

# AN MO-THEORETICAL CHARACTERIZATION OF ORGANIC REACTION MECHANISMS—IV<sup>1</sup>

## THERMAL (2 + 2) REACTIONS

T. OKADA, K. YAMAGUCHI and T. FUENO\*

Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka, Japan

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**Abstract**—Various types of thermal (2 + 2) reactions are mechanistically differentiated in terms of the phase continuity *plus* the triplet stability of the restricted Hartree-Fock molecular orbitals relevant to the entire reaction systems. The former criterion allows to discriminate between the symmetry-allowed and -forbidden reactions while the latter permits distinction between biradical and nonradical reactions. It follows that the two-step cycloaddition involving a zwitterionic intermediate, for instance, should be characterized as a symmetry-forbidden nonradical process. The mechanistic features theoretically inferred for several known examples of reactions are all found to be compatible with observation.

### INTRODUCTION

In a previous paper (referred to as Paper I hereafter),<sup>2</sup> we proposed a theoretical method of discriminating the reaction mechanisms of molecular systems in the ground singlet state, on the basis of the spin and space symmetry conservations of the Hartree-Fock molecular orbitals. The method essentially lay in the examinations of whether or not the restricted Hartree-Fock solution for the entire reacting system would involve the triplet instability at a certain stage of reaction and whether or not the nodal property of the highest occupied molecular orbital would remain invariant throughout the reaction course. Depending on the results of such a two-fold examination, given reactions were characterized to fall in one of the following four categories: The symmetry-allowed nonradical (Type 1, AN), symmetry-allowed biradical (Type 2, AR), symmetry-forbidden nonradical (Type 3, FN), and symmetry-forbidden biradical reactions (Type 4, FR).

The theory was then applied to the thermal (2 + 2) reactions of singlet molecular oxygen with olefins and the subsequent decomposition of dioxetane (Paper II).<sup>3</sup> The results were found to be wholly compatible with the experimentally proposed mechanisms (concerted, zwitterionic, or biradical).

In the present article, we will examine various types of (2 + 2) reactions along the same line, in an effort to diagnose and clarify their mechanisms. The reactions with which we will be concerned here include the ( $\pi 2_s + \pi 2_s$ ) cycloadditions of olefins and *o*-benzyne, the ( $\sigma 2_s + \sigma 2_s$ ) dehydrofluorination of ethyl fluoride, the ( $\pi 2_s + \sigma 2_s$ ) hydrochlorination of *o*-benzyne, and the ( $\pi 2_s + \pi 2_a$ ) cycloadditions of olefins and ketene.

### THEORETICAL BACKGROUND AND PROCEDURE

(A) *Triplet instability and singlet biradical character.* It is known that the restricted Hartree-Fock (RHF) single-determinant wavefunctions are not necessarily stable to fluctuations arising from removal of some of the symmetry restrictions.<sup>4</sup> Thus, the conventional RHF singlet ground state are occasionally unstable for a fluctuation in electronic configuration due to possible triplet excitations.<sup>5,6</sup>

Consider two closed-shell molecules interacting with each other at a certain spatial orientation. If the RHF singlet ground-state configuration of the entire system is unstable in the above sense, i.e., if it involves the "triplet instability," then it should be reorganized into a more stable ground state of the unrestricted Hartree-Fock (UHF) type. Therefore, the occurrence of the triplet instability at a certain stage of a given reaction course may be regarded as an indication that the reaction should proceed *via* an intermediary state of considerable (singlet) biradical character.<sup>5</sup> Conversely, nonexistence of the triplet instability throughout the course of a reaction is considered to be a necessary, though not sufficient, condition for that reaction to be nonradical in nature.<sup>1-3</sup>

In conformity to the notation used by Čížek and Paldus,<sup>7</sup> we denote the 1-electron excitations from the RHF occupied molecular orbitals  $\psi_i$  and  $\psi_j$  of the entire system to the unoccupied orbitals  $\psi_k$  and  $\psi_l$ , respectively, by

$$u = \begin{pmatrix} k \\ i \end{pmatrix} \quad \text{and} \quad v = \begin{pmatrix} l \\ j \end{pmatrix}. \quad (1)$$

The necessary and sufficient condition for the RHF

ground configuration of a given interaction system to involve the triplet instability is that the lowest eigenvalue  $\lambda_0$  of the matrix

$$\mathbf{X} = (X_{uv}) \quad (2)$$

is negative in sign.<sup>5,6</sup> The matrix elements  $X_{uv}$  are given by

$$X_{uv} = (\epsilon_k - \epsilon_i)\delta_{ij}\delta_{kl} - \langle ij|kl \rangle - \langle il|kj \rangle \quad (3)$$

where  $\epsilon_k$  and  $\epsilon_i$  are the orbital energies of  $\psi_k$  and  $\psi_i$ , respectively, and where  $\langle ij|kl \rangle$  is the familiar electronic repulsion integral

$$\langle ij|kl \rangle = \iint \psi_i(1)\psi_j(1) \frac{1}{r_{12}} \psi_k(2)\psi_l(2) d\tau_1 d\tau_2 \quad (4)$$

As is apparent from the functional form of the diagonal elements  $X_{uu}$ , the triplet instability occurs whenever a triplet-configurational excitation energy,  $\epsilon_k - \epsilon_i - \langle ii|kk \rangle$ , is surpassed in magnitude by the relevant orbital exchange energy,  $\langle ik|ki \rangle$ .

(B) *Orbital phase continuity and orbital symmetry conservation.* The rule of orbital symmetry conservation as broached by Woodward and Hoffmann<sup>7</sup> can be represented theoretically in various ways. Here we adopt the concept of orbital phase continuity, which was first introduced by Hoffmann<sup>7</sup> in the examination of sigmatropic reactions and further advanced by Goddard<sup>8</sup> in the generalized valence-bond approach to various types of concerted reactions.

We pay attention to the variation in nodal property of the highest occupied molecular orbital (HOMO) during the course of reaction. In certain reactions, the LCAO coefficient of HOMO at a reaction site first fades away and then grows up in the opposite sign with the progress of reaction. That is, the phase property of HOMO is "discontinuous" at that site. We refer to these reactions as symmetry-forbidden ones. The point where the fading-away takes place will be termed the phase transition point. Symmetry-allowed reactions are thus defined as the type of reactions which do not experience the phase transition.

When the triplet instability occurs, the HOMO as obtained by the RHF theory loses its physical meaning. In such cases, the UHF orbitals should be used for judging the phase continuity of the HOMO, as has been discussed previously.<sup>2</sup> However, for the purpose of merely locating the transition points, we may still use the RHF orbitals, by defining the transition points as those points where the RHF HOMO and lowest unoccupied molecular orbitals (LUMO) are interchanged with each other.

(C) *Calculations.* The molecular orbital energies and wavefunctions of the entire systems at given spatial orientations were obtained by the CNDO/2

method.<sup>9</sup> The molecular geometries of the composite reactants were all taken from the literature.<sup>10</sup> They were assumed to be invariant during the course of reaction. For the sake of convenience, the triplet instability matrices were constructed with only ten lower-energy configurations. The matrices were diagonalized to obtain the lowest eigenvalues  $\lambda_0$ . All computations were programmed in FORTRAN and performed on a FACOM 230-60 at the Kyoto University Computation Center.

#### ( $\pi 2_s + \pi 2_s$ ) REACTIONS

(A) *Cyclodimerization of ethylene.* The ( $\pi 2_s + \pi 2_s$ ) cyclodimerization of ethylene is one of the most familiar examples of the symmetry-forbidden cycloadditions and really does not take place. Its reverse reaction, i.e., pyrolysis of cyclobutane, proceeds with an activation energy of 62.5 kcal/mol,<sup>11</sup> which is much smaller than the value to be expected for a rectangular concerted reaction path.<sup>12</sup> Both thermochemical consideration<sup>13</sup> and extended Hückel calculation<sup>14</sup> suggest that the pyrolysis should proceed through a 1,4-biradical intermediate.

We here consider two ethylene molecules which are placed parallel to each other with the interplanar distance  $R$  and the rotation angle  $\omega$  as shown in Fig 1. The so-called ( $\pi 2_s + \pi 2_s$ ) reaction corresponds to the case where  $\omega$  is nearly  $0^\circ$ .

Fig 2 illustrates how the lowest eigenvalue  $\lambda_0$  varies with the changes in  $R$  and  $\omega$ . The region marked with dots on the  $R$ - $\omega$  plane indicates that the value of  $\lambda_0$  calculated there is negative in sign. The curve PQ is the transition line on which the phase transition of HOMO takes place.

As is apparent from Fig 2, the ( $\pi 2_s + \pi 2_s$ ) reaction path must not only pass across the transition line but traverse the triplet-instability region ( $\lambda_0 < 0$ ). Hence, the reaction should be symmetry-forbidden biradical (FR) process in our terminology.<sup>2</sup> On the transition line, the UHF HOMO is spin-polarized to a maximal extent, as has been shown previously for the ethylene- $O_2$  ( $^1\Delta$ ) system (Fig 3 of Paper II<sup>3</sup>).

(B) *Cycloaddition between strong donor and ac-*

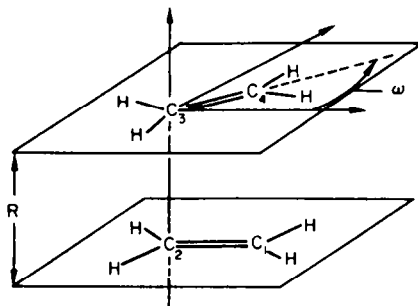


Fig 1. Geometry assumed for the ( $\pi 2_s + \pi 2_s$ ) interaction between two ethylene molecules.

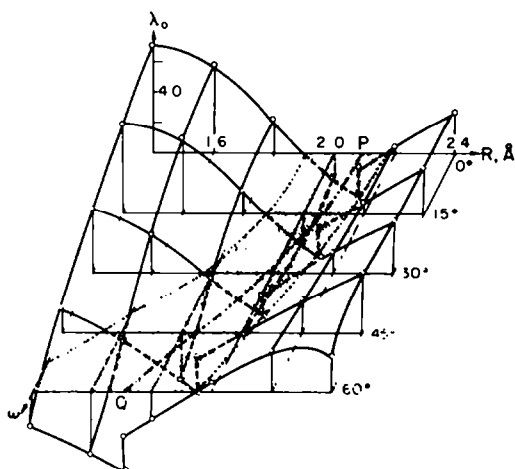
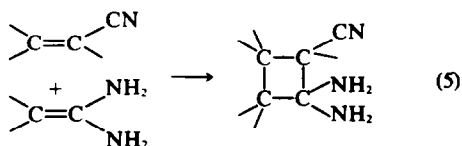


Fig 2. The  $\lambda_0$ -surface for the  $(+2, +2)$  interaction between two ethylene molecules. The dotted area indicates the triplet-instability region. The curve PQ shows the transition line.

ceptor olefin pairs. Strongly electron-donating olefins such as tetramethoxyethylene are known to readily cycloadd to strongly electron-withdrawing olefins such as dicyanoethylene in a stereospecific manner.<sup>15,16</sup> The reactions are symmetry-forbidden in the sense of Woodward and Hoffmann and are believed to proceed by a zwitterionic mechanism.<sup>15</sup> Epiotis<sup>17</sup> has emphasized the importance of the role of the CT interaction between donor and acceptor in such reactions.

Here we will examine the cycloaddition reaction between 1,1-diaminoethylene and acrylonitrile (reaction (5)) as an example. The assumed geometries of the reacting system are the same as illustrated in Fig 1.



The resulting  $\lambda_0$ -surface and the transition line PQ are shown in Fig 3. The most important feature of Fig 3 is that there appears no biradical region despite the existence of the transition line. Therefore, the reaction should be a symmetry-forbidden nonradical (FN) process, in favor of the zwitterionic mechanism.

Schematically depicted in Fig 4 is the variation in the nodal property of HOMO with the progress of reaction. In this particular example, the RHF single-determinant wavefunction shows no instability. Correspondingly, the HOMO is not subjected to spin polarization at all, and the two electrons of different spins continue to occupy the same spatial orbital throughout the course of reaction. The

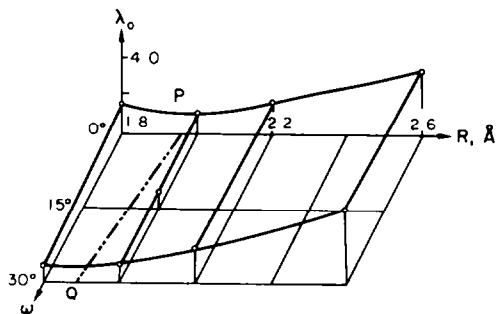


Fig 3. The  $\lambda_0$ -surface for the  $(+2, +2)$  interaction between 1,1-diaminoethylene and acrylonitrile.

HOMO experiences fading-away first at the  $\beta$ -carbon of the nitrile and then at the  $\alpha$ -carbon of the diamine. The structure of HOMO at the instance of its fading-away on the latter carbon is essentially that of a zwitterionic intermediate proposed.

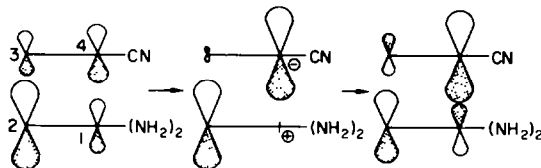
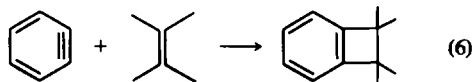


Fig 4. Variation in the nodal property of the HOMO for the 1,1-diaminoethylene—acrylonitrile system undergoing the  $(+2, +2)$  cycloaddition.

(C) *Cycloaddition between o-benzyne and ethylene.* *o*-Benzyne is capable of reacting with olefins to give cyclobutene adducts with considerable stereospecificity.<sup>18</sup> Electronic structure of *o*-benzyne is of particular interest in this connection.



Calculations<sup>19</sup> showed that the energy separation between its symmetric HOMO and antisymmetric LUMO is small and hence that interaction between the ground and doubly-excited configurations is considerably great.

As a model for *o*-benzyne, we will adopt a bent acetylene molecule. The lowest eigenvalue  $\lambda_0$  for the system comprising the benzyne model and ethylene was calculated as the function of two variables  $R$  and  $\omega$  (Fig 5). The resulting  $\lambda_0$ -surface and the transition line PQ are depicted in Fig 6.

Fig 6 clearly shows that the reaction should be a symmetry-forbidden biradical process so far as  $\omega$  is smaller than  $30^\circ$ . There, the essential features are much the same as in the ethylene dimerization (Fig 2). However, nonradical reaction paths can well exist in the region where  $\omega$  is relatively large. This latter trend may be attributed to the orbital-overlap

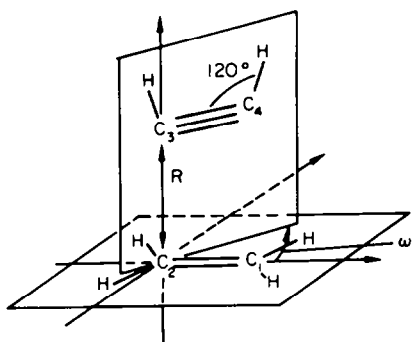


Fig. 5. Geometry assumed for the  $(\sigma_{2s} + \sigma_{2s})$  interaction of bent acetylene with ethylene.

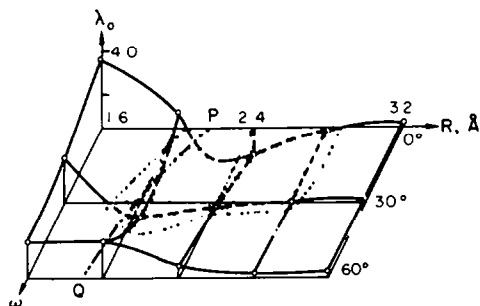


Fig. 6. The  $\lambda_0$ -surface for the  $(\sigma_{2s} + \sigma_{2s})$  interaction of bent acetylene with ethylene.

interaction developing between the  $\pi$ -MO's of ethylene and the "normal"  $\pi$ -MO's of the bent acetylene as  $\omega$  increases.

The nonradical character outweighing the biradical nature in the large  $\omega$  region could at least partly account for the apparently greater reactivity of *o*-benzynes as compared to ethylene.\* In reality, extended-Hückel calculations<sup>20</sup> of the potential surface suggest that the reaction proceeds through this region and takes on both ionic and radical characters. The reaction path as a whole may be characterized as a process intermediary in character between the cyclodimerization of ethylene (Fig 2) and the cycloaddition of 1,1-diaminoethylene toward acrylonitrile (Fig 3). The statement finds some support in the electron distributions calculated for the reaction intermediates (Fig 7). A weak zwitterionic character is discernible in the bent acetylene-ethylene system.

An alternative reason for the great reactivity of *o*-benzynes appears to lie in the biradical character of itself. As can be seen in Fig 6, the radical region shows up at an intermolecular distance as large as about 2.9 Å, which is much longer than in the case of the ethylene dimerization. Considering the small

\*It is implicitly assumed that a zwitterionic structure, whenever found appropriate, is more stable than the corresponding biradical structure.

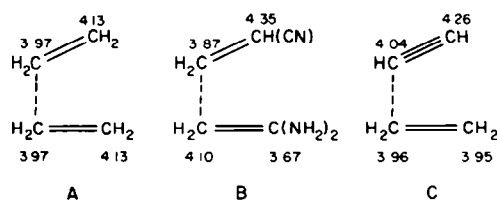


Fig. 7. Electron populations on carbon atoms in  $(\sigma_{2s} + \sigma_{2s})$  interaction systems.  $R = 1.6 \text{ \AA}$ ;  $\omega = 90^\circ$ . A, ethylene + ethylene; B, 1,1-diaminoethylene + acrylonitrile; C, ethylene + bent acetylene.

separation between the HOMO and the LUMO of *o*-benzynes,<sup>20</sup> one may draw a schematical correlation diagram as depicted in Fig 8. Even if some biradical character is still inherent, the activation energy must be sufficiently small to permit the reaction to proceed easily.

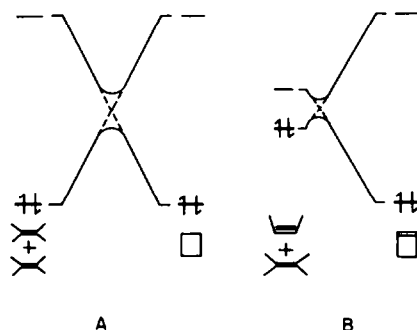
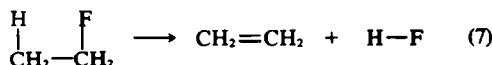


Fig. 8. Schematic correlation diagrams for  $(\sigma_{2s} + \sigma_{2s})$  cycloadditions. A, ethylene + ethylene; B, ethylene + bent acetylene.

#### $(\sigma_{2s} + \sigma_{2s})$ AND $(\sigma_{2s} + \sigma_{2s})$ REACTIONS

(A) *cis*-Elimination of hydrogen fluoride from ethyl fluoride. The thermal decomposition of halogenoalkanes into alkenes and hydrogen halide has generally been considered as a chain reaction with free radical intermediates.<sup>21</sup> However, it was demonstrated experimentally that the decomposition of ethyl fluoride (reaction (7)) can proceed by way of *cis*-elimination through a transition state with some carbonium-ion character.<sup>22</sup> The theoretic-



cal estimation of the activation parameter by Benson<sup>23</sup> for a semi-ion pair model leads to the results which closely agree with the observed values, thus corroborating the suggested mechanism.

*cis*-Elimination may formally be regarded as a  $(\sigma_{2s} + \sigma_{2s})$  reaction. We have calculated the  $\lambda_0$ -value for reaction (7), by varying the two distances  $R$  and  $L$  as defined in Fig 9. For the sake of convenience,

the  $H_3$  atom was fixed at the coordinate point where  $x = -1.4$ ,  $y = 0$ , and  $z = 1.1$  Å. The results of calculation are shown in Fig 10. The transition lines PQ and RS correspond to the phase transitions on the  $C_1$  and  $H_3$  atoms, respectively. Hatchings indicate the region where the distance between the  $H_3$  and  $F_4$  atoms is smaller than  $0.72$  Å, the sum of the covalent radii of the two atoms.

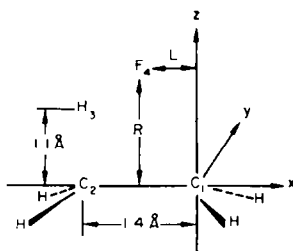


Fig 9. Geometry assumed for ethyl fluoride undergoing dehydrofluorination.

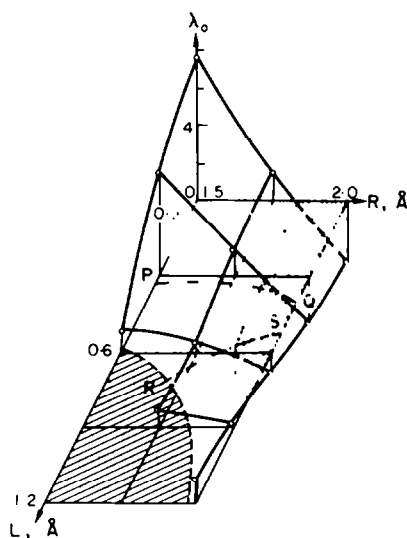


Fig 10. The  $\lambda_0$ -surface for the dehydrofluorination of ethyl fluoride. The hatched area indicates the region of a large steric repulsion between  $H_3$  and  $F_4$ , the interatomic distance being less than  $0.72$  Å.

It can be seen in Fig 10 that favorable reaction paths with no radical character do exist. The conclusion remains unaltered if we assume the  $C_2-H_3$  distance to be greater than  $1.1$  Å. Thus, the reaction could well be a nonradical process.

Fig 11 shows the variation of the HOMO during the reaction. The broken lines with dot indicate the location of the nodal plane for the HOMO. The node which initially existed between the  $C_2-H_3$  and  $C_1-F_4$  bonds 1 rotates anti-clockwise with the progress of reaction until it is displaced to region between the  $H_3-F_4$  and  $C_1-C_2$  bonds. During this

course, the coefficient of the  $2p_z$  AO of the  $C_1$  atom first disappears on the transition line PQ, thus giving rise to a zwitterionic structure with the  $C_1-F_4$  bond cleavage (2). Next, the coefficient of the  $1s$  AO of the  $H_3$  atom disappears on the transition line RS, effecting the  $C_2-H_3$  bond cleavage (3). In the meantime, the coefficient for the  $2p_z$  AO of the  $C_1$  atom is flipped over in sign and grows up to permit the  $\pi$ -bonding interaction between the  $C_1$  and  $C_2$  atoms. Finally, a bond is formed between the  $H_3$  and  $F_4$  atoms (4), and the reaction is completed.

Table 1 shows the electronic population calculated for the  $C_1 2p_z$  AO as the function of  $R$  and  $L$ . Notice that the carbonium ion character is the greatest in the neighborhood of the transition line PQ ( $L = 0.3$  Å). Experimentally, on the other hand, substitutions by the Me and OMe groups at the  $C_1$  atom are known to accelerate the reaction by factors of  $10^3$  and  $10^6$ , respectively.<sup>24</sup> These two results could best be reconciled by assuming that the structure of the transition state resembles closely that of the zwitterionic intermediate, in support of the earlier conclusion.<sup>23,24</sup>

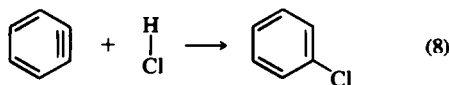
Table 1.  $2p_z$  Atomic orbital population of the  $C_1$  atom during the course of the dehydrofluorination of ethyl fluoride

$L(\text{Å})^a$	$R(\text{Å})^a$		
	1.5	1.75	2.0
0.0	0.77	0.73	0.70
0.3	0.75	0.70	0.69
0.6	0.83	0.86	0.83
0.9	—	1.14	1.00
1.2	—	—	1.09

<sup>a</sup> See Fig 9.

(B) *Hydrochlorination of o-benzyne*. In a previous section, it has been shown that even a homopolar molecule like ethylene can add to *o*-benzyne through an intermediate structure with considerable ionicity. Additions of polar molecules are more common, and often result in the formation of stereospecific adducts.<sup>25</sup>

Here, we will examine hydrochlorination of *o*-benzyne (reaction (8)) as an example. Calculations of  $\lambda_0$  were performed by varying the two



parameters  $R$  and  $\omega$  as shown in Fig 12. A bent acetylene molecule was used again as a model of *o*-benzyne. Fig 13 shows the  $\lambda_0$ -surface and the transition lines PQ and RS obtained.

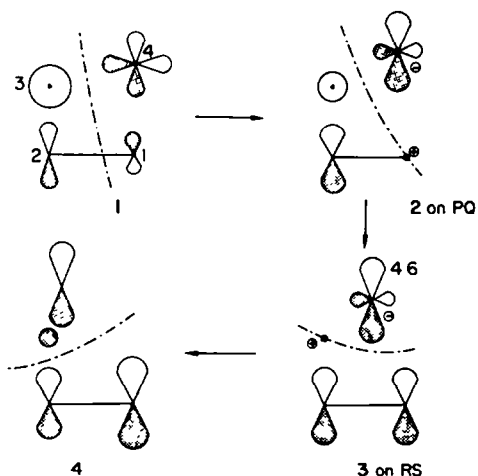


Fig 11. Variation in the nodal property of the HOMO for ethyl fluoride undergoing cis-elimination. The reaction starts with 1 ( $\text{CH}_3\text{-CH}_2\text{F}$ ) and ends up with 4 ( $\text{CH}_2=\text{CH}_2 + \text{HF}$ ).

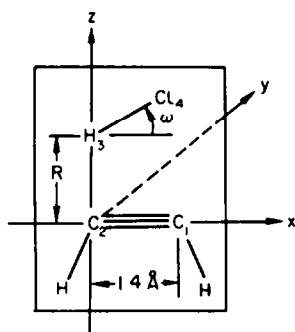


Fig 12. Geometry assumed for the hydrochlorination of bent acetylene.

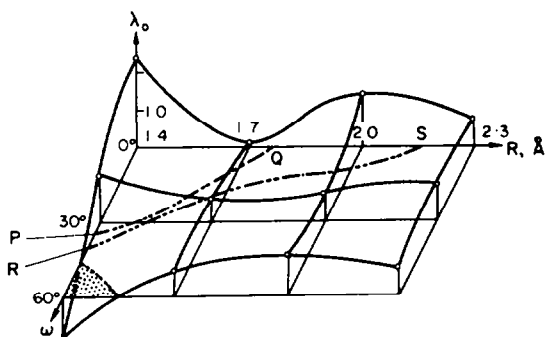


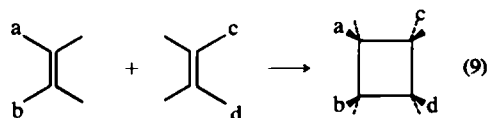
Fig 13. The  $\lambda_0$ -surface for the hydrochlorination of bent acetylene.

As is apparent from Fig 13, the reaction is a symmetry-forbidden nonradical one. The nodal property of the HOMO changes with the progress of reaction exactly in the same manner as in the reverse process of reaction (7) (Fig 11).

### ( $\pi 2_s + \pi 2_s$ ) REACTIONS

(A) *Cyclodimerization of ethylene.* The ( $\pi 2_s + \pi 2_s$ ) process is theoretically characterized as a symmetry-allowed reaction.<sup>7</sup> However, experimental studies conclude that this type of reaction is feasible to take place only in cases of twisted olefins,<sup>26</sup> singlet molecular oxygen,<sup>27</sup> and molecules like ketenes and allenes which have a cumulene bond.<sup>28</sup> We have already discussed the reaction of singlet molecular oxygen with olefins (Paper II).<sup>3</sup> Other reactive cases, i.e., the cyclodimerization of twisted olefins and the cycloaddition of ketene toward ethylene, will be treated in the sections which follow.

In this section, we will briefly consider the hypothetical ( $\pi 2_s + \pi 2_s$ ) cyclodimerization of ethylene (reaction (9)). We have calculated the



$\lambda_0$ -values for this reaction by varying the rotation angle  $\omega$  as well as the twisting angle  $\theta$  of the antarafacial ethylene as shown in Fig 14. The twisting angle  $\phi$  of the other suprafacial ethylene was fixed at  $0^\circ$ . The distance between the two ethylene molecules was assumed to be  $2.0 \text{ \AA}$ . The resulting  $\lambda_0$ -surface and the transition line PQ are depicted in Fig 15.

The reaction should start with  $\omega = \theta = 0^\circ$  (perpendicular edge-to-face placement) and end up with  $\omega = \theta = 90^\circ$  (parallel face-to-face placement). Inspection of molecular models shows that the steric repulsion between the  $\text{H}_6$  and  $\text{H}_{10}$  atoms (and likewise that between the  $\text{H}_7$  and  $\text{H}_{12}$  atoms) must be a significant hindrance against this symmetry-allowed reaction. Shown with hatchings in Fig 15 is the domain where the distance between these hyd-

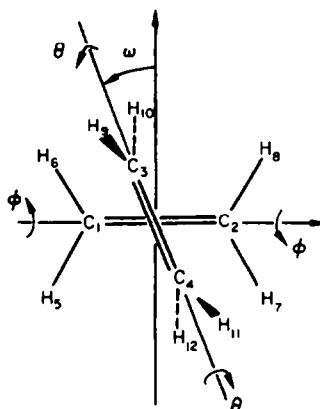


Fig 14. Geometry assumed for the ( $\pi 2_s + \pi 2_s$ ) interaction between two ethylene molecules.

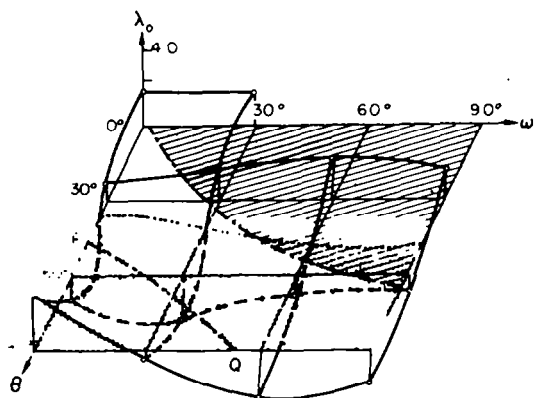


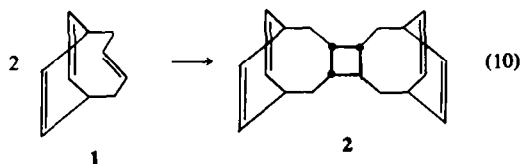
Fig 15. The  $\lambda_0$ -surface for the  $(\pi_2s + \pi_2s)$  interaction between two ethylene molecules.  $R = 2.0 \text{ \AA}$ . In the hatched area, the  $H_a-H_b$  distance is less than  $1.6 \text{ \AA}$ .

rogens is less than  $1.6 \text{ \AA}$ . Reaction paths which can avoid such a hindrance should necessarily traverse a biradical region. Thus, the reaction in question would have to assume some biradical character even though it may be a symmetry-allowed process. In other words, the reaction should be a symmetry-allowed biradical (AR) process. These results endorse the reluctance of ethylene against its symmetry-allowed  $(\pi_2s + \pi_2s)$  cyclodimerization.

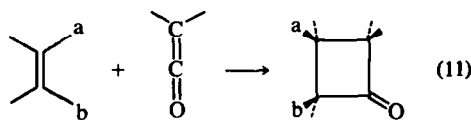
(B) *Cycloaddition between twisted ethylenes.* The geometries assumed for calculations are the same as in Fig 14 except that the suprafacial ethylene component is now twisted by a dihedral angle  $2\phi = 60^\circ$  between the two  $\text{CH}_2$  planes. The results of calculation are shown in Fig 16.

Comparison of Fig 16 with Fig 15 shows that the region of steric repulsion is largely reduced in the

case of twisted ethylene. If the reaction is assumed to be completed at  $\omega = 90^\circ$  and  $\theta = 60^\circ$ , it may well be regarded as a symmetry-allowed nonradical (AN) process. The result is compatible with the fact that bicyclo[4,2,2]deca-trans-3-cis-7,9-triene (1) spontaneously dimerizes at its twisted olefinic bond to give a cyclobutane derivative (2) stereospecifically.<sup>26</sup>



(C) *Cycloaddition of ketene toward ethylene.* Finally, we examine the antarafacial cycloaddition of ketene toward ethylene (reaction (11)). That the reaction is a  $(\pi_2s + \pi_2s)$  concerted process is almost conclusive from the high negative entropy of activation,<sup>29</sup> a modest dependence of rate on solvent polarity,<sup>29,30</sup> and a sensitive dependence of reactivity on the size of substituents attached to ketene.<sup>31</sup>



The assumed geometry is the same as in Fig 14, except that the  $\text{C}_4\text{H}_{11}\text{H}_{12}$  methylene group has been replaced by a carbonyl group. Ethylene was assumed to be planar ( $\phi = 0^\circ$ ). The results of calculation are shown in Fig 17.

The most striking feature of Fig 17 is that there exists no biradical domain in the entire range swept by  $\omega$  and  $\theta$ . Neither does the transition line show up. Therefore, the reaction in question may be

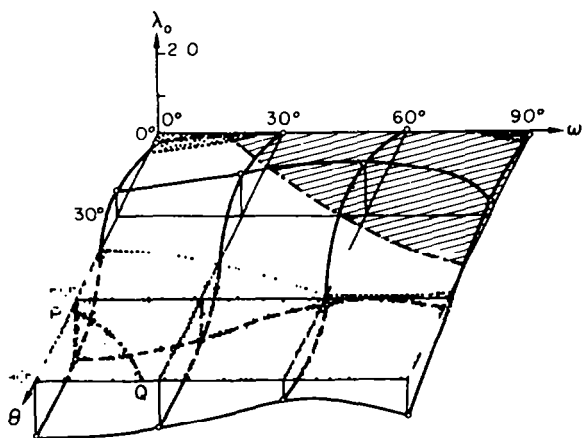


Fig 16. The  $\lambda_0$ -surface for the  $(\pi_2s + \pi_2s)$  interaction of a twisted ethylene (suprafacial) with ethylene (antarafacial). Molecular geometry of the twisted ethylene was fixed at  $\phi = 30^\circ$ . The hatched area indicates the region where the  $\text{C}_1\text{-H}_{10}$  distance is less than  $1.6 \text{ \AA}$ . The region completely covers the domain in which the  $\text{H}_a\text{-H}_b$  distance is less than  $1.6 \text{ \AA}$ .

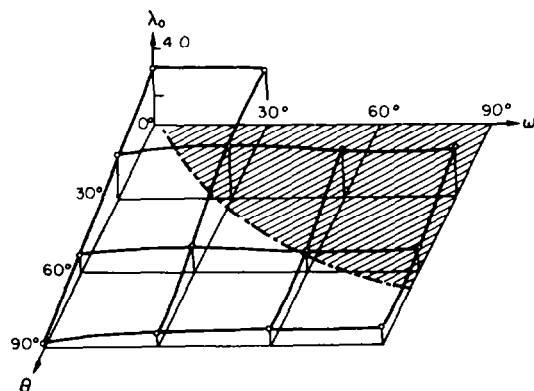


Fig 17. The  $\lambda_0$ -surface for the  $(\pi_2s + \pi_2s)$  interaction of ketene (antarafacial) with ethylene (suprafacial). The  $\text{C}_4\text{H}_{11}\text{H}_{12}$  methylene group in Fig 14 has been replaced by a carbonyl group.

characterized as a symmetry-allowed nonradical process, tantamount to the allowed concerted reaction in the sense of Woodward and Hoffmann.<sup>7</sup>

Whether or not a given type of thermal reaction could indeed proceed under usual conditions depends on how high the energy barrier for that reaction would be. The ( $\pi 2_s + \pi 2_s$ ) cyclodimerization of ethylene suffers a considerably large steric hindrance, whereas the hindrance is greatly reduced in the case of twisted olefins. Ketene could also avoid the adverse steric effect in its ( $\pi 2_s + \pi 2_s$ ) reaction toward ethylene, but more important is, in our view, that this last reaction is basically of the nonradical type, probably because of its partial polar character due to the large polarity of the CO group. Further calculations with the intermolecular distance R as a variable showed that even in the parallel planar approach ( $\omega = \theta = 90^\circ$ ), which should apparently be symmetry-forbidden, the biradical character is surprisingly small. The forbiddenness of the ( $\pi 2_s + \pi 2_s$ ) reaction of ketene with ethylene is thus not serious, in qualitative agreement with the results of the mapping analysis by Trindle.<sup>32</sup>

#### CONCLUDING REMARKS

The primary purpose of this paper has been to characterize the mechanisms of various types of thermal (2 + 2) reactions by retaining the basic concept of the Hartree-Fock molecular orbitals and therefrom to predict possible reaction paths by way of diagnosis. Determination of precise reaction courses should of course abide by the construction of exact potential-energy surfaces. Our method is only qualitative in this sense but is credited for its facility with which we may distinguish the types and structures of possible reaction intermediates. Generally speaking, no reaction should be subjected to clear-cut distinction between concerted and non-concerted or between biradical or zwitterionic. With this reservation in mind, however, one may find the present method to be useful enough to gain at least pictorial understandings of reaction mechanisms.

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