Rates of Spin-Forbidden Organic Reactions. 3. Extrusion of Nitrogen from Methylenepyrazoline[1]

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Abstract: The stereochemistry of the extrusion of molecular nitrogen from methylenepyrazoline is examined, with particular attention to the question whether the spin-forbidden production of triplet trimethylenemethane can be competitive in rate with the spin-conservative production of some singlet state of trimethylenemethane. The spin-extended orbital correspondence analysis in maximum symmetry (OCAMS) indicates that either a conrotation or a disrotation can produce triplet trimethylene directly upon N_2 extrusion. Energetic considerations suggest that a conrotation enhances the probability of singlet-triplet crossover, while disrotation favors the formation of zwitterionic singlet products. OCAMS predicts substantial spin polarization in the product triplet trimethylenemethane. The qualitative form of the potential energy surfaces is sketched by semiempirical MO computation, and a modified RRKM technique is employed to estimate the rate of triplet production relative to the rate of singlet production. Triplet production is apparently favored in spite of the spin flip required. Experimental data require a mixture of singlet and triplet production if reported energies and enthalpies are to be reproduced. The possibility that spin-forbidden processes may occur yet escape detection in routine tests is discussed.

I. Introduction

A number of small organic molecules have triplet ground states. The most well-known examples are methylene[3] and trimethylenemethane (TMM).[4] These systems may be prepared from singlet precursors such as diazomethane and methylenepyrazoline (MP) by photolysis or thermolysis.[5] Two distinct processes may be envisaged: either the hydrocarbon is formed initially in a singlet (excited) state and subsequently achieves the triplet (ground) state by collisions,[6] or the hydrocarbon is formed in the triplet state by a direct spin-forbidden process. A qualitative analysis including the spin-orbit perturbation shows that the spin-forbidden processes are not strictly forbidden in the presence of spin-orbit coupling.[7] Statistical and trajectory computations of the rate of thermolysis of diazomethane indicate that the spin-forbidden process may be competitive in rate with the spin-conservative process, for that system at least.[8] Perturbation-theoretic arguments suggest that the spin-forbidden path may be important in substituted diazomethanes as well.[9]

The purpose of this report is to examine the question whether spin-forbidden processes may be encountered in the thermolysis of methylenepyrazolines. There is some basis for expecting spin-forbidden processes to be significant in this case, since the energetic advantage in production of ground-state rather than excited-state products may cancel the penalty in rate associated with the necessity of changing spin state. Moreover, Berson and co-workers[10] have pointed out the surprising difference in the kinetics of decomposition of their bicyclic methylenepyrazoline ($\Delta S = 7$ eu) and that of Crawford and Cameron's parent methylenepyrazoline ($\Delta S = -1.1$ eu). They suggest that the parent system is undergoing a spin-forbidden step in the transition state, but that the bicyclic compound is not. The latter conclusion is based on a considerable body of experimental data, but the former relies mainly on the kinetic results.

II. Qualitative Analysis of the Dissociation of Methylenepyrazoline (MP)

We could consider two alternative modes of decomposition of methylenepyrazolines: (1) to methylenecyclopropane in its singlet ground state; (2) to trimethylenemethane, which—having two degenerate orbitals available for occupancy by only two electrons—is expected to have a triplet ground state, as has been confirmed experimentally. (Note that the e^2 assignment of electrons may produce a_1, a_2, and e symmetry states, and the $^3A_2$ state may *not* be ground state in all cases. Coulomb repulsions may dictate a singlet ground state, as seems to be the case for cyclobutadiene.)

The orbital correspondence in maximum symmetry (OCAMS) method for the qualitative description of reaction pathways will be our primary guide.[7] This method is at first glance very similar to the methods of Woodward and Hoffmann as extended by Longuet-Higgins and Abrahamson (WHLA). However, the major distinction is that while a reaction path is *presumed* in the WHLA methods, and the symmetry group is chosen so that the reaction path is totally symmetric, the OCAMS analysis arranges reactants and products in the highest common symmetry. Symmetry C_{2v} is appropriate in the case of methylenepyrazoline. All orbitals occupied in the ground states of reactants and products are assigned symmetry labels in the group of maximum symmetry. In general it will be possible to establish direct correspondence between a number of orbitals occupied in reactants and qualitatively similar orbitals bearing like symmetry labels among orbitals occupied in the ground state of products. At times, however, it will become necessary to *induce* correspondence between an orbital occupied in the ground state of reactants and an orbital occupied in the ground state of products even though the orbitals disagree in symmetry. In that case a geometric distortion can usually be found which will transform the reactant orbital of symmetry γ_R to the symmetry of the product orbital γ_P. For Abelian groups (lacking degenerate representations) the symmetry of the distortion $\gamma_D = \gamma_R\gamma_P$. The simplest illustration relevant to the system of interest here is provided by the production of methylenecyclopropane.

1. **Methylenecyclopropane (MCP).** This product is presumed to be produced in its singlet ground state, so only occupied orbitals are included in Figure 1, the correspondence diagram for its formation. Three doubly occupied molecular orbitals on each side suffice to characterize the reaction. Of the three electron pairs explicitly considered, one is delivered to the $NN\pi(a_1)$ orbital of nitrogen. No other electrons that eventually find themselves on N_2 need be considered, since the remaining orbitals occupied by its valence electrons ($NN\sigma$, $NN\pi_y$, and the lone-pair combinations n_- and n_+) have the same symmetry properties in reactant and product. Two orbital correspondence are direct, but the third, $CN\sigma_-(b_1) \leftrightarrow NN\pi(a_1)$, must be induced by motion along a b_1 symmetry coordinate, i.e., an in-plane deformation. Such a motion, perhaps accompanied by rotation of *one* of the two methylene

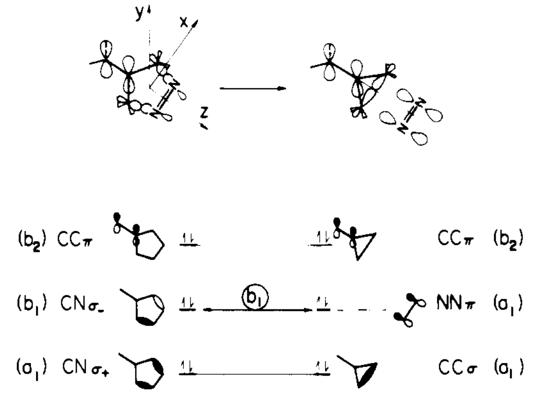


Figure 1. Correspondence diagram for formation of methylenecyclopropane from methylenepyrazoline.

groups, is appropriate for a stepwise mechanism, in which one CN bond is broken at a time, but not for the concerted rupture of both. Our analysis, therefore, indicates that direct formation of methylenecyclopropane, without a biradical intermediate, is not possible from methylenepyrazoline.

2. Construction of Correspondence Diagram for Formation of Trimethylenemethane **(TMM).** Consider the extrusion of N_2 from MP to produce TMM, sketched in Figure 2A. In Figure 2B on the right we have the four CHσ' combinations of TMM, while on the left we have the four CHσ bonds of MP. Note that of the direct correspondence lines (solid lines in Figure 2B connecting orbitals of like symmetry), two would connect CHσ orbitals with higher lying (π) orbitals of TMM, rather than with CHσ' orbitals. However, either a conrotation (a_2) or a disrotation (b_2) of the two methylene groups is capable of inducing the two recalcitrant pairs of CH orbitals to correspond among themselves.

The "direct" correspondence of the a_1 and b_1 CH orbitals of MP with a_1 and b_1 CH orbitals in TMM should not be interpreted to mean that the reaction *path* linking *these* orbitals is totally symmetric while the reaction *path* linking a_2 and b_2 CH orbitals of Mp with a_1 and b_1 CH orbitals of TMM is different in symmetry. Rather one must consider that the *perturbation* exercised by the changes in geometry has both a_1 and a_2 (or b_2) parts. Reference 7 shows that a $\Gamma_j \neq \Gamma_1$ (non-totally symmetric) reaction path will produce a perturbation of symmetry species $\Gamma_j \oplus \Gamma_j{}^2 \oplus \Gamma_j{}^3 \oplus \ldots$. The direct correspondence would be induced in these cases by the a_2 or b_2 path through the $\Gamma^2 = a_1$ part of the perturbation.

In Figures 2C and 2D the bonding levels and antibonding levels of the system (other than CH bonds) are displayed. The ordering of the MP orbitals by energy is self-evident, but the splitting of the degenerate orbitals of TMM and N_2 while those species are still close enough to interact requires comment. The interaction between the two b_2 orbitals, ψ_3 and the doubly occupied NNπ_y, makes the former slightly antibonding while it pushes the latter below NN$\pi_z(a_1)$; in contrast, $\psi_2(a_2)$ is stabilized by interaction with NN$\pi_y{}^*(a_2)$, which becomes more antibonding than NN$\pi_z{}^*(b_1)$. Most importantly, $\psi_2(a_2)$ is selected as being lower in energy than $\psi_3(b_2)$ as long as the departing nitrogen molecule has not gone completely out of interaction range.

3. Formation of TMM as a Zwitterion. It follows from Figures 2B-D that under either a conrotation (a_2) or a disrotation (b_2) (both of which ensure that the CH orbitals intercorrelate among themselves) three induced correspondences—indicated by dashed lines in Figures 2C and 2D—can be established. One doubly occupied orbital of MP, CN$\sigma_-(b_1)$, and one of its unoccupied orbitals, CN$\sigma_+{}^*(a_1)$, have no counterparts of the same symmetry species on the right, nor do $\psi_2(a_2)$ and $\psi_3(b_2)$ of TMM have any corresponding partners on the left. Either the conrotation (a_2) or the distortion (b_2) can generate a closed-shell singlet; the former would, however, be initially dominated by the doubly excited $^1A_1{}'$ state ($\psi_3{}^2$). The more stable $^1A_1$ state ($\psi_2{}^2$), which is positively charged on C_3 and has a large electron density on C_1 and C_2, and so can be regarded to be a zwitterion, is preferentially formed along the disrotatory pathway. It should be noted that these arguments neglect the CI which produces the singlet $\psi_2{}^2 \pm \psi_3{}^2$ states in D_{3h} trimethylenemethane. The mixing would be substantial only after N_2 is removed from the system so that the local symmetry is no longer C_{2v} or less.

The conrotatory (a_2) and disrotatory (b_2) reaction coordinates are sketched as "con" and "dis", respectively, in Figure 3. Taking pathway "dis" up first, we note that elongation of the CN bonds (a_1) is accompanied by two concomitant (b_2) motions, one elevating N_2 and the other rotating the methylenes. The resultant disrotatory reaction coordinate pushes the departing N_2 molecule above (or alternatively below) the XZ plane. N_2 departure along this pathway stabilizes the zwitterion particularly well, since by breaking C_{2v} symmetry it allows not only NNπ_y and NN$\pi_y{}^*$, but NNπ_z and NN$\pi_z{}^*$ as well, to contribute to the stabilization of ψ_2. The function ψ_3 is not subject to this newly available stabilization.

When the out of plane distortion is built into the reactant, as in 7-methylene-2,3-diaza[2.2.1]bicyclohept-2-ene (MDBH), shown at the top of Figure 4, the closed-shell species should be formed with particular ease. The simplified correspondence diagram, which—since reflection in the yz plane is the only symmetry element retained—reduces to a Woodward-Hoffmann-Longuet-Higgins-Abrahamson (WHLA) correlation diagram, confirms this conclusion. The experimental observation that MDBH undergoes thermolysis with a rather high Arrhenius preexponential factor is characteristic of dissociation reactions that proceed with conservation of spin. The high strain in the reactant is reflected in a lowered activation energy for its dissociation.[10]

4. Spin Nonconservative Generation of TMM in Its Triplet Ground State. The triplet ($\psi_2{}^1\psi_3{}^1$) can only be formed directly in a region where its potential surface intersects that of the lowest singlet. The nπ^* or $\pi\pi^*$ triplet states localized on the N_2 fragment would not be substantially lowered in energy as N_2 is extruded and do not correlate with the TMM ground triplet, so they need not be considered. The triplet state of the reactant which correlates with ($\psi_2{}^1\psi_3{}^1$) under either a disrotation or a conrotation is the highly excited (CN$\sigma_-{}^1$CN$_+{}^{*1}$). In order to reduce its energy sufficiently to bring it close to that of the ground-state singlet, the CN bonds will have had to be almost completely broken, and the methylene groups will have already rotated toward their eventual coplanar orientation.

In principle this could occur along either pathway "con" or "dis" of Figure 3. However, as already pointed out, the disrotatory pathway "dis" lends additional stability to ψ_2 relative to ψ_3, and thus favors initial formation of the closed-shell zwitterion. Direct formation of the triplet requires a pathway along which ψ_2 and ψ_3 are pushed together in energy. The suitability of pathway "con" is evident from the correspondence diagram (Figure 2A), according to which the correspondence lines induced by the "con" a_2 distortion, CN$\sigma_-(b_1) \leftrightarrow \psi_3(b_2)$ and CN$\sigma_+{}^*(a_1) \leftrightarrow \psi_2$ (a_2), cross one another before the fragments have separated. One of several equalizing factors can be recognized in "con" of Figure 3. As the receding N_2 molecule rotates about the z axis, its long axis moves out of the xz plane. As this occurs, NNπ_y increasingly loses overlap with ψ_3 and so can no longer destabilize it so effectively; simultaneously, NNπ_z enters into a stabilizing interaction with ψ_3.

All the above considerations suggest strongly that TMM can be produced directly in its triplet ground state by motion along a conrotatory pathway resembling "con".

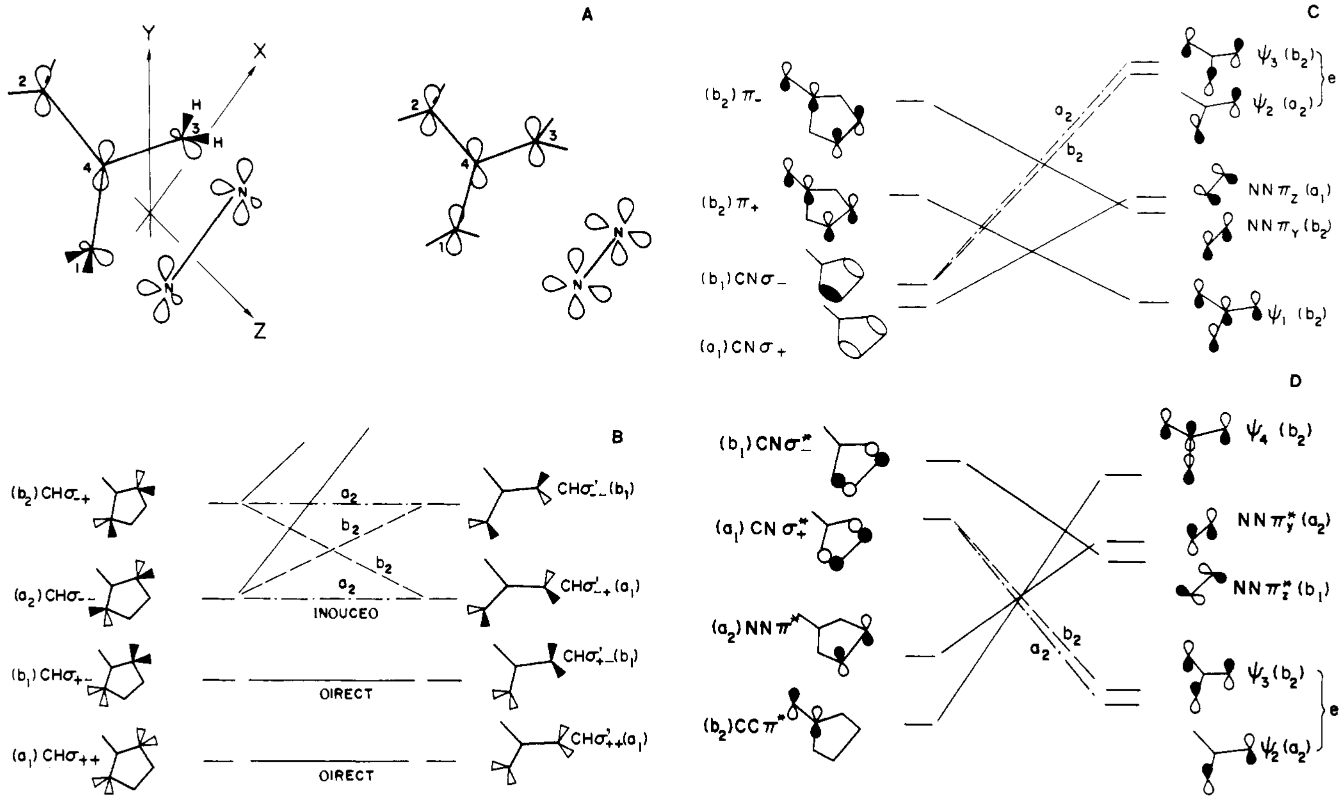
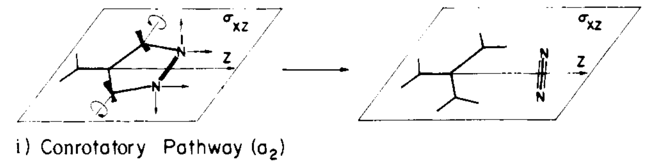
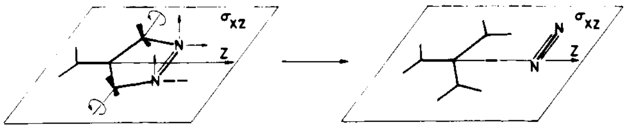


Figure 2. (A) A coordinate system and numbering convention is shown for the extrusion of molecular nitrogen from methylenepyrazoline (left), leaving planar trimethylenemethane. (B) The CH bond orbitals at the terminal methylenes 1,3 of the hydrocarbon fragment are shown, with appropriate C_{2v} irreducible representation labels. The labels for the methylenepyrazoline CH orbitals do not agree perfectly with the corresponding CH orbitals of planar trimethylenemethane. Perfect agreement in symmetry labels can be induced by an a_2 motion (conrotation of the methylenes) or by a b_2 motion (disrotation of the methylenes). These motions are the most obvious ways of producing a set of CH bonds in the molecular plane from a set of CH bonds arranged as in methylenepyrazoline. (C) Non-CH orbitals occupied in the ground states of methylenepyrazoline and nitrogen + trimethylenemethane are shown. In order to achieve correspondence in symmetry labels of these orbitals, either an a_2 or a b_2 perturbation is required. (D) Non-CH orbitals vacant in the ground states of methylenepyrazoline and nitrogen + trimethylenemethane are shown. Once again either an a_2 (conrotation) or a b_2 (disrotation) perturbation induces direct correspondence. Note that the eventually degenerate (e in D_{3h}) nonbonding orbitals of trimethylenemethane appear both in (C) and (D).



i) Conrotatory Pathway (a_2)



ii) Disrotatory Pathway (b_2)

Figure 3. Rotatory pathways for methylenepyrazoline dissociation to trimethylenemethane.

We have so far not described the operator which accomplishes the transformation of the system from singlet to triplet spin multiplicity. This is the spin-orbit coupling, which for present purposes can be represented by its one-electron component.

$$V_1(\text{spin-orbit}) = \sum_{Ai} \zeta_A \overline{L}_{Ai} \cdot \overline{S}_i$$

Here $\overline{L}_{Ai}$ is the angular momentum associated with the motion of the ith electron about the Ath nucleus, and S_i is the intrinsic ("spin") angular momentum of the ith electron. The quantity ζ_A depends on details of the atomic orbitals on center A, but will be considered here to be a parameter specified for each atom. The symmetry properties of the spin-orbit coupling

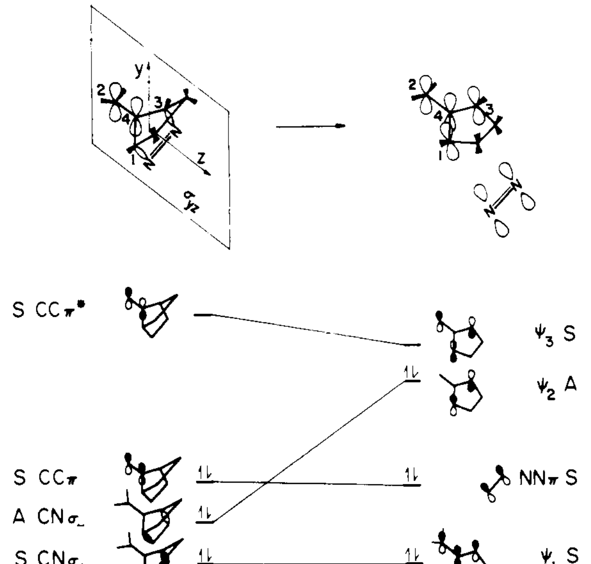


Figure 4. Correspondence diagram for a species in which the disrotatory dissociation is forced.

operator are particularly simple in Abelian groups. The operator, as a term in the Hamiltonian, must be totally symmetric, term by term. That is, the operator is a scalar product expressed as a sum made up of x, y, and z terms. Each term individually must be totally symmetric. Since the $(L_{Ai})_x$ component transforms as the rotation around the x axis, so must $(S_i)_x$ transform as the rotation about the x axis so that $\Sigma \zeta_A (L_{Ai})_x (S_i)_x$ is totally symmetric.

The effect of the spin-orbit coupling on a set of spin orbitals must be twofold. There must be an effect on the spatial symmetry due to the spatial factor in the operator, and also an effect on the spin symmetry due to the spin factor of the operator. Consider the C_{2v} case, where the spin-orbit coupling can be written

$$V_1(\text{spin-orbit}) = \text{constant} \times (W_{a_2\text{-space}}\, T_{a_2\text{-spin}} + W_{b_1\text{-space}}\, T_{b_1\text{-spin}} + W_{b_2\text{-space}}\, T_{b_2\text{-spin}})$$

This operator can transform a pair of spin orbitals of a_1 symmetry and singlet spin to any of the following states.

P_1 = singly occupied a_1 and a_2 space orbitals, a_2 component of the triplet state

P_2 = singly occupied a_1 and b_1 space orbitals, b_1 component of the triplet state

P_3 = a_1 and b_2 space orbitals, b_2 component of the triplet state

The conclusion of this argument is that, if it is necessary to use the spin-orbit coupling to establish a correspondence among space-labeled orbitals of symmetry γ_P and γ_R, a particular component of the triplet state is formed, with the symmetry of the direct product of space labels, $\gamma_P \times \gamma_R$. Figure 2A then tells us that the b_2 term in the spin-orbit operator induces the transfer of one electron from CH$\sigma_-(b_1)$ to $\psi_2(a_2)$ while the conrotatory motion delivers the other to $\psi_3(b_2)$. According to the arguments above, the $R_x(b_2)$ component of the triplet is produced first, but, because the reacting system has been distorted along an a_2 coordinate, the $R_y(b_1)$ component will be produced along with it. Symmetry species b_1 and b_2 merge as b when the symmetry is reduced from C_{2v} to C_2.

III. Quantitative Description of N_2 Extrusion from Methylenepyrazoline

Although the symmetry analysis establishes that the spin change is not forbidden if spin-orbit coupling is present, it does not permit any estimate of the relative rates of spin-allowed and spin-forbidden processes. As a first step toward this estimate, we have computed a rough surface for the N_2 extrusion from methylenepyrazoline. For economy we have used the CNDO-MO method, with complete geometry optimization by the gradient technique, to describe the concerted dissociation,[11] keeping all heavy atoms coplanar but permitting either conrotation or disrotation. Our results are summarized in Figure 5. We see a staged procedure for the concerted dissociation, in which the CN bonds are stretched in C_{2v} symmetry from about 1.4 Å at the equilibrium geometry of methylenepyrazoline to about 2.2 Å. In this neighborhood the rotation of methylenes into the plane defined by the heavy atoms becomes feasible, and the singlet and triplet surfaces cross. The conrotation is favored, and the stage is set for passage from singlet to triplet state.

In viewing Figure 5, it is necessary to keep in mind the prejudice of zero-differential overlap MO theories in favor of condensed cyclic structures. Whereas the computed dissociation energy is ca. 360 kcal/mol, a more reasonable guess based on bond energies is ca. 90 kcal/mol. This correction is most dramatic for $R_{CN} \leq 2.2$ Å, before dissociation is almost complete. This undesirable feature of the dissociation curve will influence our description of the probability of surface crossing.

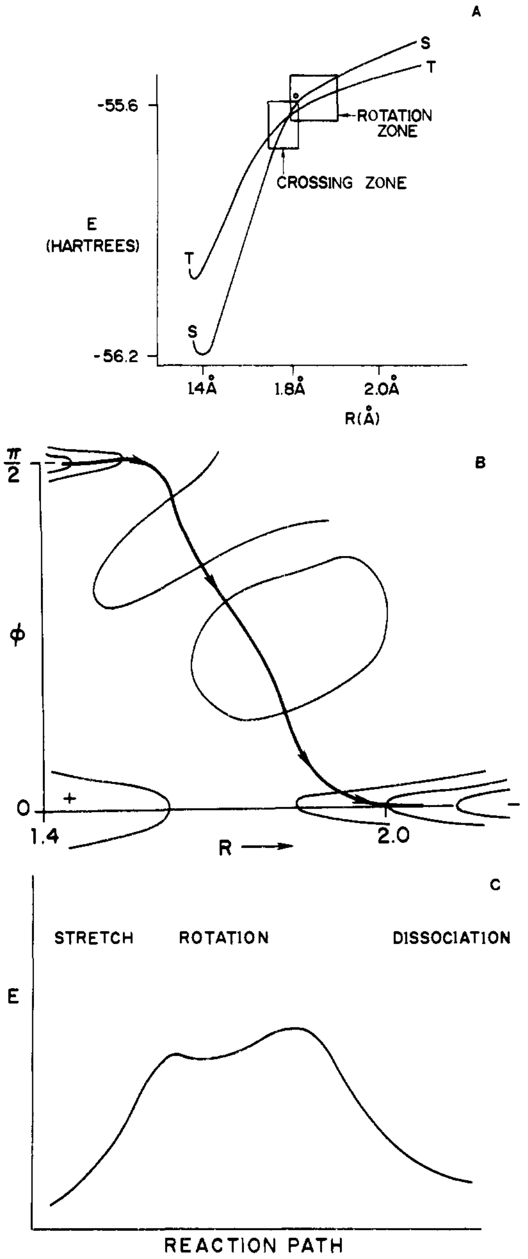


Figure 5. Dissociation surface sections for singlet (S) and triplet (T) methylenepyrazoline dissociation: (A) linear extrusion; (B) rotation zone; (C) the low-energy path.

IV. Estimation of the Probability of Crossing from Surface to Surface

A semiclassical model proposed by Landau and Zener[12] leads to an equation for the probability of crossing from surface to surface at an intersection.

$$\text{Pr} = e^{-\gamma}(1 - e^{-\gamma});\ \gamma = A^2/(V \cdot \Delta B)$$

Here A^2 is the square of the (in the present case, spin-orbit) coupling between surfaces, V is the velocity normal to the intersection, and ΔB is the difference in slopes of the surfaces in the neighborhood of the intersection. We see that crossing is favored by slow passage through a region where surfaces are almost parallel and strongly coupled.

Estimation of the slopes of the surfaces will be much in error if we use the unscaled CNDO surfaces. But since these slopes are too large for bond stretches, the error is such as to lead to an *underestimate* of the crossing probability. Therefore, we adopt the CNDO surfaces' slopes *without scaling* so as to obtain a conservative estimate of the crossing probability.

We have computed the magnitude of spin-orbit coupling in the zone near the crossing of singlet and triplet states, where R_{CN} ranges from 2.1 to 2.3 Å and ϕ (the measure of con- or disrotation) ranges from 0° (all hydrogens on the carbons in the breaking CN bonds coplanar) to $\pi/2$ (face to face CH_2 fragments). We used the one-center one-electron approximation to the total spin-orbit coupling, since two-center and two-electron contributions were shown to cancel in large part.[14] This cancellation may be expected only for molecules in which all heavy atoms (having p orbitals participating in bonding) are collinear, in view of the results of more recent computations on nonlinear polyatomics. Errors introduced by this approximation probably affect the estimate by a factor of two at most.

In the one-electron one-center approximation one may evaluate the matrix representation

$$\{V_{SO}\}_{ab} = \langle \chi_a{}^{S} | V_{SO} | \chi_b{}^{T} \rangle$$

with ease, using the relations and atomic parameters of Halevi et al. or using the relations quoted by McGlynn et al. Here $\chi_a{}^s$ is the ath atomic orbital in the basis describing the singlet state, while $\chi_b{}^T$ is the bth atomic orbital in the triplet basis. Since the singlet geometry and AO basis match the triplet geometry and AO basis at the crossing point, the matrix in the AO basis is symmetric. However, the evaluation of the expectation value of the spin-orbit coupling between states is made complicated by the fact that the MOs occupied in the singlet state are not in general orthonormal to those occupied in the triplet states even though they are expected in the same AO basis. We used the ordinary restricted Fock Hamiltonian to define the singlet state MOs while we used an unrestricted Fock operator to describe the triplet state MOs. We dealt with this problem by using the "corresponding orbital transform" defined by Amos, which constructs orbitals guaranteed to be orthogonal between the two states.

We found that the spin-orbit coupling depended on the angle of con- or disrotation ϕ in the way predicted by Salem and Rowland for trimethylene diradical. This angle dependence is well represented by

$$V_{SO} \cong 8.5 \cos\phi \sin\phi$$

where the spin-orbit coupling is written in units of cm^{-1}.

It is interesting to note that the spin-orbit coupling for MDBH is estimated to be 20% higher than the coupling in MP. Therefore the fact that MDBH follows a spin conservative dissociation path is not due to an anomalously low spin-orbit coupling; instead the cause must be the forced disrotation in MDBH not enforced in MP.

V. Rate Computation in a Rice-Ramsperger-Kassel-Marcus (RRKM) Approximation

The RRKM theory considers that the rate of dissociation of a molecule is largely determined by the relative density of states in the equilibrium geometry of the reactant and the "critical configuration", the structure along the reaction coordinate which has the minimum state density. The rate of decomposition depends on the energy available; the energy available must exceed a certain threshold E_0

$$\begin{aligned} k(E) &= 0 & E &< E_0 \\ &= f(E - E_0) & E &> E_0 \end{aligned}$$

Here f is as yet unspecified; if the system is viewed as composed of σ independent but coupled oscillators, and one insists that one critical oscillator has at least energy E_0, classical statistical arguments lead to the RRK expression[18]

$$k(E) = A\left(\frac{E - E_0}{E}\right)^{\sigma - 1}$$

A is an energy-independent factor. An important feature of the RRK argument, retained in later refinements, is that energy is "rapidly" transmitted from mode to mode. Rapid transmission in this case means that energy is randomized in the period between energization and actual dissociation. Experiment has shown that randomizations must occur in 10^{-13} s or even less, with some noteworthy exceptions.[19] Monte Carlo computations of small isolated systems show that randomization in these molecules is complete after 10^{-11} s.

Detailed evaluation of the RRK parameters A and σ was made possible by Marcus, adopting the ideas of the absolute rate theory.[20] The energy-dependent rate constant is written

$$k(E) = \frac{\alpha G^*(E - E_0)}{hN(E)}$$

where α is the reactions path degeneracy, h = Planck's constant, and E_0 is the minimum energy needed for reaction. $N(E)$ is the density of states of the reactant and G^* is the integrated density of states for the transition state. The units of N are (states/energy), and $G = \int_{E_0}^{E} N(E)\,dE$ is dimensionless. The familiar partition function Q is

$$Q = \int N(E) e^{-E/kT} dE$$

In the complex systems we are treating, this semiclassical expression is appropriate. It shows that the expression $N(E)$ is formally the (inverse) Laplace transform of the partition function

$$N(E) = \mathcal{L}^{-1}(Q(S)) \qquad (s = 1/kT)$$

Given a classical vibrational partition function

$$Q_{vib} = 1/S^{v} \sum_{i=1}^{V} h\nu_i \qquad (s = 1/kT)$$

for a system of v oscillators, the transform yields the classical density and sum of states:

$$N_v(E) = \frac{E^{v-1}}{\Gamma(v) \prod_{i=1}^{v} h\nu_i} \qquad G_v(E) = \frac{E^{v}}{\Gamma(v+1) \prod_{i=1}^{v} h\nu_i}$$

This approximation ignores zero point energy, $E_{zero\ point} = \frac{1}{2}\sum_{i=1}^{v} h\nu_i$. The problem is dealt with in an ad hoc way by shifting the energy origin to (say) $aE_{zero\ point}$, excluding lower energies from N_v. Then

$$N_v(E) = (E + aE_{zero\ point})^{v-1} \Big/ \left(\Gamma(v) \prod_{i=1}^{v} h\nu_i\right)$$

If $a = 1$, this is called the semiclassical approximation. We have used the empirical relations of Whitten and Rabinovitch,[20] wherein

$$a = 1 - \beta\omega$$

$$\log \omega = -1.0506 \left(\frac{E}{E_{zero\ point}}\right)^{1/4} \qquad E > E_{zero\ point}$$

or

$$\omega - 1 = 5\left(\frac{E}{E_{zero\ point}}\right) + 2.73\left(\frac{E}{E_{zero\ point}}\right)^{1/2 + 3.51} \qquad E < E_{zero\ point}$$

and $\beta = \nu_{disp}(v - 1)$ with $\nu_{disp} = \langle \nu^2 \rangle / \langle \nu \rangle^2$.

Molecular rotations influence the density of states if the

Table I. Input for RRKM Computation on Dissociation of Methylenepyrazoline[c,d]

moments of inertia: (amu bohr^2)
equilibrium: (34.3, 40.1, 1.51)
S-T crossing: (31.6, 87.0, 1.14)
singlet critical configuration: (31.6, 87.0, 1.14)

fundamental frequencies			
type of mode	equilibrium	triplet critical configuration	singlet critical configuration
$=CH_2$ asym str	3084^{a}	3084^{1}	3084
$=CH_2$ sym str	3005^{a}	3005^{1}	3005
	2990^{b}	2990^{1}	2990
$-CH_2-$ str	2977^{b}	2977^{1}	2977
	2928^{b}	2928^{1}	2928
	2855^{b}	2855^{1}	2855
C=C str	1662^{a}	1662	1000^{2}
N-N stretch	1552^{b}	2200^{3}	2200
$-CH_2-$ scissor	1453^{b}	1453	1453
	1433^{b}	1433	1433
$=CH_2$ def	1405^{a}	1405	1405
CH_2- (scissor)	1218^{b}	640^{4}	640
	1199^{b}	600^{4}	600
CH_2-twist	1192^{b}	596^{4}	596
	1110^{b}	555^{4}	555
C-C-C antisym bend	1015^{a}	1015	1015
antisym ring def	977^{a}	488^{4}	488
$=CH_2$ twist	977^{a}	977	50^{5}
$=CH_2$ rock	9^{a}	927	927
C-N out of plane	937^{b}	468^{6}	468
C-N sym stretch	888^{b}	*e*	*e*
$=CH_2$ wag	880^{a}	880	400^{7}
$-CH_2-$ rock	716^{b}	716	716
C-C-C sym str	673^{a}	673	673
$-CH_2$ rock	671^{b}	671	671
sym ring def	570^{a}	570	570
N-N ring twist	428^{b}	214	214
$C=CH_2$ skel wag	418^{a}	418	200^{8}
$C=CH_2$ skel rock	363^{a}	363	363
ring mode	80 (estimate)^{a}	65 (estimate)	65

[a] Methylenecyclopropane: J. R. Durig, Y. S. Li, and L. A. Carriera, *J. Chem. Phys.*, **57**, 1896 (1972); T. B. Malloy, Jr., F. Fisher, and J. Laane, *J. Mol. Spectrosc.*, **40** (1971). [b] Δ-1-Pyrazoline: J. Durig, *J. Chem. Phys.*, **52**, 6096 (1970). [c] Landau-Zener factor = 1.26×10^{-4}. At 461 K, $\Delta E^{\ddagger}$(S-T) = 31.98 kcal/mol and $\Delta S^{\ddagger}$(S-T) = −5.2 cal/mol·K, while $\Delta E^{\ddagger}$(singlet dissociation) = 39.9 kcal/mol and $\Delta S^{\ddagger}$(singlet dissociation) ≥ +6.6 cal/mol·K. Experimental values: $\Delta E^{\ddagger}$ = 32.7 kcal and $\Delta S^{\ddagger}$ = −1.1 cal/mol·K. [d] Frequencies labeled 1-8 are estimates based on qualitative bonding arguments. [e] Reaction coordinate.

moments of inertia are very different between the reactant and transition state. One may treat the rotational motion as inactive, adiabatic, or as if a hot atom influences the reaction. For simplicity we have considered only adiabatic rotations, in which the J quantum number is unaffected. The usual change in moments of inertia means that the total rotational energy will differ in the transition state from that in the reactant. Usually this difference is minor (<0.25 kcal) in these systems.

In order to compute the semiclassical $k(E)$, we need moments of inertia and vibrational frequencies for both reactant and the transition state. We can obtain the moments of inertia from the MINDO/3 optimized geometries, and in principle all the frequencies are computable by the MINDO/3 method. However, we chose to model our reactant using experimental data on rather similar molecules. The model compounds were 1-pyrazoline and methylenecyclopentane; complete vibrational analyses of these compounds were available. Those vibrations of the methylenepyrazoline derived from C-C double bond motions or ring deformations involving the sp^2 carbon were taken from the cyclopentane. Those involving aliphatic CH_2 motions or CN or NN motions were taken from the pyrazoline.

To mimic the rate of passage from singlet to triplet surface, we chose the critical configuration to lie in the crossing zone, and multiplied the conventionally computed rate of passage past that zone by the Landau-Zener crossing probability. In contrast, we chose the critical configuration for singlet, spin-conservative dissociation to lie higher on the dissociation curve than the crossing zone. This increase in energy is taken to be the estimated splitting between singlet and triplet products (7-10 kcal after scaling).[16]

The choice of characteristic frequencies can be critical to the estimate of a rate. We made a series of choices which seemed to span the set of reasonable alternatives. These are summarized in Table I. The model system was remarkably stable to our range of choices, and we consistently found computed rates of the general form

$$k_T \text{ (triplet production)} = (2.2 \times 10^{12}) \exp(-33\,000/RT)$$

$$k_S \text{ (singlet production)} = (7 \times 10^{14}) \exp(-40\,000/RT)$$

At the experimentally studied temperature, the ratio of rates is in the neighborhood of

$$k_T/k_S \simeq 5 \text{ (at } T = 461 \text{ K)}$$

The 7 kcal energy advantage of the spin-forbidden path overcomes the penalty of about −10 cal/mol·K associated with the spin flip. The triplet may also enjoy an advantage in entropy associated with the weakening of the double bond to the exo methylene.

In the course of the modeling we found it possible to match the experimental rate parameters for this system *only* by mixing roughly equal rates of the triplet process with the rates for the singlet process. The rates are so close, and differ so slightly in their activation energy and entropy values, that it is not likely that one could observe a strong curvature typical of two distinct rate processes, in a normal Arrhenius plot, over any reasonable temperature range. Therefore experimental information now available for these systems does not rule out the occurrence of a substantial fraction of spin-forbidden reaction.

VI. Summary

An approximate computation of the singlet and triplet energy surfaces for the concerted dissociation of methylene pyrazoline (MP) and 7-methylene-2,3-diaza[2.2.1]bicyclohept-2-ene (MDBH) lends support to the conclusions of symmetry arguments, that easy passage from singlet reactant to (ground state) triplet product trimethylenemethane is associated with conrotation of the hydrocarbon fragment. In MDBH, where disrotation is forced by the ring structure, the kinetics are typical of spin-conservative dissociations ($\Delta S^{\ddagger} > 0$), while MP dissociation shows a small, negative $\Delta S^{\ddagger}$. Our estimate of the spin-orbit coupling in MP, and statistical modeling of the dissociation rates, indicates that the energetically favored spin-forbidden dissociation is in fact competitive in rate with the energetically more costly singlet dissociation, and we reproduce the experimental rate parameters only by an average of parameters for spin-forbidden and spin-conservative processes.

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ESR and ENDOR Studies of a Radical Anion with Formally Nonconjugated Keto Groups: *cis*-10,11-Dimethyldiphensuccindan-9,12-dione

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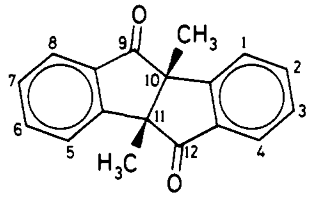
Abstract: The radical anion of *cis*-10,11-dimethyldiphensuccindan-9,12-dione (**1**), which contains two equivalent, formally nonconjugated monoketone π systems, has been studied by ESR and ENDOR spectroscopy. In the ion pairs formed by **1**$^{-}\cdot$ and its counterion, the bulk of the spin population is accommodated on one π moiety, and the cation is situated in the proximity of the pertinent oxygen atom. The rate, *k*, of interconversion between two such equivalent ion pairs is thus tantamount to the frequencies of both the intramolecular electron transfer and the migration of the cation between the preferred sites at the two oxygen atoms. The dependence of the rate *k* and the proton coupling constants on the solvent, counterion, and temperature has been investigated in detail. When *k* lies in the range of 10^6–10^9 s^{-1} it is comparable to the hyperfine time scale, and the ESR spectra exhibit effects of specific line broadening. The activation parameters (solvent, dimethylformamide; counterion, Et_4N^+) for the interconversion are $\Delta H^{\ddagger} = 26$ kJ/mol and $\Delta S^{\ddagger} = 23$ J/(mol K). The proton coupling constants, observed under a variety of experimental conditions, agree excellently with the values calculated with the use of a simple HMO model which treats **1**$^{-}\cdot$ as two weakly interacting monoketone π systems.

In a preceding paper,[2] a vibronic model was proposed to account for the unusual IR absorption of the radical anion of *cis*-10,11-dimethyldiphensuccindan-9,12-dione (**1**). The spectroscopic properties of **1**$^{-}\cdot$, which contains two formally nonconjugated monoketone fragments, depend critically on the electron exchange between the two equivalent π moieties. Since the frequency of the electron transfer must be in concert with the rate of migration of the counterion between these moieties,[3] the observed hyperfine pattern should be sensitive to the factors affecting the ion pairing, such as the polarity of the solvent, the nature of the counterion, and the temperature. Their role is examined in the present paper, which reports the results of ESR and ENDOR studies of **1**$^{-}\cdot$, performed under various experimental conditions.



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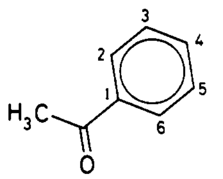

2

Experimental Section

The preparation of *cis*-10,11-dimethyldiphensuccindan-9,12-dione has been described elsewhere.[2]

The radical anion **1**$^{-}\cdot$ was produced by both "chemical" and electrolytic reduction of **1**. The chemical method consisted in reaction of **1** with potassium, sodium, and lithium in 1,2-dimethoxyethane (DME), tetrahydrofuran (THF), and 2-methyltetrahydrofuran (MTHF); the reaction of **1** with potassium was also carried out in a 2:1 mixture of DME and hexamethylphosphoric triamide (HMPA).

Electrolytic generation of **1**$^{-}\cdot$ was achieved in DME, dimethylformamide (DMF), acetonitrile (ACN), and dimethyl sulfoxide (Me_2SO). Tetraethyl- as well as tetra-*n*-butylammonium perchlorate served as the supporting electrolytes in DMF, ACN, and Me_2SO, while in DME, for reasons of solubility, only the tetra-*n*-butylammonium salt could be used. Moreover, the electrolytic reduction in all four solvents was performed with sodium tetraphenylborate, replacing tetraalkylammonium perchlorate as the supporting salt.

In general, the radical anions **1**$^{-}\cdot$ prepared under the aforementioned conditions were sufficiently stable for an investigation in the

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