



The Influence of the Structure of the Salts of Azoles upon the Processes of their Thermal and Laser Initiation^{*)}

Mikhail A. ILYUSHIN and Igor V. TSELINSKII

*Saint-Petersburg State Institute of Technology,
Moskovsky pr. 26, Saint-Petersburg
E-mail: ilyushin@lti-gti.ru*

Abstract: It is experimentally shown that for metal salts of azoles there is no universal factor determining the processes of deflagration under thermal and laser initiation. For the series of azoles having a common initial stage of thermal degradation, the step of deflagration-to-detonation transition (DDT) for the same metal cation depends on ΔH_f^0 value of the salt. At the same time within the range of silver salts of isomeric *N*-nitroaminotetrazoles ΔH_f^0 values of the compounds, their structure, reactivity of the products of the initial decomposition and the composition of gaseous products of burning all influence their initiating ability under thermal initiation. But the ionization potential of complex perchlorates of d-metals with 3(5)-hydrazino-4-amino-1,2,4-triazoles as ligands determines the intensity of initial steps of decomposition under laser initiation which, in its turn controls the threshold of ignition. Hence the knowledge of the nature of initial decomposition stages of azole salts, taking into account the mechanism of energetic effects, is necessary for prediction of their behavior under initiation.

Keywords: deflagration-to-detonation transition (DDT), salts of azidoazoles, silver salts of *N*-nitroaminotetrazoles, complex perchlorates of d-metals with 3(5)-hydrazino-4-amino-1,2,4-triazole

Introduction

Primary explosives are used to initiate detonation (explosion) processes in the charges of high explosives (HE). By initiation ability of the primary explosive charges it is meant the ability after their initiation by a simple pulse

^{*)} Presented at the 8th Int. Seminar "New Trends in Research of Energetic Materials", University of Pardubice, April 2005.

(mechanical impact, mechanical friction, beam of fire, laser beam, etc.) to initiate the detonation processes in charges of HE [1]. Detonation in charges of HE is commonly initiated by the pressure and energy of explosion products of primary explosives, which are more sensitive to external stimuli and readily detonate under the action of a thermal or mechanical pulse. Combustion in primary explosives quickly transits into detonation within a distance not exceeding several millimeters from the ignition place. The shorter the region within which combustion transforms into detonation, the higher the efficiency of a primary explosive.

Initiation of detonation processes in explosives

Modern theory of the initiation of explosives under the action of a pulsed stimulus is based on the concept of “hot spots” – the centers of intense local heating, that are responsible for the fast reactions of thermal decomposition including explosion. Local heating centers are formed due to the structural inhomogeneity of the material (dot defects, congestions of vacancies, dislocations, interfaces, etc.), chemical impurities, microinclusions occurring owing to the non-stoichiometric composition of the initial products, addition of various impurities (presence of various additives) and so on.

The defects can also arise in the field of an intense light wave. The main hypothesis of warming up the optical heterogeneities resulting in the ignition of explosives has been adopted for laser initiation due to the short duration and therefore the high power of laser impulse. Carbon inclusions contained in organic high explosives, or metal microinclusions present in azides of heavy metals can play the role of initial centers.

The mean diameter of hot spots in the case of mechanical impact or mechanical friction is of the order $\sim 10^{-3}$ - $\sim 10^{-5}$ cm [2]. The smallest sizes of the experimentally found “hot spots” under the action of laser monopulse (*Q*-switch) ($\lambda = 1064$ nm, $\tau_q = 8$ ns) depend upon the nature of an explosive. In a compound with covalent bonds (RDX, hexogen) it equals to ~ 20 nm. For ionic compounds (ammonium perchlorate, NH_4ClO_4) the size of the centers is larger and equals to about 200-300 nm and even attains ~ 1000 nm [3].

The decomposition of an explosive can be accelerated if the temperature at the reaction site is such that the heat generation by a chemical reaction exceeds the heat dissipation into the environment (the so-called “flash point”). After a certain timelag, t_{ig} , from the start of heating the specimen ignites at the decomposition site

$$t_{ig} = B \exp(E/RT_0),$$

where **B** is an empirical constant, **E** is the activation energy of thermal decomposition, **R** is the universal gas constant, and t_{ig} is the flash point of the explosive. It is necessary that the specimen should remain at this temperature during the induction period of thermal decomposition. The physical meaning of the pre-exponential factor **B** is the minimum possible ignition delay. The **B** value (10^{-8} - 10^{-13} s) depends on the sample properties and experimental conditions.

The pressure of explosion products and the detonation velocity of an explosive are related by

$$P = \frac{\rho_0 \times D^2}{n + 1}$$

where **P** is the detonation pressure, ρ_0 is the density of the explosive, **D** is the detonation velocity, and **n** is the polytropic exponent (for most explosives $n \sim 3$). To initiate an explosion in HE, a shock wave should have the pulse energy exceeding or equal to that given by the equation below.

$$J_{critical} \geq P_{critical} \int_0^{\tau} d\tau$$

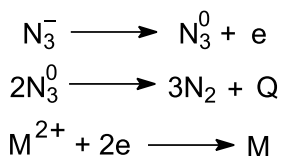
Thus, the initiating ability of a shock wave depends on the front pressure ($P_{critical}$) and the time of compression (τ). The value of $J_{critical}$ for RDX is near 46 J cm^{-2} which corresponds to $P^2 \tau = 460 \text{ GPa}^2 \mu\text{s}$ [4]. The initiating power of primary explosives can be estimated from the value of their minimal blasting charge necessary to initiate HE placed in the standard cartridge shell detonator (for example, no. 8) [4]. The initiating ability of a primary explosive mainly depends on the distance from deflagration-to-detonation transition (DDT). The chemical structure of a primary explosive and physical properties of charges both influence its initiating ability.

During the first step of the decomposition of explosives the weakest bonds in energetic molecules are broken. This is the fragmentation step. It is an endothermic step common for all explosives.

Secondary processes (for example, Red-Ox reactions, recombination of free radicals etc.) are exothermic and different in nature. They produce gaseous reaction products at high temperatures and pressures [5].

Among primary explosives metal azides are investigated in the most detail.

Under the action of an energy pulse they decompose to produce the metal and molecular nitrogen by the mechanism involving electron transfer. A simplified scheme of the decomposition of inorganic azides is as follows:



where Q is the heat of decomposition [4, 6]. The first step of decomposition of inorganic azides is the M-N bond breaking. The energy of breaking the weak bond decreases with an increasing metal ionization potential (**I**). This energy nearly equals the energy of electron excitation to the zone of conductivity [6]. Thus, the reaction $\text{N}_3^- - e \rightarrow \text{N}_3^0$ becomes more probable when the power of cation's field estimated from the sum value of their potentials of ionization divided by their ion radius ($\Sigma I/r$) increases and the crystal lattice becomes less ionic but more covalent.

Consequently, the cation's nature is the main factor determining the explosive properties of inorganic azides.

The increase in cation's enthalpy of formation, which primarily depends on the potential of ionization (**I**), leads to elevation of the enthalpy of formation of the azide.

Therefore, the values of minimal blasting charges of the salts (**W**) correlate with the enthalpy of formation of the inorganic azide (ΔH_f^0) or its heat of explosion [7]:

$$\ln W = d + b \cdot \ln \Delta H_f^0,$$

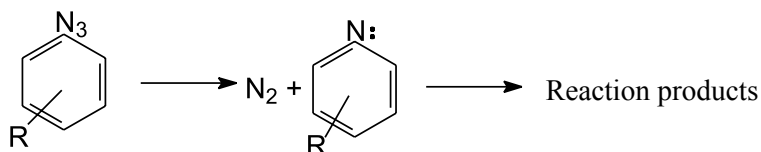
where **b**, **d** are coefficients.

The simplified scheme for the decomposition of inorganic azides given above is not fully correct and needs further refining. For example, it was found that the explosion products of $\text{Pb}(\text{N}_3)_2$ contained not only N_2 , but such species as N_3 , N_4 , N in concentration equal to the concentration of N_2 [8].

That is why the dependence of the velocity of explosion processes on DDT distance for inorganic azides may be the result of an incomplete release of potential energy during decomposition of energetic molecules.

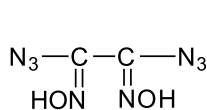
Initiation of salts of azido substituted NH- and OH-acids

The first step in the decomposition of organic azides and salts of azido substituted acids is the degradation of azido groups with the elimination of N_2 molecule [4].

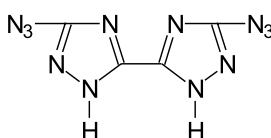


It can be stated that both the initial reaction and secondary processes will become more probable with the gain in the heat of thermal decomposition or/and enthalpy of formation of salts of azido substituted acids. Consequently, the value of the energy of degradation must affect the DDT step and minimal blasting charge of the salts of azidosubstituted acids.

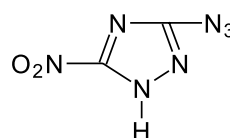
We have synthesized and investigated Cu (II), Ag (I), Pb (II) and Hg (II) salts for the following azidosubstituted acids: 1,2-diazidoglyoxim (1); bis(1-H-3-azido-1,2,4-triazol-5-yl) (2); 1-H-3-azido-5-nitro-1,2,4-triazole (3); 1-H-3-azido-5-amino-1,2,4-triazole (4); 1-H-3,5-diazido-1,2,4-triazole (5); 3-azido-4-nitramino-1,2,5-oxadiazole (6) [5, 9]:



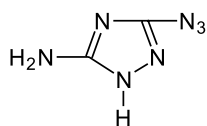
(1)



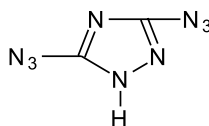
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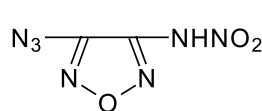
(3)



(4)



(5)



(6)

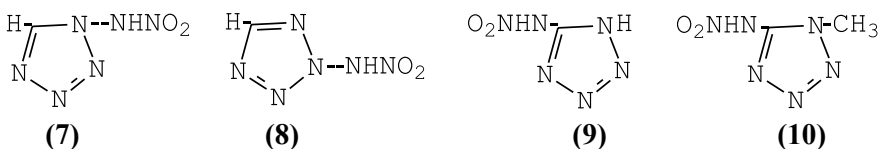
It was found that the salts of azido substituted acids with the same cation have a distinct tendency of reducing the minimal blasting charge with increasing the enthalpy of formation [10]. This tendency is the similar to that for inorganic azides [7].

Consequently, the potential energy releases only partially on the DDT step.

Initiation properties of Ag-salts of (*N*-nitramino)tetrazoles

It is known that some heavy and transition metal salts of 5-(*N*-nitramino)tetrazole have a short DDT period and thus possess initiating properties, i.e., can cause the detonation of a HE, e.g., RDX [9, 11, 12].

In order to study the influence of the position of the *N*-nitramine group on the explosive properties of salts of (*N*-nitramino)tetrazoles, we prepared silver salts of 1-(*N*-nitramino)- (**7**), 2-(*N*-nitramino)- (**8**), 5-(*N*-nitramino)- (**9**) and 1-methyl-5-(*N*-nitramino)tetrazole (**10**) [13].



The initiating power of the salts was estimated from their minimal blasting charge in RDX by the procedure described in [10]. The tests showed that the minimal blasting charges of silver salts are dependent on the position of the *N*-nitramine group and increase in the sequence:

$$\text{Ag-8: Ag-7: Ag-9: Ag-10} \approx 1:5:60:120.$$

So it can be concluded that the salts of 1- and 2-(*N*-nitramino)tetrazoles have a DDT period shorter than the salts of 5-(*N*-nitramino)tetrazoles. The average accuracy of the determination of minimal charges does not exceed 20%. Salt **Ag-8** is a more powerful initiating explosive than lead azide.

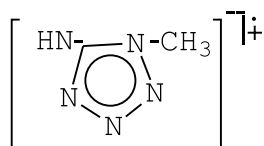
As it may be seen for such initiators as inorganic azides and salts of azidoazoles, the DDT period tends to decrease with the increasing enthalpy of formation of the salt. According to approximate calculations, the enthalpies of formation (ΔH_f^0) of 1- and 2-(*N*-nitramino)tetrazoles are by ca. 30 kJ·mol⁻¹ higher than those for 5-(*N*-nitramino)tetrazoles. However, such negligible increase in ΔH_f^0 cannot be responsible for the considerable rise in the initiating power on going from the salts of C-substituted (*N*-nitramino)tetrazoles (**9**) and (**10**) to the salts of *N*-substituted (*N*-nitramino)tetrazoles (**7**) and (**8**). Most probably, the increase in the initiating power suggests significant differences in the mechanism of decomposition of the salts of (*N*-nitramino)tetrazoles at the stage of DDT.

In order to evaluate possible differences in the composition of the primary decomposition products of (**7-10**), which can be indicative of the plausible routes of their decomposition, we examined their mass spectra, since, as it was

experimentally established for tetrazoles, the initial steps of thermal decomposition were similar to the fragmentation pattern under the electron impact [14]. As model compounds we used volatile ammonium salts of (*N*-nitramino)tetrazoles. The results are presented in Table 1.

Ammonium salts of (**7-10**) give no molecular ion peaks because of the dissociation to give ammonia and (*N*-nitramino)tetrazoles. The spectra of (**7-9**) contain the molecular ion peaks of (*N*-nitramino)tetrazoles (M^+ 129). Their intensities relative to the total ion current are 0.6, 1.0, and 0.4%, respectively. Low intensities of the molecular ion peaks of (*N*-nitramino)tetrazoles may be due to the fact that the oxygen atom of the nitro group is a strong electron acceptor and thus destabilizes the positive charge. Furthermore, the nitro group is a stable fragment and is readily eliminated under the electron impact. In the spectrum of salt (**10**) the molecular ion peak (M^+ 144) is strong: its intensity amounts to 26.1% of the total ion current. The relative stability of the molecular ion peak of (**10**) may be due to the presence of the electron-donating methyl group. The main peaks of (*N*-nitramino)tetrazoles (**8**) and (**9**) are those with m/z 28. Their intensity amounts to 35.6 and 34.1%, respectively, of the total ion current. These peaks can be assigned to three possible compounds: molecular nitrogen, CH_2N^+ , or carbon monoxide. The main peak of (*N*-nitramino)tetrazole (**7**) is that with m/z 30, which corresponds to nitrogen monoxide; its intensity amounts to 18.2% of the total ion current.

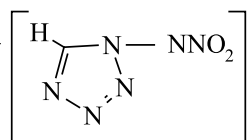
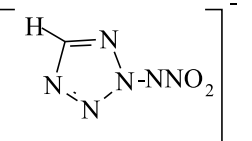
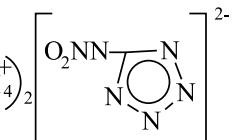
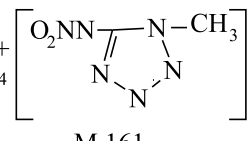
The peak with m/z 28 is also intense (17.6% of the total ion current). The main peak of (*N*-nitramino)tetrazole (**10**) is that with m/z 98, corresponding to the compound of the general formula $C_2H_4N_5$. Its intensity amounts to 29.6% of the total ion current.



The main fragmentation pathway of the molecular ions of (*N*-nitramino)tetrazoles is the loss of nitrogen dioxide. Substantially less intense is the peak of the protonated tetrazole, m/z 69 (for (*N*-nitramino)tetrazoles (**7-9**), resulting from the elimination of the N- NO_2 group. The major fragmentation pathway of the tetrazole ring in the salts of (**7-9**) is the loss of molecular nitrogen, but some portion of the product decomposes with the formation of the azide radical ion with m/z 42. In (*N*-nitramino)tetrazole (**10**) the tetrazole ring decomposes mainly with the loss of molecular nitrogen. The intermediate products of its fragmentation after the elimination of the nitro group are relatively stable to oxygen, and their further

fragmentation is practically not accompanied by oxidation, which is evidenced by the presence of free oxygen and only minor amounts of carbon dioxide (m/z 44) in the decomposition products. It may be concluded that (*N*-nitramino)tetrazole (**10**) is hardly suitable for preparing salts with a high initiating power. Salts of (**10**) should have a prolonged DDT period because of the low rate of oxidation of the initial decomposition products and, therefore, reduced heat of decomposition at the stage of acceleration of explosion. The properties of the silver salt of (**10**) have been studied experimentally, and fully support the above conclusion.

Table 1. Mass spectra of ammonium (*N*-nitramino)tetrazoles

Salt	Fragmentation peaks (% of total ion current)
NH_4^+  M 147	129(0.6), 113(0.4), 97(0.7), 83(0.1), 69(1.3), 60(1.2), 55(1.7), 46(12.0), 44(14.2), 42(6.9), 41(6.5), 36(5.5), 30(18.2), 28(17.5), 18(13.9)
NH_4^+  M 147	129(1.0), 97(0.9), 83(1.4), 69(2.3), 60(2.0), 55(2.9), 46(7.2), 44(8.1), 42(7.4), 41(4.7), 30(16.3), 28(35.5), 18(10.2)
$(\text{NH}_4^+)_2$  M 164	129(0.4), 97(0.7), 83(0.7), 69(1.2), 60(1.2), 55(1.6), 46(6.5), 44(4.0), 42(7.0), 41(2.6), 36(5.7), 30(14.0), 28(34.1), 18(20.3)
NH_4^+  M 161	145(1.7), 144(26.1), 143(0.1), 129(0.2), 128(0.2), 114(3.6), 98(29.6), 83(0.3), 82(0.1), 75(0.2), 68(0.1), 60(0.3), 56(6.3), 55(5.9), 54(0.6), 46(3.9), 44(0.4), 42(0.7), 40(0.7), 32(1.5), 30(4.7), 26(0.2), 18(2.2)

Fragmentation of the diammonium salt of (*N*-nitramino)tetrazole (**9**) gives fragment ions with m/z 28 with the intensity three times higher as compared to (**10**). Examination of the high-resolution mass spectra of the fragment ions with m/z 28 showed, that of the three possible compounds having this molecular mass nitrogen is the main component. Furthermore, in the mass spectrum of (*N*-nitramino)tetrazole (**9**) the intensity of the carbon dioxide peak is ten times

higher as compared to (10). It means that the fragmentation of this molecular ion is accompanied by more intense oxidation of carbon. These facts suggest that decomposition and oxidation at the stage of DDT are probably more close to completion for the salts of (9) than for those of (10). If this is the case, then salts of (*N*-nitramino)tetrazole (9) will have greater heats of decomposition at the stage of acceleration of explosion, higher pressures of the deflagration products, and higher initiating power. The properties of the disilver salt of (9) studied experimentally, fully confirm this suggestion.

The fragment ions of the ammonium salts of (7) and (8) are oxidized still more readily. The relative intensity of the carbon dioxide peak in their mass spectra is from two to three times higher compared to (9) and from 20 to 30 times higher compared to (10). It should be noted also that the relative intensity of the molecular nitrogen peak in the mass spectrum of (7) is by a factor of ca. 2 lower compared to (8) and (9). Therefore, out of the studied compounds the salts of (*N*-nitramino)tetrazoles (7) and (8) will have the highest heats of decomposition at the initial stages and the shortest DDT periods, the latter being probably somewhat longer for (7) because of a lesser nitrogen content in the initial decomposition products. The experimental data on the initiating power of the silver salts of isomeric (*N*-nitramino)tetrazoles (7) and (8) are in full agreement with this hypothesis.

Thus, we showed experimentally that the length of the DDT period and thus the initiating power of silver salts of isomeric (*N*-nitramino)tetrazoles (7-10) is controlled not only by their ΔH_r^0 values, but also by the structure and reactivity of their primary decomposition products and by the composition of the gas phase in the course of deflagration.

Laser initiation of metal complexes with 3(5)-hydrazino-4-amino-1,2,4-triazole as ligand

In search for new photosensitive energetic coordination compounds and for the study of the central ion effect on the sensitivity of metal complexes to laser mono pulse, we prepared and investigated complex perchlorates of copper (II) (11), cobalt (II) (12), nickel (II) (13) and cadmium (II) (14) with 3(5)-hydrazino-4-amino-1,2,4-triazole (HATr) as ligand [15]. The choice of the ligand is based on the high sensitivity of the perchlorate bis(3(5)hydrazino-4-amino-1,2,4-triazole)copper (II) to laser mono pulse [16].

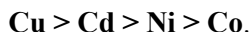
The prepared complex salts were tested for sensitivity to laser mono pulse (Table 2).

Table 2. Laser initiation of the synthesized complexes

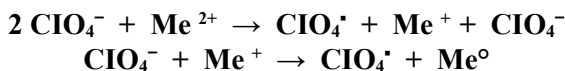
Compound	Critical energy E_{critical} , [J]	The sum of two ionization potentials of the metal cation, I_1+I_2 , Ev
[Cu (HATr) ₂](ClO ₄) ₂	$1.1 \cdot 10^{-5}$	28.02
[Cd (HATr) ₂](ClO ₄) ₂	$5.03 \cdot 10^{-4}$	25.90
[Ni (HATr) ₂](ClO ₄) ₂	$5.75 \cdot 10^{-4}$	25.78
[Co (HATr) ₂](ClO ₄) ₂	$1.36 \cdot 10^{-3}$	24.92

In this case E_{critical} is the minimum energy sufficient for the initiation of the complex resulting in its detonation.

On the basis of the results of testing it is possible to conclude that compounds (11-14) may be regarded as energetic light-sensitive primary explosives. Their sensitivity to laser mono pulse varies with the oxidizing ability of the central metal ion, expressed as the sum of two ionization potentials I_1+I_2 (Table 2). The more this value, the higher the sensitivity of a compound towards laser radiation:



It was established that at the initial stages of the process there occurs predominantly the inner-sphere ligand oxidation effected by the metal cation. The results of our study allow to assume that the following mechanism of oxidation takes place at the initial stages:



The two-stage interaction of the metal cation and the perchlorate anion results in the formation of a highly active perchlorate radical participating on the second stage of ligand oxidation.

Consequently, it is experimentally shown that for the metal salts of azoles there is no universal factor governing the processes of deflagration under thermal and laser initiation.

Conclusions

The initiating ability of heavy metal azides having a common mechanism of thermal decomposition depends on their enthalpy of formation.

The minimal charge of metal salts of azidecontaining NH- and OH- azides having a common first stage of thermal decomposition depends both on their enthalpy of formation and the catalytic properties of metal cations.

The initiating ability of silver salts of isomeric *N*-nitroaminotetrazoles is determined both by their enthalpies of formation and the composition of primary decomposition products at the deflagration stage.

The initiation threshold of complex d-metal perchlorates with 3(5)-hydrazino-4-amino-1,2,4-triazole as ligand for laser mono pulse depends on the oxidizing ability of the central ion expressed by the sum of the first and second ionization potentials of the cation.

The knowledge of both the energetic properties of compounds and the nature of initial decomposition stages is essential for the prediction of the length of deflagration-to-detonation transition for the salts of organic azides and complex d-metals perchlorates.

Acknowledgments

The work was financially supported by the Ministry of Education of the Russian Federation in the framework of the Intercollegiate Research and Development Program “Scientific Research of High School in the Field of Chemistry and Chemical Products”.

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