



Polyfunctional *N*-nitramines Structure Differentiation as a Basis for Simulation of Their Decomposition Mechanism^{*)}

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Abstract: The structural classification of different chemical classes of *N*-nitramines has been developed and the differentiation of their types throughout the functional surroundings has been proposed. Basing on it and using up-to-date experimental data on their thermal decomposition mechanisms the set of generators for chemical reactions that are typical during nitramines decomposition process has been elaborated. The original schemes for different types of *N*-nitramines thermolysis reactions have been designed and the initial stage activation energy of it has been calculated by using the B3LYP/6-31G* level of density functional theory. As the result the most favorable pathways of compounds decomposition have been displayed. The suggested methodology for thermochemical processes simulation can be used for a set of practical problems solution, including the investigations of the mechanisms of decomposition, ignition, combustion, and detonation of energetic materials as well as for “structure-properties relationships” study and for the search of prospect high-energy substances structure.

Keywords: *N*-nitramines, structural differentiation, structure-properties relationship, decomposition mechanism

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Introduction

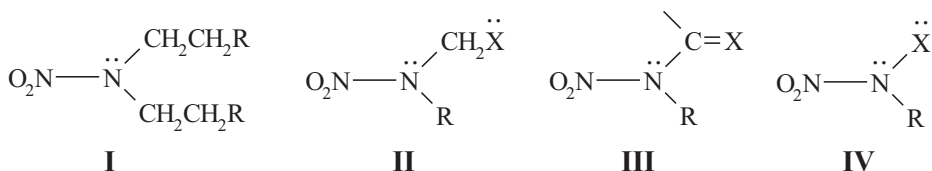
The systematical investigations of structure and properties relationships for energetic materials (aliphatic and aromatic nitrocompounds, nitramines and nitroethers, heterocycles and others) are in progress from the end of the fifties last century. Both individual compounds and the ascertainment of common features of structure-property relationships have been investigated. *N*-nitramines take the first place among energetic materials (EM) and the basic property of them is the thermostability concerned with the processes of compounds decomposition.

Although a large number of experimental investigations concerning the kinetics of (EM) thermolysis were performed, the problem of possible pathways prediction of the decomposition mechanisms remains quite topical. The problem is also of interest, from the viewpoint of assessment of the capability of potentially energetic compounds, which have not yet been synthesized. Meanwhile, theoretical methods for the solution of such a problem are very insufficient at present. In addition, they mostly deal with the interpretation of experimental data rather than with predictions. In this connection, we have formulated [1, 2] generalized problem: computer generation of possible homolysis pathways for a given compound on the basis of its structural formula, as well as correction of these pathways on the basis of some formal rules, which are specified in accordance with the experimental data.

The framed set of rules allows one to differentiate of the thermal decomposition pathways of nitramines according to its molecular structure.

During energetic materials thermal decomposition process in gas phase thermolysis reactions can pass practically throughout all known mechanisms: molecular dissociation with free radicals formation, elimination, rearrangement with the subsequent decay, disclosing of a cycle, etc. The prevalence one or other way of transformation during decomposition process depends on molecular structure, first of all [3].

Against amine nitrogen surroundings there are possible to mark out four *N*-nitrocompounds groups:



The specimens of the first group (I), where undivided pair of amine nitrogen

does not take part in conjugation or other nonvalent orbital interactions [4] are characterized by the highest thermal stability. Their decomposition begins with N–NO₂ bond homolysis.

In contrast to the first group of *N*-nitrocompounds, where are not the effects of undivided electronic pair, the effects of heminal interaction can be come out in substances of the group (II). This is a reason of the wide ranged variability in thermal constancy of the second group members. In the case of symmetric heminal systems of the group (II), when heteroatoms >N— and —X are approximately equal in basicity and inductive effect, there is practically no difference in action with compounds of the group (I), since effects of heminal interaction are multiply degenerated. In the case of assymmetric systems (II) effects of heminal interaction are fairly appeared. It deeply reduces thermal stability and changes the kinetics of initial stage of thermolysis [5-7].

In compounds of the third class (III) the amine nitrogen of *N*-nitro group is directly bonded with the unsaturated fragment. When there are no steric constraints for p_N—π*_{C=X} conjunction, the sharp decrease of N-N-bond energy is observed that facilitate its hemolytic scission or 1,3-sigmatropic shift of nitro group from nitrogen to X-atom.

The group (IV) has been formed by *N*-nitrocompounds containing amine nitrogen directly connected with heteroatom. The close contact of heterosubstitute with *N*-nitro group is accompanied by the weakening of bonds in *N*-nitro fragment according to inductive scheme and scheme of exchange interactions [8, 9].

Basic scheme of thermal induced transformations of *N*-nitro compounds are presented in Figure 1.

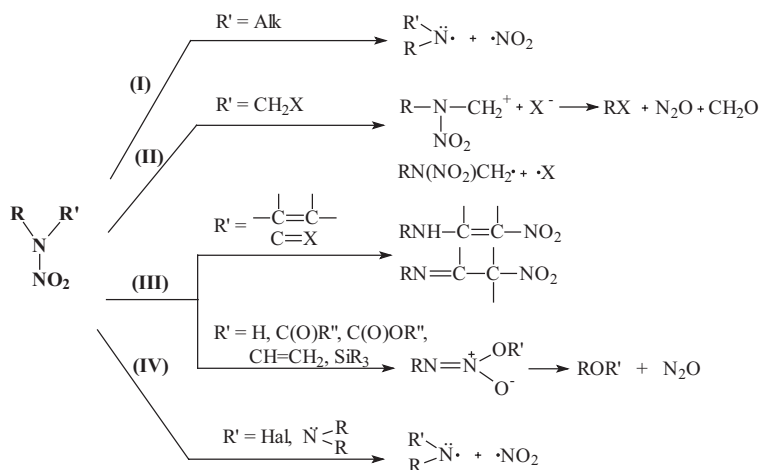


Figure 1. Thermal induced transformations of *N*-nitro compounds.

Methods

Mechanism of chemical reactions during the decomposition process we presented as a topologic structure, which is a function of source substances, intermediate and final products. It can be invariant for any concrete chemical system. To define a mechanism of decomposition we used a graph theory and formulated the general approach to the computer-assisted modeling of the mechanism of homolytical reactions for nitrocompounds. A set of chemical transformation generators based on experimental data has been formulated to follow up the more probable decomposition reactions for compounds of different chemical classes.

Screening of the most advantageous pathways from the energy standpoint were carried out by calculations of the initial stage activation energy (B3LYP/6-31G* [11] level of density functional theory [10]). Calculations were executed using GAUSSIAN 98 /12/ at the Computational Centre of Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences.

As the result the most favorable pathways of compounds decomposition have been displayed.

Results and Discussion

As a model compound of the first group (**I**) we studied *N, N'*-dimethylnitramine. Figure 2 represents four possible initial stages of decomposition of corresponding substance: (1) N-N bond homolysis, (2) HNO₂ elimination, (3) nitro-nitrite rearrangement, and (4) homolysis of the C-N bond. As a result of computer generation of probable *N, N'*-dimethylnitramine thermolysis pathways we have got a whole series of formally probable reactions. The data obtained can be used to understand the mechanism of thermal decomposition of corresponding compound as well as to clarify the formation of nitrogen, protoxide of nitrogen, H₂O, carbon monoxide and carbonic acid as the final decomposition products.

The calculated activation energy (E_a) of homolytic reaction of N–N bond cleavage is 180.7 kJ mol⁻¹, compared to 336.0 kJ mol⁻¹ for the C–N bond cleavage and to 282.2 kJ mol⁻¹ for nitro-nitrite rearrangement reactions. In this connection, one can conclude that two last-named processes are unlikely in comparison with the N–N bond homolysis reaction in *N, N'*-dimethylnitramine. The calculated activation energy (E_a) of the reaction of HNO₂ elimination is 190.2 kJ mol⁻¹ (197.8 kJ mol⁻¹ [13]) that is only for 9.5 kJ mol⁻¹ higher than for the homolytic cleavage of N–N bond. Therefore the HNO₂ elimination can be considered as the alternative pathway of decomposition for secondary nitramines.

Considerations of the presented scheme allow the conclusion that under the atom of chlorine introduction into the molecule of *N, N'*-dimethylnitramine the subsidiary channels of thermal decomposition arise through the cyclic complex with the subsequent elimination of methylchloride and homolytic cleavage of the C–Cl bond. These opportunities provide the explanation for HCl and CH₃Cl presence among the final decomposition products (the origin of which was not quite clear before).

The energy of the N–N bond cleavage in *N*-methyl-*N*-chlorine methylnitramine is 180.7 kJ mol⁻¹, for the C–N homolysis the energy is 361.1 kJ mol⁻¹, for the C–Cl cleavage bond – 295.7 kJ mol⁻¹, and (E_a) for nitro-nitrite rearrangement is 211.6 kJ mol⁻¹. Unfortunately in our calculations the transition state localization of the cyclic activated complex formation was not a success:



The experimental energy activation of the initial stage of *N*-methyl-*N*-chlorine methyl nitramine thermal decomposition is 128.5 kJ mol⁻¹ [15].

The reaction scheme of thermal decomposition process for *N*-vinyl-*N*-methyl nitramine, as one of the third type compounds representatives, is shown in Figure 4.

Analysis of the results of decomposition processes simulation follows up that under introducing an unsaturated fragment direct fixed with *N*-nitro group into a molecule, a set of rearrangements may be observed which are absent in the case of (I) and (II) groups compounds. At the same time, the possible thermo decompositions channels and resulting intermediates increase in number.

The calculated activation energy of the N–N bond cleavage in *N*-vinyl-*N*-methyl nitramine is 107.1 kJ mol⁻¹. That fits the assumption on the sharp N–N bond energy decrease for the (III) group compounds in comparison with the (I) group ones. The activation energy of the unsaturated substitute N→O shift is 226.2 kJ mol⁻¹. In case of CH₃ elimination the energy of C–N bond homolysis is 271.8 kJ mol⁻¹ and is 397.1 kJ mol⁻¹ in case of vinyl radical elimination. We failed to localize the nitro-nitrite rearrangement and the 1,3-sigmatropic shift transition states. Though, the nitro-nitrite rearrangement is not likely since the molecule has a plain configuration.

As a model of the fourth group (IV) compounds we selected *N*-methyl-*N*-chlorineamine. Figure 5 represents the scheme of its thermal decomposition process.

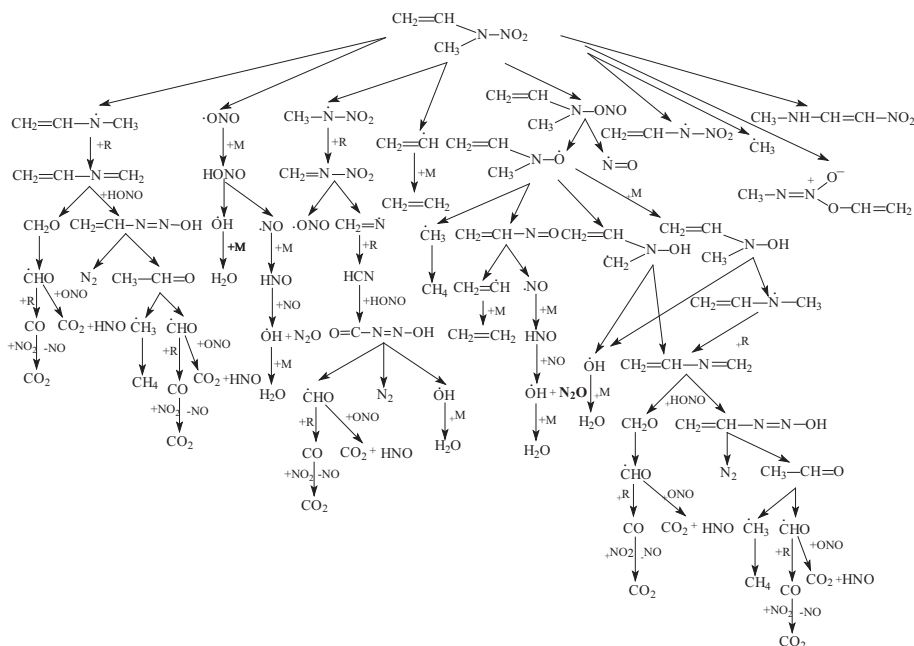


Figure 4. The fragment of *N*-vinyl-*N*-methylnitramine decomposition scheme.

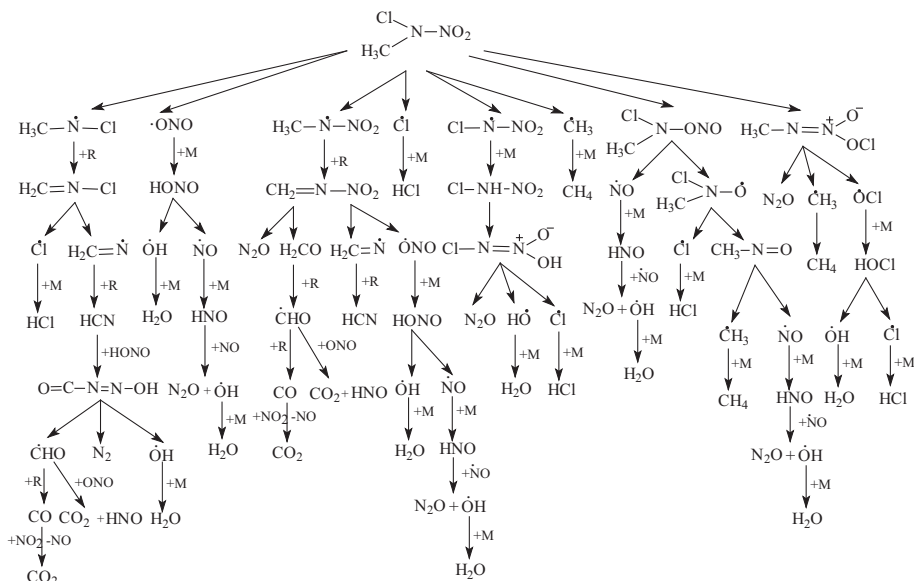


Figure 5. The fragment of *N*-methyl-*N*-chlorinenitramine decomposition scheme.

As one can see the introducing of the heteroatom, directly fixed with the NO₂ group into the *N*-nitramine molecule, makes the competitive channel decomposition rising through the C-X bond dissociation.

For the *N*-methyl-*N*-chlorinenitramine the activation energy values are: 105.8 kJ mol⁻¹ (for N–N bond homolysis), 188.8 kJ mol⁻¹ (for N–Cl bond homolysis), 302.2 kJ mol⁻¹ (for C–N bond homolysis), and 233.8 kJ mol⁻¹ (for the chlorine atom N→O shift).

As a whole, the data obtained is evidence of the radical mechanism of *N*-methyl-*N*-chlorinenitramine decomposition through the N–N bond homolytic cleavage.

Conclusion

Thus, the structural classification of various chemical classes of *N*-nitramines has been developed.

The results of thermolysis mechanisms simulations of the compounds have allowed to predict the whole spectrum of formally possible reactions.

The activation energy calculations of decomposition reactions mark out the thermochemically most preferable ones.

As is shown, the change of the amine atom surroundings has an influence upon the molecular structure that determines the modification of compounds thermostability and makes for the appearance of subsidiary channels of decomposition.

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