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Research paper

On the Mechanism of Thermal Decomposition of 1,1-Diamino-2,2-dinitroethene (FOX-7) and its Cyclic Derivatives

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Abstract: The thermal decomposition of 1,1-diamino-2,2-dinitroethene (**I**) and its cyclic derivatives 2-(dinitromethylene)-1,3-diazacyclopentane (**II**), 2-(dinitromethylene)-1,3-diazacyclohexane (**III**) and 2-(dinitromethylene)-1,3-diazacycloheptane (**IV**) was investigated by quantum chemistry methods (PBE/cc-pVDZ), as well as DSC and TG. According to both the theoretical and experimental data, the thermal stability of compounds **I-IV** increases in the sequence **IV** < **I** ≈ **III** < **II**.

Keywords: quantum-chemical calculations, FOX-7, thermal decomposition, DSC, TG

1 Introduction

1,1-Diamino-2,2-dinitroethene, C₂H₄N₄O₄ (FOX-7, Figure 1, compound **I**), is a stable high-energy compound with low friction and impact sensitivity and a high activation barrier to detonation [1-5]. In this connection, derivatives of FOX-7 are of interest as potential advanced high-energy materials, as well as models for studying the functional properties of compounds

of this class. FOX-7 is characterized by a number of specific properties, including polymorphism (α -, β -, γ - and δ -modifications are known: [6-9]), unusual kinetics of polymorphic transitions and a sharp deceleration of thermal decomposition as a result of the $\gamma \rightarrow \delta$ transformation [8, 9].

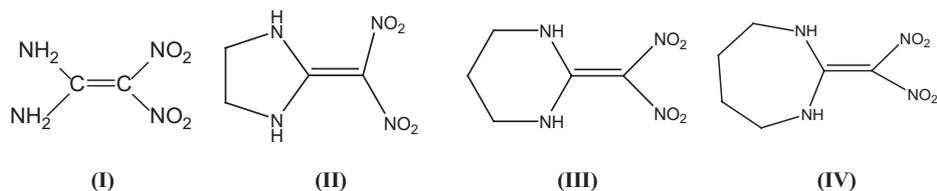


Figure 1. Molecular structure of FOX-7 (I) and its cyclic analogs (II)-(IV)

Some derivatives of FOX-7 also exhibit unusual structural features. In particular, in the crystals of compounds **III** and **IV**, the fragment $\text{N}_2\text{C}=\text{CN}_2$ is non-planar (with internal rotation angles equal to 89.0° and 79.3° , respectively), despite the existence of the formal double $\text{C}=\text{C}$ bond and the fact that planarity should be reinforced by intramolecular hydrogen bonds between the amino and nitro groups [10].

The detailed mechanism of the primary stage of FOX-7 decomposition is still debatable. In particular, it was supposed [11] that in the limiting stage of the reaction, detachment of a nitro group or a nitro-nitrite rearrangement followed by the elimination of NO may occur. However these assumptions contradict the experimentally determined activation energy (E_a) values for the thermal decomposition of FOX-7, which are reported to be 191 [12], 198.3 [13], and 197 kJ/mol [14].

It should be noted that the strength of a $\text{C}-\text{NO}_2$ bond exceeds 290 kJ/mol and that the activation energy of a nitro-nitrite isomerization followed by removal of NO is about 250 kJ/mol [11]. Consequently, the corresponding channels of FOX-7 decomposition (*i.e.* cleavage of the $\text{C}-\text{NO}_2$ bond and nitro-nitrite isomerization) are questionable. Recently, the above-mentioned reaction paths were analyzed at a high level of calculation and the following new ones were proposed [15] (Figure 2).

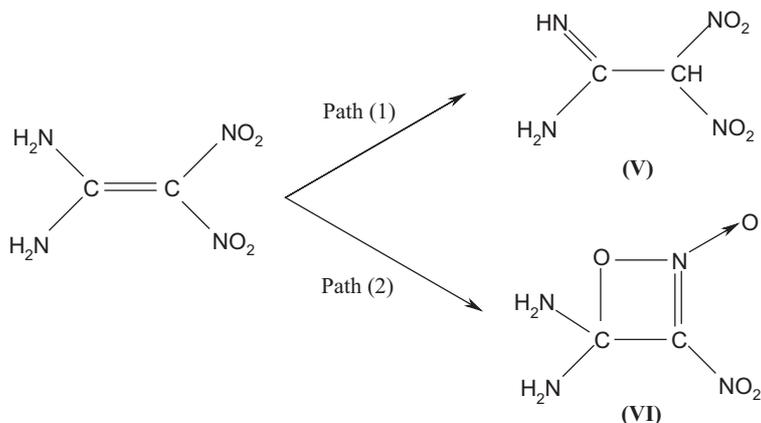


Figure 2. New reaction paths of FOX-7 decomposition

The activation energies of the processes leading to the formation of compounds **V** and **VI** were 205 and 226 kJ/mol, respectively. The first value is in good agreement with the experimental data.

Finally, another mechanism for the primary stage of thermolysis, through transfer of hydrogen from an amino group to a nitro group was proposed [13]. Theoretical estimates have shown that this stage of the reaction is accompanied by a simultaneous conformational transition, with the formation of product **VII** (Figure 3).

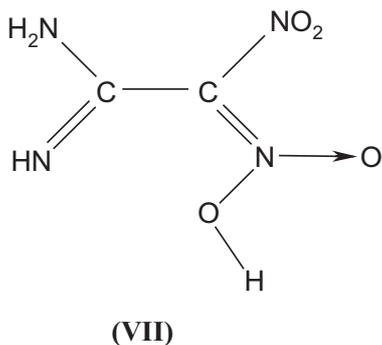


Figure 3. Molecular structure of compound **VII**

This last mechanism has the lowest activation energy of all those that have been considered: 108 [15] and 124 kJ/mol [16]. However, product **VII** is an intermediate and its further transformations lead to a total activation energy *via* this channel of 284 kJ/mol [15]. On the other hand, it was noted in [16] that

product **VII** could serve as a catalyst for the thermal conversion of FOX-7, but this issue has not yet been studied.

The reactions that FOX-7 molecules can enter into have been systematized in 2 reviews [17, 18], the second of which concluded that during the decomposition of aminonitroethylenes, the most likely channel of gas-phase decomposition is the formation of substituted oxazetes (such as **VI**, Figure 2) at the limiting stage. Along with this, based on the results of molecular dynamics and quantum calculations, it was shown [19, 20] that NO₂ elimination reactions, as well as intra- and inter-molecular hydrogen transfer, could play an important role in the thermal stability of FOX-7. The channel involving inter-molecular hydrogen transfer is energetically more favorable under static conditions, but cleavage of N–O and C–NO₂ bonds could also become dominant in primary reactions due to significant molecular distortions at high temperatures [20].

In the present paper we provide data on the thermal stability of FOX-7 and its cyclic derivatives possessing different numbers of methylene groups. A comparison of the kinetic patterns in this series of similar compounds allowed us to draw conclusions on the preferred reaction mechanism, which would be difficult to do on the basis of the kinetic data for FOX-7 alone.

2 Experimental

FOX-7 was synthesized as described in [21]. Compounds **II**, **III** and **IV** were synthesized following the methods described in [22]. Thermal decomposition of FOX-7 and the carbocyclic homologues **II**, **III** and **IV** was studied by thermal analysis. The DSC and TG measurements were performed using a NETZSCH STA 409C Luxx synchronous thermal analyzer (STA) in the temperature range 303–673 K under pure argon at a flow rate of 40 cm³/min, a sample weight of 4.0–7.6 mg, and at heating rates varying from 1 to 15 K/min.

3 Computational Methods

The calculations were performed on a multiprocessor cluster at the computational center of the Institute of Problems of Chemical Physics RAS and on an eight-core AMD computer using the GAUSSIAN 09 software [23]. All calculations were performed using the cc-pVDZ basis set and the hybrid method based on the PBE functional. This functional uses 25% exchange and 75% correlation weighting, and is known in the literature as PBE0 [24]. The choice of this level

of calculation was due to the fact that it reproduces quite well the results obtained at a much higher level of calculation and at the same time is not so resource-expensive. The last statement is based on the findings of [14], where it was shown that using the selected method gives a qualitatively correct result with an error in energy below 9 kJ/mol (*i.e.* no more than 2 kcal/mol).

This resource-saving calculation level was applied taking into account the fact that it satisfactorily reproduces the results obtained at a much higher level of calculation. To ensure the latter, we have implemented a number of calculations similar to those that have been done in [15]. The results are listed in Table 1. Thus, using the selected computation level gives us an almost correct result, with an error of 2.7-10.9 kJ/mol (*i.e.* below 2.6 kcal/mol).

Table 1. Comparison of calculated results

Parameter	This work	Ref. [15]
C-NO ₂ bond dissociation energy [kJ/mol]	300.0	306.0
E_a nitro-nitrite isomerization [kJ/mol]	262.8	251.9
E_a of V formation [kJ/mol]	199.8	202.5
E_a of VI formation [kJ/mol]	128.4	120.1

At all stationary points of the potential energy surface (PES), *i.e.* initial molecules and transition states, the frequencies of normal vibrations were calculated. The reliability of the found states was checked by the absence of imaginary frequencies in the minima and by the presence of only one imaginary frequency in the transition states (TS). Additionally, these states were controlled by scanning the internal coordinates using the IRC procedure from the TS to the initial and final states. For stationary PES points, thermodynamic corrections (enthalpy, entropy, and free energy) were calculated using the MOLTRAN software package [25] and the results of quantum calculations. The values of bond strengths and activation energy were determined taking into account the thermodynamic corrections.

4 Results and Discussion

Table 2 lists the results of quantum calculations of some parameters of the initial molecules, as well as the activation energies E_a and the thermal effects (ΔH) of the reactions proceeding through channels 1 (Figure 2, **V**) and 3 (Figure 3, **VII**). We have not yet considered channel 2 (Figure 2, **VI**), since its activation energy is much higher, and the product is relatively stable.

The TS structure corresponds to that described in [15], therefore, to save space, we do not present it here.

Table 2. Calculated data for compounds **I-IV**

Molecule	C=C bond length [Å]	C-NO ₂ bond strength [kJ/mol]	Transition of H to C		Transition of H to NO ₂		C=C bond length in crystal [Å]*
			E _a [kJ/mol]	ΔH [kJ/mol]	E _a [kJ/mol]	ΔH [kJ/mol]	
I	1.4248	300.0	199.8	57.8	131.3	123.6	1.434
II	1.4115	306.0	229.0	63.5	140.3	123.3	1.400, 1.439**
III	1.4401	300.3	193.0	58.6	130.2	126.6	1.473
IV	1.4361	299.5	183.6	61.1	136.8	127.9	1.473

* Data obtained by means of single-crystal X-ray structural analysis [10];

** For two nonequivalent molecules in the crystal structure

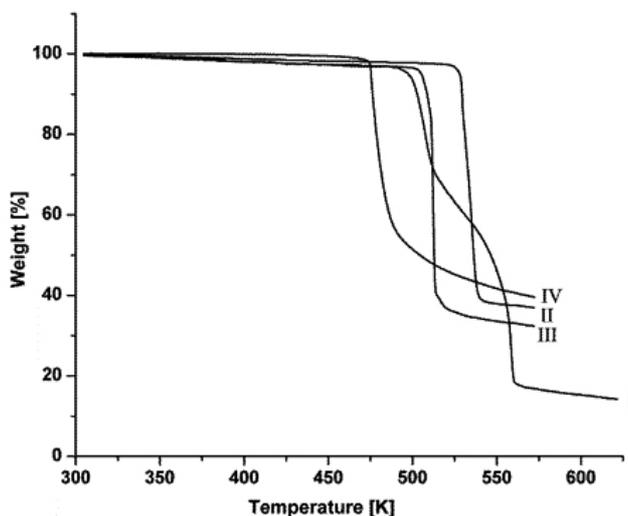
The length of the nominal double C=C bond reflects its real bond order, which may be less than 2 as a result of conjugation with the adjacent C-N bonds. Comparison of the calculation results with data on C=C bond lengths obtained by means of single-crystal X-ray structural analysis data shows that they correspond qualitatively to each other: compounds **I** and **II** have much shorter C=C bonds than **III** and **IV**.

In the reaction proceeding *via* formation of compounds like **VII**, the activation energy for all of the compounds is 130-140 kJ/mol, and the thermal effect is 123-128 kJ/mol. This means that the equilibria between **I-IV** and the products like **VII** are strongly shifted towards the starting compounds. Therefore, the contribution of this channel to the total decomposition rate is negligible despite the low E_a. Consequently, comparing the relative reactivities of compounds **I-IV** in a reaction through channel 3 is meaningless.

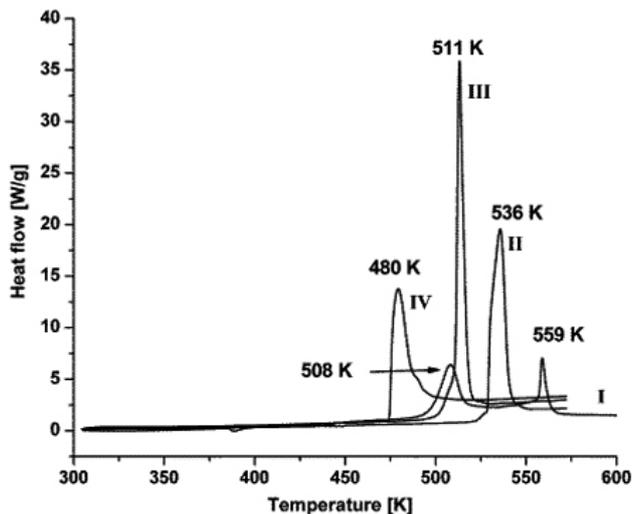
A different situation occurs when analyzing the reaction proceeding *via* channel 1. The calculated E_a of this process is in the range 183-200 kJ/mol, and the thermal effect is ~60 kJ/mol. Thus the formation of the product **V** in significant quantities and its further transformations are quite possible. The activation energy for hydrogen transfer to a carbon atom is maximal for compound **II** and is minimal for **IV**. The difference between these values, 46 kJ/mol, is very large. Based on the data obtained for channel 1, it may be expected that of the 4 compounds under consideration, **II** is the most stable, and **IV** has the lowest stability.

Unfortunately, the E_a values could not be determined correctly from available kinetic data: as noted in [14], the kinetics of thermal decomposition of **I-IV** is too complex and cannot be described by a simple kinetic law. The Arrhenius parameters (including the overrated and understated pre-exponential factors of $10^{31.3}$, $10^{6.8}$ and $10^{19.2} \text{ s}^{-1}$), found by transforming the kinetic curves to a single one or by the maximum rate time [14], do not correspond to an elementary stage of the reaction and are actually effective values. For this reason, in this work the comparison of the thermal stabilities of compounds **I-IV** was made based on the nonisothermal data.

Experimental thermal data for the compounds **I-IV** are shown in Figure 4. The sequence of temperatures at which the maximum decomposition rates are observed is maintained with varying heating rates. The presence of a second (high-temperature) maximum on the DSC curve of **I** and two inflection points on the TG curve of **I** are due to the fact that decomposition of FOX-7 below 500 K proceeds in the gas phase (as a result of sublimation) and is accompanied by a parallel polymorphic transition into the thermally more stable and non-volatile δ -modification, which decomposes in a solid-state reaction above 540 K. This phenomenon has been discussed in detail elsewhere [9]. Consequently, only the low-temperature decomposition stage of **I** (below 500 K) is to be compared with the decomposition of compounds **II-IV**, all of which are volatile and decompose predominantly in the gas phase [14].



(a)



(b)

Figure 4. TG (a) and DSC (b) curves of compounds **I-IV** at a heating rate of 5 K/min

According to the experimental data, the thermal stability of compounds **I-IV** varies in the sequence $\text{IV} < \text{I} \approx \text{III} < \text{II}$, which is in good agreement with the calculated data, according to which the stability increases in the sequence $\text{IV} < \text{III} < \text{I} < \text{II}$. These data are in agreement with the data of [14], according to which the thermal stability increases in the sequence $\text{IV} < \text{III} < \text{II}$ (data for **I** given in the cited reference cannot be used for comparison because they correspond to the decomposition of the non-volatile δ -modification).

The theoretical estimates correspond to the results of thermal measurements, not only qualitatively but also at a semiquantitative level. It is possible to estimate the difference in the decomposition temperatures of compounds **I-IV** based on the data from quantum calculations under the assumption that decomposition is determined by reaction according to channel 1 and that all of the differences in thermal stabilities are due to the differences in the activation energies. Let us also suppose that the maximum heat release rate is reached for all compounds with the same value of the rate constant of the limiting stage. For compound **I**, this value is achieved at 508 K (Figure 4(b)). The same rate constant value will be reached at 542, 502 and 492 K for the compounds **II**, **III** and **IV**, respectively. These theoretical estimates fit the experimental data quite well. Moreover, a comparison of the calculated E_a values with the experimental ones for FOX-7, which are in the range 191-198 kJ/mol [12-14] confirms

the conclusion that hydrogen transfer to a carbon atom should be considered as the most probable channel of thermal decomposition. The calculated E_a values for compounds **II**, **III** and **IV** indicate that this mechanism may be common for related compounds with more complex structures, which would be important from the viewpoint of practical applications.

Within the framework of the reaction mechanism under consideration, the thermal stability of the homologues **II-IV** depends on several factors. In these molecules, for the formation of the TS during the transfer of hydrogen from the amino group to carbon, it is necessary to rotate the plane of the amino groups relative to the plane of the nitro groups by about 90° , since in the initial states these planes are coplanar. This means that the internal rotation barrier contributes to the activation energy, which in turn is determined by the C=C bond order. The latter value can be indirectly estimated from Table 2 based on the length of this bond. As may be seen, this parameter varies in line with the activation energy and experimental data. Another factor determining the thermal stability is the distance over which the H atom is transferred. Due to the rigid structure of the cyclic compounds, this distance differs significantly within the series of homologues: 2.64 Å in **II**, 2.52 Å in **I**, 2.49 Å in **III** and 2.46 Å in **IV**. Thus, this distance changes in the same sequence as the activation energy and experimental data.

5 Conclusions

Quantum calculations as well as experimental data show that the most probable channel of the decomposition of FOX-7 and its carbocyclic homologues is channel 1, the limiting stage of which is hydrogen transfer to a carbon atom. This conclusion agrees well with the previous experimental and theoretical data on the thermal stability of these compounds [15-20].

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