The decay mechanism of 1,1,2,2-tetranitroxyethane according to theoretical calculations

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Abstract. The geometric structure was determined and the mechanisms of thermal decomposition were studied using the quantum-chemical method of the density functional B3LYP/6-31+G (2df, p) for 1,1,2,2-tetranitroxyethane and structurally similar 1,2-dinitroxyethane and nitroxyethane molecules: O-N homolytic decomposition, α-elimination of HNO₂ and various variants of β-elimination of HNO₃. It is established that the radical mechanism is the main channel for the gas-phase decomposition of the studied compounds.

1. Introduction

Organic nitrates are produced on an industrial scale and are used as explosives, drugs, and also in various composite materials [1]. The possibility of spontaneous decomposition at moderate temperatures makes it necessary to study the kinetics and mechanism of thermal decomposition of these compounds [2]. Experimental data obtained in a gaseous state are of considerable interest to understand the features of the influence of the molecular structure on the Arrhenius parameters of the primary act of the thermal decomposition of organic nitrates. These results are also important for discussing the general laws of the decay of various classes of nitro compounds, estimating the dissociation energies of chemical bonds, the enthalpies of the formation of organic radicals, and also developing the theory of monomolecular reactions. Unfortunately, the available kinetic data on the gas-phase decomposition of organic nitrates are scarce and are not of high accuracy [2–4]. In some cases, differences in the values of the activation energy of the reaction in the works of various authors are at the level of changes in these quantities in the series.

Important additional information on the molecular structure features and mechanisms of thermal decomposition of organic nitrates can be obtained using theoretical research methods [2, 5–7]. The calculation results can significantly increase the array of information on the geometry, thermochemical characteristics, dissociation energies of O-NO₂ (D(O-NO₂)) bonds in molecules.

It is known that a homolytic decomposition of this bond is the primary act of thermal decomposition of organic nitrates [2–4]. The authors of this report paid considerable attention to the theoretical study of alternative nonradical mechanisms of thermal decomposition of organic nitrates [4–6], including for compounds having several nitrate groups at one carbon atom. There was no interest in studying such compounds for a long time: it was believed that it was very difficult to obtain them, and it was even...
more difficult to study the basic properties and kinetics of thermal decomposition due to low chemical resistance.

In this publication, we consider the molecular structure and thermal decomposition mechanism of 1,1,2,2-tetranitroxyethane (I), in which each carbon atom has two nitrate groups. In [8], the synthesis of compound I was described and its most important characteristics were presented, including information on the main geometric parameters of the molecule in the crystalline state. In this regard, a theoretical study of the molecular structure of free molecules and the thermal decomposition mechanism of this very interesting compound is currently relevant.

2. Calculation methods
The calculations were carried out using the B3LYP/6-31+G (2df, p) method. It was previously shown that such a combination of the method and the basis allows obtaining reliable, experimentally consistent estimates of the barriers of monomolecular decomposition reactions for various classes of C-, N-, O-nitro compounds [9–15]. In some cases, an additional study was carried out using the method B3PW91/6-311++G (2df, p). In addition to compound I, reaction barriers of structurally similar compounds of 1,2-dinitroxyethane (II) and nitroxyethane (III) were evaluated. Structures found on the surface of potential energy were identified as transition states (TS) by the presence of one negative eigenvalue of the Hessian matrix, and their conformity to the studied processes was proved by descent from TS to the starting compounds and reaction products.

3. Results
Due to the possibility of rotation of functional groups around C—C, C—O, O—NO₂ bonds, the starting compounds have several conformers differing in energy up to 4 kJ/mol. The issue of conformational transitions in organic nitrates is rather complicated, requires special consideration, and will not be discussed in this paper. For comparability of the results, we calculated all the reaction barriers given below with respect to the conformers of compounds I, II, and III corresponding to the minimum energy (this energy is taken as zero). These data will be further presented in the text. The conformers corresponding to the directly discussed reactions are obtained from the most low-energy structure of the compounds by rotation of the O-NO₂ groups around the C-O bonds. The maximum barriers of such rotation lie in the range of 35–40 kJ/mol. For reference, the values of the activation and reaction enthalpies relative to the conformer of the compound directly involved in the discussion are indicated in parentheses.

We have studied the basic mechanisms of radical decay:
1. homolytic decomposition of O-NO₂:

\[
(R^{10})(R^{11})C(H)-C(H)(R^8)O-NO₂ \rightarrow (R)(R')C(H)-C(H)(R'')O^* + ^*NO₂
\]  

2. homolytic decomposition of C-ONO₂:

\[
(R^{10})(R^{11})C(H)-C(H)(R^8)O-NO₂ \rightarrow (R)(R')C(H)-C(H)(R'')* + ^*O-NO₂
\]  

as well as non-radical processes:
3. α- elimination of HNO₂ flowing through a five-membered transition state:
4. two variants of elimination of HNO₃ flowing through six- and four-membered transition states:

\[
\text{TS2} \quad \text{TS3}
\]

where \( R^8 = R^{10} = R^{11} = \text{ONO}_2 \) – are for the compound I; \( R^8 = R^{10} = \text{H}, R^{11} = \text{ONO}_2 \) – are for the compound II; \( R^8 = R^{10} = R^{11} = \text{H} \) are for the compound III.

The geometric parameters of the reaction center of molecules and transition states, as well as the barriers of the studied reactions of nonradical decomposition are presented in Table 1.

Geometrical parameters were obtained close to those given in [8] for a crystal for optimal conformation of compound I. The hydrogen atoms are in a trans position to each other according to the calculation in the optimal conformation. Two nitrate groups are located in the same plane as the hydrogen atom, the other two are slightly rotated. The main geometric parameters are shown in figure 1.

According to the calculation, \( \Delta H^0_{\text{fK}} \) is \(-295.4 \text{ kJ/mol}, \Delta H^2_{\text{fK}} \) is \(-321.8 \text{ kJ/mol}. \) \( \Delta f(\text{O-NO}_2) \) for two geometrical parameters of nitrate groups that differ in values, respectively, is 120.3 kJ/mol (the nitro group is in the same plane as the hydrogen atom) and 122.1 kJ/mol (the nitro group is slightly rotated).

It was not possible to evaluate the dissociation energies of the C-ONO₂ and C-C bonds in compound I, since the radicals formed during bond decomposition are not localized, but decay on NO₂ and HC(O)ONO₂.

**Table 1.** The distances between atoms in pm of the reaction center of the molecules corresponding to the most energetically favorable conformers (I, II and III), of the reactants and transition states of reactions (3) - (5) (I (n), II (n) and III (n), TS1ₜ(n), TS2ₜ(n) and TS3ₜ(n), (n), where n is the reaction number, M is the compound number) and their relative formation enthalpies in kJ/mol (the formation enthalpies of the initial compounds Iₘᵢₙ, Iₘᵢₙ and IIIₘᵢₙ, which correspond to minimum energy)².

| Structure | C-C² | C-O¹ | O-N¹ | N-O³ | C-H¹ | O-H² | C-H³ | O-H⁴ | O-H⁺ | O-H⁺ | O-H⁺ | ΔH²⁻¹⁵K |
|-----------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|---------|
| I         | 153.9 | 140.2 | 146.5 | 118.9 | 109.1 | 213.0 | 109.1 | 450.8 | 272.2 | 0.0   |       |         |
| I₁(3)     | 154.6 | 140.7 | 146.4 | 120.0 | 109.1 | 229.9 | 109.1 | 463.5 | 278.6 | 0.2   |       |         |
| TS1ₜ(3)   | 155.6 | 126.0 | 201.9 | 123.7 | 136.9 | 127.1 | 109.2 | 440.7 | 257.9 | 143.4 |       |         |
| I₄(4)     | 155.2 | 141.8 | 146.4 | 120.0 | 109.3 | 372.4 | 108.7 | 236.8 | 287.2 | 10.4  |       |         |
| TS2ₜ(4)   | 145.0 | 231.2 | 126.6 | 129.5 | 108.9 | 361.7 | 132.2 | 133.0 | 131.7 | 168.7 |       |         |
| II        | 151.4 | 144.0 | 141.7 | 120.9 | 109.3 | 253.2 | 109.3 | 447.4 | 254.1 | 0.0   |       |         |
| II₃(3)    | 152.9 | 143.7 | 142.8 | 120.7 | 109.1 | 232.6 | 109.2 | 270.7 | 277.6 | 4.1   |       |         |

\( ^² \text{D} \)
The reaction barrier \( \alpha \)-elimination of HNO\(_2\) from compound I is 145.3 (143.1) kJ/mol, which is more than 20 kJ/mol higher than the corresponding value for radical decomposition. The reaction enthalpies are respectively equal to -102.9 (-99.0) kJ/mol. The elimination of HNO\(_3\) proceeds only through a six-membered transition state. The activation barrier in this case is 168.7 (158.3) kJ/mol, the reaction enthalpy is 35.2 (24.8) kJ/mol.

In order to discuss the effect of the molecular structure on the change in barriers to alternative processes of gas-phase monomolecular decomposition of organic nitrates, it is of considerable interest to compare the various data obtained for compound I with the results of calculations by the same method and a set of basic functions for compounds II and III.

A noticeable decrease in the O-NO\(_2\) bond length and an increase in the C-ONO\(_2\) bond length occur in series I, II, III according to the calculation data. The bonds of N-O nitro groups differ slightly. In compounds II and III, the C–C bond differs little. An increase in the length of this bond in compound I by almost 30 pm may be due to the manifestation of steric stresses caused by the repulsion of negatively charged oxygen atoms of neighboring nitrate groups.

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**Figure 1.** The basic geometric parameters of 1,1,2,2-tetranitroxyethane. The data of x-ray structural analysis of the work are in parentheses [8].
An increase in the O-NO₂ bond length in compound I causes a decrease in the dissociation energy of this bond by 27.1 kJ/mol compared with compound III. It should be noted that the observed decrease in the dissociation energy associated with the appearance of the second nitro group at one carbon atom is less than the similar effect in the series of nitroalkanes. For example, according to the calculation results [10] and thermochemical data [2], the C-N bond dissociation energy in dinitromethane is almost 40 kJ/mol lower than in nitromethane.

Radical decomposition is the main mechanism of thermal decomposition of organic nitrates. The calculation results confirm this conclusion. The $D(O\text{-}NO_2)$ value is significantly lower for all studied compounds, than the activation barriers of various variants of nonradical decomposition reactions. It should also be taken into account that radical decay is characterized by higher values of the preexponential factor. The calculated values of $D(O\text{-}N)$ obtained allow estimating the activation energy of the radical decay of the studied compounds.

Let us note that, when the radical mechanism of the primary reaction event is realized, the dissociation energy of the weakest bond in the molecule practically coincides with the activation energy of gas-phase decomposition. The activation energy can be determined from the equation for organic nitrates (6):

$$E = D(O\text{-}NO_2) + RT,$$

where $T$ – is average temperature of the interval in which the experimental study of the kinetics of thermal decomposition was carried out.

$D(O\text{-}N)$ is practically independent of temperature according to the calculation data, in contrast to the enthalpies of formation of organic nitrates and radicals formed by reaction (1). Using our estimates of $D(O\text{-}NO_2)$, for compounds (2), (3), we calculated the activation energies of radical gas-phase decay. They are equal to 148.5 and 142.3 kJ/mol, respectively, which is noticeably lower than experimental estimates (166 and 149.6 kJ/mol, respectively [2]). Consequently, the calculated values of $E$ can be considered as the minimum values of the activation energy or the “lower bound” of radical decay reactions. These activation energies, according to the calculation data for different conformers of compound I, are in the range 123 - 125 kJ/mol.

The elimination of HNO₂ is the most advantageous among the mechanisms of nonradical decomposition of organic nitrates. This process can proceed in two directions: $\alpha$-elimination, when a hydrogen atom and a nitrate group attached to one carbon atom participate in the reaction, and $\beta$-elimination - in this case, a hydrogen atom and a nitrate group are attached to different carbon atoms, and as a result The reaction forms a double C=O bond. The process of $\alpha$-elimination is implemented for organic nitrates [6].

First, we consider the results of a theoretical study of the gas-phase $\alpha$-elimination of HNO₂ for compounds I, II, III. The values of the activation barrier of reaction (3) calculated using the B3LYP/6-31+G (df, p) method are given in Table 1. The B3PW91/6-311++G (2df, p) method predicts somewhat larger values of the activation enthalpy: 146.1 (145.9), 162.4 (158.1) and 165.5 (163.4) kJ/mol, respectively. An increase in the number of nitrate groups in the molecules decreases the activation enthalpy by 18.3 - 17.5 kJ / mol, respectively, and the presence of the second nitrate group at one carbon atom causes the activation enthalpy more strongly. Note that the accumulation of nitrate groups causes a relatively stronger decrease in $D(O\text{-}NO_2)$ than a decrease in the activation enthalpy of the реакции-elimination of HNO₂.

An analysis of the calculated enthalpies of the N-elimination of HNO₂ for compounds I, II, III shows that we are dealing with exothermic reactions in all cases, and the thermal effect increases with an increase in the number of nitrate groups in the molecules.

We studied the process of $\beta$-elimination of HNO₃ in two versions: a reaction proceeding through a six-membered transition state and a reaction proceeding through a four-membered transition state. The first process was studied for all the compounds under consideration. According to the calculation, the maximum thermal effect is observed for the reaction of compound II. Therefore, in this case, in contrast to the trends in $D(O\text{-}N)$ and the activation enthalpy of the $\alpha$-elimination of HNO₂, the monotonic
dependence breaks in the series Another difference is that the elimination reaction of HNO₃ is endothermic. The reaction enthalpies for the above compounds are 35.2 (24.8), 38.2 (37.5) and 59.3 (57.0) kJ/mol, respectively, according to the B3LYP/6-31+G(2df, p) method and 44.8 (34.2), 43.2 (42.6) and 65.7 (63.6) kJ/mol according to B3PW91/6-311++G(2df,p) method.

Four-membered transition state of the elimination of HNO₃ was not found for compound I. In the search process, a given four-membered transition state regrouped into a six-membered one. Reactions (4) and (5) were studied for compounds II and III. The activation enthalpies of these reactions obtained by the B3LYP/6-31+G(2df, p) method are given in table 1. The activation barriers calculated by the B3PW91/6-311++G (2df, p) method are equal to 246.2 (242.9) and 234.0 (234.0) kJ/mol, respectively. The reactions are endothermic: the reaction enthalpies are 31.8 (28.2) and 59.3 (59.3) kJ/mol, respectively (B3LYP/6-31+G (2df, p)) and 47.6 (44.2) and 65.7 (65.7) kJ/mol (B3PW91/6-311++G(2df,p)).

The barrier to the activation of the elimination of HNO₃ via the four-membered transition states for compounds II and III significantly, by almost 60 kJ/mol, exceeds the barrier to the activation of the reaction proceeding through the six-membered transition state. This is explained by the fact that, from the point of view of the rules of orbital symmetry, this process is forbidden, in contrast to the reaction proceeding through a six-membered transition state in which a conjugated electronic system is formed [16].

Thus, a theoretical study shows that radical decay is the main mechanism of thermal decomposition of the studied compounds. For all three molecules, the value of $D$(O-NO₂) is significantly lower than the activation barriers of various variants of nonradical decomposition reactions. When assessing the competition of various mechanisms, it should also be taken into account that radical decay reactions are characterized by higher values of the preexponential factor (A-factor) of the reaction. The experimental values of lg A for compounds 2 and 3, are in the range of 15–16, according to the experimental data of various authors [2–4]. Similar values are given by calculated estimates [4]. For the various elimination reactions that we studied, the calculated values of the preexponential factor are two orders of magnitude smaller than for radical decay reactions. For obvious reasons, experimental data for various options for the elimination of nitrous and nitric acids from organic nitrates are absent.

However, during thermal decomposition processes under conditions of high and ultrahigh pressures, for example, during detonation, the situation can change significantly. The reactions of homolytic decomposition of chemical bonds become unprofitable at very high pressures, since they correspond to substantially large values of the activation volume. For this reason, the primary act of thermal decomposition of the studied compounds may be the elimination of nitrous acid in reactions proceeding at very high pressures, for which, in comparison with radical decomposition reactions, a more compact transition state is observed.

4. Conclusion
The molecular structure of the free molecules of 1,1,2,2-tetranitroxyethane is determined and alternative mechanisms of its decomposition in the gaseous state are studied. Judging by the calculation results, the free molecule of 1,1,2,2-tetranitroxyethane can be a fairly stable compound. In order to consider the influence of the molecular structure, geometry was determined and various alternative mechanisms of thermal decomposition of two structurally similar compounds were studied: nitroxyethane and 1,2-dinitroxyethane. The study indicates that the main mechanism of thermal decomposition of all studied compounds is the homolytic decomposition of the O-NO₂ bond. The decay mechanism may be associated with the elimination process of HNO₂ at very high pressures when radical decay due to a significant amount of activation volume becomes unprofitable.

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