ISSN 1070-4272, Russian Journal of Applied Chemistry, 2009, Vol. 82, No. 10, pp. 1792−1798. © Pleiades Publishing, Ltd., 2009.
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STUDIES IN THE FIELD OF CHEMISTRY OF NITRO COMPOUNDS (TO 100TH BIRTHDAY ANNIVERSARY OF S. S. NOVIKOV)

Theoretical Study of the Competition between Various Mechanisms of Gas-Phase Decomposition in the Series of Primary N-Nitramines

E. A. Mazilov, E. V. Ogurtsova, A. G. Shamov, and G. M. Khrapkovskii

Center for New Information Technologies, Kazan State Technological University, Kazan, Tatarstan, Russia

Received April 29, 2009

Abstract—Nonempirical and density-functional methods were used to determine geometric parameters, enthalpies of formation of compounds and radicals, dissociation energies of the N–NO_2 bonds of primary N-nitramines and *N,N*-dinitramines. The tendencies toward variation of the geometric structure, enthalpies of formation, and dissociation energy in the series of primary N-nitramines were analyzed. Alternative mechanisms of the gas-phase thermal destruction to give experimentally observed reaction products were studied for the example of *N*-methylnitramine and its homologues.

DOI: 10.1134/S1070427209100085

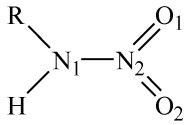
Primary *N*-nitramines are manufactured on the industrial scale. The possibility of spontaneous decomposition at comparatively low temperatures necessitates a study of the kinetics and mechanism of decomposition of the given class of compounds. Of particular interest in this class of compounds is *N,N*-methylenedinitrodiamine high explosive (medina). At present, there are only fragmentary data on the geometric and electronic structure of secondary nitramines, furnished by quantum-chemical methods and gas-phase electron diffraction analysis [1, 2]. Data on thermal stability are not distinguished by high accuracy. Frequently, the activation energy and pre-exponential factor do not agree with each other [3]. The mechanism of thermal decomposition of primary nitramines has not been conclusively elucidated; however, most of researchers believe that the radical mechanism of thermal decomposition is more advantageous. Its first stage is homolytic rupture of the N–N bond [4].

In this study, we theoretically analyzed the molecular structure and thermal decomposition mechanisms of primary amines by using B3LYP/6-31G(d) and B3LYP/6-311++G(df,p) density-functional (DFT) methods and MP2/6-31G(d) and MP2/6-311++G(df,p) nonempirical methods with Gaussian 98 and Gaussian 2003 software packages.

It has been shown previously that these methods are the most effective in determining the molecular structure, enthalpy of formation, vibrational spectra, and activation barriers of the thermal decomposition of aliphatic C- and O-nitro compounds [5].

Naturally, of particular interest in discussion of the thermal stability of N-nitro compounds are geometric characteristics of the NH–NO_2 group. The results obtained demonstrate that, in the series of both branched and unbranched primary nitramines, the length of the N–N bond remains almost unchanged (Table 1) and is, on average, 138.5 pm. The only exception is isopropylnitramine [$CH_3CH(CH_3)NHNO_2$]. In this compound, the N–N bond is the longest in the series (144.6 pm). In the case of *tert*-butylnitramine the situation changes. The existence of steric interactions makes the C–N bond longer (149.1 pm), with $r(N_1–N_2)$ decreasing to 138.1 pm. The branching of the carbon skeleton of primary nitramines at the α-carbon atom (Table 1, compound nos. 6, 8, and 9) leads to an increase in the C–N internuclear distance to 147.3 pm, with all other geometric parameters changing only slightly. In methylene-*N,N*-dinitramine and ethylene-*N,N*-dinitramine (compound nos. 10, 11), the additional nitro group has nearly no effect on the stretching of N–N and C–N bonds, and the

Table 1. Geometric parameters of primary nitramines [B3LYP/6-31G(d)]



Compd. no.	Compound	Bond length, pm				Angle, deg
		$R–N_1$	$N_1–N_2$	$N_2–O_1$	$N_2–O_2$	
1	CH_3NHNO_2	145.6 (145.3)[a]	138.5(138.2)	122.9(122.8)	122.8(122.8)	127.1(125.3)
2	$CH_3CH_2NHNO_2$	146.4	138.4	123.0	122.8	126.9
3	$CH_3(CH_2)_2NHNO_2$	146.3	138.6	122.9	122.9	126.7
4	$CH_3(CH_2)_3NHNO_2$	146.4	138.6	122.9	122.8	126.7
5	$CH_3(CH_2)_4NHNO_2$	146.3	138.5	123.0	122.8	126.6
6	$CH_3CH_2CH(CH_3)NHNO_2$	147.3	138.4	122.9	123.0	126.6
7	$CH_3CH(CH_3)CH_2NHNO_2$	146.1	138.5	122.8	123.1	126.5
8	$CH_3CH_2CH(C_2H_5)NHNO_2$	147.2	138.3	122.9	123.0	126.5
9	$CH_3CH(CH_3)NHNO_2$	147.3	138.4	123.0	123.0	126.6
10	$(CH_3)_3CNHNO_2$	149.1	138.1	123.0	123.1	126.0
11	$O_2NNHCH_2NHNO_2$	145.8	138.2	122.4	123.2	127.2
12	$O_2NNHCH_2CH_2NHNO_2$	145.9	138.3	122.7	123.0	126.9

[a] Data furnished by gas-phase electron diffraction analysis are given in parentheses [1].

NNCC angle changes insignificantly, being 179–180° for dialkyl derivatives.

With the radical mechanism of the primary event, the activation energy of thermal decomposition almost coincides with the dissociation energy of the bond being ruptured [3]:

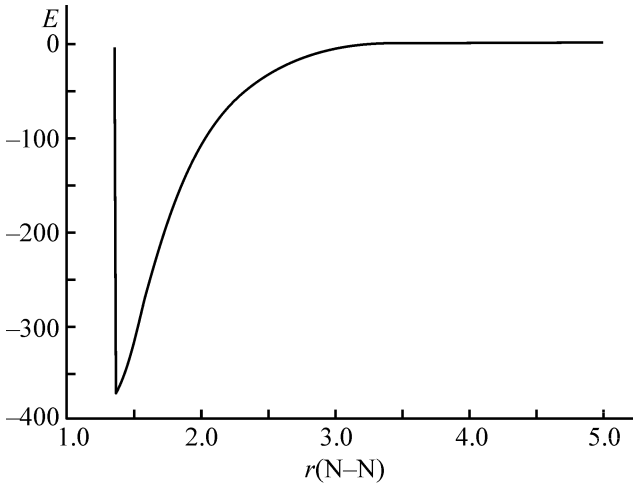
$$E_a = D(\text{N–N}) + RT.$$

If the recombination of radical formed in the course of thermal decomposition is unactivated, the enthalpy of the reaction of homolytic bond rupture is not different from the enthalpy of activation [6]. In this case, the activation energy of radical decomposition almost coincides with the bond dissociation energy and can be estimated on the basis of estimates of the enthalpy of formation of the starting compound and reaction products:

$$D(\text{A–B}) = \Delta H_A^\circ + \Delta H_B^\circ - \Delta H_{A–B}^\circ.$$

The absence of a barrier for recombination of radicals was demonstrated for the example of *N*-methylnitramine.

The results of calculation by the B3LYP/6-31G(d) method predict a minor decrease in the dissociation



A change on the total energy E (kJ mol^{-1}) of *N*-methylnitramine molecule vs. in dependence on N–N internuclear distance r(N–N) (nm).

Table 2. Enthalpies of formation of compounds and radicals and dissociation energies of the N–N bond of *N*-nitramines and fluoro and chloro derivatives of methylnitramine [B3LYP/6-31G(d)]

Compound	$\Delta H^{o}_{f,298}$, kJ mol^{-1}	Radical	$\Delta H^{o}_{f\ 298}$	D(N–N)
			kJ mol^{-1}	
		NO_2 (·)	23.0	
CH_3NHNO_2	–0.2	CH_3HN·	172.0	195.2
$CH_3CH_2NHNO_2$	–20.8	CH_3CH_2HN·	152.3	196.1
$CH_3(CH_2)_2NHNO_2$	–36.2	$CH_3(CH_2)_2HN$·	138.6	197.9
$CH_3(CH_2)_3NHNO_2$	–49.2	$CH_3(CH_2)_3HN$·	125.8	197.9
$CH_3(CH_2)_4NHNO_2$	–62.4	$CH_3(CH_2)_4HN$·	112.6	198.0
$CH_3CH_2CH(CH_3)NHNO_2$	–54.0	$CH_3CH_2CH(CH_3)$ HN·	120.2	197.2
$CH_3CH(CH_3)CH_2NHNO_2$	–48.8	$CH_3CH(CH_3)CH_2HN$·	122.6	194.4
$CH_3CH_2CH(C_2H_5)NHNO_2$	–65.3	$CH_3CH_2CH(C_2H_5)HN$·	109.2	197.5
$CH_3CH(CH_3)NHNO_2$	–44.0	$CH_3CH(CH_3)HN$·	130.3	197.4
$(CH_3)_3CNHNO_2$	–56.0	$(CH_3)_3CHN$·	109.5	188.5
$O_2NNHCH_2NHNO_2$	55.3	O_2NNHCH_2HN·	229.1	196.8
$O_2NNHCH_2CH_2NHNO_2$	43.8	$O_2NNHCH_2CH_2HN$·	211.5	190.7
$(CH_3)_2NNO_2$	–8.8	$(CH_3)_2N$·	146.4	178.2
$CH_3N(NO_2)_2$	97.3	$CH_3(NO_2)N$·	128.4	108.1
$CH_3CH_2N(NO_2)_2$	75.9	$CH_3CH_2(NO_2)N$·	163.9	110.9
$CH_3(CH_2)_2N(NO_2)_2$	62.5	$CH_3(CH_2)_2(NO_2)N$·	148.9	109.4
$CH_3(CH_2)_3N(NO_2)_2$	49.2	$CH_3(CH_2)_3(NO_2)N$·	135.6	109.4

energy of the N–N bond [D(N–N)] in the series of primary nitramines on passing from methylnitramine to *n*-pentylnitramine (Table 2). It can be noted in a comparison of compounds having NH–NO_2 groups at primary and secondary carbon atoms that values of D(N–N) for compounds with *iso*-structure are somewhat lower. Even less strong are, according to calculated data, the N–N bonds at the tertiary carbon atom. Comparison of the enthalpies of formation of compounds and radicals for isomers shows that the decrease in D(N–N) is mostly due to the additional stabilization of the radical formed upon detachment of the nitro group.

It is important to note that the D(N–N) sharply decreases if dinitramines have a second nitro group. It is noteworthy that a similar situation is observed in the series of nitro alkanes and nitro esters upon accumulation of nitro groups [7]. On the whole, values of D(N–N) of secondary nitramines are lower than those of the primary nitramines of normal structure.

Our study demonstrated comparatively narrow variation in the series of the geometric structure of the primary and secondary nitramines; accordingly, only slightly vary the D(N–N) and the activation energies of radical gas-phase decomposition.

Most of researchers tend to believe that the thermal decomposition of N-nitro compounds occurs by the unified radical mechanism, in which the homolytic rupture of N–N bonds is the primary stage. However, there is no common standpoint concerning this question. Therefore, analysis of alternative mechanisms is of indubitable interest.

We studied as possible alternative mechanisms of thermal decomposition three molecular (nonradical) processes: elimination of nitrous acid, nitro-nitrite rearrangement (NNR), and formation of the *aci*-form (2)–(4):

$$CH_3NHNO_2 \rightarrow CH_3NH\cdot + \cdot NO_2, \quad (1)$$

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

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

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

Table 3 lists geometric parameters of the reaction center of the transition state of the HNO_2 elimination reaction for primary and secondary N-nitramines.

The data in Table 3 demonstrate that the bond dissociation energies for the primary *N*-nitramines and the series of the secondary *N*-nitramines and dinitramides studied are close to the enthalpy of activation of the elimination reaction. The same is observed for aliphatic nitro esters [8].

However, the process of nitrous acid elimination is noncompetitive as an alternative to the radical decomposition because the pre-exponential factor of the reaction of homolytic rupture of the N–NO_2 bond is always larger than the molecular factor (by two order of magnitude, on average). It should also be noted that, as in the case of C-nitro compounds, the transition state of the reaction is nonpolar. For dinitramines, the barrier for the reaction of nitrous acid elimination is higher than the dissociation energy of the N–N bond, which also indicates that thermal decomposition cannot occur by this channel.

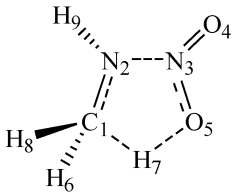
A study of the NNR mechanism demonstrated that this transition state is a three-membered ring (Table 4).

For polynitramines, a sharp decrease in the barrier height is observed for this reaction; however, the difference between D(N–N) and $\Delta H^{\#}$ remains nearly unchanged. It is remarkable that, for C-nitro compounds, the accumulation of nitro groups only slightly affects the barrier for the NNR [7].

The high values of the enthalpy of activation of the NNR reaction, which nearly twice exceed the dissociation energy of the N–N bond, indicate that this mechanism cannot be operative.

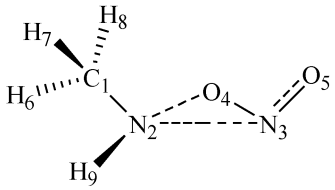
The most interesting results were obtained in a study

Table 3. Energy parameters of the transition state of the reaction of nitrous acid elimination (dissociation energy, enthalpy of activation, dipole moments of the simple and excited states) [B3LYP/6-31G(d)]



Compound	D(N–N)	$\Delta H^{\#}$	D	$D^{\#}$
	kJ mol^{-1}		D	
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

Table 4. Energy parameters of the transition state of the nitro-nitrite rearrangement (dissociation energy, enthalpy of activation, dipole moments of the simple and excited states) [B3LYP/6-31G(d)]



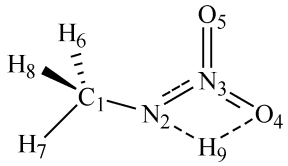
Compound	D(N–N)	$\Delta H^{\#}$	D	$D^{\#}$
	kJ mol^{-1}		D	
CH_3NHNO_2	195.2	342.3	4.23	4.76
$CH_3CH_2NHNO_2$	196.1	333.7	4.50	5.07
$CH_3(CH_2)_2NHNO_2$	197.9	335.0	4.32	5.19
$(CH_3)_2CHNHNO_2$	197.4	305.7	4.43	3.35
$(CH_3)_2NNO_2$	178.2	290.5	4.64	3.64
$(CH_3CH_2)_2NNO_2$	188.8	286.1	3.17	3.87
$CH_3N(NO_2)_2$	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

of the reaction of isomerization of the primary aliphatic N-nitramines into the *aci*-form [9].

Table 5 lists the geometric parameters of the reaction in which *aci*-forms of the primary *N*-nitramines are formed. It is clear that the isomerization reaction is possible neither for the secondary *N*-nitramines, nor for dinitro derivatives of *N*-nitramines because of the absence of a mobile hydrogen atom at the amine nitrogen atom.

The enthalpy of activation of the reaction in which the *aci*-form is produced is substantially lower (by about 150 kJ mol^{-1}, on average) than the dissociation energy of the N–N bond ruptured in the radical process. It is noteworthy that the barrier for the activation reaction is somewhat higher for *N,N*-methylenedinitrodiamine, compared with other representatives of the primary *N*-nitramines. However, in this case, too, the enthalpy of activation is substantially lower than *D*(N–N). These results are of fundamental importance because, to confirm these data, we studied the corresponding reaction for methylnitramine and *N,N*-methylenedinitrodiamine with the use of the MP2/6-31G(d) nonempricial method of the second-order perturbation theory, which confirmed the substantial decrease in the enthalpy of activation. The values calculated using this method were 152.3 kJ mol^{-1} for methylnitramine and 173.9 kJ mol^{-1} for medina, which is more than 60 kJ mol^{-1} lower than the estimate of *D*(N–N) in methylnitramine and 29 kJ mol^{-1} lower than that for *N,N*-methylenedinitrodiamine.

Table 5. Energy parameters of the transition state of formation of the aci-form (dissociation energy, enthalpy of activation, dipole moments of the simple and excited states) [B3LYP/6-31G(d)]



Compound	D(N–N)	$\Delta H^{\#}$	D	$D^{\#}$
	kJ mol^{-1}		D	
CH_3NHNO_2	195.2	149.4	4.23	3.39
$CH_3CH_2NHNO_2$	196.1	148.4	4.50	3.42
$CH_3(CH_2)_2NHNO_2$	197.9	149.8	4.32	3.49
$(CH_3)_2CHNHNO_2$	197.4	155.1	4.43	3.48
$O_2NNHCH_2NHNO_2$	196.8	166.9	3.09	3.07

Table 6. Geometric parameters of the transition state of formation of the aci-form and the enthalpy of activation of the isomerization reaction according to data furnished by different methods

Method	Bond length, pm					$\Delta H^{\#}$, kJ mol^{-1}
	C–N	N–N	N–O	N–H	O–H	
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

Table 7. Geometric parameters of the transition state of the reaction of water elimination for *N*-methylnitramine according to data furnished by different methods

Method	Bond length, pm				$\Delta H^{\#}$, kJ mol^{-1}
	C–N	N–N	N–O	O–H	
B3LYP/6-31G(d)	141.0	121.2	220.7	123.4	166.8
B3LYP/6-311++G(df,p)	141.5	119.1	225.3	126.3	146.1
MP2/6-31G(d)	140.7	125.4	221.7	119.6	128.4
MP2/6-311++G(df,p)	137.9	117.2	267.8	97.4	80.3

Table 8. Geometric parameters of the transition state of the reaction of water elimination for primary N-nitramines [B3LYP/6-31G(d)]

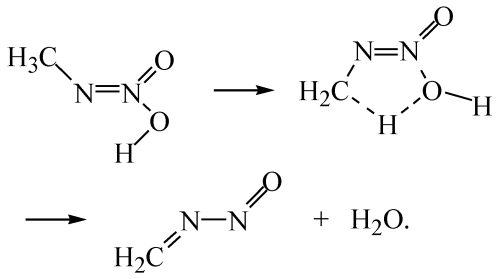
Compound	Bond length, pm				$\Delta H^{\#}$, kJ mol^{-1}
	C–N	N–N	N–O	O–H	
CH_3NHNO_2	141.0	121.2	220.7	123.4	166.8
$CH_3CH_2NHNO_2$	141.3	121.6	224.3	97.3	165.3
$CH_3(CH_2)_2NHNO_2$	141.0	121.7	224.6	97.3	165.1
$CH_3(CH_2)_3NHNO_2$	141.0	121.7	224.7	97.3	164.5
$O_2NNHCH_2NHNO_2$	150.4	119.4	214.8	120.2	159.1

Table 9. Geometric parameters of the transition state of the reaction of cyclization of *N*-nitrosomethylimine according to data furnished by different methods

Method	Bond length, pm				$\Delta H^{\#}$, kJ mol^{-1}
	C–N	N–N	N–O	C–O	
B3LYP/6-31G(d)	136.1	128.3	129.9	198.6	16.9
B3LYP/6-311++G(df,p)	135.9	127.2	129.4	198.5	14.0
MP2/6-31G(d)	135.7	130.7	131.7	196.5	15.1
MP2/6-311++G(df,p)	135.2	129.7	129.6	195.2	27.0

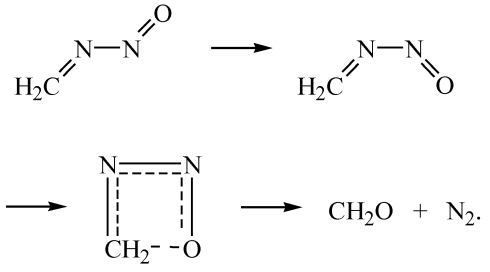
The results obtained (Table 6) predict nearly coinciding estimates for the activation barriers of the isomerization reaction for methylnitramine (147–156 kJ mol^{-1}). The only exception is MP23/6-31G(d), for which the enthalpy characteristics and reaction barrier estimates are overstated. Extending the basis to 6-311++G(df,p) commonly leads to a decrease in the barrier height.

Probably, the formation of the *aci*-form is the main channel for the primary event of the thermal destruction reaction. Therefore, its further study is of interest. Our calculations demonstrated that the reaction of water elimination has the lowest barrier among the alternative secondary reactions (Table 7):



A similar process was first studied in [10] for the example of the monomolecular decomposition of nitro methane and dinitro methane and further substantiated and analyzed in detail for the example of the nitro alkane series in [6]. The barrier for the water elimination reaction is substantially lower than that for the radical decomposition reaction. The results presented make it possible to state that the given channel of reaction development is preferable to the radical mechanism at moderate (<700 K) decomposition temperatures. It is noteworthy that, for the simplest representatives of the *N*-methylnitramine series, the height of the barrier for the water elimination reaction is in the range 164–167 kJ mol^{-1} (Table 8). For *N,N*-methylenedinitradiamine, this process occurs with a lower activation energy. All other methods employed confirm the tendencies specified above (Table 9).

Further analysis demonstrated that, in the course of the reaction, methylamine forms a cyclic intermediate decomposing to formaldehyde and nitrogen:



This reaction is not the rate-determining stage of the thermal destruction process. Therefore, its specific features are not considered for other representatives of the series of primary nitramines.

CONCLUSIONS

A theoretical analysis revealed a new, the most energetically favorable channel of the monomolecular gas-phase decomposition of primary *N*-nitramines. First, *N,N*-nitramine is isomerized into the *aci*-form via intramolecular hydrogen transfer from the ammine nitrogen atom to the nitro group. Then, the *aci*-form is cyclized, with the subsequent elimination of water. The final stage of the process is the decomposition reaction to give the corresponding aldehyde and nitrogen.

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