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Differentiation of the molecular structures of nitro compounds as the basis for simulation of their thermal destruction processes †

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Abstract. Data on the experimental and theoretical studies of thermal decomposition of *C*- and *N*-nitro derivatives of aliphatic, alicyclic, aromatic and heteroaromatic compounds, which served as the basis for the development of an *ab initio* appoach to the prediction of the mechanisms of thermolysis of energetic compounds, are described systematically. The relationships between the structures and thermolysis mechanisms of compounds based on differentiation of the structural fragments depending on the functional surrounding of nitro groups are identified. Using the RRN (Recombination Reaction Network) strategy and original CASB (Computer Assisted Structure Building) software, full reaction mechanisms for the thermal destruction of nitro compounds at different thermal decomposition levels (including extensive ones) are simulated. The full set of possible mechanisms of thermal decomposition of 38 nitro compounds of different classes is presented. The bibliography includes 201 references.

I. Introduction

The prospects of application of the high energy materials (HEM) are determined by the set of their explosive and service characteristics.[1–3] Ideally, case all characteristics of HEM materials should meet certain requirements. However, in reality the enhancement of some parameters is often accompanied by the deterioration of the others. For example, the increase in the explosive yield of compounds, as a rule, goes in parallel with the increase in mechanical sensitivity and decrease in chemical and thermal stabilities, *i.e.*, their safety level decreases.[4–10] Currently known HEM do not fully meet the criteria of entailed applications. Specifically, researchers have to pay special attention to safety requirements while designing new and more effective HEM.[11–23]

Of the most advanced directions of the design of promising HEM is the prediction of their properties prior to the synthesis,[24–32] which enables reduction of time and costs for their creation.

One of the most important applied characteristics of HEM, primarily explosives, is thermal stability associated with the peculiarities in mechanism of thermolysis for a given compound.[33–36] The elucidation of the mechanisms of thermal decomposition of explosives allows estimating their stability, while the prediction of the stability of hypothetical structures points to the expedience of their synthesis.

The goal of the present review is not to show the retrospective of numerous investigations into the thermolysis mechanism of HEM as they are rather fully represented in Russian and foreign literature.[33,37–59] Our task was to attract attention of the specialists to the paradoxical aspect of these publications, *viz.*, to the predominantly intuitive approaches to suggesting the mechanisms of thermal decomposition of HEM.

Experienced researchers are certainly aware of the hypothetical mechanisms of a particular reaction that may occur in the thermolysis of HEM. It is for this reason that the kinetic characteristics of the thermal decomposition of compounds were often related to the mechanism suggested by the investigator reckoning on his knowledge on the

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thermolysis mechanism for analogous compounds, so they were adjusted to the known schemes, voluntarily or not. Here emerged the contradictions in the interpretation of the experimental results and as a consequence the differences in the putative mechanisms of the decomposition of the same compounds. In addition, the results obtained were interpreted without consideration of other (unobvious at first glance) transformation processes, which led to additional errors.

This review is to address contradictions and to develop an *ab initio* approach for the computer simulation of the thermal destruction of HEM.

The thermal decomposition of nitro compounds, which are, as a rule, polyfunctional compounds and can decompose through different conversion pathways,[33, 35, 37–41, 60, 61] is a complicated multi-step process. In practice, however, studies of the thermal decomposition are limited to the construction of simple hypothetical schemes of the process to embrace the identified products, and/or to the investigation of the first step of thermolysis. The simulation of the full mechanisms of the thermolysis of HEM in different steps of destruction is currently a complicated problem that is difficult to formalize.

The process of the elucidation of the thermal decomposition mechanism of chemical compounds comprises two main stages:

1) construction of putative schemes of chemical transformations,

2) estimation of thermodynamic and kinetic parameters in each step.

At present, considerable progress is achieved in the second stage.[29, 30, 33, 34, 40, 47–50, 54, 55, 58] The developed methodologies and existing software enable the estimation of thermodynamic and kinetic parameters of the reactions. As far as the first stage is concerned, the theoretical approaches to the generation of hypotheses on the possible mechanisms of the decomposition of high energy materials are totally absent until now, which makes topical the investigations carried out by the authors of the present review. One of our key goals was to formalize the thermolysis mechanisms based on the revealed structure–activity relationships.

We have created a database on the thermal decomposition mechanisms for a wide range of nitro compounds in different aggregate states. For this purpose, we have considered experimental data derived from the studies of *C*- and *N*-nitro derivatives of aliphatic, alicyclic, aromatic and heteroaromatic compounds carried out with manometric, gravimetric, calorimetric methods,[35] using the method of freezing of chemical reactions in shock tubes,[62–64] and with some others. The analysis of these data allowed us to formulate the relationships between the chemical structures and mechanisms of their thermolysis.

Based on differentiation (classification) that we suggested of structural fragments depending on the features of the functional surrounding of the nitro group, the formalization of such relationships was carried out. Then, the methodology of computer-assisted generation of a complete array of possible reactions that occur in the thermal decomposition of the nitro compounds at different stages of their destruction could be derived. Such an approach of generating a hypothesis excludes the intuitive nature of the prediction of the thermolysis mechanism.[27, 60, 65–93] The hypotheses on the mechanisms of thermolysis of a particular compound were formed based solely on its structural formula regardless of its phase state. We intended to limit the number of the generated hypotheses by subsequent estimation of the most probable decomposition using the available experimental data and calculation results considering the phase state.

In the choice of the hypotheses, along with the experimental data, we used the calculation methods for the estimation of the energetic preference of the possible decomposition pathways, which were determined using the results of the activation energy calculation (E_a) of the gas-phase thermolysis reaction. The necessary calculations were performed with the density functional theory (DFT) using the hybrid potential B3LYP[94–96] and the standard valence-split basis set 6-31G* (Ref. 97) implemented in GAUSSIAN 98 (Ref. 98) at the Centre of Computer Assistance in Chemical Research of the N D Zelinsky Institute of Organic Chemistry, RAS. The calculation results of the main characteristics for a series of compounds using 6-31G** and 6-311++G** basis sets were rather close to those obtained for 6-31G* basis set. This allowed us to confine ourselves to the latter basis set, which requires substantially lesser computation time. It should be noted that the B3LYP/6-31G* method produces the values for the activation energy of the unimolecular decomposition of nitro compounds quite close to the experimental activation energies for the gas-phase decomposition (the difference does not exceed 2.4 kcal mol^{-1}, which is comparable with the experimental error).[42] Molecules with heavy atoms were calculated using the LANL2DZ basis set. For the biradical structures, we considered triplet spin states, while of all possible biradical conformers, we chose the most thermodynamically stable ones.

In the estimation of the activation barriers of the radical decomposition reactions, we proceeded from an assumption[33, 40, 99, 100] that in the case of the radical mechanism of decomposition the activation energy of thermolysis virtually coincides with the energy (D) of the R–A bond cleavage.

$$E_a = D(\mathrm{R-A}) + RT,$$

$$D(\mathrm{R-A}) = \Delta H^\circ_{\mathrm{R}} + \Delta H^\circ_{\mathrm{A}} - \Delta H^\circ_{\mathrm{R-A}},$$

where $\Delta H^\circ_{\mathrm{R}}$, $\Delta H^\circ_{\mathrm{A}}$ and $\Delta H^\circ_{\mathrm{R-A}}$ are the enthalpies of the formation of reaction products and initial state, respectively, R is the universal gas constant, T is temperature. Thus, the absence of a barrier to the recombination of the radicals formed upon bond cleavage was assumed.

In contrast to the reactions that follow the radical mechanism, one cannot estimate the activation energies for the molecular reactions from the enthalpies of the initial state and the product[101] due to the necessity of the determination of the transition state structure and its energy. In such cases, the activation energy was calculated as the difference between the energy of the transition state and the energies of the reactants. The positions of all the stationary points were determined by the analysis of the Hessian matrices from the absence of pseudo-frequencies. The structures of the transition states were confirmed by the calculations of the inner reaction coordinate.

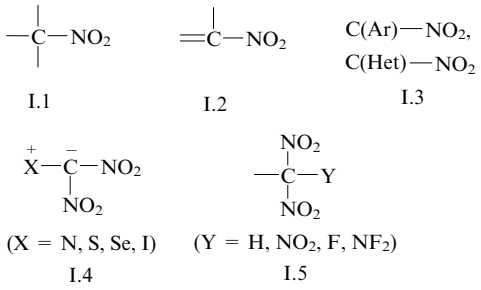
The high energy materials can be obtained starting from compounds of different chemical classes.[1, 3, 11–19, 25, 26, 102, 103] The nitro group is an explosophoric group most often used for the design of such

compounds.[1, 3, 11–19, 25, 26, 102–105] This is why it is very important to reveal relationships between the mechanisms of decomposition of nitro compounds and the features of the functional surroundings of the nitro groups in the structures of these compounds.

II. The differentiation of the molecular structures of nitro compounds

1. *C*-Nitro compounds

The *C*-nitro compounds we investigated can be divided into several groups depending on the nature of the fragment the nitro group is attached to.



I.1 I.2 I.3

(X = N, S, Se, I) I.4

(Y = H, NO_2, F, NF_2) I.5

Group I.1 contains compounds with one nitro group at the sp^3 hybridized carbon atom;

group I.2 includes compounds with one or two nitro groups at the sp^2 hybridized carbon atom, while aromatic and heteroaromatic compounds are included into separate group I.3. Group I.4 includes dinitromethylides, while group I.5 comprises compounds with two or three nitro groups at the sp^3-hybridized carbon atom.

The mechanisms of thermal decomposition of all five types of nitro compounds are presented below.

a. Compounds of group I.1

Three simplest aliphatic nitro derivatives of group I.1, *viz*., nitromethane (**1**), nitroethane (**2**) and fluoronitromethane (**3**) will be considered.

The gas-phase decomposition of nitromethane (**1**) and nitroethane (**2**) was investigated by pyrolysis[106–113] and photolysis[114–117] methods and in shock tubes.[62–64] The experimental conditions included wide ranges of temperatures and pressures. Despite numerous investigations, no unambiguous interpretation of the mechanisms of thermal decomposition of nitroalkanes has been achieved so far. Thus different initial steps of the decomposition processes have been suggested:[37, 38, 118]

for nitromethane (**1**)

$$CH_3NO_2 \longrightarrow {}^{\bullet}CH_3 + {}^{\bullet}ONO, \quad (1)$$

$$CH_3NO_2 \longrightarrow CH_3ONO \longrightarrow CH_3O^{\bullet} + {}^{\bullet}NO, \quad (2)$$

$$CH_3NO_2 \longrightarrow CH_3ONO \longrightarrow CH_2O + HNO; \quad (3)$$

for nitroethane (**2**)[37, 38, 118]

$$C_2H_5NO_2 \longrightarrow {}^{\bullet}C_2H_5 + {}^{\bullet}ONO, \quad (4)$$

$$C_2H_5NO_2 \longrightarrow C_2H_4 + HNO_2. \quad (5)$$

For example, Crawforth and Waddington[119] reported high methane yield and large amount of nitrogen dioxide formed in the first step of pyrolysis of nitromethane (**1**). This suggests the decomposition of nitromethane by cleavage of the C–N bond [reaction (1)]. Study of the emission from the CH_3NO_2–Ar system at temperatures up to 2300 °C showed[62] that the radical $^{\bullet}ONO$ had a very short lifetime and reacted presumably according to the following equation:

$$^{\bullet}CH_3 + {}^{\bullet}ONO \longrightarrow CH_3O^{\bullet} + {}^{\bullet}NO. \quad (6)$$

Thus, the main role in the thermal decomposition of compound **1** is played by the C–N bond cleavage reaction.[33, 37, 38]

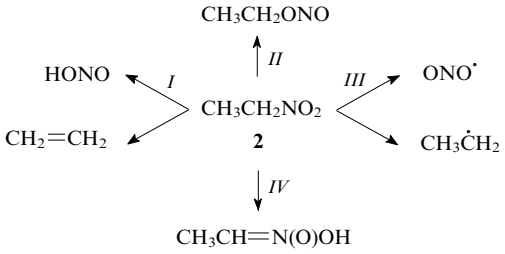
In contrast to nitromethane, in the thermal decomposition of nitroethane (**2**) the elimination of nitrous acid dominates, which leads to the formation of ethylene [reaction (5)]. The theoretical estimation[43, 120] of the value of the activation barrier to the elimination reaction of HNO_2 from nitroethane performed by the DFT/B3LYP/6-31G* method gave 45.3 kcal mol^{-1}. This is in very good agreement with the experimental value[37] for the energy required for the first step of the decomposition of nitroethane (45.0 kcal mol^{-1} at 320–380 °C). At temperatures above 450 °C, the decomposition mechanism for compound **2** changes so that the homolytic cleavage of the C–NO_2 bond occurs, which, according to the experimental data,[33] has the activation energy of 55.6 kcal mol^{-1}. Note that according to our calculations (DFT/B3LYP/6-31G*), the activation energy of the decomposition reaction of nitroethane *via* this pathway is equal to 56.4 kcal mol^{-1}. The prevalence of the decomposition of compound **2** through the dissociation of the C–NO_2 bond at high temperatures is explained by a higher value of the pre-exponential factor in the Arrhenius equation for this reaction [$\log A = 15.90$ (s^{-1})] compared with the elimination reactions of nitrous acid [$\log A = 12.24$ (s^{-1})].[33]

In various investigations, the intramolecular nitro–nitrite rearrangement was often regarded as a possible way of the thermal decomposition of the aliphatic nitro derivatives.[33, 38, 40, 42, 43, 121] Thus in the investigation of the decomposition of nitromethane (**1**) in a molecular beam[122, 123] under laser heating, the formation of formaldehyde was observed, which may result from the nitro–nitrite rearrangement [see reaction (3)]. However, according to the results of DFT/B3LYP/6-31G* calculations performed for a number of aliphatic nitro derivatives,[42, 43, 121] the activation barrier to the nitro–nitrite rearrangement turned out to be higher than the dissociation energy for the C–NO_2 bond. The latter suggests that this rearrangement cannot noticeably compete with the homolytic dissociation reactions of the nitro group or elimination of nitrous acid.[42, 43, 121] In particular, in the case of decomposition of nitroethane (**2**) the value of the activation barrier to the nitro–nitrite rearrangement is equal to 62.6 kcal mol^{-1}, which is 6.2 kcal mol^{-1} higher than the dissociation energy for the C–NO_2 bond and 17.3 kcal mol^{-1} higher than the activation barrier to elimination of nitrous acid.[43] At present, the only known exception in this series is fluoronitromethane (**3**) for which the activation energy of the nitro–nitrite rearrangement is 3.6 kcal mol^{-1} lower (according to DFT/B3LYP/6-31G* calculations) than the energy of the C–NO_2 bond dissociation.[43]

Possible directions of the first step of thermolysis of nitroethane (**2**) as an example of the group I.1 nitro derivatives are shown in Scheme 1. Depending on the temperature mode, the decomposition can occur both with

the elimination of nitrous acid (decomposition pathway *I* in Scheme 1), and with the homolytic cleavage of the $C-NO_2$ bond (pathway *III*).[33,40] The possibility of the nitro–nitrite rearrangement (pathway *II*) cannot be excluded.[33,40,121] Of note also is that in the gas phase at high pressures as well as in the condensed state the decomposition through the formation of the *aci*-form of a nitro compound (pathway *IV*) is possible.[33]

Scheme 1



The activation barrier that we calculated to the intramolecular isomerization of nitroethane to the *aci*-form with 1,3-sigmatropic proton shift (pathway *IV* in Scheme 1) is equal to 63.8 kcal mol^{-1}. In the gas phase, this is the most energetically unfavourable direction of the decomposition. However, it was stated[33] that the decomposition of compound **2** *via* the *aci*-form is possible both in the gas phase at the elevated pressures and in the condensed state. Under these conditions, the prototropic tautomerism can be regarded as the intermolecular rather than the intramolecular process.[124–127] Using the known calculation procedure,[128] we estimated the tautomerization energy of nitroethane (**2**) into *aci*-form from the difference in the thermodynamic stabilities of the tautomeric forms, this was shown to be equal only to 10.4 kcal mol^{-1}.

One should also take into account that if the barriers to the secondary reactions are significantly higher than those to the initial steps of decomposition the low-barrier reactions can be reversible. In this case, estimation of the energetic parameters of the subsequent steps of decomposition is required for obtaining a correct estimation of the mechanisms of thermal decomposition of a compound.

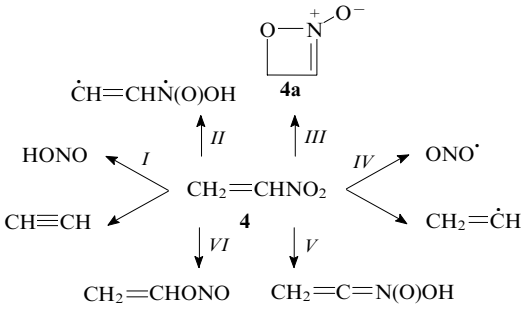
Thus, from the analysis of the experimental and calculated data one can infer that in the general case the possible directions of the initial decomposition of compounds of group I.1 are the homolytic cleavage of the $C-NO_2$ bond, the elimination of nitrous acid, the nitro–nitrite rearrangement and the decomposition *via* the *aci*-form of a nitro compound.

b. Compounds of group I.2

The presence of a nitro group at the double bond in compounds of group I.2 enables an additional (compared with group I.1) decomposition pathway, *viz., via* 1,2-oxazete 2-oxide. Scheme 2 displays the directions of the first step of decomposition of nitroethylene (**4**) as an example.‡

‡ In the present review, the capital letters at the number of a compound indicate the intermediates derived from it, while the small letters denote different isomeric forms of the initial compound (including tautomers and configurational isomers); arrows departing form one point show the destruction products of one molecule.

Scheme 2



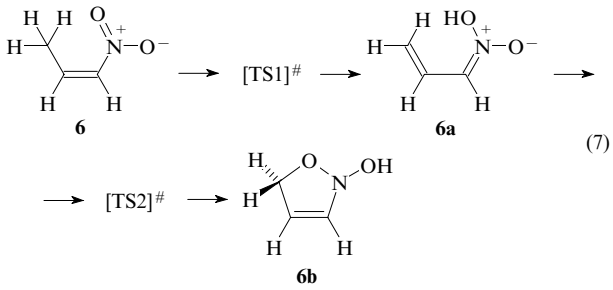
The possibility for the reaction to proceed by pathway *III* with the formation of compound **4a** is based on the experimental data on the thermolysis of nitrostyrene[129] and on theoretical investigations of the decomposition mechanisms of nitroalkanes.[42,43,130] According to DFT/B3LYP/6-31G* calculations,[43,130] the activation barrier to the pyrolysis for the compounds of group I.2 *via* a cyclic transition state is equal to 48.0 kcal mol^{-1} for nitroethylene (**4**) and 44.6 kcal mol^{-1} for *trans*-nitropropene (**5**), which is close to the experimental values (E_a = 45.8 and 42.2 kcal mol^{-1}, respectively).[33]

For nitroethylene (**4**), the $C-NO_2$ bond dissociation energy (pathway *IV* in scheme 2; E_a = 67.1 kcal mol^{-1})[43] is 19.1 kcal mol^{-1} higher than the energy required for the formation of 1,2-oxazete ring. The value of the activation barrier to the reaction of HNO_2 elimination (pathway *I*) is 58.1 kcal mol^{-1} (Ref. 43), while the activation energy of the nitro–nitrite rearrangement (pathway *VI*) is 57.6 kcal mol^{-1} (Ref. 43). The energy of 61.5 kcal mol^{-1} is required for the intramolecular isomerization of nitroethylene (**4**) to *aci*-form with 1,3-sigmatropic proton shift (pathway *V*).

The energetically least favourable pathway of the decomposition of compound **4** is pathway *II* with 1,4-proton shift, which requires 71.7 kcal mol^{-1} for its realization.

Thus, the activation energies for the initial reactions of the decomposition of nitroethylene (**4**) through pathways *I*, *II*, *IV* and *VI* (see scheme 2) are significantly higher than the activation energy for the decomposition reaction *via* cyclic intermediate **4a**. Analogous dependence was observed for the *trans*- (**5**) and *cis*-nitropropene (**6**).[43]

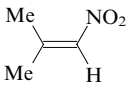
At the same time, the isomerization to *aci*-form **6a** (Ref. 43) with 1,5-proton shift [reaction (7)] is possible for *cis*-nitropropylene (**6**). This reaction requires 33.6 kcal mol^{-1}, which is 13.5 kcal mol^{-1} lower than the activation barrier to the decomposition of compound **6** *via* 1,2-oxazete 2-oxide (E_a = 47.1 kcal mol^{-1}).

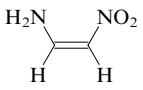


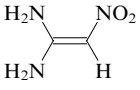
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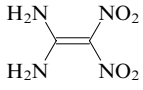
TS is transition state.

For 1-nitroisobutene (**7**), as well as for aminonitroethylenes **8**–**10**, the activation barriers to the intramolecular isomerization reaction to *aci*-form with 1,5-proton shift is even lower: E_a = 33.4, 10.3, 7.5 and 29.6 kcal mol^{-1}, respectively.[43]


7


8


9


10

The activation energies for the decomposition reactions of compounds **7**–**10** *via* 1,2-oxazete 2-oxide are given below:

Compound	E_a /kcal mol^{-1}
7	43.5
8	43.9
9	29.9
10	29.7

However, the limiting step of the decomposition of *cis*-nitropropylene (**6**) is the transformation of *aci*-nitro compound **6a** into 2-hydroxy-2,5-dihydroisoxazole (**6b**) rather than the primary step, *i.e.*, the formation of **6a** [see reaction (7)].[43, 131, 132] The value of the activation barrier to this reaction is 43.6 kcal mol^{-1}, which is 10.0 kcal mol^{-1} higher than that to the primary step (the formation of intermediate **6a**) and 3.5 kcal mol^{-1} lower than the activation energy of the decomposition of compound **6** *via* 1,2-oxazete 2-oxide.

For the aminonitroethylenes **8**–**10**, the isomerization of the *aci*-form to 2-hydroxy-2,5-dihydroisoxazole is also the limiting step.[43, 131, 132] Nevertheless, the activation energy for this reaction (E_a = 62.8, 65.6 and 54.4 kcal mol^{-1} for aminoethylenes **8**, **9** and **10**, respectively)[132] turned out to be significantly higher than the activation barrier to the isomerization of these compounds into 1,2-oxazete 2-oxide (E_a = 43.9, 29.9 and 29.7 kcal mol^{-1}).[43, 131, 132] Thus, the formation of the cyclic 1,2-oxazete 2-oxide intermediates in the unimolecular decomposition of the aminonitroethylenes is most probable.[132]

The energy required for the formation of 1,2-oxazete 2-oxide in the case of 1-fluoronitroethylene (**11**) is 52.3 kcal mol^{-1} and is close to the value of the activation barrier to the nitro–nitrite rearrangement (54.4 kcal mol^{-1}),[43, 130] *i.e.*, energetically these processes are equally probable.

It was noted[43, 120, 130, 133] that at temperatures up to 400–500 °C and above the mechanism of the homolytic C–NO_2 bond cleavage becomes competitive in the thermal destruction of the nitroalkenes due to the positive activation entropy of this reaction.

Thus, the homolytic cleavage of the C–NO_2 bond, the elimination of nitrous acid, the nitro-nitrite rearrangement, the decomposition *via* the *aci*-form or 1,2-oxazete 2-oxide are the possible pathways of the primary decomposition of nitroalkenes by the unimolecular mechanism of pyrolysis.

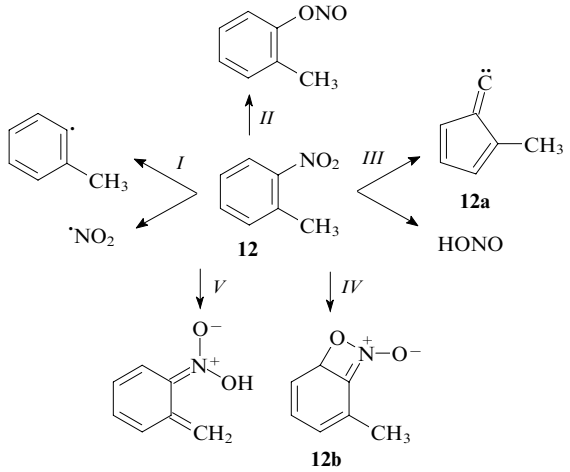
The quantum chemical estimation (DFT/B3LYP/6-31G*) of the activation barriers to the bimolecular decomposition reactions of nitroalkenes has been performed along with the investigation of the unimolecular mechanisms of their thermal destruction. Based on the results of the calculations, one can infer that bimolecular decomposition reactions of nitroalkenes, which are the most probable in the thermal destruction of these compounds in the liquid and gas phases at high pressure, can compete with unimolecular pyrolysis reactions. For example, in the case of nitroethylene the activation barriers to the limiting steps of the bimolecular decomposition [23.0–25.0 kcal mol^{-1} (Refs 120, 132 and 134)] are about twice higher than the value of the activation barrier to the isomerization of this compound into 1,2-oxazete 2-oxide (48.0 kcal mol^{-1}).

c. Compounds of group I.3

Formally, aromatic and heteroaromatic nitro derivatives can be attributed to the compounds of group I.2 (the nitro group is at the sp^2-hybridized carbon atom). However, we failed to find in the literature a single example of the elimination of nitrous acid or formation of 1,2-oxazete 2-oxide in the destruction of the aromatic and heteroaromatic nitro compounds, therefore, we have placed such derivatives into separate group I.3.

The majority of the compounds for which the mechanisms of the thermal decomposition have been studied belong to the series of the aromatic nitro compounds. Scheme 3 shows the possible pathways of the primary decomposition of *o*-nitrotoluene (**12**) as an example. The most typical are three pathways of the first step of thermolysis,[33, 42, 43] *viz.*, the homolytic cleavage of the C–NO_2 bond (pathway *I*), the nitro–nitrite rearrangement (pathway *II*) and 1,5-sigmatropic proton shift in nitrobenzenes with the hydrogen-containing substituents in the *ortho*-position to the nitro group (pathway *V*).

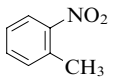
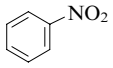
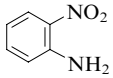
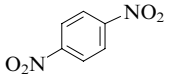
Scheme 3



One should note that the analysis of the variants of the primary destruction of the aromatic nitro derivatives takes into account the pathways of the decomposition of these compounds with the concomitant elimination of nitrous acid (pathway *III* in scheme 3), as well as that *via* 1,2-oxazete 2-oxide (pathway *IV*), which cannot be excluded for certain combination of substituents in a molecule.

According to the data from the calculations (DFT/B3LYP/6-31G*),[43] the energy required for the homolytic removal of the nitro group (pathway *I* in Scheme 3) from the series of aromatic nitro derivatives comprising 23 com-

Table 1. The energy characteristics (kcal mol^{-1}) of the initial step of thermolysis of nitroarenes **12**–**15**.

Compound	Formula	E_a (Ref. 43)		H (see [b])
		I	*II*	
12		67.3	58.1	113.8
13		69.8	62.9	117.4
14		74.1	63.2	122.4
15		66.8	60.0	116.4

[a] Enthalpy (the total thermal effect of the reaction), the calculation was performed by the authors of the present review using the DFT/B3LYP/6-31G* method.

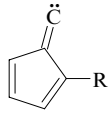
pounds lie in the range of 58.4–77.8 kcal mol^{-1}. Analogous values for the nitroarenes **12**–**15** are given in Table 1.

The activation barrier to the nitro–nitrite rearrangement (pathway *II*) for 20 aromatic nitro compounds [43] lie in the range of 53.2–67.6 kcal mol^{-1} (see Table 1). For compounds **12**–**15**, this value is 9.2, 6.9, 10.9 and 6.8 kcal mol^{-1} lower, respectively, than the energy required for the homolytic removal of the nitro group.

Experimental values [33] of the activation barriers to the first step of the decomposition of nitroarenes that do not contain hydrogen atoms in the *ortho*-substituents relative to the nitro group (for example, $E_a = 69.7$ and 68.6 kcal mol^{-1} for compounds **13** and **15**, respectively, at 400–500 °C) correspond to the energy required for the homolytic cleavage of the C–NO$_2$ bond (pathway *I* in Scheme 3). Due to higher activation entropy under the experimental conditions and larger value of the preexponential factor in the Arrhenius equation for this reaction [$\log A = 16.7$–17.3 (s^{-1}) for a selected series containing eight nitro derivatives], [134] the thermal destruction by the radical mechanism proceeds at a higher rate.[42,43] The ratio of the decomposition rates by the radical mechanism and by the mechanism of the nitro–nitrite rearrangement for nitroarenes at 400 °C is 5 : 1. With the decrease in temperature, the contribution of the nitro-nitrite rearrangement to the total reaction rate increases.[42,121]

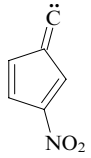
The isomerization to the *aci*-form with 1,5-sigmatropic hydrogen shift (path *c* in scheme 3) [33,42] is possible in the first step of the decomposition for the aromatic compounds with substituents containing hydrogen atoms in the substituents in the *ortho*-position relative to the nitro group. The activation barrier to this reaction for *o*-nitrotoluene (**12**) according to the results of the calculations [42] by DFT/B3LYP/6-31G* method is 44.1 kcal mol^{-1} (the experimental value [33] is 49.5 kcal mol^{-1} at 350–420 °C), for *o*-nitroaniline (**14**) it is 42.7 kcal mol^{-1} (the experimental [33] value is 57.5 kcal mol^{-1} at 400–470 °C). This is lower than the energy required for the nitro-nitrite rearrangement and the homolytic cleavage of the C–NO$_2$ bond. The explicit correlation between the theoretical estimation and the results of the experiment is lacking; presumably, the contribution of the decomposition process *via* the *aci*-form into the overall energetics of the pyrolysis is substantial for such *ortho*-substituted nitrobenzenes.[42]

The elimination of HONO from the aromatic nitro derivatives **12**–**15** (pathway *III* in Scheme 3) leads to the formation of the corresponding singlet carbenes **12a**–**15a**.



12a–**14a**

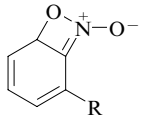
R = CH$_3$ (**12a**), H (**13a**), NH$_2$ (**14a**).



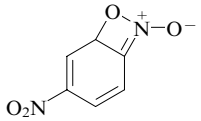
15a

In line with our calculations, the heat of this reaction lies in the range of 113.8–122.4 kcal mol^{-1} (see Table 1), which is significantly higher (by 50–80 kcal mol^{-1}) than the energy required for the decomposition of compounds **12**–**15** by the pathways *I*, *II* and *V* (see Scheme 3). Thus, the decomposition of the aromatic nitro compounds with the elimination of nitrous acid is energetically unfavourable. The decomposition *via* this pathway has not been detected experimentally either.

Yet another possible pathway of the decomposition of compounds **12**–**15** is pathway *IV* (see Scheme 3) with the formation of the bicyclic structures **12b**–**15b**, respectively.



12b–**14b**

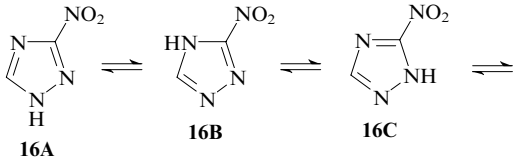


15b

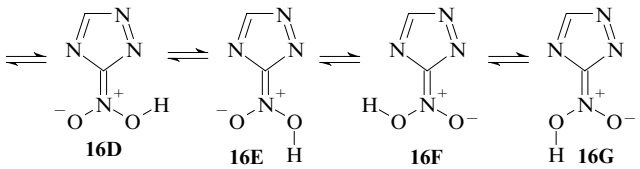
R = CH$_3$ (**12b**), H (**13b**), NH$_2$ (**14b**).

The calculated enthalpies of formation of intermediates **12b** and **14b** are equal to 53.5 and 58.6 kcal mol^{-1}, respectively, which is 9.4 and 15.9 kcal mol^{-1} higher than the values of the activation barrier to the decomposition of these compounds *via* pathway *V* (see Scheme 3). Thus, the decomposition of nitroarenes **12** and **14** *via* pathway *IV* is less probable.

According to our estimation,[74] the most preferable decomposition mechanism in the series of heteroaromatic nitro derivatives with a labile hydrogen atom in the ring is the decomposition *via* the *aci*-form. Below are shown possible tautomers and rotamers of 3(5)-nitro-1,2,4-triazole (**16**) including its *aci*-forms (compounds **16D**–**16G**) differing in configuration of the oxygen-containing groups with respect to the exocyclic C–N bond (*Z*,*E*; *Z*,*Z*; *E*,*E* and *E*,*Z*, respectively). The conclusion on the existence of the tautomeric forms is in agreement with the experimental data on the studies of the thermal decomposition of compound **16** in



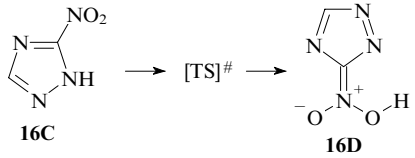
16A **16B** **16C**



16D **16E** **16F** **16G**

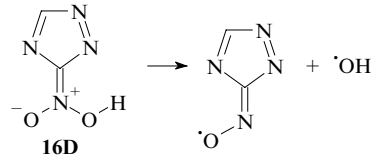
the solid state (with a pre-melting stage) in the temperature range of 180–200 °C.[74, 135] As mentioned above, the prototropic tautomerism is regarded under these conditions not as an intramolecular, but as an intermolecular process.[124–127]

The estimation[74] of the energies of tautomerization of 3(5)-nitro-1,2,4-triazoles **16A–16C** to the isomeric *aci*-forms (**16D–16G**) based on the difference in their thermodynamic stabilities gives the values from 22.9 to 27.9 kcal mol^{-1}. It should be noted that the value of the activation barrier to the intermolecular proton migration affording *aci*-form **16D** for the tautomeric *C*-nitro-1,2,4-triazole (**16C**) [reaction (8)] is also small (29.2 kcal mol^{-1}, DFT/B3LYP/6-31G* method) and is comparable to the values required for the intermolecular proton exchange.



16C **16D** (8)

As the activation barrier to the first step of the isomerization of *C*-nitro-1,2,4-triazoles **16A–16C** to *aci*-form **16D** is rather low, we have analyzed[74] the energy required for the possible reactions of the secondary decomposition of the isomers **16D–16G**. It was established that among all possible directions of the decomposition of the nitrotriazole *aci*-form (*e.g.*, isomer **16D**) the homolytic elimination of the hydroxyl radical is energetically the most preferable one [reaction (9)].

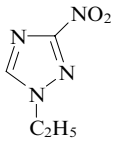


16D (9)

The activation energy for this reaction is in the range of 46.4 to 51.5 kcal mol^{-1} depending on the structure of the tautomers **16D–16G**,[74] which is higher than the energy required for the isomerization of *C*-nitro-1,2,4-triazoles to the *aci*-form. This suggests the reversibility of this reaction. However, the values of the activation barriers to the more energy demanding secondary decomposition reactions of the *aci*-forms **16D–16G** are lower than the activation energies for the destruction of the C-nitroforms **16A–16C**:[74] 67.2–68.2 kcal mol^{-1} for the homolytic elimination of the nitro group, 60.2–63.5 kcal mol^{-1} for the nitro–nitrite rearrangement, 66.7–71.3 and 89.6–105.6 kcal mol^{-1} for the homolytic cleavage of the endocyclic N–N and C–N bonds, respectively.

Thus, taking into account the energy expenditure for the secondary destruction reactions of *aci*-nitro-1,2,4-triazole, the decomposition of compound **16** *via* its *aci*-form seems to be energetically the most favourable.

At the same time, for alkyl-substituted 3-nitro-1,2,4-triazole **17**,[136] which cannot produce the *aci*-form upon proton migration, the experimental value of the activation energy of the thermal destruction in the gas phase (at 380–410 °C) is equal to 65.1 kcal mol^{-1}. This value is typical of the aromatic nitro compounds where the thermal decomposition proceeds with the primary cleavage of the C–NO$_2$ bond.



17

According to our calculations, the energy expenditure for the homolytic elimination of the nitro group from compound **17** is 67.9 kcal mol^{-1}, which is in good agreement with the experimental data (see above). It is of note that, although the value of the activation barrier to the nitro–nitrite rearrangement for 1-ethyl-3-nitro-1,2,4-triazole (58.8 kcal mol^{-1}, DFT/B3LYP/6-31G*) is 9.1 kcal mol^{-1} lower than the activation energy for the radical elimination of the nitro group due to the higher activation entropy, in this temperature range the second process turns out to be more favourable.

Thus, in keeping with the data presented above, one can state that the most probable pathways of the first stage of decomposition of aromatic and heteroaromatic nitro compounds are the homolytic cleavage of the C–NO$_2$ bond, the nitro–nitrite rearrangement and its decomposition *via* the *aci*-form of a nitro compound.

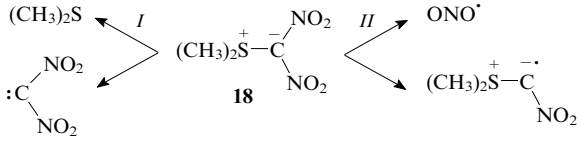
d. Compound of group I.4

Dinitromethylides, which belong to compounds of the group I.4 according to our classification, are characterized by the presence of a semi-polar bond between the carbon atom to which the nitro group is bound and the heteroatom on which the positive charge is localized (for example, compounds **18–21** in Table 2). Scarce data on the prediction of thermal stability of dinitromethylides[24] are available in the literature, while the kinetic investigations of their thermolysis are absent. The structural peculiarities of this type of compounds exclude the possibility of their decomposition with the elimination of nitrous acid as well as their decomposition *via* 1,2-oxazete 2-oxide. Theoretically, apart from the destruction pathways for the compounds of group I.1 and I.2 presented above, another additional decomposition pathway is possible for dinitromethylides through the homolytic cleavage of the zwitter-ionic bond carbon–heteroatom [pathway *I* in Scheme 4, thermolysis of dimethylsulfonium dinitromethylide (**18**) is given as an example].

Table 2. The dissociation energies (in kcal mol^{-1}) for the zwitter-ionic carbon–heteroatom (X^+-C^-) and C–NO$_2$ bonds in dinitromethylides **18–21** (according to DFT/B3LYP/LANL2DZ calculations).

Compound	Formula	Bond	
		X^+-C^-	C^--NO_2
18	$(CH_3)_2S^+-C^-(NO_2)_2$	56.6	56.2
19	$(CH_3)_3N^+-C^-(NO_2)_2$	76.7	55.3
20	$(CH_3)_2Se^+-C^-(NO_2)_2$	63.4	59.1
21	$CH_3I^+-C^-(NO_2)_2$	30.0	42.9

Scheme 4



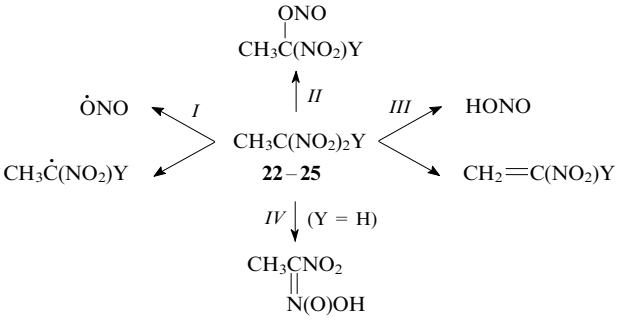
The energy expenditure for the decomposition of dinitromethylides *via* this pathway greatly depends on the nature of the heteroatom (see Table 2). According to our calculations (DFT/B3LYP/LANL2DZ), the X^+-C^- bond dissociation energy decreases with the substitution of the heteroatom in the dinitromethylide molecule in the series N > Se > S > I. At the same time, for trimethylammonium (**19**) and dimethylselenonium (**20**) dinitromethylides the homolytic elimination of the nitro group is thermally preferable (pathway *II*, see Scheme 4), the activation barrier of this process being lower than the dissociation energy for the zwitter-ionic bond carbon–heteroatom by 21.4 and 4.3 kcal mol^{-1}, respectively. The homolytic elimination of the nitro group and the cleavage of the zwitter-ionic bond carbon–heteroatom for dimethylsulfonium dinitromethylide (**18**) are energetically equal, while cleavage of the I^+-C^- bond is the most thermally favourable for methyliodonium dinitromethylide (**21**).

Thus, the results of the calculations suggest that the decomposition through the homolytic elimination of the nitro group and cleavage of the bipolar bond carbon–heteroatom are most probable for dinitromethylides (group I.4) under the thermolysis conditions.

e. Compound of groups I.5

We placed polynitroalkanes containing dinitro-, trinitro-, fluorodinitro- and (difluoroamino)dinitromethyl fragments into a separate group. Different assumptions exist on the decomposition mechanisms of such derivatives. Due to the steric hindrance between the nitro groups in the polynitromethyl fragment, the strength of the $C-NO_2$ bond is decreased. Compounds of this type decompose with the homolytic elimination of the nitro group.[33,38] Scheme 5 illustrates this decomposition pathway (pathway *I*) by the example of polynitroethane derivatives **22**–**25**.

Scheme 5

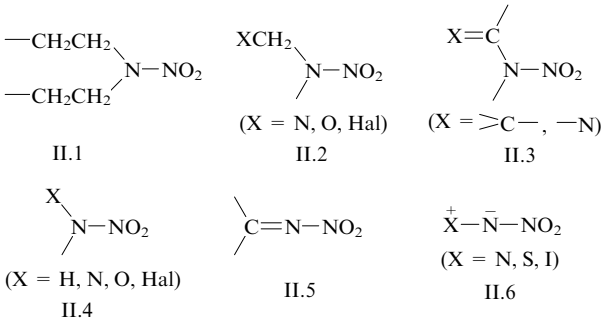


Y = H (**22**), NO_2 (**23**), F (**24**), NF_2 (**25**).

The radical mechanism of decomposition of 1,1-dinitroalkanes is confirmed by the results of the investigations of the kinetics of the gas-phase decomposition of these compounds.[137] Thus $^{\bullet}CH_3$ radical was observed in the thermolysis products of 1,1,1-trinitroethane (**23**).[138] Hence, the possibility of the intramolecular elimination of nitrous acid in the thermal decomposition of compound **23** was excluded. The radical mechanism of the decomposition in the gas phase is typical also of fluorodinitromethyl derivatives.[139] Experimental studies[140] on the thermal decomposition of *N,N*-difluoroamines with the general formula $RC(NO_2)_2NF_2$ (R = NO_2, F, CH_3) showed that they differ little in stability from the corresponding nitro analogues $RC(NO_2)_3$. Decomposition of α-difluoroamino-α-dinitroalkanes proceeds at equal rates in both gas and liquid states and is limited by the stage of the $C-NO_2$ bond cleavage. In the condensed state, the decomposition of dinitromethyl compounds, apparently, proceeds via *aci*-form (pathway *IV* in Scheme 5).[33,141]

2. *N*-Nitro compounds

Depending on the functional surrounding of the nitramino group, we have selected six groups of *N*-nitro compounds.

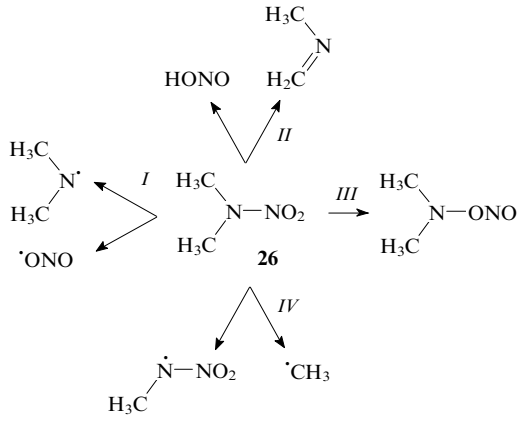


Derivatives of group II.1 include nitramines in which the orbital of the lone electron pair of the amine nitrogen atom is not involved in the non-valence interactions with the vacant frontier orbitals of the substituents, nor it is involved in conjugation.[142] For compounds of group II.2, the geminal orbital interactions occur ($p_N-\sigma^*_{C-X}$, $p_X-\sigma^*_{N-N}$)[142] in which the neighbouring heteroatom is involved. *N*-Nitroenamines and *N*-nitroamidines are included into group II.3. Nitramines containing heteroatom or hydrogen atom at the amine nitrogen atom are included into group II.4. Compounds with the nitrimine group constitute group II.5, while onium *N*-nitrimides form group II.6.

a. Compounds of group II.1

N,N-Dimethylnitramine (**26**) is the simplest representative of nitramines of group II.1. Its destruction products were identified and the activation energy of the decomposition reaction was estimated in the experimental investigations of its thermal destruction.[33,39,41,56] The radical elimination of the nitro group[33,39–41] (pathway *I* in Scheme 6), elimination of HNO_2 (pathway *II*)[41] and the nitro–nitrite rearrangement (pathway *III*)[143,144] are considered as the principal mechanisms of the first step of decomposition of compound **26**. In order to obtain the complete set of pathways of the initial decomposition of *N,N*-dimethylnitramine (**26**), we have also considered the possibility of the C–N bond homolytic cleavage (pathway *IV*).

Scheme 6



The homolytic elimination of the nitro group is the most energetically favourable route of the initial decomposition of compound **26**, the values $E_a = 40.8$ kcal mol^{-1} [$\log A = 14.1$ (s^{-1})] were found experimentally.[41] According to our calculations (DFT/B3LYP/6-31G*), the activation barrier to this reaction is 42.3 kcal mol^{-1}. The calculated energy expenditure (45.4 kcal mol^{-1}) for the elimination of HNO_2 *via* pathway *II* (see Scheme 6) is 3.1 kcal mol^{-1} lower than *via* pathway *I*. Pathway *II* characterized by the negative activation entropy cannot compete with pathway *I* as the contribution of this thermolysis route to the destruction of *N*,*N*-dimethylnitramine (**26**) is insignificant. Indeed, according to the experimental data,[145] the reaction rate for nitrous acid elimination from compound **26** is approximately 100 times smaller than the reaction rate for the homolytic elimination of the nitro group.

The energy expenditure for the nitro – nitrite rearrangement (pathway *III*, see Scheme 6) is even greater. The activation energy of the destruction reaction *via* this pathway is 67.4 kcal mol^{-1} (DFT/B3LYP/6-31G*). Note that in the experiments at ~900 °C the fraction of the nitro – nitrite rearrangement in the mechanism of the *N,N*-dimethylnitramine decomposition is less than 10%.[145] The nitro – nitrite rearrangement is the major channel of photolysis-induced decomposition of a series of secondary nitramines.[47,48]

Finally, according to the calculations, the most energetically demanding is the C – N bond cleavage (pathway *IV* in Scheme 6) in compound **26**: $E_a = 80.2$ kcal mol^{-1}. Hence, this pathway for the decomposition of nitramine **26** is unlikely.

The experimentally determined[41] kinetic parameters of thermolysis for a number of compounds of group II.1 are given bellow:

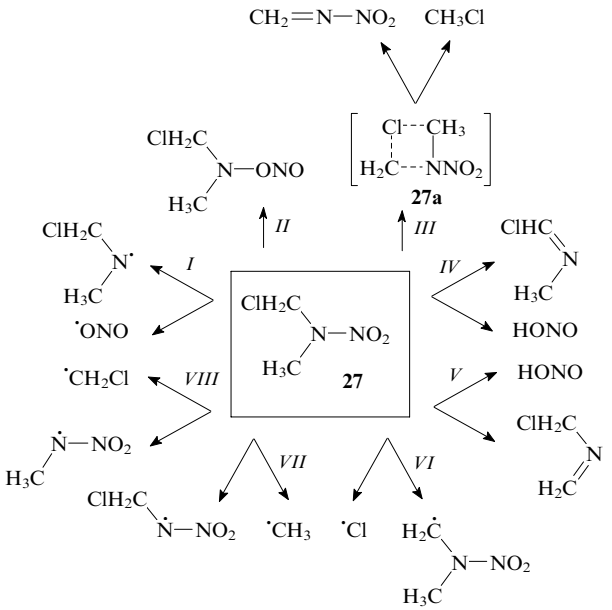
Compound	E_a /kcal mol^{-1}	$\log A$ (s^{-1})
N,*N*-Diethylnitramine	41.6	15.1
N,*N*-Dipropylnitramine	42.0	14.8
N,*N*-Diisopropylnitramine	42.6	15.9
N-Nitromorpholine	38.9	13.6
N-Nitropiperidine	42.1	14.8
N,*N*′-Dinitropiperazine	38.2	13.6

These data are also in favour of the preferential homolytic cleavage of the N – NO_2 bond.

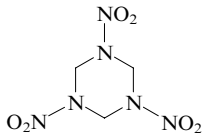
b. Compounds of group II.2

Geminal orbital interactions $p_N - \sigma^*_{C-X}$ and $p_X - \sigma^*_{N-N}$[142] play an important role in compounds of group II.2 in contrast to *N*-nitro compounds of the first group in which the lone electron pair of the amine nitrogen atom of the nitramine fragment does not participate in the orbital interactions. For the symmetrical systems where the nitrogen atom and the heteroatom X are close in basicity and inductive effect, the mechanisms of the thermal decomposition do not differ from the mechanisms of the decomposition of compounds of group II.1 since the effects of the geminal interactions therein are degenerate.[142] The consequence of the orbital interactions in the asymmetric systems II.2 is the increase in the number of possible thermolysis pathways associated with the cleavage of the C – X bond. For example, Scheme 7 shows the possible pathways of the destruction of *N*-chloromethyl-*N*-methylnitramine (**27**) including the homolytic cleavage of the C – Cl bond (pathway *VI*) as well as its decomposition through the formation of cyclic transition state **27a** (pathway *III*).[60,142]

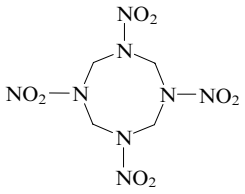
Scheme 7



Hexogen (1,3,5-trinitro-1,3,5-triazacyclohexane, RDX, **28**) and octogen (1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane, HMX, **29**) are representatives of compounds of group II.2, which belong to the symmetrical geminal systems; the mechanisms of their thermal decomposition are studied in detail.[33,39,41]

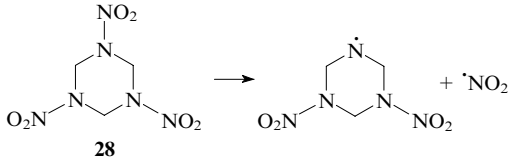


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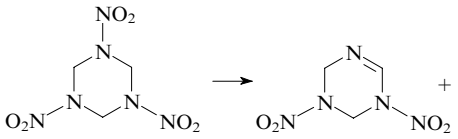
29

The schemes of the decomposition of compounds **28** and **29** follow similar trends, while the differences in the spatial arrangement of the nitramine groups [trigonal in octogen (**29**) and one trigonal and two pyramidal in hexogen (**28**)] influence only the initial rates of the decomposition of these compounds rather than the mechanisms on the whole.[33,146] A plethora of hypotheses on the possible mechanisms of the initial step of decomposition of compounds **28** and **29** have been forwarded in the studies of their thermolysis, they are highlighted in a review.[41] However, homolytic cleavage of the N – NO_2 bond [reaction (10) for hexogen] should be considered as the principal initial step of the decomposition that was confirmed experimentally.[41,147,148]



28 (10)

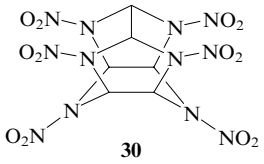
Moreover, it was established experimentally that at 240 – 290 °C the elimination of nitrous acid from compound **28** is also possible [reaction (11)].[149,150]



(11)

28

The polyhedral nitramine hexanitrohexaazaisowurtzitane (2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatetracyclo[5.5..0.0^{5,9}.0^{3,11}]dodecane, HNIW, CL-20, **30**), which is intensively studied nowadays, should be ranged to the same group of compounds.[151, 152]



30

Compound **30** is one of the most powerful explosives.[151, 153] Since the early 1990s, the systematic investigations have been carried out on both the optimal ways of its synthesis [151, 152] and its physicochemical properties,[151] in particular the mechanism and kinetics of its thermal decomposition. For example, the kinetics of the thermal decomposition of this compound was studied by thermogravimetry and IR spectroscopy.[154, 155] It was shown that the major gaseous decomposition products of CL-20 in the initial step of the destruction are NO_2 and, as a continuation of decomposition of the latter, NO. On this basis, it was concluded that the homolytic cleavage of the $N-NO_2$ bond is the main pathway of the thermal destruction of this compound. The formation of the NO_2 radicals was registered by EPR spectroscopy in a study of the low-temperature photolysis (at 80 K) of single-crystalline CL-20.[156] NO_2 was identified in the thermal decomposition products by rapid-scan IR spectroscopy.[157] The activation energy of the initial step of decomposition was estimated to be 40.8 kcal mol^{-1} in kinetic studies on the thermal decomposition of CL-20 by thermogravimetry and manometry.[158, 159] This value is close to the dissociation energy for the $N-NO_2$ bond in hexogen (39.7 kcal mol^{-1}) and octogen (44.9 kcal mol^{-1}).[33] The calculated [57] energy of the homolytic cleavage of the $N-NO_2$ bond of CL-20 in the gas phase is 37.6 kcal mol^{-1} (DFT/B3YP/6-31G*).

N-Chloromethyl-*N*-methylnitramine (**27**) is an example of asymmetric *N*-nitro compounds of the group II.2. The introduction of the chlorine atom significantly decreases the thermal stability of the molecule compared to *N*,*N*-dimethylnitramine (**26**) and is accompanied by the change in the kinetics of the thermolysis process.[160] Thus the energy expenditure for the initial step of decomposition of symmetrical compound **26** was assessed from 40.6–40.8 (Refs 40 and 141) to 46.2 kcal mol^{-1} (Ref. 40), while for *N*-chloromethyl-*N*-methylnitramine (**27**) this was experimentally estimated [160] as 30.7 kcal mol^{-1}. Besides, the initial decomposition of compound **27** is characterized by a lower value of the pre-exponential factor in the Arrhenius equation [log A = 10.5 (s^{-1})] and by the negative activation entropy,[160] while log A for compound **26** is 15.8 (s^{-1}) and the activation entropy is positive.[40]

We have calculated (DFT/B3LYP/6-31G*) the activation energies for all possible pathways of the decomposition of the monochloro derivative **27** shown in Scheme 7:

Pathway	E_a/kcal mol^{-1}
I	43.2
II	50.5
III	78.4
IV	41.3
V	44.3
VI	70.6
VII	86.2
VIII	103.6

Analysis of the obtained results suggests that the elimination reaction of nitrous acid (pathway *IV*) is energetically preferable.

Experimental data [160] testify the negative value of the activation entropy of the initial step of decomposition of *N*-chloromethyl-*N*-methylnitramine (**27**). This is characteristic of the reaction proceeding through a cyclic transition state and is more probable (taking into account the activation energies) for the intramolecular elimination of HONO. The calculated values of the energy expenditure for the initial decomposition of compound **27** *via* this pathway are slightly overestimated compared to the experimentally estimated value of the activation barrier (30.7 kcal mol^{-1}).[160] The decomposition through the cyclic transition state **27a** (pathway *III*),[160] is unlikely due to the energetical disadvantage of the process (the calculated activation energy for this reaction is 78.4 kcal mol^{-1}).

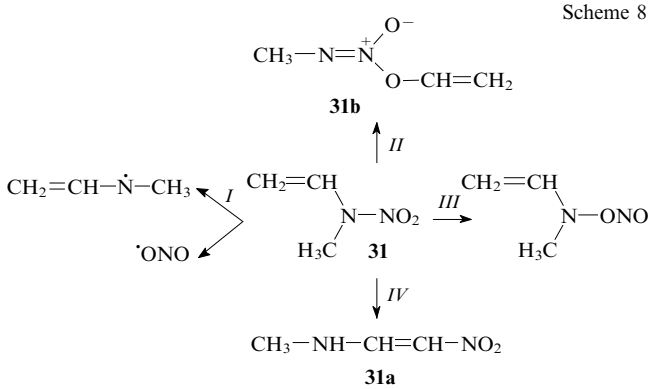
Apparently, given the diversity of the possible thermolysis pathways of *N*-chloromethyl-*N*-methylnitramine (**27**) (see Scheme 7), the question of the preferable mechanism of the initial step is still debatable. In the present paper, we consider only the variants of the homolytic and molecular decompositions of compound **27**; we also plan to investigate the possible mechanisms of its heterolytic destruction during which the preferable cleavage of the carbon–heteroatom bond cannot be excluded.

Thus, the possible pathways of the decomposition of group II.2 compounds include the homolytic elimination of the nitro group, the elimination of nitrous acid, the nitro–nitrite rearrangement and the cleavage of the carbon–heteroatom bond.

c. Compounds of group II.3

Scheme 8 shows as an example the mechanism of the decomposition of *N*-methyl-*N*-vinylnitramine (**31**). In the absence of steric hindrance, the $n_N-\pi^*_{C=X}$ interaction is

Scheme 8



typical of *N*-nitroenamines, derivatives of the group II.3, which leads to the decrease in the $N-NO_2$ bond strength.[60] This facilitates both its radical cleavage and 1,3-sigmatropic shift of the nitro group from the nitrogen atom to the unsaturated fragment with the formation of compound **31a** (pathway *IV*). The N→O-shift of the unsaturated substituent is also possible with the formation of unstable alkoxydiazene oxides **31b** (pathway *II*).[60]

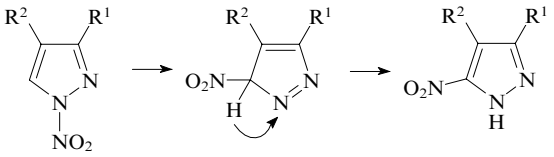
It was established experimentally[161] that β-nitroenamine **31a** formed upon thermolysis of *N*-methyl-*N*-vinylnitramine (**31**), albeit in small yield (see Scheme 8, pathway *IV*). However, the major direction of thermal destruction of compound **31** was the decomposition *via* intermediate **31b** (pathway *II*).

We have performed the calculation of the energy expenditure for each step of the thermolysis of nitramine **31** shown in Scheme 8:

Pathway	E_a /kcal mol^{-1}
I	25.6
II	54.0
III	51.3
IV	45.4

According to the calculations, the homolytic elimination of the nitro group is the energetically favourable direction of the initial step of the destruction of *N*-vinyl-*N*-methylnitramnie (**31**) in gas phase (pathway *I*). This pathway is more favourable than the 1,3-sigmatropic shift of the nitro group to the carbon atom of the C=C bond (pathway *IV*) (by 19.8 kcal mol^{-1}), than the nitro–nitrite rearrangement (pathway *III*) (by 25.7 kcal mol^{-1}) and than the migration of the vinyl fragment to the oxygen atom (pathway *II*) (by 28.4 kcal mol^{-1}). In addition, it is of note that the three latter processes (pathways *II*–*IV*) have negative activation entropy compared to the radical elimination of the nitro group for which the activation entropy is positive. Nitrogen(I) oxide identified experimentally in the thermal destruction of *N*-methyl-*N*-vinylnitramine (**31**)[161] appears probably in the later steps of the decomposition of NO_2,[74] which is formed in the decomposition *via* pathway *I*.

Group II.3 also includes azole *N*-nitro derivatives. Thus 5-unsubstituted *N*-nitropyrazoles undergo intramolecular rearrangement with the formation of 3(5)-nitropyrazoles in high-boiling solvents at 120–190 °C.[162,163] The 1,2-sigmatropic shift of the nitro group is considered as the first step of this rearrangement, which is followed by fast rearomatization of the intermediate product [reaction (12)].[164] '[1,5] Sigmatropic Nitro Migration'



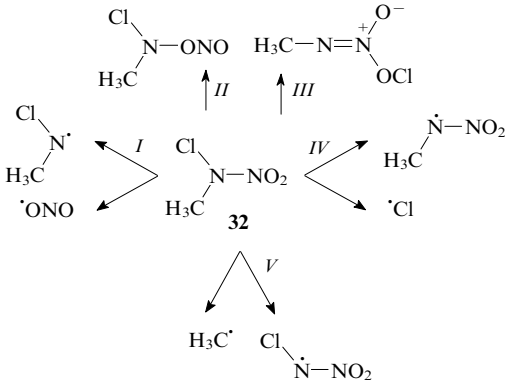
(12)

Analogous rearrangements occur in the thermal treatment of other *N*-nitroazoles,[165] including *N*-nitroimidazoles[166] and *N*-nitro-1,2,4-triazoles.[74,167,168] Our calculations of the activation barriers to the decomposition reactions of the latter are in good agreement with the experimental data.[74]

d. Compounds of group II.4

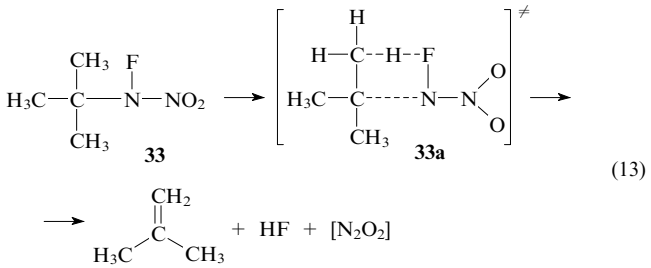
The $N-NO_2$ and N–X bonds are weakened due to the inductive effects and $p_N-\sigma^*_{N-X}$, $p_X-\sigma^*_{N-N}$ exchange interactions in the nitramines containing a heteroatom at the amine nitrogen atom (group II.4).[60] The experimental data on the investigations into the mechanisms of the thermal destruction of such compounds are scarce. The decomposition can proceed with both the homolytic elimination of the nitro group and the cleavage of the bond between the nitrogen atom and the heteroatom. Scheme 9 shows the possible pathways of the destruction of *N*-chloro-*N*-methylnitramine (**32**).

Scheme 9



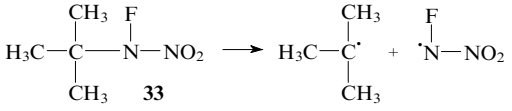
According to our calculations (DFT/B3LYP/6-31G*), the radical elimination of the nitro group from *N*-chloro-*N*-methylnitramine (**32**) is energetically the most favourable in the gas phase (pathway *I* in Scheme 9, E_a = 25.3 kcal mol^{-1}). To compare, the energy expenditure for the homolytic dissociation of the N–Cl bond in this compound (pathway *IV*) is 45.1 kcal mol^{-1}, while for the migration of the chlorine atom to the oxygen atom (pathway *III*) it is 55.8 kcal mol^{-1}.

It has been established experimentally[169,170] that *N*-fluoro-*N*-nitramines decompose at 50–80 °C, they have low activation barriers to the decomposition (23–30 kcal mol^{-1}) and positive activation entropies. Judging by the formation of a complex multiproduct mixture, it is assumed[169] that the decomposition of *N*-*tert*-butyl-*N*-fluoronitramine (**33**) can proceed simultaneously according to two mechanisms, *viz*., molecular [reaction (13)]



(13)

and radical [reaction (14)].



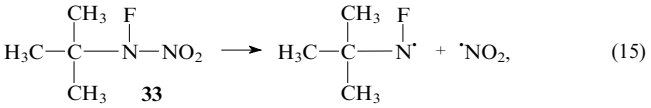
(14)

However, the decomposition through the cyclic transition state **33a** according to Eqn (13) assumes *a priori* the high probability of the negative entropy of activation,

which contradicts the experimental data.[169,170] The value of the activation barrier to the reaction (14) calculated by us is 72.0 kcal mol^{-1}, which is substantially higher (by a factor of 2.4–3.1) than the experimentally estimated energies of the decomposition activation energies for *N*-fluoro-*N*-nitramines.

The results of calculations of the activations barriers to other reactions of the homolytic decomposition of *N*-*tert*-butyl-*N*-fluoronitramine (**33**), which are characterized by the positive entropy of activation, are given below:

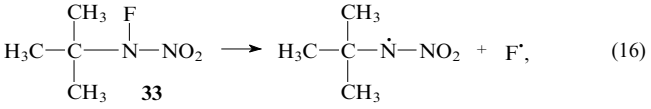
for the radical elimination of the nitro group



(15)

E_a = 22.9 kcal mol^{-1};

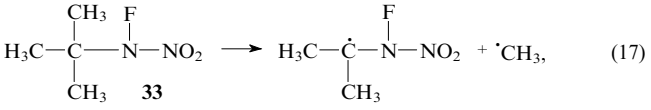
for the radical elimination of the fluorine atom



(16)

E_a = 63.6 kcal mol^{-1};

for the elimination reaction of the methyl radical



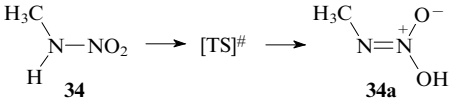
(17)

E_a = 43.3 kcal mol^{-1}.

The listed values of E_a show that the radical elimination of the nitro group dominates in the thermal decomposition of *N*-chloro- and *N*-fluoronitramines [reaction (15)].

The primary *N*-nitramines (X = H) formally can also be ranged in group II.4 due to their structure. These compounds are often characterized by a lower thermal stability than the secondary nitramines, which is explained [39] by the differences in the decomposition mechanisms due to the lability of the N–H hydrogen atom.

It should be noted that the thermal decomposition of primary nitramines is less investigated than that of the secondary ones. Two main points of view exist on the mechanism of the decomposition of primary nitramines in the gas phase. According to the one of them (Refs 60, 73, 102, 104, 105, 171–174), the decomposition of, *e.g.*, *N*-methyl-*N*-nitramine (**34**) proceeds *via aci*-form **34a** [reaction (18)].

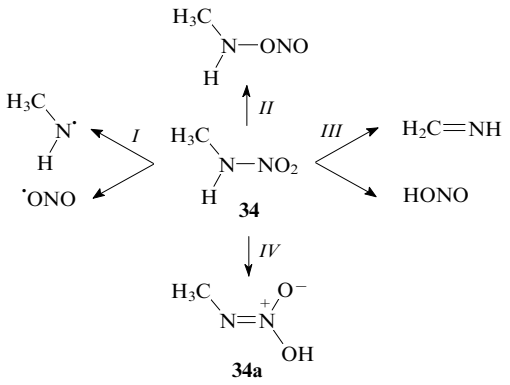


(18)

Other directions of the thermolysis of this compound are shown in Scheme 10.

According to the results of quantum chemical calculations (DFT/B3LYP/6-31G*),[73,174] the activation barrier to the formation of the *aci*-form of *N*-methyl-*N*-nitramine (**34a**) (pathway *IV* in Scheme 10) is lower than those to the homolytic elimination of the nitro group (by 10.9 kcal mol^{-1}, pathway *I*), the elimination of HNO_2 (by

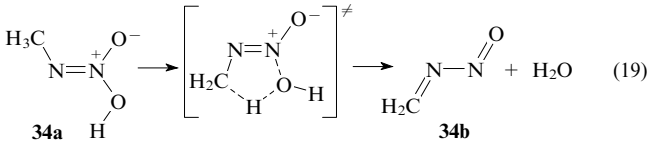
Scheme 10



11.7 kcal mol^{-1}, pathway *III*) and the nitro–nitrite rearrangement (by 46.0 kcal mol^{-1}, pathway *II*).

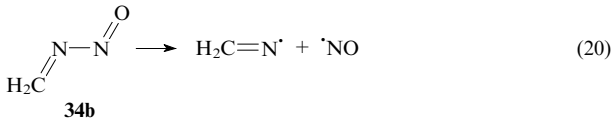
Pathway	E_a/kcal mol^{-1}
I	46.6
II	81.7
III	47.4
IV	35.7

The theoretical investigation [174] of the secondary reactions of the decomposition of *N*-methyl-*N*-nitramine (**34**) *via* pathway *IV* has shown that among the alternative variants of the destruction of the intermediate **34a** the elimination of water has the lowest activation barrier Eqn (19)]. Depending on the calculation method used, this value is 19.2 (MP2/6-311++G**), 30.6 (MP2/6-31G*), 34.9 (B3LYP/6-31++G**) or 39.8 kcal mol^{-1} (B3LYP/6-31G*).



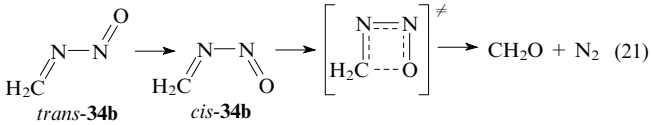
(19)

The activation barrier to subsequent decomposition of nitrosomethylimine **34b** *via* the radical cleavage of the N–N bond [reaction (20)] is 21.1 kcal mol^{-1} (B3LYP/6-31G*).[174]



(20)

The decomposition of intermediate **34b** is accompanied by the substantially lower energy expenditure *via* the alternative molecular mechanism of the thermolysis [reaction (21)].



(21)

The energy required for the isomerization of the *trans*-isomer **34b** into its *cis*-form is ~1.5 kcal mol^{-1} (B3LYP/6-31++G**, MP2/6-31G*, B3LYP/6-31G*, MP2/6-311++G**).[174] The transformation of the *cis*-**34b** intermediate

to formaldehyde and nitrogen requires from 3.3 (B3LYP/6-31++G**, MP2/6-31G*) to 4.0 (B3LYP/6-31G*) and 5.9 kcal mol^{-1} (MP2/6-311++G**).[174]

Thus, in the sequence of the decomposition reactions of *N*-methyl-*N*-nitramine (**34**)[174] *via* pathway *IV* (see Scheme 10) to the simplest final products [Eqns (19)–(21)], the first step, *i.e.*, the prototropic isomerization of the initial nitramine **34** into the b *aci*-form **34a**, is the most energy demanding.

According to another point of view,[175] the decomposition of the primary nitramines in the gas phase proceeds by the radical mechanism with the initial cleavage of the N–NO$_2$ bond (pathway *I*, see Scheme 10). This conclusion was made on the basis of the experimental investigation of the thermal decomposition of a series of primary alkylnitramines in the gas phase.[175] An assumption was made[176] that the decomposition of *N*-methyl-*N*-nitramine (**34**) in the gas phase includes the reversible cleavage of the N–NO$_2$ bond. According to the experimental data,[175] the activation barrier to the first step of the gas-phase decomposition of *N*-methyl-*N*-nitramine (**34**) in the temperature range of 230–280 °C is 41.0 kcal mol^{-1} and the reaction is accompanied by the positive entropy of activation. Thus, the radical mechanism through the homolytic elimination of the nitro group was inferred.[175] The calculated value of the N–NO$_2$ bond dissociation (46.6 kcal mol^{-1})[73,174] is rather close to the experimental value of the activation barrier to the initial decomposition of *N*-methyl-*N*-nitramine (**34**) (41.0 kcal mol^{-1}).[175]

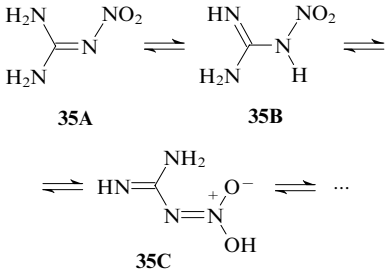
As mentioned above, the energy expenditure for the intramolecular proton transfer in compound **34** with the formation of the *aci*-form **34a** is lower than the activation barrier to the homolytic elimination of the nitro group, which suggests that the former pathway of the destruction of compound **34** is thermally preferable to the latter. However, it is known[33] that the thermal decomposition reactions proceed under kinetic control. That is why the pre-exponential factors in the Arrhenius equation should be taken into account along with the theoretical estimation of the activation barriers to the decomposition reactions to allow correct comparison with the experiment.

Thus the calculated value of the pre-exponential factor [log A = 13.4 (s^{-1})][174] for the formation of *N*-methyl-*N*-nitramine *aci*-form (**34a**) in the temperature range of 250–350 °C is in good agreement with the experimental one [log A = 13.65 (c^{-1})].[175] The calculation for the homolytic elimination of the nitro group from compound **34** gives the value of log A equal to 14.5 (s^{-1}).[174] Nevertheless, our point of view is that the conclusions drawn from the analysis of parameter log A are not indisputable. For example, the range of variation of log A for the homolytic elimination of the nitro group from secondary nitramines is 13.6–15.9 (s^{-1}).[41] This value correlates well with the experimental data[175] according to which the interval of log A variation for the gas-phase destruction of the primary nitramines is 13.55–15.34 (s^{-1}). Apparently, the question on the mechanism of the thermal decomposition of primary nitramines in the gas phase requires additional investigations.

e. Compounds of group II.5

Compounds of group II.5 are characterized by the presence of the C=N bond at the nitro group. There is no generally accepted point of view on the mechanism of thermal decomposition of the compounds of the nitroguanidine series. Experimental investigations of the mechanisms of thermal decomposition of this type of compounds are generally limited to the most practically important nitroguanidine derivatives.[45,177–182]

The peculiarity of the nitroguanidine (**35**), the parent compound of this series, is the presence of two amino groups at the carbon atom bonded to the nitrimine fragment. The nitrimino–nitramine tautomerism is possible for compound **35** (**35A** ⇄ **35B**). The tautomer **35B** can undergo subsequent hydride shift yielding *aci*-nitramino form **35C**.[65]



35A **35B** **35C**

It should be noted that various groups of researchers usually considered only the simplest hypothetical pathways of decomposition of only one arbitrary tautomeric form.[45] However, no experimental evidence for predominant presence or absence of a particular tautomer under the thermolysis conditions is available .

Theoretically, the existence of ten tautomeric forms and rotamers of nitroguanidine is possible (structures **35A**–**35J**), which differ in thermodynamic stabilities (Table 3).[65,75] In the gas phase, the nitrimine tautomer **35A** is the most stable. The X-ray diffraction data point to the nitrimine structure of nitroguanidine in the solid state as well.[183] Nevertheless, one cannot exclude the interconversion of the tautomers under the thermolysis conditions. The decomposition of the least thermally stable isomer is energetically favourable.

The full energy with the zero point energy correction for tautomer **35A** ($E + ZPE$) is −409.776420 a.u., which is 0.017674 a.u. (11.09 kcal mol^{-1}) lower than that for the second most stable tautomer **35B** (see Table 3). Eight rotamers are possible for the *aci*-nitramino form of nitroguanidine (**35C**–**35J**), the energies of tautomerization of structure **35A** leading to them are in the range 20.7 to 25.3 kcal mol^{-1}, which points to their lower thermodynamic stability.

The thermal decomposition of the nitramine form of nitroguanidine **35B** proceeds possibly according to four pathways (Scheme 11): the homolytic elimination of the

Scheme 11

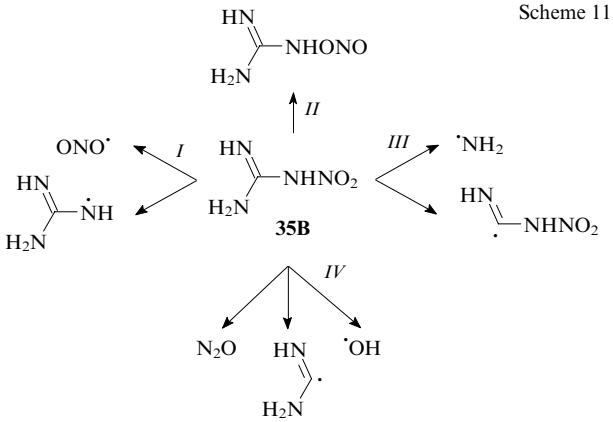
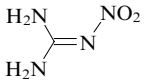
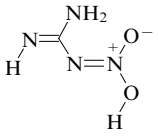
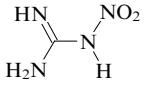
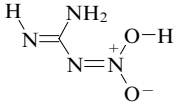
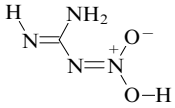
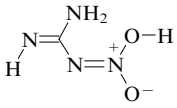
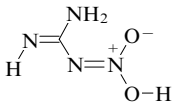
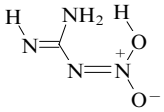
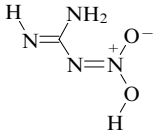
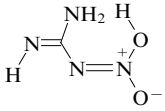


Table 3. The energy characteristics for the tautomers and rotamers of nitroguanidine in the gas phase (calculation at the DFT/B3LYP/6-31G* level).

Compound	Formula	$E+ZPE$ (a.u.)	ΔE/kcal mol^{-1} (see [a])	Compound	Formula	$E+ZPE$ /(a.u.)	ΔE/kcal mol^{-1} (see [a])
35A		−409.776420	0.0	**35F**		−409.739156	23.4
35B		−409.758746	11.1	**35G**		−409.743440	20.7
35C		−409.743230	20..8	**35H**		−409.743129	20.9
35D		−409.743363	20.7	**35I**		−409.738276	23.9
35E		−409.738131	24.0	**35J**		−409.736059	25.3

[a] The energy of tautomerization of the original structure to the corresponding tautomer (ΔE) was calculated by the formula

$\Delta E = [(E + ZPE)_x - (E + ZPE)_y] \times 627.5$ (kcal mol^{-1}),

where ZPE is the zero-point energy correction, x is the original tautomer, y applies to other tautomers.[128]

nitro group (pathway *I*), the elimination of the radical $^{\bullet}NH_2$ (pathway *III*), the nitro–nitrite rearrangement (pathway *II*) and the destruction with extrusion of N_2O and elimination of the $^{\bullet}OH$ radical (pathway *IV*).

The calculated activation energies of the decomposition *via* these pathways are as follows:

Pathway	E_a/kcal mol^{-1}
I	35.8
II	65.1
III	98.2
IV	66.6

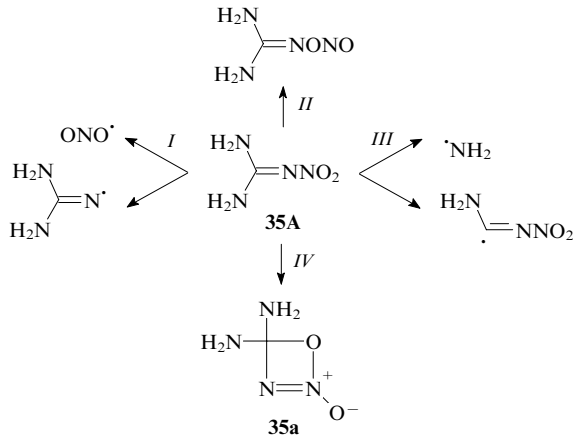
The calculation of the E_a values for the reactions proceeding in the first step of the thermal decomposition of compound **35B** suggests that homolytic cleavage of the $N-NO_2$ bond (pathway *I*) is thermally much more preferable than other decomposition pathways.

The possible directions of the destruction of the nitrimine form of nitroguanidine (**35A**) are given in Scheme 12.

The calculated activation energies for the homolytic elimination of NO_2 (pathway *I*), elimination of an NH_2 group (pathway *III*), the nitro–nitrite rearrangement (pathway *II*) and the decomposition through 1,2,3-oxadiazete 2-oxide cyclic transition state (pathway *IV*) are 46.4, 102.5, 72.7 and 27.7 kcal mol^{-1}, respectively.

The mechanism of the decomposition of nitroguanidine depends on the thermolysis conditions.[184] Thus, the analysis of the decomposition products suggested that the decomposition of compound **35A** began at 210 °C on slow heating and occurred with the cleavage of the $N-NO_2$ bond (pathway *I* in Scheme 12).

Scheme 12

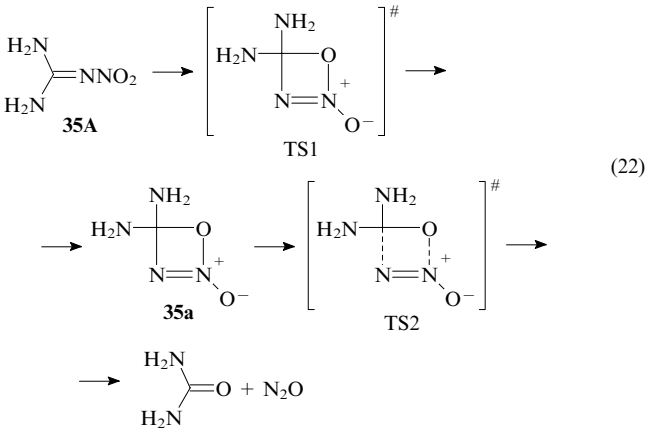


On rapid heating, the destruction began at 240 °C with the elimination of the amino group, *i.e.*, it occurred through the cleavage of the C–N bond (pathway *III*). No detailed description of the decomposition mechanism of nitroguanidine was given.[184]

According to the calculations (DFT/B3LYP/6-31G*),[65] the homolytic elimination of the nitro group from compound **35A** is energetically more than twice as favourable as the elimination of the NH_2 radical, *i.e.*, the former process is thermally preferable to the latter.

By analogy with nitroalkenes (group I.2), the decomposition of nitrimines through the 1,2,3-oxadiazete 2-oxide

cyclic transition state TS1 [reaction (22); the decomposition of isomer **35A** is given as an example] is theoretically possible. This mechanism has not been considered for the nitrimine so far. In the case of nitroguanidine, the implementation of this mechanism can result in urea and N_2O.



(22)

Nitrogen(I) oxide and urea have been detected experimentally in the decomposition products of compound **35**.[45, 185, 186] The compounds identified upon thermolysis of nitroguanidine, *viz.*, NH_3, HNCO, CO_2 and H_2O, are also the decomposition products of urea.[65]

The activation barrier to the formation of the cyclic transition state TS1 calculated by us (DFT/B3LYP/6-31G*) for reaction (22) is 27.7 kcal mol^{-1}, which is 18.7 kcal mol^{-1} lower than the energy required for the homolytic elimination of the nitro group from nitroguanidine. The experimental value [187] of the activation barrier to the initial step of the decomposition of compound **35** is 31.0 kcal mol^{-1}.

The decomposition of the cyclic structure **35a** to nitrogen(I) oxide and urea is energetically favourable and exothermic (66.9 kcal mol^{-1}) (Fig. 1). The activation barrier to the simultaneous cleavage of the C—N and N—O bonds in compound **35a** *via* transition state TS2 is only 11.7 kcal mol^{-1}. This is 16.0 kcal mol^{-1} lower than the barrier to the initial isomerization reaction of nitroguanidine (**35A**) to intermediate **35a**, *i.e.*, the first step of this mechanism is limiting.

The data presented above indicate that the decomposition of the nitrimine form of nitroguanidinium **35A** *via* the cyclic transition state TS1 is thermally preferable to the homolytic elimination of the nitro group (see Scheme 12, pathway *I*).

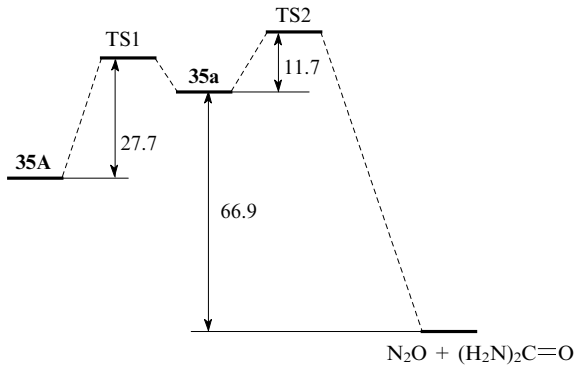
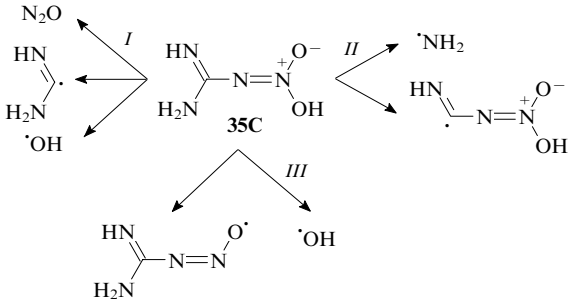


Figure 1. The energy diagram of the stepwise decomposition of nitroguanidine (**35A**) into nitrogen(I) oxide and urea (the energies are given in kcal mol^{-1}).

The decomposition of the *aci*-forms of nitramine (**35C**–**35J**) occurs along three pathways (Scheme 13) including elimination of N_2O (pathway *I*), the NH_2 radical (pathway *II*) and the hydroxyl radical (pathway *III*). The calculated values of the activation energies of the decomposition *via* these pathways for the isomer **35I** are 53.6, 118.7 and 42.7 kcal mol^{-1}, respectively.

Scheme 13



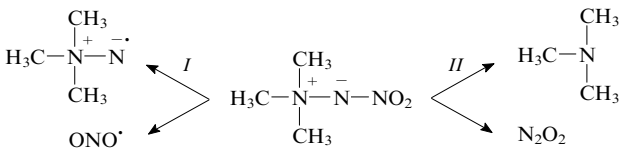
However, the activation barrier even to the most favourable pathway of thermolysis of the conformer **35I** *via* the pathway *III* (see Scheme 13) turned out to be higher than the barriers to the decomposition of isomers **35A** and **35B** *via* the most thermally preferable routes (pathway *IV* in Scheme 12 and pathway *I* in Scheme 11, respectively). In addition, the *aci*-nitramino forms of nitroguanidine **35C**–**35J** are thermodynamically less probable than tautomers **35A** and **35B**. In general, the thermal decomposition of the nitroguanidine *via* the *aci*-nitramino forms is unlikely.

Thus, the nitrimine form **35A** is the least thermally stable form of nitroguanidine, the mechanism of its decomposition *via* 1,2,3-oxadiazete 2-oxide cyclic transition state TS1 is the most energetically favourable. The energy expenditure for the destruction of nitramine form **35B** by the radical mechanism with the homolytic elimination of the nitro group are 8.1 kcal mol^{-1} higher. Presumably, both decomposition routes of nitroguanidine should be considered as competing, while the kinetic preference of any of them will be governed by the temperature conditions of the thermolysis.

f. Compounds of group II.6

In the onium *N*-nitrimides (group II.6), the N—NO_2 bond is stronger than the semi-polar (zwitter-ionic) X^+—N^- bond where X is a heteroatom. Decomposition of trimethylammonium *N*-nitrimide (**36**) is given as an example in Scheme 14. The decomposition of this type of compounds with the cleavage of the semi-polar bond (pathway *II*) is the most preferable.

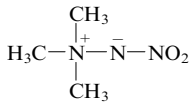
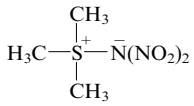
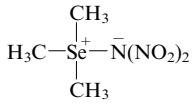
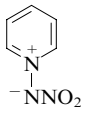
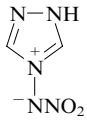
Scheme 14



36

As the mechanisms of the thermal decomposition of compounds of group II.6 have not been investigated in detail and only the data on the prediction of their thermal stability are available,[24, 75] we made a theoretical estimation of the dissociation energies of the zwitter-ionic bond of the

Table 4. The dissociation energy for the zwitter-ionic X^+-N^- bond and for the $N-NO_2$ bond in the onium *N*-nitrimides (DFT/B3LYP/6-31G* calculation).

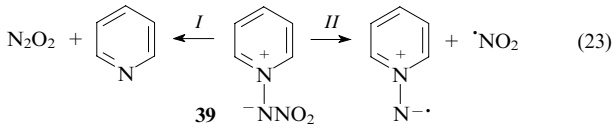
Compound	Formula	E_a (X^+-N^-) /kcal mol^{-1}	E_a ($N-NO_2$) /kcal mol^{-1}
36		42.5	67.8
37		40.9	47.8
38		50.5	61.2
39		42.9	44.2
40		38.3	59.2

nitrogen atom with a heteroatom (X^+-N^-) and the $N-NO_2$ bond in compounds **36**–**40** (Table 4).

As one can see from Table 4, the energy expenditure for the cleavage of the semi-polar X^+-N^- bond in aliphatic *N*-nitrimides **36**–**38** gradually increases on going from sulfonium (**37**) to ammonium (**36**) and then to selenonium *N*-nitrimide (**38**). The height of the activation barrier to the homolytic elimination of the nitro group in compounds **36**–**38** increases on going from sulfonium (**37**) to selenonium (**38**) and then to ammonium *N*-nitrimide (**36**), exceeding the dissociation energy value for the X^+-N^- bond by 6.9, 10.7 and 25.3 kcal mol^{-1} for compounds **37**, **38** and **36,** respectively.

The difference in the dissociation energies of the N^+-N^- bond in ammonium *N*-nitrimides **36**, **39**, **40** does not exceed 4.6 kcal mol^{-1}. The strength of the N^+-N^- bond is lower than that of the $N-NO_2$ bond by 1.3, 20.9 and 25.3 kcal mol^{-1} for compounds **39**, **40** and **36,** respectively. Among these compounds, 1,2,4-triazolium *N*-nitrimide (**40**) is the most stable;[75] according to our calculations, E_a (N^+-N^-) = 38.3 kcal mol^{-1} (the experimental value[44] is 40.0 kcal mol^{-1}).

It is of note that the activation barriers to both decomposition pathways of pyridinium *N*-nitrimide (**39**) [reaction (23)]



(23)

are rather close (the difference is only 1.3 kcal mol^{-1}). In this case, both pathways of the thermal destruction are possible with some energetic preference of the pathway *I*.

* * *

Thus, the differentiation of the nitro compounds into several structural types depending on the peculiar features of the functional surrounding of the nitro group made it possible to estimate both putative and the most feasible mechanisms of the initial step of decomposition of each of them.

III. The methodology of computer simulation of thermal decomposition processes of organic compounds. The fundamentals of simulation

To date, computer-aided generation of reaction networks is a rather well developed area of the modern mathematical chemistry.[188–194] Taking into account the specific mechanisms of the decomposition of high energy compounds, we have developed the corresponding software based on the classification discussed above. This enables computer simulation of the thermolysis mechanisms of nitro compounds belonging to different classes.[27,65–92] Two basic concepts underlie this methodology. First, all reactions that occur during thermolysis are potentially competitive. Second, the intermediates formed *via* different pathways can react with each other and all other species present in a closed chemical system (CS). Such an approach produces the most detailed representation of the processes that may occur during the thermolysis, which is close to the real one. The relationships between the intermediates are represented as a complex directed reaction network, the recombination reaction network (RRN). The basis of the RRN representation is the bipartite graph (Fig. 2) in which one type of vertices corresponds to the generated species, while the second corresponds to the description of the reactions. The vertices are joined by the oriented edges with straight lines, which allows distinguishing the reactants (incoming lines) and the products (ongoing lines).

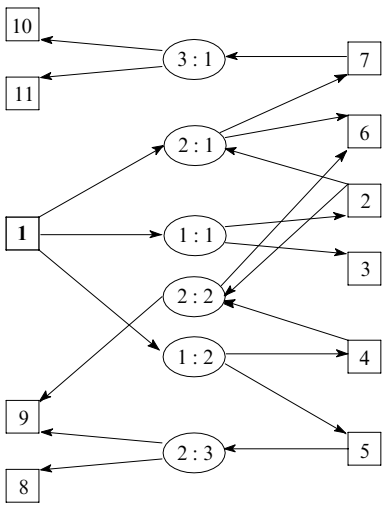


Figure 2. A fragment of the recombinant reaction chain.
The vertices of the bipartite graph denoted by numbers in squares represent chemical compounds (starting compounds, intermediates and products). Vertices as ovals represent chemical reactions (first digit denotes the iteration number at which this particular reaction was generated, while the second one denotes the corresponding ordinal number of the reaction).

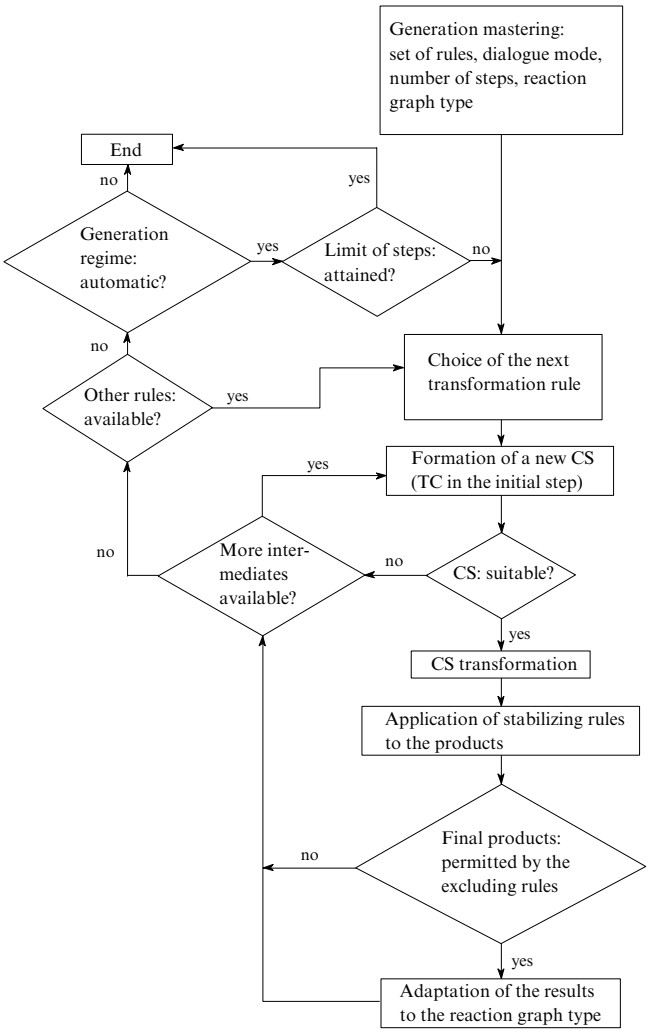


Figure 3. Flow chart of the generation process of the recombinant reaction chains.

The flow chart of the RRN generation is given in Fig. 3.

The decomposition reactions of a starting compound and reactions of the intermediates are described as the expert rules (reactions generators) formulated on the basis of the empirical data and operating following the 'if – then' principle.[66, 72–74] These generators can be general or more specific, *i.e.*, describe both the general reactions, such as the radical recombination, and particular cases, for example the nitro – nitrite rearrangement. Each rule has its own particular molecular graph and the description of the corresponding transformation.

The chemical reaction generators are defined as follows. A chemical compound (S) is described as a set of N atoms (subset A) and M chemical bonds (subset B):

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

Each atom A_i possesses a number of parameters X, for example, $X = \{$chemical element, valence, hybridization type, *etc.*$\}$. Accordingly, the bonds B_j are characterized by their own sets of properties Y, for example, Y = {bond energy, bond length, atom identifiers linked by this bond, *etc.*}.

Using combinatorial enumeration, unique reaction systems are designed from the entire set of chemical structures generated from the starting compound in the initial step. The reaction system can comprise one or several (at most three) molecules of the same or different compounds. Then a chemical reaction (R) represents an operation that describes the mechanism of transformation of a set of the reaction centres that meet the specified structural conditions $C^0(A,B)$ to the reaction products by changing the necessary characteristics of atoms and chemical bonds, for example, redistribution of electrons, the change in the bond order, *etc.*

The generation of the RRN is carried out using the software CASB (Computer Assisted Structure Building),[27, 66, 72] which can be used for the computer simulation of different processes in chemistry, in particular, for the simulation of the decomposition mechanisms of organic compounds.

1. The generation of thermal decomposition reactions of organic compounds

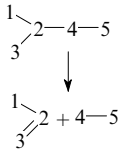
As mentioned in the previous Section, the simulation of a process using the developed methodology requires that parameterization of this class of compounds was performed, *i.e.*, the rules of chemical transformation were defined. These rules are formulated on the basis of the experimental data from the investigations into the thermolysis mechanisms of nitro compounds in different aggregate states. The set of rules consists of three groups that differ in the action steps, *viz.*, the transforming, stabilizing and excluding rules.

Table 5 displays examples of the rules that simulate, in particular, elimination of HNO_2, closure of vicinal biradicals and the exclusion of the reactions that lead to polyradicals from RRN (for the list of the principal rules, see Refs 66, 72–74).

For example, the rule No. 1 is the transforming one and describes the HNO_2 elimination reaction, which can be presented as follows for secondary nitramines:

$$\begin{matrix} R^1{-}H_2C \\ \\ R^2{-}H_2C \end{matrix}\!\!\!

Table 5. Examples of the 'if – then' principles for the simulation of thermal decomposition reactions of *C*- and *N*-nitro compounds.

Rule No.	Graph	Description [a]	Mode	Settings [b]				
				atom	property	relation	value	operation
1		HNO_2 elimination	transformation	1	atom type	=	C	no
					heteroatoms	=	1	BD
					hybridization	=	sp^3	BD
				2	atom type	=	C, N	no
				3	the same	=	C	no
					heteroatoms	=	1	BD
					hybridization	=	sp^3	BD
					atoms H	>	0	BD
				4	atom type	=	N	no
					charge	=	1	set equal to 0
				5	atom type	=	O	no
					charge	=	−1	set equal to 0
2		closure of vicinal biradicals	stabilization	1	UE	>	1	change to −1
				2	UE	>	1	change to −1
3		non-vicinal biradicals	exclusion	1	valence	<	2	BD
					UE	>	1	no
				2	valence	<	2	BD
					UE	>	1	no

Note. The following notations are used: BD stands for 'by default' peration; UE stands for unpaired electrons. [a] Reaction name; [b] description of atomic characteristics in the system of chemical procedures that should be done for each atom.

2. The discrimination of hypotheses on the decomposition mechanisms of compounds

The application of the combinatorial elements for the generation of the hypothetical reaction schemes of thermal decomposition of compounds stipulates certain requirements to the calculation resources and sets limits to the analysis of the results. The choice of the most probable mechanisms of the thermal destruction is based on the estimation of the energetic preference of the elementary steps for every generated pathway of the homolytic and molecular decomposition, which is inferred from the results of the calculation of the activation energy for the corresponding reactions.

IV. Simulation of the thermal decomposition of nitro compounds

In the generation of the decomposition mechanisms, we conformed to the following rules:

1) consider the homolytic and molecular reactions;

2) cover the whole spectrum of all possible experimental conditions of the process;

3) use the experimental data from pyrolysis, mass spectrometry and other methods of investigation into the thermal decomposition of nitro compounds in different aggregate states.

1. Thermal decomposition of *C*-nitro compounds

We simulated of the thermal decomposition mechanisms of representatives of all types of *C*-nitro compounds including the hypothetical structures (the dash denotes the authors' unpublished results).

Group	Compound	Ref.
I.1	nitromethane (**1**)	72
	nitroethane (**2**)	72, 78, 91
I.2	nitroethylene (**4**)	78, 91
	1,1-diamino-2,2-dinitroethylene	89
	5-dinitromethylidene-4,5-dihydro-1,2,4-triazole	—
I.3	5-nitro-1,2,4-triazole (**16C**)	74
	3-*aci*-nitro-1,2,4-triazole (**16D**)	74
I.4	1,2,4-triazolium 1-dinitromethylide	—
I.5	1,1-dinitroethane (**22**)	—
	1,1,1-trinitroethane (**23**)	78, 91
	1-dinitromethyl-1,2,4-triazole	—
	5-dinitromethyl-1,2,4-triazole	—

To illustrate the application of the developed approach and the software as a whole, we present the results of the simulation of the mechanisms of thermal decomposition of 3(5)-nitro-1,2,4-triazole (**16**) as an example.[74]

In compound **16**, the methine fragment bearing the nitro group is incorporated into the heteroaromatic ring (group I.3). In this case, the existence of several isomeric structures is possible (see above). In the gas phase, tautomer **16C** is the most thermodynamically favourable (Table 6).

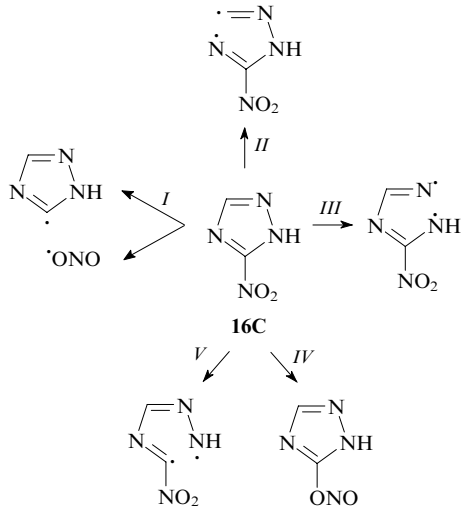
The simulation of the thermolysis mechanisms has been performed for all isomers **16A** – **16G**, because heat impact favours the proton migration in compound **16**. It was established that the decomposition mechanisms of structures **16A** – **16G** are similar.[74] For example, the following processes can occur in the initial step of the thermal destruction of isomer **16C** (Scheme 15): the homolytic elimination of the nitro group (pathway *I*), the cleavage of the N – N bond (pathway *III*) or the C – N bond (pathways *II*, *V*) in the heterocycle and the nitro – nitrite rearrangement (pathway *IV*).

Table 6. The energy characteristics of tautomers **16A**–**16G**.

Compound	$E+ZPE$ (a.u.)	ΔE/kcal mol^{-1} (see [a])
16A	−446.67369	0.8
16B	−446.66551	5.9
16C	−446.67490	0.0
16D	−446.63714	22.9
16E	−446.63057	27.8
16F	−446.63636	24.2
16G	−446.63048	27.9

[a] See comment to Table 3.

Scheme 15



The estimation of the decomposition pathways for compound **16C** gives the following values of the energy expenditure for each of them:

Pathway	E_a/kcal mol^{-1}
I	67.4
II	104.7
III	67.8
IV	60.1
V	93.3

These data suggest that the thermal decomposition of compound **16C** through the nitro–nitrite rearrangement (pathway *IV*) is the most preferable.

Similar thermolysis mechanism is typical of isomers **16D**–**16G** as well.[74] A fragment of the generated mechanism of the thermal destruction of structure **16G** or **16F** is given in Scheme 16 as an example. Here the homolytic elimination of the hydroxyl radical (pathway *I*), the destruction of the 1,2,4-triazole ring with extrusion of the nitrogen molecule (pathway *II*), the cleavage of the C–N bond (pathway *III*) and the elimination of the oxygen atom from the *aci*-nitro fragment (pathway *IV*) are the most probable pathways of the initial step of the decomposition; their activation energies are equal to 46.4, 55.4, 91.0 and 73.7 kcal mol^{-1}, respectively. Hence, the homolytic elimination of the hydroxyl radical upon thermolysis (pathway *I*) is the most preferable for this isomer.

Based of the performed calculations, we can state that the *aci*-form of 3(5)-nitro-1,2,4-triazole **16G** is the least thermally stable against thermolysis. Hence, the thermal decomposition of compound **16** through the *aci*-nitro-tautomer **16G** is energetically favourable.

The simulation of the possible mechanisms of the thermal decomposition of compound **16G** has shown (see Scheme 16) that, in addition to the experimentally[135] detected products [N_2, N_2O, NO, CO_2, HCN, HNCO, 3(5)-nitroso-1,2,4-triazole and 1,2,4-triazolone], other thermolysis products (H_2O, CO, NO_2, cyanamide, isocyanuric acid, melamine, 1,2,4-triazole) can also form. The fact that these compounds have not been detected experimentally can be connected with both the limitations of the applied methods and the imperfection of the instruments.

Triazine-type fused products are usually formed upon thermal decomposition of organic compounds containing several nitrogen atoms (including the high-energy materials).[59, 195–197] In addition to melamine and isocyanuric acid shown in Scheme 16, ammeline, ammelide, heptazine and polymers derived from the latter can be formed.[198, 199] All these compounds constitute the condensed residue X shown in the scheme.

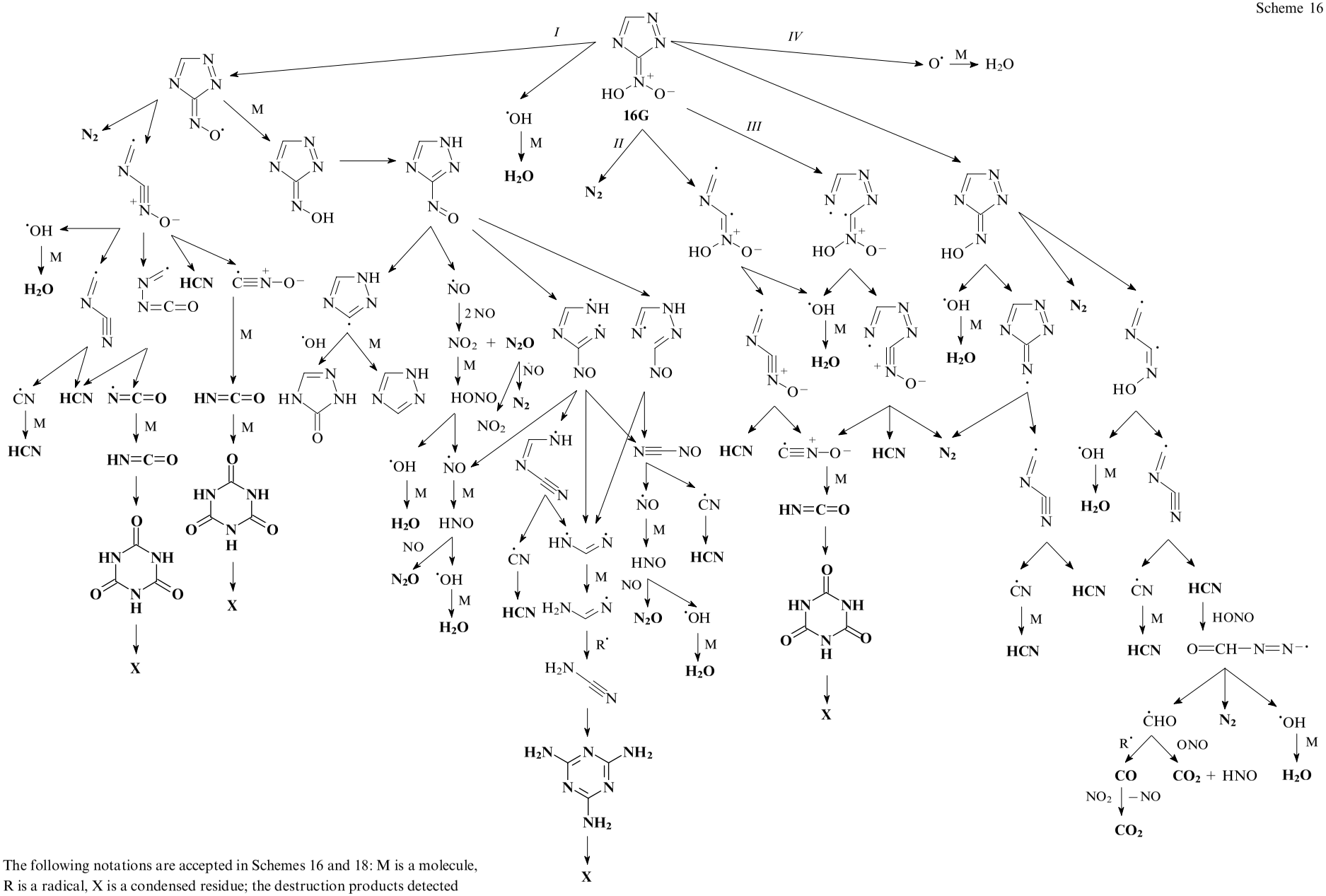
The calculation of the activation energies for all reactions generated for the thermal decomposition of 3-*aci*-nitro-1,2,4-triazole **16G** (Ref. 74) suggests that the final thermolysis products of this compound are formed *via* the predictable decomposition pathways that are the thermally favourable.

2. Thermal decomposition of *N*-nitrocompounds

We have performed the simulation of the complete stepwise mechanisms of the thermal decomposition of the following *N*-nitro compounds (some polyfunctional compounds can be attributed to two groups at once):

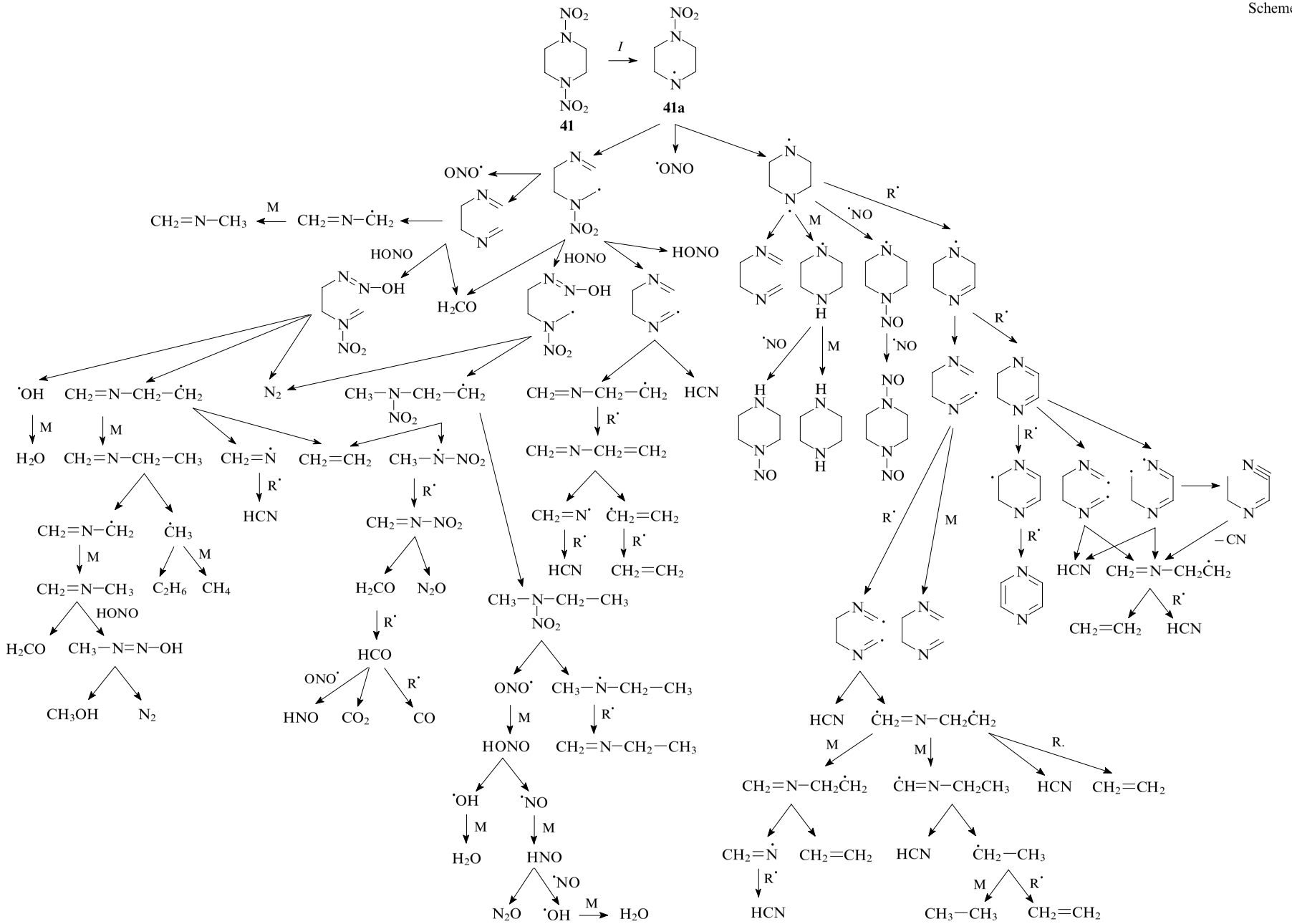
Group	pound	Com-Ref.
II.1	*N*,*N* -dimethylnitramine (**26**)	73, 77, 87
	N,*N*′-dinitropiperazine (**41**)	73, 81
	trans-1,4,5,8-tetranitrodecahydropyrazino[2,3-*b*]pyrazine	79, 92
II.2	*N*-chloromethyl-*N*-methylnitramine (**27**)	73, 77, 87
	1,3,5-trinitro-1,3,5-triazacyclohexane (hexogen, **28**)	72
	1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (octogen, **29**)	72
	hexanitrohexaazaisowurtzitane (CL-20, **30**)	88
	1,3-dinitro-1,3-diazacyclobutane (tetrogen)	73
	1-nitro-1-azacyclobutane	72
	1,3-dinitro-1-azacyclobutane	72
	1,3,3 -trinitro-1-azacyclobutane (trinitroazetidine)	72
II.3	*N*-methyl-*N*-vinylnitramine (**31**)	73, 77, 87
	N-nitro-1,2,4-triazole	74
	N,*N*′-dinitrofurazano [3,4-*b*]piperazine	73, 81
	N-methylnitramine (**34**)	73
	zwitter-ionic form of 3-nitramino1,2,4-triazole	75
II.3, II.4	3-nitramino-1,2,4-triazole	75
	3-*aci*-nitramino-1,2,4-triazole	75
	nitramine form of *N*-nitroguanidine	65
II.4	*N*-chloro-*N*-methylnitramine (**32**)	73, 81
	N-*tert*-butyl-*N*-fluoronitramine	73
	4-nitramino-1,2,4-triazole	75
	4-*aci*-nitramino 1,2,4-triazole	75
	1,2,4-triazolium 4-nitrimide	75
II.5	5-nitrimino-1,2,4-triazole	75
	N-nitroguanidine (**35**)	65

Scheme 16

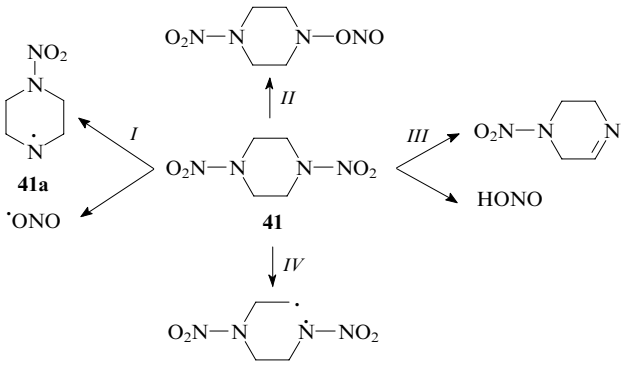


The following notations are accepted in Schemes 16 and 18: M is a molecule, R is a radical, X is a condensed residue; the destruction products detected experimentally are given in bold type.

Scheme 17


41
41a
I
ONO•
•ONO
HONO
H2CO
M
R•
•NO
•OH
H2O
HCN
HNO
CO2
CO
N2
CH3OH
C2H6
CH4
HCO
N2O
HNO2

Scheme 18



We consider the thermolysis of *N*,*N*′-dinitropiperazine (**41**), which belongs to the compounds of group II.1 (see above) as an example of the generation of mechanisms of the thermal destruction of *N*-nitramines.[73, 81] The generated mechanism (Schemes 17, 18) includes the following pathways of the initial step of the decomposition of this compound: the radical elimination of the nitro group (pathway *I*), the intramolecular elimination of nitrous acid (pathway *III*), the nitro–nitrite rearrangement (pathway *II*) and the homolytic cleavage of the C—N bond (pathway *IV*). The energetic characteristics of these processes are as follows:

Pathway	E_a /kcal mol^{-1}
I	40.7
II	68.7
III	69.4
IV	80.4

The energetically preferable thermolysis pathway for this compound is the homolytic elimination of the nitro group (pathway *I*), which is confirmed by the experimental data.[200] The energy expenditure for the homolytic elimination of the nitro group calculated by us are closest to the experimentally estimated activation barrier to the thermal decomposition reaction of *N*,*N*′-dinitropiperazine (38.2 kcal mol^{-1}).[41]

It is of note that for a number of cyclic nitramines (including *N*,*N*′-dinitropiperazine) the possibility of the formation of nitrous acid in the initial step of the decomposition has been discussed.[201] However, it was shown [73, 81] that HONO results from secondary processes. This is confirmed by the calculated value of the activation barrier to the decomposition of compound **41** *via* pathway *III*, which is 28.7 kcal mol^{-1} higher than the energy expenditure for its destruction *via* pathway *I*. The simulation of the mechanisms of the deeper steps of thermolysis of *N*,*N*′-dinitropiperazine (**41**) gives a complicated pattern of conversions. Scheme 18 illustrates secondary processes involving intermediate **41a**, which is formed in the initial step of the decomposition of compound **41** only *via* pathway *I*.

The simulated overall mechanism of the destruction of compound **41** allows predicting the whole spectrum of possible reactions. It is in good agreement with the experimental data and explains the formation of such products as N_2, N_2O, NO, NO_2, CO, CO_2, piperazine, *N*-nitrosopiperazine and *N*,*N*′-dinitrosopiperazine.[56] According to the calculations the formation of CH_3OH, HCN, CH_4, C_2H_4 and C_2H_6, which have not been detected in the experimental conditions, is also possible.

V. Conclusion

Thus, experimental data on the thermal decomposition of organic nitro compounds allowed us to reveal the structure–property relationship as applied to the thermolysis mechanism, thermal decomposition reactions of polyfunctional *C*- and *N*-nitro compounds, which resulted in creation of the formal-logical generators of such reactions. The review presents an effective scheme of the differentiation of *C*- and *N*-nitro compounds depending on the functional surrounding of the nitro group, which allows predicting the mechanisms of their thermolysis on the basis of this classification as well as facilitating the interpretation of the experimental data.

The developed method of computer-aided generation of the mechanisms of thermal destruction of nitro compounds allows predicting the whole spectrum of the potential products of the destruction. The proposed mechanisms of the thermal decomposition can be used for the calculation of the kinetic parameters of thermolysis and the estimation of stability of the high-energy compounds, *e.g.*, to address safety concerns.

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