Thermal decomposition mechanisms of nitro-1,2,4-triazoles: a theoretical study

V. L. Korolev,[a] T. V. Petukhova,[b] T. S. Pivina,[a] A. A. Porollo,[c] A. B. Sheremetev,[a] K. Yu. Suponitskii,[d] and V. P. Ivshin[b]*

[a]*N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky Prosp., 119991 Moscow, Russian Federation. Fax: +7 (495) 135 5328. E-mail: tsp@ioc.ac.ru*
[b]*Mari State University, 1 Lenin Sq., 424000 Yoshkar-Ola, Mari El Republic, Russian Federation.*
[c]*Biomedical Informatics, Children´s Hospital Research Foundation, 3333 Burnet Av., Cincinnati, OH 45229, USA.*
[d]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 119991 Moscow, Russian Federation.*

Possible decomposition mechanisms of *C*-nitro- and *N*-nitro-1,2,4-triazoles were simulated. We showed that in addition to the experimentally detected thermolysis products including N_2, N_2O, NO, CO_2, HCN, HNCO, 1,2,4-triazole, 3(5)-nitroso-1,2,4-triazole, and 1,2,4-triazolone, some other decompositon products (H_2O, CO, NO_2, cyanamide, cyanuric acid, and melamine) can be formed. Using the density functional approach (B3LYP/6-31G* approximation), we assessed the most favorable thermal decomposition pathways of nitrotriazoles and studied the relationships between the thermolysis pathways of these substances and their molecular and electronic structures. We found a correlation between the energy gap width (energy difference between the frontier molecular orbitals) and the stabilities of the *C*-nitro-1,2,4-triazole tautomers to thermal decomposition.

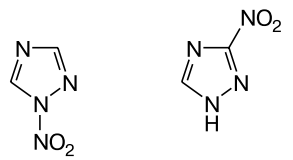
Key words: thermal decomposition, nitro-1,2,4-triazoles, quantum chemical calculations, simulation of mechanisms of chemical processes, structure—property relationships.

Thermal stability is an important operating characteristic of energetic compounds, which is related to thermal decomposition of substances.[1] Thermal decomposition of high-energy materials is a complex multistep process. In most experimental studies, the processes occurring in the course of thermal decomposition are described using the simplest hypothetical schemes that do not go beyond the analysis of the final products and/or the initial step of the decomposition.[1,2] These experiments are preceded by labor-consuming synthesis of the target compounds. Nevertheless, there is no assurance that a given substance will possess the desired properties (in particular, thermal stability) that make it a promising energetic compound. In this connection one intensively developing avenue of energetic materials design includes prediction of their properties. This allows one to choose the most promising compounds prior to the synthetic stage, thus shortening the time and reducing the expenditure for the synthesis and subsequent investigations of the potentially promising substances.[3—6] Using mathematical modeling of thermal decomposition processes of hypothetical substances, it is possible to assess the whole spectrum of corresponding thermolysis pathways and to predict certain features of the thermal stability of the compounds. Additionally, mathematical modeling can help in interpreting the experimental data on the ignition, combustion, or explosive decomposition of the substances synthesized.

Often, energetic compounds for various applications[7—11] are synthesized based on a combination of the nitro groups with polynitro heterocycles (in particular, 1,2,4-triazole). However, there are only a few experimental studies[10,12—16] of the thermolysis of *N*-nitro-1,2,4-triazoles, in which the initial stage of the decomposition was considered. Thermal decomposition of *C*-nitro-1,2,4-triazoles[10,17—22] and 3-nitro-1,2,4-triazolone-5 (NTO, a promising compound for various applications)[23] was studied in more detail both experimentally and theoretically. However, these studies also report only on the most probable initial stage of decomposition and on the final products of the thermal decomposition, leaving alternative decomposition pathways out of consideration. In this work we theoretically studied a whole spectrum of the

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 8, pp. 1338—1358, August, 2006.
1066-5285/06/5508-1388

reactions that can occur in the course of thermal decomposition of two regioisomeric nitrotriazoles, namely, *N*-nitro-1,2,4-triazole (**1**) and *C*-nitro-1,2,4-triazole (**2**).



1 **2**

Experimental data on the compositions of the thermal decomposition products of compounds **1** and **2** as well as the kinetic parameters and a possible mechanism of the initial stage of thermolysis are available.[13,18,20] This allows the substances in question to be considered as model objects for a theoretical study.

Thermolysis of compounds: methods of modeling

In order to describe multistage thermal decomposition processes, we developed a methodology[24—31] that allows one to study and assess possible pathways of thermal decomposition of aliphatic and alicyclic nitro derivatives. Here, this approach was used for modeling the mechanisms of thermolysis of heteroaromatic nitro compounds **1** and **2**.

Our methodology is based on the assumption that any intermediate formed in the course of thermolysis can react with all other species and their combinations that are formed in different stages of thermolysis.[25] The decomposition reactions of the initial compound and the interactions between intermediates are described by the expert rules (reaction generators) formulated based on empirical data and operating following the "if—then" principle. The reaction generators can describe both general (*e.g.,* radical recombination) and particular (*e.g.,* nitro-nitrite rearrangement) reactions, *i.e.*, be both general or particular in character.[1,32] Each expert rule is related to a particular molecular graph and corresponding transformation rules.

The chemical reaction generators were defined as follows. A chemical compound S can be represented by a set of N atoms (subsets A) and M chemical bonds (subsets B):

$$S = \{A_1, ..., A_N, B_1, ..., B_M\}.$$

Any atom A_i is characterized by its parameters X, *e.g.*, X = {chemical element, valence, hybridization, *etc.*}. Therefore, the bonds B are characterized by their own set of properties Y, *e.g.*, Y = {bond energy, bond length, identificators of the atoms connected by this bond, *etc.*}.

The chemical compound has at least one reaction center $C(A,B)$ that can be described by a particular set (more exactly, by corresponding characteristics) of the atoms and/or bonds:

$$C(A,B) = \{A_1...A_n,B_1...B_m\} = \\ = \{X_1^1...X_k^1,...,X_1^n...X_k^n,Y_1^1...Y_l^1,...,Y_1^m...Y_l^m\},$$

where n and m are respectively the numbers of atoms and chemical bonds in the reaction center and X_i^j and Y_i^j are the ith characteristics of the jth atom or chemical bond, respectively. For the same reaction center the sets of the properties analyzed can be different for the constituent atoms or bonds. Then, the chemical compound can be treated as a set of r reaction centers

$$S = \{C_1(A,B), ..., C_r(A,B)\}.$$

The applicability of a reaction generator to a chemical system is determined by the intersection $C^0(A,B) \cap S$ of two sets, namely, the reaction-center set $C^0(A,B)$ incorporated into the generator and the set S corresponding to the chemical structure under consideration. In terms of the molecular graphs this means that the total graph of the chemical system includes a subgraph of the reaction center.

Using combinatorial enumeration, the non-repeated reaction systems are designed from the whole set of the chemical structures generated (at the first step, they are generated from the initial compound). A reaction system can comprise one or more (at most three) molecules of the same compound or different compounds. Then, the chemical reaction R can be treated as an operation which describes the mechanism of transformation of a set of the reaction centers that meet the specified structural conditions $C^0(A,B)$ to reaction products by changing the necessary characteristics of atoms and chemical bonds, *e.g.*, redistribution of electrons, change in bond orders, *etc.* (for more detail, see Table 1):

$$A' = R_a(A|C^0(A,B)), \qquad B' = R_b(B|C^0(A,B))$$

or, generally,

$$S' = R(S|C^0(A,B)),$$

where R_a and R_b are respectively the operations on the atoms A and chemical bonds B allowed when the conditions $C^0(A,B)$ are met; A' and B' are the subsets of the atoms and chemical bonds possessing new properties and involved in the reaction; and S' is the new chemical system formed as a result of the reaction.

Once tested for correctness of the operation using model compounds, the generators designed can be applied to objects that were not studied at all or were poorly studied.

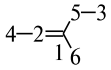
The basis sets of rules for the generators of hypotheses of the chemical reactions for modeling thermal decomposition pathways of nitroalkanes, nitroamines, and nitroethers were reported earlier.[25,33,34] Our analysis showed that the decomposition of heterocyclic compounds can involve a number of processes that were not taken into account in the early studies. In order to describe them, we formulated some additional expert rules based on the experimental data on thermolysis of different classes of chemical compounds.[1,35] They are listed in Table 1. The reactions conditions imply that most reactions proceed by a homolytic mechanism.

Rule (1) represents the nitro-nitrite rearrangement[1,32]:

$$R—NO_2 \longrightarrow R—ONO.$$

Rules (2) and (3) describe free-radical reactions. The initial set of rules[34] describing the propagation of a free-radical chain included severe restrictions. In this work, in order to construct a generalized model, we introduced additional rules. The first rule accounts for chain propagation by proton transfer involving cyclic radicals (*e.g.*, 1,2,4-triazolyl radical). The second rule represents a restriction describing the recombination with a cyclic radical.

Table 1. Expert rules for generation of thermal decomposition pathways of heterocyclic compounds

Rule	Graph	Description[a]	Settings[b]				
			Atom	Property[c]	Relation	Value	Operation[d]
(1)		Nitro—nitrite rearrangement	1	Atom type	=	N, C	No
				UE	=	0	No
				Charge	=	0	No
	↓		2	Atom type	=	N	No
	1—3—2=4			Charge	=	1	Set equal to 0
			3	Atom type	=	O	No
				Charge	=	−1	Set equal to 0
			4	Atom type	=	O	No
(2)	1 + 2	Chain propagation	1	Atom type	=	C, N, O	No
				Valence	=	3	BD
				UE	≥	1	Change to −1
				Charge	=	0	No
			2	Atom type	=	C,N,O	No
				Heteroatoms	≥	1	BD
				H atoms	≥	1	BD
				UE	=	0	Set equal to 1
				Charge	=	0	No
(3)	1 + 2—3	Radical recombination	1	Atom type	=	N	No
	↓			Heteroatoms	=	0	No
	1—2—3			Hybridization	=	sp^3	BD
				UE	≥	1	Change to −1
			2	Atom type	<>	C	No
				Heteroatoms	≥	1	BD
				Valence	≤	2	BD
				UE	≥	1	Change to −1
				Charge	=	0	No
			3	Atom type	<>	C	No
				Heteroatoms	=	2	BD
				Hybridization	<	sp^3	BD
				Heteroatoms	=	0	BD
				Valence	=	3	BD
				UE	≥	1	Change to −1
				Charge	=	0	No
(4)		Decomposition $H_2N—NO_2$	1	Atom type	=	N	No
				H atoms	≥	2	BD
				UE	=	0	No
	↓			Charge	=	0	Set equal to −1
	1=2=3 + 4		2	Atom type	=	N	No
				Charge	=	1	No
			3	Atom type	=	O	No
			4	Atom type	=	O	No
				Charge	=	−1	Set equal to 0
(5)		Rearrangement to *aci*-form	1	Atom type	=	N	No
				Charge	=	1	No
			2	Atom type	=	N, C	No
	↓			UE	=	0	No
				Charge	=	0	No
			3	Atom type	=	C	No
				UE	=	0	No
				Charge	=	0	No
			4	Atom type	=	C	No
				Heteroatoms	=	1	BD

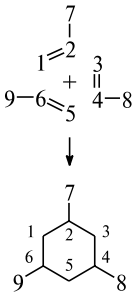
(*to be continued*)

Table 1 (*continued*)

Rule	Graph	Description[a]	Settings[b]				
			Atom	Property[c]	Relation	Value	Operation[d]
			5	Atom type	=	O	No
				Charge	=	0	No
			6	Atom type	=	O	No
				Charge	=	−1	No
				Valence	=	4	BD
				UE	=	0	Set equal to 1
				Charge	=	0	No
(6)	1=2—3 + 4=5 ↓ 1=2 + 3=4=5	Formation of CO_2	1, 5	Atom type	=	O	No
				UE	=	0	No
				Charge	=	0	No
			2	Atom type	=	N	No
				UE	=	0	No
				Charge	=	0	No
			3	Atom type	=	O	No
				UE	=	1	Set equal to 0
			4	Atom type	=	C	No
				H atoms	=	1	BD
				UE	=	1	Set equal to 0
				Charge	=	0	No
(7)	5=4—3 + 1≡2 ↓ 5—4 3 ‖ ‖ 1—2	$HCN + HNO_2$	1, 4	Atom type	=	N	No
				UE	=	0	No
				Charge	=	0	No
			2	Atom type	=	C	No
				H atoms	=	1	BD
				UE	=	0	No
				Charge	=	0	No
			3	Atom type	=	O	No
				H atoms	=	1	BD
				UE	=	0	No
				Charge	=	0	No
			5	Atom type	=	O	No
				UE	=	0	No
				Charge	=	0	No
(8)	1—2=3—4 ↓ 2≡3 + 1+4	Formation of nitrogen	1	Atom type	=	C	No
				UE	=	0	No
				Charge	=	0	No
			2, 3	Atom type	=	N	No
				UE	=	0	No
				Charge	=	0	No
			4	Atom type	=	C, N, O	No
				H atoms	=	1	BD
				UE	=	0	No
				Charge	=	0	No
(9)	1—2≡3 ↓ 1=2=3	Isomeri-zation	1	Atom type	=	O	No
				UE	=	0	No
				Charge	=	0	No
			2	Atom type	=	C	No
				UE	=	0	No
				Charge	=	0	No
			3	Atom type	=	N	No
				UE	=	0	No
				Charge	=	0	No

(*to be continued*)

Table 1 (*continued*)

Rule	Graph	Description[a]	Settings[b]				
			Atom	Property[c]	Relation	Value	Operation[d]
(10)		Trimerization	1, 3, 5	Atom type	=	N	No
				Heteroatoms	=	0	BD
				UE	=	0	No
				Charge	=	0	No
			2	Atom type	=	C	No
				Heteroatoms	=	2	BD
				UE	=	0	No
				Charge	=	0	No
			4, 6	Atom type	=	C	No
				UE	=	0	No
				Charge	=	0	No
			7, 8, 9	Atom type	=	C, N, O	No
				Valence	≤	2	BD
(11)	1 + 3=2—4 ↓ 1≡2 + 3 + 4	Interaction of ammonia with nitrous acid	1	Atom type	=	N	No
				H atoms	≥	3	BD
				UE	=	0	No
				Charge	=	0	No
			2	Atom type	=	N	No
				UE	=	0	No
				Charge	=	0	No
			3	Atom type	=	O	No
			4	Atom type	=	O	No
				H atoms	=	1	BD
(12)	4=5 + 1=2=3 ↓ 4≡5 + 1≡2 + 3	Decomposition of N_2O	1	Atom type	=	N	No
				Charge	=	−1	Set equal to 0
			2	Atom type	=	N	No
				Charge	=	1	Set equal to 0
			3	Atom type	=	O	No
			4	Atom type	=	C	No
				H atoms	=	2	BD
				Charge	=	0	Set equal to −1
			5	Atom type	=	O	No
				Charge	=	0	Set equal to 1
(13)	1=2=3 ↓ 1≡2 + 3	High-temperature decomposition of N_2O	1	Atom type	=	N	No
				UE	=	0	No
				Charge	=	−1	Set equal to 0
			2	Atom type	=	N	No
				UE	=	0	No
				Charge	=	1	Set equal to 0
			3	Atom type	=	O	No
				Charge	=	0	No
(14)	1=2=3 + 4=5 ↓ 1≡2 + 3—4=5	Formation of dinitrogen	1	Atom type	=	N	No
				UE	=	0	No
				Charge	=	−1	Set equal to 0
			2	Atom type	=	N	No
				UE	=	0	No
				Charge	=	1	Set equal to 0
			3	Atom type	=	O	No
				UE	=	0	Set equal to 1
				Charge	=	0	No
			4	Atom type	=	N	No
				UE	=	1	Set equal to 0
				Charge	=	0	No

(*to be continued*)

Table 1 (*continued*)

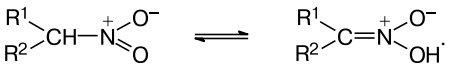
Rule	Graph	Description[a]	Settings[b]				
			Atom	Property[c]	Relation	Value	Operation[d]
			5	Atom type	=	0	No
				UE	=	0	No
				Charge	=	0	No
(15)	1=2 + 3=4 + 5=6 ↓ 1=2=3 + 4—5=6	Decomposition of NO_2	1	Atom type	=	N	No
				UE	=	1	Set equal to 0
				Charge	=	0	Set equal to 1
			2, 6	Atom type	=	O	No
			3	Atom type	=	N	No
				UE	=	1	Set equal to 0
				Charge	=	0	Set equal to −1
			4	Atom type	=	O	No
				UE	=	0	Set equal to 1
			5	Atom type	=	N	No
				UE	=	1	Set equal to 0

[a] Reaction name.
[b] Description of atomic characteristics in the system of chemical procedures that should be done for each atom.
[c] UE stands for "Unpaired Electrons".
[d] BD stands for "By-Default" operation.

The decomposition of nitramide to nitrous oxide and water[36,37] is included by rule (4):

$$NH_2NO_2 \longrightarrow N_2O + H_2O.$$

Rule (5) describes the rearrangement of nitro compounds to the *aci*-form[1,32]:



Rule (6) describes the formation of carbon dioxide in the oxidation of formaldehyde[1]:

$$2\,NO_2 + CH_2O \longrightarrow 2\,NO + CO_2 + H_2O.$$

Rule (7) takes into account the interaction of nitrous acid with hydrogen cyanide by analogy with Ref. 38:

$$HONO + HCN \longrightarrow HO—N=N—CH=O.$$

Structures containing the —N=N— fragment decompose with elimination of nitrogen molecule.[39] This is described by rule (8). Rule (9) describes the isomerization of cyanic acid into isocyanic acid.[40] Rule (10) describes trimerization of isocyanic acid and cyanamide.[41] Rule (11) corresponds to the interaction of ammonia with nitrous acid with elimination of nitrogen molecule and water[42]:

$$HONO + NH_3 \longrightarrow N_2 + 2\,H_2O.$$

Rule (12) describes the reaction of nitrous oxide with formaldehyde[43]:

$$N_2O + H_2CO \longrightarrow N_2 + H_2O + CO.$$

Rule (13) illustrates high-temperature decomposition of nitrous oxide[44]:

$$N_2O \longrightarrow N_2 + O.$$

Rule (14) describes the formation of molecular nitrogen upon disproportionation of nitrogen oxides[45]:

$$N_2O + NO \longrightarrow N_2 + NO_2.$$

Rule (15) describes the disproportionation of nitrogen monoxide[45]:

$$3\,NO \longrightarrow N_2O + NO_2.$$

The use of combinatorial calculus elements for generating hypothetical schemes of thermal decomposition of compounds imposes particular requirements on the computational resources and limitations on the analysis of the results obtained. The complexity of the combinatorial approach to modeling of chemical processes and methods of limitation of the growth of chains generated in the model were assessed and discussed earlier.[34] In this work we present an improved approach to the determination of the most probable pathways of thermal decomposition. It is based on assessment of thermochemical preferableness of a particular pathway in the initial stage of decomposition of a given compound. The preferableness is determined based on the results of activation energy[1] (E_a) calculations for the initial stage of thermal decomposition for each generated pathway of homolytic decomposition.

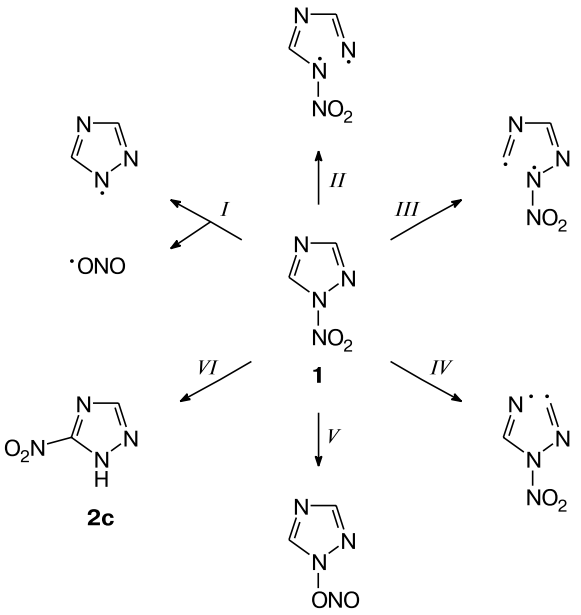
To this end, we calculated the geometric, electronic, and energy characteristics of the initial compounds in the gas phase, as well as those of the transition states and final products of the reactions using the density functional theory (DFT) with the B3LYP hybrid functional[46] and a conventional split-valence basis set 6-31G*.[47] Calculations of the characteristics of particular compounds using extended basis sets (6-31G** and 6-311G**)

gave similar results; because of this, the 6-31G* basis set was used. Additionally, the enthalpies of activation of monomolecular decomposition of nitro compounds calculated[48] by the B3LYP/6-31G* method are similar to the experimental activation energies for the gas-phase decomposition (differences were at most 2.4 kcal mol^{-1}, which is comparable with the experimental error). Positions of all stationary points were confirmed by analysis of the Hesse matrices. Check for transition states was done by calculating the intrinsic reaction coordinates. Biradical structures were assumed to be in the triplet spin states. All calculations were carried out using the GAUSSIAN-98 program package[49] at the Computational Center of the N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences.

Results and Discussion

Six possible pathways of decomposition of compound **1** revealed upon generation of thermolysis pathways (Scheme 1) are as follows: radical elimination of the nitro group (pathway *I*), homolytic cleavage of bonds in the heterocycle (N—N, pathway *II*, and C—N, pathways *III* and *IV*), nitro-nitrite rearrangement (pathway *V*), and 1,5-sigmatropic shift of the nitro group with the formation of 5-nitro-1,2,4-triazole (**2c**) (pathway *VI*).

Scheme 1



The results of calculations of the geometric parameters and bond orders according to Wiberg for compound **1** are shown in Fig. 1. It follows that the introduction of the nitro group at the ring nitrogen atom causes the delocalization in the ring to weaken to some extent due to the partial interaction of the lone electron pair of the N(1) atom with the nitro group. The exocyclic bond N(1)—N(6) is longer than that in conventional nitramines;[50] its calculated length is in good agreement with the data obtained by X-ray analysis (1.445 Å).[51] Analysis of the bond orders shows that this bond is weaker than the transannular bonds N—N. This favors cleavage of the N(1)—N(6) bond, which is accompanied by either elimination or migration of the nitro group to the other nucleophilic center, namely, the neighboring carbon atom in compound **1**. The transannular bonds C(3)—N(4) and C(5)—N(1), which are dissociated in the initial stage of the decomposition of compound **1** (see Scheme 1), are characterized by lower orders compared to the noncleaved bonds C(3)—N(2) and C(5)—N(4).

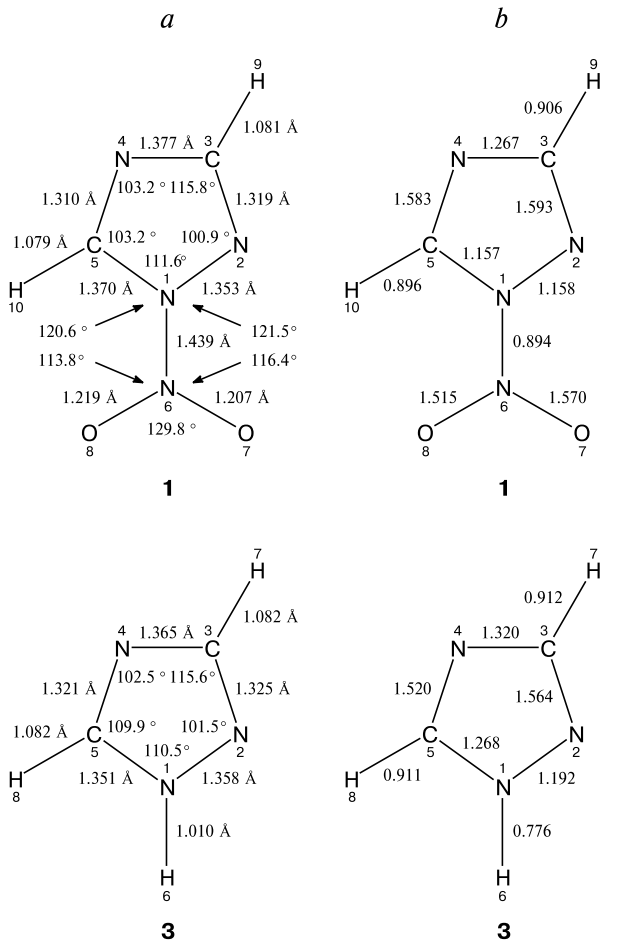
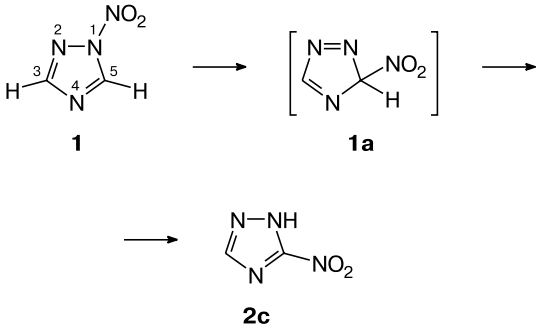


Fig. 1. Geometric parameters of molecules (*a*) and bond orders according to Wiberg (*b*) for 1-nitro-1,2,4-triazole (**1**) and unsubstituted 1,2,4-triazole (**3**).

Activation energy calculations for the reactions occurring in the initial stage of decomposition of compound **1** showed that the energy expenditure for radical elimination of the nitro group (see Scheme 1, pathway *I*) is 39.4 kcal mol^{-1} and the energies of the N(1)—N(2) (pathway *II*), C(5)—N(1) (pathway *III*), and C(3)—N(4) (pathway *IV*) ring bond rupture processes are 62.2, 84.6, and 71.1 kcal mol^{-1}, respectively. We failed to locate the

transition state of nitro-nitrite rearrangement (pathway *V*), but according to published data[1] for *N*-nitro derivatives, this rearrangement is thermochemically less favorable than homolytic elimination of the nitro group. The rearrangement **1** → **2c** (pathway *VI*)[7,12] involves two stages (Scheme 2).

Scheme 2



1 **1a** **2c**

The initial stage represents a sigmatropic shift of the nitro group with the formation of intermediate **1a**. According to calculations, the geometric parameters of planar initial molecule **1** are strongly changed in transition state **TS1** (Fig. 2), namely, the nitro group is above the plane of the heterocycle, the N—NO_2 bond is stretched to 2.054 Å, and the distance between the nitrogen atom of the nitro group and the carbon atom C(5) is shortened to 2.154 Å (*cf.* 1.439 and 4.748 Å, respectively, for compound **1**). In **TS1**, the H—C(5) bond length remains almost unchanged compared to the corresponding bond in compound **1** (1.083 *vs.* 1.079 Å, respectively). The C(5)—N(1)—NO_2 bond angle decreases from 127.0° (**1**) to 74.0° (**TS1**). The calculated activation energy for this process is 31.8 kcal mol^{-1}. Experimental data on the energies E_a of thermal rearrangements of *N*-nitro-1,2,4-triazoles to *C*-nitro isomers are unavailable. The activation energies for a similar process in pyrazole derivatives lie between 30 and 36 kcal mol^{-1} depending on the substituents.[52] Migration of the nitro group results in an intermediate product (**1a**), which, by analogy with the pyrazole nitro derivatives,[52] undergoes a rapid re-aromatization to a thermodynamically more stable compound **2c** with a release of an energy of 30.9 kcal mol^{-1}. The calculated activation energy for hypothetical proton shift to the N(1) nitrogen atom occuring *via* the transition state **TS2** (see Fig. 2) is 29.7 kcal mol^{-1}. The H(10)—C(5) bond in **TS2** elongates to 1.289 Å and the distance between the hydrogen atom and the N(1) nitrogen atom is shortened to 1.317 Å. The C(5)—NO_2 bond length in **TS2** is 1.480 Å. Thus, the activation barrier to proton transfer from the C(5) carbon atom to the N(1) nitrogen atom is 1.9 kcal mol^{-1} lower than the energy expenditure for the sigmatropic shift of the nitro group from the N(1) to the C(5) atom. The C(5)—NO_2 bond length in the final product **2c** is 1.449 Å, which is in agreement with the X-ray analysis data[53] for 3-nitro-1.2.4-triazole (**2**)). In molecule **2c**, the nitro group and the heterocycle lie in the same plane, which favors conjugation between them and stabilization of the whole system. The geometric parameters of the initial compound (**1**), intermediate (**1a**), final product (**2c**), and transition states **TS1** and **TS2** are shown in Fig. 2.

The activation energy calculations suggest that sigmatropic shift of the nitro group (E_a = 31.8 kcal mol^{-1}, pathway *VI*) is 7.6 kcal mol^{-1} energetically more favorable than homolytic elimination of this species (E_a = 39.4 kcal mol^{-1}). This is consistent with the data[13] on thermolysis of compound **1** in benzonitrile, where the *C*-nitro product **2c** was isolated in more than 50% yield. At the same time, NO_2 radical elimination (pathway *I*) should be considered as a competing reaction. This is indicated by the experimental detection[13] of unsubstituted 1,2,4-triazole (**3**) among the thermolysis products of compound **1**.

The propagation of further transformations of the intermediates generated in the course of the decomposition of compound **1** following pathways *I* and *VI* was studied in more detail. Scheme 3 presents the generated chains of intermediates and possible routes of their transformations in the course of thermolysis of compound **1** following pathway *I*.

One of the primary decomposition products (see Schemes 1 and 3) is 1,2,4-triazole (**3**), which can undergo further decomposition. Earlier,[37] a simple scheme of concerted decomposition of compound **3** was proposed (Scheme 4).

Comparison of Schemes 3 and 4 suggests that our modeling makes it possible to obtain a complete picture of processes occurring in the course of decomposition.

It should be noted that theoretically 1,2,4-triazole can exist as a mixture of two tautomers (**3a** and **3b**) that can be in equilibrium (Scheme 5).

According to calculations, tautomer **3a** is 6.3 kcal mol^{-1} energetically more stable than **3b**. Simulation of the thermal decomposition pathways of compound **3a** (see Scheme 3) revealed three possible pathways involving dissociation of the C(3)—N(4), C(5)—N(1), and N(1)—N(2) bonds. Calculations of the geometric parameters and electronic characteristics of 1,2,4-triazole (see Fig. 1) show that the broken bonds C(3)—N(4) and C(5)—N(1) are 0.026—0.044 Å longer than the C(5)—N(4) and C(3)—N(2) bonds retained in this stage of thermal decomposition and have lower bond orders according to Wiberg. The bond dissociation energies of C(3)—N(4) and C(5)—N(1) are 84.7 and 102.5 kcal mol^{-1}, respectively. The homolytic bond dissociation energy of N(1)—N(2) is the lowest, being equal to 71.0 kcal mol^{-1}; this is the most thermochemically

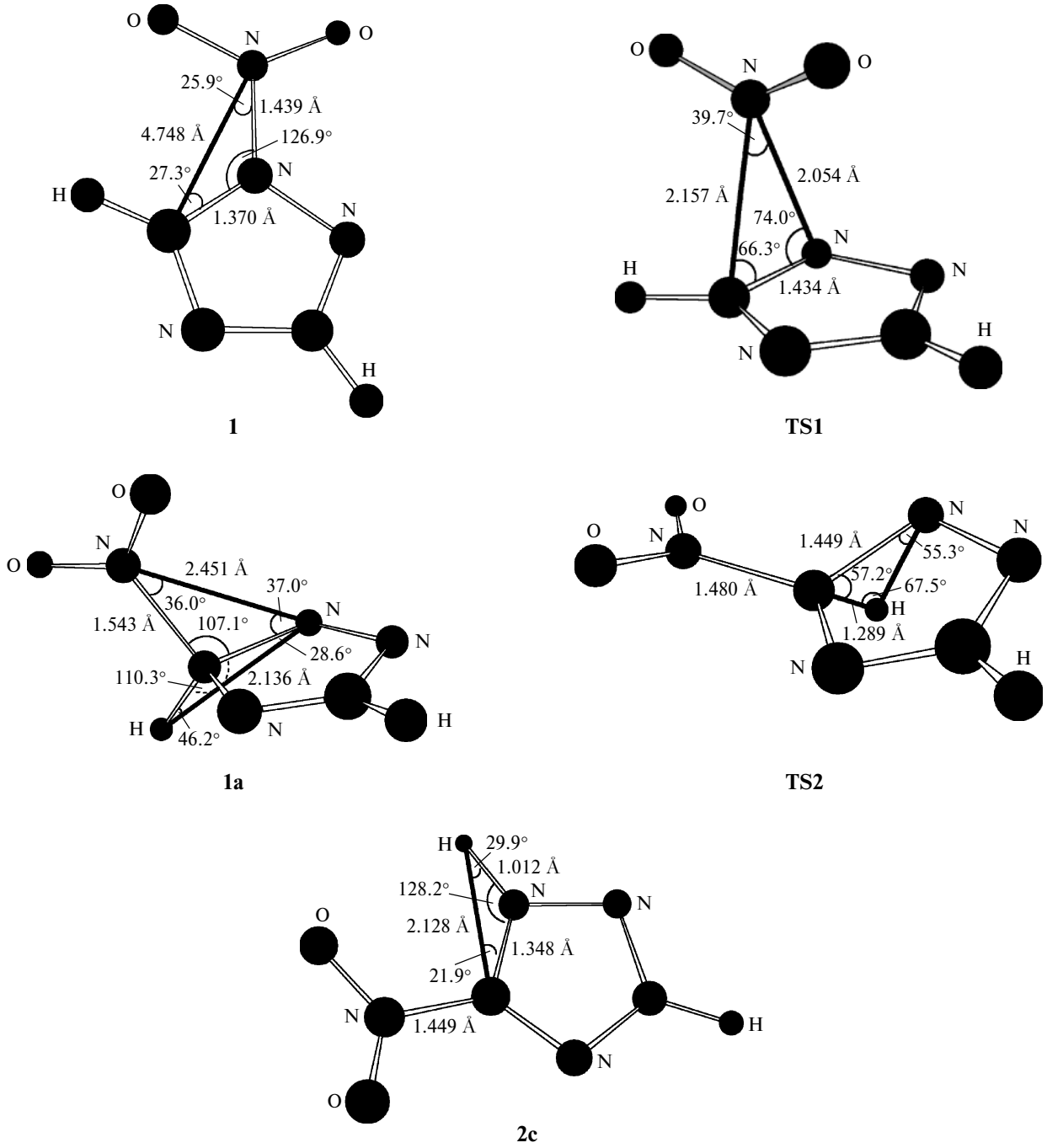


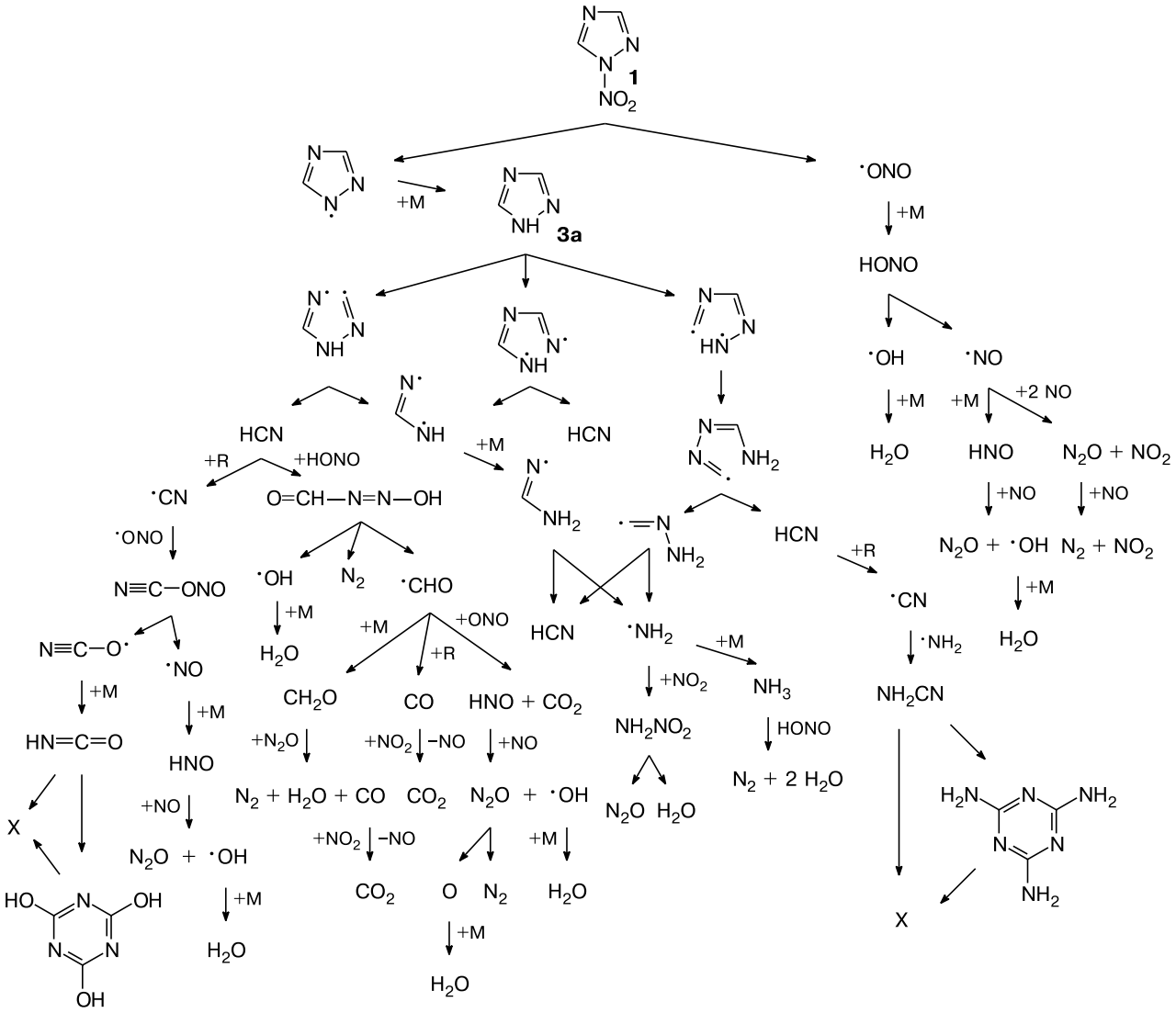
Fig. 2. Structures and selected geometric parameters of molecules **1**, **1a**, **2c**, and transition states **TS1** and **TS2**.

preferable step of the decomposition of compound **3a**. Note that all pathways of the decomposition of compound **3a** lead to the same final products, namely, N_2, N_2O, NO, H_2O, CO_2, HCN, HNCO, as well as cyanamide, cyanuric acid, and melamine. Modeling of the decomposition of tautomer **3b** also gave an identical set of final products. The ratio of these components in the resulting mixture of products is determined by the decomposition pathways of the compound.

As mentioned above, thermal rearrangement of compound **1** involves the formation of its regioisomer **2** (see Scheme 1, pathway *VI*), which can exist in several tautomeric forms (Scheme 6).

From the ^1H, ^{13}C, and ^{15}N NMR data (see Ref. 54) and analysis of the dipole moments[55,56] of 3(5)-nitro-1,2,4-triazoles unsubstituted at nitrogen atom it follows that in solution the hydrogen atom is localized at the ring nitrogen atom that is distal relative to the nitro group.

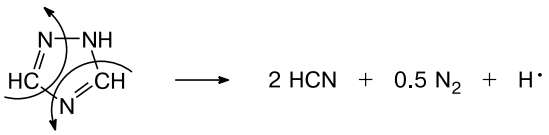
Scheme 3



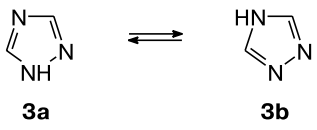
X is condensed residue

From this point on M denotes a molecule and R denotes a radical.

Scheme 4



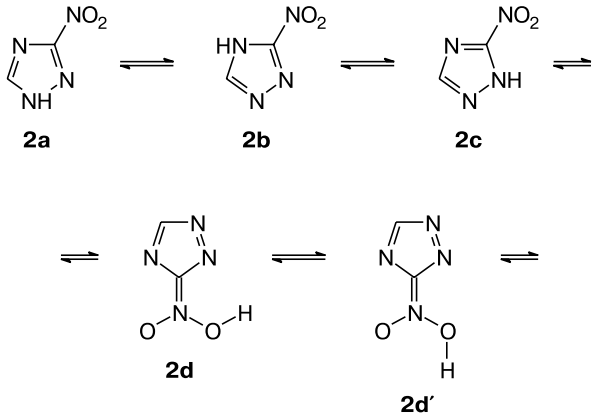
Scheme 5



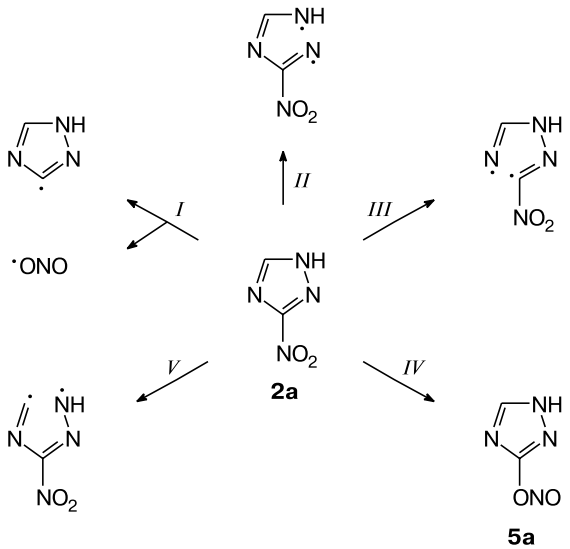
This corresponds to tautomer **2a**. The presence of a certain tautomer of compound **2** will be determined by particular conditions. Since heating can cause interconversion of tautomers, we simulated thermolysis of all tautomers **2a—2e**. The tautomerization energies of nitro-1,2,4-triazoles were determined by analogy with the calculations for nitro-1,2,3-triazoles.[57] The calculations revealed the highest stability of tautomer **2c** (Table 2).

Now we will consider the results of simulation of the thermolysis pathways of the tautomers. Scheme 7 illustrates the initial stage of the decomposition of 1*H*-3-nitro-1,2,4-triazole (**2a**).

Scheme 6



Scheme 7



Scheme 8 describes the initial stage of thermal decomposition of 4*H*-3-nitro-1,2,4-triazole (**2b**).

Scheme 9 corresponds to the initial stage of decomposition of 1*H*-5-nitro-1,2,4-triazole (**2c**).

Scheme 10 presents the results obtained by simulating the initial stage of decomposition of 3-*aci*-nitro-1,2,4-triazole (**2d**).

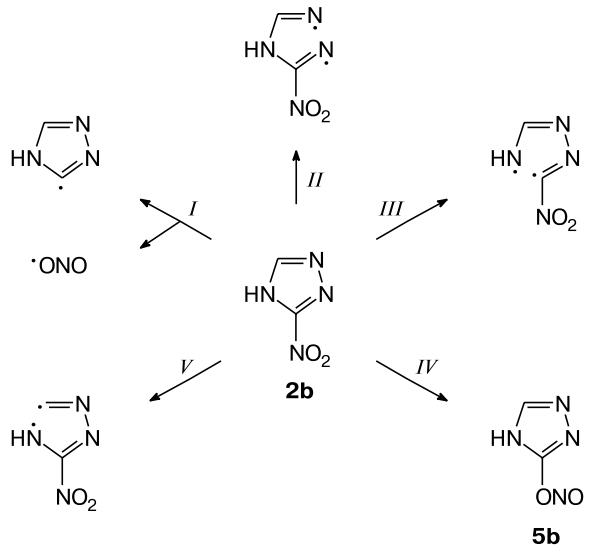
Scheme 11 corresponds to the initial stage of the decomposition of 3-*aci-nitro*-1,2,4-triazole (**2e**).

Table 2. Energy characteristics of tautomers **2a—e**

Compound	$-(E + ZPE)$ /au	Energy of tautomerization of **2c*** to corresponding tautomer /kcal mol^{-1}
2a	446.67369	0.8
2b	446.66551	5.9
2c	446.67490	0.0
2d	446.63714	22.9
2d′	446.63057	27.8
2e	446.63636	24.2
2e′	446.63048	27.9

* Calculated using the expression $[(E + ZPE)_x - (E + ZPE)_y] \cdot 627.5$ kcal mol^{-1} (see Ref. 57), where ZPE is the zero-point vibrational energy correction, x denotes tautomer **2c**, and y stands for all other tautomers.

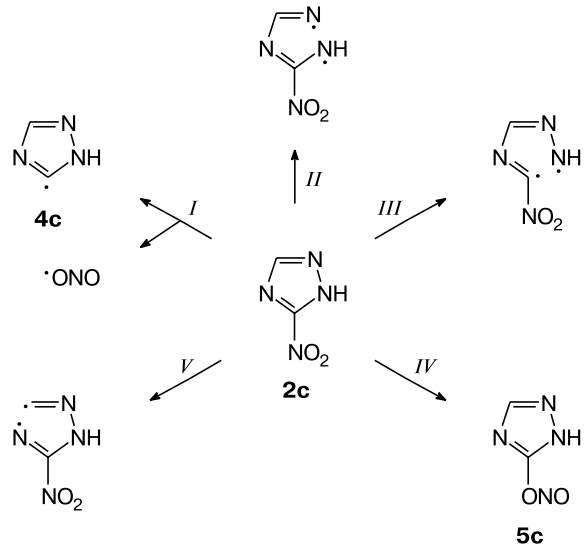
Scheme 8



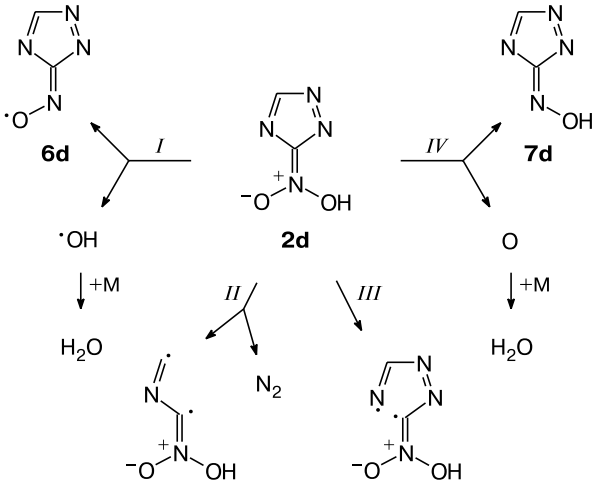
Our simulation revealed five decomposition pathways of tautomers **2a—c**, namely, homolytic elimination of the nitro group (pathway *I*), cleavage of the N—N bond in the heterocycle (pathway *II*), cleavage of the C—N bonds (pathways *III* and *V*), and the nitro-nitrite rearrangement (pathway *IV*). The probable pathways of thermal decomposition of the thermodynamically less stable tautomers (**2d,e**) include homolytic elimination of the hydroxyl radical (pathway *I*), opening of the 1,2,4-triazole ring with release of nitrogen (pathway *II*), cleavage of C—N bond (pathway *III*), and elimination of oxygen from the *aci*-nitro fragment (pathway *IV*). The results of calculations of the geometric and electronic parameters of the tautomers of compound **2** are shown in Fig. 3 and listed in Table 3.

The ring bonds C(3)—N(4) and C(5)—N(1) in molecule **2a**, C(3)—N(4) and C(5)—N(4) in molecule **2b**,

Scheme 9

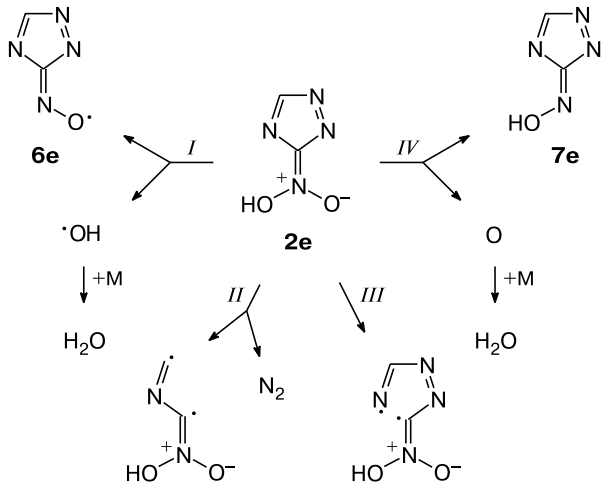


Scheme 10



and C(3)—N(2) and C(5)—N(4) in molecule **2c**, which are cleaved in the thermolysis of compounds **2a—c** (see Schemes 7—11), are 0.01—0.06 Å longer than the non-dissociating ring bonds C—N (see Fig. 3) and their orders are 0.14—0.42 lower than those of the ring bonds. At the same time the N(1)—N(2) bonds in tautomers **2d,e** are on the average 0.05 Å shorter than the corresponding bonds in tautomers **2a—c**, their orders being 0.337 higher. The adjacent bonds, C(3)—N(2) and C(5)—N(1), in compounds **2d,e** are longer than the other C—N bonds in the ring. The exocyclic bonds C(3)—N(6) in molecules **2d,e** are on the average 0.09 Å shorter and the orders of these bonds are 0.266 higher compared to the corresponding bonds in tautomers **2a—c**. The N—O bonds in compounds **2d,e** are different, namely, the N—O(H) bond is on the

Scheme 11



average 0.17 Å longer than the N→O bond. Therefore, the order of the former bond is 0.56 lower. Tautomers **2d** and **2e** are energetically more favorable than compounds **2d´** and **2e´** due to the formation of a hydrogen bond (this was confirmed by analysis of the electron density distribution in the framework of the "Atoms in molecules" theory[58]). Tautomers **2a—e** have a planar molecular structure. Comparison of the geometric parameters and bond orders according to Wiberg in the simulation of thermolysis pathways of tautomers **2a—e** indicates preferableness of the dissociation of the longest same-type bonds characterized by lower bond orders. From the data in Table 3 it follows that the energy gap between the frontier orbitals successively decreases in the order **2a** > **2b** > **2c** > > **2d,e** > **2d´—e´**.

The results of activation energy calculations for the reactions occurring in the initial stage of thermolysis of tautomers **2a—e** are listed in Table 4. Pathway *IV* is the thermochemically most favorable for the decomposition of compounds **2a—c** (*cf.* pathway *I* for compounds **2d—2e´**). Comparison of the data listed in Tables 3 and 4 suggests

Table 3. Electronic characteristics of molecules tautomers **2a—e**

Compound	Ionization potential	Δ*
	eV	
2a	10.301	9.068
2b	10.297	9.041
2c	10.275	9.017
2d	10.279	9.006
2d´	10.265	8.993
2e	10.275	8.995
2e´	10.265	8.994

* Energy gap between the frontier orbitals.

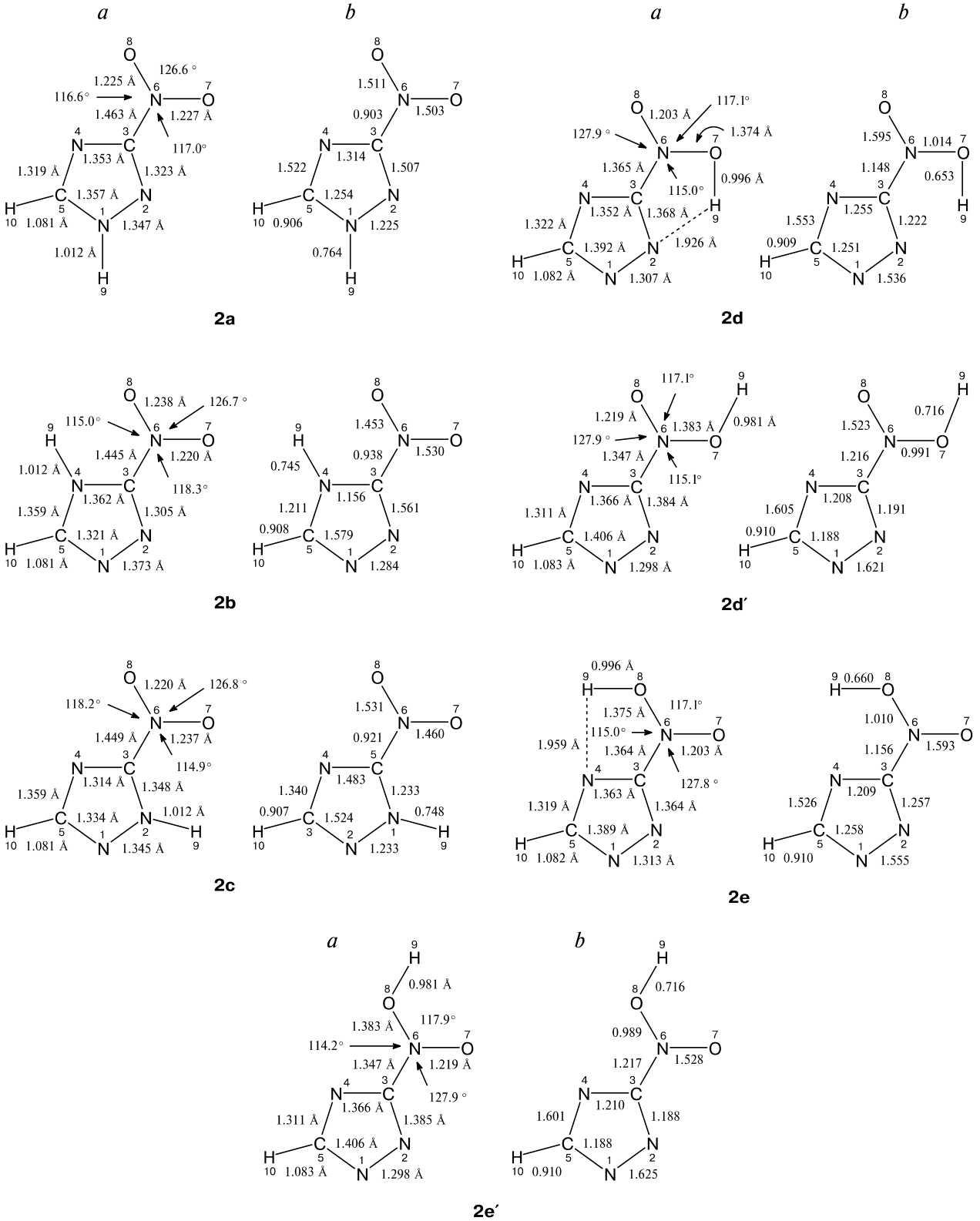


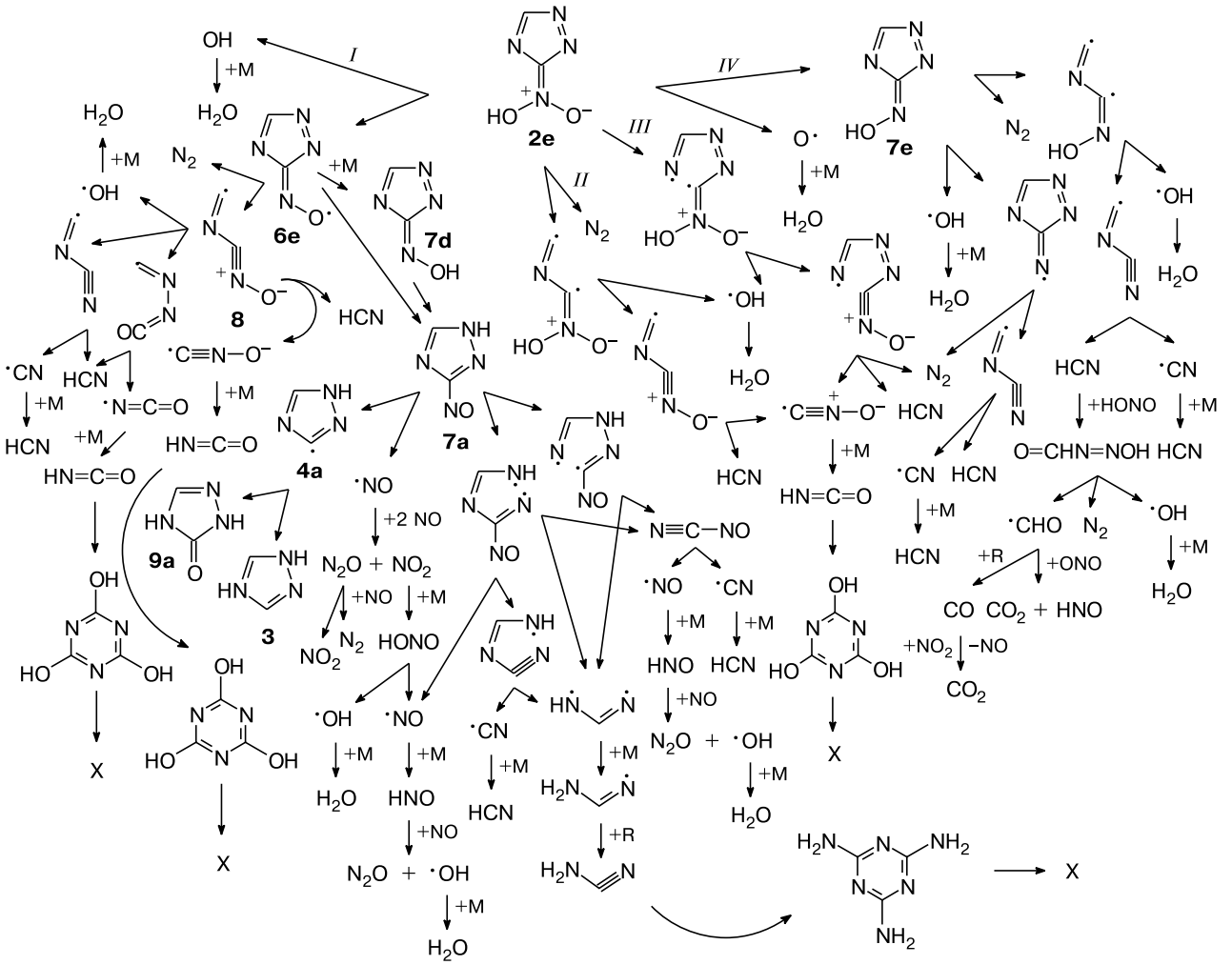
Fig. 3. Geometric parameters of molecules (*a*) and bond orders according to Wiberg (*b*) for tautomers **2a—e**.

a correlation between the energy gap width (energy difference between the frontier orbitals) and the stability of the *C*-nitro-1,2,4-triazole tautomers to thermal decomposition. From the results presented in Table 4 it also follows that tautomers **2d´** and **2e´** are the thermochemically least stable under the thermolysis conditions. For these compounds, homolytic dissociation of the N—O bond (pathway *I*) accompanied by elimination of the hydroxyl radical (48.2 and 46.4 kcal mol^{-1} for **2d´** and **2e´**, respectively) is most favorable in the initial stage. Dissociation of the N→O bond (pathway *IV*) with elimination of the oxygen atom (75.0 and 73.3 kcal mol^{-1} for **2d´** and **2e´**, respectively) is much less favorable. The energy expenditure for the decomposition of tautomers **2d´** and **2e´** following pathway *II* (see Scheme 11, Table 4) is slightly higher than that needed for the decomposition of these compounds following pathway *I*; pathway *III* is the thermochemically least favorable. The experimentally determined activation energy for the initial stage of thermal decomposition of 3-nitro-1,2,4-triazole in the solid phase (including a pre-melting stage) is 38.28 kcal mol^{-1} at 180—200 °C,[20] which is the closest value to the energy expenditure for homolytic elimination of the hydroxyl radical (pathway *I*). Similar values were also obtained for the other two *C*-nitrotriazoles unsubstituted at the nitrogen atom, namely, 38.97 kcal mol^{-1} (bis(3-nitro-1,2,4-

Table 4. Activation energies (E_a) for reactions occurring in the initial stage of the decomposition of tautomers **2a—e**

Thermolysis pathway	E_a/kcal mol^{-1}						
	2a	**2b**	**2c**	**2d**	**2d´**	**2e**	**2e´**
I	67.2	68.2	67.4	51.5	48.2	50.2	46.4
II	71.3	66.7	67.8	59.7	55.4	59.2	55.4
III	105.6	90.4	93.3	95.4	91.1	94.9	91.0
IV	65.2	63.5	60.1	78.0	75.0	75.9	73.7
V	98.0	89.6	104.7	—	—	—	—

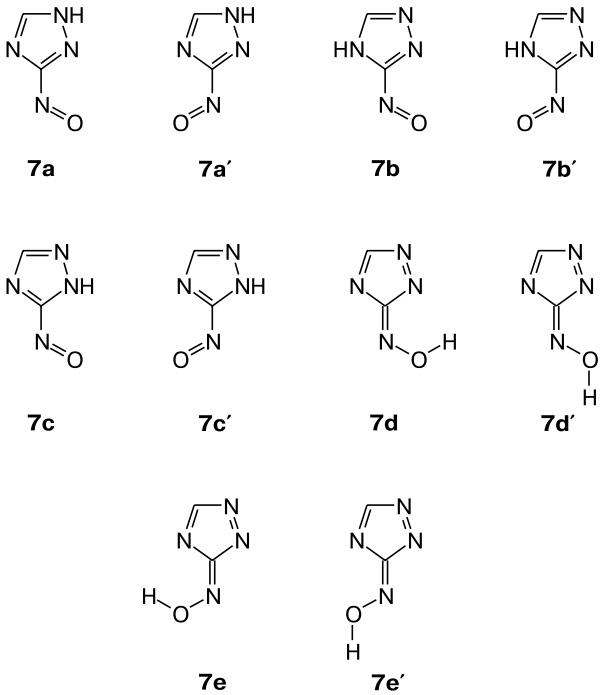
Scheme 12



triazol-5-yl))[20] and 39.57 kcal mol^{-1} (bis(3-nitro-1,2,4-triazol-5-yl)methane).[20] This is much lower than the activation barriers to radical elimination of the nitro group or to the nitro-nitrite rearrangement. At the same time the activation energy for the gas-phase decomposition of 3-nitro-1-ethyl-1,2,4-triazole (here, formation of the *aci*-nitro tautomeric form involving migration of the NH proton is impossible) is 65.06 kcal mol^{-1}.[19] This is characteristic of aromatic nitro compounds whose thermal decomposition begins with dissociation of the C—NO_2 bond (see Ref. 1). Therefore, the assumption of the possibility of existence of energetically less favorable tautomers **2d** and **2e** among the intermediate products of thermolysis seems to be true.

Scheme 12 presents a possible mechanism of deep decomposition of 3-*aci*-nitro-1,2,4-triazole (**2e**), which was obtained using the expert rules developed; it illustrates the generated chains of intermediates and probable sequences of their transformations.

The energetically most favorable pathway of thermolysis of tautomers **2d,e**, which is accompanied by elimination of the OH group (pathway *I*), leads to the corresponding nitroxyl radicals **6d,e** (see Schemes 10—12). Here, further transformations can follow three pathways (see Scheme 12), namely, the formation of nitroso-1,2,4-triazoles **7a—c** (see below), formation of 3-hydroxyimino-1,2,4-triazoles **7d,e**, and decomposition with elimination of nitrogen molecule and formation of the oxynitrile radical **8**.

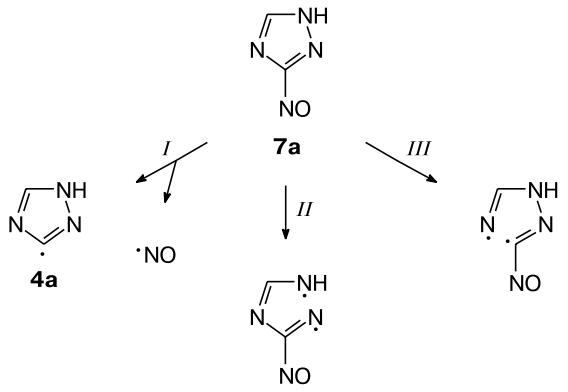


According to the published data,[20] the mass spectrum of the decomposition products of *C*-nitro-1,2,4-triazole (**2**) exhibits a peak of a fragment ion with $m/z = 98$ corresponding to radical cation **7**. Our calculations showed that the formation of corresponding nitroso derivatives is thermochemically most favorable. For instance, the formation of compound **7a** upon attack of the nitroxyl radical **6e** on the HNO_2 molecule is accompanied by energy release ($E_a = -10.6$ kcal mol^{-1}). The formation of the hydroxyimino derivative **7d** from the same nitroxyl radical (**6e**) requires absorption of an energy of 0.7 kcal mol^{-1} and the energy expenditure for this process is 11.3 kcal mol^{-1} lower than that for the former process. Decomposition of the nitroxyl radical **6e** (see Scheme 12) with elimination of nitrogen molecule is even less favorable ($E_a = 17.1$ kcal mol^{-1}).

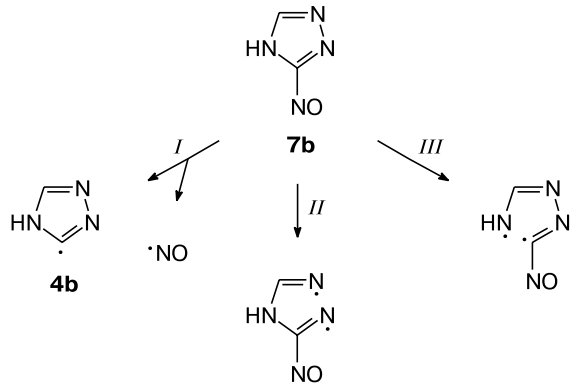
In order to obtain a complete picture of the mechanisms of thermal decomposition of the intermediate **7** and to assess the thermochemical preferableness or particular decomposition pathways, we generated the thermolysis pathways of compounds **7a—e** (Schemes 13—17).

The decomposition of each of the isomers **7a—c** can follow three pathways. These are the homolytic elimination of the nitroso group (pathway *I*), cleavage of the N—N bond in the heterocycle (pathway *II*), and cleavage

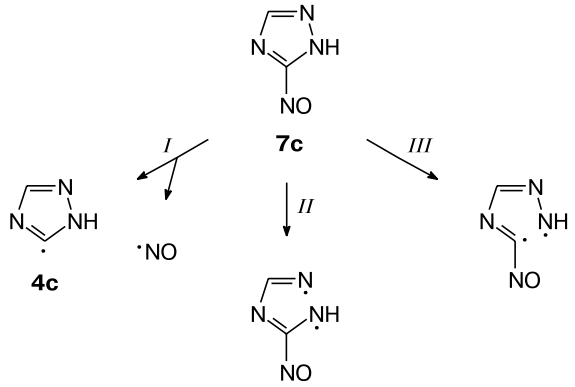
Scheme 13



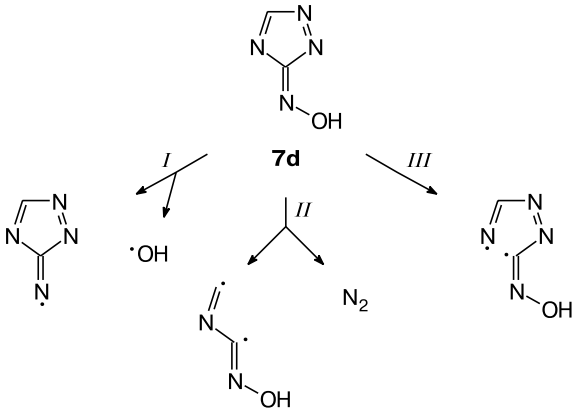
Scheme 14



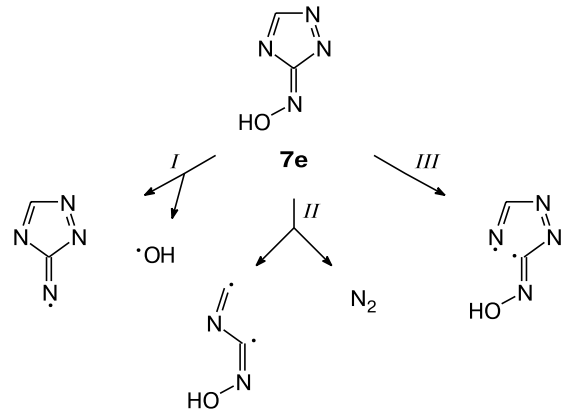
Scheme 15



Scheme 16



Scheme 17



of the ring bond C—N (pathway *III*). Possible decomposition pathways of oximes **7d,e** (see Schemes 16 and 17) include elimination of the hydroxyl radical (pathway *I*), opening of the heterocycle with elimination of the nitrogen molecule (pathway *II*), and opening of the 1,2,4-triazole ring due to the cleavage of one C—N bond (pathway *III*).

Table 5. Activation energies (E_a) for reactions occurring in the initial stage of the decomposition of intermediates **7**

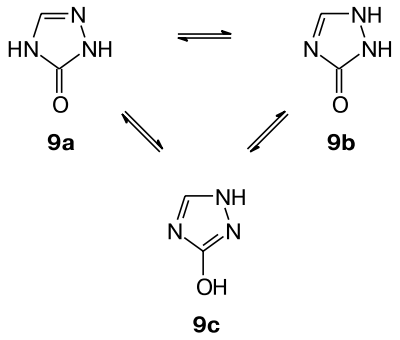
Compound	Pathway			Compound	Pathway		
	I	*II*	*III*		*I*	*II*	*III*
7a	53.6	—*	70.3	**7c´**	54.1	70.6	65.1
7a´	54.7	—*	71.5	**7d**	67.2	39.1	73.0
7b	54.6	64.0	58.9	**7d´**	65.8	37.7	66.9
7b´	57.8	67.2	62.1	**7e**	68.7	40.7	75.6
7c	55.6	72.3	66.6	**7e´**	67.1	39.0	68.2

* We failed to calculate the E_a value for the decomposition of compounds **7a** and **7a´** following pathway *II*.

The results of the activation energy calculations for the reactions occurring in the initial stage of thermolysis of compounds **7a—e** are listed in Table 5. Energetically, the decomposition of hydroxyimines **7d,e** with opening of the triazole ring (pathway *II*) and elimination of nitrogen is the most preferable; this requires an energy expenditure of 37.7—40.7 kcal mol^{-1}. Thermolysis following this pathway results in N_2, N_2O, NO, CO_2, HCN, HNCO, H_2O, and cyanuric acid as the final products. Elimination of the hydroxyl radical (pathway *I*) and cleavage of the C—N bond in the ring (pathway *III*) in compounds **7d,e** is less favorable compared to pathway *II* (by 28.1 and 29.2—33.9 kcal mol^{-1}, respectively). In the nitroso derivatives **7a—c** (their formation is thermochemically preferable compared to hydroxyimines **7d,e**), homolytic elimination of NO is accompanied by absorption of 53.6—57.8 kcal mol^{-1}, which is 15.9—17.1 kcal mol^{-1} larger than in the decomposition of compounds **7d,e** following pathway *II*. The energy expenditure for cleavage of the ring bonds N—N (pathway *II*) and C—N (pathway *III*) in the intermediates **7a—c** is respectively 9.4—16.7 and 4.3—16.7 kcal mol^{-1} larger than for the decomposition following pathway *I*. Radical **4** that is formed in the thermolysis of triazole can either undergo a transformation to unsubstituted 1,2,4-triazole (**3**) with a release of 44.8 kcal mol^{-1} (with M = HONO, see Scheme 12) which then decomposes (see Scheme 3) or recombine with the hydroxyl radical (−116.8 kcal mol^{-1}) to give a tautomeric mixture of 1,2,4-triazolones (**9a,b**) and 3-hydroxy-1,2,4-triazole (**9c**) (Scheme 18).

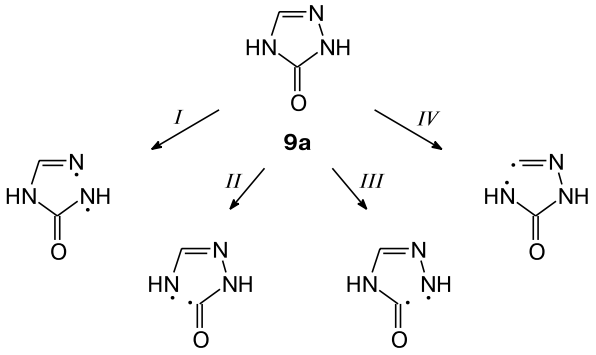
Tautomer **9a** is the most thermodynamically stable. According to our calculations, the energies of its tautomerization to **9b** and **9c** are 15.5 and 11.2 kcal mol^{-1}, respectively. The possibility of formation of triazolone **9a** in thermolysis of 3(5)-nitro-1,2,4-triazole (**2**) was considered earlier.[17] Indeed, a mass spectrometric study[20] of decomposition products of compound **2** revealed a peak with m/z = 86 corresponding to compound **9** which can

Scheme 18



undergo further transformations accompanied by cleavage of the N—N and C—N bonds in the heterocycle (Scheme 19).

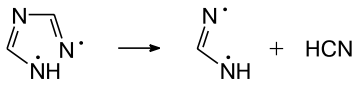
Scheme 19



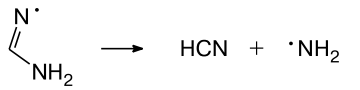
The energy expenditure for cleavage of the bonds shown in Scheme 19 is 70.5 (pathway *I*), 79.5 (pathway *II*), 81.2 (pathway *III*), and 106.3 kcal mol^{-1} (pathway *IV*). Thus, the decomposition following pathway *I* is the thermochemically most favorable. A complete pattern of the decomposition of 1,2,4-triazolone following pathway *I* is shown in Scheme 20, which illustrates the chains of intermediates and possible sequences of their transformations, which accompany the deep decomposition of 1,2,4-triazolone **9a**.

From Scheme 20 it follows that the final products of the decomposition of 1,2,4-triazolone include N_2, N_2O, NO, CO_2, HCN, HNCO, H_2O, cyanamide, cyanuric acid, and melamine, *i.e.*, the same products as those formed in the decomposition of 1,2,4-triazole **3**.

In order to substantiate the efficiency of the methodology proposed, we calculated the enthalpies of all the reactions generated assuming thermal decomposition of 3-*aci*-nitro-1,2,4-triazole (**2e**) to the final products. The results obtained show that the final products of thermolysis of compound **2e** following the predicted decomposition pathways are formed in thermochemically favorable processes. Below we present a number of reactions that can occur in the course of thermal decomposition of 3(5)-nitro-1,2,4-triazole (**2**) and list their enthalpies (ΔH_f°/kcal mol^{-1}).


(9.8)


(−17.9)


(25.4)

$H_2N^{\bullet} + {}^{\bullet}NO_2 \longrightarrow H_2N{-}NO_2$ (−48.9)

$H_2N{-}NO_2 \longrightarrow N_2O + H_2O$ (−27.1)

${}^{\bullet}NH_2 + HONO \longrightarrow NH_3 + {}^{\bullet}ONO$ (−30.4)

$NH_3 + HONO \longrightarrow N_2 + 2\,H_2O$ (−64.5)

$HCN + HONO \longrightarrow O{=}CH{-}N{=}N{-}OH$ (−19.6)

$O{=}CH{-}N{=}N{-}OH \longrightarrow {}^{\bullet}CHO + N_2 + {}^{\bullet}OH$ (27.8)

${}^{\bullet}CHO + {}^{\bullet}NO_2 \longrightarrow CO_2 + HNO$ (−78.2)

$HNO + {}^{\bullet}NO \longrightarrow N_2O + {}^{\bullet}OH$ (−17.3)

${}^{\bullet}OH + HONO \longrightarrow H_2O + {}^{\bullet}NO_2$ (−38.2)

$2\,N_2O \longrightarrow O_2 + 2\,N_2$ (−31.6)

$O + 2\,HONO \longrightarrow H_2O + 2\,ONO^{\bullet}$ (−64.8)

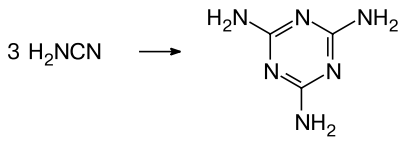
$HCN + {}^{\bullet}OH \longrightarrow {}^{\bullet}CN + H_2O$ (16.9)

${}^{\bullet}CN + {}^{\bullet}NO_2 \longrightarrow N{\equiv}C{-}ONO$ (−79.7)

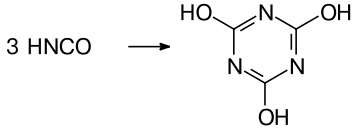
$N{\equiv}C{-}ONO \longrightarrow N{\equiv}C{-}O^{\bullet} + {}^{\bullet}NO$ (13.9)

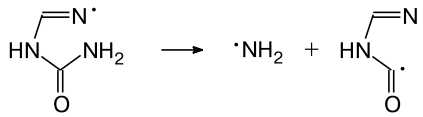
${}^{\bullet}NO + HONO \longrightarrow HNO + {}^{\bullet}ONO$ —

${}^{\bullet}CN + {}^{\bullet}NH_2 \longrightarrow H_2N{-}CN$ (−118.0)

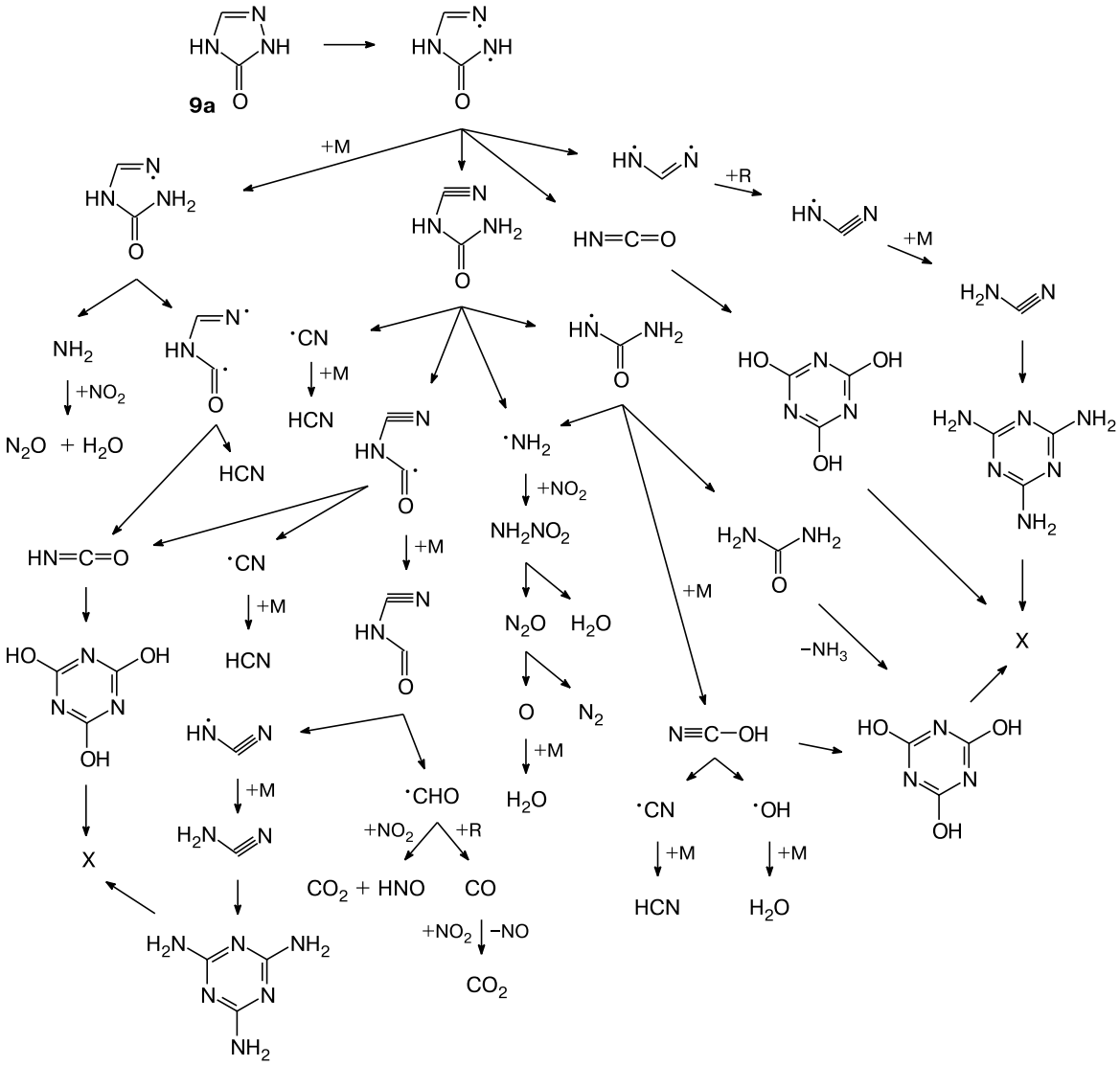

(−89.0)

$N{\equiv}C{-}O^{\bullet} + H_2O \longrightarrow HNCO + {}^{\bullet}OH$ (4.8)

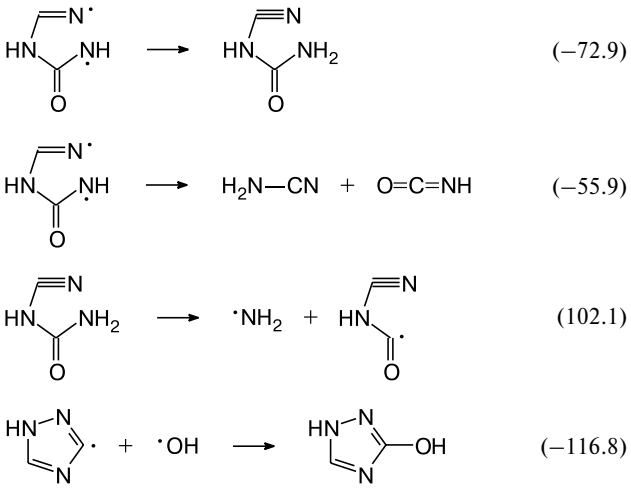

(−18.6)

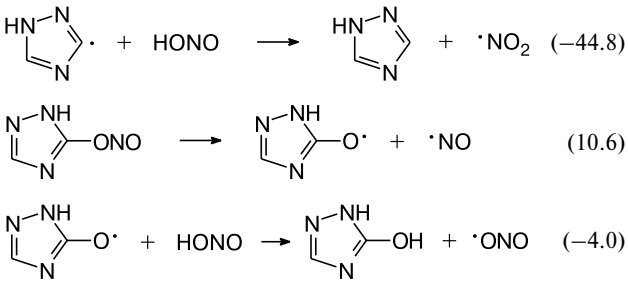

(99.4)

Scheme 20



X is a condensed residue





According to published data,[17] thermal decomposition of 3(5)-nitro-1,2,4-triazole (**2**) can theoretically be accompanied by the nitro-nitrite rearrangement (pathway *IV*, see Schemes 7—9). We calculated the geometric parameters and energy of hypothetical transition state of this process (Fig. 4). Comparison of the geometric pa-

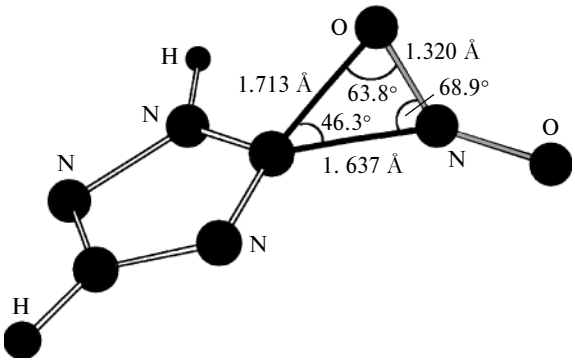


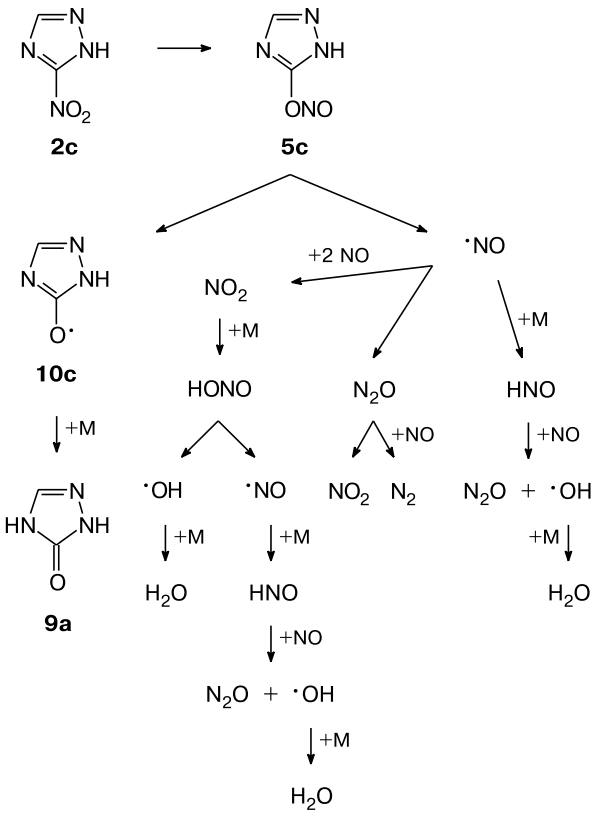
Fig. 4. Transition-state structure for nitro-nitrite rearrangement in **2c**.

rameters of the initial molecule **2c** and the transition state of the nitro-nitrite rearrangement shows elongation of the C—NO_2 bond by 0.188 Å, formation of the new C—O bond 1.713 Å long (*cf.* 2.267 Å in **2c**), and a nearly two-fold decrease in the C—N—O angle. The nitro group is above the triazole ring plane, lying almost orthogonal to it, whereas molecule **2c** has a planar structure.

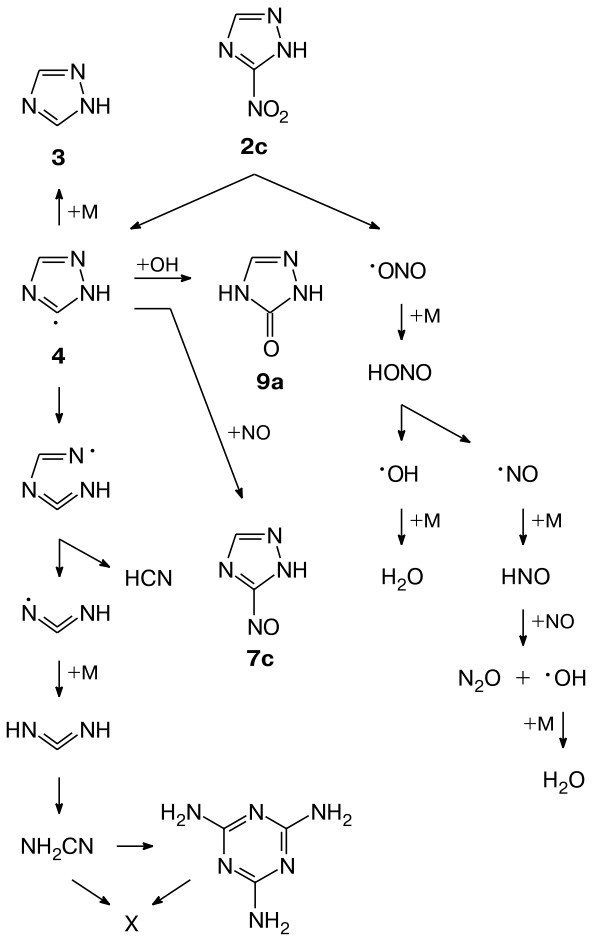
According to calculations, the energy expenditure for the nitro-nitrite rearrangements in compounds **2d,e** is 13.7—18.8 kcal mol^{-1} lower than the energy expenditure for elimination of the hydroxyl group (see Schemes 10 and 11, pathway *I*). Further decomposition of the rearrangement product **5c** to triazolone radical **10c** (Scheme 21) is expected to occur quite easy and be accompanied by absorption of an energy of 10.6 kcal mol^{-1} (see above). Moreover, further transformation of **10c** to 1,2,4-triazolone **9a** is accompanied by energy release (−15.2 kcal mol^{-1}, see above), which indicates an exothermic process. Possible decomposition mechanisms of **9a** are shown above (see Schemes 19 and 20).

However, the nitro-nitrite rearrangement excludes the possibility of formation of the nitroso (**7a—c**) and hydroxyimino (**7d,e**) derivatives of triazole, which were experimentally detected among the decomposition products of 3(5)-nitro-1,2,4-triazole **2**.[20] The energy expenditure for the nitro-nitrite rearrangement (see Schemes 7—9, pathway *IV*) and the activation energies for homolytic elimination of the NO_2 group (see Schemes 7—9, pathway *I*) and cleavage of the ring bond N—N (see Schemes 7—9, pathway *II*) are very similar (see Table 4). Thus, according to the thermochemical data, these three

Scheme 21



Scheme 22



X is a condensed residue

thermolysis pathways of tautomers **2a—c** are almost equiprobable. However, only the decomposition of compounds **2a—c** with radical elimination of the nitro group leads to the same products as those formed in the thermolysis of **2d,e** (N_2, N_2O, NO, CO_2, HCN, HCNO, H_2O, cyanamide, cyanuric acid, melamine, **3**, **7**, and **9**).

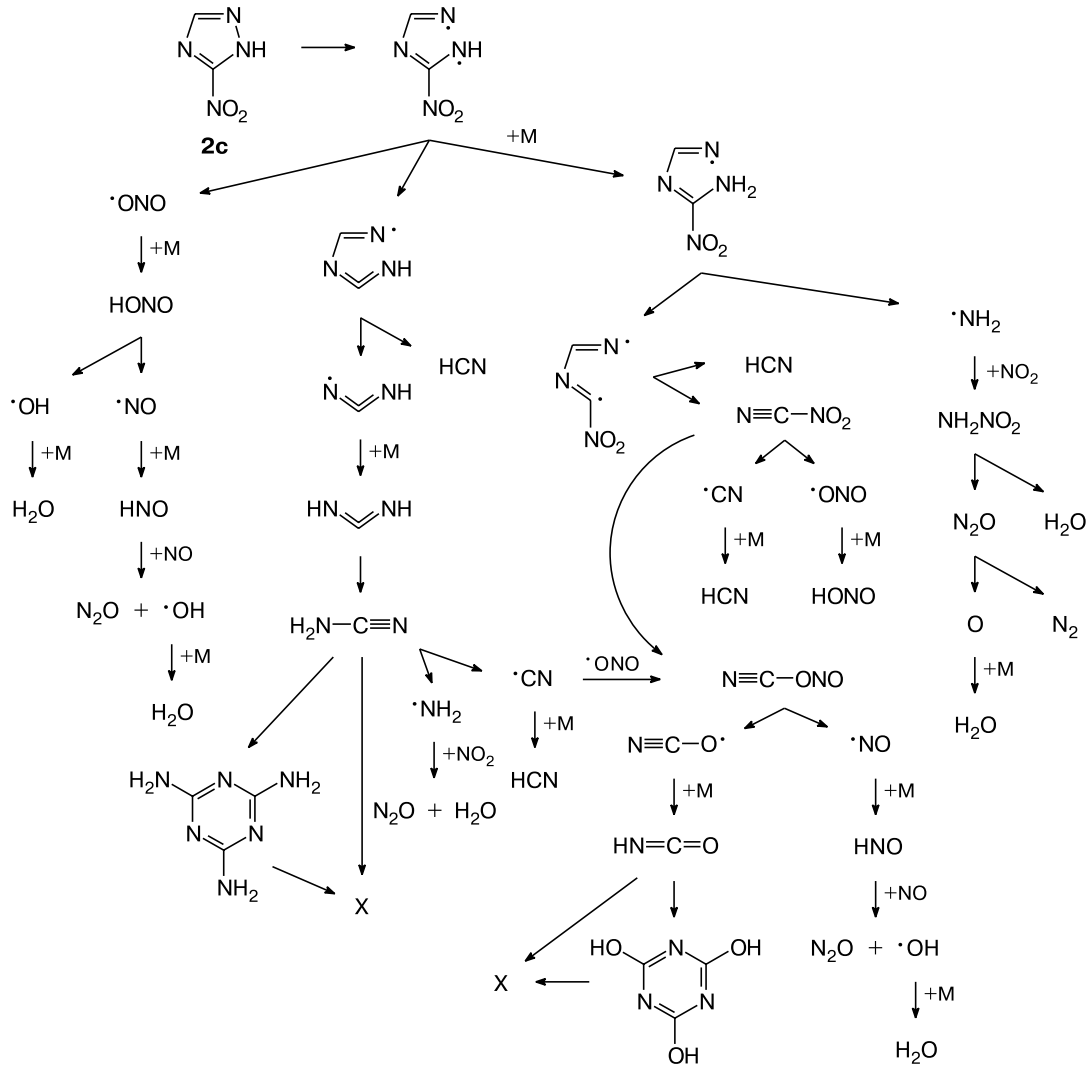
Scheme 22 illustrates a stepwise deep decomposition of compound **2c** following pathway *I*.

Modeling of the mechanism of thermal decomposition of compound **2c** following pathway *II* (Scheme 23), which involves the opening of the triazole ring through cleavage of the N—N bond as the initial stage of thermolysis, provides no explanation for the presence of experimentally detected 1,2,4-triazole derivatives **7** and **9** among the decomposition products.

The energy expenditure for cleavage of the heteroaromatic bonds C—N (see Schemes 7—9, pathways *III* and *V*) in molecules **2a—c** is 21.4—44.6 kcal mol^{-1} higher than the energy expenditure for the corresponding processes following pathways *I*, *II*, and *IV*. Here (Scheme 24, the decomposition of **2c** following pathway *III*), similarly to the decomposition following pathway *II*, the decomposition of the triazole ring in the initial stage rules out the formation of the experimentally detected 1,2,4-triazole derivatives. Therefore, the probability of this decomposition pathway of the compound is low.

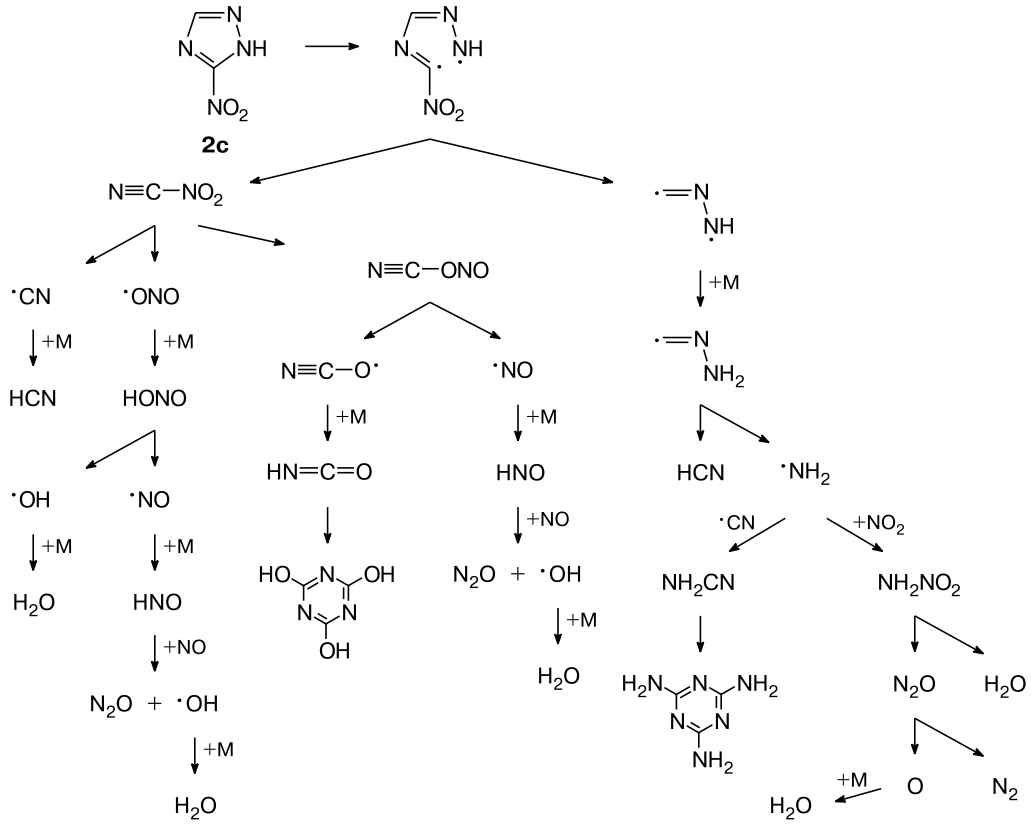
Experimental data on the composition of the condensed residue formed in the thermolysis of nitro-1,2,4-triazoles are unavailable. However, it was reported[59—62] that thermal decomposition of various classes of organic

Scheme 23



X is a condensed residue

Scheme 24



nitrogen compounds is followed by the formation of condensed triazine-type products with similar compositions. It is this feature that gives grounds to suggest the presence of rather complex molecular systems including the triazine and heptazine fragments among the products of thermolysis of nitrotriazoles.[59—64]

Our study made it possible to generate models for the mechanisms of thermal decomposition of nitro-1,2,4-triazoles. These models not only allow possible pathways of the initial stage of decomposition of the compounds to be considered, but also permit obtaining a comprehensive spectrum of deeper transformations of intermediates on the way to the final products of thermolysis.

Our calculations predicted the formation of a number of products (H_2O, CO, NO_2, cyanamide, cyanuric acid, melamine) that were previously not detected but which can be formed during the thermolysis of nitrotriazoles.

Based on the hypotheses of the decomposition mechanisms of nitrotriazoles, we assessed the thermochemical preferableness of the following decomposition pathways of these compounds: a sigmatropic shift of the nitro group with the formation of *C*-nitro-1,2,4-triazole for *N*-nitro-1,2,4-triazole and tautomerization of *C*-nitro-1,2,4-triazole to the *aci*-nitro form followed by removal of the hydroxyl radical.

The results obtained can be used for thermal stability prediction and interpretation of experimental data on the decomposition of nitro-1,2,4-triazoles.

References

1. G. B. Manelis, G. M. Nazin, Yu. I. Rubtsov, and V. A. Strunin, *Termicheskoe razlozhenie i gorenie vzryvchatykh veshchestv i porokhov* [*Thermal Decomposition and Combustion of Explosives and Powders*], Nauka, Moscow, 1996, 223 pp. (in Russian).
2. Yu. Shu, B. L. Korsunskii, and G. M. Nazin, *Usp. Khim.*, 2004, **73**, 320 [*Russ. Chem. Rev.*, 2004, **73** (Engl. Transl.)].
3. G. A. Olah and R. Squire, in *Chemistry of Energetic Materials*, Ed. G. A. Olah, Academic Press, San Diego, 1991, p. 212.
4. P. L. Marinkas, in *Organic Energetic Compounds*, Ed. P. L. Marinkas, Nova Science Publishers, Inc., New York, 1996, p. 425.
5. V. F. Sopin and G. A. Marchenko, *Sovremennye problemy tekhnicheskoi khimii. Materialy dokl. Vseros. nauchno-tekhnicheskoi konf.* [*Modern Problems of Technical Chemistry. Proc. All-Russia Res. and Technol. Conf.*] *(Kazan´, November 21—22, 2003)*, Kazan´, 2003, 40 (in Russian).
6. L. P. Smirnov, *Usp. Khim.*, 2004, **73**, 1210 [*Russ. Chem. Rev.*, 2004, **73** (Engl. Transl.)].
7. M. S. Pevzner, *Ros. Khim. Zh.*, 1997, **41**, 73 [*Mendeleev Chem. J.*, 1997, **41** (Engl. Transl.)].

8. H. H. Licht, H. Ritter, and B. Wanders, *Proc. 25 Intern. Ann. Conf. of ICT (Energetic Materials)*, Karlsruhe (Germany), 1994, 45(1).
9. H. H. Licht, S. Braun, M. Wanders, and H. Ritter, *Proc. 29 Intern. Ann. Conf. of ICT (Energetic Materials)*, Karlsruhe (Germany), 1998, 47(1).
10. H. H. Licht and H. Ritter, *Propellants, Explosives, Pyrotechnics*, 1997, **22**, 333.
11. US Pat. 5889161; *Chem. Abstr.*, 1999, **130**, 239630.
12. C. L. Habraken and P. Cohen-Fernandez, *Chem. Commun.*, 1972, **2**, 37.
13. M. S. Pevzner, T. N. Kulibabina, S. L. Ioffe, I. A. Maslina, B. V. Gidaspov, and V. A. Tartakovsky, *Khim. Geterotsikl. Soedin.*, 1979, 550 [*Chem. Heterocycl. Compd.*, 1979 (Engl. Transl.)].
14. M. S. Pevzner, T. N. Kulibabina, N. A. Povarova, and L. V. Kilina, *Khim. Geterotsikl. Soedin.*, 1979, 1132 [*Chem. Heterocycl. Compd.*, 1979 (Engl. Transl.)].
15. A. M. Astakhov, V. A. Revenko, and E. S. Buka, *Sovremennye problemy tekhnicheskoi khimii. Materialy dokl. Vseros. nauchno-tekhnicheskoi konf.* [*Modern Problems of Technical Chemistry. Proc. All-Russia Res. and Technol. Conf.*] *(Kazan´, November 21—22, 2003)*, Kazan´, 2003, 209 (in Russian).
16. A. M. Astachov, V. A. Revenko, and E. S. Buka, *Proc. Seventh Seminar "New Trends in Research of Energetic Materials"*, Pardubice (the Czech Republic), 2004, 424.
17. J. C. Oxley, J. L. Smith, Z. L. Zhou, and R. L. McKenney, *J. Phys. Chem.*, 1995, **99**, 10383.
18. R. S. Stepanov, L. A. Kruglyakova, and M. A. Stepanova, *Tez. dokl. mezhinstitutskogo kollokviuma "Khimiya azotistykh geterotsiklov"* [*Abstrs Inter-Institute Colloq. "Chemistry of Nitrous Heterocycles"*], Chernogolovka, 1995, 38 (in Russian).
19. R. S. Stepanov and L. A. Kruglyakova, *Kinet. Katal.*, 1996, **37**, 339 [*Kinet. Catal.*, 1996, **37** (Engl. Transl.)].
20. R. S. Stepanov, L. A. Kruglyakova, and M. A. Stepanova, *Zh. Obshch. Khim.*, 1997, **67**, 324 [*Russ. J. Gen. Chem.*, 1997, **67** (Engl. Transl.)].
21. A. K. Sikder, M. Geetha, D. B. Sarwade, and J. P. Agrawal, *J. Hazardous Materials*, 2001, **A82**, 1.
22. R. S. Stepanov, L. A. Kruglyakova, O. A. Golubtsova, and A. M. Astakhov, *Khim. Geterotsikl. Soedin.*, 2003, 699 [*Chem. Heterocycl. Compd.*, 2003 (Engl. Transl.)].
23. Wai-Leung Yim and Zhi-Feng Liu, *J. Am. Chem. Soc.*, 2001, **123**, 2243.
24. A. A. Porollo, D. E. Lushnikov, T. S. Pivina, and V. P. Ivshin, *J. Mol. Struc. (THEOCHEM)*, 1997, **391**, 117.
25. A. A. Porollo, D. E. Lushnikov, T. S. Pivina, V. P. Ivshin, and N. S. Zefirov, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 1869 [*Russ. Chem. Bull.*, 1999, **48**, 1845 (Engl. Transl.)].
26. A. A. Porollo, T. V. Petukhova, V. P. Ivshin, T. S. Pivina, and D. E. Lushnikov, *Proc. "Energetic Materials" of the 30th Intern. Ann. Conf. of ICT*, Karlsruhe (Germany), 1999, 15(1).
27. T. S. Pivina, A. A. Porollo, T. V. Petukhova, and V. P. Ivshin, *Proc. 26th Intern. Pyrotechnics Seminar*, Nanjing (China), 1999, 438.
28. T. S. Pivina, A. A. Porollo, T. V. Petukhova, and V. P. Ivshin, *Proc. 5th Intern. Symp. on Special Topics in Chemical Propulsion (5-ISICP)*, Stresa (Italy), 2000, 343.
29. A. A. Porollo, T. V. Petukhova, V. P. Ivshin, T. S. Pivina, and E. A. Smolenskii, *Tez. dokl. 2-j Vseros. konf. "Molekulyarnoe modelirovanie"* [*Abstrs 2nd All-Russia Conf. "Molecular Modeling"*], Moscow, 2001, 94 (in Russian).
30. A. Porollo, T. Petukhova, V. Ivshin, T. Pivina, B. Korsunskii, and O. Golovanov, *Proc. 32nd Intern. Ann. Conf. of ICT*, Karlsruhe (Germany), 2001, 87(1).
31. T. V. Petukhova, A. A. Porollo, V. L. Korolev, V. P. Ivshin, Y. N. Surikova, and T. S. Pivina, *Proc. 33rd Intern. Ann. Conf. of ICT*, Karlsruhe (Germany), 2002, 60(1).
32. G. M. Khrapkovskii, G. N. Marchenko, and A. G. Shamov, *Vliyanie molekulyarnoi struktury na kineticheskie parametry monomolekulyarnogo raspada S- i O- nitrosoedinenii* [*Effect of Molecular Structure on Kinetic Parameters of Monomolecular Decomposition*], FEN, Kazan´, 1997 (in Russian).
33. E. V. Sokerina, D. E. Lushnikov, T. S. Pivina, A. A. Porollo, and V. P. Ivshin, *Proc. 21st Intern. Pyrotechnics Seminar*, Moscow, 1995, 849.
34. A. A. Porollo, Ph.D. (Chem.) Thesis, Mari State University, Yoshkar-Ola, 1999, 135 pp. (in Russian).
35. D. C. Nonhebel and J. Walton, *Free-Radical Chemistry; Structure and Mechanism*, University Press, Cambridge, 1974.
36. A. L. Fridman, V. P. Ivshin, and S. S. Novikov, *Usp. Khim.*, 1969, **38**, 1448 [*Russ. Chem. Rev.*, 1969, **38** (Engl. Transl.)].
37. A. M. Astakhov, Ph.D. (Chem.) Thesis, Sibirskii State Technological University, Krasnoyarsk, 1999, 118 pp. (in Russian).
38. J. C. Oxlye, M. Hiskey, D. Naud, and R. Szekeres, *J. Phys. Chem.*, 1992, **96**, 2505.
39. J. March, *Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*, J. Wiley and Sons, New York, 1985.
40. A. N. Nesmeyanov and N. A. Nesmeyanov, *Nachala organicheskoi khimii* [*The Foundations of Organic Chemistry*], Khimiya, Moscow, 1977, **1**, 624 pp. (in Russian).
41. E. N. Zil´berman, *Reaktsii nitrilov* [*Reactions of Nitriles*], Khimiya, Moscow, 1972, 445 pp. (in Russian).
42. T. Brill, *Mat. Res. Soc. Symp. Proc.*, 1993, **296**, 269.
43. T. Brill, *J. Propulsion and Power*, 1995, **11**, 740.
44. V. I. Avdeev, S. F. Ruzankin, and G. M. Zhidomirov, *Kinet. Katal.*, 2005, **46**, 191 [*Kinet. Catal.*, 2005, **46** (Engl. Transl.)].
45. *Fiziko-khimicheskie i teplofizicheskie svoistva rastvorov na osnove chetyrekhokisi azota* [*Physicochemical and Thermal-Physical Properties of Solutions Based on Nitrogen Tetroxide*], Ed. V. B. Nesterenko, Nauka i Tekhnika, Minsk, 1981, 303 pp. (in Russian).
46. W. Koch and M. C. Holthausen, *A Chemists´s Guide to Density Functional Theory*, Wiley-VCH, Weinheim, 2001, 300 p.
47. T. Clark, *A Handbook of Computational Chemistry*, J. Wiley and Sons, New York, 1985.
48. E. V. Nikolaeva, Ph.D. (Chem.) Thesis, Kazan´ State Technological University, Kazan´, 2002, 203 pp. (in Russian).
49. M. J. Frish, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komazomi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara,

M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzales, M. Head-Gordon, E. S. Replogle, and J. A. Pople, *GAUSSIAN 98. Revision A.9*, Gaussian, Inc., Pittsburgh (PA), 1998.
50. *Cambridge Structural Database, Version 5.26*, November, 2004.
51. B. D. T. Cromer, K.-Y. Lee, and R. R. Ryan, *Acta Crystallogr.*, 1988, **C44**, 1673.
52. J. Janssen, C. L. Habraken, and R. Louw, *J. Org. Chem.*, 1976, **41**, 1758; M. I. Kanishchev, N. V. Korneeva, S. A. Shevelev, and A. A. Fainzil´berg, *Khim. Geterotsikl. Soedin.*, 1988, 435 [*Chem. Heterocycl. Compd.*, 1988 (Engl. Transl.)].
53. G. Evrard, F. Durant, A. Michel, J. G. Fripiat, J. L. Closset, and A. Copin, *Bull. Soc. Chim. Belg.*, 1984, **93**, 233.
54. H. H. Licht, H. Ritter, H. R. Bircher, and P. Bigler, *Magn. Reson. Chem.*, 1998, **36**, 343.
55. M. S. Pevzner, E. Ya. Fedorova, I. N. Shokhor, and L. I. Bagal, *Khim. Geterotsikl. Soedin.*, 1971, 275 [*Chem. Heterocycl. Compd.*, 1971 (Engl. Transl.)].
56. M. S. Pevzner and R. E. Trifonov, *Zh. Org. Khim.*, 1998, **34**, 784 [*Russ. J. Org. Chem.*, 1998, **34**, 748 (Engl. Transl.)].
57. P. Politzer, M. E. Grice, and J. M. Seminario, *J. Quantum Chem.*, 1997, **61**, 389.
58. R. F. W. Bader, *Atoms in Molecules. A Quantum Theory*, Clarendron Press, Oxford, 1990.
59. A. Gao, A. L. Reingold, and T. B. Brill, *Propellants, Explosives, Pyrotechnics*, 1991, **16**, 97.
60. A. Gao, Y. Oyumi, and T. V. Brill, *Comb. and Flame*, 1991, **83**, 345.
61. T. V. Brill, *Prog. Energy Combast. Sci.*, 1992, **18**, 91.
62. T. V. Brill and H. Ramanathan, *Comb. and Flame*, 2000, **122**, 165.
63. V. M. Karlik, V. I. Zagranichnyi, and L. N. Al´tshuler, *Khimicheskaya promyshlennost´* [*Chem. Industry*], 1981, **8**, 16 (464) (in Russian).
64. A. I. Finkel´shtein and N. V. Spiridonova, *Usp. Khim.*, 1964, **33**, 900 [*Russ. Chem. Rev.*, 1964, **33** (Engl. Transl.)].

Received December 19, 2005;
in revised form August 9, 2006