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Another Look at the Decomposition of Methyl Azide and Methanimine: How Is HCN Formed?

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Ab initio molecular orbital calculations have been used to study the decomposition of methyl azide (CH_3N_3), methanimine, and its isomers (CH_3N) in both lowest lying singlet and triplet states. Geometries were optimized using UMP2/6-31G(d,p) level of theory while energies of the stationary points on potential energy surfaces were obtained from QCISD(T) calculations with larger 6-311++G(d,p) and 6-311++G(3df,2p) basis sets and corrected for zero-point energies. The temperature dependence of the rate constants of various dissociative processes has also been calculated using the conventional transition-state theory. While the decomposition of methyl azide occurs, in the singlet state, through a concerted motion of N_2 elimination with hydrogen shift, giving methanimine, the triplet methyl azide does not exist as a discrete species but falls apart, giving triplet methylnitrene plus N_2 . Starting from singlet methanimine, 1,1- H_2 elimination giving HNC is found to be favored over 1,2- H_2 elimination giving HCN, a 1,2-H shift yielding aminocarbene, and N–H bond cleavage producing the H_2CN radical. The hot HNC molecule is expected to rearrange rapidly to HCN. From singlet aminocarbene (HCNH_2), 1,2- H_2 loss giving HNC is also a less energy-demanding step than the 1,2- H_2 loss, generating HCN. Overall, it appears that, in the lowest singlet state, HCN is not directly formed upon fragmentation of methanimine but rather from rearrangement of HNC which is the primary product. In the triplet state, the HCN formation from either methylnitrene or methanimine passes through successive losses of H atoms.

Introduction

Since the discovery of phenyl azide by Griesse¹ in 1864 and the subsequent proposal for formation of nitrene intermediates by Tiemann² in 1891, the chemistry of these compounds continues to attract intense interest. Azides constitute beyond doubt one of the most versatile classes of building blocks in organic and heterocyclic syntheses.³ The photochemistry of aromatic azides has also been widely investigated, in part owing to their use in photoresist technologies and vesicular light-sensitive materials and in biological methods of photoaffinity labeling.⁴ Recent experimental studies⁵ by different groups have demonstrated convincingly that singlet phenylnitrene is actually produced as a discrete intermediate upon photolysis of phenyl azide. Thus, the transient singlet nitrene undergoes subsequent ring expansion to azacycloheptatetraene and also intersystem crossing to its triplet ground state.⁵ Regarding alkyl azides, the question whether singlet nitrenes are formed during their Curtius rearrangement (eq 1) is yet to be answered completely.



Methanimine ($\text{H}_2\text{C}=\text{NH}$) was first identified by Milligan⁶ as the major product upon photolysis of methyl azide (CH_3N_3) by argon matrix IR spectrometry at 4 K. Similarly, this product was characterized by photoelectron spectroscopic techniques following thermolysis of methyl azide.⁹ At 720 K, characteristic PE bands of $\text{H}_2\text{C}=\text{NH}$ were already observed; at 850 K, methyl azide was pyrolyzed completely and the recorded PE spectrum contained bands due to HCN and H_2 . Formation of HCN was

rationalized as coming directly and exclusively from dehydrogenation of methanimine.

Earlier^{8,9} as well as more recent¹⁰ ab initio molecular orbital calculations consistently suggest that, in the closed-shell singlet state ($^1\text{A}'$), conversion of methylnitrene to methanimine is a barrier-free process, implying that singlet CH_3N does not correspond to an equilibrium structure. In a 1984 review, Wentrup¹¹ summarized well the conventional wisdom on this matter: “it is very difficult, if not impossible, to prove that singlet methylnitrene is an intermediate in this reaction”. The question of concerted versus stepwise decomposition of methyl azide has been addressed by Bock and Dammel¹² using semiempirical MNDO calculations. These authors considered that both thermal formation and subsequent reactions of methylnitrene should occur on the singlet potential energy surface and found that on the MNDO energy surface, both concerted and stepwise reaction paths exist with comparable activation energies. Despite these findings, they argued, on the basis of the observed temperature dependence of the decomposition of various alkyl azides, that the methyl azide pyrolysis occurs concertedly with coupled N_2 extraction and hydrogen shift. Nevertheless, these results should be regarded with much caution, because the MNDO method predicts an energy barrier of about 5 kcal/mol for the $\text{CH}_3\text{N} \rightarrow \text{CH}_2=\text{NH}$ rearrangement, in clear contrast with ab initio results.^{9,10} Regarding methylnitrene, it is to be noted that when C_s symmetry is enforced, the open-shell singlet state ($^1\text{A}''$), a component of the Jahn–Teller splitting from the ^1E state, exists as a local minimum with a high-energy barrier to rearrangement.⁹ Nevertheless, due to the small $^1\text{A}'-^1\text{A}''$ energy splitting,^{9,10} this excited state of methylnitrene is presumably not survived upon slight geometry

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distortion removing C_s symmetry. More recent evidence for the extremely short-lived existence of singlet methylnitrene has been collected from a photodetachment spectroscopic study of the CH_3N^- anion.¹³ If this remarkable fact could be confirmed, it indicates that a chemical species which does not correspond at all to an equilibrium structure, when vertically generated, could briefly respond to a spectrometer before decomposing or rearranging irreversibly to a more stable isomer. On the other hand, HCN might not be directly generated from methanimine as postulated by Bock and Dammel.¹² An earlier theoretical study,¹⁴ overlooked by these authors, has in fact suggested that 1,2 elimination of H_2 yielding HCN is less favored than the 1,1 elimination giving HNC, the latter rapidly rearranging to HCN.

Both methanimine and hydrogen cyanide have also been identified as initial products in the reaction between atomic carbon and ammonia ($\text{C} + \text{NH}_3$).¹⁵ Thus, although these species are apparently situated at the center of an interesting network of reactions, their formation mechanism is not yet clearly established. None of the previous theoretical studies examined the entire network, making reliable comparison of energetic parameters somewhat difficult. In an attempt to construct a consistent and reliable potential energy surface and thereby to resolve the various questions left open in previous studies, we have carried out ab initio molecular orbital calculations at uniform and high levels of theory on the decomposition of methyl azide and interconnections between possible $[\text{CH}_3\text{N}]$ isomers. Both lowest-lying closed-shell singlet and triplet electronic states have been examined. Subsequently, calculated geometrical and energetic results have been utilized to calculate the temperature dependence of the apparent rate constants of relevant reaction channels making use of the conventional absolute rate theory. This kinetic analysis allows the possibilities of HCN formation from the CH_3N species via different routes to be unambiguously established.

Calculation

Ab initio molecular orbital calculations were performed using a local version of Gaussian 92 program.¹⁶ Initial geometry optimizations and harmonic vibrational analyses were carried out at the Hartree–Fock level of theory (HF) with the 6-31G-(d,p) basis set. The identity of each transition structure is established, when necessary, by intrinsic reaction coordinate (IRC) calculations. Geometries of the equilibrium and transition structures were then reoptimized at the second-order Møller–Plesset perturbation theory with the same atomic basis (MP2/6-31G(d,p)). Improved energies of all relevant stationary points on various potential energy surfaces were obtained via single-point electronic energy computations using the quadratic configuration interaction method, QCISD(T),¹⁶ in conjunction with the larger 6-311++G(d,p) and 6-311++G(3df,2p) basis sets at the MP2 geometries. Throughout this paper, bond lengths are given in angstroms, bond angles in degrees, total energies in hartrees, zero-point and relative energies, unless otherwise stated, in kcal/mol.

Results and Discussion

Decomposition of Methyl Azide. Geometries of equilibrium methyl azide (MA) and transition (TS) structures for N_2 elimination are displayed in Figure 1. The MP2/6-31G(d,p)-optimized geometry of MA has been reported and abundantly commented in a recent paper.¹⁷ We have found that in its singlet ground state, hydrogen transfer from C to N and cleavage of the $\text{N}_1\text{—N}_2$ bond take place concertedly at the transition state. In TS, the $\text{N}_1\text{—N}_2$ bond is in fact lengthened from 1.244 to 1.935 Å, whereas the migration of the H_m atom is also initiated with

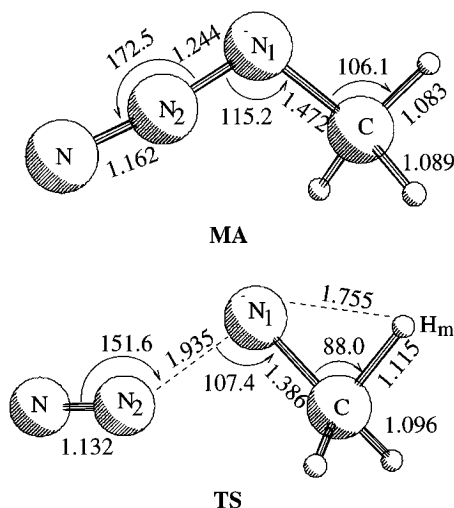


Figure 1. Selected MP2/6-31G(d,p)-geometrical parameters of methyl azide (MA) and transition structure (TS) for N_2 elimination.

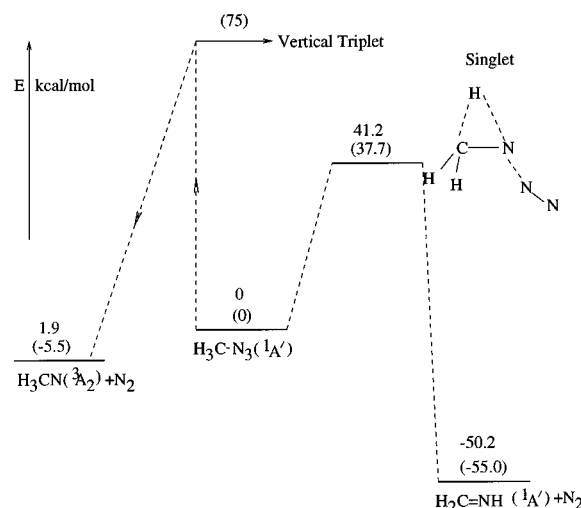


Figure 2. Relative energies (kcal/mol) for the decomposition of methyl azide in both lowest lying singlet and triplet states. Energies obtained from QCISD(T)/6-311++G(3df,2p)+ZPE and QCISD(T)/6-311++G-(d,p)+ZPE (values in parentheses) calculations.

a small stretching of the C—H_m distance and a marginal closure of the $\text{H}_m\text{—C—N}$ bond angle. The IRC calculations confirm that beyond the TS, the H_m atom is progressively transferred to N. Calculated relative energies are summarized in Figure 2. The singlet decomposition is slightly exothermic, requiring also a substantial activation energy. Extension of the one-electron basis function tends to increase the barrier. On the basis of these observations we suggest an energy barrier of $\text{ca. } 40 \pm 3$ kcal/mol for the singlet concerted decomposition of methyl azide. Using the available heat of formation of methanimine, $\Delta H_{f,0}^\circ(\text{H}_2\text{C=NH}) = 22.9$ kcal/mol at 0 K,¹⁸ the corresponding value for methyl azide can be estimated as $\Delta H_{f,0}^\circ(\text{H}_3\text{CN}_3) = 73.1$ kcal/mol with a probable error of ± 3 kcal/mol; the latter value differs somewhat from an earlier estimate of 67 kcal/mol using the group additivity scheme.¹⁹

In the excited triplet state, the $\text{N}_1\text{—N}_2$ bond breaks without any energy barrier giving rise to triplet methylnitrene (CH_3N , $^3\text{A}_2$). Thus, triplet methyl azide does not exist as a genuine energy minimum. The vertical triplet methyl azide having the singlet geometry lies 75 kcal/mol above MA and thus positioned well above the singlet TS (cf. Figure 2). As could be expected from the barrier height, the decomposition is rather slow, but this is not inconsistent with the experimental fact that methyl azide pyrolysis begins to occur at 720 K at 10^{-2} mbar pressure.¹²

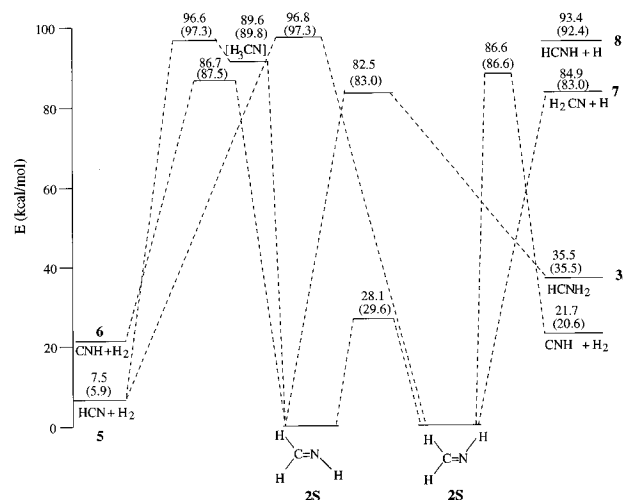


Figure 3. Schematic energy profiles showing the 1,2-H shift, H_2 eliminations, and bond cleavages of singlet $H_2C=NH$. Relative energies are derived from QCISD(T) calculations with the 6-311++G(3df,2p) and 6-311++G(d,p) (values in parentheses) basis sets and ZPE corrections.

At that temperature the absolute rate constant of decomposition is calculated to be about $k = 1.2 \times 10^2 \text{ s}^{-1}$. Note, however, that under the experimental conditions, it is not sure whether the observed temperature really corresponds to that reached the decomposing molecules.

Decomposition of Singlet Methanimine. Methanimine has been observed as the primary product upon thermolysis and photolysis of methyl azide.^{6,12} Since this process is exothermic (cf. Figure 2), the product formed therein contains a certain amount of excess internal energy which could then be utilized to undergo further reactions. The crucial role of the hot molecules could in fact be demonstrated by experimental findings. While HCN is detected already at 770 K during methyl azide pyrolysis, decomposition of cool methanimine as starting materials proceeds only at 1300 K.¹² Since an accurate calculation of energy partitioning between both fragments, $H_2C=NH$ and N_2 , requires a chemical dynamics treatment which is beyond the scope of the present work, we are, for the time being, not able to treat the HCN formation from methyl azide using chemical activation process. We have therefore considered the various pathways proceeding from cool methanimine, assuming, in other words, no excess energy available in the forming products. This presumably leads to the lower values of rate constants than that of the true ones; the calculated values are at best considered as the lower limits. Nevertheless, this separate treatment which corresponds to methanimine decomposition still might give a clue to the understanding of methyl azide decomposition mechanism. The geometrical parameters of all the structures considered are not reported here as most of them are simple and can be reproduced rapidly. Geometries of some interesting transition structures will however be displayed.²⁰ Calculated potential energy curves for various reaction channels arising from methanimine and its isomer aminocarbene in the singlet ground state are illustrated in Figures 3 and 4.

The $[C,H_3,N]$ system contains in principle four isomers including methylnitrene H_3C-N (1), methanimine $H_2C=NH$ (2), aminocarbene $HC-NH_2$ (3), and a carbyne structure, $C-NH_3$ (4), and a number of fragments including $HCN + H_2$ (5), $HNC + H_2$ (6), $H_2CN + H$ (7), $HCNH + H$ (8), $CNH_2 + H$ (9), and finally $C + NH_3$ (10). In Figures 3 and 4 and the following discussion, the letter **S** stands for singlet. Transition structure (TS) connecting two equilibrium structures, **X** and **Y**,

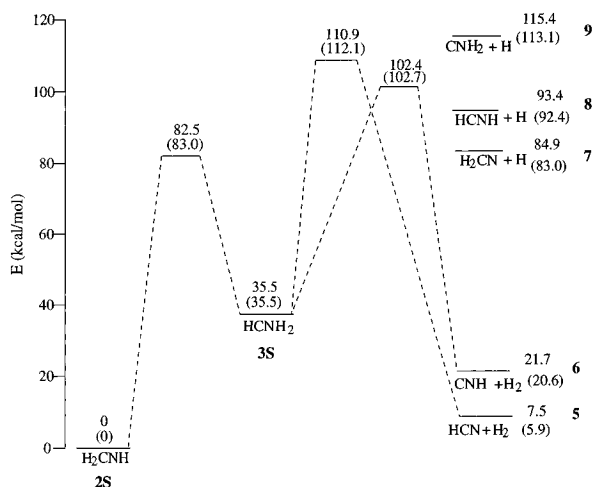
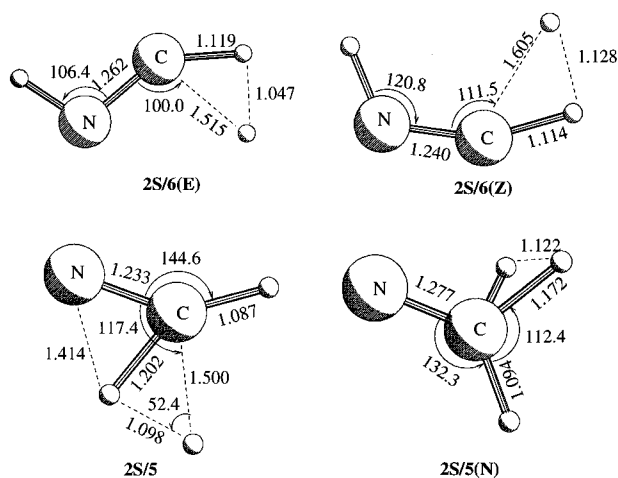


Figure 4. Schematic energy profiles showing the rearrangements and H_2 eliminations of aminocarbene ($HCNH_2$). Relative energies are derived from QCISD(T)/6-311++G(3df,2p)+ZPE and QCISD(T)/6-311++G(d,p)+ZPE (values in parentheses).

CHART 1



is designated as **X/Y**. Our calculations show that singlet carbyne (**4S**) is a high-energy isomer lying about 142 kcal/mol above **2S** and 27 kcal/mol above the fragments, $C-NH_2 + H$ (**9**). Although **4S** is 26 kcal/mol more stable than $C(^1D) + NH_3$ (**10**), it readily dissociates into **9** with an energy barrier of only 4 kcal/mol. These points lie thus in a potential energy region much higher than that released during rearrangement of methanimine. It is therefore reasonable to admit that $C-NH_3$ (**4S**) does not take part in the transformation under consideration. The species **4S** is of course important in the $C + NH_3$ reaction. The heat of formation of aminocarbene (**3S**) has been evaluated in a recent paper.^{18a}

From $H_2C=NH$ (**2S**), a number of reaction channels are open, including 1,1 elimination, 1,2 elimination, 1,2 hydrogen shift, and N-H and C-H bond cleavages. A few points are worth mentioning:

(i) There are two distinct transition states for 1,1 elimination of H_2 . In **2S/6(E)** (Chart 1) both departing H atoms are situated in trans position with respect to the nitrogen H atom. In **2S/6(Z)** they are in a cis configuration relative to the C=N bond. Energetically, however, both TS are quasiidentical.

(ii) There are also two transition states which correspond to 1,2- H_2 elimination. While **2S/5** is formally the transition state for this process, **2S/5(N)** appears to be a transition state connecting $HCN + H_2$ with methylnitrene (**1S**). In reality, IRC calculations reveal that, upon removal of C_s symmetry, it

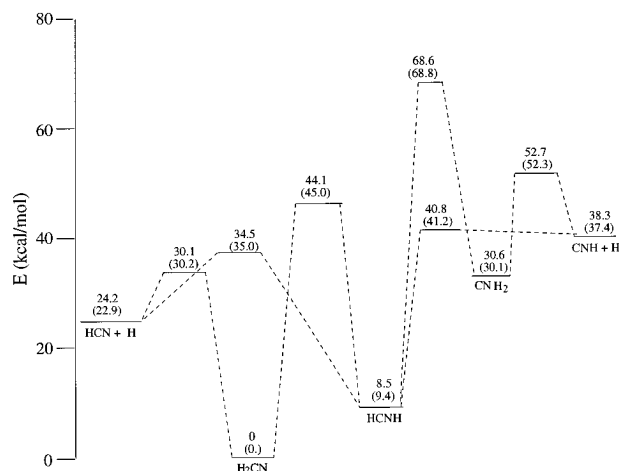


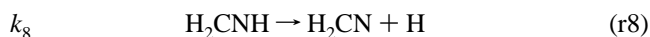
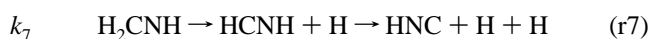
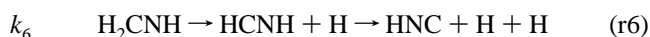
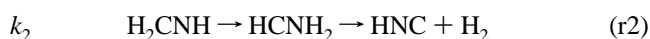
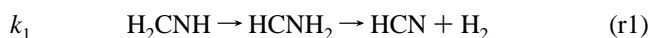
Figure 5. Schematic energy profiles showing the interconversions of CH_2N radicals. Relative energies are derived from QCISD(T)/6-311++G(3df,2p)+ZPE and QCISD(T)/6-311++G(d,p)+ZPE (values in parentheses).

optimizes to methanimine (**2S**). Again, both TS possess similar energy content. Hence, 1,2- H_2 elimination from methanimine is found to be intrinsically less favored than 1,1- H_2 elimination.

(iii) Aminocarbene (**3S**) also undergoes both 1,1- and 1,2- H_2 elimination. Even though HNC is less stable than HCN, its formation is again more favorable via a 1,2- H_2 departure.

(iv) The methanimine–aminocarbene interconversion by a 1,2-H shift is associated with the smallest energy barrier. However, the corresponding TS **2S/3S** lies only a few kcal/mol below the $\text{H}_2\text{C}=\text{N} + \text{H}$ (**7**) dissociation limit. Therefore it is crucial to establish the possible reaction channels of the latter radical. Figure 5 displays the energy profile for the $[\text{CH}_2\text{N}]$ radicals using the same theoretical model. It shows that a H loss from $\text{H}_2\text{C}=\text{N}$ yielding HCN is the most facile pathway.

We can now define the rate constants for different reaction routes starting from singlet methanimine (**2S**) as follows:



It should be noted that all above reactions could be responsible for HCN formation. Reactions (r1) and (r2) were treated via the following equation:



The overall rate constant k can readily be derived by considering the steady-state of B formulated as

$$k = \frac{k_P k_F}{k_B + k_P}$$

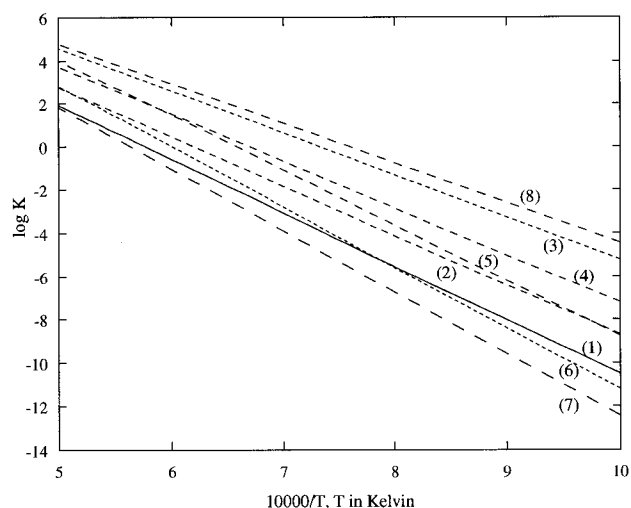


Figure 6. Variation of the rate constants of various reactions of methanimine with temperature using energies obtained by QCISD(T)/6-311++G(3df,2p) calculations given in Figures 3–5.

The individual rate constants k_F , k_B , and k_P were calculated from the absolute rate theory as

$$k_i = \frac{k_b T}{h} \frac{Q^\ddagger}{Q} \exp(-E/RT)$$

where Q^\ddagger and Q are the complete partition functions for the reactant(s) and transition state, respectively, E is the activation energy, k_b the Boltzmann constant, T the temperature, and h the Planck constant. Q^\ddagger and Q are calculated from the vibrational wavenumbers using the HF/6-31G(d,p) wave functions and rotational constants from the MP2/6-31G(d,p)-optimized geometries. The initial steps of reactions r5 and r6 involve the direct dissociation of N–H and C–H bonds, respectively. Since these dissociative processes do not have a transition state, we have taken the N–H and C–H vibrational frequencies of $\text{H}_2\text{C}=\text{NH}$ as the frequency factors for the initial steps of both reactions r5 and r6, respectively. We thus assume that the reverse processes of initial steps of reactions r5 and r6 are unimolecular. A similar kind of treatment was also used earlier.²¹ It should be noted that the complication of energy partitioning among the fragments does not arise after the initial dissociation of reactions r5 and r6 as they are direct dissociation processes. With the above assumption, both reactions r5 and r6 can be treated in the framework similar to eq 2. A survey of several dissociation and recombination reactions shows that the ratio of the frequency factors for dissociation and recombination is about 10^2 .²² Hence we have calculated the frequency factors for recombination (i.e., $\text{B} \rightarrow \text{A}$ process in eq 2) by dividing for the dissociation process by a factor of 10^2 . Figure 6 also shows the variation of all the rate constants with temperature. Direct formation of HNC from $\text{H}_2\text{C}=\text{NH}$ via 1,1- H_2 elimination (r3) is shown to be the most favorable pathway at all temperatures. The HNC species, thus formed, could undergo rapid isomerization to HCN due to its high internal energy acquired during its formation from $\text{H}_2\text{C}=\text{NH}$. The energy barrier for the $\text{HNC} \rightarrow \text{HCN}$ isomerization amounts to about 30 kcal/mol.²³ Production of HCN directly from $\text{H}_2\text{C}=\text{NH}$ through 1,2- H_2 elimination (r4) is the next favorable process until the temperature rises to 1600 K. Above 1600 K, generation of HCN via the $\text{H}_2\text{C}=\text{N}$ radical (r5) becomes almost equal to that via reaction r4. Reactions r1, r2, r6, and r7 remain less important at all temperatures. Figure 6 also suggests that the rate constant for reaction r8, i.e., the H_2CN formation, is always very high. Hence, the radical may be detected following thermolysis of the cool methanimine species.

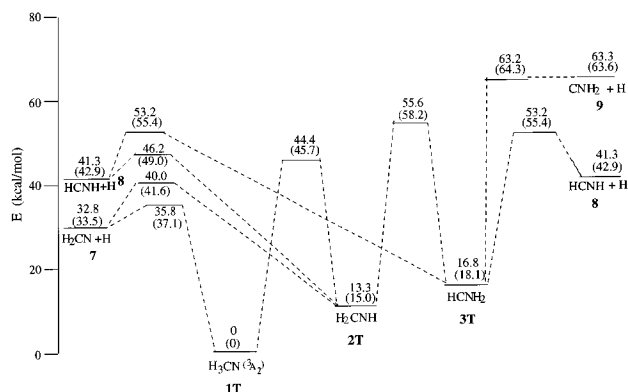


Figure 7. Schematic energy profiles showing the interconversions between CH_3N species in the triplet electronic state. Relative energies are derived from QCISD(T)/6-311++G(3df,2p)+ZPE and QCISD(T)/6-311++G(d,p)+ZPE (values given in parentheses) calculations.

Decomposition of Triplet Species. As discussed above, triplet methyl azide does not exist as a discrete species but falls apart giving methylnitrene ($^3\text{A}_2$) plus N_2 . Figure 7 summarizes the potential energy surface of the triplet $[\text{CH}_3\text{N}]$ species. Our best estimate predicts that **1T** is the lowest-lying triplet form which lies about 52 kcal/mol above singlet methanimine (**2S**, cf. Figure 2). Accordingly, its heat of formation at 0 K can be estimated as $\Delta H_{f,0}^\circ(\text{H}_3\text{CN}) = 75 \pm 3$ kcal/mol. Several dissociation channels of H_3CN , H_2CNH , and HCNH_2 which lead to either HCNH or H_2CN are endothermic (cf. Figure 7). As a consequence, the kinetic analysis, as stated above, cannot be applied for the CH_3N energy surface due to the lack of knowledge about the distribution of the excess energy among fragments. It is however possible to identify the most probable route for the HCN formation. The most facile path from **1T** is obviously a H-loss producing $\text{H}_2\text{CN} + \text{H}$ (cf. Figure 7) followed by a subsequent H loss, $\text{H}_2\text{CN} \rightarrow \text{HCN} + \text{H}$ (cf. Figure 5). The associated energy barriers are significantly smaller than other fragmentations arising from CH_3N (**1T**).

In the event that methyl azide could be photochemically sensitized to its triplet excited state, then a large amount of energy (>70 kcal/mol, cf. Figure 2) could be released from the vertical azide during formation of triplet methylnitrene (**1T**). Assuming that a considerable portion of this excess energy is gathered in CH_3N , it might then easily undergo most of the processes seen in Figure 7 which consistently led to the production of the H_2CN radical and thereby the HCN molecule.

Summary

Three important results emerge from the present study on the decomposition of methyl azide and methanimine: (i) Decomposition of singlet methyl azide produces methanimine plus molecular nitrogen is a single step in which both N_2 departure and H-migration movements are in concert. Triplet methyl azide does not exist as a discrete species but fragments to triplet methylnitrene. (ii) During decomposition of singlet methanimine, formation of hydrogen isocyanide, HNC, is the most favorable process via a 1,1- H_2 elimination. The primary

product, HNC, presumably undergoes rapid isomerization to HCN due to its high internal energy. (iii) In the triplet state, the most probable route for HCN formation is due to a successive H loss from methylnitrene, $\text{CH}_3\text{N}_3 \rightarrow \text{N}_2 + \text{CH}_3\text{N}(^3\text{A}_2) \rightarrow \text{H} + \text{H}_2\text{CN}(^2\text{B}_1) \rightarrow \text{HCN} + \text{H}$.

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References and Notes

- (1) Griess, P. *Philos. Trans. R. Soc. London* **1864**, 13, 377.
- (2) Tiemann, F. *Ber. Dtsch. Chem. Ges.* **1891**, 24, 4162.
- (3) Scriven, E. F. V.; Turnbull, K. *Chem. Rev.* **1988**, 88, 298 and references therein.
- (4) (a) Schuster, G. B.; Platz, M. S. *Adv. Photochem.* **1992**, 17, 69. (b) Chowdhry, V.; Westheimer, F. H. *Annu. Rev. Biochem.* **1979**, 48, 293. (c) Mijer, E. W.; Nijhuis, S.; Van Vroonhoven, F. C. B. M. *J. Am. Chem. Soc.* **1988**, 110, 7209.
- (5) (a) Marcinek, A.; Leyva, E.; Whitt, D.; Platz, M. S. *J. Am. Chem. Soc.* **1993**, 115, 8609. (b) Tomioka, H.; Ichikawa, N.; Komatsu, K. *J. Am. Chem. Soc.* **1993**, 115, 8621. (c) Albini, A.; Bettinetta, G.; Minoli, G. *J. Am. Chem. Soc.* **1991**, 113, 6928.
- (6) (a) Milligan, D. E. *J. Chem. Phys.* **1961**, 35, 1491. (b) Jacox, M. E.; Milligan, D. E. *J. Mol. Spectrosc.* **1975**, 56, 333.
- (7) Bock, H.; Dammel, R.; Horner, L. *Chem. Ber.* **1981**, 114, 221.
- (8) (a) Demuyck, J.; Fox, D. J.; Yamaguchi, Y.; Schaefer, H. F. *J. Am. Chem. Soc.* **1980**, 102, 6204. (b) Pople, J. A.; Raghavachari, K.; Frisch, M. J.; Binkley, J. S.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1983**, 105, 6389.
- (9) Nguyen, M. T. *Chem. Phys. Lett.* **1985**, 117, 290.
- (10) (a) Richards, C.; Meredith, C.; Kim, S.-J.; Quelch, G. E.; Schaefer, H. F. *J. Chem. Phys.* **1994**, 100, 481. (b) Sumathi, R. *J. Mol. Struct. (THEOCHEM)*, in press.
- (11) Wentrup, C. In *Reactive Molecules*; Wiley: New York, 1984; pp 204–205.
- (12) (a) Bock, H.; Dammel, R. *Angew. Chem., Int. Ed. Engl.* **1987**, 26, 504. (b) Bock, H.; Dammel, R. *J. Am. Chem. Soc.* **1988**, 110, 5261.
- (13) Travers, M. J.; Cowels, D. C.; Clifford, E. P.; Ellison, G. B.; Engellang, G. B., quoted in ref 10a.
- (14) McPherson, D. W.; McKee, M. L.; Shevlin, P. B. *J. Am. Chem. Soc.* **1983**, 105, 6193.
- (15) (a) Shevlin, P. B.; McPherson, D. W.; Melius, P. J. *J. Am. Chem. Soc.* **1981**, 103, 7006. (b) Schevlin, P. B.; McPherson, D. W.; Melius, P. J. *J. Am. Chem. Soc.* **1983**, 105, 488.
- (16) Gaussian 92/DFT, Revision F.4; Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Wong, M. W.; Foresman, J. B.; Robb, M. A.; Head-Gordon, M.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; DeFrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. Gaussian, Inc.: Pittsburgh, PA, 1993.
- (17) Costa Cabral, B. J.; Costa, M. L.; Almaster Ferreira, M. A. A. *J. Mol. Struct. (THEOCHEM)* **1993**, 281, 185.
- (18) (a) Nguyen, M. T.; Rademakers, J.; Martin, J. M. L. *Chem. Phys. Lett.* **1994**, 221, 149. (b) Smith, B. J.; Pople, J. A.; Curtius, L. A.; Radom, L. *Aust. J. Chem.* **1992**, 45, 285.
- (19) Benson, S. W.; Cruickshank, F. R.; Golden, D. M.; Haugen, G. R.; O'Neal, H. E.; Rogers, A. S.; Shaw, R.; Walsh, R. *Chem. Rev.* **1969**, 69, 279.
- (20) MP2/6-31G(d,p)-optimized geometries of CH_3N and CH_2N structures and QCISD(T) energies with 6-311++G(d,p) and 6-311++G(3df, 2p) basis sets can be obtained from the authors.
- (21) (a) Chandra, A. K.; Malar, E. J. P.; Sengupta, D. *Int. J. Quantum Chem.* **1992**, 41, 351. (b) Sengupta, D.; Chandra, A. K. *Ibid.* **1994**, 52, 1317.
- (22) Bozzelli, J. W.; Dean, A. M. *J. Phys. Chem.* **1989**, 93, 1058; **1993**, 97, 4427.
- (23) Nguyen, M. T.; Groarke, P. J.; Malone, S.; Hegarty, A. F. *J. Chem. Soc., Perkin Trans. 2* **1994**, 807.

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