

(31) Note also that only one triplet has been observed below these two singlets. This feature is an inconsistency that suggests the existence of other triplets between the T_1 and T_2 levels shown in Figure 5. They may not have been observed because they lie only slightly above T_1 or because the corresponding $T_1 \rightarrow T_1$ transitions are weak. See, e.g., T. Takemura, K. Hara,

and H. Baba, *Bull. Chem. Soc. Jpn.*, **44**, 977 (1971). The existence of such states might modify the extreme favor that our hypothesis gives toward the singlet channel in the case of naphthalene. On the other hand, it is possible that symmetry factors leading to low oscillator strength in $T_1 \rightarrow T_1$ transitions are also manifested in triplet-triplet annihilation.

Photochemical Extrusion of Nitrogen in Azo Compounds. An ab Initio SCF-CI Study

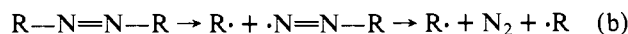
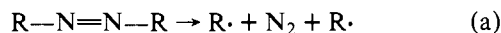
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Abstract: Ab initio SCF-CI methods have been used to simulate the behavior of the ground and low-lying excited states of *cis*-diimide when a nitrogen molecule is expelled via a concerted scission of the pair of NH bonds or a stepwise mechanism. The analysis of the states correlation diagrams shows that the successive rupture of the NH bond is the preferred pathway and might be initiated by the light-induced population of the lowest $n\pi^*$ singlet state of the azo chromophore.

Thermal nitrogen extrusion in azo compounds may proceed via concerted (a) or successive (b) scissions of the pair of N-C bonds coupling the N=N unit to the rest of the molecule.²

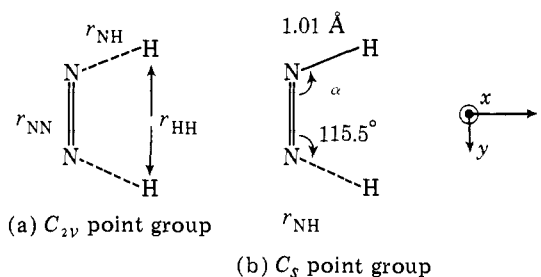


Of course these simple mechanisms have been improved to include, for example, cage effects, but nevertheless the refined versions retain their close parentage with (a) or (b). Recent ab initio SCF calculations³ have shown that no clear-cut choice can be made between (a) and (b) in the thermal decomposition of 1-pyrazolines. Simultaneous cleavage of both CN bonds leading to a planar trimethylene diradical has a calculated activation energy of 44.1 kcal/mol. On the other hand, a two-step reaction involving an intermediate diazenyl radical requires 44.5 kcal/mol. Undoubtedly small perturbations may favor one mechanism or its partner. This in turn might account for the conflicting interpretations of experimental results whether they favor concerted⁴ or successive⁵ scissions.

The same basic mechanisms have been invoked to rationalize the spin correlation effects noted in the photochemically induced expulsion of N_2 .⁶ The aim of this paper is to compare the behavior of the various excited states of azo compounds when pathways (a) and (b) are theoretically simulated. The prototype of this ab initio SCF study is *cis*-diimide.⁷ This choice requires a word of caution. In this model one or two N-H linkages will be broken whose bond energies (92 ± 2 kcal/mol) are notably different from those of the N-C bonds experimentally investigated (78 kcal/mol).⁸ In addition our scheme does not take into account the release of ring strain energy (~ 15 – 20 kcal/mol) which intervenes in the cleavage of cyclic azo compounds. Therefore these calculations will not provide us with an accurate estimation of the activation energies involved (which in turn might be compared with experimental values) but rather with the basic characteristics of the excited states correlation patterns in both alternatives (a) and (b). This approach closely parallels the study of acyclic and cyclic ketones with formaldehyde as a convenient model.⁹

Methodology

Mechanisms (a) and (b) have been treated in the following fashion. In the case of the concerted path (a), for each value of the elongated NH bonds we have minimized the SCF energy of the ground state (without CI) with respect to the r_{NN} and r_{HH} distances.¹⁰ In the second case we have restricted ourselves to the primary feature of the complete reaction, that is, the breaking of one of the NH linkages. For a given NH distance the ground-state energy has been optimized with respect to the NN bond length (r_{NN}) and the NNH angle (α).¹¹ The



ground-state energy was obtained using the ab initio SCF Gauss 70 series of programs¹² in its STO-3G minimum basis set version.¹³ The ground-state MOs were then used to carry out the CI segment of the complete calculation of the excited states wave functions. Singly and doubly excited configurations were constructed, that is, configurations obtained by promoting one or two electrons from the six highest occupied to the four lowest empty MOs.¹⁴ It is important to add that two theoretical procedures were tested at each point of the reaction path to ensure that, for each state under study, the best set of ground-state MOs was used to generate the Slater determinants to be included in the CI calculation. This forces the CI treatment, which, for practical reasons, had to be limited, to approach as closely as possible the results of a complete investigation. The first procedure is Roothaan closed-shell SCF formalism^{15a} which gives adequate MOs in the vicinity of the reactant; the second is Nesbet's brand of open-shell calculations^{15b} which is more adapted in regions where occupied and empty MOs eventually intersect. We accepted as final result

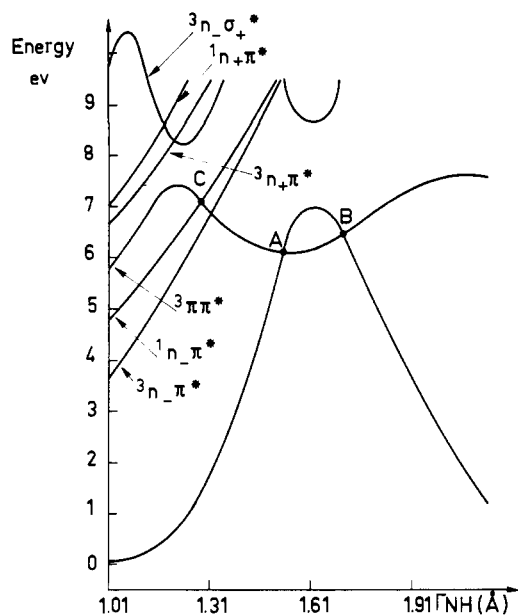


Figure 1. Potential energy curves of the ground and low-lying excited states of *cis*-diimide in the concerted elongation of the pair of N-H linkages.

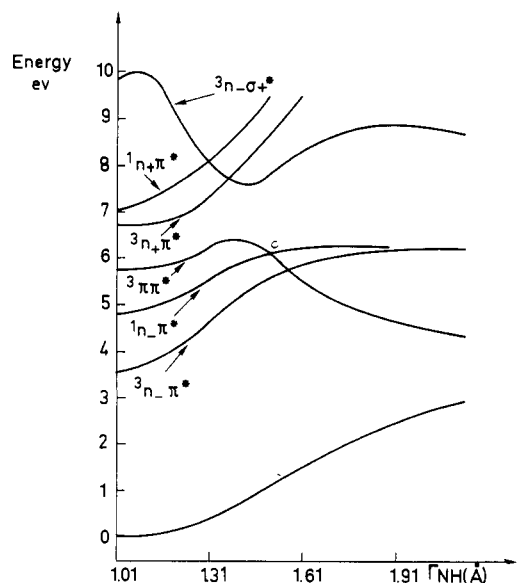


Figure 2. Potential energy curves of the ground and low-lying excited states of *cis*-diimide in the one-bond cleavage.

the lowest of the two energies obtained, at each point, for each state. Let us consider as a test the first excited singlet state of *cis*-diimide. This singlet results from the excitation of an electron out of the out-of-phase combination of the nitrogen lone pairs (n_- , see Figure 3) to the π_x^* molecular orbital. Let us note first that our calculated vertical excitation energy¹⁶ (4.67 eV) is in good agreement with previous theoretical evaluations¹⁷ (4.35 eV¹⁷). The experimental value has not been yet determined. However, *trans*-azomethane $n-\pi^*$ vertical excitation energy is 3.67 eV¹⁸. *Cis* azoalkanes $n-\pi^*$ maxima being red shifted from the maxima of the parent spectra,¹⁹ *cis*-azomethane should therefore have an excitation energy smaller than 3.6 eV. As pointed out by a referee, only if the difference between H and CH₃ is much greater than expected could the 4.67-eV value for *cis*-diimide be correct. This discrepancy results from the sharp variation of the $n-\pi^*$ energy as a function of the HNN angle.¹⁸ A small change of this nuclear variable—recall that such an optimization is not carried out here—is sufficient to reconcile *cis*-diimide and

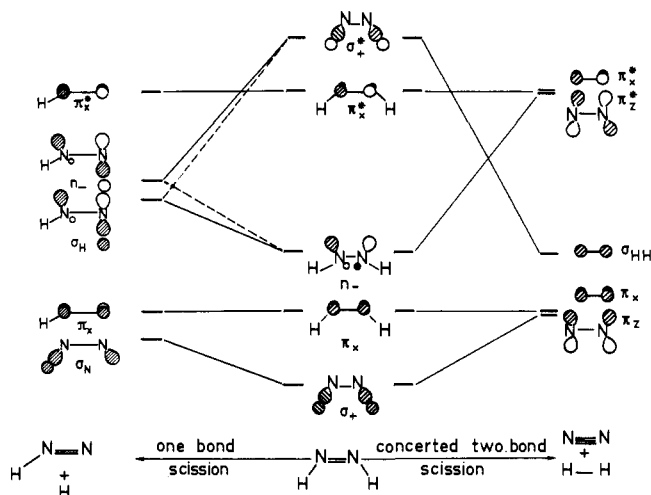


Figure 3. Molecular orbitals correlation diagrams in the two-bond (on the right) and one-bond (on the left) scissions of *cis*-diimide.

azomethane $n-\pi^*$ vertical excitation energies. Figures 1 and 2 respectively represent the ab initio SCF-CI potential energy curves (PEC) for the concerted (a) and stepwise (b) mechanisms. We shall now proceed to the detailed analysis of their main characteristics.

Discussion of the Potential Energy Curves

A. MO Correlation Diagram. The discussion rests on the MO correlation diagram (Figure 3). The π -type orbitals (noted π_x) are not sensibly affected in both processes. The in-plane MOs present similar features in both reaction paths, though one might say that their evolution is "stopped halfway" in the one-bond scission.

The MO pattern associated with the concerted distortion shows that (1) the in-phase combination of the bonding and antibonding MOs of the NH linkages (σ_+ and σ_+^*) are (as would be expected) strongly destabilized and stabilized, respectively. They correlate with an in-plane π type MO (π_z ; bonding) and the bonding function of the H₂ fragment (σ_{HH}); (2) n_- raises in energy to become the in-plane antibonding π_x^* orbital of the N₂ moiety. In the one-bond scission σ_+ and σ_+^* behave in a fashion qualitatively similar to that encountered in the concerted path. σ_+ correlates with an MO (σ_N) which is the bonding combination of the σ_{NH} bonding orbital of the unaffected NH bond and the lobe on the N atom which results from the elongation of the second NH linkage. On the other hand, n_- is destabilized, though its antibonding character is retained and easily recognized. σ_+^* is strongly stabilized and would intend to correlate with the 1s atomic orbital on the "free" hydrogen atom (σ_H). This "natural" behavior of the MOs (dotted lines in Figure 3) is somewhat obscured by two features. At the final point of our calculations ($r_{NH} = 1.91$ Å) there is still some mixing between n_- and σ_H . As a result the HOMO of the system is the bonding combination $\sigma_H + n_-$, with a dominant contribution of σ_H , hence its denomination. Similarly the antibonding $n_- - \sigma_H$ LUMO is mainly located on the diazenyl fragment (n_-). The second remark is that the "natural" correlation involves a symmetry-forbidden orbital crossing which is taken into account in the SCF correlation diagram represented as full lines in Figure 3.

These correlations will now be used to discuss the behavior of the various excited states.

B. States Correlation Diagram. Concerted Reaction. For the sake of clarity these states will be labeled according to their electronic nature but also, whenever necessary, to their symmetry with respect to the molecular (yz) and bisector (xz) planes of symmetry, in that order. The ground state of diimide intends to correlate with a doubly excited $\sigma_{HH}^2 \rightarrow \pi_x^*{}^2$ state

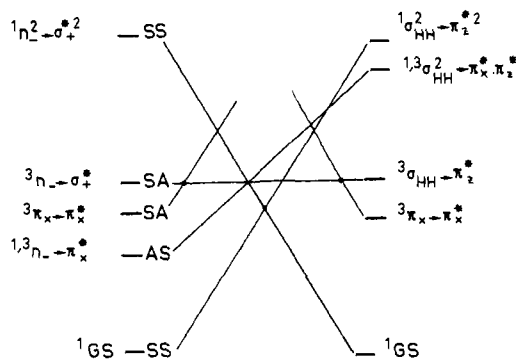


Figure 4. States correlation diagram in the concerted extrusion of N_2 . The dots represent the crossings which become avoided at the CI level of calculation.

of the fragments while, at the same time, the ground state of the products is linked to the doubly excited $n_{-2} \rightarrow \sigma_{+}^{*2}$ state of the reactant (Figure 4). The symmetry (SS) of this duo results in an avoided crossing in the transition region ($r_{NH} \sim 1.56 \text{ \AA}$). This situation is analogous to that encountered in Woodward and Hoffmann analysis of various π electrocyclic reactions where four electrons are forced to coexist in an antiaromatic fashion.²⁰ Indeed the energy gap between the adiabatic potential energy curves (PEC) is 1.75 eV here as compared to, for example, 2 eV in the disrotatory closure of butadiene.²¹ The pair (singlet, triplet) of $n_{-}\pi_x^*$ excited states of diimide correlates with high-lying zwitterionic doubly excited states of the products where both electrons occupying the H_2 bonding MO have been transferred to the π^* manifold of N_2 (one in π_x^* , the other in π_z^*). No other state of similar symmetry (AS) appears in the part of Figure 1 of mechanistic interest, hence the sharp quasi-linear increase of the $1,3n_{-}\pi_x^*$ PECs when the NH bond scissions develop. Let us consider finally the $\pi\pi^*$ triplet state. The diimide $\pi\pi^*$ triplet and its N_2 fragment homologue both tend to reach high-lying triplet excited states of the products and reactant, respectively. A third member of similar transformation properties (SA), however, intervenes: the $n_{-}\sigma_{+}^*$ triplet of *cis*-diimide which correlates with the $3\sigma_{HH} \rightarrow \pi_z^*$ state of the fragments. The relative position of these three curves results in two avoided crossings which, when taken into account in the CI step of the calculations, produce the sinuous shape of the $\pi\pi^*$ triplet PEC.

C. States Correlation Diagram. One-Bond Scission. In this case the symmetry of the reacting system collapses to C_s with a unique plane of symmetry (that of the molecule, yz). Let us briefly comment on the nature of the low-lying states of the scission products. The lowest singlet-triplet pair of states exhibits diradical $D_{\sigma\sigma}$ character. As usual in homosymmetric diradicals the singlet function is the out-of-phase mixing of the σ_H^2 and n_{-2} configurations while the triplet is none other than the pure $\sigma_H^1 n_{-1}$ triplet configuration. The second pair of states possesses diradical $\sigma\pi$ (heterosymmetric) character ($1,3D_{\sigma\pi}$) with one electron mainly located on the hydrogen atom (σ_H) and its partner in the π_x^* MO of the diazenyl fragment.²¹

The correlation diagram is straightforward (Figure 5). The diimide ground state correlates with the singlet $D_{\sigma\sigma}$, the $1,3n_{-}\pi_x^*$ states with the $D_{\sigma\pi}$ states of the fragments. The most interesting feature is that the $n_{-}\sigma_{+}^*$ triplet, in the course of its intended correlation with the $D_{\sigma\sigma}$ triplet diradical, would cross the $\pi_x\pi_x^*$ triplet which is destabilized in the bond-breaking process. This crossing is symmetry forbidden. The maximum in the $\pi\pi^*$ triplet PEC and the well in that of the $n_{-}\sigma_{+}^*$ triplet are the remnants of the "natural" behavior of these states.

Mechanistic Implications

Figures 1 and 2 clearly show that both mechanisms have two

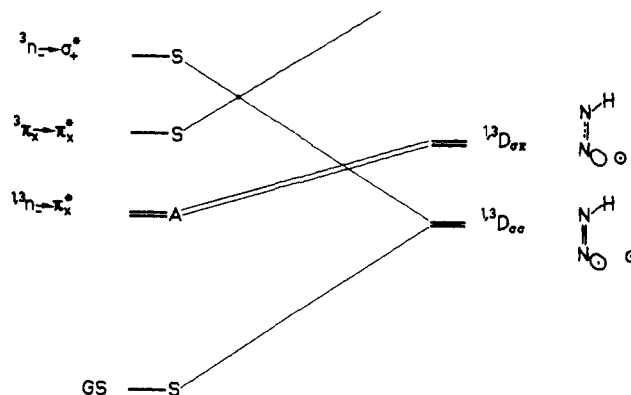


Figure 5. States correlation diagram in the one bond cleavage of *cis*-diimide. The dots represent the crossings which become avoided at the CI stage of the calculations.

qualitatively analogous though quantitatively different characteristics. On one hand the pair of singlet-triplet $\pi_{-}\pi^*$ excited states are destabilized when the concerted or dissymmetric distortions are turned on. The initial destabilization of the raising curve in (a) (where two NH bonds are broken) is roughly twice that in (b) (where only one bond is affected). On the other hand the overall shape of the $3\pi\pi^*$ PEC is similar in both cases. This triplet, which is the lowest state in the transition region ($r_{NH} \sim 1.56 \text{ \AA}$) of the concerted rupture (0.75 eV below the maximum of the ground state PEC), becomes nearly degenerated with the ground state in the final stages ($r_{NH} > 2.5 \text{ \AA}$) of the stepwise mechanism. Here again the initial slope of the destabilized $3\pi\pi^*$ PEC is much larger in the two-bond scission.

In both cases potentially reactive systems must end up on the $3\pi\pi^*$ PEC. In the transition state area of (a) this triplet crosses twice the ground-state PEC (A and B in Figure 1). Intersystem crossing might take place and bring back the reacting species on the ground state surface whether this leakage is unproductive (A) or allows the final separation of N_2 and H_2 (B). In the competing possibility (b) the $D_{\sigma\sigma}$ triplet may proceed further along the reaction path, that is, elongate its second NH bond or intersystem cross to the parent degenerate $D_{\sigma\sigma}$ singlet.

The potentially reactive triplet $\pi\pi^*$ may be populated in two ways: adequate sensitization by an energy (triplet) donor is the first, direct irradiation generating the dipole-allowed $n_{-}\pi^*$ singlet the second. Let us note that in this second alternative the jump (at C, Figure 2) from the $1n_{-}\pi^*$ to the $3\pi\pi^*$ PEC is very efficient, the flipping of the electron spin being compensated by a 90° rotation of this electron's position in space (from the in-plane n_{-} to the out-of-plane π^* orbital).²³ In both strategies an activation energy is necessary whether to attain the maximum in the $3\pi\pi^*$ PEC or the intersystem crossing region around C. Even though our calculations were not specifically designed to obtain precise energy values, they clearly show that the activation energies required by the concerted mechanism (a) are almost twice those of the stepwise concurrent (b) (via the $3\pi\pi^*$, (a) and (b) necessitate 1.65 and 0.95 eV respectively; via the $1n_{-}\pi^*$ state these energies are larger, 2.25 and 1.3 eV). This ratio is directly related to the number of NH bonds elongated in both processes.

To conclude let us first recall that our calculations quantitatively suffer from limited basis set and configuration interaction and the lack of individual optimization of the excited states under scrutiny. Still they exhibit the fundamental differences between both processes. If we cannot affirm that the two-bond scission is totally unrealistic in all cases it appears that the activation energies it would require cannot be reduced to such an extent as to allow the $3\pi\pi^*$ or $1n_{-}\pi^*$ states to rea-

sonably acquire them in a time compatible with their lifetime. In any case the concerted mechanism cannot compete with the one-bond scission. This alternative pathway necessitates activation energies which, even though they still appear somewhat too large in our semiquantitative scheme, are much smaller. Any improvement in our calculations (not to mention the substituent effects on the azo group) would bring these energies in a range where they could be acquired by the reacting excited states (be it the $\pi\pi^*$ sensitization experiments or the $n-\pi^*$ singlet via direct irradiation) in a photochemically decent period of time. With the aforementioned restrictions in mind, nitrogen extrusion appears to follow a stepwise breaking mechanism of the pair of NH bonds which is initiated by the light-induced population of the lowest $n-\pi^*$ singlet state of the azo chromophore.

References and Notes

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- (10) Such a reaction path involves two successive steps. In the first the elongation of the two NH linkages releases (at least partially) two hydrogen atoms. In the second these atoms recombine to generate a hydrogen molecule. Strictly speaking reaction path (a) is then represented by the early stages of our calculated reaction mechanism. A referee suggested that the concerted breaking of the NH bonds should be accompanied by an increase of the NNH angles. This is indeed what is observed at the beginning of our simulated reaction (recall that the energies are minimized with respect to r_{HH} and r_{NH}). When the two hydrogen atoms recombine the NNH angles decrease but they have partly lost their meaning.
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Activity Coefficients of an Electrolyte A or B in a Ternary Mixture (A + B + H₂O) and a Transition Model

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Abstract: Based on a transition model, as applied to solutions of a single electrolyte, a semiempirical expression has been proposed to predict the activity coefficients of a 1:1 electrolyte A or B in a ternary mixture (A + B + H₂O). The calculated activity coefficients compare well with their experimental values. Glueckauf and other relations of mixed electrolyte solutions follow as a consequence of cross-differentiation of the fundamental expression.

Recent years have witnessed considerable interest in the thermodynamic properties of aqueous electrolyte mixtures. Much of this interest stems from the importance of mixed electrolytes in such fields as oceanography and geochemistry and considerable attention¹⁻³ has been paid to predict the activity coefficients of each component of an aqueous mixed electrolyte solution. Lietzke and Stoughton⁴ have recently

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extended their two-structure model,⁵ as applied to solutions of a single electrolyte, to predict the activity coefficients of each component in a mixed electrolyte solution with surprising accuracy. However, their fundamental equation does not explain some of the other features of these aqueous mixed electrolyte solutions (e.g., Glueckauf relations, etc.). The present work is a semiempirical extension of a transition model⁶ to predict the activity coefficient data of the components A or B of a ternary (A + B + H₂O) mixture. Glueckauf and other rela-