(10) J. H. Freed, *Ann. Rev. Phys. Chem.*, **23**, 265 (1972).
(11) R. G. Kooser, W. V. Volland, and J. H. Freed, *J. Chem. Phys.*, **50**, 5243 (1969).
(12) S. A. Goldman, G. V. Bruno, and J. H. Freed, *J. Chem. Phys.*, **59**, 3071 (1973).
(13) J. S. Hwang, R. P. Mason, and J. H. Freed, to be submitted for publication.
(14) D. S. Leniart, Ph.D. Thesis, Cornell University, 1971; H. D. Connor, Ph.D. Thesis, Cornell University, 1972; H. D. Connor, D. S. Leniart, and J. H. Freed, to be submitted for publication.
(15) See ref 10 for a review and references through 1971.
(16) J. S. Hyde, L. E. G. Eriksson, and A. Ehrenberg, *Biochim. Biophys. Acta*, **222**, 688 (1970).
(17) J. S. Hyde and L. S. Dalton, *Chem. Phys. Lett.*, **16**, 568 (1972).
(18) J. H. Freed, G. V. Bruno, and C. F. Polnaszek, *J. Phys. Chem.*, **75**, 3385 (1971).
(19) S. A. Goldman, G. V. Bruno, C. F. Polnaszek, and J. H. Freed, *J. Chem. Phys.*, **56**, 716 (1972).
(20) G. V. Bruno and J. H. Freed, *Chem. Phys. Lett.*, **25**, 328 (1974).
(21) G. V. Bruno, Ph.D. Thesis, Cornell University, 1973.
(22) A. Abragam, "The Principles of Nuclear Magnetism," Oxford University Press, New York, N. Y., 1961.
(23) H. C. Torrey, *Phys. Rev.*, **76**, 1059 (1949).
(24) (a) C. F. Polnaszek, G. V. Bruno, and J. H. Freed, *J. Chem. Phys.*, **58**, 3185 (1973). (b) This is based on a rigorous definition of **d** as a transition moment. However, in previous usage we have set $d_{i,j} = 0$ for any transition which is not excited even though it is allowed.[3-8] Such a usage is a convenience for well-separated lines, but it breaks down for overlapping lines or in the slow tumbling region, so we return here to the rigorous definition of **d** for general discussions.
(25) The special case of $\Delta\omega = 0$ and $T_1 = T_2 \equiv T$, which, as noted, represents a breakdown of the expansion eq 2.24a, results in $\Delta Z'(t)$ decaying as $e^{-t/T}$, while the coupled modes $[\Delta Z''(t) \pm \frac{1}{2}\Delta X(t)]$ decay as $e^{-t}(T^{-1} \pm i\omega_1)$. Since we are assuming $\omega_1^2 T_1 T_2 = (\omega_1 T)^2 \ll 1$, it follows that $e^{-t}(T^{-1} \pm i\omega_1) \cong e^{-t/T}(1 \pm i\omega_1 t)$, essentially an exponential decay in T_1.
(26) When the $w_{\beta\beta}$ are very different, *e.g.*, b and/or $b'' \gg 1$, such that $w_{22}, w_{33} \gg w_{11}$, then other steady-state approximations appropriate to pulses of duration Δt fulfilling $w_{22}^{-1}, w_{33}^{-1} \ll w_{11}^{-1} = 2T_1$ may be used by solving for the steady-state solutions appropriate for $W_e \approx 0$ but W_n and/or $\omega_{EX} \neq 0$. This steady-state solution yields equal degrees of saturation of all the eigenstate pairs, and thus gives comparable results to that for case (2) above. [Note, however, that for a steady-state approximation to apply here, $\Delta t \gtrsim 2(T_1^{-1} + T_2^{-1})^{-1}$ and $\omega_1^2 \geq (T_1^{-1} - T_2^{-1})$.[22,23]
(27) This perturbation approach was first used by FBP in ref 18 to discuss effects of nonsecular g tensor contributions to saturation behavior. There are some minor errors in eq 60 of that reference, due to a use of nonsymmetric matrices (*i.e.*, the unnormalized $\mathfrak{D}_{KML}$ were used as the basis), but this has no effect on the discussion which follows, nor on the final result of eq 61.

A Molecular Orbital Study of the Addition of Singlet Methylene to Butadiene

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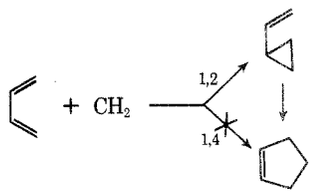
A simple molecular orbital method is proposed to deal with chemically reacting systems in terms of the molecular orbitals of two isolated reactants. The electron population of a reacting system is partitioned into several orbital interaction terms, allowing a tracing of the origin of intermolecular bond formation and of the intramolecular reorganization of the electron distribution. The method is applied to the interaction between singlet methylene and butadiene. Both 1,2- and 1,4 addition are electronically allowed, but the 1,4 addition is discriminated against by excessive closed-shell repulsive interactions.

Introduction

The interpretation of chemical interactions between two systems in terms of the electronic structures of isolated reactants is a problem of crucial importance to chemistry. Some useful reactivity indices and generalized stereoselection rules have been derived by rather simplified molecular orbital (MO) methods.[1-8] There perturbation theory and orbital correlation diagrams have been found to be quite powerful. Several more detailed MO theoretical methods have been proposed in order to calculate the interaction energy and the electron distribution of chemically interacting systems from the wave functions of two isolated reactants.[9-17] Although the application of the "isolated-molecule-approximation"[18] is limited to the case of relatively weak interactions, *e.g.*, the early stage of chemical reactions, it can often be very informative in disclosing the governing factors of complicated chemical reactions.

The typical reactions of methylenes, namely, addition to a double bond, insertion into a single bond, and dimerization, have proven a useful testing ground for approximate calculations of bimolecular potential energy surfaces and reaction coordinates.[19,20] In the present work we continue our study of methylene reactions, returning to the addition reaction. We seek to understand a negative result; experiments on the reaction of singlet methylene with dienes have given no direct evidence of 1,4 concerted addition.[21] Normal 1,2 addition apparently prevails as the initial step.[22] This is so despite the least-motion cheletropic reaction of 1,4 addition clearly being a symmetry allowed process.[7]



In this paper we first present a simple way of discussing the reorganization of the electronic distributions of two interacting molecules, and then apply our formalism to the reaction of singlet methylene and butadiene.

Population Analysis of Chemically Reacting Systems

Let us consider an interaction between two molecular systems, A and B. The MO's of A and B in their isolated states are given by linear combinations of atomic orbitals (AO's) as

$$a_i = \sum_r^{A} c_{ir}\chi_r \qquad \text{for the system A}$$

$$b_i = \sum_s^{B} c_{is}\chi_s \qquad \text{for the system B}$$

The MO's of the composite system A–B of the two reactants, retaining the nuclear configurations they possessed when isolated, are given by

$$\psi_n = \sum_t^{A-B} c_{nt}\chi_t$$

ψ_n can be rewritten in terms of the a_i's and b_l's as a linear combination of MO's

$$\psi_n = \sum_i^{occ} k_{ni}a_i + \sum_j^{unocc} k_{nj}a_j + \sum_l^{occ} k_{nl}b_l + \sum_m^{unocc} k_{nm}b_m \quad (1)$$

where Σ^{occ} and Σ^{unocc} imply summation over all the occupied MO's and over all the unoccupied MO's, respectively. The coefficients k can be obtained exactly, for example, by solving the secular equation, or approximately, by the use of perturbation theory. It should be noted here that the a's form an orthonormal set, the b's another orthonormal set, and that a's and b's are not in general mutually orthogonal. All the functions are assumed to be taken as real.

The spin-free electron density of the systems A and B in their isolated states is defined by

$$\rho_A{}^0 = 2\sum_i^{occ}(a_i)^2 \quad (2)$$

and

$$\rho_B{}^0 = 2\sum_l^{occ}(b_l)^2 \quad (3)$$

The electron density of the system A–B is given by

$$\rho = 2\sum_n^{occ}(\psi_n)^2 = \rho_A + \rho_B + \rho_{A-B} \quad (4)$$

where

$$\rho_A = 2\sum_n^{occ}\Bigg[\sum_i^{occ}(k_{ni}a_i)^2 + \sum_j^{unocc}(k_{nj}a_j)^2 + \sum_i^{occ}\sum_{i'\neq i}^{occ}(k_{ni}k_{ni'}a_ia_{i'}) + \sum_j^{unocc}\sum_{j'\neq j}^{unocc}(k_{nj}k_{nj'}a_ja_{j'}) + \sum_i^{occ}\sum_j^{unocc}k_{ni}k_{nj}(a_ia_j + a_ja_i)\Bigg] \quad (5)$$

and

$$\rho_{A-B} = \Bigg[\sum_i^{occ}\sum_l^{occ}\rho_{A-B,il} + \sum_i^{occ}\sum_n^{unocc}\rho_{A-B,in} + \sum_j^{unocc}\sum_l^{occ}\rho_{A-B,jl} + \sum_j^{unocc}\sum_n^{unocc}\rho_{A-B,jn}\Bigg] \quad (6)$$

$$\rho_{A-B,il} = 4\sum_n^{occ}k_{ni}k_{nl}a_ib_l \quad \text{etc.}$$

The first and the second terms in eq 5 reflect the strength of the charge transfer and local excitation in the course of reaction, and the last three terms give the electron reorganization, *i.e.*, polarization, in the system A. The density ρ_{A-B} measures the changes in the electron densities of the intermolecular region and is responsible for the formation of chemical bonds between A and B.

The distortion of the electron density distribution due to the interaction of the two systems is given by

$$\Delta\rho = \Delta\rho_A + \Delta\rho_B + \rho_{A-B} \quad (7)$$

where

$$\Delta\rho_A = \rho_A - \rho_A{}^0 \quad \text{etc.}$$

From the condition of the conservation of the total number of electrons throughout the reaction, we have

$$\int\Delta\rho\ d\upsilon = 0 \quad (8)$$

That is, the intermolecular bond is formed at the cost of electron densities in the neighborhood of the two reactants.

The intermolecular electron density ρ_{A-B} can be expanded in terms of the AO's of A and AO's of B

$$\int\rho_{A-B,il}\ d\upsilon = 4\sum_n^{occ}k_{ni}k_{nl}S_{il} = 4\sum_r^{A}\sum_s^{B}\Bigg(\sum_n^{occ}k_{ni}k_{nl}c_{ir}c_{ls}s_{rs}\Bigg) = V_{A-B,il} \quad (9)$$

where

$$S_{il} = \int a_ib_l\ d\upsilon \text{ and } s_{rs} = \int\chi_r\chi_s\ d\upsilon$$

The quantity $V_{A-B,il}$ gives the overlap population between A and B as a result of interaction of MO a_i with MO b_l. The total overlap population is given by

$$V_{A-B} = \sum_i^{occ}\sum_l^{occ}V_{A-B,il} + \sum_i^{occ}\sum_m^{unocc}V_{A-B,im} + \sum_j^{unocc}\sum_l^{occ}V_{A-B,jl} + \sum_j^{unocc}\sum_n^{unocc}V_{A-B,jn} \quad (10)$$

According to the Mulliken population analysis scheme,[23] the overlap population between AO r and AO s is divided evenly into two parts, one of which contributes to the gross population of AO r and the other to that of AO s. The overlap population $V_{A-B,il}$ arises from the interaction between MO a_i and MO b_l. Therefore, it is natural to divide this quantity into two parts, one belonging to MO a_i and the other to MO b_l. Thus, we may define the number of electrons occupying MO a_i in the interacting state by

$$\nu_i = 2\sum_n^{occ}(k_{ni})^2 + 2\sum_n^{occ}\sum_l^{B}k_{ni}k_{nl}S_{il} \quad (11)$$

We can thus see the complete analogy between ν_i and the Mulliken gross population and between $V_{A-B,il}$ and the Mulliken overlap population.[23]

ν and V_{A-B} may be useful in analyzing what happens in a given chemical interaction. When the reactants are separated, isolated, the overlap population V_{A-B} is zero. In the framework of a single-electron-configuration approximation the numbers of electrons occupying the originally occupied MO's a_i's and b_l's are two and those occupying the originally unoccupied MO's a_j's and b_m's are zero. As the interaction grows, the originally occupied MO's will lose some fraction of their electron pairs and the originally unoccupied MO's will correspondingly gain electrons. This process, of course, will be accompanied by an energy destabilization, except for the case of some strong donor–acceptor interactions in which the zero- and/or first-order perturbation stabilizes a charge-transferred configuration. However, this destabilization will be overcome or partly compensated by the stabilization originating from intermolecular bond formation. The situation is very similar to the promotion of electrons from an atomic state to a valence state, familiar to us for the case of molecule forma-

tion from atoms. The question is then how to diminish the unnecessary destabilization due to electron promotion in the course of reaction, so as to facilitate the progress of the reaction. The distinction between so-called "allowed" and "forbidden"[7] reaction paths is clearly related to this problem.

By introducing the MO's ψ_n which are expanded in terms of the MO's of A and B into the total wave function Ψ of the composite system, we can analyze Ψ as a linear combination of various electron configurations of two reactants, *e.g.*, the original, charge-transferred, locally excited configuration and so on.[24,25] Such a configuration analysis can also furnish us with a clearer perception of the factors influencing chemical interaction.

Orbital Crossing and Correlation Diagrams

Before proceeding to the discussion of our calculation on the interaction of singlet methylene and butadiene, it may be worth mentioning here briefly how orbital correlation diagrams[7] relate to our present MO treatment. The expansion coefficients k provide much the same information that is contained in correlation diagrams, which interrelate the orbitals of reactants with products, or in simple orbital interaction diagrams.

To make the correspondence clear we first examine the addition of singlet methylene to ethylene. This reaction is an excellent example of an orbital symmetry directed preference for a non-least-motion path of low symmetry over a least-motion approach of higher symmetry. It also forms an obvious departure point for analysis of the interaction of methylene with butadiene.

Consider two configurations of a methylene and an ethylene (Figure 1). The first, marked A, represents a waypoint in the orbital symmetry allowed approach of the two molecules.[19a,d] The second, marked B, is a higher symmetry, C_{2v}, geometry, corresponding to the least-motion, forbidden approach.[26] π and π^* are the usual ethylene orbitals, σ the highest occupied molecular orbital (HOMO) of a singlet methylene, p the lowest unoccupied molecular orbital (LUMO) of the methylene, in reality a 2p orbital on carbon.[27]

The numbers of electrons occupying the various orbitals in geometry A are the following: $\nu_{\pi^*} = 0.040$, $\nu_p = 0.427$, $\nu_\sigma = 1.909$, $\nu_\pi = 1.629$. Charge transfer has clearly taken place primarily from π to p. This, of course, is in agreement with the experimental results on the polarity developed in the transition state for methylene addition.[28]

In a complementary analysis,[25] one can expand the total wave function of the composite system in terms of various states of the components

$$\Psi = 0.718\Psi_0 + 0.445\Psi_{\pi\to p} + 0.135\Psi_{\pi\to p,\pi\to p} + 0.122\Psi_{\sigma\to\pi^*} + 0.179\Psi_{\sigma\to p} + \cdots$$

where Ψ_0 is the original state ($\pi^2\sigma^2$), $\Psi_{\pi\to p}$ the one-electron transferred state, with an electron moving from π to p ($\pi^1\sigma^2p^1$), $\Psi_{\sigma\to p}$ the locally-one-electron-excited state, σ to p ($\pi^2\sigma^1p^1$), and so on.[29,30] The magnitude of the various coefficients shows again the important role of the charge transfer from π to p.

The population analysis we have developed allows an informative partitioning of the total overlap population between ethylene and methylene: $V_{\pi\sigma} = -0.026$, $V_{\pi p} = 0.167$, $V_{\pi^*\sigma} = 0.028$, and $V_{\pi^* p} = -0.002$. Note the antibonding character of the closed-shell interaction between π and σ, and once again the dominant bonding interaction between π and p.

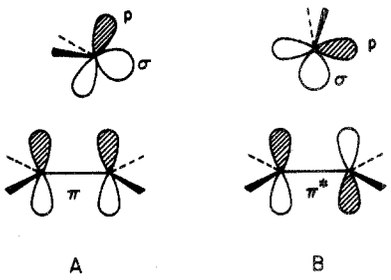


Figure 1. Geometries of two approaches of methylene to ethylene: A, non-least-motion allowed; B, least-motion forbidden. The two illustrations also show the shape of the σ and p orbitals of methylene and π and π^* levels of ethylene.

The above results are to be contrasted with the least-motion approach B. The occupation numbers in that case are $\nu_{\pi^*} = 0.059$, $\nu_p = 1.940$, $\nu_\sigma = 0.743$, and $\nu_\pi = 1.270$. Decomposition of the state wave function gives

$$\Psi = 0.292\Psi_{\pi\to p,\pi\to p} + 0.545\Psi_{\sigma\to p,\sigma\to p} + 0.570\Psi_{\pi\to p,\sigma\to p} + 0.116\Psi_{\sigma\to\pi^*,\sigma\to p} + \cdots$$

In the isolated state, four electrons occupy π and σ. Therefore, it is clear from examining the occupation numbers that a level crossing had taken place at $R > 2.5$ Å. Indeed, if the calculation is repeated at $R = 3.0$ Å, prior to that crossing, $\nu_\sigma = 1.999$, $\nu_\pi = 2.000$.[31]

The above example demonstrates how the ν's can show the type of electron shift, *i.e.*, transfer and/or excitation, which accompanies the orbital crossing. By expanding the wave function of the composite system as a linear combination of various electron configurations, one can define still more clearly the type of reorganization of electrons required to facilitate the occurrence of a reaction. It should be noted that neither the changes in the occupation numbers, nor the transfer from one electron configuration to another will take place discontinuously. An electronic state can and does interact with other states of the same spatial symmetry and the same spin multiplicity. Such configuration interaction is of particular importance when one is dealing with nearly degenerate levels, and may endow a system with biradical character.[32]

Addition of Singlet Methylene to Butadiene

As mentioned in the Introduction, there is no convincing evidence that singlet methylene can add in a concerted fashion to the termini of a butadiene. Instead 1,2 addition to a single double bond appears to be favored. This is so despite the 1,4 addition being a symmetry-allowed least-motion process. The problem at hand is thus to analyze how in this system a choice is made between two allowed reactions.

To study the difference between 1,2 and 1,4 addition we set up two reaction models for a methylene interacting with an *s-cis*-butadiene, as shown in Figure 2. In mode I, suited to 1,4 addition, C_s symmetry is maintained. The methylene is allowed to move in the mirror plane of butadiene orthogonal to the molecular plane. The separation of the two molecules was measured by the distance R from the methylene carbon to the midpoint of the line joining C_1 and C_4 of butadiene. The constraint to a plane allowed two angular degrees of freedom in addition to R. No particular symmetry constraint was used in mode II. The separation R here was measured from the midpoint of the $C_1{=}C_2$ double bond. The full six degrees of freedom were studied. For both modes the geometries of the buta-

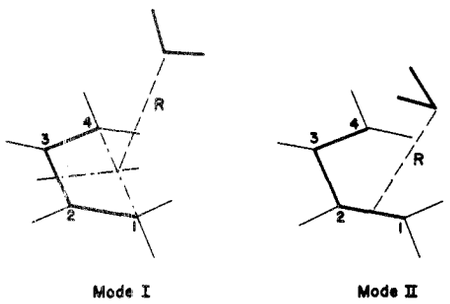


Figure 2. Two modes of approach of methylene to butadiene.

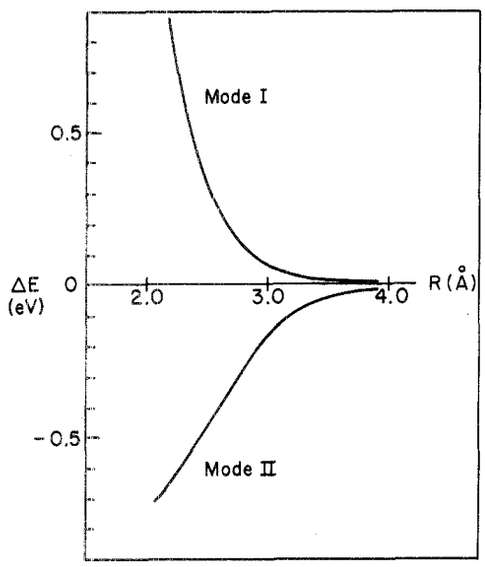


Figure 3. Energy as a function of R for modes I and II. Note that R is measured from a different origin (Figure 2) for the two modes.

diene and the methylene were frozen throughout the optimization.[33]

At a given R all the angular degrees of freedom were optimized. Figure 3 shows the energy as a function of R for both modes. The energy goes up along mode I, uniformly down along mode II in the region shown in Figure 3. Apparently mode I is not a real local minimum. When an optimized mode I geometry is used as a starting point for a mode II optimization (R measured from midpoint of $C_1{=}C_2$ instead of the C_1C_4 line), it moves smoothly over to a type II geometry. The preference for 1,2 addition is confirmed, though it must be noted that we did not allow full freedom to the reaction partners to relax their internal geometries in the course of the reaction.

We next turn to the analysis of what makes the mode II approach preferred over mode I. Figure 4 gives two projections of a pair of "snapshots" of angularly optimized geometries along the two reaction paths,[34] and Table I lists partitioned intermolecular overlap populations.

In both modes the sum of the overlap populations between occupied MO's of butadiene and occupied MO's of methylene is negative, as noted before for ethylene and methylene and as would be expected for the interaction between two closed-shell systems.[14b,23,35] The sum of the overlap populations between the occupied MO's of butadiene and the unoccupied MO's of methylene, and the converse, is positive, mainly coming from mutual charge-transfer interactions. Interactions between the unoccupied MO's are not important. Of all the combinations of the

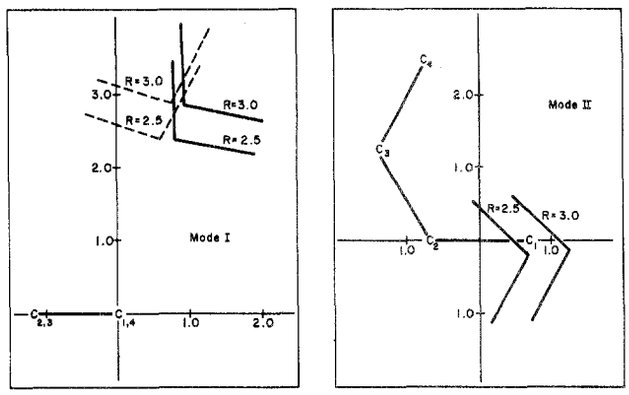


Figure 4. Projections of two optimized geometries along the modes of approach of methylene to butadiene. See text for a description of this drawing. The projection for mode I is on the vertical mirror plane of butadiene, and for mode II on the horizontal mirror plane containing the butadiene. Reference 34 explains the dashed geometries for mode I.

TABLE I: Partitioned Overlap Populations between Butadiene and Methylene

	Mode I		Mode II	
	R = 3.0 Å	R = 2.5 Å	R = 3.0 Å	R = 2.5 Å
$\sum_{i}^{\text{occ}}\sum_{l}^{\text{occ}} V_{\text{A-B},il}$	−0.0146	−0.0752	−0.0173	−0.0537
$\sum_{i}^{\text{occ}}\sum_{m}^{\text{unocc}} V_{\text{A-B},im}$	0.0086	0.0478	0.0699	0.1816
$\sum_{j}^{\text{unocc}}\sum_{l}^{\text{occ}} V_{\text{A-B},jl}$	0.0041	0.0180	0.0057	0.0351
$\sum_{j}^{\text{unocc}}\sum_{m}^{\text{unocc}} V_{\text{A-B},jm}$	0.0000	0.0001	0.0005	−0.0029
Total	−0.0019	−0.0094	0.0587	0.1601

MO's of the two species, the interaction between the HOMO of butadiene and the LUMO of methylene plays the dominant role in intermolecular bond formation. As R gets smaller, the total overlap population between butadiene and methylene, however, becomes more negative in mode I, while it becomes more positive in mode II.

The calculation further showed that the σ electronic system of butadiene remained almost unaffected at distances of R = 2.5 Å and greater. It is thus sufficient to consider interactions with the π orbitals of butadiene, here labeled π_1 through π_4. Table II gives the numbers of electrons occupying the π MO's of butadiene and σ and p of methylene at R = 2.5 Å. The values in parentheses indicate the contributions from the second term of eq 11, *i.e.*, the intermolecular part. It is interesting to note that the HOMO of diene, π_2, donates more electrons than the lower orbital π_1, and that the LUMO, π_3, accepts more electrons than the higher orbital π_4. Moreover, the contribution from the intermolecular term in π_2 is about four times as large as that in π_1. The same is true with respect to π_3 and π_4. These results show quantitatively the important role of the frontier orbitals π_2 and π_3.

Returning to an examination of Tables I and II, we can first confirm that both reaction modes are symmetry allowed. This follows from the uniform increase with decreasing separation in the charge transfer part of the overlap populations, and the corresponding smooth depopulation of bonding levels and population of antibonding ones. There are no pathological features similar to those en-

TABLE II: Number of Electrons Occupying the MO's of Interacting Butadiene and Methylene at R = 2.5 Å

MO	Mode 1	Mode 2
Butadiene		
π_4	0.000	0.008(0.003)
π_3	0.038	0.044(0.012)
π_2	1.836	1.586(0.065)
π_1	1.998	1.918(0.016)
Methylene		
p	0.170	0.562(0.088)
σ	1.966	1.891(0.016)

countered in the least-motion approach of methylene to ethylene.

Nevertheless, there is a significant and obvious differential between the two modes. The charge transfer in mode I, the 1,4 addition, is considerably smaller than in mode II. The corresponding positive overlap population arising from the interaction between the occupied MO's of one component and unoccupied MO's of the other is, in mode I, insufficient to compensate for the negative, antibonding population arising from closed-shell interactions. At R = 2.5 Å the net overlap population between methylene and butadiene is in fact slightly negative.

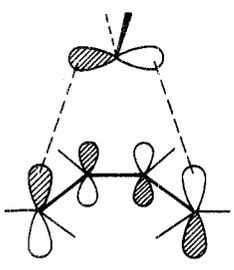
A decomposition of the wave functions at R = 2.5 Å yields[36]

$$\Psi_{\mathrm{I}} = 0.881\Psi_0 + 0.350\Psi_{\pi_2 \rightarrow \mathrm{p}} + 0.144\Psi_{\sigma \rightarrow \pi_3} + 0.026\Psi_{\pi_1 \rightarrow \pi_3} + 0.008\Psi_{\pi_2 \rightarrow \pi_3} + \cdots$$

and

$$\Psi_{\mathrm{II}} = 0.644\Psi_0 + 0.184\Psi_{\pi_1 \rightarrow \mathrm{p}} + 0.457\Psi_{\pi_2 \rightarrow \mathrm{p}} + 0.116\Psi_{\sigma \rightarrow \pi_3} + 0.045\Psi_{\sigma \rightarrow \pi_4} + 0.003\Psi_{\pi_1 \rightarrow \pi_3} + 0.001\Psi_{\pi_1 \rightarrow \pi_4} + 0.022\Psi_{\pi_2 \rightarrow \pi_3} + 0.004\Psi_{\pi_2 \rightarrow \pi_4} + 0.185\Psi_{\sigma \rightarrow \mathrm{p}} + \cdots$$

We observe that the original state Ψ_0 is still dominant. The $\pi_1 \rightarrow$ p and $\pi_2 \rightarrow$ p transfers in II are considerably more important than the $\pi_2 \rightarrow$ p transfer in I. This indeed is the crux of the difference between modes I and II. In any reaction of methylene the crucial orbital is its acceptor orbital, p. The primary interaction is between that acceptor, LUMO, p and whatever donor orbital is offered up by the substrate. In the 1,2 addition both π_1 and π_2 serve as donors, with the latter dominating. In the 1,4 addition mode by symmetry only π_2 can interact with p. And that overlap, shown schematically in 1 is basically inefficient. The methylene has to approach very close to the butadiene to make that overlap significant, and in doing so it encounters excessive closed-shell repulsions.



1

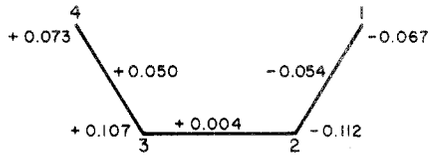
Charge Transfer and Polarization

It is worthwhile to analyze in somewhat greater detail the reorganization, in course of the favored 1,2 addition, of the π electrons in butadiene and the mixing of σ and p orbitals in the attacking methylene. As seen in the preceding section, the donation of electrons from the HOMO of butadiene to the LUMO of methylene is the dominant term. Such donation will weaken the 1,2 and (equally) the 3,4 bonds of the diene, and strengthen the 2,3 bond, because π_2, the HOMO, has a node between carbons 2 and 3. The effect would appear to be symmetric with respect to the bond being attacked, $C_1{=}C_2$, and its untouched partner, $C_3{=}C_4$. But, of course, there is a differential between the two ends of the molecule, set by polarization terms. The π-electron density of the butadiene in the interacting state is given by[37]

$$\rho_\pi = 1.9015\pi_1^2 + 1.5206\pi_2^2 + 0.0325\pi_3^2 + 0.0047\pi_4^2 - 0.2241(\pi_1\pi_2 + \pi_2\pi_1) - 0.0053(\pi_1\pi_3 + \pi_3\pi_1) - 0.0009(\pi_1\pi_4 + \pi_4\pi_1) + 0.0502(\pi_2\pi_3 + \pi_3\pi_2) + 0.0112(\pi_2\pi_4 + \pi_4\pi_2) + 0.0122(\pi_3\pi_4 + \pi_4\pi_3)$$

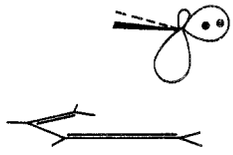
Here we note that the number of electrons occupying the π MO's is calculated to be less than four in the interacting state, because a part is transferred to methylene and another part is consumed in bond formation. The cross terms are the ones which yield the polarization.[38]

The effect of polarization may be seen by the changes in electron densities and overlap populations specified in **2**. A positive sign implies an increase in electronic density or overlap population due to polarization. An electron flow from the 1,2 bond region to the 2,3 and 3,4 bond regions will be observed. The interaction weakens the 1,2 π bonding and strengthens somewhat the 3,4 bond.



2

Another interesting effect may be seen at the attacking methylene. The σ and p orbitals of the methylene, which are orthogonal in the isolated state, will be intermixed through their interaction with butadiene orbitals. Figure 5 shows the electron density of methylene, ρ_{CH_2}, in the x'–z' plane at $y' = 0$. The coordinate axes are defined in the figure. They refer to a local coordinate frame fixed in the methylene. It is most interesting to see that spatial rearrangement of electron density takes place in such a way that the maximum electron distribution in methylene is almost parallel to the molecular plane of butadiene. Qualitatively it may be said that the repulsive nature of the closed-shell interaction between σ and π is "remembered" to the extent that even when the primary attack of the methylene is through its p orbital, it still attempts to remove the σ electron pair as far as possible from possible interaction. In another way of thinking, the bonding situation, shown in **3**, represents a transition from the symmetry-enforced σ–p picture of methylene bonding to a hybridized state associated with the product cyclopropane.



3

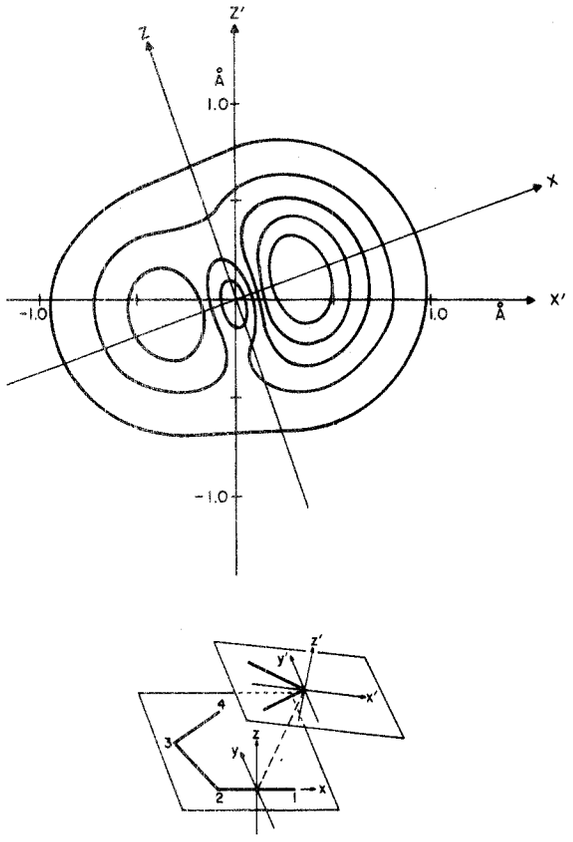


Figure 5. The electronic density of methylene is shown at top. The coordinate system is specified in detail in the small figure at bottom. Primed axes refer to a coordinate system fixed in the methylene, unprimed axes to one fixed at the midpoint of $C_1{=}C_2$.

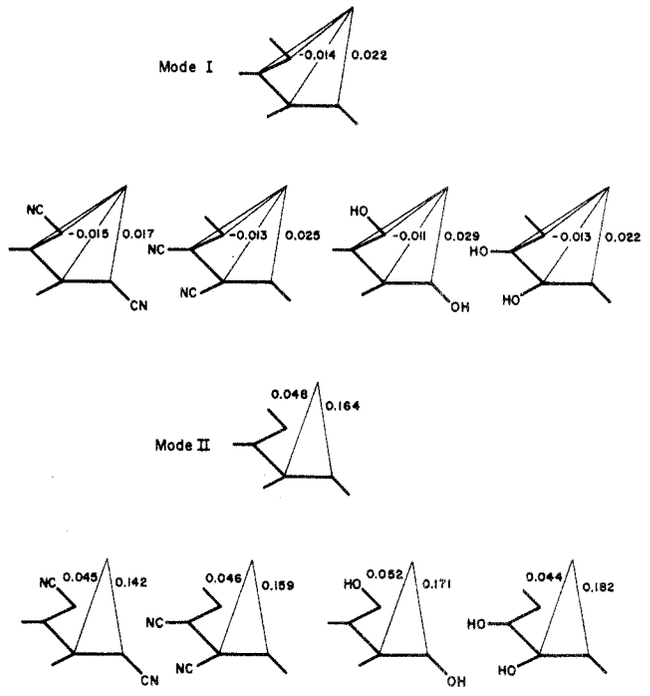


Figure 6. Overlap populations for some substituted butadienes in mode I and II geometries at R = 2.5 Å.

Effect of Substituents

We conclude by examining the effect of electron-donating and accepting substituents on the relative merits of 1,2 and 1,4 addition. Taking the R = 2.5 Å geometry for modes I and II, we substituted the 1 and 4 or 2 and 3 positions with sample donors, hydroxyl groups, or sample acceptors, cyano groups. Though a comparison of energetics can be made, we have found it illuminating to examine the methylene–butadiene overlap populations in the substituted compounds relative to the unsubstituted case. This is done in Figure 6. Donor substituents, either at the terminal or central carbons, increase the intermolecular overlap populations for mode II. Acceptor substituents, on the contrary, make for weaker interaction. It is easy to trace this effect to the perturbation of the HOMO of the diene, π_2, by the substituents.

The overall effect on mode I, the model for 1,4 addition, is disappointingly small. The placement of electron accepting groups at the 2 and 3 positions increases slightly the intermolecular overlap populations. This can be traced to increased charge transfer from methylene σ to π_3 of diene. One strategy to bring about a preference of 1,4 over 1,2 addition might then be the placement of π-electron accepting groups at the 2 and 3 positions of the diene, coupled with substitution by σ-electron-releasing groups at the methylene carbon. However, we are pessimistic whether a reversal of the preference can be achieved; the calculated substituent effects are so small.[39]

To summarize we have analyzed in detail the origins of the preference for 1,2 addition of methylene to butadiene over 1,4 addition. Both processes are allowed, but the stabilizing charge transfer interaction in the 1,2 addition is much more efficient. The simple methodology of intermolecular population analysis and orbital decomposition which we have developed here covers and connects the perturbation, orbital and state correlation, configuration interaction, and frontier orbital approaches to chemical interactions. The method may be extended easily to open-shell systems and the interaction of more than two reagents.

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References and Notes

(1) C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc., Ser. A*, **192**, 16 (1947).
(2) F. H. Burkitt, C. A. Coulson, and H. C. Longuet-Higgins, *Trans. Faraday Soc.*, **47**, 553 (1951).
(3) G. W. Wheland, *J. Amer. Chem. Soc.*, **64**, 900 (1940).
(4) (a) M. J. S. Dewar, *J. Amer. Chem. Soc.*, **74**, 3341, 3345, 3350, 3353, 3355 (1952). (b) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969.
(5) (a) K. Fukui, T. Yonezawa, and H. Shingu, *J. Chem. Phys.*, **20**, 722 (1952); (b) K. Fukui, T. Yonezawa, and C. Nagata, *Bull. Chem. Soc. Jap.*, **27**, 423 (1954); (c) K. Fukui in "Molecular Orbitals in Chemistry, Physics and Biology," P.-O. Löwdin and B. Pullman, Ed., Academic Press, New York, N. Y., 1964.
(6) R. D. Brown, *J. Chem. Soc.*, 2232 (1959).
(7) (a) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 395, 2511 (1965); (b) R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 2046, 4388, 4389 (1965); (c) *Accounts Chem. Res.*, **1**, 17 (1968); (d) R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **81**, 797 (1969).
(8) R. F. Hudson, *Angew. Chem., Int. Ed. Engl.*, **12**, 36 (1973).
(9) J. N. Murrell, M. Randić, and D. R. Williams, *Proc. Roy. Soc., Ser. A*, **284**, 566 (1965).
(10) G. Klopman and R. F. Hudson, *Theor. Chim. Acta*, **8**, 165 (1967).
(11) G. Klopman, *J. Amer. Chem. Soc.*, **90**, 223 (1968).

(12) A. Imamura, *Mol. Phys.*, **15**, 225 (1968).
(13) L. Salem, *J. Amer. Chem. Soc.*, **90**, 543, 553 (1968).
(14) (a) K. Fukui and H. Fujimoto, *Bull. Chem. Soc. Jap.*, **41**, 1989 (1968); **42**, 3399 (1969); (b) H. Fujimoto, S. Yamabe, and K. Fukui, *ibid.*, **44**, 2936 (1971).
(15) L. Salem and A. Devaquet, *J. Amer. Chem. Soc.*, **91**, 3793 (1969).
(16) A. Devaquet, *Mol. Phys.*, **18**, 233 (1970).
(17) R. Sustmann and G. Binsch, *Mol. Phys.*, **20**, 1, 9 (1971).
(18) R. D. Brown, *Quart. Rev., Chem. Soc.*, **6**, 63 (1952).
(19) (a) R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968); (b) R. Hoffmann, R. Gleiter, and F. B. Mallory, *ibid.*, **92**, 1460 (1970); (c) R. C. Dobson, D. Hayes, and R. Hoffmann, *ibid.*, **93**, 6188 (1971); (d) R. Hoffmann, D. M. Hayes, and P. S. Skell, *J. Phys. Chem.*, **76**, 664 (1972).
(20) (a) H. Kollmar, *Tetrahedron Lett.*, 3337 (1970); *Tetrahedron*, **28**, 5893 (1972); (b) M. J. S. Dewar, E. Haselbach, and M. Shanshal, *J. Amer. Chem. Soc.*, **92**, 3505 (1970); N. Bodor, M. J. S. Dewar, and J. S. Wasson, *ibid.*, **94**, 9095 (1972); (c) H. Basch, *J. Chem. Phys.*, **55**, 1700 (1971); *Theor. Chim. Acta*, **28**, 151 (1973); (d) I. S. Y. Wang and M. Karplus, *J. Amer. Chem. Soc.*, **95**, 8160 (1973); (e) J. P. Snyder, R. J. Boyd, and M. A. Whitehead, *Tetrahedron Lett.*, 4347 (1972); (f) J. E. Del Bene, *J. Amer. Chem. Soc.*, **94**, 3713 (1972); (g) G. F. Tantardini and M. Simonetta, *Isr. J. Chem.*, **10**, 581 (1972); (h) J. N. Murrell, J. B. Pedley, and S. Durmat, *J. Chem. Soc., Faraday Trans. 2*, 1370 (1973); (i) S. P. Kolesnikov, A. I. Ioffe, and O. M. Nefedov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2622 (1973).
(21) (a) The literature contains several cases of possible 1,4 addition: B. Grzybowska, J. H. Knox, and A. F. Trotman-Dickinson, *J. Chem. Soc.*, 4402 (1961); 3826 (1962); V. Franzen, *Chem. Ber.*, **95**, 571 (1962); J. A. Berson and E. S. Hand, *J. Amer. Chem. Soc.*, **86**, 1978 (1964); T. V. Domareva-Mandelshtam and I. A. Dyakonov, *Zh. Obsch. Khim.*, **34**, 3844 (1964); H. Nozaki, M. Yamabe, and R. Noyori, *Tetrahedron*, **21**, 1657 (1965); E. Müller and H. Kessler, *Justus Liebigs Ann. Chem.*, **692**, 58 (1966); P. Hodge, J. A. Edwards, and J. H. Fried, *Tetrahedron Lett.*, 5175 (1966). (b) The 1,4 addition of triplet dicyanocarbene to cyclooctatetraene is discussed by A. G. Anastassiou, R. P. Cellura, and E. Ciganek, *Tetrahedron Lett.*, 5267 (1970). The related additions of triplet cyanonitrene have been treated in detail by A. G. Anastassiou, *J. Amer. Chem. Soc.*, **87**, 5512 (1955); **90**, 1527 (1968). (c) See the recent discussion of C. W. Jefford, nT. Kabengele, J. Kovacs, and U. Burger, *Tetrahedron Lett.*, 257 (1974); *Helv. Chim. Acta*, **57**, 104 (1974).
(22) A careful analysis of the parent system of methylene and butadiene has been carried out by H. M. Frey, *Trans. Faraday Soc.*, **58**, 516 (1972).
(23) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833, 1841 (1955).
(24) H. Baba, S. Suzuki, and T. Takemura, *J. Chem. Phys.*, **50**, 2078 (1969).
(25) S. Yamabe, S. Kato, H. Fujimoto, and K. Fukui, *Theor. Chim. Acta*, **30**, 327 (1973).
(26) In both A and B, R, the distance from the carbene carbon to the midpoint of the C=C bond is the same and equal to 2.5 Å. For further details see ref 19a and 19d. The molecular orbitals in this paper were calculated by the extended Hückel method: R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); R. Hoffmann and W. N. Lipscomb, *ibid.*, **36**, 2179, 3489 (1962); **37**, 2872 (1962).
(27) For a discussion of the electronic structure of methylenes see J. F. Harrison in W. Kirmse, "Carbene Chemistry," 2nd ed, Academic Press, New York, N. Y., 1971, p 159; R. Hoffmann, G. D. Zeiss, and G. W. Van Dine, *J. Amer. Chem. Soc.*, **90**, 1485 (1968).
(28) P. S. Skell and A. Y. Garner, *J. Amer. Chem. Soc.*, **78**, 3409 (1956).
(29) In this type of analysis the wave functions are given by the proper antisymmetrized products of molecular orbitals.
(30) The locally excited state $\Psi_{\sigma\rightarrow p}$ can also be regarded as a successive charge-transfer process, *e.g.*, $\Psi_{\sigma\rightarrow\pi^*,\pi^*\rightarrow p}$. Such a forward and backward charge-transfer interaction may be important in strong donor–acceptor interactions. On this point, see the discussion by Epiotis [N. D. Epiotis, *J. Amer. Chem. Soc.*, **94**, 1924 (1972); **95**, 1191 (1973)]. In that case, however, the charge-transferred state, $\Psi(A^-D^+)$ or $\Psi(A^{2-}D^{2+})$, should be the dominant term in the wave function. We think this is rarely so, even when the reactants are highly polar.
(31) In an interesting approach to concerted reactions, E. B. Wilson and P. S. C. Wong, *Chem. Phys. Lett.*, **15**, 400 (1972), have suggested following the change in occupation numbers of natural orbitals as a criterion of allowedness. At large separation $\Psi = \Psi_0$. If we form the wave function Ψ' for the doubly excited state (two electrons shifted from HOMO to LUMO) at R = 2.5 Å, we get $\Psi' = 0.994\Psi_0 + \ldots$. The corresponding occupation numbers for this Ψ' state are $\nu_\pi = 1.999$, $\nu_{\pi^*} = 0.000$, $\nu_\sigma = 1.994$, $\nu_p = 0.002$. Thus the crossing is confirmed in another way.
(32) (a) L. Salem, *Chem. Commun.*, 981 (1970); (b) E. F. Hayes and A. K. Q. Siu, *J. Amer. Chem. Soc.*, **93**, 2090 (1971); (c) L. Salem and C. Rowland, *Angew. Chem., Int. Ed. Engl.*, **11**, 92 (1971); (d) H. Fukutome, *Progr. Theor. Phys.*, **47**, 1156 (1972).
(33) The following geometrical assumptions were made: $C_1{=}C_2$ 1.35 Å, C_2–C_3 1.46 Å, all C–H 1.10 Å. The HCH angle in methylene was taken as 102°, all valence angles in butadiene at 120°.
(34) Within the constraints of a type I approach we actually locate two local energy minima at a given value of R. They are both shown in Figure 4. The two minima differ only in the cant of the methylene group, they possess virtually identical energies and yield nearly identical population partitions. In the subsequent discussion we use the geometries corresponding to one of these minima, the one drawn in solid in Figure 4.
(35) (a) L. Salem, *Proc. Roy. Soc., Ser. A*, **264**, 379 (1961); (b) V. Magnasco, *Theor. Chim. Acta.*, **21**, 267 (1971).
(36) Only singly transferred and singly excited electron configurations are shown, in order to simplify the representation of Ψ. The contributions of highly transferred and highly excited electron configurations are not necessarily small. The doubly transferred configuration from π_2 of butadiene to p of methylene $\Psi_{\pi_2\rightarrow p,\pi_2\rightarrow p}$, for example, has a coefficient of 0.075 in Ψ_I and 0.161 in Ψ_{II}.
(37) The σ–π separability does not hold in the interacting state. Here the π electron density means the distribution of electrons occupying those levels which, in the isolated butadiene, were strictly π levels.
(38) For a further discussion of polarization see L. Libit and R. Hoffmann, *J. Amer. Chem. Soc.*, **96**, 1370 (1974).
(39) One might note the negative overlap populations in mode I between the methylene carbon and C_2 or C_3 of butadiene. These can be traced to the σ–π_3 interaction and the nature of π_3, that it has a different phase of the wave function at C_2 and C_3 relative to C_1 and C_4. The σ–π_3 interaction, governed by σ overlap with butadiene p orbitals at C_1 and C_4, thus has a destablizing secondary interaction with C_2 and C_3. This is still another component of the troubles with the 1,4 addition.