Computer Simulation of Thermal Decomposition Mechanism for Compounds with Nitroguanidine Fragment[*]

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Abstract: The application efficiency of energetic compounds depends on the set of their characteristics. The most important of them is a thermal stability, which is connected with the thermal decomposition mechanism of compounds.
Nitroguanidine and its analogs have been of interest as an example of energetic compounds. However, currently there is no general view for the thermolysis of nitroguanidine analogs. Having labile hydrogen atoms, theoretically, nitroguanidine and its analogs may exist in different tautomeric forms. Meanwhile, there are no experimental evidences if this or other tautomeric form domination during a decomposition process.
In order to fill this gap, the simulation of mechanism of all nitroguanidine tautomers and 3-nitramine-1,2,4-triazole thermal decomposition was carried out. Subsequent evaluation of different tautomeric forms in terms of thermodynamic stability and activation energy for initial steps of their decomposition reactions has been conducted using DFT approach (B3LYP/6-31G*). Thermochemical preferences of some decomposition pathways have been determined.

Keywords: nitroguanidine, 1,2,4-triazole, simulation of mechanism, decomposition reaction

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Introduction

As is known, experimental investigations of multi-stepped thermolysis processes for energetic materials are complicated. That is why in a set of works a theoretical approach to simulate mechanisms of organic compounds thermolysis processes has been proposed [1-5]. In the present work, this approach has been used for nitroguanidine (**1**) and 3-nitramino-1,2,4-triazole (**2**) thermolysis channels modeling (the latter compound was considered because it contains nitroguanidine in the nitrimine form as a fragment of the structure).

$$\underset{H_2N}{\overset{H_2N}{>}}C=N-NO_2$$

1

2

Methods of Investigations

Based on analysis of experimental data on mechanisms of thermal decomposition reactions for nitroguanidine and 1,2,4-triazoles, a generator of hypothesis for the mechanisms of the compounds thermolysis has been elaborated. At the heart of the methodology was the representation of decomposition processes as Recombination Reaction Nets (RRN). The approach was realized in the CASB computer program [1-2] and allows one to get the whole spectrum of reactions occurring in the course of compounds thermal decomposition. Having probable mechanism, to evaluate the thermochemical preference of these or other pathways of decay, quantum-chemical calculations of the activation energy for reactions at the first step of decomposition were carried out. All calculations were accomplished by the method of density functional (DFT) using hybrid potential B3LYP and standard valence-split basic 6-31G* [6]. Calculations were executed using GAUSSIAN 98 [7] at the Computational Centre of Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences.

Results and Discussion

For nitroguanidine (**1**) it is possible ten tautomeric forms and rotational isomers. Experimental evidences of one or other tautomer prepotency under

thermolysis conditions are lacking. Apparently, the opportunity of one or another tautomer or their mixture existence depends on particular conditions. That is why the simulation of nitroguanidine thermolysis mechanism was carried out for all (**1a-1c**) tautomeric forms.

As the measure of isomer stability the calculated tautomerisation energy [9] of different forms we used. The results (Table 1) show that in gas phase the tautomer (**1b**) is the most thermodynamic stable: its total energy is the least relatively to all others forms.

Table 1. Energy characteristics of nitroguanidine tautomers (1a-c)

Compounds	Total energy (E), a.e.	Tauto-meriza-tion energy, kcal/mol	Compounds	Total energy (E), a.e.	Tauto-meriza-tion energy, kcal/mol
1a	-409.758746	11.09	**1c4**	-409.739156	23.4
1b	-409.776420	0.00	**1c5**	-409.743446	20.7
1c1	-409.743239	20.8	**1c6**	-409.743129	20.9
1c2	-409.743363	20.7	**1c7**	-409.738276	23.9
1c3	-409.738131	24.0	**1c8**	-409.736059	25.3
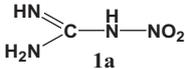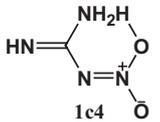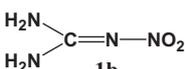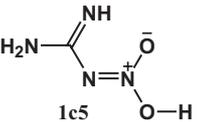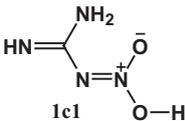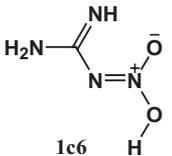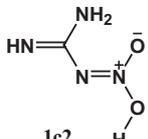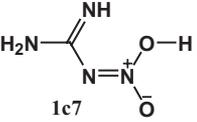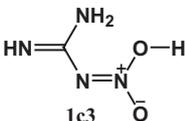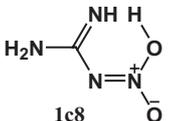
The energy of tautomerization was calculated by formula $[(E + ZPE)_x - (E + ZPE)_y] \times 627.5$ kcal/mol [9], where ZPE is a correction for the energy

of zero-point oscillations, x – the data for the tautomer (**1b**) and y – the data for any other isomers.

Computer generation of possible pathways for (**1b**) decomposition gave three hypotheses of the initial stage (Figure 1): homolytic cleavage of nitro-group (channel 1), NH_2 group breakage (channel 2), and nitro-nitrite rearrangement (channel 3).
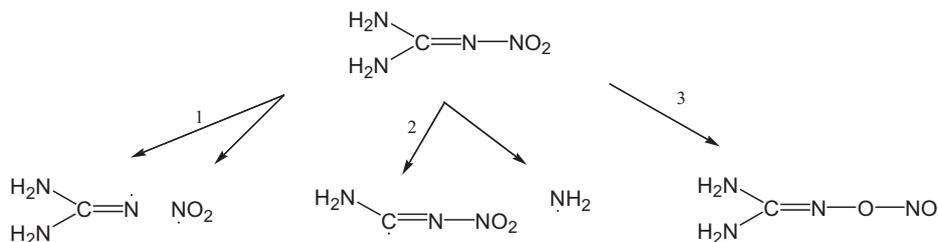
Figure 1.   The initial stages of nitroguanidine (**1b**) thermal decomposition.

The results of activation energy (E_a) calculations of the presented decomposition reactions showed the thermochemical preference of (**1b**) destruction along the channel 1 with $E_a = 46.4$ kcal mol^{-1}. The radical NH_2 cleavage energetic input (channel 2) is higher ($E_a = 56.1$ kcal mol^{-1}). Unfortunately, we failed to localize the nitro-nitrite rearrangement transition state (channel 3). However, according to [10] for N-nitro derivatives this rearrangement is thermochemicaly less favorable than homolytic cleavage of nitro-group.

In Figure 2 the fragment of consequent stages for nitroguanidine (**1b**) decomposition along the channel 1 is presented as an illustration of generated net intermediates and of the order of their transformations.

The generated mechanism of (**1b**) thermolysis allows one to describe the whole spectrum of reactions occurring in the course of thermal decomposition and of the experimentally confirmed final products [11] of thermolysis: N_2O, NH_3, CO_2, HNCO, cyanamide, dicyanamide, urea, cyanuric acid, melamine.

For the second compound that we present in the paper (C-nitramino-1,2,4-triazole (**2**)) 30 tautomeric forms and rotational isomers are possible. The same as in the case of nitroguanidine, for the compound (**2**) there is no evidence of thermochemical preferences of this or other form. The results of our calculations (DFT/B3LYP/6-31G*) done for all isomers (Table 2) show that in gas phase the tautomer (**2a**) is the most thermodynamic stable one.
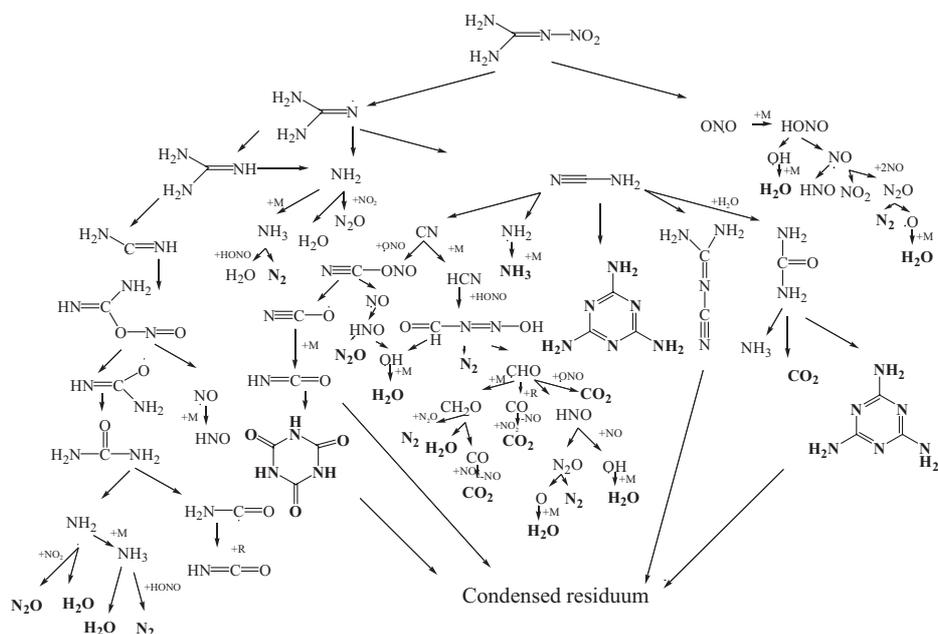
Figure 2. The fragment of consequent stages for nitroguanidine (**1b**, channel 1) thermal decomposition.

Table 2. Energy characteristics of C-nitramino-1,2,4-triazole tautomers (2a-i)

Compounds	Total energy (E), a.e.	Tauto-merization energy, kcal mol⁻¹	Compounds	Total energy (E), a.e.	Tauto-merization energy, kcal mol⁻¹
2a	-502.0856	0.0	**2g7**	-502.0711	9.0
2b	-502.0854	0.3	**2h1**	-502.0699	9.5
2c	-502.0748	6.6	**2h2**	-502.0597	15.6
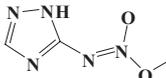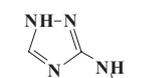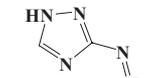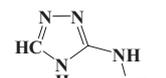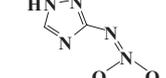
Compounds	Total energy (E), a.e.	Tauto-merization energy, kcal mol^{-1}	Compounds	Total energy (E), a.e.	Tauto-merization energy, kcal mol^{-1}
2d1	-502.0835	1.4	**2h3**	-502.0639	13.1
2d2	-502.0842	0.9	**2h4**	-502.0637	13.3
2e1	-502.0581	16.8	**2h5**	-502.0662	11.6
2e2	-502.0472	23.8	**2h6**	-502.0593	15.9
2f1	-502.0460	24.5	**2h7**	-502.0637	13.0
2f2	-502.0602	15.5	**2i1**	-502.0672	10.6
2g1	-502.0771	5.0	**2i2**	-502.0531	19.7
2g2	-502.0637	13.3	**2i3**	-502.0540	18.9
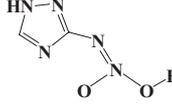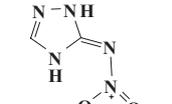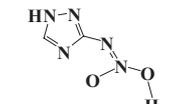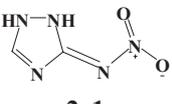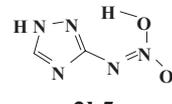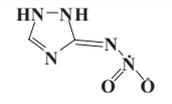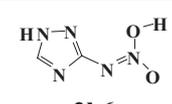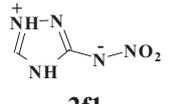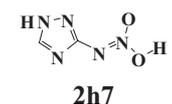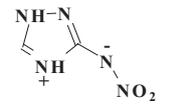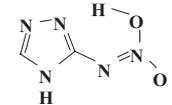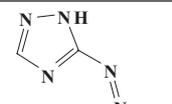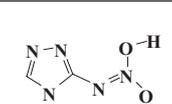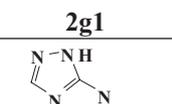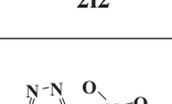
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2g4	-502.0672	11.3	**2i5**	-502.0604	15.1
2g5	-502.0635	13.3	**2i6**	-502.0611	14.7
2g6	-502.0716	8.7	**2i7**	-502.0523	19.8
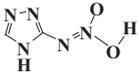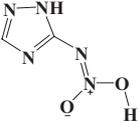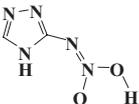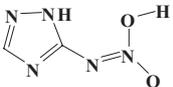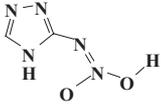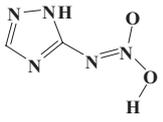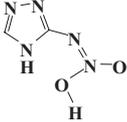
Therefore in the paper we present the result of simulation of thermal decomposition mechanism for tautomer (**2a**). Generation of possible pathways of (**2a**) decomposition gave three probable channels of the initial stage (Figure 3): homolytic cleavage of nitro-group (channel 1), N-N bond breakage in heterocycle (channel 2), and C-N out-of-cycle bond breakage (channel 3).

In nitro-1,2,4-triazoles [12] it takes 23.7-34.3 kcal mol^{-1} more energy for heteroaromatic C-N bond breakage than for transannular N-N bond breakage (channel 2). According to our calculations for (**2a**) tautomer at the initial step the most benefit is the C-NO$_2$ homolysis (channel 1). This mechanism is estimated to have the activation energy of 27.9 kcal mol^{-1}. The initial steps of nitro-1,2,4-triazole decomposition processes of other channels (2 and 3) are almost twice as many (E_a = 68.1 and 87.1 kcal mol^{-1}, correspondingly) compared with the channel 1 process.

Figure 3. Consequent stages for 3-nitramino-1,2,4-triazole (**2a**) thermal decomposition.

The computer generation of the possible pathways of (**2a**) thermal decomposition (Figure 3) provided a wide number of reactions and the final decomposition products. It is significant that during HS-thermolysis of 3-nitramino-1,2,4-triazole [13] only NO, NO_2, HCN, CO, N_2O have been detected experimentally. However, in this study we showed (Figure 3) the

possibility of formation for a set of some other products being experimentally not found: H_2O, N_2, O_2, CO_2, HNCO, ammonia, cyanamide, dicyanamide, dicyane, urea, cyanuric acid, melamine, 3(5)-amino-1,2,4-triazole, 4-amino-1,2,4-triazole, 1,2,4-triazole, 1,2,4-triazolon, 3(5)-nitro-1,2,4-triazole, 3(5)-nitrozo-1,2,4-triazole.

Conclusion

As the result of nitrimine form for nitroguanidine and of 3-nitramino-1,2,4-triazole thermal decomposition mechanisms simulation the comprehensive spectrum of possible pathways for their thermal decay has been suggested. Based on the suggested hypotheses on the mechanisms of thermal decomposition the estimation of thermochemical preferences of decomposition pathways have been carried out. The data obtained can be used to propose the thermal stability of compounds and for understanding of experimental thermal decomposition kinetic investigations.

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