Simulation of *trans*-1,4,5,8-Tetranitrodecahydro-pyrazino[2,3-b]pyrazine Decomposition Mechanism

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Abstract: On the basis of the earlier methodology developed for generation of thermal decomposition mechanisms for organic compounds, computer simulation of *trans*-1,4,5,8-tetranitrodecahydro-pyrazino[2,3-*b*]pyrazine (TNAD) degradation is performed. The probable pathways of this decomposition are examined. The activation energies of reactions at the initial step of TNAD degradation are calculated using the B3LYP/6-31G* level of the density functional theory. The results are compared with the experimental data. The preferable pathway of TNAD thermal decomposition is revealed.

Keywords: computer simulation, pathways of degradation, activation energy calculations

Introduction

As is known, there are numerous effective high-energy compounds among nitramines. Cyclic nitramines evoke special interest in this respect; for example, we can mention 1,3,5-trinitro-1,3,5-triazinane (RDX), 1,3,5,7-tetranitro-1,3,5,7-

tetraazacyclooctane (HMX), and 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaaza tetracyclo[5.5.0.0^{5,9}.0^{3,11}]dodecane (CL-20). T*rans*-1,4,5,8-tetranitrodecahydro-pyrazino[2,3-*b*]pyrazine (TNAD), a comparatively little known compound, also belongs to this group.

In this study, we investigated the thermal stability of TNAD. Such stability is one of the most important characteristics of high-energy compounds, determined by the mechanism of their thermolysis [1]. For this purpose, we performed computer simulation of the mechanism of TNAD thermal decomposition. Literature data on this process are lacking: in [2] the experimental activation parameters for TNAD decomposition in gas phase were studied (E_a=156.5 kJ·mol^{-1}, log(A/s^{-1}) = 13.8). These results are essentially different from kinetic parameters at the initial step of TNAD solid-phase decay: E_a=196.0 kJ·mol^{-1}, log(A/s^{-1}) = 17.5 [3]; E_a=209.1 kJ·mol^{-1}, log(A/s^{-1}) = 18.8 [4]; and E_a=101.6 kJ·mol^{-1}, log(A/s^{-1}) = 17.5 [5].

We simulated the mechanism of TNAD decomposition from the initial step to deeper stages of thermolysis. Further, we calculated the activation energies for reactions that are possible in the process of TNAD degradation and, as a result, revealed the most preferable pathway of *trans*-1,4,5,8-tetranitrodecahydro-pyrazino[2,3-*b*]pyrazine decomposition.

Methods

Using the experimental data and reviewing the thermal decomposition mechanisms for high-energy compounds of various chemical classes, we formulated the empirical rules for simulating the possible reactions in the process of thermolysis. These rules were formalized in so-called transformation generators. Actually, they form a set of expert rules which structure is based on the criteria for selection of thermal decomposition reactions. Using these rules, Recombination Reaction Networks (RRNs) are generated. Such RRNs list the initial compounds and intermediate structures appearing during thermal decomposition process. The methodology used for simulation of the possible thermal decomposition pathways of organic compounds is presented in more detail in [6].

After computer simulation of degradation mechanisms, the preferable decomposition pathways were estimated on the basis of calculations using the density functional theory (DFT) approach with the B3LYP hybrid functional [7] and the conventional 6-31G* split-valence basis set [8]. All calculations were performed using the GAUSSIAN-98 program package [9] at the Computational Center of Zelinskii Institute of Organic Chemistry, Russian Academy of Sciences.

Results and Discussion

Scheme 1 presents the possible pathways for the initial step of *trans*-1,4,5,8-tetranitrodecahydro-pyrazino[2,3-*b*]pyrazine (TNAD) (compound **1**) thermal decomposition. Activation energy calculations show that free-radical detachment of the nitro group requires 160.1 kJ·mol^{-1} (*pathway 1*). The energy corresponding to HNO$_2$ elimination (*pathway 2*) is 261.3 kJ·mol^{-1}. We failed to localize the transition state of HNO$_2$ elimination along *pathway 3*. However, one can assume that the activation energy for the reaction along this route will be comparable to the activation energy of the reaction occurring along *pathway 2*. We also failed to localize the transition state of the nitro-nitrite rearrangement, but, as is shown in [1], the nitro-nitrite rearrangement is energetically unfavorable for nitramines (*pathway 4*).

The energies estimated for homolytic cleavage of the C–N bond (*pathways 5, 6*) are presented in [6]. The resultant energy values are 376-418 kJ·mol^{-1} and a fact that allows us to characterize this process as energetically unfavorable for the initial stage of TNAD thermolysis.

Thus, on the basis of the above data, one can conclude that free-radical detachment of the nitro group (*pathway 1*) is energetically favorable and, consequently, this process is the most likely initial step in thermal decomposition of *trans*-1,4,5,8-tetranitrodecahydro-pyrazino[2,3-*b*]pyrazine.
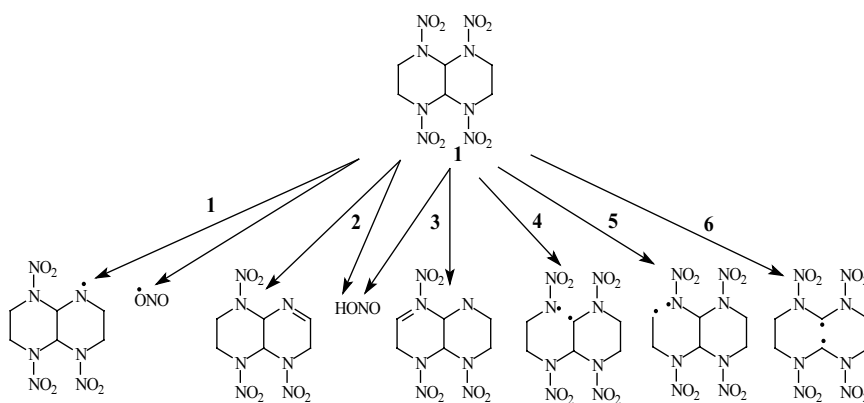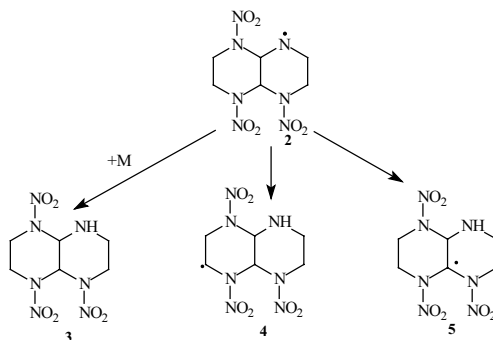

Scheme 1.

Then we performed computer generation of TNAD thermal decomposition along *pathway 1* as the most favorable one. Schemes 2-6 demonstrate the chains of intermediates thus generated and the possible routes of their transformations.

Scheme 2 illustrates the initial step of TNAD thermal decomposition and subsequent transformation of the NO_2 radical. As follows from this scheme, the final products of NO_2 transformation are N_2O and H_2O.
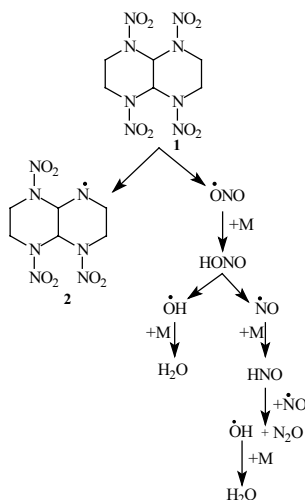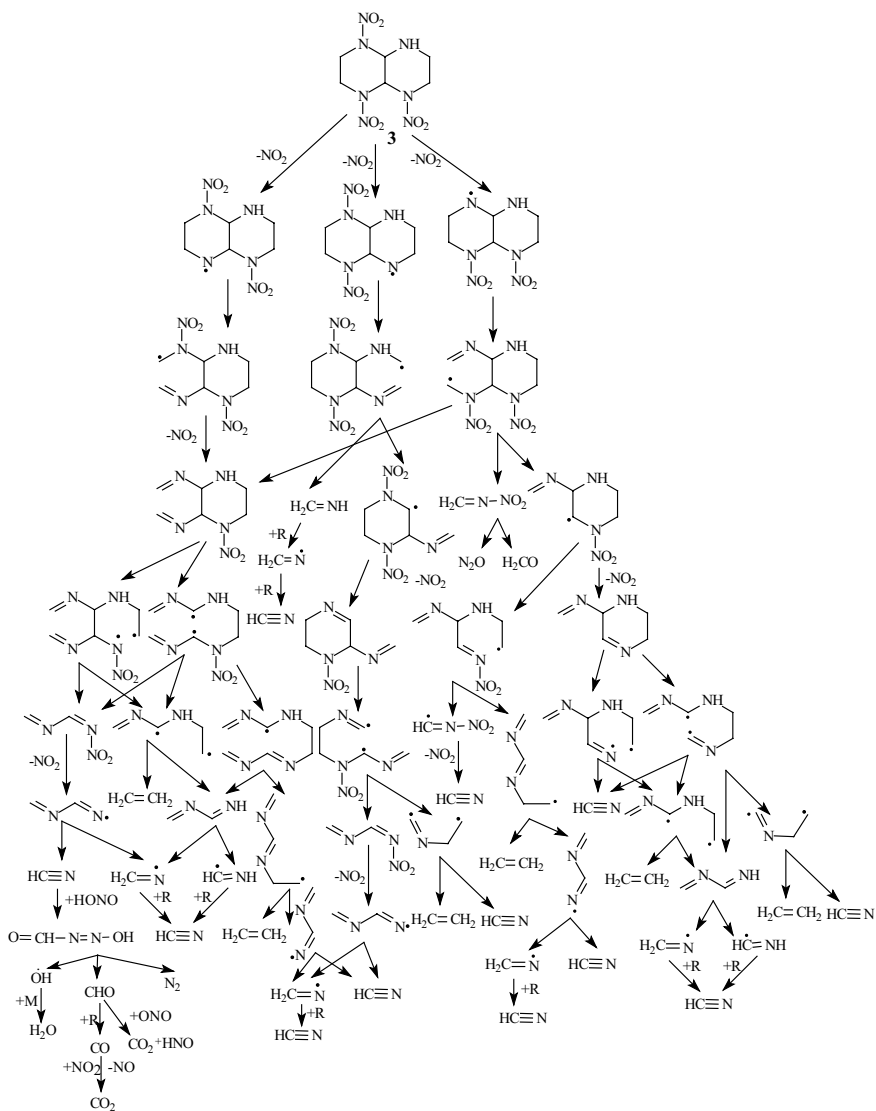

Scheme 2.

Scheme 3 presents some versions of transformations for radical **2**, which is formed at the initial step of TNAD thermal decomposition. They indicate the possibility of interaction between **2** and the initial molecule with formation of compound **3**, as well as intramolecular transfer of the free-radical center with formation of radicals **4** and **5**.
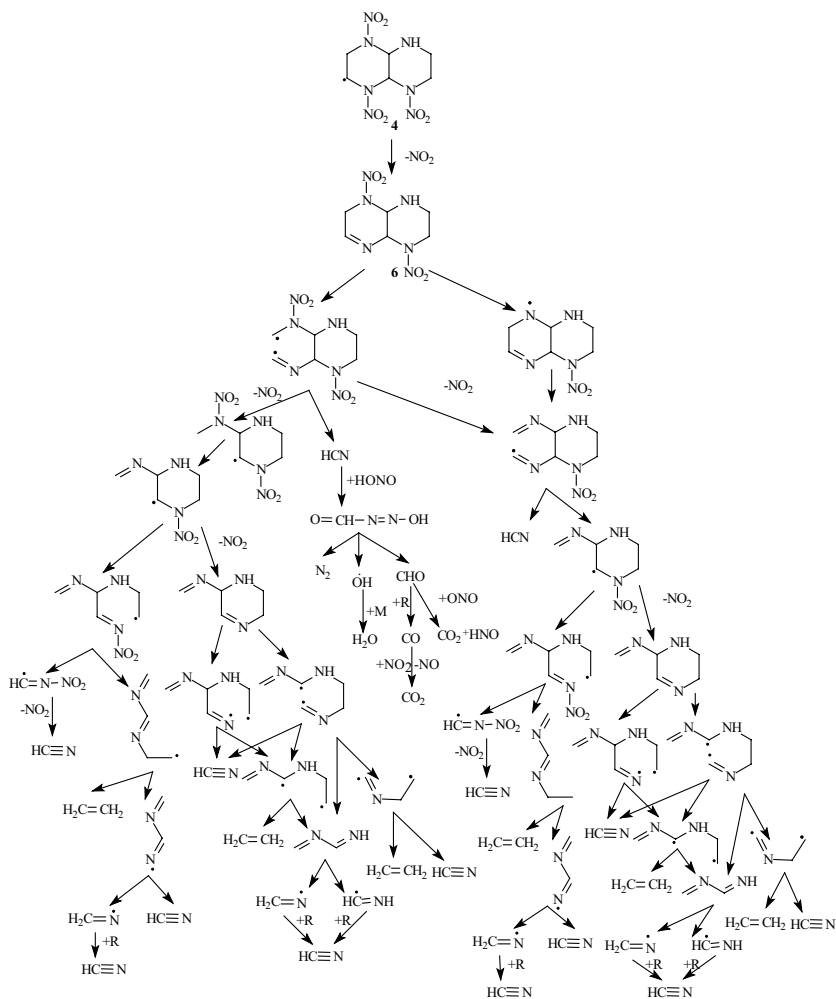

Scheme 3.

Decomposition of compound **3** (Scheme 4) occurs via homolytic detachment of nitro group. Further, one of six-membered cycles is opened. TNAD thermolysis

along this pathway results in H_2O, CO_2, CO, N_2O, CH_2O, N_2, HCN, and C_2H_4. It is essential to note that in [2] the authors performed the analysis of gas-final products for TNAD decay using IR-spectroscopy and revealed the presence of CO_2, CO, HCN, N_2O, NO_2 and NO.

Scheme 4.

Schemes 5 and 6 illustrate stepwise decomposition of radicals **4** and **5**. At the initial stage of this process, free-radical detachment of the nitro group leads to formation of compounds **6** (Scheme 5), **7** and **8** (Scheme 6).
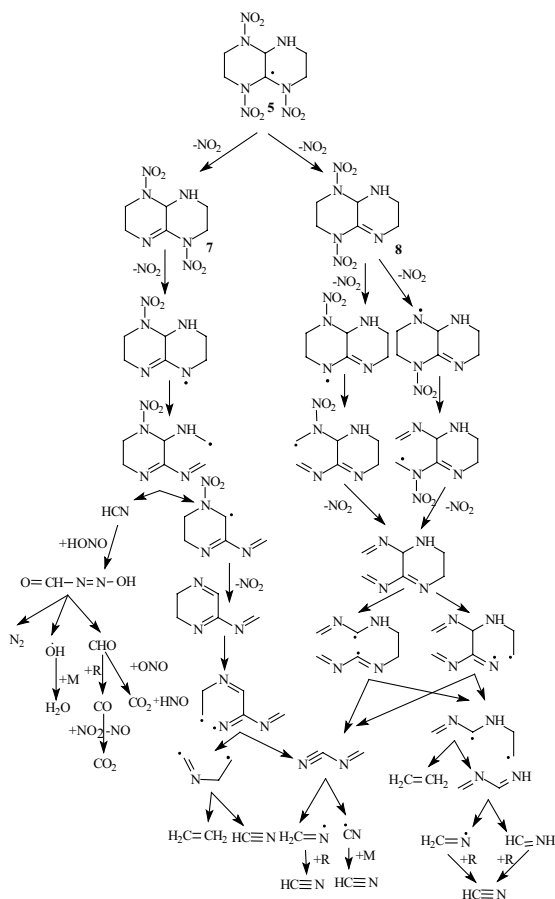

Scheme 5.

Subsequent decomposition of compound **6** may take place along two pathways: free-radical detachment of the nitro group and ring opening.

Compounds **7** and **8** decompose with nitro group detachment at the first stage and cycle opening at the next one. Degradation of these radicals results in the formation of final products: H_2O, CO_2, CO, N_2, HCN, and C_2H_4. As is

seen, N_2O and CH_2O (earlier obtained in computer simulation of the thermal degradation mechanism of compound **3**) are absent among the decomposition products of **4** and **5**.

Scheme 6.

Let us compare our results concerning the mechanism of TNAD thermal degradation with the published data on thermal decomposition of other cyclic nitramines: RDX and HMX.

As is pointed out in [10], reactions of RDX and HMX decomposition obey the same rules. Thermal degradation of these compounds starts with homolytic detachment of the nitro group. The set of the final products of RDX and HMX thermolysis in the gaseous phase almost entirely consists of simple compounds:

HCN, N_2O, H_2O, NO_2, NO, CO_2, CO, CH_2O, and N_2 [11-13]. It is significant that thermal degradation of TNAD also leads to the same set of simple final products. However, in addition to all the above products, thermolysis of compound **1** (Schemes 4-6) can also lead to the formation of ethylene.

Conclusion

The thermal decomposition mechanisms of *trans*-1,4,5,8-tetranitrodecahydro-pyrazino[2,3-*b*]pyrazine (TNAD) were generated, and the activation energies corresponding to possible reactions at the initial step of its degradation were calculated using quantum-chemical techniques. The most favorable way of TNAD thermolysis was revealed: it proceeds via homolytic detachment of the nitro group. The calculated activation energy of NO_2 radical elimination is 160.1 kJ·mol^{-1} (*pathway 1*) and does agree with the experimental data [2] in gas phase (156.5 kJ·mol^{-1}). The proposed mechanisms of TNAD decay illuminate the formation of such products as CO_2, NO_2, NO, N_2O, CO, and HCN, which were revealed experimentally too [2]. Besides we suppose the possibility of additional final products formation: H_2O, CH_2O, N_2, and C_2H_4.

The thermochemical preference of simulated secondary reactions within the TNAD decomposition mechanism will be analyzed in our further publications.

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