Russian Chemical Bulletin, International Edition, Vol. 50, No. 6, pp. 952—957, June, 2001

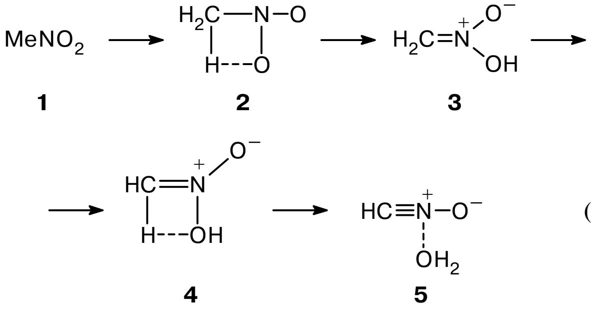
Mechanism of formation and monomolecular decomposition of *aci*-nitromethanes: a quantum-chemical study

G. M. Khrapkovskii,[a] A. G. Shamov,[a]★ G. A. Shamov,[a] and V. A. Shlyapochnikov[b]

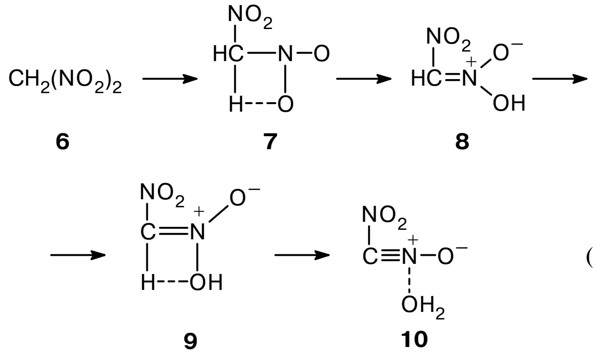
[a]*Kazan State Technological University,*
68 ul. K. Marksa, 420015 Kazan, Russian Federation.
Fax: +7 (843 2) 37 6263. E-mail: shamov@kstu.ru
[b]*N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,*
47 Leninsky prosp., 119991 Moscow, Russian Federation.
Fax: +7 (095) 135 5328

A quantum-chemical study of the reactions of formation of *aci*-nitromethane (*aci*-NM) and *aci*-dinitromethane (*aci*-DNM) and their decomposition with elimination of water was carried out. The methods employed were the *ab initio* RHF method with inclusion of electron correlation at the MP2 level of theory and the Dunning—Hay double zeta basis set augmented with polarization d-functions on heavy-element atoms, the DFT approach at the B3LYP level, and the semiempirical PM3 method. The formation of *aci*-NM and *aci*-DNM was found to be the limiting stage of the mechanism under study. For DNM, the barrier to reaction is substantially lower than for NM. The estimates of the heights of the barriers to formation found from density functional calculations at the B3LYP/6-311++G(df,p) level (258 kJ mol^{-1} for *aci*-NM and 218.5 kJ mol^{-1} for *aci*-DNM) are thought to be the most reliable.

Key words: thermal decomposition, *ab initio* quantum-chemical calculations, nonempitrical quantum-chemical calculations, elimination, nitromethane, dinitromethane, trinitromethane, *aci*-nitromethane, *aci*-dinitromethane, *aci*-trinitromethane.



(1)



(2)

Studies of tautomeric transformations are of considerable interest to gain a deeper insight into general relationships between the reactivities of aliphatic nitro compounds.[1–3] In this case, processes involving various transformations of nitronic acids in, *e.g.*, thermal decomposition of nitroalkanes[4–6] play an important role. It is known[7] that liquid-phase decomposition of nitromethane (NM) and nitroethane as well as gas-phase decomposition of NM under supercritical conditions[4,8] (at high pressures and temperatures of 600 to 800 °C) proceed *via* the corresponding *aci*-forms. However, the kinetics and mechanisms of the reactions of nitronic acids have been poorly studied as yet. This precludes establishment of general regularities of proceeding the reactions of liquid-phase thermal decomposition of *C*-nitro compounds.[4,6] Previously,[9] a mechanism of thermal decomposition of dinitromethane (DNM) was proposed. The mechanism involves elimination of water from *aci*-DNM and provides an explanation for low thermal stability of DNM. However, the enthalpies of formation of NM, DNM, *aci*-NM, and *aci*-DNM obtained from MINDO/3 calculations were found to be incorrect. For the last two compounds, they appeared to be unrealistic (too low),[9] even lower than for NM and DNM. The activation barriers to the formation of *aci*-NM obtained from the MINDO/3 and *ab initio* MP2/6-31G(d) calculations differ substantially (227 *vs.* 314 kJ mol^{-1}, respectively).[10] Taking into account that the above-mentioned mechanism[9] not only does provide an explanation for "DNM anomaly", but is also of considerable interest for understanding of regularities of monomolecular decomposition of nitro compounds both in the gas phase and in the condensed phase, in this work we carried out a detailed quantum-

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 6, pp. 913—917, June, 2001.

Table 1. Selected geometric parameters (*r*) of the molecules under study and TS of reactions (1) and (2) obtained from *ab initio* and semiempirical PM3 (given in parentheses) calculations

Structure	*r*/pm			
	C—N	N—O	C—H	O—H
1	148.4 (151.4)	119.7 (121.4)	107.8 (110.1)	—
2	149.8 (143.0)	127.2 (130.6)	152.9 (159.5)	115.7 (121.8)
3	126.9 (130.7)	135.2 (144.1)	106.8 (108.7)	95.4 (95.6)
4	123.1 (123.1)	220.9 (187.5)	115.4 (137.5)	149.0 (141.6)
5+H_2O	113.1 (116.6)	121.6 (121.1)	105.8 (107.0)	94.7 (95.2)
6	148.5 (154.8)	119.1 (120.7)	107.4 (111.7)	—
7	151.5 (146.2)	126.3 (129.2)	148.5 (110.9)	118.2 (130.7)
8	128.9 (133.3)	134.7 (142.6)	106.5 (110.9)	95.6 (95.7)
9	125.8 (125.3)	194.7 (182.1)	126.4 (142.0)	130.6 (138.4)
10+H_2O	113.0 (117.6)	119.6 (120.7)	—	94.7 (95.1)

chemical study of this process. The methods employed were the semiempirical PM3 method, the *ab initio* RHF method, and the density functional theory. Reactions (1) and (2) proceed involving elimination of water from *aci*-NM and *aci*-DNM and were taken as examples.

These reactions can proceed in nitro compounds containing two or three H atoms in α-position relative to the nitro group and cannot proceed in trinitromethane (TNM) or tetranitromethane.[9]

Calculation procedure

Ab initio calculations were carried out using the Dunning—Hay double zeta basis set[11] augmented with polarization d-functions on heavy-element atoms (hereafter, DZV-1d). Full optimization of geometric parameters was performed by the RHF method and followed by inclusion of electron correlation at the second-order level of Møller—Plesset perturbation theory (MP2).[12] No zero-point vibrational energy corrections were introduced. Additionally, we estimated the effect of higher-order corrections of perturbation theory (MP3, MP4(DQ)) taking reaction (1) as an example and compared all the results obtained in this work with those found previously by the coupled clusters method with inclusion of double substitutions (CCD).[18] Density functional (DFT) calculations with the three-parameter B3LYP functional[13] were carried out in the 6-31G(d) and 6-311++G(df,p) basis sets with inclusion of zero-point vibrational energy corrections. Stationary points were identified by analyzing the Hesse matrices. The correspondence between the transition states (TS) located and reactions studied was additionally proved by moving from the saddle points to the neighboring critical points corresponding to the reaction products. All calculations were carried out using the GAMESS[14] and GAUSSIAN-94 [15] program packages.

Results and Discussion

Selected geometric parameters of the reaction centers of initial compounds, products of the reactions (1) and (2), and the corresponding TS are listed in Table 1. The energies of structures **1**—**10** are listed in Table 2 and the relative energies of the processes studied are listed in Table 3.

Geometric parameters of initial compounds, TS of the reactions of formation of *aci*-NM and *aci*-DNM, and reaction products obtained from both semiempirical (PM3) and *ab initio* calculations are close. Main distinctions between the results obtained by different methods are as follows. According to PM3 calculations, the C—NO_2 bond in DNM is appreciably longer than in NM. This is consistent with the main trends of changes in the geometric parameters of nitroalkanes.[16,18] However, *ab initio* calculations predict nearly equal *r*(C—N) distances in the NM and DNM molecules and substantial shortening of the *r*(N—O) distances owing to accumulation of nitro groups in the latter molecule. Semiempirical PM3 calculations also revealed a shortening of the *r*(N—O) distance, but it is less pronounced. For the TS of reactions (1) and (2) both computational methods predict that the C—H and N—O bond lengths change to the greatest extent, whereas the *r*(C—NO_2) distances appear to be only slightly lengthened according to *ab initio* and only slightly shortened according to semiempirical calculations.

Thus, the geometric parameters of the TS of reactions (1) and (2) obtained from *ab initio* calculations are

Table 2. Enthalpies of formation of structures **1**—**10** calculated by the PM3 and MINDO/3 methods and the total energies of the corresponding stationary points obtained from *ab initio* calculations

Structure	ΔH_f/kJ mol^{-1}		*E*/au	
	PM3	MINDO/3	HF/DZV-1d	MP2/DZV-1d
1	−66.68	−44.00	−243.7183165	−244.3811414
2	201.53	182.50	−243.5847085	−244.2606494
3	−16.05	−45.50	−243.6876754	−244.3475762
4	164.92	101.00	−243.5544207	−244.2432007
5	−105.57	−192.50	−243.7055519	−244.3696817
6	−49.98	−72.00	−247.2135503	−448.4124691
7	140.93	84.50	−447.1004550	−448.3097009
8	−47.27	−144.00	−447.1836414	−448.3829176
9	128.48	−30.00	−447.0408109	−448.2889181
10	−138.40	−347.00	−447.1704994	−448.3778192

Table 3. Relative energies (in kJ mol^{-1}) of processes studied

Method	$\Delta H_{1,2}/\Delta E_{1,2}$	$\Delta H_{1,3}/\Delta E_{1,3}$	$\Delta H_{3,4}/\Delta E_{3,4}$	$\Delta H_{3,5}/\Delta E_{3,5}$	$\Delta H_{6,7}/\Delta E_{6,7}$	$\Delta H_{6,8}/\Delta E_{6,8}$	$\Delta H_{8,9}/\Delta E_{8,9}$	$\Delta H_{8,10}/\Delta E_{8,10}$
	Nitromethane				Dinitromethane			
PM3	268.21	50.63	180.98	−89.14	191.91	2.72	175.74	−91.01
MINDO/3 [8]	227.0	−1.50	146.50	−147.0	156.5	−72.0	104.0	−203.0
RHF/DZV-1d	350.78	80.44	349.95	−46.94	296.92	76.10	375.0	34.50
MP2/RHF/DZV-1d	316.35	88.24	274.00	−46.94	269.81	77.21	238.43	13.38
MP3	317.82	69.45	311.33	−34.14				
MP4(DQ)	318.23	72.17	307.19	−39.50				
CCD	319.41	71.79	306.85	−41.09				

Table 4. Geometric parameters of nitromethanes obtained from DFT calculations at the B3LYP/6-31G(d) level and experimental values (Ref. 16)

Compound	*r*/pm			Angle/deg	
	C—N	N—O	C—H	H—C—N	O—N—O
NM	150.0	122.6	109.1	107.2	126.0
	(148.9±5)	(122.4±5)	(108.8±1)	(107.2)	(125.3)
DNM	150.7	122.2	108.8	108.2	127.5
TNM	151.7	122.0	108.5	109.4	128.8
	(105.5±5)	(121.9±3)			(128.6±1.0)
Tetranitro-	154.1	121.5	—	—	129.3
methane	(152.6±6)	(121.8±2)	—	—	(129.3±1.0)

closer to those of *aci*-NM and *aci*-DNM, respectively. Therefore, the *ab initio* estimates of the heights of the barriers to these reactions are substantially higher (by 60—80 kJ mol^{-1}) than those found by the PM3 method. On the other hand, comparison of changes in the main bond lengths in the TS of reaction (2) relative to those in the initial molecules shows that they are much less than analogous changes for the TS of reaction (1). This can be responsible for a decrease of 46.5 (*ab initio*) and 76.3 kJ mol^{-1} (PM3) in the barrier to the reaction.

The data listed in Table 3 suggest that the formation of *aci*-NM and *aci*-DNM is the limiting stage of reactions (1) and (2), respectively. The barrier to the second stage, *viz.*, elimination of water, is much lower and remains virtually unchanged with accumulation of nitro groups in the molecule.

The barrier to formation of *aci*-TNM calculated by the PM3 method is 142.5 kJ mol^{-1}, which is nearly 50 kJ mol^{-1} lower than for *aci*-DNM. Hence, the decrease in the barriers to the reactions of formation of *aci*-NM, *aci*-DNM, and *aci*-TNM (a total of 125.5 kJ mol^{-1} according to PM3 calculations) is substantially larger than the decrease in the C—N bond dissociation energies, *D*(C—N), for the same molecules (a total of 57 to 71 kJ mol^{-1} according to different experimental estimates[4]).

If the heights of the barriers to reactions of isomerization and monomolecular decomposition of aliphatic *C*-nitro compounds are estimated both semiempirically and using *ab initio* calculations with inclusion of electron correlation at the MP*n* (n = 2—4) level of theory, the results obtained can differ substantially from the experimental values. Recently,[19] we studied transition states of the reactions of β-elimination of nitrous acid from nitroethane and *n*-nitropropane by the MP2/6-31G(d) method and showed that the calculated enthalpies of activation were nearly 60 kJ mol^{-1} higher than the experimental activation energies of gas-phase decomposition. It was found[20] that the MP2/6-31G(d) method substantially overestimates the barrier to nitro-nitrous rearrangement in the NM molecule. This suggests that the barriers to reactions (1) and (2) obtained from *ab initio* calculations should be regarded as upper bounds.

To obtain additional information on the energies of monomolecular decomposition of NM, DNM, and TNM, we studied the key stage of the reaction mechanism, *viz.*, the formation of *aci*-NM, *aci*-DNM, and *aci*-TNM, using the density functional theory (DFT) with the three-parameter B3LYP functional and the 6-31G(d) basis set. Recently,[21] it was shown that the barrier to reaction of elimination of HNO_2 from nitroethane estimated by this method is nearly equal to the experimental value (188.3 and 190.3 kJ mol^{-1}, respectively). Density functional calculations can also be used for correct prediction of the activation energies of gas-phase radical decomposition of aliphatic nitro compounds.[22]

Table 5. Geometric parameters of *aci*-NM, *aci*-DNM, and *aci*-TNM obtained from DFT calculations at the B3LYP/6-31G(d) level

Compound	*r*/pm						Angle N—O—H /deg
	C—N	C=N	N=O	N—O	N—OH	O—H	
aci-NM	—	130.0	—	124.1	142.3	97.7	100.0
aci-DNM	142.8	131.8	122.8, 123.7	122.2	141.6	97.9	100.9
aci-TNM	146.7, 147.2	132.7	122.4, 123.0	122.5	138.0	98.1	109.3

Table 6. Atomic charges (q) and dipole moments (μ) of nitromethanes and *aci*-NM, *aci*-DNM, and *aci*-TNM obtained from DFT calculations at the B3LYP/6-31G(d) level

Compound	q/e						μ/D
	C	N	O	O(H)	H	H(O)	
NM	−0.334	0.454	−0.370	−0.369	0.208	0.203	3.47
DNM	−0.056	0.470	−0.350	−0.339	0.246	0.247	3.18
TNM	0.213	0.489	−0.335	−0.314	—	0.269	2.23
aci-NM	−0.196	0.381	−0.479	−0.500	0.187	0.416	1.42
aci-DNM	0.185	0.339	−0.385	−0.473	0.236	0.431	4.62
aci-TNM	0.693	0.416	−0.382	−0.449	—	0.443	4.27

Tables 4—6 present selected geometric parameters and characteristics of the electronic structure of NM, DNM, TNM, *aci*-NM, *aci*-DNM, and *aci*-TNM. The geometries of the TS of reactions (1) and (2) are shown in Fig. 1.

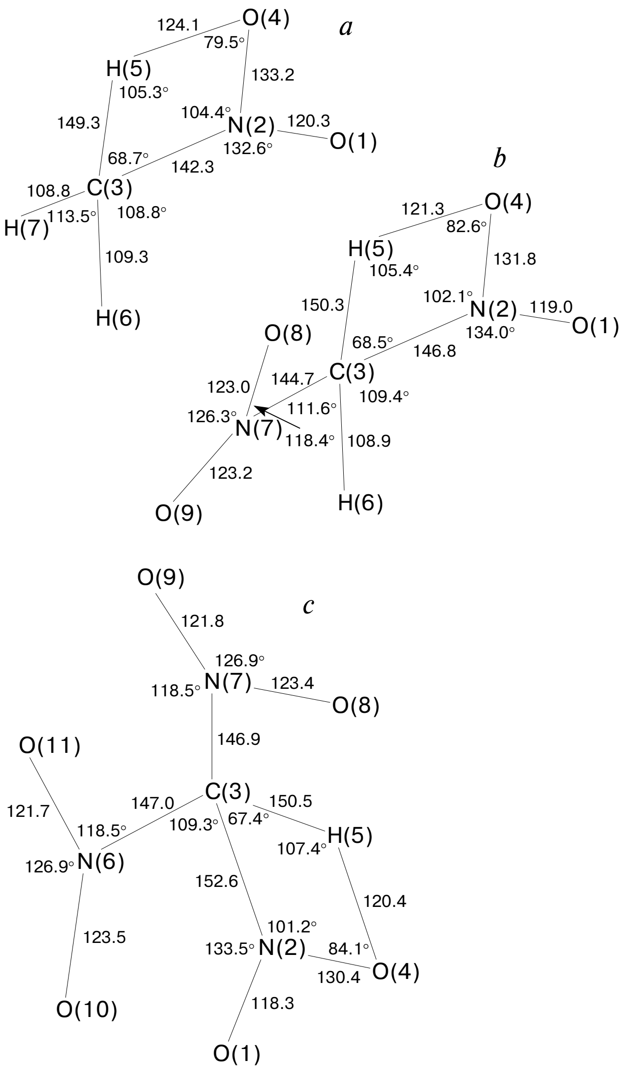


Fig. 1. Transition state geometries of the reactions of formation of *aci*-NM (*a*), *aci*-DNM (*b*), and *aci*-TNM (*c*) molecules (the bond lengths are given in pm).

Analysis of the results obtained in this work shows that the B3LYP/6-31G(d) method correctly reproduces the molecular geometries of the NM, DNM, and TNM molecules (see Table 4). To get a deeper insight into the problem, we also present information on the geometry of the C—NO_2 group in the tetranitromethane molecule. A comparison of the calculated and experimental bond lengths in the four molecules shows that they are close. The maximum difference does not exceed 1.5 pm (for the C—NO_2 bond length in tetranitromethane molecule). The differences between the calculated and experimental C—H and N—O bond lengths are no larger than 0.3 pm. For the O—N—O angles, the differences between the calculated and experimental values lie within the limits of experimental error. It should be noted that the method employed correctly reproduces the experimentally observed character of changes in the geometric parameters of the molecules under study. In particular, accumulation of the NO_2 groups leads to appreciable lengthening of the C—NO_2 bond and to substantial shortening of the r(N—O) and r(C—H) distances. This can be thought to be correlated with the corresponding decrease in the C—NO_2 bond strength, an increase in the C—H bond strengths,[4] and an increase in the O—N—O angle. The aforesaid suggests that the B3LYP/6-31G(d) method reproduces the geometry of aliphatic *C*-nitro compounds much more correctly than the MP2/DZV-1d method.

From the data listed in Table 5 it follows that accumulation of NO_2 groups in the *aci*-NM, *aci*-DNM, and *aci*-TNM molecules leads to substantial lengthening of the C=N bonds and the corresponding shortening of the r(N—OH) distances. On the other hand, changes in the OH bond lengths are very small, though a tendency has been toward lengthening of the r(O—H) distance in the molecules studied. The r(C—N) distances in *aci*-DNM and *aci*-TNM are much shorter than in DNM and TNM, respectively.

Analysis of the electron density distribution reveals substantial differences in the atomic charges of carbon atoms in NM, DNM, and TNM and the corresponding *aci*-forms. According to calculations, the negative charge on the C atom of *aci*-NM is much smaller than in NM, whereas carbons in *aci*-DNM and *aci*-TNM carry rather large positive charges (see Table 6). These compounds (especially, *aci*-TNM) must be highly reactive in the reactions of nucleophilic substitution and elimination.

The differences between the negative atomic charges of oxygens in the N—O and O—H groups are relatively small. On the other hand, an appreciable decrease in the negative atomic charge of the O atom of the N—O group on going from *aci*-NM to *aci*-DNM should be noted. The magnitude of this charge remains virtually unchanged with accumulation of NO_2 groups (in *aci*-TNM). A tendency for a decrease in the negative atomic charges of oxygens in the OH groups on going from *aci*-NM to *aci*-DNM is much less pronounced. The atomic charges of hydrogen atoms of the OH groups in the compounds under study are larger than those on the H atoms bound to the C atom. Yet another feature of the electronic structure is a dramatic increase in the dipole moment of *aci*-DNM as compared to *aci*-NM.

The above-mentioned features of the effect of accumulation of nitro groups on changes in the reaction center geometry are supported by analyzing the TS geometry of the formation reaction of *aci*-NM. The C—H bond length in the TS changes to the greatest extent as compared to the initial molecule. Taking into account this fact, one would assume that the reaction under study begins with intramolecular hydrogen transfer to an O atom of the NO_2 group. On the other hand, other geometric parameters of the reaction center (C—N and N—O bond lengths) also significantly change in the course of the reaction. We found that the Δr(C—H)* values for the reactions of NM, DNM, and TNM (40.2, 41.5, and 42 pm, respectively) increase only slightly. This seemingly should lead to an increase in the enthalpy of activation of the reaction (or the barrier to reaction). However, the calculations predict the reverse, namely, a substantial decrease in the barrier heights (Table 7). This contradicts the assumption that the mechanism of formation of *aci*-NM, *aci*-DNM, and *aci*-TNM involves intramolecular hydrogen transfer.

Table 7. Enthalpies of formation and barriers to reactions of formation (in kJ mol^{-1}) of *aci*-NM, *aci*-DNM, and *aci*-TNM

Compound	ΔH_f°			$\Delta H^\#$	
	Expt.[23]	PM3	B3LYP /6-31G(d)	PM3	B3LYP /6-31G(d)
NM	−74.6, −80.8	−43.9	−67.8	269.5	270.0
DNM	−59.8	−28.9	−32.7	192.0	227.8
TNM	−0.8	−30.1	29.2	142.7	201.7

Therefore, the reactivity can be thought to be due to changes in other geometric parameters. Indeed, the absolute values of Δr(C—N) for the reactions of NM, DNM, and TNM (7.7, 4.0, and 0.9 pm, respectively) decrease substantially. The Δr(N—O) values for the reactions of NM, DNM, and TNM (10.6, 9.6, and 8.9 pm, respectively) also follow this pattern, though the tendency is less pronounced. The results of analysis of the bond dissociation energies and force constants of different bonds in the reaction center suggest that opposing changes in the Δr(N—O) and Δr(C—H) values for these reactions nearly cancel each other. Therefore, a decrease in the heights of the barriers to reactions of formation of *aci*-NM, *aci*-DNM, and *aci*-TNM with accumulation of NO_2 groups should mainly be associated with a decrease in the $\Delta r(C—NO_2)$ differences between the TS and initial molecules. In this case, the mechanism of formation of *aci*-NM seems to involve a synchronous elimination of hydrogen, thus leading to significant changes in several geometric parameters (r(C—H), r(C—N) and r(N—O)) rather than intramolecular hydrogen transfer. This is also consistent with the results of semiempirical PM3 and *ab initio* MP2 calculations (see Table 1).

Thus, accumulation of nitro groups leads to substantial decrease in the heights of the barriers to formation of *aci*-NM, *aci*-DNM, and *aci*-TNM. It should be noted that extension of the basis set leads to a decrease in the activation barriers to these reactions. The estimates of the barrier heights obtained from density functional B3LYP/6-311++G(df,p) calculations are thought to be the most reliable. Their values for the reactions of NM and DNM are 258.1 and 218.5 kJ mol^{-1}, respectively, which is close to the thermochemical estimates of D(C—N) values (253.3 kJ mol^{-1} for NM and 225.5 kJ mol^{-1} for DNM).[23]

On the other hand, high barriers to the reactions of NM, DNM, and TNM studied in this work prevent them from proceeding during monomolecular gas-phase decomposition of these compounds, especially having regard to the pre-exponential factors of gas-phase radical decomposition reactions that are much larger than those of any competing molecular reactions.[4,5] On the other hand, it is known that the activation energy of the primary act of liquid-phase thermal decomposition of NM is substantially lower (by 80—100 kJ mol^{-1})[4–6] than that of the gas-phase decomposition of this compound. As mentioned above, liquid-phase decomposition of NM involves the formation of *aci*-NM as intermediate. Therefore, the processes studied in this work can be of interest for the development of our understanding of relationships of the liquid-phase decomposition of nitromethanes and for rationalization of abnormally low stability of DNM.

This work was carried out with the financial support of the Russian Foundation for Basic Research (Project No. 00-03-33039).

References

1. S. S. Novikov, V. V. Sevost′yanova, G. A. Shveikhgeimer, and V. A. Shlyapochnikov, *Khimiya alifaticheskikh i alitsiklicheskikh nitrosoedinenii* [*Chemistry of Aliphatic*

---

* Hereafter Δr denotes the change in the length of a particular bond in the TS relative to that in the initial molecule.

and Alicyclic Nitro Compounds], Mir, Moscow, 1974 (in Russian).

2. The Chemistry of the Nitro and Nitroso Groups, Vol. 1, Ed. H. Feuer, Interscience Publishers, a division of John Wiley and Sons, New York—London—Sydney—Toronto, 1969.
3. K. L. Lammertsma and B. V. Prasad, *J. Am. Chem. Soc.*, 1993, **115**, 2348.
4. G. M. Nazin and G. B. Manelis, *Usp. Khim.*, 1994, **63**, 327 [*Russ. Chem Rev.*, 1994, **63** (Engl. Transl.)].
5. G. B. Manelis, G. M. Nazin, Yu. I. Rubtsov, and V. A. Strunin, *Termicheskoe razlozhenie i gorenie vzryvchatykh veshchestv and porokhov* [*Thermal Decomposition and Combustion of Explosives and Propellants*], Nauka, Moscow, 1996 (in Russian).
6. G. M. Khrapkovskii, G. N. Marchenko, and A. G. Shamov, *Vliyanie stroeniya molekul na kineticheskie parametry monomolekulyarnogo raspada S- i O-nitrosoedineniya* [*Molecular Structure Effect on the Kinetic Parameters of Monomolecular Decomposition of S-Nitro and O-Nitro Compounds*], FEN, Kazan′, 1997 (in Russian).
7. R. Engelke, W. I. Earl, and C. M. Rohlfing, *Int. J. Chem. Kinet.*, 1986, **18**, 1205.
8. K. R. Brower, *J. Org. Chem.*, 1988, **53**, 3776.
9. G. M. Khrapkovskii, A. M. Rozin, V. A. Tikhomirov, and A. G. Shamov, G. N. Marchenko, *Dokl. Akad. Nauk SSSR*, 1988, **298**, 921 [*Dokl. Chem. USSR*, 1988 (Engl. Transl.)].
10. M. L. McKee, *J. Am. Chem. Soc.*, 1986, **108**, 5784.
11. T. H. Dunning and P. J. Hay, in *Methods of Electronic Struct. Theory*, Ch. 1, Ed. H. F. Shaefer, III, Plenum Press, New York, 1977, 1.
12. C. Møller and M. Plesset, *Phys. Rev.*, 1934, **46**, 618.
13. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648; C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785; B. Mierhlich, A. Savin, H. Stoll, and H. Preuss, *Chem. Phys. Lett.*, 1989, **157**, 200.
14. M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. J. Jensen, S. Koseki, N. Matsunaga, K. A. Nguen, S. Su, T. L. Dupius, and J. A. Montgomery, *J. Comput. Chem.*, 1993, **14**, 1347.
15. M. J. Frisch, G. W. Trucks, H. B. Schelegel, P. M. W. Gill, P. M. W. Jonson, P. M. W. Robb, J. R. Cheeseman, T. Keith, A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, *Gaussian-94*, *Revision E1*, Gaussian, Inc., Pittsburgh (PA), 1995.
16. N. I. Sadova and L. V. Vilkov, *Usp. Khim.*, 1982, **51**, 153 [*Russ. Chem. Rev.*, 1982, **51** (Engl. Transl.)].
17. G. M. Khrapkovskii, A. G. Shamov, G. A. Shamov, and V. A. Shlyapochnikov, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 2438 [*Russ. Chem. Bull.*, 1996, **45**, 2309 (Engl. Transl.)].
18. G. M. Khrapkovskii, A. G. Shamov, G. A. Shamov, and V. A. Shlyapochov, *Mendeleev. Commun.*, 1997, 169.
19. G. M. Khrapkovskii, A. G. Shamov, G. A. Shamov, and V. A. Shlyapochnikov, *Zh. Org. Khim.*, 1996, **35**, 891 [*J. Org. Chem.*, 1996, **35** (Engl. Transl.)].
20. M. L. McKee, *J. Phys. Chem.*, 1989, **93**, 7365.
21. A. G. Shamov, G. M. Khrapkovskii, and G. A. Shamov, in *Struktura i dinamika molekulyarnykh sistem* [*Structure and Dynamics of Molecular Systems*], Ioshkar-Ola—Kazan—Moscow, 1998, **3**, 183 (in Russian).
22. A. G. Shamov and G. M. Khrapkovskii, in *Struktura i dinamika molekulyarnykh sistem* [*Structure and Dynamics of Molecular Systems*], Kazan′, 1999, 347 (in Russian).
23. Yu. A. Lebedev, E. A. Miroshnichenko, and Yu. K. Knobel′, *Termokhimiya nitrosoedinenii* [*Thermochemistry of Nitro Compounds*], Nauka, Moscow, 1970.

Received in May 19, 2000;
in revised form November 9, 2000