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Energy Barriers to Gas-Phase Unimolecular Decomposition of Mono- and Dinitrotoluenes

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Abstract—Alternative paths of gas-phase unimolecular decomposition of three nitrotoluenes and six dinitrotoluenes, in particular homolytic dissociation of the C–N bond, nitro–nitrite rearrangement, intramolecular hydrogen transfer from the methyl to nitro group with formation of isomeric *aci*-nitrotoluenes, and various paths involving formation of bicyclic intermediates, have been studied at the DFT B3LYP/6-31+G(2*df*,*p*) level of theory using GAUSSIAN 09 software package. The most energetically favorable path for *o*-nitrotoluene and 2,3-, 2,4-, 2,5-, and 2,6-dinitrotoluenes is the formation of *aci*-nitrotoluenes. The effect of the substrate structure on the competition between different mechanisms of these reactions has been analyzed.

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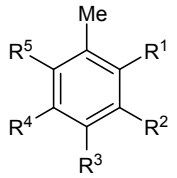
Nitrotoluenes, including those produced on a large scale, are capable of undergoing spontaneous decomposition at moderate temperatures [1–10]. Therefore, much attention is given to the kinetics and mechanisms of their thermal decomposition. There is a considerable dispersion of the Arrhenius parameters reported in the literature for thermal decomposition of nitrotoluenes. Apart from experimental studies, various mechanisms of unimolecular decomposition of nitrotoluenes were extensively studied by modern quantum chemical methods [11–20]. Nevertheless, there are considerable gaps in understanding of the mechanism of thermal decomposition of nitrotoluenes. The same also applies to specific features of the competition between different mechanisms of the primary act of gas-phase unimolecular decomposition of these compounds, though new interesting results have recently been obtained in this line of research [13, 15–18].



1–9

1, $R^1 = NO_2$, $R^2 = R^3 = R^4 = R^5 = H$; **2**, $R^1 = R^3 = R^4 = R^5 = H$, $R^2 = NO_2$; **3**; $R^1 = R^2 = R^4 = R^5 = H$, $R^3 = NO_2$; **4**, $R^1 = R^2 = NO_2$, $R^3 = R^4 = R^5 = H$; **5**, $R^1 = R^3 = NO_2$, $R^2 = R^4 = R^5 = H$; **6**, $R^1 = R^4 = NO_2$, $R^2 = R^3 = R^5 = H$; **7**, $R^1 = R^5 = NO_2$, $R^2 = R^3 = R^4 = H$; **8**, $R^1 = R^4 = R^5 = H$, $R^2 = R^3 = NO_2$; **9**, $R^1 = R^3 = R^5 = H$, $R^2 = R^4 = NO_2$.

Herein, we report the results of our theoretical study on the main mechanisms of the primary act of gas-phase unimolecular decomposition of *o*-, *m*-, and *p*-nitrotoluenes **1**–**3** and 2,3-, 2,4-, 2,5-, 2,6-, 3,4-, and 3,5-dinitrotoluenes **4**–**9**.

We considered three alternative mechanisms of the primary decomposition act of compounds **1**–**9**:

(1) Homolytic dissociation of the C–NO_2 bond:

$$Me(R')C_6H_3–NO_2 \longrightarrow Me(R')C_6H_3^{\bullet} + NO_2^{\bullet} \quad (1)$$

(2) Homolytic dissociation of the C–CH_3 bond:

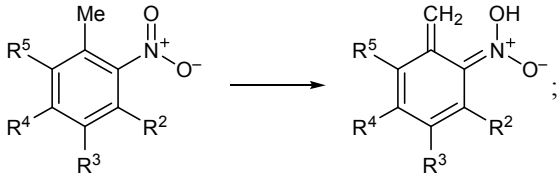
$$Me(R')C_6H_3–NO_2 \longrightarrow O_2N(R')C_6H_3^{\bullet} + CH_3^{\bullet} \quad (2)$$

(3) Nitro–nitrite rearrangement:

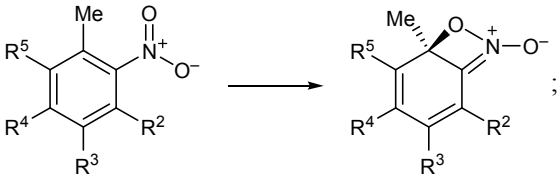
$$Me(R')C_6H_3–NO_2 \longrightarrow Me(R')C_6H_3–O–NO \quad (3)$$

where R′ = H (**1**–**3**), NO_2 (**4**–**9**).

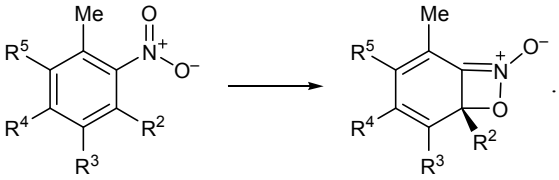
For compounds **1** and **4**–**7** containing a nitro group in the *ortho* position with respect to the methyl group (RH) we also considered formation of *aci*-nitro forms:


; (4)

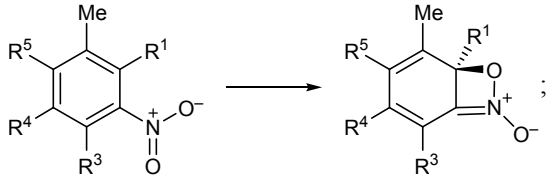
formation of substituted 6-methyl-7-oxa-8-azabicyclo-[4.2.0]octa-1(8),2,4-triene 8-oxides [18]:


; (5)

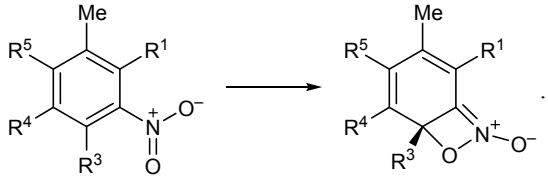
and formation of substituted 2-methyl-7-oxa-8-azabicyclo[4.2.0]octa-1(8),2,4-triene 8-oxides [18]:


. (6)

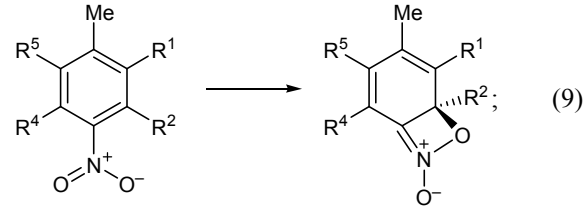
For compounds **2**, **4**, **6**, **8**, and **9** with a nitro group in the *meta* position with respect to the methyl group, we also considered (in addition to the first three mechanisms) the formation of substituted 5-methyl-7-oxa-8-azabicyclo[4.2.0]octa-1(8),2,4-triene 8-oxides [18]:

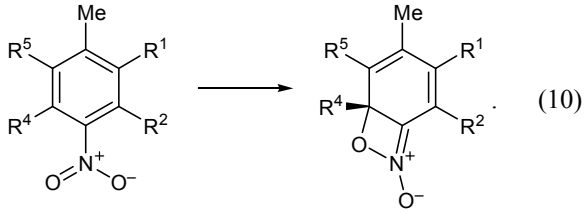

; (7)

and formation of substituted 3-methyl-7-oxa-8-azabicyclo[4.2.0]octa-1(8),2,4-triene 8-oxides [18]:


. (8)

For *p*-nitrotoluenes **3**, **5**, and **9** we considered two alternative mechanisms in addition to the first three: the formation of substituted 4-methyl-7-oxa-8-azabicyclo[4.2.0]octa-1(8),2,4-triene 8-oxides and formation of substituted 4-methyl-7-oxa-8-azabicyclo[4.2.0]-octa-1(8),2,4-triene 8-oxides [18] [reactions (9) and (10), respectively]:


(9)


. (10)

For all these processes we determined the enthalpies of activation and enthalpies of reaction. It is known [21, 22] that these values coincide for many radical decomposition reactions. The calculations were performed at the DFT B3LYP/6-31+G(2*df*,*p*) level of theory. The given combination of the functional and basis set was shown to ensure reliable evaluation of the barriers to unimolecular decomposition of *C*-nitro compounds [22, 23]. The most important mechanisms of the primary act of thermal decomposition of nitrotoluenes, such as homolytic dissociation and formation of *aci*-nitro compounds [reactions (1), (4)] were studied in more detail using different DFT methods and basis sets. The reaction enthalpies ΔH_r were calculated from the enthalpies of formation ΔH_f of the most favorable conformations of the initial and resulting structures. The ΔH_f values were estimated by standard methods [18] on the basis of the total electronic energies. In all cases, transition states were identified by the presence of one imaginary eigenvalue in the corresponding second derivative matrix and were mapped to a definite process by descend to the initial reagent and product along the reaction coordinate. All calculations were performed for the singlet surface, and the solutions found were checked for stability to wave function perturbations by the STABLE procedure implemented in Gaussian [24].

The activation barriers of the examined processes for nitrotoluenes in which the methyl group is located in the *ortho*, *meta*, or *para* position with respect to the nitro group are given in Tables 1–3, respectively. The most interesting are the results obtained for *o*-nitrotoluenes for which all the above considered mechanisms of unimolecular decomposition are possible. Among them, the most favorable is intramolecular hydrogen transfer with formation of *aci*-nitro compounds. Increase of the number of nitro groups in the

Table 1. Enthalpies of activation ($\Delta H^{\neq}$) and reaction (ΔH_r) for possible primary acts of thermal decomposition of *o*-nitrotoluenes **1** and **4**–**7** (kJ/mol); B3LYP/6-31+G(2*df*,*p*) calculations

Reaction no.	**1**		**4**		**5**		**6**		**7**	
	$\Delta H^{\neq}$	ΔH_r	$\Delta H^{\neq}$	ΔH_r	$\Delta H^{\neq}$	ΔH_r	$\Delta H^{\neq}$	ΔH_r	$\Delta H^{\neq}$	ΔH_r
1	–	271.9	–	236.2	–	259.9	–	259.9	–	252.4
2	–	403.2	–	415.9	–	409.9	–	409.1	–	398.6
3	238.7	–3.0	225.6	–21.2	236.7	–12.6	228.9	–15.5	234.0	–14.9
4	169.3	154.6	171.4	154.5	164.3	147.1	169.8	149.1	164.9	146.2
5	247.2	221.7	232.7	195.8	231.7	213.8	250.6	220.6	221.3	196.5
6	240.4	220.9	219.6	194.4	225.8	209.0	244.1	220.0	215.7	200.8

Table 2. Enthalpies of activation ($\Delta H^{\neq}$) and reaction (ΔH_r) for possible primary acts of thermal decomposition of *m*-nitrotoluenes **2**, **4**, **6**, **8**, and **9** (kJ/mol); B3LYP/6-31+G(2*df*,*p*) calculations

Reaction no.	**2**		**4**		**6**		**8**		**9**	
	$\Delta H^{\neq}$	ΔH_r	$\Delta H^{\neq}$	ΔH_r	$\Delta H^{\neq}$	ΔH_r	$\Delta H^{\neq}$	ΔH_r	$\Delta H^{\neq}$	ΔH_r
1	–	284.8	–	246.3	–	272.9	–	239.5	–	273.0
2	–	408.2	–	415.9	–	409.1	–	414.2	–	413.5
3	258.1	8.7	236.8	–16.1	248.4	–3.5	224.6	–19.6	255.8	–0.4
7	256.2	231.2	232.4	199.0	257.9	229.1	232.9	196.2	240.6	221.8
8	261.1	236.4	243.8	209.1	266.2	241.0	233.7	202.3	248.6	227.6

Table 3. Enthalpies of activation ($\Delta H^{\neq}$) and reaction (ΔH_r) for possible primary acts of thermal decomposition of *p*-nitrotoluenes **3**, **5**, and **8** (kJ/mol); B3LYP/6-31+G(2*df*,*p*) calculations

Reaction no.	**3**		**5**		**8**	
	$\Delta H^{\neq}$	ΔH_r	$\Delta H^{\neq}$	ΔH_r	$\Delta H^{\neq}$	ΔH_r
1	–	288.9	–	277.0	–	243.5
2	–	409.4	–	409.9	–	414.2
3	262.1	11.4	260.3	2.3	229.4	–17.5
9	257.4	238.9	244.8	227.9	227.1	202.1
10	257.4	238.9	249.3	236.6	233.4	205.2

molecule weakly affects the activation barrier of this reaction.

The activation barriers for the formation of *aci*-nitro compounds are considerably (by 35–40 kJ/mol) lower than the energies of activation for thermal decomposition of nitro toluenes (Table 2) [2, 6, 13, 15–18]. Therefore, this process cannot be the rate-determining step of unimolecular decomposition of nitrotoluenes in which the methyl group is located in the *ortho* position with respect to the nitro group. On the other hand, intramolecular hydrogen transfer is the most advantageous isomerization version of *o*-nitrotoluenes, and there are serious reasons to believe that this process is the primary act of thermal decomposition of *o*-nitrotoluene and its nitro derivatives. Analogous assumption was made in almost all publications on the mechanism of thermal decomposition of aromatic nitro compounds [2, 6, 13, 15–18], which determines the necessity of more detailed investigation of the reaction mechanism.

The results obtained for 2,3- and 2,5-dinitrotoluenes do not match the tendency of the enthalpy of activation of reaction (4) to monotonically decrease as the number of nitro groups in the molecule increases. The calculations for 2,3- and 2,5-dinitrotoluenes predict a slight increase of the enthalpy of activation as compared to *o*-nitrotoluene. In the case of 2,3-dinitrotoluene, the observed differences may be related to the

fact that the nitro group involved in the process is additionally turned with respect to the benzene ring plane due to effect of the neighboring nitro group. Trends in the variation of the enthalpy of activation are discussed below on the basis of analysis of changes of geometric parameters of the reaction center in the transition states and nitrotoluene molecules.

An interesting peculiarity of the process under study is monotonic change of the enthalpy of activation and enthalpy of reaction [correlation coefficient 0.83 according to the B3LYP/6-31+G(2*df*,*p*) data]. The enthalpy of reaction in the examined series of compounds changes in a way similar to the enthalpy of activation. For example, the enthalpies of reaction for 2,3- and 2,5-dinitrotoluenes are higher than those found for 2,4- and 2,6-dinitrotoluenes, and the enthalpies of reaction for the latter almost do not differ from each other. On the other hand, the change of the enthalpy of reaction in the examined series considerably exceeds the change in the enthalpy of activation (17.1 and 9.7 kJ/mol, respectively).

In order to obtain additional information on the mechanism of formation of *aci*-nitrotoluenes, the calculations were carried out by different methods using different basis sets. Insofar as the goal of this work was to study reaction mechanism for a fairly large series of compounds, the choice of the calculation method was based on different versions of DFT methods. Taking into account published data and preliminary estimates of the reaction barriers for nitrotoluenes, additional studies were performed using wB97XD functional and 6-31G(*d*,*p*), 6-311+G(*df*,*p*), and 6-311++(3*df*,3*pd*) basis sets. To obtain as complete data as possible, B3LYP functional and 6-31G(*d*) and 6-311++G(3*df*,3*pd*) basis sets with considerably different sizes were also used.

The main conclusions on the effect of substituents on the enthalpy of activation $\Delta H^{\neq}$ for the formation of *aci*-nitro compounds were consistently confirmed by all methods used in this work, which indicated reliability of our results.[1] The range of variation of $\Delta H^{\neq}$ did not exceed 12–14 kJ/mol (Table 4). The largest value was predicted for 2-nitro- and 2,3- and 2,5-dinitrotoluenes. In all cases, extension of the basis set resulted in decrease of the activation barrier in absolute value.

Table 4. Enthalpies of activation ($\Delta H^{\neq}$), reaction (ΔH_r) and activation of reverse reaction ($\Delta H^{\neq}_{rev}$) for the isomerization of *o*-nitrotoluenes **1** and **4**–**7** into *aci*-nitro compounds (kJ/mol); B3LYP/6-31+G(2*df*,*p*) calculations

Compound no.	$\Delta H^{\neq}$	ΔH_r	$\Delta H^{\neq}_{rev}$
1	169.3	154.6	14.7
4	171.4	154.5	16.9
5	164.3	147.1	17.2
6	169.8	149.1	20.6
7	164.9	146.2	18.8

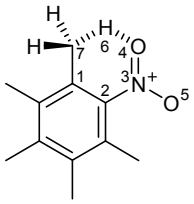
The observed variation of the enthalpy of activation may be rationalized by analysis of changes in the geometric parameters of transition states in comparison to initial molecules (Δr; Tables 5, 6). As the number of nitro groups increases in going from molecule **1** to **5** and **7**, the difference in the C^2–N^3, H^3–O^4, and C^7–H^6 bond lengths at the reaction center decreases. The C^1–C^2 and C^7–C^1 bond lengths showed an opposite trend, but the first trend prevails, so that the enthalpy of activation decreases as the number of nitro groups increases. However, due to the opposite tendency, the effect of decrease of the activation barrier to the formation of *aci*-nitro compounds is very weak. Furthermore, the small change of the activation barrier in the examined series of compounds is also related to the small change of the bond lengths ($\Delta r_{for} = |\Delta r_{TS-S}|_{max} - |\Delta r_{TS-S}|_{min.}$), which does not exceed 2.5 pm (Table 6).

Herein, we do not consider the O^4–H^6 bond since it is absent in the initial compound and the contribution of long-range interactions of atoms is insignificant. However, this distance is likely to affect the enthalpy of activation of *aci*-nitro forms of 2,5-dinitrotoluene, which increases as compared to **1**, **5**, and **7**. Although this distance in **6** is shorter than in **7**, molecule **6** lacks additional steric interaction between the neighboring substituents, nitro groups in positions *2* and *6* and methyl group in position *1*.

As noted above, the highest activation barrier to the formation of *aci*-nitro form was also found for 2,3-dinitrotoluene. This is most likely to be related to greater variation of the geometric parameters in going from the initial molecule to the transition state than that observed for any other nitrotoluene. As a result, the activation barrier to the transformation of *o*-nitrotoluene to the *aci*-nitro compound is lower than that for 2,3-dinitrotoluene: 169.3 and 171.4 kJ/mol, respectively, according to the B3LYP/6-31+G(2*df*,*p*) calculations (Table 5).

[1] The results of calculations by all methods used in this work are available from the authors by e-mail.

Table 5. Bond lengths (pm) and enthalpies of formation (kJ/mol) of initial compounds (S), transition states (TS), and products (P) for the isomerization of nitrotoluenes **1** and **4–7** into *aci*-nitro compounds; B3LYP/6-31+G(2*df*,*p*) [wB97XD/6-31+G(2*df*,*p*)] calculations



Compound no.		C^1–C^2	C^2–N^3	N^3–O^4	O^4–H^6	C^7–H^6	C^7–C^1	$\Delta H^\circ_{f,298}$
1	S	140.6 [140.0]	147.4 [146.9]	122.6 [121.7]	256.8 [258.5]	109.3 [109.2]	150.8 [150.5]	91.8 [138.8]
	TS	144.2 [143.5]	138.7 [138.0]	132.2 [130.8]	113.9 [112.5]	149.7 [149.9]	141.5 [140.7]	261.1 [327.2]
	P	147.3 [146.8]	134.6 [133.9]	139.4 [137.5]	97.9 [97.4]	210.6 [211.4]	136.7 [135.9]	246.4 [309.3]
4	S	139.8 [139.2]	148.1 [147.4]	121.8 [121.0]	274.2 [274.0]	109.4 [109.3]	150.8 [150.6]	113.0 [194.6]
	TS	144.3 [143.5]	138.9 [138.2]	131.7 [130.2]	114.8 [113.7]	147.7 [147.6]	141.2 [140.3]	284.4 [385.7]
	P	147.2 [147.2]	134.2 [133.2]	139.2 [137.2]	98.0 [97.5]	206.5 [208.3]	136.0 [135.0]	267.5 [366.8]
5	S	140.7 [140.0]	147.8 [147.3]	122.5 [121.6]	257.6 [257.3]	109.4 [109.2]	150.6 [150.3]	80.4 [165.4]
	TS	144.3 [143.7]	139.7 [138.9]	131.6 [130.2]	115.2 [113.6]	148.4 [148.8]	141.1 [140.3]	244.8 [348.7]
	P	147.4 [147.2]	135.5 [134.3]	138.6 [136.7]	98.0 [97.6]	210.6 [210.1]	136.3 [135.4]	227.5 [331.5]
6	S	140.5 [139.8]	147.8 [147.3]	122.4 [121.5]	259.9 [258.3]	109.3 [109.2]	150.8 [150.5]	81.6 [166.5]
	TS	143.9 [143.2]	139.2 [138.5]	131.8 [130.4]	114.8 [113.3]	148.6 [149.0]	141.5 [140.6]	251.3 [355.8]
	P	147.2 [146.5]	134.7 [134.5]	139.5 [137.7]	97.7 [97.2]	216.4 [220.8]	136.6 [136.6]	230.7 [331.2]
7	S	140.5 [139.8]	147.8 [147.2]	122.4 [121.5]	284.8 [284.5]	109.3 [109.2]	150.8 [150.5]	100.5 [182.3]
	TS	145.0 [144.4]	139.7 [138.9]	131.5 [130.1]	114.9 [113.3]	148.0 [148.6]	140.9 [140.2]	265.5 [367.8]
	P	148.1 [147.8]	134.9 [133.6]	139.1 [137.3]	97.9 [97.4]	214.4 [216.4]	135.6 [134.8]	246.7 [348.5]

Table 6. Change of the bond lengths at the reaction center (Δr, pm) in the formation of *aci*-nitro compounds from nitrotoluenes **1** and **4–7**; B3LYP/6-31+G(2*df*,*p*) [wB97XD/6-31+G(2df,p)] calculations

Compound no.	Δr	C^1–C^2	C^2–N^3	N^3–O^4	O^4–H^6	C^7–H^6	C^7–C^1
1	TS–S	3.6 [3.5]	–8.7 [–8.9]	9.6 [9.1]	–142.9 [–146.0]	40.4 [40.7]	–9.3 [–9.8]
	TS–P	–3.1 [–3.3]	4.1 [4.1]	–7.2 [–6.7]	16.0 [15.1]	–60.9 [–61.5]	4.8 [4.8]
4	TS–S	4.5 [4.3]	–9.2 [–9.2]	9.9 [9.2]	–159.4 [–160.3]	38.3 [38.3]	–9.6 [–10.3]
	TS–P	–2.9 [–3.7]	4.7 [5.0]	–7.5 [–7.0]	16.8 [16.2]	–58.8 [–60.7]	5.2 [5.3]
5	TS–S	3.6 [3.7]	–8.1 [–8.4]	9.1 [8.6]	–142.4 [–143.7]	39.0 [39.6]	–9.5 [–10.0]
	TS–P	–3.1 [–3.5]	4.2 [4.6]	–7.0 [–6.5]	17.2 [16.0]	–62.2 [–61.3]	4.8 [4.9]
6	TS–S	3.4 [3.4]	–8.6 [–8.8]	9.4 [8.9]	–145.1 [–145]	39.3 [39.8]	–9.3 [–9.9]
	TS–P	–3.3 [–3.3]	4.5 [4.0]	–7.7 [–7.3]	17.1 [16.1]	–67.8 [–71.8]	4.9 [4.0]
7	TS–S	4.5 [4.6]	–8.1 [–8.3]	9.1 [8.6]	–169.9 [–171.2]	38.7 [39.4]	–9.9 [–10.3]
	TS–P	–3.1 [–3.4]	4.8 [5.3]	–7.6 [–7.2]	17.0 [15.9]	–66.4 [–67.8]	5.3 [5.4]
1, **4–7**	$\lvert\Delta r_{TS-S}\rvert_{max}$	4.5 [4.6]	9.2 [9.2]	9.9 [9.2]	169.9 [171.2]	40.4 [40.7]	9.9 [10.3]
	$\lvert\Delta r_{TS-S}\rvert_{max}$	3.4 [3.4]	8.1 [8.3]	9.1 [8.6]	142.4 [143.7]	38.3 [38.3]	9.3 [9.8]
	$\lvert\Delta r_{TS-P}\rvert_{max}$	3.3 [3.7]	4.8 [5.3]	7.7 [7.3]	17.2 [16.2]	67.8 [71.8]	5.3 [5.4]
	$\lvert\Delta r_{TS-P}\rvert_{min}$	2.9 [3.3]	4.1 [4.0]	7.0 [6.5]	16.0 [15.1]	58.8 [60.7]	4.8 [4.0]
$\Delta r_{for} = \lvert\Delta r_{TS-S}\rvert_{max} - \lvert\Delta r_{TS-S}\rvert_{min}$		1.1 [1.2]	1.1 [0.9]	0.8 [0.6]	27.5 [27.5]	2.1 [2.4]	0.6 [0.5]
$\Delta r_{rev} = \lvert\Delta r_{TS-P}\rvert_{max} - \lvert\Delta r_{TS-P}\rvert_{min}$		0.4 [0.4]	0.7 [1.3]	0.7 [0.8]	1.2 [1.1]	9.0 [11.1]	0.5 [1.4]

The barriers to the reverse reactions (isomerization of *aci*-nitrotoluenes into nitrotoluenes) are very low, and the substrate structure, in particular increase of the number of nitro groups, almost does not affect the $\Delta H^{\neq}$ value. Analysis of the geometric parameters of the reaction center in the transition states and *aci*-nitrotoluenes provides a simple explanation. The reason is that the change of the geometric parameters both in the reverse reaction ($|\Delta r_{TS-P}|$) and in the series of compounds under study ($\Delta r_{rev} = |\Delta r_{TS-P}|_{max} - |\Delta r_{TS-P}|_{min.}$) is considerably smaller than in the forward reaction (formation of *aci*-nitrotoluenes; $|\Delta r_{TS-P}|$, Δr_{for}).

The structure of the transition state is closer to the structure of the isomerization products than to the structure of initial nitrotoluenes. For example, the length of the O^4–H^6 bond being formed in *o*-nitrotoluene differs from the corresponding bond in the transition state by 142.9 pm [B3LYP/6-31+G(2*df*,*p*)], whereas the difference for the reverse reaction is as small as 16 pm (Table 6). During the forward reaction, the C^2–N^3 bond changes by 1.1 pm against 0.7 pm for the reverse reaction. Analogous pattern is observed for other geometric parameters. The corresponding variations of the C^1–C^2 bond length are 1.1 and 0.4 pm, and for the N^3–O^4 bond, 0.8 and 0.7 pm, respectively (Table 6). Therefore, it is not surprising that, unlike clearly endothermic intramolecular hydrogen transfer with formation of *aci*-nitrotoluenes, the reverse isomerization of nitronic acids into nitroarenes should be accompanied by significant heat evolution.

Among other nonradical paths of decomposition of aromatic nitro compounds, the most theoretically studied is their isomerization into nitrites (nitro–nitrite rearrangement) [14, 16, 18]. It was reliably found that $\Delta H^{\neq}$ for the nitro–nitrite rearrangement is lower by 20–40 kJ/mol than the dissociation energy of the C–N bond [*D*(C–N)], which increases the contribution of this process to the apparent rate constant at reduced temperature as compared to the radical mechanism. No systematic studies of the nitro–nitrite rearrangement of nitrotoluenes were performed; therefore, analysis of the results given in Table 1–3 is of considerable interest. The activation barrier for reaction (3) is much lower than *D*(C–N). The largest difference (33.2 kJ/mol) is observed for *o*-nitrotoluene, and the smallest difference (9.5 kJ/mol), for 2,3-dinitrotoluene when the nitro group on C^3 is involved.

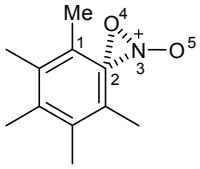
As the number of nitro groups increases, the difference in the *D*(C–N) and $\Delta H^{\neq}$ values for nitro–nitrite rearrangement decreases. Furthermore, this difference is appreciably smaller for nitrotoluenes containing a nitro group in the *meta* or *para* position (Table 1–3). For example, the differences between *D*(C–N) and $\Delta H^{\neq}$ for the nitro–nitrite rearrangement of **1**–**3** are 33.2, 26.7, and 26.8 kJ/mol, respectively. In going from compound **1** to **5** and **7**, this difference decreases to 23.2 and 18.4 kJ/mol, respectively, for reactions (1) and (3) at the nitro group in the *ortho* position with respect to the methyl group, and to 16.7 kJ/mol for compound **5** reacting at the *para*-nitro group. 2,3- and 3,4-Dinitrotoluenes are characterized by the smallest difference between *D*(C–N) and enthalpy of activation of the nitro–nitrite rearrangement, regardless of the position of the nitro groups, which is determined mainly by reduction of the energy of homolytic dissociation of the C–N bond. Presumably, steric repulsion between the neighboring nitro groups is important here. The effect of the second nitro group in 2,5-dinitrotoluene on the difference in the *D*(C–N) and $\Delta H^{\neq}$ values is insignificant. The differences are 31.0 and 24.5 kJ/mol, respectively, and are very similar to those found for *o*- and *m*-nitrotoluenes. 3,5-Dinitrotoluene occupies an intermediate position between 2,3- and 2,5-dinitrotoluenes.

The enthalpy of activation $\Delta H^{\neq}$ of the nitro–nitrite rearrangement strongly depends on the position of the nitro group relative to the methyl group. In the series of isomeric mononitrotoluenes, the lowest $\Delta H^{\neq}$ value was obtained for *o*-nitrotoluene, and the highest, for *p*-nitrotoluene. In most cases, increase of the number of nitro groups leads to reduction of the enthalpy of activation. This effect is relatively stronger for dinitrotoluenes with the nitro groups in the *ortho* position with respect to each other, i.e., for 2,3- and 3,4-dinitrotoluenes.

The enthalpies of reaction (3) generally have small negative values which change monotonically in parallel with $\Delta H^{\neq}$. The highest correlation coefficients (0.96 and 0.97) were found for the nitro–nitrite rearrangements of substrates with a nitro group in the *meta* or *para* position with respect to the methyl group. If the nitro group occupies *ortho* position with respect to the methyl group, the correlation coefficient appreciably decreases (0.88).

The activation barriers to the reverse isomerization of tolyl nitrites to nitrotoluenes are slightly higher than those to forward reactions (3) for all substrates, except for *m*- and *p*-nitrotoluenes and 2,4-dinitrotoluene reacting at the *para*-nitro group. Analysis of the geometric parameters of the reaction center showed that in

Table 7. Geometric parameters and enthalpies of formation of initial compounds (S), transition states (TS), and products (P) in the nitro–nitrite rearrangement of *o*-nitrotoluenes **1** and **4–7**; B3LYP/6-31+G(2*df*,*p*) calculations



Compound no.		C^2–N^3, pm	N^3–O^4, pm	C^2–O^4, pm	∠$C^2N^3O^4$, deg	$\Delta H^\circ_{f,298}$, kJ/mol
1	S	147.4	122.6	232.1	118.2	91.8
	TS	171.0	130.9	180.0	71.8	330.5
	P	237.2	146.6	138.7	32.7	88.8
4	S	148.1	121.8	230.4	116.8	113.0
	TS	166.4	131.3	171.5	68.2	338.6
	P	243.3	156.7	135.9	31.1	91.8
5	S	147.8	122.5	231.8	117.8	80.4
	TS	169.9	131.0	178.1	71.3	317.1
	P	238.8	149.8	137.8	32.2	67.8
6	S	147.8	122.4	231.7	117.8	81.6
	TS	169.0	130.9	176.5	70.8	310.5
	P	239.4	150.0	137.3	31.9	66.0
7	S	147.8	122.4	231.6	117.8	100.5
	TS	169.6	131.1	177.8	71.2	334.5
	P	238.3	149.4	137.9	32.4	85.6

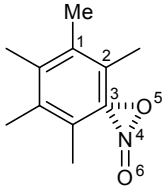
the reaction reverse to (3) the C–N and N–O bond lengths change to a greater extent than in the forward process (Tables 7–9). Unlike forward reactions, the isomerization of tolyl nitrites into nitrotoluenes is characterized by a slight increase of the activation barrier in going from mono- to dinitro-substituted compounds. The only exception is 3,4-dinitrotoluene for which the enthalpy of activation of both nitro–nitrite rearrangement and reverse reaction was lower than those for *m*- and *p*-nitrotoluenes (Tables 1–3).

Summarizing the results of studying the nitro–nitrite rearrangement of nitrotoluenes, it is necessary to emphasize once more that this process is unlikely to compete with alternative formation of *aci*-nitro compounds of *ortho*-substituted substrates **1** and **4–7**; however, it may contribute (in addition to the radical mechanism) to the apparent rate constant of gas-phase unimolecular decomposition of nitrotoluenes with *meta* and *para* arrangement of the methyl and nitro groups (Tables 1–3).

One more nonradical mechanism implying isomerization of nitroarenes into bicyclic intermediates has been proposed relatively recently [18, 25]. This isomerization can take two paths for each nitro group. The cyclization of nitrotoluenes with a nitro group on C^2 may follow schemes (5) and (6) with participation of the neighboring C^1 and C^3 atoms, 3-nitro-substituted substrates could give rise to bicyclic structures according to reactions (7) and (8) with participation of C^2 and C^4, and the nitro group on C^4 may be involved in intramolecular ring closure with participation of C^3 and C^5 [reactions (9) and (10)]. The most energetically favorable is reaction (6) for **1** and **4–7** (nitro group in the *ortho* position with respect to the methyl group), reaction (7) for **2** and **9** (*meta*-nitro group), and reaction (9) for **3** and **8** (*para*-nitro group). The activation barriers for alternative reactions (5), (8), and (10), where C^1 and C^2, C^3 and C^4, and C^4 and C^5 are shared between the two rings in the corresponding bicyclic intermediates, are higher by 2–13 kJ/mol (Tables 1–3).

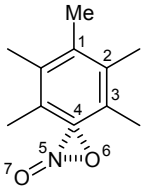
As follows from the data in Tables 1–3, the enthalpy of activation $\Delta H^{\neq}$ for all isomerizations into bicyclic intermediates decreases in going from mono- to dinitrotoluenes. Here, as well as in the isomerization to *aci*-nitro compounds, 2,5-dinitrotoluene is an exception. The enthalpies of activation of reactions (5)–

Table 8. Geometric parameters and enthalpies of formation of initial compounds (S), transition states (TS), and products (P) in the nitro–nitrite rearrangement of *m*-nitrotoluenes **2**, **4**, **6**, **8**, and **9**; B3LYP/6-31+G(2*df*,*p*) calculations



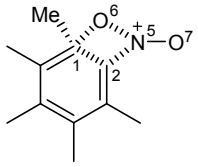
Compound no.		C^3–N^4, pm	N^4–O^5, pm	C^3–O^5, pm	∠$C^3N^4O^5$, deg	$\Delta H^\circ_{f,298}$, kJ/mol
2	S	147.5	122.6	231.6	117.8	79.7
	TS	172.5	130.7	179.9	71.3	337.9
	P	236.8	146.4	138.6	32.8	88.4
4	S	147.4	122.2	230.9	117.5	113.0
	TS	166.9	131.3	171.4	69.0	349.8
	P	241.4	155.0	136.4	31.7	96.9
6	S	147.9	122.4	231.3	117.4	81.6
	TS	171.5	130.4	176.5	70.1	329.9
	P	238.9	149.7	137.2	32.0	78.1
8	S	147.7	122.1	230.3	116.9	108.8
	TS	166.4	131.0	170.2	68.6	333.4
	P	243.1	156.8	135.7	31.1	89.2
9	S	147.9	122.4	231.4	117.4	70.1
	TS	171.0	130.8	177.6	70.7	325.9
	P	238.4	149.6	137.6	32.3	69.7

Table 9. Geometric parameters and enthalpies of formation of initial compounds (S), transition states (TS), and products (P) in the nitro–nitrite rearrangement of *p*-nitrotoluenes **3**, **5**, and **8**; B3LYP/6-31+G(2*df*,*p*) calculations



Compound no.		C^4–N^5, pm	N^5–O^6, pm	C^4–O^6, pm	∠$C^4N^5O^6$, deg	$\Delta H^\circ_{f,298}$, kJ/mol
3	S	147.0	122.6	231.2	117.8	78.0
	TS	170.8	131.0	179.2	71.5	340.1
	P	236.7	146.5	138.5	32.8	89.4
5	S	147.4	122.3	231.1	117.7	80.4
	TS	170.6	131.0	177.8	70.9	340.8
	P	237.7	149.1	137.6	32.5	82.8
8	S	147.1	122.2	230.2	117.2	108.8
	TS	165.6	131.3	170.0	68.9	338.2
	P	242.6	156.3	135.8	31.3	91.3

Table 10. Geometric parameters and enthalpies of formation of initial compounds (S), transition states (TS), and products (P) in the transformation of *o*-nitrotoluenes **1** and **4–7** into 6-methyl-7-oxa-8-azabicyclo[4.2.0]octa-1(8),2,4-triene 8-oxides [reaction (5)]; B3LYP/6-31+G(2*df*,*p*) calculations



Compound no.		C^1–C^2, pm	C^2–N^5, pm	N^5–O^6, pm	O^6–C^1, pm	∠$C^2N^5O^6$, deg	$\Delta H^\circ_{f,298}$, kJ/mol
1	S	140.6	147.4	122.6	282.7	118.2	91.8
	TS	147.5	134.9	136.2	181.4	101.5	339.0
	P	149.5	132.5	147.3	149.3	94.6	313.5
4	S	139.8	148.1	121.8	300.9	116.8	113.0
	TS	147.4	136.5	134.7	185.3	102.1	345.7
	P	149.8	133.0	147.2	148.7	94.3	308.9
5	S	140.7	147.8	122.5	283.5	117.8	80.4
	TS	147.7	136.2	135.3	179.8	100.8	312.1
	P	149.4	133.5	145.2	150.4	94.8	294.2
6	S	140.5	147.8	122.4	284.0	117.8	81.6
	TS	147.2	135.4	136.0	181.2	101.3	332.1
	P	149.4	132.6	148.2	148.4	94.2	302.1
7	S	140.5	147.8	122.4	286.9	117.8	100.5
	TS	148.1	136.2	134.7	181.2	101.2	321.8
	P	150.0	133.2	145.6	149.2	94.7	297.1

(8) for 2,5-dinitrotoluene were higher than those calculated for all other substrates. Unfortunately, these findings cannot be explained on the basis of variation of geometric parameters of the initial compounds during the process (Tables 10–15).

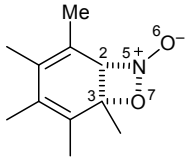
All reactions (5)–(10) are highly endothermic. This may be rationalized by the fact that in all cases changes in the geometric parameters of the reacting species in the reverse reactions (transformation of bicyclic intermediates into nitrotoluenes) are much smaller than in the forward reactions (Tables 10–15). The enthalpies of reactions (5)–(10) (ΔH_r) change monotonically in parallel with $\Delta H^{\neq}$. The correlation coefficients for the $\Delta H^{\neq}$ and ΔH_r values calculated by the B3LYP/6-31+G(2*df*,*p*) method are 0.84, 0.93, 0.93, 0.96, 0.99, and 0.96 for reactions (5)–(10), respectively.

To complete the study of the mechanisms of isomerization of nitrotoluenes to bicyclic intermediates, one more peculiarity of these mechanisms should be noted. It may be crucial for the choice of the main mechanism of thermal decomposition of nitrotoluenes. Specifically, increase of the number of nitro groups in nitrotoluene molecules is accompanied by greater decrease of the activation barrier to the isomerization to bicyclic intermediates than in the alternative nitro–nitrite rearrangement (Tables 1–3).

The enthalpies of activation for the formation of bicyclic intermediates from *o*-nitrotoluene and its rearrangement into nitrite differ insignificantly (247.2, 240.4, and 238.7 kJ/mol, respectively). The formation of bicyclic intermediates together with homolytic dissociation and nitro–nitrite rearrangement may contribute to the apparent rate constant of thermal decomposition of *m*- and *p*-nitrotoluenes. This especially applies to 3,5-dinitrotoluene, for which the enthalpies of activation of reactions (7) and (8) are lower by 7–15 kJ/mol than the activation barrier to reaction (3) (Table 2).

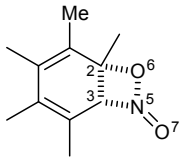
Finally, let us discuss some peculiarities of the effects of molecular structure of nitrotoluenes on the energy of dissociation of the C–NO_2 bond and on the energy of activation of radical thermal decomposition. Table 16 contains the calculated enthalpies of formation of nitrotoluenes and radicals generated by homolytic dissociation of the C–NO_2 bond, and energies of

Table 11. Geometric parameters and enthalpies of formation of initial compounds (S), transition states (TS), and products (P) in the transformation of *o*-nitrotoluenes **1** and **4**–**7** into 2-methyl-7-oxa-8-azabicyclo[4.2.0]octa-1(8),2,4-triene 8-oxides [reaction (6)]; B3LYP/6-31+G(2*df*,*p*) calculations



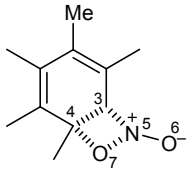
Compound no.		C^2–C^3, pm	C^2–N^5, pm	N^5–O^7, pm	O^7–C^3, pm	∠$C^2N^5O^7$, deg	$\Delta H^\circ_{f,298}$, kJ/mol
1	S	136.6	147.4	122.6	269.9	117.7	91.8
	TS	146.9	134.7	137.2	176.7	100.7	332.2
	P	148.9	132.6	147.7	148.6	94.4	312.7
4	S	139.5	148.1	122.0	309.2	116.6	113.0
	TS	145.2	135.4	137.2	176.7	100.7	332.6
	P	147.5	132.5	151.6	145.8	93.3	307.5
5	S	139.1	147.8	122.3	270.0	117.4	80.4
	TS	147.2	135.9	136.1	175.4	100.4	306.2
	P	149.5	133.2	145.8	148.5	94.8	289.4
6	S	139.4	147.8	122.4	272.2	117.3	81.6
	TS	146.6	135.2	137.0	176.6	100.5	325.7
	P	148.7	132.7	148.7	147.5	94.0	301.6
7	S	139.2	147.8	122.4	274.9	117.1	100.5
	TS	146.8	136.2	135.9	176.0	100.3	316.2
	P	148.6	133.7	145.3	149.5	94.7	310.3

Table 12. Geometric parameters and enthalpies of formation of initial compounds (S), transition states (TS), and products (P) in the transformation of *m*-nitrotoluenes **2**, **4**, **6**, **8**, and **9** into 5-methyl-7-oxa-8-azabicyclo[4.2.0]octa-1(8),2,4-triene 8-oxides [reaction (7)]; B3LYP/6-31+G(2*df*,*p*) calculations



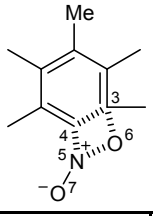
Compound no.		C^2–C^3, pm	C^3–N^5, pm	N^5–O^6, pm	C^3–O^6, pm	∠$C^3N^5O^6$, deg	$\Delta H^\circ_{f,298}$, kJ/mol
2	S	139.3	147.5	122.6	271.9	117.8	79.7
	TS	146.3	134.8	137.3	178.1	100.7	335.9
	P	148.5	132.5	148.9	148.0	94.0	310.9
4	S	139.5	147.4	122.2	280.0	117.5	113.0
	TS	145.0	135.5	137.1	178.4	100.8	345.4
	P	147.5	132.3	153.3	145.1	92.8	312.0
6	S	138.8	147.9	122.4	271.7	117.7	81.6
	TS	145.9	135.2	137.1	177.8	100.4	339.5
	P	148.2	132.5	149.8	147.3	93.5	310.6
8	S	138.5	147.7	122.1	283.3	116.9	108.8
	TS	146.0	136.3	136.0	181.5	101.1	341.7
	P	148.8	133.0	149.1	147.2	93.6	305.0
9	S	139.1	147.9	122.4	271.7	117.4	70.1
	TS	146.4	136.0	136.3	177.1	100.2	310.7
	P	148.4	133.5	146.7	148.9	94.2	291.9

Table 13. Geometric parameters and enthalpies of formation of initial compounds (S), transition states (TS), and products (P) in the transformation of *m*-nitrotoluenes **2**, **4**, **6**, **8**, and **9** into 3-methyl-7-oxa-8-azabicyclo[4.2.0]octa-1(8),2,4-triene 8-oxides [reaction (8)]; B3LYP/6-31+G(2*df*,*p*) calculations



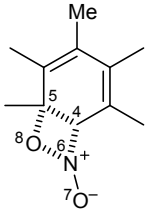
Compound no.		C^3–C^4, pm	C^4–N^5, pm	N^5–O^6, pm	C^3–O^6, pm	∠$C^4N^5O^6$, deg	$\Delta H^\circ_{f,298}$, kJ/mol
2	S	139.0	147.5	122.5	272.0	117.7	79.7
	TS	146.3	134.7	137.5	177.5	100.6	340.9
	P	148.6	132.4	148.9	147.9	94.0	316.1
4	S	139.0	147.4	122.3	271.6	117.2	113.0
	TS	146.0	135.9	136.2	180.3	100.0	356.8
	P	148.7	132.9	148.8	147.2	93.8	322.1
6	S	139.0	147.9	122.4	271.6	117.4	81.6
	TS	146.2	135.2	137.3	176.4	100.2	347.8
	P	148.5	132.7	149.2	147.3	93.7	322.6
8	S	139.5	147.7	122.0	292.3	116.8	108.8
	TS	144.7	135.6	137.4	177.5	100.6	342.6
	P	147.4	132.4	153.1	144.8	92.7	311.1
9	S	138.8	147.9	122.3	271.0	117.5	70.1
	TS	146.8	135.9	136.4	175.6	100.1	318.7
	P	149.3	133.1	147.0	147.8	91.3	297.8

Table 14. Geometric parameters and enthalpies of formation of initial compounds (S), transition states (TS), and products (P) in the transformation of *p*-nitrotoluenes **3**, **5**, and **8** into 4-methyl-7-oxa-8-azabicyclo[4.2.0]octa-1(8),2,4-triene 8-oxides [reaction (9)]; B3LYP/6-31+G(2*df*,*p*) calculations



Compound no.		C^3–C^4, pm	C^4–N^5, pm	N^5–O^6, pm	C^3–O^6, pm	∠$C^4N^5O^6$, deg	$\Delta H^\circ_{f,298}$, kJ/mol
3	S	139.2	147.0	122.6	272.4	117.8	78.0
	TS	146.6	134.6	137.5	176.4	100.4	335.4
	P	148.6	132.6	147.7	148.8	94.3	316.9
5	S	138.5	147.4	122.3	271.7	117.7	80.4
	TS	146.5	135.9	136.3	175.1	99.9	325.2
	P	148.8	133.2	146.1	148.6	94.4	308.3
8	S	139.5	147.1	122.2	285.6	117.2	108.8
	TS	144.9	135.4	137.4	176.8	100.5	335.9
	P	147.3	132.5	151.6	145.8	93.1	310.9

Table 15. Geometric parameters and enthalpies of formation of initial compounds (S), transition states (TS), and products (P) in the transformation of *p*-nitrotoluenes **3**, **5**, and **8** into 4-methyl-7-oxa-8-azabicyclo[4.2.0]octa-1(8),2,4-triene 8-oxides [reaction (10)]; B3LYP/6-31+G(2*df*,*p*) calculations



Compound no.		C^4–C^5, pm	C^4–N^6, pm	N^6–O^8, pm	C^5–O^8, pm	∠$C^4N^6O^8$, deg	$\Delta H^\circ_{f,298}$, kJ/mol
3	S	139.2	147.0	122.6	272.4	117.8	78.0
	TS	146.6	134.6	137.5	176.4	100.4	335.4
	P	148.6	132.6	147.7	148.8	94.3	316.9
5	S	139.1	147.4	122.5	272.4	117.3	80.4
	TS	146.4	135.9	136.9	173.4	99.4	329.8
	P	148.3	133.5	146.0	149.5	94.3	317.0
8	S	138.8	147.1	122.3	277.9	117.0	108.8
	TS	146.5	136.1	136.1	179.7	100.9	342.2
	P	149.0	133.1	147.7	148.0	94.0	314.1

Table 16. Enthalpies of formation (ΔH_f) of nitrotoluenes **1**–**9** and energies of dissociation of the C–N bond therein [D(C–N)]; B3LYP/6-31+G(2*df*,*p*) calculations[2]

Compound no.	ΔH_f, kJ/mol	Radical[a]	ΔH_f, kJ/mol	D(C–N), kJ/mol
1	91.8	*o*-$MeC_6H_4^\bullet$	350.5	271.9
2	79.7	*m*-$MeC_6H_4^\bullet$	351.3	284.8
3	78.0	*p*-$MeC_6H_4^\bullet$	353.6	288.9
4	113.0	1-Me-3-$NO_2C_6H_3$-2-$^\bullet$	335.9	236.2
		1-Me-2-$NO_2C_6H_3$-3-$^\bullet$	346.0	246.3
5	80.4	1-Me-4-$NO_2C_6H_3$-2-$^\bullet$	327.0	259.9
		1-Me-2-$NO_2C_6H_3$-4-$^\bullet$	344.1	277.0
6	81.6	1-Me-5-$NO_2C_6H_3$-2-$^\bullet$	328.2	259.9
		1-Me-2-$NO_2C_6H_3$-5-$^\bullet$	341.1	272.9
7	100.5	1-Me-6-$NO_2C_6H_3$-2-$^\bullet$	339.7	252.4
8	108.8	1-Me-4-$NO_2C_6H_3$-3-$^\bullet$	335.0	239.5
		1-Me-3-$NO_2C_6H_3$-4-$^\bullet$	339.0	243.5
9	70.1	1-Me-5-$NO_2C_6H_3$-3-$^\bullet$	329.8	273.0

[a] Arbitrary atom numbering.

dissociation of that bond. Insofar as the energy of dissociation is calculated from the enthalpies of formation of nitrotoluenes, it is necessary to consider, at least briefly, the main trends in their variation. It should also be taken into account that the gas-phase enthalpies of formation of nitrotoluenes and dinitrotoluenes calculated by different quantum chemical methods may be interesting per se.

Among isomeric mononitrotoluenes, the lowest ΔH_f value was found for *p*-nitrotoluene (Table 16), and the highest, for *o*-nitrotoluene, which is consistent with the

[2] The results of calculations by the other methods [B3LYP/6-31G(*d*,*p*), B98/6-31G(*d*,*p*), wB97XD/TZVP*p*] are available from the authors by e-mail.

experimental data [26]. Increased enthalpy of formation of *o*-nitrotoluene may be related to steric repulsion between the neighboring nitro and methyl groups. The lower enthalpy of formation of *p*-nitrotoluene may be attributed to direct polar conjugation between the donor (CH_3) and acceptor (NO_2) substituents. These factors also affect the enthalpies of formation of isomeric dinitrotoluenes. The lowest enthalpy of formation was predicted for 3,5-dinitrotoluene which is the only dinitrotoluene with spatially separated large substituents.

Among 2,4-, 2,5-, and 2,6-dinitrotoluenes, the latter is characterized by the highest enthalpy of formation according to the computational data obtained by all methods used in this work. This may result from interaction of the methyl groups with two nitro groups. A slightly lower enthalpy of formation of 2,4-dinitrotoluene relative to 2,5-dinitro isomer may be accounted for by direct polar conjugation in the former. This assumption is supported by the close ΔH_f values of *m*- and *p*-nitrotoluenes, on the one hand, and of 2,5- and 2,4-dinitrotoluenes, on the other. These values are 1.2 and 1.7 kJ/mol, respectively, according to the B3LYP/6-31+G(2*df*,*p*) calculations (Table 16). The other methods gave fairly similar values. In the series of dinitrotoluenes, the highest enthalpy of formation was found for the 2,3-dinitro isomer in which strong steric repulsion exists between oxygen atoms of the neighboring nitro groups.

Insofar as the main goal of this section of our study was to estimate activation barriers to radical decomposition reactions, we will not discuss here other peculiarities of the effect of molecular structure on the enthalpies of formation of nitrotoluenes, though the results given in Table 16 provide rich information for such discussion. We only note that our estimates of the enthalpies of formation obtained by different methods, as well as the tendencies in their variation, are fairly consistent. For instance, the correlation coefficient between the ΔH_f values of nitrotoluenes, calculated by the B3LYP/6-31G(*d*,*p*) and wB97XD/TZVPp methods is 0.96, by the B98/6-31G(*d*,*p*) and wB97XD/TZVPp methods, 0.99, by the B98/6-31G(*d*,*p*) and B3LYP/6-31G(*d*,*p*) methods, 0.98, and by the B3LYP/6-31+G(2*df*,*p*) and other methods, 0.99–1.00.

Apart from the enthalpies of formation of the initial compounds, enthalpies of formation of the corresponding products (Table 16) are necessary to estimate the enthalpy of dissociation of the C–NO_2 bond in nitrotoluenes. Substitution of a hydrogen atom in nitrobenzene molecule by methyl group changes the enthalpy of dissociation of the C–NO_2 bond. The enthalpy of dissociation of that bond also depends on mutual position of the methyl and nitro groups. The highest *D*(C–N) values was predicted for *p*-nitrotoluene, and the lowest, for *o*-nitrotoluene. Presumably, this is related to steric interaction between the neighboring substituents. Analysis of the ΔH_f values of the initial compounds and resulting radicals (Table 16) shows that considerable decrease of *D*(C–N) in *o*-nitrotoluene compared to other mononitrotoluenes is determined mainly by the difference in the enthalpies of formation of the initial molecules. The difference in the enthalpies of formation of isomeric methylphenyl radicals is smaller.

A slightly increased energy of dissociation of the C–NO_2 bond in *p*-nitrotoluene compared to the *meta* isomer may be rationalized by two factors acting in the same direction. The calculated ΔH_f value for *p*-nitrotoluene is slightly lower than that for *m*-nitrotoluene. On the other hand, the enthalpy of formation of *p*-methylphenyl radical is higher than the enthalpy of formation of *m*-methylphenyl radical. Both these factors enhance the C–NO_2 bond in *p*-nitrotoluene in comparison to *m*-nitrotoluene, but the effect is fairly weak. The only reason why we consider these factors here is that they are reflected fairly clearly in this simplest case. Thus, the main trends in the variation of the energy of dissociation of the C–NO_2 bond in mononitrotoluenes are related to steric and electronic factors.

As we already noted, the reduced strength of the C–NO_2 bond in *o*-nitrotoluene is likely to be determined by steric factor. On the other hand, increased strength of that bond in *p*-nitrotoluene in comparison to *m*-nitrotoluene is related in part to direct polar conjugation between a weak donor (methyl group) and strong acceptor (nitro group). On the basis of these factors we can interpret variation of *D*(C–N) for isomeric dinitrotoluenes. We estimated the C–NO_2 bond strength for different positions of nitro groups in their molecules; therefore, the number of calculated *D*(C–N) values is considerably larger than the number of examined compounds [13 values of *D*(C–N) for 9 nitro compounds]. Among isomeric dinitrotoluenes, the strongest C–NO_2 bonds are those at C^4 and C^5 (C^3) in 2,4- and 2,5-dinitrotoluenes, respectively, as well as in 3,5-dinitro isomer. According to the B3LYP/6-31+G(2*df*,*p*) data, the energies of dissociation of the C–NO_2 bond are 273.0 (3,5-dinitrotoluene), 277.0

(2,4-dinitrotoluene), and 272.9 kJ/mol (2,5-dinitrotoluene; Tables 1–3). The C^4–NO_2 bond in 2,4-dinitrotoluene is stronger than the C^3–NO_2 bond in 3,5-dinitrotoluene. From the viewpoint of structural differences between the initial molecules, the different strengths of those bonds may be accounted for by possible direct polar conjugation in 2,4-dinitrotoluene and by the lack of such conjugation in 3,5-dinitrotoluene. On the other hand, analysis of the calculated enthalpies of formation of the initial compounds and products of their radical decomposition makes it possible to estimate the contribution of different factors on a quantitative level.

Comparison of the enthalpies of formation of nitrotoluenes and radicals derived therefrom shows that the C^4–NO_2 bond in 2,4-dinitrotoluene is stronger than the C^3–NO_2 bond in 3,5-dinitrotoluene due mainly to the higher enthalpy of formation of the corresponding radical. According to the data of B3LYP/6-31+G(2*df*,*p*) calculations (this method was preferentially used for quantitative estimations), the difference exceeds 14.3 kJ/mol. The difference in the ΔH_f values of 2,4- and 3,5-dinitrotoluenes is slightly smaller (10.3 kJ/mol), so that the C^4–NO_2 bond in molecule **5** is stronger by 4 kJ/mol than in **9**.

Dinitrotoluenes with nitro groups in the *ortho* position with respect to each other (2,3- and 3,4-dinitro isomers) are characterized by weakest C–NO_2 bonds. The lowest D(C–N) value was predicted for the C^2–NO_2 bond in 2,3-dinitrotoluene, which is weaker than the C^3–NO_2 bond by almost 10.1 kJ/mol [B3LYP/6-31+G(2*df*,*p*) calculations; Tables 2, 3, 16). Additional weakening of the C–NO_2 bond neighboring to the methyl group may be rationalized by steric repulsion between the nitro and methyl groups.

The energies of dissociation of the C–NO_2 bond almost do not differ from the energies of activation for radical decomposition of nitrotoluenes. Therefore, the calculated values can also be used for that purpose. Temperature dependence of the energy of activation is usually expressed by the formula

$$E = D(\text{C–N}) + RT. \quad (11)$$

Unlike enthalpies of formation of aromatic nitro compounds and radicals generated by homolytic dissociation of the C–NO_2 bond, the energy of dissociation of that bond is almost temperature independent [22]. Therefore, the energies of dissociation calculated for 298 K (Tables 1–3, 16) can be used to estimate the energy of activation for thermal decomposition of nitroarenes by formula (11).

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