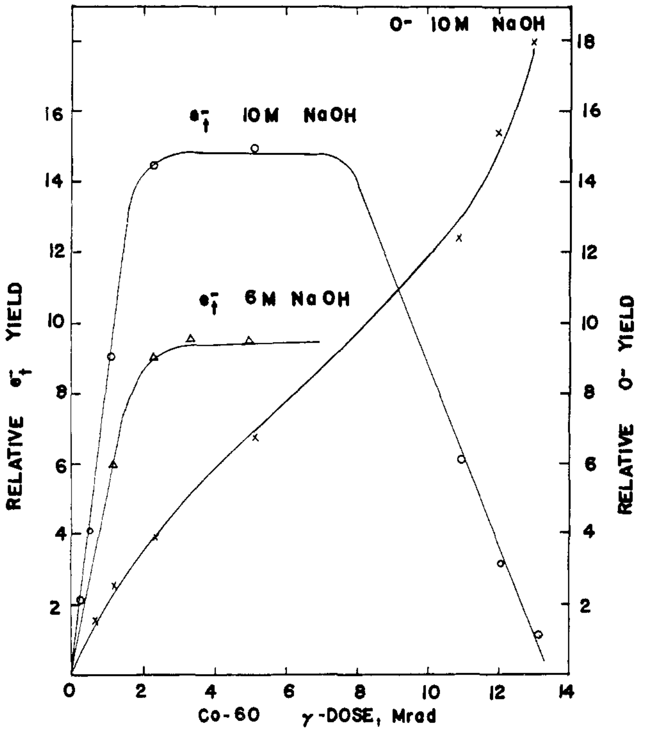


Figure 1. Relative e_t^- and O^- yields as a function of γ radiation dose in alkaline ices at 77°K.

magnetic species are observed, the e_t^- must react above 8 Mrads with a species other than O^- to form a diamagnetic species.

A plausible explanation for the dose saturation behavior is suggested by considering reactions which can compete with the trapping reaction for radiation-produced mobile electrons, e_m^-. The trapping reaction is shown by (1) where T denotes an available trap for e_m^-, and possible competing reactions for e_m^- are given by (2) and (3).

$$e_m^- + T \xrightarrow{k_1} e_t^- \tag{1}$$

$$e_m^- + e_t^- \xrightarrow{k_2} e_{2t}^{2-} \tag{2}$$

$$e_t^- + (H_2O)^+ \xrightarrow{k_3} H_2O \tag{3}$$

From the dose saturation data for 6 and 10 *M* NaOH, it is seen that the number of traps available in the system is proportional to $[OH^-]$. Reaction 3 involving the radiation-produced hole, $(H_2O)^+$, predicts that the dose saturation yield should be independent of $[OH^-]$ and that the dose at which saturation occurs should depend on $[OH^-]$. Neither prediction is observed experimentally, so reaction 3 does not explain the results.

The formation of e_{2t}^{2-} by reaction 2 is consistent with our results. The onset of dose saturation occurs when a specific fraction of the available traps are filled; hence it is independent of $[OH^-]$. At low doses, $k_1[T] >> k_2[e_t^-]$; saturation occurs when $k_1[T] = k_2[e_t^-]$; and for $k_2 > k_1$, $[e_t^-]$ decreases at high doses.

In an e_{2t}^{2-} center we expect that the second electron would be bound more weakly than the first electron. In this case thermal dissociation could lead to $e_{2t}^{2-} \rightarrow e_t^-$. We searched for this reaction by warming colorless spheres of 10 *M* NaOH that had been irradiated to 15 Mrads at 77°K and showed no epr spectrum due to e_t^-. Above 120°K a blue color was observed to appear; this was trapped by suddenly recooling to 77°K. Both the epr line and optical band of e_t^- were then observed for the warmed samples. We believe this experiment conclusively demonstrates the existence of e_{2t}^{2-}.

The direct analogy of e_{2t}^{2-} in hydroxide ices is the F′ center in irradiated alkali halides.[4] The F′ center consists of two electrons trapped in the same halide ion vacancy; it is diamagnetic, has broad optical absorption in the near-infrared, can be thermally dissociated to yield the F center which is analogous to e_t^-, and can be produced by optical bleaching of the F center. Symons and co-workers[5] have studied optical bleaching of e_t^- and indeed find a new, broad absorption in the near-infrared, although no maximum could be observed. This observation is additional evidence for e_{2t}^{2-}.

The binding of two electrons in the same anion vacancy can be understood qualitatively as follows. The wave function of e_t^- extends over a greater volume than that of the OH^- which it replaces; consequently, there will be a small potential well in the e_t^- volume which can bind a second electron. This argument implies that the second electron is bound more weakly than the first. Vinetskii and Giterman[6] have calculated the interaction of two electron centers in a dielectric medium. They find a minimum in the potential curve at an ~4-A separation between the two electrons. The radius of the e_t^- charge distribution has been previously estimated as 3–4 A from experimental data.[3] Hence the existence of e_{2t}^{2-} seems compatible with the approximate theoretical calculations.

Acknowledgment. This research was generously supported by the Air Force Rocket Propulsion Laboratory and the U. S. Atomic Energy Commission. This is AEC Document No. COO-1528-11. J. Z. is grateful to the U. S. Atomic Energy Commission for an Advanced Health Physics Fellowship and to Professor F. E. Hoecker for his cooperation. We thank Professor R. N. Adams for making available the epr equipment and Professor R. Friauf and D. Renneke for helpful discussions.

---

[4] J. H. Schulman and W. D. Compton, "Color Centers in Solids," The Macmillan Co., New York, N. Y., 1962, pp 107–112.

[5] M. J. Blandamer, L. Shields, and M. C. R. Symons, *J. Chem. Soc.*, 4352 (1964).

[6] V. L. Vinetskii and M. Sh. Giterman, *Soviet Phys. JETP*, **6**, 560 (1958); see also J. Jortner, S. A. Rice, and E. G. Wilson in "Metal Ammonia Solutions," W. A. Benjamin, Inc., New York, N. Y., 1964, p 245.

John Zimbrick, Larry Kevan
Departments of Chemistry and Radiation Biophysics
University of Kansas, Lawrence, Kansas 66044

Received March 20, 1967

Molecular Orbital Symmetry Conservation in Transition Metal Catalyzed Transformations

Sir:

Woodward and Hoffmann have published a series of communications extending simple molecular orbital theory into the area of reaction chemistry.[1] This

---

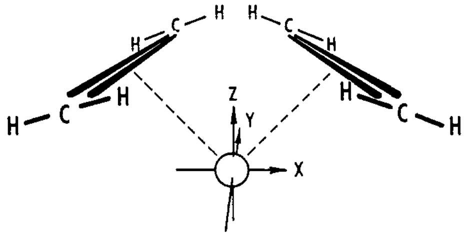
[1] (a) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395, 2511, 4389 (1965); (b) *ibid.*, **87**, 2046 (1965); (c) *ibid.*, **87**, 4388 (1965); (d) see also H. C. Longuet-Higgins and E. W. Abrahamson, *ibid.*, **87**, 2045 (1965); and K. Fukui, *Tetrahedron Letters*, 2009 (1965).

fresh approach to understanding reacting systems underlines a fundamental concept which correlates, with respect to symmetry, the molecular orbitals of reactants with those of products. The Woodward–Hoffmann postulate, dividing molecular transformations into "allowed" and "forbidden" categories, has proven a powerful tool for understanding a large body of complex chemistry. This communication extends the concept of symmetry conservation into transition metal catalysis.

Bicyclo[2.2.1]hepta-2,5-diene undergoes smooth dimerization to cyclobutane derivatives in the presence of zerovalent Fe,[2] Ni,[3a-c] and Co[4] catalysts, and tetracyclo[2.2.1.$0^{2,6}$.$0^{3,5}$]heptane (quadricyclene) has recently been reported to undergo a facile valence isomerization to bicyclo[2.2.1]hepta-2,5-diene catalyzed by various noble metal complexes.[5] Since, in the metal-free system, a mechanism involving a concerted molecular transformation in these reactions is strictly forbidden by the Woodward–Hoffmann rules,[1b] the role of the transition metal catalysts invites examination.

The concerted fusion of two olefins to a ground-state cyclobutane ring requires the introduction of two electrons into the olefin AS orbital and the removal of two electrons from the olefin SA orbital (A = antisymmetric; S = symmetric).[1b] A transition metal system containing d orbitals of sufficient energy and possessing the appropriate number of d electrons can, conceivably, carry out these operations. We propose a mechanism for metal-catalyzed cycloaddition in which the metal orbitals combine with the olefin orbitals, giving a set of occupied molecular orbitals of the symmetry required for an allowed reaction path.

Consider the metal–diolefin complex I. For the concerted cyclobutanation, the elements of symmetry are the *ZX* and *YZ* planes. The symmetry classifications of the π-orbital combinations of I (C_{2v}) are the same as those reported for the uncatalyzed reaction.[1b] These orbitals interact with combinations of metal atomic orbitals as follows: SS (a_1) with metal s, p_z, d_{z^2}, and $d_{x^2-y^2}$; SA (b_1) with metal p_x and d_{zx}; AS (b_2) with metal p_y and d_{yz}; AA (a_2) with metal d_{xy}. Metal orbitals of the appropriate energy could combine with the olefin orbitals yielding a set of new molecular orbitals of the same symmetry classification; bonding between the metal and the olefin, then, could result with electronic population of the bonding molecular orbitals.



I

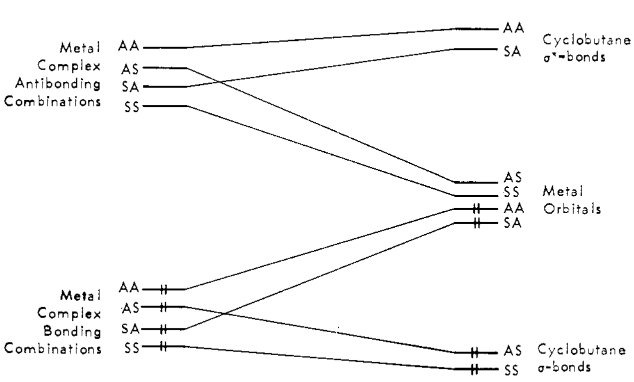


Figure 1.

A correlation diagram for the cyclobutanation of the ligand-bound olefins is illustrated in Figure 1, which describes an orbital pathway for the placement of electron pairs into the cyclobutane σ bonds and for the removal of the appropriate olefin π electrons. In this process, the electron density in the AS and SA orbitals of the complex is redistributed; in the AS orbital, electron density shifts into the incipient cyclobutane σ bond while in the SA orbital, electron density is localized in the metal d_{zx} orbital. This can be envisaged as a change in ligand-to-metal bonding as the system moves across the reaction coordinate. Ring closure draws the olefin SA combination sharply upward in energy, thereby diminishing the ligand-to-metal orbital mixing and increasing the electron density in the d_{zx} orbital. The olefin AS orbital, rehybridizing to a σ bond, undergoes an increase in electron density with diminished metal d_{yz} orbital mixing. An electronically excited product can conceivably result depending on the nature and geometry of the metal system, but, given the general ordering of orbitals pictured in Figure 1, a reaction path to a ground-state cyclobutane ligand exists. This simple description is supported by extended Hückel molecular orbital calculations[6] carried out on the cyclobutanation of two olefin ligands attached to nickel dicarbonyl, a system reported to cyclobutanize bicyclo[2.2.1]hepta-2,5-diene.[3a] The calculations yielded correlation diagrams describing the allowed transformation.[7]

Other transition metal catalyzed reactions suggest metal participation of this sort. The nickel-catalyzed conversion of acetylene to cyclooctatetraene, the Reppe synthesis,[8] is an example. In a close examination of this reaction, Schrauzer has favored a concerted mechanism in which the four σ bonds of the cyclooctatetraene are formed essentially simultaneously.[9] Since the isolated transformation is thermally forbidden,[1b] such a mechanism suggests the electronic participation by the metal. The molecular orbital symmetry aspects of this reaction were examined using as a model the structure II proposed by Schrauzer.[9]

The four π orbitals of the acetylene ligands in II can be treated as two sets, each containing a pair of

---

(2) C. W. Bird, D. L. Colinese, R. C. Cookson, J. Hudec, and R. O. Williams, *Tetrahedron Letters*, 373 (1961); P. W. Jolly, F. G. A. Stone, and K. Mackenzie, *J. Chem. Soc.*, 6416 (1965).

(3) (a) C. W. Bird, R. G. Cookson, and J. Hudec, *Chem. Ind.* (London), 20 (1960); (b) G. N. Schrauzer and S. Eichler, *Chem. Ber.*, **95**, 2764 (1962); (c) L. G. Cannell, U. S. Patent 3,258,502 (1966).

(4) D. R. Arnold, D. J. Trecker, and E. B. Whipple, *J. Am. Chem. Soc.*, **87**, 2596 (1965).

(5) H. Hogeveen and H. C. Volger, *ibid.*, **89**, 2486 (1967).

(6) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

(7) Orbital functions were taken from E. Clementi and D. L. Raimondi, *ibid.*, **38**, 2686 (1963); J. W. Richardson, W. C. Nieuwpoort, R. R. Powell, and W. R. Edgell, *ibid.*, **36**, 1057 (1962); J. W. Richardson, R. R. Powell, and W. C. Nieuwpoort, *ibid.*, **38**, 796 (1963); H. Basch, A. Viste, and H. B. Gray, *ibid.*, **44**, 10 (1966).

(8) W. Reppe, O. Schlichting, K. Klager, and T. Towpel, *Ann. Chem.*, **560**, 1 (1948).

(9) G. N. Schrauzer, *Angew. Chem. Intern. Ed. Engl.*, **3**, 185 (1964).

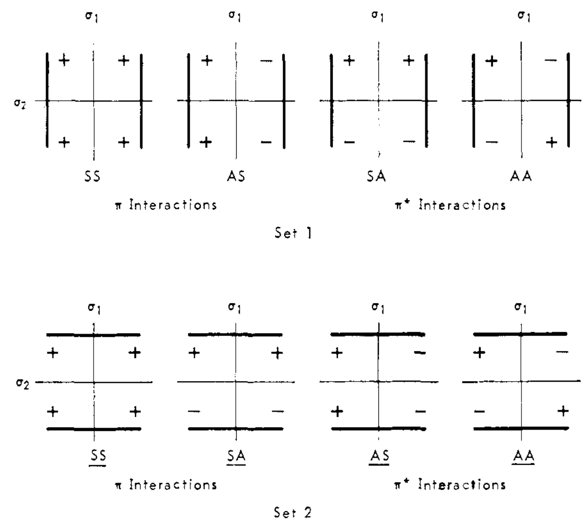
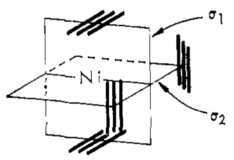


Figure 2.

π orbitals (Figure 2). The ligands seated at the corners of σ_2 comprise set 1 and the ligands positioned on the edges of σ_1 constitute set 2. The members of each set interact yielding the following combinations. Orbitals in set 1 will interact with orbitals in set 2 of the same symmetry yielding a new set, half the members of which are bonding in the region of space between the sets and the other half antibonding. The SS and SS orbitals, for example, combine giving two orbitals, both of SS symmetry, one bonding in the region of the incipient cyclooctatetraene σ bonds and the other antibonding in that region. The four bonding members of the final set correspond in symmetry to the incipient σ bonds of cyclooctatetraene. If the interaction between the orbitals of the metal system and the olefin combinations results in the electronic population of these four molecular orbitals, then an orbital pathway to the concerted cycloaddition exists.



11

The application of symmetry conservation concepts to the selected reactions[10] introduces a novel mechanism involving a role for the transition metal unique in catalysis. The results suggest that certain metal systems containing orbital configurations of the prerequisite energy are capable of rendering otherwise forbidden cycloaddition reactions allowed by providing a template of atomic orbitals through which electron pairs of transforming hydrocarbon ligands and metal systems can interchange and flow into the required regions of space.

Acknowledgment. We are grateful to Drs. J. Merritt, F. S. Mortimer, Isaac Dvoretzky, and J. H. Raley for stimulating discussions and helpful comments.

Frank D. Mango, J. H. Schachtschneider
Shell Development Company
Emeryville, California
Received December 9, 1966

---

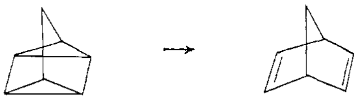
[10] Electronic involvement by a transition metal is suggested in other systems. The cobalt-catalyzed isomerization of allylbenzene to β-methylstyrene is an example.[11] Back donation of d electrons converts the suprafacial [1,3] sigmatropic change of order[10] to an allowed process.

[11] L. Roos and M. Orchin, *J. Am. Chem. Soc.*, **87**, 5502 (1965).

Valence Isomerization of Quadricyclene[1a] to Norbornadiene[1b] Catalyzed by Transition Metal Complexes

Sir:

The thermal isomerization of quadricyclene (I) to norbornadiene (II) is known to proceed slowly ($t_{1/2}$ > 14 hr at 140°).[2] It has now been found that the rate of this reaction is dramatically increased by transition metal–olefin complexes. For instance, $t_{1/2}$ at −26° was found to be 45 min for a 0.7 *M* solution of I in $CDCl_3$ in the presence of 2 mole % of di-μ-chloro-bis-(bicyclo[2.2.1]hepta-2,5-diene)dirhodium(I).



I II

Complexes such as di-μ-chloro-tetrakis(ethylene)-dirhodium(I), dichloro(1,5-cyclooctadiene)palladium-(II), di-μ-chloro-bis(π-methallyl)dipalladium(II), and dichloro(bicyclo[2.2.1]hepta-2,5-diene)platinum(II) behave similarly. For all complexes a quantitative conversion of I into II was observed. The isomerization catalyzed by di-μ-chloro-bis(bicyclo[2.2.1]hepta-2,5-diene)dirhodium(I) was followed kinetically by integration of the olefinic triplet (δ 6.82 ppm) in the nmr spectrum of the norbornadiene formed. The samples were prepared at about −60° in $CDCl_3$, warmed up rapidly to the desired temperature, and then transferred to the cavity of the nmr spectrometer (being at the same temperature).

The reaction proved to be first-order in quadricyclene and, as shown in Table I, about first order in catalyst.

Table I. Pseudo-First-Order Rate Constants of the Reaction[a] Quadricyclene → Norbornadiene

$[Rh_2(norbornadiene)_2Cl_2]$, *M*	10^2k, sec^{-1}
0.02	0.025
0.06	0.068

[a] At −26°; [quadricyclene] = 0.7 *M* ($CDCl_3$).

The apparent values of the activation parameters (inaccurate because of experimental difficulties, such as temperature control and instability of the catalyst solution) are $\Delta H^{\ddagger}$ 21 ± 5 kcal $mole^{-1}$, $\Delta S^{\ddagger}$ = 45 ± 18 eu (catalyst concentration 0.036 *M*).

The mechanism of the reaction is thought to involve a coordination of quadricyclene to the transition metal either *via* an exchange with the originally coordinated olefin or by extension of the coordination around the metal. For the rhodium–olefin complexes and for the

---

[1] (a) IUPAC designation tetracyclo[$3.2.0.0^{2,7}.0^{4,6}$]heptane; (b) IUPAC designation bicyclo[2.2.1]hepta-2,5-diene.

[2] G. S. Hammond, N. J. Turro, and A. Fischer, *J. Am. Chem. Soc.*, **83**, 4674 (1961).