allowed and correlation diagrams reveal that the conversion of the latter complex to ground-state product is also allowed. In short, photochemical polar [4s + 2s] cycloadditions can indeed be very favorable.

Although the intricacies of correlation diagrams were fully discussed in the original work of Woodward and Hoffmann, it may be appropriate to stress some points. Thus the correlation diagram for the photoaddition of butadiene and ethylene involves crossing of levels of different symmetry and, thus, either a MO correlation diagram or a state correlation diagram provide a fully satisfactory depiction of the transformation. On the other hand, the correlation diagram for the photoaddition of a donor butadiene and an acceptor ethylene constitutes a simplified description of the transformation. Thus, if all the MO's of the two reactants were drawn, crossing of levels of the same symmetry would occur. However, this violation of the noncrossing rule could have been alleviated by the construction of state correlation diagrams which would have provided an adequate theoretical description of the transformation. Nonetheless, it is much simpler to construct MO correlation diagrams for systems where crossing of levels of the same symmetry occurs and discuss the so-called *intended* correlations of MO's. Hence, the correlation diagrams for the polar [4 + 2] photocycloadditions are perfectly adequate for our qualitative discussions.

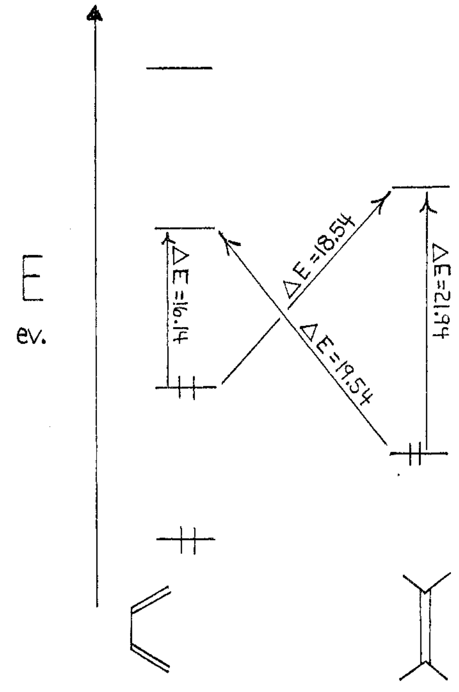

Figure 4. Interaction diagram for a semipolar [4 + 2] cycloaddition. The locally excited state is the lowest energy excited state. Energy levels from a CNDO/2 calculation.

The [4 + 2] photocycloadditions are not restricted to acyclic dienes and olefins. For example, aromatic molecules, like naphthalene, anthracene, etc., can potentially act as the diene component in photochemical [4 + 2] cycloadditions. The MO correlation diagram for the [4 + 2] photocycloaddition of anthracene and ethylene is shown in Figure 3. The intended MO correlations make it unambiguously clear that the situation is identical with that encountered in the case of the butadiene–ethylene photocycloaddition. A MO correlation diagram for the [4 + 2] photocycloaddition of donor anthracene–acceptor ethylene can be constructed and the conclusion drawn will be identical with those arrived at on the basis of the correlation diagrams for the photocycloaddition of donor butadiene–acceptor olefin.

We have sought to provide some kind of quantitative support for these ideas and we have calculated various diene–dienophile pairs in order to determine whether the locally excited or excited charge-transfer state will constitute the lowest excited state of the reactants to be correlated with the various states of the product. The calculation results shown in Figures 4–8 demonstrate clearly that in typical semipolar cycloadditions (Figures 4 and 7) the locally excited state is the lowest excited state, while in typical polar cycloadditions (Figures 5, 6, and 8) the excited charge-transfer state is the lowest excited state. The numbers in Figures 4, 5, and 6 were obtained by simple subtraction of CNDO/2 orbital energies and, thus, two electron correction terms are neglected in the calculation of the energy difference between a ground state and an excited state complex. A similar procedure is followed in Figures 7 and 8 where the orbital energies are eigenvalues of an effective one-electron Hamiltonian. We feel that the qualitative trends revealed by such an approach will not be altered significantly when electron interaction is incorporated in the

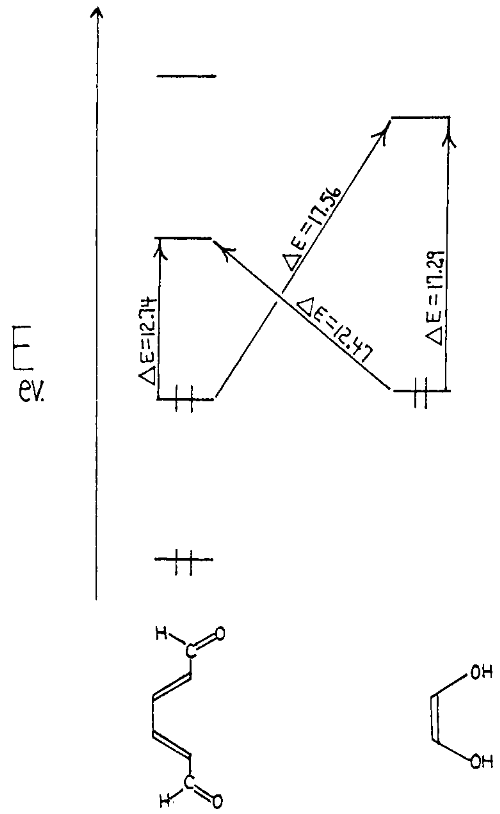

Figure 5. Interaction diagram for a typical polar [4 + 2] cycloaddition between an electron-deficient diene and an electron-rich olefin. The excited charge-transfer state is lower in energy than the locally excited state. Energy levels from a CNDO/2 calculation.

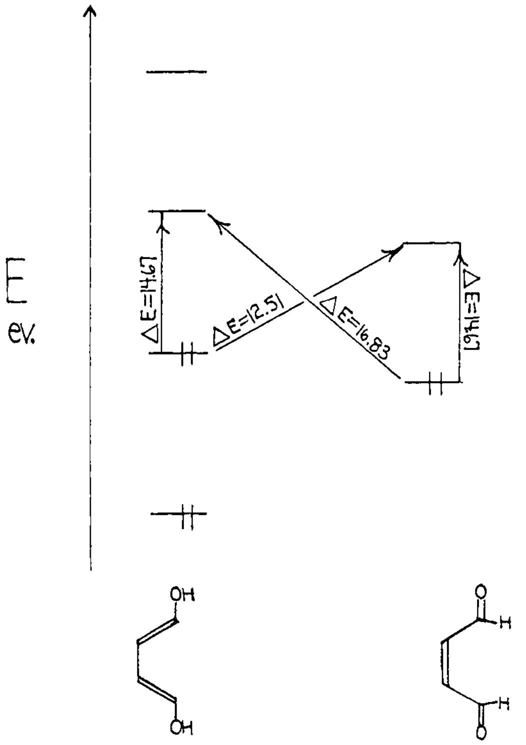

Figure 6. Interaction diagram for a polar cycloaddition between an electron-rich diene and an electron-deficient dienophile. The charge-transfer excited state is the lowest energy excited state. Energy levels from a CNDO/2 calculation.

theoretical treatment. Such an approach is discussed elsewhere.[7]

Our analysis is consistent with the following interesting

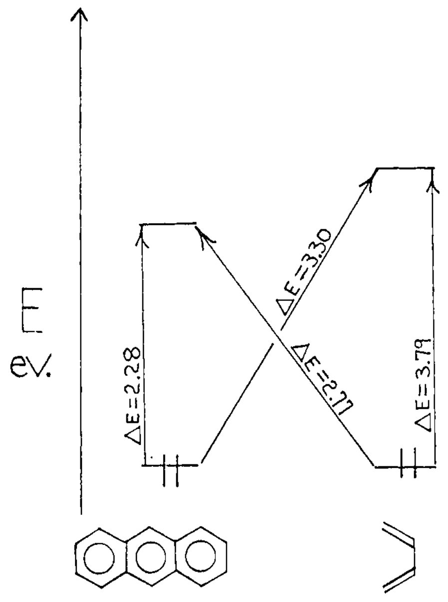

Figure 7. Interaction diagram for the cycloaddition of anthracene and butadiene. The locally excited state is lower in energy than the charge-transfer excited state. Energy levels from a Wolfsberg–Helmholtz–Mulliken calculation.

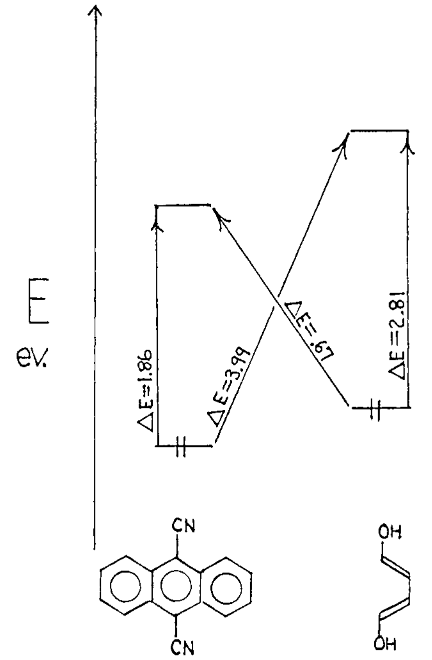

Figure 8. Interaction diagram for the cycloaddition of 9,10-dicyanoanthracene and 1,4-dihydroxybutadiene. The charge-transfer excited state is the lowest excited state. Energy levels from a Wolfsberg–Helmholtz–Mulliken calculation.

experimental facts.

(1) Anthracene adds to dienes stereospecifically in a [4s + 4s] manner, but 9-cyanoanthracene adds to dienes stereospecifically in a [4s + 2s] manner.[8]

(2) Retrograde homo-Diels–Alder reactions of azo compounds exhibit the same [4s + 2s] stereoselectivity under both thermal and photochemical conditions.[9]

(3) Maleic anhydride adds photochemically to benzene, a poor electron donor aromatic (ionization potential = 9.25 eV)[10] in a [2 + 2] manner.[11] On the other hand, it adds photochemically to anthracene, a good electron donor aromatic (ionization potential = 7.55 eV)[10] in a [4 + 2] manner.[12,13]

We suggest that polar [4 + 2] photocycloadditions can be useful synthetic reactions and that the orbital symmetry approach[14] can be used in connection with many photochemical problems such as the effect of substituents on the mechanism and stereochemistry of photochemical pericyclic reactions.

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Registry No.—Butadiene, 106-99-0; ethylene, 74-85-1; anthracene, 120-12-7; 2,3-dimethyl-2-butene, 563-79-1; 2,4-hexadienediol, 3249-28-3; 1,2-ethenediol, 1571-60-4; 1,3-butadiene-1,4-diol, 42466-41-1; malealdehyde, 3675-13-6; 9,10-dicyanoanthracene, 1217-45-4.

References and Notes

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(13) However, the [4 + 2] photoadditions of the esters of maleic and fumaric acids to anthracene appears to proceed *via* diradical intermediates rather than a stereoselective [4s + 2s] fashion: G. Kaupp, *Chimia*, **25**, 230 (1971). This may be due to the fact that these olefins are much inferior acceptors compared to maleic anhydride, for example.

(14) The correlation diagrams for semipolar and polar [4 + 2] photocycloadditions are constructed by reference to symmetrical reactants. However, the same conclusions are valid for unsymmetrical reactants, since the local symmetry of the ethylenic and butadienic MO's is the important factor.

The Activation Volume for Single-Bond Homolysis From Empirical Internal Solvent Pressure

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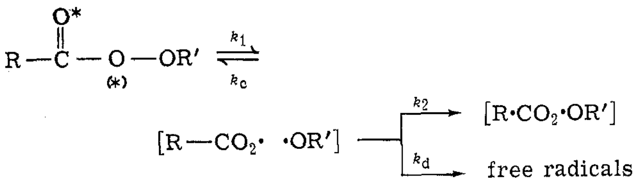
Neuman and coworkers[1] have measured apparent activation volumes for a number of free-radical initiators. These parameters (ΔV_e*) were small for peresters previously proposed[2] to undergo concerted (C–C and O–O) decomposition and large for *tert*-butyl perbenzoate. The activation volumes were thus considered an additional criterion of mechanism. We,[3] as well as others,[4] have examined viscosity effects on overall rates of decomposition of peroxides. We have used Scheme I as a general one in analyzing the results quantitatively. Equations 1 and 2 (where k_o and k_s are observables) give the predictions of this scheme for overall disappearance of initiators.

Scheme I



$$\frac{1}{(k_1/k_o) - 1} = \frac{k_2}{k_c} + \frac{k_d}{k_c} = (\frac{1}{f_{\text{recombination}}} - 1) = \frac{k_o}{k_s} \tag{1}$$

$$k_1 = k_o + k_s \tag{2}$$

Assuming k_d is the only viscosity-sensitive (interpretive) rate constant and *knowing* the value of k_1 allows the analysis of the k_o–fluidity dependence in terms of fraction recombination. Pryor and coworkers[4] have used essentially the same scheme and proposed extrapolation of $1/k_o$ *vs.* η^{α} to zero viscosity as a means of estimating the value of $1/k_1$. An alternative is to measure the rate constant for scrambling of carbonyl-^{18}O (k_s). Under the assumption above, the sum of $k_o + k_s$ (k_1) should be constant.

These sums were not constant for either of the two cases which we investigated[3] (Table I, Scheme I; R = Ph, CH_3; R′ = *t*-Bu). We wish to point out that the positive activation volumes determined by the external pressure variation[1] imply that k_1 could only *fortuitously* be constant over the range of solvents investigated because of differences in internal solvent pressure.[5]

It is possible to circumvent the problems of calculating internal pressures by defining an empirical set of differential solvent pressures (DSP) from a reaction of known activation volume. This is analogous to the definition of Hammett[10] substituent constants from an arbitrary reaction. The apparent activation volume for *tert*-butyl perbenzoate is reported[11] to be +10.4 cc/mol in cumene and +12.9 cc/mol in chlorobenzene. Assuming that the activation volume in the hydrocarbon solvents which we have used is similar[12] and that the differential solvation energy is zero, the relative rates (Table I) can be used to determine the differential solvent pressures for the solvent series at 130° (Figure 1, Table I). A plot of ln ($k_o + k_s$) for the peracetate, also at 130°, *vs.* the DSP values is linear, giving an activation volume of +5 cc/mol (Figure 1), which is in agreement with

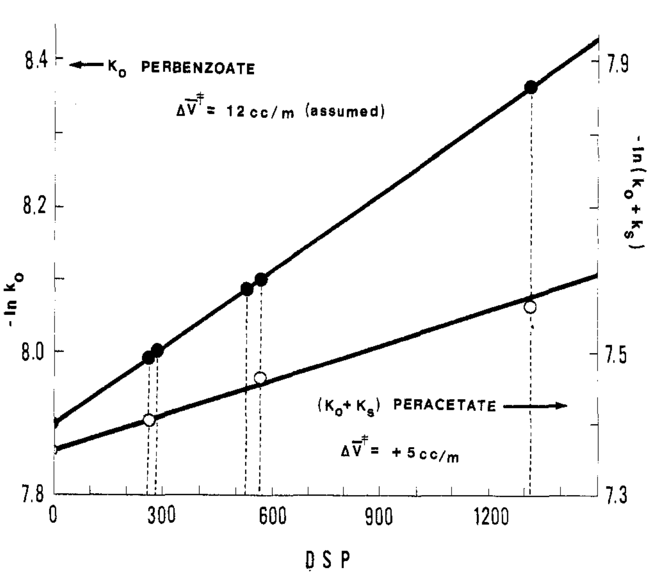


Figure 1. Activation volumes from empirical differential solvent pressures.