

JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Registered in U. S. Patent Office. © Copyright, 1974, by the American Chemical Society

VOLUME 96, NUMBER 19

SEPTEMBER 18, 1974

Hierarchy of Symmetry Conservation Rules Governing Chemical Reaction Systems¹

David M. Silver

Contribution from the Applied Physics Laboratory, The Johns Hopkins University,
Silver Spring, Maryland 20910. Received June 6, 1973

Abstract: A comparison is presented of two sets of symmetry conservation rules that govern the course of various chemical reactions. The Wigner–Witmer rules are shown to operate on the basis of total electronic orbital symmetry conservation, whereas the Woodward–Hoffmann rules utilize individual electronic orbital symmetry conservation for their operation. A three-level hierarchy of symmetry control is generated by these sets of rules: namely, “allowed” reactions conserve both total and individual orbital symmetry, “forbidden” reactions conserve total but not individual orbital symmetry, and “unfeasible” reactions conserve neither of these symmetries. The parallel application of both sets of rules to several particular reactions is presented.

The elucidation of numerous chemical reaction phenomena is greatly facilitated by the use of symmetry conservation rules that correlate the electronic states of reactant species with appropriate electronic states of possible product species. One of these sets of symmetry rules, proposed by Wigner and Witmer² in 1928, has been the subject of numerous discussions, applications, and extensions.^{3–10} Another set of symmetry rules, proposed by Woodward and Hoffmann^{11–14} in 1965, has also attracted considerable attention.^{9, 10a, 15–36}

(1) This work was supported by the Department of the Navy, Naval Ordnance Systems Command under Contract N00017-72-C-4401.

(2) E. Wigner and E. E. Witmer, *Z. Phys.*, **51**, 859 (1928).

(3) R. S. Mulliken, *Rev. Mod. Phys.*, **4**, 1 (1932); *Phys. Rev.*, **43**, 279 (1933).

(4) M. Kotani, *Proc. Phys. Math. Soc. Jap.*, **19**, 460 (1937).

(5) G. Herzberg, “Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules,” 2nd ed, Van Nostrand, Princeton, N. J., 1950, pp 315–322.

(6) K. E. Shuler, *J. Chem. Phys.*, **21**, 624 (1953).

(7) G. Herzberg, “Molecular Spectra and Molecular Structure. III. Electronic Spectra and Electronic Structure of Polyatomic Molecules,” Van Nostrand, Princeton, N. J., 1966, pp 276–296 and 563–577.

(8) A. G. Gaydon, “Dissociation Energies and Spectra of Diatomic Molecules,” 3rd ed, Chapman and Hall, London, 1968, pp 52–60.

(9) M. Karplus and R. N. Porter, “Atoms and Molecules,” W. A. Benjamin, Menlo Park, Calif., 1970, pp 397–404 and 489.

(10) (a) T. F. George and J. Ross, *J. Chem. Phys.*, **55**, 3851 (1971); (b) Y.-N. Chiu, *ibid.*, **58**, 722 (1973).

(11) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 395, 2046, 2511 (1965).

(12) R. B. Woodward, *Chem. Soc., Spec. Publ.*, No. 21, 217 (1967).

(13) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968); *Science*, **167**, 825 (1970).

(14) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(15) H. C. Longuet-Higgins and E. W. Abrahamson, *J. Amer. Chem. Soc.*, **87**, 2045 (1965).

Because of their usefulness and the wide interest in these two sets of symmetry rules, it would be particularly pertinent to demonstrate the relationship between the two and examine their applicability to similar problems.

(16) K. Fukui, *Tetrahedron Lett.*, 2009, 2427 (1965); *Bull. Chem. Soc. Jap.*, **39**, 498 (1966); *Accounts Chem. Res.*, **4**, 57 (1971).

(17) K. Fukui and H. Fujimoto, *Tetrahedron Lett.*, 251 (1966); *Bull. Chem. Soc. Jap.*, **39**, 2116 (1966); **40**, 2018 (1967).

(18) P. Millie, *Bull. Soc. Chim. Fr.*, 4031 (1966).

(19) H. E. Zimmerman, *J. Amer. Chem. Soc.*, **88**, 1564, 1566 (1966); *Science*, **153**, 837 (1966); *Accounts Chem. Res.*, **4**, 272 (1971).

(20) M. J. S. Dewar, *Tetrahedron, Suppl.*, **8**, 75 (1966); ref 12, p 177; *Angew. Chem., Int. Ed. Engl.*, **10**, 761 (1971).

(21) L. Salem, *J. Amer. Chem. Soc.*, **90**, 543, 553 (1968).

(22) J. A. Berson, *Accounts Chem. Res.*, **1**, 152 (1968).

(23) J. I. Brauman and D. M. Golden, *J. Amer. Chem. Soc.*, **90**, 1920 (1968).

(24) W. Th. A. M. van der Lugt and L. J. Oosterhoff, *Chem. Commun.*, 1235 (1968); *J. Amer. Chem. Soc.*, **91**, 6042 (1969); *Mol. Phys.*, **18**, 177 (1970).

(25) J. J. C. Mulder and L. J. Oosterhoff, *Chem. Commun.*, 305, 307 (1970).

(26) C. Trindle, *J. Amer. Chem. Soc.*, **92**, 3251, 3255 (1970).

(27) W. A. Goddard, III, *J. Amer. Chem. Soc.*, **92**, 7520 (1970); **94**, 793 (1972).

(28) R. G. Pearson, *Accounts Chem. Res.*, **4**, 152 (1971); *Pure Appl. Chem.*, **27**, 145 (1971); *Theor. Chim. Acta*, **16**, 107 (1970).

(29) N. D. Epiotis, *J. Amer. Chem. Soc.*, **94**, 1924, 1935, 1941, 1946 (1972).

(30) W. Schmidt, *Tetrahedron Lett.*, 7, 581 (1972).

(31) J. E. Baldwin, A. H. Andrist, and R. K. Pinschmidt, Jr., *Accounts Chem. Res.*, **5**, 402 (1972).

(32) J. A. Berson and L. Salem, *J. Amer. Chem. Soc.*, **94**, 8917 (1972).

(33) J. A. Berson, *Accounts Chem. Res.*, **5**, 406 (1972).

(34) W. J. van der Hart, J. J. C. Mulder, and L. J. Oosterhoff, *J. Amer. Chem. Soc.*, **94**, 5724 (1972).

(35) E. B. Wilson and P. S. C. Wang, *Chem. Phys. Lett.*, **15**, 400 (1972).

(36) R. F. Hudson, *Angew. Chem., Int. Ed. Engl.*, **12**, 36 (1973).

The two sets of symmetry rules share a fundamental basis, although they differ in certain essential respects that allow them to form a hierarchical structure. Unfortunately, the traditional manner of deriving, treating, and applying the two sets of rules tends to over-emphasize their differences. For instance, the Wigner–Witmer rules are customarily conceived in terms of (1) conservation of angular momentum and (2) selection rules specifying accessible product states of a reaction. The Woodward–Hoffmann rules, on the other hand, are customarily conceived in terms of (1) conservation of symmetry and (2) energy considerations determining the course of a reaction. However, (1) the symmetry designation of a wavefunction signifies that the wavefunction is an eigenfunction of a particular symmetry operation, but such an invariance of a symmetry operation implies the existence of a constant of motion and a conservation law. For instance, rotational symmetry invariance implies conservation of angular momentum. Furthermore, (2) a selection rule represents a statement that a particular reaction path is most feasible. From an energy point of view, that means that the internuclear potential along that selected path has the least high energy barrier between reactant and product. Alternatively, energy considerations themselves allow a selection to be made of a most feasible final state; hence, energy considerations lead to selection rules. Thus, both Wigner–Witmer and Woodward–Hoffmann rules should be regarded in the same terms: namely, (1) conservation of angular momentum *ergo* conservation of symmetry; and (2) selection rules *ergo* energy considerations. Although straightforward, the similarity and interdependence of these concepts have not been generally recognized.

A number of prerequisites must be satisfied^{10a} in order to apply the symmetry rules to a reaction system. Common to the two sets of symmetry rules^{2,14} is the assertion that the Born–Oppenheimer³⁷ approximation be valid so that nuclear and electronic motions can be separated. For the isolated reaction system, the total angular momentum is necessarily conserved.³⁸ However, it is further assumed that three separate components of angular momentum are separately conserved during the reaction process:^{2–7} namely, the nuclear angular momentum, the electronic spin angular momentum, and the electronic orbital angular momentum. In addition, all electronic spin interactions and nuclear dynamic effects^{10a,39} are assumed negligible. Under these conditions, the treatment of the conservation of electronic orbital angular momentum generates two fundamentally similar, but separate, sets of symmetry rules. The Wigner–Witmer rules assume conservation of *total* electronic orbital angular momentum, whereas the Woodward–Hoffmann rules assume conservation of *individual* electronic orbital momenta. In both cases, the electronic energy plays the role of an effective internuclear potential function governing the motions of the nuclei. Thus, the feasibility of a given reaction mechanism can be assessed by determining the electronic energy along the reaction coordinate as the

system undergoes the transformation from reactants to products. This reaction path energy profile is of course influenced by the effects of angular momentum conservation considerations.

When the positions of the nuclei are such that they conform to a symmetry point group,⁴⁰ then the orbital angular momentum functions, both *total* and *individual*, form a basis for the irreducible representations of the point group and the *total* and *individual* orbital symmetry designations become the instruments for the determination of energy characteristics along the reaction path as embodied in the symmetry rules. In the present work, the distinction between conservation of *total*² vs. *individual*¹⁴ electronic orbital symmetry is used to classify the symmetry rules into a hierarchy of symmetry control over the course of chemical reactions.

The present work is concerned with the total electronic energy (*i.e.*, the internuclear potential energy in the Born–Oppenheimer approximation) along an *entire* trajectory from reactant, through transition state, and into product conformation, that is, an *entire* reaction path on the potential energy surface. Thus, reactant-type and product-type wave functions are developed and both combined into a configuration interaction series that is valid throughout the course of the reaction regime. This allows bona fide variational energy expressions to be derived that correspond to the energy along the entire reaction path. In addition, this scheme provides a qualitative means for assessing reaction feasibilities concurrently from both the Wigner–Witmer and Woodward–Hoffmann points of view. In contrast, the customary approach is to consider the molecular orbital arrangement specifically at the reactant and product positions only. Another approach is that of Hudson³⁶ who uses a perturbation treatment to deal with a small region on the potential energy surface that is only very close to the reactant (or product) state. A further and very different approach has been reported by George and Ross^{10a} who treat the problem from the vantage point of collision theory to assess the consequences of symmetry conservation on the transition matrix.

In the following, a general wave function description is developed for reacting systems that allows for both the Wigner–Witmer and Woodward–Hoffmann treatments to be applied. The corresponding symmetry conservation rules are described and their effects on the electronic energy of the system are assessed. These energy considerations lead to a justification for the operation of the symmetry rules, since the feasibility of a reaction is related to the height of the energy barrier encountered by the system along the given reaction path. Finally, several examples of the qualitative application of these rules to the same chemical systems are presented to illustrate the relationship between the two approaches.

I. Wigner–Witmer Rules

Since all spin and nuclear effects are separated from the electronic orbital motions in the current regime, the wave function description of a reaction system need only be concerned with the electronic orbital or spatial characteristics. Of particular interest is the assignment

(37) M. Born and R. Oppenheimer, *Ann. Phys. (Leipzig)*, **84**, 457 (1927).

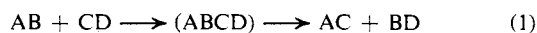
(38) P. A. M. Dirac, "The Principles of Quantum Mechanics," 4th ed, Oxford University Press, London, 1958, p 115.

(39) R. Englman, "The Jahn–Teller Effect in Molecules and Crystals," Wiley-Interscience, London, 1972.

(40) F. A. Cotton, "Chemical Applications of Group Theory," Interscience, New York, N. Y., 1963.

of orbital symmetry labels derived from the molecular point group corresponding to the geometrical conformation of the nuclear framework.

Consider the following bimolecular chemical reaction.



Following Shuler's extension⁶ of the Wigner–Witmer rules, the reactant wave function, ψ_R , is obtained by taking a properly antisymmetrized product of wave functions: one, ψ_{AB} , describing the AB molecule and constructed from molecular orbitals spanning the space of AB; and the other, ψ_{CD} , describing the CD molecule and built from CD molecular orbitals. Thus, one obtains

$$\psi_R = \mathcal{A}[\psi_{AB}\psi_{CD}] \quad (2)$$

where \mathcal{A} is the appropriate antisymmetrization operator which makes ψ_R satisfy the Pauli principle⁴¹ for fermions. The total symmetry of each of the two isolated constituents ψ_{AB} and ψ_{CD} must be resolved into a linear combination of symmetry species corresponding to the point group of the intermediate complex, ABCD of eq 1. This resolution is easily accomplished by means of available symmetry correlation tables.^{3,6,7} This procedure imposes certain geometrical restrictions on the system since particular symmetry elements in the original point group of one of the reactant molecules must be aligned so as to coalesce into certain symmetry elements in the point group of the complex and similarly for the point group symmetry elements of the other reactant. The symmetry of the total reactant function, ψ_R , is then obtained by taking the direct product of the set of resolved symmetry species of AB with those of CD. This process produces a manifold of possible symmetry species corresponding to ψ_R in the point group of the incipient intermediate complex arising from the reactants.

The product wave function, ψ_P , is built from wave functions that describe the AC and BD systems as follows.

$$\psi_P = \mathcal{A}[\psi_{AC}\psi_{BD}] \quad (3)$$

Here, as in the reactant case, the total symmetry of each of the two isolated constituents, ψ_{AC} and ψ_{BD} , must be resolved into a linear combination of symmetry species of the point group of the intermediate complex. Taking the direct product of the AC with the BD symmetry species gives the manifold of species corresponding to ψ_P in the point group of the complex.

In order for the reactants and products to correlate, the symmetry conservation rule states that the intermediate complex, formed during the reaction, must have at least one symmetry species in its term manifold that arises both from the resolved reactant and resolved product manifolds. The entity of symmetry being conserved from reactant to product wave function is therefore a total electronic orbital symmetry or state symmetry, as opposed to an individual electronic orbital symmetry. That is, the combination of reactants must form at least one total electronic state symmetry that can also be produced from the combination of product molecules, and these state symmetries must be correlated by a resolution through the point group of an appropriate intermediate complex.

(41) W. Pauli, Jr., *Z. Phys.*, **31**, 765 (1925).

The total wave function ψ corresponding to the given reaction system is formed from a linear combination of the reactant and product wave functions

$$\psi = C_R\psi_R + C_P\psi_P \quad (4)$$

where the C 's are appropriate linear coefficients. This represents a two-state variational wave function approximation, or in valence bond language, the total description ψ arises from the two structures, reactant ψ_R and product ψ_P . Initially, C_R would have a magnitude close to unity and C_P would have a magnitude close to zero. At the end of the reaction process, these values would be interchanged. Throughout the process, the structures ψ_R and ψ_P would retain the localized descriptions indicated by the subscripts in eq 2 and 3, respectively. Symmetry conservation implies a matching of the set of possible state symmetries of ψ_R with those of ψ_P . These concepts regarding ψ are further developed in the sequel.

II. Woodward–Hoffmann Rules

Following the general procedures of the preceding section, the total electronic wave function description of a chemical reaction system to be used within the context of the Woodward–Hoffmann rules is again a two-state configuration interaction approximation.^{34,35} Thus, the total wave function ψ for any reaction system has the same form as that given in eq 4 although the reactant and product structures, ψ_R and ψ_P , are constructed in a different manner.

Again, consider the reaction given in eq 1. Here, molecular orbitals are formed that span the entire AB + CD reactant system. A localization to a reactant description is indicated by writing the reactant wave function ψ_R in terms of the fully antisymmetrized wave function ψ_{AB+CD} as follows.

$$\psi_R = \psi_{AB+CD} \quad (5)$$

The product structure ψ_P is composed of molecular orbitals spanning the space of AC + BD.

$$\psi_P = \psi_{AC+BD} \quad (6)$$

As before, these structures retain localized reactant and product characteristics, respectively, throughout the reaction process. The geometrical conformation of the nuclear framework is constrained to conform to a certain symmetry point group that is present during the reactant, intermediate complex, and product stages. This allows each of the molecular orbitals to be labeled with a symbol corresponding to the irreducible symmetry species that it represents.

In order for the reactants and products to correlate, the symmetry conservation rule states that the symmetries of each of the individual principal occupied molecular orbitals of the reactant structure must be the same as the symmetries of the individual principal occupied molecular orbitals of the product structure. For an N -electron system, the entity of symmetry being conserved from reactant to product wave function is therefore a set of N individual electronic molecular orbital symmetries. That is, the symmetry of each occupied molecular orbital in the reactant wave function must correlate with a similarly occupied orbital of the same symmetry in the product wave function.

In addition to these individual electronic orbital

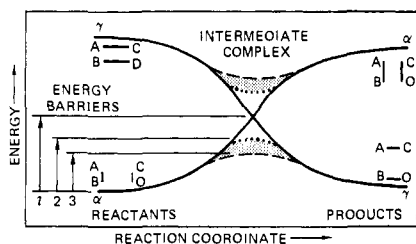


Figure 1. The energy as a function of reaction coordinate for the hypothetical bimolecular process. Solid curves represent energy of wavefunctions describing "reactant" $AB + CD$ (α) and "product" $AC + BD$ (γ) structures. No interaction between curves α and γ gives high energy barrier indicated by the arrow labeled 1 on the left of the diagram; the exchange interaction between α and γ gives the dotted curve and energy barrier 2; and full interaction between α and γ gives the dashed curve corresponding to barrier 3.

symmetry labels, each of the N -electron structures, ψ_R and ψ_P of eq 5 and 6, has total electronic orbital symmetry or state symmetry as well. This state symmetry can be obtained from the successive direct products of the N individual orbital symmetries corresponding to each occupancy of a molecular orbital. This total symmetry quantity finds its usefulness in relating the Woodward-Hoffmann and Wigner-Witmer rules to one another.

The use of a two-term expression for ψ provides needed flexibility for the present purposes over the conventional use of a single-determinantal approach.¹⁴ This is especially true in the region of the intermediate complex and particularly when energy considerations are tackled. The qualitative results are nevertheless equivalent for both the present regime and the canonical description of these symmetry rules.¹⁴

III. Energy Considerations

The motions of the nuclei, as they pass from a reactant conformation into a product conformation, constitute a chemical reaction path. The relative probability that the reaction might follow a given path depends on the relative ease with which the nuclei can traject this path. Since the electronic energy is assumed to be playing the role of an effective internuclear potential, the feasibility of a given reaction depends upon the nature of the electronic energy profile along the reaction coordinate. In particular, a reaction path encountering a high electronic energy barrier is associated with a low reaction probability, while a reaction path encountering a lower electronic energy barrier is associated with a higher reaction probability. Since the orbital symmetry characteristics of reactant and product wave functions can strongly influence the relative magnitude of these electronic energy barriers, these symmetry characteristics become useful indices for predicting the relative heights of these barriers and, hence, for predicting the relative feasibilities of various reaction paths. Thus a justification for the operation of the symmetry rules can be developed on the basis of electronic energy and symmetry considerations. In this section, the symmetry properties of the wave functions, developed in the preceding sections, are used to assess the electronic energy along the entire course of a reaction from reactants to products, including the point where the maximum energy barrier occurs. In this way, the relationship between the Wigner-Witmer and Wood-

ward-Hoffmann rules is elucidated and their operation justified.

An appropriate electronic wave function ψ has been defined in eq 4 to describe the motions of the electrons during the course of a chemical reaction. The feasibility of the reaction process is determined by the nature of the energy expectation value E along the reaction coordinate as follows

$$E = \langle \psi | \mathcal{H} | \psi \rangle / \langle \psi | \psi \rangle \quad (7)$$

with the Hamiltonian \mathcal{H} given by

$$\mathcal{H} = \sum_{\alpha < \beta} Z_{\alpha} Z_{\beta} / R_{\alpha\beta} + \sum_i (-1/2 \nabla_i^2 - \sum_{\alpha} Z_{\alpha} / r_{\alpha i} + \sum_{j(>i)} r_{ij}^{-1}) \quad (8)$$

where α and β label nuclei, i and j label electrons, and Z_{α} is the charge on nucleus α . From eq 7, a set of secular equations is derived, from which the linear coefficients C_R and C_P of eq 4 are determined. The corresponding eigenvalues can be written as follows

$$E = \{ 1/2(\alpha + \gamma) - \beta S \pm [1/4(\alpha - \gamma)^2 + \beta^2 - \beta S(\alpha + \gamma) + \alpha\gamma S^2]^{1/2} \} (1 - S^2)^{-1} \quad (9)$$

where the energy of the reactant structure is α

$$\alpha = \langle \psi_R | \mathcal{H} | \psi_R \rangle / \langle \psi_R | \psi_R \rangle \quad (10)$$

the energy of the product structure is γ

$$\gamma = \langle \psi_P | \mathcal{H} | \psi_P \rangle / \langle \psi_P | \psi_P \rangle \quad (11)$$

the interaction, resonance or exchange energy between the two structures is termed β

$$\beta = \langle \psi_R | \mathcal{H} | \psi_P \rangle [\langle \psi_R | \psi_R \rangle \langle \psi_P | \psi_P \rangle]^{-1/2} \quad (12)$$

and since no orthogonality has been assumed to exist between the two structures, the overlap integral S is defined by

$$S = \langle \psi_R | \psi_P \rangle [\langle \psi_R | \psi_R \rangle \langle \psi_P | \psi_P \rangle]^{-1/2} \quad (13)$$

The quantities α , γ , β , and S of eq 10-13, respectively, are each strong functions of the internuclear coordinates and hence each of these quantities varies along the entire reaction path. This is illustrated in Figure 1, where the energy of a reactant structure, α , is shown to vary along the reaction coordinate from a low to a high value, whereas the energy of a product structure, γ , is shown to vary from a high to a low value as the reaction proceeds.

The basis for the operation of symmetry rules is the strong influence exerted on the energy of the system, E in eq 9, by the symmetry properties of the structures ψ_R and ψ_P through their effects on the exchange and overlap integrals, β and S of eq 12 and 13. Since the Hamiltonian transforms as the totally symmetric species of the point group of the system, the direct product of the symmetry species, Γ , of ψ_R and ψ_P

$$\Gamma[\psi_R] \Gamma[\psi_P] \quad (14)$$

must have a totally symmetric component in order for either β or S to be nonzero. This is simply a consequence of the Wigner-Eckart theorem.^{42,43} In terms of the Wigner-Witmer rules, if total symmetry is conserved

(42) A. R. Edmonds, "Angular Momentum in Quantum Mechanics," 2nd ed, Princeton University Press, Princeton, N. J., 1960, pp 73-75.

(43) P. Roman, "Advanced Quantum Theory," Addison-Wesley, Reading, Mass., 1965, pp 576-590.

(*vide supra*), then β and S can be nonzero; otherwise, these quantities vanish. This is illustrated in Figure 1 for the hypothetical reaction of eq 1. If total symmetry is not conserved, the two structures ψ_R and ψ_P do not correlate with one another and the energy expression in eq 9 reduces to $E = \alpha$, shown by the solid line in Figure 1. In other words, without total symmetry conservation, the energy states α and γ cross without interacting with one another in the vicinity of the intermediate complex. However, if total symmetry is conserved, the two structures do correlate with one another and the energy, corresponding to eq 9, lies in the shaded region of Figure 1 along the course of the reaction. In this case, the two energy states α and γ do interact and give rise to configurational mixing in the intermediate complex region. At the point along the reaction coordinate where $\alpha = \gamma$, the energy expression in the symmetry conserved case reduces to

$$E|_{\alpha=\gamma} = (\alpha \pm \beta)/(1 \pm S) \quad (15)$$

giving an energy lowering ΔE of

$$\Delta E|_{\alpha=\gamma} = \pm(\beta - \alpha S)/(1 \pm S) \quad (16)$$

over the symmetry nonconserved case.

The total electronic symmetry labels described in section II with respect to the Woodward–Hoffmann rules yield results that are identical with those just described. If total symmetry is not conserved, there is again no interaction between the two structures ψ_R and ψ_P . However, if total symmetry is conserved, then the individual electronic orbital symmetry labels give rise to a further distinction between the correlation of various reactant and product molecules. That is, the composition and value of β and S are governed by the individual electronic orbital symmetry properties of the reactant and product wave functions. To examine these effects, it is sufficient¹⁴ to consider the single determinant comprising a self-consistent-field molecular orbital approximation, the leading term in a configuration interaction series, or the principal determinant in a natural orbital expansion.³⁵

No orthogonality is assumed between reactant and product molecular orbitals or between ψ_R and ψ_P . However, since each of the reactant and product molecular orbitals has been constructed to be an eigenfunction of the particular point group that is present during the entire course of the reaction, symmetry can produce orthogonality between reactant and product molecular orbitals. Thus, in general, any one-electron molecular orbital, for instance, $\varphi_R^i(q)$, the i th molecular orbital of the reactant structure describing the q th electron, is nonorthogonal to any other molecular orbital, for instance, $\varphi_P^j(q)$, the j th molecular orbital of the product structure; however, if the symmetry species, $\Gamma[\varphi_R^i]$ and $\Gamma[\varphi_P^j]$, of the two orbitals are not identical, then the two orbitals are orthogonal by symmetry. Moreover, an N -electron determinant describing the reactants is nonorthogonal to an N -electron determinant describing the products unless there does not exist a complete concordance of symmetry species between the component molecular orbitals of the two determinants. Therefore, the overlap integral, S of eq 13, vanishes unless all individual orbital symmetries are conserved. In addition to zero-particle operators, the matrix elements of one-particle operators in \mathfrak{H} also vanish for two

determinants when all individual orbital symmetries are not conserved. The remaining terms included in β from \mathfrak{H} are the two-electron repulsion terms and these integrals allow two orbitals of the reactant structure to have symmetry species different than two orbitals of the product structure, under the following conditions: (i) all other individual orbital symmetries of the two structures must be concordant and (ii) the discordant symmetry species must be such that their direct product

$$\Gamma[\varphi_R^i(1)]\Gamma[\varphi_P^k(1)]\Gamma[\varphi_R^j(2)]\Gamma[\varphi_P^l(2)] \quad (17)$$

has a totally symmetric component of the point group of the system. Where these conditions are met, aside from orbital overlaps, the interaction term β , as written in eq 12, consists solely of two-electron exchange integral contributions and this is denoted by appending a subscript 2 on the symbol, β_2 . In this case, the energy expression of eq 9 reduces to

$$E = 1/2(\alpha + \gamma) \pm [1/4(\alpha - \gamma)^2 + \beta_2^2]^{1/2} \quad (18)$$

and is depicted by the dotted curves for the hypothetical reaction illustrated in Figure 1.

Recapitulating, where total or state symmetry is conserved and individual orbital symmetry is not conserved but nevertheless the individual symmetries satisfy the conditions set forth with respect to eq 17 above, the reactant and product states do correlate and there is an energy lowering encountered along the reaction coordinate as embodied in eq 18. Now consider again the point along the reaction path where $\alpha = \gamma$. The energy now reduces to

$$\Delta E|_{\alpha=\gamma} = \alpha \pm \beta_2 \quad (19)$$

giving an energy lowering of

$$\Delta E|_{\alpha=\gamma} = \pm\beta_2 \quad (20)$$

A reaction having the symmetry characteristics just described is termed a “forbidden” process in the Woodward–Hoffmann regime. This terminology is discussed further, *vide infra*.

The other important situation involving conservation of individual orbital symmetries gives rise to an “allowed” process in the Woodward–Hoffmann vocabulary. Here, in addition to total symmetry being conserved, each of the individual orbital symmetries is also conserved from reactant to product structures. That is, each of the symmetry species $\Gamma[\varphi_R^i]$ of the reactant structure can be matched one-for-one with identical species found in the product structure, $\Gamma[\varphi_P^j]$. Now the corresponding N -electron determinants are nonzero for zero-, one-, and two-particle operators, allowing both S and β to be nonzero, where β consists of contributions from each term appearing in \mathfrak{H} . The relevant energy expression is now eq 9 and is represented by the dashed curve in Figure 1. At the point where $\alpha = \gamma$, eq 15 and 16 are relevant and the greater energy lowering in this case, over the “forbidden” reaction described by eq 19 and 20, is seen to arise both from the full exchange interaction β and from overlap effects, S .

A comparison of the Wigner–Witmer and Woodward–Hoffmann rules can now be made *via* Figure 2. Where total orbital symmetry is not conserved, individual orbital symmetry is also not conserved and the two rules give the same answer: namely, that the reaction is “unfeasible.” In the case where total sym-

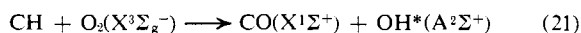
IS ORBITAL SYMMETRY CONSERVED?		WHAT IS REACTION FEASIBILITY?	
TOTAL	INDIVIDUAL	WIGNER-WITMER RULES	WOODWARD-HOFFMANN RULES
NO	NO	UNFEASIBLE	FORBIDDEN
YES	NO	FEASIBLE	FORBIDDEN
YES	YES		ALLOWED

Figure 2. The hierarchy of electronic orbital symmetry conservation showing the effect of various categories of symmetry conservation on reaction feasibility.

metry is conserved, the Woodward–Hoffmann rules make a further distinction on the basis of individual orbital symmetries, giving rise to a subtlety not considered by the Wigner–Witmer rules; namely, “feasible” reactions are further classified as “allowed” or “forbidden.” Thus, on energy grounds, there exists a three-level hierarchy of symmetry control over chemical reactions.

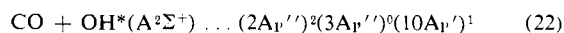
IV. Examples

A. Reaction of CH with O₂. The reaction of various electronic states of CH with ground state oxygen to yield ground state CO and excited state OH*



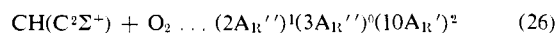
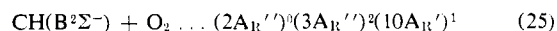
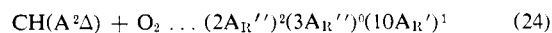
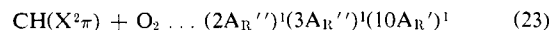
has been discussed by Shuler⁶ in connection with hydrocarbon flame reactions. The intermediate complex, CHO₂, is assumed to be planar and to possess C_s symmetry. Resolution of the symmetry species of the products into the C_s point group gives the species A' for each molecule. The resulting direct product A' × A' yields A' for the possible symmetry species of the intermediate. Resolution of the reactant O₂ symmetry species into C_s gives A''. Resolution of the ground or first excited state of CH, X²π, or A²Δ into C_s yields both A' and A'' for each state. Combining these with the A'' species of O₂ gives a manifold of possible intermediate symmetry species of A' and A''. Thus, both of these states of CH when reacted with O₂ correlate with the product species indicated in eq 21 via an intermediate of species A'. The second excited state of CH, B²Σ⁻, resolves into an A'' species of C_s and since its direct product with the O₂ species gives A'' × A'' = A', this reaction also correlates with products in the same manner as above. Finally, the third excited state of CH, C²Σ⁺, resolves into the A' species of C_s and since the direct product of A' × A'' gives A'', reaction of CH in this electronic state with O₂ does not correlate with the products given in eq 21.

In contrast to the Wigner–Witmer rules, the Woodward–Hoffmann rules require the construction of molecular orbitals spanning the planar four nuclei system. The s and p atomic orbitals lying in the plane form a set of A' molecular orbitals, while the p orbitals perpendicular to the plane form a set of A'' orbitals. For the product conformation CO + OH*, the molecular orbitals, 1 A_{P'} to 9 A_{P'} and 1 A_{P''}, are each taken to be doubly occupied and the remaining three electrons are taken to be distributed as follows.



This gives nineteen A' and four A'' orbitals and total symmetry of A'. The orbitals being referred to here describe the product conformation with bonding characteristics in CO and OH. For the reactant conforma-

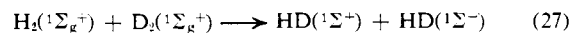
tion, CH + O₂, the corresponding molecular orbitals, 1A_{R'} to 9A_{R'} and 1A_{R''}, are also each taken to be doubly occupied and the remaining three electrons are distributed as follows.



These orbitals differ from those describing the product structure in that these orbitals describe the reactant bonding arrangement of CH and O₂. The ground and first two excited states then have nineteen A' and four A'' orbitals and total symmetry of A'. For these three reactions, both individual and total symmetry are therefore conserved as the reaction proceeds to products. With the third excited state, there are twenty A' and three A'' orbitals giving total symmetry of A'' and neither individual nor total symmetry is conserved.

The Wigner–Witmer and Woodward–Hoffmann rules therefore give equivalent results for the reaction in eq 21. In particular, the reactions involving the first three electronic states of CH are “feasible” processes, whereas the reaction involving the C²Σ⁺ state of CH is “unfeasible.”

B. Bimolecular Hydrogen–Deuterium Exchange. The chemical exchange reaction between ground state hydrogen and deuterium molecules to form the mixed isotope, diatomic HD



is easily subjected to the two symmetry rules. Assuming a planar complex for the geometry of the four-atom intermediate,⁶ the Σ_g⁺ symmetry of each reactant is resolved into A' species of the C_s point group. The direct product of the resulting two A' species is A' × A' = A'. The Σ⁺ species of each product molecule is also resolved into the A' representation of C_s. Therefore, total symmetry is conserved through an A' intermediate state. With respect to the C_s point group, the Woodward–Hoffmann rules give this same result, since the four electrons each occupy an orbital of A' symmetry in both reactant and product configurations and consequently total and individual orbital symmetries are conserved. Through C_s symmetry, the reaction is therefore both “feasible” and “allowed.”

However, from the Woodward–Hoffmann point of view, the symmetry of C_s is too low to be useful in this case since no symmetry element of the group bisects a bond that is made or broken during the reaction.¹⁴ Hence, higher symmetries are of more interest;^{44,45} for instance, a rectangle–square–rectangle geometrical arrangement, where the nuclei are situated at the corners of a rectangle in the reactant stage, form a square intermediate and form a new rectangle in the product conformation, maintaining D_{2h} symmetry throughout. For Wigner–Witmer rules, the Σ_g⁺ and Σ⁺ species each resolve into A_g species of D_{2h} and again total symmetry is conserved. For Woodward–Hoffmann rules, the four electrons in the reactant structure occupy two A_g and two B_{3u} molecular orbitals in the D_{2h} group giving a total symmetry of A_g. The product structure is

(44) R. Hoffmann, *J. Chem. Phys.*, **49**, 3739 (1968).

(45) D. M. Silver, *Chem. Phys. Lett.*, **14**, 105 (1972).

comprised of two A_g and two B_{2u} orbitals corresponding to A_g total symmetry. Again, in agreement with the Wigner–Witmer rules, total symmetry is conserved. However, the individual orbital symmetries are not conserved and, although the reaction can be considered “feasible” on total symmetry grounds, it is a “forbidden” reaction on individual symmetry grounds through the D_{2h} point group. This same result is found when a number of other higher symmetry groups are examined⁴³ for this reaction.

C. Butadiene–Cyclobutene Stereoisomerization. The classic example¹¹ of an electrocyclic, ring-chain stereoisomerization is that of butadiene–cyclobutene depicted in Figure 3. Only the four p-type orbitals, situated one per carbon atom, need be considered in order to ascertain whether the disrotatory or conrotatory process¹¹ is most likely to occur.

With respect to a mirror plane of symmetry perpendicular to the plane of the four carbon nuclei and bisecting the BC internuclear axis, the reactant butadiene molecule has two A' and two A'' orbitals, giving a total symmetry of A' . All four occupied product cyclobutene molecular orbitals have the symmetry species A' , giving rise to a total symmetry of A' . Here, total symmetry is conserved but individual symmetry is not conserved and the disrotatory reaction is termed “feasible” on the former grounds but “forbidden” on the latter grounds.

With respect to a two-fold axis of symmetry lying in the plane of the four carbon nuclei and bisecting the BC axis, there are two A and two B occupied reactant butadiene orbitals, giving total symmetry of A . The symmetry species of the occupied product cyclobutene orbitals is also two A and two B , with total symmetry A . Therefore, both total and individual orbital symmetries can be conserved for this conrotatory process, making it both a “feasible” and “allowed” reaction.

By considering only total orbital symmetries, Wigner–Witmer-type rules would predict both the disrotatory and conrotatory modes of reaction to be equally feasible. Consideration of individual orbital symmetries allows the further distinction to be drawn regarding the relative feasibility of these two reaction paths.

There is an important consequence of the fact that there are two distinct reaction paths involved in this example: namely, that along each path (conrotatory and disrotatory) there is a distinct set of reaction path dependent quantities, α , γ , β , and S of eq 10–13, respectively. This is particularly evident for S , since S vanishes along the disrotatory path but not along the conrotatory, and also for β , which reduces to β_2 along the disrotatory but not along the conrotatory path. In addition, it is equally true that α (disrotatory) and γ (disrotatory) differ from α (conrotatory) and γ (conrotatory), respectively, along the two reaction paths. These latter sets of quantities differ from one another both because of symmetry-imposed differences in the electronic structures along the two paths and because the nuclear geometries should differ in general along the two different paths. Hence, it is not simply the energy lowerings of eq 16 for the symmetry conserved conrotatory process and of eq 20 for the symmetry nonconserved disrotatory process that alone can be compared to one another to assess the relative favorability of one mode of reaction over the other. This is because

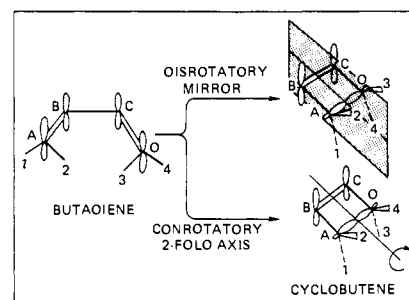


Figure 3. Two possible modes of ring closure are depicted for the butadiene–cyclobutene isomerization. The disrotatory and conrotatory reactions produce different stereoisomers as indicated by the substituent labels 1 to 4 on the product molecules.

the two energy lowerings refer to two different reference energies, α (conrotatory) and α (disrotatory), located at different positions on the potential energy surface. However, the full energy expressions, of eq 9 for conrotatory and eq 18 for disrotatory, are valid over the entire course of the respective reaction paths. Proper quantitative comparisons of the two modes of reaction can therefore be made *via* eq 15 and 19, when the energy at the intermediate point along each path corresponds to the maximum barrier.

V. Discussion

The chemical reactions treated thus far all involve the rearrangement of various nuclei from reactant positions into product conformations. Although nuclear motions perform a central role in these chemical reactions, the concern throughout this work has not been with nuclear motion per se but rather with the internuclear potential that governs this nuclear motion. The possible occurrence of violations of the electronic orbital symmetry rules and the further influence on reaction feasibility due to the effect of nuclear motions are discussed in the present section.

There is a distinction between “violation” of the electronic orbital symmetry rules and “nonapplicability” of these rules. The applicability of the rules extends over systems for which (a) effects due to the Born–Oppenheimer approximation are negligible, (b) nuclear angular momenta, electronic spin angular momenta, and electronic orbital angular momenta are separately conserved, (c) electronic spin interactions and nuclear dynamic effects are negligible, and (d) elements of symmetry exist among the nuclear positions along the course of the reaction path. A proper formulation of the symmetry rules must include these conditions as prerequisites. It is important to realize that if these constraints are not obeyed with respect to a given system, then the electronic orbital symmetry rules cannot strictly be applied to that system. These constraints therefore represent a limitation on the *universality* of the symmetry rules. Indeed, several examples of chemical systems have been cited^{10a} (although incorrectly designated to be violations, *vide infra*) for which one or another of these conditions do not hold and for which therefore the rules cannot logically be applied.

It is with respect to the subset of chemical reactions, for which the conditions a–d hold true, that the total electronic energy (internuclear potential) can be evaluated from appropriate electronic wave functions as in

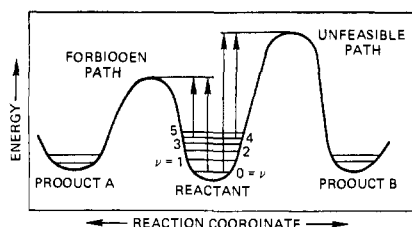


Figure 4. The energy as a function of reaction coordinate for a hypothetical reaction involving two alternative pathways. The electronic orbital symmetry properties of reactant, product A, and product B are assumed to be such that the reaction from reactant to product A is forbidden, while reaction to product B is unfeasible. Arrows indicate the magnitude of energy barriers for the two reaction paths with respect to each of two initial nuclear states, $\nu = 0$ and $\nu = 4$.

section III and the effects of various electronic orbital symmetry situations can be assessed. Thus, it is under these conditions that the electronic orbital symmetry rules predict the relative heights of the electronic energy barriers along certain reaction paths: namely, along an allowed path, the barrier is predicted to be lower than the barrier along a forbidden path; and similarly, the barrier along a forbidden path is predicted to be lower than the barrier along an unfeasible path. A violation of these rules, with respect to a given chemical reaction, must consist of the observation that conditions a–d are satisfied and the predicted ordering of barrier heights is incorrectly specified by the rules. If a violation of these rules is to be found, it must be sought among those chemical systems for which the rules can properly be applied: *i.e.*, the above prerequisite constraints must be satisfied. In this sense, there has not yet been a demonstration of a true violation of the rules.

It should be noted, however, that the symmetry rules have had an enormous impact precisely in cases where condition d, regarding symmetry among nuclear positions, is not strictly satisfied, *e.g.*, the butadiene-cyclobutene isomerization where the presence of various nonequivalent substituents, numbered 1–4 in Figure 3, violates condition “d” in a strict sense, but nevertheless, these same substituents provide both the motivation for the rules and the means for distinguishing between the conrotatory and disrotatory modes of reaction. In such cases, the substituent groups are considered to be peripheral to the reaction zone and hence, as an *approximation*, the effects of these peripheral groups on the reaction process are considered to be negligible. To a large extent, this approximation is found¹⁴ to be valid; however, it is certainly conceivable that there might be molecular situations where this approximation may not be valid. In particular, the presence of a certain peripheral substituent might lead to steric hindrance in a product conformation or hindered rotation along a certain reaction path. This could lead to an inaccessibly high product state energy, γ , or an unusually high barrier along the reaction path, causing an otherwise “allowed” reaction to be rendered unfavorable. The energy considerations of section III take account of such effects by consistently employing total wave functions which, in principle, contain all such pertinent information about the reaction system. Thus, although such effects may not necessarily be evident in a simple qualitative application of the symmetry rules, quantitative predictions based on calculations using the energy

expressions of section III should always agree with the corresponding experimental observations.

Further consideration of condition “a” is warranted since, even within the confines of the Born–Oppenheimer approximation, the effects of nuclear motions can alter the character of a chemical reaction.^{9, 23, 46–48} Such considerations can be appreciated by reference to Figure 4. Consider the reactant species to be in a certain nuclear state (*e.g.*, nuclear vibrational state, $\nu = 0$). The characteristics of the internuclear potential along the two alternative reaction coordinates are determined by the electronic orbital symmetry properties of the reactant species and the product A and product B species. The material in section III of the present work provides expressions for the energy as a function of reaction coordinate, including the maximum barrier position, for the various symmetry situations. In the example given in Figure 4, the “forbidden” path has the lower energy barrier and thus from strictly static, electronic considerations, the “forbidden” path toward product A is predicted to be the more feasible of the two alternatives. Now consider the effect of the initial nuclear state on the reaction feasibility. Reaction from the lowest nuclear state (*i.e.*, $\nu = 0$) should be less feasible than reaction from a higher nuclear state (*e.g.*, $\nu = 4$), since the effective energy barriers with respect to these two states are considerably different. Moreover, reaction along the “forbidden” path might be entirely inaccessible due to the magnitude of the barrier with respect to the lower nuclear state but easily accessible from the higher nuclear state. In the absence of the forbidden path, even the “unfeasible” reaction mode to product B could possibly become accessible if enough energy were present in appropriate modes of nuclear motion including vibration, rotation, and translation. These and other effects arising from nuclear motion itself as well as temperature and pressure effects need to be assessed from appropriate dynamical and statistical considerations. That such strictly dynamic, nuclear considerations are important to an absolute determination of reaction feasibility does not, however, negate the importance and usefulness of the underlying electronic aspects that provide the overall character of the internuclear potential. That is to say, within the confines and constraints under which the electronic orbital symmetry rules are properly defined, these rules can be expected to play a dominant and legitimate role in the elucidation of chemical reaction phenomena.

VI. Conclusions

Group theory and symmetry are extremely useful tools in many areas of molecular quantum mechanics. In the present context, symmetry is used for the evaluation of matrix elements between wave functions representing reactant and product structures along the course of a reaction coordinate. In particular, the total orbital symmetry of an N -electron wave function and the N individual electronic orbital symmetries of the N electrons comprising the system are used to separate symmetry rules into a hierarchy of three levels, indicated in Figure 2. Quantitative energy relations between these various categories of reaction feasibility can be obtained from eq 9, where electron spin interactions,

(46) R. F. W. Bader, *Can. J. Chem.*, **40**, 1164 (1962).

(47) L. Salem, *Chem. Phys. Lett.*, **3**, 99 (1969).

(48) L. Salem and J. S. Wright, *J. Amer. Chem. Soc.*, **91**, 5947 (1969).

coupling of electronic and nuclear motions, and other nuclear dynamic effects can be assumed to be negligible. It should be emphasized that the same fundamental basis governs the operation of both sets of symmetry rules and in this respect the two sets of rules are fundamentally similar.

The examples, given in section IV, show that Wigner-Witmer and Woodward-Hoffmann rules give equivalent results to the extent that *total* orbital symmetry can be useful but that the Woodward-Hoffmann rules can often provide a further distinction between possible reaction paths by considering *individual* orbital symmetries as well. The examples include cases where total symmetry is sufficient to analyze a reaction and

also cases where an examination of individual symmetries is required.

The hierarchy of symmetry control rests on the occurrence of energy barriers of different heights being encountered, along various reaction coordinates, corresponding to the degree of concordance or discordance of symmetry species from reactant to product wave function structures. The possible experimental observation of "forbidden" processes^{2,3,29-33} presages the need to emphasize that these different barrier heights do not control the reaction destiny in an absolute sense but only affect the various probabilities of reaction along different paths. However, for many purposes,¹⁴ this degree of reaction control is quite important.

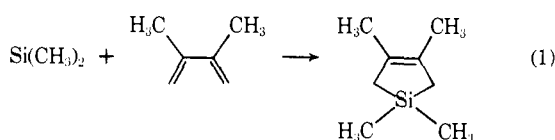
Ground Electronic State of Silylene¹

O. F. Zeck, Y. Y. Su, G. P. Gennaro, and Y.-N. Tang*²

Contribution from the Department of Chemistry, Texas A & M University, College Station, Texas 77843. Received September 7, 1973

Abstract: Silylene-³¹Si adds to 1,3-butadiene to give silacyclopent-3-ene-³¹Si. Studies using nitric oxide as a scavenger demonstrate that the reacting silylene is present as 80% triplet and 20% singlet, while studies using neon as a moderator prove that the ground electronic state of silylene is a singlet.

The chemistry of silylene and its derivatives has been the subject of several recent review articles.³⁻⁵ Ever since dimethylsilylene was formed by the reduction of dimethyldichlorosilane and trapped through the Si-H insertion process in the pioneering work of Skell and Goldstein,⁶ numerous investigations on reactions of various substituted silylenes have been performed.³⁻⁵ One such investigation which pertains to our study is the addition of dimethylsilylene to 2,3-dimethyl-1,3-butadiene.⁷



It was further established that conjugated dienes were more reactive toward dimethylsilylene than molecules with only one double bond.⁴ While studies such as these have provided a considerable amount of information about substituted silylenes, the knowledge about unsubstituted silylene, SiH₂, itself is rather limited.

Silylene has been successfully produced by two different methods: (i) the nuclear recoil technique which

was developed by Gaspar and coworkers,⁸⁻¹² and (ii) the decomposition studies stemming from the pyrolysis and photolysis of compounds such as SiH₄ and Si₂H₆.¹³⁻¹⁷



The only well-established silylene reaction to date is the insertion of SiH₂ into Si-H bonds.^{8,9,11-16}



The possible insertion of silylene into other types of bonds such as Si-Si bonds has also been suggested.^{11,15} On the other hand, it has been demonstrated that SiH₂ is inert toward C-H, C-C, and Si-C bonds.³⁻⁵ The predicted products from the silylene addition to olefins are substituted silacyclopropanes which have never been detected experimentally.^{9,15} Their absence can be explained by the instability of such highly

(8) P. P. Gaspar, B. D. Pate, and W. C. Eckelman, *J. Amer. Chem. Soc.*, **88**, 3878 (1966).

(9) P. P. Gaspar, S. A. Bock, and W. C. Eckelman, *J. Amer. Chem. Soc.*, **90**, 6914 (1968).

(10) P. P. Gaspar, S. A. Bock, and C. A. Levy, *Chem. Commun.*, 1317 (1968).

(11) P. P. Gaspar and P. Markusch, *Chem. Commun.*, 1331 (1970).

(12) P. P. Gaspar, P. Markusch, J. D. Holten III, and J. J. Frost, *J. Phys. Chem.*, **76**, 1352 (1972).

(13) M. A. Nay, G. N. C. Woodall, O. P. Strausz, and H. E. Gunning, *J. Amer. Chem. Soc.*, **87**, 179 (1965).

(14) J. H. Purnell and R. Walsh, *Proc. Roy. Soc., Ser. A*, **293**, 543 (1966).

(15) M. Bowrey and J. H. Purnell, *J. Amer. Chem. Soc.*, **92**, 2594 (1970).

(16) P. Estacio, M. D. Sefcik, E. K. Chan, and M. A. Ring, *Inorg. Chem.*, **9**, 1068 (1970).

(17) I. DuBois, G. Herzberg, and R. D. Verma, *J. Chem. Phys.*, **47**, 4262 (1967).

(18) P. S. Skell and E. J. Goldstein, *J. Amer. Chem. Soc.*, **86**, 1442 (1964).

(1) Preliminary information concerning this work was reported in, G. P. Gennaro, Y.-Y. Su, O. F. Zeck, S. H. Daniel, and Y.-N. Tang, *J. Chem. Soc., Chem. Commun.*, 637 (1973).

(2) Address correspondence to this author.

(3) I. M. T. Davidson, *Quart. Rev., Chem. Soc.*, **25**, 111 (1971).

(4) W. H. Atwell and D. R. Weyenberg, *Angew. Chem., Int. Ed. Engl.*, **8**, 469 (1969).

(5) P. P. Gaspar and B. J. Herold in "Carbene Chemistry," 2nd ed, W. Kirmse, Ed., Academic Press, New York, N. Y., 1971.

(6) P. S. Skell and E. J. Goldstein, *J. Amer. Chem. Soc.*, **86**, 1442 (1964).

(7) W. H. Atwell and D. R. Weyenberg, *J. Amer. Chem. Soc.*, **90**, 3438 (1968).