Differentiation of C-Nitrocompounds as the Basis for Thermolysis Mechanisms Formalization

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Abstract: Classification of thermolysis mechanisms for C-nitrocompounds has been performed based on empirical data for different classes of chemical compounds. Focus was placed on the functional environment surrounding the nitro-group of interest. Finding specific structural characteristics allowed us to formalize the possible mechanisms of its degradation. The results of subsequent computer generation for decomposition mechanisms of several aliphatic C-nitrocompounds demonstrated a good prediction capability of our methodology for modeling processes of thermolysis in organic compounds.

Keywords: computer simulation, structure-thermal stability relationships, reactions of decay

Introduction

Thermal decomposition of high-energy materials, which, as a rule, represent polyfunctional compounds and decay along different channels of transformations, is a complex multi-step process. However, the most investigations of compounds decomposition add up to the construction of simple hypothetical schemes based on the information about final products obtained and/or on the initial step of decomposition study. But theoretical description of energetic materials thermal decomposition mechanism on today represents an intricate problem which is difficult to formalize, that's why similar investigations are few in number. In

this connection the elaboration of effective approaches to the solution of this problem is extremely important.

It is generally known that the preferable direction of compounds thermal destruction mainly depends on the molecular structure of substances. Our approach is based on structure and compounds decomposition relationships examination and on depending of nitro-group functional surrounding features. The fulfilled differentiation of compounds depend upon molecular structure allowed us to formalize the possible mechanisms of their thermal decomposition. Formalization of these relationships was performed using database on decomposition mechanisms of different chemical classes compounds: aliphatic, alicyclic, aromatic and heteroaromatic C- and N-nitrocompounds.

In present study C-nitrocompounds were the object of our investigation. Depending on nitro-group surrounding it is possible to mark out four types of structures:
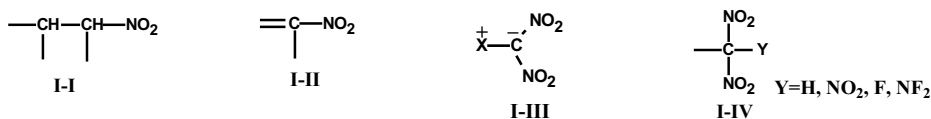
In nitro-derivatives of the group **I-I** with the nitro methyl fragment both nitrous acid elimination and homolytic C-NO$_2$ bond cleavage are possible depending on the temperature of a process [1]. Theoretically, the opportunity of nitro-nitrite rearrangement is not excluded [2]. In condensed phase the decomposition process is possible via *aci*-nitroform [1, 3].

In nitro-derivatives of the group **I-II** (with the nitro methene fragment) C=C double bond in α-position to the nitro group causes the additional (compared with the group **I-I** compounds) possibility of decomposition through 4H-1,2-oxazet-2-oxide cycle [4, 5]. In liquid phase thermolysis of nitro-olefins or in gas phase under high pressures the bimolecular mechanism of decay is possible [4]. For compounds with the methene fragment combined with the nitro group is included in aromatic or heteroaromatic systems there are no examples of nitrous acid elimination or of decomposition process via 4H-1,2-oxazet-2-oxide cycle.

Dinitromethilydes (**I-III**) are characterized by the presence of a semi polar bond between the carbon atom in α-position to nitro-group and the adjacent heteroatom. The structural features of this type compounds exclude the possibility of decomposition via 4H-1,2-oxazet-2-oxide cycle. All rest decomposition channels (typical for compounds **I-I** and **I-II** groups) can take place during thermolysis of **I-III** type compounds. Theoretically, in addition to described above cases it is possible supplementary pathway with the zwitter carbon-heteroatom bond cleavage.

Dinitro-, trinitro-, as well as fluorodinitro and difluoroaminodinitro derivatives have been singled out in the group **I-IV**. Because of the reduced bond strength caused by the steric effects of the nitro-groups of polynitro fragment, these compounds undergo decomposition via homolytic nitro-group elimination. In condensed phase dinitromethyl compounds can decompose via *aci*-nitroform [1, 3].

Methods

Based on the above presented classification for describing of multi step processes for C-nitrocompounds thermodestruction, we elaborated a methodology to assess a computer simulation of the whole mechanisms of thermolysis for different types of nitrocompounds. At the heart of methodology the assumption underlies that reactions can be rated as the competitive existent processes. At that intermediates can be got by different ways and potentially can react with all other species in a separate chemical system. That presentation allows one to perform a whole spectrum of the reactions that can occur in the course of compounds thermal decomposition [6-9].

The chemical reactions of initial substance decay and its interaction with the intermediates of a reactor medium are performed as a set of expert rules [6, 8]. They were formulated using the experimental data on thermolysis mechanism of compounds from different chemical classes. The energetic preferableness of the most probable pathways of compounds decomposition by computer generation obtained is determined on the results of activation energy (E_a) calculations for corresponding elementary reactions of compounds decay process.

The necessary calculations were performed within the framework of density functional theory (DFT) with hybrid potential B3LYP[10] and standard valence-split basis 6-31G*[11] using the GAUSSIAN-98 program package [12] at the computer center of Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences.

Results and Discussion

To estimate the elaborated methodology for generation of compounds **I-I** type decay mechanism we selected nitroetane (1). The choice of the compound occurs to simplicity of this compound structure and on the other hand, the availability of sufficiently detailed experimental and theoretical data of its

mechanism thermolisys and information of final products composition [1, 13].

The generated mechanism of compound **1** thermolysis (the *fragment* of it is presented in Scheme 1) show four possible pathways at the initial step of decomposition: homolytic removal of the nitro group (*channel I*, E_a=56.4 kcal/mol), intramolecular HNO_2 elimination (*channel II,* E_a=45.3 kcal/mol), nitro-nitrite rearrangement (*channel III*, E_a=62.6 kcal/mol), and decay through *aci*-form (*channel IV*, E_a=63.8 kcal/mol).
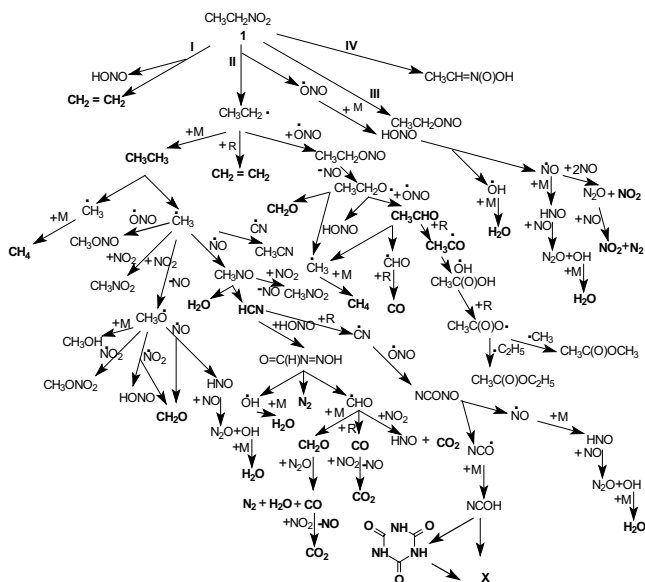
Scheme 1.

* Here and subsequently: M is molecule, R is radical, X is condensed residuum;
The experimentally registered products are set off in bond.

Thermo chemically the most advantageous direction for thermolysis of nitroetane decomposition is the *channel II*, that has the experimental confirmation under temperature below 450 ° C [1, 13]. The competition for this pathway performs *channel I* that is confirmed by the experimental data for the process of compound **1** decomposition at the temperatures higher then 450 °C [1, 13]. The activation barrier for nitro-nitrite rearrangement (*channel III*) is 6.2 kcal/mol higher in comparison with the $C–NO_2$ bond homolytic cleavage barrier (*channel I*). Because of it the possibility for nitroethane decomposition along the *channel III* can not be excluded, although the probability for this pathway of destruction is essentially less in comparison with *channels I* and *II* [2].

Calculated activation barrier for nitroethane intramolecular isomerization into *aci*-nitro form with the 1,3-sigmatrop shift of proton is 63.8 kcal/mol. For gas phase that is the most unfavorable way of compound **1** decomposition. However on the matter /1/ the nitroethane decomposition is possible via *aci*-nitroform (*channel IV*) in gas phase under high pressures, as well as, in condensed phase.

The generated mechanism of nitroetane thermolysis allows one to clarify the formation of all experimentally registered final products [13] of decomposition: C_2H_4, C_2H_6, CH_4, CH_2O, CO, CO_2, H_2O, N_2, NO_2, NO, CH_3CHO, HCN (Scheme 1). Besides, under nitroetane decay the formation of simple products N_2O and HNCO is possible (see Scheme 1). Oxidation of acetaldehyde can result in CH_3COOH rise. Under recombination of the radicals presented in a reaction system the following compounds can be formed as intermediates: CH_3OH, CH_3CN, CH_3NO, CH_3NO_2, CH_3ONO, CH_3ONO_2, $CH_3C(O)OCH_3$, $CH_3C(O)OC_2H_5$. Trimerization of HNCO can result in cyanur acid with the subsequent isomerization of it into thermodynamically more stable isocyanuric acid. However, at the same time, it is necessary to take into account not high probability of trimerization process passing in gas phase.

The simulation of the whole mechanism of decomposition for compounds of the **I-II** group was carried out for nitro ethylene (**2**). The compound (**2**) is the representative of nitro olefins. It is essential to note that the experimental studies for this class of compounds are noticeably less than for above analyzed nitro derivatives of paraffin hydrocarbons (**I-I**).

Thus in [20] as the result of thermolysis process investigation for five substances with the general formula $RCH=CHNO_2$ using gas-liquid chromatography was determined: at the shallow depth of degradation (5-15%) the main organic products of nitro olefins decay are the corresponding alkynes. Besides of it there was proved that at the initial step of α-nitro olefins decay the process proceeds not as radical one but rather as molecular with the activation barrier amounts in the range from 40 to 45 kcal/mol. Based on it as the mechanism of initial step decomposition for these compounds it is logically to assume the HNO_2 elimination. However later fulfilled theoretical (DFT/B3LYP/6-31G*) estimation of activation barriers for reactions [4, 14] that are characteristic for different mechanisms decomposition of one of representatives for this series of compounds (namely, nitro ethylene (**2**)) showed the activation barrier of nitrous acid molecular elimination of (**2**) equal to 58.1 kcal/mol. That is for 12.3 kcal/mol higher than the experimental value (45.8 kcal/mol [20]).

At the same time, according to the results of calculations [4, 14] energy spending for molecular decay of nitro ethylene via 4H-1,2-oxazet-2-oxide cycle

is essentially lower than for HONO elimination and is equal to 48.0 kcal/mol, that shows the good correlation with the experimental value (45.8 kcal/mol).

Generation of possible pathways for the compound **2** decomposition (the *fragment* of it is presented in Scheme 2) gave six probable channels [4, 14] at the initial stage of decay: homolytic cleavage of nitro-group (*channel I*, E_a=67.1 kcal/mol), intramolecular HNO_2 elimination (*channel II,* E_a=58.1 kcal/mol), nitro-nitrite rearrangement (*channel III*, E_a=57.6 kcal/mol), formation of 4H-1,2-oxazet-2-oxide cycle (*channel IV,* E_a=48.0 kcal/mol), 1,4H-shift to *aci*-nitroform (*channel V,* E_a=71.7 kcal/mol), and 1,3H-shift to *aci*-nitroform (*channel VI,* E_a=61.5 kcal/mol).

In accordance with the theoretical estimation [4, 14] of activation barriers at the initial step of nitro ethylene decomposition, the destruction of **2** with the nitro-nitrite regrouping (*channel III*) is thermally more preferable (for 0.5 kcal/mol) than the HNO_2 elimination (*channel II*). In other words, these directions of decomposition at the initial step are approximately equiprobable throughout the energy spending. Thermally the most advantageous pathway is nitro ethylene decomposition along *channel IV*.
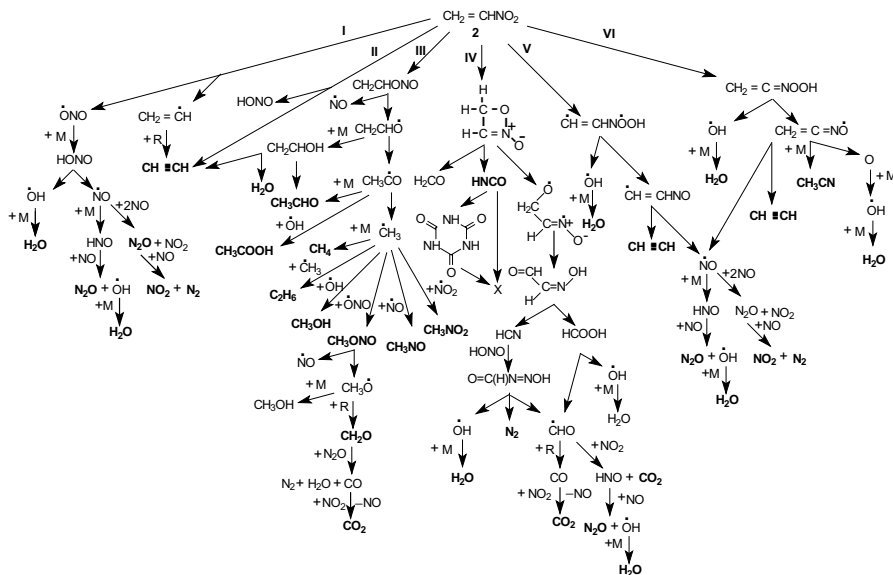
Scheme 2.

As noted above, only acetylene [20] was experimentally notified in decomposition products of compound **2**. As a result of generation for compound **2** thermolysis mechanism the possibility of formation such compounds as:

NO_2, NO, N_2O, N_2, H_2O, CO, CO_2, HCN, $HCOOH$, $HNCO$, CH_4, C_2H_2, C_2H_6, CH_2O, CH_3CHO, CH_3OH, CH_3CN, CH_3NO, CH_3NO_2, CH_3ONO, CH_3COOH, iso-cyanuric acid was shown. At that the formation of experimentally registered acetylene is possible at the initial step of compound **2** decay (*channel II*), as well as at the more deep stages of thermodestruction (*channels I, III, V, VI*).

As experimentally established, aliphatic 1,1-dinitro-, 1,1,1,-trinitro-, 1-fluoro-1,1-dinitro- and 1-difluoroamino-1,1-dinitrometilene derivatives are destructed through homolytical elimination of nitro group [1]. For trinitro-, fluorodinitro- and difluoroaminodinitromethilene derivates this mechanism of decomposition occurs in gas phase, as well as in condensed state [1].

Taking it into account, we simulated the probable mechanism of stage wise destruction for 1,1,1-trinitroetane (**3**). Homolytical separation of the nitro group is the most probable pathway for compound **3** decomposition. In Scheme 3 the *fragment* of the mechanism is presented. Schemes 1 and 2 illustrate the most probable mechanisms of CH_2O and ONO-radical decomposition. The choice of compound **3** as a model of the **I-IV** group compounds is connected with the presence of experimental data on final decomposition products [21] for **3**.

Scheme 3.

As a result of mechanism thermolysis generation of compound **3** the pathways for formation of experimentally registered intermediate and final decomposition products in gas phase [21] were displayed: N_2, N_2O, NO, NO_2, CO, CO_2, CH_3CN, CH_3NO_2, CH_3OH, CH_3ONO_2, CH_3ONO, CH_3COOH, CH_3COOCH_3, CH_3NO, HCN, H_2O. It was shown that in addition to above-enumerated compounds it is possible a formation of the set of other substances ($HNCO$, CH_2O and acetone).

Thus the getting of the whole set of experimentally registered products as a result of computer modeling for the process of compound **3** decay is evidence of a good predictable capability of elaborated methodology and its application for simulation of thermodecomposition mechanisms for compounds with the polynitromethylene substitutes.

Calculations of activation barriers for the elementary reactions at the subsequent steps of simulated process of decay up to the final products for studied nitrocompounds will be the subject for our further investigations.

Conclusion

On the basis of experimental data on mechanisms of different chemical classes organic compounds decomposition the differentiation of C-nitro compounds depend upon peculiarities of functional surrounding of the nitro group was carried out.

The possible decomposition mechanisms are formalized depending on the structure of substances.

As a result of computer modeling of possible pathways for thermodecomposition of nitro ethane, nitro ethylene and 1,1,1-thrinitroetane the whole spectrum of reactions formally possible during thermodestruction of studied compounds was obtained.

The high prediction capability of elaborated methodology to simulate C-nitro compounds decomposition mechanisms was demonstrated.

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