J. Org. Chem. 1982, 47, 4529–4534

A Theoretical Study of the Mechanism of the Thermal Decomposition of Azoalkanes and 1,1-Diazenes

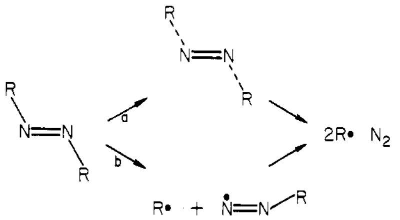
J. J. Dannenberg* and D. Rocklin

Department of Chemistry, City University of New York-Hunter College, New York, New York 10021

Received February 5, 1982

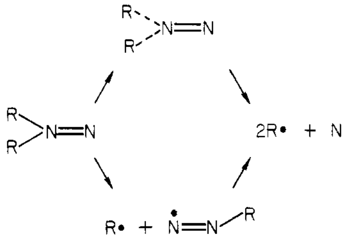
The MNDO approximation to molecular orbital theory with 2 × 2 CI and extensive geometrical optimization was used to study the reaction paths for the thermolyses of *trans*- (**1**) and *cis*- (**2**) azoethane and 1,1-diethyldiazene (**3**). In all cases, the stepwise reaction was clearly preferable to the concerted, two-bond cleavage. **1** isomerizes to **2** and then dissociates. The calculated energies of activation (48.9, 43.9, and 24.3 kcal/mol for **1**, **2**, and **3**, respectively) agree remarkably well with experimental measurements and theoretical estimates. The mechanism indicated by this study is discussed in the context of the previously reported experimental data.

The mechanism of thermal decomposition of azoalkanes has been the subject of continued interest. In particular, the question of whether a concerted, two-bond cleavage (reaction 1a) or a two-step mechanism (reaction 1b) is operative remains unresolved. Engel's recent summary of the current thinking on this question is that "azoalkane thermolysis seems to proceed by a continuum of mechanisms...; the more unsymmetrical the azo compound, the more unsymmetrically it cleaves".[1]



(1)

The chemistry of 1,1-diazenes has been recently studied by Dervan[2] and others. Similar questions about the mechanism of their thermal decompositions (see reaction 2) can be posed.



(2)

In this study, we have investigated the reaction paths for the thermal decomposition of *trans*- and *cis*-azoethane (**1** and **2**) and 1,1-diethyldiazene (**3**). Our goal is to suggest a detailed mechanism that would be useful as a model for designing future experiments in the manner we have previously discussed elsewhere.[3] Azoethane, rather than the simpler azomethane, was chosen for this study as the primary radicals formed should be more comparable to those involved in the decompositions of cyclic diazenes, which will be the subject of further work.

There have been several previous theoretical treatments of diimide, 1,1-diazene, and their derivatives,[4] but there have been no detailed theoretical studies of the decomposition reaction paths of azoalkanes other than a study of 1-pyrazolines that considered several specific decomposition paths.[4u]

Methods

The MNDO approximation to molecular orbital theory has been used with 2 × 2 CI for all closed shell states.[5a] A reaction coordinate was chosen for each reaction path to be studied. Geometrical optimization was performed with the Fletcher–Powell–Davidon algorithm incorporated in the MNDO program.[5a] Each stable or metastable species that corresponds to a local minimum on the reaction surface was completely optimized using all (up to 42) internal parameters independently. The reaction paths were first calculated without CI by stepping through the appropriate reaction coordinates (C–N bond lengths for the bond-breaking steps, N–N-angle and C–N–N–C dihedral angle for the cis/trans isomerization) while optim-

---

(1) (a) For a review, see Engel, P. S. *Chem. Rev.* **1980**, *80*, 99. (b) Ramsperger, H. C. *J. Am. Chem. Soc.* **1929**, *51*, 2134. (c) Perona, M. J.; Beadle, P. C.; Golden, D. M. *Int. J. Chem. Kinet.* **1973**, *5*, 495. (d) Koga, G.; Koga, N.; Anselme, J-P. In "The Chemistry of the Hydrazo, Azo, and Azoxy Groups"; Patai, S., Ed.; Wiley: New York, 1975. (e) Hinz, J.; Oberlinner, A.; Ruchardt, C. *Tetrahedron Lett.* **1973**, 1975. (f) Crawford, R. J.; Takagi, K. *J. Am. Chem. Soc.* **1972**, *94*, 7406. (g) Strausz, O. P.; Lown, J. W.; Gunning, H. E. *Compr. Chem. Kinet.* **1972**, *100*, 4910. (h) Koenig, T. *Free Radicals* **1973**, 1. (i) Green, J. G.; Dubay, G. R.; Porter, N. A. *J. Am. Chem. Soc.* **1977**, *99*, 1264. (j) Porter, N. A.; Marnett, L. J. *Ibid.* **1973**, *95*, 4361. (k) Porter, N. A.; Dubay, G. R.; Green, J. G. *Ibid.* **1978**, *100*, 920. (l) Tsolis, A.; Mylonakis, S. G.; Nieh, M. T.; Seltzer, S. *Ibid.* **1972**, *94*, 1264. (m) Neuman, R. C.; Lockyer, G. D.; Amrich, M. J. *Tetrahedron Lett.* **1972**, 1221. (n) Kopecky, K. R.; Pope, P. M.; Sastre, J. *Can. J. Chem.* **1976**, *54*, 2639. (o) Johnson, R. A.; Seltzer, S. *J. Am. Chem. Soc.* **1973**, *95*, 938. (p) Seltzer, S.; Dunne, F. T. *Ibid.* **1965**, *87*, 2628. (q) Timberlake, J. W.; Garner, A. W. *J. Org. Chem.* **1976**, *41*, 1666. (r) Engel, P. S.; Bishop, D. J. *J. Am. Chem. Soc.* **1975**, *97*, 6754. (s) Snyder, J. P.; Harpp, D. N. *Ibid.* **1976**, *98*, 7821. (t) Firestone, R. A. *J. Org. Chem.* **1980**, *45*, 3604. (u) Neumann, R., paper given at the 183rd Natioal Meeting of American Chemical Society, Las Vegas, NV, March 1982. (v) McMillen, D. F.; Lewis, K. E.; Smith, G. P.; Golden, D. M. *J. Phys. Chem.* **1982**, *86*, 709.

(2) (a) Dervan, P. B.; Uyehara, T.; Santelli, D. S. *J. Am. Chem. Soc.* **1979**, *101*, 2069. (b) Hinsberg, D. H., III; Dervan, P. B. *Ibid.* **1979**, *101*, 6142.

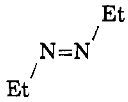
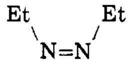
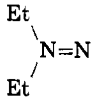
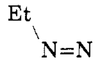
(3) Dannenberg, J. J. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 519.

(4) (a) Casewit, C. J.; Goddard, W. A., III *J. Am. Chem. Soc.* **1080**, *102*, 4057. (b) Parsons, C. A.; Dykstra, C. E. *J. Chem. Phys.* **1979**, *71*, 3025. (c) Howell, J. M.; Kirschenbaum, L. J. *J. Am. Chem. Soc.* **1976**, *98*, 877. (d) Camp, R. N.; Epstein, I. R.; Steel, C. *Ibid.* **1977**, *98*, 2453. (e) Slanina, Z. *Chem. Phys. Lett.* **1977**, *50*, 418. (f) Baird, N. C.; Wernette, D. A. *Can. J. Chem.* **1977**, *55*, 350. (g) Bigot, B.; Sevin, A.; Devaquet, A. *J. Am. Chem. Soc.* **1978**, *100*, 2639. (h) Davis, J. H.; Goddard, W. A., III *Ibid.* **1980**, *102*, 4058. (i) Lehn, J. M.; Munsch, B. *Theor. Chim. Acta* **1978**, *12*, 91. (j) Schaad, L. J.; Kinser, H. B. *J. Phys. Chem.* **1969**, *73*, 1901. (k) Wong, D. P.; Fink, W. H.; Allen, L. C. *J. Chem. Phys.* **1970**, *52*, 6291. (l) Radom, L.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 289. (m) Baird, N. C.; Swenson, J. R. *Can. J. Chem.* **1969**, *51*, 3097. (n) Wagniere, G. *Theor. Chim. Acta* **1973**, *31*, 269. (o) Vasudevan, K.; Peyerimhoff, S. D.; Buenker, R. J.; Kammer, W. E. *Chem. Phys.* **1975**, *7*, 187. (p) Winter, N. W.; Pitzer, R. M. *J. Chem. Phys.* **1975**, *62*, 1269. (q) Alrichs, R.; Staemmler, V. *Chem. Phys. Lett.* **1976**, *37*, 77. (r) Cimiraglia, R.; Riera, J. M.; Tomasi, J. *Theor. Chim. Acta* **1977**, *46*, 223. (s) Pople, J. A.; Krishnan, R.; Schlegel, H. B.; Binkley, J. S. *Int. J. Quant. Chem.* **1978**, *14*, 545. (t) Talaty, E. R.; Schwartz, A. K.; Simons, G. *J. Am. Chem. Soc.* **1975**, *97*, 972. (u) Hiberty, P. C.; Jean, Y. *Ibid.* **1979**, *101*, 2538.

(5) (a) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899. (b) Dewar, M. J. S.; Ford, G. P. *Ibid.* **1979**, *101*, 5558. (c) Frenking, G.; Schmidt, J.; Schwarz, H. *Z. Naturforsh. B: Anorg. Chem. Org. Chem.* **1980**, *35*, 3513. (d) Burkholder, D.; Jones, W. E.; Ling, K. W.; Wasson, J. S. *Theor. Chim. Acta* **1980**, *55*, 325. Decoret, C.; Royer, J.; Dannenberg, J. J. *J. Org. Chem.* **1981**, *46*, 4074. (f) Dannenberg, J. J.; Brown, N.; Bunch, B., unpublished results.

0022-3263/82/1947-4529$01.25/0

Table I. Energies (kcal/mol) of Various Species and Energies of Activation for Their One-Bond and Concerted Two-Bond Cleavages

		energy of activation		
	heat of formation	one-bond cleavage	two-bond cleavage (concerted)	reported
	8.3	52.3[a] 48.9[b]	77.3[a] 74.2[b]	47.2[c] 48.5[d] 49.7[e] 44.5[f]
	13.3	43.9	69.2	
	48.9	24.3	32.6	24[g]
	33.8	14.0		13[h]

[a] Direct cleavage. [b] Overall E_a for trans → cis → cleavage. [c] Reference 8a. [d] Reference 8b. [e] Reference 1c. [f] Toluene used as carrier, ref 8c. [g] Estimated from 1,1-diimide ab initio calculations, ref 4a. [h] For diazenyl radical ref 9.

izing all the remaining (up to 41) internal coordinates individually, to determine the approximate geometries of the *cols*, as optimization with CI is extremely costly. The points along the reaction path near the *cols* (those points on the reaction surfaces that correspond in geometry to the transition states) were then recalculated with use of CI and progressively fewer constraints on the geometrical optimization until complete optimization in all internal parameters other than the reaction coordinate was achieved with CI. In the concerted reaction, the two C–N bond lengths were constrained to be equal. Parameters that were calculated to be equivalent without CI were coupled for the CI calculations.

The MNDO method has been reported to calculate relative energies better than most other commonly used ab initio and semiempirical methods. The results are particularly good for compounds with NN bonds.[5b] Few detailed studies of specific reaction paths have been reported.[5c–f] Our own experience has indicated MNDO to be particularly useful for the study of reactions involving neutral free radicals and radical pairs.[5f]

Results and Discussion

The structures and heats of formation of all the optimized species as well as the activation energies for the various processes are collected in Tables I and II and depicted in Figures 1 and 2. Figure 3 depicts the reaction paths calculated for the various processes considered. The complete geometries can be obtained as supplementary material.

The structures of **1** and **2** fall well within the range of previous calculations. The largest differences among the calculations are found for the N–N distance. The values reported for this bond length obtained from various optimized ab initio calculations of diimide fall between 1.21 and 1.29 Å with the cis isomer generally having a N–N distance less than or equal to the trans isomer calculated by the same method.[4] The experimental value is reported to be 1.252 Å.[6] The CNN angles are reported to be 111.9° and 119.4° for *trans*-[6] and *cis*-[7] azomethane. Previously reported calculated values for these angles are 109.6° and 119.2° (STO-3G)[4c] 112° and 119.5° (PRDDO).[4d] Ab initio calculations on trans diimide have predicted HNN angles of 102.5–110.5°,[4b,f,h,j,k,m,n,p,q] for which an experimental value of 106.85° has been reported.[6] Cis diimide angles have been calculated from 111.5 to 116.0°.[4b,c] It is likely that the N–N distance and N–NR angles are coupled as longer NN distances tend to be predicted by the same calculations that predict small NNR angles. Nevertheless, MNDO predicts larger CNN angles for **2** than do other calculations on different but analogous molecules. It is interesting to note that **2** does not have a plane of symmetry in its optimized geometry (see Figure 1). To avoid eclipsing the methylene H's on the two α carbons, one ethyl group is turned along the C–N bond so that the β carbon is below the plane of the three other carbons and two nitrogens.

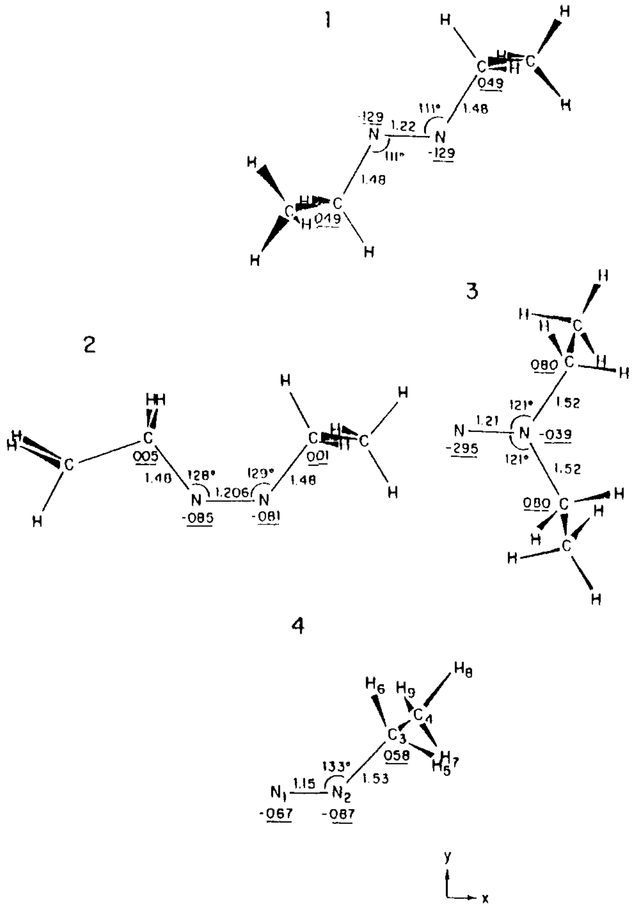


Figure 1. The geometries of the stable and metastable species. Bond lengths are in angstroms; atomic charges (×1000) are underlined.

The calculated relative energies of **1** and **2** are in good agreement with the 7–8 kcal/mol difference in energy estimated by Engel.[1r] The difference in energy between **3** and **1** also agrees well with the 40 kcal/mol difference between the cyclic tetramethylene analogues predicted by Goddard.[4h]

This study clearly predicts the concerted, two-bond cleavage (reaction 1a) to be unfavorable relative to the stepwise bond cleavage of either the *cis*- or *trans*-azoethane. The activation energy for the first bond cleavage in reaction 1b is 52.3 and 43.9 kcal/mol for the trans and cis isomers, respectively. The activation energy for the

---

(6) Carlotti, M.; John, J. W. C.; Trambetti, A. *Can. J. Phys.* **1974**, *52*, 340.

(7) Stevens, J. F., Jr.; Curl, R. F., Jr.; Engel, P. S. *J. Phys. Chem.* **1979**, *83*, 1432.

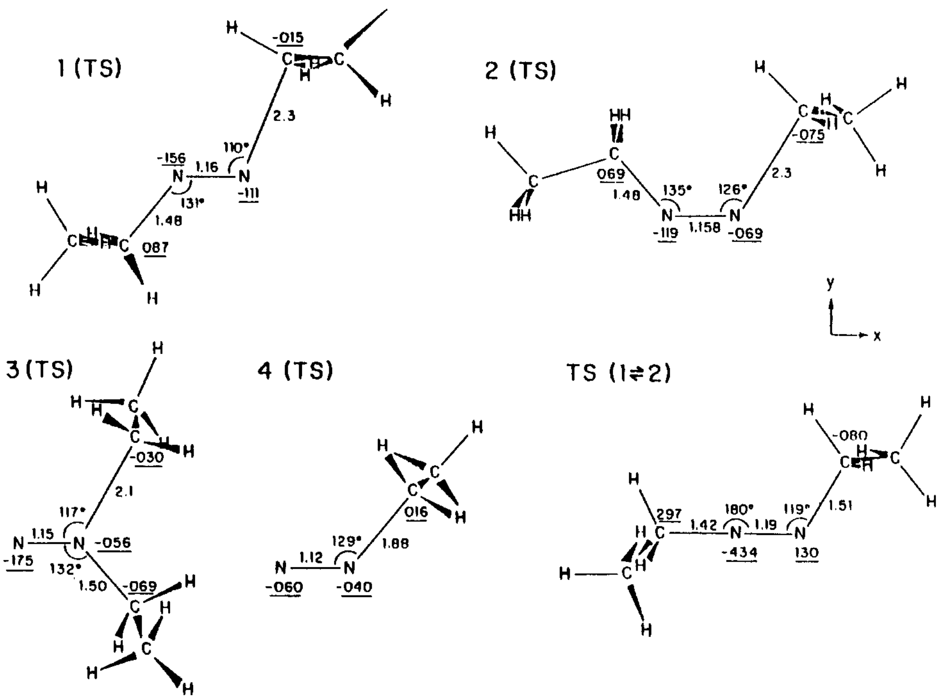


Figure 2. The geometries of the transition states. See caption of Figure 1 for explanation.

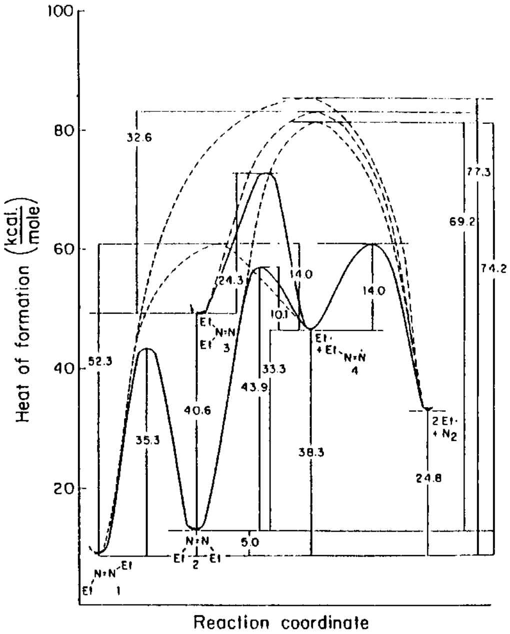
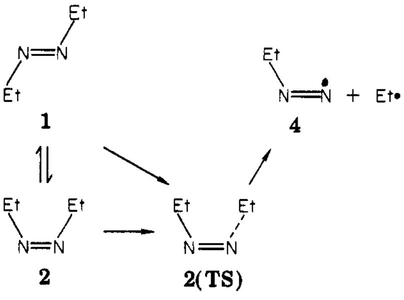
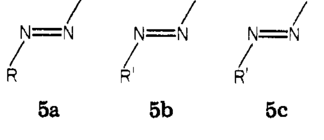


Figure 3. Reaction coordinate diagram for the thermolysis of 1–3. The solid line represents the best path for each reaction. The broken lines represent other paths that were considered in this study (see text).

trans to cis isomerization is calculated to be 35.3 kcal/mol, which suggests that the most facile path for breaking the first bond of 1 is via the cis transition state (**2TS** in Figure 2) with an overall activation energy of 48.9 kcal/mol. The experimental values reported for the gas-phase decomposition of 1 (47.2–49.7 kcal/mol in the absence of a carrier gas)[1c,8a,b] are in remarkably good agreement with the calculated value. An interesting aspect of the reaction path is that the ethyldiazenyl radical, 4, has an activation energy of 14.0 kcal/mol for its decomposition to ethyl radical and molecular nitrogen. This compares with a reported experimental E_a value for HNN· of 13 kcal/mol[9] and a theoretical value of 22.6 kcal/mol.[10a] Fukui has recently calculated the activation energy for the decomposition of methyldiazenyl radical to be 13 kcal/mol.[10b] Since the activation energies for recombination of the ethyl and ethyldiazenyl radicals are calculated to be 10.1 and 14.0 kcal/mol to *cis*- and *trans*-azoethane (2 and 1, respectively; see below), the second step of the reaction may influence the observed rate of the reaction.



Much of the experimental evidence generally interpreted in support of a concerted, two-bond cleavage (reaction 1a) are comparisons of the rates of thermolysis of symmetrically and unsymmetrically substituted azoalkanes of the type **5a–c**. The basic argument is that if reaction 1b be the correct mechanism and the R–N bond be weaker than the R′–N bond, **5a** and **5b** would have similar activation energies for thermolysis, while that of **5c** would be higher. However, if a concerted mechanism be operative (reaction a), then the E_a value of **5b** should be intermediate between **5a** and **5c**. Engel suggests that the more different are R



5a **5b** **5c**

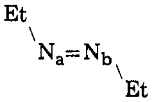
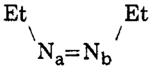
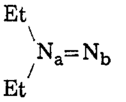
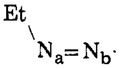
---

(8) (a) Sandhu, H. S. *J. Phys. Chem.* **1968**, *72*, 1857. (b) Clark, W. D.; Swinehart, D. F.; McCoy, R. D., "Abstracts of Papers", 132nd National Meeting of the American Chemical Society, New York, 1957; American Chemical Society: Washington, DC, 1957, p 475. (c) Martin, G.; Maccoll, A. *J. Chem. Soc., Perkin. Trans. 2* **1977**, 1887.

(9) Willis, C.; Back, R. A.; Parsons, J. M. *J. Photochem.* **1976/77**, *6*, 253.

(10) (a) Baird, N. C. *J. Chem. Phys.* **1975**, *62*, 300. (b) Yamashita, K.; Kaminoyama, M.; Yamabe, T.; Fukui, K. *Chem. Phys. Lett.* **1981**, *83*, 78.

Table II. Selected Features of the Critical Points for the Reaction Paths

	bond lengths, Å[c]			angles, deg		charge (×10³)				bond order (N–N) ×10³	
	$R_{N=N}$	$R_{C\text{-}N_a}$	$R_{C\text{-}N_B}$	CN_aN_b	CN_bN_a	N_a	N_b	Et(N_a)	Et(N_b)	π_y	π_z
	1.221	1.480	1.480	116.6	116.6	−129	−129	+129	+129	187	971
TS[a]	1.162	<u>2.3</u>	1.482	109.8	130.5	−111	−156	+154	+113	474	986
Δ[b]	−0.059	+0.8	+0.002	−6.8	+13.9	+018	−027	−016	+025	+287	+015
	1.213	1.483	1.483	128.7	128.0	−081	−085	+082	+084	327	972
TS[a]	1.158	<u>2.3</u>	1.479	126.3	135.1	−068	−119	+038	0.149	540	985
Δ[b]	−0.055	+0.8	−0.004	−2.3	+7.1	+013	−034	−044	+065	+213	+013
	1.211	1.515	1.515	121.3	121.3	−295	−039	+167	+167	339	898
TS[a]	1.153	<u>2.1</u>	1.495	117.3	131.6	−056	−175	+074	+157	567	963
Δ[b]	−0.058	+0.585	−0.020	−4.0	+10.3	+239	−136	−093	−010	+228	+065
	1.154	1.487		133.2		−087	−067	+159		632	983
TS[a]	1.121	<u>1.88</u>		129.4		−040	−060	+100		861	998
Δ[b]	−0.033	+0.39		−3.8		+047	+007	−053		+229	+015

[a] Transition state (*col* on the surface). [b] Differences between starting point and TS for each reaction step. [c] Reaction coordinates are underlined.

and R′, the greater tendency toward the one-bond cleavage mechanism (reaction 1b).

The effect upon our proposed reaction path of changing one of the ethyl groups to an alkyl group that would have a lower C–N dissociation energy is illustrated in Figure 4. Since the bond cleavage becomes less endothermic than for 1, the Hammond postulate[11] suggests that the transition state should look less like the diazenyl, alkyl radical pair and the barrier to recombination should increase. This kind of analysis suggests that the influence of the second step of the reaction on the overall rate ought to be greatest for symmetrical azoalkanes. The entropy of activation for the recombination reaction ought to be negative, while that for the decomposition of the diazenyl radicals ought to be positive. Thus, increasing temperature should make the first step more rate determining. Also, recombination ought to be less favorable in low-pressure gas-phase reactions than in condensed-phase reactions.

It is instructive to reconsider much of the reported experimental results on the thermolyses of azoalkanes in terms of the mechanism suggested by these calculations. First of all, the comparisons between the E_a of unsymmetrically and symmetrically substituted azoalkanes can be explained by the two-step mechanism as discussed previously. Secondly, the observations that both trans and cis isomers decompose through transition states that have the same heat of formation[14] is very well-explained by the proposed mechanism as the cis transition state is common to both isomers. No cis isomer would normally be detected in the reaction mixtures as the ΔE between trans and cis isomers (5 kcal/mol) implies the concentration of cis would be significantly less than 1% of an equilibrium mixture. The similar substituent effects in cycloazoalkanes and *trans*-azoalkanes are also[12] consistent with a cis transition state for most *trans*-azoalkanes. The dipole moment of 2 is calculated to decrease from 2.54 to 2.20 D in the transition state for one-bond cleavage. This observation suggests that 2 should be better stabilized by polar solvents than either its transition state or 1, in agreement with observed solvent effects.[13]

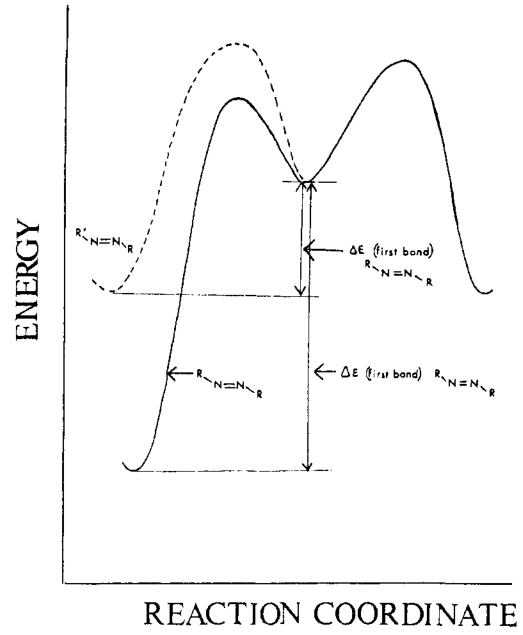


Figure 4. The effect of changing one of the alkyl groups on an azoalkane. The solid line represents the reaction of a symmetrical azoalkane. The broken line represents the probable effect of substituting an alkyl group, R′, that has a weaker N–C bond for one of the original alkyl groups. Since the second reaction is less endothermic, the transition state looks less like the diazenyl radical. The broken line lies higher than the solid line as the unsymmetrical azoalkane is more active in this hypothesis. As the second step is the same for both reactants, the two curves are drawn to meet at the intermediate radical pair.

A recent review compiles many cases of symmetrical and unsymmetrical azoalkane homolyses.[1a] It is noteworthy that in all reports dealing with gas-phase homolyses, the

---

[11] Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334.

[12] Duismann, W.; Ruchardt, C. *Chem. Ber.* **1978**, *111*, 596.

[13] Schulz, A.; Ruchardt, C. *Tetrahedron Lett.* **1976**, 845.

[14] Chae, W-K; Baughman, S. A.; Engel, P. S.; Bruch, M.; Qzmeral, C.; Timberlake, J. W. *J. Am. Chem. Soc.* **1981**, *103*, 4824.

unsymmetrical azoalkane **5b** had an activation energy within about 1 kcal of the less stable of **5a** and **5c**, except for R = *tert*-butyl, R′ = allyl where **5b** had an activation energy lower than either symmetrical molecule **5a** or **5c**. Clearly, recombination ought to be less likely in gas-phase reactions than in solution. In the latter case, frequent collisions will rapidly change the trajectories that separate the radical pairs, causing a greater probability of recombination. In the gas phase, recombination becomes unlikely after the radicals become relatively distant from each other. The anomalous case R = *tert*-butyl, R′ = allyl is also interesting as azo-2-methylisopropane (**5a**, where R = *tert*-butyl) is one of the few azoalkanes for which the activation energy for homolysis of the trans isomer is less than the trans to cis barrier. The activation energy for this compound should, then, be somewhat higher than expected if the trans isomer were able to react via the cis transition state as would normally be the case.

The mechanism of the cis–trans isomerization was studied by using the C–N–N–C dihedral angle as a stepped reaction coordinate and allowing complete optimization of the other 31 internal coordinates. The calculation indicated semilinearization provided the best route between *cis*- and *trans*-**1** as one of the C–N–N valence angles opened to 180° during this process. The E_a value of 35.3 kcal/mol is in fair agreement with the 42 kcal observed for the free energy of activation of most trans to cis isomerizations of azoalkanes.[14] Other theoretical studies on diimide are in agreement with the semilinear transition state.[4a–c,m,q,r]

There have been several reports of CIDNP observed for recombination of radical pairs derived from thermolysis of 1,2-diazenes.[1i–k,n] Most involve studies of diazenes that decompose to a phenyldiazenyl radical although there is at least one documented case that involves an alkyl (1-norbornyl) diazenyl radical. Other evidence supporting a stepwise mechanism involves stereochemical studies,[11n,o] isotope effects,[1p] and measurement of activation volumes.[1m] Interestingly, CIDNP is observed from the cis as well as trans isomers of the recombined diazenes, even in cases where the cis isomers are very sterically hindered.[1n] Very recently, Neumann has observed a pressure dependence for the thermolysis of *cis*-azoadamantane. This is the first direct evidence for a stepwise mechanism in a symmetrical azoalkane.[1u] These observations are consistent with our proposed mechanism. On the other hand, a recent finding of a low Arrhenius preexponential factor has led Golden to favor a synchronous mechanism.[1v]

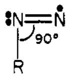
Table II shows the changes in various geometric parameters and charge densities for the first bond cleavage from the three isomers of azoethane, **1**–**3**. The departing ethyl group tends to have a smaller C–N–N angle in the transition state than in the stable isomer, while the reverse is true for the other C–N–N angle. These observations are consistent with an increase in p_y–p_y, in plane, π-bond character in the transition states (where the axes are defined in Figures 1 and 2). The π_y-bond order increases more for the trans transition state than for the cis (presumably because the π_y-bond order is already high in the cis isomer). The total π-bond order is greater in the cis transition state, which is probably the reason that the total energy of the cis *col* is lower than that of the trans. The Hammond postulate[11] would ordinarily predict the *col* for **1** to be lower than that for **2** as the homolysis of **1** is more endothermic.

Table III. Spin Densities on the Ethyldiazenyl Radical and the Transition State for Its Cleavage to Ethyl Radical and N_2 [a]

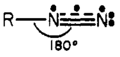
	spin density (×10³)				
atom	25	p_x	p_y	p_z	total
N_1	000 (000)	029 (017)	510 (218)	000 (000)	539 (236)
N_2	072 (039)	030 (013)	112 (039)	000 (000)	214 (093)
C_3	023 (022)	105 (266)	091 (330)	000 (005)	219 (622)
C_4	000 (001)	000 (001)	000 (001)	002 (002)	003 (004)
H_5					000 (002)
H_6					016 (007)
H_7					000 (004)
H_8					007 (030)
H_9					000 (004)

[a] Values for the transition state are in parentheses; see Figure 2 for numbering convention.

The ethyldiazenyl radical is of primary importance to the proposed mechanism. Table III gives the spin densities in this radical and in the transition state for its decomposition. Two extreme structures that this species could assume are represented by **6a** and **6b**. In **6a** the 90° angle for R–N–N requires that the p_y orbital on the substituted nitrogen be very much involved in the N–C bond, thereby localizing the unpaired electron on the terminal N. In **6b** the linear arrangement of the C–N–N bond allows the unpaired electron to be in an antibonding orbital as part of a three-electron π-bond between the nitrogens. The ethyl group cannot accept π electrons very readily. At some intermediate angle, the three-electron bond can mix with the C–N σ bond, allowing spin density to be effectively delocalized into the ethyl group.



6a

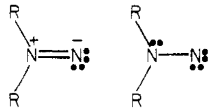


6b

The transition state for breaking the second bond has a smaller C–N–N angle than the diazenyl radical. Ideally this angle should tend toward 90° to allow the electron from the C–N bond to go to the nitrogen p_y orbital (or the new π bond of nitrogen), but CNN angle strain will prevent this. Opening of the C–N–N angle toward 180° will leave a nitrogen molecule with one electron in an sp orbital and a three-electron π bond, which would correspond to the n–π^* excited state of nitrogen. This aspect of the stability of diazenyl radical itself has been previously discussed by Baird.[10a]

Firestone recently published an analysis of the thermolysis of azoalkanes using arguments based upon Linnett structures.[1t] It is extremely interesting that our MNDO results agree very well with his analysis so far as direct comparison is possible. In particular, there is agreement in the charge pattern of the transition state and the tendency to planarization of the departing carbon (see supplementary material for complete geometries).

The thermolysis of 1,1-diethyldiazene is also predicted to be a stepwise process with an activation energy of 24.3 kcal/mol. This value accords well with the observations of Dervan[2] and the predictions of Goddard.[4a] The transition state for the first bond cleavage resembles that of the azoalkane transition states, except, of course, for the position of the departing ethyl radical. It may at first seem surprising that the activation energy is 24.3 kcal/mol for this reaction, which is exothermic by 2.3 kcal/mol. The apparent reason for this high activation energy becomes evident upon inspection of the π orbitals. The formal (p_z) π bond is not completely formed in the 1,1-diazene (bond order = 0.90). This phenomenon is surely due to the unsymmetrical nature of the molecule. The substituted nitrogen tends to have more than half of the p_z π electrons as suggested by the resonance structures, in which the π-bonding electrons are sometimes localized on that nitrogen. To compensate, the terminal nitrogen has an almost completely filled p_y orbital (population 1.87). In the transition state the p_y–π bond is virtually completely formed. The three-electron p_y–π bond involves the p_y–π^* orbital. This orbital has a node near the substituted nitrogen so the bonding interaction between this orbital and the departing ethyl group must not contribute very much to the stabilization of the transition state.



Conclusion

The MNDO reaction paths reported agree remarkably well with the observed and best theoretical estimates of the relative energies of the stable species and transition states for stepwise thermolyses of **1**–**3**. Concerted paths are much higher in energy. The preferred reaction sequence for most *trans*-azoalkanes should involve the cis transition state.

Acknowledgment. This work was supported by PSC-BHE Grant 13361.

Registry No. **1**, 15463-99-7; **2**, 58911-62-9; **3**, 38534-43-9.

Supplementary Material Available: The complete geometries of all the optimized species (4 pages). Ordering information is given on any current masthead page.

Conversion of Nitro Paraffins into Aldehydes and Ketones[1]

Nathan Kornblum,* Allen S. Erickson, William J. Kelly, and Barbara Henggeler

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

Received April 13, 1982

The use of potassium permanganate provides a simple and effective means for converting nitro paraffin salts to pure aldehydes and ketones in 81–96% yields. Even the carbon–carbon double bond is less readily attacked by permanganate than a nitro paraffin anion. Thus, the salt of ω-nitroundecylene is converted to undecylenic aldehyde in 59% yield.

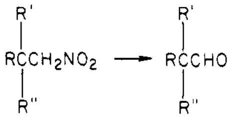
Many years ago Nef found that the salt of primary nitro paraffins are transformed into aldehydes, and those of secondary nitro compounds into ketones, when they are treated with aqueous mineral acid (eq 1 and 2).[2] Although

$$RC^{-}HNO_2 \xrightarrow{H_3O^+} RCHO + N_2O \tag{1}$$

$$R_2C^{-}NO_2 \xrightarrow{H_3O^+} R_2C{=}O + N_2O \tag{2}$$

the Nef reaction has repeatedly been employed to advantage, reports exist of its inadequacy and, indeed, downright failure. This, coupled with a heightened awareness of the utility in synthesis of aliphatic nitro compounds, has led a number of investigators to devise alternate procedures for converting nitro paraffins into aldehydes and ketones.[3]

In 1981 we described a general synthesis of quaternary carbon compounds (**1**) in which a CH_2NO_2 group is bonded to the quaternary carbon.[1] Conversion of these compounds into quaternary aldehydes (**2**), i.e., the reaction of eq 3,



$$\underset{R''}{\overset{R'}{RCCH_2NO_2}} \longrightarrow \underset{R''}{\overset{R'}{RCCHO}} \tag{3}$$

1 **2**

would make these difficultly accessible aldehydes readily available. Efforts to achieve the transformation of eq 3 by the Nef reaction, and by procedures employing $TiCl_3$, were unpromising, and attention was then directed to the use of potassium permanganate. We were encouraged to do so because Shechter and Williams,[3] following the early work of Nametkin,[3] had shown that aqueous potassium permanganate oxidizes nitro paraffin salts almost instantaneously and had reported that it is an effective reagent for converting the salts of primary nitro compounds to aldehydes. However, even though 20 years have elapsed since potassium permanganate was proposed as a reagent for converting the salts of primary nitro paraffins into aldehydes, its use has not achieved the status of a synthetically useful procedure. Indeed, the numerous alternatives to the Nef reaction have all been published since the Shechter–Williams paper appeared.[3a]

The original permanganate procedure[3a] has some less than satisfactory aspects and, in our hands, it gave erratic

---

[1] A preliminary report of a portion of this work has been published: Kornblum, N.; Erickson, A. S. *J. Org. Chem.* **1981**, *46*, 1037.

[2] Nef, J. U. *Justus Liebigs Ann. Chem.* **1894**, *280*, 264.

[3] (a) $KMnO_4$: Shechter, H.; Williams, F. T. *J. Org. Chem.* **1962**, *27*, 3699. Nametkin, S. S.; Zabrodina, A. S. *Ber. Dtsch. Chem. Ges.* **1936**, *69*, 1789. (b) Modified Nef reactions: Black, D. St. C. *Tetrahedron Lett.* **1972**, 1331. Jacobson, R. M. *Ibid.* **1974**, 3215. Keinan, E.; Mazur, Y. *J. Am. Chem. Soc.* **1977**, *99*, 3862. (c) Ozonolysis: McMurry, J. E.; Melton, J.; Padgett, H. *J. Org. Chem.* **1974**, *39*, 259. (d) $TiCl_3$: McMurry, J. E.; Melton, J. *J. Am. Chem. Soc.* **1971**, *93*, 5309; *J. Org. Chem.* **1973**, *38*, 4367. (e) VCl_2: Kirchhoff, R. *Tetrahedron Lett.* **1976**, 2533. (f) *t*-BuOOH: Bartlett, P. A.; Green, F. R., III; Webb, T. R. *Ibid.* **1977**, 331. (g) $Ce(NH_4)_2(NO_3)_6$: Olah, G. A.; Gupta, B. G. B. *Synthesis* **1980**, 44. (h) H_2O_2: Olah, G. A.; Arvanaghi, M.; Vankar, Y. D.; Prakash, G. K. S. *Synthesis* **1980**, 662. (i) $NaNO_2$ + RONO: Kornblum, N.; Wade, P. A. *J. Org. Chem.* **1973**, *38*, 1418. (j) MoO_5: Galobardes, M. R.; Pinnick, H. W. *Tetrahedron Lett.* **1981**, 5235.

0022-3263/82/1947-4534$01.25/0