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The thermal decomposition of aminotetrazoles. Part 2. 1-Methyl-5-aminotetrazole and 1,5-diaminotetrazole

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Abstract

The thermal decompositions of 1-methyl-5-aminotetrazole and of 1,5-diaminotetrazole have been studied using thermogravimetry, differential scanning calorimetry and thermal volumetric analysis. The solid residues, and the high boiling point and gaseous products of the decompositions have been collected and identified using IR spectroscopy and mass spectrometry.

Both aminotetrazoles start to decompose just after melting: 1-methyl-5-aminotetrazole at 495 K and 1,5-diaminotetrazole at 460 K. The decomposition is accompanied by elimination of gaseous and high boiling point products, partial evaporation of the original substances and formation of thermally stable residues.

Both 1-methyl-5-aminotetrazole and 1,5-diaminotetrazole, in the solid state and probably in the melt, coexist in amino and imino tautomeric forms. Therefore, two competing mechanisms of tetrazole ring-breaking, with elimination of respectively nitrogen or hydrogen azide molecule, are proposed.

INTRODUCTION

Aminotetrazoles are prospective gas-generating and blowing agents for polymeric systems, because they are sufficiently thermally stable and yield a large volume of gas on thermal decomposition. In Part 1 of this investigation [1], the mechanism and kinetics of the thermal decomposition of 5-aminotetrazole (5-AT) were studied using both experimental and theoretical considerations. It was shown that the temperature-dependent

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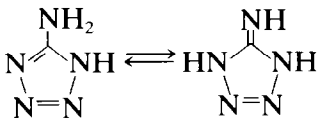
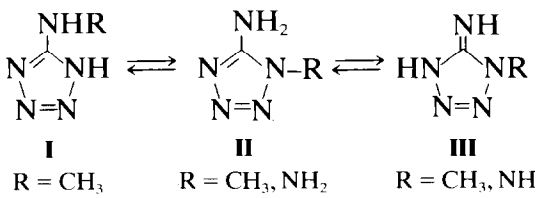
tautomeric amino–imino and prototropic transformations are the important preliminary steps of 5-AT thermal decomposition. Crosslinked triazine structures were identified in the solid residue of its thermal decomposition. They are thermally stable and, hence, 5-AT can be considered as a prospective blowing agent for flame retardant intumescent compositions.

The amino–imino tautomerism of 5-AT involves the reversible transition of a proton from the amino substituent to position 4 of the tetrazole ring



However, because the amino form of 5-AT has a proton in position 1 of the tetrazole ring which becomes identical to the proton in position 4 of the imino form, analytical identification of the transferred proton in 5-AT is ambiguous [1].



(1)

The present investigation was undertaken to study the mechanism and kinetics of the thermal decomposition of 1-methyl-5-aminotetrazole (MAT) and 1,5-diaminotetrazole (DAT) which are the simplest 1-substituted derivatives of 5-AT and do not have a proton in position 1. The existence of amino–imino tautomerism (**II** ⇌ **III**, eqn. (1)) for MAT [2–5] and DAT [4, 5] is controversial. Moreover, the isomerization at elevated temperatures of MAT to 5-methyltetrazole (**II** ⇌ **I**, eqn. (1)) was also considered by Henry et al. [6]. The expected peculiarities of the thermal decomposition of MAT and DAT, provoked by their possible tautomerism, are the reasons for our particular interest in these compounds.

EXPERIMENTAL

1-Methyl-5-aminotetrazole was obtained by methylation of 5-aminotetrazole by methyl iodide [7]. The resulting mixture of 1-methyl- and 2-methyl-5-aminotetrazole was separated by dissolution in hot benzene. The benzene-insoluble 1-isomer was purified by multiple recrystallization from water (m.p. 495 K) and characterized by IR.

1,5-Diaminotetrazole was synthesized by reacting thiosemicarbazide, sodium azide and ammonium chloride in dimethylformamide in the presence of PbO [8]. Crude DAT was purified by recrystallization from water (m.p. 459 K) and characterized by IR. To recognize the absorptions of groups involved in hydrogen bonding, the spectra were recorded at either elevated ($\approx$440 K) or low temperatures ($\approx$100 K) [9].

The thermal decompositions of MAT and DAT were investigated at a heating rate of 10 K min^{-1} in flowing nitrogen (60 ml min^{-1}) on a Du Pont thermoanalyser, equipped with a DSC cell, and on a 951 thermogravimetric analyser (TG). In the DSC cell, experiments were performed either in a static nitrogen atmosphere at a pressure of 4 MPa or in sealed aluminium pans in a self-generated atmosphere. The thermal volumetric analysis (TVA) was carried out in glass ampoules on a DAGV-70-2M volumeter [10] in a static argon atmosphere at heating rates ranging from 0.63 to 40 K min^{-1}.

The identification of the solid residues of the decomposition and of high boiling point products condensed on the water-cooled walls of the ampoules was carried out by IR. The evolved gases were identified by IR and mass spectrometry. A detailed description of the methods for collecting and analysing the products was given in our previous paper [1].

RESULTS

Figures 1 and 2 show the DSC curves of MAT and DAT carried out under inert gas flow (a), at elevated pressures in an inert atmosphere (b), and in sealed crucibles in a self-generated atmosphere (c). Both MAT and DAT show a melting exotherm, at 495 and 460 K respectively, followed by exothermal degradation at 520–620 K (MAT, Fig. 1) and at 470–540 K

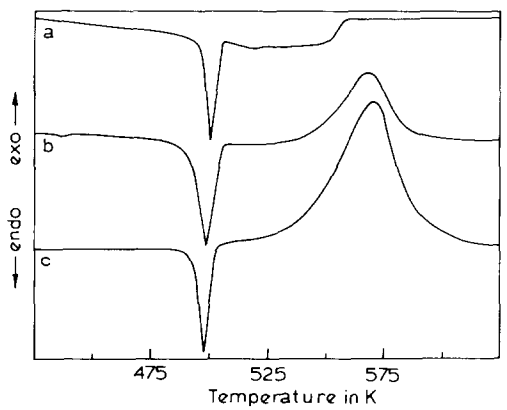


Fig. 1. DSC curves of thermal decomposition of 1-methyl-5-aminotetrazole, heating rate 10 K min^{-1}: curve a, nitrogen flow at 60 mol min^{-1}; curve b, nitrogen at 4 MPa; curve c, sealed aluminium pan.

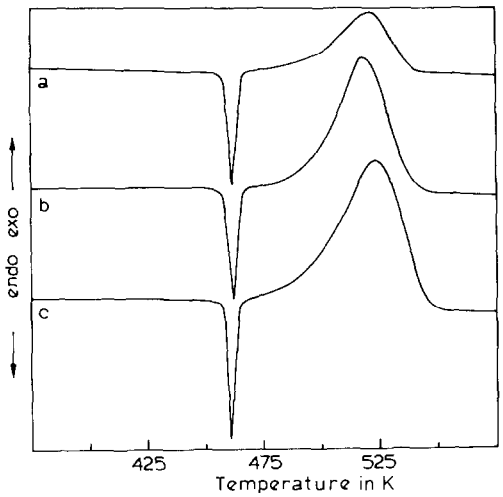


Fig. 2. DSC curves of thermal decomposition of 1,5-diaminotetrazole. Conditions and curves as in Fig. 1.

(DAT, Fig. 2). The exothermal effect increases when the degradation is carried out under pressure or in sealed pans, in which the endothermal evaporation of the aminotetrazoles is prevented. Under pressure or when using sealed pans, the loss of secondary products from the pans on decomposition is also restricted. If these products decompose exothermically, as with HN_3 in the case of 5-AT [1], they can also contribute to the exothermal peak.

Both compounds under study lose up to 85% of their weight in the first stage of thermal decomposition under nitrogen flow (Fig. 3). Thermally

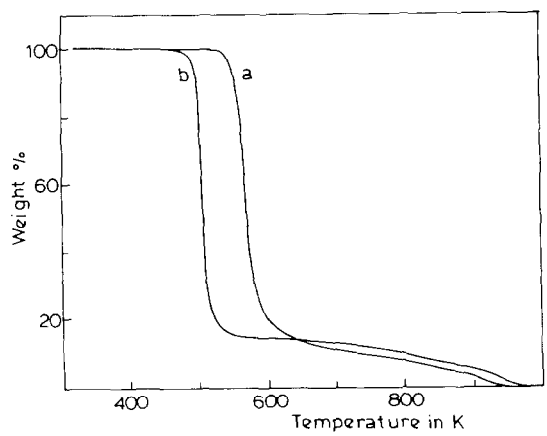


Fig. 3. Weight loss curves of thermal decomposition of (curve a) 1-methyl-5-aminotetrazole and (curve b) 1,5-diaminotetrazole. Heating rate, 10 K min^{-1}; nitrogen, 60 ml min^{-1}.

stable solid residues are formed, which ultimately decompose at temperatures above 900 K.

The major gaseous product for both MAT and DAT is nitrogen, as shown by mass spectrometry. For MAT, hydrogen cyanide and hydrogen azide were also present in considerable amounts, as indicated by IR and mass spectrometry. In addition, propane and methylamine were detected as minor products in the mass spectra of the degradation products of MAT. In the gaseous products of DAT, the presence of HCN and ammonia was observed by both IR and mass spectrometry.

Figures 4 and 5 (curves (a)) show IR spectra of the original MAT and DAT, respectively. Both have characteristic absorptions of their parent compound, 5-aminotetrazole [1]. In the region of ν(NH), MAT has two strong bands at 3320 and 3150 cm^{-1}, whereas DAT has three bands at 3325, 3240 and 3160 cm^{-1}. The bands of MAT and DAT at 3150 and 3160 cm^{-1},

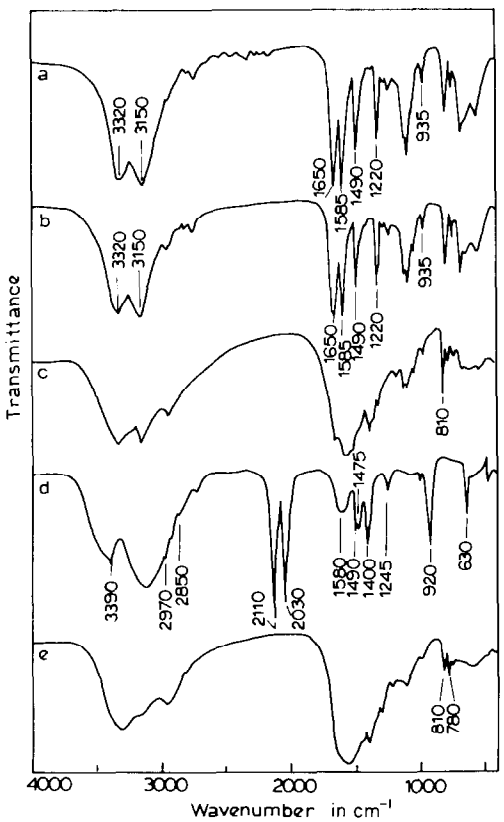


Fig. 4. IR spectra of 1-methyl-5-aminotetrazole and of the products of its thermal decomposition recorded in KBr pellets: curve a, original material; curve b, high boiling point products condensing in the lower ring; curve c, high boiling point products condensing in the middle ring; curve d, high boiling point products condensing in the upper ring; curve e, solid residue of thermal decomposition.

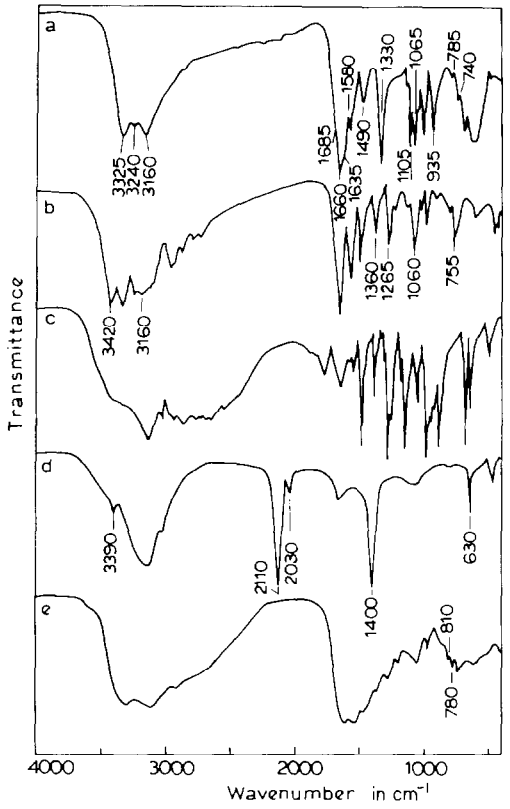


Fig. 5. IR spectra of 1,5-diaminotetrazole and products of its thermal decomposition recorded in KBr pellets. Spectra as in Fig. 4.

respectively, lie far removed from the region of amine NH stretching [9, 11], even taking into consideration the possibility of band shifts due to hydrogen bonding [12]. Indeed, on recording the spectra of DAT between 100 and 440 K, there is only a 13 cm^{-1}, shift for this band which is typical for weak H-bonding.

In the case of 5-aminotetrazole, it was shown [1, 4] that ν(NH) in the >NH ring group is lowered to 3200 cm^{-1}. The presence of the substituents on the ring might be responsible for the further decrease in ν(NH) to 3150 cm^{-1} for MAT and 3160 cm^{-1} for DAT. We did not record spectra of MAT at low and high temperatures, as for DAT, but it seems likely that both the initial MAT and DAT have >NH groups in the ring. These groups can be derived from their tautomeric forms, **I** or **III** (eqn. (1)).

The bands of DAT at higher wavenumbers (3325 and 3240 cm^{-1}) also change their position with decreasing or increasing temperature. Therefore, all the NH bonds of DAT and probably of MAT are influenced by hydrogen bonding [9]. Moreover at 100 K, DAT shows additional bands at 3315 and 3290 cm^{-1}.

The strong bands at 1650 cm^{-1} for MAT, and at 1660 and 1635 (shoulder) cm^{-1} for DAT, can be attributed to NH_2 deformation [1, 9, 11, 12]. These two bands for DAT decrease in wavenumber with increasing temperature, which is an additional indication of the participation of NH_2 groups in hydrogen bonding.

Nevertheless, in this region, DAT also has a band at 1685 (shoulder) cm^{-1}, the position of which does not depend on the temperature, which rules out its involvement in hydrogen bonding. The band can probably be attributed to ν_{exo}(C=N), which is possible in the imino form (**III**) but not in the amino form (**II**). The C–N_{exo} stretching is detectable only in the spectrum of MAT at 1220 cm^{-1}. Absorptions at 1585 and 1490 cm^{-1} for MAT and at 1580 and 1490 cm^{-1} for DAT, are probably the two modes of ring stretching due to out-of-phase and in-phase ν_{endo}(C=N) respectively, [9, 13].

Both compounds under study show a strong absorption at 1330 cm^{-1} (Figs. 4 and 5, spectra (a)) which is due to semicircle stretching of the tetrazole ring [9]. Three bands of medium intensity in the region 1110–1000 cm^{-1}, which are present in the spectra of MAT and DAT, are probably pseudo-alternating and radial stretching modes of the ring [9, 11]. We also cannot exclude the possibility of absorption in this region due to δ(NH) of the tetrazole ring.

The band of medium intensity at 935 cm^{-1} in the spectrum of DAT (Fig. 5, spectrum (a)) is very sensitive to a decrease in temperature. In the spectrum obtained at 100 K, this band is shifted to 950 cm^{-1}. It is probably due to a wagging of associated >NH · · · H of the tetrazole rings [11]. Moreover, both MAT and DAT show absorptions due to NH_2 wagging in the region 670–800 cm^{-1}.

The high boiling point products of MAT and DAT thermolysis which condense on the water-cooled part of the TVA apparatus, form three rings at different levels on the wall of the glass ampoules. The IR spectra of the lower ring, where the least volatile products condense, are shown in Fig. 4 (spectrum (b)) for MAT and in Fig. 5 (spectrum (b)) for DAT. In the case of MAT, the IR spectra of the initial substance and of the lower ring (spectra (a) and (b) in Fig. 4) are practically identical. This means that, on heating, some of the original MAT evaporates without decomposition.

In contrast, DAT shows significant changes between spectra (a) and (b) (Fig. 5). However after recrystallization of the lower ring product of DAT from acetone, its IR spectrum becomes identical to the original DAT. Moreover, its thermogravimetry is very similar to the TG curve of the original DAT. This shows that DAT undergoes reversible structural changes on evapoaration and condensation.

The changes affect mainly the groups containing N–H bonds (Fig. 5, spectra (a) and (b)). An intense new band at 3420 cm^{-1} appears in the region of ν(NH) of –NH_2 groups. The band at 3160 cm^{-1}, which was

attributed to ν(NH) of the tetrazole ring, is broadened and its intensity considerably decreased. Instead of two weak bands at 785 and 740 cm^{-1} (Fig. 5, spectrum (a)), there is one intense band at 755 cm^{-1} (Fig. 5, spectrum (b)) in the region of NH_2 wagging. The wagging band of associated $>NH \cdots H$ of the tetrazole ring disappears completely in the evaporated DAT. Considerable changes are also observed in the region of 3100–2500 cm^{-1}, where there is a series of broad bands caused by the associated N–H stretching [11, 12].

The bands attributed above to the absorptions of the tetrazole heterocycle of DAT, also shift their position and change in intensity in the evaporated sample (Fig. 5, spectra (a) and (b)). Instead of the doublet at 1105 and 1065 cm^{-1}, a singlet band is observed at 1060 cm^{-1}. However, instead of the absorption at 1330 cm^{-1} which was assigned to semicircle stretching of the tetrazole ring in the evaporated sample, two bands at 1360 and 1265 cm^{-1} are observed. The last band can probably be assigned to ν_{exo}(C–N) [9, 11, 12].

The character of the changes of the IR spectra on evaporation and condensation is similar to that previously observed and discussed for 5-aminotetrazole [1]. Probably, as in the case of 5-aminotetrazole, at room temperature, solid state DAT coexists in both amino and imino forms and on heating (melting, evaporation) the tautomeric equilibrium is shifted towards the amino form. However, it is difficult to draw this conclusion about the existence and shift of such an equilibrium for MAT from the comparative analysis of the initial (Fig. 4, spectrum (a)) and condensed (Fig. 4, spectrum (b)) IR spectra. However, the possible existence of the imino form of MAT cannot be excluded.

The IR spectra of the products of decomposition of MAT and DAT which are more volatile and condense in the middle ring, are shown in Figs. 4 and 5 (spectra (c)) respectively. From its characteristic absorptions at the 3350–3100 cm^{-1} and 1650–1500 cm^{-1} regions, as well as the band at 810 cm^{-1} (Fig. 4, spectrum (c)), *N,N',N''*-trimethylmelamine [13] has been identified in the middle ring of the volatile products of MAT. In the case of DAT, the IR spectrum of the product of the middle ring (Fig. 5, spectrum (c)) is identical to the IR spectra of 1,2,4-triazole [14].

In the thermal decomposition of MAT, a mixture of products condenses in the upper ring (Fig. 4, spectrum (d)). One component of the mixture is ammonium azide (3390, 2110, 1400 and 630 cm^{-1}) [15]. The intense absorption at 2030 cm^{-1} suggests an excess of free N_3^- [16], probably from HN_3, which can also condense in this ring (b.p. 37°C) [17]. Additional bands at 2970, 2850, 1580, 1490, 1475 and 1245 cm^{-1} might be due to the absorption of $CH_3NH_2HN_3$ [9, 11, 12]. The medium-intensity absorption at 990 and the strong band at 920 cm^{-1} shown in Fig. 4, (spectrum (d)) cannot be reliably assigned at this stage of our investigation. In the case of DAT,

only ammonium azide (Fig. 5, spectrum (d)) is found in the upper ring of the high boiling point products.

The thermal decomposition residues after the first stage of weight loss (Fig. 3) for both aminotetrazoles under study, have IR spectra (Figs. 4 and 5, spectra (e)) similar to those of the products of thermal decomposition of 5-aminotetrazole, showing characteristic absorptions (3400–3100, 1670–1350, 810 and 780 cm^{-1}) of condensed crosslinked melamine derivatives [1, 18]. They probably consist of crosslinked structures with –NH– or –NR– bridges which are the products of interaction between, 1,3,5-triamino-s-triazines formed by degradation of MAT and DAT. The residues are thermally stable on further heating to 900 K (Fig. 3).

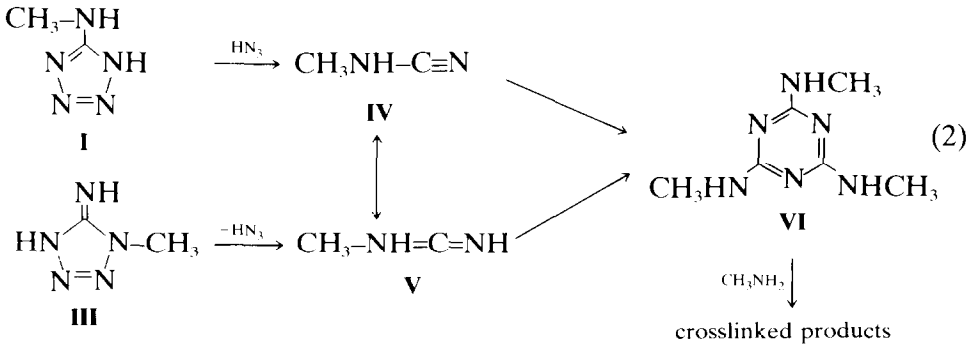
We have calculated the dependences of the apparent activation energy E_α on the degree of decomposition α of MAT and DAT using the Ozawa isoconversion method [19] (Fig. 6, curves (a) and (b), respectively). Three sections can be distinguished in both curves: the initial section up to $\alpha = 0.15$ where the activation energy decreases; the middle section $0.15 < \alpha < 0.8$ where the activation energy remains unchanged and is about 175 kJ mol^{-1} for both MAT and DAT; and, finally, the third section $\alpha > 0.8$ where the activation energy decreases.

DISCUSSION

Both 1-methyl-5-aminotetrazole and 1,5-diaminotetrazole give several gaseous and high boiling point products in the first step of their decomposition. Moreover, the dependence of the activation energy of the degree of decomposition at this stage (Fig. 6) is complex. Thus we can assume that the decomposition of MAT and DAT, even at the beginning, goes through several (parallel or successive) chemical processes.

A recent review [20] showed that nitrogen or hydrogen azide/organic azides are the primary products of tetrazole decomposition. The thermal decomposition of 1,5-disubstituted tetrazoles, in particular, is accompanied, as a rule, by elimination of only nitrogen as a volatile product. In the case of MAT and DAT, we also found hydrogen azide. It is evident (see eqn. (1)) that the opening of the MAT and DAT rings with elimination of hydrogen azide is only possible in the tautomeric forms **I** and **III** which have a proton in position 4 of the tetrazole ring.

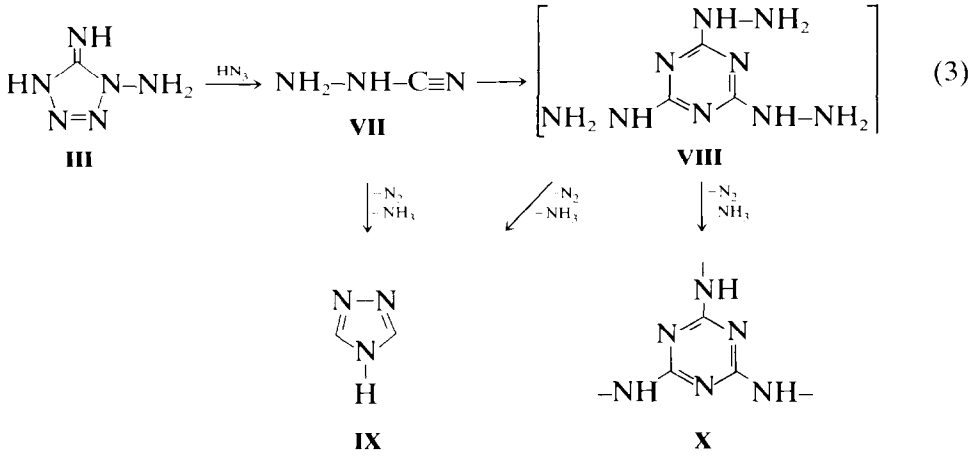
In the case of MAT, the transfer of proton can be due to the isomerization to 5-methylaminotetrazole occurring on heating. However, the concentration of 5-methylaminotetrazole in MAT treated at 460–467 K, according to the data of Henry et al. [6], does not exceed 4.2%. Because hydrogen azide is one of the major products of MAT decomposition, it seems that the imine form which is probably present in the initial sample also contributes to the elimination of HN_3



(2)

Methylcyanamide **IV** or methylcarbodiimide **V** which remains after evolution of HN_3 are likely to undergo in situ cyclotrimerization, as was shown previously for cyanamide and carbodiimide in the case of 5-aminotetrazole [1]. We found *N,N',N''*-trimethylmelamine **VI** in the middle ring of the high boiling point products but did not detect the presence of **IV** or **V**. By analogy, trimethylmelamine **VI** is likely to condense to melamine [18] giving crosslinked products. Methylamine, which would be eliminated in this reaction, has indeed been identified by mass spectrometry in the gaseous degradation products.

In the case of DAT, as shown above, the imino form **III** is present in the initial substrate. It is probable that this form undergoes decomposition with evolution of NH_3



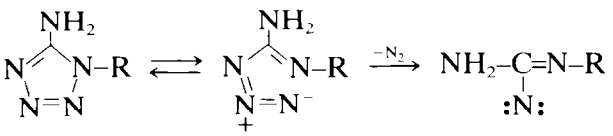
(3)

In contrast to MAT, in the thermal decomposition of DAT, the trimerization product of aminocyanamide **VII**, *N,N',N''*-triaminomelamine **VIII**, was not detected. Instead, 1,2,4-triazole **IX** condenses in the middle ring of the high boiling point products. Perhaps the product **VIII** only forms as an intermediate because it is unstable at the high temperatures at which

the decomposition of DAT occurs. For instance, it is known from the literature [21, 22] that *N,N',N''*-triaminomelamine is not formed in the reaction of triazine with hydrazine hydrochloride. Moreover, triazine ring-narrowing with formation of 1,2,4-triazole was observed [21, 22]. At this stage of our investigation, we cannot exclude the possibility that 1,2,4-triazole **IX** is formed directly from aminocyanamide **VII**.

In the solid residue of DAT, triazine structures crosslinked by –NH– bridges **X** were identified. The data obtained enable us to propose the two parallel decomposition routes of the intermediate **XIII** shown in eqn. (3).

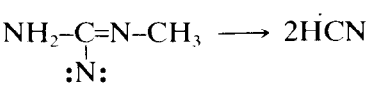
The other possible route of MAT and DAT degradation which is operative for many 1,5-disubstituted tetrazoles [20] involves scission of the N1–N2 bond of the tetrazole ring with formation of an intermediate non-cyclic form, azidoazomethine **XI**



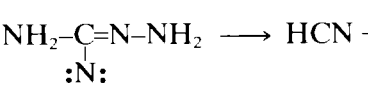
XI **XII**

where R is $-NH_2$, $-CH_3$ (4)

This form of aminotetrazole **XI** is unstable and decomposes with elimination of nitrogen. Nitrene **XIII** which is the product of this reaction is also likely to decompose to hydrogen cyanide and ammonia in the case of MAT (eqn. (5a)) and to hydrogen cyanide, ammonia and nitrogen in the case of DAT (eqn. (5b))

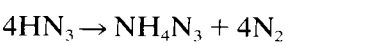


(5a)



(5b)

It was shown above that nitrogen prevails among the gaseous products of decomposition of the investigated 5-aminotetrazoles. In addition to reactions (4) and (5b), nitrogen might be produced in the course of decomposition of hydrogen azide [23]



(6)

This reaction is exothermic and its contribution to the overall exothermocity of the degradation as measured by DSC depends on the hindrance of HN_3 elimination from the sample pan. The results of the DSC experiments shown in Figs. 1 and 2 probably provide evidence in favour of this assumption.

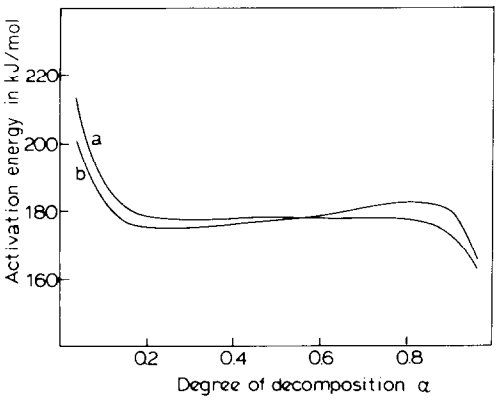


Fig. 6. Dependence of the activation energy on the degree of decomposition of (curve a) 1-methyl-5-aminotetrazole and (curve b) 1,5-diaminotetrazole.

The dependences of the activation energy on the degree of decomposition obtained for MAT and DAT (Fig. 6, curves (a) and (b)) confirm that the thermal decomposition of both aminotetrazoles at the stage of heterocycle cracking is a complex process, including several competing reactions. The similar shape of the curves for the both compounds suggest a similiar decomposition mechanism, or at least similar limiting stages. Because the activation energy values in the middle section ($0.15 < \alpha < 0.8$) of MAT and DAT thermolysis (175 kJ mol^{-1}) are comparable with the activation energy of 5-iminotetrazole thermolysis (165 kJ mol^{-1}) [1], it may be presumed that the elimination of HN_3 from the imino form **III** is a limiting stage in this section. In contrast to 5-aminotetrazole [1], in the case of MAT and DAT, the thermal decomposition might only be limited by the evolution of nitrogen (eqn. (4)) in the later stages of thermolysis ($\alpha > 0.8$).

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