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High-Energy Salts of 5,5′-Azotetrazole. I. Thermochemistry and Thermal Decomposition

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Abstract: Thermal decomposition of disubstituted salts of high-energy 5,5′-azotetrazole (sodium, ammonium, hydrazine, guanidine, aminoguanidine, and triaminoguanidine salts) under isothermal and nonisothermal conditions in solid and liquid phases is studied. The relationship between the basicity and the thermal stability of the 5,5′-azotetrazole salt is demonstrated. The boundary of possible existence of 5,5′-azotetrazole salts in terms of the basicity index pK_a is determined. Gaseous and condensed products of decomposition are analyzed, and a mechanism of thermal decomposition of 5,5′-azotetrazole is proposed. The enthalpies of formation of some 5,5′-azotetrazole salts are determined, and the most reliable values are chosen on the basis of the analysis of the data obtained in the present study and those available in publications.

Keywords: 5,5′-azotetrazole salts, thermal decomposition, kinetics, heat of combustion, enthalpy of formation.

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INTRODUCTION

Salts of 5.5′-azotetrazole (H_2AzT) with metals have been known for longer than a century [1–3]. Salts of H_2AzT with sodium, potassium, barium, and calcium were synthesized for the first time in [1], where it was shown that they contained crystallization water, which is why they did not manifest explosive properties. However, copper, mercury, silver, and lead salts of H_2AzT [4] synthesized later turned out to be explosives with low thermal stability and high sensitivity to impact, friction, and flame. The basic lead salt of H_2AzT was used in Germany during World War II as an explosive for hot bridge wires [4].

Recently, in many countries, salts of azotetrazole with nitrogenous bases are synthesized and studied, being viewed as promising oxygen-free high-enthalpy low-sensitivity components of explosive compositions, gas-generating compositions [5–9], and rocket propellants [5, 6, 10]. Salts of H_2AzT with nitrogenous bases contain a large amount of nitrogen, many of them are highly thermostable, possess high positive enthalpy of formation, low hygroscopicity and solvability in water, and small molecular weight of gaseous combustion products. The most attention of researchers is paid to salts of H_2AzT with such bases as ammonia, hydrazine, guanidine, aminoguanidine, and triaminoguanidine [7–9, 11].

Enthaplies of formation of salts of H_2AzT with hydrazine [12], ammonia, guanidine, and triaminoguanidine [9] were experimentally determined to be 858, 444, 410, and 1075 kJ/mol, respectively. For most salts of H_2AzT, the enthalpy of formation was obtained by means of quantum chemical calculation of this value in a gaseous phase with subsequent conversion into a solid state by accounting for the enthalpy of sublimation also calculated in any way. Note that, for oxidizer-free compounds, the energy released in their combustion and explosion was only due to their internal energy. Thus, the accuracy in determining the enthalpy of formation of those compounds became very important.

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Azotetrazole in free form at room temperature is unstable. In water, it quickly converses into hydrazinotetrazole, which is accompanied by the release of nitrogen [1]. The methanol solution of sodium salt of azotetrazole under the action of $HBF_4 \cdot Et_2O$ at low temperature can produce crystalline solvate with two methanol molecules, stable at −30°C. Free acid can be stored without decomposition for several months at −80°C [13]. It is shown in [14] that the primary decomposition of one of the tetrazole rings of H_2AzT leads to intermediate formation of unstable diazomethylazotetrazole whose interaction with two water molecules produces hydrazinotetrazole and formic acid.

Decomposition of salts of H_2AzT with alkaline, alkaline-earth, and certain trivalent metals was investigated by differential scanning calorimetry (DSC) [13]. All salts were crystalline hydrates, and water losses were observed when heating up to 100°C. The heat release maximum was reached in a temperature range of 211–335°C, with lithium salt being the most stable and barium salt being the least stable. Decomposition of salts of H_2AzT with Na, Ba, Pb, and Hg was studied by means of DSC and thermogravimetric analysis (TGA) in [15], and the decomposition activation energies, obtained in detecting the heat release peaks in DSC, were quite high (for example, 285–368 kJ/mol or 68–88 kcal/mol for sodium salt) and probably fail to reflect the real strength of broken bonds.

The DSC method under nonisothermal conditions was also used to investigate the decomposition of salts of H_2AzT with such bases as guanidine, aminoguanidine, diaminoguanidine, and triaminoguanidine [16]. The salt of guanidine was the most stable ($T_{\max} = 261.5$°C), and the salts of diaminoguanidine and triaminoguanidine ($T_{\max} = 200.9$ and 209.2°C) were the least stable (Table 1). The estimated values of the decomposition activation energy, determined from nonisothermal data by the Ozawa and Kissinger methods, for these salts lie in a range of 167–209 kJ/mol (40–50 kcal/mol). It is noteworthy that, according to the data obtained by TGA at 130°C in [8], the decomposition of salts of aminoguanidine and triaminoguanidine proceeds with strong acceleration, which means that the kinetic parameters obtained in nonisothermal conditions are formal and fail to reflect the kinetics of the primary stage of decomposition. In the composition of the gaseous phase of decomposition products, the mass spectrometry and infrared spectrometry are used to find nitrogen, ammonia, HCN, and HNCNH carbodiimide. It is assumed that thermal decomposition begins with dissociation of the salt into free acid and a base with subsequent decomposition of the latter. Azotetrazole decomposes into nitrogen and HCN (6 moles of gas per 1 mole of azotetrazole), and guanidine bases decompose into ammonia (hydrazine) and carbomiimide, which, in its turn, decomposes into ammonia, nitrogen, and hydrocyanic acid. Hydrazine is also unstable at temperatures of decomposition of salts and decomposes according to the known mechanism with the formation of H_2 and N_2 and traces of ammonia. Note that the proposed mechanism can only produce gaseous products, while the TGA data indicate a large amount of the condensed products that remains after decomposition.

The products of pyrolysis of the triaminoguanidine salt of azotetrazole $(TAG)_2$AzT was studied in [17, 18] using mass spectrometry. It was also assumed therein that the initial stage of decomposition of salt is dissociative evaporation of the free acid and base. Azotetrazole decomposed with the formation of two N_2 molecules and a compound with a gross formula $C_2H_2N_6$, with an eight-membered heterocycle attributed to it. In parallel to that, triaminoguanidine decomposed to form hydrazine, ammonia, nitrogen, HCN, and a polymer product of the composition $C_2H_5N_5$. The interaction of hydrazine with $C_2H_2N_6$, formed in the decomposition of azotetrazole, produced a polymer $[{=}NCH_2N{=}NCH_2N{=}]_n$.

The decomposition of the triaminoguanidine salt of azotetrazole $(AG)_2$AzT in solid phase in nonisothermal (DSC) and isothermal (TGA) conditions is described in [19]. It is shown by tests in isothermal conditions that the decomposition of $(AG)_2$AzT proceeds with acceleration. In nonisothermal conditions, the energy activation is quite high: $E_a = 207$ kJ/mol (49.5 kcal/mol). The mass spectrometric analysis of the pyrolysis products of $(AG)_2$AzT indicates the presence of molecular nitrogen and ammonia.

The decomposition of the hydrazine salt of azotetrazole $(N_2H_5)_2$AzT was described in isothermal conditions by TGA in a temperature range $T = 110$–130°C [12]. The substance decomposed with weak acceleration, lost 43% of its weight, and was accompanied by a strong heat effect (1450 J/g), while the rate constants of the initial stage had parameters $E_a = 169.3$ kJ/mol (40.5 kcal/mol) and $A = 2.1 \cdot 10^{17}$ s^{-1}. On the basis of the kinetic data obtained, it was predicted by the authors that the storage time of $(N_2H_5)_2$AzT (1% of decomposition) was ten years at $T \leqslant 48$°C. According to the TGA and DSC data [20], that substance lost 77% of weight in the range $T = 160$–180°C per one heat releasing stage (1650 J/g). The decomposition activation energy in nonisothermal conditions ($E_a = 136.2$ kJ/mol), published in [20], was apparently erroneous as the DSC data were recalculated and a different value was obtained: $E_a = 241.9$ kJ/mol (57.8 kcal/mol).

Table 1. Thermochemical properties of salts of H_2AzT

Substance	$T_{\max}$, °C*	Weight loss, % (temperature, °C)	E_a, kJ/mol	Source
$Na_2AzT \cdot 5H_2O$	248	—	285–367	[13]
	265	33.7–36.5 (240–290)	418	[15]
$(NH_4)_2AzT$	195	—	—	[10]
	190			[9]
	212			[28]
$(N_2H_5)_2AzT$	163	43 (110–130)	169.3	[12]
	188	77 (150–185)	136.2 (241.9)**; 220.74	[20]
Gu_2AzT	240	—	—	[9]
	261.5	—	205.9	[16]
	265	—	—	[29]
	242.3	59 (200–265)	—	[23]
	260.8	70 (177–447)	218	[30]
$(AG)_2AzT$	223.4	—	212	[16]
	243		207	[19]
	216		—	[29]
$(DAG)_2AzT$	200.9	—	182.7	[16]
$(TAG)_2AzT$	195	—	164.5	[9]
	209	—		[16]
	191.8	93 (141–273)		[23]

*Maximum temperature, DSC exotherm (10°C/min); **Recalculation of the data from [20].

That was confirmed also by the kinetic parameters obtained in the TGA study [20]: $E_a = 220.7$ kJ/mol (52.7 kcal/mol) and $\ln A = 54.04$. The analysis of the decomposition products, carried out using FTIR spectroscopy, indicated the formation of NH_3 and HCN [20]. In view of the data obtained, an absolutely unreal decomposition mechanism of $(N_2H_5)_2AzT$ was proposed in [20], which included the primary scission of the double bond N=N in the azo-group with subsequent decomposition of tetrazole cycles into N_2 and HCN and reduction of HCN by hydrazine to CH_4. The proposed mechanism yielded 10 moles of gaseous products per 1 mole of $(N_2H_5)_2AzT$, while the TGA data indicated the large amount of condensed products, remaining after decomposition.

The density functional theory (a level of B3LYP/6-31G(d,p)) and nonempirical methods MP2/6-31G(d,p) and HF/6-31G(d) were used in [21] to simulate the decomposition of guanidine salt of azotetrazole Gu_2AzT. Based on the simulation results, the authors assumed that the primary stage could be dissociation of the salt into cation and anion with their subsequent decomposition into CN^+, NH_3 and CN^-, and N_2 with activation energies of 210 and 250 kJ/mol (50.2 and 59.8 kcal/mol), respectively. The obvious disagreement between the experimental observations of stability H_2AzT and AzT^{2-} and the mechanism proposed, as well as the unusual and highly improbable decomposition products made those calculations quite questionable. Continuing with that kind of research the authors of [22] proposed using the decomposition mechanism of Gu_2AzT, which did not imply salt dissociation into cation and anion. The tetrazole cycles of anion of tetrazolate were decomposed, then the protonated guanidines transferred their protons to the azo group, forming a hydrazine compound N_2C–NHNH–CN_2, which decomposed with the formation of molecular nitrogen and HNC. According to the calculations shown, free guanidine decomposed in an unimaginable way into CH_3NH_2 and molecular nitrogen.

The results obtained in [23] were not any less surprising from the standpoint of chemistry. In it, polynitrogen compounds were subjected to thermoanalytical screening in order to search for additives that increased the burning rate of propellants with a high content of RDX. The primary stage of decomposition of the guanidine salt Gu_2AzT was assumed to be the proton transfer, which, however, did not result in the expected formation of free acid and base, but continued further, while the base protonated the acid. According to those authors, the hydrazine salt $(N_2H_5)_2AzT$ decomposed in the same way, with hydrazine protonating the azotetrazole. As strange as it could be, that idea absolutely unacceptable from the standpoint of chemistry was also used in [19] in the description of the decomposition of aminoguanidine salt $(AG)_2AzT$.

The replacement of guanidine by the related triaminoguanidine is, according to [23], capable of fundamentally changing the decomposition mechanism of the salt $(TAG)_2AzT$. The authors of [23] ignored the proton transfer for $(TAG)_2AzT$ and proposed the release of a nitrogen molecule from quite a stable anion of azotetrazole as a primary stage (for example, the heat release maximum in the decomposition of sodium salt is observed at $T = 265°C$ [15]) and only then the decomposition of triaminoguanidine in an unimaginable way into three radials NH_2 and a three-radical residual of guanidine.

The decomposition of $(TAG)_2AzT$ is described in [24]. The analysis of the gaseous phase of the decomposition products of $(TAG)_2AzT$ during fast heating in a cell of a Fourier spectrophotometer shows the presence of 6.46 mol of N_2, 5.06 mol of NH_3, 4.00 mol of HCN, and trace amounts of NH_2CN per 1 mol of the original salt. The heat effect of this reaction (770 kJ/mol), which is about 65% of all the energy left in $(TAG)_2AzT$, is attributed to a condensed phase. Apparently, the authors do not realize that the condensed phase in this case would have to heat up to a temperature above 1400 K.

The decomposition of guanidine azotetrazole Gu_2AzT was investigated in [25] using a combined (experimental and computational) approach. The infrared FTIR spectroscopy and time-of-flight mass-spectroscopy were used to identify N_2, NH_3, HCN, guanidine, and melamine as decomposition products of Gu_2AzT at $T = 553$–573 K. Because the bands belonging to dianion AzT^{2-} in the infrared range vanished and a large amount of molecular nitrogen was formed, it was concluded in [25] that decomposition began with the release of a N_2 molecule from dianion. The quantum-mechanical calculation of this reaction yielded an activation energy of 159.6 kJ/mol (37.5 kcal/mol). Unlike the accepted preliminary dissociation of salt, it was assumed that the proton transfer occurred only after opening of the tetrazole ring. In that case, the final decomposition of the dianion AzT^{2-} led to the formation of the $CH_2{=}N{-}NC$ compound, whose existence was barely probable.

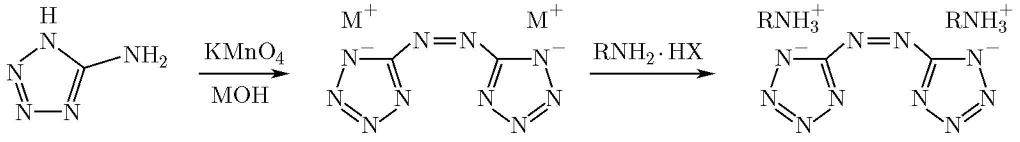
A quite unique mechanism for the formation of melamine by the interaction of guanidine cation with a free guanidine was proposed in [25], which also raised many questions. The problem was that the formation of melamine by the trimerization of cyanamide, formed during the pyrolysis of guanidine, was an industrial method for the production of melamine [26]. In the following paper [27], the authors numerically calculated the weight loss in TGA and the heat release in DSC on the basis of the decomposition mechanism proposed in [25], which contained 107 elementary reactions and 76 reaction products, many of which were questionable and improbable.

Thus, the analysis of the publications shows that the thermal decomposition of the salts of H_2AzT mainly occurs in nonisothermal conditions, and the resulting kinetic parameters mostly turn out to be formal and sometimes even erroneous. The study of the chemical mechanism of decomposition of the salts of H_2AzT, required to predict the compatibility of components and guaranteed storage life of compositions based on the salts of H_2AzT with nitrogen bases, is in most cases quite far from perfect from the standpoint of chemistry. The known thermochemical and physicochemical properties of the salts of H_2AzT are given in Tables 1 and 2. As seen from Table 2, the enthalpies of formation of the salts differ very much in many cases.

Thus, the purpose of this paper is the systematic study of thermal stability and determination of the decomposition mechanism of the salts of H_2AzT. Moreover, the enthalpies of formation of a series of salts are determined experimentally, and the reliability of the results obtained is estimated.

EXPERIMENT

Salts of 5,5′-azotetrazole are synthesized in two stages. The first stage is the oxidation of 5-aminotetrazole with potassium permanganate in an alkaline aqueous solution according to the standard procedure [1], which results in azotetrazole salts with sodium (Na_2AzT) and barium (BaAzT). Then, these salts are used as starting materials for the preparation of the salts of 5,5′-azotetrazole with nitrogen bases (R1):



(R1)

$M^+ = Na^+, Ba^{2+}/2.$

Table 2. Physical and chemical properties of the salts of H_2AzT

Substance	ρ, g/cm^3	ΔH_f^0, kJ/mol	D, m/s	p, GPa	V, l/kg	Source
$(NH_4)_2AzT$	1.53	444	7600^a	187^a	979	[9]
	1.562 (200 K)	551^a	7788^b	216^b	824^b	[10]
$(N_2H_5)_2AzT$	—	858	6330^b	247^b	—	[12]
		—	—	—	1436	[20]
Gu_2AzT	1.538	410	7100^a	155^a	979	[9]
			6192^b	154^b	975^c	[16]
	1.569 (200 K)	—	—	—	—	[31]
	1.69	452.2	—	—	—	[29]
$(AG)_2AzT$	1.559	435^a	6418^b	165.6^b	999^c	[16]
	1.59	782				[29]
$(DAG)_2AzT$	1.599	708.8	7045^b	204.5^b	1026^c	[16]
$(TAG)_2AzT$	1.602	1075	9050^a	292^a	981	[9]
			7654^b	241.7^b	1058^c	[16]
	1.634 (193 K)	—	—	—	—	[31]

Here ρ is the density, ΔH_f^0 is the enthalpy of formation, D is the detonation rate, V is the volume of the detonation products, and p is the pressure in the shock wave front. ^{a}Estimated value; ^{b}Calculated using the Kamlet semiempirical formula; ^{c}ICT Thermodynamic Code.

The salts of nitrogenous bases poorly soluble in water (the guanidine salts Gu_2AzT, $(AG)_2AzT$, and $(TAG)_2AzT$ and the hydrazine salt $(N_2H_5)_2AzT$) are obtained by mixing the hot aqueous solutions of soluble salts of nitrogenous bases (X = Cl, NO_3) and Na_2AT with subsequent crystallization of the salt of azotetrazole. The ammonia salt of azotetrazole $(NH_4)_2AzT$ that is soluble in water is obtained by mixing hot aqueous solutions of $(NH_4)_2SO_4$ and BaAzT with subsequent removal of the barium sulfate residue and evaporation of the mother solution. The yield of the final products is 70–85%. The qualitative and quantitative compositions of the salts obtained are confirmed using infrared spectrometry and element analysis, respectively. All these salts except for $(NH_4)_2AzT$, Gu_2AzT and TAG_2AzT comprise 1–3 molecules of crystallization water, which is removed by dehydration in a vacuum oven at $T = 80$–100°C.

The thermal stability of the salts under study is preliminarily determined in nonisothermal conditions by means of DSC. The sample of the tested substances (1–3 mg) is placed into sealed aluminum pans. The rate constants of nonisothermal decomposition are calculated using the Kissinger method [32] in the assumption of the first order of reaction based on the maximal decomposition temperatures measured at different heating rates (Table 3). The decomposition kinetics in a liquid phase is obtained using samples with mixtures of the substances under study with low-melting thermostable compounds (Table 4).

Thermal decomposition in isothermal conditions is investigated using a manometric method. The substance is placed into a glass Bourdon pressure gauge (the ratio of the sample weight to the free volume is $m/V = (10 \pm 2) \cdot 10^{-4}$ g/cm^3, and the sample weight is about 10 mg) located in a thermostat with Rose's alloy (the accuracy of temperature and pressure measurements is ±1°C and ±1 torr, respectively). An error in determining the rate constant is nearly 10%. In a usual temperature range of measurements of 30–40°C this error allows obtaining the Arrhenius equation parameters with an accuracy of ±0.4–0.6 for the exponent of the pre-exponential factor and ±4–8 kJ/mol for activation energy.

The quantitative analysis of gaseous decomposition products is carried out by measuring their pressure at fixed temperatures (cryoscopic analysis). The first temperature is the temperature of the end of the experiment, and the second temperature is room temperature. Then the measurements are carried out at lower temperatures until the boiling point of liquid nitrogen is reached (−196°C).

Calorimetric measurements are carried out using a B-08M standard bomb calorimeter equipped by a modified oxygen bomb 210.5 ml in volume, which can withstand an explosion of 2 g of a powerful explosive. Distilled water is added into the shell of the calorimeter until a total weight of 4587 ± 0.1 g is reached, the temperature of the filled calorimetric bucket is brought to 298 ± 0.1 K.

Table 3. Data of the DSC analysis of the salts of 5,5′-azotetrazole with nitrogen bases

Heating rate, °C/min	$T_{\max}$, °C					
	Na_2AzT	$(NH_4)_2AzT$	$(N_2H_5)_2AzT$	Gu_2AzT	$(AG)_2AzT$	$(TAG)_2AzT$
2	254	210	—	243	211	195
4	265	219	184	253	218	203
8	273	226	191	261	224	210
16	283	232	202	267	231	218
32	292	—	212	276	238	226

Table 4. Data of the DSC analysis of the mixtures of the salts of 5,5′-azotetrazole with solvents

Heating rate, °C/min	$T_{\max}$, °C				
	1 / 4 $(NH_4)_2AzT$/sorbitol	1/1 $(N_2H_5)_2AzT/N_2H_4 \cdot HCl$	1/19 $Gu_2AzT/Gu \cdot HCl$	1/9 $AG_2AzT/AG \cdot HCl$	1/9 TAG_2AzT/sulfolane
2	165	161	230	—	187
4	169	167	238	181	192
8	175	175	249	190	201
16	183	180	253	199	208
32	187	192	262	208	—

Table 5. Calorimetric data of the salts of azotetrazole

Salt	$-\Delta_c U$, J/g*	$-\Delta_c U$, kJ/mol	ΔH_f^0, kJ/mol
$(NH_4)_2AzT$	11 963 ± 110	2393 ± 23	452 ± 23
$(N_2H_5)_2AzT$	12 551 ± 59	2887 ± 14	659 ± 14
Gu_2AzT	12 986 ± 160	3688 ± 44	387 ± 44
$(AG)_2AzT$	12 900 ± 130	4051 ± 40	462 ± 40
$(TAG)_2AzT$	13 977 ± 98	5228 ± 37	1065 ± 37

*The heat generated from the combustion of the wire cotton thread, Joule heat, and correction for non-condensed water vapors, as well as the heat generated from the formation of a solution of nitric acid are taken into account.

The temperature rise is measured using a Testo 735 electronic thermometer with a measurement accuracy of ±0.001°C. The calorimeter is calibrated by a reference benzoic acid of a thermochemical grade with an internal combustion energy $\Delta_c U = -26\,434.9$ J/g (−6318.1 cal/g) [33, 34]. The thermal equivalent of the calorimeter is $\varepsilon = 14\,670.8 \pm 12.5$ J/K (3506.4 ±3.0 cal/K).

The samples of the salts of azotetrazole (0.5–1 g) in the form of pressed pellets are burned in pure form at an oxygen pressure of 1.5–3.5 MPa. The pellets are placed into crucibles of stainless steel or attached directly to the igniter wire. The samples are ignited by a wire with a combustion energy $\Delta_c U = -6694$ J/g (−1600 cal/g) [33]). The contributions of current heating energy of the wire and its combustion energy are taken into account, and the latter is determined by weighing the mass of unburned wire fragments and calculating the mass of the burned wire. In some experiments, the role of an ignition aid could be played by small thin cotton threads binding the substance pellet with the igniter wire, whose internal combustion energy is $\Delta_c U = -16\,238$ J/g (−3881 cal/g) [33]. All experiments are carried out in 99.95% pure oxygen (no nitrogen impurity). Considering the fact that there is nitrogen in the tested samples, the formation of nitrogen acid during combustion is determined by potentiometry. The resulting calorimetric values of the salts of azotetrazole are given in Table 5. The error is calculated with a confidence level of 95%.

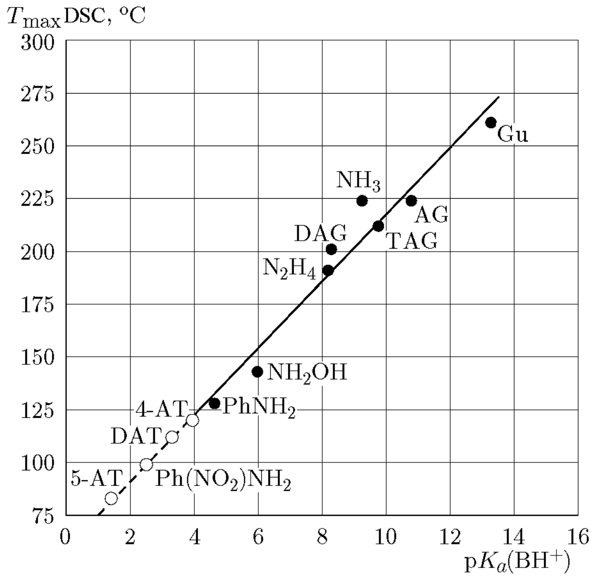


Fig. 1. Temperature maximum of the exothermal peak of DSC of the salts of H_2AzT versus basicity: the bright dots denote the estimated decomposition temperatures with weak bases.

RESULTS AND DISCUSSION

Synthesis of the Salts of Azotetrazole

Azotetrazole is unstable in free form and decomposes at room temperature within a few seconds [1, 13]. In an acid medium, H_2AzT decomposes with the formation of 5-tetrazolylhydrazine and other products [14]. Salt formation increases the stability of azotetrazole, and most of its salts with metals have an exoeffect temperature of 211–248°C [13]. The stability of salts with organic bases depends on basicity: the larger it is, the higher the ignition point of salt (Fig. 1).

The salts of 5-aminotetrazole and 1.5-diaminotetrazole, obtained by ion transfer from sodium salt [7], have the explicit features of decomposition. These features include the vanishing of the bright yellow color of the solution, which is characteristic of the salts of H_2AzT, and deposition of a bright colorless residue identified by infrared spectrometry as salt of hydrazinotetrazole of the corresponding acid.

It was shown that salts with bases whose basicity $pK_a > 4.6$ can stably form in aqueous media, with signs of decomposition observed in the case of smaller values of pK_a (5-aminotetrazole 5-AT with pK_a 1.3, 1.5-diaminotetrazole DAT with pK_a 3.3, 3-nitroaniline with pK_a 3.54, and 4-amino-1.2.4-triazole 4-AT with pK_a 3.92). The salts cannot be obtained with base excess, with the use of salts of weak acids, and at lowered temperature (20°C). Thus, the claim about the synthesis of the salts of tetrazole [7] is probably mistaken. It is also noted in further studies [35] that the synthesis of these salts cannot be reproduced. There is a description of the properties of only salts with more basic alkylated triazole and tetrazole derivatives.

Themochemical Characteristics of the Salts of Azotetrazole

For reliable determination of the thermodynamic characteristics of explosives, not only the purity of the substance is important, but also the method of determination and the conditions of sample preparation. In order to prevent incomplete combustion, the samples are burned without a crucible, with the pressed pellet of the substance under study placed into an igniter coil rolled out of a nichrome wire. This allows igniting the sample over its entire surface and eases the access of oxygen to the substance.

In the case of ignition in a calorimetric bomb in an oxygen medium, the pressed charges of salts burn with a sharp sound. Despite the explosive character of conversion of the salts, the combustion energy measurements indicate satisfactory reproducibility in parallel tests.

The salts under study burn according to the following reactions:

$$C_2H_8N_{12}(s) + 4O_2(g) \\ \to 2CO_2(g) + 4H_2O(liq) + 6N_2(g), \quad (1)$$

$$C_2H_{10}N_{14}(s) + 4.5O_2(g) \\ \to 2CO_2(g) + 5H_2O(liq) + 7N_2(g), \quad (2)$$

$$C_4H_{12}N_{16}(s) + 7O_2(g) \\ \to 4CO_2(g) + 6H_2O(liq) + 8N_2(g), \quad (3)$$

$$C_4H_{14}N_{18}(s) + 7.5O_2(g) \to \\ \to 4CO_2(g) + 7H_2O(liq) + 9N_2(g), \quad (4)$$

$$C_4H_{18}N_{22}(s) + 8.5O_2(g) \\ \to 4CO_2(g) + 9H_2O(liq) + 11N_2(g). \quad (5)$$

Here (s), (liq), and (g) denotes the solid, liquid, and gaseous states.

The molar standards of the enthalpy of combustion $\Delta_c H$ are calculated from the values of the internal combustion energy $(-\Delta_c U)$ using the equation

$$\Delta_c H = \Delta_c U + \Delta n RT, \quad (6)$$

where Δn is the quantity difference of moles of the gaseous reaction products and original reagents. In accordance with stoichiometry of reactions (1)–(5) and resulting values of the internal combustion energy of the salts $(NH_4)_2AzT$, $(N_2H_4)_2AzT$, Gu_2AzT,

Table 6. Enthalpy of formation of salts

Base	ΔH_f^0, kJ/mol					
	Acid					
	H_2AzT	$HClO_4$	$HN(NO_2)_2$	HNO_3	NT+	HCl
NH_3	443.9 [9] 452 ± 23	−295.3 [37]	−134.6 [38]	−365.1 [39]	−269.9 [40]	−314.4 [37]
N_2H_4	659 ± 14	−176.6 [37]	−13.6 [38]	−246.3 [37]	−159.0 [41]	−196.6 [37]
NH_2OH	—	−277.6 [42]	−140.2 [43]	−366.5 [37]	—	−317.6 [37]
Gu	410.0 [9] 387 ± 44	−311.1 [44]	−157.8 [38]	−386.9 [44]	−297.1 [45]	−324.9 [44]
AG	434.3 [16]	−192.0 [46]	43.7 [38]	−278.7 [46]	−177.8 [47]	−220.6 [46]
DAG	708.8 [16]	—	—	−157.3 [48]	−87.9 [47]	—
TAG	1075 [9] 1065 ± 37	36.3 [49]	182.9 [38]	−50.2 [49]	58.6 [47]	5.2 [49]
const*	—	1018	706	1171	978	1060

Here *const = $\Delta H_f^0 (HL)_2$AzT − $2\Delta H_f^0 LHB$.

$(AG)_2$AzT, and $(TAG)_2$AzT, their enthalpies of formation are calculated. The following standard enthalpies of formation of the reaction products are used: CO_2(g) ($\Delta_f H_{298}^0 = -393.51 \pm 0.13$ kJ/mol) and H_2O(liq) ($\Delta_f H_{298}^0 = -285.81 \pm 0.04$ kJ/mol) [36]. The calorimeter data of the salts of azotetrazole are given in Table 5. The standard deviation of the resulting enthalpies of formation ranges from 14 kJ/mol for $(N_2H_5)_2$AzT to 44 kJ/mol for Gu_2AzT.

Naturally, along with methodical errors, the uncontrollable presence of impurities in the sample under study highly contributes to errors in measuring the enthalpy of formation. Many experimental studies of salts of various acids with organic bases allow one to statistically choose the most correct value from the differing experimental data. It can be assumed that the enthalpy of salt comes from the sum of enthalpies of formation of free components in solid form and the energy of salt formation [50]:

$$\Delta H_f^0 LHA = \Delta H_f^0 L + \Delta H_f^0 HA - \Delta H_{\text{diss}}. \quad (7)$$

In this case, the difference between the enthalpies of formation of salts of different acids with identical bases is a constant. The known enthalpies of formation of a series of salts of two acids can be used to obtain an average value of this constant (Table 6). In turn, if this constant and enthalpy of formation of one of the acids are known, it is possible to quite correctly calculate the enthalpy of formation of a similar salt of another acid:

$$\Delta H_f^0 (LH)_2\text{AzT} = 2\Delta H_f^0 LHB + \text{const}. \quad (8)$$

Thus, based on data for similar salts of nitric, perchloric, dinitramidic, and hydrochloric acids, as well as nitrotriazolone, the enthalpies of formation of ammonium, hydrazine, hydroxylamine, guanidine, aminoguanidine, diaminoguanidine, and triaminoguanidine salts of azotetrazole are calculated. The calculation results are given in Table 7.

It can be assumed that the averaged enthalpy of formation obtained from several series of similar salts of different acids may minimize the error introduced through methodical errors and impurities. As seen from Table 8, the experimental data obtained for $(NH_4)_2$AzT, $(N_2H_5)_2$AzT, Gu_2AzT, and $(TAG)_2$AzT are in good agreement with the calculation results (the deviation is 6–24 kJ/mol). The enthalpy of formation of aminoguanidine salt is significantly different from the expected value (lower by 159 kJ/mol), which is probably due to the fact that it is quite difficult to produce in pure form. Note that the reference values of the enthalpy of formation of this salt also differ from the estimated one: some of them are larger (161 kJ/mol [29]) and some smaller (187 kJ/mol [16]). It is also noteworthy that, in [9], all the three results for $(NH_4)_2$AzT, Gu_2AzT, and $(TAG)_2$AzT are valid (the difference from the estimated values does not exceed 17 kJ/mol).

The proposed approach also allows estimating the enthalpy of formation of unstable azotetrazole H_2AzT (with lower accuracy because the heat of salt formation is different for different acids) in the comparison of the salts of azotetrazole with similar salts of nitrotriazolone and bistetrazole $\Delta H_f^0 = 705 \pm 29$ kJ/mol.

Table 7. Enthalpies of formation of the salts of azotetrazole, calculated from several series of similar salts of different acids

Base	ΔH_f^0, kJ/mol					
	Acids whose salts are used for the calculations					
	$HClO_4$	$HN(NO_2)_2$	HNO_3	NT+	HCl	Average value
NH_3	427.3	436.7	440.2	437.9	430.7	428 ± 16
N_2H_4	664.8	678.5	678.0	659.6	666.2	669 ± 8
NH_2OH	462.8	425.5	437.5	—	424.4	442 ± 19
Gu	395.7	390.2	396.6	383.5	409.7	393 ± 10
AG	634.8	617.4	613.0	622.0	618.3	621 ± 8
DAG	—	—	855.9	801.9	—	829 ± 38
TAG	1090.5	1072.2	1070.1	1094.8	1069.8	1079 ± 15

Table 8. Comparison of experimental and averaged enthalpies of formation of the salts of azotetrazole

Salt	ΔH_f^0, kJ/mol*	ΔH_f^0, kJ/mol**	Δ, kJ/mol
$(NH_4)_2$AzT	452 ± 23 444 [9] 551 [10]	428 ± 16	24 16 123
$(N_2H_5)_2$AzT	659 ± 14 858 [12]	669 ± 8	−10 189
$(NH_2OH)_2$AzT	—	442 ± 19	—
Gu_2AzT	387 ± 44 410 [9] 452 [29]	393 ± 10	−6 17 59
$(AG)_2$AzT	462 ± 40 434[16] 782 [29]	621 ± 8	−159 −187 161
$(DAG)_2$AzT	709 [16]	829 ± 38	−120
$(TAG)_2$AzT	1065 ± 37 1075 [9]	1079 ± 15	−14 −4

*Experimental data; **The data averaged over several series of salts.

Decomposition of Na_2AzT

According to the DSC data, for the sodium salt of azotetrazole, there is an endothermic peak in the range $T \approx 120$°C which is related to dehydration of the salt and an exothermic peak at higher temperatures (250–300°C), indicating the thermal decomposition of anhydrous salt. The sodium salt of azotetrazole decomposes without melting.

The activation energy for Na_2AzT, calculated from the DSC data by the Kissinger method (see Table 3) is 41.0 kcal/mol, and the kinetic data are described by the expression $k = 3.3 \cdot 10^{14} \cdot \exp(-20\,815/T)$ (k in [s^{-1}] everywhere). This significantly differs from the decomposition activation energy of Na_2AzT (E_a = 68–88 kcal/mol), obtained previously from the DSC data [15].

To prepare for thermal decomposition in isothermal conditions, the sodium salt of azotetrazole is loaded into a manometric device in the form of pentahydrate and then vacuumed for dehydration at $T = 100$°C on a boiling water bath for 30 min. However, as the manometer is immersed into the thermostat at $T \geqslant 200$°C the salt explodes after 10–15 s.

In the case of lower temperatures (160–190°C), the decomposition rate noticeably slows down after release of 0.5–1.0 mol of gas per 1 mol of the starting substance (Fig. 2). In order to obtain the final volume of gases in the conducted experiments and avoid an explosion, the temperature is risen in two stages: initially up to 190–210°C and then, as 1.5 mol of gas per 1 mol of the starting substance is released, up to 230–240°C (Figs. 2 and 3). The final gas release is about 3 mol/mol. As temperature rises further to 350°C, at least 0.1 mol/mol is released.

The gas release curves in the first section are described by the first-order equation and the resulting rate constants are described by the expression $k = 2.0 \cdot 10^{11} \cdot \exp(-16\,560/T)$.

The cryoscopic analysis of gaseous products of decomposition of sodium salt shows that the gaseous phase contains only nitrogen (3 mol of nitrogen per 1 mol of the starting compound). Consequently, the element composition of the condensed product corresponds

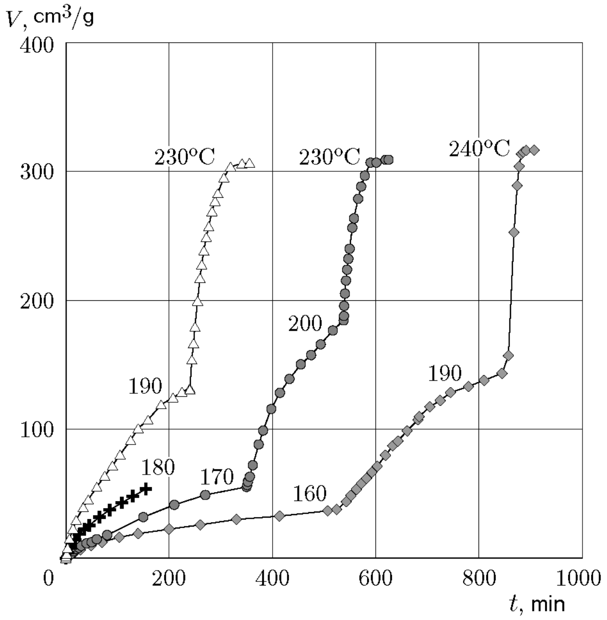


Fig. 2. Gas release in the decomposition of Na_2AzT at different temperatures.

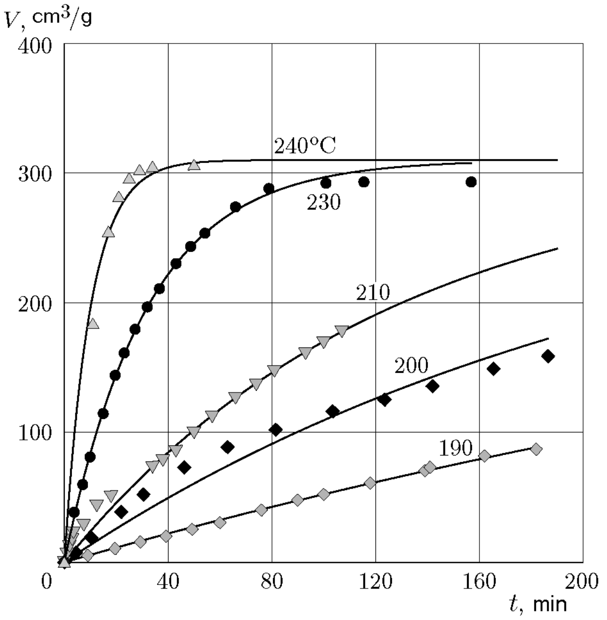


Fig. 3. Gas release in the decomposition of reduced samples of Na_2AzT at different temperatures.

to $NaCN_2$. This product is stable at temperatures up to 400°C.

The release of 3 mol of nitrogen corresponds to 40% loss of weight, which agrees well with the TGA data (36.5%) [15].

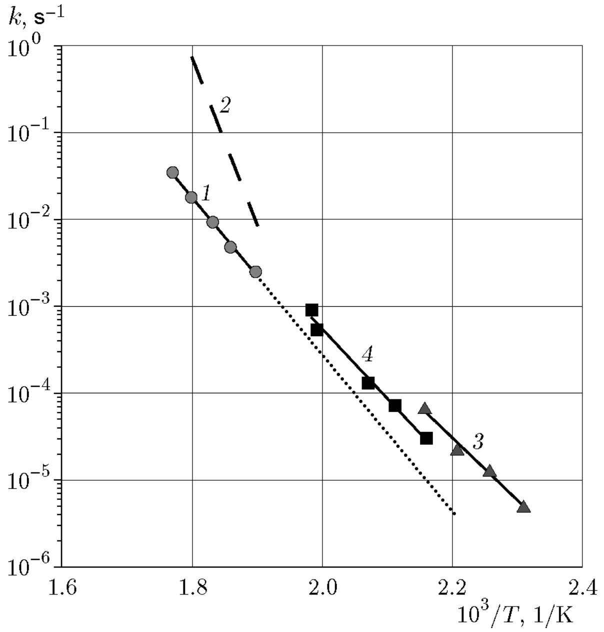


Fig. 4. Kinetic parameters of decomposition of Na_2AzT, obtained in nonisothermal conditions (points *1* and dotted curve; curve *2* [15]) and isothermal conditions (*3* and *4* for the weight of the sample about 10 and 1 mg, respectively).

The curves of gas release of decomposition of the reduced samples are also described by the first-order equation (Fig. 3), but the kinetic parameters are slightly different from those obtained previously: $k = 5.6 \cdot 10^{12} \times \exp(-18\,430/T)$. As seen from Fig. 4, as the sample is reduced, the kinetic data obtained in isothermal conditions begin approaching the kinetics obtained in the DSC experiments. The influence of the amount of substance on the kinetic parameters of decomposition apparently indicates the self-heating of a 10-mg sample in the decomposition in isothermal conditions. The published kinetic data of decomposition of Na_2AzT, shown in Fig. 4 is very different from the data obtained in the work, indicating an incorrect description of the experimental data.

Decomposition of $(NH_4)_2AzT$

The ammonia salt of azotetrazole is a compound whose decomposition is not complicated by the decomposition of its base. According to the DSC data (see Table 3), the salt of $(NH_4)_2AzT$ is less stable than sodium salt and decomposes without melting. Its decomposition rate constants in nonisothermal conditions in the coordinates $\ln k$–$1/T$ are described by the equation with an activation energy of 182.4 kJ/mol (43.6 kcal/mol): $k = 1.5 \cdot 10^{17} \cdot \exp(-21\,930/T)$.

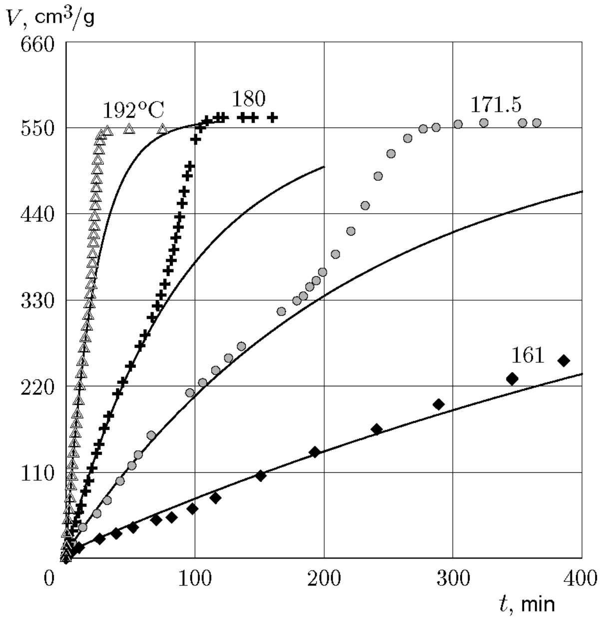


Fig. 5. Gas release in the decomposition of the salt of $(NH_4)_2$AzT at different temperatures: the points refer to the experimental date, and the curves refer to the description by the first-order model.

The shape of gas release curves for $(NH_4)_2$AzT in tests on isothermal decomposition is unusual (Fig. 5). Until a decomposition depth of 0.6, this salt decomposes according to the first-order reaction, after which the decomposition accelerates. The final volume of gases for $(NH_4)_2$AzT has a constant value in the entire temperature range under study and equals 550 cm^3/g (5 mol/mol). According to the cryoscopic analysis, the gaseous phase of ammonium salt contains 3 mol of nitrogen and 2 mol of ammonia per 1 mol of the starting compound.

The gas release curves in the decomposition of $(NH_4)_2$AzT in the range $T = 161$–192°C until a degree of decomposition of 0.6–0.7 is reached is described by the first-order equation, which yields a set of rate constants that obey the expression $k = 2.3 \cdot 10^{17} \times \exp(-22\,000/T)$. The data obtained in nonisothermal conditions in the DSC tests virtually match the kinetic parameters obtained in isothermal conditions (Fig. 6). In the range $T = 161$–210°C the decomposition of $(NH_4)_2$AzT is described by the equation with a high activation energy of 172.8 kJ/mol (41.3 kcal/mol): $k = 1.81 \cdot 10^{16} \cdot \exp(-20\,860/T)$.

One of the reasons for the accelerating decomposition of $(NH_4)_2$AzT in isothermal conditions at a large degree of decomposition could be dissolution of the substance in decomposition products, which results in that the process transfer from the solid phase to liquid one. In order to validate this assumption, the DSC at different heating rates is used to determine the decomposition kinetics of $(NH_4)_2$AzT in a mixture of low-melting ($T_{\rm melt} = 112$°C) and relatively thermostable (stable until 295°C) alcohol sorbitol. The stability of the mixture of $(NH_4)_2$AzT with sorbitol (1 : 4) is much lower than that of solid $(NH_4)_2$AzT. In the range $T = 165$–187°C the resulting rate constants are described by the expression $k = 7.6 \cdot 10^{19} \cdot \exp(-22\,430/T)$ (curve *3* in Fig. 6).

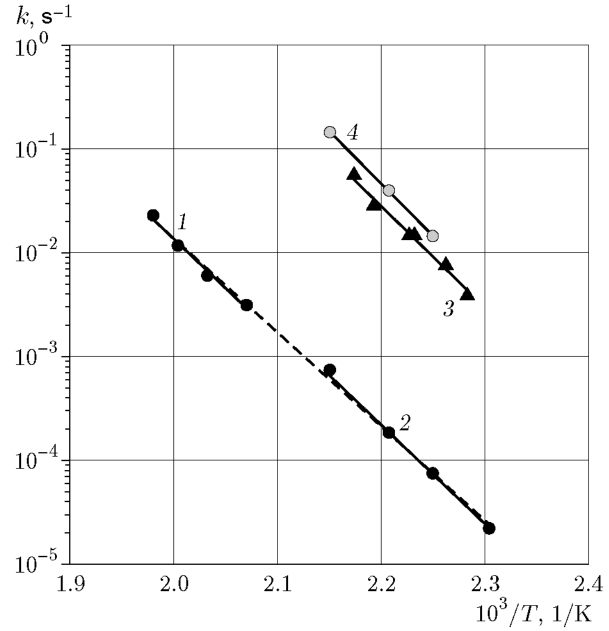


Fig. 6. Kinetic parameters of decomposition of $(NH_4)_2$AzT obtained in nonisothermal condition (*1* and *3*) and isothermal condition (*2* and *4*): decomposition in the solid phase (*1* and *2*) and decomposition in the liquid phase (*3* and *4*).

As seen from Fig. 6, the rate constants of the self-acceleration of $(NH_4)_2$AzT in isothermal conditions $k = 7.0 \cdot 10^{20} \cdot \exp(-23\,210/T)$ (curve *4*) are close to the decomposition constants of the solution $(NH_4)_2$AzT in the sorbitol melt. This confirms the statement that the decomposition of $(NH_4)_2$AzT in isothermal conditions accelerates because the starting substance dissolved in the decomposition products. The decomposition rate $(NH_4)_2$AzT in the liquid phase is 120–240 times higher than that in the solid phase.

Decomposition of $(N_2H_2)_2$AzT

The decomposition activation energy of the hydrazine salt of azotetrazole, calculated using the Kissinger method from the DSC data (see Table 3), turns out to be lower than that of ammonia salt: 125.1 kJ/mol (29.9 kcal/mol). In the range $T = 184$–212°C the resulting rate constants are described by the expression $k = 1.2 \cdot 10^{12} \cdot \exp(-15130/T)$.

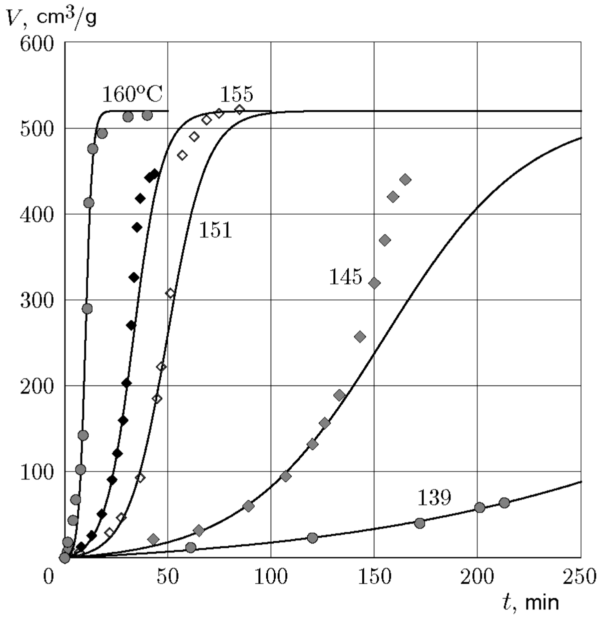


Fig. 7. Gas release in the decomposition of the salt of $(N_2H_5)_2$AzT at different temperatures: the points refer to the experimental data, and the curves refer to the description by the first-order model with autocatalysis.

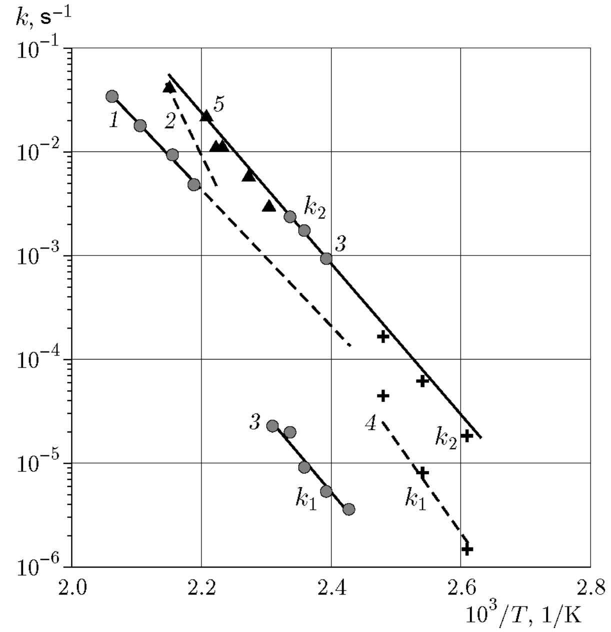


Fig. 8. Kinetic parameters of the decomposition of $(N_2H_5)_2$AzT obtained in nonisothermal conditions [*1* (points and curve), *2* (curve of [20]), and *5* (points)] and isothermal conditions: *3* (k_1 and k_2, points and curves) and *4* (curve of [12], k_1 and k_2); *3*(k_1) refers to the reaction in the solid phase; *3*(k_2), *4*(k_2), and *5* refer to the liquid phase.

The tests in isothermal conditions show that the decomposition accelerates. The final volume of gases is about 520 cm^3/g (5.2 mol/mol) (Fig. 7).

According to the cryoscopic analysis, the gas phase after the decomposition of hydrazine salt contains 3 mol of nitrogen, 1.3–1.5 mol of ammonia, and about 1 mol of hydrazine (that does decompose at these temperatures) per 1 mol of the starting compound.

In the range $T = 139$–$160°C$ the decomposition of $(N_2H_5)_2$AzT is described by the first-order autocatalysis equation [51] up to the high degrees of decomposition: $k_1 = 2.9 \cdot 10^{12} \cdot \exp(-17\,020/T)$ and $k_2 = k_k \cdot V_\infty = 2.3 \cdot 10^{14} \cdot \exp(-16\,740/T)$. Thus, the data obtained in nonisothermal conditions in the DSC tests are formal and represent averaging of the kinetics parameters of the process with autocatalysis (Fig. 8). Visual signs of melting appear during the decomposition of the hydrazine salt. It is likely that the decomposition accelerates in isothermal conditions because of submelting. In order to test this assumption, DSC at different heating rates is used to determine the decomposition kinetics of the mixture of $(N_2H_5)_2$AzT with low-melting ($T_{\text{melt}} = 92°C$) and relatively thermostable ($T_{\text{dec}} = 240°C$) hydrazine hydrochloride N_2H_5Cl with a ratio of 1 : 1. As seen from Fig. 8, the resulting decomposition constants fall into the dependence of the rate constant of self-acceleration k_2 on temperature, which is extrapolated onto the high-temperature range, and this confirms the assumption that the decomposition of $(N_2H_5)_2$AzT in isothermal conditions accelerates due to submelting. The decomposition rate $(N_2H_5)_2$AzT in the liquid phase is 140–175 times higher than that in the solid phase.

The rate constants obtained in nonisothermal conditions in [20] are close to the constants of this study, but the kinetic parameters have a very large difference (see Fig. 8). The kinetic data of the noncatalytic stage, obtained by means of TGA in isothermal conditions [12], also differ from the kinetic parameters of this study. Describing the data of the thermogravimetric study from [12] by the first-order autocatalysis equation helps obtaining both the constants of the noncatalytic stage k_1 and the constants of the acceleration stage k_2, which are in good agreement with the constants k_2 obtained by the manometric method (Fig. 8). Thus, the resulting isothermal kinetics of decomposition $(N_2H_5)_2$AzT in the liquid phase (k_2) describes the decomposition in a wide temperature range of 110–192°C. The difference in the rate constants k_1 (curves *3* and *4* in Fig. 8) is probably due to the fact that TGA (curve *4*) allows for the substance to evaporate, which overstates the observed initial rate.

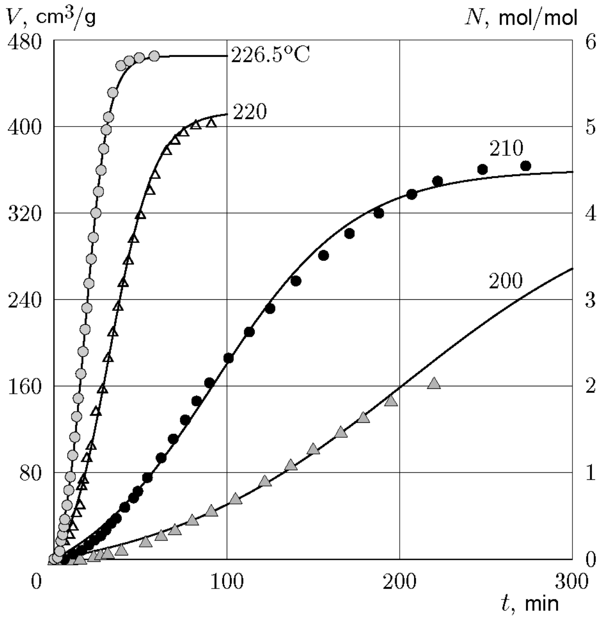


Fig. 9. Gas release in the decomposition of Gu_2AzT at different temperatures: the points refer to the experimental data, and the curves stand for the description by the first-order autocatalysis model.

Decomposition of $(Gu)_2AzT$

The guanidine azotetrazole is an onium salt with the strongest thermostability among those studied. According to the DSC data (see Table 3), the decomposition rate constants of Gu_2AzT in nonisothermal conditions, which are described in the coordinates $\ln k$–$1/T$ by the equation with a high activation energy of 210.9 kJ/mol (50.4 kcal/mol): $k = 1.06 \cdot 10^{17} \times \exp(-22\,290/T)$.

In the tests in the isothermal decomposition, the gas release curves indicate that decomposition accelerates with time. The final volume of gases is about 450 cm^3/g (6 mol/mol) (Fig. 9). According to the cryoscopic analysis, the gas phase of guanidine azotetrazole contains 3 mol of nitrogen and about 3 mol of ammonia per 1 mol of the starting compound.

In the range T = 200–226.5°C, the decomposition of Gu_2AzT is described by the first-order catalysis equation: $k_1 = 8.7 \cdot 10^{15} \cdot \exp(-22\,630/T)$ and $k_2 = k_k \cdot V_\infty = 4.2 \cdot 10^{17} \cdot \exp(-23\,320/T)$. As in the case of hydrazine salt, the data for the decomposition of Gu_2AzT, obtained in nonisothermal conditions in DSC tests, are formal and represent averaging of the kinetic parameters of the process with autocatalysis (Fig. 10). It is noteworthy that the extrapolation of kinetic data of the noncatalytic stage k_1 onto the low-temperature range is in good agreement with the decomposition rate constant of Gu_2AzT obtained at T = 130°C using the weight loss data [8]. Thus, it can be stated that, in a very wide range of temperatures of 130–226.5°C the decomposition of Gu_2AzT in the solid phase is described by the above-given equation k_1 with an activation energy of 187.4 kJ/mol (44.8 kcal/mol).

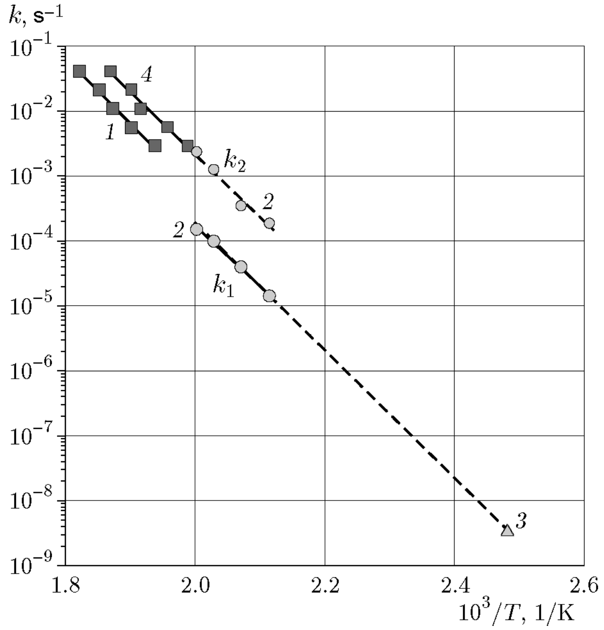


Fig. 10. Kinetic parameters of the decomposition of solid Gu_2AzT obtained in nonisothermal conditions (*1*, points and curve) and isothermal conditions [*2* (k_1, points and curves) and *3* (k_2, points)]; points and curve *4* refer to the decomposition of Gu_2AzT in the liquid phase in nonisothermal conditions.

According to the DSC data, the decomposition of Gu_2AzT starts before melting, but the condensed residue in the pressure gauge manifests the signs of liquefaction after decomposition. It can be assumed that the reason for the acceleration during the decomposition of Gu_2AzT in isothermal conditions is submelting. This assumption can be validated by using DSC at different heating rates to obtain the decomposition kinetics of Gu_2AzT in the mixture with low-melting (T_{melt} = 178–185°C) and relatively thermostable (stable until 265°C) guanidine hydrochloride. In the range T = 249–262°C the resulting rate constants are described by the expression $k = 4.0 \cdot 10^{16} \cdot \exp(-22\,200/T)$. In the Bourdon pressure gauge at T = 230°C this mixture (5% Gu_2AzT + 95% Gu · HCl) is described by the first-order equation up to large depths of decomposition, which allows considering data obtained in nonisothermal conditions (DSC) as correct.

As seen from Fig. 10), the rate constants of the self-acceleration stage k_2 fall into the above-given dependence extrapolated onto the lower-temperature range, which confirms the idea that the decomposition of Gu_2AzT in isothermal conditions accelerates because of submelting. Thus, in the wide range temperatures 210–262°C the decomposition of Gu_2AzT in the liquid phase is described by the equation with an activation energy of 183.7 kJ/mol (43.9 kcal/mol). The decomposition rate of Gu_2AzT in the liquid phase is only 13–16 times higher than that in the solid phase.

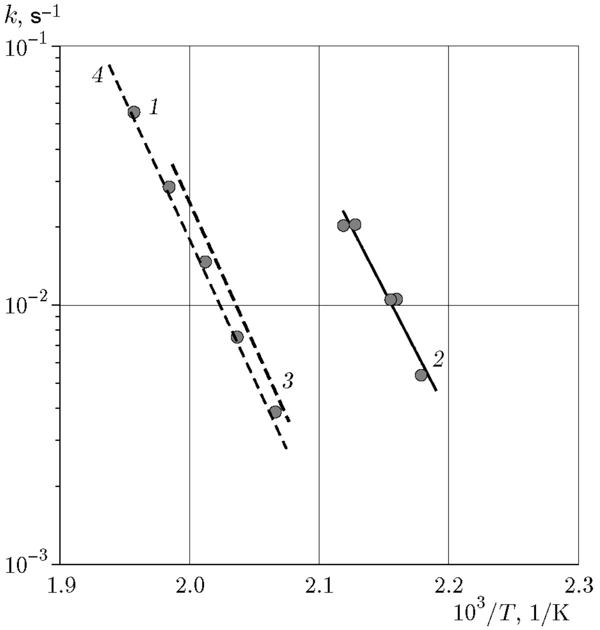


Fig. 11. Kinetic parameters of decomposition of $(AG)_2AzT$ in solid phase (*1*, *3* [16], and *4* [19]) and liquid phase (*2*) in nonisothermal conditions.

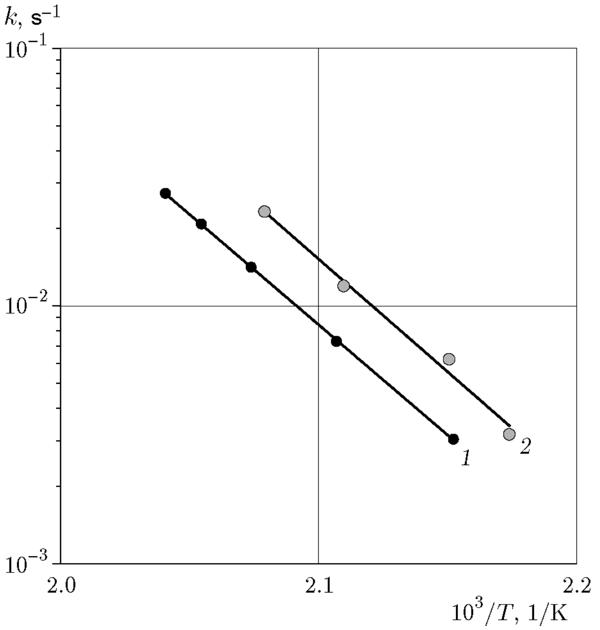


Fig. 12. Kinetic parameters of decomposition of $(TAG)_2AzT$ in solid phase (*1*) and liquid phase (*2*) in nonisothermal conditions.

Decomposition of $(AG)_2AzT$ *and* $(TAG)_2AzT$

The stability of the salts of amino- and triaminoguanidine with H_2AzT is studied in this paper only in nonisothermal conditions using DSC. As noted above, the data obtained in isothermal conditions [8] conclude that the decomposition of the salts of aminoguanidine and triaminoguanidine proceeds with strong acceleration, so the kinetic parameters determined in nonisothermal conditions are formal and fail to reflect the kinetics of the initial stage of decomposition. As shown on the examples of ammonia, hydrazine, and guanidine salts, acceleration is due to the melting or dissolution of the original substance in the decomposition products. In other words, it can be expected that the decomposition of these compounds in the liquid phase obeys the first- order equation, and the data obtained in nonisothermal conditions can be used to calculate the correct rate constants. The DSC method at different heating rates is applied to obtain the decomposition kinetics of aminoguanidine salt in a mixture with aminoguanidine chloride $AG \cdot HCl$ ($T_{\rm melt} = 165$°C) and triaminoguanidine salt with sulfolane ($T_{\rm melt} = 27$°C and $T_{\rm boil} = 285$°C). The data are given in Figs. 11 and 12.

As seen from Figs. 11 and 12 and Table 9, showing all the kinetic data obtained in this study, the decomposition rates of $(AG)_2AzT$ and $(TAG)_2AzT$ in solid and liquid phases at identical temperatures have only nine- and two-fold differences, respectively. It should be noted that the processing of the kinetic data by the Kissinger method in the assumption of the first order of reaction in the case where the real process proceeds with self-acceleration yields averaged kinetic parameters of the noncatalytic stage and acceleration stage. Thus, the kinetic parameters of decomposition in solid phase are overestimated. However, the difference in the kinetic parameters of decomposition of Gu_2AzT in different physical states is not large either (13- to 16-fold). It is noteworthy that there is a significant difference in the kinetic parameters of the salts of ammonia and hydrazine in different physical states (more than two orders of magnitude) as compared with the salts of random guanidine derivatives (one order of magnitude).

Table 9. Data on the thermal decomposition of the salts of H_2AzT in different conditions

H_2AzT salt	T, °C	Physical state; Test conditions	A	E_a, kJ/mol (kcal/mol)	Correlation coefficient	$k_{250°C}$, s^{-1}
Na_2AzT	254–292	Solid; DSC	$3.3 \cdot 10^{14}$	173.1 (41.4)	0.9966	0.0017
	160–190	Solid; Isothermal	$2.0 \cdot 10^{11}$	137.7 (32.9)	0.9867	0.0036
	190–231	Solid; Isothermal 1-mg sample	$5.6 \cdot 10^{12}$	153.2 (36.6)	0.9880	0.0028
Gu_2AzT	243–276	Solid; DSC	$1.1 \cdot 10^{17}$	185.3 (44.3)	0.9910	0.032*
	200–227	Solid; Isothermal	$8.7 \cdot 10^{15}$	188.2 (45.0)	0.9955	0.0014
	230–262	Solution; DSC	$4.0 \cdot 10^{16}$	184.4 (44.1)	0.9822	0.015
	200–227	Liquid; Isothermal	$4.2 \cdot 10^{17}$	193.9 (46.3)	0.9769	0.018
$(AG)_2AzT$	186–199	Solid; DSC	$6.3 \cdot 10^{20}$	214.3 (51.2)	0.9994	0.25*
	181–209	Solution; DSC	$6.3 \cdot 10^{18}$	184.6 (44.1)	0.9544	2.26
$(TAG)_2AzT$	195–226	Solid; DSC	$1.3 \cdot 10^{16}$	166.9 (39.9)	0.9999	0.28*
	187–208	Liquid; DSC	$3.6 \cdot 10^{16}$	167.5 (40.0)	0.9922	0.67
$(NH_4)_2AzT$	210–232	Solid; DSC	$1.5 \cdot 10^{17}$	182.3 (43.6)	0.9879	0.092
	161–192	Solid; Isothermal	$2.3 \cdot 10^{17}$	182.9 (43.70)	0.9998	0.13
	165–187	Solution; DSC	$7.6 \cdot 10^{19}$	186.5 (44.6)	0.9833	18.0
	172–192	Liquid; Isothermal	$7.0 \cdot 10^{20}$	193.0 (46.1)	0.9998	37.6
$(N_2H_5)_2AzT$	184–212	Solid; DSC	$1.2 \cdot 10^{12}$	125.7 (30.1)	0.9933	0.33*
	139–160	Solid; Isothermal	$2.9 \cdot 10^{12}$	141.5 (33.8)	0.9572	0.021
	161–192	Solution; DSC	$6.5 \cdot 10^{14}$	143.7 (34.4)	0.9748	2.85
	145–160	Liquid; Isothermal	$2.3 \cdot 10^{14}$	139.2 (33.3)	0.9944	2.89

*The substance decomposes with self-acceleration, and the kinetic data calculated in the assumption of the first order of reaction are the averaged kinetic parameters of the initial stage and self-acceleration.

Decomposition of the Onium Salts of Azotetrazole

The characteristic feature of onium salts, which include the salts of 5,5′-azotetrazole with organic bases, is the possibility of reversible formation of the original acid and base:

$$(\mathrm{BH})_2\mathrm{AzT} \leftrightarrow 2\mathrm{B} + \mathrm{H_2AzT}.$$

The thermal decomposition of onium salts usually proceeds through the decomposition of the molecules of the less stable base or acid, formed in equilibrium at this temperature [52]. In this case, it is known that the acid H_2AzT is characterized by low thermal stability. Consequently, the decomposition rate of its salts is determined by the decomposition of free acid:

$$W = k[\mathrm{H_2AzT}].$$

As the transfer velocities of proton in the liquid phase are large (the relaxation time is 10^{-5}–10^{-10} s) and equilibrium is established quickly [53], the decomposition of the onium salt of azotetrazole can be considered as the decomposition of the free acid whose concentration is given by the strength of the acid and base:

$$[\mathrm{H_2AzT}] = \frac{K[(\mathrm{BH})_2\mathrm{AzT}]}{[\mathrm{B}]^2}.$$

In view of the determination of the acid-base equilibrium constants, the expression for the decomposition rate is written in the form:

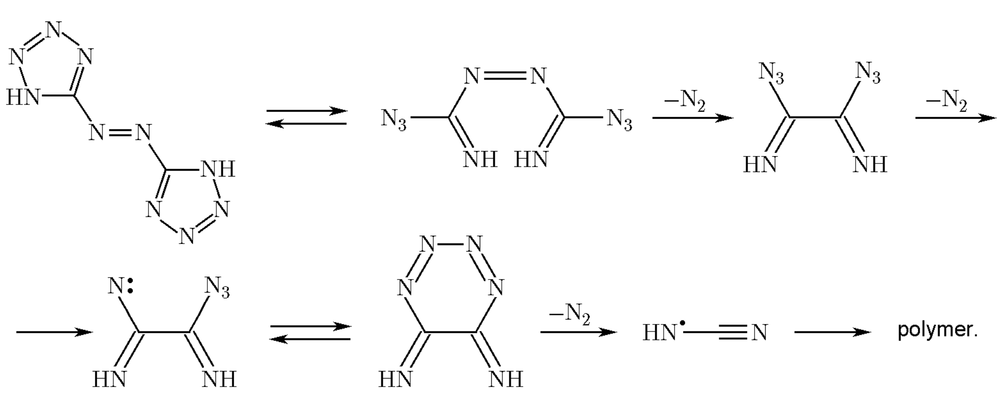
$$W = k[\mathrm{H_2AzT}] = \frac{kK_W^2}{K_bK_a}\frac{[(\mathrm{BH})_2\mathrm{AzT}]}{[B]^2} = k_f[(\mathrm{BH})_2\mathrm{AzT}].$$

Here K_W is the water autoprotolysis constant, K_a is the acid dissociation constant, K_b is the base protonation constant, and k_f is the observed constant.

Thus, for the salts of the same acid with different bases, the observed constants are different due to the differing basicity of the organic base, even though the decomposition of salts is determined by the decomposition of the same molecule, i.e., the free acid molecule.

Basicity is determined by the base protonation constant K_b (or the dissociation constant K_a) of the acid conjugates with it), which is usually measured in water. An acidity value significantly varies in nonaqueous media, which may include a melt (or solution) of salt. Nevertheless, in the absence of other data, the indicators $\mathrm{p}K_a$ of conjugate acids are used to establish correlation between the thermal stability of the salts of azotetrazole (e.g., $k_{180^\circ\mathrm{C}}$) and basicity. The analysis of the decomposition rate constants of the salts of azotetrazole in the liquid phase shows that there is an increase in the decomposition rate with a decrease in the basicity of amines. The largest difference from the correlation dependence is observed in the hydrazine salt, and it largely vanishes if it is assumed that the values of $\mathrm{p}K_a$ of hydrazine and ammonia in the melt of salts are close.

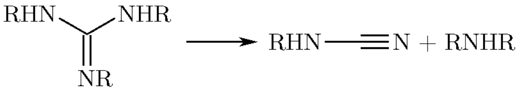
The low stability of free azotetrazole is quite surprising. Azocompounds with heterocycles, such as furazan and triazole, have high thermal stability [54, 55]. Also 5-(4-amidinum-1-tetrazene) tetrazole (tetrazene), bearing an azogroup bound to a tetrazole cycle, has quite acceptable stability [2, 4]. It is known [56] that the decomposition of an azocompound can begin with scission of a C—N bond or proceed according to a concerted mechanism with the release of a N_2 molecule and the formation of a new C—C bond. The activation energy of the concerted mechanism is usually lower than that of the scission of the C—N bond [57, 58]. The finding of the $C_2H_2N_6$ ion [17, 18] in the mass spectrum of the decomposition products of Gu_2AzT, which can be formed according to the reaction (R2), plays in favor of the concerted mechanism:



(R2)

The decomposition is preceded by tetrazole-imine isomerization and the transition of the azogroup from trans- to cis-conformation. This assumption is confirmed by the good stability of hydrazotetrazole (T_{exo} = 235°C and DSC 5°C/min [59]), incapable of this transition.

Guanidine bases in free form possess low stability and decompose in parallel to azotetrazole:



(R3)

$R = H, NH_2.$

Hydrazine is characterized by good stability and the fact that it partially vanishes during the decomposition of salt indicates the reaction of hydrazine and nitrene formed in the decomposition of tetrazole cycles.

The cryoscopic analysis of onium salts shows that the decomposition of the salts of azotetrazole results in the formation of N_2 and NH_3 and condensed products. The presence of melamine (meleme) in condensed products is confirmed by infrared spectra and the results of the element analysis. These data agree well with the results of other studies [25].

CONCLUSIONS

The performed studies of the thermal stability of the onium salts of azotetrazole shows that the stability of salts increases along with the basicity of the bases. This relationship indicates the preliminary dissociation of salt and further decomposition of the free acid and base. Azotetrazole is the least stable among the salt dissociation products, and its decomposition is the key factor determining the stability of salt. The basicity determines the concentration of the free azotetrazole, thereby affecting the decomposition rate of salt. The active particles resulting from the decomposition of azotetrazole can involve more stable bases into the process. It is assumed that the decomposition of azotetrazole proceeds according to the concerted mechanism with low activation energy. As the decomposition is preceded by tetrazole-imine izomerization and transfer of the azocompound from the trans- to cis-conformation, the observed activation energy in the liquid phase lies in the range 163–193 kJ/mol (39–46 kcal/mol).

The thermodynamic characteristics of a series of salts of azotetrazole are determined. On the basis of the comparative analysis of the experimental and estimated enthalpies of formation of salts of different acids with organic compounds, the most reliable values are chosen and the approach to calculating the enthalpies of formation of new salts is proposed.

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