J. Am. Chem. Soc. 1983, 105, 7681-7685

Gas-Phase Reactions. 36.[1] Pyrolysis of Vinyl Azide[⊥] [2-4]

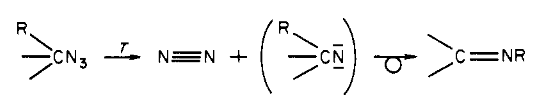
Hans Bock,*[†,‡] Ralph Dammel,[†] and Sitki Aygen[†]

Contribution from the Departments of Chemistry, Universities of Frankfurt and Michigan, D-6000 Frankfurt, Niederurseler Hang, West Germany, and Ann Arbor, Michigan 48109.

Received April 4, 1983

Abstract: The gas-phase pyrolyses of vinyl azide as well as of 1*H*-1,2,3-triazole have been investigated by means of PE spectroscopy. In accordance with predictions from MNDO hypersurface studies, vinyl azide in its lowest thermal decomposition channel splits off nitrogen to yield predominantly 2*H*-azirine as identified by the PE spectrum of the cool-trapped compound, which at higher temperatures rearranges to the most stable C_2H_3N isomer, acetonitrile. The experimental observations and the quantum chemical calculations both indicate that among those reaction pathways, which can readily be characterized by a suitably selected pair of reaction coordinates from the 12-dimensional hyperspace for the C_2H_3N moiety, synchronous nitrogen extrusion–azirine ring formation is the energetically most favorable one.

Thermal decompositions of simple azides in the gas phase[5-10] are attractive both from synthetic as well as theoretical points of view. The prototype reaction combines the following intriguing features: (a) the nitrogen molecule is a thermodynamically favorable leaving moiety, the kinetically feasible extrusion of which frequently[5-9] leads into a uniform, well-defined decomposition channel; (b) the short-lived nitrene intermediate and its transparent unimolecular rearrangement, e.g., for R = H by 1,2-hydrogen shift,[2,5,10,11] provides a quantum chemical testing ground, and (c) the resulting imines, especially for R = H, are quite often best[6-8] accessible via (1) on a preparative scale.


(1)

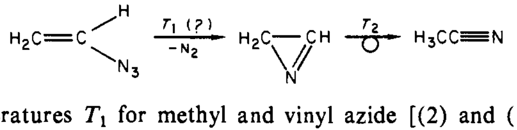
Among the analytical methods suited for the study of gaseous flow systems such as (1), photoelectron spectroscopy offers distinct advantages:[2,3,5] Only small amounts of dangerous compounds need be handled at pressures below 10^{-2} mbar. Above all, the products are identified and characterized by their radical cation state fingerprints, i.e., their ionization patterns, which via Koopmans theorem,[2] $\mathrm{IE}_n^{\mathrm{v}} = -\epsilon_J^{\mathrm{SCF}}$, can be linked to quantum chemical calculations.

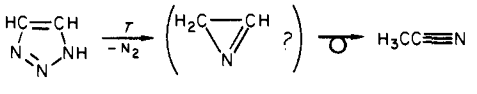
The gas-phase pyrolysis of methyl azide,[5] PE spectroscopically monitored over the temperature range between 300 and 1300 K,

$$\mathrm{H_3CN_3} \xrightarrow[-\mathrm{N_2}]{T_1 > 800\ \mathrm{K}} \mathrm{H_2C{=}NH} \xrightarrow[-\mathrm{H_2}]{T_2 > 850\ \mathrm{K}} \mathrm{HC{\equiv}N} \qquad (2)$$

starts only above a remarkable 800 K! Corroborating MNDO calculations[5] likewise predict a high activation barrier for the nitrogen extrusion followed by fast nitrene rearrangement on a nearly repulsive hypersurface slope.[5]

Vinyl azide reportedly[12] is a highly sensitive material which may detonate on mechanical shock or at 350 K. Its pyrolysis reported here has been monitored PE spectroscopically over the full temperature range, since a microwave study[6] gave some indication that 2*H*-azirine and acetonitrile were among the decomposition products. Rationalizing these results by the postulated[8] reaction pathway, a comparison of the decomposition temperatures T_1 for methyl and vinyl azide [(2) and (3)] in conjunction with calculated hypersurface activation barriers should provide clues whether the nitrogen extrusion in the latter is supported by the neighboring vinyl group. An analogous argument holds for 1*H*-1,2,3-triazole, whose thermal decomposition[9] therefore has also been investigated PE spectroscopically both in an empty quartz tube as well as catalyzed by cuprous oxide, Cu_2O.


(3)


(4)

Experimental Section

Vinyl Azide. The starting material for the known synthesis,[12] β-chloroethyl azide, was prepared by the reaction of β-chloroethyl *p*-toluenesulfonate with sodium azide in methanol/water, extraction with ether, and vacuum distillation (bp 46 °C at 33 mbar, yield 54%). Dehydrohalogenation with potassium hydroxide in ethylene glycol/water[12] and removal of water from the distillate by repeated high-vacuum condensation from a 200 to a 77 K cold trap yielded 40% product. Although the vinyl azide had been stored under vacuum below 240 K, some decomposition to a yellowish-red contaminant had occurred when the sample was reinspected after a few weeks. Fortunately, no explosion occurred during the course of this work, but strong advice is given[12] against handling substantial amounts of vinyl azide using only normal laboratory precautions.

1*H*-1,2,3-Triazole. 1-Benzyl-1,2,3-triazole-4,5-dicarboxylic acid[13] was prepared via addition of benzyl azide[13] to acetylenedicarboxylic acid.

[⊥] Dedicated to Professor Werner Schultheis on the occasion of his 80th birthday.

[†] University of Frankfurt.

[‡] University of Michigan.

(1) Part 35: Bock, H.; Aygen, S.; Solouki, B.; *Z. Naturforsch., B* **1983**, *38B*, 611.

(2) Cf. the summary by: Bock, H.; Solouki, B. *Angew. Chem.* **1981**, *93*, 425–442; *Angew Chem., Int. Ed. Engl.* **1981**, *20*, 427–444.

(3) Part of: Aygen, S. Ph.D. Thesis University of Frankfurt, 1982. Dammel, R., Ph.D. Thesis University of Frankfurt, in preparation.

(4) Semiempirical hyperstructure calculations of the Frankfurt PES group have been summarized: Bock, H.; Dammel, R.; Roth, B. In "Inorganic Rings and Clusters"; Ralph W. Rudolph Memorial Symposium at the ACS Meeting, Kansas City, September, 1982, Cowley, A., Ed.; American Chemical Society: Washington, D.C., in print.

(5) For the photoelectron spectroscopically optimized pyrolysis of methyl azide, cf.: Bock, H.; Dammel, R.; Horner, L. *Chem. Ber.* **1981**, *114*, 220–226 and references cited therein.

(6) Ford, R. G. *J. Am. Chem. Soc.* **1977**, *99*, 2389–2390. Cf. also the recent summary by: Brown, R. F. C. "Pyrolytic Methods in Organic Chemistry"; Academic Press: New York, 1980, and literature cited therein.

(7) Cf., e.g.: Lwowski, W., Ed., "Nitrenes"; Interescience: New York, 1970 and literature cited therein.

(8) L'abbé, G. *Angew. Chem.* **1975**, *23*, 831–838; *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 775–783 and literature cited therein.

(9) Winnewisser, M.; Vogt, J.; Ahlbrecht, H. *J. Chem. Res., Synop.* **1978**, 298–299. For substituted triazoles, see: Gilchrist, T. L.; Gymer, G. E.; Rees, C. W. *J. Chem. Soc., Perkin Trans. 1* **1975**, 8 and literature cited therein.

(10) Since our first report on the vinyl azide pyrolysis,[2] L. L. Lohr and K. Morokuma have performed ab initio calculations on a double Z basis level, which would favor methyl isonitrile as an additional intermediate. Cf.: Lohr, L. L., Jr.; Hanamura, M.; Morokuma, K. *J. Am. Chem. Soc.* **1983**, *105*, 5541–5547.

(11) Schaefer, H. J., III. *Acc. Chem. Res.* **1979**, *12*, 288–296. For methyl nitrene, see also: Yarkony, D. R.; Schaefer, H. F., III; Rothenberg, S. *J. Am. Chem. Soc.* **1974**, *96*, 5974–5977; Demuynck, J.; Fox, D. J.; Yamaguchi, Y.; Schaefer, H. F., III. *Ibid.* **1980**, *102*, 6204–6207.

(12) Wiley, R. H.; Moffat, J. *J. Org. Chem.* **1957**, *22*, 995–996 and literature cited therein.

(13) Wiley, R. H.; Hussung, K. F.; Moffat, J. *J. Org. Chem.* **1956**, *21*, 190–192.

0002-7863/83/1505-7681$01.50/0

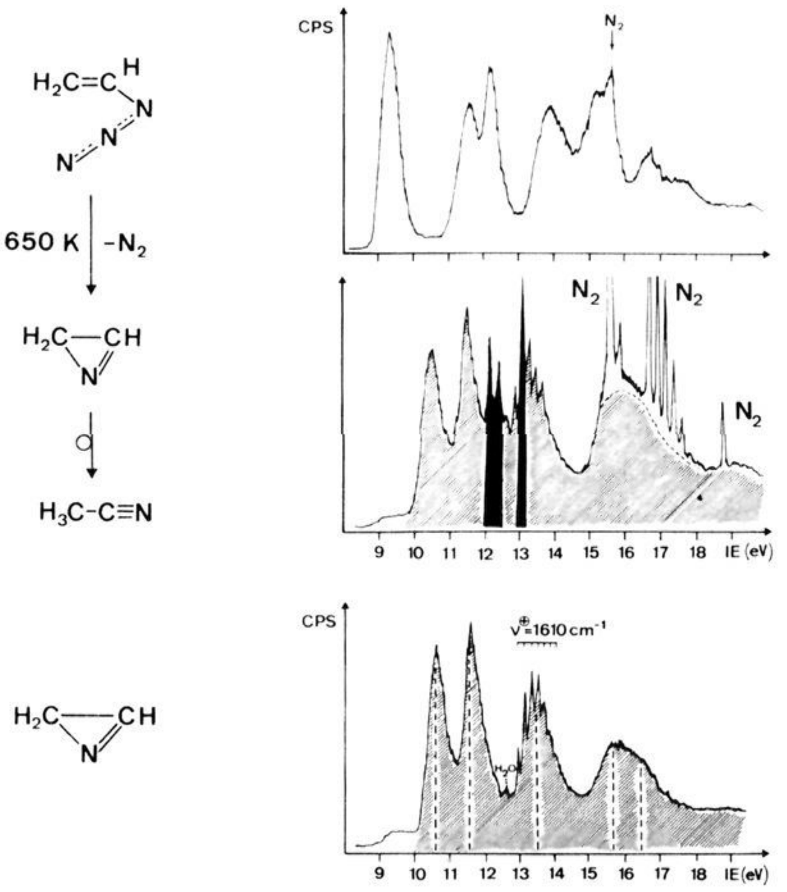


Figure 1. He I PE spectra of vinyl azide evaporated from a 200 K cold bath and its pyrolysis products at 650 K, 2H-azirine (shaded) and acetonitrile (blackened), as well as of cool-trapped and reevaporated pure 2*H*-azirine (for detailed assignment of PE-spectra cf. text).

After decarboxylation of the diacid, the resulting 1-benzyl-1,2,3-triazole was transformed into 1*H*-1,2,3-triazole by hydrogenolytic cleavage of the *N*-benzyl bond during three days in an autoclave at about 50 bar of hydrogen pressure.

Photoelectron spectra were recorded on a modified Perkin-Elmer PE 16 spectrometer and calibrated with the xenon $^2P_{3/2}$ and argon $^2P_{3/2}$ and $^2P_{1/2}$ lines. Resolution was of the order of 30 mV throughout the experiments.

Pyrolyses were carried out in a quartz tube (length 35 cm, diameter 1.5 cm) connected via Teflon-brand valves to the PE spectrometer at one and to the storage vessel at the other end. The compounds were evaporated from the storage vessel held at 200 K via the Teflon-brand valves (cf. Figure 7 in ref 2). The quartz tube was heated in a temperature-controlled oven of 30-cm length.

MNDO calculations were carried out at the Hochschul-Rechenzentrum of Frankfurt University using the program kindly provided by M. J. S. Dewar and W. Thiel.[14] Full geometry optimization was carried out for all compounds. Hypersurfaces were calculated by assigning fixed values to the appropriate coordinates and optimizing all others. The distance between grid points was 5–10° for the angle-dependent hypersurfaces. For the two-dimensional hypersurfaces checks were made by calculating reaction pathways from different starting points. Results were consistent to within ±1 kJ/mol.

PE Spectroscopically Monitored Pyrolyses

For illustration of the advantages of PE spectroscopic gas analysis[2] also for the vinyl azide and triazole pyrolyses, the essential PE spectra of the precursors as well as those recorded during the thermal decomposition and of the reaction products are presented in Figures 1 and 2. Their assignment will be commented upon in the following.

Vinyl Azide. As only few PE spectra of azides RN_3, e.g., R = H,[15] CH_3,[5] C_3H_5,[16] C_6H_5,[17] SiH_3,[18] or $Si(CH_3)_3$,[16,18] have been recorded and/or published so far, the MNDO assignment for vinyl azide in its syn form ($\Delta H_f^{\mathrm{MNDO}}(\mathrm{syn}) = +366$ kJ/mol; $\Delta H_f^{\mathrm{MNDO}}(\mathrm{anti}) = +376$ kJ/mol) shall be given:

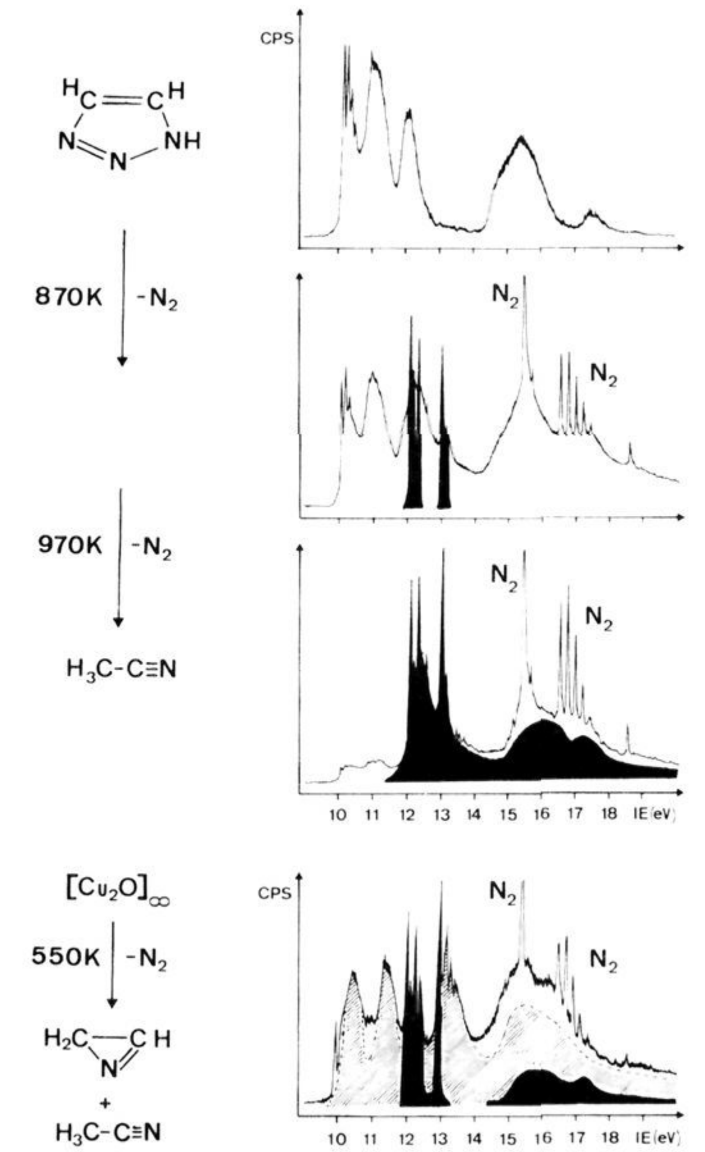
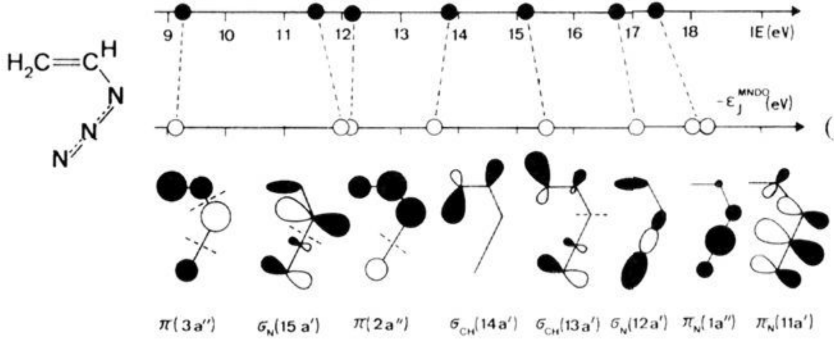


Figure 2. He I PE spectra of 1*H*-1,2,3-triazole and its pyrolysis products at 870 K and 970 K in an empty quartz tube as well as at 550 K over cuprous oxide (shaded: 2*H*-azirine; blackened: acetonitrile).



(5)

This assignment of the vinyl azide ionization pattern leads to a Koopmans' correlation with a satisfactorily small standard error:

$$\mathrm{IE}_n^{\,v} = 0.93(-\epsilon_J^{\mathrm{MNDO}}) + 0.87;\ \mathrm{SE} = 0.3\ \mathrm{eV} \qquad (6)$$

According to (5), the second ionization at 11.56 eV and the two ionizations at 16.77 and 17.4 eV, which according to the MNDO orbitals (5) are predominantly nitrogen radical cation states, are obviously characteristic for the azido group.[5,15–18]

Vinyl Azide Pyrolysis. Two representative experiments shall be described here, which were carried out as follows:

(a) After recording the PE spectrum of vinyl azide (Figure 1) at 300 K, the temperature of the oven was raised, until at 620 K the vinyl azide ionization pattern quickly began to disappear, and the characteristic nitrogen PES bands[19] began to emerge. At

---

(14) Cf., e.g.: Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4907–4917.

(15) Bastide, J.; Maier, J. P. *Chem. Phys.* **1976**, *12*, 177–190. Lee, T. H.; Colton, R. J.; White, M. G.; Rabalais, J. W. *J. Am. Chem. Soc.* **1975**, *97*, 4845–4851.

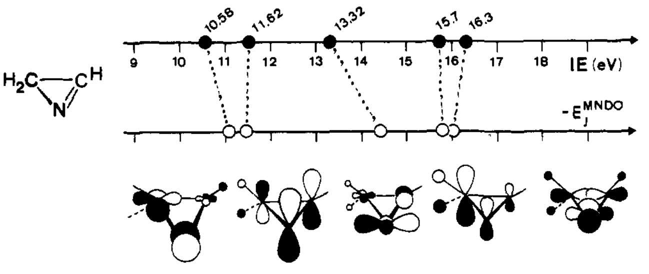
(16) Bock, H.; Dammel, R., unpublished results. Cf.: Herrmann, W. A.; Kriechbaum, G. W.; Dammel, R.; Bock, H.; Ziegler, M. L.; Pfisterer, H. *J. Organomet. Chem.* **1983**, *254*, 219–241.

(17) Bastide, J.; Maier, J. P.; Kubota, T. *J. Electron Spectrosc. Relat. Phenom.* **1976**, *9*, 307–316.

(18) Cradock, S.; Ebsworth, E. A. V.; Murdoch, J. D. *J. Chem. Soc. Faraday Trans. 2* **1972**, *68*, 86–100.

(19) Cf., e.g.: Turner, D. W.; Baker, C.; Baker, A. D.; Brundle, C. R. "Molecular Photoelectron Spectroscopy—A Handbook of He 584 Å Spectra"; Wiley-Interscience: New York, 1970. Or: Kimura, K.; Katsumata, S.; Achiba, Y.; Yamazaki, T.; Iwata, S. "Handbook of HeI Photoelectron Spectra of Fundamental Organic Molecules"; Japan Scient. Soc. Press: Tokyo; Halsted Press: New York, 1981.

the optimized decomposition temperature of 650 K, the vinyl azide bands have vanished completely, giving way to those of nitrogen,[19] of acetonitrile,[19] and of another product, for which new bands were observed at 10.58, 11.57, in the region between 13.0 and 14.0, and around 16 eV (Figure 1). The pyrolysis products were then frozen out in a U-tube between oven and spectrometer, held at 77 K, with nitrogen being continuously removed by pumping. After 1 h, the gas flow through the pyrolysis tube was stopped, the temperature of the U-tube was raised to about 190 K, and the gas pressure in the spectrometer was readjusted. Under these conditions acetonitrile remains frozen out in the U-tube, and the PE spectrum of pure 2*H*-azirine can be recorded (Figure 1), which according to geometry optimized MNDO calculations is assigned as in (7). Again (cf. ref 16), a Koopmans' correlation with a



(7)

resonably small standard error is obtained for all radical cation states but B̃ ($^2A'$), thus confirming the assignment (7) of the 2*H*-azirine PE spectrum.

$$\mathrm{IE}_n^{\mathrm{V}} = 0.94(-\epsilon_j^{\mathrm{MNDO}}) - 0.82;\ \mathrm{SE} = 0.37\ \mathrm{eV} \tag{8}$$

The deviation from experiment for the B̃ ($^2A'$) state is reduced to 0.4 eV by ΔSCF(CI)-MNDO calculations.

(b) In another experiment, a second oven was placed between the U-tube and the PE spectrometer inlet. When the temperature of the second oven was increased to 750 K, the characteristic bands of acetonitrile began to appear. Reaction was complete above 1000 K with no other products but acetonitrile being formed.

1*H*-1,2,3-Triazole pyrolyses were carried out both in an empty quartz tube and after filling it with cuprous oxide dispersed over quartz wool:

(a) The pyrolysis of 1*H*-1,2,3-triazole (PE spectrum;[20] cf. Figure 2) at 10^{-2} mbar began at 840 K with evolution of nitrogen and formation of acetonitrile. At 970 K, the reaction was virtually complete with acetonitrile and nitrogen being the only products observed (Figure 2).

(b) The pyrolysis of 1*H*-1,2,3-triazole was repeated over cuprous oxide as a catalyst. A quantity of quartz wool sufficient for a loose fill of the reaction tube was impregnated with finely powdered Cu_2O. Nitrogen evolution began at 515 K. At 550 K, the triazole bands had almost disappeared (Figure 2). Besides nitrogen,[19] 2*H*-azirine was found to be the main reaction product, with some acetonitrile[19] also present (Figure 2). Copper powder was found to be ineffective as a catalyst for 2*H*-azirine formation. This finding suggests that it might be the electron deficiency of $(Cu_2O)_\infty$, a p-type semiconductor,[21] that opens the 2*H*-azirine decomposition channel for the adsorbed electron-rich triazole.

MNDO Hypersurface Studies for the Ensemble C_2H_3N

The close correspondence between experiment and theory as exemplified in the Koopmans' correlations for both vinyl azide (6) and 2*H*-azirine (8) can be used as tested basis, to explore other possible products of nitrogen extrusion from vinyl azide, which form the ensemble C_2H_3N. The either known or energetically most favorable isomers[2,11,22] are compiled together with some triplet species in the MNDO total-energy diagram displayed in Figure 3.

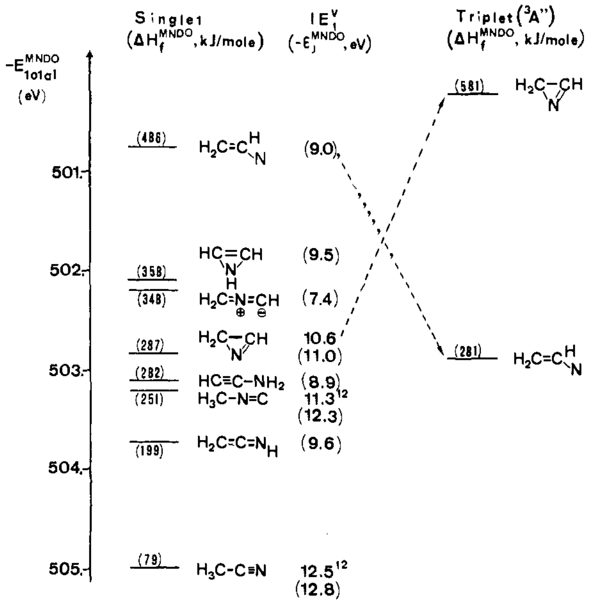


Figure 3. MNDO total energies, $-E_{1\mathrm{otal}}{}^{\mathrm{MNDO}}$ (eV), and heats of formation, $\Delta H_f{}^{\mathrm{MNDO}}$ (kJ/mol) for some of the more stable isomers of the C_2H_3N ensemble in their singlet ground state, together with MNDO eigenvalues, $-\epsilon_J{}^{\mathrm{MNDO}}$ (eV), for the highest occupied molecular orbitals and known first vertical ionization energies, $\mathrm{IE^v}$ (eV). Also listed are the $\Delta H_f{}^{\mathrm{MNDO}}$ values for the triplet ground states ($^3A''$) of vinyl nitrene and 2*H*-azirine (calculated values in brackets; cf. text).

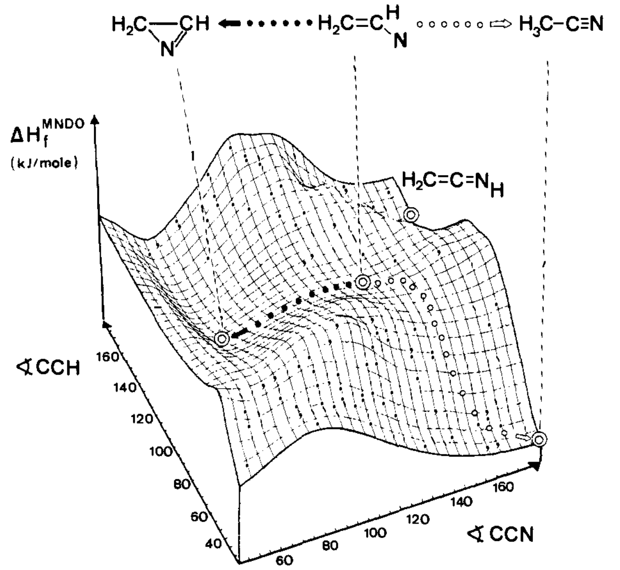


Figure 4. MNDO heat of formation hypersurface for singlet vinyl nitrene rearrangements to 2*H*-azirine, ketene imine, and the thermodynamically most favorable isomer, acetonitrile (see text).

By far the most stable isomer calculated is acetonitrile; followed by the ketene imine and, higher up in the scale, methyl isocyanide, aminoacetylene, and 2*H*-azirine. The tautomer, 1*H*-azirine, however, and in accordance with chemical experience,[23] turns out to be rather unstable. As concerns the "parent" isomer, vinyl nitrene, the MNDO total energy of its triplet ground state matches that of the 2*H*-azirine singlet and lies some 2 eV below the singlet nitrene (Figure 3). Nevertheless, thermal decomposition of azides

---

(20) For the assignment of the 1*H*-1,2,3-triazole spectrum, see: Cradock, S.; Findlay, R. H.; Palmer, M. H. *Tetrahedron* **1973**, *29*, 2173–2181.

(21) Cf., e.g.: Bond, G. C. "Principles of Catalysis", rev. 2nd ed.; The Chemical Society: London, 1972.

(22) For the energies of some other triplet species, cf.: Torres, M.; Lown, E. M.; Bunning, H. E.; Strausz, O. P. *Pure Appl. Chem.* **1980**, *52*, 1623–1643. See also, Dewar, M. J. S.; Ramsden, C. A. *J. Chem. Soc., Chem. Commun.* **1973**, 688.

(23) Cf., e.g.: Fowler, F. W. *Adv. Heterocycl. Chem.* **1973**, *13*, 45–76 and literature cited therein.

should, in general, yield both singlet nitrogen[24] and singlet nitrene because of spin conservation[25] and for energetic reasons.

Several of the C_2H_3N isomers displayed in Figure 3, however, cannot readily be formed from vinyl nitrene; for example, the rearrangement to aminoacetylene would require shifting two hydrogens, or the formation of methyl isocyanide can only be achieved by skeletal resequencing. On the other hand, simple processes may lead to the energetically reasonably close isomers 2*H*-azirine and ketene imine and to the thermodynamically most favorable product, acetonitrile (Figure 3). All these essential isomers can be projected onto a single two-dimensional hypersurface (Figure 4), if both the angles ∠CCH and ∠CCN are chosen out of the $3n - 6 = 12$ possible reaction coordinates leading to $\binom{12}{2} = 66$ individual combinations.

Inspection of the MNDO hypersurface (Figure 4) shows vinylnitrene to lie in a very shallow minimum with the activation barrier for ring closure to 2*H*-azirine (Figure 4: ●●●→) calculated to be only a few kilojoules per mole. Whereas the separating hypersurface "ridge" to ketene imine seems insurmountable ($\Delta\Delta H_f^{MNDO} \sim 70$ kJ/mol), the rearrangement to acetonitrile (Figure: ○○○→) can proceed along a more favorable "mountain pass" ($\Delta\Delta H_f^{MNDO} \sim 40$ kJ/mol).

Thus, the MNDO hypersurface studies for the C_2H_3N ensemble suggest preferential formation of 2*H*-azirine on nitrogen extrusion from vinyl azide with the thermodynamically favored product, acetonitrile, predominating at higher temperature—a theoretical prediction that could be verified in all its facets experimentally by the PE spectroscopically monitored pyrolysis of the hazardous starting material (Figure 1).

Mechanistic Rationalization

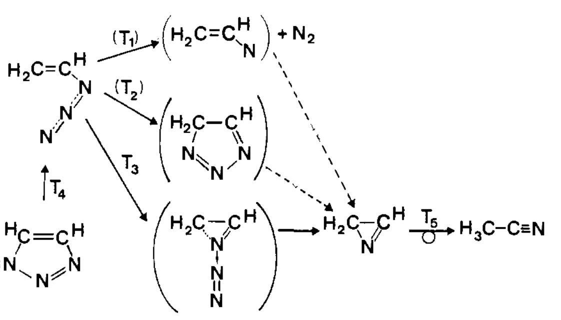
The results of the PE spectroscopically monitored thermal decompositions of methyl azide,[5] vinyl azide, and 1*H*-1,2,3-triazole can be summarized as follows:

(a) Vinyl azide decomposes at 650 K—a temperature lower by some 200 K than does methyl azide under similar conditions—to yield 2*H*-azirine and nitrogen.

(b) 1*H*-1,2,3-Triazole, the electronically stabilized five-center 6π-electron tautomer of vinyl azide, splits off nitrogen above 870 K to yield acetonitrile.

(c) 2*H*-Azirine rearranges to acetonitrile above 750 K, also the triazole yields predominatly 2*H*-azirine, if its decomposition temperature is lowered to 550 K by Cu_2O catalysis.

Although neither the experiments nor the MNDO hypersurface study provide any information concerning the dynamics of the reaction, i.e., about the changes in the internal-energy distribution along the reaction pathway, one is tempted to establish a rationale for the above facts very much in the way of conventional mechanistic classification. In the literature,[8,9,23,26] three possible mechanisms have been proposed for the thermal decomposition of vinyl azide derivatives: the "free nitrene" route (9), cyclization to a 4*H*-1,2,3-triazole intermediate (10), and a neighboring group assistance, i.e., N_2 extrusion supported by three-membered ring formation (11). The 1*H*-1,2,3-triazole pyrolysis also investigated here would fit into all three mechanistic possibilities via a preceding 1*H*-triazole ⇄ vinyl azide tautomer equilibrium activated at a temperature T_4 higher than (T_1) to T_3.[27]



(9)

(10)

(11)

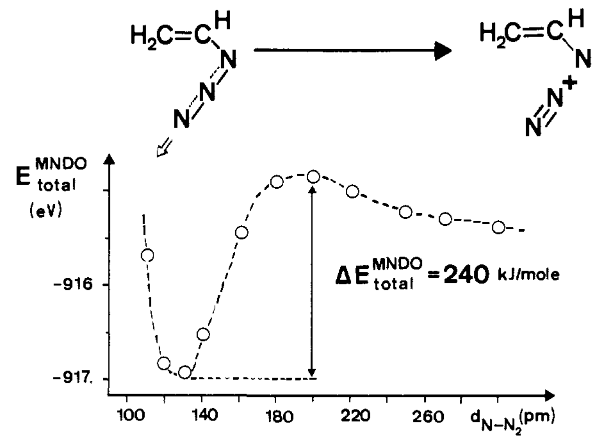


Figure 5. One-dimensional MNDO total-energy hypersurface for withdrawal of the N_2 subunit in the direction of the (vinyl) azide stretching frequency with all fragment geometries optimized for each individual point.

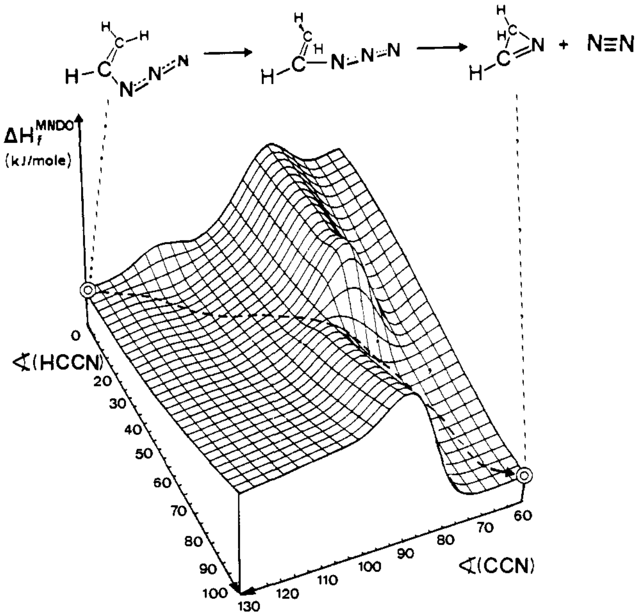


Figure 6. MNDO heat of formation hypersurface for vinyl azide decomposition via synchronous N_2 extrusion plus azirine ring formation (11).

On the basis of our experiments and of additional MNDO hypersurface studies, we can advance the following arguments for the evaluation of the mechanisms 9–11:

The free nitrene route (9) can be exluded for two reasons. MNDO calculations predict almost identical barriers for nitrogen extrusion and nitrene formation for both methyl[5] and vinyl azides in either syn or anti conformation (Figure 5).

However, the flash-vacuum decomposition temperatures observed for saturated azides, e.g., 850 K for H_3CN_3[5] or 880 K for $(H_3C)_5SiN_3$,[16] are much higher than the 650 K needed for the unsaturated vinyl azide. This lower value is consistent with experimental activation parameters for the decomposition of substituted vinyl azides in solution, typical values for which are $\Delta H^{\ddagger} \sim 100$ to 120 kJ/mol and $\Delta S^{\ddagger} \sim -12$ to -30 kJ/mol.[26] Reactions

---

[24] Herzberg, G. "Molecular Spectra and Molecular Structure: I. Spectra of Diatomic Molecules", 2nd ed.; Van Nostrand: Princeton, NJ, 1950.

[25] However, spin-forbidden reactions may become allowed when the overall space x spin symmetry is considered; for the role of direct space x spin coupling, cf., e.g.: Cracauer-Ninio, M.; Halevi, E. A. 2nd IUPAC Conference on Physical Organic Chemistry, Noordwijkerhout, Holland, April, 1974; Abstracts of Papers, p 22.

[26] L'abbé, G.; Mathys, G. *J. Org. Chem.* **1974**, *39*, 1778–1780.

[27] Burke, L. A.; Leroy, G.; Nguyen, M. T.; Sana, M. *J. Am. Chem. Soc.* **1978**, *100*, 3668–3674. Surprisingly, ab initio calculations for the barrier of the thermal vinyl azide/triazole isomerization yield the rather low value of 120–150 kJ/mol.

J. Am. Chem. Soc. 1983, 105, 7685–7690

proceeding via free nitrenes exhibit higher activation energies, and, above all, positive activation entropies.[8]

The 4*H*-1,2,3-triazole route[8,27] **(10)** runs contrary to chemical intuition, since the bending of an azido group requires a strong force. Moreover, the resulting 4*H*-triazole lacks the advantageous stabilization that a 6π-electron system as in its anion would provide. Therefore, the facile base-catalyzed rearrangement of vinyl azide derivatives[27,28] to triazoles in solution bears no relevance to the gas-phase process. In accordance with the above arguments, MNDO hypersurface studies[29] predict a rather high activation energy of around 230 kJ/mol.[27]

A synchronous process via a three-membered ring supported nitrogen extrusion (11) has been studied as a refinement of the C_2H_3N MNDO hypersurface presented in Figure 4 for the following reasons: upon reinspection of the free nitrene mechanism, i.e., the N_2 expulsion with higher barrier followed by nitrene rearrangement with close-to-zero barrier, a more concerted reaction suggests itself. When both the dihedral angle $\angle HCCN$ and the bond angle $\angle CCN$ are used as reaction coordinates, the activation energy for the synchronous N_2 extrusion plus ring formation is lowered to 138 kJ/mol (Figure 6).

The synchronous process presented in Figure 6 would be in agreement with the negative activation entropies found in the decomposition of substituted vinyl azides,[26] since a geometrically highly strained transition state must be passed through in the course of 2*H*-azirine formation. At the same time, the "neighboring" group effect, which lowers the N_2 extrusion barrier for vinyl azide by over 100 kJ/mol, explains not only its decomposition temperature T_3 (11) lowered by 200 K relative to that of methyl azide[5] but also its instability at room temperature as well as its hazardous explosive properties.

Acknowledgment. This work was made possible by the State of Hesse and the University of Frankfurt, which provided the PE spectrometers and the computer time. We also like to thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for generous support.

Registry No. Vinyl azide, 7570-25-4; 1,2,3-triazole, 288-36-8; 2*H*-azirine, 157-16-4; ketene imine, 17619-22-6; methyl isocyanide, 593-75-9; aminoacetylene, 52324-04-6; *N*-methylidynemethanaminium hydroxide, inner salt, 61170-69-2; 1*H*-azirine, 157-17-5; vinyl nitrene, 64987-66-2; acetonitrile, 75-05-8; cuprous oxide, 1317-39-1.

---

[28] Meek, J. S.; Fowler, J. S. *J. Am. Chem. Soc.* **1967**, *89*, 1967; *J. Org. Chem.* **1968**, *33*, 985-987 and literature cited therein.

[29] Kos, A.; Schleyer, P. von R., private communication.

Zwitterionic Bicyclobutane: An Intermediate in the Course of a Nucleophilic Vinylic-like Substitution Reaction on 3-Halobicyclobutanecarbonitrile[1]

Shmaryahu Hoz* and Doron Aurbach

Contribution from the Department of Chemistry, Bar-Ilan University, Ramat-Gan 52100, Israel.
Received December 29, 1982. Revised Manuscript Received August 1, 1983

Abstract: In the nucleophilic reaction of the alkoxides MeO$^-$, EtO$^-$, *i*-PrO$^-$, and $CF_3CH_2O^-$ with 3-halobicyclobutanecarbonitrile (**1**-Cl, -Br), the ketal 3,3-dialkoxycyclobutanecarbonitrile (**2**) together with small amounts of the vinylic compound **3** were obtained. Rate constants for the reaction of **1** with MeO$^-$, EtO$^-$, and *i*-PrO$^-$ in the parent alcohols were determined at 25 °C. In the reaction of MeO$^-$ in MeOH, the reversible formation of the iminomethoxy compound **4** was also observed. The element effect $k_{Cl/Br} \approx 4$ indicates that in the first step of the reaction the nucleophile cleaves the central bond of **1** rather than the bond to the leaving group. In this step, a cyano-stabilized carbanion is formed on C-1 and a halo ether on C-3 of the molecule. Evidence is presented to show that unlike the addition–elimination mechanism in nucleophilic vinylic substitution reactions, there is no ring closure coupled with the expulsion of the nucleofuge to give the alkoxybicyclobutane **5**. Instead, the halo ether decomposes to give oxocarbenium paired with both the carbanion on C-1 and the halide ion (path b, Scheme I). In the reactions of **1** with $CF_3CH_2O^-$ in *t*-BuOH, the (2,2,2-trifluoroethoxy)carbenium is captured by a trifluoroethoxy ion to give **2** (R = CF_3CH_2) and by *t*-BuOH (which is otherwise unreactive) to give the two cis–trans isomers of the mixed ketal **6**. In these reactions, the less stable isomer **6t** is obtained preferentially over the more stable one **6c**. This behavior is typical in cases where protonation of the cyclobutanic carbanion is the stereochemically controlling step. The ratio **2** (R = CF_3CH_2):**6** is significantly affected by the halogen identity (Cl or Br), whereas there is no element effect on the cis–trans partition of the two isomers of **6**. These last two observations together with analysis of rate constant ratios for similar reactions strongly support a reaction pathway in which the nucleofuge departs to give a zwitterionic intermediate before the carbanion is protonated or nucleophilically displaces the nucleofuge to form the covalent alkoxybicyclobutane **5**. The zwitterionic species is in fact a bicyclobutane derivative in which the central bond is ionic rather than covalent. The origin of the barrier for the transformation of this ionic bond to a covalent one is discussed.

Although formally a single bond, the central bond of bicyclobutane closely resembles a carbon–carbon double bond in its chemical behavior. This is manifested, for example, in its ability to participate in polymerization reactions,[3a,b] to add various electrophiles such as acids and halogens,[3a,b] to trap benzyne intermediates,[3c] and when suitably activated, to undergo nucleophilic addition reactions.[2,4] Nevertheless, to the best of our knowledge it was not reported to undergo a nucleophilic substitution reaction at the bridgehead carbon ("vinylic-like" position) analogously to suitably substituted olefins.[5]

Nucleophilic vinylic substitution reactions are extensively documented in the literature.[5,6] The most common mechanism

---

[1] Presented in part in the 49th Israel Chemical Society Meeting, Oct 1982. This is part 5 in the series Cyclobutane–Bicyclobutane Systems. For part 4, see: Hoz, S.; Aurbach, D.; Avivi, C. *Tetrahedron Lett.* **1983**, 1639.

[2] Hoz, S.; Aurbach, D. *J. Am. Chem. Soc.* **1980**, *104*, 2340.

[3] (a) Wiberg, K. B.; Lampman, G. M.; Ciula, R. P.; Connor, D. S.; Schertler, P.; Lavanish, J. *Tetrahedron* **1965**, *21*, 2749. (b) Hall, J. K.; Blanchard, E. P.; Cherkofsky, S. C.; Sieja, J. B.; Sheppard, W. A. *J. Am. Chem. Soc.* **1971**, *93*, 110. (c) Pomerantz, M.; Wilke, R. N.; Gruber, G. W.; Roy, U. *Ibid.* **1972**, *94*, 2752.

[4] Hoz, S.; Aurbach, D. *Tetrahedron* **1979**, *35*, 883.

[5] (a) Rappoport, Z. *Acc. Chem. Res.* **1981**, *14*, 7. (b) Modena, G. *Ibid.* **1971**, *4*, 73.

0002-7863/83/1505-7685$01.50/0