Molecular structure, enthalpies of formation and dissociation energies of the O – N bond for a number of aliphatic nitrates and nitrites

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Abstract. The optimal conformations of nitrates and nitrites of aliphatic alcohols C₁-C₄, as well as radicals formed during homolytic cleavage of O-NO₂ and O-NO bonds were determined using the multistep (composite) method G4, as well as a large number of different density functional (DDF) methods and basis sets. The enthalpies of formation and dissociation energies of breaking bonds were calculated for the studied compounds. Comparison with the available experimental data shows that the best agreement with experiment is achieved when using the G4 method. In this case, the error in the enthalpies of formation does not exceed 1 kcal/mol. The paper also discusses the features of the influence of the molecular structure on the change in the series of enthalpies of formation and dissociation energies.

1. Introduction
Modern quantum chemical methods are widely used to study the structure and reactivity of various classes of nitro compounds, including the kinetics and mechanism of thermal decomposition of molecules in a gaseous state [1-3]. In many cases, the results of theoretical studies can significantly increase the number of discussed mechanisms, simplify, and deepen the interpretation of experimental data, and sometimes change it. For C- and N-nitro compounds, the results of calculating the geometric parameters and enthalpies of formation of molecules, as well as the barriers of chemical reactions, are in good agreement with the available experimental data. The best agreement between the experimental values of the enthalpies of formation of compounds and radicals formed upon homolytic cleavage of chemical bonds, as well as the barriers of gas-phase radical decomposition reactions, is achieved using the multistep (composite) methods G3, G3B3 and G4.

The calculated data are much less for O-nitro compounds, and the results of experimental studies in the gaseous state, which are of particular interest in studying the effect of the molecular structure on the change in the series of Arrhenius parameters of monomolecular decomposition reactions, are also few and not highly accurate [4-7]. In a number of cases, the differences in the values of the activation energy of the radical decomposition reaction for compounds studied by different authors exceed the observed changes in the series [5]. For example, for methyl nitrate, the experimental values of the activation energy in the works of different authors vary in the range from 36.0 to 40.5 kcal/mol, and for nitroglycerin - from 36.0 to 39.0 kcal/mol; rather large differences are observed for other aliphatic nitrates, for which the kinetics of thermal decomposition was studied in the gaseous state.

The kinetics of thermal decomposition of nitrites of aliphatic alcohols is also clearly insufficiently studied; only a few of the simplest compounds have been studied in the gaseous state [5]. All this
significantly complicates the study of the peculiarities of the influence of the structure of molecules on changes in the series of the activation energy of gas-phase monomolecular decomposition. This situation calls for an additional experimental and theoretical study of the radical decomposition of O-nitro compounds since this mechanism is the main channel for the thermal decomposition of nitrates and nitrites of aliphatic alcohols.

2. Calculation methods
This paper presents the results of a theoretical study of the radical decomposition of 16 nitrates and nitrites of the simplest aliphatic alcohols C₁-C₄. The calculations were carried out using the Gaussian program [8]. Earlier, we showed by the example of the simplest nitroalkanes C₁-C₄ that the results of calculations using multistep methods are in good agreement with the results of thermochemical and kinetic studies. For example, when using the G4 method, the mean in the series of the error modulus of the dissociation energy of the C-NO₂ bond does not exceed 0.8 kcal/mol, and the standard deviation is 1 kcal/mol. The results obtained show that the results of a theoretical study can be used not only to discuss the main regularities of changes in the series of enthalpies of formation of compounds and radicals, but also to replenish and, in some cases, to refine the experimental data.

The values of the enthalpies of formation of the starting compounds and products of the reactions of homolytic cleavage of O-NO₂ and O-NO bonds presented below were calculated from the total electronic energies by standard methods for optimal conformations. The calculations were carried out using many non-empirical, multi-step methods, as well as density functional methods. The limited volume of publication allows us to cite only a part of the results obtained, which we consider the most interesting. We present relatively more detailed calculated data for aliphatic nitrates, for which the kinetics and mechanism of thermal decomposition have been studied for many years [4-7].

3. Results
Tables 1 and 2 show the calculated values of the enthalpies of formation of nitrates of aliphatic alcohols, obtained using various methods of density functional and basis sets, as well as multistep methods. All the methods used in this work practically equally convey the tendencies of change in the enthalpies of formation in the series. As an illustration, we give correlation between the calculated values of the enthalpies of formation obtained by the wB97X/Def2TZVPP and G4 methods in Figure 1. With an increase in the number of carbon atoms in a molecule, a monotonic decrease (increase in modulus) of the enthalpy of formation occurs. Among isomeric propyl nitrates and butyl nitrates, the highest values of enthalpies of formation (the smallest in modulus) are observed for compounds in which the nitrate group is attached to the primary carbon atom. The lowest value of the enthalpy of formation in the series is observed for tert-butyl nitrate, which is the only one among the studied compounds in which the nitrate group is attached to a tertiary carbon atom. It is interesting to note that, despite the relatively small differences in the values of the enthalpies of formation, it is possible to distinguish between the cedium isomers of the molecule having nitrate groups attached, respectively, to the primary (compounds 3, 5, 7) or secondary (compounds 4, 6) carbon atoms. On the example of compounds 5 and 7, it can be seen that the branching of the carbon skeleton in the isomer leads to a decrease in the enthalpy of formation.

The values of the enthalpies of formation obtained using various methods and basis sets differ markedly. Comparison with the available thermochemical data (unfortunately, incomplete) suggests that the most reliable are the results obtained using multistep (composite) methods. Among them, the best agreement with experiment is achieved when using the G4 method. In this case, the mean modulus of deviation of the calculated and experimental values is 0.78 kcal/mol, and the standard deviation is 0.91 kcal/mol. Above, we have already noted that this method also best conveys the thermochemical characteristics of C-nitro compounds. Given these data, it can be assumed that the results of the G4 method are reliable.
Table 1. Enthalpies of formation of nitrates of aliphatic alcohols C\textsubscript{1}–C\textsubscript{4} according to the results of DFT methods (kcal/mol).

| № | Compound          | B3LYP/6-31G(d) | B3LYP/6-31G(2df,p) | B98/6-31G(d) | B98/6-31G(d,p) | B98/6-31G(2df,p) | wB97X/Def2TZVPP |
|---|------------------|----------------|---------------------|-------------|--------------|-----------------|-----------------|
| 1 | CH\textsubscript{3}ONO\textsubscript{2} | -29.68 | -39.84 | -29.42 | -31.92 | -40.32 | -30.77 |
| 2 | CH\textsubscript{2}CH\textsubscript{2}ONO\textsubscript{2} | -36.35 | -48.15 | -36.08 | -40.30 | -48.67 | -38.72 |
| 3 | CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}ONO\textsubscript{2} | -39.39 | -53.00 | -39.26 | -45.16 | -53.72 | -43.23 |
| 4 | CH\textsubscript{2}CHONO\textsubscript{2}CH\textsubscript{3} | -42.75 | -56.28 | -42.60 | -48.63 | -56.96 | -46.78 |
| 5 | CH\textsubscript{2}4CH\textsubscript{2}CH\textsubscript{2}ONO\textsubscript{2} | -42.51 | -57.93 | -42.50 | -50.08 | -58.84 | -47.89 |
| 6 | CH\textsubscript{2}CHONO\textsubscript{2}CH\textsubscript{3}CH\textsubscript{3} | -43.00 | -58.48 | -43.00 | -50.73 | -59.34 | -48.68 |
| 7 | (CH\textsubscript{2})\textsubscript{3}CH\textsubscript{2}CH\textsubscript{2}ONO\textsubscript{2} | -43.34 | -58.88 | -43.43 | -51.07 | -59.84 | -49.31 |
| 8 | (CH\textsubscript{2})\textsubscript{4}ONO\textsubscript{2} | -45.78 | -61.21 | -45.81 | -53.65 | -62.03 | -52.01 |

Table 2. Enthalpies of formation of nitrates of aliphatic alcohols C\textsubscript{1}–C\textsubscript{4} according to the results of ab initio and composite methods (kcal/mol).

| № | Compound          | HF/6-31G(d,p) | MP2/6-31G(d,p) | CCSD/6-31G(d,p) | G3 | G3B3 | G4 | Exp. [5] |
|---|------------------|-------------|---------------|----------------|----|-----|----|--------|
| 1 | CH\textsubscript{3}ONO\textsubscript{2} | 293.66 | 4.59 | 52.68 | -29.51 | -30.47 | -29.79 | -29.16 |
| 2 | CH\textsubscript{2}CH\textsubscript{2}ONO\textsubscript{2} | 354.48 | 7.56 | 59.93 | -37.82 | -38.62 | -37.74 | -37.05 |
| 3 | CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}ONO\textsubscript{2} | 419.19 | 14.03 | 70.68 | -42.70 | -43.42 | -42.45 | -41.60 |
| 4 | CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}ONO\textsubscript{2}CH\textsubscript{3} | 416.25 | 9.40 | 66.62 | -46.96 | -47.58 | -46.54 | -45.60 |
| 5 | CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}ONO\textsubscript{2} | 483.92 | 20.34 | 81.30 | -47.72 | -48.39 | -47.41 | - |
| 6 | CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}ONO\textsubscript{2}CH\textsubscript{3} | 484.22 | 18.05 | 79.72 | -49.89 | -50.56 | -48.92 | - |
| 7 | (CH\textsubscript{2})\textsubscript{3}CH\textsubscript{2}CH\textsubscript{2}ONO\textsubscript{2} | 483.30 | 17.94 | 79.54 | -49.70 | -50.12 | -49.53 | - |
| 8 | (CH\textsubscript{2})\textsubscript{4}ONO\textsubscript{2} | 481.46 | 13.30 | 75.71 | -54.19 | -54.70 | -53.47 | - |

Figure 1. Correlation dependence of the calculated values of the enthalpies of formation obtained using the wB97X/Def2TZVPP and G4 methods. Correlation coefficient is 0.998.

Close values of the enthalpies of formation of alkyl nitrates are predicted by the G3 method, for which the average error modulus is 0.9 kcal/mol, and the standard deviation is 1.12 kcal/mol. The
G3B3 method systematically underestimates the enthalpies of formation, and the errors observed in this case are about 1.5 times higher. Density functional methods convey the enthalpies of formation much worse; relatively best estimates among them are given by the wB97X/Def2TZVPP method.

As mentioned above, the number of experimental estimates of the enthalpies of formation of aliphatic nitrates is small and they are not highly accurate. Much more complete and reliable information is available on thermochemical estimates of the enthalpies of formation of alkoxyl radicals, which are formed during homolytic cleavage of the O-N bond in nitrates and nitrites. Tables 3 and 4 show the calculated values obtained, as well as experimental data, when choosing which we used the recommendations of the handbook [9].

Table 3. Enthalpies of formation of products of radical decomposition of aliphatic nitrates and nitrites according to the results of DFT methods (kcal/mol).

| № | Compound       | B3LYP/6-31G(d) | B3LYP/6-31G(2df,p) | B98/6-31G(d) | B98/6-31G(2df,p) | wB97X/Def2TZVPP |
|---|----------------|----------------|---------------------|--------------|------------------|-----------------|
| 1 | CH₃O           | 1.98           | -1.39               | 3.44         | 0.85             | -0.12           | 3.48           |
| 2 | CH₃CH₂O        | -5.23          | -10.09              | -4.50        | -8.78            | -8.87           | -4.56           |
| 3 | CH₃CH₂CH₂O     | -8.49          | -15.16              | -7.16        | -13.21           | -14.19          | -9.21           |
| 4 | CH₃CHOCH₃      | -10.68         | -17.25              | -9.40        | -15.35           | -16.26          | -11.49          |
| 5 | CH₃CH₂CH₂CH₂O  | -11.49         | -20.00              | -10.30       | -18.04           | -19.17          | -13.81          |
| 6 | CH₃CHOCH₂CH₃   | -14.67         | -23.13              | -13.48       | -21.21           | -22.27          | -16.82          |
| 7 | (CH₃)₂CHOH     | -12.87         | -21.48              | -11.77       | -19.5            | -20.69          | -15.69          |
| 8 | (CH₃)₂CO       | -16.56         | -24.96              | -15.52       | -23.24           | -24.21          | -19.54          |
| 9 | NO             | 22.03          | 18.50               | 23.45        | 23.45            | 19.70           | 20.51           |
| 10| NO₂            | 5.71           | 0.15                | 6.51         | 6.51             | 0.30            | 5.43            |

Table 4. Enthalpies of formation of products of radical decomposition of aliphatic nitrates and nitrites according to the results of ab initio and composite methods (kcal/mol).

| №  | Compound       | HF/6-31G(d,p) | MP2/6-31G(d,p) | CCSD/6-31G(d,p) | G3   | G3B3 | G4   | Exp. [9] |
|----|----------------|--------------|---------------|-----------------|------|------|------|---------|
| 1  | CH₃O           | 114.79       | 28.51         | 31.35           | 4.99 | 4.49 | 4.36 | 3.49    |
| 2  | CH₃CH₂O        | 175.63       | 31.81         | 37.88           | -2.95| -3.28| -3.55| -4.90   |
| 3  | CH₃CH₂CH₂O     | 240.28       | 38.19         | 48.56           | -7.78| -8.07| -8.59| -9.89   |
| 4  | CH₃CHOCH₃      | 238.08       | 35.13         | 46.52           | -10.93| -10.66| -11.55| -12.50  |
| 5  | CH₃CH₂CH₂CH₂O  | 305.05       | 44.64         | 59.29           | -12.75| -12.87| -13.74| -14.70  |
| 6  | CH₃CHOCH₂CH₃   | 302.62       | 40.87         | 56.53           | -14.99| -15.22| -17.04| -17.90  |
| 7  | (CH₃)₂CHH₂O    | 304.26       | 42.04         | 58.02           | -16.04| -16.34| -16.62| -16.58  |
| 8  | (CH₃)₂CO       | 300.14       | 36.75         | 53.06           | -20.51| -20.45| -21.06| -21.70  |
| 9  | NO             | 125.61       | 38.08         | 49.11           | 21.99| 21.85| 21.45| 21.56   |
| 10 | NO₂            | 187.23       | 21.09         | 55.83           | 8.23 | 7.61 | 7.33 | 7.90    |

Before proceeding to the comparison of the calculation results with the experiment, let us briefly consider some tendencies in the change in the enthalpies of formation in the series, which all the calculation methods used in this work convey practically in the same way, in which they are quite consistent with the experimental results. With an increase in the number of carbon atoms in radicals, a significant decrease in the enthalpy of formation is observed. According to the G4 method, this effect exceeds 25 kcal/mol. Among the isomers, the lowest values of the enthalpies of formation are observed for radicals in which the unpaired electron is localized predominantly at the primary carbon atom (radicals 3, 5, 7). As in the case of the enthalpies of formation of aliphatic nitrates, the branching of the hydrocarbon skeleton causes a decrease in the enthalpy of formation of the corresponding alkoxy radicals in the isomers. Similar tendencies of change in the series of enthalpies of formation of
compounds and radicals suggests the presence of a correlation dependence in the change in these two quantities in the series. An analysis of the results obtained shows that such a relationship really exists. According to the G4 method, the correlation coefficient is 0.91.

Comparison of the calculated and experimental data shows that the use of multistep (compositional) methods makes it possible to obtain reliable estimates of the enthalpies of formation of alkoxy radicals. The best agreement with experiment is achieved when using multistep methods. Among them, the G4 method gives the best results. When using it, the average error modulus in the series of the studied radicals reaches 0.89, and the standard deviation does not exceed 1.21. The use of the G3 and G3B3 methods give close, but somewhat worse performance. Among the density functional methods, the wB97X/Def2TZVPP and B98/6-31G(d) methods give the best results. Note that the above methods better convey the enthalpies of formation of alkyl radicals.

The calculated values of the enthalpies of formation of molecules and products of the reaction of homolytic cleavage of the O-NO₂ bond make it possible to estimate the dissociation energies of this bond. Based on these data, it is easy to determine the values of the activation energy of radical decomposition in the gaseous state of the simplest aliphatic nitrates. The results of calculating the dissociation energies are presented in Tables 5 and 6.

When assessing the reliability of the results of calculating the energies of dissociation, we use the available thermochemical data; the calculated values of the activation energies of radical decomposition in the gaseous state are compared with the available kinetic estimates summarized in the monograph [6]. Unfortunately, as noted above, the available experimental data are not complete and are not highly accurate.

Comparison of thermochemical estimates of the dissociation energy of the O-NO₂ bond with quantum-chemical calculations of this value by the G4 method allows concluding that the calculated and experimental values are in good agreement with each other. The maximum difference between the calculated and experimental values of the dissociation energies does not exceed 0.65 kcal/mol, and in all cases the calculated values exceed the experimental estimates. Estimates of methods G3 and G3B3 exceed thermochemical values by 1.5-2.5 kcal/mol. Among the DFT methods, the wB97X/Def2TZVPP method predicts rather close to the experimental values of the dissociation energy, and in all cases, these are lower estimates.

The ab initio values of the dissociation energy of the O-NO₂ bond are generally in poor agreement with the experimental data. The mean difference in the moduli of these values in the series exceeds 5 kcal/mol. Moreover, if the MP2 method greatly overestimates the value of the dissociation energy, then the CCSD method underestimates it.

Comparison of the calculated values of the activation energy of radical decomposition with the corresponding kinetic estimates shows that the quantum-chemical (as well as thermochemical) estimates exceed the values of the activation energy of radical decomposition in the gaseous state. However, the observed differences are at a level of the order of 1 kcal/mol, which is comparable with the error of experimental determination.

Table 5. The dissociation energies of the O–N bond in the nitrates of aliphatic alcohols C₁–C₄ (D(O-N)) according to the results of DFT methods (kcal/mol).

| №  | Compound          | B3LYP/  | B3LYP/  | B98/  | B98/  | B98/  | wB97X/  |
|----|-------------------|---------|---------|-------|-------|-------|---------|
|    |                   | 6-31G(d)| 6-31G(2df,p) | 6-31G(d) | 6-31G(d,p) | 6-31G(2df,p) | Def2TZVPP |
| 1  | CH₃ONO₂           | 37.37   | 38.30   | 39.37 | 39.28 | 40.50 | 39.68   |
| 2  | CH₂CH₂ONO₂       | 36.83   | 37.91   | 38.09 | 38.03 | 40.10 | 39.59   |
| 3  | CH₃CH₂CH₂ONO₂    | 36.61   | 37.69   | 38.61 | 38.46 | 39.83 | 39.45   |
| 4  | CH₂CHONO₂CH₃     | 37.78   | 38.88   | 39.71 | 39.79 | 41.00 | 40.72   |
| 5  | CH₂CH₂CH₂ONO₂    | 36.73   | 37.78   | 38.71 | 38.55 | 39.97 | 39.51   |
| 6  | CH₂CHONO₂CH₂CH₃ | 34.04   | 35.20   | 36.03 | 36.03 | 37.37 | 37.29   |
| 7  | (CH₃)₂CHCHONO₂   | 36.18   | 37.25   | 38.17 | 38.08 | 39.45 | 39.05   |
| 8  | (CH₃)₂CONO₂       | 34.93   | 36.10   | 36.8  | 36.92 | 38.12 | 37.90   |
We estimated the activation energy of the radical decomposition of aliphatic nitrates based on the calculated values of the dissociation energy of the O-NO₂ bond using the equation

\[ E = D(O-N) + RT, \]  

(1)

When evaluating the activation energies of radical decomposition, a temperature of 175°C (the average temperature of the interval in which the experimental study was carried out) was used based on the available experimental data on the conditions of the kinetic experiment. The calculated data allow analyzing the influence of the molecular structure on the change in the series of C₁–C₄ nitrates in the dissociation energy of the O-NO₂ bond and the activation energy of radical decomposition in the gaseous state in sufficient detail. Thermochemical and kinetic data cannot be used for this purpose due to their incompleteness and insufficient accuracy. First, we note that, according to the data of all methods, the changes in the dissociation energy observed in a series in most cases do not exceed 3 kcal/mol. In contrast to nitroalkanes, the tendencies of changes in the dissociation energy of the O-NO₂ bond breaking during the reaction, as well as the activation energy of radical decomposition of aliphatic nitrates, are transferred by all methods used in this work in almost the same way.

The highest values of the dissociation energy are observed for compounds in which the nitrate group is attached to the primary carbon atom: compounds 1, 2, 3, 5, 7 in table. 5, 6. The calculation predicts relatively lower activation energies for compounds 4, 6, 8, in which the nitrate group is attached to the secondary or tertiary (compound 8) carbon atoms. It is essential that within the groups indicated above, the values of the dissociation energy and the activation energy of radical decomposition in the gaseous state are very close; the differences for compounds of the first group in this case do not exceed 0.8 kcal/mol, and for compounds of the second group - 0.5 kcal/mol.

We consider the results obtained using the G4 method to be the most reliable estimates of the dissociation energy of the O-NO₂ bond and the activation energy of radical decomposition in the gaseous state. The results obtained using the G3B3 method, which gives overestimated values, and the wB97X/Def2TZVPP method, which slightly underestimates the estimates of the G4 method, are in good agreement with them. The calculated values of the dissociation energy of the O-NO₂ bond can be used not only to discuss the effect of the molecular structure on the barrier for the reaction of gas-phase decomposition of nitrates of aliphatic alcohols, but also to assess the reliability of various kinetic data, which, as noted above, do not agree well with each other in publications of different authors.

We also determined the enthalpies of formation of nitrates in aliphatic alcohols C₁–C₄. The results are shown in Table 7. As in the study of nitrates of aliphatic alcohols, the results obtained for the optimal conformations of the compounds were used to discuss the enthalpies of formation. Previously, for comparison, various conformations were studied and their enthalpies of formation were determined. When using one method, the differences in the values of the enthalpies of formation for a given compound do not exceed 2.5-3.0 kcal/mol. At the same time, the differences in the calculated

### Table 6. Dissociation energies of the O–N bond in the nitrates of aliphatic alcohols C₁–C₄ (D (O-N)) based on ab initio and composite methods (kcal/mol).

| №  | Compound                  | HF/6-31G(d,p) | MP2/6-31G(d,p) | CCSD/6-31G(d,p) | G3   | G3B3   | G4   | Exp.   |
|----|--------------------------|--------------|---------------|----------------|------|--------|------|--------|
| 1  | CH₃ONO₂                  | 8.36         | 45.01         | 34.5           | 42.73| 42.57  | 41.48| 40.55  |
| 2  | CH₂CH₂ONO₂               | 8.38         | 45.34         | 33.78          | 43.10| 42.95  | 41.52| 40.05  |
| 3  | CH₂CH₂CH₂ONO₂            | 8.32         | 45.25         | 33.71          | 43.15| 42.96  | 41.19| 39.61  |
| 4  | CH₃CHONO₂CH₃             | 9.06         | 46.82         | 35.73          | 44.26| 44.53  | 42.32| 41.00  |
| 5  | CH₂CH₂CH₂CH₂ONO₂         | 8.36         | 45.39         | 33.82          | 43.20| 43.13  | 41.00| -      |
| 6  | CH₂CHONO₂CH₂CH₃          | 5.63         | 43.91         | 32.64          | 43.13| 42.95  | 39.21| -      |
| 7  | (CH₃)₂CHCH₂ONO₂          | 8.19         | 45.19         | 34.31          | 41.89| 41.39  | 40.84| -      |
| 8  | (CH₃)₃CONO₂              | 5.91         | 44.54         | 33.18          | 41.91| 41.86  | 39.74| -      |
values of the enthalpies of formation for a compound obtained using different methods can exceed 15 kcal/mol.

Table 7. Enthalpies of formation of nitrites of aliphatic alcohols C\textsubscript{1}–C\textsubscript{4} according to calculation data (kcal/mol).

| №  | Compound       | B3LYP/6-31+G(3df,p) | B98/6-31G(d) | wB97X/Def2TZVPP | wB97X/TZVP | wB97X/TZVP | G4 | Exp. [10] |
|----|----------------|---------------------|-------------|------------------|------------|------------|----|----------|
| 1  | CH\textsubscript{2}ONO | -17.84              | -13.22      | -14.85           | -6.30      | -5.47      | -15.28 | -15.60   |
| 2  | CH\textsubscript{2}CH\textsubscript{2}ONO | -24.08              | -20.07      | -22.35           | -12.84     | -12.20     | -23.25 | -25.80   |
| 3  | CH\textsubscript{3}CH\textsubscript{2}CH\textsubscript{2}ONO | -26.86              | -23.40      | -27.02           | -16.47     | -15.08     | -28.10 | -28.40   |
| 4  | CH\textsubscript{3}CH\textsubscript{2}CH\textsubscript{3}ONOCH\textsubscript{3} | -30.33              | -26.76      | -30.76           | -20.84     | -18.70     | -32.34 | -31.80   |
| 5  | CH\textsubscript{3}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}ONO | -29.63              | -26.58      | -31.64           | -20.05     | -18.54     | -33.01 | -34.90   |
| 6  | CH\textsubscript{3}OCH\textsubscript{2}CH\textsubscript{3}CH\textsubscript{3} | -30.68              | -28.22      | -33.92           | -22.63     | -20.96     | -35.97 | -36.60   |
| 7  | (CH\textsubscript{3})\textsubscript{2}CH\textsubscript{2}ONO | -30.41              | -27.67      | -33.26           | -21.79     | -20.33     | -35.31 | -36.10   |
| 8  | (CH\textsubscript{3})\textsubscript{3}CONO | -34.17              | -31.36      | -37.94           | -26.78     | -24.68     | -41.10 | -41.10   |

The minimum values of the enthalpies of formation are predicted by the B3LYP method, and the maximum (minimum in modulus since all values of the enthalpies of formation are negative) are predicted by the wB97XD/TZVP method. The tendencies of change in the enthalpies of formation of aliphatic nitrites in the series are conveyed by all the methods we used in the same way. It is interesting that these tendencies are like the above-described features of the change in the enthalpies of formation of nitrites (the correlation coefficient in the series of compounds studied by one method reaches 0.99), so we will not specifically consider them. Comparison with the available experimental values of the enthalpies of formation of nitrites of aliphatic alcohols shows that the most reliable calculated values are obtained by the G4 method. We have already noted above that this method transfers the enthalpies of formation of aliphatic nitrites better than all others.

Using the calculated values of the enthalpies of formation of compounds and alkoxy radicals (Tables 3, 4), we calculated the dissociation energies of the O-NO bond. The results obtained are presented in Table 8.

All the methods used in this work convey the tendencies of changes in dissociation energies in a series practically in the same way. The estimates of the activation energy of radical decomposition for nitrites of aliphatic alcohols were given, as for nitrites, for a temperature of 175°C, adding RT to the dissociation energies of the O-N bond, equal to 0.88 kcal/mol.

Table 8. Dissociation energies of O–N bonds in nitrites of aliphatic alcohols C\textsubscript{1}–C\textsubscript{4} (D(O-N)) based on the calculation results (kcal/mol).

| №  | Compound  | B3LYP/6-31+G(3df,p) | B98/6-31G(d) | wB97X/Def2TZVPP | wB97X/TZVP | wB97X/TZVP | G4 | Exp.[10] |
|----|-----------|---------------------|-------------|------------------|------------|------------|----|----------|
| 1  | CH\textsubscript{2}ONO | 37.18              | 40.11       | 38.84            | 37.31      | 37.22      | 41.09 | 40.65    |
| 2  | CH\textsubscript{2}CH\textsubscript{2}ONO | 36.83              | 39.02       | 38.3             | 36.69      | 37.29      | 41.15 | 42.46    |
| 3  | CH\textsubscript{3}CH\textsubscript{2}CH\textsubscript{2}ONO | 36.92              | 39.69       | 38.32            | 36.67      | 36.72      | 40.96 | 40.07    |
| 4  | CH\textsubscript{3}CH\textsubscript{2}CH\textsubscript{3}ONOCH\textsubscript{3} | 38.32              | 41.81       | 39.79            | 38.77      | 38.28      | 42.24 | 40.46    |
| 5  | CH\textsubscript{3}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}ONO | 36.98              | 39.73       | 38.34            | 36.7       | 36.74      | 40.72 | 41.76    |
| 6  | CH\textsubscript{3}OCH\textsubscript{2}CH\textsubscript{3}CH\textsubscript{3} | 35.36              | 39.9        | 38.74            | 36.21      | 36.32      | 40.38 | 41.57    |
| 7  | (CH\textsubscript{3})\textsubscript{2}CH\textsubscript{2}ONO | 36.47              | 37.64       | 36.92            | 36.45      | 36.64      | 40.74 | 39.76    |
| 8  | (CH\textsubscript{3})\textsubscript{3}CONO | 36.71              | 39.29       | 38.91            | 37.55      | 37.48      | 41.48 | 40.96    |

According to the calculation data, the dissociation energy of the breaking bond and the activation energy of radical decomposition in the gaseous state with the breaking of this bond change insignificantly in the series of compounds studied. Due to the fact that the most reliable estimates of
the enthalpies of formation of compounds and radicals, as noted above, are provided by the G4 method, we will analyze the change in the dissociation energies of the O-NO bond using the results of this method. Analyzing the results obtained, we note that the changes in the strength of the O-NO bond observed in a series are relatively small and do not exceed 3.4 kcal/mol. According to the calculation data, the strongest are CO-NO bonds formed with the participation of the primary carbon atom; less durable are formed with the participation of primary and tertiary carbon atoms. Within the indicated groups of compounds, the difference in the strength of O-NO bonds does not exceed 1.2 kcal/mol for compounds of the first group and 0.55 kcal/mol for compounds of the second group. The change in the activation energy of radical gas-phase decomposition in the series of nitrites of aliphatic alcohols occurs in a similar way. An interesting feature of this study is the closeness of the dissociation energies of O-NO₂ and O-NO bonds. As noted above, the tendencies of their change in the series also coincide. When calculating the dissociation energies of O-NO₂ and O-NO bonds, the difference in the values of the enthalpies of formation of nitrates and nitrites is compensated by differences in the values of the enthalpies of formation of NO₂ and NO radicals.

4. Conclusion
Using various quantum-chemical methods, the enthalpies of formation of nitrates and nitrites of aliphatic alcohols C₁-C₄, as well as products of homolytic cleavage of O-NO₂ and O-NO bonds in these compounds, have been calculated. The best agreement with experiment is achieved when using the G4 method. The observed changes in the dissociation energies in the series do not exceed 2.5–3.0 kcal/mol. A similar change in the series of enthalpies of formation of the studied compounds was noted, as well as a correlation dependence in the change in the series of enthalpies of formation of compounds and radicals, which explains the closeness of the calculated values of dissociation energies. According to the calculation results, the strongest are the O-NO₂ and O-NO bonds attached to the primary carbon atom.

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