High-Nitrogen Energetic Materials of 1,2,4,5-Tetrazine Family: Thermal and Combustion Behaviors

Valery P. Sinditskii, Viacheslav Yu. Egorshev, Gennady F. Rudakov, Sergey A. Filatov, and Anna V. Burzhava

Abstract Considerable recent attention has been focused on research and development of high-nitrogen energetic materials. Among polynitrogen energetic materials, 1,2,4,5-tetrazine derivatives are of particular interest owing to their high density, thermostability, and remarkable insensitivity to electrostatic discharge, friction, and impact. The purpose of the present work is to analyze possible application areas of different types of tetrazine-based energetic materials reasoning from their peculiar combustion properties. Study of thermal stability of tetrazine derivatives has shown that, in most cases, the stability of the substance is determined by decomposition of the less stable substitute rather than the tetrazine cycle itself. Combustion and thermocouple-aided studies have revealed that tetrazines are mostly low-volatile substances with high burning surface temperatures that, in turn, predetermine the condensed-phase combustion mechanism. The lack or low content of oxygen in tetrazine-based energetic materials results in formation of high-enthalpy species among combustion products, thus preventing from full release of energy stored in the material.

1 Introduction

Energetic materials that burn at the expense of energy derived from positive heat of formation rather than oxidation of the carbon backbone have recently attracted attention not only as explosives but also as components of gas-generating and propellant compositions because they are capable of producing relatively high specific impulse despite low combustion temperature [1]. 1,2,4,5-Tetrazine (also known as s-tetrazine) derivatives are among these compounds. 1,2,4,5-Tetrazines are unique heterocyclic compounds containing the maximum number of nitrogen atoms in the cycle among the stable azines. Introduction of nitrogen atoms in the

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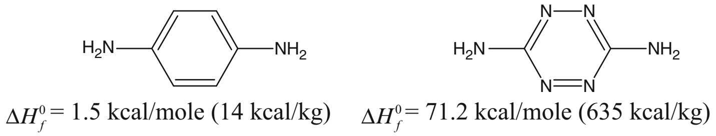
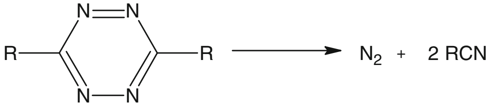


Scheme 1



Scheme 2

molecule leads to an increase in the enthalpy of formation. As it can be seen from Scheme 1, the tetrazine ring even without explosophoric groups has a high enough enthalpy of formation, providing TNT coefficient as large as 0.6.

Decomposition mechanism of photochemically excited 1,2,4,5-tetrazines, proposed by Hochstrasser in 1975, consists of the triple concerted dissociation [2] (Scheme 2).

It was theoretically proved by Schaefer in 1986 [3]. In 2000, J. Oxley et al. [4] investigated the thermal decomposition of a large number of tetrazine derivatives and found out that thermal decomposition might follow this pathway, but it was not concerted and not the only pathway. It was shown that the tetrazines exhibit two principal modes of decomposition: elimination of N_2 from the tetrazine ring followed by cleavage of the remaining N-N bond and loss of the substituent group, in some cases assisted by proton transfer. Tetrazine ring possesses high thermal stability; elementary representatives, for example, diaminotetrazine, decompose at temperatures over 300 °C.

It was discovered that some of tetrazine derivatives can be surprisingly insensitive toward destructive stimuli such as impact, friction, and electrostatic discharge. Furthermore, some of these compounds display interesting explosive performance and extraordinary combustion properties: high burning rates and a weak dependence of the burning rate on the pressure. The latter was attributed to the occurrence of the leading combustion reaction in the condensed phase [5] that is not quite correct. The low dependence of the burning rate on the pressure is typical of the systems with the invariable surface temperature, for example, of some thermites. If the temperature of the burning surface (the place of the leading combustion reaction) is defined by boiling, it grows with pressure, and, correspondingly, the exponent in the combustion law can change in a wide interval and even exceed unity.

Due to their remarkable properties, tetrazine-based energetic materials have been proposed for using in various fields: insensitive "green" explosives, components of powders and solid rocket propellants, gas-generating and fire-fighting compositions, monopropellants, and fuel components for microengines.

In recent years, there have been a number of reviews, dedicated to s-tetrazines as building blocks for new functional molecules, including energetic materials [1, 6]. However, an analysis of the combustion behaviors of tetrazines, their place among other energetic materials, has not been carried out yet. The purpose of the present work was to analyze burning behavior of these compounds, try to establish a connection between their physicochemical properties and combustion mechanism, and propose possible application areas of different types of tetrazine-based energetic materials reasoning from their peculiar combustion properties.

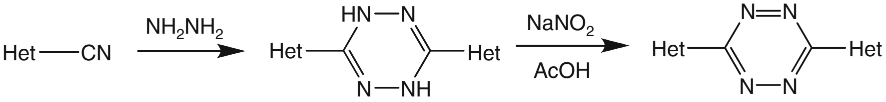
A wide range of derivatives of 1,2,4,5-tetrazine have been synthesized to date. They can be conventionally divided into four groups: (1) compounds that contain no oxidizing elements in the molecule (CHN-tetrazines), (2) compounds that contain active oxygen in the molecule (CHNO-tetrazines), (3) salts of tetrazine derivatives with oxidizing acids, and (4) salts of tetrazine derivatives with metals and coordination compounds with metal nitrates and perchlorates.

2 General Schemes of Synthesis of Substituted s-Tetrazines

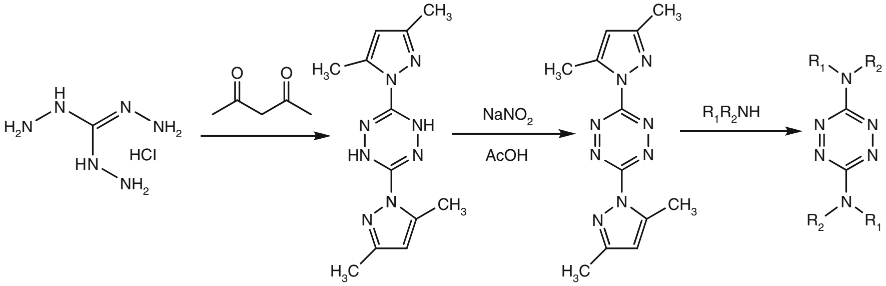
s-Tetrazines have long been discovered; the first report dates back to the end of the nineteenth century. A convenient method for the synthesis of symmetrically disubstituted tetrazine, containing alkyl, aryl, or hetaryl moieties, is the Pinner method, which comprises cycling the corresponding nitriles under the action of hydrazine followed by oxidation of the intermediate dihydrotetrazine [7] (Scheme 3).

The tetrazine chemistry reached its peak after the 1990s, when American researchers from Livermore Laboratory have proposed a method of synthesis of 3,6-bis(dimethylpyrazolyl)tetrazine from available and cheap starting materials – triaminoguanidine and acetylacetone [1, 8]. Dipyrazolyltetrazines are remarkably versatile starting synthons for preparation of a huge number of tetrazines by simply using nucleophilic displacement of the pyrazolyl groups by various nucleophiles (Scheme 4).

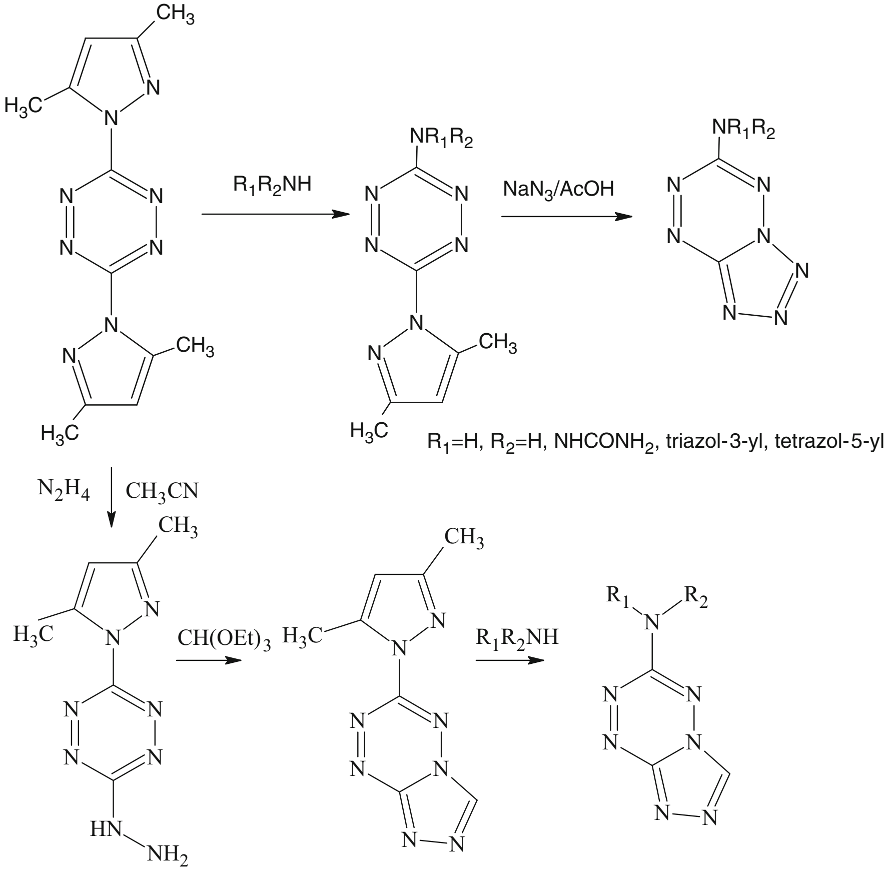
Dimethylpyrazolyltetrazine reacts with weakly based hetarylamines such as aminofurazans, aminoimidazoles, aminotriazoles, aminotetrazoles, or aminotetrazines to afford 3-hetaryl-amino-s-tetrazines [9]. Dipyrazolyltetrazine can react to form monosubstituted products, which, in turn, can be transformed to derivatives of annulated azolotetrazines: triazolotetrazines and tetrazolotetrazines (Scheme 5).



Scheme 3



Scheme 4



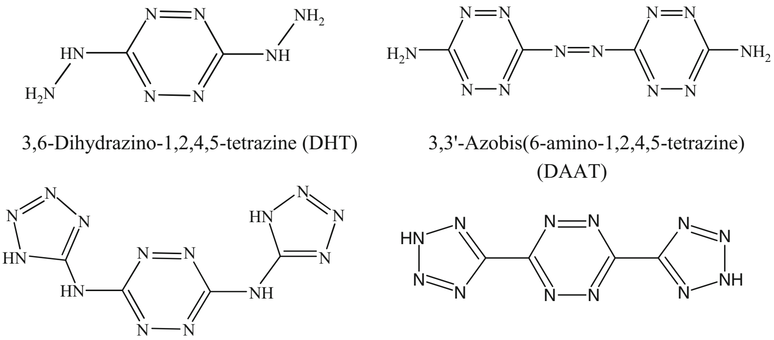
R_1=H, R_2=H, $NHCONH_2$, triazol-3-yl, tetrazol-5-yl

Scheme 5

3 Energetic Materials Based on CHN-Tetrazines

The main representatives of tetrazine-based energetic materials without active oxygen are shown in Scheme 6. As it can be seen from the Scheme and Table 1, the introduction of endothermic substituents, such as hydrazine, tetrazole, or diazo group in the tetrazine cycle leads to energetic materials with the enthalpy of formation up to 900–1000 kcal/kg. Such high-energy content makes these materials explosive with detonation velocity of about 7500 m/s and more.

Dihydrazino-tetrazine (DHT) was previously calculated to perform well in both rocket and gun propellant applications [12]. DHT is described as a highly energetic fuel having a heat of formation measured as 128 kcal/mol or 900 kcal/kg [9]. The hot flame and carbon-free combustion of DHT have made it ideal for a new generation of reduced-toxicity fireworks [10].



3,6-Dihydrazino-1,2,4,5-tetrazine (DHT)

3,3'-Azobis(6-amino-1,2,4,5-tetrazine) (DAAT)

3,6-Bis(tetrazol-5-amino)-1,2,4,5-tetrazine (BTATz)

3,6-Bis(tetrazol-5-yl)-1,2,4,5-tetrazine (BTT)

Scheme 6

Table 1 Some physicochemical properties of main CHN-tetrazines

Compound	Density (density of pressed sample), g/cm^3	ΔH_f^0, kcal/mol (kcal/kg)	DSC exotherm, °C (heat effect, kcal/kg)	Detonation velocity, m/s (density, g/cm^3)
DHT	1.69 [17] (1.59)	128 (900) [11]	164 (307) and 307 (196) [4][b]	7540 (1.56) [18]
DAAT	1.78 [19]	206 (936) [13, 21]	>252 [15]	7400 (1.65) [14]
	1.76 (1.65) [20]	247 (1123) [14]	320 (714) [14]	7900 (1.78) [22]
BTATz	1.76 [23]; 1.742 [24] (1.71)	211 (850) [25]; 170 (685)[a] [26]	264[c] [12]; 320 (374) [27]	7520[a] (1.76) [12]
BTT	1.68 [28]	224 (1026) [22]	235 (633) [22]	7950[a] (1.68)

[a] Estimation

[b] Two-stage decomposition

[c] DSC onset

Experimental test of 3,3′-azobis(6-amino-1,2,4,5-tetrazine) (DAAT) with 5 mass % Kel-F 800 binder yielded a detonation velocity of 7400 m/s at a pellet density of 1.65 g/cm^3, the detonation velocity at TMD (1.78 g/cm^3) was extrapolated to reach 7900 m/s. A density of 1.76–1.78 g/cm^3 was measured by gas pycnometry [13, 14] which is somewhat lower than the value reported by Hiskey et al. (1.84 g/cm^3, Ref. [13]). Sensitivity properties of DAAT demonstrate that the material is relatively insensitive to impact and resistant to initiation by electrical discharge and friction.

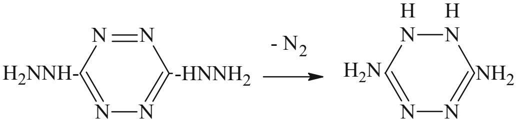
Bis(tetrazolylamino)tetrazine (BTATz) was treated as the key component for new generation propellants [12, 17], fire suppressing gas generators [11, 12], and automobile airbags [13]. BTATz can sustain burning when packed in glass tubes as small as 250 μm in diameter [12], which may well find an application as monopropellant for microthrusters [14, 15]. In addition, BTATz is ballistic modifier for propellants: adding 22 % BTATz to ammonium dinitramide (ADN) leads to 1.5 times increase in the burning rate and reduces the pressure exponent [18]. As a substitute of hexogen (RDX) in the composite modified double-base (CMDB) propellant, BTATz can improve the burning rate and reduce the pressure exponent [16].

As with DAAT, 3,6-bis(tetrazol-5-yl)-1,2,4,5-tetrazine (BTT) also can be described as low-sensitive energetic material. The high-nitrogen content of this energetic material makes it highly attractive as a component for energetic applications like gas-generating airbag formulations.

As it was noted above, the thermal stability of the tetrazine ring is quite good. The pure DAAT was found to be thermally stable up to melting point 252 °C [13, 15]. BTATz is also thermally stable substance, demonstrating DSC exotherm maximum at 320 °C [21]. It is interesting to note that BTT which is similar to BTATz, but free of NH-bridges between heterocycles, shows much less temperature of DSC exotherm [22]. DHT decomposes in two steps, demonstrating exotherms at 164 and 307 °C [4]. The low thermal stability of DHT has been explained by primary decomposition of the exocyclic substituent or by its loss [4]. This explanation is not quite obvious, since the hydrazine moiety is stable enough.

In our lab, we studied two compounds from this class, DHT and BTATz [20]. The experiments on thermal decomposition of DHT under isothermal conditions were carried out in thin-walled glass manometers of the compensation type (the glass Bourdon gauge) in the temperature interval of 110–130 °C. There is a sharp rise of the gas release curves preceded by a section with small decomposition rate, which is typical for decomposition with self-acceleration. The reason for such a behavior is topochemistry. Most likely, the section of fast gas release is associated with the DHT decomposition on the crystal defects. The rate constants were evaluated from experimental data using a model of first-order reaction with self-acceleration. The difference in rate constants between first-order reaction and self-acceleration is two orders of magnitude. Taking into account complex behavior of DHT decomposition, the rate constants obtained under DSC nonisothermal conditions should be considered as formal.

Scheme 7



Maximum gas release at DHT decomposition at 110–130 °C is not big (208 cm^3/g or 1.32 mol of gas per one mole of DHT), which is close to data of work [29] (0.79–0.83 mol/mol). It has been determined that the first stage of DHT decomposition is not the loss of the exocyclic hydrazine moiety but the redox process, in which the tetrazine ring is reduced by the hydrazine groups to form diaminodihydrotetrazine and molecular nitrogen [20] (Scheme 7).

This is because the tetrazine is the electron-poorest aromatic system that makes the tetrazine ring a strong electron attractor. The easy reduction of tetrazines was reported by Stone et al. as soon as 1963 [30]. Decomposition of the formed diaminodihydrotetrazine occurs at higher temperatures during the second stage.

BTATz is a much more thermally stable substance. Its decomposition under isothermal conditions in the temperature interval of 250–285 °C follows a first-order reaction to high extent of decomposition, and no self-accelerations is observed. Maximum gas release at BTATz decomposition is 280 cm^3/g or 3 mol of gaseous products per one mole of BTATz. The study of BTATz decomposition allows assumption that the decomposition involves all three heterocyclic rings. The rate constants obtained in different works [21, 31] in isothermal and nonisothermal conditions are in a good agreement with each other. All rate constants obtained in the our work [20] in the interval of 250–334 °C are well described by the Arrhenius equation with activation energy of 57.5 kcal/mol: $k = 2.0 \cdot 10^{19} \exp(-28900/T),\ s^{-1}$.

The kinetic parameters of BTATz decomposition proved to be rather high for typical first-order reaction. Decomposition reactions of the tetrazole ring include preliminary isomerization of 1H-tautomer in 2H-tautomer with subsequent elimination of a molecule of nitrogen by means of the concert mechanism [32, 33] or isomerization of 1H-tautomer of tetrazole in azidoimine with subsequent elimination of molecular nitrogen from the azido group [34-36]. Because of preliminary isomerization, the observable activation energy is higher than the activation energy of nitrogen elimination reaction itself.

According to Son et al. [37], DHT has a high burning rate, slightly <50 mm/s at 10 MPa. In our experiments [20], DHT in the form of samples, pressed into 4-mm acrylic tubes, is capable of stable burning starting from a pressure of 0.2 atm (Fig. 1). Pressure dependence of the burning rate is described by two laws ($r_b = 3.63p^{0.69}$; $r_b = 2.04p^{0.67}$) for different pressure intervals (0.02–2 MPa and 4–10 MPa, respectively), which are divided by the combustion instability region. Literature data agree with ours at high pressures only. The difference at low pressures is likely to be connected with some admixtures to the samples, for example, trace amounts of a volatile solvent, acting as the coolant.

BTATz also demonstrates high burning rates. Available data on burning rates of BTATz vary over a wide range. Addition of binder and mode of purification

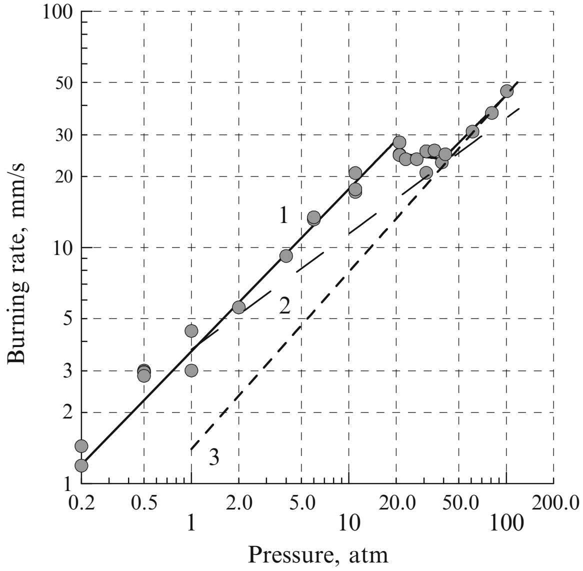


Fig. 1 Comparison of DHT burning rates measured in [20] (*1*, *points*) and [37]: DHT + 3 % estane (*2*), pure DHT (*3*)

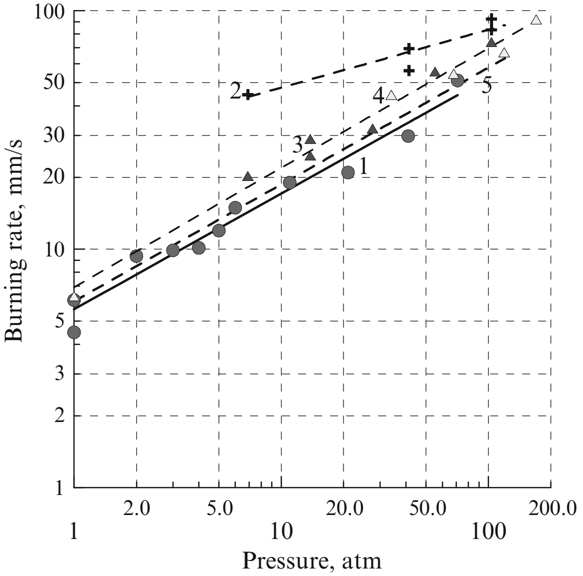


Fig. 2 Comparison of burning rates of BTATz samples obtained in different labs: data of [20] (*1*, *solid line* and *points*), data of [18] (*2*, *3*, *4*, *points* and *dashed lines*), data of [37] (*5*, *dashed line*)

both exert effect on the burning rate [18, 37]. A comparison of results obtained in the present work ($r_b = 5.6p^{0.49}$) with available data on burning rates of BTATz is presented in Fig. 2. Our burning rates are practically coincident with those for BTATz with 3 % of binder Kel-F [37] and slightly lower than data for samples of BTATz thoroughly washed by alcohol (points 3 and 4 in Fig. 2) [18]. Surprisingly, the maximum burning rates were observed in combustion of BTATZ samples treated with dimethylformamide (points 2 in Fig. 2).

Fig. 3 Temperature distribution in the combustion wave of BTATz at pressures 0.2 atm (*1*) and 4 atm (*2*)

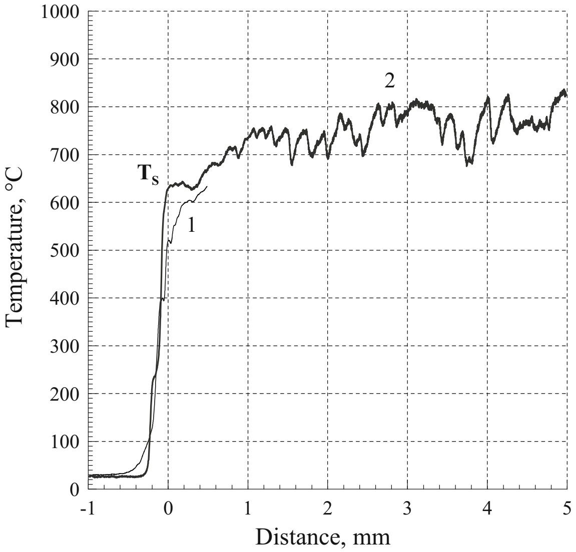
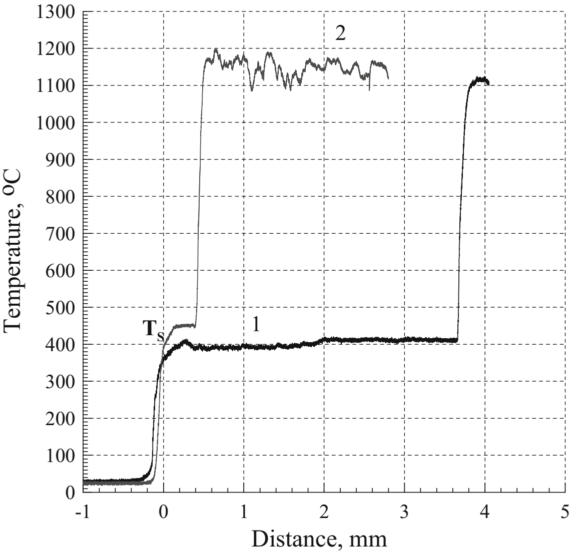
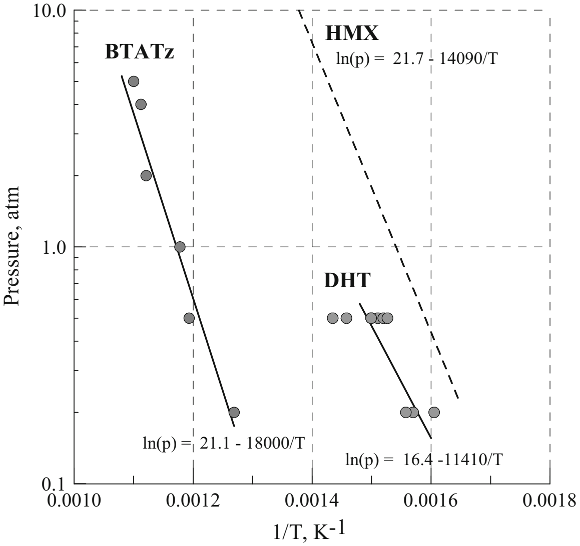


Fig. 4 Temperature distribution in the combustion wave of DHT at pressures 0.2 atm (*1*) and 0.5 atm (*2*)



Temperature profiles in the BTATz and DHT combustion wave were obtained with the help of thin tungsten-rhenium thermocouples at low pressures [20]. Both compounds burn with little or no luminous flame, indicating low flame temperatures. Indeed, the maximum measured flame temperature of BTATz does not exceed 800 °C (Fig. 3), which is 1060 °C less than the adiabatic temperature. Combustion of DHT proceeds in two-stage regime: there is a region between the surface and flame with a weak growth of temperature (Fig. 4).

Fig. 5 Surface temperature against pressure for BTATz, DHT, and HMX



The maximum measured flame temperature is also less than the adiabatic temperature, which is caused by formation of high-energy products in the flame, such as endothermic nitrile derivatives. The thermocouple measurements show that condensed-phase reactions play a dominant role in combustion of DHT and BTATz.

The effect of pressure on the measured surface temperatures of DHT and BTATz is shown in Fig. 5 in comparison with HMX [38]. Both tetrazines have surface temperatures significantly higher than those for such low-volatile substance as HMX. DHT is a low-volatile substance with boiling temperature of about 425 °C and heat of vaporization of 22.7 kcal/mol. BTATz is a nonvolatile substance with boiling temperature of about 580 °C and heat of vaporization of 35.8 kcal/mol.

Comparison of surface temperatures of various explosives at atmospheric pressure shows that temperatures of DHT and BTATz are, respectively, 50 and 200° higher than the surface temperature of HMX (Fig. 6). It is believed that so high temperatures of the rate-limiting combustion zone are responsible for the observed high burning rates of the tetrazines.

The DHT decomposition mechanism allows explanation of its combustion behavior. Since DHT combustion is controlled by a reaction in the condensed phase, one can derive kinetic parameters of this reaction if the residence time of the substance at the burning surface is known [39, 40]. Kinetics of the leading reaction of DHT combustion at low pressures $\left(k = 10^{12.26}\exp\left(-15850/T\right),\ \mathrm{s}^{-1}\right)$ coincide with kinetics of initial reaction of the first decomposition stage (Fig. 7).

The heat effect of this reaction averages about 280 cal/g. Since the surface temperature grows with pressure, at pressures above 2 MPa, the reaction heat effect becomes comparable with the heat required for warming up the condensed phase to the surface temperature and melting. The further increase of pressure results in occurrence of heat instability. At pressures higher than 4 MPa, the

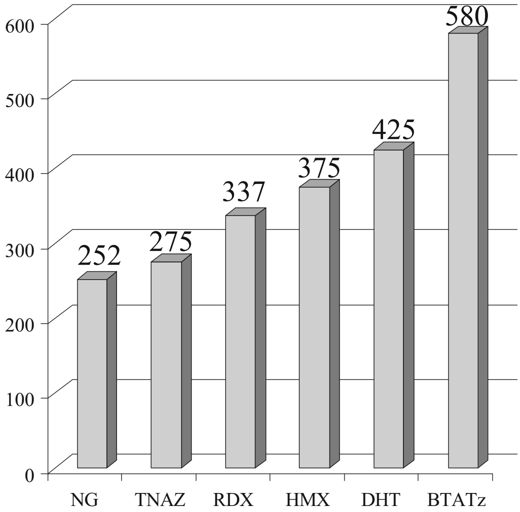


Fig. 6 Comparison of burning surface temperatures (in °C) of various explosives at atmospheric pressure

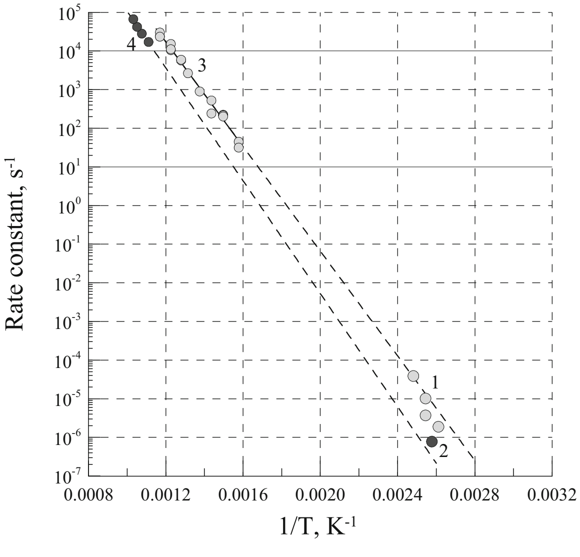


Fig. 7 Comparison of rate constants of initial reaction of the first (*1*) and second (*2*) decomposition stages and kinetics of the leading reaction of DHT combustion at low (*3*) and high (*4*) pressures

instability disappears. The burning rate at high pressures is obviously controlled by decomposition kinetics $\left(k = 10^{12.33}\exp\left(-16830/T\right),\ \mathrm{s}^{-1}\right)$ of the second stage with total heat effect of approximately 575 cal/g.

The comparison of the obtained rate constants of the leading reaction of combustion with rate constants of BTATz decomposition is shown in Fig. 8. As can be seen in the Figure, the kinetic parameters derived from the combustion model, $k\left(s^{-1}\right) = 10^{10.44}\exp\left(-16150/T\right)$, considerably differ from kinetics of decomposition BTATz in the condensed phase. The slope of dependence *lnk* vs. *1/T* for the leading reaction of combustion strongly differs from the slope of a

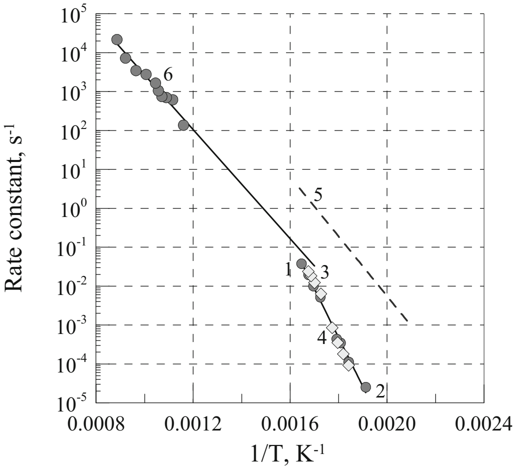


Fig. 8 Comparison of decomposition kinetics of BTATz (*1–4*), aminotetrazole (*5*) [41], and kinetics of leading reaction of BTATz combustion (*6*) [20]: *1* and *2* [20], *3* [21], *4* [31]

straight line *lnk* (*1/T*) for reaction of BTATz in the condensed phase and is close to the slope of *lnk* (*1/T*) dependence for the decomposition reaction of 5-AT [41]. As mentioned above, the decomposition of tetrazole ring includes preliminary reactions of isomerization. At high temperatures, which are realized at the burning surface of BTATz, all these preliminary reactions have been already finished, and there is only decomposition of the last product of isomerization reaction. The similar situation was observed at study of decomposition kinetics of 5-nitro-1,2,4-triazol-3-one (NTO) in a wide interval of temperatures [42]. The activation energy of the leading combustion reaction of BTATz (32.1 kcal/mol) is in a good agreement with calculated activation energy of azidoimine decomposition (~28 kcal/mol) [33, 34].

A comparison of the rate constants of the leading reaction of BTATz combustion $\left(k = 2.8 \cdot 10^{10} \cdot \exp\left(-16150/T\right),\ s^{-1}\right)$ with rate constants of 5-aminotetrazole decomposition ($k = 1.3 \cdot 10^{13} \cdot \exp\left(-17680/T\right),\ s^{-1}$ [41]) shows (Fig. 8) that combination of two heterocyclic systems has resulted in increasing stability of aminotetrazole moiety.

The data obtained make it possible to explain low pressure index for combustion of DHT and BTATz. If the rate-limiting reaction occurs in the condensed phase, the pressure index will be dependent on the ratio of activation energy of the reaction to heat of evaporation [40]. This ratio for DHT and BTATz is correspondingly equal to 0.69 and 0.45 that is in a good agreement with experimental pressure index (0.69 and 0.49, respectively).

In combustion of CHN-tetrazines, the formation of high-energy products in the flame, such as endothermic nitrile derivatives, occurs that results in lowering of measured flame temperatures as compared with adiabatic values. Most likely it was the main reason for the measured specific impulses being of approximately 14 % of the theoretical one in a study on possible application of BTATz in micropropulsion systems [14].

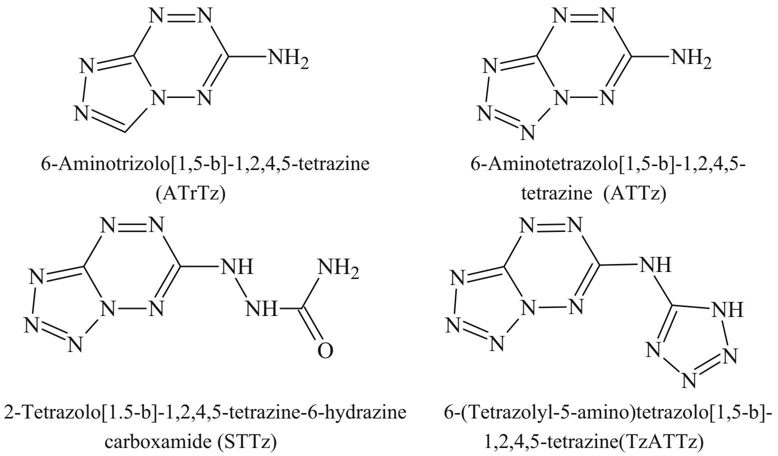
4 Energetic Materials Based on CHN-Tetrazines Annulated with Azoles

Azoloannulated tetrazines are of current interest as energetic materials. Of all the possible azolo[1,2,4,5]tetrazines, derivatives of [1,2,4]triazolo[4,3-b]-s-tetrazine and tetrazolo[1,5-b]-s-tetrazine are of particular interest. The main method of synthesis of [1,2,4]triazolo[4,3-b]-s-tetrazines is condensation of hydrazine derivatives of tetrazine with orthoesters of carboxylic acids [43, 44].

The derivatives of tetrazolo[1,5-b][1,2,4,5]tetrazine can be synthesized by treatment of 3-hydrazine-[1,2,4,5]tetrazines by nitrous acid [1] or by substitution of leaving groups in the tetrazine cycle with sodium azide [1, 45]. All the tetrazolo[1,5-b][1,2,4,5]tetrazines demonstrate the azido-tetrazole tautomerism, with the azido form being predominant [45-47]. However, substituted 6-amino-tetrazolo[1,5-b]-1,2,4,5-tetrazines and their salts in the solid states were shown to exist in the tetrazole form at ambient and elevated temperatures [48, 49]. A reason for such a behavior is, apparently, the donor properties of substituted 6-amino group, since it is known that the open-ring azidoimine form is favored by electron-withdrawing groups and the tetrazole form is favored in the presence of electron-donating groups [50].

Some representatives of azolotetrazine-based energetic materials are shown in Scheme 8. As shown from Table 2, all of them possess high positive enthalpy of formation, for some of them it is higher than 1000 kcal/kg.

Licht and Ritter [51] synthesized 6-amino-tetrazolo[1,5-b]-1,2,4,5-tetrazine (ATTz) (deflagration point ~200 °C), by the diazotization of 3,6-diamino-1,2,4,5-tetrazine with $NaNO_2$, followed by reacting the non-isolated diazonium salt compound with NaN_3. They found that the tetrazolotetrazine ATTz should be



6-Aminotrizolo[1,5-b]-1,2,4,5-tetrazine (ATrTz)

6-Aminotetrazolo[1,5-b]-1,2,4,5-tetrazine (ATTz)

2-Tetrazolo[1.5-b]-1,2,4,5-tetrazine-6-hydrazine carboxamide (STTz)

6-(Tetrazolyl-5-amino)tetrazolo[1,5-b]-1,2,4,5-tetrazine(TzATTz)

Scheme 8

Table 2 Some physicochemical properties of main CHN-azolotetrazines

Compound	Density (density of pressed strand), g/cm^3	ΔH_f^0, kcal/mol (kcal/kg)	DSC exotherm, °C (heat effect, kcal/kg)	Detonation velocity, m/s (density, g/cm^3)
ATrTz	1.60 [52]	116 (847)[a]	300 (159) [53]	7200 (1.60)[c] [52]
		148 (1080)[b] [52]		
ATTz	1.68 [52]	146 (1060)[a] [54]	203 (948) [54]	7970 (1.68)[c] [52]
	(1.6) [54]	175 (1268)[b] [52]		
STTz	1.84 (1.43) [54]	114 (584)[a] [54]	215 (758) [54]	7720 (1.84)[c] [54]
TzATTz	(1.52) [54]	221 (1077)[a] [54]	188 (937) [54]	7390 (1.52)[c] [54]

[a] Estimation
[b] Gas phase, DFT calculation
[c] Calculation

regarded as a primary explosive because of its distinct shock and friction sensitivity and strongly exothermal decomposition in the thermal analysis.

According to work [54], ATTz possesses good initiating properties. The minimum initiating charge of ATTz for RDX in detonator No. 8 brass caps was found to be <0.05 g. It is notable that sensitivity of triazolotetrazines to mechanical stimuli is significantly less than sensitivity of tetrazolotetrazines.

According to calculations at the B3LYP/6-311G** level, the introduction of annulated azole cycle leads to increase in the length of N-N and C-N bonds in the tetrazine cycle and decrease in the bond order in comparison with simple representative, diaminotetrazine, leading to reduction in the thermal stability of azolotetrazines. Indeed, DSC exotherm of 6-aminotrizolo[1,5-b]-1,2,4,5-tetrazine (ATrTz in Table 2) is observed at lower temperature (300 °C) than DSC exotherm of diaminotetrazine (347 °C) [4], although remaining still thermally stable. Despite the fact that calculated bond lengths and bond orders of ATrTz and ATTz are close, the latter substance is less stable; according to DSC data, the maximum of ATTz exotherm is observed at considerably lower temperatures (~200 °C).

The experimental data on thermal decomposition of ATrTz and ATTz under isothermal conditions in the temperature interval of 230–260 and 165–180 °C, respectively, are shown in Figs. 9 and 10. The decomposition of both substances follows the reaction of first order up to high extents of the decomposition.

Maximum gas release at ATrTz decomposition is not large (~130 cm^3/g or 1 mol of gases per 1 mol of ATrTz). The decomposition of ATTz at 165–180 °C produces up to 335 cm^3/g or 2 mol of gaseous products per 1 mol of ATTz, which corresponds to destruction of both tetrazole and tetrazine cycles.

As the decomposition of both ATrTz and ATTz follows a first-order reaction until high extent of decomposition, the kinetic data obtained under nonisothermal conditions (DSC) can be compared with corresponding data obtained under isothermal conditions. As Fig. 11 shows, all the kinetic data for both substances are well described by straight lines in wide temperature

Fig. 9 *Curves* of the gas release in decomposition of ATrTz at different temperatures. *Lines* are fittings; *points* are experimental data

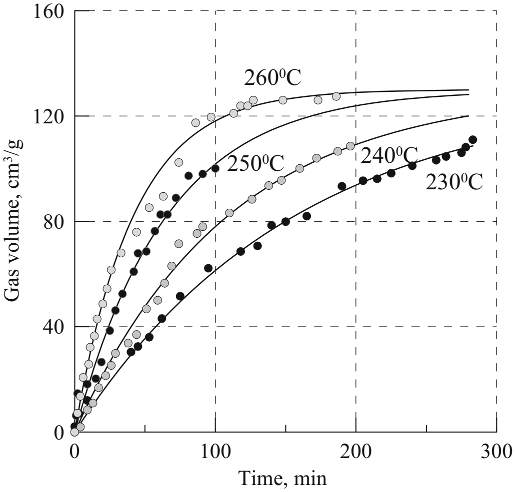
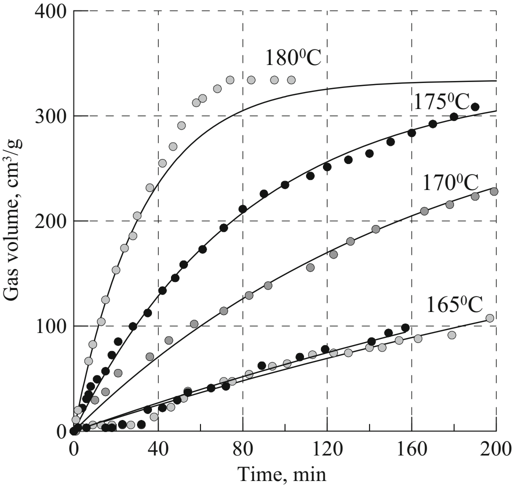


Fig. 10 *Curves* of the gas release in decomposition of ATTz at different temperatures. *Lines* are fittings; *points* are experimental data

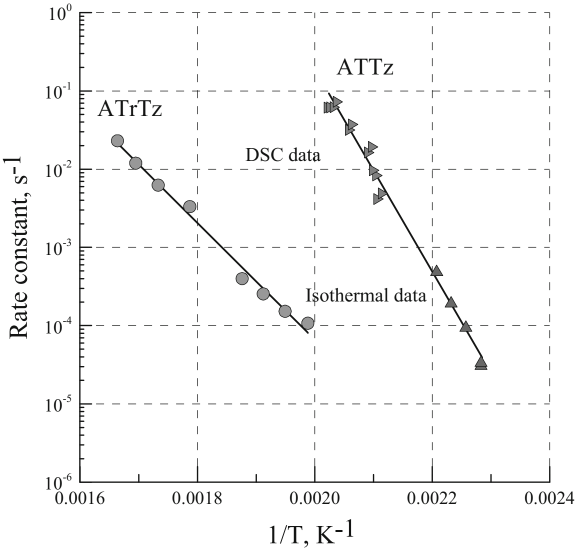


intervals: $k\,(230-328\ \ °\mathrm{C}) = 5.8\cdot 10^{10}\exp(-17205/T)$, s^{-1} for ATrTz and $k\,(164-221\ \ °\mathrm{C}) = 1.3\cdot 10^{25}\exp(-29750/T)$, s^{-1} for ATTz.

As might be expected from results of calculation at the B3LYP/6-311G ** level, the simplest representatives of azolotetrazines, ATrTz and ATTz, have rate constants of decomposition higher than rate constants of decomposition of the simplest tetrazine – diaminotetrazine [4].

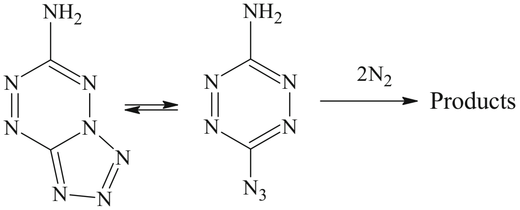
Many researches are apt to relate thermal stability of energetic material to the activation energy. A comparison of thermal stabilities of tetrazolotetrazine and triazolotetrazine shows that such approach is not always correct. Tetrazolotetrazine, being considerably less stable than triazolotetrazine (e.g., ATrTz and ATTz decomposition rate constants at 500 K differ each other by more than three orders of

Fig. 11 Comparison of thermal stability of triazolotetrazine ATrTz and tetrazolotetrazine ATTz, obtained by different methods. *Lines* are fittings through both isothermal and nonisothermal experimental points



magnitude), possesses at the same time a very high value of the activation energy 57.5 kcal/mol, and, vice versa, stable triazolotetrazine shows a rather low activation energy of 34.2 kcal/mol.

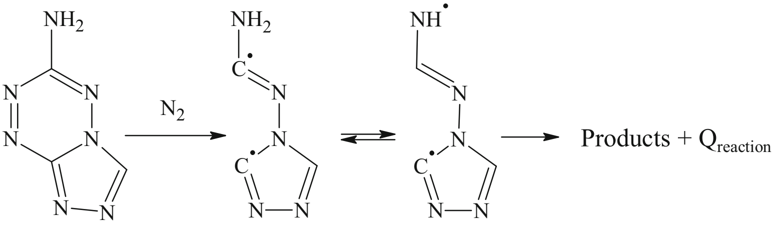
The abovementioned activation energies do not relate to any elementary decomposition stage but are characteristics of more complex transformation. It is well known that higher temperatures generally favor the azide form [47, 55]. In the case of tetrazolotetrazines, for example, BTATz [20], this transformation includes preliminary isomerization into the azide followed by its decomposition. Apparently, the decomposition of the azido group induces simultaneous decomposition of the tetrazine ring:



As a result, the observed activation energy is a sum of activation energies of these two elementary stages:

$$E_{obs} = E_{isom} + E_{dec}$$

Low activation energies of decomposition of triazolotetrazines can be linked with concerted mechanism of decomposition of the tetrazine cycle as it has been postulated in the case of photochemically excited 1,2,4,5-tetrazines [2, 3]. Here, elimination of nitrogen takes place synchronously with recombination of formed radicals [56] to give one kinetically indistinguishable stage:



As a result, the observed activation energy is a difference between activation energy of bond rupture and heat effect of the subsequent radical reaction:

$$E_{obs} = E_{dec} - Q_{reaction}$$

Annulated tetrazolotetrazines appeared to burn faster than similarly structured open tetrazine derivatives. For example, tetrazolotetrazine with aminotetrazole substituent (TzATTz) burns four to seven times faster than its structural analog BTATz (Fig. 12).

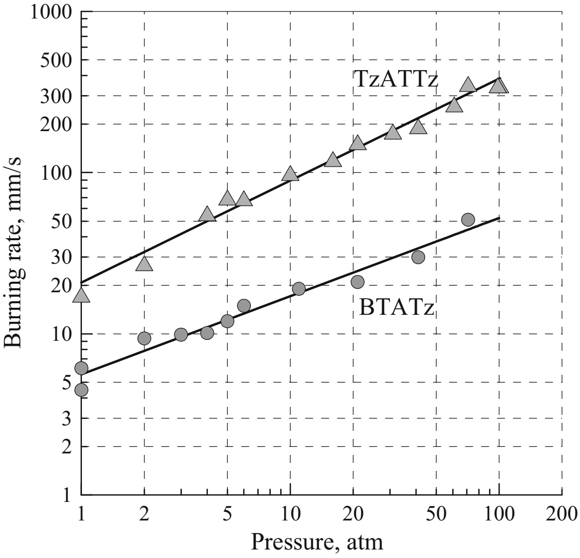


Fig. 12 Comparison of burning rates of similarly structured tetrazolotetrazines

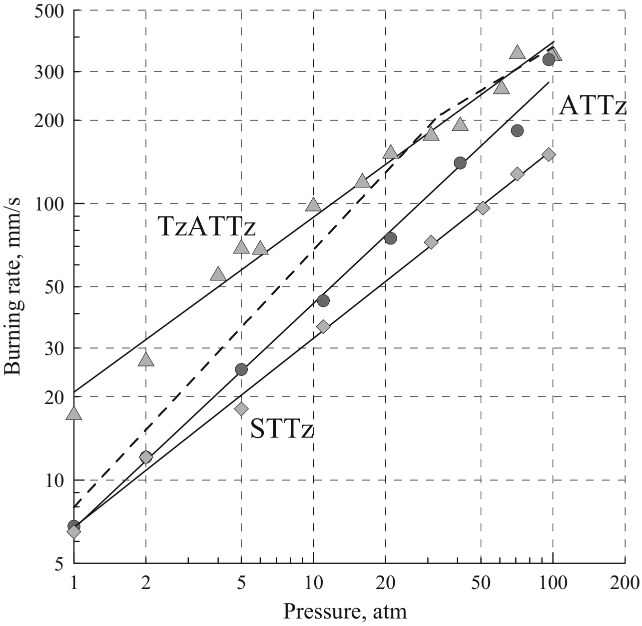


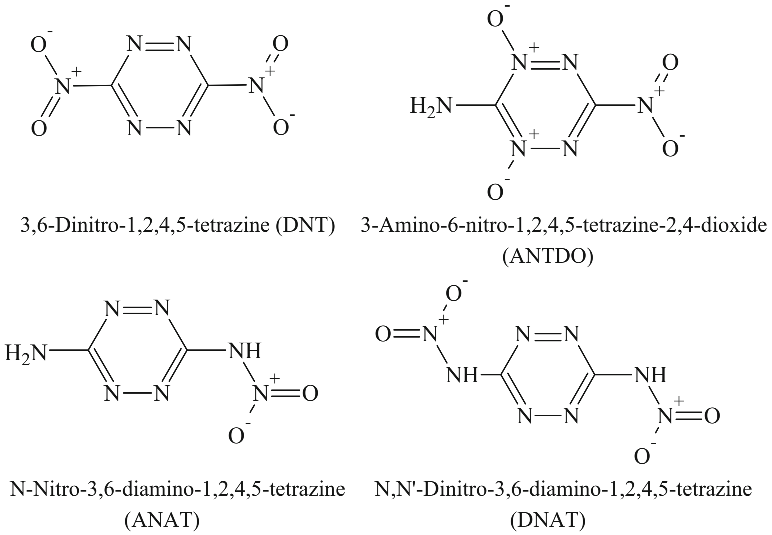
Fig. 13 Comparison of burning rates of tetrazolotetrazines and primary explosive tetrazene (*dashed line*)

High burning rates of many of tetrazolotetrazines allow considering these materials as potential primary explosives. Figure 13 shows a comparison of burning rates of some of tetrazolotetrazines with burning rates of a well-known initiating explosive tetrazene.

Because of high burning rates, temperature profiles in the combustion of tetrazolotetrazines can hardly be obtained with the help of thin thermocouples. However, supposing that the surface temperature (i.e., boiling point) of annulated azolotetrazines has changed little in comparison with ordinary tetrazines, it is reasonable to assume that higher burning rates of tetrazolotetrazines are stipulated by their lower thermal stability.

5 Energetic Materials Based on CHNO-Tetrazines

The best energetic performance can be reached if endothermic tetrazine cycle and active oxygen are joined together in one molecule. As shown in Scheme 9 and Table 3, the enthalpies of formation of CHNO-tetrazines containing nitroamino groups are lower than enthalpies of formation of CHN-tetrazines. Nevertheless, the calculated detonation velocities of CHNO-tetrazines are comparable to those of such explosives as RDX and HMX. However, all attempts to synthesize 3,6-



3,6-Dinitro-1,2,4,5-tetrazine (DNT)

3-Amino-6-nitro-1,2,4,5-tetrazine-2,4-dioxide (ANTDO)

N-Nitro-3,6-diamino-1,2,4,5-tetrazine (ANAT)

N,N'-Dinitro-3,6-diamino-1,2,4,5-tetrazine (DNAT)

Scheme 9

Table 3 Some physicochemical properties of main CHNO-tetrazines

Compound	Density, g/cm^3	ΔH_f^0, kcal/mol (kcal/kg)	DSC exotherm, °C	Detonation velocity, m/s (density, g/cm^3)
DNT	1.88 [57]	128 (744)[a] [57] 60 (350)[b]	Too unstable to isolate [8]	9380 (calc.) (1.88) [57]
ANTDO	1.92 [58]	53.4 (307) [58]	110 [8] 192 [58]	9120 (calc.) (1.92)
ANAT	1.82 [59]	105 (671)[a] [59]	164 [1, 59]	8230 (calc.) (1.82) [57]
DNAT	1.83 [57]	135 (670)[a] [57]	Unstable [60]	9150 (calc.) (1.83) [57]

[a] Gas phase, DFT calculation

[b] Estimation

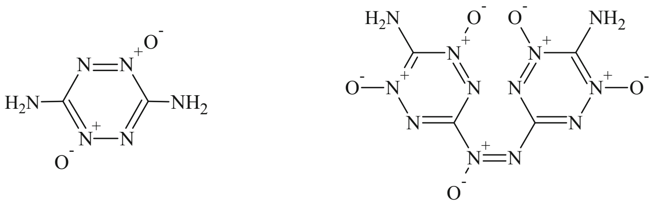
dinitro-1,2,4,5-tetrazine (DNT) failed due to extreme hydrolytic and thermal instability [8].

According to calculations at the B3LYP/6-311G** level [57], the substitution of amino group for nitro group leads to increase in the lengths of N-N and C-N bonds in the tetrazine ring and to decrease in their bond order in comparison with diaminotetrazine, but the least stable bond is the bond between nitro group and the tetrazine ring. It should be noted that according to work [58], tetrazine mononitro derivatives, 3-amino-6-nitro-1,2,4,5-tetrazine and its 2,4-dioxide, have quite a satisfactory thermal stability: substantial decomposition is observed at temperatures higher than 190 °C.

The stability of nitroamino derivatives is not much better. N,N′-Dinitro-3,6-diamino-1,2,4,5-tetrazine (DNAT) was readily hydrolyzed back to starting material in contact with traces of moisture [1]. It is known that nitroamines, containing electron-withdrawing groups like NO_2 and F, have weak hydrolytic and thermal stability [34]. In this connection, it is not surprising that nitroamines, containing such a strong electron attractor as the tetrazine ring, possess unsatisfactory thermal stability. Nevertheless, unlike nitrotetrazines, the stability of nitroaminotetrazines can be increased by transforming them into anionic form. Thus, some salts of N-nitro-3,6-diamino-1,2,4,5-tetrazine (ANAT) are described as relatively dense (>1.55 g/cm^3) materials, exhibiting relatively good thermal stability (T_d >148 °C) [59].

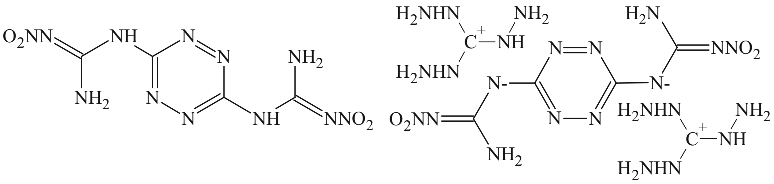
Another way to incorporate the active oxygen into the tetrazine molecule is to obtain N-oxide fragment in the cycle or to introduce the nitro group into the side chain (Scheme 10 and Table 4). However, such approach does not allow obtaining energetic materials with well-balanced oxidizer/fuel ratio.

In 1993, Coburn et al. [8] reported the synthesis of 3,6-diamino-1,2,4,5-tetrazine-1,4-dioxide (LAX-112), an example of a cycloaromatic energetic material without oxidizing nitro groups. LAX-112 has relatively high heat of formation, good density, and detonation velocity that initially led to a much higher predicted performance than measured. This tetrazine compound was extensively evaluated as an insensitive explosive in the early 1990s. Then, LAX-112 was considered as fuel for solid-fuel digital microthrusters [16]; however, slow burning rates and formation of solid particles during combustion prevented further studying it as a monopropellant.



3,6-Diamino-1,2,4,5-tetrazine-1,4-dioxide (LAX-112)

3,3'-Azoxybis(6-amino-5-N-oxide-s-tetrazine) (DAATO3.5)



3,6-Bis(nitroguanidine-1,2,4,5-tetrazine (NQ2Tz)

Triaminoguanidinium salt of 3,6-bis(nitroguanidine)-1,2,4,5-tetrazine (TAG2NQ2Tz)

Scheme 10

Table 4 Some physicochemical properties of main CHNO-azolotetrazines

Compound	Density (density of pressed sample), g/cm^3	ΔH_f^0, kcal/mol (kcal/kg)	DSC exotherm, °C	Detonation velocity, m/s (density, g/cm^3)
LAX-112	1.85 [51]	48 (330) [51]	220 [8]	8786 (calc.)(1.85) [51]
			266 [51]	
DAATO3.5	1.88 [16]	131 (440)[a] [26]	177[a] [16]	9000 (calc.)(1.88) [16]
NQ2Tz	1.76 (1.70) [62]	93 (330) [62]	269 [63]	7840 (1.7) [63]
TAG2NQ2Tz	1.61 (1.51) [62]	300 (606) [62]	175 [63]	7620 (1.51) [63]
		153 (309) [67]		

[a] For a mixture of compounds

In the effort to improve the density and explosive performance of DAAT, Los Alamos chemists [16] obtained a mixture of various N-oxides of DAAT with an average oxygen content of approximately 3.5. This mixture of N-oxides, which was called DAATO3.5, has the calculated detonation velocity (at measured density of 1.88 g/cm^3) of 9.0 km/s [16]. DAATO3.5 proved to be sensitive to friction and spark. The density of DAATO3.5 was found to be relatively high; however, it could not be pressed to densities >80 % of theoretical maximum density (TMD), which was attributed to unusual morphology.

DAATO3.5 with an addition of 5 % polyvinyl alcohol and 1 % triethylene glycol (6.35-mm diameter, 1.52 g/cm^3 pressed pellet) burns at high rates (r_b at 10 MPa is 58.6 mm/s) and shows low dependence on pressure ($r_b = 16.9P^{0.27}$, P in atm); both parameters are desirable in high-performance propellant applications [26]. Because it was not possible to press neat DAATO3.5 without a binder and because binders generally suppress burn rates, it may be expected that the burn rate of pure DAATO3.5 is higher than that published.

A 6:2:1 mixture of nitro compound 3,6-bis-(3-nitrofurazan-4-ylamino)-s-tetrazine with mono- and di-N-oxides in tetrazine ring was synthesized by oxidation of 3,6-bis(3-aminofurazan-4-ylamino)-s-tetrazine [61]. In analogical way, the triazolotetrazine-substituted aminofurazan was oxidized into the nitro analog. A mixture of triazolotetrazine-substituted diaminoazofurazan and diaminoazoxyfurazan as by-products was formed. The synthesized nitro compounds are strong NH-acids. The acidity of these compounds allows a large variety of energetic salts to be prepared.

3,6-Bis(nitroguanidine)-1,2,4,5-tetrazine (NQ2Tz) and its triaminoguanidinium salt (TAG2NQ2Tz) were studied as promising components in gas-generating and propellant applications because they have low pressure indexes [62, 63]. Compound NQ2Tz has a DSC onset of 228 °C, with fast decomposition at 269 °C, and a gas pycnometry density of 1.76 g/cm^3. The heat of formation was measured using combustion calorimetry, and a value of 93 kcal/mol was obtained [63]. Compound TAG2NQ2Tz has a density of 1.61 g/cm^3 as determined by gas pycnometry. The thermal stability of triaminoguanidinium salt is lower than NQ2Tz as determined by DSC analysis. The onset of decomposition begins at 166 °C, with a fast exotherm at 175 °C. Compound TAG2NQ2Tz was determined by combustion calorimetry to have a very high heat of formation of 300 kcal/mol. Such a high value of enthalpy is somewhat doubtful. Indeed, simple summation of enthalpies of formation of TAG2NQ2Tz composing fragments – triaminoguanidine (68.8 kcal/mol [64]) and NQ2Tz (93 kcal/mol [62]) – gives a considerably lower value of 230.6 kcal/mol. Taking into account the heat of salt formation (~39 kcal/mol, an estimate from enthalpies of formation of triaminoguanidinium nitrate -12.0 kcal/mol [65], liquid nitric acid -41.6 kcal/mol [66], and triaminoguanidine), the resulting enthalpy of TAG2NQ2Tz formation is calculated as ~153 kcal/mol, i.e., almost twice as less as published in [62].

As indicated in work [63], both NQ2Tz and TAG2NQ2Tz exhibit very low pressure dependence during combustion; the former has been shown to demonstrate the lowest pressure exponent known in the literature for a neat material. The combustion study of NQ2Tz pressed into 4-mm i.d. plexiglass tubes to a density of 1.6 g/cm^3 has shown that NQ2Tz burning rate is very sensitive to impurities [67]. At low pressures, including subatmospheric region, it burns in flameless mode with a large scatter of burning rates. A luminous flame appears at pressures higher than 20 atm. A comparison of burning rates of NQ2Tz measured in different labs (Fig. 14) shows that burning rates are different and that the pressure index obtained

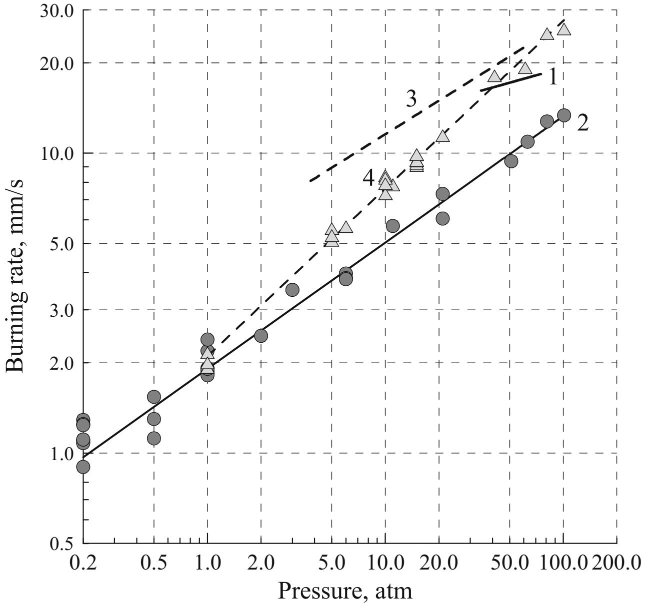


Fig. 14 Comparison of burning rates of NQ2Tz (*1*, *2*) and TAG2NQ2Tz (*3*, *4*), obtained in different labs: *1*, *3* – work [63]; *2*, *4* – work [67]

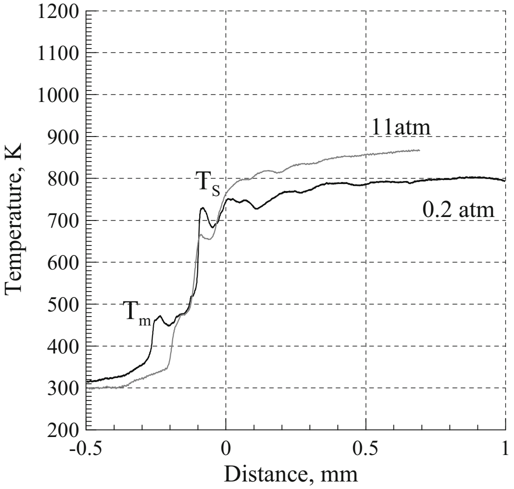


Fig. 15 Typical temperature profiles for NQ2Tz at different pressures

in our lab ($r_b = 1.91P^{0.42}$) [67] is significantly larger that pressure index published in [63] ($r_b = 8.97P^{0.16}$). Nevertheless, it is still less than the pressure index of HMX.

TAG2NQ2Tz pressed into 4-mm plexiglass tubes to a density of 1.55 g/cm^3 burns a little faster than the parent NQ2Tz compound. Combustion of the triaminoguanidine salt proceeds without luminous flame at all pressures up to 100 atm. As with NQ2Tz, the pressure exponent of the salt measured in our lab [67] ($r_b = 2.1P^{0.56}$) appeared to be significantly more than published one ($r_b = 4.92P^{0.37}$). A possible reason for such different combustion behaviors is likely purity of the materials and different sample preparation technique for burning rate tests.

Temperature profiles in the NQ2Tz and TAG2NQ2Tz combustion waves were obtained with the help of thin tungsten-rhenium thermocouples at low pressures, where both compounds burn without luminous flame. The maximum measured flame temperature of NQ2Tz in the pressure interval of 0.2–11 atm does not exceed 900 °C (Fig. 15), which is 1210 °C less than the adiabatic temperature. Reactions in the NQ2Tz flame do not reach their thermodynamic equilibrium (2115 K) even at 50 atm, resulting in the measured combustion temperature being no more than 1700 K. The temperature gradient above the surface is low ($\sim$4000 K/cm).

Unlike NQ2Tz, the temperature gradient above the burning surface of the triaminoguanidinium salt (Fig. 16) is much higher. A considerable heat flow from the gas phase is spent on warming up the dispersed substance over the burning surface, thus not affecting the heat balance of the condensed phase and leaving the dominant role for the condensed phase.

Thus, the thermocouple-aided measurements show that condensed-phase reactions play a dominant role in combustion of both NQ2Tz and TAG2NQ2Tz. As with NQ2Tz, the maximum measured flame temperature (910–1035 K) for TAG2NQ2Tz in the pressure range of 0.7–15 atm is less than adiabatic temperature (1590 K). This difference is caused by formation of high-energy products in the flame, such as

Fig. 16 Typical temperature profiles for TAG2NQ2Tz at different pressures

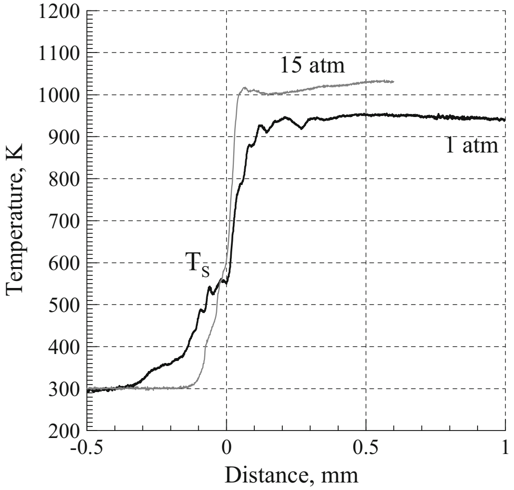
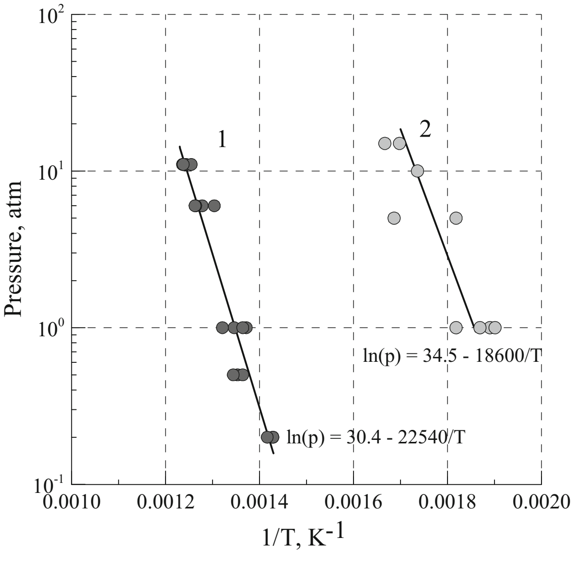


Fig. 17 Surface temperatures vs. pressure for NQ2Tz (*1*) and TAG2NQ2Tz (*2*)



endothermic nitrile derivatives, favored by deficiency of oxygen in both molecules. Besides, T-Jump/FTIR spectroscopy indicates that NO_2 and N_2O are formed in the gaseous products from the flash pyrolysis of NQ2Tz [68].

NQ2Tz is a low-volatile substance with boiling temperature of about 743 K and heat of vaporization of 44.8 kcal/mol. The surface temperatures of TAG2NQ2Tz are within the interval of 530–600 K (Fig. 17) that is considerably lower than the surface temperature of the parent NQ2Tz acid (705–805 K). NQ2Tz possesses weak acidic properties, and, therefore, the dissociation temperature of the salt cannot be very high. After dissociation of the salt and evaporation of volatile triaminoguanidine, the remaining NQ2Tz acid evaporates in the flame at higher temperatures.

The experiments on thermal decomposition of NQ2Tz under isothermal conditions have been carried out at temperatures 200–240 °C. The curve of gas evolution is described by the first-order reaction to high extents of decomposition. The final volume of gases is 320 cm^3/g (4.1 mol/mol). In *lnk – 1/T* coordinates, the experimental points are fitted by a straight line as $k = 5.4 \cdot 10^{12} \exp(-19140/T)$, s^{-1}. The nonisothermal kinetics derived from DSC analysis is in a good agreement with the above kinetic equation for isothermal decomposition. According to T-jump/FTIR spectroscopy [68], the evolution of NO_2 indicates that N-NO_2 homolysis in nitroguanidine substituent is a trigger reaction of decomposition process. It is interesting to note that a comparison of the decomposition rate constants of NQ2Tz with those of nitroguanidine (NQ) ($k = 5.9 \cdot 10^9 \cdot \exp(-14188/T)$, s^{-1} [69]) indicates that bonding of the tetrazine ring to nitroguanidine has resulted in increasing stability of nitroguanidine moiety.

TAG2NQ2Tz has a considerably lower stability than NQ2Tz: the peak of exothermal decomposition in the DSC curves is observed at 197–230 °C depending on the heating rate. Experiments on thermal decomposition of TAGNQ2Tz under isothermal conditions have been carried out at 150–160 °C. The curves of gas evolution have a significant induction period which decreases with temperature. A sharp rise in the decomposition rate begins after the induction period is over. The final volume of released gases is 365 cm^3/g (~8 mol/mol). The experimental points can be satisfactorily described by a kinetic equation with autocatalysis to give the following rate constants: $k_1 = 1.9 \cdot 10^{15} \exp(-21090/T)$, s^{-1} and $k_2 = 3.1 \cdot 10^{17} \exp(-19460/T)$, s^{-1}. Composition of formed gases [68] indicates that the TAG cation dramatically affects the decomposition pathway. The formation of large amounts of NH_3 suggests that bond cleavage in the TAG cation is the dominant reaction of the thermal decomposition of TAG2NQ2Tz.

As burning rates of NQ2Tz and TAG2NQ2Tz are defined by chemical reactions in the condensed phase, the kinetics of the leading reaction on combustion can be derived from the burning rates and data of thermocouple measurements [39, 40]. A comparison of thus obtained rate constants of the leading reaction with decomposition rate constants in DSC and manometric experiments is shown in Fig. 18. A good correspondence between the kinetics of the leading combustion reaction and the kinetics of decomposition, defined at considerably lower temperatures, is observed for NQ2Tz. In the case of TAG2NQ2Tz, the kinetics of the leading combustion reaction coincides with the kinetics of decomposition acceleration, extrapolated to the high-temperature range. At high temperatures, the substance on the burning surface is in the molten state. The coincidence of combustion kinetics and the auto acceleration shows that the reason for the acceleration of decomposition is submelting of the sample.

Thus, the experiments have shown that the combustion mechanism of both substances is based on the reactions in the condensed phase and their burning rates are defined by the decomposition kinetics at the surface temperatures.

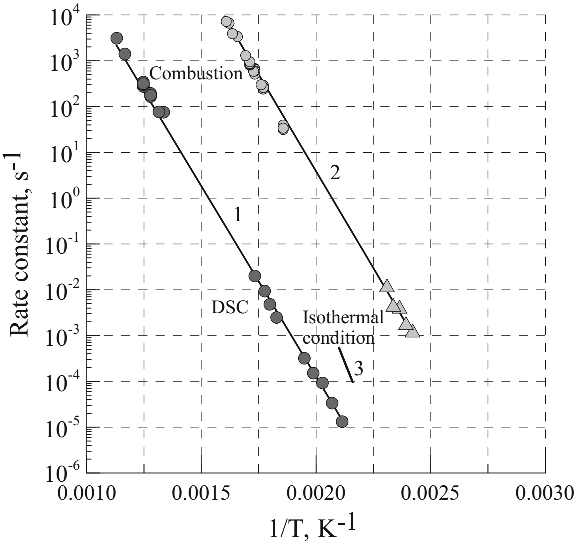


Fig. 18 Comparison of rate constants of the leading reaction on combustion and rate constants of decomposition under nonisothermal (*DSC*) and isothermal conditions for NQ2Tz *(1)* and TAG2NQ2Tz (*2*). *Line 1* is fitting of NQ2Tz isothermal decomposition data, *line 2* is kinetics of the leading reaction of TAG2NQ2Tz combustion, and *line 3* is rate constants of NQ decomposition

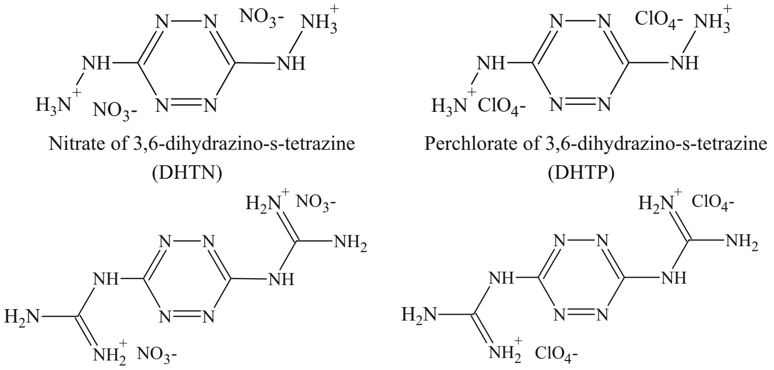
6 Salts of Substituted Tetrazines with Oxidizing Acids

Active oxygen can be introduced into the molecule by synthesizing tetrazine salts with such inorganic oxidizing acids as nitric and perchloric ones. In this case, the tetrazine molecule must contain some substituent groups of basic nature, for example, hydrazine or guanidine.

Several energetic salts of DHT were synthesized including bisdinitramide, diperchlorate, dinitrate, and 4,4′,5,5′-tetranitro-2,2′-biimidazolate, all having fairly low drop weight impact values and decomposition points [1]. Other tetrazine-based explosives of this class include nitrate and perchlorate salts of 3,6-diguanidino-s-tetrazine (DGT) [16, 19] (Scheme 11).

The reaction of salt formation reduces the total enthalpy of formation of the compounds. The heat of formation of DGT was determined to be 47 kcal/mol. The heat of formation of DGTN and DGTP was estimated on the base of thermodynamic data for guanidine, guanidine nitrate, and guanidine perchlorate [19]. Enthalpies of formation of DHTN and DHTP (Table 5) were calculated in similar way. However, due to good oxidizer/fuel ratios and high densities of these compounds, they possess high detonation velocities: 7.5 km/s and higher (Table 5). Among these substances, one can find insensitive explosives.

The use of different heterocycles containing nitro groups and acting as acids in the reaction with DHT, such as 5-nitrotetrazole, 3-amino-5-nitrotriazole, or 4,4′,5,5′-tetranitro-2,2′-bisimidazole [72], helps to increase enthalpies of formation of the salts, but at the same time decreases the oxidizer/fuel ratio. As the result, the salts proved to possess energetic characteristics not exceeding characteristics of RDX.



Nitrate of 3,6-dihydrazino-s-tetrazine (DHTN)

Perchlorate of 3,6-dihydrazino-s-tetrazine (DHTP)

3,6-Diguanidino-1,2,4,5-tetrazine nitrate (DGTN)

3,6-Diguanidino-1,2,4,5-tetrazine perchlorate (DGTP)

Scheme 11

Table 5 Some physicochemical properties of salts of substituted tetrazines with oxidizing acids

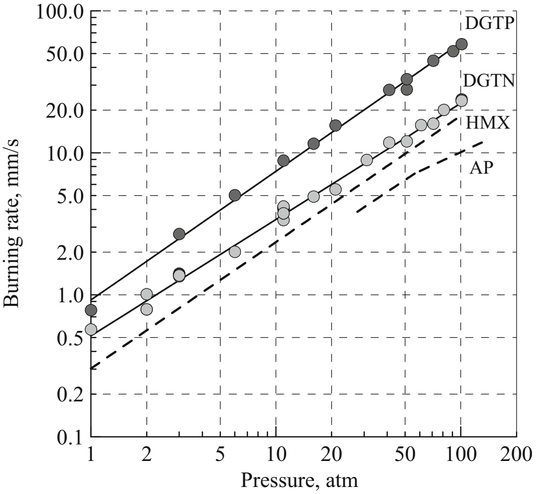
Compound	Density (density of pressed strand), g/cm^3	ΔH_f^0, kcal/mol (kcal/kg)	DSC exotherm, °C (heat effect, kcal/kg)	Detonation velocity, m/s (density, g/cm^3)
DHTN	1.80 [1]	−30 (−112)[a]	117 [1], 161 (1200)	8300 (1.65)[c]
	(1.65) [70]		[29], 156 [70]	
DHTP	1.96 (1.76) [1]	6 (18)[a]	200 [1], 191 (67) and 288 (355) [29]	7520 (1.76)[c]
DGTN	1.72 (1.6) [16]	−61 (−189)[a] [19]	226[b] [16]	7310 (1.6) [16, 19]
			276 (200) [73]	
DGTP	1.905 (1.79) [16, 19]	−30 (−75)[a] [19]	265[b] [16]	8070 (1.79) [16, 19]
	1.977 (at 93 K) [71]		272 [71]	

[a] Estimation
[b] DSC onset
[c] Calculation

The thermal stability of DHT salts has been examined in [29]. It has been shown that the salts exist in the reversible equilibrium with the parent base and acid; thus, in several cases, the decomposition rate of the parent DHT and the salt are essentially identical. The thermal stability of DHT salts strongly depends on the acidity of the corresponding acid [72]. When strong acids are used, the thermal stability is enhanced.

Burning rate behaviors and temperature profiles have been investigated for salts of 3,6-diguanidino-1,2,4,5-tetrazine with perchloric and nitric acids [73] (Fig. 19). The burning rate-pressure dependences for pressed samples of DGTN and DGTP are expressed in the pressure interval of 1–100 atm as $r_b = 0.535p^{0.816}$ and $r_b = 0.92p^{0.906}$, respectively. Both salts burn faster than HMX: 1.3 times for

Fig. 19 Comparison of burning rates of DGTP, DGTN, HMX, and AP



nitrate and 3 times for perchlorate. Comparing DGTP with ammonium perchlorate, one can see a six-time increase in the burning rate, which is not surprising, since the combustion temperature of DGTP is two times higher than the combustion temperature of AP. It should be noted that the burning rates of DGTP are relatively moderate among other energetic salts of perchloric acid. For example, the burning rate of both 1,5-diaminotetrazole perchlorate [74] and carbohydrazide perchlorate [75] approaches 150 mm/s at pressure of 100 atm.

Temperature profiles in the DGTN combustion wave were studied with the help of thin tungsten-rhenium thermocouples at pressures of 0.5, 1, 3, and 11 atm (Fig. 20). At low pressures, temperature profiles demonstrate the absence of high-temperature flame. At pressure 100 atm, the maximum flame temperature T_f does not exceed 900 °C. It is much lower than the calculated adiabatic flame temperature (1396 °C), and the observed 460° difference cannot be connected with radiant heat losses by the thermocouple.

Flameless combustion makes it easy to determine the surface temperature up to 100 atm (Fig. 21). All experimental points give the dependence of DGTN vapor pressure on temperature as $\ln(P) = 10860/T + 16.07$, allowing estimation of the heat of vaporization as 64.8 kcal/mol. Comparison of effect of pressure on the surface temperatures of TAGN [76], DGTN, and AN [77] shows that DGTN surface temperature is close to TAGN surface temperature but is higher than AN surface temperature. The surface temperatures of DGTN and TAGN are close, which, in our opinion, is caused by the close basicity of guanidine fragments in both molecules.

According to DSC analysis, DGTN shows no melting point and exhibits one intense exotherm between 272 and 280 °C at heating rate 4–16 °C/min. Kinetic data of thermal decomposition of DGTN were calculated by Kissinger's equation, suggesting the first reaction order. The calculation gives unrealistically high activation energy (~76 kcal/mol), which is likely due to fact that the decomposition does not obey the first order.

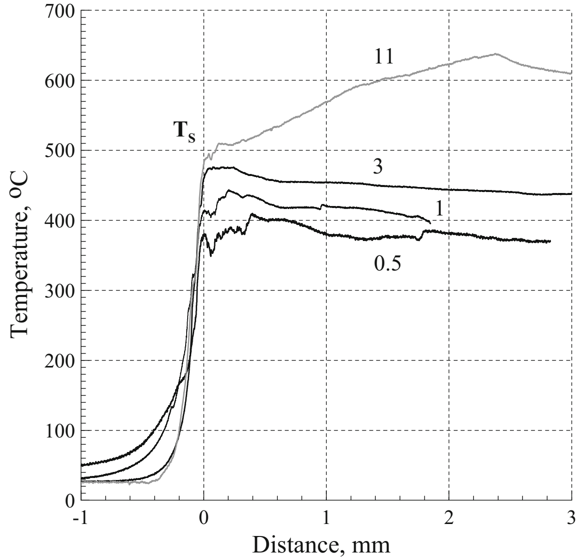


Fig. 20 Typical temperature profiles of DGTN at 0.5, 1, 3, and 11 atm

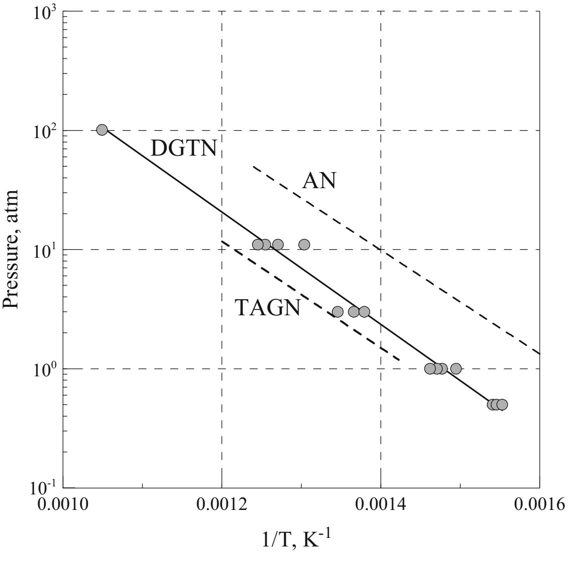


Fig. 21 Effect of pressure on the surface temperatures of TAGN, DGTN, and AN

Flameless combustion of DGTN in a wide range of pressures clearly testifies the leading role of reactions in the condensed phase. Therefore, one can use the experimental data on the burning rates and surface temperatures to extract kinetic parameters of the leading combustion reaction. Kinetic parameters of DGTN decomposition derived from the condensed-phase combustion model, $k\left(\mathrm{s}^{-1}\right) = 10^{13.14}\exp(-37200/RT)$, are in a good agreement with rate constants obtained

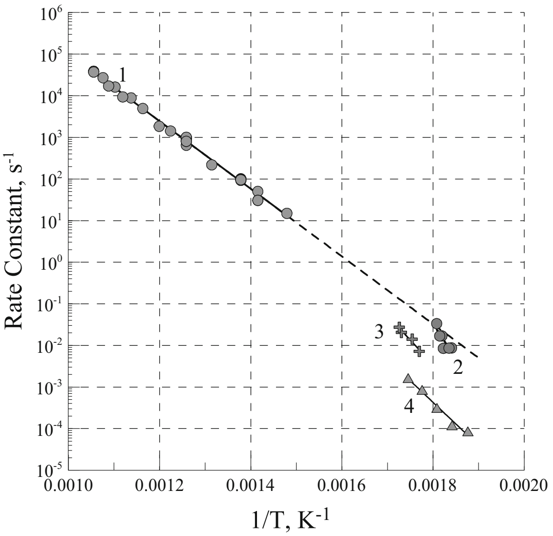


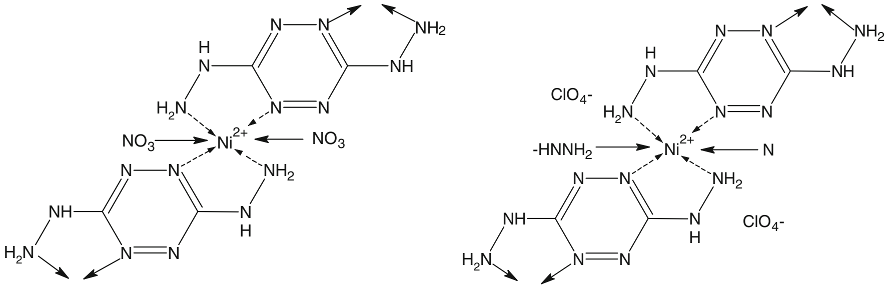
Fig. 22 Comparison of rate constants of the leading reaction of DGTN combustion (*1*) and rate constants of DGTN decomposition derived from DSC measurements (*2*) with kinetic parameters of DGT (*3*) and GuN (*4*) decomposition

by Kissinger's method from DSC curves (Fig. 22). It should be noted that the leading combustion reaction acquires more realistic activation energy (37 kcal/mol) if calculated over a wide temperature range. As can be seen from the figure, DGTN is significantly less stable than guanidinium nitrate GuN [78]. The comparison of rate constants of DGTN and GuN shows that the introduction of tetrazine ring into guanidine molecule decreases thermal stability of the salt. This is in correspondence with the abovementioned facts [29, 72] that the decrease in the salt stability is caused by decreasing strength of the acid. The tetrazine ring is an electron-withdrawing substituent, and, consequently, it reduces the basic properties of guanidine. The weaker the bond strength between acid and base, the more shifted the equilibration toward free acid and base, which possesses lower thermal stability than the initial salt.

Thus, the investigation carried out allow conclusion that the mechanism of DGTN combustion is similar to that of other onium salts, such as ammonium nitrate, perchlorate, and dinitroamidate [79]. The surface temperature on combustion of DGTN is controlled by reaction of dissociation as well. The burning rate of DGTN is determined by processes in the condensed phase.

7 Coordination Compounds of Tetrazine

Tetrazine-based energetic materials can be obtained in synthesis of coordination compounds of metal perchlorates or nitrates by using the tetrazine ring as the ligand. The presence of at least four nitrogen donor atoms in tetrazine and its derivatives allows for potentially rich coordination chemistry. The most common arrangement



Dihydrazino-s-tetrazine nickel(II) Nitrate $[Ni(DHT)(NO_3)_2]$

Tris(dihydrazino-s-tetrazine)dinickel(II) Perchlorate $[Ni_2(DHT)_3](ClO_4)_4$

Scheme 12

Table 6 Some physicochemical properties of explosive coordination compounds of tetrazine

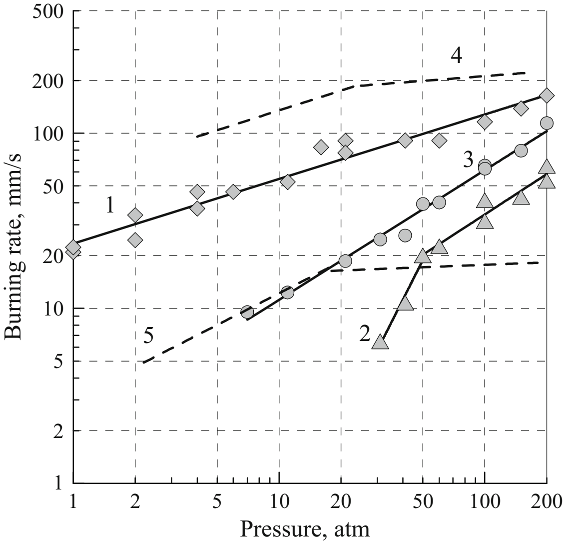
Compound	Density (density of pressed sample), g/cm^3	ΔH_f^0, kcal/mol (kcal/kg)	DSC exotherm, °C	Flame temperature at 100 atm, K
$[Ni(DHT)(NO_3)_2]$	(1.85)	29 (90)	130	3040
$[Ni_2(DHT)_3](ClO_4)_4$	–	258 (275)	242	3290
$[Cu_2(DPT)_3](ClO_4)_4$	(1.65)	175 (174)	302	2250
$[Ni(DPT)(ClO_4)_2]$	(1.57)	79 (164)	332	2400

with tetrazine itself involves it as a bridging ligand via the one and four positions. Discrete dinuclear complexes or linear coordination oligomers and polymers may result [80]. Basicity, and therefore coordination ability of tetrazine cycle, is low, that is why stable complexes can be better obtained if one uses tetrazines with donor substitutes. In this regard, most interesting compounds, from energetic point view, are dihydrazino-s-tetrazine and diguanidino-s-tetrazine. However, complexing of diguanidino-s-tetrazine with metal perchlorate results in hydrolysis of guanidine groups. Dihydrazino-s-tetrazine forms coordination compounds with nickel nitrate and perchlorate (Scheme 12). The nitrate complex still proved to be thermally unstable: its ignition temperature was as low as 130 °C, and the perchlorate complex was prone to spontaneous explosion [70] (Table 6).

Therefore, stable coordination compounds with tetrazines have been synthesized from the well-known pyridyltetrazines. The most frequently used tetrazine ligand 2,2′-bispyridyltetrazine usually acts as transoid symmetrically bis-chelating ligands [80]. In our lab, explosive complex compounds of 3,6-di(2-pyridinyl)-1,2,4,5-tetrazine (DPT) with nickel and cobalt perchlorates have been obtained and studied [70].

Explosive coordination compounds (CC) can be considered as model propellants containing the catalyst, which is the central metal ion; fuel, which is the ligand; and oxidizer, which is the anion, all mixed at the molecular level. For this reason, the

Fig. 23 Burning behaviors of complex perchlorates: (*1*) $[Cu_2(DPT)_3(ClO_4)_4]$, (*2*) $[Ni(DPT)(ClO_4)_2]$, (*3*) DPT·$2HClO_4$, (*4*) $[Cu(PhDA)_2](ClO_4)_2$, and (*5*) $[Ni(PhDA)_3](ClO_4)_2$



study of CC combustion allows one to avoid problems of interpretation of results associated with inhomogeneity of the catalyst distribution and particle size effect. The effect of the metal atom nature on combustion of a coordination compound can be estimated by comparing its burning rates with burning rates of the corresponding metal-free system containing the same fuel and oxidizer [74, 81].

The leading reactions in combustion of coordination compounds of DPT as well as DPT salt with perchloric acid (DPT·$2HClO_4$) was assumed to proceed in the gas phase because of low decomposition depths in the condensed phase and high flame temperatures [70]. By its chemical nature, this leading reaction is a redox transformation. It is interesting to note that burning rates of $[Cu_2(DPT)_3](ClO_4)_2$ appeared to be much higher than burning rates of DPT·$2HClO_4$ that has been naturally explained by high efficiency of copper ion acting as the catalyst. In its turn, nickel does not show any catalytic activity in its perchlorate complex with DPT (Fig. 23).

The burning rates of complexes with energetic tetrazine ligands turned out to be close or even slower than burning rates of analogous complexes with non-energetic phenylenediamine (PhDA). This fact suggests that the activity of tetrazine derivatives in redox reactions is low.

As an example, the reduced reactivity of tetrazine derivatives can be illustrated by comparison of burning rates for complexes of DHT and hydrazine with nickel nitrate, which is as replacement of lead azide in a new type of detonators [82]. It is evident that, despite a significant difference in the combustion temperatures of $[Ni(DHT)(NO_3)_2]$ (3040 K) and $[Ni(N_2H_4)_3(NO_3)_2]$ (2500), both complexes have the same burning rates (Fig. 24).

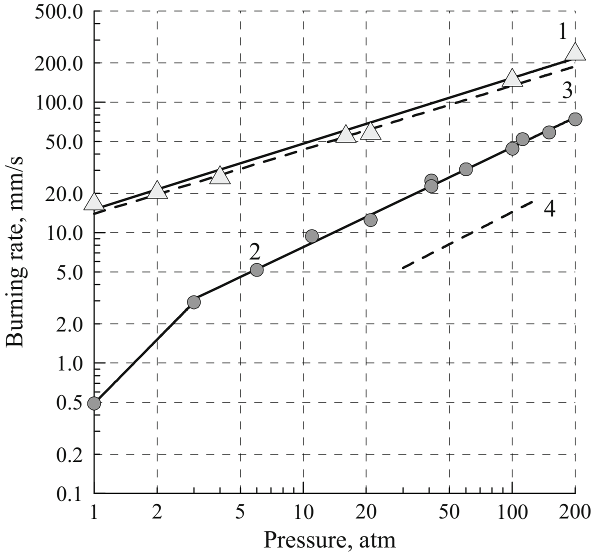


Fig. 24 Burning behaviors of complex nitrates: (*1*) [Ni(DHT)$(NO_3)_2$], (*2*) DHT·$2HNO_3$, (*3*) $[Ni(N_2H_4)_3](NO_3)_2$, and (*4*) $N_2H_4{\cdot}HNO_3$

8 Conclusions

High enthalpy of formation and good thermal stability of tetrazine cycle allow producing tetrazine-based energetic materials, which can be used as insensitive, thermostable, environmentally friendly explosives, components of fast-burning propellants, gas-generating compositions, and nonmetal primary explosives.

A drawback of tetrazines is their poor solubility in organic solvents along with the tendency to give solvates, which makes obtaining these substances in pure form difficult.

Investigation of the thermal stability of tetrazine derivatives has shown that the least stable group in the molecule is usually the substituent in the tetrazine cycle which decomposition controls decomposition of whole molecule. Electron-withdrawing properties of the tetrazine cycle, in its turn, tend to increase thermal stability of the substituents.

Study of combustion behavior along with thermocouple-aided measurements has shown that most of tetrazines are low-volatile substances with high surface temperatures, which determines a dominant role of the condensed phase in combustion of many tetrazine derivatives.

The tetrazine cycle shows low reactivity in redox reactions, leading to rather moderate burning rates of its salts with oxidizing acids and coordination compounds despite high energetic characteristics.

The absence of oxygen or low-oxygen content in the tetrazine-based energetic materials leads to formation of high-enthalpy species (nitriles) in the combustion products, resulting in the incomplete heat release.

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