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Secondary Processes in the Mechanism of Gas-Phase Monomolecular Destruction of *o*-Nitrotoluene

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Abstract—A density functional theory method, B3LYP/6-31+G(2df,p), has been used to study the secondary processes of the most probable mechanism of gas-phase thermal decomposition of *o*-nitrotoluene (accompanied with formation of the *aci*-form at the first stage). The secondary processes of isomerization of aci-nitrotoluene have been recognized as the rate-limiting steps. This is consistent with results of earlier theoretical studies. The results on isomerization of the HONO group in the *aci*-form of *o*-nitrotoluene reported herein have substantially corrected the earlier suggested mechanism of thermal degradation of *o*-nitrotoluene.

Keywords: quantum-chemical simulation, reaction mechanism, thermal decomposition, *o*-nitrotoluene, *aci*-form, primary stage, secondary process

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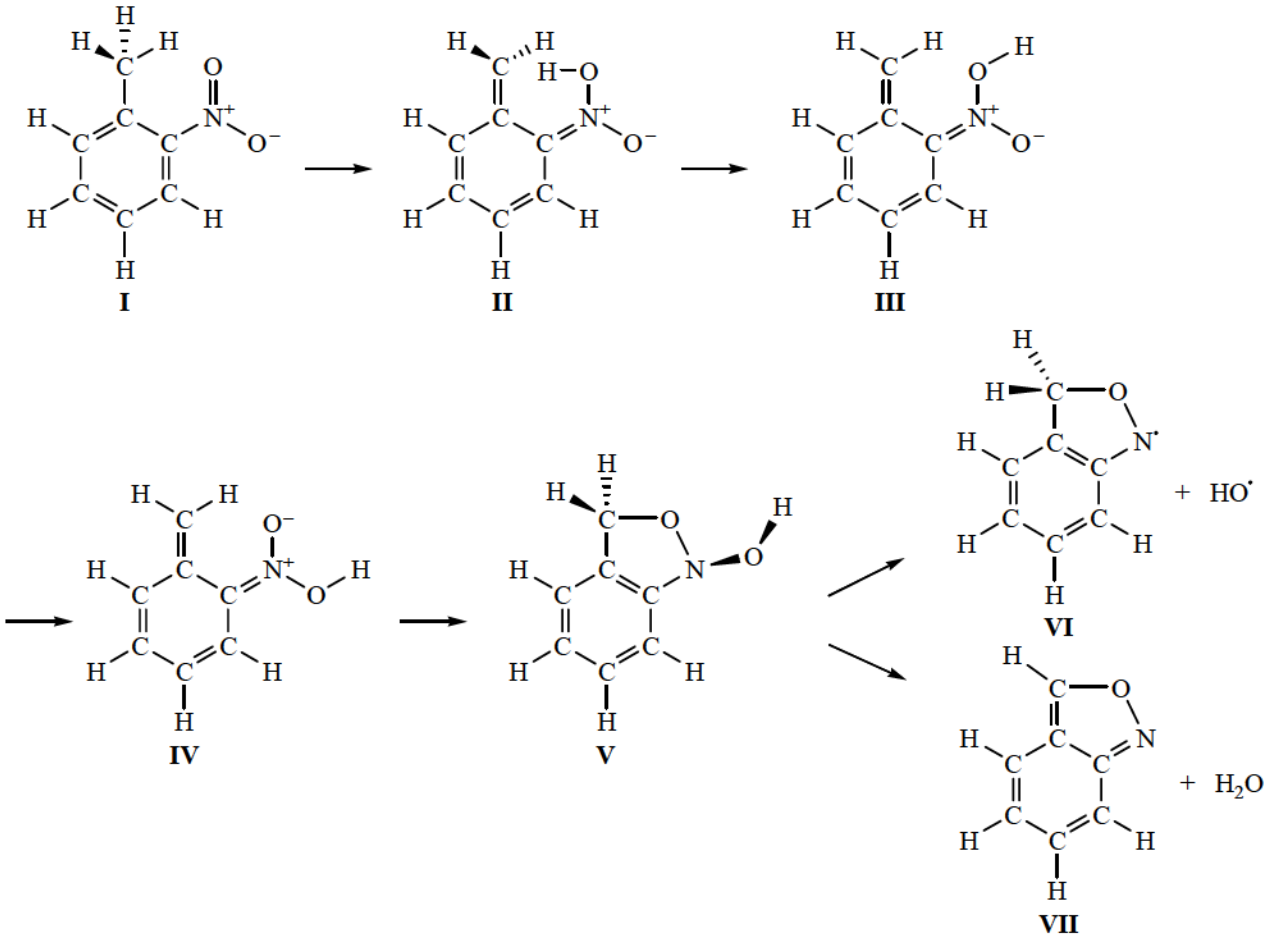
Study of mechanism of thermal decomposition of *o*-nitrotoluene (**I**) and its nitro derivatives is of fundamental as well as of practical interest. The known mechanisms of thermal destruction of nitro compounds [1–5] have not explained the observed substantial decrease of the Arrhenius parameters of *o*-nitrotoluene decomposition with respect to those of its *meta*- and *para*-isomers [6–9]. The experimentalists have suggested that this decrease is due to the special feature of the reaction mechanism including formation of the *aci*-form of *o*-nitrotoluene (**II**) at the first stage. The enthalpy of activation ($\Delta H^{\neq}$) of thermal decomposition of compound **I** as derived from the experimental activation energy via the $\Delta H^{\neq} = E_a - RT_{av}$ (T_{av} is the average temperature of the experiment) equation are substantially scattered. For example, $\Delta H^{\neq}$ has been found equal to 172.8 kJ/mol at 300–350°C [7, 8]; to 201.6 ± 3 kJ/mol (in 400–450°C) [6], and to 206.2 kJ/mol in 797–907°C [9]. Taking into account that the enthalpy of activation is only slightly dependent on temperature, it is natural to assume that the reaction mechanism is changed depending on the temperature range. The very low activation enthalpy found in [7] most likely corresponds to the primary act of the process, formation of the *aci*-form of the substrate; whereas the other reported values apparently refer to some secondary processes occurring in the course of thermal destruction of *o*-nitrotoluene.

Analysis of theoretical studies of mechanism of thermal destruction of compound **I** [1, 10–14] suggested the following scheme of the process (Scheme 1).

Enthalpy of formation of the transition states in the above-given mechanism ($\Delta H_f^{\neq}$) (referred to enthalpy of formation of *o*-nitrotoluene) substantially differ depending on the quantum-chemical method applied [1, 10–14]. For example, $\Delta H_f^{\neq}$ of the primary stage of compound **II** formation (**I** → **II**) varies from 172 (B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d,p) [10]) to 202.9 kJ/mol (BHLYP/6-311+G(2d,p)//B3LYP/6-31G(d,p) [10]). However, all the simulations reported suggest that the limiting step of the overall process is not the primary act (**I** → **II**) but subsequent transfer of the hydrogen atom between the two oxygen atoms in the *aci*-form (**III** → **IV**). The activation barrier of this step, according to the most accurate simulation with the G2M(RCC,MP2) method [11] is of 221.3 kJ/mol, about 20 kJ/mol higher than the experimental estimation of 201.6 ± 3 [6] and 15 kJ/mol higher than the value of 206.2 kJ/mol from [9]. For the primary act **I** → **II**, $\Delta H_f^{\neq}$ = 193.7 kJ/mol is given in [11] (likely, the most accurate experimentally determined enthalpy of activation of this reaction is of 172.8 kJ/mol [5, 8]). These differences can be assigned to inaccuracy of the applied method, although authors of [11] have not analyzed the systematic simulation errors.

Scheme 1.



According to our simulation using the B3LYP/6-31+G(2df,p) DFT method [1, 13–14], the primary act **I** → **II** revealed $\Delta H_f^{\neq}$ of 169.3 kJ/mol, about 6 kJ/mol lower than the experimental estimation (175.4 kJ/mol). The rate-limiting process **III** → **IV** showed $\Delta H_f^{\neq}$ = 216.4 kJ/mol, exceeding the experimental estimation of the activation barrier in the case of *o*-nitrotoluene (201.6 ± 3 kJ/mol) by about 15 kJ/mol [6, 8]. On the one hand, those deviations were within the the experimental uncertainty of 8–15 kJ/mol. At the same time, according to our data, the B3LYP/6-31+G(2df,p) method gave somewhat underestimated values of activation enthalpy [15, 16]. On top of that, the sign of the deviation was opposite for the two processes. Hence, that destruction pathway was most probably unrealistic.

The above-shown mechanism could be realized if the **III** → **IV** isomerization occurred via rotation of the $=N^+(OH)O^-$ groups around the C=N double bond. The value of $\Delta H_f^{\neq}$ for that process was of 188 kJ/mol. Is so, the reactions of water (**V** → **VII**) or hydroxyl radical (**V** → **VI**) elimination from 2,1-benzisoxazol-2(3*H*)-ol (**V**) with the barriers of 193.0 and 204.9 kJ/mol, respectively, became the rate-limiting steps. Taking into account that we likely obtained the underestimated values, the data could be interpreted as follows. At lower temperature range, the **V** → **VII** transformation should likely occur, as $\Delta H_f^{\neq}$ for that process was in agreement with the experimental estimate of 201.6 ± 3 kJ/mol. At higher temperature range, elimination of ·OH from compound **V** (**V** → **VI**) became possible, since the value of $\Delta H_f^{\neq}$ for that process was consistent with the experimental value of 206.2 kJ/mol. The conclusion is supported by systematic character of deviations (1–9 kJ/mol towards lower values) of the calculated enthalpies of activation from the experimental values.

Therefore, the presented results eliminated contradictions between the experimental and theoretical studies of *o*-nitrotoluene thermal decomposition.

The presented simulation results were obtained for the singlet surface, and all the solutions were tested for stability with respect to perturbations imposed on the wave function. We plan to further confirm the results with a multideterminant method such as TD DFT.

The computations were performed at Kazan Branch of Interdisciplinary Supercomputer Center of Russian Academy of Sciences.

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