Ethynamine – Ketenimine – Acetonitrile Rearrangements:
A Computational Study of Flash Vacuum Pyrolysis Processes.

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Abstract: The rearrangement of ethynamine 3 (H-C≡C-NH₂) to ketenimine 4 (CH₂=C=NH) and acetonitrile 5 (CH₂CN) has been investigated by ab initio theory up to the MP4(SDTQ)/6-31G*//MP2(FU)/6-31G* level. Multiconfigurational calculations at the CASPT2/CASSCF(6,5) (2σ + 3π) level were performed in selected cases. The most direct rearrangements 3 → 4 → 5 involve two consecutive 1,3-H shifts, which are formally forbidden by the Woodward-Hoffmann rules. The ab initio barrier for the concerted first step 3 → 4 via TS1 is very high, 74 kcal/mol at the MP4 level, and the structure of the transition state TS1 very unusual with a linearized CCN angle (169.4°), which suggest that the observed reaction may not proceed in this way. In fact, a lower barrier of about 60 kcal/mol via aminovinylidene 2 and imidoylcarbene 15 has been found. Thus, the direct 1,3-shift via TS1 is discredited.

The ab initio barrier for the concerted second step, 4 → 5 via TS2, is 61 kcal/mol, and the transition state structure is again very unusual with a virtually linear CCN backbone. In TS2 the migrating H atom is bonded to the central sp-type carbon atom with C-H distances of 1.5 Å. However, this transition state does not appear to correspond to physical reality, as it cannot be confirmed by CASPT2/CASSCF calculations. Instead, the CASPT2/CASSCF calculations predict reaction via vinylnitrene 9, but the calculated barrier of 78 kcal/mol for 4 → 9 is seriously higher than the experimental shock-tube activation energy of 70 ± 3 kcal/mol for the 4 → 5 rearrangement. The activation energy for formation of the radical pair •CH₂CN + H• (11) from 4 is estimated as...
67-70 kcal/mol in excellent agreement with the experimental shock-tube value. There is strong experimental evidence for homolytic paths in pas-phase pyrolys and keteninines.

**Introduction**

The parent ethynamine (aminoacetylene), H$_2$N-C≡CH 3, is a very unstable molecule, which can be generated by flash vacuum pyrolysis (FVP) of aminomethylideneisoxazolone 1 via aminovinylidene 2 (Scheme 1) with an activation energy of the order of 50 kcal/mol. It is possible to observe 3 by matrix-isolation IR spectroscopy, and especially by mass spectrometry using a pyrolysis reactor installed inside the source housing of the mass spectrometer. The mass spectrum of 3 was distinguished from those of ketenimine 4 and acetonitrile 5 by means of the collisionally induced dissociation (CID) mass spectra. The rearrangement of 3 to 5 is very facile under FVP conditions and takes place without ketenimine 2 being directly observable.

**Scheme 1.** Formation of ethynamine, ketenimine and acetonitrile.

In our experience, the rearrangements of easily tautomerizable molecules like 3 often take place via *intermolecular* H-exchange and/or collisions with the hot wall of the reactor. For example, cyanic acid, HOCN, is very difficult to observed in FVP experiments under the usual reaction conditions because of its easy tautomerization to isocyanic acid, HNCO. It (HOCN) has been observed by microwave spectroscopy in a supersonic jet expansion. Similarly, 2-imino-1H-pyridine is difficult to observe because of its tautomerization to 2-aminopyridine. Secondary ethynamines 7 are kinetically more stable than 3, and their isomerization to keteninines 8 has been observed directly (Scheme 2; e.g. R = Ph).
Scheme 2. Formation of secondary ethynamines 7 and isolable ketenimines 8.

Scheme 3. Vinylnitrene pathway. Energies of ground and transition states in kcal/mol. 9 is the open-shell singlet vinylnitrene lying ca. 12 kcal/mol above the triplet.10,11

We have posited that a homolytic process via •CH₂CN 11 + H• has a lower barrier of 70 kcal/mol.
kcal/mol, which is in excellent agreement with the experimental value (Scheme 4). This path will be elaborated further below.

**Scheme 4.** The homolytic (dissociative) pathway. Energies in kcal/mol

\[
\begin{align*}
4 & \xrightarrow{102} 11 & 11 & \rightarrow & 5 \\
31.8 & & 94.8 & & 0
\end{align*}
\]

Osman has carried out several single-determinant calculations for the reaction \(4 \rightarrow 5\) and found a TS at 57-71 kcal/mol with a nearly linear NCC backbone very similar to the one calculated by us (TS2) and presented below.\(^{12}\) Osman formulated this structure in terms of a long bond (1.58 Å) between N and the migrating H in the TS, a very acute angle HNC (≈60°), and no bond between the migrating H and C2 or C1.\(^{12}\)

Han-Gook Cho has generated ketenimine 4 by laser ablation from acetonitrile and interpreted the reaction as unimolecular.\(^{13}\) He also performed B3LYP calculations for the ground-state reaction and again, unsurprisingly, found the same TS as described by us below in Figure 2 (TS2) lying 88 kcal/mol above the ketenimine; this energy is evidently far too high compared with the experimental value and the homolytic path described above (70 kcal/mol).

The analogous 1,3-shift converting allene 12 to methylacetylene 13 (Scheme 5) has been investigated by detailed MCSCF calculations and found to proceed via vinylmethylene, cyclopropene, and propenylidene with an overall activation energy of ~66 kcal/mol.\(^{14}\)

**Scheme 5.** Allene – Methylacetylene Rearrangement.

\[
\begin{align*}
12 & \rightarrow & 13 \\
\end{align*}
\]

The barrier estimated for a direct 1,3-H shift 12\(\rightarrow\)13 was ~95 kcal/mol. The reaction has been investigated by shock-tube pyrolysis and was reported to be intramolecular with an extremely high activation energy of 92 kcal/mol in the temperature range 1400-1700 K.\(^{15}\) A more reasonable value of 61 kcal/mol and a purely unimolecular reaction were determined in a second shock-tube study at 1000-1200 K.\(^{16}\) The results of a shock tube experiment on the propyne to allene isomerization\(^{17}\) were in agreement with those of Lishitz.\(^{16}\) The overall energy barriers calculated at the G2(B3LYP)
level\textsuperscript{18} were in good agreement with those of Yoshimine et al.,\textsuperscript{14} and the results of flow pyrolysis experiments\textsuperscript{18} were found to be in agreement with Hidaka’s\textsuperscript{17} shock-tube results.

Further high-level \textit{ab initio} calculations on this and related systems have been published.\textsuperscript{19,20,21} Using QCISD(T) theory and RRKM calculations of rate constants the isomerization mechanism suggested by Yoshimine and co-workers\textsuperscript{14} was essentially confirmed;\textsuperscript{22} the highest calculated barrier of 66.8 kcal/mol corresponds to the 1,2-H shift from allene to vinylmethylene. As expected, the putative, direct 1,3-H shift from allene to propyne was found to have a much higher barrier of 88.8 kcal/mol. In this case too, the homolytic C-H bond dissociation energies for allene and propyne were found to be 89.2 and 89.9 kcal/mol, respectively, i.e. very close to the barrier for the putative, direct 1,3-H shift.\textsuperscript{23}

**Results and Discussion**

1. Direct 1,3-H Shifts.

The calculated structures of 3-5 as well as 2\textit{H}-azirine 10, the cyanomethyl radical 11, and aziridin-2-ylidene 14 at the MP2/6-31G* level are presented in Figure 1. The calculated structures of ketenimine 4 and acetonitrile 5 are in excellent agreement with the available experimental\textsuperscript{24,25} parameters as well as previous calculations.\textsuperscript{26} Overall, the computed energies given in Table 1 are in broad agreement with recent calculations at MP4(SDTQ)\textsuperscript{27} and CCSD(T) levels\textsuperscript{28,29} as far as comparisons are possible. The relative energies of 3-5, 10, 11 and 14 up to the MP4(SDTQ)/6-31G* level are given in Table 1. Ethynamine 3 is calculated to be less stable than ketenimine 4 by 19 kcal/mol, and 4 is less stable than acetonitrile 5 by 34 kcal/mol.
Figure 1. Calculated equilibrium structures of compounds 3, 4, 5, 10, 11, and 14 (MP2(FU)/6-31G*//MP2(FU)/6-31G*)

The transition state TS1 for the direct, intramolecular 1,3-H shift 3→4 lies 74 kcal/mol above 3 at the MP4 level including ZPE correction (Table 1). It is characterized by a high imaginary frequency of 1201 i cm\(^{-1}\) and was confirmed as a proper TS by an IRC calculation. The terminal groups C\(_1\)H\(_1\) and NH\(_2\) rotate concertedly in such a way that the migrating hydrogen (H\(_3\)) approaches C\(_1\) in a plane perpendicular to the plane of the molecule (\(\angle H_3C_1C_2N = 0^\circ\)) (Figure 2). H\(_3\) is loosely bonded to the central carbon atom, C\(_2\), with a bond length of 1.171 Å.

The transition state TS2 for the 1,3-H shift 4→5 lies 61 kcal/mol above 4 at the MP4 level (Table 1). The vibrational analysis showed a single, large imaginary frequency of 1668 i cm\(^{-1}\), and the transition state was confirmed by an IRC calculation. TS2 has an unusual, almost linear C\(_1\)C\(_2\)N structure (Figure 3), with H\(_3\) again migrating in a plane perpendicular to the molecular plane and bonded to C\(_2\) with a bond length of 1.153 Å. This structure is very similar to those reported by Osman\(^{12}\) and Cho.\(^{13}\) The TS is early as expected for a highly exothermic reaction, and it can be regarded as a ketenimine with a highly distorted C\(_2\)-N-H angle of 49\(^\circ\).
2. The Homolytic Pathway 4→11→5

The transition state for the homolytic dissociation, H₂C≡C=NH 4 → •CH₂CN 11 + H• (Scheme 4) is calculated to lie only 2.6 kcal/mol above TS2 (structure: Figure 1; energy: Table 1). Therefore, this homolytic pathway must be considered as a strong contender for the true reaction mechanism under high-temperature pyrolysis conditions. Calculations at a higher level and inclusion of the entropy term are expected to further lower the energy of this path. The recombination of the radical pair, •CH₂CN + H• → CH₃CN 5, may take place by a roaming mechanism.

There is good experimental evidence that rearrangement of N-substituted ketenimines to acetonitriles is a free radical process, particularly in the gas-phase,¹¹,³⁰,³¹ but also sometimes in solution.³² For example, FVP of N-phenylketenimines afford the isomeric phenylacetonitriles in very modest yields together with the products of H-abstraction and recombination, i.e. acetonitrile, benzenes, succinonitriles and biphenyls.¹¹,³⁰ The products formed from fulvenimines in the FVP of 1-acylbenzotriazoles are largely due to free radical reactions.³¹,³³ However, it must be kept in mind that under reaction conditions where intermolecular hydrogen transfer is possible, this causes facile and rapid tautomerization of N-H ethynamines and ketenimines, i.e. 3 → 4 and 4 → 5.

3. 2-Aziridinylidene Mechanisms 14→4.

An alternative isomerization of ketenimine 4 to 2-aziridinylidene 14 (structure: Figure 1) has been
considered by Wang and Deng (Scheme 6).\textsuperscript{34} We find a transition state TS\textsubscript{3} (Figure 4) for 14 \rightarrow 4 at 125.9 kcal/mol relative to CH\textsubscript{3}CN, or ca. 23 kcal/mol higher than the dissociative pathway via CH\textsubscript{2}CN + H\bullet (11) at the MP2 computational level (Table 1), which therefore makes the 14 \rightarrow 4 pathway very unlikely. Even with the somewhat lower Gibbs free energies computed by Pinto et al. at the MP2 level, TS\textsubscript{3} is still at ca. 109 kcal/mol and therefore uncompetitive.

**Scheme 6.** Interconversion and rearrangement of aziridinylidene 14 and 2\textit{H}-azirine 10

![Scheme 6](image)

**Figure 4.** TS\textsubscript{3} and TS\textsubscript{4} for rearrangements of aziridinylidene 14 to ketenimine 4 and acetonitrile 5.

If formed, 14 could have isomerized to acetonitrile via TS\textsubscript{4} (Figure 4), which lies 26 kcal/mol above 14 (Table 1). Aziridinylidene 14 could also have isomerized to 2\textit{H}-azirine 10 in a 1,2-H shift with a transition state TS\textsubscript{5} (Figure 5) lying 33 kcal/mol above 14, which is still 17 kcal/mol above the homolytic pathway via 11 and therefore not competitive. As reported previously, on pyrolysis 2\textit{H}-azirine 10 can ring-open to vinylnitrene 9 and then isomerize to both ketenimine 4 and acetonitrile 5 (Scheme 3).\textsuperscript{11} The transition state TS\textsubscript{6} for the reaction 10 \rightarrow CH\textsubscript{3}NC \rightarrow 5 is
shown in Figure 5.

![Diagram](attachment:image.png)

**Figure 5.** TS5 and TS6 for isomerization of aziridinylidene 14 to 2H-azirine 10 and for 2H-azirine to methyl isocyanide CH₃NC, which then isomerizes to CH₃CN 5.

4. **Imidoylcarbene 15 and Aminovinylidene 16.**

A shown above, the direct 1,3-H shift converting ethynamine 3 to ketenimine 4, requires a very high transition state TS1 of the order of 74 kcal/mol at the single-determinant MP4 level. The existence of a high barrier is undoubted, since it permits the experimental observations of 3, which is otherwise only a fleeting, metastable compound susceptible to rapid tautomerization under bimolecular reaction conditions or by wall collisions. But the highly unusual structure of TS1 suggest that 3 might instead rearrange to the lower-lying imidoylcarbene 15 (Scheme 7), which is estimated to lie considerably lower in energy (~105 kcal/mol above 5 or ~52 kcal/mol above 3). Carbone 15 would then undergo a rapid 1,2-H shift to afford ketenimine 4. Most 1,2-H shifts in carbenes have low activation barriers of just a few kcal/mol. Therefore, this reaction, 3→15→4 is preferred over the unrealistic 1,3-H shift 3→4 via TS1.

**Scheme 7.** Ethynamine-Imidoylcarbene-Ketenimine Path 3→15→4 (energies in kcal/mol)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Energy (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>52.8</td>
</tr>
<tr>
<td>15ZZ</td>
<td>~105</td>
</tr>
<tr>
<td>4</td>
<td>34.4</td>
</tr>
</tbody>
</table>

Acetylenes are known to undergo thermal interconversion with vinylidenes (the Roger Brown Rearrangement) with an energy barrier of ~40 kcal/mol, whereby the barrier for the
reverse reaction is extremely small (< 2 kcal/mol). Ethynamine 3 is formed in such a rearrangement from aminovinylidene 2 (Scheme 1) in the FVP reaction. Thus, the reverse reaction, 3→2 should generate 2 lying ca. 40 kcal/mol above 3 at ~93 kcal/mol relative to acetonitrile. A 1,2-H shift in 2 would generate imidoylcarbene 15 with an energy of about 105 kcal/mol with respect to acetonitrile (Scheme 8).

**Scheme 8.** The Ethynamine-Aminovinylidene-Imidoylcarbene-Ketenimine Path 3→2→15→4 (energies in kcal/mol relative to acetonitrile 5)).

Thus the overall barrier for the rearrangement of 3 to 4 is expected to be no more than about 113 kcal/mol relative to acetonitrile, or ~60 kcal/mol relative to ethynamine 3. This reaction therefore becomes the overall most preferred path for the isomerization 3→4, removing the need for TS1. In contrast, N-H bond dissociation energies in amines are over 100 kcal/mol, so unlike the dissociative path 4→11→5 described above, a homolytic path for 3→4 is not to be expected. The reason that the homolytic path in Scheme 4 is preferred for the second isomerization, 4→5, lies in the much lower bond dissociation energy of the C-H bonds in 5 (~70 kcal/mol) and consequential relatively low energy of the radical pair CH₂CN’ + H’ (11).

**Conclusion and Outlook**

Transition states were calculated for the concerted 1,3-H shifts converting ethynamine 3 to ketenimine 4 (TS1) and ketenimine 4 to acetonitrile 5 (TS2) in the gas-phase. However, the lowest-energy route for 3→4 passes through aminovinylidene 2 and imidoylcarbene 15. The lowest-energy route for 4→5 is not the direct 1,3-H shift but instead a homolytic dissociation of ketenimine 4 to the radical pair CH₂CN’ + H’ (11), which then recombines to form acetonitrile 5.
A roaming mechanism for this recombination may apply. Higher-level multideterminant calculations of these reactions will be reported.\textsuperscript{42}

More generally, the deceptively simplest reaction mechanisms are not always the best. Concerted 1,3-H shifts in linear systems are generally unlikely. That is the case for the unimolecular rearrangements of allene to propyne and of ethynamine to ketenimine to acetonitrile, and also for the unsubstantiated, direct interconversion of nitrile imine, \( \text{H-C(}^\dagger\text{)}=\text{N(}^\dagger\text{)}=\text{NH} \) with diazomethane \( \text{H}_2\text{C}=\text{N(}^\dagger\text{)}=\text{N(}\cdot\text{)} \).\textsuperscript{43,44} However, in condensed phases and in surface reactions, the tautomerizations of \( N\)-H ethynamines and ketenimines, e.g. \( 3 \rightarrow 4 \) and \( 4 \rightarrow 5 \), are rapid and take place via intermolecular proton transfer.

**Computational Methods**

Calculations were carried out initially using the Gaussian 90 suite of programs.\textsuperscript{45} All geometries were fully optimized using gradient optimization at the Hartree-Fock (HF) level. Harmonic vibrational frequencies were calculated at the HF/6-31G* to characterize minima and first-order saddle points. Geometry optimizations at the correlated level were performed using second-order Møller-Plesset perturbation theory\textsuperscript{46,47} (MP2) with the 6-31G* basis set, denoted MP2(FU)/6-31G*//MP2(FU)/6-31G*. Single point calculations in the frozen core (FC) approximation at the Mp4 level including single, double, triple and quadruple substitutions are denoted MP4(SDTQ)/6-31G*//MP2(FU)/6-31G*. Harmonic vibrational frequencies were calculated for TS1 and TS2 at the MP2(FU)/6-31G* level. All TS structures were subjected to internal reaction coordinate tests in forward and reverse directions. The final energies were corrected for zero-point vibrational energies (ZPVE) calculated at the HF/6-31G* level and scaled by a factor 0.89. All bond lengths and bond angles referred to in the text are at the MP2(FU)/6-31G*//MP2(FU)/6-31G* level.

**ASSOCIATED CONTENT**

Supporting Information Available.

Further computational details are obtainable from the authors.

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Notes
The authors declare no competing financial interest.

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Table 1. Relative Energies$^a$

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<thead>
<tr>
<th>Basis set/Species</th>
<th>3 Ethyn-</th>
<th>4 keten-</th>
<th>5 aceto-</th>
<th>TS1 3-4</th>
<th>TS2 4-5</th>
<th>10 2H-azirine</th>
<th>14 aziridinylidene</th>
<th>TS3 14-4</th>
<th>TS4 14-5</th>
<th>TS5 14-10</th>
<th>TS6 10-CH$_3$CN</th>
<th>11$^b$ CH$_2$-CN$^+$ + H$^-$</th>
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<tr>
<td>HF/6-31G*</td>
<td>51.4</td>
<td>35.3</td>
<td>0.0</td>
<td>155.6</td>
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<td>128.3</td>
<td>121.6</td>
<td>129.0</td>
<td>1112.3</td>
<td>84.5</td>
</tr>
<tr>
<td>MP2(FC)/6-31G*//HF/6-31G*</td>
<td>51.8</td>
<td>36.0</td>
<td>0.0</td>
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<td>119.9</td>
<td>95.2</td>
<td>102.7</td>
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<td>MP2(FU)/6-31G*/MP2(FU)6-31G*</td>
<td>52.8 (52.5)</td>
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<td>87.6 (87.0)</td>
<td>127.9 (125.9)</td>
<td>116.1 (112.6)</td>
<td>122.5 (119.6)</td>
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<td>MP3(FC)/6-31G*/MP2(FU)/6-31G*</td>
<td>49.7</td>
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<td>3.9</td>
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$^a$ See Computational Methods. All values are in kcal/mol relative to CH$_3$CN 5.

$^b$ The free radical pair CH$_2$CN$^+$ + H$^-$

$^c$ Values in parentheses include ZPVE corrections scaled by 0.89.

$^d$ ZPVE corrections (unscaled).
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