The effect of molecular structure on the O – NO$_2$ bond dissociation energy and the activation energy of the radical decay of cellotriose nitrates

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Abstract. The molecular structure was determined using the method B3LYP/6-31+G(2df, p), and the dissociation energies of the O – NO$_2$ bond in dimethylcellobiose and cellotriose nitrates were calculated. It has been established that the O – NO$_2$ bonds attached to the secondary carbon atom at C$_2$ are the least strong in cellotriose nitrates. With an increase in the degree of substitution, a slight decrease in the dissociation energy of radical decay is observed. The results can be used to discuss the mechanism of thermal decomposition of cellulose nitrates.

1. Introduction

Cellulose nitrates (CN) are used as the polymer base of pyroxylin and ballistic powders, as well as in the manufacture of various paints and varnishes [1]. In recent decades, the use of CNs has expanded significantly in connection with the manufacture of ionizing radiation detectors, biological indicators, semipermeable membranes of selective sorbents, and other high technology products [2]. This stimulated research on the directional regulation of the basic physicochemical characteristics of CNs to obtain materials with desired properties.

The longest stage of CN production is the stabilization process, in which the chemical resistance of cellulose nitrates is formed. The rate constant of thermal decomposition of CN can be a quantitative assessment of chemical resistance. The kinetics of thermal decomposition of CN has been studied for over 120 years. During this period, a huge array of experimental data was obtained, fairly simple and reliable methods for assessing the chemical resistance of samples produced at enterprises were developed, the main directions for improving stabilization technology were determined [2-6]. However, many issues of fundamental interest for understanding the laws of changes in the chemical resistance of CNs remain unresolved.

For example, based on the available experimental data, it is not clear whether the degree of substitution (nitrogen content) in the CN samples affects the activation energy of the thermal decomposition reaction. Some studies claim that there is no such effect [3]. This conclusion raises serious doubts. First of all, the interval in which the kinetics of thermal decomposition of nanocrystals was studied is small; only samples with a nitrogen content of 11 to 13.8% were studied [3, 4]. In addition, the experimental data for samples with the same degree of substitution differ significantly among...
different authors. A serious drawback of experimental work is the absence in most cases of information about the features of stabilization of the studied CN samples. At the same time, it is quite obvious that the rate of thermal decomposition of nanocrystals varies significantly during stabilization \[1, 2\]. And finally, the available results do not allow drawing conclusions about the mechanism of thermal decomposition of cellulose nitrates.

One of the serious obstacles to studying the mechanism is the lack of information on the molecular structural inhomogeneity (MSI) of CN in studies of the kinetics of thermal decomposition. Reliable experimental methods have been developed for assessing MSI at various levels of the structural organization of CN: elementary unit, macromolecule, nitrocellulose matrix \[2\]. The first of these levels is the most important to study the mechanism of thermal decomposition reactions. The same nitrogen content (degree of substitution) in different samples can correspond to the most diverse ratios of the content of nitrate groups in the elementary unit of the carbon atoms C_2, C_3, C_6 of the glucopyranose cycle. Unfortunately, studies on the kinetics of thermal decomposition and MSI of cellulose nitrates were carried out in isolation from each other.

2. Calculation methods

The missing information can be obtained using quantum chemical methods; however, the published results do not allow any specific conclusions. The fact is that a significant part of the calculations for assessing the barriers of the thermal decomposition of organic nitrates was carried out using semi-empirical methods, which can produce very large errors. These results are mainly of historical interest \[6\].

Estimates of non-empirical and DFT methods are much more reliable, however, much simpler compounds – mononitrates or polynitrates of aliphatic alcohols – were used as models for studying the mechanism of thermal decomposition of nanocrystals \[2\]. These are too crude models that do not take into account the structural features of the CN. In several works, bond dissociation energies in glucose nitrates were estimated, however, the calculations were carried out using methods and bases that can give large errors in determining barriers \[2\]. All this necessitates an additional study of the mechanism of thermal decomposition of CN using adequate calculation methods and molecular models.

In our work, we present the results of studying the influence of the molecular structure on the change in the strength of O–N bonds in dimethyl celllobiose and cellotriose nitrate molecules. These compounds are much closer to the structure of cellulose nitrates than previously used models. The calculations were performed using the B3LYP method and the basic set 6-31+G(2df,p). It was found for a large number of organic compounds, including nitro compounds, that this method and basis provide good agreement with experimental data on the enthalpies of the formation of reagents and products, as well as barriers to chemical reactions \[7–15\].

3. The results

The following tables use the short descriptions of the compounds given in the table 1.

Table 2 shows the calculated values of the O–N bond length and charges on the atoms forming this bond in dimethicellulose nitrates. Atom charges were calculated by two different methods. An analysis of our results shows that the bond lengths and charges on the atoms of nitrate groups attached to different carbon atoms in the compounds studied differ markedly. In mononitrates, the smallest value of the O–N bond length is predicted by the calculation for the nitrate group at C_6, and the largest at C_3. The bond lengths and atomic charges in the mononitrates of various glucopyranose cycles are practically the same.

With the accumulation of nitrate groups in the molecules, the bond lengths increase slightly. This tendency is weakest for primary nitrate groups at C_6 and most strongly for nitrate groups at C_2. In the series mononitrate-trinitrate, an increase in the positive charge on the nitrogen atom and the negative charge on the oxygen atom is observed. However, the noted trends are expressed rather weakly.
– specifically specified, we analyze the results obtained for the first mononitrates and dinitrates show that the degree of substitution weakly affects both the enthalpy and enthalpy of the reaction is accompanied by a decrease in the entropy of the reaction. The data obtained the O–N bond dissociation energies decrease for nitrate groups in the series C6–C2. Interestingly, an increase in the O–N bond dissociation energy, which coincide in the series of compounds reactions were evaluated from the entropies and radicals formed upon breaking the O–N bond, the calculation predicts the lowest enthalpy of formation for the radical in which C6 is present. The O–N bond dissociation energies decrease for nitrate groups in the series C3, C6, C2. Hereinafter, if this is not specifically specified, we analyze the results obtained for the first glucopyranose cycle. Interestingly, an increase in the O–N bond dissociation energy is accompanied by a decrease in the reaction entropy. Similar trends are observed when analyzing the results obtained for dimethylcellobiose dinitrates. The strongest bonds are O–N bonds at C3, and the least strong bonds are at C2. An increase in the enthalpy of the reaction is accompanied by a decrease in the entropy of the reaction. The data obtained for mononitrates and dinitrates show that the degree of substitution weakly affects both the enthalpy and
the entropy of the reaction. According to the calculation data, in 2, 3, 6-trinitrate 1,4-dimethylcellobiose, the O-N bonds at C₆ are the strongest in the first glucopyranose cycle, and the least strong at C₁. Thus, the relative bond strength in the series of isomers changes for trinitrates.

Table 3. Thermochemical characteristics of compounds and radicals ($\Delta H_{f, \ 298K}$, kJ/mol; $\Delta S_{f, \ 298K}$, J/(mol· deg)) and thermochemical characteristics of the radical decomposition reaction ($\Delta H_{p, \ f}$, kJ/mol; $\Delta S_p$, J/(mol· deg)) of cellobiose nitrates. In parentheses there are atom numbers of the cellobiose cycle at which the O-NO₂ bond breaks. The sign ' denotes a glucose cycle having, as a substituent at position 1, another glucose cycle; group CH₃ acts as terminal substituents.

| Compound          | Thermochemical specifications of the compound | Thermochemical specifications of the radical | $\Delta H_p$=D(O-NO₂) | $\Delta S_p$ |
|-------------------|-----------------------------------------------|---------------------------------------------|------------------------|-------------|
|                   | $\Delta H_{f, \ 298K}$ $S_{f, \ 298K}$       | $\Delta H_{p, \ f}$ $S_{p, \ 298K}$        |                        |             |
| 2-N-1,4'-DMCB     | -1560.4 1052.7                                | -1441.0 976.8                               | 133.6                  | 180.9       |
| 3-N-1,4'-DMCB     | -1561.5 1067.5                                | -1436.5 983.3                               | 139.2                  | 172.6       |
| 6-N-1,4'-DMCB     | -1574.9 1052.5                                | -1451.3 972.5                               | 137.8                  | 176.9       |
| 2'-N-1,4'-DMCB    | -1559.5 1059.4                                | -1440.8 982.9                               | 132.9                  | 180.3       |
| 3'-N-1,4'-DMCB    | -1568.9 1055.4                                | -1450.7 969.2                               | 132.4                  | 170.6       |
| 6'-N-1,4'-DMCB    | -1575.4 1052.0                                | -1450.0 974.2                               | 139.6                  | 179.1       |
| 2,6-DN-1,4'-DMCB  | -1475.7 1135.1                                | -1357.0 1060.7                              | 132.9                  | 182.4       |
| 2,6-DN-1,4'-DMCB  | -1476.3 1148.9                                | -1343.5 1061.5                              | 138.5                  | 177.3       |
| 2',6'-DN-1,4'-DMCB| -1477.5 1141.0                                | -1353.2 1061.5                              | 138.5                  | 177.3       |
| 2',6'-DN-1,4'-DMCB| -1463.7 1148.9                                | -1338.5 1062.9                              | 139.4                  | 170.8       |
| 3,6-DN-1,4'-DMCB  | -1468.2 1139.6                                | -1350.6 1056.7                              | 131.8                  | 173.9       |
| 3',6'-DN-1,4'-DMCB| -1469.1 1134.0                                | -1344.9 1061.6                              | 137.5                  | 178.9       |
| 6,6'-DN-1,4'-DMCB | -1492.1 1134.0                                | -1369.2 1055.7                              | 137.1                  | 178.5       |
| 6',6'-DN-1,4'-DMCB| -1473.5 1135.5                                | -1367.5 1056.2                              | 138.7                  | 179.1       |
| 2,3,6-TN-1,4'-DMCB| -1379.8 1221.7                                | -1262.5 1148.5                              | 131.5                  | 183.6       |
| 2,3,6-TN-1,4'-DMCB| -1257.3 1143.7                                | -1262.5 1148.5                              | 131.5                  | 183.6       |
| 2',3',6'-TN-1,4'-DMCB| -1246.9 1151.0                               | -1250.1 1142.5                              | 127.6                  | 169.6       |
| 2',3',6'-TN-1,4'-DMCB| -1241.3 1149.3                               | -1250.1 1142.5                              | 127.6                  | 169.6       |

Let us note that the O-N bonds at C₆ are the most durable for mononitrates, dinitrates and trinitrates of the second glucopyranose cycle, according to the calculation data. It is rather difficult to explain such differences in the relative bond strength in different cycles, since various factors can influence the change in bond strength in a series of isomers. An important role among them, obviously, is played by the possibility of the formation of intramolecular hydrogen bonds in compounds and radicals that stabilize the structure.

Analysis of changes in the length of O-N bonds depending on the degree of substitution is also of particular interest. Let us note that the observed changes are not large. The calculation predicts the strongest changes for the O-N bond at C₂; the smallest – for this compound is at C₆. In the latter case, with an increase in the degree of substitution from 1 to 3, the bond length decreases by only 0.005 Å (0.5 pm). Such very weak changes in the bond length indicate the absence of any significant steric interactions involving this nitrate group. It is possible that a very weak change in the O-N dissociation energy at C₆ (only 1.1 kJ/mol) in trinitrate compared with mononitrate is also associated with this.

The observed decrease in bond strength is 7.7 kJ/mol for nitrate groups at C₂; in this case, the bond length increases by 0.014 Å (1.4 pm). The calculation predicts not a decrease, but an increase in bond strength for nitrate groups at C₂; with an increase in its length in trinitrate compared to mononitrate by 0.028 Å (2.8 pm), the strength of this bond increases by 1.7 kJ/mol. This effect, which is obviously an
artifact, is predicted only for nitrate in the first glucopyranose cycle. The calculation predicts a decrease in O-N bond strength by 2.1 kJ/mol in trinitrate for the nitrate group at C$_3$ attached to the second glucopyranose cycle.

If we briefly summarize the results obtained in the study of dimethylcellobiose nitrates, it should be noted that the differences in the bond strength O-N both in the series of isomers and with an increase in the degree of substitution are small enough so that one can speak of any preferred variant of one or another mechanism of the primary act of radical thermal decomposition. The differences in the dissociation energy of the least strong O–N bond in the studied compounds does not exceed 8–12 kJ/mol, which does not exclude the possibility of parallel reactions of the decomposition of nitrate groups attached to different carbon atoms. An interesting feature of the studied processes is the fact that an increase in the O–N bond strength is usually accompanied by a decrease in the entropy of the radical decomposition reaction.

In the final part of the work, we will consider the results obtained for cellotriose nitrates. In order to evaluate the effect of neighboring nitrate groups, a model was considered in which the hydroxyl groups at position 2,3,6 were nitridated for two peripheral glucopyranose cycles, and the hydroxyl groups were sequentially replaced with nitrate groups in the central cycle. Thus, we studied 3 heptanitrates (mononitrates in the central cycle), 6 octanitrates (dinitrates in the central cycle), and 3 nonanitrates (trinitrates in the central cycle, respectively).

Table 4 shows the calculated values of the dissociation energies of O-N bonds in the studied compounds. They were obtained on the basis of calculated estimates of the enthalpies of formation of compounds and radicals shown in the table 5.

According to the calculation data, in the series of heptanitrates, the O-N bonds in the central ring at C$_3$ are the strongest, and the least strong at C$_2$. A similar trend is observed in the series of cellotriose octanitrates. In this case, the bonds at C$_3$ are also the strongest in the central cycle, and the least strong at C$_2$. It does not change in the series of non-nitrate cellotrioses. Here, O-N bonds at C$_3$ are most durable; least durable – at C$_2$.

The results of a theoretical study of cellotriose nitrates show that in most cases, according to the calculation, O-N bonds of secondary nitrate groups attached to the C$_3$ carbon atom are stronger. The least durable are the corresponding groups attached to the carbon atom C$_2$. The bond strength of O-N primary nitrate groups at C$_6$ is intermediate.

| Compound | radical | D(O-N), kJ/mol |
|----------|---------|---------------|
| 2,3,6,2',2'',3'',6''-HN CT | 2,3,6,(.)',2'',3'',6'' | 128.2 |
| 2,3,6,3',2'',3'',6''-HN CT | 2,3,6,(.)',2'',3'',6'' | 144.2 |
| 2,3,6,6',2'',3'',6''-HN CT | 2,3,6,(.)',2'',3'',6'' | 137.6 |
| 2,3,6,2'3',2'',3'',6''-ON CT | 2,3,6,(.)',2'',3'',6'' | 133.3 |
| 2,3,6,2'3',2'',3'',6''-ON CT | 2,3,6,(.)',2'',3'',6'' | 139.7 |
| 2,3,6,26',2'',3'',6''-ON CT | 2,3,6,(.)'6'',2'',3'',6'' | 131.2 |
| 2,3,6,2'6',2'',3'',6''-ON CT | 2,3,6,(.)'6'',2'',3'',6'' | 137.0 |
| 2,3,6,3'6',2'',3'',6''-ON CT | 2,3,6,(.)'6'',2'',3'',6'' | 144.3 |
| 2,3,6,3'6',2'',3'',6''-ON CT | 2,3,6,(.)'6'',2'',3'',6'' | 136.4 |
| 2,3,6,2'3'6',2'',3'',6''-NN CT | 2,3,6,(.)'3'6'',2'',3'',6'' | 135.1 |
| 2,3,6,2'3'6',2'',3'',6''-NN CT | 2,3,6,(.)'3'6'',2'',3'',6'' | 139.8 |
| 2,3,6,2'3'6',2'',3'',6''-NN CT | 2,3,6,(.)'3'6'',2'',3'',6'' | 135.6 |
Table 5. The enthalpies of the formation of cellotriose polynitrates and radicals formed upon breaking the O-N bond. Data for radicals are given after the information about the compounds. In radicals, the position of nitrate groups is indicated. The site of bond cleavage during the formation of radicals is indicated by a dot in parentheses.

| Compound | \( \Delta H_f \), \( \text{kJ/mol} \) | \( \Delta H_f \), \( \text{298.15K} \), \( \text{kJ/mol} \) | \( \Delta G_f \), \( \text{298.15K} \), \( \text{kJ/mol} \) | \( S_f \), \( \text{298.15K} \), \( \text{J/(mol-K)} \) |
|----------|-----------------|-----------------|-----------------|-----------------|
| 2,3,6,2\',3\',6\'-HN CT | -1657.4 | -1778.9 | -710.9 | 1787.7 |
| 2,3,6,3\',2\',3\',6\'-HN CT | -1682.0 | -1803.0 | -735.5 | 1789.4 |
| 2,3,6,6\',2\',3\',6\'-HN CT | -1675.6 | -1797.9 | -725.2 | 1771.7 |
| 2,3,6,2\',3\',2\',6\'-HN CT | -1582.9 | -1704.9 | -590.8 | 1867.5 |
| 2,3,6,2\',6\',2\',3\',6\'-HN CT | -1573.4 | -1696.4 | -578.8 | 1855.9 |
| 2,3,6,3\',6\',2\',3\',6\'-HN CT | -1595.6 | -1718.1 | -603.2 | 1865.1 |
| 2,3,6,2\',3\',6\',2\',3\',6\',6\'-NN CT | -1495.0 | -1618.7 | -457.2 | 1943.6 |
| 2,3,6,(\'3\',2\',3\',6\',6\',6\') | -1548.2 | -1664.9 | -662.5 | 1707.8 |
| 2,3,6,(\'3\',2\',3\',6\',6\',6\') | -1557.1 | -1673.0 | -674.8 | 1721.8 |
| 2,3,6,(\'3\',2\',3\',6\',6\',6\') | -1557.8 | -1674.5 | -672.1 | 1707.5 |
| 2,3,6,(\'3\',2\',3\',6\',6\',6\') | -1468.3 | -1585.9 | -537.5 | 1788.0 |
| 2,3,6,2\'(\'3\',2\',3\',6\',6\') | -1462.2 | -1579.5 | -535.5 | 1803.0 |
| 2,3,6,(\'3\',2\',3\',6\',6\') | -1461.1 | -1579.4 | -528.7 | 1780.4 |
| 2,3,6,2\'(\'3\',2\',3\',6\',6\') | -1455.9 | -1573.6 | -524.7 | 1786.3 |
| 2,3,6,(\'3\',2\',3\',6\',6\') | -1470.5 | -1588.0 | -543.2 | 1800.2 |
| 2,3,6,3\'(\'3\',2\',3\',6\',6\') | -1478.5 | -1595.9 | -548.7 | 1791.9 |
| 2,3,6,(\'3\',2\',3\',6\',6\') | -1379.0 | -1497.8 | -406.9 | 1880.3 |
| 2,3,6,2\'(\'3\',2\',3\',6\',6\') | -1374.4 | -1493.1 | -403.5 | 1884.7 |
| 2,3,6,2\',3\'(\'2\',3\',6\',6\') | -1378.8 | -1497.2 | -404.4 | 1873.7 |

Our results significantly differ from previously published data on the bond strength in glucose nitrites, which were used earlier to discuss the mechanism of thermal decomposition of cellulose nitrites [2, 6]. According to these data, the bond strength in the series of glucose mononitrates, dinitrates and trinitrates decreases with the transition from primary nitrate groups to secondary ones. We consider these results to be erroneous; in most cases, they were obtained using semiempirical methods, or density functional methods with small basis sets. In addition, which is especially significant, the previously obtained results do not sufficiently reflect the specificity of cellulose nitrites.

The results of our work also show that the influence of changes in the degree of substitution on the value of the dissociation energy of O–N bonds and the activation energies of radical decomposition in the gaseous state for the studied compounds, as well as cellulose nitrites, is rather weakly expressed. At the same time, one can expect a slight, no more than 8-10 kJ/mol, decrease in the activation energy during the transition from mononitrates to cellulose trinitrates. This forecast does not contradict the available experimental data [2–4]. It should also be noted that the calculated estimates of the O–N bond dissociation energies in the studied compounds are obviously underestimated by 12–15 kJ/mol, which is typical of the method used in the work, which at the same time correctly conveys the trends in the reaction barriers in the series.

Such an assumption can be made on the basis of our assessment of the barriers of the reactions of thermal decomposition of mono-nitrites of simple alcohols (C1–C4), as well as 5 glycerol nitrites, by various quantum-chemical methods. In this case, it was found that a multistep method G4 gives estimates of the enthalpies of formation of compounds, radicals, and dissociation energies of O–N bonds, which are almost identical with experiment. However, at present, it is not possible to use this method to study changes in a number of reaction barriers of such complex compounds as dimethylcellobiose nitrites and cellotriose nitrites. Even our study of cellotriose nitrites using the method B3LYP/6-31+G(2df, p) was associated with a very large expenditure of machine time.
4. Conclusion
A theoretical study of the molecular structure and estimation of the dissociation energies of O-NO₂ bonds in dimethylcellobiose and cellotriose nitrates shows that nitrate groups at different carbon atoms interact weakly with each other in these compounds. This determines, obviously, the proximity of the values of bond dissociation energies and the activation energies of the radical decay of the studied compounds and the weak dependence of the barriers of the radical decay reactions on the degree of substitution. Similar patterns can be expected for the thermal decomposition of cellulose nitrates, since the radical mechanism of the primary act of this reaction is beyond doubt.

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