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Thermal decomposition of aminotetrazoles.
Part 1. 5-Aminotetrazole

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Abstract

The thermal decomposition of 5-aminotetrazole (5-AT) has been studied by thermogravimetry, thermal volumometry, DSC, DTA and EGA. Solid products of thermal decomposition have been identified by IR spectroscopy and gaseous products by IR and mass spectrometry. Theoretical considerations of thermodynamic characteristics and energies of atomic bonding in the 5-AT tautomeric forms and intermediates have been carried out by the MO SCF method in the MNDO approximation. On the basis of IR and available literature data it is shown that dehydrated 5-AT exists mainly in the imino form in the solid state. Thermal treatment leads to increasing content of the amino form. The thermal decomposition of the imino form of 5-AT starts just after melting and results in hydrogen azide and carbodiimide. The linear polymer of carbodiimide and melamine derivatives have been identified in the solid residue. Further increase of temperature in the course of linear heating leads to another route of thermal decomposition involving the amino form of 5-AT accompanied by the evolution of nitrogen. Apparent activation energies of these routes determined from non-isothermal thermogravimetric data amount to 165 and 135 kJ mol^{-1}, respectively.

INTRODUCTION

The 5-aminotetrazole (5-AT) is a commercially available derivative of tetrazole. It contains more than 80 wt% of nitrogen, is thermally stable and nonexplosive. Therefore 5-AT is a prospective material for the generation of gases at high temperatures.

The thermal decomposition of the 5-AT has been studied by Reimlinger [1]. Hydrogen azide was found among the gaseous products and hydrazonium azide ($N_2H_4 \cdot HN_3$) among the solid products of decomposition. The

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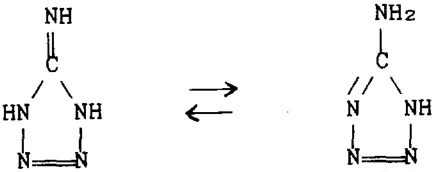
author did not identify cyanamide in the condensed products but the proposed scheme of thermolysis assumed the formation of this substance.

The electron impact-induced fragmentation of 5-AT in the ion source of a mass spectrometer was studied by Brady [2] and surveyed by Shurukhin et al. [3]. Two routes for the fragmentation of the 5-AT molecule were proposed: splitting to cyanamide and hydrogen azide and eliminaton of nitrogen with formation of the metastable fragment CH_3N_3.

The high interest of the study of thermal decomposition of 5-AT is caused by a tautomerism of the substance. There are contradicting points of view in the literature [4] on the amino–imino tautomerism of 5-AT.



(Ia) (Ib)

The presence of 5-iminotetrazole (5-IT) (**Ia**) in the solid state was identified by IR spectroscopy in ref. 5–7. In contrast, Murphy and Picard [8] analysed the melting points and UV and IR spectra of some alkyl derivatives of 5-AT in the solid state and explained the existence of $C{=}N_{exo}$ absorption by the resonance of structures with division of charges. In contrast, a prototropic 1H ↔ 2H tautomerism is usual for 5-substituted derivatives of tetrazole [4].

The present investigation was undertaken to study the mechanism and kinetics of the thermal decomposition of 5-AT. Great attention was paid to the role of tautomerism in this process.

EXPERIMENTAL

Material

A commercial sample of 5-AT twice recrystallised from water and dried at 375 K under vacuum 0.1 kPa ($T_{melt.} = 476$ K) was used.

Thermal analysis

The thermal degradation was carried out either under nitrogen flow (60 $cm^3\ min^{-1}$) on a Du Pont Thermal Analyser 2100 fitted with a differential scanning calorimetry cell 901 (DSC) and thermogravimetric analyser 951 (TG), or under self-generated atmosphere in hermetic steel holders using a derivatograph OD-102 (Paulik–Paulik–Erdey). Some DSC experiments were done under nitrogen at 4 MPa. Thermal volumometric analysis (TVA) was carried out on a thermal volumometer DAGV-70-2M in glass ampoules under argon [9]. The TG and TVA experiments were carried out at different heating rates from 0.63 to 40 K min^{-1}.

Identification of degradation products

A solid residue and volatile products condensable on the walls of the ampoules cooled by running water were collected at different steps of decomposition. Gaseous products were collected either by cooling the output gas flow in a U tube at 77 K in TG or by decomposition of 5-AT in hermetic ampoules under argon at 10 Pa. An identification of the solid products from the TG experiments was carried out by FTIR at room temperature in KBr pellets. The gaseous products obtained in the hermetic ampoules were analysed by a Varian MAT-311 mass spectrometer and those obtained in the gas output of TG were analysed by FTIR coupled with gas chromotography. Evolution of gases of an acidic or alkaline nature was studied by coupling thermogravimetry to evolved gas analysis (EGA). Volatile gaseous products were monitored by changing the conductivity of a 0.1 N NaOH or 0.1 N H_2SO_4 aqueous solution respectively into which the stream of the thermobalance output was bubbled.

Calculations

An activation energy at different steps of decomposition was calculated from TG and TVA data by the Ozawa method [10]. An electronic and geometric structure of the tautomeric forms of 5-AT was estimated by the semiempirical MO SCF method in the MNDO approximation [11], which allowed us to calculate the electron density distribution, the geometry and the energetic characteristics of tetrazole derivatives with sufficient accuracy [12,13].

RESULTS

Thermal analysis

5-AT starts to decompose just after melting at 480 K at a heating rate of 10 K min^{-1}. Figure 1, curve a shows the TG curve of the 5-AT thermal decomposition. About 50% of mass is lost at the first step of degradation in the temperature interval 480–540 K. Degradation is completed at 1000 K (100% mass loss). The EGA curves (Fig. 1, curves b and c) show three steps of evolution of acidic gases (curve b, at 520, 800 and 990 K) and one broad peak (curve c, at 620 K) of evolution of alkaline gases.

Unlike tetrazole [9] 5-AT, having a high positive standard enthalpy of formation [14], decomposes in an open holder practically without heat evolution. Figure 2, curve a shows a small exothermic peak (495 K) just

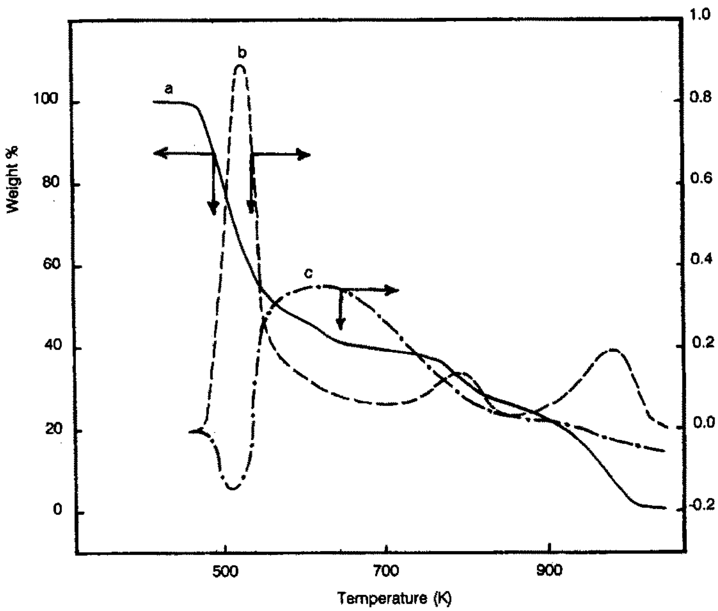


Fig. 1. TG (%) (curve a), and rate of evolution of acidic (curve b) and akaline (curve c) gases in arbitrary units; curves of 5-AT thermal decomposition under nitrogen at a heating rate of 10 K min^{-1}.

after a deep endothermic one (488 K). However, the DTA curve (Fig. 2, curve b) of 5-AT thermal decomposition in a hermetic holder under self-generated atmosphere has a very strong exothermic peak in the tem-

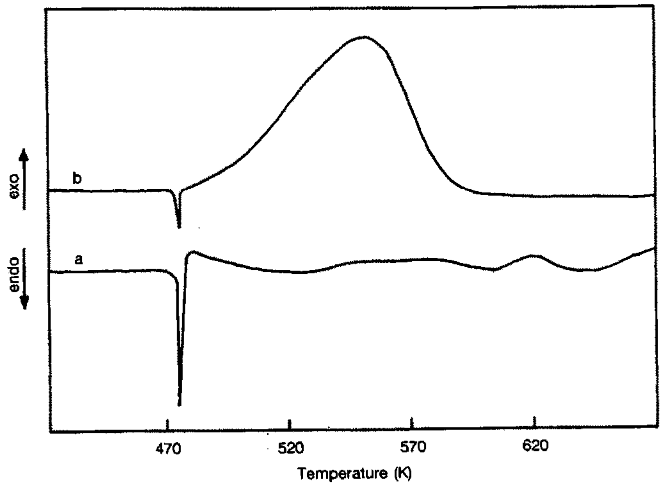


Fig. 2. DSC (curve a) under nitrogen and DTA (curve b) under self-generated atmosphere of 5-AT. Heating rate is 10 K min^{-1}.

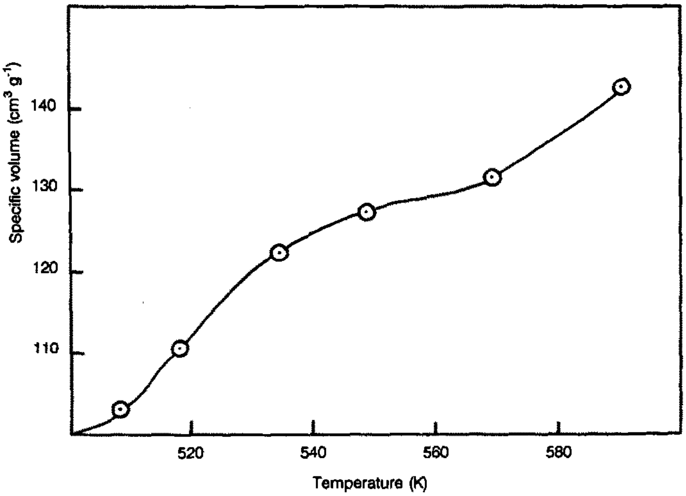


Fig. 3. Dependence of specific volume of evolved gases on temperature of 5-AT semitransformation at the first step.

perature interval 490–600 K. The endothermal decomposition of 5-AT cannot be explained by partial evaporation of 5-AT from the open holder in the DSC cell, because additional experiments in a high pressure cell (4 MPa of nitrogen) did not change the shape of the curve in Fig. 2, curve a. In our opinion, such different behaviour of 5-AT in the open and hermetic holders is due to the removal from the open holder of volatile products having very high enthalpies of formation.

The volume of evolved gases from the thermal decomposition of 5-AT depends on the heating rate, i.e., and on the temperature interval where the decomposition is observed. Figure 3 shows the dependence of the specific volume of evolved gases measured in dynamic volumometric experiments on the temperatures of the end of the first step of 5-AT decomposition. An increase of the temperature by 90 K leads to an increase of the specific volume of about 45%. In contrast, the mass loss in the first step is practically independent of the heating rate.

Analysis of evolved gases

The FTIR of the gaseous products collected after the first step of decomposition shows the absorption bands at 2155, 2125, 1165 and 1140 cm^{-1} that are typical hydrogen azide (HN_3). The mass spectrum (Fig. 4) besides the characteristic fragments of HN_3 ($m/z = 15$ (NH^+), 29 (N_2H^+), 42 (N_3^+) and 43 (HN_3^+) also has a strong peak of N_2 ($m/z = 28$). The N_2 can be formed by electron impact fragmentation of HN_3 or by thermal decomposition of 5-AT.

Study of thermally induced tautomerism

To study a possible tautomeric transformation of 5-AT, the sample was heated either to melting point 478 K and rapidly quenched to room temperature (IR of Fig. 5, curve b), or to evaporation under vacuum (1 Pa) in the apparatus (IR of condensed product, Fig. 5, curve c). Heating and quenching of 5-AT proceeded without mass loss or evolution of gases but IR spectra (compare Figs. 5, curve a, b and c and see also Table 1) changed noticeably. Two strong bands at 3485 and 3380 cm^{-1} and the medium band at 3280 cm^{-1} characteristic for ν_{NH} absorptions in the initial sample (Fig. 5, curve a) become weaker in the melted and quenched sample (Fig. 5, curve b) and disappear completely in the evaporated sample (Fig. 5, curve c). Instead, two strong bands at 3420 and 3350 cm^{-1} (Fig. 5, curve c) appear. Significant changes of absorption in the region 3080–2510 cm^{-1} of partially ionised ν_{NH} due to H bonding and in the region 775–740 cm^{-1} of δ_{NH} rocking were also detected after melting or evaporation of 5-AT. These data prove that transformation of N–H-containing groups occurs due to the thermal treatment described above.

Furthermore the absorptions belonging to ν_{C-N} and $\nu_{C=N}$ also change. The strong bands at 1680 cm^{-1} ($\nu_{exo=N}$) and the comparatively weak bands at 1590 cm^{-1} ($\nu_{endoC=N}$) and at 1265 cm^{-1} (ν_{exoC-N}) (Fig. 5, curve a and Table 1) probably indicate the presence of the imino form in the initial sample. The band of $\nu_{exoC=N}$ at 1680 cm^{-1} decreases and bands of $\nu_{endoC=N}$ and ν_{exoC-N} at 1264 cm^{-1} increase in Fig. 5, curves b and c. Strong absorptions of δ_{NH} at 1655 and 1640 cm^{-1} become evident in the spectrum of the sample after melting (Fig. 5, curve b) and increase in the sample after evaporation (Fig. 5, curve c). Instead of one characteristic absorption

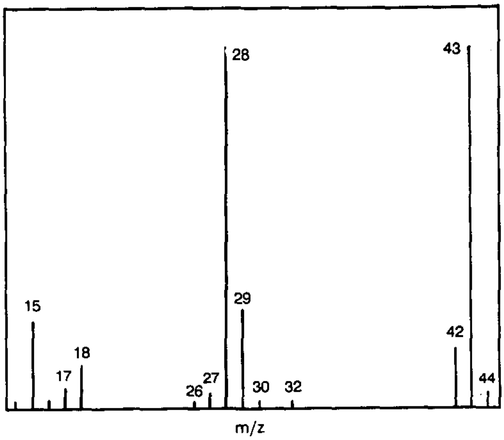


Fig. 4. Mass spectrum of gaseous products.

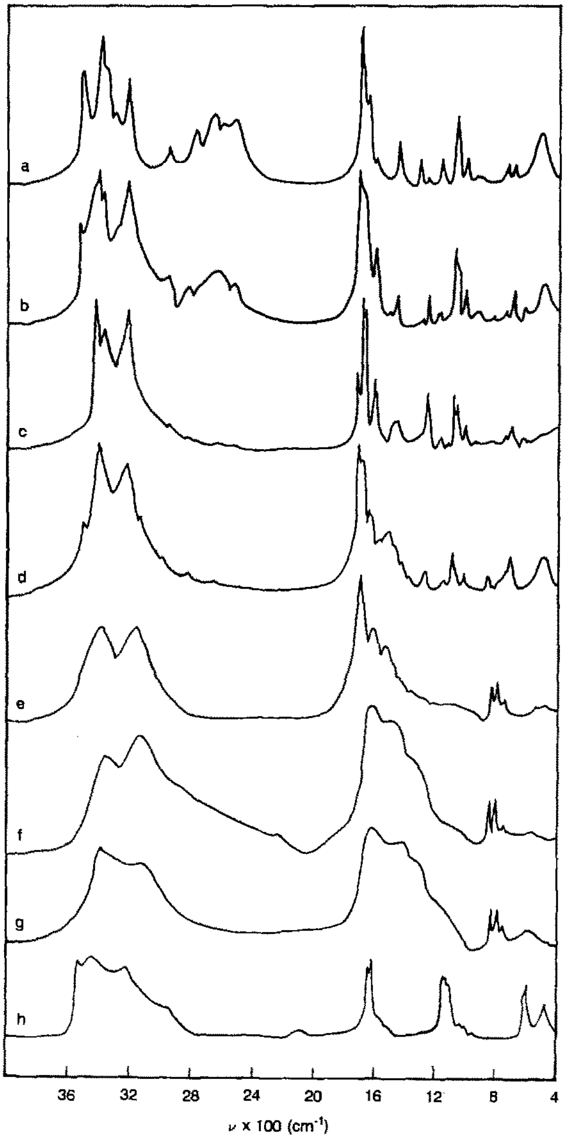


Fig. 5. Infrared spectra (KBr pellets) of 5-AT: initial dehydrated 5-AT (curve a); melted and quenched (curve b); evaporated under vacuum (curve c); residue at 25% mass loss (500 K) (curve d); residue at 50% mass loss (540 K) (curve e); residue at 670 K (curve f); residue of thermal decomposition of 3,5,7-triamino-s-triazole[4,3-a]-s-triazine (670 K) (curve g); fraction of 5-AT residue soluble in DMSO (670 K) (curve h).

of the tetrazole ring at 1070 cm^{-1} (Fig. 5, curve a) we found two bands at 1070 and 1050 cm^{-1} in the thermally treated sample (Fig. 5, curves b and c).

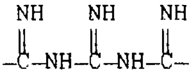
The above data show that in the initial dehydrated sample, mainly the imino form (**Ia**) of 5-AT is present. The melting or evaporation of the sample results in an increase of the content of the amino form.

Analysis of condensed products

The residue of the first step of degradation of 5-AT (550 K, Fig. 1) is a light yellow product which remains at the bottom of the ampoule of the volumometer and is partially soluble in DMSO. The residue decomposes in three steps on further heating: 610, 790 and 975 K (Fig. 1).

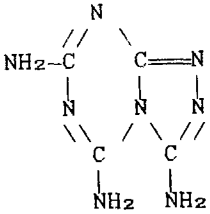
Figure 5, curve d, e and f show IR spectra of a nonvolatile product collected in the bottom of the ampoule at different steps of 5-AT thermal decomposition. From the Fig. 5, curve e and assignments listed in Table 1 it is clear that absorption of the tetrazole ring (3200, 1455, 1160, 1070, 1000 and 915 cm^{-1}) disappear at 540 K where mass loss is about 50%. The absorptions at 1570, 1525, 1420, 1360 and 810 cm^{-1} of the 1,3,5-s-triazine ring (melamine) start to appear at the initial stage of 5-AT thermal decomposition at 500 K (Fig. 5, curve d). The residue at 540 and 670 K also shows characteristic bands of melamine and its condensed forms (melem, melam [22]) at 1360 and 1240 cm^{-1}. Besides these absorptions the band at 780 cm^{-1} characteristic for isotriazine structures [26] is detected at 540 and 670 K. At high temperature (above 670 K) the absorptions of carbodiimide groups at 2170 and 1590 cm^{-1} become noticeable.

The IR spectrum of the part of residue which is insoluble in DMSO does not differ from the spectrum of the residue obtained at 540 K (Fig. 5, curve e). The spectrum of the soluble part (Fig. 5, curve h) shows strong absorptions at 3550 and 3420 cm^{-1} which are likely to be due to ν_{NH}. The strong band at 1635 cm^{-1} is assigned to δ_{NH}, that at 1615 cm^{-1} to $\nu_{C=N}$ and at 1140 cm^{-1} to ν_{C-N} [14,15]. This product is likely to consist of polymeric chains with the structure



$$-\overset{\overset{NH}{\|}}{C}-NH-\overset{\overset{NH}{\|}}{C}-NH-\overset{\overset{NH}{\|}}{C}- \qquad (III)$$

which can be formally derived from carbodiimide polymerisation. To study the structure of the nonvolatile residue, the 3,5,7-triamino-s-triazolo [4,3-a]-s-triazine



(IV)

was synthesised by the method described in ref. 26. A small mass loss due

TABLE 1

Infrared absorptions and assignments of 5-AT, thermally treated 5-AT and its products of thermal decomposition

Wave numbers (cm^{-1})	Intensity of bands [a]						Assignments	References
	Initial	Melted	Evaporated	Residue 500 K	Residue 540 K	Residue 670 K		
3485	st	m		sh			ν_{NH}	15, 16
3420		sh	st					
3380	st	st		st				
3350	sh	st	st		st			
3320						st		
3280	m	sh						
3200	st	st	st	st			$\nu_{NH\text{ of tetrazole ring}}$	5, 7
3160					st			
3100	Series of absorptions of medium and weak intensity						$\nu_{NH\text{ of ionized forms}}$	15, 16
2500								
2170							$\nu_{N=C=N}$	15,16
1680	st	st	m	st			$\nu_{exoC=N}$	8, 16–18
1655		st	st					5,16, 17
1640	st	st	st	st	st		δ_{NH}	19–21
1590	w	m	m			st	$\nu_{endoC=N}$	5, 7, 19
1570				m			$\nu_{triazine\ ring}$	22
1525				m	st			
1490		w	w	m	st		non identified	
1455	m	m	w	sh			$\nu_{tetrazole\ ring}$	5, 23
1435						st	$\nu_{triazine\ ring}$	22
1420				sh	sh			
1360				w	sh	sh		
1300	m	w		w			$\nu_{N-N=N}$	19, 24, 25
1265	w	m	m				ν_{exoC-N}	5
1240				w	sh		$\nu_{triazine\ ring,\ melam}$	22
1160	m	w		w			$\nu_{tetrazole\ ring}$	5–7, 20
1145		w	w					
1070	st	st	m	m				
1050		sh	m					
1000	m	m	w	w				
935			w					
915	w	w		w				
890			w				non identified	
835		w		w				
810				w	m	m	$\delta_{triazine\ ring}$	22
780				sh	w	m	$\delta_{isotriazine\ ring}$	26
775		w	w				$\delta_{NH\ rocking}$	5
760	w			w				
745				m	w	w		
740	w	m	m					

[a] Key: st, strong; m, medium; w, weak; sh, shoulder.

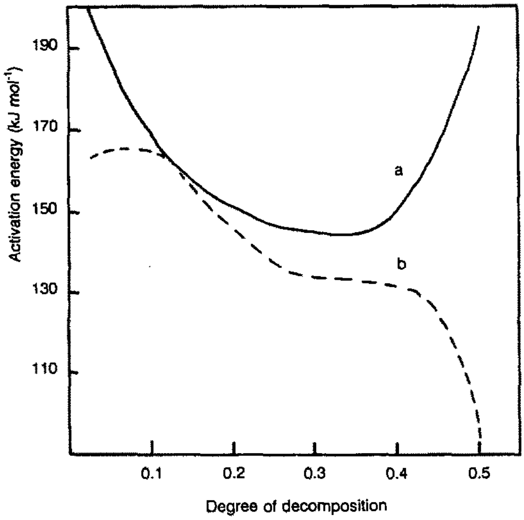


Fig. 6. Dependence of activation energy on degree of decomposition obtained from TG data (curve a) and TVA data (curve b).

to evolution of ammonia was detected on heating **IV** to 670 K. The IR spectrum of the residue of **IV** (Fig. 5, curve g) is very similar to the spectrum of the solid residue of 5-AT thermal decomposition at the same temperature (Fig. 5, curve f), showing the same characteristic bands of triazine (810 cm^{-1}) and isotriazine (780 cm^{-1}) rings. Deformation absorptions of triazole rings are masked by a strong wide band in the region 1100-950 cm^{-1}

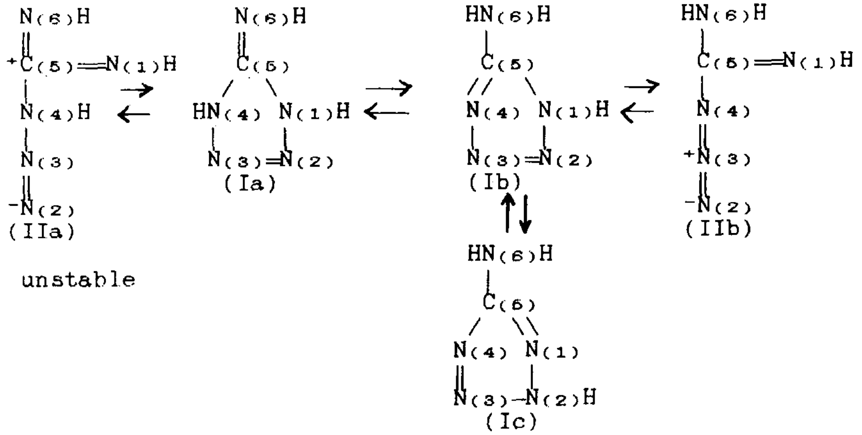
The volatile products of degradation of 5-AT condense as white crystalline substances in the form of two rings at different levels. The upper product explodes on fast heating and its IR spectrum is identical to that of ammonium azide [27]. The lower ring shows an IR spectrum identical to that of melamine [22].

Kinetic analysis

Figure 6 shows the dependence of activation energy of the first step of the thermal decomposition of 5-AT calculated by the Ozawa method from TG (Fig. 6, curve a) and TVA (Fig. 6, curve b) data. There are at least three sections in the curve obtained from TG data: at $\alpha < 0.25$, E decreases from 200 to 145 kJ mol^{-1}; at $0.25 < \alpha < 0.4$, E is approximately constant at 145 kJ mol^{-1} and at $0.4 < \alpha < 0.5$, E decreases from 145 to 195 kJ mol^{-1}. There are four sections in the curve obtained from TVA: at $\alpha < 0.1$, E is fixed at the level of 165 kJ mol^{-1}; at $0.1 < \alpha < 0.25$, E decreases from 165 to 135 kJ mol^{-1}, at $0.25 < \alpha < 0.4$, E is approximately the same at about 135 kJ mol^{-1} and at $0.4 < \alpha < 0.5$, E decreases again from 135 to 90 kJ mol^{-1}. A difference between the behaviour of the curves is due to the fact that ammonium azide and melamine condense on the surface of the ampoule in the TVA experiments and they do not contribute to the gas evolution and therefore to the estimation of E, whereas in TG experiments these products evacuate from the holder and so contribute to the kinetic curves. Nevetheless, both curves indicate the complex character of the first step ($\alpha < 0.5$) of the thermal decomposition of 5-AT.

Theoretical considerations

To obtain additional information on the possible routes of the thermal decomposition of 5-AT, different energetic parameters for closed ring and open ring structures of the amino and imino forms



and of 2-H-5-aminotetrazole were estimated by the MNDO method [9]. The calculations for the intermediate **IIa** show the instability of this form. Separate molecules of hydrogen azide and carbodiimide are more preferable. The results of calculations are collected in Table 2. It is clear that the N_1–N_2 bond is the weakest nitrogen–nitrogen bond in all the ring forms (**Ia**, **Ib** and **Ic**). Although the differences with the energies of some other

TABLE 2

Energetic parameters of tautomeric forms and intermediates of 5-AT

Substance	Energies of bonds (eV)						H_f^0 (kJ mol^{-1})	Ionization potential (eV)
	N1–N2	N2–N3	N3–N4	N4–C5	N1–C5	C5–N6		
Ia	−16.5	−22.8	−16.7	−17.7	−17.2	−24.1	291	9.63
Ib	−17.0	−21.4	−17.8	−20.2	−18.2	−17.1	215	10.78
Ic	−17.3	−17.5	−21.7	−17.0	−20.6	−17.4	241	11.08
IIb		−32.0	−19.6	−16.0	−24.4	−16.0	352	10.11

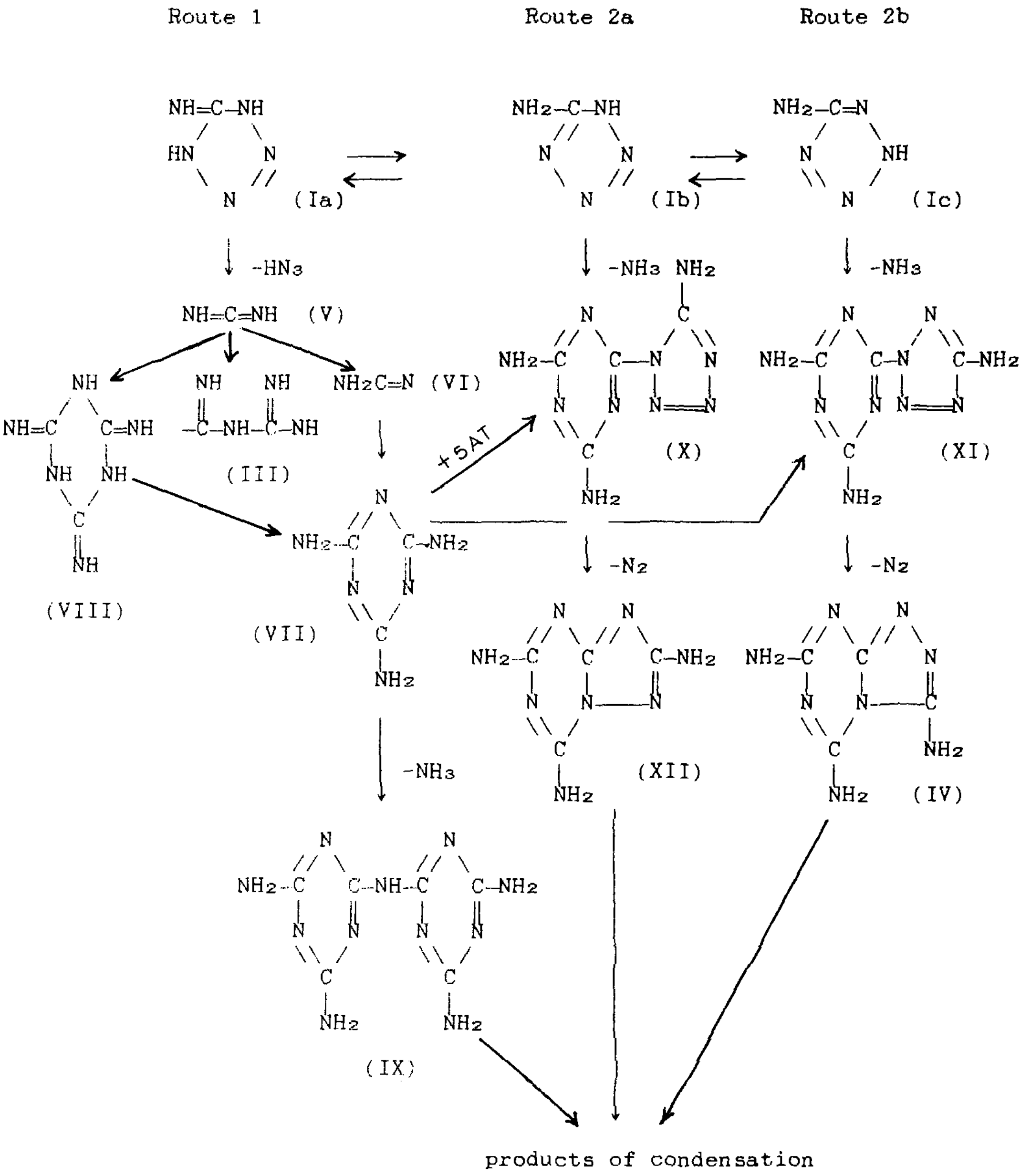
bonds are not sufficient the breaking of this bond is likely to be the first step of the thermal decomposition. The intermediate **IIb** probably eliminates a nitrogen molecule, because the energy of the N_2–N_3 bond (−32.0 eV) is close to that of a triple bond.

DISCUSSION

The initial sample of 5-AT consists mostly of the imino form. Apart from the data presented in this paper the imino form in the solid state has been identified by other researchers [5–7] using IR analysis. Ansell [28] surveyed the experimentally measured bond lengths of different tetrazole derivatives and found that the geometric structure of 5-AT determined from X-ray analysis was different from the other compounds considered because the bond lengths N_1–N_2 (1.381 Å) and N_3–N_4 (1.373 Å) of 5-AT are practically equal and look like single bonds. The bond length N_2–N_3 (1.255 Å) corresponds to a localised double bond. This is the independent confirmation of the existence of the imino form in the solid state. The thermal treatment of the initial sample, as was shown above on the basis of IR data (Fig. 5), leads to an increase of the content of the amino form **Ib**.

Because the heats of formation for the separate molecules of **Ib** and **Ic** form are less than that of **Ia** (Table 2) the equilibrium in gas phase has to shift to **Ib** and **Ic** forms. The shift is also possible in liquid phase, for example in the melt. Thus the imino and amino forms of 5-AT may coexist in the liquid phase just after melting. We also cannot exclude the prototropic tautomerism (**Ib** ↔ **Ic**) in the melt; therefore all three forms (**Ia**, **Ib** and **Ic**) of 5-AT are able to decompose under these conditions and consequently three routes of 5-AT decomposition are considered below.

Because we found the thermal decomposition just after melting it is reasonable to assume that at the initial stage some part of the imino form undergoes destruction because it is less stable than the amino form (Table 2) and its concentration in the melt is sufficient. The energies of N_1–N_2 or N_3–N_4 bonds in the **Ia** form are somewhat less than that of N_1–N_2 in the **Ib** form (Table 2), so there is a great possibility of breaking the N_1–N_2 or N_3–N_4 bonds of the imino form as during the decomposition of tetrazole [29]. The intermediate **IIa**, which can be formed upon breaking of N_1–N_2 of N_3–N_4 bonds in **Ia**, is unstable as shown by MNDO calculation and it decomposes into ammonium azide and carbodiimide **V**. Carbodiimide **V** is also unstable at high temperatures [30] and is probably inclined to isomerise into cyanamide **VI** or to polymerise. Linear polymer **III** was identified by FTIR (Fig. 5, curve h) in the solid residue. A sum of enthalpies of formation of HN_3 (264.0 kJ mol^{-1}) and cyanamide **VI** (61.2 kJ mol^{-1}) is more than the heat of 5-AT formation (207.9 kJ mol^{-1}). Therefore the thermal splitting of the 5-AT ring resulting in HN_3 and **V** can proceed endothermically (Fig. 2, curve a). If the removal of HN_3 from the holder is



impossible (experiments in hermetic holders on a derivatograph) the first step of 5-AT thermal decomposition becomes exothermic (Fig. 2, curve b) owing to decomposition of HN_3.

Cyanamide **VI** at high temperatures transforms into melamine **VII** [31] directly or through dicyandiamide formation. This reaction is exothermic and that is why the small exothermic peak at 495 K was observed on the DSC curve (Fig. 2, curve a). We also cannot exclude the possibility of trimerization of carbodiimide **V** [32] and formation of isotriazine (isomelamine **VIII**), which transforms in melamine **VII** on heating. Some amount of the melamine is sublimated from the melt, therefore melamine was found on the cooled part of the ampoule in volumometric experiments. The major part of melamine undergoes condensation with evolution of ammonia (Fig. 1, curve c). We observe the condensation reaction at temperatures 100 K lower than in refs. 23, 33, 34 because it proceeds in the melt of 5-AT. Finkel'stein [35] proved that condensation of **VII** could start at lower temperatures in the melt. The evolution of ammonia due to the condensation process starts at the end of the first step (530 K) of the 5-AT thermal decomposition (Fig. 1, curve c) and continues up to 900 K, when condensation products start to decompose. This means that all products of melamine condensation (melam, melem and melon [23,33–35]) may be obtained at different temperatures. The evolving ammonia interacts with HN_3 forming ammonium azide which was detected on the cooled walls of the ampoule

$$HN_3 + NH_3 \rightarrow NH_4N_3 \qquad (1)$$

By analogy with the aminotriazoles [26] it is also possible to assume that, besides the above condensation, the interaction of the amino form **Ib** with melamine or their products of condensation occurs in the melt. The 5-aminotetrazole-1-yl-1-(3,5-diamino)-s-triazine **X** eliminates nitrogen and results in formation of 3,5,8-triamino-s-triazole[4,3-a]-s-triazine **XII**. The substance **XII** contains an isotriazine ring that was identified in the IR spectrum (Fig. 5, curve f) of the solid residue of the 5-AT thermal decomposition. Moreover, the IR spectrum (Fig. 5, curve g) of the residue of thermal decomposition of the reference substance **IV**, which is an isomer of **XII**, is very similar to the spectrum shown in curve f in Fig. 5. The considered route is a suitable mechanism by which to explain the appearence of isotriazine structures identical to **IV**.

The possible 2-H form of 5-AT (**Ic**) probably also condenses with melamine (route 2b) giving 5-aminotetrazole-2-yl-1-(3,5-diamino)-s-triazine **XI** that undergoes splitting with elimination of N_2. The residue of decomposition is the reference substance **IV**.

Hydrogen azide starts to decompose slowly at 525 K [36]

$$HN_3 \rightarrow NH_4N_3 + N_2 \qquad (2)$$

and it produces an additional amount of ammonium azide and nitrogen. Since the temperature range of 5-AT thermal decomposition shifts to high temperatures if the heating rate increases, the contribution of the decomposition of the amino form **Ia** and thermolysis of HN_3 increase. This leads to the increase of specific volume of gases evolved in the first step (Fig. 3).

The dependence of apparent activation energy on degree of decomposition in the first step (Fig. 6) is complex. Splitting of the tetrazole ring is likely to be a limiting stage of thermal decomposition of tetrazole [9,37]. Therefore the apparent activation energy in the initial stage, including all the processes of 5-AT thermal decomposition, mainly reflects the splitting of the imino form (**Ia**). The further elimination of HN_3 from intermediate **IIa**, as MNDO calculation shows, can proceed without or with very small activation energy. The increase of degree of decomposition and simultaneous increase of temperature result in accumulation of the amino form (**Ia**) and the increasing contribution of route 2a, b to 5-AT thermal decomposition. The sections of decreasing E on curves in Fig. 6 correspond to the complex mechanism. The splitting of the amino form of the tetrazole ring (**X** → **XII**, route 2 and **XI** → **IV**, route 2b) and the other accompanying reactions probably become limiting in the interval $0.25 < \alpha < 0.4$. The further changing of E at $\alpha > 0.4$ (Fig. 6) probably reflects the kinetics of condensation of products, **VII**, **IX**, **XII** and **IV**. Ammonia evolved in these processes evacuates from the holder in TG experiments but condenses on the cooled walls of the ampoule in TVA experiments. Therefore the condensation is detected by TG and TVA in different ways.

The above considerations show that the thermolysis of 5-aminotetrazole is a complex process including at least three interdependent parallel routes. The equilibrium between amino and imino forms and the prototropic tautomerism of the substance under study determines the contribution of different routes. Therefore the mechanism of thermal decomposition of 5-aminotetrazole is dependent on temperature and heating rate.

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