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AN MO THEORETICAL CHARACTERIZATION OF ORGANIC REACTION MECHANISMS—V[1]

TRANSITION METAL CATALYZED (2+2) REACTIONS

K. TATSUMI, K. YAMAGUCHI and T. FUENO*
Department of Chemistry, Faculty of Engineering Science,
Osaka University, Toyonaka, Osaka 560, Japan

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Abstract—The concept of the triplet instability for the conventional Hartree-Fock molecular orbitals has been applied to metal-catalyzed cyclodimerizations to olefin and acetylene as well as hydrogenation of olefin. It is found that the rectangular approach of reactants should be accompanied by the appearance of a significant biradical character. Hence, the concerted (one-step) reactions cannot necessarily be energetically favorable processes, even though transition metal catalyst can formally remove the orbital-symmetry restriction. It is emphasized that correlation diagrams which are usually drawn only on the basis of the knowledge of reactants and products are incapable of providing an adequate description of metal catalyzed reactions.

INTRODUCTION

Applications of the Woodward-Hoffmann orbital symmetry rule[2] to metal catalyzed reactions have been a research subject of considerable significance.[3–6] Among others, Mango and Schachtschneider[6a] have presented an important concept that cyclodimerization of olefins, which is basically a symmetry-forbidden process, can be rendered symmetry-allowed through a unique interaction of olefin ligands with transition metal catalyst. On the basis of the orbital correlation diagram involving metal d orbitals, they propose that a smooth interflow of electron pairs between metal and fusing olefins can lead the fusion to a thermally allowed reaction.

However, considerations of reaction processes in terms of orbital correlation alone generally lack information of the nature of the intermediary stage of reactions. Metal catalyzed reactions may well be a more intricate process than would appear from simple orbital correlation diagrams. In fact, recent experimental evidence suggests that the reactions which are considered to be symmetry-allowed in the sense of Mango and Schachtschneider proceed by a stepwise mechanism.[7] Theoretical reexamination of the mechanism would thus be still rewarding. For the more complex cases of cyclodimerization and oligomerization of acetylene,[6b] details of the reaction process are still less transparent.

In the present work, we have undertaken all-valence-electron SCF treatments of the metal catalyzed (2+2) type reactions of ethylene and acetylene. For the sake of simplicity, hypothetical nickel hydride complexes have been considered. Special attentions have been directed to the role of the catalyst. For this purpose, the triplet stability-instability index (λ_0) has been calculated for the entire reaction systems of several assumed geometries with and without the catalyst component. Hopefully, the results greatly assist proper understandings of the nature of transition metal catalyzed reactions.

METHOD

(a) *Hartree-Fock calculations.* Hartree-Fock MO calculations were conducted for total systems comprising ligands and nickel hydride NiH_2 which were placed at various relative positions. Only the valence-shell electrons including nickel d electrons were treated within the framework of the ZDO approximation. The relevant Hartree-Fock hamiltonian matrix elements[8] are:

$$F_{rr}^{AA} = U_{rr} + \frac{1}{2}P_{rr}(rr|rr) + \sum_{s\neq r}^{A} P_{ss}(rr|ss) + \sum_{s}^{B} (P_{ss} - N_s)(rr|ss) \tag{1}$$

$$F_{rs}^{AA} = -\frac{1}{2}P_{rs}(rr|ss) \quad r \neq s \tag{2}$$

$$F_{rs}^{AB} = H_{rs}^{AB} - \frac{1}{2}P_{rs}(rr|ss) \tag{3}$$

where P_{rs} and $(rr|ss)$ are the customary bond order and electron repulsion integral, respectively, and where N_s is the number of valence electrons belonging to atomic orbital χ_s. The off-diagonal core integrals, H_{rs}, were evaluated in the work according to the Wolfsberg-Helmholtz formula[9]

$$H_{rs}^{AB} = \frac{1}{2}S_{rs}\kappa(I_r^A + I_s^B) \tag{4}$$

where I_r^A is the valence-state ionization potential of atomic orbital χ_r of atom A and where S_{rs} is the overlap integral between χ_r and χ_s. The value of κ was assumed to be 1·1.

Numerical values for $(rr|rr)$ and U_{rr} were taken from Oleari's table.[10] The ionization potentials were evaluated by assuming the configuration of Ni to be d^{10}. The atomic orbital exponents ζ were all chosen from the data due to Zerner and Gouterman.[11] These input parameters are summarized in Table 1. No *a priori* assumption was made for the oxidation state of the metal. The two-center Coulomb repulsions were estimated by the Nishimoto-Mataga approximation.[12]

(b) *Triplet instability.* The stationary point as obtained by the usual (restricted) Hartree-Fock theory may not necessarily be a true minimum,[13] particularly when the theory is applied to molecular systems deviated from

Table 1. Parameters used for calculation

Atomic orbital		ζ	I_p(eV)	(rr|rr)(eV)
Ni	3d	2.960	5.02	16.71
	4s	1.473	7.19	7.96
	4p	1.473	3.10	6.40
C	2s	1.608	21.36	12.23
	2p	1.568	11.56	11.08
H	1s	1.000	13.60	12.85

equilibrium geometry.[14,15] Thus, the Hartree-Fock solution for a molecular system is often unstable to a fluctuation in electronic configuration of the system due to possible triplet excitation.[16,17] When this is the case, i.e. when the conventional Hartree-Fock singlet ground state involves the triplet instability, a more stable singlet state should exist such that the electronic structure is better depicted by wave functions of the spin density wave type.[17] The occurrence of the triplet instability may therefore be regarded as a criterion of the (singlet) biradical character of the system.[17,18] The criterion has already been used fairly extensively for the discussion of the biradical vs zwitterionic mechanisms of a number of thermal (2+2) type reactions.[2,18]

The conventional Hartree-Fock ground configuration of a given system is triplet unstable, whenever the lowest eigenvalue λ_0 of the matrix $X = (X_{uv})$ is negative in sign.[16,17] The matrix elements X_{uv} are defined by

$$X_{uv} = (\epsilon_k - \epsilon_i)\delta_{ij}\delta_{kl} - \langle ij|kl\rangle - \langle il|kj\rangle \qquad (5)$$

where ϵ_k and ϵ_i are the energies of molecular orbitals ψ_k and ψ_i, respectively, and where (ij|kl) is the two-electron repulsion integral.

$$\langle ij|kl\rangle = \int\!\!\int \psi_i(1)\psi_j(1)\frac{1}{r_{12}}\psi_k(2)\psi_l(2)\,d\tau_1\,d\tau_2. \qquad (6)$$

In eqn (5), the symbols u and v stand for one-electron excitations from occupied molecular orbitals ψ_i and ψ_j to virtual vacant orbitals ψ_k and ψ_l, respectively. The sign and magnitude of λ_0 can now be regarded as a quantitative index of the biradical character of the system in question.

In the case of the transition metal catalyzed systems, the central metals themselves possess an open-shell character due to the small d–d splitting. Apparently, however, the triplet instability associated with metal d orbitals alone is of no direct significance to our present purpose. Therefore, the instability of this sort has entirely been left out of account in this work.

RESULTS AND DISCUSSION

(a) *Cyclodimerization of olefin.* Frequent occurrence of metal-catalyzed $({}_{\pi}2_s + {}_{\pi}2_s)$ cycloadditions of olefins was first interpreted by Mango[6] in terms of the exchange of electron pairs between the metal and the transforming ligands. That is to say, the AS(π) combination of the carbon $p_x(\pi)$ orbitals [antisymmetric(A) and symmetric(S) with respect to the yz and xz planes, respectively, as shown in Fig. 1] is considered to inject a pair of electrons into the metal d_{xz} orbital, while the vacant SA(π^*) orbital accepts a flow of an electron pair from the metal d_{yz} orbital. The net result is a dismissal of the crossing between the AS(π–σ^*) and SA(π^*–σ) correlations which was present in the non-catalyzed reaction. The reaction is thus switched formally from a symmetry-forbidden transformation to a symmetry-allowed one.

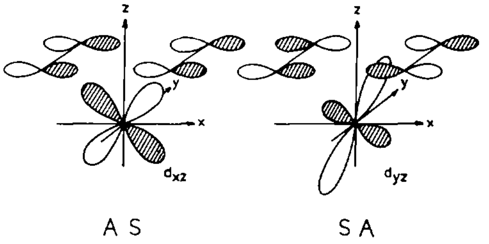


Fig. 1. Spatial arrangement of the orbitals relevant to transition metal catalyzed cyclodimerization of olefin.

In order to gain a better insight into the proposed mechanism, we have dealt with a bisethylene-nickel hydride complex, $(C_2H_4)_2NiH_2$, by an empirical SCF method. In the first place, calculations were carried out for a rectangular approach model as shown in Fig. 2. It was assumed throughout this work that the ligand molecules are not deformed structurally by the formation of metal complex and hence that the metal catalysis, if any, is purely a matter of electronic effects. A special effect of ligand deformation will be discussed later.

Figure 3 shows the variations in electron density on the metal d orbitals in question as the functions of the intermolecular distance R. Interesting to note here is the trend that the electron densities on the d_{xz} (initially vacant) and d_{yz} (initially filled) orbitals are interchanged at a critical distance R ≃ 2·1 Å. The overall features of Fig. 3 corroborate the afore-mentioned view of Mango, who

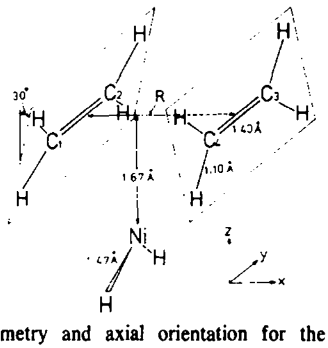


Fig. 2. Geometry and axial orientation for the rectangular approach of metal-catalyzed cyclodimerization of ethylene. The Ni atom is placed equidistant from the four C atoms.

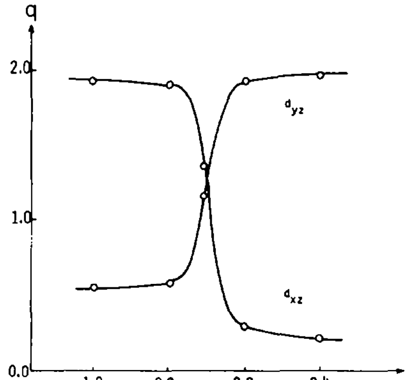


Fig. 3. Electron population of Ni d-orbitals as a function of R for the rectangular approach of two ethylenes.

emphasizes the special role of the d_{xz} and d_{yz} orbitals (Fig. 1) in the metal-catalyzed olefin dimerizations. The view that the reaction should be a symmetry-allowed process thus seems to be basically correct.

Consideration of the nature of this reaction in terms of the triplet stability-instability criterion is more illuminating. Figure 4 compares the variations in λ_0 with R for both the metal-catalyzed (solid line) and non-catalyzed (broken line) systems. The non-catalyzed reaction, which is obviously a symmetry-forbidden process,[2] takes on negative λ_0-values over the range $1{\cdot}9 < R(\text{Å}) < 2{\cdot}4$, indicating that the incipient ethylene dimer possesses an appreciably large biradical character.[2,18] The result is a natural consequence of the relatively small energy gap between the frontier π and π^* orbitals in this range of molecular separation.[18] The λ_0-value for the catalyzed system is seen to be uniformly greater than that for the non-catalyzed system. Importantly, however, the λ_0-value is still negative in sign at $R = 2{\cdot}0\text{–}2{\cdot}2$ Å, where the d_{xz} and d_{yz} orbitals interchange their electron populations (Fig. 3). In other words, the diolefinic moiety is predicted to bear some biradical character at this critical region. The entire process of the metal catalyzed cycloaddition involving a rectangular intermediate should therefore be characterized as a symmetry-allowed but biradical (AR) process.[18]

The situation can best be interpreted schematically in terms of the orbital correlations illustrated in Fig. 5. At an early stage of reaction the AS(π) orbital of the reactant system would be destablized abruptly as if it were correlated with the AS(σ^*) orbital of the product, rather than with the AS(d_{xz}) orbital directly. The AS(π) orbital would then be repelled down by the higher-lying AS orbital. In the meantime, a sudden exchange of electrons takes place between metal and ligands, which now permits the AS(π) orbital to correlate with the final AS(d_{xz}) orbital. Likewise, the SA(d_{yz}) orbital of the reactant system, which is destined to be correlated with the product SA(σ) orbital, would first be destablilized because of its decreasing electron population and then tend to be stabilized on account of the developing σ-bond formation between olefins. Correlations between the antibonding orbitals could be visualized in a similar manner. The net result is that the energy gap between the AS(π) and SA(π^*) orbitals [as well as that between the SA(σ) and AS(σ^*) orbitals] at an intermediary stage of reaction is sufficiently small to give negative λ_0-values, i.e. the triplet instability.

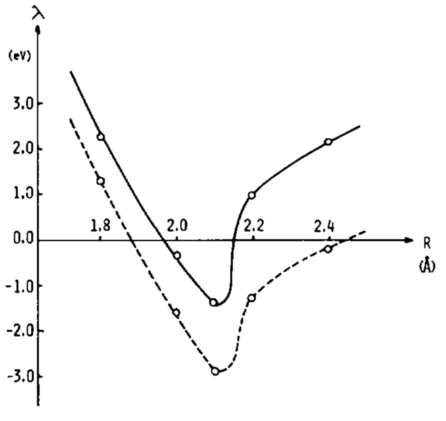


Fig. 4. λ_0-value as a function of R for the rectangular approach of cyclodimerization of ethylenes. ———, Reaction catalyzed by a transition metal; ----, Noncatalyzed reaction.

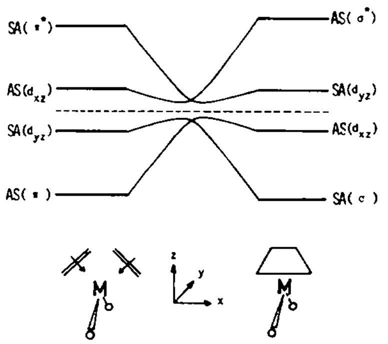


Fig. 5. Schematic representation of the orbital correlations in the metal-catalyzed cyclodimerization of ethylenes.

On the grounds presented above, it may be concluded that the concerted cyclodimerization of ethylene proceeding along the pathway for rectangular approach cannot be a very favorable process even in the presence of transition metal complex.

Triplet stability considerations were extended to a trapezoidal model as shown in Fig. 6. The distance R_2 between the C_1 and C_4 atoms was assumed to be 1·4 Å greater than the interatomic distance R_1 between C_2 and C_3. The nickel atom was allowed to shift by R_3 in the $-y$ direction.

Figure 7 shows the variation in the λ_0-value as the function of R_1 and R_3. Most conspicuous here is the tendency that the radical character diminishes with the increasing R_3. It appears that the reaction would be nonradical in character at $R_3 > 0{\cdot}7$ Å. The disappearance of the biradical character in the diolefinic moiety must be due to the formation of bonds between the metal atom and the terminal C atoms, C_1 and C_4. The metal-carbon bonds

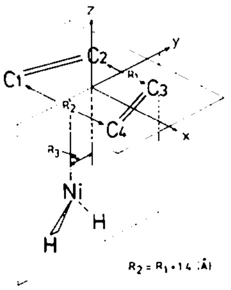


Fig. 6. Geometry and axial orientation for the trapezoidal approach of the metal-catalyzed olefin dimerization.

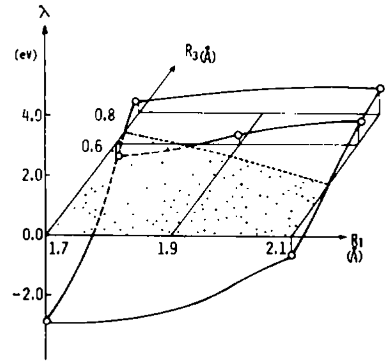


Fig. 7. The λ_0-surface for the trapezoidal approach of metal-catalyzed olefin dimerization with R_1 and R_3 as variables.

would eventually be destructed by subsequent processes such as elimination of metal complex and insertion of other ligands. At any rate, the results of our analysis strongly suggest that the entire process of the metal-catalyzed reaction should essentially be a two-step reaction involving a 5-membered cyclic intermediate,[7] if it is to be free from a biradical character.

(b) *Cyclodimerization of acetylene.* Unlike the simple olefin transformation, the transition metal catalyzed interconversion of bisacetylene to cyclobutadiene cannot be a symmetry-allowed process. According to Mango and Schachtschneider,[6c] this is due to the crossing of the additional AS and SA orbital correlations which are not present in the case of olefin dimerization.

Figure 8 shows the geometry of a rectangular approach model used for our calculations. The combinations of two acetylene orbitals are treated as two sets; one (⊥) containing π and π^* orbitals vertical to the fusing diacetylene plane and the other (∥) being parallel to the x axis. The lowest eigenvalues of the instability matrices were calculated separately for those Hartree-Fock orbitals involving the vertical and parallel p_π orbitals. The results ($\lambda_\perp$ and $\lambda_\parallel$) are shown as the function of R in Fig. 9.

The $\lambda_\perp$-value calculated for non-catalyzed reaction is negative in sign at distances smaller than 1·8 Å. In fact, the ground electronic configuration of free quadrate cyclobutadiene is triplet, and even if it is deformed to a rectangular form due to the Jahn-Teller effect, it would still have some biradical character. In the presence of metal complex, however, $\lambda_\perp$ remains to be positive in sign even at a distance R = 1·5 Å, a typical C–C bond length. The results suggest that the biradical character of cyclobutadiene disappears on metal. A number of stable cyclobutadiene-metal complexes have indeed been isolated.[19] In a sense, the radical character of ligand diene has been "absorbed" into the metal center. The $\lambda_\parallel$-value, on the other hand, shows a pattern which is completely different from that of $\lambda_\perp$ and resembles closely in shape with the λ_0-curve obtained for the case of bisolefin (Fig. 4). With $\lambda_\perp$ and $\lambda_\parallel$ together, the characteristics of the metal-catalyzed bisacetylene fusion is expected to be essentially the same as that of the olefin dimerization.

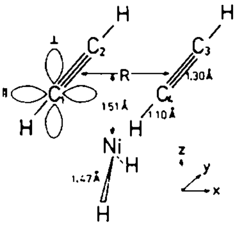


Fig. 8. Geometry and axial orientation for the metal-catalyzed cyclodimerization of acetylene.

Figure 10 shows variations in the electron population on the metal d_{xz} and d_{yz} orbitals with R. The two orbitals interchange their electron populations in the region R = 2·0 – 2·1 Å, as in the case of olefin dimerization (Fig. 3). However, they mutually exchange electrons once again in the vicinity of R = 1·7 Å, to resume their original electron populations. The two-fold electron migration, ebb and flow, should importantly govern the nature of this particular metal-catalyzed reaction.

Here, it deserves special mention that, in the domains R = 1·7 and 2·1 Å, our procedure to obtain Hartree-Fock solutions did not converge on iteration. This reflects enormous reorganizations in electronic structure of the system there. According to Koutecký and Bonačić-Koutecký,[15,20] the problem of such a convergence difficulty itself is closely related to the biradical character of the molecular system treated.

With the above two theoretical indications in mind, we have reexamined the orbital correlations in the bisacetylene-cyclobutadiene transformation. The essential part of the correlation is diagramatically illustrated in Fig. 11. The electronic configuration shown in the middle corresponds to the intermediary molecular geometry

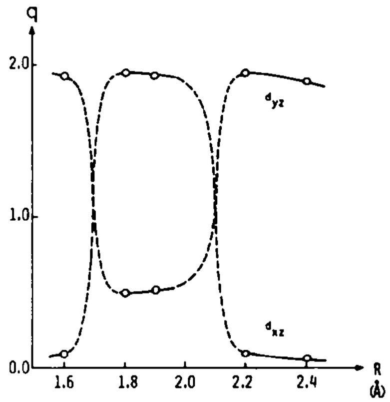


Fig. 10. Electron population of Ni d-orbitals as a function of R for the metal-catalyzed cyclodimerization of acetylene.

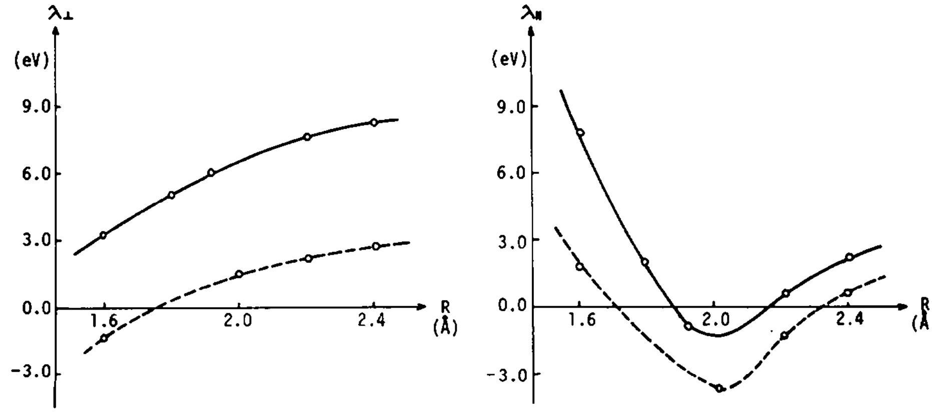


Fig. 9. λ_0-value as a function of R for the cyclodimerization of acetylene. ———, Reaction catalyzed by a transition metal; - - - -, Noncatalyzed reaction.

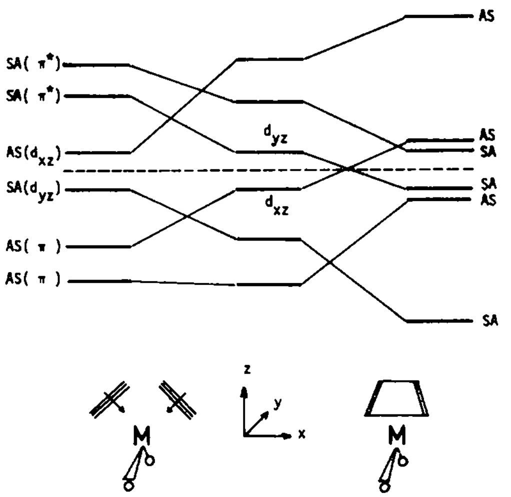


Fig. 11. Schematic representation of the orbital correlation in the metal-catalyzed cyclodimerization of acetylene.

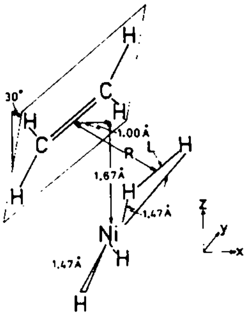


Fig. 12. Geometry and axial orientation for the metal-catalyzed hydrogenation of ethylene.

(R = 1·8 – 1·9 Å) at which the d_{xz} orbital attains a maximal electron population. The transformation between bisacetylene and the intermediary structure is a symmetry-allowed but biradical (AR) process exactly in the same token as used for the olefin dimerization (Fig. 5). The transformation between the intermediary structure and the cyclobutadiene complex involves a crossing of the AS and SA orbitals associated with the metal d orbitals alone. The radical character arising from this crossing should be relatively immaterial to the reaction of our concern. The overall rectangular process, which is certainly symmetry-forbidden, is thus considered not to be a particularly high-energy process as compared to the corresponding olefin conversion.

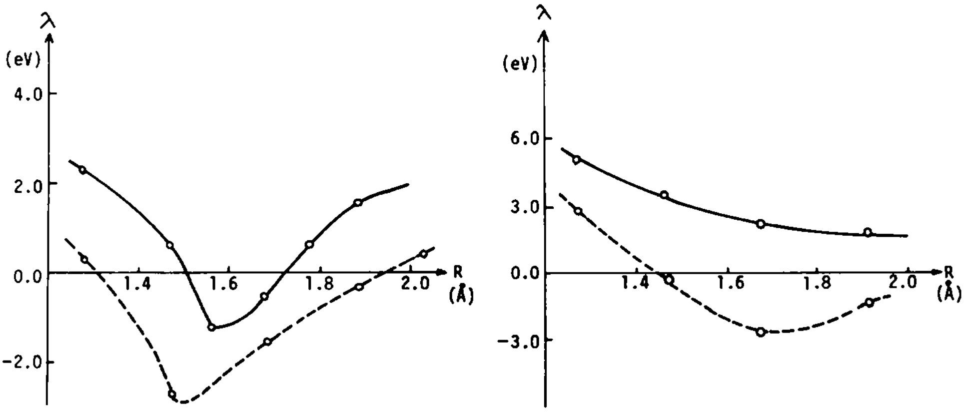
(c) *Hydrogenation of olefin.* Hydrogenation of olefin is a typical example of (${}_{\pi}2+{}_{\sigma}2$) reaction. Its ground-state process is symmetry-forbidden but can be rendered allowed by the presence of transition metal catalyst as in the case of olefin dimerization.

We here treat the reaction between hydrogen and ethylene in the presence of NiH_2 as a model for metal catalyzed hydrogenation of olefin. Figure 12 shows geometry of the reacting system assumed for calculation. The H–H bond length L was fixed at 0·8 and 1·4 Å. The former (model A) corresponds to the case where the hydrogen molecule is not considerably deformed from its equilibrium structure, while the latter (model B) is aimed at representing the cases where the H–H bond has already been weakened substantially. The λ_0-values were calculated as the function of R for both models A and B. The results are shown in Fig. 13.

In model A, the catalyzed reaction still has a biradical region around R = 1·6 Å. The λ_0-curve closely resembles that for the noncatalyzed reaction. The metal catalyzed hydrogenation proceeding by way of model A would thus be an AR process.

In the case of model B, on the other hand, the catalyzed reaction takes on relatively large positive λ_0-values over the R range of our interest. In the absence of metal catalysis, the λ_0-value is negative in sign even at distances far greater than R = 1·8 Å. This is because at the outset the hydrogen molecule has been assumed to be greatly deviated in structure from its equilibrium geometry. The biradical character which persisted to the reacting system is completely removed by NiH_2. The metal catalyzed hydrogenation of model B may thus be characterized as a symmetry-allowed nonradical (AN) process.[17,18]

All the concerted cycloadditions such as Diels–Alder reactions and carbene additions to olefins can also be characterized as the AN processes. The ready occurrence of transition metal catalyzed hydrogenation may be understood from this similarity in reaction type. Probably, the hydrogenation proceeds via a low-energy path involving a transition state similar to our model B, in which the bonding of hydrogen molecule is considerably loosened but is biradical character is effectively "absorbed" into the metal center.



L = 0.8 Å

L = 1.4 Å

Fgi. 13. λ_0-value as a function of R for the hydrogenation of ethylene. ———, Reaction catalyzed by a transition metal; ----, Noncatalyzed reaction.

CONCLUSIONS

(1) The transition metal catalyzed cyclodimerization of ethylene is formally a symmetry-allowed reaction but possesses a considerable biradical character in the fusing bisethylene moiety, depending on the geometry of the reacting system.

(2) The corresponding reaction of acetylene is no doubt symmetry-forbidden but the symmetry restriction should not be too severe for the reaction to take place thermally.

(3) Metal catalyzed hydrogenation of ethylene appears to proceed via a transition state in which the bonding of hydrogen molecule is considerably loosened.

REFERENCES

[1] Part IV: T. Okada, K. Yamaguchi and T. Fueno, *Tetrahedron* **30**, 2293 (1974).

[2a] R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.* **87**, 395 (1965); [b] R. B. Woodward and R. Hoffmann, *The Conservation of Orbital Symmetry*. Academic Press, New York (1970).

[3] D. R. Eaton, *J. Am. Chem. Soc.* **90**, 4272 (1968).

[4] C.-C. Su, *Ibid.* **93**, 5653 (1971).

[5] R. Pettit, H. Sugahara, J. Wristers and W. Merck, *Discuss. Faraday Soc.* **47**, 71 (1969).

[6a] F. D. Mango and J. H. Schachtschneider, *J. Am. Chem. Soc.* **89**, 2484 (1967); [b] F. D. Mango, *Advan. Catal.* **20**, 291 (1969); [c] F. D. Mango and J. H. Schachtschneider, *J. Am. Chem. Soc.* 91, 1030 (1969); [d] F. D. Mango, *Tetrahedron Letters* 4813 (1969); [e] F. D. Mango and J. H. Schachtschneider, *J. Am. Chem. Soc.* **93**, 1123 (1971); [f] F. D. Mango and J. H. Schachtschneider, *Transition Metals in Homogeneous Catalysis* (Edited by G. N. Schrauzer). Marcel Dekker, New York (1971).

[7a] T. J. Katz and S. A. Cerefice, *J. Am. Chem. Soc.* **91**, 6519 (1969); [b] T. J. Katz and S. A. Cerefice, *Ibid.* **93**, 1049 (1971); [c] L. Cassar, P. E. Eaton and J. Halpern, *Ibid.* **92**, 3535 (1970); [d] J. E. Byrd, L. Cassar, P. E. Eaton and J. Halpern, *Chem. Commun.* 40 (1971); [e] R. H. Grubbs and T. K. Brunck, *J. Am. Chem. Soc.* **94**, 2538 (1972); [f] L. G. Cannel, *Ibid.* **94**, 6867 (1972); [g] A. R. Fraser, P. H. Bird, S. A. Bezman, J. R. Shapley, R. White and J. A. Osborn, *Ibid.* **95**, 597 (1973); [h] J. X. McDermott and G. M. Whitesides, *Ibid.* **96**, 947 (1974).

[8] C. C. J. Roothaan, *Rev. Mod. Phys.* **23**, 69 (1951).

[9] M. Wolfsberg and L. Helmholtz, *J. Chem. Phys.* **20**, 837 (1952).

[10] L. Di Sipio, E. Tondello, G. De Michelis and L. Oleari, *Chem. Phys. Lett.* **11**, 287 (1971).

[11] M. Zerner and M. Gouterman, *Theoret. Chim. Acta Berl.* **4**, 44 (1966).

[12] K. Nishimoto and N. Mataga, *Z. Phys. Chem. N. F.* **13**, 140 (1957).

[13] D. J. Thouless, *The Quantum Mechanics of Many-Body Systems*. Academic Press, New York (1961).

[14] J. Koutecký, *J. Chem. Phys.* **46**, 2443 (1967).

[15] J. Koutecký and V. Bonačić, *Ibid.* **55**, 2408 (1971).

[16] J. Čížek and J. Paldus, *Ibid.* **47**, 4976 (1967); J. Paldus and J. Čížek, *Ibid.* **52**, 2919 (1970).

[17] H. Fukutome, *Prog. Theor. Phys.* **47**, 1156 (1972).

[18] K. Yamaguchi, T. Fueno and H. Fukutome, *Chem. Phys. Lett.* **22**, 461, 466 (1973).

[19] B. W. Roberts and A. Nissner, *J. Am. Chem. Soc.* **94**, 7168 (1972).

[20] V. Bonačić and J. Koutecký, *Intern. J. Quant. Chem.* 137 (1971). [b] J. Koutecký and V. Bonačić-Koutecký, *Chem. Phys. Lett.* **15**, 558 (1972).