ISSN 1990-7931, Russian Journal of Physical Chemistry B, 2022, Vol. 16, No. 5, pp. 862–868. © Pleiades Publishing, Ltd., 2022.
Russian Text © The Author(s), 2022, published in Khimicheskaya Fizika, 2022, Vol. 41, No. 9, pp. 19–25.

The Effect of Molecular Structure on the Strength of $C–NO_2$ Bonds of Nitropentanes

G. M. Khrapkovskii[a], **I. V. Aristov**[a], **D. L. Egorov**[a, *], **Ya. V. Denisova**[a], **and E. V. Nikolaeva**[a]
[a] *Kazan National Research Technological University, Kazan, Russia*
**e-mail: egorovdl2015@yandex.ru*

Received December 12, 2021; revised January 17, 2022; accepted January 20, 2022

Abstract—The enthalpies of the formation of eight nitropentanes and pentyl radicals are calculated using the G3B3 and G4 multistep (composite) quantum chemical methods, as well as the B3LYP, CAM-B3LYP, and wB97XD density functional methods. Based on these results, the dissociation energies of the $C–NO_2$ (D(C–N)) compounds are determined. The features of the influence of the molecular structure on the value D(C–N) of nitropentanes are considered. The calculated and thermochemical values of the enthalpies of formation of radicals are compared, which show that the most reliable estimates are given by the G4 method (the average absolute value of the error is 2.2 kJ/mol). According to the G4 method, the dissociation energy of the studied compounds varies from 252.8 to 268.2 kJ/mol.

Keywords: nitropentanes, pentyl radicals, radical decomposition, enthalpies of formation, dissociation energies

DOI: 10.1134/S1990793122040066

INTRODUCTION

The study of the kinetics and mechanism of thermal decomposition is one of the important areas of research in the field of chemistry of nitro compounds [1–12]. Currently, the most detailed information on the kinetics of thermal decomposition is available for nitroalkanes [2, 3, 8]. Nitroalkanes in the gaseous state decompose according to two main mechanisms: radical, with homolytic cleavage of the $C–NO_2$ bond; and molecular, associated with the elimination of nitrous acid [3]. The experimental data on the kinetics of thermal decomposition in the gaseous state are of particular interest for discussing the influence of the structure of molecules on the change in the series of Arrhenius parameters of the primary reaction. A significant place in the study of the mechanisms of thermal destruction of nitro compounds is occupied by calculations by quantum chemical methods [13–15]. The use of these methods makes it possible to significantly expand the number of discussed mechanisms of thermal destruction of various classes of nitro compounds [15–34]. In addition, in many cases this makes it possible to clarify, supplement, and sometimes fundamentally change the interpretation of the experimental data.

The bulk of the experimental data on the kinetics of the gas-phase radical decomposition of nitroalkanes was obtained for polynitro compounds. Much less information is available on the radical mechanism of the gas-phase decomposition of mononitroalkanes [2, 3]. Mononitroalkanes decompose predominantly according to the molecular mechanism with the elimination of nitrous acid; therefore, experimental estimates of the barriers of radical decomposition reactions are available only for a few simple compounds and are not very accurate [2, 3]. The energy (enthalpy) of dissociation of the C–N (D(C–N)) bond can be calculated from the enthalpies of formation of nitroalkanes and reaction products. In the work [35] using various ab initio and density functional theory (DFT) methods, the values D(C–N) of the eight simplest nitroalkanes C_1–C_4, which are in good agreement with the most reliable thermochemical estimates, were determined.

This report presents the results of calculating the strength of the $C–NO_2$ bond in nitropentanes, for which the experimental values D(C–N) obtained using thermochemical or kinetic methods are absent. The use of the calculated data for nitropentanes is of considerable interest, since it allows us to consider in more detail some features of the influence of the molecular structure on the D(C–N) value in the nitroalkanes series and obtain important additional information about the comparative strength of the $C–NO_2$ bonds formed with the participation of primary, secondary, and tertiary carbon atoms.

CALCULATION METHODS

The calculations were carried out using the GAUSSIAN 09 application software package [36]. The enthalpies of formation were estimated from the total electronic energies by the standard methods [37,

Table 1. Enthalpies of formation (in kJ/mol) of nitropentanes

Compound number	Compound	B3LYP/ 6-31G(*d*,*p*)	CAM-B3LYP/ 6-31+G(2*df*,*p*)	wB97XD/ TZVP	wB97XD/ TZVPP	G3B3	G4
1	1-Nitropentane	−174.5	−192.2	−107.3	−161.4	−171.9	−169.9
2	2-Nitropentane	−185.9	−204.2	−121.0	−174.1	−189.7	−187.7
3	3-Nitropentane	−186.3	−204.6	−122.9	−175.8	−192.9	−190.5
4	2-Methyl-1-nitrobutane	−172.9	−192.4	−110.4	−164.2	−178.8	−177.0
5	2-Methyl-2-nitrobutane	−190.0	−208.5	−128.7	−180.7	−202.8	−200.5
6	2-Methyl-3-nitrobutane	−183.9	−203.6	−122.8	−175.7	−194.7	−193.0
7	3-Methyl-1-nitrobutane	−172.9	−192.3	−111.2	−165.7	−175.5	−173.9
8	2,2-Dimethyl-1-nitropropane	−177.3	−197.9	−116.5	−169.9	−189.0	−189.5

38] for the optimal conformations. Composite methods G3B3 [38] and G4 [39], which convey the thermochemical characteristics of nitroalkanes better than other quantum chemical methods, were used [35, 37, 38, 40]. In order to obtain more detailed data, we also applied the DFT methods B3LYP [41, 42] with basis 6-31G(*d*,*p*), wB97XD [43] with bases TZVP and TZVPP, and CAM-B3LYP [44] with basis 6-31+G(2*df*,*p*).

RESULTS

Table 1 shows the calculated values of the enthalpies of formation of nitropentanes. Unfortunately, there are no reliable experimental data on the enthalpies of formation of mononitropentanes [45, 46]. However, in the works [35, 40], it was shown that for nitromethane, nitroethane, nitropropanes, and nitrobutanes, the thermochemical and calculated values of the enthalpies of formation obtained using the G3B3 and G4 methods are in good agreement with each other. The error of the G4 calculation averaged in the series does not exceed 3.8 kJ/mol. Taking into account these data, it can be assumed that the calculated values of the enthalpies of formation for nitropentanes will also be quite reliable. In the work [47], the thermochemical value is given of the enthalpy of formation of 1-nitropentane in the gaseous state, equal to −164 kJ/mol, which agrees satisfactorily with the estimate by the G4 method: −169.9 kJ/mol.

All methods used in the work equally convey the trends in the enthalpies of formation in the series of nitropentanes. The calculation predicts the highest values of the enthalpies of formation (the smallest in absolute value) for the following compounds: 1-nitropentane, 2-methyl-1-nitrobutane, 3-methyl-1-nitrobutane, and 2,2-dimethyl-1-nitropropane, in which the nitro group is attached to the primary carbon atom (compounds **1**, **4**, **7**, and **8** are given in Table 1). In this case, the presence of the branching of the carbon skeleton increases the absolute value of the enthalpy of formation. The calculation predicts the lowest value of the enthalpy of formation in the series for 2-methyl-2-nitrobutane (compound **5**), in which the nitro group is attached to the tertiary carbon atom. Nitropentanes in which the nitro group is attached to a secondary carbon atom (compounds **2**, **3**, and **6**), have average enthalpies of formation in the series.

Table 2 shows the calculated values of the enthalpies of formation of pentyl radicals. According to the calculation results, relatively large values of the enthalpies of formation are observed for those in which the unpaired electron is localized mainly on the primary carbon atom (pentyl, 2-methylbutyl, 3-methylbutyl, 2,2-dimethylpropyl). Radicals in which the unpaired electron is localized predominantly on the secondary carbon atom (pentan-2-yl, pentan-3-yl, 3-methylbutan-2-yl) have lower enthalpies of formation. The calculation predicts the minimum value of the enthalpy of formation in the series for the pentyl radical, in which the unpaired electron is localized mainly on the tertiary carbon atom (2-methyl-2-nitrobutane).

Comparison of the calculated and experimental values of the enthalpies of formation of pentyl radicals is a rather complicated problem. For a long time in various reference books [48–50] for hydrocarbon radicals, the recommended values of the enthalpies of formation were given, which differed by 12–17 kJ/mol. In recent years, considerable attention has been paid to the analysis of the reliability of the experimental data. As a result of the work done, the spread of recommended values of the enthalpies of formation of radicals has significantly decreased. With this in mind, for comparison with the calculated values, we use the results recommended in a relatively recent paper [51]. These values are in good agreement with the data of authoritative thermochemical reference books [48, 49]. The absolute values of the deviations of the calculated values of the enthalpies of formation of pentyl radicals from the recommended experimental ones are given in Table 2.

Table 2. Enthalpies of formation ($\Delta H_{f,\,298}$) and absolute values of their deviations from experimental estimates (Δ) for radicals formed upon cleavage of the C—NO_2 bond in nitropentanes (in kJ/mol)

Compound no.	Radical	B3LYP/6-31G(*d*,*p*)		CAM-B3LYP/6-31+G(2*df*,*p*)		wB97XD/TZVP		wB97XD/TZVPP		G3B3		G4		Experiment
		$\Delta H_{f,\,298}$	Δ	$\Delta H_{f,\,298}$	Δ	$\Delta H_{f,\,298}$	Δ	$\Delta H_{f,\,298}$	Δ	$\Delta H_{f,\,298}$	Δ	$\Delta H_{f,\,298}$	Δ	
9	Pentyl	37.1	17.3	33.5	20.9	84.5	30.1	64.4	10.0	61.0	6.6	56.1	1.7	54.4
10	Pentan-2-yl	20.6	29.6	19.0	31.3	73.2	23.0	50.2	0.0	51.0	0.8	45.7	4.5	50.2
11	Pentan-3-yl	21.9	25.1	20.0	27.0	75.0	28.0	52.1	5.1	51.9	4.9	46.9	0.0	47.0
12	2-Methylbutyl	38.5	9.4	33.5	14.4	85.5	37.6	63.1	15.2	56.4	8.5	51.5	3.6	47.9
13	2-Methylbutan-2-yl	9.4	19.6	8.7	20.3	61.2	32.2	38.6	9.6	39.7	10.8	33.9	4.9	29.0
14	3-Methylbutan-2-yl	20.7	19.6	18.1	22.2	70.2	29.9	47.8	7.5	45.5	5.2	40.0	0.3	40.3
15	3-Methylbutyl	34.6	13.4	30.0	18.0	81.2	33.2	60.0	12.0	53.3	5.3	48.2	0.2	48.0
16	2,2-Dimethylpropyl	33.9	2.5	26.0	10.4	77.9	41.5	56.2	19.8	44.1	7.7	39.1	2.7	36.4
17	NO_2	23.0	10.1	21.3	11.8	53.9	20.8	22.6	10.5	31.8	1.3	30.7	2.4	33.1
	Mean value Δ (excluding NO_2)		17.1		20.5		31.9		9.9		6.2		2.2	

According to the calculation data, the best agreement between these values is observed when using the G4 method. In this case, the average error modulus in the series is 2.2 kJ/mol, which is even less than the possible errors of the experimental determination indicated in the reference books [48–51]. Note that a similar picture is also observed when comparing the experimental and calculated enthalpies of formation of hydrocarbon radicals C_1–C_4 [40]. In this case, the average modulus of the error in determining the enthalpy of formation of radicals using the G4 method is 3.5 kJ/mol. The data presented also show that in a number of cases the calculation results can be used to assess the reliability of the experimental data. This is important in cases where the results recommended in various thermochemical handbooks differ significantly. A similar situation existed for pentyl radicals for a long time. The enthalpies of formation recommended in the guide [50] for them in the gaseous state were significantly lower than those given in [48, 49].

When using the directory data [50] the average error modulus of the G4 method increases significantly and reaches a value of 18.6 kJ/mol. Relatively recently, in [51], with the participation of the authors of the reference book [50], these results were revised taking into account the new experimental data. At the same time, the values recommended for alkyl radicals C_2–C_5 barely differed from the results given in the works [48, 49]. The considered situation shows that the results of quantum chemical calculations in a number of cases can be used not only to fill in the missing data but also to assess the reliability of the available experimental data.

When using the G3B3 method, the average value of the error modulus in the series of studied compounds almost triples (6.2 kJ/mol). The DFT methods used in this work agree much worse with the thermochemical data. For the B3LYP and wB97XD methods, the mean modulus of difference between the calculated and experimental values in the series is 17.0 and 31.9 kJ/mol, respectively. At the same time, the B3LYP method systematically underestimates, while the wB97XD method overestimates, the enthalpies of formation of radicals. These trends should be taken into account when analyzing the calculated values of the dissociation energies of the C—NO_2 bond of nitropentanes. The corresponding results are presented in Table 3.

The lack of reliable experimental data on the enthalpies of formation of nitropentanes makes it impossible to compare the obtained calculated values with the thermochemical estimates of D(C—N). At the same time, a comparison of the calculated and experimental values of the enthalpies of formation of the reaction products of the radical decomposition of nitropentanes (alkyl radicals and NO_2) suggests that the calculated values D(C—N) obtained using the G4 method will be sufficiently close to the most reliable thermochemical estimates. The results of a comparison of the calculated and experimental values of D(C—N) of

Table 3. Dissociation energies (in kJ/mol) of the C—NO_2 (D(C—N)) bond in the reaction of the radical decomposition of nitropentanes

Compound number	B3LYP/6-31G(*d,p*)	CAM-B3LYP/6-31+G(2*df,p*)	wB97XD/TZVP	wB97XD/TZVPP	G3B3	G4
1	234.6	246.9	245.7	248.4	264.7	256.6
2	229.5	244.4	248.0	246.9	272.6	264.1
3	231.2	245.9	251.8	250.5	276.7	268.2
4	234.4	247.1	249.8	249.9	267.0	259.1
5	222.4	238.5	243.8	241.9	274.4	265.1
6	227.6	242.9	246.9	246.1	272.1	263.6
7	230.5	243.5	246.3	248.3	260.6	252.8
8	234.2	245.2	248.3	248.7	265.0	259.3

nitroalkanes C_1—C_4 can also serve as an additional argument in favor of this assumption [35, 40]. In this case, the average absolute value of the error in the calculated and experimental values of *D*(C—N) when using the G4, G3, and G3B3 methods does not exceed 6.6 kJ/mol.

All the methods used in our work predict a relatively insignificant change of *D*(C—N) in the series of isomeric nitropentanes (by not more than 8–13 kJ/mol (G3B3)). The calculations predict the changes of the enthalpies of formation of nitropentanes and pentyl radicals to be 2–2.5 times greater in the series. Based on these data, it can be assumed that the change in the series of enthalpies of formation of compounds and radicals occurs in a consistent manner and when calculating *D*(C—N) the noted differences are partially compensated.

An analysis of the obtained data shows that the correlation between the enthalpies of formation of the nitropentanes and radicals formed during the homolytic cleavage of the C—NO_2 bond indeed takes place in them. For example, according to the G4 method, the correlation coefficient between these values is 0.906. The estimated values of *D*(C—N) predicted by different methods differ markedly. For example, for 1-nitropentane, this difference reaches 30.1 kJ/mol. The maximum values for the C—NO_2 bond strength are predicted by the G3B3 method, and the minimal values are predicted by the B3LYP/6-31G(*d,p*) method. As noted, we consider the estimates of *D*(C—N) obtained by the G4 method to be the most reliable. For example, for 1-nitropentane, they predict the value of *D*(C—N) to be 256.6 kJ/mol, which is very close to the calculated estimates of the strength of this bond obtained using this method for nitroethane, 1-nitropropane, and 1-nitrobutane: 256.9, 258.6, and 256.5 kJ/mol, respectively [35].

According to the G4 and G3B3 methods, relatively stronger bonds in nitropentanes are formed with the participation of a secondary carbon atom: 2-nitropentane, 3-nitropentane, and 2-methyl-3-nitrobutane. The strongest C—NO_2 bond in nitropentanes is observed in 3-nitropentane. Increasing the strength of the C—NO_2 bond in compounds **2**, **3**, and **6**, in which the nitro group is located in the secondary carbon atom, compared with nitropentanes, in which this bond is formed with the participation of the primary carbon atom (compounds **1**, **4**, **7**, and **8**) is related to different trends in the enthalpies of formation of nitropentanes and alkyl radicals.

In isomeric pentyl radicals, the maximum value of the enthalpies of formation is observed for those that are formed upon cleavage of the C—N bond in the primary carbon atom (compounds **9**, **12**, **15**, and **16**). However, this increase does not compensate the decrease in the enthalpies of formation in 1-nitropentanes compared to 2-nitropentanes. The observed trends explain the increase of *D*(C—N) in 2-nitropentanes compared to 1-nitropentanes. A similar trend, according to the G4 method, is also observed for nitroalkanes C_1—C_4 [35, 40], which is also consistent with the thermochemical data. According to the results of the DFT methods used in the work, the opposite trend is observed. The C—NO_2, bonds formed with the participation of primary carbon atoms are relatively stronger and bonds formed with the participation of secondary carbon atoms are less strong. Since these data contradict the thermochemical estimates, in the future, when considering the regularities of the influence of the molecular structure on the change in the series of the dissociation energy of the C—NO_2 bond the corresponding results obtained by the DFT methods are not used. The discussion below is based on the results of the G4 method.

The *D*(C—N) values in the group of compounds having C—NO_2 bonds formed with the participation of primary (compounds **1**, **4**, **7**, **8**) or secondary (compounds **2**, **3**, **6**) carbon atoms are sufficiently close. At the same time, among isomeric nitrobutanes having bonds formed with the participation of secondary carbon atoms, the calculation notes differences in 2-nitropentane and 3-nitropentane. In the last of these compounds, in which the nitro group is attached to the central carbon atom, the calculation predicts a noticeable increase in the strength of the $C-NO_2$ bond. Analysis of data on the enthalpies of formation of compounds and radicals (Tables 1, 2) shows that this is due to a slight decrease in the enthalpy of formation of 3-nitropentane compared to 2-nitropentane, as well as the increase in the enthalpy of formation of the radical formed upon homolytic cleavage of the $C-NO_2$ bond in 3-nitropentane. The strength of the $C-NO_2$ bond, formed with the participation of the tertiary carbon atom in 2-nitro-2-methylbutane, barely differs from the calculated values predicted for compounds in which the nitro group is attached to the secondary carbon atom: 2-nitropentane and 3-nitro-2-methylbutane.

Comparison with calculated data obtained for the other nitroalkanes studied using the G4 method [35, 40] shows that the D(C–N) values predicted for compounds with similar structures differ insignificantly. For example, for 1-nitrobutane and 1-nitropentane, these values are the same. Interestingly, method G4 predicts fairly close D(C–N) values for nitrohexanes[1]. For them, similar patterns of influence of the molecular structure on the change in the strength of the $C-NO_2$ bond in series are also observed. For example, according to the calculation data, the bonds formed with the participation of primary carbon atoms are the weakest. The estimated D(C–N) values in 1-nitrohexane are only 1.2 kJ/mol less than in 1-nitropentane (255.43 and 256.6 kJ/mol). The $C-NO_2$ bonds are noticeably stronger. in nitrohexanes and nitropentanes formed with the participation of secondary carbon atoms. It is important that in this case the calculated D(C–N) values for structurally similar compounds differ insignificantly. Thus, for 2-nitrohexane and 2-nitropentane, the G4 method predicts values of 263.1 and 264.1 kJ/mol, respectively. For 3-nitrohexane and 3-nitropentane, the D(C–N) values are 267.3 and 268.2 kJ/mol, respectively.

Similar D(C–N) values are also predicted by the calculation for nitroalkanes in which the nitro group is attached to the tertiary carbon atom. The D(C–N) estimates according to the G4 method in 2-nitro-2-methylpentane and 2-nitro-2-methylbutane are 264.8 and 265.1 kJ/mol, respectively. The estimates obtained using the G3B3 method in most cases overestimate the results obtained using the G4 method by about 6–7 kJ/mol. However, they convey the same effect of the molecular structure on the change in the bond strength in a number of the studied compounds. Note that similar trends can also be observed for all C_1-C_6 mononitroalkanes. These results are of considerable interest for understanding the general patterns of the influence of the molecular structure on the change in the series of enthalpies of formation of compounds and radicals, as well as the dissociation energies of the $C-NO_2$ bond and activation energies of the radical gas-phase decomposition of aliphatic nitro compounds.

We also evaluated the barriers of the other main alternative mechanisms of the primary act of the gas-phase monomolecular decomposition of nitropentanes. The scope of this article does not allow us to present all our results. Therefore, we present only estimates of the activation barriers for the studied reactions obtained by the G4 method.

For the isomerization reaction of nitropentanes into pentylnitrites (nitro-nitrite rearrangements) in a number of compounds **1**–**8**, the activation enthalpies were determined to be 265.3, 251.9, 252.6, 267.8, 248.5, 250.6, 268.2, and 262.8 kJ/mol, respectively. A characteristic feature of the process is the proximity of the activation enthalpies of the forward and reverse reactions. The difference between these values does not exceed 20 kJ/mol. Since the barriers for the reactions of nitro-nitrite rearrangements of compounds **1**–**8**, although somewhat lower, are still close to the values of D(C–N), given in Table 3, and the activation entropy is significantly lower than for radical decomposition reactions, this mechanism cannot compete with the process of homolytic C–N bond cleavage.

For reactions of the β-elimination of HNO_2 from compounds **1**–**7**, the activation enthalpies were obtained to be 199.1, 195.6, 199.0, 200.9, 185.9, 198.2, and 194.3 kJ/mol, respectively, which is significantly lower than the dissociation energy of C–N bonds in nitropentanes (Table 3). This process is the most energetically favorable among all the alternative processes of the primary process that we studied. A comparison of the activation enthalpies of reactions of the β-elimination of HNO_2 from compounds **1**–**7** with the calculated D(C–N) values for these compounds shows that there is no correlation between them. It should be noted that the G4 method for all the studied C_1-C_5 nitroalkanes predicts the absence of such a dependence, while according to the results of the density functional methods, it should exist [13]. Apparently, this derivation of density functional methods is an artifact.

CONCLUSIONS

In summary, we can assume that the calculated values of the enthalpies of formation of nitropentanes and pentyl radicals, as well as the dissociation energies of the $C-NO_2$ bond obtained using the G4 method in nitropentanes, will be quite reliable. They can be used to fill in the missing experimental data and discuss the results of studying the kinetics of the gas-phase decomposition of nitroalkanes.

---

[1] We have not completed the work on the study of the thermochemical properties of nitrohexanes; therefore, we present the results for only a few of the studied compounds.

REFERENCES

1. E. Yu. Orlova, *Chemistry and Technology of High Explosives* (Khimiya, Leningrad, 1981) [in Russian].
2. G. B. Manelis, G. M. Nazin, Yu. I. Rubtsov, and V. A. Strunin, *Thermal Decomposition and Combustion of Explosives and Gunpowder* (Nauka, Moscow, 1996) [in Russian].
3. G. M. Nazin and G. B. Manelis, Russ. Chem. Rev. **63**, 313 (1994).
4. G. M. Nazin, G. B. Manelis, and F. I. Dubovitskii, Russ. Chem. Bull. **37**, 603 (1968).
5. G. M. Nazin and G. B. Manelis, Russ. Chem. Bull. **21**, 768 (1972).
6. T. B. Brill and K. J. James, Chem. Rev. **93**, 2667 (1993).
7. I. S. Zaslonko, Yu. P. Petrov, and V. N. Smirnov, Kinet. Catal. **38**, 321 (1997).
8. G. M. Khrapkovskii, G. N. Marchenko, and A. G. Shamov, *Influence of the Molecular Structure on the Kinetic Parameters of the Thermal Decomposition of C- and O-nitro Compounds* (FEN, Kazan, 1997) [in Russian].
9. G. M. Nazin, V. V. Dubikhin, T. K. Goncharov, A. I. Kazakov, A. V. Nabatova, and A. V. Shastin, Russ. J. Phys. Chem. B **15**, 604 (2021).
10. G. M. Nazin, V. V. Dubikhin, T. K. Goncharov, A. I. Kazakov, A. V. Nabatova, and A. V. Shastin, Russ. J. Phys. Chem. B **15**, 483 (2021).
11. G. M. Nazin and B. L. Korsunskiy, Russ. J. Phys. Chem. B **15**, 271 (2021).
12. B. E. Krisyuk, Russ. J. Phys. Chem. B **14**, 1 (2020).
13. G. M. Khrapkovskii, A. G. Shamov, E. V. Nikolaeva, and D. V. Chachkov, Russ. Chem. Rev. **78**, 903 (2009).
14. V. L. Korolev, T. S. Pivina, A. A. Porollo, T. V. Petukhova, A. B. Sheremetev, and V. P. Ivshin, Russ. Chem. Rev. **78**, 945 (2009).
15. L. P. Smirnov, Russ. Chem. Rev. **79**, 421 (2010).
16. G. M. Khrapkovskii, A. G. Shamov, G. A. Shamov, and V. A. Slyapochnikov, Mendeleev Commun., No. 5, 169 (1997). https://doi.org/10.1070/MC1997v007n05ABEH000825
17. A. G. Shamov and G. M. Khrapkovskii, Mendeleev Commun., No. 4, 163 (2001). https://doi.org/10.1070/MC2001v011n04ABEH001423
18. E. A. Mazilov, E. V. Nikolaeva, A. G. Shamov, and G. M. Khrapkovskii, Mendeleev Commun., No. 17, 359 (2007). https://doi.org/10.1016/j.mencom.2007.11.022
19. G. M. Khrapkovskii, A. M. Rozin, V. A. Tikhomirov, A. G. Shamov, and G. N. Marchenko, Dokl. Akad. Nauk SSSR **298**, 921 (1988).
20. A. G. Shamov, E. V. Nikolaeva, and G. M. Khrapkovskii, Russ. J. Appl. Chem. **82**, 1741 (2009).
21. A. G. Shamov, E. V. Nikolaeva, and G. M. Khrapkovskii, Russ. J. Gen. Chem. **74**, 1227 (2004).
22. S. C. Chen, S. C. Xu, E. Diau, and M. C. Lin, J. Phys. Chem. A **110**, 10130 (2006). https://doi.org/10.1021/jp0623591
23. E. V. Nikolaeva, A. G. Shamov, and G. M. Khrapkovskii, Russ. J. Gen. Chem. **84**, 2076 (2014).
24. G. M. Khrapkovskii, A. G. Shamov, R. V. Tsyshevsky, et al., Comput. Theor. Chem. **966**, 265 (2011). https://doi.org/10.1016/j.comptc.2011.03.016
25. R. V. Tsyshevsky, G. G. Garifzianova, D. V. Chachkov, A. G. Shamov, and G. M. Khrapkovskii, J. Energ. Mater. **27**, 263 (2009). https://doi.org/10.1080/07370650902733004
26. G. M. Khrapkovskii, T. F. Shamsutdinov, D. V. Chachkov, and A. G. Shamov, J. Mol. Struct.: THEOCHEM **686**, 185 (2004). https://doi.org/10.1016/j.theochem.2004.09.001
27. G. M. Khrapkovskii, A. G. Shamov, R. V. Tsyshevsky, et al., Comput. Theor. Chem. **985**, 80 (2012). https://doi.org/10.1016/j.comptc.2012.02.003
28. D. D. Sharipov, D. L. Egorov, D. V. Chachkov, A. G. Shamov, and G. M. Khrapkovskii, Russ. J. Gen. Chem. **81**, 2273 (2011).
29. E. Martinez-Nunez, I. Borges, Jr., and S. A. Vasquez, J. Phys. Org. Chem. **15**, 123 (2002). https://doi.org/10.1002/poc.460
30. W. F. Hu, T. J. He, D. M. Chen, and F. C. Liu, J. Phys. Chem. A **106**, 7294 (2002). https://doi.org/10.1021/jp020070n
31. M. T. Nguyen, H. T. Le, B. Hajgato, T. Veszpremi, and M. C. Lin, J. Phys. Chem. **107**, 4286 (2003). https://doi.org/10.1021/jp027532h
32. S. C. Chen, S. C. Xu, E. Diau, and M. C. Lin, J. Chem. Phys. A **110**, 10130 (2006). https://doi.org/10.1021/jp0623591
33. G. Fayet, L. Joubert, P. Rotureau, and C. Adamo, J. Phys. Chem. A **113**, 13621 (2009). https://doi.org/10.1021/jp905979w
34. G. M. Khrapkovskii, E. V. Nikolaeva, D. V. Chachkov, and A. G. Shamov, Russ. J. Gen. Chem. **74**, 908 (2004).
35. G. M. Khrapkovskii, D. L. Egorov, E. V. Nikolaeva, D. V. Chachkov, and A. G. Shamov, Russ. J. Gen. Chem. **85**, 1801 (2015).
36. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, et al., *Gaussian 09, Rev. D.01* (Gaussian, Inc., Wallingford CT, 2009).
37. L. A. Curtiss, P. C. Redfern, and K. Raghavachari, J. Chem. Phys. **123**, 124107 (2005). https://doi.org/10.1063/1.2039080
38. A. G. Baboul, L. A. Curtiss, P. C. Redfern, and K. Raghavachari, J. Chem. Phys. **110**, 7650 (1999). https://doi.org/10.1063/1.478676
39. L. A. Curtiss, P. C. Redfern, and K. Raghavachari, J. Chem. Phys. **126**, 084108 (2007). https://doi.org/10.1063/1.2436888
40. G. M. Khrapkovskii, R. V. Tsyshevsky, D. V. Chachkov, D. L. Egorov, and A. G. Shamov, J. Mol. Struct.: THEOCHEM **958**, 1 (2010). https://doi.org/10.1016/j.theochem.2010.07.012
41. A. D. Becke, Phys. Rev. A **38**, 3098 (1988). https://doi.org/10.1103/PhysRevA.38.3098

42. C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B **37**, 785 (1988). https://doi.org/10.1103/PhysRevB.37.785

43. J.-D. Chai and M. Head-Gordon, Phys. Chem. Chem. Phys. **10**, 6615 (2008).

44. T. Yanai, D. Tew, and N. Handy, Chem. Phys. Lett. **393**, 51 (2004). https://doi.org/10.1016/j.cplett.2004.06.011

45. E. A. Miroshnichenko, T. S. Kon'kova, Ya. O. Inozemtsev, and Yu. N. Matyushin, Russ. Chem. Bull. **59**, 890 (2010).

46. E. A. Miroshnichenko, T. S. Kon'kova, Ya. O. Inozemtsev, V. P. Vorob'eva, and Yu. N. Matyushin, Russ. J. Phys. Chem. B **2**, 595 (2008).

47. E. A. Miroshnichenko, T. S. Kon'kova, Yu. N. Matyushin, Ya. O. Inozemtsev, and V. P. Vorob'eva, Butlerov. Soobshch **26** (11), 46 (2011).

48. *Energetics of Organic Free Radicals,* Ed. by J. A. Martinho Simoes, A. Greenberg, and J. F. Liebman (Blackie Acad. Profess., London, 1996), p. 22. https://doi.org/10.1007/978-94-009-0099-8_2

49. *NIST Chemistry WebBook, NIST Standart Reference Database No. 69* (Natl. Inst. Stand. Technol., Gaithersburg MD). http://webbook.nist.gov.

50. Yu. D. Orlov, Yu. A. Lebedev, and I. Sh. Saifullin, *Thermochemistry of Organic Free Radicals* (Nauka, Moscow, 2001) [in Russian].

51. M. Yu. Orlov, E. M. Chernova, V. V. Turovtsev, and Yu. D. Orlov, Russ. Chem. Bull. **63**, 2620 (2014).