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Confined rapid thermolysis/FTIR/ToF studies of methyl-amino-triazolium-based energetic ionic liquids

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ABSTRACT

Thermal decomposition of the energetic ionic liquids 1-methyl-4-amino-1,2,4-triazolium iodide (Me4ATI), 1-methyl-4-amino-1,2,4-triazolium nitrate (Me4ATN), 1-amino-3-methyl-1,2,3-triazolium iodide (Me1ATI), and 1-amino-3-methyl-1,2,3-triazolium nitrate (Me1ATN) was studied by confined rapid thermolysis. Sub-milligram quantities of the compounds were subjected to decomposition under isothermal conditions achieved by initially heating the sample at rates of approximately 2000 K/s. The products formed by decomposition under the afore-mentioned conditions were sampled by rapid scan FTIR spectroscopy and time-of-flight mass spectrometry. Decomposition studies involving the iodide salts were carried out around 270–290 °C, whereas the nitrate salts were subjected to 320–340 °C. The amino group was found to be involved in the initiation reaction, forming copious quantities of ammonia from the iodide compounds and, N_2O and H_2O from the nitrate compounds. The extent of decomposition of the triazole ring was minimal at the considered temperatures.

1. Introduction

A wide range of attractive properties [1–8] have drawn the interest of the scientific community to ionic liquids, a unique class of compounds with melting points below 100 °C. The exceptional chemical and thermal stability of these compounds, coupled with their low vapor pressures and low melting points have put them forth as potential replacements of many noxious organic solvents used in the chemical industry [9,10]. Also their easy recoverability after usage has made them popular as 'green solvents'. However, attention has recently been drawn to energetic heterocyclic ionic liquids with nitrogen-rich cations, such as imidazoles, triazoles and, tetrazoles, coupled with oxygen-rich anions such as nitrates, nitramides, and perchlorates, because of their thermal stability and high energy density. These compounds are easy to synthesize, and their properties can be tailored to suit specific requirements by minor alterations in their molecular structure.

A comprehensive overview of recent studies regarding triazolium-based salts has been presented in our previous work [11]. Significant effort in developing salts based on various derivatives of 1,2,4-triazole or 1,2,3-triazole as cations and nitrates, perchlorates, and dinitramides as anions have been exerted by Shreeve et al. [12–19] and Drake et al. [20–22]. Since the hydrogen atoms on these azoles can be substituted easily by various functional groups, the family of the triazole salts has been expanded to include azido, amino, nitro, and nitramino azolium salts. However, most of the thermal decomposition studies have been carried out using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under slow heating rates without any particular emphasis on the chemical kinetics of these decomposition reactions. Though these studies were carried out under low heating rates, the underlying trends provide valuable insights into the thermal stability of these compounds, the effects of various groups substituting the protons on the triazole ring, and their decomposition behavior under elevated heating rates.

Nitrate, perchlorate and dinitramide salts of 3,4,5-triamino-1,2,4-triazole were synthesized and characterized by Drake et al. [21]. The dinitramide salt of the cation was found to be the least stable, followed by the nitrate and the perchlorate. Replacement of two ring H atoms with amino groups had no effect on the decomposition temperature of the dinitramide salt, but the perchlorate and the nitrate salts demonstrated an increased thermal stability. 1-amino-3-alkyl-1,2,3-triazolium nitrates (alkyl = methyl, ethyl, *n*-propyl, 2-propenyl, and *n*-butyl) were also synthesized and characterized by vibrational spectra, multinuclear NMR analyses, and DSC studies [22]. The DSC studies on these compounds showed that the thermal stability was decreased as the alkyl chain length increased. Salts formed by pairing the 1-methyl-3,4,5-triamino-1,2,4-triazolium cation with azide, nitrate, perchlorate, dinitramide, nitrotetrazolate, and azotetrazolate were characterized by Darwich et al. [23]. The order of thermal stability was found to be perchlo-

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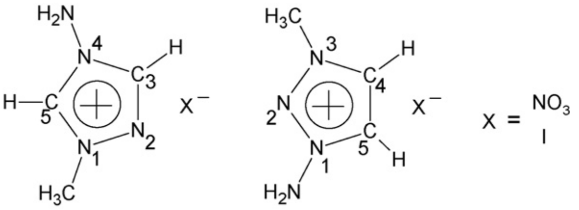


Fig. 1. Structure of 1-methyl-4-amino-1,2,4-triazolium X (X = iodide and nitrate) and 1-amino-3-methyl-1,2,3-triazolium X (X = iodide and nitrate).

Table 1
Vibrational frequencies of experimentally observed gaseous products.

Description	Wavenumber (cm^{-1})	Reference
H_2O	3657, 1595	[31]
HCN	3311, 712	[31]
NH_3	3337, 1627, 950	[31]
CH_3I	2974, 1435, 1252, 882	[31]
HNO_3	3551, 1710, 1326, 879	[32]
$MeONO_2$	2962, 1667, 1291, 1019, 855	[33]
CO_2	2349, 667	[31]
N_2O	2224, 1285	[31]
NO	1875	[27]
NO_2	1617, 1320	[32]
HNCO	3530, 2269	[34]

rate > nitrate > azide > azotetrazolate > nitrotetrazolate > dinitramide. The introduction of the methyl group increased the decomposition temperature from 245 to 261 °C for the nitrate salt.

The aim of the current work is to identify the mechanism determining the initiation of decomposition of energetic amino-methyl-triazolium salts under high temperatures and heating rates. The synergistic diagnostic tools, Fourier transform infrared (FTIR) spectroscopy and time-of-flight (ToF) mass spectrometry (MS), were utilized to afford better probabilities of identifying the decomposition products and thus, determining the reaction pathways. The energetic salts of primary interest are Me4ATN and Me1ATN. Since the complexity of the secondary reactions is considerably higher for the oxygen-rich anions, the relatively simple iodides Me4ATI and Me1ATI were studied initially. The molecular structures of the molecules are shown in Fig. 1. Studies were also conducted on the building blocks for these rather complex molecules, including 4-amino-1,2,4-triazole (4AT), 1-methyl-1,2,4-triazole (1MeTA), and 1-amino-1,2,3-triazole.

2. Experimental approach

The experimental setup as well as the data-reduction techniques utilized to extract mole fractions of individual species from the FTIR spectra were discussed is earlier works [24–26]. The technique utilized to study the rapid thermal decomposition of energetic materials, termed confined rapid thermolysis (CRT), is used in conjunction with two synergistic diagnostic tools, a Fourier transform infrared spectrometer and a time-of-flight mass spectrometer. The method is very sensitive to decomposition processes occurring in the condensed phase, compared to the gas phase, as the molecules are quenched by the relatively cooler atmosphere into which they evolve. Typically, a small quantity, 0.5 mg of a solid or 0.5 μL of a liquid, of the sample is rapidly heated in between two heated surfaces maintained under isothermal conditions in a constant pressure chamber purged by an inert gas. The use of a small sample volume enclosed in a confined space, roughly 300 μm in height, enables heating rates in the range of 2000 K/s.

The gaseous products evolving from the condensed phase are sampled by a modulated FTIR beam passing through two ZnSe windows. Thus the spectra are obtained in near real-time with a spectral resolution of 2 cm^{-1} and a temporal resolution of 50 ms. The gaseous species are also sampled by a ToFMS system, equipped with a 1 m flight tube and a 44 mm microchannel plate detector, via a 100 μm orifice plate. The molecular beam entering the third stage, maintained at 10^{-7} Torr, is ionized by electron impact ionization set at 70 eV. Individual mass spectra are acquired at 1000 Hz, and time-to-mass scaling is performed using the expressions $m = a(t - t_0)^2$, where the two constants for each mass spectrum are obtained from known positions of helium and argon. The species concentrations of various species, such as H_2O, N_2O, NO_2, NO, NH_3, CO_2, CO, MeOH, HCN, and HNO_3 are extracted by a non-linear, least-squares method by comparison with theoretical transmittance. The radiative properties, such as partition function, halfwidth of spectral lines, and its temperature exponent, are determined from the HITRAN database [27].

3. Results and discussion

3.1. Thermal decomposition pathways of Me4ATI

Me4ATI is a light orange crystalline solid under standard conditions, with a melting point of 101 °C [17]. Approximately 0.5 mg of the sample was rapidly thermolyzed in the temperature range of 230–300 °C. Fig. 2a shows the products evolving from the decomposition of Me4ATI at a representative temperature of 270 °C and 1 atm. The vibrational frequencies of the experimentally observed species evolving from the compounds studied are listed in Table 1. As seen from Fig. 2a and Table 1, the major decomposition prod-

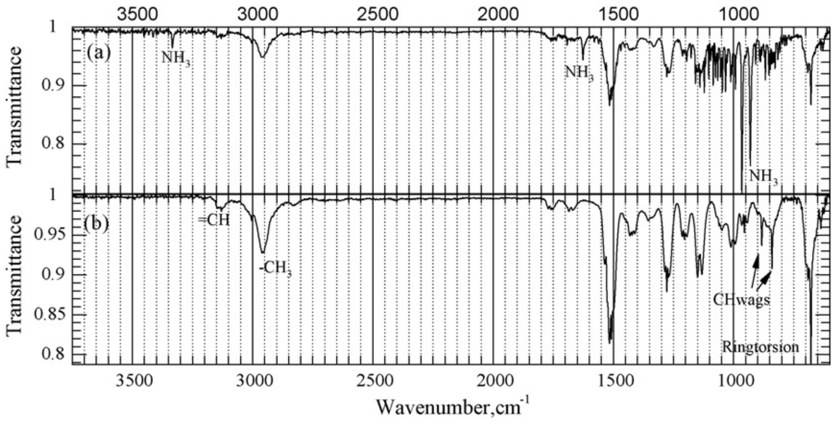


Fig. 2. FTIR spectrum of species from rapid thermolysis of (a) Me4ATI at 270 °C and 1 atm N_2, and (b) MeTA at 250 °C and 1 atm N_2.

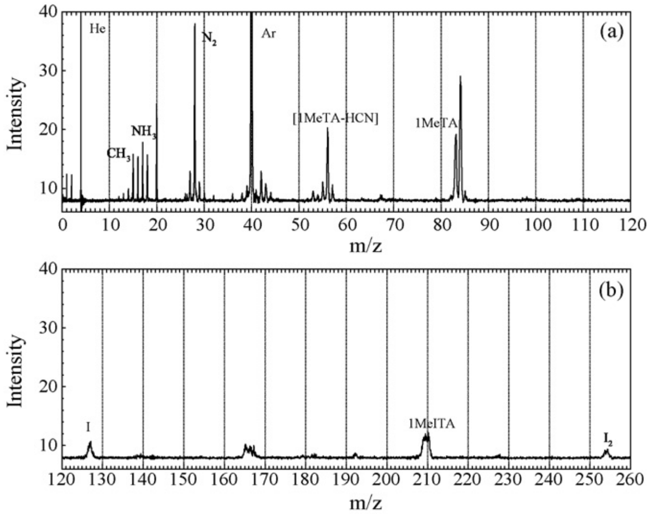


Fig. 3. Mass spectrum from rapid thermolysis of Me4ATI at 270 °C and 1 atm Ar, He and residual air (average of 10 spectra).

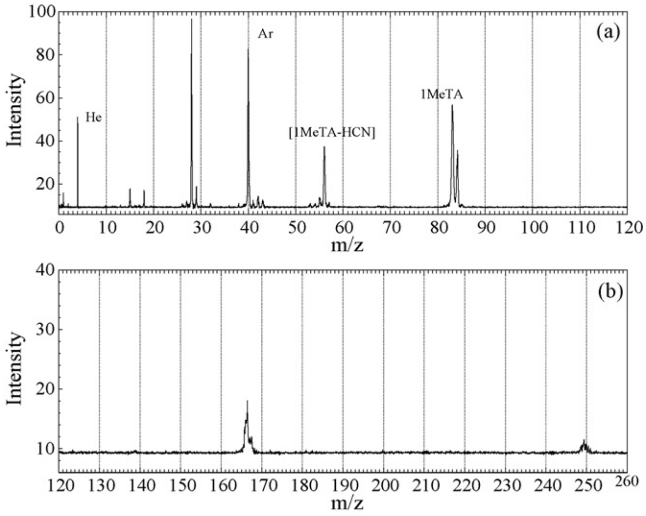


Fig. 4. Mass spectrum from rapid thermolysis of MeTA at 250 °C and 1 atm Ar, He and residual air (average of 10 spectra).

uct is ammonia, with its rotational doublet near 900 cm^{-1}, as well as peaks at 1626 and 3336 cm^{-1}. The rotational lines due to the protonated anion HI or the vibrational bands from CH_3I were not detected.

In order to identify the source of the rovibrational bands from 1500 to 1000 cm^{-1}, 1MeTA was acquired from Sigma-Aldrich and used without further purification, and the resulting FTIR spectrum of vaporized 1MeTA attained at 250 °C and 1 atm is displayed in Fig. 2b. 1MeTA was found to be stable under comparable conditions, as evident from the lack of detection of any smaller products, such as HCN or CH_3CN. Although the presence of the NH_3 rotational lines from 1200 to 750 cm^{-1} proved to be a hindrance in clearly identifying the vibrational bands from 1MeTA in that region, the presence of 1MeTA among the decomposition products of Me4ATI is recognized by the ring torsion frequency around 680 cm^{-1} and the strong band around 1500 cm^{-1}. The lack of HCN among the products shows that the ring structure is intact at the applied temperatures. N_2 could not be detected due to its IR-inactivity. Based on the prodigious quantities of ammonia liberated and the formation of 1MeTA, the initiation of decomposition occurs most likely through the amino group. Proton transfer does not occur directly to form HI.

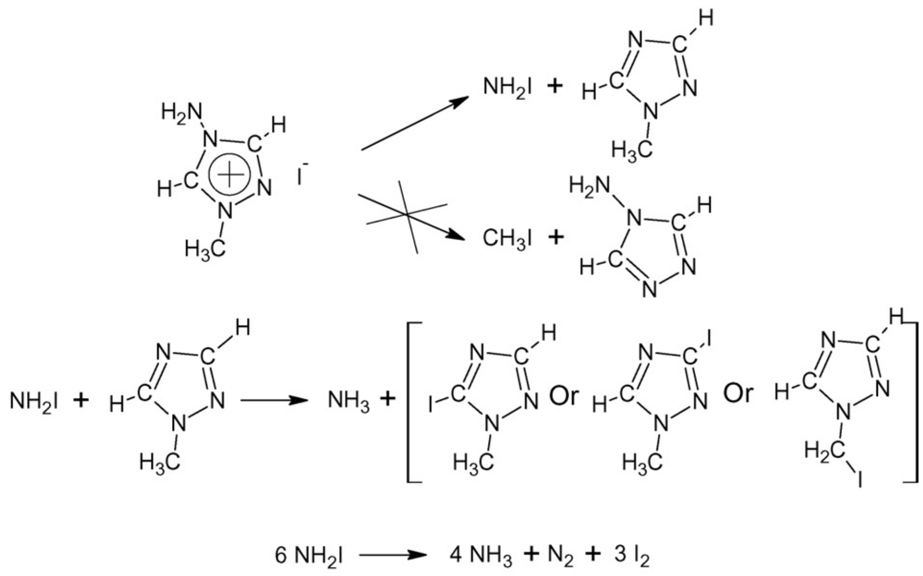
To assist in the identification of species evolved during the decomposition of Me4ATI, Fig. 3a and b shows the results from the thermolysis of Me4ATI under an inert atmosphere of Ar and He, acquired at 270 °C and 1 atm Ar, He and residual air, under an ionization potential of 70 eV at 1000 Hz. In order to provide better signal-to-noise ratios in the mass spectra, 10 consecutive spectra were averaged, providing a temporal resolution of 0.01 s. Although the mass spectrum in Fig. 3a and b, split in order to provide clarity, appears at a first glance as quite complicated due to the fact that a high ionization potential is used, it facilitates comparison with available mass spectral data bases for a wide range of chemical compounds [28].

The prominent peaks at $m/z = 17$ and $m/z = 83$ attests to the formation of ammonia and 1MeTA, respectively. The signal at $m/z = 84$ was formed by the excess protonation of 1MeTA, due to the presence of H^+ ions in the flight tube of the ToFMS. The fragmentation of the ring of 1MeTA is seen in Fig. 4a, with the most prominent one seen at $m/z = 56$, due to the loss of an HCN fragment. Similar fragments found in Fig. 3a substantiate the formation of 1MeTA during the decomposition of Me4ATI. 1MeTA also dimerizes to a limited extent, as seen by the peak at $m/z = 166$. The peak at $m/z = 209$ can be explained by the formation of methyl-iodo-triazole, produced as a by-product during the formation of ammonia from the amino group. The lack of a peak at $m/z = 142$ proves the absence of CH_3I. The peak at $m/z = 28$ has contributions from molecular N_2 as well as fragmentation of 1MeTA.

The availability of the ToFMS data facilitates the determination of the decomposition pathways of Me4ATI. As postulated earlier, the presence of large quantities of ammonia and 1MeTA indicates the involvement of the amino group in the initiation stage of decomposition. The most probable initiation pathway, as shown in Scheme 1, is the deamination of the Me4AT cation to form 1MeTA and NH_2I. Similar decomposition pathways were observed during the decomposition of 1-amino-4,5-dimethyl-tetrazolium iodide [29]. NH_2I being a reactive species, promptly reacts with the neutral 1MeTA to abstract an H-atom to form NH_3 and methyl-iodo-triazole. The exact location of abstraction is difficult to ascertain due to the existence of two similar locations on the ring carbon atoms (position C_3 and C_5), as well as the methyl group. NH_2I subsequently decomposes to form NH_3, N_2 and molecular iodine. The lack of HI among the FTIR spectra or the mass spectra precludes the possibility of a proton transfer from the methyl group or the amino group as an initiation reaction. Also, due to almost undetectable levels of CH_3I among the decomposition spectra, a nucleophilic transfer involving the methyl group to form CH_3I is neglected as a significant decomposition pathway.

3.2. Thermal decomposition pathways of Me4ATN

Unlike its iodide salt, the nitrate salt of the methyl-amino-triazolium cation is a clear viscous liquid with a melting point of −60 °C. Thermal decomposition measured by DSC was initiated at 221 °C [17]. Confined rapid thermolysis of approximately 0.5 μL of the sample was carried out at temperatures around 320 °C. The hygroscopic nature of the salt made it difficult to clearly study the decomposition behavior of the compound. The sample was dried for 24 h under vacuum (40 mTorr) and then stored in a sealed container to avoid contamination by moisture. Fig. 5a depicts an FTIR spectrum of species from rapid thermolysis of Me4ATN at 320 °C and 1 atm. Nitric acid (HNO_3), with several rovibrational bands from 1700 to 800 cm^{-1} and an overtone above 3500 cm^{-1}, was immediately discernable as a major species. The other major species detected were H_2O, N_2O, and CO_2. Also identified were small quantities of HNCO and HCN. Fig. 5b shows the spectrum obtained by



Scheme 1. Proposed reaction pathway for Me4ATI.

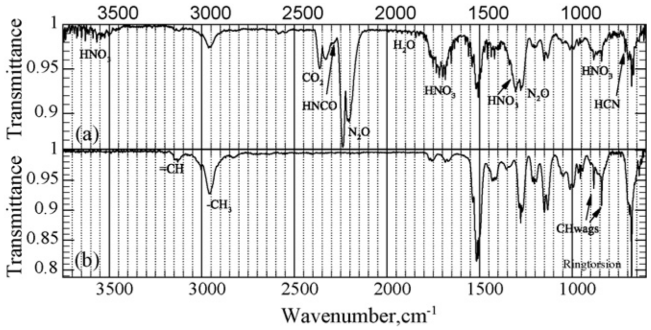


Fig. 5. FTIR spectrum of species from rapid thermolysis of (a) Me4ATN at 320 °C and 1 atm N_2, and (b) MeTA at 250 °C and 1 atm N_2.

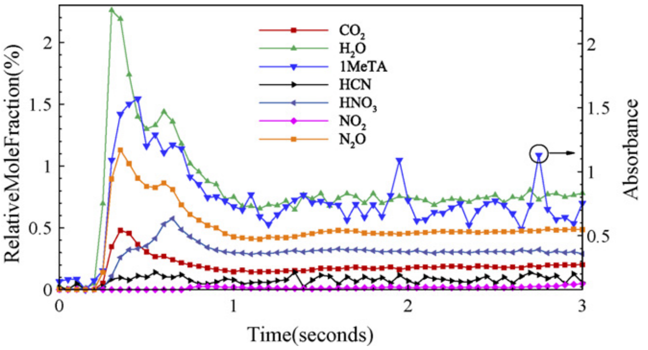


Fig. 7. Species evolution from rapid thermolysis of Me4ATN at 320 °C and 1 atm N_2.

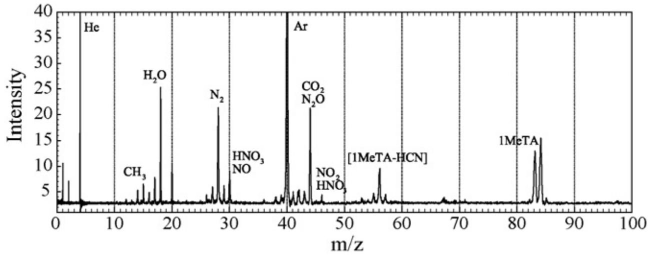


Fig. 6. Mass spectrum from rapid thermolysis of Me4ATN at 320 °C and 1 atm Ar, He and residual air (average of 10 spectra).

vaporizing 1MeTA for identification of the bands in the ‘fingerprint region’. It was clear that the decomposition products of Me4ATN contained the stable compound 1MeTA, as evident from the presence of the C–H wags near 850 cm^{-1}, and the ring torsion near 680 cm^{-1}. As expected, methyl nitrate (CH_3ONO_2) was not detected among the products.

The findings obtained from FTIR analysis were confirmed by ToF mass spectra. Fig. 6 shows a spectrum from the ToFMS acquired during the pyrolysis of Me4ATN at 320 °C and 1 atm Ar, He and residual air. At a first glance, the HNO_3 detected from the FTIR spectra seem to be absent due to the lack of a strong peak at $m/z = 63$. However, previous studies [30] showed that HNO_3 readily decomposes under the high ionization potential used to form NO_2^+ ($m/z = 46$), NO^+ ($m/z = 30$), H^+ ($m/z = 1$) and a number of other smaller ions, which were present in the mass spectra acquired during the event. Similar to the decomposition of Me4ATI, the signal at $m/z = 84$ was formed by the excess protonation of 1MeTA, due to the presence of H^+ ions in the flight tube of the ToFMS. The peak at $m/z = 44$ is attributed to N_2O and CO_2, also present in the FTIR spectra. Additionally, the lack of a peak at $m/z = 69$ proves the absence of 1-*H*-triazole, a by-product of the decomposition of 4-amino-triazole under similar conditions [11], hence negating the possibility of involvement of the methyl group during the initiation reaction.

As shown in Fig. 7, the species evolution profiles, extracted from the FTIR spectra acquired at 320 °C, reveals further information on the decomposition pathways of Me4ATN. Although HNO_3 was found to be a major product during the decomposition of Me4ATN, its rate of evolution was significantly delayed compared to the faster rates of H_2O and N_2O. CO_2 and HCN were found to evolve at smaller quantities. The right vertical axis shows the absorbance of the band from 1100 to 1175 cm^{-1} arising from 1MeTA. As seen from this plot, 1MeTA desorbs at a rate comparable to H_2O and N_2O from the condensed phase.

The nitrate anion and the complex structure of the amino-methyl-triazole results in a wide variety of reactions leading to the decomposition of Me4ATN. However, the formation of H_2O and N_2O early in the event, and the lack of methyl nitrate suggest that the initiation reaction involves the amino group. As shown in Scheme 2, the initiation reaction is through an N_4–N bond scission to form 1MeTA and the reactive species, NH_2ONO_2. NH_2ONO_2 subsequently forms N_2O, H_2O and N_2 through secondary reactions with

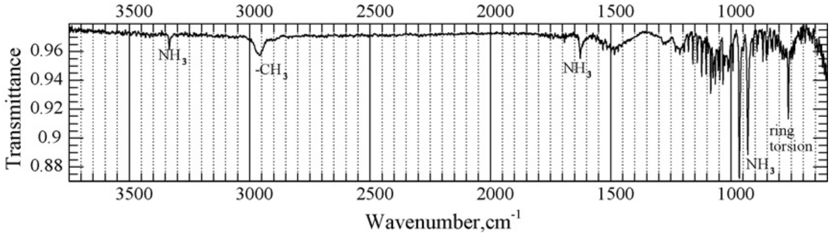
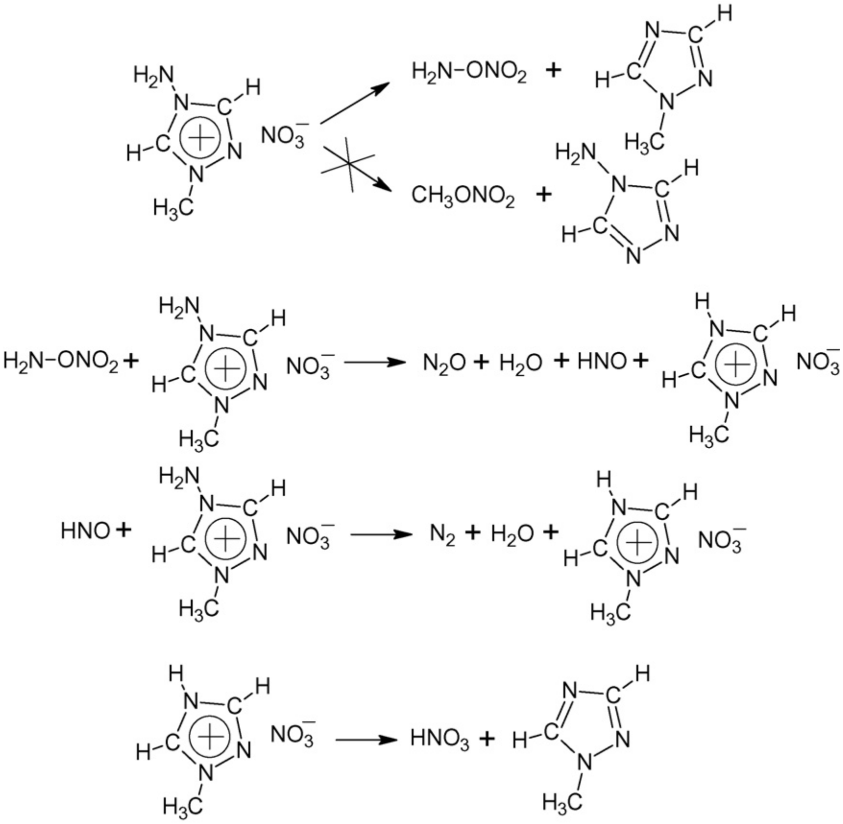


Fig. 8. FTIR spectrum of species from rapid thermolysis of Me1ATI at 290 °C and 1 atm N_2.



Scheme 2. Proposed reaction pathway for Me4ATN.

the parent molecule Me4ATN. Methyl-triazolium nitrate, formed as a by-product during these reactions, decomposes to form the HNO_3 detected at a later stage, and additional 1MeTA. 1MeTA produced during the initiation and secondary steps is further reduced to a limited extent to CO_2, HCN, HNCO, H_2O and N_2 by the strong oxidizer, HNO_3.

3.3. Thermal decomposition pathways of Me1ATI

Me1ATI, an isomer of Me4ATI, is a light yellow crystalline solid under standard conditions. The decomposition temperatures for Me1ATI were found to be relatively similar to those of Me4ATI. Thermolysis tests were typically conducted at 290 °C. Fig. 8 shows the species evolving from rapid thermolysis at 290 °C and 1 atm. As listed in Table 1, the principal product is ammonia, with its prominent rotational doublet and numerous rotational lines near 900 cm^{-1}, similar to the decomposition products of Me4ATI. Unlike Me4ATI, the lack of the reference compound 3-methyl-1,2,3-triazole (3MeTA) rendered accurately determining the peaks in the ‘fingerprint region’ difficult. However, the presence of a sharp peak at 760 cm^{-1}, typically attributed to ring torsion, confirms the

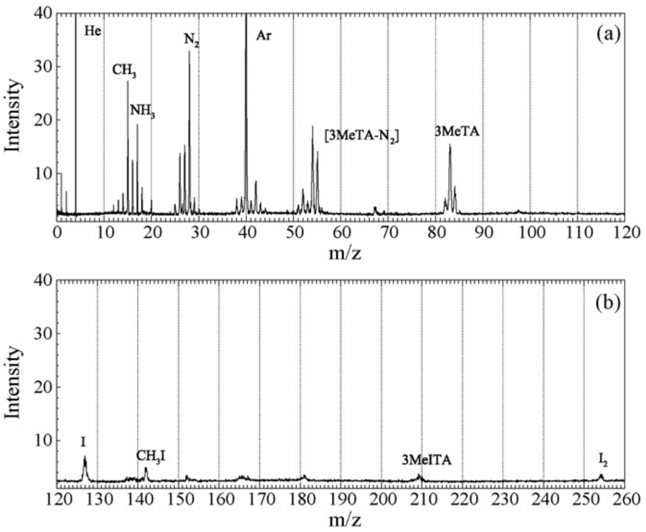


Fig. 9. Mass spectrum from rapid thermolysis of Me1ATI at 290 °C and 1 atm Ar, He and residual air (average of 10 spectra).

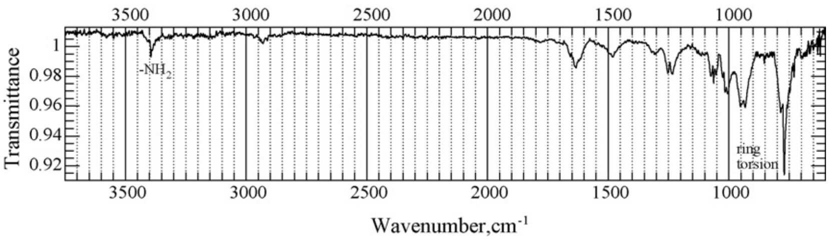


Fig. 10. FTIR spectrum of species from rapid thermolysis of 1ATA at 350 °C and 1 atm N_2.

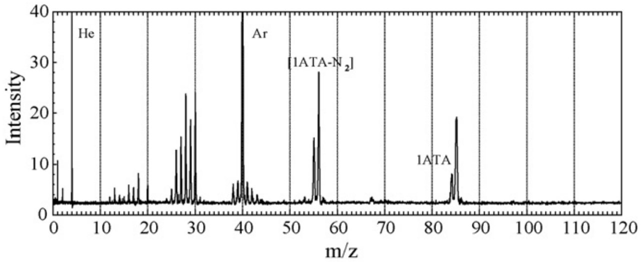


Fig. 11. Mass spectrum from rapid thermolysis of 1ATA at 350 °C and 1 atm Ar, He and residual air (average of 10 spectra).

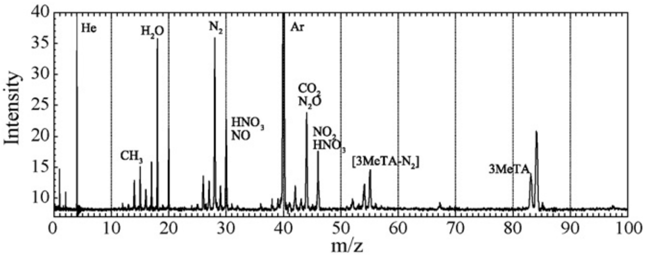


Fig. 13. Mass spectrum from rapid thermolysis of Me1ATN at 340 °C and 1 atm Ar, He and residual air (average of 10 spectra).

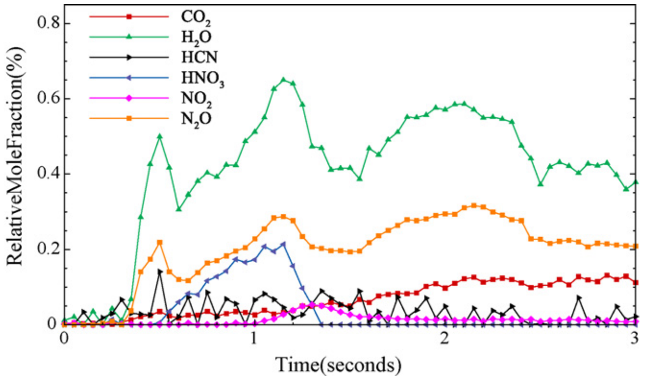


Fig. 14. Species evolution from rapid thermolysis of Me1ATN at 340 °C and 1 atm N_2.

presence of a cyclic triazole. The presence of a $-CH_3$ stretch near 3000 cm^{-1} indicates the possibility of the formation of 3MeTA. HCN and HI were not detected among the products. Due to overlapping of bands, it was not possible to accurately identify CH_3I in the spectra. As in the case of Me4ATI, the copious amount of ammonia leads to the possibility of the involvement of the involvement of the amino group in the initiation reaction.

Results from the use of the ToFMS provide additional details on the rapid thermolysis behavior of Me1ATI. Fig. 9a and b shows a spectrum from the ToFMS acquired during the pyrolysis of Me1ATI at 290 °C and 1 atm Ar, He and residual air. Careful observation of the spectrum reveals that $m/z = 17$ (NH_3) and $m/z = 83$ (3MeTA) are the major species. The peaks at $m/z = 55$, 54, 52, 42, and 27 were suspected to be formed due to fragmentation of 3MeTA. Similar to the fragmentation of 1MeTA, the large peak at $m/z = 28$ is partially formed by the fragmentation of 3MeTA. The major deviation from the mass spectra obtained from Me4ATI was the formation of the methyl iodide (CH_3I), evident from the peak at $m/z = 142$. This shows the presence of a secondary reaction pathway through a nucleophilic methyl group transfer to the iodide anion. The smaller peaks at $m/z = 209$ and $m/z = 166$ account for methyl-iodo-triazole and the 3MeTA dimer, respectively.

From the information revealed by the ToFMS and FTIR spectra, it is clear that the decomposition of Me1ATI proceeds primarily through a ring N_1–N bond scission to form NH_2I and 3MeTA. However, there exists a secondary reaction pathway, leading to the formation of CH_3I and 1-amino-1,2,3-triazole (1ATA). 1ATA was found to be stable when subjected to thermolysis at 350 °C. The FTIR and mass spectra of 1ATA are shown in Figs. 10 and 11, respectively. However, proton transfer to form HI is not a possibility. The NH_2I formed in the initiation step reacts with 3MeTA at position C_4 or C_5, or the methyl group to form methyl-iodo-triazole or iodo-methyl-triazole. The initiation reaction pathways and the subsequent secondary steps are shown in Scheme 3. Decomposition of NH_2I also takes place in a manner similar to those observed in Scheme 1, forming NH_3, N_2, and I_2.

3.4. Thermal decomposition pathways of Me1ATN

Me1ATN is a colorless crystalline solid with a high degree of hygroscopicity. Hence, this salt was also dried under vacuum for

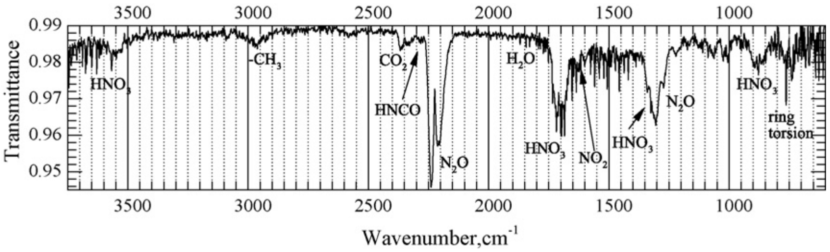
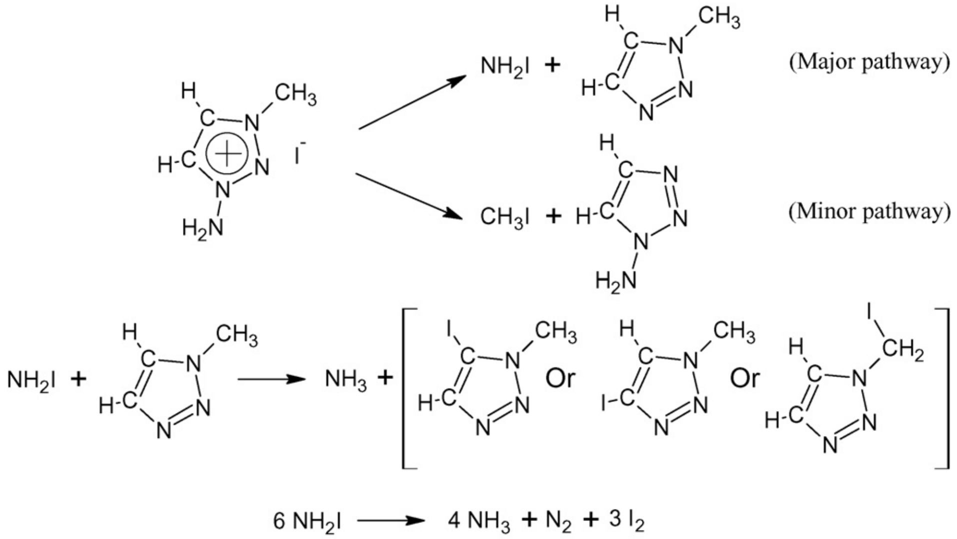


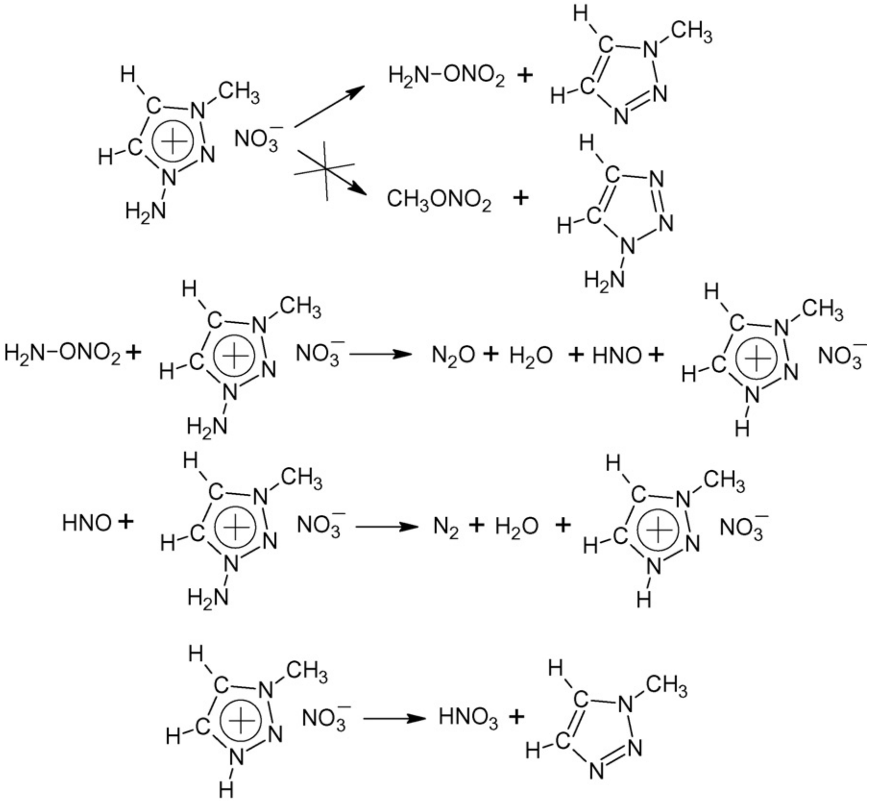
Fig. 12. FTIR spectrum of species from rapid thermolysis of Me1ATN at 340 °C and 1 atm N_2.



Scheme 3. Proposed reaction pathway for Me1ATI.

24 h and stored in a desiccator. Me1ATN has a melting point of 86–88 °C, and decomposition is initiated at 185 °C, as measured by DSC [22]. Small quantities of the sample were thermolyzed at temperatures near 340 °C. Fig. 12 shows an FTIR spectrum of the gaseous products generated during thermolysis of Me1ATN at 340 °C and 1 atm. According to Table 1, the major species present among the decomposition products were HNO_3, H_2O and N_2O, similar to the FTIR spectra obtained from Me4ATN. Besides these principal species, smaller quantities of CO_2, NO_2, and HNCO were also detected. Though it was difficult to exactly ascertain the presence of 3MeTA, the band due to ring torsion around 760 cm^{-1} and the –CH_3 stretch near 3000 cm^{-1} indicate its formation. Due to overlapping of bands, it was not possible to exactly identify CH_3ONO_2, if present, among the products.

Fig. 13 shows a ToFMS spectrum from the thermolysis of Me1ATN taken at 340 °C and 1 atm Ar, He and residual air. Similar to Me4ATN, the decomposition products include HNO_3, as seen from the peaks at $m/z = 46$ and $m/z = 30$. Although these peaks are also indicative of CH_3ONO_2, formation of this species is most likely limited due to lack of conclusive evidence. The peaks at $m/z = 83$ and $m/z = 84$ shows the presence of 3MeTA and its protonated form. The smaller species found in the FTIR spectra, such as H_2O at $m/z = 18$,



Scheme 4. Proposed reaction pathway for Me1ATN.

N_2O and CO_2 at $m/z = 44$ are also present. The fragmentation of 3MeTA leads to the smaller peaks at $m/z = 55$, 54, 52, 42, and 27.

In order to further elucidate the decomposition pathways of Me1ATN, the species evolution profiles were extracted from the FTIR spectra at 340 °C and displayed in Fig. 14. The pattern of evolution of various species was found to be remarkable similar to Me4ATN, with H_2O and N_2O desorbing from the condensed phase at a fast rate, followed by HNO_3. As observed in case of Me4ATN, the evolution of HNO_3 is considerably delayed. Based on the FTIR and ToFMS spectra, and the knowledge gained from studying the decomposition of Me1ATI and Me4ATN, the decomposition pathways of Me1ATN are shown in Scheme 4. The decomposition of Me1ATN was mostly similar to that of Me4ATN, barring the ambiguity regarding the involvement of the methyl group in the initiation reaction, as seen in Me1ATI. The primary reaction pathway involves the formation of NH_2ONO_2 and 3MeTA. The smaller species N_2O and H_2O are formed via fast secondary reactions. Methyl-triazolium nitrate, formed as a by-product during these reactions, decomposes to form the HNO_3 detected at a later stage, and more 3MeTA. Additionally, 3MeTA was oxidized by nitric acid to form the smaller molecular weight species.

4. Conclusions

Confined rapid thermolysis studies with FTIR spectroscopy and ToF mass spectrometry as the diagnostic tools were conducted on four methyl-amino-triazolium-based compounds, Me4ATI, Me4ATN, Me1ATI, and Me1ATN. The change in the ring structure from a 1,2,4-triazole to a 1,2,3-triazole did not have a significant effect on the thermal stability and the major decomposition pathways for the compounds. For both the iodide compounds Me4ATI and Me1ATI, the amino group was involved in the initiation reaction, leading to the formation of NH_3 and methyl-iodo-triazoles. However, unlike Me4ATI, in case of Me1ATI, the secondary initiation pathway involving a methyl group transfer to form CH_3I was found to be active. In case of the nitrate compounds, decomposition was initiated by the nitrate ion scavenging the amino group to form NH_2ONO_2 and the corresponding methylated triazole. NH_2ONO_2 reacted vigorously with the parent nitrates to form H_2O, N_2O and N_2 through secondary reactions. The methylated triazoles were subsequently oxidized by HNO_3 to form smaller molecular weight species.

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