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Molecular Structure and Mechanisms of Unimonomolecular Decomposition of Primary *N*-Nitramines

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Abstract—By means of nonempirical and the density functional methods the geometrical parameters, the enthalpies of formation of the compounds and radicals, and the dissociation energies of the N–NO_2 bond in primary and secondary *N*-nitramines were evaluated. The tendencies to the variation of spatial arrangement, of the formation enthalpies, and of the dissociation energies in the series of simplest *N*-nitramines were analyzed. Alternative mechanisms of the initial stage of the gas phase unimolecular decomposition were considered. It is noted that among all the processes of unimolecular decomposition the formation and destruction of *aci*-form according to the complex multy-stage mechanism was the most energetically favored.

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N-nitramines form one of the most interesting and practically important classes of nitro compounds. But just this class remains the less studied one. Only scarce data on spatial arrangement and the electronic structure of secondary *N*-nitramines obtained by gas-phase electronography and various quantum-chemical methods exist [1, 2]. Experimental studies of the kinetics of thermal decomposition are incomplete and of low accuracy. In many cases experimental data reported by several workers are in poor agreement [3, 4]. For instance, for octogene the scatter in the activation energy value exceeds 100 kJ, and the reported pre-exponential factors are in the range 11.7–19.2 [3, 4]. The mechanism of decomposition of primary and secondary nitramines is not completely established up to now. In the majority of works it is presumed that the initial act of the reaction is determined by the homolytic cleavage of the N–N bond [4, 5]. But the absence of detailed data on the composition of products on the initial stages of *N*-nitramines decomposition, and of the sufficient number of the reliable theoretical evaluations of barriers to the alternative reactions of unimolecular decomposition is the main obstacle for the understanding of the reaction mechanism. Primary *N*-nitramines remain the least studied.

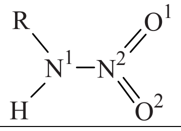
In the work presented an attempt is made of investigation of the molecular structure and the reaction mechanisms of the thermal decomposition of primary *N*-nitramines using modern quantum-chemical methods. In some cases our data on the molecular structure and the mechanism of the gas phase decomposition of secondary nitramines was used for discussion.

The variations in the molecular structure and the mechanism of unimolecular decomposition of primary *N*-nitramines were studied by means of the density functional methods (DFT-methods) B3LYP/6-31G(d) and B3LYP/6-311++G(df,p) within the framework of the Gaussian 98 and Gaussian 2003 programs. It was shown recently [6,7] that these methods well reflected the geometrical parameters, the enthalpies of formation, the vibrational spectra [8], and the barriers of the reaction of the molecular decomposition in the gas phase of the aliphatic C- and O-nitro compounds. The calculations were carried out with a complete optimization of geometric parameters without symmetry limitations. When several local minimum points were found, the one with the lowest energy value was used. All compounds presented in this contribution have positive Hessian values in the extremum points.

Direct contact of the amine fragment with nitro groups in primary nitramines attracts the interest to the investigation of geometry of the reaction center and of the charge distribution between the two contacting nitrogen atoms. In the consideration of problems of thermal stability of *N*-nitro compounds the greatest interest present naturally the geometrical characteristics of NH–NO_2 group. Our results show that in the series both of branched and unbranched primary nitramines the N–N interatomic distance does not practically vary (Table 1) and reaches on the average 138.5 pm. Branching of the carbon skeleton of primary nitramines at the α-carbon atom (compounds **VI, VIII,** and **IX** causes the increase in the C–N distance to 147.3 pm.

The rest geometrical parameters vary insignificantly. Introduction of a halogen in the methylnitramine molecule leads to a decrease in the C–N

Table 1. Geometrical parameters of primary nitramines and also of the fluorine and chlorine derivatives of methylnitramine [B3LYP/6-31G(d)]



Comp. no.	Compound	Interatomic distance, pm				Angle, deg
		$R–N^1$	$N^1–N^2$	$N^2–O^1$	$N^2–O^2$	ON^2O
I	CH_3NHNO_2	145.6 (145.3)[a]	138.5 (138.2)	122.9 (122.8)	122.8 (122.8)	127.1 (125.3)
II	$CH_3CH_2NHNO_2$	146.4	138.4	123.0	122.8	126.9
III	$CH_3(CH_2)_2NHNO_2$	146.3	138.6	122.9	122.9	126.7
IV	$CH_3(CH_2)_3NHNO_2$	146.4	138.6	122.9	122.8	126.7
V	$CH_3(CH_2)_4NHNO_2$	146.3	138.5	123.0	122.8	126.6
VI	$CH_3CH_2CH(CH_3)NHNO_2$	147.3	138.4	122.9	123.0	126.6
VII	$CH_3CH(CH_3)CH_2NHNO_2$	146.1	138.5	122.8	123.1	126.5
VIII	$CH_3CH_2CH(C_2H_5)NHNO_2$	147.2	138.3	122.9	123.0	126.5
IX	$CH_3CH(CH_3)NHNO_2$	147.3	138.4	123.0	123.0	126.6
X	$(CH_3)_3CNHNO_2$	149.1	138.1	123.0	123.1	126.0
XI	CH_2FNHNO_2	143.0	141.0	122.3	122.2	127.6
XII	CHF_2NHNO_2	143.6	140.4	122.2	122.3	127.7
XIII	CF_3NHNO_2	141.7	141.2	122.2	121.7	128.4
XIV	$CHFClNHNO_2$	142.5	140.6	122.2	122.2	127.9
XV	$CClF_2NHNO_2$	143.6	141.0	122.2	121.7	128.5
XVI	CCl_2FNHNO_2	143.4	141.8	122.2	121.6	128.6
XVII	$CH_2ClNHNO_2$	142.1	140.9	122.3	122.1	127.9
XVII	$CHCl_2NHNO_2$	142.1	141.1	122.0	122.1	128.1
XIX	CCl_3NHNO_2	143.2	141.9	122.1	121.5	128.6
XX	$O_2NNHCH_2NHNO_2$	145.8	138.2	122.4	123.2	127.2
XXI	$O_2NNHCH_2CH_2NHNO_2$	145.9	138.3	122.7	123.0	126.9

[a] Gas electronography data are given in parentheses [1].

Table 2. Geometrical parameters of secondary nitramines [B3LYP/6-31G(d)]

Compound	Interatomic distance, pm			Angle, deg	
	C–N	N–N	N–O	CNC	NNN
$(CH_3)_2NNO_2$	145.5	136.4	123.5	125.8	–
$(CH_3CH_2)_2NNO_2$	146.4	136.6	123.6	123.4	–
$(CH_2F)_2NNO_2$	143.2	140.9	122.3	122.1	–
$(CHF_2)_2NNO_2$	144.8	140.9	122.3	121.5	–
$(CF_3)_2NNO_2$	145.1	143.7	121.4	124.3	–
$CH_3N(NO_2)_2$	147.0	146.9	122.0	–	112.9
$CH_3CH_2N(NO_2)_2$	148.3	145.7	122.2	–	115.1
$CH_3(CH_2)_2N(NO_2)_2$	148.2	145.6	122.3	–	115.2
$CH_3(CH_2)_3N(NO_2)_2$	148.3	145.6	122.3	–	115.2

interatomic distance and to elongation of the N–N bond. The calculations predict a monotonous change in the ONO angle value due to the nonvalent interactions of the F···O and Cl···O atoms. Analogous trends may be observed also for the mixed halides. Comparison of data for the halide derivatives of methylnitramine and nitromethane [9] permits a conclusion that whereas for C-nitro compounds an important role in variation of geometrical parameters is played by sterical factors (for the chlorine derivatives of nitromethane accumulation of bulky chlorine atoms results in sterical strain leading to the abnormal elongation of interatomic distance and to decrease in strength of the C–N bond [9]), for *N*-nitro compounds the decisive role is played by electronic effects.

In the methylene-*N*,*N*-dinitramine (medina) and ethylene-*N*,*N*-dinitramine (EDNA) additional nitro group practically does not affect the length of the N–N and C–N bonds. Note also that nitro groups are located in different amine fragments.

During the investigation of secondary nitramines the attention was attracted by the significant variation in the N–N interatomic distance. Dinitramines have a strong electron-acceptor NO_2 group which is bound directly to the amine nitrogen atom. At the transfer from primary nitramines to dinitro- and dialkylnitramines the NNCX angle (where X = Alk or NO_2) changes insignificantly. For example, for dinitro derivatives NNNC angle is 140°–142°, and for dialkyl compounds it is 179°–180° (see Table 2).

Calculation of the vibration frequences of molecules by means of various quantum-chemical methods makes it possible to obtain information about their belonging to a certain symmetry group and also to evaluate the vibrational statistic sum which provides the main contribution to the preexponential factor (A-factor) of the gas phase unimolecular decomposition. In Table 3 the calculated values of the vibration frequencies of *N*-methylnitramine obtained by different DFT methods (B3LYP) and nonempirical calculations (MP2, MP3, MP4, QSISD, G2) together with the experimental values measured for the gas phase [10] are presented.

The analysis performed shows that the best correlation between the calculation results and the experimental data is provided by the MP4/6-31G(d) and QCISD/6-31G(d) methods. The correlation coefficients are 0.9927 and 0.9922, respectively. As the experimental data on the frequencies in the far IR range were obtained for nitramines in the crystalline and the condensed states [11], the correlation coefficients were calculated on the basis of frequencies up to 700 cm^{-1}. DFT methods to some extent overrate the frequencies above 2000 cm^{-1}, and broadening of basis [B3LYP/6-311++G(df,p)] leads to the greater scattering while for nitro ethers the reversed dependence is observed. Greatest disagreement with the experiment was observed for the MP3/6-31G(d) and G2 methods. It could be expected because the accounting for the odd corrections (MP3, MP5) in the Møller–Plesset perturbation theory gives significant oscillation in the calculation of the force constants. The calculation of frequencies in the G2 method proceeds according to HF/6-31G(d) method which significantly overestimates the frequencies for N- and C-nitro compounds.

A significant interest presents the investigation of the value and the form of the rotation barriers for the functional groups (Fig. 1).

A high value of the rotation barrier for NO_2 group indicates a significant p–π conjugation between the unshared electronic pair of the amine nitrogen and the π-electronic system of the nitro group. The analogous tendency was observed also in the aliphatic nitro ethers [12]. The form of barrier permits to conclude that the inversion in the amine fragment is present. The molecule posesses C_1 symmetry. Besides, we studied the variations in the interatomic distances and the bond angles arising from the rotation of functional group. The most interesting was the observed elongation of

Table 3. Spectral characteristics (vibration frequencies, cm^{-1}, and the correlation coefficients) for *N*-methylnitramine according to different methods

IR spectrum, pairs [10]	B3LYP/ 6-31G(d)	B3LYP/ 6-311++G(df,p)	MP2/ 6-31G(d)	MP3/ 6-31G(d)	MP4/ 6-31G(d)	G2	QCISD/ 6-31G(d)	Assignment
3446	3594	3604	3598	3647	3548	3867	3596	ν(NH)
3430	3182	3147	3254	3245	3203	3357	3210	$\nu_{as}(CH_3)$
	3143	3113	3212	3205	3158	3317	3167	$\nu_{as}(CH_3)$
	3056	3033	3114	3116	3066	3236	3080	$\nu_{sim}(CH_3)$
1621	1701	1639	1823	1818	1715	1888	1711	$\nu_{as}(NO_2)$
1492	1541	1510	1573	1572	1554	1663	1560	
1440	1509	1476	1543	1546	1525	1648	1532	$\nu_{as}(CH_3)$
1430	1482	1457	1514	1528	1490	1624	1505	$\nu_{sim}(CH_3)$
1401	1445	1421	1482	1503	1456	1605	1470	σ(NH)
1386	1383	1349	1410	1467	1356	1572	1416	σ(NH)
1340	1213	1199	1238	1248	1219	1324	1233	$\sigma(CH_3)$
1332	1156	1143	1181	1185	1165	1260	1176	$\sigma(CH_3)$
1092	1122	1113	1142	1175	1108	1256	1142	ν(CN)
928	952	945	962	993	932	1056	965	ν(NN)
785	780	780	775	807	772	907	792	$\rho(NNO_2)$
772	752	740	774	791	756	827	782	$\rho(NNO_2)$
	586	585	603	614	583	656	599	
	553	514	582	593	568	597	584	
	309	302	323	329	321	340	326	$\sigma(CH_3)$
	186	178	210	209	210	213	211	$\rho(NCH_3)$
	143	135	153	153	148	159	151	
Correlation coefficient	0.9917	0.9913	0.9916	0.9906	0.9927	0.9885	0.9922	

N–N bond during the rotation of NO_2 group. The largest elongation (up to 1.29 pm) of the above-mentioned bond was found at the turn of functional group by 120° and 300°. At 0° and 180° the variations are the smallest, but in this position the other more labile characteristics such as CNN and ONO angles change That is why small characteristic maximum points are observed on the diagram of alteration of the rotation barrier with the rotation angle of the nitro group (Fig. 2).

After the brief discussion of the features in the changes of the geometric parameters in the *N*-nitramine series we go to the main subject of our work, that is the investigation of the effect of spatial arrangement on the variation in the activation barriers for the alternative mechanisms of unimolecular decomposition in the gas phase. At first we would consider the rules of radical mechanism of the first step of the reaction consisting in the homolytic cleavage of the N–NO_3 bond. In the radical mechanism

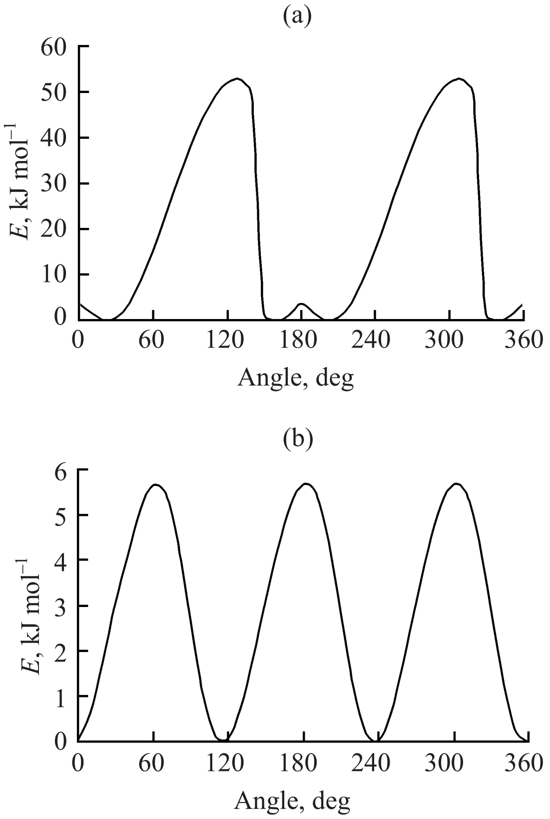


Fig. 1. Form of the rotation barriers for (a) NO_2 and (b) CH_3 groups in *N*-methylnitramine [B3LYP/6-31G(d)].

of the initial act the activation energy of thermal decomposition practically coincides with the dissociation energy of the bond suffering the cleavage [4].

$$E_a = D(\text{N–N}) + RT.$$

If the recombination of radicals formed in the course of thermal decomposition requires no activetion, the enthalpy of homolytic cleavage of the RA bond, RA = $R^{\cdot}$ +$A^{\cdot}$ is equal to the activation enthalpy [13]. In this case the activation energy of radical decomposition practically coincides with the dissociation energy of the RA bond and it can be evaluated according to the Hess' law through the quantum-chemical evaluations of the formation enthalpies of the starting compound and the reaction products.

$$D(\text{R–A}) = \Delta H^0_{\text{R}} + \Delta H^0_{\text{R}} - \Delta H^0_{\text{R–A}}.$$

On an example of *N*-methylnitramine it was shown that the barrier to radical recombination is absent (see Fig. 3). We have used the procedure described in detail in [14].

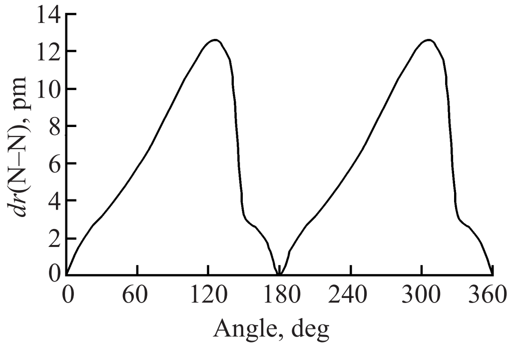


Fig. 2. Dependence of variation of the N–N bond length on the rotation angle of NO_2 group in *N*-methylnitramine [B3LYP/6-31G(d)].

Results of calculations by the B3LYP/6- 31G(d) method predict small increase in the dissociation energy of the N–N bond [*D*(N–N)] in the series of primary nitramines in going from methylnitramine to *n*-pentylnitramine (Table 4). A monotonous increase in the dissociation energy is confirmed also by the B3LYP/6-311++G(df,p) method.

Comparison of the compounds containing NH–NO_2 group at the primary and the secondary carbon atoms reveals that the *D*(N–N) values for the compounds of *iso*-structure are to some extent smaller. Calculations show that N–N bonds at the tertiary carbon atom are even less strong. The comparison of the enthalpies of formation of the isomeric compounds and radicals shows that the decrease in *D*(N–N) is connected mainly with the additional stabilization of the radical formed by the elimination of the nitro group. Note that the analogous effect is observed in the series of nitro alkanes and nitro ethers [9].

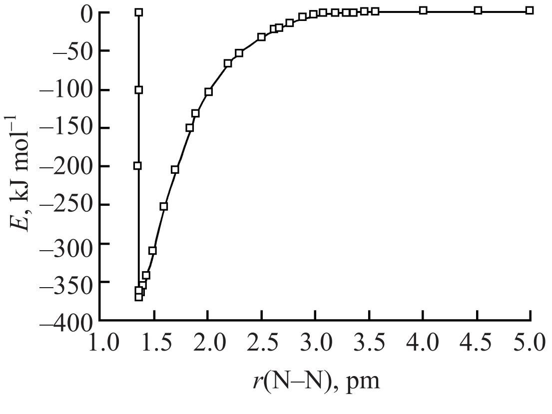


Fig. 3. Dependence of the variation of the total energy of *N*-methylnitramine molecule on the N–N interatomic distance [B3LYP/6=31G(d)].

Table 4. Formation enthalpies of compounds and radicals and the dissociation energies of N–N bond in *N*-nitramines, fluorine and chlorine derivatives of methylnitramine [B3LYP/6-31G(d), kJ mol^{-1}]

Compound	$\Delta H^{0}_{\mathrm{f},\,298}$	Radical	$\Delta H^{0}_{\mathrm{f},\,298}$	*D*(N–N), kJ mol^{-1}
		NO_2 ($^{\bullet}$)	23.0	
CH_3NHNO_2	–0.2	$CH_3HN^{\bullet}$	172.0	195.2
$CH_3CH_2NHNO_2$	–20.8	$CH_3CH_2HN^{\bullet}$	152.3	196.1
$CH_3(CH_2)_2NHNO_2$	–36.2	$CH_3(CH_2)_2HN^{\bullet}$	138.6	197.9
$CH_3(CH_2)_3NHNO_2$	–49.2	$CH_3(CH_2)_3HN^{\bullet}$	125.8	197.9
$CH_3(CH_2)_4NHNO_2$	–62.4	$CH_3(CH_2)_4HN^{\bullet}$	112.6	198.0
$CH_3CH_2CH(CH_3)NHNO_2$	–54.0	$CH_3CH_2CH(CH_3)HN^{\bullet}$	120.2	197.2
$CH_3CH(CH_3)CH_2NHNO_2$	–48.8	$CH_3CH(CH_3)CH_2HN^{\bullet}$	122.6	194.4
$CH_3CH_2CH(C_2H_5)NHNO_2$	–65.3	$CH_3CH_2CH(C_2H_5)HN^{\bullet}$	109.2	197.5
$CH_3CH(CH_3)NHNO_2$	–44.0	$CH_3CH(CH_3)HN^{\bullet}$	130.3	197.4
$(CH_3)_3CNHNO_2$	–56.0	$(CH_3)_3CHN^{\bullet}$	109.5	188.5
CH_2FNHNO_2	–195.6	$CH_2FHN^{\bullet}$	–33.7	184.9
CHF_2NHNO_2	–414.5	$CHF_2HN^{\bullet}$	–249.2	188.3
CF_3NHNO_2	–647.4	$CF_3HN^{\bullet}$	–498.8	171.5
$CHFClNHNO_2$	–194.9	$CHFClHN^{\bullet}$	–47.2	170.7
$CClF_2NHNO_2$	–400.6	$CClF_2HN^{\bullet}$	–270.1	153.5
CCl_2FNHNO_2	–167.1	$CCl_2FHN^{\bullet}$	–38.1	152.0
$CH_2ClNHNO_2$	–10.1	$CH_2ClHN^{\bullet}$	151.0	184.1
$CHCl_2NHNO_2$	9.1	$CHCl_2HN^{\bullet}$	155.2	169.1
CCl_3NHNO_2	58.8	$CCl_3HN^{\bullet}$	180.4	144.6
$O_2NNHCH_2NHNO_2$	55.3	$O_2NNHCH_2HN^{\bullet}$	229.1	196.8
$O_2NNHCH_2CH_2NHNO_2$	43.8	$O_2NNHCH_2CH_2HN^{\bullet}$	211.5	190.7
$(CH_3)_2NNO_2$	–8.8	$(CH_3)_2N^{\bullet}$	146.4	178.2
$(CH_3CH_2)_2NNO_2$	–52.0	$(CH_3CH_2)_2N^{\bullet}$	113.8	188.8
$(CH_2F)_2NNO_2$	–389.3	$(CH_2F)_2N^{\bullet}$	–239.7	172.6
$(CHF_2)_2NNO_2$	–825.1	$(CHF_2)_2N^{\bullet}$	–675.2	172.9
$(CF_3)_2NNO_2$	–1273.7	$(CF_3)_2N^{\bullet}$	–1166.6	130.1
$CH_3N(NO_2)_2$	97.3	$CH_3(NO_2)N^{\bullet}$	128.4	108.1
$CH_3CH_2N(NO_2)_2$	75.9	$CH_3CH_2(NO_2)N^{\bullet}$	163.9	110.9
$CH_3(CH_2)_2N(NO_2)_2$	62.5	$CH_3(CH_2)_2(NO_2)N^{\bullet}$	148.9	109.4
$CH_3(CH_2)_3N(NO_2)_2$	49.2	$CH_3(CH_2)_3(NO_2)N^{\bullet}$	135.6	109.4

The calculations show that introduction of halogen in the methylnitramine molecule results in the decrease in *D*(N–N). Note also sharp decrease in *D*(N–N) (almost on 80 kJ mol^{-1}) in the presence of the second nitro group in dinitramines. In this case N–N bond is strongly elongated and a weak electrostatic interaction between the nitrogen atoms leads to the strong decrease in the dissociation energy (Tables 2, 4). Analogous variations take place in aliphatic C-nitro compounds at the accumulation of nitro groups [9], but for *N*-nitramines this effect is expressed more clearly. In general, *D*(N–N) values of secondary nitramines are lower as compared to the primary nitramines of normal structure.

The studies performed show that variations in the parameters of spatial arrangement of primary and secondary nitramines are relatively small, and consequently the variations in the *D*(N–N) values and the activation energies of the radical gas phase decomposition are insignificant [12–14].

Although the majority of researchers consider that thermal decomposition of *N*-nitrocompounds proceeds according to the general radical mechanism where the first stage is the homolytic cleavage of the N–N bond, nowadays the common viewpoint is not yet attained, and investigation of alternative mechanisms presents the undoubtful interest.

We studied as alternative mechanisms of thermal decomposition three molecular (nonradical) processes including the elimination of nitrous acid, the nitro-nitrite rearrangement and the formation of an *aci*-form [Eqs. (2)–(4)].

$$CH_3NHNO_2 \rightarrow CH_3NH^{\bullet} + {}^{\bullet}NO_2, \quad (1)$$

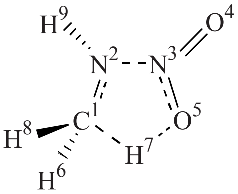
$$CH_3NHNO_2 \rightarrow CH_2{=}NH + HNO_2, \quad (2)$$

$$CH_3NHNO_2 \rightarrow CH_3NHONO, \quad (3)$$

$$CH_3NHNO_2 \rightarrow CH_3N{=}N(OH)O. \quad (4)$$

In the Table 5 geometrical parameters of the reaction centers in the transition state of the elimination of HNO_2 for primary and secondary *N*-nitramines are listed.

Table 5. Geometrical parameters of the transition state for the elimination of nitrous acid [B3LYP/6-31G(d)]



Compound	Interatomic distance, pm					Angle, deg		
	C^1–N^2	N^2–N^3	N^3–O^5	C^1–H^7	O^5–H^7	$C^1N^2N^3$	$N^2N^3O^5$	$C^1H^7O^5$
CH_3NHNO_2	134.4	212.5	126.8	133.8	129.8	96.4	102.0	150.4
$CH_3CH_2NHNO_2$	134.9	214.1	126.5	131.2	132.7	96.6	101.8	152.1
$CH_3(CH_2)_2NHNO_2$	134.9	214.4	126.6	131.2	132.8	96.5	101.8	152.0
$(CH_3)_2CHNHNO_2$	135.2	214.9	126.3	129.7	134.7	96.9	101.5	153.5
$(CH_3)_2NNO_2$	135.8	198.4	130.2	133.9	129.1	97.4	105.9	147.2
$(CH_3CH_2)_2NNO_2$	136.1	205.2	129.8	127.9	133.8	96.1	104.6	150.1
$CH_3N(NO_2)_2$	134.1	217.4	126.3	133.1	129.8	95.5	100.5	150.6
$CH_3CH_2N(NO_2)_2$	135.7	217.9	126.4	131.5	131.2	96.0	100.4	153.0
$CH_3(CH_2)_2N(NO_2)_2$	135.7	218.2	126.4	131.5	131.5	95.9	100.5	152.9
$CH_3(CH_2)_3N(NO_2)_2$	135.7	218.1	126.4	131.4	131.5	95.9	100.4	152.9
CH_2FNHNO_2	132.5	215.4	126.2	131.4	132.7	95.9	101.9	150.3
$CH_2ClNHNO_2$	133.0	210.7	126.4	133.3	128.9	96.4	102.4	149.6

It follows from the obtained data that the transition state for each compound under investigation is the planar five-membered cycle. As compared to the starting molecules the greatest variations are observed for the N–N bond (which is practically ruptured in the transition state), for the C–N bond (its shortening indicates the formation of the C=N multiple bond), and for the C–H bond, and therewith the hydrogen atom H^7 begins its movement to the nitro group. In the series *N*-methylnitramine–isopropylnitramine the insignificant elongation of the reaction center bonds is observed, but on the whole the structure of the transition state practically does not alter. Due to the influence of substituent the elongation of the N–N bond in the secondary nitramines is to some extent smaller, while in dinitramines it is larger.

Data presented in Table 6 show that the energy of bond dissociation for primary *N*-nitramines, and for the series of secondary *N*-nitramines and dinitramines under investigation is close to the activation enthalpy of HNO_2 elimination [15]. Meanwhile, elimination of nitrous acid is uncompatible as compared to the homolytic decomposition because the preexponential factor of the homolytic cleavage of the $N–NO_2$ bond is always higher (by 1.5–2 orders of magnitude approximately by our estimations) than for the heterolytic process. Note also that in the case of C-nitro compounds the transition state of the reaction is nonpolar contrary to the predictions of the modified McCole–Benson theory [16]. In the case of dinitramines the barrier of elimination of nitrous acid proves to be higher than the dissociation energy of the N–N bond.

It also shows that the thermal decomposition along this pathway is impossible. Investigation of the nitro-nitrite rearrangement mechanism showed that in this case the transition state is a three-membered cycle. Analysis of its geometrical parameters permits the understanding of the sharp increase in the reaction barrier as compared to the eliminaton of nitrous acid (Table 7). First of all strong elongation of the N–N and N–O bonds is observed. Main energy expenditures are connected with it. Variations in the rest geometrical parameters are not large as compared to the starting molecules.

Similarly to polynitramines, N–N bond of secondary nitramines is strongly elongated. Note that contact of the nitro group oxygen atom with the amine nitrogen atom in the case of secondary and polynitramines is provided by the decrease in the $N_2N_3O_4$ angle, and not by elongation of the N–O bond observed for the primary *N*-nitramines.

Table 6. Energy parameters of the transition state for the elimination of nitrous acid (dissociation energy, activation enthalpy, dipole moments in the ground and the excited state) [B3LYP/6-31G(d)]

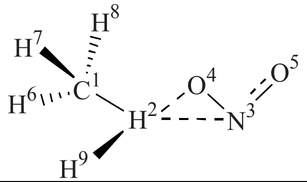
Compound	*D*(N–N), kJ mol^{-1}	$\Delta H^{\#}$, kJ mol^{-1}	*D*, Debye	$D^{\#}$, Debye
CH_3NHNO_2	195.2	198.6	4.23	3.04
$CH_3CH_2NHNO_2$	196.1	194.1	4.50	3.27
$CH_3(CH_2)_2NHNO_2$	197.9	195.0	4.32	3.31
$(CH_3)_2CHNHNO_2$	197.4	193.5	4.43	3.61
$(CH_3)_2NNO_2$	178.2	188.8	4.77	3.41
$(CH_3CH_2)_2NNO_2$	188.8	186.5	4.64	3.70
$CH_3N(NO_2)_2$	108.1	149.7	3.17	3.74
$CH_3CH_2N(NO_2)_2$	110.9	150.9	3.42	4.01
$CH_3(CH_2)_2N(NO_2)_2$	109.4	150.7	3.58	4.23
$CH_3(CH_2)_3N(NO_2)_2$	109.4	150.4	3.68	4.36
CH_2FNHNO_2	184.9	206.4	3.48	3.31
$CH_2ClNHNO_2$	184.1	202.9	3.40	3.18

For polynitramines sharp increase in the barrier of this reaction is observed, but the difference between *D*(N–N) and $\Delta H^{\neq}$ remains practically the same. It is noteworthy that for C-nitro compounds accumulation of nitro groups weakly affects the value of barrier of the nitro-nitrate rearrangement, and the decrease in enthalpy of this reaction in fluoronitromethane is so significant that the possibility of thermal decomposition in the gaseous state according to this pathway is considered [9] (Table 8).

High values of the activation enthalpy of nitro-nitrite rearrangement which are almost two times higher that the N–N bond dissociation energy show that this mechanism cannot take place.

Most interesting results were obtained in the investigation of isomerization of the primary aliphatic *N*-nitramines to the *aci*-form [17, 18]. In Table 9 geometrical parameters of the formation of the aci-form for primary aliphatic *N*-nitramines are presented. It is clear that isomerization of secondary *N*-nitramines as well as *N*-dinitramines is impossible because of the absence of the mobile hydrogen on the amine nitrogen

Table 7. Geometrical parameters of the transition state for the nitro-nitrite rearrangement [B3LYP/6-31G(d)]



Compound	Interatomic distance, pm				Angle, deg	
	C^1–N^2	N^2–N^3	N^2–O^4	N^3–O^4	$C^1N^2N^3$	$N^2N^3O^4$
CH_3NHNO_2	143.3	218.2	220.5	128.6	112.3	73.9
$CH_3CH_2NHNO_2$	142.9	219.3	223.5	128.5	119.8	74.9
$CH_3(CH_2)_2NHNO_2$	142.7	219.9	223.8	128.6	118.9	74.8
$(CH_3)_2CHNHNO_2$	142.3	252.8	259.6	121.5	110.1	79.4
$(CH_3)_2NNO_2$	142.1	265.4	121.2	122.1	110.7	77.2
$(CH_3CH_2)_2NNO_2$	142.8	271.3	121.9	121.4	99.2	81.6
$CH_3N(NO_2)_2$	144.4	262.2	119.2	118.6	110.3	79.6
$CH_3CH_2N(NO_2)_2$	144.7	263.3	119.3	118.7	110.3	79.3
$CH_3(CH_2)_2N(NO_2)_2$	144.2	263.9	119.5	118.7	110.1	79.3
$CH_3(CH_2)_3N(NO_2)_2$	144.2	264.1	119.4	118.9	109.9	79.3

atom. During the intramolecular hydrogen transfer N–N distance shortens corresponding to the formation of the double N=N bond. Geometrical parameters of the transition state in the series of primary nitramines practically do not vary.

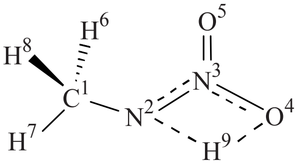
In Table 10 geometrical parameters of *aci*-forms of primary *N*-nitramines are listed. It follows from the presented data that increased basis leads to elongation of the C–N and N–O bonds and to shortening of the N–N bond. Nitramines having a non-branched carbon skeleton (*N*-methyl, *N*-ethyl, *N*-propylnitramine) have a symmetric structure (C_{2v}). In isopropylnitramine the nitramine group is oriented to one of methyl groups, and the symmetry in this case is broken.

Frequencies of vibrations of the *N*-methylnitramine *aci*-form were calculated (Table 11). As no reported experimental measurements of spectral characteristics exist, it can be stated only that the vibration frequencies change in accordance with the variations in the basis. Evaluations obtained by means of all four methods are fairly close. The activation enthalpy of the aci-form formation (on the average ~150 kJ mol^{-1}) is significantly lower than the dissociation energy of the

Table 8. Energy parameters of the transition state for the nitro-nitrate rearrangement (dissociation energy, activation enthalpy), dipole moments of the starting molecule and the transition state [B3LYP/6-31G(d)]

Compound	D(N–N), kJ mol^{-1}	$\Delta H^{\#}$, kJ mol^{-1}	D, Debye	$D^{\#}$, Debye
CH_3NHNO_2	195.2	342.3	4.23	4.76
$CH_3CH_2NHNO_2$	196.1	333.7	4.50	5.07
$CH_3(CH_2)_2NHNO_2$	197.9	335.0	4.32	5.19
$(CH_3)_2CHNHNO_2$	197.4	305.7	4.43	3.35
$(CH_3)_2NNO_2$	178.2	290.5	4.64	3.64
$(CH_3CH_2)_2NNO_2$	188.8	286.1	3.17	3.87
$CH_3N(NO_2)_2$	108.1	230.6	3.42	4.24
$CH_3CH_2N(NO_2)_2$	110.9	228.3	3.58	4.16
$CH_3(CH_2)_2N(NO_2)_2$	109.4	225.7	3.68	4.30
$CH_3(CH_2)_3N(NO_2)_2$	109.4	225.3	4.64	4.40

Table 9. Geometrical parameters of the transition state of formation of the *aci*-form [B3LYP/6-31G(d)]



Compound	Interatomic distance, pm					Angle, deg	
	$C^1–N^2$	$N^2–N^3$	$N^3–O^4$	$N^2–H^9$	$O^4–H^9$	$N^2N^3O^4$	$N^2H^9O^4$
CH_3NHNO_2	145.0	131.1	132.6	130.6	131.6	103.5	104.3
$CH_3CH_2NHNO_2$	145.8	131.2	132.5	131.0	131.2	103.5	104.4
$CH_3(CH_2)_2NHNO_2$	145.6	131.3	132.6	131.1	131.1	103.5	104.5
$(CH_3)_2CHNHNO_2$	147.1	131.3	132.9	131.2	130.6	103.4	104.7

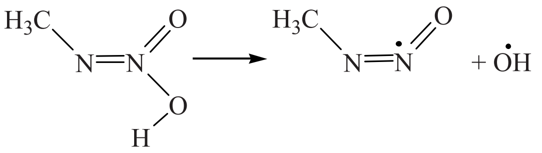
Table 10. Geometrical parameters of *aci*-form of *N*-nitramines [B3LYP/6-31G(d)]

Compound	Interatomic distance, pm					Angle, deg	
	$C^1–N^2$	$N^2–N^3$	$N^3–O^4$	$N^2–H^9$	$O^4–H^9$	$N^2N^3O^4$	$N^2H^9O^4$
CH_3NHNO_2	145.9	126.5	140.1	212.7	97.9	113.7	83.3
$CH_3CH_2NHNO_2$	146.7	126.4	140.3	213.1	97.9	113.8	83.0
$CH_3(CH_2)_2NHNO_2$	146.6	126.4	140.2	213.0	97.8	113.7	83.1
$(CH_3)_2CHNHNO_2$	147.7	126.3	140.5	212.4	97.9	113.5	83.3

N–N bond in the homolysis. This result is fundamental, and therefore for its confirmation we have carried out the investigation of the corresponding reaction for methylnitramine using the nonempirical method of the second order pertrubation theory MP2/6-31G(d) which confirmed the significant decrease in the activation enthalpy. The value obtained by this method for *N*-methylnitramine was 152.3 kJ mol^{-1} what is 65 kJ mol^{-1} higher than the *D*(N–N) evaluation. This result is the additional independent con-formation of compatibility of such mechanism. Note that the activetion enthalpy of isomerization in the series including *N*-methyl, *N*-ethyl, *N*-propyl, and *N*-isopropylnitramine increases monotonously from 148.4 to 155.1 kJ mol^{-1}.

The results presented (Table 12) predict close evaluations of the activation barriers of isomerization (147.0–156.0 kJ mol^{-1}). The only exception is MP3/6-31G(d) method leading to overestimation of enthalpies and the reaction barrier evaluations. Broadening of basis to 6-311++G(df,p) in general leads to a decrease in the barrier value. Geometrical parameters obtained from nonempirical calculations vary insignificantly. The greatest difference is observed in the evaluations of the N–N and N–H interatomic distances (see Table 12).

The calculations show that the most favorable version of the reaction first step is connected with rearrangement, and for complete establishment of the reaction mechanism different pathways of decomposition of the *N*-methylnitamine *aci*-form must be studied to evaluate the most energetically favorable pathway of unimolecular decomposition. The studies performed showed that homolytic decomposition of the *aci*-form is energetically unacceptable because the activation enthalpy of the reaction (5) is considerably higher than the activation energy of the radical decomposition.



(5)

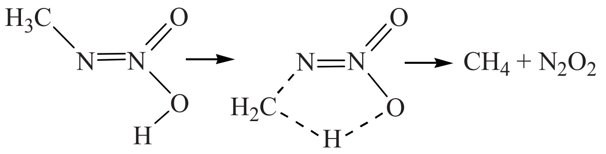
The nonempirical MP2/6-31G(d) and MP2/6-311+++G(df,p) methods significantly overestimate the

Table 11. Vibration frequencies (cm^{-1}) of *N*-methylnitramine *aci*-form according to different nonempiricalal and DFT methods

B3LYP/6-31G(d)	B3LYP/6-311++G(df,p)	MP2/6-31G(d)	MP2/6-311++G(df,p)
3653	3717	3641	3768
3172	3149	3245	3226
3098	3068	3177	3148
3042	3016	3099	3072
1725	1674	1834	1813
1510	1474	1541	1489
1506	1472	1538	1483
1460	1433	1489	1451
1364	1343	1380	1373
1335	1302	1326	1325
1196	1181	1209	1190
1121	1102	1139	1109
1050	1032	1077	1084
943	932	927	936
724	723	708	699
651	651	662	680
540	541	540	553
474	442	469	384
313	308	319	320
250	245	248	231
150	150	187	191

energy of N–OH bond (288.3 and 287.1 kJ mol^{-1} respectively). Introduction of the polarizational and the diffusive orbitals in the case of B3LYP/6-311++G (df,p) and MP2/6-311++G(df,p) methods leads to the decrease in the dissociation energy (207.4 and 192.6 kJ mol^{-1} respectively). Note that the dissociation energy of N-OH bond in the *N*-methylnitramine *aci*-form is close to the dissociation energy of the N–NO_2 bond in the ground state of *N*-methylnitramine. It indicates the significant conjugation of the nitro group (its rotation barrier is 55.2 kJ mol^{-1}) and the amine fragment leading to the leveling the multiplicity of bonds.

Reactions (6) and (7) involved with the liberation of methane and the transfer of hydroxyl also proceed with the lagre energy consumption.



(6)

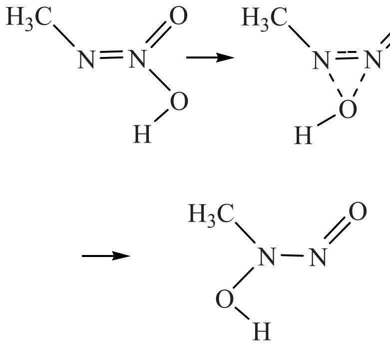
The barrier of the reaction (6) is the highest [359.3 and 368.5 kJ mol^{-1} for B3LYP/6-31G(d) and MP2/6-31G(d) methods] among all the processes under investigation because in this process the greatest structural changes of molecules take place. C–N and O–H bonds undergo the greatest elongation (191.3 pm and 159.9 pm respectively). Evaluation of barrier of the methane liberation by means of B3LYP/6-31G(d) and MP2/6-31G(d) methods differ insignificantly (on 9.2 kJ mol^{-1}).

In the case of the hydroxy group transfer [reaction (7)] the broadening of basis [B3LYP/6-311++G(df,p) and MP2/6-311++G(df.p)] leads to an increase in the

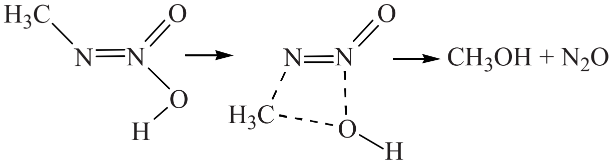
Table 12. Geometrical parameters of the transition state of formation of *aci*-form and the activation enthalpy of isomerization obtained by different methods

Method	Interatomic distance, pm					$\Delta H^{\#}$, kJ mol^{-1}
	C_1–N_2	N_2–N_3	N_3–O_4	N_2–H_9	O_4–H_9	
B3LYP/6-31G(d)	145.0	131.1	132.6	130.6	131.6	149.4
B3LYP/6-311++G(df,p)	144.7	130.8	132.4	129.8	130.9	148.0
MP2/6-31G(d)	144.9	131.5	132.6	129.5	134.0	152.3
MP2/6-311++G(df,p)	144.4	131.1	130.7	127.5	132.2	147.0
MP3/6-31G(d)	144.9	129.8	131.5	129.3	132.3	169.1
MP4/6-31G(d)	145.6	132.2	133.6	130.4	133.9	156.2

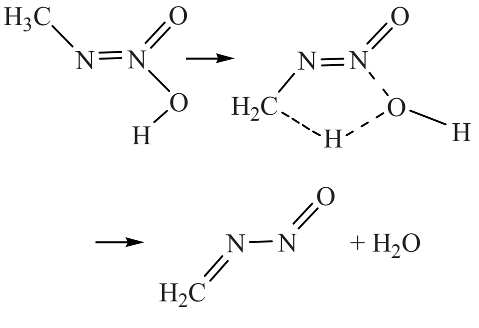
activation barrier to 285.5 and 331 kJ mol^{-1}. Use of the diffusive and the polarizational orbitals leads to the elongation of the N-OH bond on 7.6 (for B3LYP method) and on 5.8 pm (for MP2 method) in the structure of the transition state for *N*-methylnitramine. Hence, use of the broadened basis leads to the shift of hydroxy group to the alkyl fragment of molecule.


(7)

Reaction (8), promising on the first glance (the corresponding reaction products were found during the liquid phase decomposition of *N*-nitramines [19]), proved to be unacceptable from the energy point of view. Data obtained by us exclude this patway of decomposition of the *aci*-form at least in the unimolecular reaction in the gas phase. The mean value of the activation barrier obtained by different methods is 297.7 kJ mol^{-1}.


(8)

Among the alternative pathways of decomposition of the *N*-methylnitramine aci-form the lowest barrier corresponds to the elimination of water [reaction (9)].

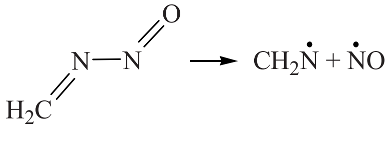

(9)

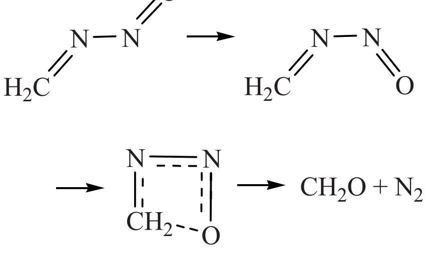
Analogous process was for the first time studied in [19] on an example of unimolecular decomposition of nitromethane and dinitromethane. Later it was substantiated and thoroughly studied by an example of the series of nitoalkanes [13]. According to B3LYP/6-31G(d) calculations the barrier of this process (166.8 kJ mol^{-1}) in the case of methylnitramine to some extent exceeds the activation enthalpy of formation of the *aci*-form, but it is to some what lower than that of the radical decomposition reaction. Evaluation of the preexpotential factor of the reaction (log *A* ~13.0) permits to state that this reaction pathway is preferred as compared to the radical process at moderate (<700 K) decomposition temperatures. Note that all the other methods used by us show that evaluation of the activation enthalpy for the elimination of water is lower than the barrier of the *aci*-form formation (Table 13).

Table 13. Geometrical parameters of the transition state of elimination of water and the activation barriers for methyl, ethyl, propyl, and butylnitramine [B3LYP/6-31G(d)]

Compound	Interatomic distance, pm				$\Delta H^{\#}$, kJ mol^{-1}
	C–N	N–N	N–O	O–H	
CH_3NHNO_2	141.0	121.2	220.7	123.4	166.8
$CH_3CH_2NHNO_2$	141.3	121.6	224.3	97.3	165.3
$CH_3(CH_2)_2NHNO_2$	141.0	121.7	224.6	97.3	165.1
$CH_3(CH_2)_3NHNO_2$	141.0	121.7	224.7	97.3	164.5

Subsequent studies permitted to find out two energetically acceptable pathways of further development of the process. They include the homolytic cleavage of N–N bond [reaction (10)] [according to B3LYP/6-31G(d) and B3LYP/6-311++G(df,p) the dissociation energy is 88.4 and 80.7 kJ mol^{-1} respectively] and cyclization with the formation of formaldehyde and nitrogen [reaction (11)]. The latter process is the most favorable.


(10)


(11)

Formation of the transition state in the reaction (11) is preceded by the conformational transformation shown in the scheme. The barrier of the latter is not high (3–6 kJ mol^{-1}), and the activation barrier of cyclization according to B3LYP/6-31G(d) and MP2/6-31G(d) methods is 16.9 and 15.1 kJ mol^{-1} respectively.

Hence, theoretical studies permitted the establishment of a new and the the most energetically favorable pathway of the gas phase unimolecular decomposition of *N*-methylnitramine. The first stage is isomerization of *N*-nitramine to its *aci*-form by the intramolecular hydrogen transfer from the amine nitrogen atom to nitro group. After that *aci*-form undergoes cyclization with the subsequent liberation of water. The process is completed by the ring opening with the formation of formaldehyde and nitrogen. Kekin et al. [20] reported on the Arrhenius parameters of the initial act of the gas phase decomposition of *N*-methylnitramine [$E =$ 171.0 kJ mol^{-1}, log A 13.65 (s^{-1})] that were interpreted from the point of view of the radical mechanism. But we consider that they do not fit to the homolytic rupture of the N–NO$_2$ bond. Quantum chemical (Table 1) and thermochemical (207.5 kJ mol^{-1} [21]) evaluations of D(N–N) are considerably higher than the effective value of the activation energy. The value of the preexponential factor (log A) in the reaction of *N*-methylnitramine is significantly underestimated as compared to the other simplest aliphatic nitro compounds decomposing in the gas phase according to the homolytic mechanism (*N*,*N*-dimethylnitramine, nitromethane [14]). Our quantum chemical evaluations show that log A of homolytic decomposition must be not lower than 14.5 s^{-1}.

At the same time experimental values of E and log A quite agree with the mechanism suggested by us and the parameters of its main steps [reactions (4), (9), and (11)]. Depending on the experimental conditions the competition between the radical mechanism and isomerization to *aci*-form with its subsequent decomposition may be observed. Reported data [20] and our calculations show that in the gas phase the nonradical mechanism significantly prevails. As is known [22] the liquid phase decomposition of *N*-methylnitramine proceeds significantly faster than the gas phase reaction may be because of the heterolytic pathways. But considering the experimental conditions in [20] their contribution into the kinetic parameters of the reaction cannot be to any extent significant.

Results of the present work may be important not only for understanding of the mechanism of thermal decomposition of *N*-nitramines, but also of the general rules of the gas phase decomposition of nitro compounds as a whole.

The possibility of proceeding of the gas phase thermodecomposition of primary *N*-nitramines according to the molecular mechanism beginning from isomerization is suggested. Analysis of molecular mechanisms of thermal decomposition of secondary nitramines confirmed the proceeding of thermolysis according to the mechanism of homolytic cleavage of the N–N bond. Results of calculations significantly supplement the existing experimental data on the geometry of molecules and thermochemical characteristics of *N*-nitro compounds.

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