negative net charge (the C_β and, possibly, O atom),[4g-i] thus confirming the view that the *intrinsic* positional selectivity of simple heteroaromatic toward powerful ionic electrophiles is governed by factors strictly related to the charge distribution developed in the encounter pair.

The preferred O and C_α substitution previously observed when the gaseous electrophile is a bidentate ion ($CH_3FCH_3^+$ or t-$C_4H_9^+$) is therefore attributed to a preliminary "hydrogen-bond-like" interaction (prevented in $^3HeT^+$) between the hydrogens of the electrophile and the hard site (the n electrons) of furan, which would favor α substitution.[20]

The available gas-phase experimental results are in good agreement with recent semiempirical calculations of the attractive potentials generated by the interaction of an isolated molecule of **1**–**4** and a positively charged electrophile.[21b] It should be emphasized that the agreement is complete when the experiments are carried out under conditions as close as possible to the ideal ones of theoretical calculations. Thus, use of a free unsolvated heteroaromatic molecule and the gaseous electrophile $^3HeT^+$ (which can be reasonably assumed as a positive point charge) shows that the aforementioned theoretical approach correctly predicts site selectivity in heteroaromatic substitution, without requiring those forced assumptions necessary to provide a theoretical justification for data obtained in solution, i.e., under conditions totally different from those pertaining to the theoretical approach itself.[21]

Conclusions

The essential features of gas-phase electrophilic substitution on simple five-membered heteroaromatics are exhibited by the gas-phase reaction of $^3HeT^+$ ions, formed from the β decay of molecular tritium, with pyrrole, *N*-methylpyrrole, furan, and thiophene. The low substrate discrimination of the $^3HeT^+$ ion, comparable with that observed in related substitutions with gaseous electrophiles, such as $CH_3FCH_3^+$ and t-$C_4H_9^+$,[3] can be explained by the exceedingly high reactivity of the unsolvated ionic reactant. The *intrinsic* directive properties of simple heteroaromatics toward powerful gaseous electrophiles, especially $^3HeT^+$, are found to correlate well with theoretical predictions based upon the molecular electrostatic potential established in the encounter pair.[21] In particular, β (and Y) substitution predominantly takes place in furan and pyrrole, β attack in *N*-methylpyrrole, and α displacement in thiophene. This kinetic behavior appears in substantial disagreement with the conclusions of related gas-phase ICR investigation based on the behavior of $C_4H_5Y^+$ species after attaining thermodynamic equilibrium.[15,22]

Acknowledgment. The authors wish to express their gratitude to Dr. Arturo Razzini for his interest in the present work and useful suggestions in the preparation of substituted heteroaromatics. Acknowledgment is also due to the Mass Spectrometry Service of the Area della Ricerca di Roma, C.N.R., for running the CIMS experiments.

Registry No. 1, 109-97-7; **2**, 96-54-8; **3**, 110-00-9; **4**, 110-02-1; $^3HeT^+$, 87568-71-6.

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(20) Pepe, N.; Speranza, M. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1179–1186.

(21) (a) Politzer, P.; Weinstein, H. *Tetrahedron* **1975**, *31*, 915–923. (b) Chou, D.; Weinstein, H. *Ibid.* **1978**, *34*, 275–286. (c) Politzer, P.; Donnelly, R. A.; Daiker, K. C. *J. Chem. Soc., Chem. Commun.* **1973**, 617. (d) Bertheir, G.; Bonaccorsi, R.; Scrocco, E.; Tomasi, J. *Theor. Chim. Acta* **1972**, *26*, 101–105.

(22) Houriet, R.; Schwarz, H.; Zummack, W. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 905–906.

Qualitative Valence Bond Theory and Firestone's Extended Diradical for 1,3-Dipolar Cycloadditions

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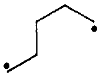
Abstract: A qualitative valence bond analysis of the nature of Firestone's extended diradical



for the "1,3-dipolar" cycloaddition reaction is provided. It is deduced that the ground state for this species corresponds approximately to a (geometrically) nonsymmetrical transition state for a concerted mechanism for the cycloaddition. It is also deduced that the energy minimum for an electronic excited state lies immediately above this transition state. The excited state does not correlate with the ground states of the reactants or the cycloaddition product. If it is populated, subsequent reaction may lead to H atom abstraction and oxime product formation, as is observed to occur together with cycloaddition, for the thermal reaction of PhCNO with PhCCH. If the transition state for the cycloaddition has a symmetrical geometry, Firestone's cyclo diradical

corresponds neither to the transition state nor to an intermediate, but rather to an entity whose electronic structure lies between that of the transition state and the cycloaddition product. The excited state that lies immediately above the symmetrical transition state is probably not thermally accessible. Regardless of the geometry, a two-step mechanism will pertain if secondary structures, which involve the transfer of at least one electron between the reactants, are dominant after the first transition state has been reached.

The controversy between Huisgen[1] and Firestone[2] concerning the mechanism for 1,3-dipolar reactions—for example, benzonitrile oxide + phenylacetylene (**1**) → 2,5-diphenylisoxazole (**3**)—is longstanding. Whereas Huisgen has postulated that the mech-

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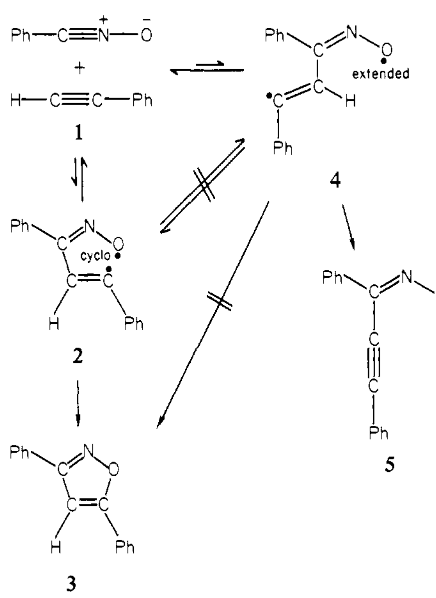


anism is concerted, Firestone has proposed a two-step mechanism, which is assumed to proceed via a cyclo spin-paired diradical intermediate, **2**. The existence of extended diradical intermediates such as **4** is also assumed in order to account for the formation on occasions of 1,4-addition products such as the oxime **5**.[3] Of course the intermediates **2** and **4** for Firestone's mechanisms do not correspond to the initial transition states in Firestone's theory. These are attained prior to the formation of and at a higher energy than the intermediates.

The results of different molecular orbital calculations[9-16] for the cycloaddition reaction have provided support for both the one-step and two-step mechanisms (see ref 15 and 16 for recent discussions of the conclusions obtained from these calculations). The most recent of these are the ab initio studies reported in ref 16 for the cycloaddition of fulminic acid to acetylene. The transition state for this reaction is calculated to be highly unsymmetrical,[17] with a geometry resembling that of the extended diradical **4**. Using RHF/4-31G + 3 × 3 CI procedures, Hiberty et al.[16] have calculated the optimized geometries of **6** and **7** for

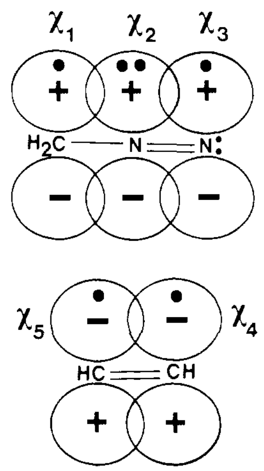
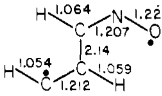


Figure 1. Atomic orbitals for separated reactants.



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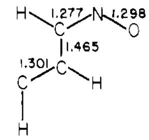

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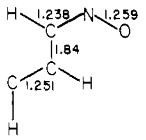

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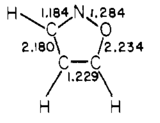

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the extended transition state and an extended diradical intermediate, with an energy separation of 1.1 kcal mol^{-1}. A further refined CIPSI calculation gave the geometry of **8** for the extended transition state, whose energy is 3.6 kcal mol^{-1} lower than that for a cyclo transition state. (The ab initio geometry of **9** calculated by Komornicki et al.[14] for the latter species is similar to that reported by Poppinger.[9]) Hiberty et al. have concluded[16] that because the extended transition state is of lower energy, Firestone's diradical mechanism "merits serious consideration" at least for this and some related cycloaddition reactions. It is also claimed that if the diradical mechanism passes through **4**, "Huisgen's and Firestone's proposals are unreconcilable".

The purpose of the present paper is to use qualitative valence bond theory to suggest that there are at least two entities that could correspond to Firestone's extended diradical. If the cycloaddition proceeds by means of a concerted mechanism, one of these entities corresponds to the transition state. We shall then deduce that another extended diradical species also exists; it corresponds to an electronic excited state whose energy minimum lies immediately above the transition state for the concerted mechanism. Thus with the aid of qualitative valence bond theory, we are proposing a reinterpretation of the nature of the extended diradical species. Further comments concerning the nature of Firestone's cyclo diradical **2**, which we have discussed previously,[5-8] for essentially symmetrical transition states will also be provided. We consider that the difference between cyclo and extended diradicals for cycloadditions is one of degree but not of kind and that Huisgen's and Firestone's mechanisms are not entirely unreconcilable. We shall also show that if secondary charge-transfer structures are dominant beyond an initial transition state, then a second transition state will arise, and therefore a two-step

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(1) Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 565, 633; *J. Org. Chem.* **1968**, *33*, 2285; **1976**, *41*, 403; *Pure Appl. Chem.* **1981**, *53*, 171.

(2) Firestone, R. A. *J. Org. Chem.* **1968**, *33*, 2285; *J. Chem. Soc. A.* **1970**, 1570; *J. Org. Chem.* **1972**, *37*, 2181; *Tetrahedron* **1977**, *33*, 3009.

(3) In **1-5**, we have used Firestone's valence bond representation, as is displayed in Scheme I of ref 4. These are not necessarily the optimum valence bond structures—especially for the 1,3-dipolar molecule; see, for example, ref 5-8.

(4) Firestone, R. A. *Lect. Heterocycl. Chem.* **1980**, *5*, S-89.

(5) Harcourt, R. D. *J. Mol. Struct.* **1972**, *12*, 351.

(6) Harcourt, R. D. *Tetrahedron* **1978**, *34*, 3125; **1979**, *35*, 901.

(7) Harcourt, R. D.; Roso, W. *Can. J. Chem.* **1978**, *56*, 1093.

(8) Harcourt, R. D. "Qualitative Valence-Bond Descriptions of Electron-Rich Molecules" Springer-Verlag: New York, 1982; p 239. A list of typographical errata for this reference, and also for ref 21, is available from the author. In particular on p 70, an O-O Pauling "3-electron bond" can be developed between a pair of oxygen atoms for NO_3 and CO_3^- with C_{2v} symmetry. The three electrons occupy $\bar{\pi}$ orbitals; cf. p 133 where $\bar{\pi}$ should replace π. Also, replace trans with gauche on p 45, line 8.

(9) Poppinger, D. *J. Am. Chem. Soc.* **1975**, *97*, 7486; *Aust. J. Chem.* **1976**, *29*, 465.

(10) Dewar, M. J. S. *Faraday Discuss. Chem. Soc.* **1977**, *62*, 197. Dewar, M. J. S.; Olivella, S.; Rzepa, H. S. *J. Am. Chem. Soc.* **1978**, *100*, 5650.

(11) Caramella, P.; Houk, K. N.; Domelsmith, L. N. *J. Am. Chem. Soc.* **1977**, *99*, 4511. For frontier molecular orbital studies of 1,3-dipolar cycloaddition reactions, see: Houk, K. N. *Acc. Chem. Res.* **1975**, *8*, 361 and ref 12.

(12) Sustmann, R. *Tetrahedron Lett.* **1971**, 2717, 2721; *Pure Appl. Chem.* **1974**, *40*, 569. Sustmann, R.; Trill, H. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 838.

(13) Leroy, G.; Nguyen, M. T.; Sana, M. *Tetrahedron* **1978**, *34*, 2459. Leroy, G.; Sana, M.; Burke, L. A.; Nguyen, M.-T. In "Quantum Theory of Chemical Reactions"; Daudel, R., Pullman, A., Salem, L., Veillard, A., Eds.; Reidel: Dordrecht, Holland, 1980; Vol. I, p 91.

(14) Komornicki, A.; Goddard, J. D.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1980**, *102*, 1763.

(15) Lluch, J. M.; Bertrãn, J. *Tetrahedron* **1979**, *35*, 2601; **1982**, *38*, 1847; *J. Chem. Soc., Perkin Trans. 2* **1982**, 1419.

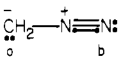
(16) Hiberty, P. C.; Ohanessian, G.; Schlegel, H. B. *J. Am. Chem. Soc.* **1983**, *105*, 719.

(17) Similar geometries have also been calculated for the transition states of this and other 1,3-dipolar cycloaddition reactions using MINDO/2 and MINDO/3 procedures.[10,15]

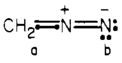
mechanism will pertain. Our intention here is not necessarily to adjudicate between the concerted and two-step pathways for 1,3-dipolar cycloaddition but rather it is to indicate the nature of the valence bond requirements for these two types of mechanisms.

Valence Bond Structures and Reaction Orbitals

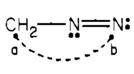
For ease of pictorial representation only, we shall use the cycloaddition reaction diazomethane + acetylene → pyrazoline to develop the valence bond theory. The relevant atomic orbitals are displayed in Figure 1 for the separated reactants, for which the primary canonical valence bond structures, together with that for the product, are the Lewis octet structures **10–14**. For 1,3-dipolar molecules, the results of calculations from different laboratories[18,19] indicate that zwitterionic structures such as **10** and **11** and "long-bond" (or spin-paired diradical) structures such as **12** are the dominant canonical forms and that sometimes the latter may have larger weights than the former. Sextet canonical structures, such as **15–17**, have been calculated to be of lesser importance. Occasionally, the alternative designation "zwitterionic diradical hybrid" is used to describe a 1,3-dipolar molecule.[5–8]


$\overset{-}{C}H_2-\overset{+}{N}\equiv N{:}$

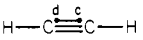
10


$CH_2=\overset{+}{N}=\overset{-}{N}{:}$

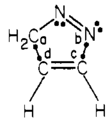
11


$CH_2-N=N{:}$

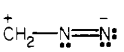
12


$H-C\equiv C-H$

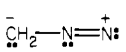
13



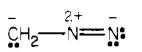
14


$\overset{+}{C}H_2-N=\overset{-}{N}{:}$

15


$\overset{-}{C}H_2-N=\overset{+}{N}{:}$

16


$\overset{-}{C}H_2-\overset{2+}{N}=\overset{-}{N}{:}$

17

When proceeding from reactants to products, the spin pairings between the electrons of four singly occupied orbitals need to be changed, as will be described below in some detail. Although the nature of these "reaction orbitals" must alter throughout the course of the reaction,[20] at each stage we may label them as a, b, c, and d. For simplicity here, we shall assume that a and b are the carbon and nitrogen atomic orbitals χ_1 and χ_3 of the "long-bond" structure **12** and that c and d are a pair of orbitals (χ_4 and χ_5) that overlap to form one of the C–C π-bonds in free acetylene. (In the Appendix, we elaborate upon the form of the a and b orbitals in order to include other canonical structures in the mechanism.) These four orbitals feature as singly occupied in important valence bond structures for each of the reactants and the product.

Spin Wave Functions and Potential Energy Curves

In the separated reactants, the a and b π-electrons of CH_2N_2 are spin paired, as are the c and d π-electrons of C_2H_2. The

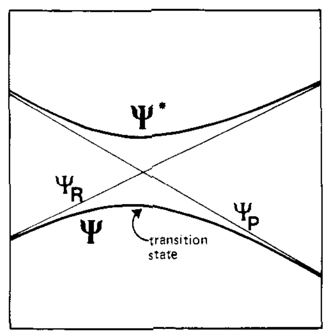


Figure 2. Potential energy curves for primary (or "covalent") reactant-like and product-like wave functions.

appropriate singlet-spin ($S = 0$) wave function for these four electrons is given by[5,22] eq 1,

$$\Psi_R = N_R\{|a^\alpha b^\beta c^\alpha d^\beta| + |a^\beta b^\alpha c^\beta d^\alpha| - |a^\alpha b^\beta c^\beta d^\alpha| - |a^\beta b^\alpha c^\alpha d^\beta|\} \quad (1)$$

For the pyrazoline product, the a–b and c–d π-bonds of the reactants are replaced by a–d and b–c σ-bonds in the product. The a and d electrons must then have opposed spins, as must the b and c electrons. The appropriate $S = 0$ wave function is given by eq 2.

$$\Psi_P = N_P\{|a^\alpha b^\beta c^\alpha d^\beta| + |a^\beta b^\alpha c^\beta d^\alpha| - |a^\alpha b^\alpha c^\beta d^\beta| - |a^\beta b^\beta c^\alpha d^\alpha|\} \quad (2)$$

The course of the reaction may be described[5,6,8] (approximately) by the lower energy linear combination of the reactant-like and product-like wave functions, Ψ_R and Ψ_P, i.e.:

$$\Psi \approx C_R\Psi_R + C_P\Psi_P \quad (3)$$

Near the commencement of the reaction, $|C_R| >> |C_P|$, whereas $|C_P| >> |C_R|$ near the conclusion.[5,6] Schematic potential energy curves are displayed in Figure 2. Because the C–N, N–N, and C–C bonds of the reactants are stretched when proceeding from $CH_2N_2 + C_2H_2$ to pyrazoline, the a–b and c–d bonding interactions[23] are reduced as the reaction proceeds. Therefore the energy of Ψ_R increases along the reaction coordinate. Similarly, a–d and b–c bonding interactions are favored as the reactants approach each other, and therefore the energy of Ψ_P decreases as the reaction proceeds. Consequently when only Ψ_R and Ψ_P of eq 1 and 2 are used to describe the reaction profile, a concerted mechanism must obtain,[24] regardless of how the a and b orbitals of CH_2N_2 and the c and d orbitals of C_2H_2 are defined.

In a later section we shall discuss the effect of including secondary charge-transfer structures on the reaction profile. The primary structures are defined here to be those for which there is no charge transfer between the reactants at any stage along the profile. In this and the next section, we need give consideration only to the primary structures in order to determine the nature of Firestone's extended diradical.

For the (singlet-spin) extended diradical **4**, the a and c electrons are spin-paired as are the b and d electrons. These spin-pairings occur in the $S = 0$ wave function of eq 4,

$$\Psi_{D,ext} = N_{D,ext}\{|a^\alpha b^\beta c^\beta d^\alpha| + |a^\beta b^\alpha c^\alpha d^\beta| - |a^\alpha b^\alpha c^\beta d^\beta| - |a^\beta b^\beta c^\alpha d^\alpha|\} \quad (4)$$

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(18) See ref 7, 8, and 12 of ref 6 and: Hiberty, P. C.; Ohanessian, G. *J. Am. Chem. Soc.* **1982**, *104*, 66. (b) Hiberty, P. C. *Isr. J. Chem.*, in press. (We thank the author for providing us with a preprint.)

(19) In the "long-bond" structure **12**, the pecked line (---) represents the formal π-bond that exists between the nonadjacent atoms.[6–8] Because the overlap integral for the singly occupied atomic orbitals of this bond is very small (~0.02), the bond has negligible strength. In structures **19** and **20**, pecked lines are also used to represent "long" or formal bonds involving pairs of well-separated atoms. Sometimes formal bonds are omitted from the valence bond structures.

(20) The orbitals a and b of CH_2N_2 in particular can be replaced by various types of 2-center orbitals within either the "increased-valence" or nonpaired spatial orbital framework;[5,6] see Appendix. Alternatively within the MOCI formation, we may write[21]

$$\Psi \approx C_1|\psi_1{}^\alpha\psi_1{}^\beta\psi_2{}^\alpha\psi_2{}^\beta| + C_2|\psi_1{}^\alpha\psi_1{}^\beta\psi_3{}^\alpha\psi_3{}^\beta| \equiv |\psi_1{}^\alpha\psi_1{}^\beta\psi_+{}^\alpha\psi_-{}^\beta| + |\psi_1{}^\alpha\psi_1{}^\beta\psi_-{}^\alpha\psi_+{}^\beta|$$

in which the ψ_i are the canonical molecular orbitals, $\psi_+ = \psi_2 + l\psi_3$, $\psi_- = \psi_2 - l\psi_3$, and $l = (-C_2/C_1)^{1/2}$. The singly occupied orbitals have their electrons spin paired in each of these alternative treatments.

(21) Harcourt, R. D. In "Quantum Science"; Calais, J.-L., Goscinski, O., Linderberg, J., Öhrn, Y., Eds.; Plenum: New York, 1976; p 105; *Aust. J. Chem.* **1979**, *31*, 933.

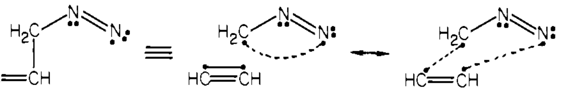
(22) Pilar, R. "Elementary Quantum Chemistry"; McGraw-Hill: New York, 1968; p 553.

(23) The a–b bonding interactions are sensitive to N–N and C–N bond stretching when the a and b orbitals are modified as described in the Appendix and ref 5–8 so that the zwitterionic structures **10** and **11** with N–N and C–N π-bonds, as well as the diradical structure **12**, are included as components of Ψ_R and Ψ_P.

(24) Shaik, S. S. *J. Am. Chem. Soc.* **1981**, *103*, 3692. Pross, A.; Shaik, S. S. *Ibid.* **1981**, *103*, 3702; **1982**, *104*, 187.

$$\equiv N_{\mathrm{D,ext}}(N_{\mathrm{R}}\Psi_{\mathrm{P}} - N_{\mathrm{P}}\Psi_{\mathrm{R}}) \qquad (5)$$

which may be expressed as a linear combination of the Ψ_R and Ψ_P of eq 1 and 2, according to eq 5. If it is assumed[25] that Ψ_R and Ψ_P have the same values for their normalization constants N_R and N_P, then $\Psi_{D,ext} = N(\Psi_P - \Psi_R)$; i.e., Firestone's extended diradical **18** is equivalent[26] to resonance between the "reactant-like"



18 19 20

and "product-like" structures **19** and **20**, with the latter structures having equal weights. This occurs when $E_R = E_P$.

Because the potential energy curves for Ψ_R and Ψ_P must cross (Figure 2), $\Psi_{D,ext}$ must correspond (approximately) to either the transition state for the reaction (which occurs when $E_R = E_P$, cf. ref 24) or an electronic excited state whose minimum energy lies immediately above that of the transition state. To ascertain which of these is appropriate, it is necessary to determine the signs of the coefficients C_R and C_P in eq 3 when $|C_R| = |C_P|$. This is done in the following section.

Transition State for Concerted Mechanism and Excited-State Intermediate

(a) Extended Diradicals. Using the procedures described in ref 27, it may be deduced that the overlap integral Δ ($\equiv\langle\Psi_R|\Psi_P\rangle$) is approximately equal to $^1/_2$ and that the energy separation $E_- - E_+$ for the wave functions of eq 6 is given approximately by eq 7, in which the A_{ij} are exchange integrals defined as in eq 8 for A_{ab}. For orbital overlap integrals ($S_{ij} = \langle i|j\rangle$) > 0 the A_{ij} are

$$\Psi_+ = (\Psi_P + \Psi_R)/(2 + 2\Delta)^{1/2} \quad \Psi_- = (\Psi_P - \Psi_R)/(2 - 2\Delta)^{1/2} \qquad (6)$$

$$E_- - E_+ \approx {}^1\!/_3\{2(A_{bd} + A_{ac}) - (A_{ab} + A_{cd} + A_{bc} + A_{ad})\} \qquad (7)$$

$$A_{ab} = \langle a(1)b(2)c(3)d(4)|\hat{H}|b(1)a(2)c(3)d(4)\rangle \qquad (8)$$

< 0, and their magnitudes are strongly dependent on the magnitude of S_{ij}^2.

For the extended diradical **4** or **18**, only the a–c and c–d overlap integrals S_{ac} and S_{cd} can have appreciable magnitudes, and therefore $E_- - E_+ \approx {}^1/_3(2A_{ac} - A_{cd})$. Using the geometries of **6** and **7** for the extended diradical transition state and intermediate, approximate estimates of the overlap integrals[28,29] are 0.48 and 0.52 for S_{ac} and 0.28 and 0.29 for S_{cd}, respectively. These values provide a qualitative guide to the relative magnitudes of A_{ac} and A_{cd}, and therefore we may conclude that $E_- < E_+$, i.e., that $\Psi_{D,ext}$ is the wave function for the transition state of the cycloaddition reaction when the transition state has a geometry which is similar to that of Firestone's extended diradical.

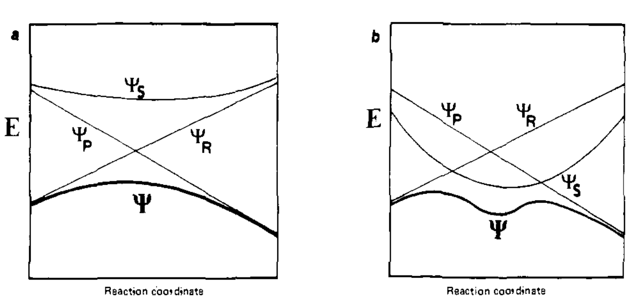
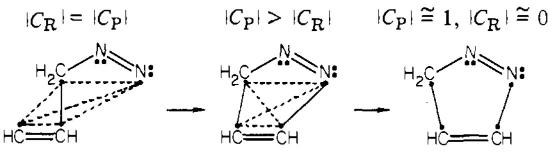


Figure 3. Potential energy curves with secondary (or "ionic") wave function included:[24] (a) concerted cycloaddition; (b) two-step cycloaddition.

Because only one maximum occurs between reactants and products along the ground-state potential energy curve (Figure 2) for eq 3, this potential energy curve describes a concerted mechanism. Therefore rotation around the C–C bond (which requires an activation energy) is not required in order to convert the extended diradical into the pyrazoline product. Increasing contributions from Ψ_P after the transition state of Figure 2 has been reached will bring about the geometrical changes that are required to arrive at the final product. This may be represented schematically as follows.[19]



21 22 23

The energy minimum for the higher energy wave function Ψ_+ lies immediately above that for the transition state (Figure 2). The wave function at this energy minimum is $\Psi_+ = \Psi_P + \Psi_R$, and the associated state will be thermally populated if $E_+ - E_- < kT$. Because eq 7 has both negative and positive terms, the geometrical conformations for the transition states of at least some reactions would enable this requirement to be satisfied. The Ψ_+ state cannot revert to the ground states of either the reactants or the cycloaddition product by moving along its potential energy curve. However, it may be responsible for subsequent hydrogen atom abstraction, as occurs in the oxime formation for the reaction **1** → **4** → **5**. Further, because $E_+ - E_- < kT$ for thermal population of Ψ_+, the activation energies for both H atom abstraction and cycloaddition must be very similar, as is observed to be the case.[30] Thus, if the transition state for the cycloaddition has an unsymmetrical geometry, as in **4**, a second electronic state may lie close in energy to it.

(b) Cyclo Diradicals. In previous publications,[5,6] we have shown that the wave function for Firestone's cyclo diradical **2** corresponds to the Ψ_P component of eq 3, and therefore it does not represent a distinct intermediate. No barrier to ring closure should arise in **2** prior to the formation of the final product; some incipient b–c bond formation already exists in **2**, because the b and c orbitals must overlap (however slightly).

If the transition state is relatively symmetrical, with the cyclo geometry of **9**, we may also use eq 6 to deduce its properties. For this case $E_- - E_+ \approx {}^1/_3(-A_{bc} - A_{cd} - A_{ad})$, because the nonneighbor overlap integrals S_{ab}, S_{ac}, and S_{bd} all have very small magnitudes. Therefore $E_- - E_+ > 0$; i.e., the transition state now has the wave function $\Psi_+ = \Psi_R + \Psi_P$. Because the exchange integral A_{cd} must always have appreciable magnitude (S_{cd} varies from 0.37 in C_2H_2 to ~0.12 in pyrazoline), it is probable that $E_- - E_+ >> kT$, and therefore, in contrast with the extended diradical (vide supra), a symmetrical transition state should generate only the products

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[25] The normalization constants N_R and N_P of eq 1 and 2 are given approximately by

$$^1\!/_2(1 - S_{ad}^2 - S_{bc}^2 - S_{ac}^2 - S_{bd}^2 + 2S_{ab}^2 + 2S_{cd}^2)^{-1/2}$$

and

$$^1\!/_2(1 - S_{ab}^2 - S_{cd}^2 - S_{ac}^2 - S_{bd}^2 + 2S_{ad}^2 + 2S_{bc}^2)^{-1/2}$$

At or near the transition state, each of the atomic orbital overlap integrals S_{ab}, S_{cd}, S_{bc}, S_{bd}, and S_{ad} is <0.3 in magnitude, and therefore it is a good approximation to assume that $N_R = N_P \approx {}^1/_2(1 - S_{ac}^2)^{-1/2}$.

[26] Alternatively, the use of Rumer diagrams for four singly occupied orbitals shows that there are only two independent canonical structures. See, for example, ref 22, p 553.

[27] Pauling, L. *J. Chem. Phys.* **1933**, *1*, 280. See also ref 22, p 551.

[28] For illustrative purposes here, we have assumed that the bond angles calculated by Hiberty et al.[16] fix the hybridization of carbon atomic orbitals a, c, and d. Slater orbitals with neutral atom exponents have been used to calculate the overlap integrals.[29]

[29] Mulliken, R. S.; Rieke, C. A.; Orloff, D.; Orloff, H. *J. Chem. Phys.* **1949**, *17*, 158.

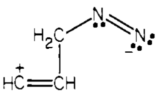
[30] Morrocchi, S.; Ricca, A.; Zanarotti, A.; Bianchi, G.; Gandolfi, R.; Grünanger, P. *Tetrahedron Lett.* **1969**, 3329. Battaglio, A.; Dondoni, A.; Mangini, A. *J. Chem. Soc. B* **1971**, 554. Beltrame, P.; Sartirana, P.; Vintani, C. *J. Chem. Soc. B* **1971**, 814. Additional references are provided in Firestone, R. A. *Tetrahedron* **1978**, *33*, 3009.

of cycloaddition in a thermal reaction.[31] We therefore predict that there will be an increasing propensity for H atom abstraction (or some alternative) reactions to occur photochemically, if no such reaction is observed to occur thermally.

In the above treatments for the concerted mechanism, we have not allowed for contributions from charge transfer or secondary valence bond structures. These structures do not interact with the valence bond structures for the infinitely separated reactants. Inclusion of the secondary structures for a concerted pathway (Figure 3a) will alter the magnitude of the energy separation between the transition state and the electronic excited state, but the primary description of the transition state must still approximate to either $\Psi_R - \Psi_P$ or $\Psi_R + \Psi_P$ according to the nature of the geometry for the transition state.

Two-Step Mechanism

Shaik and Pross[24] have shown that a two-step mechanism may arise if a secondary valence bond structure has a lower energy than have the primary reactant-like and product-like structures at any stage along the reaction coordinate between the reactants and products. Schematically the potential energy curves are displayed in Figure 3b; two transition states arise. For 1,3-dipolar cycloadditions proceeding through an initial extended transition state, a two-step mechanism will occur if secondary "ionic" structures, such as the dipolar sextet and zwitterionic octet structures **24–26**, are dominant immediately beyond this transition state. Each of these structures involves the transfer of one electron from one reactant molecule to the other, and therefore it does not contribute to the valence bond description of the infinitely separated reactants. In Figure 3, Ψ_S is the wave function for the secondary structures.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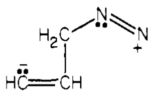
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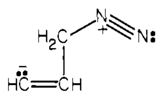
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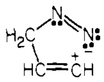
It may be noted that if secondary structures such as **24–26** are the dominant forms at all stages beyond the first transition state, they cannot generate a cycloaddition product unless a rotation around the C–C single bond occurs. This will require an activation energy if a barrier to rotation exists. However, this rotation can be bypassed as Ψ_P of eq 2 becomes increasingly dominant beyond the second transition state of Figure 3b. We may also note that the wave functions for each of **24–26** do not overlap well with either Ψ_R or Ψ_P for the extended diradical. The wave functions for secondary structures that are similar to **27–32** below, but with extended geometry, are better suited for overlap with Ψ_R and Ψ_P.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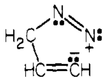
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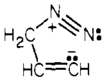
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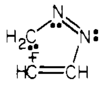
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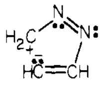
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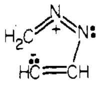
32

Our discussion for this and the previous sections show that if a transition state for cycloaddition has an extended geometry, the cycloaddition mechanism is either concerted or two-step if, immediately beyond the transition state, the reacting system is primarily either "covalent" (i.e., involving no charge transfer between the reactants) or "ionic" in character. Even if the transition state is relatively symmetrical with the cyclo geometry of **2**, as was originally assumed by Huisgen,[1] one-step and two-step mechanisms will pertain according to Figures 3a and 3b, if either primary "covalent" structures or secondary "ionic" structures such as **27–32** are, respectively, dominant immediately beyond the first transition state.

The possibility that zwitterionic or dipolar intermediates might be involved in cycloadditions between very-electron-rich 1,3-dipoles and very-electron-deficient dipolarophiles has been discussed by Houk,[11] Black et al.,[32] and Oshima et al.,[33] for example. Yoshimura et al.[34] have found that the rate constants for the 1,3-dipolar cycloaddition of diazodiphenylmethane with several dipolarophiles do not depend on the solvent polarity and have concluded that it is unlikely that zwitterionic intermediates are formed in the ractions studied.

The considerations of this section are based on the following formulation of the valence bond wave function for the 1,3-dipolar cycloaddition. Let R_1 and R_2 represent the reactant components (e.g., CH_2N_2 and C_2H_2); these are present in both the primary reactant-like and product-like valence bond structures with wave functions Ψ_R and Ψ_P. Then at any stage along the reaction coordinate, we may write

$$\Psi \approx \Psi(R_1,R_2) + \lambda_1\Psi(R_1^+,R_2^-) + \mu_1\Psi(R_1^-,R_2^+) + \lambda_2\Psi(R_1^{2+},R_2^{2-}) + \mu_2\Psi(R_1^{2-},R_2^{2+}) \tag{9}$$

$$\equiv \Psi(R_1,R_2) + C_S\Psi_S \tag{10}$$

$$\equiv C_R\Psi_R + C_P\Psi_P + C_S\Psi_S \tag{11}$$

If $\Psi(R_1,R_2)$ and Ψ_S are assumed to be normalized, a concerted mechanism will pertain if $|C_S|$ is always less than unity, whereas a two-step mechanism can occur if $|C_S| > 1$ at some intermediate stage along the reaction coordinate.

Sustmann's[12] molecular orbital classification of 1,3-dipolar cycloadditions can also be fitted into the context of eq 9. This classification is based on HOMO–LUMO interactions. Type I cycloaddition involves charge transfer from the HOMO of the 1,3-dipole (R_1 here) into the LUMO of the dipolarophile (R_2); this charge transfer generates the $\Psi(R_1^+,R_2^-)$ and $\Psi(R_1^{2+},R_2^{2-})$ configurations of eq 9. The sum of the weights for "ionic" valence bond structures such as **25**, **26**, **28**, **29**, **31**, and **32** (+ others) will then be larger than the sum of the weights for "ionic" structures **24**, **27**, and **30** (+ others). The converse holds for Type II cycloaddition, for which the energy of the HOMO of the 1,3-dipole is lower than that for the LUMO of the dipolarophile. No matter in which direction charge transfer primarily occurs, a two-step mechanism can only pertain if $|C_S| > 1$ in eq 10 at any stage along the reaction profile.

Conclusions

By using qualitative valence bond theory, we have shown how the primary electronic structure of the initial transition state determines whether or not the 1,3-dipolar cycloaddition is concerted or proceeds as a two-step mechanism via a second transition state. The theory also indicates that if the first transition state is primarily an extended diradical, the energy minimum for an electronic excited state for the extended diradical must lie immediately above and energetically close to the transition state. To our knowledge, this point has not been recognized previously. We have suggested that this excited state may be the entity involved in oxime formation for reactions such as **1** → **4** → **5**.

One of us has previously suggested[5-8] that 1,3-dipolar cycloadditions proceed by means of a concerted diradical mechanism. The present paper provides further support for this hypothesis, if secondary "ionic" structures do not become dominant at any

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[31] It is possible that a geometrical arrangement for the transition state could exist for which Ψ_- and Ψ_+ are degenerate, i.e., when $2A_{ac} + 2A_{bd} = A_{ab} + A_{bc} + A_{cd} + A_{ad}$. A Jahn–Teller distortion will then produce a double maximum in the potential energy curve.

[32] Black, D. St. C.; Crozier, R. F.; Rae, I. D. *Aust. J. Chem.* **1978**, *31*, 2239.

[33] Oshima, T.; Yoshioka, A.; Nagai, T. *J. Chem. Soc., Perkin Trans. 2* **1978**, 1283.

[34] Yoshimura, Y.; Osugi, J.; Nakahara, M. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3325.

Table I. Structural Weights $(W_I)^{15}$ and Bond-Eigenfunction Coefficients $(C_I)^{7}$ for Valence Bond Structures 10–12 and 15–17

	10	11	12	15	16	17
W_i (STO-3G)	0.164	0.414	0.281	0.042	0.010	0.089
W_I (4-31G)	0.162	0.396	0.303	0.050	0.011	0.078
C_i (STO-5G)	0.307	0.230	0.377	0.047	0.153	*a*

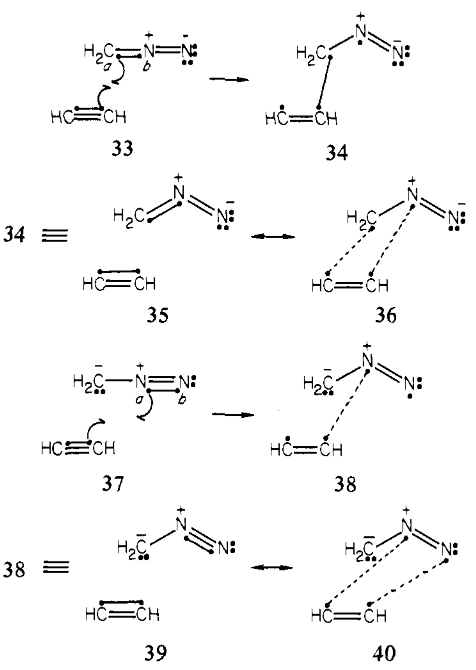
[a] Not included in the calculations.

stage along the reaction profile.

Acknowledgment. R.D.H. thanks the University of Melbourne for S.S.P. leave and Professor B. Kirtman for the use of the facilities in his department at U.C.S.B., Santa Barbara, where this work was carried out.

Appendix

For CH_2N_2, weights and bond-eigenfunction coefficients for the primary zwitterionic and "long-bond" structures **10**–**12**, and for the less important structures **15**–**17**, are reported in Table I. In order that $CH_2N_2 + C_2H_2 \rightarrow$ the cycloaddition product pyrazoline **14** via an extended diradical transition state, the importance of **12** must increase as the reaction proceeds, otherwise $2 + 2 \rightarrow 4$ as well as $3 + 2 \rightarrow 5$ cycloaddition would be observed. Thus if only the zwitterionic structures **10** and **11** are used to represent CH_2N_2 and the singly occupied a and b orbitals are those indicated in **33** and **37**, we may represent the formation of the extended diradical as follows:

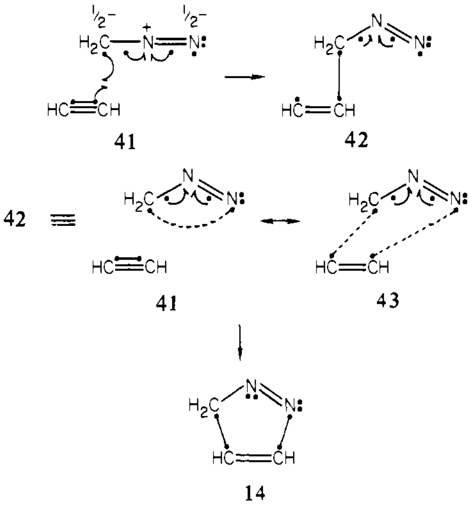


Therefore, consideration of only the zwitterionic octet structures cannot generate the pyrazoline from the extended diradicals **34** and **38**, unless further electronic reorganization occurs.

By modifying the nature of the lone-pair orbital χ_2 in **12**, the zwitterionic structures as well as **12** may also be included in the cycloaddition theory. For the symmetrical transition state **9**, this has been done in ref 5–8 in various ways. Similar procedures are also appropriate for the extended diradical. In essence, it involves the replacement of the doubly occupied nitrogen atomic orbital configuration $(\chi_2)^2$ in **12** by any of the configurations $(\phi_{12})^1(\chi_2)^1$, $(\chi_2)^1(\phi_{23})^1$, or $(\phi_{12})^1(\phi_{23})^1$ in which $\phi_{12} = \chi_2 + k\chi_1$ and $\phi_{23} = \chi_2 + l\chi_3$ are C–N and N–N bonding molecular orbitals. In ref 5 and 8, it is shown that use of the first two configurations is equivalent to using the C–N and N–N antibonding orbitals $\phi^*_{12} = k^*\chi_2 - \chi_1$ and $\phi^*_{23} = l^*\chi_2 - \chi_3$ as the a or b orbitals in eq 1 and 2. Each of Ψ_R, Ψ_P, and $\Psi_{D,ext}$ is then a linear combination of two $S = 0$ configurations, cf. ref 5, p 360.

When $(\chi_2)^2$ is explicitly included in the Slater determinants of eq 1, 2, and 4, 6 × 6 determinants such as $|a^\alpha b^\beta c^\alpha d^\beta \chi_2{}^\alpha \chi_2{}^\beta|$ replace the 4 × 4 determinants. Replacing $(\chi_2)^2$ with, for example, $(\phi_{12})^1(\phi_{23})^1$ generates eight Slater determinants for each of eq 1, 2, and 4, which then remain as $S = 0$ singlet-spin eigenstates. Each Slater determinant in eq 1, 2, and 4 is replaced by two Slater determinants. For example, $|a^\alpha b^\beta c^\alpha d^\beta|$ is replaced by $|a^\alpha b^\beta c^\alpha d^\beta \phi_{12}{}^\alpha \phi_{23}{}^\beta| - |a^\alpha b^\beta c^\alpha d^\beta \phi_{12}{}^\beta \phi_{23}{}^\alpha|$.

Inclusion of $(\phi_{12})^1(\phi_{23})^1$ generates the Linnett nonpaired spatial orbital structure[2,5–8,35] of **41** for CH_2N_2. This structure is equivalent[5–8,35] to resonance between the Lewis canonical structures **10**–**12** and **17**. For the cycloaddition via the extended diradical transition state, we may write **41** → **42** (≡ **41** ↔ **43**) → **14**, with the magnitudes of the bonding parameters k and l decreasing in the molecular orbitals ϕ_{12} and ϕ_{23} as the reaction proceeds.



Registry No. H_2, 1333-74-0; PhCNO, 103-71-9; PhCCH, 536-74-3; diazomethane, 334-88-3.

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(35) Linnett, J. W. "The Electronic Structures of Molecules"; Methuen: London, 1964.