

- (78) N. R. Carlsen and H. F. Schaefer, *Chem. Phys. Lett.*, **48**, 390 (1977).
 (79) G. Herzberg, "Molecular Spectra and Molecular Structure III. Electronic Spectra and Electronic Structure of Polyatomic Molecules", Van Nostrand-Reinhold, New York, N.Y., 1966.
 (80) F. Herman, A. R. Williams, and K. H. Johnson, *J. Chem. Phys.*, **61**, 3508 (1974).
 (81) P. J. Hay and W. A. Goddard III, *Chem. Phys. Lett.*, **14**, 46 (1972).
 (82) P. J. Hay, T. H. Dunning, Jr., and W. A. Goddard III, *Chem. Phys. Lett.*, **23**, 457 (1973).
 (83) W. A. Goddard III, T. H. Dunning, Jr., W. J. Hunt, and P. J. Hay, *Acc. Chem. Res.*, **6**, 368 (1973).
 (84) P. J. Hay, T. H. Dunning, Jr., and W. A. Goddard III, *J. Chem. Phys.*, **62**, 3912 (1975).
 (84) W. A. Goddard III, P. J. Hay, and T. H. Dunning, to be published.
 (86) R. L. Kuczkowski, *J. Am. Chem. Soc.*, **86**, 3617 (1964).
 (87) A. E. Foti, V. H. Smith, Jr., and D. R. Salahub, *Chem. Phys. Lett.*, **57**, 33 (1978).
 (88) J. Kao, *Inorg. Chem.*, **16**, 2085 (1977).
 (89) J. Kao and N. L. Allinger, *Inorg. Chem.*, **16**, 35 (1977).
 (90) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", Wiley-Interscience, New York, N.Y., 1966.
 (91) D. R. Salahub and R. P. Messmer, *J. Chem. Phys.*, **64**, 2039 (1976).
 (92) D. R. Salahub and R. P. Messmer, *Phys. Rev. B*, **14**, 2592 (1976).
 (93) H. Köpf, *Angew. Chem., Int. Ed. Engl.*, **8**, 375 (1969).
 (94) L. B. Clark, Ph.D. Thesis, University of Washington, 1963, quoted in ref 9.
 (95) B. D. Sharma and J. Donohue, *Acta Crystallogr.*, **16**, 891 (1963).
 (96) A. E. Foti, V. H. Smith, Jr., and J. W. D. Connolly, to be published.
 (97) D. A. Lokben, T. W. Couch, and J. D. Corbett, Abstracts of the 160th National Meeting of the American Chemical Society, Chicago, Ill. 1970.

Ground- and Excited-State Correlations in Bond Rupture Reactions

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Abstract: Semiempirically based molecular orbital configuration interaction ground- and excited-state correlation diagrams are generated for the bond ruptures in cyclobutane, water, ammonia, hydrogen peroxide, and hydrazine. All calculations confirm the topicity rules of Dauben, Salem, and Turro. It is shown, however, that the diagrams have some deceptive features with regard to correlations to Rydberg states.

Introduction

We will demonstrate that valence orbital level semiempirical self-consistent field configuration interaction (SCF-CI) calculation can be used to elucidate some of the correlative features of the potential energy surfaces for ground and excited singlet and triplet state bond rupture reactions. We will also analyze some of the deceptive features of such valence level correlations. The kinds of diagrams we will generate are the computational counterparts of the topicity rules formulated by Dauben, Salem, and Turro.¹

We will deal specifically with certain cross sections of the surfaces for ruptures of CC, OO, NN, CN, NH, and OH single bonds. Although the calculation of all these surfaces is obtainable by current ab initio methods, only a few have been reported.² More importantly, it is common practice for various investigators to report only portions of surfaces for a few states of the molecule under study. Rarely is the reader given a total view of the interrelationships between various states of spectroscopic and/or photochemical interest and the ground state. We will attempt to do that here. The major goal of the work presented here is to confirm the topicity rules and to prepare the methodology for larger molecular systems for which good quality ab initio SCF-CI calculation of excited-state surfaces is presently too expensive. We have previously reported portions of the singlet surfaces on NH₃, N₂H₄,^{3a} and H₂O₂.^{3b}

Method of Calculation

A. Parametrization. The calculations presented here used the Eaker-Hinze parametrization for all bonds except CC and OO.⁴ This parametrization retains most of the features of the CNDO/2 approximation but changes the resonance terms, β_{pq} , and the electron-other-core term, V_{ab} . In the CNDO/2 approximation, $V_{ab} = Z_b(aa|bb)$, Z_b is the core charge on atom b as seen by an electron in one of the orbitals on atom a, and $(aa|bb)$ is the two-centered electron-electron repulsion inte-

gral. The Eaker-Hinze approximation is (in atomic units)

$$V_{ab} = Z_b[(1 - \alpha)(aa|bb) + \alpha(R_{ab}^2 + 1/\rho_a^2)^{-1/2}] \quad (1)$$

where R_{ab} is the distance between atoms a and b and ρ_a is the Slater orbital exponent for atom a. Eaker and Hinze found a best fit value for α of 0.3143 in calibrating their multiconfiguration (MCSCF) calculations to a number of physical observables. However, we found their parametrization not satisfactory for the OO bond energy in H₂O₂ (calcd, after CI, 155 kcal/mol; exptl, 51).⁵ Likewise, their parametrization yielded a computed enthalpy for the cyclobutane \rightarrow 2 ethylene reaction of about -70 kcal/mol (after 60 \times 60 CI) whereas the experimental value is +18.⁶ We chose to superimpose on the Eaker-Hinze parametrization that of Das Gupta and Huzinaga.⁷

$$V_{ab} = Z_b(1 + Be^{-CR_{ab}})(aa|bb) \quad (2)$$

For the case of the OO bond, $B = -0.069$, $C = 1$. For the CC bond $B = 1.29407$, $C = 1.87204$. In the case of carbon the resonance terms were also slightly modified: $\beta_{2s} = -0.5404$ au, $\beta_{2p} = -0.3985$.

It should be stressed that the use of either eq 1 or 2 is without theoretical justification. However, our parametrization, or that of the previous workers, does not differ from the classical CNDO/2 term for V_{ab} by more than 2% in the region where R_{ab} is greater than 1 Å.⁸ Using this parametrization the OO bond in H₂O₂ has a dissociation energy of about 45 kcal/mol.^{2b} The cyclobutane \rightarrow 2 ethylene reaction has a calculated enthalpy of +4 kcal/mol at the 60 \times 60 CI level. This latter value is deceptive because it is dependent on the amount of CI, becoming more exothermic as the level of CI is increased.⁹ Likewise, the parametrization in H₂O₂ was not directly applicable to large-size peroxides. However, the use of eq 2 allows the enthalpy of a particular reaction to be calibrated to the experimental value after which the rest of the surface can be

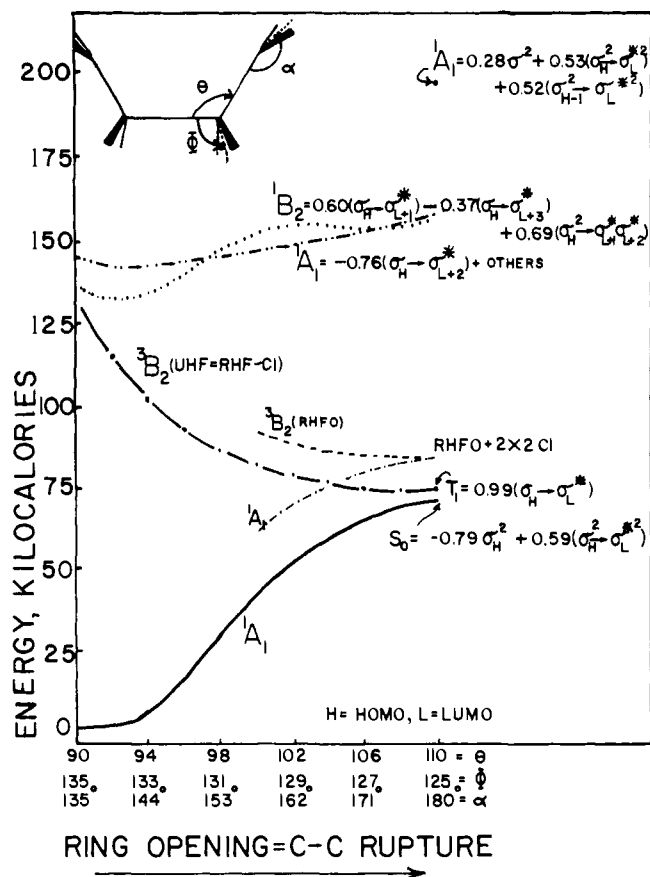


Figure 1. Topicity 2 bond rupture in cyclobutane: CC and CH bond distances kept constant at 1.54 and 1.08 Å, respectively. RHF-CI, restricted Hartree-Fock at about 94×94 level. UHF, unrestricted Hartree-Fock. RHFO, open-shell restricted Hartree-Fock (see text). Given are the major configurations.

computed with greater confidence. Because the V_{ab} terms are numerically large, only small parameter variations yield large computed changes in the enthalpy of a particular reaction.

B. SCF Techniques. Although Eaker and Hinze applied their parametrization to a MCSCF technique,⁴ we choose the classical route of obtaining an SCF closed shell solution followed by a separate CI mixing of the various same symmetry ground and excited singlet and triplet states. The CI treatment was limited to between 50 and 110 configurations. Both single and the various types of double excitation virtual states were used in the CI calculation. The configurations were selected on the basis of their importance at the dissociation limit rather than at the ground-state equilibrium geometry. The closed-shell SCF calculations were generally stable out to about 2–2.5 Å. At all geometries the off-diagonal elements of the SCF energy matrix, e_{ij} , were computed¹⁰ and included in the CI treatment.

A standard UHF treatment of one of the triplet states was also performed.¹¹ Finally, an open-shell Nesbet-type¹² SCF calculation was also performed in the diradical region of the cyclobutane ring opening surface.

Finally, it is pointed out that the degeneracy of the singlet and triplet $n\sigma^*$ states for certain planar configurations of the molecules dealt with here is an artifact of the CNDO method.

Results and Discussion

A. General Considerations. The following discussion of specific molecules will deal with the cases having topicity numbers 2, 3, and 4. As shown by Dauben, Salem, and Turro,¹ these cases will yield respectively one, two, and four pairs of diradical states. For the hypothetical molecule A:B, composed

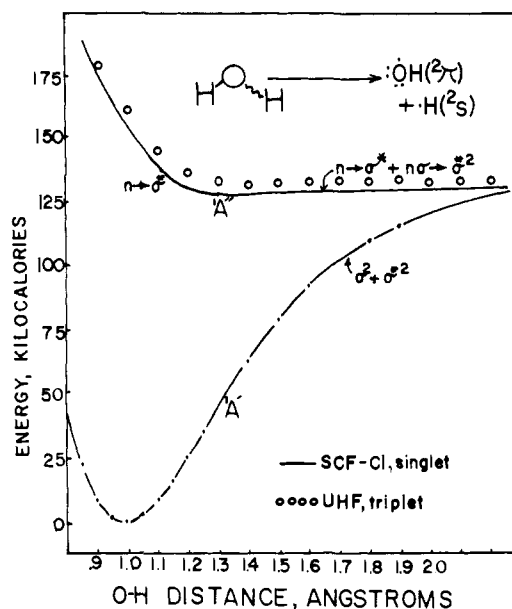


Figure 2. Topicity 3 bond rupture in H₂O. Initial geometry, HOH, 105°; OH, 0.96 Å; other OH varied.

Table I. Relationships between the Topicity Numbers and the Ground and Radical Pair Electronic Configurations

topicity	confign	example	possible radical pair confign ^a
2	A:B (σ)(σ)	H ₂	^{1,3} (A· + ·B)
3	A:B ($\sigma\pi$)(σ)	H ₂ O	^{1,3} (A· + ·B); ^{1,3} (A· + ·B)
4	A:B ($\sigma\pi$)($\sigma\pi$)	H ₂ O ₂	^{1,3} (A· + ·B); ^{1,3} (A· + ·B); ^{1,3} (A· + ·B); ^{1,3} (A· + ·B)

^a 1 = singlet radical pair; 3 = triplet radical pair.

of radical fragments A and B, joined by a σ bond and also containing 0, 2, and 4 nonbonding electrons in the ground state, Table I can be constructed.

Since the topicity numbers are just the total number of available valence radical sites, the number of radical pair states shown in Table I merely reflects the possible combinations of the occupations of those sites by either one or two electrons. Since the calculations presented here are done at the valence orbital level, it will be found that the radical pair states will correlate directly with only theoretical valence states of the molecule. However, the theoretical situation is more complicated in that most of the actual excited states for the simple molecules dealt with here are Rydberg in character. Even at the semiempirical level a correlative treatment of molecular Rydberg states would require adding additional diffuse higher energy basis orbitals of the proper symmetry. In the cases of topicity 3 and 4 we will deal with this issue carefully and show that in some circumstances the valence orbital calculations give the proper symmetry information for correlative purposes. In some other cases some aspects of the calculation are deceptive. The cases in which proper information is given merely result from the fact that certain Rydberg molecular orbitals will evolve directly into valence molecular orbitals with geometry change. The symmetry rules for such an evolution between Rydberg molecular states and valence or Rydberg radical states have already been dealt with in the case of the united atom treatment of polyatomic molecules.¹³

For those interested in making a comparison between the known ground-state bond dissociation energies and those calculated here, the experimental values are OH(H₂O),⁵ 119 kcal/mol; NH(NH₃),¹⁴ 110; NN(N₂H₄),¹⁴ 71; OO(H₂O₂),⁵ 51; and CC(C₄H₈, ring opening),¹⁵ 63. It should be stressed that whatever the magnitude of our values these are artifacts

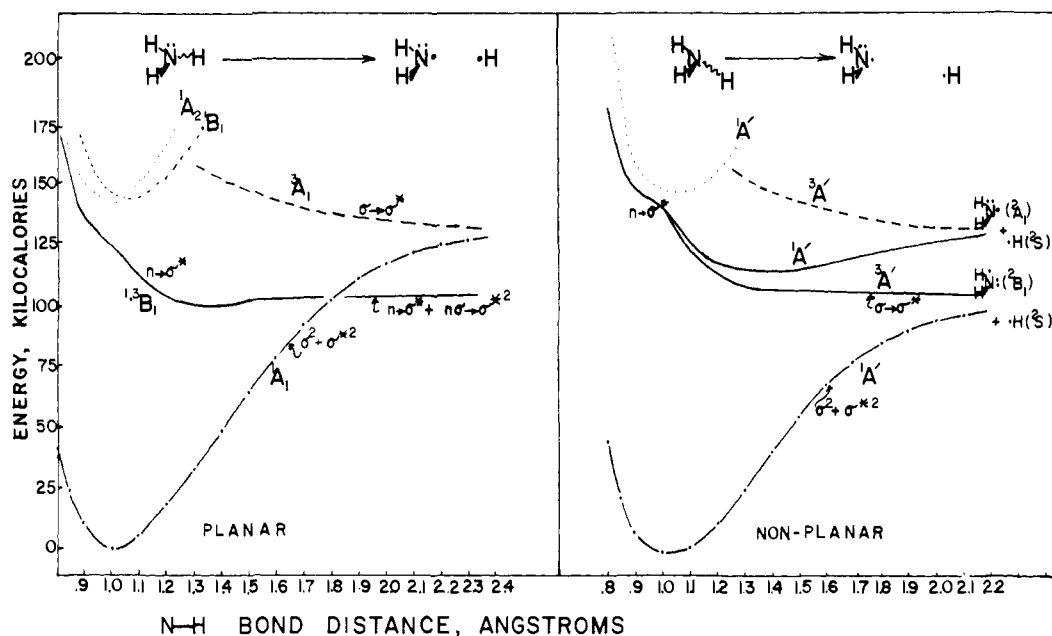


Figure 3. Topicity 3 bond rupture in NH_3 . Planar geometry, HNH , 120° ; NH , 1.01 \AA . Nonplanar geometry, HNH , 120° ; NH , 1.01 \AA ; other H approaches N at 45° to the HNH plane.

of both the parametrization and the amount of CI included in the treatment. Because of this we will stress the correlative features of the diagrams. From this point, it can be stated that all the calculations were in accord with the topicity rules and followed our expectations based on symmetry considerations alone.

B. Topicity 2 CC Bond Ruptures. The CC bond ruptures in ethane and cyclobutane ring opening to give the tetramethylene diradical were studied. Figure 1 shows various features of the latter case. The simplest closed-shell MO-CI theoretical view¹⁶ of the CC bond rupture involves discussion of only the σ and σ^* CC bond rupture orbitals. Four states are generated from various orbital occupations. These are the ground-state singlet diradical pair, $^1\psi = 1/\sqrt{2}(\sigma^2 - \sigma^{*2})$; the triplet diradical pair, $^3\psi = ^3\sigma\sigma^*$; and two zwitterions, $Z_1(^1\sigma\sigma^*)$ and Z_2 (same composition as $^1\psi$, with a positive phase). In the C_{2v} point group ring opening shown in Figure 1, these states would correspond respectively to symmetries 1A_1 , 3B_2 , 1B_2 , and 1A_1 . As can be seen from the CI compositions given in Figure 1, the simple view of the singlet and triplet diradical states is adequate at the large CI level. However, the CI compositions of the lowest energy excited 1B_2 and 1A_1 states do not correspond to the classical Z_1 and Z_2 states. In the 1B_2 state, the HOMO (mostly terminal carbon localized) does play the role of the departing MO. A number of non-LUMO CC and CH antibonding orbitals play the role of accepting MOs. Thus, while there is some charge transfer character to this state, it is not the classical Z_1 state. Likewise, the lowest energy excited 1A_1 state is not configurationally related to the Z_2 state. There is a higher energy 1A_1 state which does have a configurational composition which would qualify it as being a Z_2 state.

The case of CC bond breaking in ethane, not shown diagrammatically, is similar to that of cyclobutane in that the S_0 and T_1 diradical states are nearly degenerate at large CC distances. More importantly, the excited singlet surfaces lie at least 5 eV above the diradical surface. Thus, as expected from the topicity rules, there is no close approach of the ground and excited singlet states along the CC coordinate.

There are several additional interesting features in Figure 1. The large CI (94×94) estimate of the lowest triplet state, 3B_2 , is energetically identical with the much simpler UHF estimate. Thus the UHF calculation contains the same correlation energy as the more expensive CI calculation. Finally,

the simple open-shell Nesbet-Salem estimate of the triplet (single determinate) and the singlet (2×2 CI) energies were only 10–15 kcal/mol above a more complete 94×94 CI treatment of the closed-shell MOs. It was found, however, that in order to make a marriage between closed-shell and open-shell CI surfaces a nearly equivalent large CI treatment was necessary. Truncating the CI calculation at a low level, as has been done for certain portions of the ab initio surface of the cyclobutane ground-state ring opening,¹⁷ was found to be inadequate. However, the 2×2 CI surface mimics the behavior of the more complete surface. It may be that a low level CI will pick up the necessary information to characterize the important features of certain portions of some kinds of surfaces.^{18,19}

C. Topicity 3 Bond Ruptures—Water and Ammonia. Figures 2 and 3 show the valence state correlation diagram for bond ruptures in H_2O and NH_3 . In the case of water, $A = \text{OH}(^2\pi)$; $B = \text{H}(^2S_0)$. It is the double degenerate character of the OH radical which controls the topicity number. For correlation purposes the π -orbital sequence in the degenerate pair of $\text{OH}(^2\pi)$ can be thought to be $\pi_x^2\pi_y$ and $\pi_x\pi_y^2$,¹³ corresponding to \dot{A} and \dot{A}' of Table I. An insertion of the H atom in the π_y orbital will produce configurations $\dot{A}:B$ and $\dot{A}':B$, respectively. The former configuration is the ground state of water; the latter is a $n\sigma^*(^1B_1)$ excited state at C_{2v} symmetry (A'' , C_s). The correlation in Figure 2 shows clearly the degeneracy of the excited- and ground-state surfaces at the diradical limit. This diagram is also correct at the Rydberg level, since the lowest excited state ($n, 3s$) is of the same symmetry.²⁰ This is true because there is an orbital correlation, $3s \leftrightarrow \sigma^*$ (both a' symmetry), along the bond rupture coordinate.

The situation with NH_3 is more complicated since NH bond rupture can occur in a coplanar or nonplanar fashion.^{3a} The ground state of the amino radical $\text{NH}_2(^2B_1)$ has a configuration $\sigma^2\pi \equiv \dot{A}$; whereas the first excited state (2A_1) has a configuration $\sigma\pi^2 \equiv \dot{A}'$. Thus, insertion of the H atom in a coplanar mode into the NH_2 ground state will produce an $\dot{A}:B$ excited state configuration. Therefore the 2B_1 excited state of NH_2 will correlate with the ground state of NH_3 for this coplanar reaction coordinate. This is shown clearly in Figure 3. For nonplanar NH bond rupture of NH_3 both the ground and the lowest energy and excited singlet states have the same symmetry (A') and there will be no ground-excited state crossings.

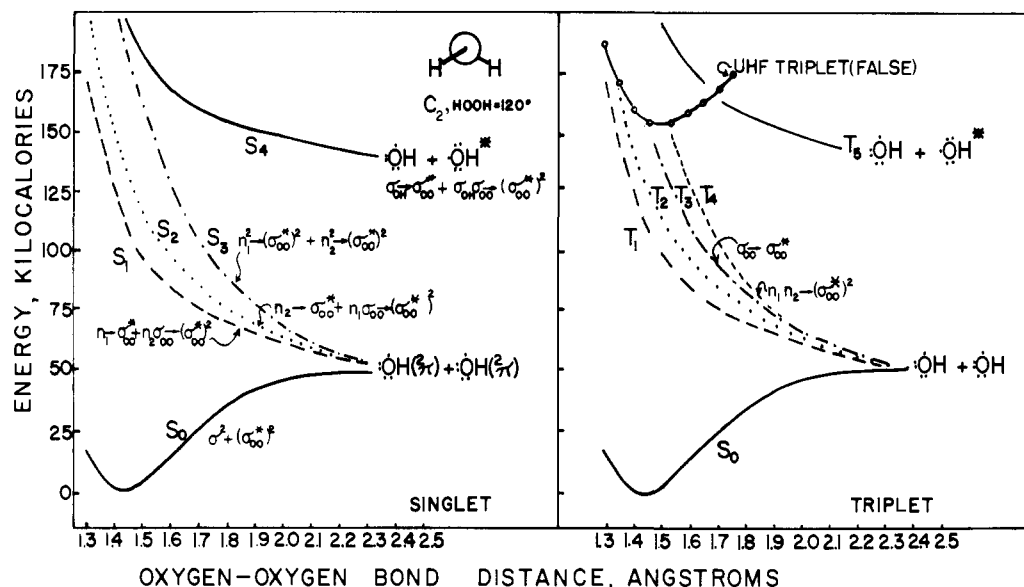


Figure 4. Topicity 4 bond rupture in H_2O_2 (C_2 symmetry). HOO , 105° ; OH , 0.96 \AA . Symmetries: S_1 (A), S_2 (B), S_3 (A), $T_1 = S_1$, $T_2 = S_2$, T_3 (B), T_4 (B), n_1 (b), n_2 (a), σ_{00} (A), σ_{00}^* (B).

As in the case of H_2O , the lowest excited singlet-triplet states of NH_3 are Rydberg in character (n , $3s$).^{2d} However, as with H_2O , Figure 3 shows that these states are correlatively correct.

Comparison of Figure 3 with the planar excited state ab initio calculations^{2d} of Runau et al. shows that the surfaces shown for 1A_2 and 1B_1 may be deceptive. However, the 3A_1 surface is not deceptive; it is a required feature of the triplet rupture of the NH bond having a $^3\sigma\sigma^*$ configuration at large NH distances. In spectroscopic terms, this surface will correlate with a high energy triplet in-plane (n , $3p$) Rydberg state. Runau et al. argue that a second low-energy 1A_1 Rydberg state will attempt to correlate with the 2A_1 state of NH_2 and that this may be the origin of NH_2^* fluorescence ($^2A_1 \rightarrow ^2B_1$) in NH_3 photolysis. However, the 2A_1 state of NH_2 correlates directly with the ground state of planar NH_3 . Likewise, the excited singlet counterpart of the 3A_1 state is the above-mentioned Z_1 state which could be Rydberg in character at long distances and correlate with a Rydberg 2A_1 of NH_2 . In conclusion, all the features shown in Figure 3 appear correlatively correct with the exception of the 1A_2 and 1B_1 states for planar NH rupture and the third $^1A'$ state in the nonplanar rupture.

Some comment must be made on the role of CI in our calculations vs. the current ab initio treatments of Rydberg states. Our Figures 2 and 3 show that the $n\sigma^*$ states have a major double excited component ($n\sigma\sigma^*$) at long distances whereas the ab initio calculations on NH_3 ^{2b,d} indicate essentially single determinate character for the $n3s$ Rydberg state along the bond rupture coordinate. Part of the discrepancy results from the fact that our CI basis functions were constructed from ground-state MO function rather than SCF excited-state minimized functions. In addition, the restricted atomic basis set in the MO functions forces the excited state to be written using σ and σ^* orbitals. This, in turn, permits the writing of resonance structures of the type $\text{A} \cdot | \cdot \text{B} \leftrightarrow \cdot \text{A} | \cdot \text{B}^-$. This would require CI to remove the contaminating ionic structure at the intermediate or the dissociation limits. In addition, the $3s$ orbital, being spatially large, will avoid some of this correlation problem.

Finally, one of the most deceptive features of the calculations presented here is that they cannot differentiate between the known preference²¹ for photochemical rupture of OH and NH over CO and CN bonds in alcohols and amines. Although not

shown here, our computations indicate no correlative preference for NH over CN rupture in the $n\sigma^*$ state of methylamine. Although no such ab initio surfaces have yet been generated,²² the recent calculations of Wadt and Goddard²³ show that in the sequence water, methanol, and dimethyl ether, the $3s$ orbital avoids the electron-rich methyl group region while not avoiding the electron-deficient H atom region. Thus it is easy to speculate that even if CO and OH rupture are correlatively similar, the excited-state CO rupture surface will have an energy barrier.

D. Topicity 4 Bond Ruptures, Hydrogen Peroxide and Hydrazine. Portions of the singlet surfaces of H_2O_2 (C_{2h}) and N_2H_4 (D_{2h} and C_2) have already been reported with regard to their significance to the ground- and excited-state chemistry.³ The possibility of a multisurface correlation for the OO rupture in H_2O_2 was discussed as long as 50 years ago²⁴ and is included in the correlation tables of Herzberg.¹³ However, we have found no comment on its significance in the publications on peroxide photochemistry or in peroxide-connected chemiluminescence.^{3b} Figure 4 shows that there are four singlet and four triplet states which correlate with two ground-state OH radicals. Their symmetries and configurational compositions are what one would expect from valence orbital arguments. No ab initio surfaces on H_2O_2 have been reported. The ab initio spectra calculations of HOCl ²⁵ indicate that the lower excited states are valence in nature, described by a promotion of an electron from a nonbonding into the OO antibonding orbital. Recent calculations on H_2O_2 (C_2 symmetry)²⁶ indicate Rydberg character for the S_1 and S_2 states, their symmetries being identical with those shown in Figure 4 (S_1 (A; $n_13s\sigma^*$); S_2 (B; $n_23s\sigma^*$). As with our S_1 and S_2 states both these Rydberg states will correlate with two OH ground-state radicals. Since these ab initio calculations did not include doubly excited configurations they will not generate our S_3 (A) doubly excited valence state. The ab initio calculations also predict a low-lying (A; $n_13s\sigma$) state which could correlate with the two ground-state OH radicals after an avoided crossing with an even higher lying A state (our S_3) of the valence type shown in Figure 4. Thus Figure 3 must be considered partially deceptive with regard to the higher lying excited-state correlations. The fact that three singlet and four triplet excited states of the proper symmetry must eventually correlate with the two OH ground-state radicals remains. However, while all our valence excited states are repulsive in nature, some of the upper

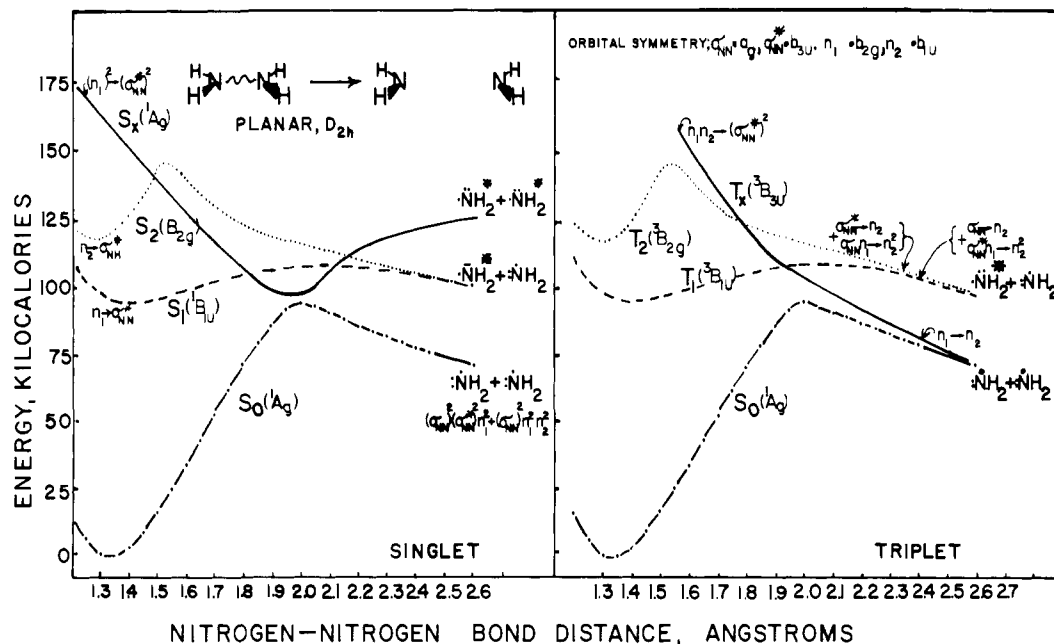


Figure 5. Topicity 4 bond rupture in N_2H_4 (D_{2h} symmetry). Geometry the same as planar NH_3 with variation of NN distance.

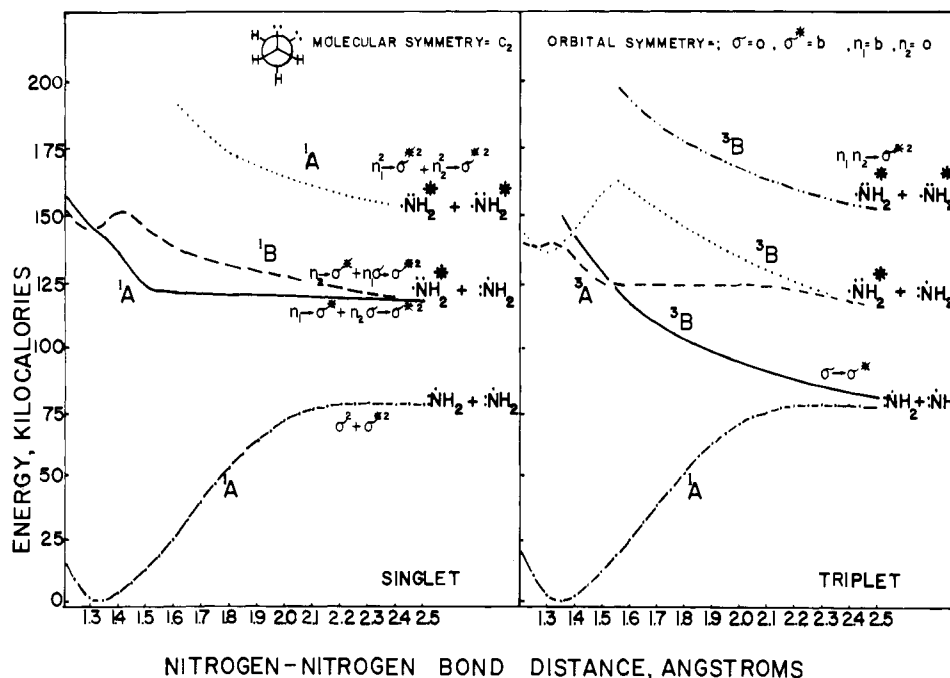


Figure 6. Topicity 4 bond rupture in nonplanar N_2H_4 (C_2 symmetry). NH distances the same as NH_3 . HNH, HNN bond angles tetrahedral; conformation staggered as shown.

Rydberg states may be nonrepulsive in the region of the equilibrium geometry of the ground state of H_2O_2 .

Another deceptive feature in Figure 4 is the bonding nature of the UHF triplet. While it is commonly recognized that a UHF computation may not select the lowest energy triplet,²⁷ the false nature of the UHF surface shown in Figure 4 (and also found in the case of N_2H_4) is more fundamental in nature. Such a false surface will be encountered when one is attempting to break a symmetrical three-electron bond. Even a UHF function may have ionic components, in this case of the type $\dot{A}:\dot{A} \leftrightarrow +\dot{A}:\dot{A}^-$. These ionic components cannot disappear unless the radical partners are asymmetric by geometry or electronegativity.

Because of the number of geometrical variations the problem of the correlation diagrams in N_2H_4 is more complex than in

the case of H_2O_2 . However, at the dissociation limit there must be four singlet and four triplet surfaces. The generated radical pairs are not all degenerate as was the case in H_2O_2 . In the case of D_{2h} hydrazine, there will be two 1A_g surfaces of different energies having configurations $\dot{A}:\dot{A}$ and $\dot{A}::\dot{A}$ at the diradical limit. There will also be, at the diradical limit $^1B_{1u}$ and $^1B_{2g}$ states having different linear combinations of the configuration $\dot{A}:\dot{A}$. Two triplet states will also have the same symmetries while two others will be $^3B_{3u}$. We have shown all the correlations for these states in Figure 5 except the higher energy $^3B_{3u}$.

The major complication in the D_{2h} surface of N_2H_4 is the interaction of two ground-state NH_2 radicals ($\sigma^2\pi + \sigma^2\pi$) in a manner which places four σ electrons in the same spatial region. This is a highly repulsive configuration. The symmetry

of this pathway, 1A_g , is the same as that for the bonding interaction of two excited NH_2^* radicals ($\sigma\pi^2 + \sigma\pi^2$). In the CNDO approximation only a barely avoided crossing occurs for these two states because of the neglect of orbital-orbital exchange terms on the same atom ($K_{\sigma\pi} = 0$, the off-diagonal element in the CI matrix between the two most important configurations). This is only a partial artifact of the CNDO approximation, since the term will be smaller than normally encountered in avoided crossings of virtual states having electrons all occupying the same spatial regions.

The bond rupture in planar D_{2h} hydrazine is unusual in that an orbital inversion for the ground-state SCF solution occurs along the reaction pathway passing from $\sigma^2n_2^2n_1^2$ to either $\sigma^2\sigma^*n_2^2$ or $\sigma^2\sigma^*n_1^2$ at the diradical limit. Neither this orbital inversion nor the configuration of the diradical pair function used causes difficulty if a sufficient number of the proper virtual states are used in the CI treatment. As seen from Figure 5, the surfaces make a perfect marriage across the orbital inversion point without a discontinuity. In the case of the C_2 configuration (Figure 6) no orbital inversion occurs and the evolution and type of CI functions found are fundamentally no different than found in the ruptures of H_2O and NH_3 .

No ab initio calculations of either the surfaces or spectroscopic states in hydrazine are published. We can anticipate that low-lying Rydberg states of the type $n_13s\sigma^*$ (B_{1u}) and $n_23s\sigma^*$ (B_{2g}) will have the same general correlations as valence states of the same symmetry shown in Figure 5 since $3s\sigma^* \leftrightarrow \sigma^*$ for the NN bond. However, the possibility of a low-lying $3s$ (a_g) orbital would also generate two low-lying states of the same symmetry. Thus, the actual ab initio low-lying excited-state surfaces for D_{2h} rupture will be much more complex than indicated by Figure 5, possibly containing several avoided crossings between Rydberg states of the same symmetry. Therefore, Figures 5 and 6 are essentially more deceptive than the case of H_2O_2 . All we know is that with NN rupture three Rydberg states of planar hydrazine must eventually degenerate into valence states and give valence state diradical pairs. Finally, the actual route of photodecomposition of N_2H_4 gives NH, not NN, bond rupture.²⁸ While we found computationally that NH rupture occurred without a significant barrier,^{3a} we tend to believe, as with methylamine (vide supra), that the explanation rests in the nature of the Rydberg orbitals rather than any valence state arguments. However, the photoexcitation of tetraphenylhydrazine yields prompt NN bond rupture followed by an extraordinarily slow rate of radical-radical recombination.²⁹ The radical pair recombination may be stimulated by infrared excitation of one of the radical pairs, an event which is only easy to understand by the examination of Figures 5 and 6 if ground-excited state surfaces approach one another.

Conclusions

The most general conclusion is that the correlation diagrams computationally generated here are better than we would have expected from our general prejudice against semiempirical calculations. In fact, we see no methodological barrier preventing the inclusion of Rydberg-type orbitals at the semiempirical level and the generating of semiempirical surfaces

of the same relative value as much more expensive ab initio calculations. We would tend to be pessimistic about any details of surfaces or the order of spectroscopic states generated here or by such a fashion. Personally, we learned a great deal about the correlative features of the bond rupture events studied here. From a photochemical viewpoint it is evident that surface touching-crossing can computationally occur in topicity 3 or higher conditions. These conditions arise with all the intercombination of bonds between the elements of C, H, O, and N except between CC and CH in the hydrocarbons and HH in H_2 . Thus, the crossing of excited singlet- and ground-state surfaces is a general event in bond rupture reactions.

References and Notes

- (1) W. G. Dauben, L. Salem, and N. J. Turro, *Acc. Chem. Res.*, **8**, 41 (1975).
- (2) (a) A correlation surface for the ground and excited states of H_2O is shown by C. R. Claydon, G. A. Segal, and H. S. Taylor, *J. Chem. Phys.*, **54**, 3799 (1971). (b) Excited-state surfaces for H_2O are shown by J. A. Horsley and F. Flouquet, *Chem. Phys. Lett.*, **5**, 165 (1970); F. Flouquet and J. A. Horsley, *J. Chem. Phys.*, **60**, 3767 (1974). (c) Ground-state bond dissociations in CH_4 , NH_3 , and H_2O are calculated by K. Ishida, K. Kondo, and T. Yonezawa, *ibid.*, **66**, 2883 (1977). (d) A comprehensive set of excited-state surfaces is computed for NH_3 by R. Runau, S. D. Peyerimhoff, and R. J. Buenker, *J. Mol. Spectrosc.*, **68**, 253 (1977).
- (3) (a) E. M. Evleth, *Chem. Phys. Lett.*, **38**, 516 (1976); (b) *J. Am. Chem. Soc.*, **98**, 1637 (1976).
- (4) C. W. Eaker and J. Hinze, *J. Am. Chem. Soc.*, **96**, 4084 (1974).
- (5) J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966).
- (6) S. W. Benson and H. E. O'Neal, "Kinetic Data on Gas Phase Reactions", NSRDS-NBS 21, U.S. Government Printing Office, Washington, D.C.
- (7) A. Das Gupta and S. Husinaga, *Theor. Chim. Acta*, **35**, 329 (1974).
- (8) The form of eq 1 is such that the deviation from the CNDO/2 V_{ab} term varies from positive to negative in the bonding region, whereas in eq 2 the deviation is either positive or negative depending on the value of B .
- (9) For instance, the CI energy for planar ground-state ethylene varied from about -1.2 eV at the 60×60 level to -2.4 eV at the 110×110 level.
- (10) R. Daudel, R. Lefebvre, and C. Moser, "Quantum Chemistry", Interscience, New York, N.Y., 1959; p 554, eq 35.
- (11) Unrestricted Hartree-Fock; see J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory", McGraw-Hill, New York, N.Y., 1970.
- (12) See L. Salem, *J. Am. Chem. Soc.*, **96**, 3486 (1974), for a discussion.
- (13) See G. Herzberg, "Electronic Spectra of Polyatomic Molecules", Van Nostrand, Princeton, N.J., 1967, Chapter 3.
- (14) D. M. Golden, R. K. Solly, N. A. Gac, and S. W. Benson, *J. Am. Chem. Soc.*, **94**, 363 (1972).
- (15) F. Kern and W. D. Walters, *J. Am. Chem. Soc.*, **75**, 6196 (1953). See also ref 5.
- (16) L. Salem and C. Rowland, *Angew. Chem., Int. Ed., Engl.*, **11**, 92 (1972).
- (17) G. A. Segal, *J. Am. Chem. Soc.*, **96**, 7892 (1974).
- (18) C. Leforestier, *Nouveau J. Chim.*, **2**, 73 (1978).
- (19) However, see D. A. Dixon, R. Foster, T. A. Halgren, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **100**, 1359 (1978).
- (20) This is shown in ref 2a and 2d. Of particular interest is the challenging of the concept of "avoided crossings" in the NH_3 surface in ref 2d, a concept developed in detail by L. Salem, C. Leforestier, G. Segal, and R. Wetmore, *J. Am. Chem. Soc.*, **97**, 479 (1975). In NH_3 the concept of avoided crossings is best replaced by the concept of "derydbergization".
- (21) (a) C. G. Freeman, M. J. McEwan, R. F. C. Claridge, and L. F. Phillips, *Chem. Phys. Lett.*, **8**, 177 (1971). (b) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry", Wiley, New York, N.Y., 1966, pp 441, 456-459.
- (22) The CN and NH bond rupture excited state surfaces in methylamine are presently under investigation using ab initio methods by the authors.
- (23) W. A. Wadt and W. A. Goddard III, *Chem. Phys.*, **18**, 1 (1976).
- (24) H. C. Urey, L. H. Dawsey, and F. O. Rice, *J. Am. Chem. Soc.*, **51**, 1371 (1929).
- (25) G. Hirsch, P. J. Bruna, S. D. Peyerimhoff, and R. J. Buenker, *Chem. Phys. Lett.*, **52**, 442 (1977).
- (26) A. Rauk and J. M. Barriol, *Chem. Phys.*, **25**, 409 (1977).
- (27) For instance, see T. Koenig, R. A. Wielesek, and S. C. Huntington, *Tetrahedron Lett.*, 2283 (1974).
- (28) M. Arvis, C. Deviller, M. Gillois, and M. Curtat, *J. Phys. Chem.*, **78**, 1356 (1974).
- (29) R. W. Anderson, Jr., and R. M. Hochstrasser, *J. Phys. Chem.*, **80**, 2155 (1976).