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Thermal decomposition of aminotetrazoles

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Abstract

The thermal decomposition of 5-aminotetrazole (5-AT), 1-methyl-5-aminotetrazole (MAT), 1,5-diaminotetrazole (DAT), poly-1-vinyl-5-aminotetrazole (PVAT) and sodium salt of 5-aminotetrazole (SAT) have been studied by thermogravimetry, thermal volumetric analysis (TVA), DSC, DTA and evolved gas analysis (EGA). The kinetic parameters of the thermal decomposition of aminotetrazoles were calculated either by the Ozawa method or by the method of invariant kinetic parameters (IKP). The gaseous products, volatile condensed products and solid residues were identified by FTIR and gas chromatography–mass-spectrometry (GS/MS). The total energies and the energies of chemical bonds of various isomeric forms of 5-AT and MAT have been calculated ab initio using MP2/6-31G** theory level and MNDO approximation. Based on the content of products of thermal decomposition and the kinetic consideration, the mechanism of thermal decomposition of aminotetrazoles has been derived. Two routes of the splitting of tetrazole ring leading either to elimination nitrogen or hydrogen azide are suggested. The contribution of each route is changing upon the advancement of the process. It was assumed, that hydrogen azide splits out from the prothotropic forms of the tetrazole ring, which have hydrogen atoms by nitrogens in the ring. Experimental study as well as literature data on the amino-imino tautomerism are in agreement with the suggested mechanism of the decomposition of the tetrazole ring. It is shown that secondary reactions significantly extend variety of the products of thermal decomposition of aminotetrazoles.

Keywords: Aminotetrazoles; Thermal decomposition; Tetrazole ring

1. Introduction

Aminotetrazoles possess a unique combination of properties. In spite of large positive enthalpies of formation [1], they exhibit surprisingly high thermal stability [2–5]. Aminotetrazoles have the highest content of nitrogen among all organic substances (e.g. 82.3 wt.% for 5-aminotetrazole (5-AT) and 84.0 wt.% for 1,5-diaminotetrazole (DAT)). Therefore, aminotetrazoles are prospective materials for generation of gases, as blowing agents, solid propellants and other combustible and thermally decomposing systems [6,7]. The kinetics and mechanism of thermal decomposition of aminotetrazoles is of high interest. Since aminotetrazoles show the tendency to prototropic, ring-chain and mesoionic isomerization [2,3,8], the investigation seemed to be important for revealing and evaluation the role of structural factors in the thermal transformations.

Recently, we have studied the thermal decomposition behavior of tetrazole [9–11] and some aminotetrazoles

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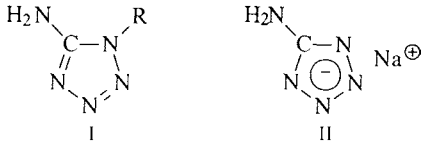
[2–4]. This paper presents an overview of the comprehensive study on kinetics and mechanism of thermal decomposition of a series of aminotetrazoles of the following structures.



I II

Which include 5-AT, (I, R = H), 1-methyl-5-aminotetrazole (MAT, I, R = CH_3), DAT, (I, R = NH_2), poly-1-vinyl-aminotetrazole (PVAT, polymer of 1-vinyl-5-aminotetrazole I, R = CH=CH_2), and 5-aminotetrazole sodium salt (SAT, II), where the tetrazole ring exists in the anionic form.

2. Experimental

Synthesis and purification of 5-AT, MAT, DAT and PVAT were described elsewhere [2–4]. The purified 5-AT was reacted with sodium ethylate at equivalent ratio in ethanol to prepare SAT. After completion of the reaction, solvent was distilled out under vacuum. The results of chemical analysis for SAT are as following.

CH_2N_5Na (107,05)	Calc.	C 11.21	H 0.019	N 65.39	Na 21.49
	Found	C 11.26	H 0.021	N 66.02	Na 21.18

The thermal decomposition of the aminotetrazoles was studied either in the sealed steel holders using derivatograph OD-102 (Paulic-Paulic-Erdey) or under nitrogen flow or under high pressure (N_2, DSC) at various heating rates on a Du Pont Thermal analyser equipped with a 901 DSC cell and a 951 thermogravimetric analyser (TG). Evolution of acidic or basic gases was monitored at the outlet of exhaust gases from the TG apparatus by using an electrical conductivity cell (evolved gas analysis, EGA). Thermal volumetric analysis (TVA) was carried out on a DAGV-70-2 M dynamic volumeter [9] in glass test-tubes under argon atmosphere at different heating rates ranging from 0.63 to 40 K min^{-1}.

Solid products of thermal decomposition were studied by FTIR (Perkin Elmer 2000) in KBr pellets. The gaseous and volatile products were analyzed using gas chromatography–mass-spectrometry (GS 5890/MS 5970, Hewlett-Packard) and FTIR. More details about collection, preparation and analysis of the products of thermal decomposition are reported elsewhere [2–4].

The activation energies at different degrees of thermal decomposition were calculated from TVA data by the Ozawa method [12]. The activation energies ($\hat{E}$) and the pre-exponent factors ($\hat{A}$) were also calculated using the method of invariant kinetic parameters (IKP) [13]. This method is based on existence of the linear relationship between the log A and E calculated from the Eq. (1) when various kinetic functions $g(\alpha)$ are used.

$$\log[g(\alpha)] = \log\left(\frac{AE}{\beta R}\right) - 0.475\frac{E}{RT_0} - 2.315 \quad (1)$$

$$\log A = aE + b \quad (2)$$

As it was shown [13], the parameters a and b in the Eq. (2) are also linearly related, when the heating rate is changed. These relationships allow eliminating the dependence of the $\hat{A}$ and $\hat{E}$ on the heating rate and selection of the kinetic function [13]. Besides the Ozawa equation, the Coats–Redfern [14] and Flynn methods [15] were used for calculations of a and b parameters. If $\hat{A}$ and $\hat{E}$ for each aminotetrazole are known, appropriate kinetic function $f(\alpha)$ can be selected by the statistical procedure described elsewhere [16].

Quantum calculations the total energies of the molecules and the energies of chemical bonds were performed ab initio using MP2/6-31G** theory level [17]. The bond energies in different isomeric forms of 5-AT were calculated by the MNDO approximation [18]. Both methods provide the reliable evaluation of the energetic parameters of the tetrazoles as well as good approximation of the relative stability of different isomeric forms [19,20].

3. Results and discussion

3.1. Thermal analysis

As thermogravimetry shows (Fig. 1), 5-AT, PVAT and SAT have two step of weight loss within the

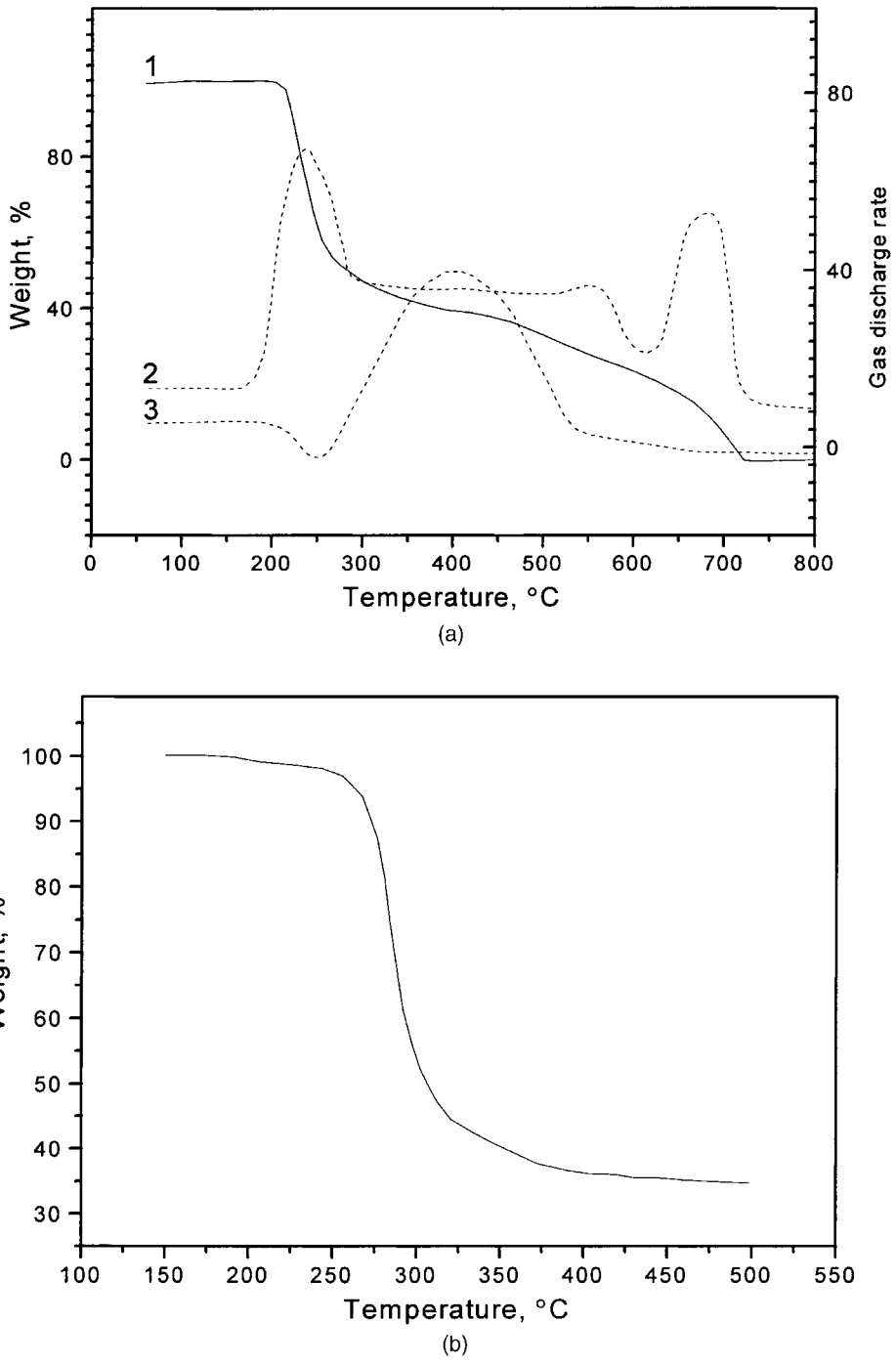
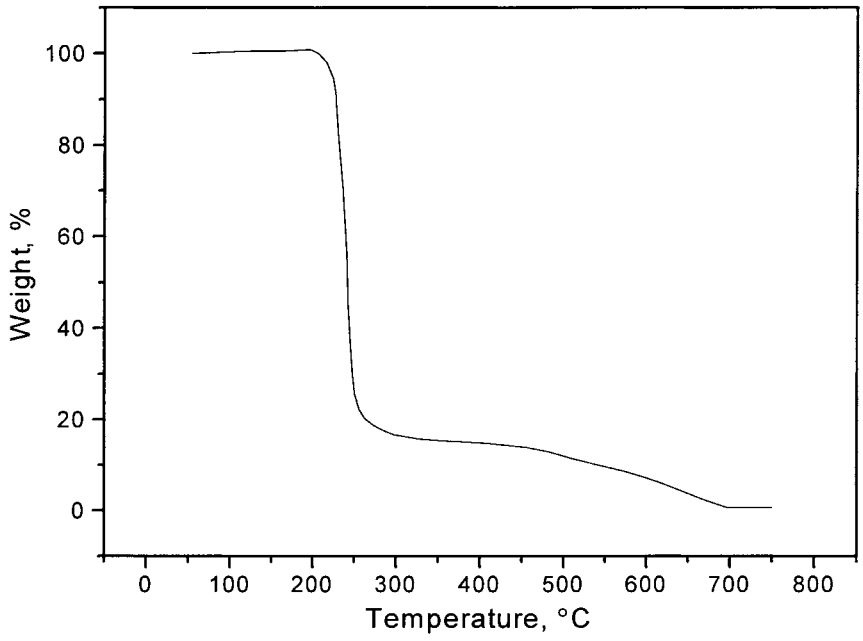
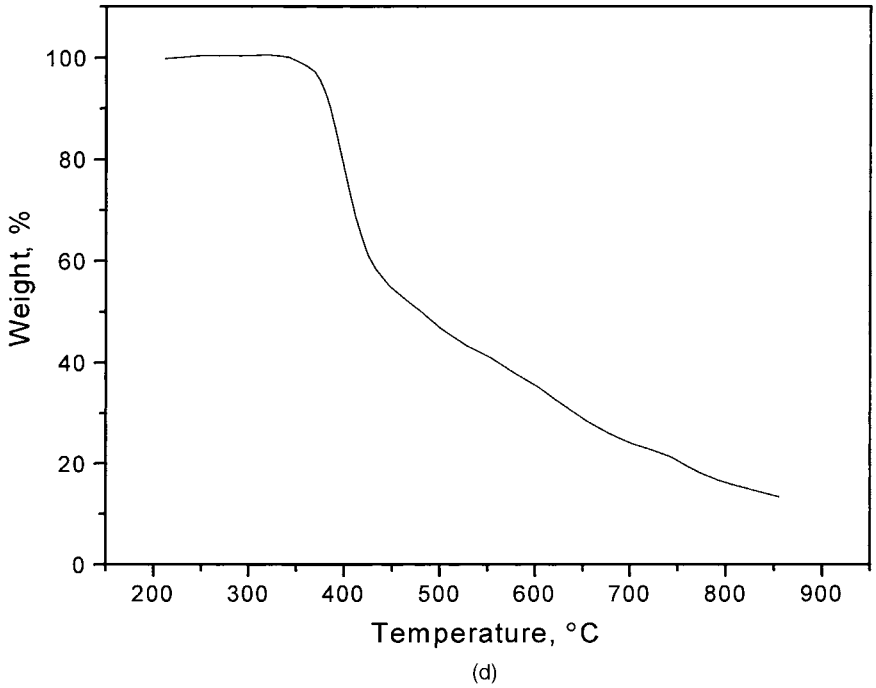


Fig. 1. TG curves of thermal decomposition of aminotetrazoles under nitrogen of 60 ml min^{-1} at a heating rate 10 K min^{-1}. (a) 5-AT: (1) TG curve; (2) rate of evolution of acidic gases; (3) rate of evolution of alkaline gases; (b) MAT; (c) DAT; (d) PVAT; (e) SAT.



(c)



(d)

Fig. 1. (*Continued*).

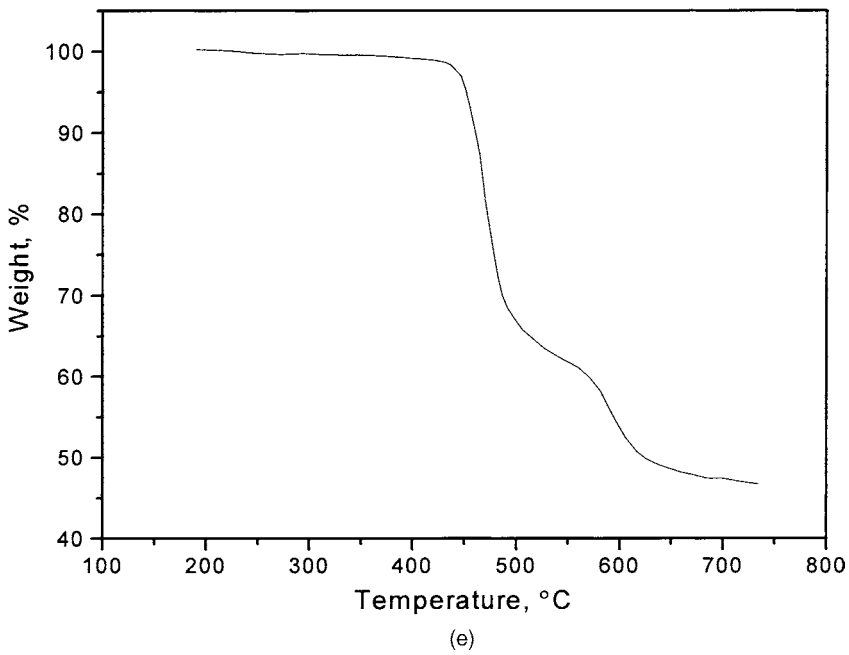


Fig. 1. (*Continued*).

temperature interval of 460–900 K, whereas, MAT and DAT decompose in one main step at 470–620 K followed by a slow weight loss till 870 K (Fig. 1). The temperature intervals, heats of decomposition, specific volumes of gas evolved and weight losses for the first step of thermal decomposition of aminotetrazoles are presented in Table 1. The decomposition of 5-AT, MAT and DAT starts right after the melting. This process is exothermal when experiments are carried out in the sealed holders or at the elevated pressures under nitrogen; the thermal effect being increased for 5-AT and MAT as the pressure raises [3]. In spite of high positive enthalpies of formations ($\Delta H^{\circ}_{f(\mathrm{gas})} = 77.42$ kcal mol^{-1} for 5-AT and 72.31 kcal mol^{-1} for MAT [1]), 5-AT, MAT and SAT decompose endothermic under nitrogen flow (Fig. 2). Such an unusual behavior can be explained by the evolution of highly energetic ($\Delta H^{\circ}_{f(\mathrm{gas})} = 63.15$ kcal mol^{-1} [21]) and readily volatile hydrogen azide (evolution from 5-AT, MAT) or the mixture of HN_3 and sodium azide (evolution from SAT). These products are being removed from the reaction zone under nitrogen flow, they partially decompose with heat evolution when decomposition proceeds under the elevated pressures but they are subjected to the complete destruction in the sealed holders. In contrast, the melting of PVAT

Table 1
Characteristic parameters for the first stage of thermal decomposition of aminotetrazoles (TG, DSC, TVA)

Compound	T_{melt} (K)	Decomposition interval (K)	$-\Delta H_{\mathrm{decomp}}$[a] (kJ mol^{-1})	Gas evolution (cm^3 g^{-1})	Weight loss (%)
5-AT	478	480–610	8.5	130	50
MAT	495	520–620	220	240	65
DAT	460	470–540	850	550	85
PVAT	–	493–615	70	250	40
SAT	–	563–635		230	35

[a] Measured in DSC experiments, heating rate: 10 K min^{-1}; pressure of nitrogen: 10 atm.

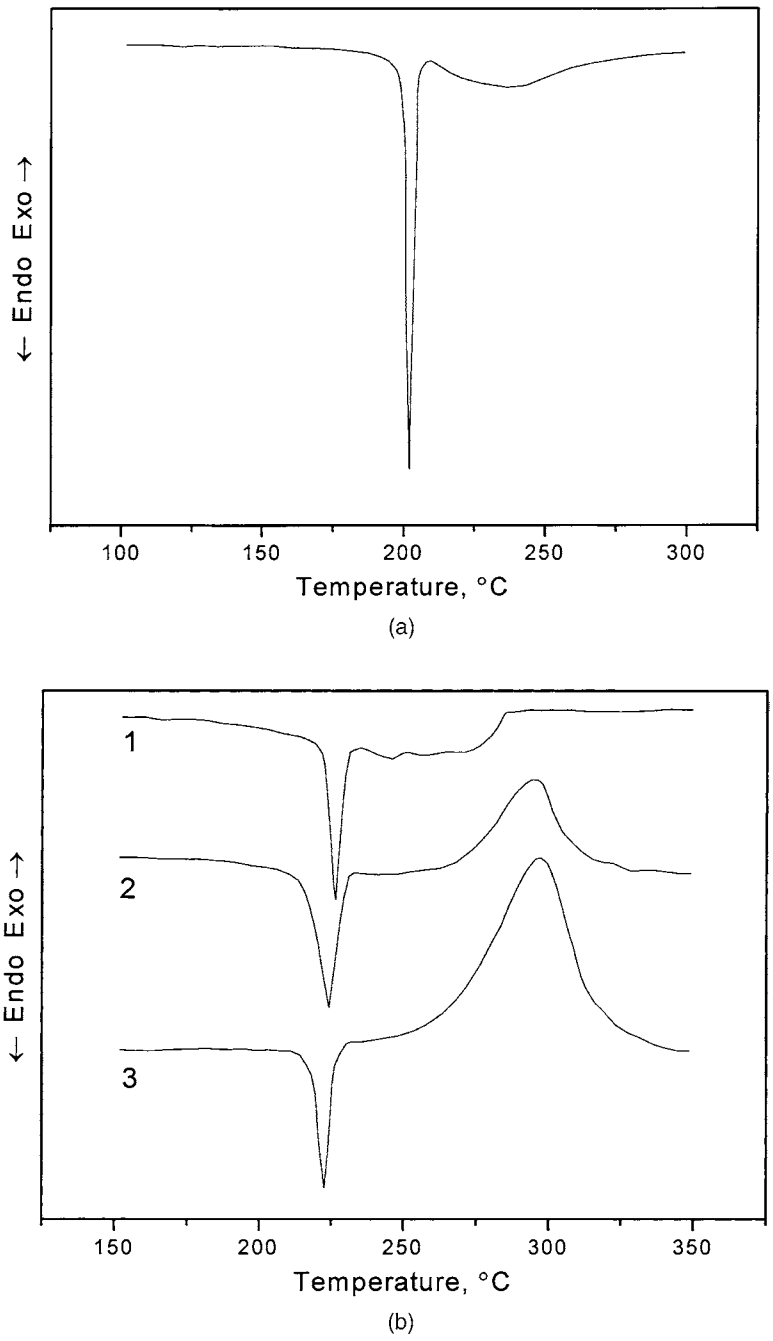


Fig. 2. DSC curves of thermal decomposition of aminotetrazoles under nitrogen flow of 60 ml min^{-1} at a heating rate 10 K min^{-1}. (a) 5-AT; (b) MAT: (1) nitrogen flow of 60 ml min^{-1}; (2) nitrogen pressure, 4 MPa; (3) sealed aluminium pan; (c) DAT; (d) PVAT; (e) SAT.

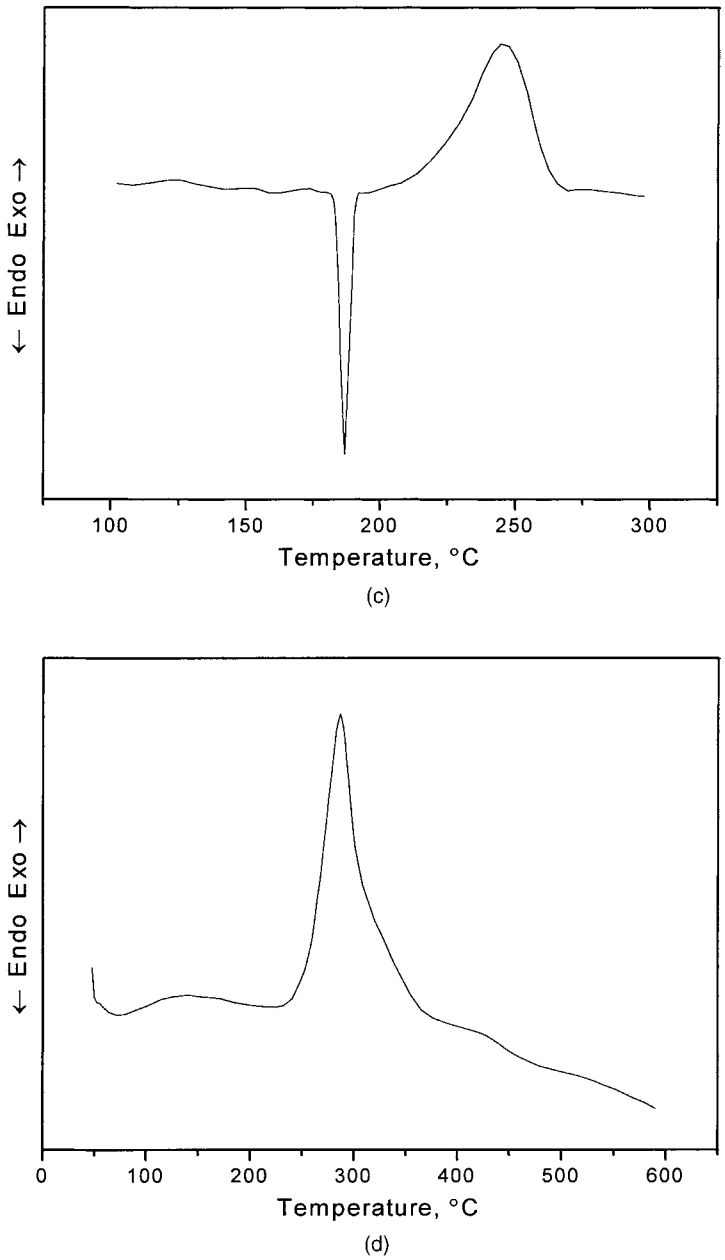
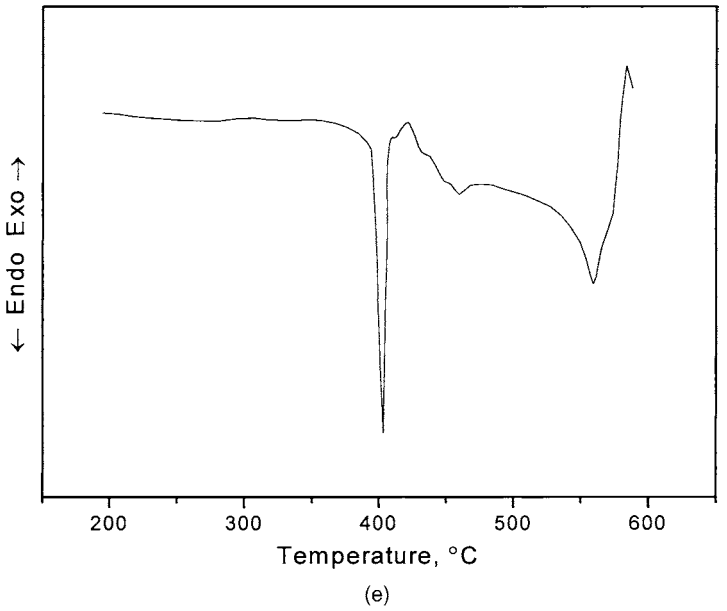


Fig. 2. (*Continued*).

and SAT is observed after they start to decompose. The DSC curves for all aminotetrazoles under study are shown in Fig. 2.

Upon thermal decomposition of the aminotetrazoles we were able to separate the gaseous products, volatile condensed products and solid non-volatile residue. Table 2 summarizes the data on gaseous and volatile products of thermal decomposition of aminotetrazoles. Nitrogen, hydrogen azide and ammonia were always identified among the gaseous products. DAT additionally shows hydrogen cyanide, while MAT results in formation of HCN and methylamine. Melamine and



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ammonium azide are the major volatile condensed products of the decomposition of 5-AT, PVAT and SAT. DAT in addition to these products gives some 1,2,4-triazole. Methylammonium azide and trimethylmelamine were found at the thermal decomposition of MAT (Table 2). According to the FTIR data [2–4], solid residues formed upon the decomposition of all aminotetrazoles contain cross-linked simm-triazine and simm-isotriazine structures. The formation of similar structures upon thermal decomposition of 5-AT was observed by Williams et al. [22].

The EGA experiments for 5-AT, DAT and PVAT show that the highest rate of evolution of acidic species observed at the initial stage of thermal decomposition (an example with 5-AT is shown in Fig. 1a). According to the FTIR (absorptions at 2155, 2125, 1165 and 1140 cm^{-1}) and mass-spectrometry, this is due to the evolution of HN_3. Hydrogen azide as a major volatile product of 5-AT thermolysis was identified in [5,22,23]. On the other hand, the evolution of volatile basic products usually starts after the completion of the first stage of thermal decomposition [2–4].

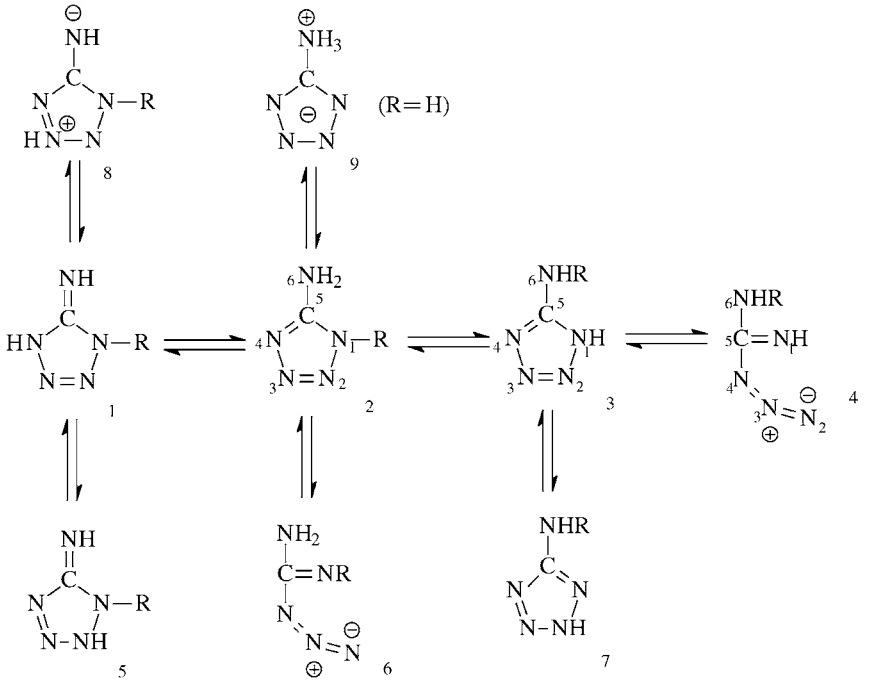
Table 2
Gaseous and volatile condensed products of thermal decomposition of aminotetrazoles

Compound	Gaseous products	Volatile condensed products
5-AT	N_2, HN_3, NH_3	NH_4N_3, melamine
MAT	N_2, HN_3, NH_3, HCN, CH_3NH_2	NH_4N_3, $CH_3NH_2{\cdot}HN_3$, trimethylmelamine
DAT	N_2, HN_3, NH_3, HCN	NH_4N_3, 1,2,4-triazole
PVAT	N_2, HN_3, NH_3	NH_4N_3, melamine
SAT	N_2, HN_3, NH_3	NH_4N_3, melamine

3.2. Isomerization of 5-aminotetrazoles

5-ATs with substituents at the position "1" of the tetrazole ring may exist in various isomeric forms according to prototropic, ring-chain or mesoionic isomerization as well as due to the migration of the substituent to the position "5" of the ring (Scheme 1).

Therefore, any experimental data proving presence of the different isomeric forms of aminotetrazoles in solid state, melt form or solutions are of great importance for understanding the mechanism of thermal decomposition of the aminotetrazoles. According to [24], the amino-imino tautomerizm (**1** ⇔ **2**) of 5-ATs is controversial. In the solid state, 5-iminotetrazole **1** was identified by the IR spectroscopy [25–27]. On the



Scheme 1.

other hand, the absorption of $\nu_{C=N\ exocyclic}$ was detected in some alkyl derivatives of 5-AT, but was attributed the structures bearing divided charges [28]. According to ^{15}N CP/MAS NMR, solid 5-AT monohydrate exists in the 1H-form (**2**, R = H) with a strong hydrogen bonding between the nitrogen atoms of the cycle and water molecules [8], while in the solution of dimethyl sulfoxide it is mainly in the form **2** which is prone to the fast proton exchange between the N_1 and N_4 atoms [29]. The ^{13}C NMR data of the substituted 1-phenyl-5-aminotetrazoles and 1-substituted-5-phenylaminotetrazoles in $CDCl_3$ shows that the chemical shifts of the tetrazole C-5 and the phenyl C-1 correspond to the 5-amino form [30]. The ^1H NMR data shows that in the DMF solution, 5-AT predominately exists in the imino form **1**, whereas, in the toluene or CCl_4 solution, there are resonance peaks attributed to both amino and imino forms [31]. Knowing that 5-ATs and 5-alkylaminotetrazoles exist only in the amino form in DMSO and alcohol solvents [32], the last finding seems to be surprising.

The isomerization of MAT to 5-methylaminotetrazole (**2** ⇔ **3**, R = CH_3) at the elevated temperatures was studied by Henry [33]. The content of 5-methylaminotetrazole in the melt of MAT was found to account for about 4%. Transformation of 1-alkylamino-5-aminotetrazoles into 5-tetrazolylhydrazones in solutions of dimethyl sulfoxide or xylene at elevated temperatures was also revealed [34]. As far as the prototropic 1H ⇔ 2H tautomerizm (**3** ⇔ **7**) is concerned, such kind of isomerization is usual for N-unsubstituted 5R-tetrazoles including 5-AT [32].

Since the most contradicting points of view on the isomerization of aminotetrazoles relate to amino-imino tautomerizm, we have studied **1** ⇔ **2** transformations of such kind for 5-AT [2]. The IR spectra of samples subjected to dehydration or heating either to melting point 478 K and rapid quenching or evaporation under vacuum and quenching, proved that the dehydrated 5-AT represents a mixture of the amino and imino forms with predominance of the imino form. The hydration, heating or evaporation of 5-AT result in increase of the content of amino isomer. This conclusion is based on the changes in the relative intensities of the absorptions at 1680 cm^{-1} ($\nu_{C=N\ exocyclic}$), 1264 cm^{-1} ($\nu_{C-N\ exocyclic}$), 740–775 cm^{-1} (δ_{N-H}), 2510–3080 cm^{-1} ($\nu_{of\ partially\ ionized\ N-H}$) and 3280, 3380, 3485 cm^{-1} (ν_{N-H}) [2].

In our experiments, we believed that the composition of the products released at the initial stage of the fragmentation of aminotetrazoles, may serve as an indicator of the isomeric form of the tetrazole ring. In the case of 5-AT, the evolution of hydrogen azide (HN_3) at the initial stage of the decomposition was observed (Table 2). According to the Scheme 1, we assume that HN_3 may evolve upon fragmentation of the isomers containing hydrogen atom at one of the ring nitrogen atoms (compounds **1**, **3**, **5**, **7**, and, possible, mesoionic form **8**). This is confirmed by the mass-spectrometric fragmentation of tetrazoles [35], which shows similarity to the reactions of thermal decomposition. The tetrazole derivatives which do not contain hydrogen at the nitrogen atoms of the cycle, for example poly-1-vinyltetrazole [36], sodium salt of tetrazole [37], 1,5-dimethyltetrazole and 1-phenyltetrazole [38] decompose without evolution of HN_3 independently on the conditions. It is known [2–4,39] that 1H,5H-tetrazole and 1,5-substituted tetrazoles decompose with formation of the azides **4** or **6** followed by splitting out of the nitrogen molecule and stabilization of the formed nitrene. Therefore, we believe that the compound **3** should mainly decompose via the elimination of nitrogen. Furthermore, as it has already been mentioned, the content of 5-methylaminotetrazole (**3**, R = CH_3) in the melt of MAT is relatively small [33] and it can not contribute sufficiently to the formation of HN_3. Thus, aminotetrazoles containing the imino form may produce the hydrogen azide at the initial stage of thermal decomposition. However, it should be noted that amino-imino tautomerizm in the solid aminotetrazoles has not been understood enough and it requires further profound investigation.

According to the quantum-chemical evaluation of the total energies of various isomeric forms of 5-AT in the gaseous state, the most stable is 2H-tautomer **7**, which is somewhat (by 19,14 kJ mol^{-1}) more stable than 1H-tautomer **2** (Table 3). These data are in good agreement with the experimental results on relative stability of N-substituted tetrazoles, where 2-isomers were found the most stable [19]. The imino form **1** is less stable than amino tautomers **2** (**7**) as well as the

Table 3
Total energies of the molecules and the energies of the chemical bonds in the tetrazole ring for different isomeric forms for 5-AT and MAT

Compound[a]	Calculation method							
	MP2/6-31G**		MNDO					
	Total energy E_T (a.u.)	ΔE (kJ mol^{-1})	Bond energies (eV)					
			N_1–N_2	N_2–N_3	N_3–N_4	N_4–C_5	N_1–C_5	C_5–N_6
7, R = H	−312.7663122467	0.0	−17.3	−17.5	−21.7	−17.0	−20.6	−17.4
2, R = H	−312.7590132584	19.14[b]	−17.0	−21.4	−17.8	−20.2	−18.2	−17.1
4, **6**, R = H	−312.7480744139	47.81[b]	–	−32.0	−19.6	−16.0	−24.4	−16.0
1, R = H	−312.7362685938	78.76[b]	−16.5	−22.8	−16.7	−17.7	−17.2	−24.1
8, R = H	−312.7192731092	123.31[b]	−17.1	−19.9	−18.2	−15.8	−14.9	−24.1
9, R = H	−312.7104257716	146.50[b]	−20.5	−18.0	−20.5	−18.0	−18.0	−16.1
5, R = H	−312.7051929754	160.22[b]	−14.5	−15.1	−24.3	−14.5	−15.1	−24.9
2, R = CH_3	−351.9427086519	0.0						
7, R = CH_3	−351.9393182647	8.90[c]						
3, R = CH_3	−351.9315824202	29.18[c]						
6, R = CH_3	−351.9225967550	52.71[c]						
4, R = CH_3	−351.9200091865	59.52[c]						
1, R = CH_3	−351.9198370112	59.94[c]						
8, R = CH_3	−351.9038836158	101.78[c]						
9, R = CH_3	−351.8934100610	129.25[c]						
5, R = CH_3	−351.8867288631	135.11[c]						

[a] The numbering of compounds refers to Scheme 1.
[b] Relative to 2H-5-aminotetrazole **7** (R = H).
[c] Relative to 1-methyl-5aminotetrazole **2** (R = CH_3).

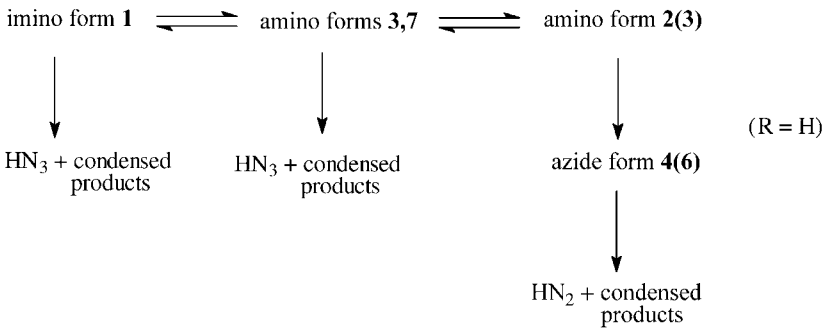
azide form **4** (**6**). Other isomers and mesoionic forms are characterized by substantially larger values of total energy (Table 3).

In contrast, for various isomers of MAT where hydrogen atom at the position "1" is substituted by the methyl group, the difference in total energies is not so big (Table 3). As in the case of 5-AT, the least stable isomers of MAT are 1H(R), 3H-5-iminotetrazole **5** and the mesoionic forms **8**, **9**. Since the proton transfer in the melt proceeds more readily that in the gas phase [40], we assume that isomeric forms **1**, **2**, **4** and **7** are the most likely to exist in the melt of 5-AT; the imino form **1** being thermodynamically the least stable isomer. In the case of 1-substituted 5-aminotetrazoles, the presence of isomeric forms **3** and **7** in the melt is also possible (Table 3).

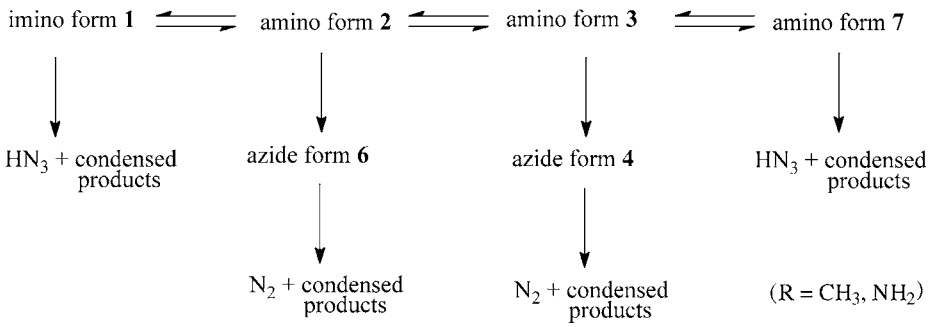
3.3. Mechanism of thermal decomposition

The quantum-chemical calculations of the bond energies indicate that fragmentation of the imino form **1** most likely will give HN_3, whereas amino tautomer **2** converts easily to the azide form **4(6)**, which should result in splitting out of a nitrogen molecule (Table 3). Since the dehydrated 5-AT mostly exists in the imino form, this form will, probably, undergo decomposition first with evolution of hydrogen azide. On the other hand the imino form transforms upon heating to the amino forms, which decompose with the evolution hydrogen azide or nitrogen. Taking into consideration the relative stability of the isomers (Table 3), the scheme of thermal decomposition of 5-AT can be represented as following in (Scheme 2).

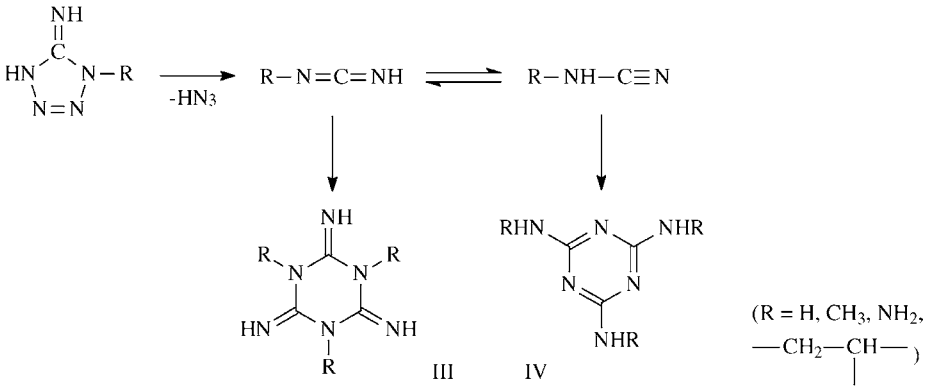
Since 1-substituted 5-aminotetrazoles are able to isomerize to 5-aminosubstituted-1(2)-H-tetrazoles (**2** ⇔ **3** ⇔ **7**) which are relatively stable (Table 3), the general scheme of MAT and DAT thermal decomposition should be as following in (Scheme 3).Because the content of 5-methylaminotetrazole in the melt of MAT is low [33], we assume that the contribution of the amino forms **3** and **7** to the thermal decomposition of MAT and DAT is likely to be relatively small.



Scheme 2.



Scheme 3.

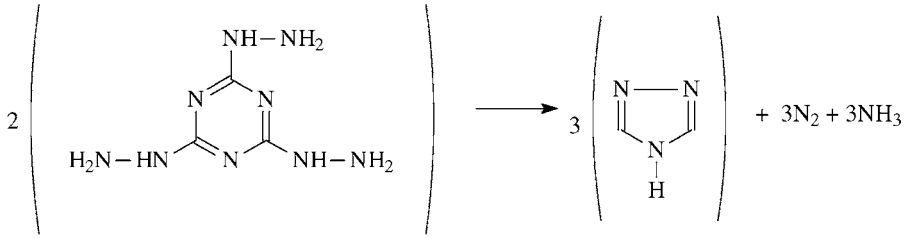


Scheme 4.

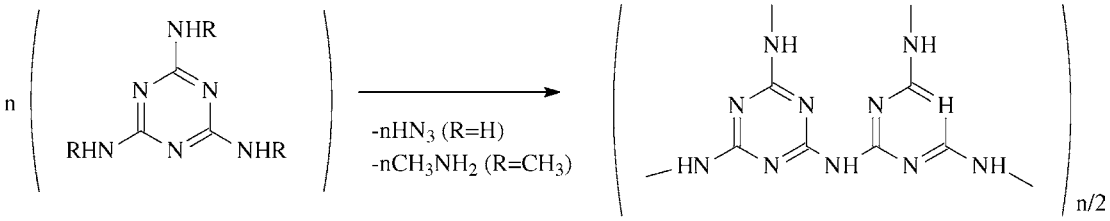
5-AT, MAT, DAT and PVAT decompose with evolution of HN_3 and formation of monosubstituted carbodiimides which is indicative of the imino form **1**. The carbodiimides are non-stable and they undergo isomerization to cyanamides [41] or cyclotrimerization to simm-isotriazines. The cyanamides can cyclotrimerize to simm-triazines as well [42] (Scheme 4).

The formed melamine (IV, R = H) and *N*,*N*′,*N*″-trimethylmelamine (IV, R = CH_3) were identified among the volatile condensed products of 5-AT and MAT (Table 2) correspondingly. In contrast to 5-AT and MAT, DAT did not produce the trimerization product of aminocyanamide, *N*,*N*′,*N*″-aminomelamine (IV, R = NH_2), but instead it gives 1,2,4-triazole. This is explained by the low stability of *N*,*N*′,*N*″-aminomelamine which decompose with the formation of 1,2,4-triazole and evolution of nitrogen and ammonia [3] (Scheme 5).

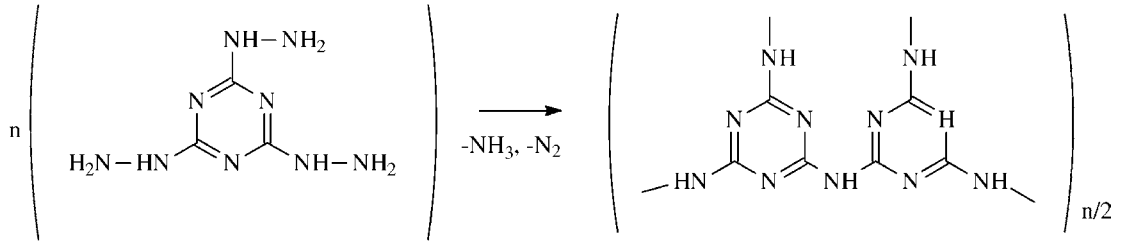
While some melamine or *N*,*N*′,*N*″-trimethylmelamine produced from 5-AT or MAT evaporate, some other undergo condensation forming the crosslinked simm-triazine structures (melam, melem and melon) [43], which tend to reside in the solid residue (Scheme 6).



Scheme 5.



Scheme 6.



Scheme 7.

Ammonia or methylamine are evolved in this reaction and they were identified among the volatile products (Table 2). The evolution of ammonia or methylamine is observed towards the end of the first step of the decomposition (Fig. 1a). They react with HN_3 forming ammonium or methylammonium azides, respectively (Table 2).

The simm-triazine structures crosslinked by –NH– bridges (V) were also found in the solid residue of DAT. It is likely that along with the decomposition of *N*,*N*′,*N*″-aminomelamine according to Scheme 5, the condensation with splitting out of nitrogen takes place (Scheme 7).

The amino forms **2** and **3** decompose via azide isomers **4**, **6** followed by the elimination of nitrogen molecule and formation of the corresponding nitrenes, which are unstable when $R = CH_3$, NH_2 and are subject of breakdown to the gaseous products (Scheme 8).

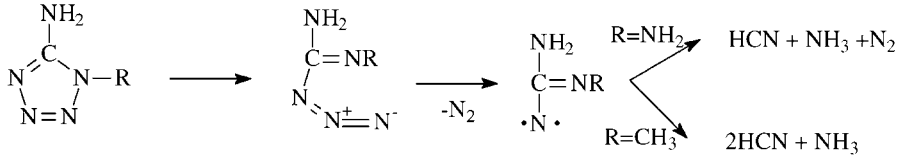
The presence of HCN in the gaseous products and relatively high specific volume of the gases evolved (due to N_2) at the decomposition of MAT and DAT (Table 1) are, probably, due to the decomposition of the corresponding nitrenes.

The solid residue from PVAT showed the presence of carbodiimide and polyamine structures, which suggests that the thermal decomposition of the amino form of PVAT can be described by the following scheme (Scheme 9) [4].

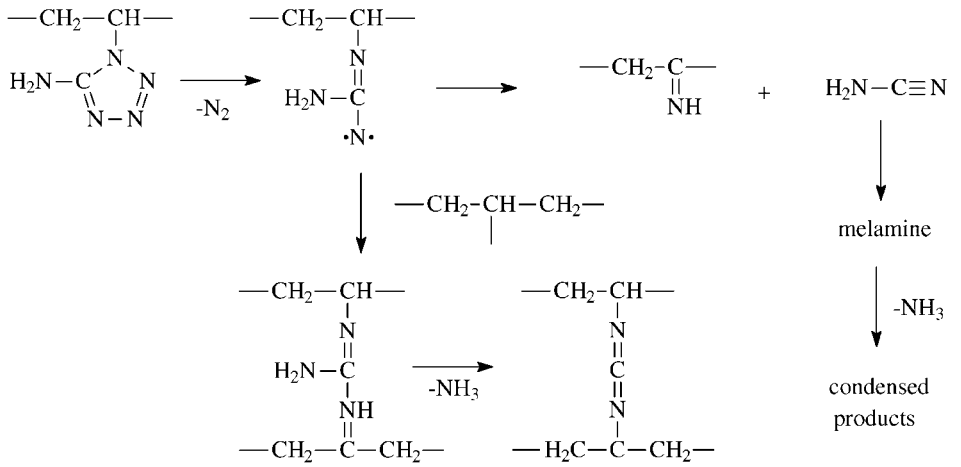
However, the thermal decomposition of aminotetrazolesis is likely to be more complex because of the condensation of amino forms of the original product with the simm-triazines formed in the course of the process. This gives intermediates which decompose later evolving nitrogen and resulting in crosslinked structures similar to the melem and melam [2].

SAT was found to be very thermally stable comparing to other aminotetrazoles (Table 1). This is typical of tetrazoles in the anionic form, e.g. sodium salt of tetrazole [37] or sodium salt of poly-5-vinyltetrazole [44]. The high stability of the tetrazole salts is due to the ‘‘aromaticity’’ of the tetrazolate anions compare to the corresponding 5-substituted tetrazoles [45]. In contrast to other aminotetrazoles, SAT decomposes to sodium azide and cyanamide at the initial stage.

The decomposition of NaN_3 with evolution of nitrogen [21] and cyclotrimerization of cyanamide to melamine and its condensation products occurs in the secondary reactions. Similar mechanism was observed for the thermal decomposition of sodium salt of poly-5-vinyltetrazole, which gave polyacrylonitrile (non-condensable to simm-triazines) and sodium azide [44]. Evolution of HN_3 in the course of thermal decomposition of SAT (Table 2) suggests that proton transfer from the amine group to N_1 or N_4 nitrogen may occur. The formed intermediate decomposes with elimination of hydrogen azide and gives thermally stable sodium cyanamide (Scheme 10).



Scheme 8.

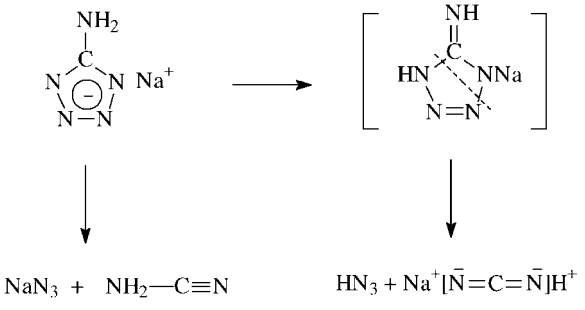


Scheme 9.

3.4. Kinetics

All the aminotetrazoles under study show complex dependences of the effective energy of activation on the degree of decomposition $E(\alpha)$ (Fig. 3). This suggests that the thermal decomposition of aminotetrazoles involves few simultaneous chemical reactions, which contribution is being changed in the course of the process.

We can split all aminotetrazoles into two groups according to the shape of $E(\alpha)$ dependences. The first group consists of 5-AT, MAT and DAT which show a downgoing shape of $E(\alpha)$, while the $E(\alpha)$ curves for PVAT and SAT show a maximum (Fig. 3). The downgoing dependence $E(\alpha)$ is typical for the complex process with the reversible stage [46]. It is likely that the transition between imino and amino forms **1** ⇔ **2** 5-AT, MAT, DAT and additionally transition **3** ⇔ **7** in the case of 5-AT are the reversible chemical processes occurring upon the thermal decomposition of these aminotetrazoles. On the other hand, the dependence $E(\alpha)$ with a maximum is attributed to the process involving two competitive parallel reactions [47]. Since PVAT and SAT start decompose without melting, the reversible transitions between different isomeric forms are hindered and the dominant process at the initial stage is the competitive decomposition of the corresponding amino and imino forms.



Scheme 10.

It is likely that the part of the curve $E(\alpha)$ where $E_a \sim 200$ kJ mol^{-1} $(0.1 < \alpha < 0.2)$ and another part where $E_a \sim 150$ kJ mol^{-1} $(0.5 < \alpha < 0.8)$ correspond to two different mechanisms of the decomposition of 5-AT (Fig. 3a): the elimination of HN_3 from the imino form and the elimination of the nitrogen molecule from the amino form, respectively. This is based on the assumption that at the initial stage of the decomposition 5-AT mostly consists of the imino form **1**, which is less stable then the other isomers and therefore, upon heating it decomposes and transforms into the amino forms **2(3)** and **7** simultaneously. Poly-1-vinyltetrazole, which mostly decompose through elimination of nitrogen show the E_a of 145 kJ mol^{-1} [37] and this value is similar to that of the 5-AT at $(0.5 < \alpha < 0.8)$. Further change of E_a for 5-AT is observed at $\alpha > 0.9$, which is likely to be due to the secondary processes of condensation in the solid residue.

At $0.2 < \alpha < 0.7$, which apparently corresponds to the decomposition of the imino forms, MAT and DAT show the $E_a \sim 200$ and ~ 180 kJ mol^{-1} respectively (Fig. 3b and c). As expected, SAT show relatively high $E_a \sim 300$ kJ mol^{-1} (Fig. 3e) because it is the most thermally stable among the aminotetyrazoles under study.

The IKP and the statistically selected kinetic functions for the thermal decomposition of the aminotetrazoles are listed in Table 4. It is seen that the values

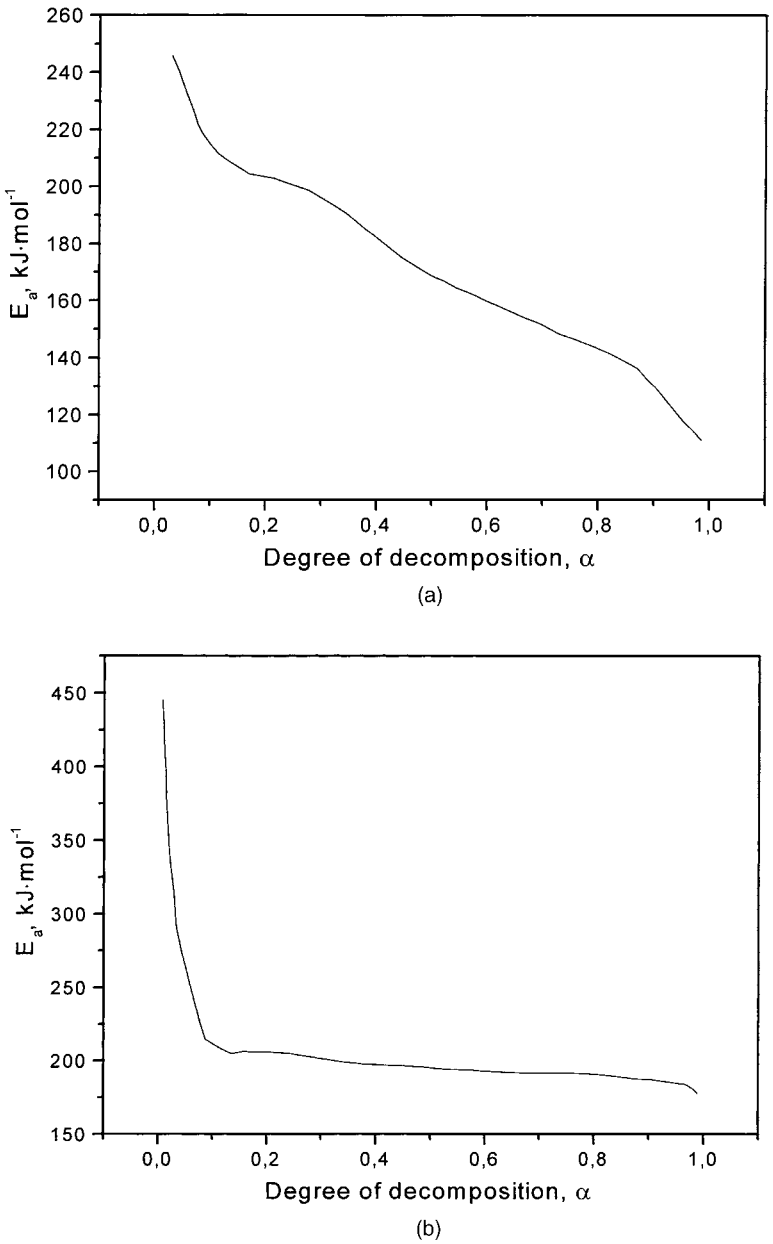
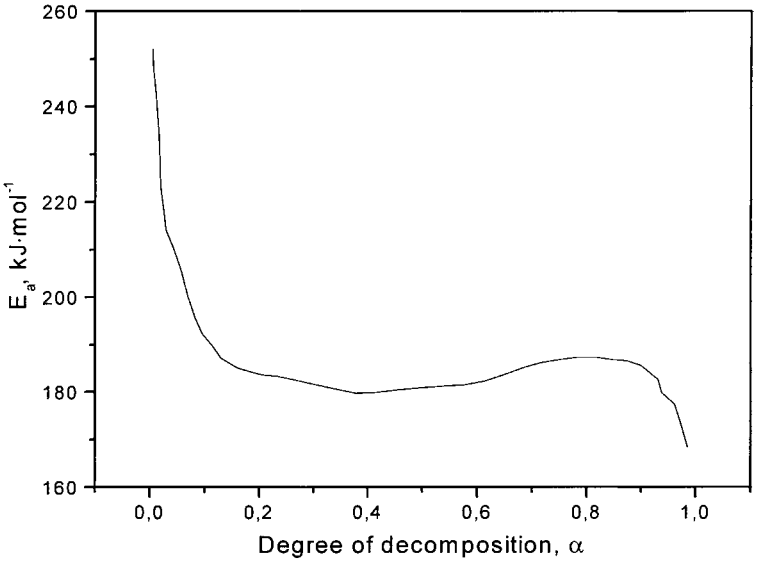
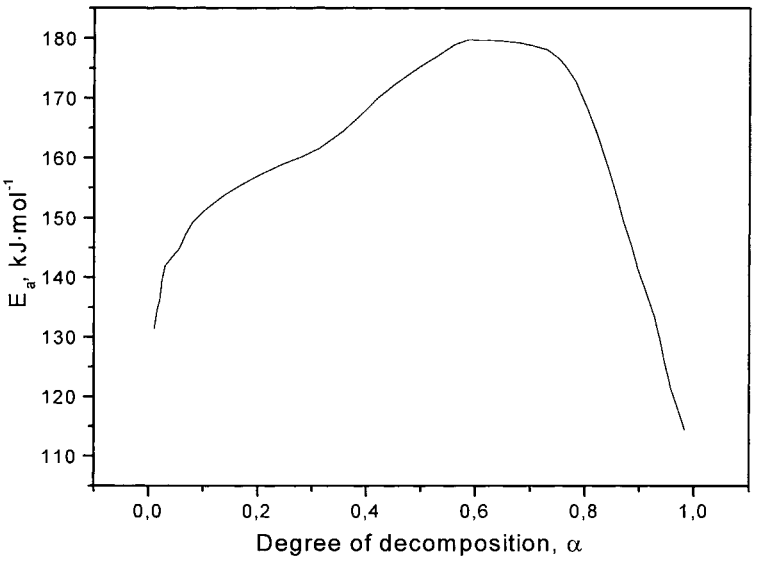


Fig. 3. Dependences of the activation energy on the degree of decomposition of aminotetrazoles. (a) 5-AT; (b) MAT; (c) DAT; (d) PVAT (e) SAT.



(c)



(d)

Fig. 3. (*Continued*).

of $\hat{E}$ and $\log\hat{A}$ are similar for the various methods of calculation (Ozawa, Flynn or Coats–Redfern). All aminotetrazoles, apart from MAT, decompose via first order process (Table 4). The $\hat{E}$, $\log\hat{A}$ and statistically selected kinetic functions $f(\alpha)$ correspond to the range of maximum decomposition rate and can be used in the modeling of combustion for evaluation of the combustion rates.

In general, the kinetics of thermal decomposition of the aminotetrazoles agree with the chemical mechanisms proposed from the composition of the products.

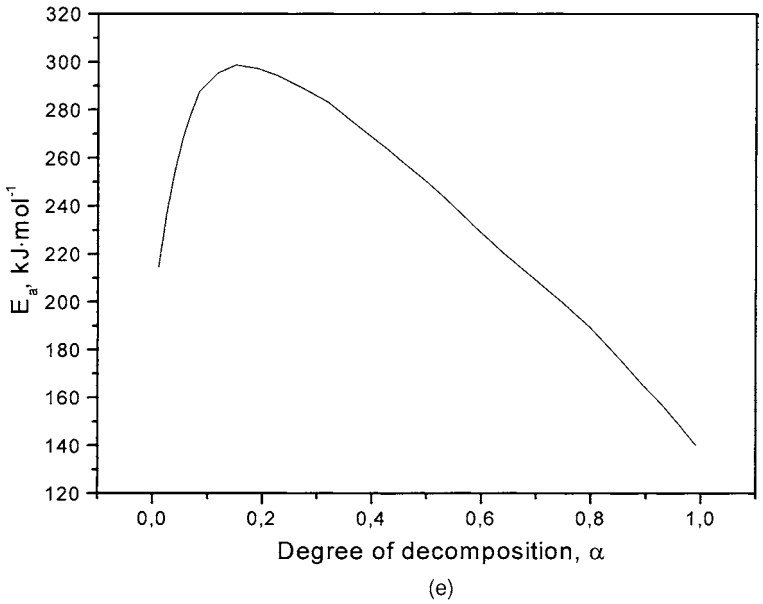


Fig. 3. (*Continued*).

Table 4
IKP and kinetic functions for the first stage of thermal decomposition of aminotetrazoles

Compound	Method of calculation	$\hat{E}$ (kJ mol^{-1})	log$\hat{A}$, $\hat{A}$: c^{-1}	$f(\alpha)$
5-AT	Ozawa	147 ± 10	13.1 ± 1.0	1−α
	Flynn	153 ± 10	13.7 ± 1.0	
	Coats–Redfern	136 ± 13	11.8 ± 1.4	
MAT	Ozawa	178 ± 4	14.8 ± 0.4	$(1-\alpha)[-\ln(1-\alpha)]^{1/3}$
	Flynn	169 ± 7	13.9 ± 0.6	
	Coats–Redfern	179 ± 6	14.8 ± 0.5	
DAT	Ozawa	175 ± 7	15.9 ± 0.7	1−α
	Flynn	183 ± 9	16.6 ± 0.9	
	Coats–Redfern	181 ± 6	16.4 ± 0.6	
PVAT	Ozawa	164 ± 8	13.2 ± 0.8	1−α
	Flynn	172 ± 10	13.9 ± 0.8	
	Coats–Redfern	175 ± 6	14.1 ± 0.7	
SAT	Ozawa	189 ± 3	14.3 ± 0.3	1−α
	Flynn	199 ± 4	15.1 ± 0.3	
	Coats–Redfern	168 ± 6	12.3 ± 0.5	

4. Conclusions

Two mechanisms of splitting of the tetrazole ring are effective in aminotetrazoles: (1) evolution of hydrogen azide from the tautomeric forms with hydrogen atom by nitrogens in the ring and (2) evolution of nitrogen molecule from the amino-tautomeric form. This assumption is based on the composition of volatile products of the thermal decomposition as well as data of the study of amino-imino tautomerism. The ab

initio calculations of the total energies and the energies of chemical bonds in 5-AT and MAT are in favor of these two mechanisms.

In the case of 5-AT, MAT and DAT, the thermal decomposition of the imino form starts just after the melting and results in evolution of hydrogen azide. An increase of the temperature leads to another pathway of thermal decomposition involving corresponding amino forms, which decompose with elimination of nitrogen. Similar general pattern of thermal decomposition is observed for PVAT and SAT, however, these substances start to decompose prior melting. All aminotetrazoles produce ammonium azide, simmtriazines and the products of their condensation.

The apparent activation energies of thermal decomposition of imino forms are in the range of 180–200 kJ mol^{-1}, whereas amino forms decompose with the activation energies close to 150 kJ mol^{-1}. Two mechanisms of splitting of the tetrazole ring are in agreement with the data of kinetics of thermal decomposition. SAT has significantly higher activation energy because the tetrazole ring of SAT is more ''aromatic'' then rings of other aminotetrazoles.

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