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Effect of Molecular Structure of Nitroalkanes on the C–NO$_2$ Bond Strength and Activation Energy of the Gas-Phase Radical Decomposition According to the Quantum-Chemical Simulation

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Abstract—The non-empirical (MP2 and CCSD), composite (G4), and DFT (B3LYP, CAM-B3LYP, B98, and wB97XD) methods with different basis sets have been employed to compute the formation enthalpies of a series of C$_1$–C$_4$ nitroalkanes and the hydrocarbon radicals formed via the C–N bond rupture as well as the C–N bond dissociation energies. For the series of isomeric nitroalkanes, the effects of the nature of the participating carbon atom (primary, secondary, or tertiary) and the size of adjacent alkyl group on the C–N bond strength have been analyzed. The reasons for different thermochemical and kinetic estimates of the C–N bond dissociation energy in nitroalkanes have been discussed.

Keywords: nitroalkane, alkyl radical, radical decomposition, enthalpy of formation, dissociation energy

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Experimental data on the kinetics of thermal decomposition of organic compounds is an important source of information about the bond dissociation energies and formation enthalpies of the radicals [1–3]. In the case of the homolytic rupture, the C–NO$_2$ bond dissociation energy [D(C–N)] can be determined from the experimental value of the reaction activation energy (E) using Eq. (1).

$$D(\text{C–N}) = E - RT. \quad (1)$$

Having known the values of D(C–N) and formation enthalpy of the RCNO$_2$ compound, the formation enthalpy of the corresponding radical RC$^{\cdot}$ can be determined using Eq. (2):

$$\Delta_f H^0_{\text{RC}^\bullet} = D(\text{C–N}) + \Delta_f H^0(\text{RC–NO}_2) - \Delta_f H^0(\text{NO}_2)^{\cdot}, \quad (2)$$

with $\Delta_f H^0_{\text{RC}}$, $\Delta_f H^0(\text{NO}_2)$, and $\Delta_f H^0(\text{RC–NO}_2)$ standing for the enthalpies of formation of the substrate and the products of reaction (3).

$$\text{RCNO}_2 \rightarrow \text{RC}^{\cdot} + \text{NO}_2^{\cdot}. \quad (3)$$

The D(C–N) values and enthalpies of formation of the organic radicals have been determined for polynitroalkanes using the described approach. However, the experimental data on the decomposition kinetics of mononitroalkanes are available only for nitromethane, nitroethane, and isomeric nitropropanes. Noteworthily, the unsubstituted mononitroalkanes other than nitromethane at temperatures below 700 K are predominantly decomposed via HNO$_2$ elimination (the non-radical mechanism) [1]. The contribution of the radical mechanism is increased upon heating, allowing determination of the activation energy of the radical decomposition. However, such estimates are not very accurate.

Taking advantage of the thermochemical method, the C–NO$_2$ bond dissociation energy can be determined experimentally using Eq. (2); fairly accurate estimates of the formation enthalpies of mononitroalkanes have been obtained [4–7]. Accuracy of the estimates of formation enthalpies of the hydrocarbon radicals required for calculation of D(C–N) has been much worse: the two poorly correlated sets of values have been reported in the literature [8–10], the difference between the values often exceeding 12–15 kJ/mol. The use of so called “accepted values” in many cases has led to contradictory results. For example, the correlation coefficient between the estimates of D(C–N) obtained using the data extracted from most reliable handbooks [8–10] is below 0.50. Moreover, the trends of the bond strength variation as determined using different recommended estimates are different. The thermochemical and the kinetic estimates of the D(C–N) value are substantially different; in all the cases the former estimate is higher, although the opposite could be anticipated from Eq. (1). No convincing explanation of the described discrepancies has been available in the literature.

Independent estimates of the formation enthalpy and the dissociation energy can be made from quantum-chemical simulations. Initially, such estimates have been obtained via the semiempirical methods [11–13]. The accuracy of the so determined formation enthalpies of the molecules and the radicals is poor, but the errors are partially compensated when calculating the dissociation energy using Eq. (2). However, the results of semiempirical quantum-chemical simulation have allowed the semi-quantitative estimates of the bond strengths in the nitroalkanes. Application of the non-empirical and density functional theory (DFT) methods has been much more efficient [14–17]. Nevertheless, the formation enthalpies and the bond dissociation energies of nitroalkanes simulated via the different methods have been often in poor agreement. In view of this, at the current state of the art it is impossible to unambiguously discuss the effects of molecular structure on the C–NO_2 bond strength in the mononitroalkanes using the available experimental and simulated data. The very basic questions have been still open, for example: (a) how does the C–N bond strength depends on the nature of the carbon atom (primary, secondary, or tertiary) forming the bond; (b) what is the effect of the adjacent alkyl size on the C–N bond strength; and c) what is the reason for the discrepancy between the thermochemical and the kinetic estimates of D(C–N).

In this work, we attempted to answer the posed questions analyzing the new computational data obtained using the non-empirical and DFT methods. The choice of the DFT methods was based on the fact that majority of the published results has been obtained via the B3LYP method [18–22]. We have examined the advantages of other modern methods using the non-empirical MP2 method [23–28] with different basis sets and the CCSD method [29, 30] with the 6-31G(d,p) basis set.

Potential of the composite methods for determination of energy parameters of nitroalkanes has been earlier studied in detail [31]. Herein, we limit the report to the results obtained using the G4 method [32, 33], not discussed in [31]. We have trialed different basis sets in the DFT simulation; in this contribution we only discuss the data relevant to the three basis sets having given the best results. For non-empirical methods, we only report the simulated dissociation energy that is generally in satisfactory agreement with the experimental data in spite of poor accuracy of determination of the formation enthalpies of the molecules and the radicals.

All simulations were performed using the Gaussian09 package of quantum-chemical software [34, 35] installed in the Kazan Division of Joint Supercomputer Center of Russian Academy of Sciences. The dissociation energies were calculated from the formation enthalpies of the nitroalkanes and the products of their radical decomposition using Eq. (2). The enthalpies of formation were determined for the optimized conformations of the compounds via the standard procedures [36, 37].

Table 1 shows the calculated values of formation enthalpies of the C_1–C_4 nitroalkanes (the detailed thermochemical data are available for these compounds). As expected, the best agreement with the experiment was obtained when using the G4 composite method. Noteworthily, small deviations were obtained for the G3 and G3B3 methods [31, 36, 37] as well. Among the hybrid DFT methods, the agreement between the calculated and the experimental values of the formation enthalpy was the best in the case of the B98 method [38]. Importantly, all the applied methods correctly reproduced the general trends of the formation enthalpy variation. In the case of the linear nitroalkanes, the formation enthalpy decreased with the growing alkyl chain length. In the case of the branched isomers, the formation enthalpy decreased along the primary > secondary > tertiary nitroalkanes series.

Interestingly, expansion of the basis set used in the B3LYP and B98 simulations deteriorated the results agreement with the thermochemical data, whereas in the cases of the CAM-B3LYP [39] and wB97XD [40] methods expansion of the basis set improved the agreement with the experiment. Therefore, the results obtained using the the latter two methods seemed more reliable.

Comparative analysis of the simulated formation enthalpy of the hydrocarbon radicals (Table 2) with the

Table 1. Enthalpies of formation of the nitroalkanes (kJ/mol)[a]

Method	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	Δ_{av}
B3LYP/6-31G(d,p)	–79.1 (4.6)	–113.0 (10.9)	–135.6 (11.3)	–144.8 (5.4)	–153.6 (8.8)	–166.1 (4.6)	–153.1	–174.1 (1.3)	6.7
B3LYP/6-31+G(2df,p)	–84.5 (10.0)	–105.4 (3.3)	–116.3 (7.9)	–126.8 (12.6)	–127.2 (17.6)	–132.2 (29.3)	–130.1	–142.7 (32.6)	16.3
B3LYP/6-311++G(3df,3pd)	–85.8 (11.3)	–105.4 (3.3)	–114.2 (10.0)	–125.4 (13.8)	–123.8 (20.9)	–134.7 (26.8)	–127.2	–139.3 (36.0)	17.6
CAM-B3LYP/6-31G(d,p)	–85.8 (11.3)	–131.0 (28.9)	–163.2 (38.9)	–174.9 (35.6)	–196.2 (51.5)	–204.6 (43.1)	–198.7	–218.0 (42.7)	36.0
CAM-B3LYP/6-31+G(2df,p)	–94.1 (19.7)	–126.4 (24.3)	–148.5 (24.3)	–159.8 (20.5)	–169.0 (24.3)	–177.0 (15.5)	–174.5	–190.0 (14.6)	20.5
CAM-B3LYP/6-311++G(3df,3pd)	–94.1 (19.7)	–124.3 (22.2)	–144.3 (20.1)	–155.6 (16.3)	–163.2 (18.4)	–171.1 (9.6)	–168.6	–183.3 (7.9)	16.3
B98/6-31G(d,p)	–72.8 (1.7)	–106.7 (4.6)	–127.6 (3.3)	–138.5 (0.8)	–149.4 (4.6)	–156.9 (5.0)	–151.5	–168.2 (7.1)	3.8
B98/6-31+G(2df,p)	–86.2 (11.7)	–109.2 (7.1)	–122.6 (1.7)	–133.1 (6.3)	–135.1 (9.6)	–141.4 (20.1)	–139.3	–151.9 (23.4)	11.3
B98/6-311++G(3df,3pd)	–85.4 (10.9)	–106.3 (4.2)	–117.6 (6.7)	–128.0 (11.7)	–128.0 (16.7)	–134.3 (27.2)	–132.2	–144.8 (30.5)	15.5
wB97XD/6-31G(d,p)	–77.4 (2.9)	–123.8 (21.8)	–153.6 (29.3)	–165.3 (25.9)	–185.4 (40.6)	–197.1 (35.6)	–191.2	–210.0 (34.7)	27.2
wB97XD/6-31+G(2df,p)	–90.4 (15.9)	–122.2 (20.1)	–145.6 (21.3)	–156.5 (17.2)	–169.0 (24.3)	–177.4 (15.9)	–174.5	–189.1 (13.8)	18.4
wB97XD/6-311++G(3df,3pd)	–89.1 (14.6)	–116.3 (14.2)	–137.2 (13.0)	–148.1 (8.8)	–158.2 (13.4)	–166.9 (5.4)	–163.6	–178.2 (2.9)	10.5
G4	–79.9 (5.4)	–106.7 (4.6)	–128.4 (4.2)	–143.9 (4.6)	–147.7 (2.9)	–162.3 (0.8)	–159.0	–179.5 (4.2)	3.8
Experiment [5, 7]	–74.5	–102.1	–124.3	–139.3	–144.8	–161.5		–175.3	

[a] (**1**) CH_3NO_2; (**2**) $CH_3CH_2NO_2$; (**3**) $CH_3(CH_2)_2NO_2$; (**4**) $CH_2C(H)NO_2CH_3$; (**5**) $CH_3(CH_2)_3NO_2$; (**6**) $CH_2C(H)NO_2CH_3CH_3$; (**7**) $(CH_3)_2CHCH_2NO_2$; (**8**) $(CH_3)_3CNO_2$; absolute errors of the calculations are given in parentheses; Δ_{av}—method-averaged values.

experimental data was complicated: as mentioned above, at least two sets of the substantially different values have been reported in the literature [8–10]. In this work we used the thermochemical data from [9, 10], in view of the lower errors of the experimental determination reported in those collections.

The best agreement with the experiment was obtained for the results of the composite G4 method: the averaged absolute deviation from the experimental data was only slightly higher than the errors determination given in [9, 10].

In the cases of the DFT methods, the deviation of the calculated formation enthalpy of the hydrocarbon radicals from the experimental values was much higher, although all the methods used in this study correctly reproduced the parameter variation along the series. Similarly to the commented above, the B3LYP and B98 methods showed better agreement with the experimental data on the radicals formation enthalpy for smaller basis sets, whereas in the case of the CAM-B3LYP and the wB97XD methods, extension of the basis set improved the agreement with the experimental data.

The results obtained for the $NO_2^{\cdot}$ radical deserve special discussion. In all the cases except for the wB97XD method with the 6-31G(d,p) basis set, the

Table 2. Enthalpies of formation of the radicals formed via rupture of the C–NO_2 bond (kJ/mol)[a]

Method	**1'**	**2'**	**3'**	**4'**	**5'**	**6'**	**7'**	**8'**	**9'**	Δ_{av}
B3LYP/6-31G(d,p)	133.1 (13.8)	98.7 (20.1)	80.8 (19.2)	59.8 (32.2)	59.0	41.4 (25.5)	55.6 (15.5)	23.8 (22.2)	23.0 (10.0)	21.3
B3LYP/6-31+G(2df,p)	133.5 (13.4)	110.5 (8.8)	100.0 (0.0)	83.7 (8.4)	90.0	76.6 (9.6)	85.8 (14.6)	56.9 (10.9)	14.2 (18.8)	9.2
B3LYP/6-311++G(3df,3pd)	137.2 (9.6)	114.6 (4.2)	107.5 (7.5)	89.1 (2.9)	97.5	80.3 (13.4)	93.7 (22.6)	64.4 (18.4)	6.3 (26.8)	11.3
CAM-B3LYP/6-31G(d,p)	129.6 (17.2)	86.4 (32.2)	55.9 (44.4)	39.3 (52.7)	25.6	11.6 (55.2)	21.0 (50.2)	-8.6 (54.8)	32.6 (0.4)	43.9
CAM-B3LYP/6-31+G(2df,p)	130.1 (16.7)	98.3 (20.5)	77.4 (23.0)	61.9 (30.1)	57.3	44.4 (22.6)	51.9 (19.2)	24.7 (21.3)	21.3 (11.7)	21.8
CAM-B3LYP/6-311++G(3df,3pd)	135.1 (11.7)	104.6 (14.2)	85.4 (14.6)	69.9 (22.2)	67.8	54.8 (12.1)	62.3 (8.8)	35.6 (10.5)	13.8 (19.2)	13.4
B98/6-31G(d,p)	146.0 (0.8)	111.7 (7.1)	92.0 (7.9)	74.5 (17.6)	72.0	56.9 (10.0)	69.5 (1.7)	37.2 (8.8)	27.2 (5.9)	7.5
B98/6-31+G(2df,p)	146.4 (0.4)	120.9 (2.1)	108.4 (8.4)	92.0 (0.0)	96.2	82.0 (15.1)	92.0 (20.9)	62.8 (16.7)	13.0 (20.1)	9.2
B98/6-311++G(3df,3pd)	152.3 (5.4)	128.0 (9.2)	117.6 (17.6)	100.8 (8.8)	107.9	93.3 (26.4)	103.3 (32.2)	74.1 (28.0)	6.3 (27.2)	18.4
wB97XD/6-31G(d,p)	142.3 (4.6)	101.7 (17.2)	69.9 (30.1)	55.6 (36.4)	41.8	27.2 (39.7)	38.1 (33.1)	7.9 (38.5)	33.9 (0.8)	28.5
wB97XD/6-31+G(2df,p)	143.9 (2.9)	113.4 (5.4)	90.4 (9.6)	77.8 (14.2)	72.4	59.0 (8.4)	66.5 (4.6)	39.7 (6.3)	18.4 (15.1)	7.5
wB97XD/6-311++G(3df,3pd)	150.2 (3.3)	121.8 (2.9)	100.8 (0.8)	87.9 (4.2)	85.4	71.5 (4.6)	79.5 (8.4)	52.7 (6.7)	13.4 (19.7)	4.2
G4	144.8 (2.1)	120.5 (1.7)	100.4 (0.4)	88.7 (3.3)	79.5	69.9 (2.9)	71.5 (0.4)	51.5 (5.4)	29.7 (3.3)	2.5
Experiment [11, 12]	146.9	118.8	100.0	92.0	–	66.9	71.1	46.0	33.1	

[a] (**1'**) $CH_3^{\bullet}$; (**2'**) $CH_3CH_2^{\bullet}$; (**3'**) $CH_3CH_2CH_2^{\bullet}$; (**4'**) $CH_2CHCH_3^{\bullet}$; (**5'**) $CH_3(CH_2)_2CH_2^{\bullet}$; (**6'**) $CH_2CHCH_3CH_3^{\bullet}$; (**7'**) $(CH_3)_2CHCH_2^{\bullet}$; (**8'**) $(CH_3)_3C^{\bullet}$; (**9'**) $NO_2^{\bullet}$; absolute errors of calculations are given in parentheses; Δ_{av}—method-averaged values ($NO_2^{\bullet}$ data excluded).

calculated formation enthalpy of that radical was below the experimental value. Importantly, in the all cases expansion of the basis set increased the resulting value deviation from the experimental one. Obviously, the value of the formation enthalpy of the $NO_2^{\cdot}$ radical affected the absolute value of the C–NO_2 bond dissociation energy, but not its variation along the series.

The calculated values of *D*(C–N) are presented in Table 3. According to the simulation, the C–NO_2 bond strength revealed only slight variation, by 10.5–20 kJ/mol, in the series of the studied nitroalkanes. That was consistent with the thermochemical and kinetic data. Note that the variation of that bond strength in the studied series was differently described by different theoretical and experimental methods.

All the non-empirical methods revealed similar variations of the *D*(C–N) in the studied series (see figure). In particular, the C–NO_2 bonds formed by the secondary carbon atom were the strongest. The results presented in Tables 1 and 2 rationalized the observed trend as follows: decrease of the formation enthalpy in the series of primary nitroalkanes exceeded the decrease of the formation enthalpy of the radicals formed via the C–NO_2 bond rupture. The respective thermochemical and kinetic data were in agreement with that conclusion.

Table 3. Energies of dissociation of the C–NO_2 bond (kJ/mol)[a]

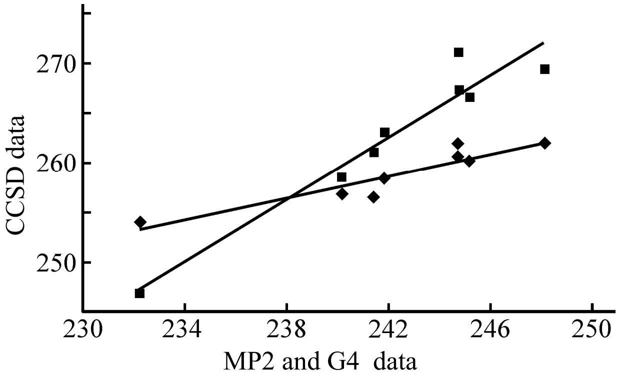
Method	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	Δ_{av}
B3LYP/6-31G(d,p)	235.1	234.7	239.3	227.6	235.6	230.5	231.8	220.9	26.4
	(19.2)	(19.2)	(18.0)	(36.8)		(31.0)		(33.5)	
B3LYP/6-31+G(2df,p)	232.2	230.1	230.1	224.7	231.4	223.0	230.5	213.8	32.2
	(22.2)	(23.8)	(27.2)	(39.7)		(38.5)		(40.6)	
B3LYP/6-311++G(3df,3pd)	229.3	226.4	228.0	220.9	227.6	221.3	227.2	210.0	35.1
	(25.1)	(27.6)	(29.3)	(43.5)		(40.2)		(44.4)	
CAM-B3LYP/6-31G(d,p)	247.7	250.2	251.9	246.9	254.4	248.9	252.3	242.3	9.6
	(6.7)	(3.8)	(5.4)	(17.6)		(13.0)		(12.1)	
CAM-B3LYP/6-31+G(2df,p)	246.0	246.0	246.9	243.1	247.7	243.1	247.7	236.0	14.2
	(8.4)	(7.9)	(10.5)	(21.3)		(18.4)		(18.4)	
CAM-B3LYP/6-311++G(3df,3pd)	243.1	242.7	243.5	239.3	244.8	239.7	244.8	232.6	17.6
	(11.3)	(11.3)	(13.8)	(25.1)		(21.8)		(21.8)	
B98/6-31G(d,p)	246.4	245.6	246.9	240.6	248.5	240.6	248.1	232.6	15.5
	(7.9)	(8.4)	(10.5)	(23.8)		(20.9)		(21.8)	
B98/6-31+G(2df,p)	245.6	243.1	243.5	237.7	244.3	236.4	243.9	227.6	18.8
	(8.8)	(10.9)	(13.8)	(26.8)		(25.1)		(26.8)	
B98/6-311++G(3df,3pd)	243.5	240.2	241.0	234.7	241.8	233.9	241.8	225.1	21.3
	(10.9)	(13.8)	(16.3)	(29.7)		(27.6)		(29.3)	
wB97XD/6-31G(d,p)	253.6	259.4	257.3	254.8	261.1	258.2	263.2	251.9	3.8
	(0.8)	(5.4)	(0.0)	(9.6)		(3.3)		(2.5)	
wB97XD/6-31+G(2df,p)	252.3	254.0	254.4	252.3	259.4	254.4	259.0	247.3	5.4
	(2.1)	(0.0)	(2.9)	(12.1)		(7.1)		(7.1)	
wB97XD/6-311++G(3df,3pd)	252.7	251.0	251.5	248.9	256.5	251.9	256.5	243.9	7.5
	(1.7)	(2.9)	(5.9)	(15.5)		(9.6)		(10.5)	
MP2/6-31G(d,p)	246.9	258.6	263.2	267.4	261.1	269.4	266.5	271.1	7.5
	(7.5)	(4.6)	(5.9)	(2.9)		(7.9)		(16.7)	
G4	254.0	256.9	258.6	261.9	256.5	261.9	260.2	260.7	2.1
	(0.4)	(2.9)	(1.3)	(2.5)		(0.4)		(6.3)	
CCSD/6-31G(d,p)	232.2	240.2	241.8	244.8	241.4	248.1	245.2	244.8	15.9
	(22.2)	(13.8)	(15.5)	(19.7)		(13.4)		(9.6)	
QCISD/6-31G(d,p)	230.5	238.5	240.2	243.1	239.7	246.4	243.5	243.5	17.2
	(23.8)	(15.5)	(17.2)	(21.3)		(15.1)		(10.9)	
Experiment [11, 12]	254.4	254.0	257.3	264.4	–	261.5	–	254.4	

[a] See note for Table 1.

At the same time, all the applied DFT methods showed that the C–NO_2 bonds formed by secondary carbon atoms were weaker. In that case, the absolute variation of the formation enthalpy of the radicals exceeded that of the corresponding isomeric nitroalkanes. The conclusion contradicted the available experimental data and the results of non-empirical simulation, and apparently was an artifact.

Another question of considerable interest is the effect of the alkyl chain length on the *D*(C–N) value; the available experimental data cannot give the unambiguous conclusion on the matter. Our non-empirical simulations confirmed that the increased alkyl chain length led to slight strengthening of the C–NO_2 bond in the cases of the 1-nitroalkanes (nitromethane, nitroethane, and 1-nitropropane). The available thermochemical and kinetic data did not contradict the conclusion.

Experimental activation energies of the gas-phase nitroalkanes decomposition were lower than the



Correlation of the CCSD and MP2 [6-31G(d,p) basis set] data, the correlation coefficient of 0.965 (♦); and of the CCSD and G4 data, the correlation coefficient of 0.930 (■).

thermochemical or quantum-chemical estimates of the *D*(C–N) value. Although quite small, the difference was above the possible experimental (simulation) error. According to Eq. (1), the opposite trend was expected in the case of radical mechanism of the primary stage of the reaction. The observed discrepancy could be explained by the contribution of various non-radical pathways of the reaction into the experimentally measured rate constant of thermal decomposition.

Detailed analysis of experimental results was beyond the scope of this study. However, it should be noted that the substantial difference between the activation energy of the gas-phase decomposition of nitromethane and the corresponding *D*(C–N) value could not be explained exclusively by the contribution of competitive non-radical reactions. Indeed, the activation enthalpy of all the known mechanisms of the primary stage of nitromethane gas-phase decomposition exceeds the *D*(C–N) value [16, 41–43]. Probably, the gas-phase decomposition of nitromethane was complicated by faster reactions at the walls of the reaction vessel, where liquid-phase decomposition might occur under certain conditions.

In the cases of nitroethane and nitropropanes, the difference between the activation energy of the gas-phase monomolecular decomposition and the *D*(C–N) value could be explained by the contribution of the gas-phase elimination of HNO_2 [22]. Its activation energy [188.5 (nitroethane), 188.1 (1-nitropropane), and 182.3 (2-nitropropane) kJ/mol] is substantially lower than the *D*(C–N) of the nitroalkanes; therefore, the contribution of elimination could lower the effective activation energy of the gas-phase decomposition. The assumption was supported by the variations of the activation energy of the radical decomposition of nitroethane (233.1 kJ/mol), 1-nitropropane (245.1 kJ/mol), and 2-nitropropane (226.3 kJ/mol), otherwise unexplainable in the frame of a unified mechanism of the primary reaction stage.

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