On the Formation of N$_3$H$_3$ Isomers in Irradiated Ammonia Bearing Ices: Triazene (H$_2$NNNH) or Triimide (HNHNNH)

Marko Förstel$^{[a, d]}$, Yetsaw A. Tsegaw$^{[b]}$, Pavlo Maksyutenko$^{[a, d]}$, Alexander M. Mebel$^{[c]}$, Wolfram Sander$^{[b]}$, and Ralf I. Kaiser$^{*}$

The remarkable versatility of triazenes in synthesis, polymer chemistry, and pharmacology has led to numerous experimental and theoretical studies. Surprisingly, only very little is known about the most fundamental triazene: the parent molecule with the chemical formula N$_3$H$_3$. Here we observe molecular, isolated N$_3$H$_3$ in the gas phase after it sublimes from energetically processed ammonia and nitrogen films. Combining theoretical studies with our novel detection scheme of photoionization-driven reflectron time-of-flight mass spectrometry we can obtain information on the isomers of triazene formed in the films. Using isotopically labeled starting material, we can additionally gain insight in the formation pathways of the isomers of N$_3$H$_3$ under investigation and identify the isomers formed as triazene (H$_2$NNNH) and possibly trimide (HNHNNH).

1. Introduction

During the last decades, triazenes—a class of organic molecules carrying the \textit{=N=N=—} moiety—have received substantial attention both from the theoretical and organic chemistry communities.$^{[1]}$ Derived from \textit{cis-} and \textit{trans-}triazene (HN\textsubscript{3}NH\textsubscript{2}; Scheme 1), the substituted counterparts have significant applications in synthetic chemistry,$^{[1a, d]}$ polymer science,$^{[1e]}$ and pharmacology as antitumor drugs such as Dacarbazine, Temozolomide, and Mitozolomide$^{[2]}$ with their biological activity attributed to their purported capability to alkylate deoxyribonucleic acid (DNA).$^{[3]}$ Although triazenes have been synthesized for over 65 years, their stem compound$^{[4]}$ \textit{trans}- and \textit{cis-}triazene (Scheme 1) could not be isolated since triazene undergoes facile acid-catalyzed decomposition.$^{[5]}$ An unknown isomer of N$_3$H$_3$ has been detected mass spectrometrically via signal at mass-to-charge $m/z$ = 45 as a transient species by discharging hydrazine (N$_2$H$_4$); the ionization energy of the unknown isomer was reported to be 9.6 ± 0.1 eV.$^{[6]}$ Triazene (N$_3$H$_3$) has a half-life time of at least 1 ms was also inferred as an intermediate in the radiolysis of an aqueous solution of hydrazine based on a single absorption feature at 230 nm.$^{[7]}$ The cyclic isomer of triazene, cyclo-triazene, was first reported crystallographically in zeolate A, where it was stabilized by a silver cation as Ag(N$_3$H$_3$)$_2$. Finally, lithium-ion-complexed species Li(N$_3$H$_3$)$^{+}$ of unknown structures were generated in a microwave discharge of hydrazine–helium mixtures.$^{[8]}$

The aforementioned spurious indication of “triazene” isomers (N$_3$H$_3$) triggered significant computational efforts spanning three decades.$^{[9]}$ An early study by Nguyen et al. identified a \textit{cis-} and \textit{trans-} isomer of triazene (HN\textsubscript{3}NNH$_2$) with all six atoms arranged in the same plane (C$_2$ symmetry); the \textit{trans-} isomer is thermodynamically more stable by 27 to 38 kJ mol$^{-1}$ compared to the \textit{cis} structure (Scheme 1).$^{[9a, c]}$ A later study by Magers et al. identified two additional isomers of triazene, triimide (azine) and cyclo-triazene (triaziridine) with trimide about 54 to 130 kJ mol$^{-1}$ and cyclo-triazene about 170 to 190 kJ mol$^{-1}$ less stable than \textit{trans}-triazene. Therein it was pointed out that triazene is “not exactly planar” and that “low-temperature isolation of these species would likely succeed”.$^{[9d]}$ These findings were refined by Pye et al.$^{[9e]}$ \textit{1-}amino-1,1-diazened was first located on the potential energy surface by Salter et al.$^{[9f]}$ who suggested that this isomer (called isotriazene in their paper) is 42 to 50 kJ mol$^{-1}$ lower in energy than cyclo-triazene. Combined, these results show that the stabilities of triazenes decrease in the order \textit{trans-}triazene, \textit{cis-}triazene, trimide, \textit{1-}amino-1,1-diazened and cyclo-triazene (Scheme 1).

Here, we exploit a novel experimental approach to synthesiz-\textsuperscript{[15]}e N$_3$H$_3$ in low-temperature matrices via an interaction of ionizing radiation with frozen films containing ammonia (NH$_3$) and nitrogen (N$_2$) along with their deuterated (ND$_3$) and $^{15}$N-labeled (\textsuperscript{15}N$_3$H$_3$) counterparts. Upon sublimation of the newly formed molecules, N$_3$H$_3$ is identified for the first time via fragment-free single-photon vacuum ultraviolet (VUV) photoionization cou-
pled to a reflectron time-of-flight mass spectrometer (PI-ReTOF-MS) through its parent ion at mass-to-charge \( m/z = 45 \). This observation is substantiated by the detection of its isotopically labeled counterparts \( \text{N}_3\text{D}_3 \) \( (m/z = 48) \) along with \( ^{15}\text{N}_3\text{H}_3 \) \( (m/z = 46), ^{15}\text{N}_2\text{NH}_3 \) \( (m/z = 47), \) and \( ^{15}\text{N}_3\text{H}_3 \) \( (m/z = 48) \), respectively.

Scheme 1. Structures, ionization energies, and relative energies with respect to the most stable isomer of the triazene. Distances are given in Ångstrom, angles in degrees. Plain and italic numbers are calculated at the B3LYP/6-311G** and CCSD(T)/6-311G** levels of theory, respectively. Ionization energies are adiabatic values. Numbers in parenthesis in \textit{italics} denote values derived with CCSD(T)/6-311G** optimized geometries. The two bottom rows show the structures of the ionic species used for the calculation of the adiabatic ionization energy.

Experimental Section

Ice layers with thicknesses of 600 ± 50 nm were prepared from four different gases along with their mixtures. These ices were ammonia \( (\text{NH}_3) \), D3-ammonia \( (\text{ND}_3) \), ammonia and nitrogen \( (\text{NH}_3, \text{N}_2; 1:1.0 ± 0.2) \) and ammonia and 15N-nitrogen \( (\text{NH}_3, ^{15}\text{N}_2; 1:1 ± 0.2) \) with purities as follows: NH\(_3\) (Matheson; 99.999%), ND\(_3\) (Isotopes Inc; 99+% D), N\(_2\) (Matheson; 99.9999%) and \(^{15}\text{N}\) (Cambridge Isotope...
The composition of the ice mixtures was determined by relating the NH3 absorption features at 1092 cm\(^{-1}\) with a value of 1.7 \(\times 10^{-17}\) cm\(^{-1}\) to the ice thickness determined by interferometry. Each sample was then irradiated for 60 min with 5 keV electrons at a current of 15 \(\pm 2\) nA by scanning the electron beam over the target surface of 0.9 \(\pm 0.1\) cm\(^2\) at an angle of 70\(^\circ\) with respect to the surface normal of the substrate. The average deposited dose \(D\) per irradiated molecule can be calculated using Equation (2):

\[
D = \frac{lt}{\sum N_e \rho A} \left( E_{\text{ion}} - f_{\text{trans}} E_{\text{trans}} - f_{\text{bs}} E_{\text{bs}} \right)
\]  

where \(l\), \(t\), \(m\), \(N_e\), \(\rho\), \(A\) and \(E_{\text{ion}}\) are the irradiation current, irradiation time, molecular mass of the molecule, the electron charge, Avogadro’s constant, the density of the ice, the irradiated area of the ice, and the initial kinetic energy of the electrons, respectively. The values \(f_{\text{trans}}, f_{\text{bs}}, E_{\text{bs}}\) and \(l\) denote the fraction of electrons transmitted through the ice, the fraction of electrons which are backscattered, the average kinetic energy of the backscattered electrons, the average kinetic energy of the transmitted electrons, and the average penetration depth of the electrons, respectively. These values are determined exploiting the Monte Carlo simulation program CASINO\(^{[11]}\) averaging over 20000 trajectories. The deposited energy per ammonia molecule in these experiments is 1.5 \(\pm 0.2\) eV. In the mixed ices we determined a dose of 1.3 \(\pm 0.2\) eV per irradiated ammonia molecule and 1.9 \(\pm 0.2\) eV per irradiated nitrogen molecule. The simulation parameters are summarized in Table 1. After the irradiation, each ice was kept at 5.5 K for one hour. During the irradiation and the equilibration phase, infrared spectra (FTIR, Nicolet6700) were recorded from 6000 to 500 cm\(^{-1}\) with a resolution of 4 cm\(^{-1}\). The substrate was then warmed up with a rate of 0.5 K/min\(^{-1}\) to 300 K.

Molecules subliming into the gas phase were photoionized at 10.49 eV, 9.67 eV and 9.1 eV and detected using a reflection time-of-flight mass spectrometer (ReTOF).\(^{[20]}\) The 10.49 eV photons were generated by frequency tripling of the third harmonic of an Nd:YAG (354.7 nm) (Spectra Physics, PRO-250, 30 Hz) laser in a jet of pulsed xenon (Xe) gas.\(^{[17]}\) 9.67 eV and 9.1 eV photons were produced using resonant four-wave difference mixing of two frequencies \((2\omega_1 - \omega_2)\).\(^{[18]}\) 9.67 eV photons were generated from two beams overlapping in krypton gas, where the first beam was generated using the frequency-tripled (202 nm) output of a dye laser (606 nm, Rhodamine 610, Sirah, Cobra-Stretch) which was pumped by the second harmonic of an Nd:YAG laser (532 nm). The second laser beam was generated using the direct output of a dye laser (478 nm, Coumarin 480, Sirah, Precision Scan). This dye laser was pumped with the third harmonic of an Nd:YAG laser (355 nm). 9.1 eV photons were via mixing in xenon gas. The first beam was generated using the frequency doubled (222.6 nm) output of a dye laser (445.1 nm, Coumarin 450, Sirah, Cobra-Stretch) which was pumped by the third harmonic of an Nd:YAG laser (355 nm). The second laser beam was generated using the direct output of a dye laser (607 nm, Rhodamine 610, Sirah, Precision Scan). This dye laser was pumped with the second harmonic of an Nd:YAG laser (532 nm). The respective laser beams where then coupled using a dichroic mirror and led into a differentially pumped vacuum chamber through a magnesium fluoride (MgF\(_2\)) window. A fused silica bi-convex lens (Thorlabs LB4265, f = 150 mm) focused the respective beams into a section of a pulsed jet of krypton (9.67 eV) or xenon (9.1 eV) released by a piezoelectric pulsed valve operated at 30 Hz. A lithium fluoride (LIF) lens mounted off-center from the beam path of the generated and fundamental laser beams separated the beams according to their refractive indices spatially. A pin hole behind this lens was then used to block the fundamentals \((\omega_1; \omega_2)\) from entering the interaction region, and only the desired light was introduced into the main chamber. A schematic of the experimental setup is shown in Scheme 2.

### Computational Methods

Calculated structures, ionization energies and relative energies with respect to the lowest-energy isomer of NH\(_3\), are shown in Scheme 1. Geometries of various NH\(_3\) isomers and transition states as well as of products of NH\(_3\) dissociation were optimized at the hybrid density functional B3LYP level of theory\(^{[19]}\) with the 6–311G** basis set\(^{[20]}\) and vibrational frequencies were computed using the same B3LYP/6–311G** method to characterize stationary points as local minima or transition states and to obtain zero-point energy corrections (ZPE). For selected isomers and their cations we additionally performed geometry optimization at the coupled clusters CCSD(T) level of theory\(^{[21]}\) with the same 6–311G** basis set. Single-point energies at the optimized geometries were then refined employing the explicitly correlated coupled clusters CCSD(T)-F12 method\(^{[22]}\) with Dunning’s correlation-consistent cc-pVTZ-F12
basis set,

the CCSD(T)-F12/cc-pVTZ-f12 energy is expected to closely approach the complete basis set frozen core \(\text{CCSD(T)}\)/CBS limit and hence the relative energies from the present calculations are anticipated to provide accuracy within 5 \(\text{kJ mol}^{-1}\) or better. Vertical and adiabatic ionization energies for all \(\text{N}_2\text{H}_3\) isomers were evaluated at the same CCSD(T)-F12/cc-pVTZ-f12//B3LYP/6–311G** + ZPE(B3LYP/6–311G**) level and also calculated were appearance energies of fragmentation pathways. The CCSD(T) and CCSD(T)-F12 energies were computed within the restricted closed (open) shell scheme with restricted HF wavefunction used as a reference, RHF-\text{RCCSD(T)}. All electronic structure calculations were carried out using the Gaussian 09\(^{[24]}\) and MOLPRO 2010\(^{[25]}\) program packages. The potential energy diagram including \(\text{N}_2\text{H}_3\) isomers, transition states, and dissociation products is illustrated in Figure 1. Energy calculations are summarized in Table S1. Geometrical structures of all isomers and transition states are summarized in Table S2. Calculated vibrational frequencies are summarized in Table S3. Vertical and adiabatic ionization energies are presented in Table S4. The transition states in these tables are labeled according to Figure 1.

2. Theoretical Results

Our computations identified seven \(\text{N}_2\text{H}_3\) isomers. In agreement with earlier theoretical calculations, \(\text{trans-} (\text{trans-H}_2\text{NNNH})\) and \(\text{cis-triazene} (\text{cis-H}_2\text{NNNH})\) are the most stable isomers of \(\text{N}_2\text{H}_3\) with the \(\text{trans}\) isomer residing 21 \(\text{kJ mol}^{-1}\) below the \(\text{cis}\) structure. Both are connected via a transition state lying 187 \(\text{kJ mol}^{-1}\) higher in energy than \(\text{trans-H}_2\text{NNNH}\). The next group of isomers in the order of stability includes trimidines (\(\text{HNHNNH}\)), which can exist as \(\text{trans–trans}, \text{trans–cis},\) and \(\text{cis–cis}\); 78, 81, and 102 \(\text{kJ mol}^{-1}\) above \(\text{trans-H}_2\text{NNNH}\), respectively. The different trimidines are connected to one another via rotational barriers around the N–N bonds ranging between 107 and 132 \(\text{kJ mol}^{-1}\). The nitrene (\(\text{HNHNNH}\)) and cyclic isomer (\(\text{N}_2\text{H}_5\)) are the least stable isomers being 120 and 178 \(\text{kJ mol}^{-1}\) higher in energy than \(\text{trans-triazene}\). It should be noted that we performed CCSD(T)/6–311G** geometry optimization for selected most favorable \(\text{N}_2\text{H}_3\) isomers, \(\text{trans-}\) and \(\text{cis-H}_2\text{NNNH}\) and \(\text{trans–trans-NHHNNH}\), and their cations. The differences between optimized B3LYP and CCSD(T) geometric parameters (Scheme 1) appeared to be rather minor and did not exceed 0.03 Å and 4° and in most cases were much lower than those maximal values. The effect of the use of the CCSD(T)/6–311G** optimized geometries on the relative energies of the \(\text{N}_2\text{H}_3\) isomers obtained by single-point CCSD(T)-F12 calculations were below 1 \(\text{kJ mol}^{-1}\). For adiabatic ionization energies, the differences between the values obtained with B3LYP and CCSD(T) geometries were only 0.01 \(\text{eV}\) for \(\text{trans-H}_2\text{NNNH}\) and \(\text{trans–trans-NHHNNH}\) and 0.05 \(\text{eV}\) for \(\text{cis-H}_2\text{NNNH}\).

Triimides can be formed from triazenes by 1,2-H migrations from the terminal \(\text{NH}_2\) group to the central nitrogen atom overcoming barriers of 265 \(\text{kJ mol}^{-1}\) (\(\text{trans-H}_2\text{NNNH}\)→\(\text{trans–cis-NHHNNH}\)) and 259 \(\text{kJ mol}^{-1}\) (\(\text{cis-H}_2\text{NNNH}\)→\(\text{trans–trans-NHHNNH}\)). Alternatively, a 1,2-H shift from the terminal \(\text{NH}_2\) moiety to the central nitrogen leads from \(\text{trans-H}_2\text{NNNH}\) to \(\text{H}_2\text{NNNH}\) via a 299 \(\text{kJ mol}^{-1}\) barrier. The latter can ring-close to \(\text{c-N}_3\text{H}_4\), overcoming a significant barrier of 272 \(\text{kJ mol}^{-1}\). An alternative pathway is the decomposition to molecular nitrogen plus ammonia via a lower barrier of only 81 \(\text{kJ mol}^{-1}\). The cyclic \(\text{c-N}_3\text{H}_4\) isomer can also be formed by ring closure in \(\text{trans–cis-NHHNNH}\) going through a barrier of 238 \(\text{kJ mol}^{-1}\). The thermodynamically most favorable dissociation channel of \(\text{trans-triaze}\) ne is \(\text{trans-H}_2\text{NNNH}\)→\(\text{H}_2\text{NNNH}\)→\(\text{N}_2\) \(+\) \(\text{NH}_3\), leading to the products exoeergic by 193 \(\text{kJ mol}^{-1}\) but the highest barrier on this pathway is at 299 \(\text{kJ mol}^{-1}\). \(\text{Trans-triazene}\) can also directly lose molecular hydrogen (\(\text{H}_2\)) producing hydrogen azide (\(\text{HN}_3\)) with an endoeergency of 62 \(\text{kJ mol}^{-1}\) and overcoming a barrier of 304 \(\text{kJ mol}^{-1}\). Both \(\text{trans-}\) and \(\text{cis}\) conformations of triazene can dissociate to amidogen (\(\text{NH}_2\)) plus dinitrogen monohydride (\(\text{N}_2\text{H}\)) by a cleavage of the N–N single bond without an exit barrier. The products lie 199 \(\text{kJ mol}^{-1}\) higher in energy than
Finally, various trimides can in principle decompose to ground triplet state imidogen (NH, $X\Sigma^+$) plus diimide ([Z]/([E]-N$_2$H$_2$), 322 and 342 kJ mol$^{-1}$ above trans-triazene. The triplet ground state of imidogen (NH, $X\Sigma^+$) lies 150 kJ mol$^{-1}$ above trans-triazene.
below the first excited state singlet state (the spin allowed product), and a decay involving a N–N bond rupture is likely to proceed via singlet–triplet intersystem crossing (ISC). Both possibilities are shown in Figure 1.

3. Experimental Results

The PI-ReTOF-MS results are shown in Figure 2 and Figure 3, which include the data of irradiated ammonia measured at three different ionization energies (left) and, measured all at an ionization energy of 10.49 eV, the PI-ReTOF-MS data of irradiated ND₃, NH₃:N₂ and NH₃:¹⁵N₂ ice (right). Dominating all spectra measured with 10.49 eV is the signal at mass-to-charge ratio of 17 from the host matrix molecule ammonia (NH₃) and, respectively at m/z = 20 from ND₃. This signal depicts a sublimation onset of 75 ± 2 K, peaks at around 105 ± 2 K and reaches zero intensity above 130 K ± 5 K. A second TPD peak is observed at this m/z ratio between 150 K and 190 K, with a maximum at around 175 K. The next strongest contribution is observed at a mass-to-charge ratio of m/z = 32, which is observable at all three ionization energies. This TPD peak is observed in the 145 to 200 K range, peaking at around 155 K. The experiment at 10.49 eV with the isotopically labeled compounds show a peak with the same TPD profile at mass-to-charge ratios of m/z = 36 (ND₃ ice) and at m/z = 34, 35 and 36 with intensity decreasing in that order in the NH₃:¹⁵N₂ ice. The next highest contribution is found in the 10.49 eV probed NH₃ ice at a mass-to-charge ratio of m/z = 45. This TPD profile is observed in the 150 to 190 K region with a peak at around 175 K. This profile is also observed in the 9.67 eV experiment but not in the 9.1 eV experiment. The ND₃ experiment reveals a peak with similar shape at a mass-to-charge ratio of m/z = 48, but reduced in intensity by a factor of six compared to the ammonia ice. The NH₃:N₂ experiment also exposes this feature, but with an intensity reduced by a factor of 2.5 compared to the ammonia experiment. The NH₃:¹⁵N₂ experiment depicts intensity with a similar TPD profile at mass-to-charge ratios of m/z = 45, 46 and 47 (Figure 2 f and Figure 3 f). Again, the intensity decreases as the mass-to-charge ratio rises with factors of 0.24, 0.12 and 0.06 compared to the peak at m/z = 45 from the pure NH₃ ice. At a mass-to-charge ratio of m/z = 30 we also observe a TPD profile in the range from 157 to 180 K, peaking at 172 K. This peak is observed in the pure ammonia ice only in the 10.49 eV experiment, where it reveals a peak intensity comparable to that

Figure 2. PI-ReTOF-MS spectra with the initial ice composition and the ionization energy given in each panel.
of the TPD profile at a mass-to-charge ratio of \( m/z = 45 \) (Figure 2a and Figure 3a). In the NH\(_3\):N\(_2\) ice mixture, this peak is a factor of two higher in intensity than that of \( m/z = 29 \) (Figure 2e and Figure 3e). We also observe a very small signal at a mass-to-charge ratio of \( m/z = 29 \) in the ammonia ice at 10.49 eV (Figure 2a and Figure 3a). The TPD profile of this signal shows some intensity in the same range as that of \( m/z = 45 \). However, the signal-to-noise ratio of that signal is very poor. No signal is observed at a mass-to-charge ratio of \( m/z = 28 \).

4. Discussion

Due to the simplicity of the host ice, consisting only of two different atoms, the molecular identification of the observed mass-to-charge ratios is straightforward. The signal at \( m/z = 30 \) must stem from a molecule with the chemical formula N\(_2\)H\(_2\), \( m/z = 32 \) from N\(_2\)H\(_4\) and \( m/z = 45 \) from N\(_3\)H\(_3\). Molecular nitrogen (N\(_2\)) is not observed because its ionization energy (IE = 15.58 eV\(^{[26]}\)) resides well above our highest ionization energy of 10.49 eV. The N\(_2\)H\(_2\) isomer was identified as cis- and/or trans-dimide (\( m/z = 30 \), IE = 9.58 eV).\(^{[27]}\) The N\(_2\)H\(_4\) isomer is hydrazine (\( m/z = 32 \), IE = 8.1 eV). With this low ionization energy it is the only molecule observed in the 9.1 eV experiment. In order to identify the isomers of N\(_3\)H\(_3\) we have to use data obtained at different ionization energies. Figure 3a depicts the TPD profile of all subliming molecules with \( m/z = 45 \) and an ionization energy below 10.49 eV. Sublimation starts at 150 K and the intensity increases slowly up to a temperature of 173 K. After that we observe a further sharp increase in intensity, which reaches its maximum at 180 K. At 185 K the intensity is back to 20% of its maximum value and then slowly decreases towards zero at around 200 K.

![Figure 3. TPD profiles extracted from the PI-ReTOF-MS spectra shown in Figure 2. For intensity and shape comparison, the TPD trace of NH\(_3\) ice at 10.49 eV (a) is included normalized to the respective spectrum as a dotted line in (b), (d) and (e).](image-url)
Figure 3b shows the result when the subliming molecules are probed using an ionization energy of 9.67 eV. It can be seen that the total observed intensity is a factor of six lower than that measured in the 10.49 eV experiment. The TPD profile, however, shows the same shape as that measured at 10.49 eV. For comparison, the normalized 10.49 eV TPD profile is shown in Figure 3b as a dotted line. Decreasing the ionization energy further we arrive at Figure 3c. Here, at 9.1 eV ionization energy, we observe no signal at this mass-to-charge ratio at all. Comparing these observations with the calculated ionization energies we can already conclude that neither iso-triazene nor cyclo-triazene are detected. Iso-triazene can be excluded because the ionization energy in the 9.1 eV experiment is well above the ionization energy of iso-triazene (IE = 8.62 eV). The fact that the shape of the TPD profile remains unchanged when changing the ionization below that of cyclo-triazene (Figure 3b) is a very strong indication that cyclo-triazene is not observed in our experiment.

A discrimination between the remaining isomers, triazene and trimide, based solely on their ionization energies is complicated because of the small differences in their ionization energies and the uncertainty of the calculated ionization energies in the order of up to ±0.2 eV.\(^{29}\) However, there is one observation that suggests that the observed isomers are cis- and/or trans-triazene, but not trimide. That is, we observe a small signal at a mass-to-charge ratio of \(m/z = 29\), which has a TPD profile that matches that of the trace at \(m/z = 45\). The appearance energy of the \(N_2H^+\) fragment from trans-triazene is 10.26 eV and from cis-triazene it is 10.03 eV. This suggests that signal at \(m/z = 29\) can only stem from fragmented cis- and/or trans-triazene. It cannot originate from trimide because our computations suggest that this isomer cannot fragment to \(N_2H^+ + NH_2\) upon ionization at 10.49 eV. It needs to be noted that the observed intensity is barely above the noise level and that even if it were higher, it would not exclude that trimide is formed. However, it does imply that at least some of the observed signal stems from cis- and/or trans-triazene. Another argument why the observed isomer could be trans-triazene is the fact that only hydrogen tunneling is necessary to arrive from any of the trimides or the cis-triazene to the energetically lowest lying trans-triazene. Processes like this were shown to have half-life times of two hours at temperatures as low as 11 K and a barrier of 126 kJ mol\(^{-1}\).\(^{26}\) We reach the sublimation temperature of around 170 K 6 h 40 min after irradiation stopped and the calculated barriers are in the same order of magnitude as in the systems discussed in Ref. [29] (Figure 1).

After having established that mostly triazene and also possibly trimide are forming in the ice, let us now concentrate on the potential formation pathways of these molecules. We suggest that the most likely formation pathway towards \(N_2H_4\) occurs via the diimide (\(N_2H_4\)) intermediate after reaction with either imidogen via \(N_2H_4 + NH\rightarrow N_2H_3\) or with amidogen via \(N_2H_4 + NH_2\rightarrow N_2H_3 + H\) as shown in the last step in Scheme 3. Both, imidogen and amidogen, are primary formation products of the irradiation process. Besides the computationally predicted decomposition pathways and energetics, the four following experimental observations strongly suggest that diimide (\(N_2H_4\)) and not the main final irradiation product hydrazine (\(N_2H_4\)) or other intermediates like \(HN\) or \(HN_2\) are intermediates in the \(N_2H_4\) formation. They also show that a formation of \(N_2H_4\) involving molecular nitrogen (\(N_2\)) is unlikely.

First, the \(N_2H_4\) yield decreases by a factor of 2.5 when comparing the \(NH_3\) to the \(NH_3\) \(N_2\) ices. The yield of \(N_2H_3\) decreases by a factor of 1.6 in these ices. These values are only in agreement with each other if we assume that \(N_2H_4\) is a precursor in \(N_2H_4\) formation. This first point is further backed by the observation that the ratio of diimide molecules with no \(^{15}\)N atoms to diimide molecules with one \(^{15}\)N atom is, with 0.53 ± 0.05, the same as that of \(N_2H_3\) to \(^{15}\)N\(N_2H_4\) (0.52 ± 0.05).

Second, using the same argument we can exclude hydrazine (\(N_2H_4\)) as a precursor because the yield of \(N_2H_4\) decreases by a factor of 4.3 when comparing its yields in the \(NH_3\) and the \(NH_3\) \(N_2\) ice. This means that if \(N_2H_4\) were a precursor in \(N_2H_4\) production, the \(N_2H_4\) yield should decrease at least as much as the \(N_2H_4\) yield.

Third, in the \(NH_3\) \(N_2\) ices, we observe a decrease in the yield of \(N_2H_4\) compared to pure ammonia ice of about 2.5. The shape of the TPD curve is, however, unchanged. This indicates

---

**Scheme 3.** Principal reaction pathways towards the formation of \(N_2H_4\) starting with \(NH_3\) and with \(N_2H_4\) as an intermediate. The primary irradiation products are shown in blue. Also included are two principal reaction pathways towards \(N_2H_4\),
that the same isomers are forming in both systems. The isoto-
pically labeled ices reveal the reason for the strong decrease in N₂H₃ yield: even though the ¹⁵N₂ part of the ice contributes two thirds of all the nitrogen atoms available in the ice, 56 ± 3% of the observed triazene molecules did not incorporate any ¹⁵N atom. 29 ± 2% of the molecules built in only one ¹⁴N, and merely 14 ± 2% hold two ¹⁴N atoms. A possible reaction pathway leading to triazene including isotopically labelled mole-
cular nitrogen without initial N₂ cleavage would be ¹⁵N₂ + H → ¹⁵N₂H followed by ¹⁴N₂H + NH₂ → ¹⁴N₃H₂. Only 14% of the observed N₂H₃ molecules have that signature despite the abundance of ¹⁴N atoms. This means that hypothetical forma-
tions of N₂H₃ via NH₃ (from N₂+H) or via NH₂ (from N₂+NH) are not important pathways.

Fourth, the remaining possibility to form N₂H₃ starts with a cleavage of molecular nitrogen (N₂) to two nitrogen atoms, which could then form imidogen (NH) after recombination with a hydrogen atom; imidogen can react with diimide (N₂H₄) to N₂H₃. Also these pathways can only play a minor role in the formation of N₂H₃ since they would result in ¹⁵N₂N₂H₂. All these experimental considerations together with our energetic calcula-
tions are pointing to N₂H₃ as the reaction intermediate in the N₂H₃ formation.

As depicted in the reaction scheme (Scheme 3), there are two possibilities to arrive from N₂H₃ to N₂H₅. Using our tech-
nique we cannot differentiate between these two. The same holds for the formation of N₂H₅. Here, four different formation pathways are feasible. One starting with the primary irradiation product NH and three possibilities starting with the primary irradiation product NH₂.

5. Conclusions

We have processed homogeneous ammonia (NH₃) and deutera-
ted ammonia (ND₃) films as well as mixed NH₃ : N₂ and NH₃ : ¹⁵N films with energetic electrons at low temperatures to study the formation of the hitherto poorly described N₂H₅ iso-
mers. N₂H₅ as well as its isotopically labeled counterparts ND₃, ¹³¹⁵N₂H₅, ¹⁴¹⁵N₂H₅ and ¹⁴¹³¹⁵N₂H₅ are observed via their mass-to-
charge ratios m/z = 45, 48, 48, 47 and 46, respectively, after they are photoionized upon sublimation. Using our newly es-
tered method of photoionization driven reflectron time-of-
flight mass spectroscopy (PI-ReTOF-MS), a sensitive detection scheme utilizing tunable photon energies, in combination with the calculation of ionization energies of the possible N₂H₅ iso-
mers, we show that the observed N₂H₅ signal can only stem from the triazene and/or the trimide isomers. Both the iso-tra-
zene and the previously described cyclo-triazenes are not ob-
erved. Further, by calculating the appearance energy of the fragment ions of triazene and trimide and comparing those to our experimental observations we present evidence that at least parts of the observed N₂H₅ signal must originate from trans- and/or cis-triazenes. To elucidate the formation mecha-
nism of N₂H₅ we have then conducted isotopic substitution studies and suggest that the N₂H₅ formation occurs preferably with the diimide (N₂H₄) as a precursor via the reaction with imi-
dogen (NH). These considerations are backed by energetic cal-
culations of the possible decomposition pathways of N₂H₅. Summarizing we can conclude that our study gives a detailed insight in the formation of N₂H₅ in energetically processed films and hope that it helps in future attempts to isolate mole-
cular triazene to make it available as a direct component in the synthesis of more complex molecules.

Acknowledgements

The authors thank the W. M. Keck Foundation and the U. S. Army Research Office (W911NF-14-1-0167) for support. M. F. acknowledges funding from the DFG (FO 941/1). The Bochum team (YAT, WS) thanks the Cluster of Excellence RESOLV (EXC 1069), funded by the Deutsche Forschungsgemeinschaft, for support.

Keywords: ammonia • matrix isolation • nitrogen chain molecules • triazene • trimides


