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Effect of tertiary amines on the thermal stability of high-energy trinitroalkyl compounds

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ABSTRACT

The influence of complex formation on the thermal stability of promising energetic materials containing trinitromethyl and amino groups in the molecule has been studied by quantum chemistry methods. Several different model molecules were used for calculations. Geometry optimization of the initial molecules and their complexes was performed using the PBE0 DFT method with the cc-pVDZ basis set. The electron energy was calculated by the CCSD, DLPNO-CCSD, DLPNO-CCSD(T) methods with the cc-pVDZ, aug-cc-pVDZ, aug-cc-pVTZ basis sets and the CBS-QB3 method. It has been shown that for model molecules containing a double C=C bond, complex formation has little effect on the strength of the C–NO_2 bond whereas for model molecules with an alkyl or triazine substituent, the C–NO_2 bond in the complex is 25–30 kJ/mol weaker than in an isolated molecule.

KEYWORDS: *Quantum-chemical calculation, complexes of trinitromethyl groups with tertiary amines, C–NO_2 bond energy.*
AMS Subject Classification: 05C12.

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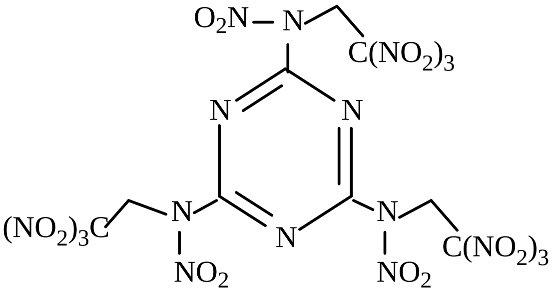
I. INTRODUCTION

Substances containing a trinitromethyl group are among promising high-energy compounds, since this group not only causes a significant energy release during thermal transformations, but also improves the oxygen balance in mixed fuels [1 - 4]. As a rule, such compounds are characterized by satisfactory thermal stability, however, they are inferior in this indicator to a number of important high-energy compounds, such as HMX, CL-20 and FOX-7. When using energetic compounds in mixed fuels, not only their own thermal stability is important, but also compatibility with other components of the composition should be taken into account. The compatibility (in terms of thermal stability) of an energetic group (for example, trinitroalkyl one) with other functional groups of the same molecule is also important.



I

Figure: 1

In particular, for the energetic compound 2,4,6-tris(2,2,2-trinitroethylnitramino)-1,3,5-triazine (**I**), it was shown that as a result of its transformation into a low-density β-modification and even as a result of the activation of fragmentary movements in the crystal (a process preceding the α→β transformation), is accompanied by a sharp acceleration of thermal decomposition (Fig. 2) [5].A possible explanation for this phenomenon is the assumption that the abstraction of the NO_2 group from the trinitroethyl fragment can be catalyzed by the secondary amino group, since close contacts between the $C(NO_2)_3$ and $C–N(NO_2)–C$ fragments become possible only as a result of a sharp increase in the free volume in the crystal due to the activation of fragmentary motions, which is recorded in the X-ray diffraction analysis of the heated crystal.

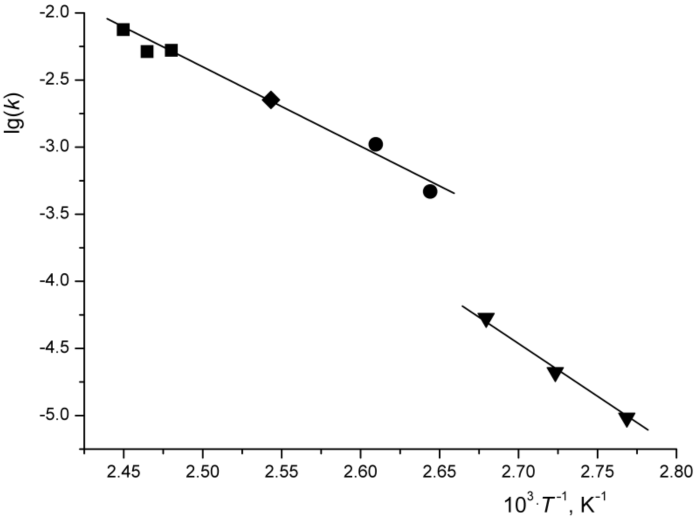
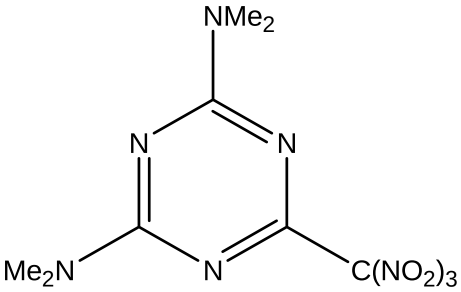


Figure: 2

Temperature dependence of the catalytic rate constant of decomposition of **I** in Arrhenius coordinates. The triangles correspond to the low-temperature a-modification of **I**, the circles correspond to the disordered α-modification **I** with activated fragmentary movements, the rhombus corresponds to the β-modification of **I**, and the squares correspond to the melt of **I**.

Another representative of this class of substances, 2,4-bis(N,N-dimethylamino)-6-trinitromethyl-1,3,5-triazine (**II**), has recently been synthesized and characterized in detail [6, 7]. The compound **II** is of interest as a model for elucidating the extent to which the simultaneous presence of tertiary amino groups and trinitromethyl substituents in triazine derivatives affects their thermal stability.

The kinetics of thermal decomposition of substances containing trinitromethyl group is well studied [8]. In these reactions, the first, rate-limiting stage of the reaction is the monomolecular homolytic cleavage of the $C–NO_2$ bond with an activation energy of 146–167 $kJ\cdot mol^{-1}$ and a pre-exponential factor of $10^{15} – 10^{17}\ s^{-1}$. However, for **II**, the first-order rate constants corresponding to the initial stages of decomposition are described by the Arrhenius equation with an activation energy of 66.9 ± 9.6 $kJ\cdot mol^{-1}$ and an anomalously low value of the pre-exponential factor of $10^{4.6\pm1.2}\ s^{-1}$ [7]. These data show that in this case a compensation effect is observed and the compound **II** decomposes according to a different mechanism.



II

Figure: 3

It was shown that at 92°C **II** undergoes a polymorphic transformation preceded by an abrupt drop in density. Polymorphic transformation occurs with the destruction of crystals and is accompanied by partial mechanochemical decomposition of **II**. Melting **II** at about 123°C leads to a sharp acceleration of decomposition. When passing from a melt to a dilute solution in an inert solvent, the decomposition rate is significantly reduced. The thermal decomposition kinetic curves are S-shaped (Fig. 4) and are described by the 1st order autocatalysis equation [7]. When passing from a melt to a dilute solution, the rate of thermolysis of **II** in the stationary section of the kinetic curve decreases by 4–6 times, and in the initial section, by tens of times. The ratio of initial reaction rates in the melt and dilute solution extrapolated to the moment of the beginning of the process is 30±5. Note also that in solutions of different but low concentrations (2.5 and 5 wt.%), the rate of thermal decomposition of **II** is almost the same [7].

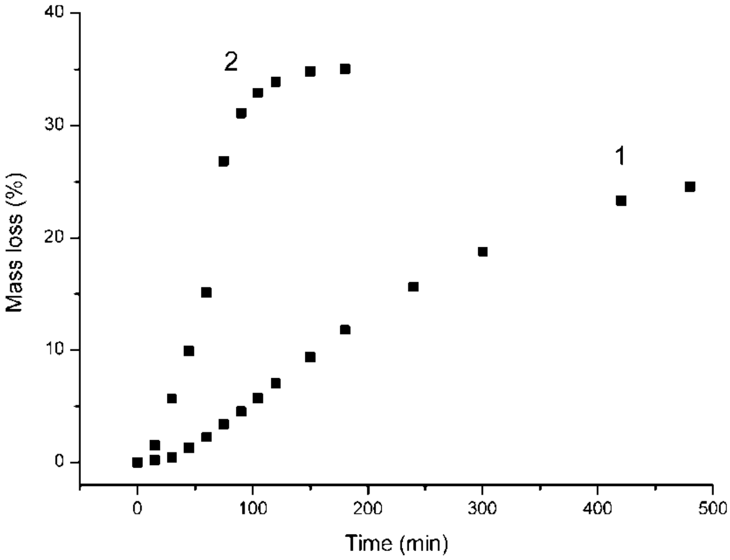


Figure: 4
Thermogravimetric kinetic curves of the decomposition of **II** at 120°C, in 2.5% solution in dinonyl phthalate (1) and in the melt (2) (according to [7]).

Based on these data, it was suggested that the interaction of the trinitromethyl group with the dimethylamino group, which has basic (nucleophilic) properties, may be the cause of this behavior. This assumption was confirmed by a specially conducted experiment, which showed that in the presence of N-phenylmorpholine, a significant decrease in the thermal stability of **II** occurs even in a dilute solution. However, the mechanism of the influence of the tertiary amino group on the kinetics of the thermal decomposition of **II** remained unclear. In particular, it is not clear whether this group is capable of catalyzing the reaction, or its role is only that it is directly involved in the limiting stages of decomposition. The aim of this work is an attempt to answer this question.

II. Materials And Methods

2.1 Computational methods

The calculations were carried out on a multiprocessor cluster in the computer center of the IPCP RAS. Preliminary calculations were performed using the GAUSSIAN 09, Revision C.01 program [9] based on the DFT method with the PBE0 hybrid functional [10] and the cc-pVDZ basis set. The choice of this level of calculation is due to the fact that for nitrogen-containing high-energy compounds (for example, 1,1-Diamino-2,2-dinitroethylene **(DADNE)** [11]orNitroguanidine(**NQ**)[12]) it reproduces the results obtained at higher levels of calculation with a sufficient degree of accuracy, and at the same time it is more resource efficient. The electron energy of stationary points obtained by the DFT method was calculated using the GAUSSIAN 09 software at the CCSD/aug-cc-pVDZ level and ORCA 5.0.2 software [13, 14] using the DLPNO-CCSD method with the aug-cc-pVDZ basis set. The latter approach makes it possible to significantly speed up the calculation while maintaining accuracy in comparison with CCSD/aug-cc-pVDZ calculation in the GAUSSIAN 09 program. A basis set superposition error (BSSE) was taken into account for the TS of the reactions in which two or more molecules are formed.

For control the results obtained, some stationary points were also calculated using the DLPNO-CCSD(T) method with aug-cc-pVDZ and aug-cc-pVTZ basis sets as well as CBS-QB3 method. However, the comparison showed that the values of activation parameters differ insignificant from those calculated at the

DLPNO-CCSD/aug-cc-pVDZ level. Thermodynamic corrections to the energy were found using the MOLTRAN software package [15] using the calculated normal vibration frequencies.

The energy (enthalpy) of the C–NO_2 bond ($\Delta H_{C\text{-}NO2}$) in the studied molecules was determined as the difference between the sum of the enthalpies of the products (i.e. R radical and NO_2) and the enthalpy of the reagent (initial molecule M):

$$\Delta H_{C\text{-}NO2} = \Delta H_R + \Delta H_{NO2} - \Delta H_M$$

In the case of complexes, instead of the parent molecule and the final radical, the corresponding complexes with a tertiary amine are meant.

2.2 Molecules with TNM and TA groups used as models

The compound **II** is bifunctional, that is, it has two kinds of functional groups, trinitromethyl (TNM) and tertiary amino (TA) ones. Between themselves, these groups of different molecules are able to enter into a fairly strong donor-acceptor interaction, which leads to the formation of well-bound complexes. To model these complexes and elucidate the causes of the change in the thermal stability of **II** with a change in its concentration in solution, we used various molecules containing TNM and TA groups. The following TNM compounds were used as models:

TNM1 TNM2 TNM3

Figure: 5

The first of these, (trinitromethyl)methane, is the simplest. There are no multiple and conjugated bonds in TNM1, and only external causes can affect the strength of the C–NO_2 bond. A double bond is added to the TNM2 molecule, which can lead to electron delocalization, involving nitro groups. The TNM3 molecule contains a triazine ring, and this molecule is the closest model for the compound **II**.

The trinitromethyl groups in all three model molecules are in similar states: the planes of two nitro groups are nearly perpendicular to the C–C bond, and the third one is almost parallel to the C–C bond. It can be expected that, if this configuration is preserved in the complexes with tertiary amines, the strength of the C–NO_2 bond in the complexes for two nitro groups will be close to each other, while for the third nitro group it may be different. In isolated TNM molecules, there is no such difference, since no matter which nitro group is removed, the structure (and energy) of the final radical is the same.

The following compounds with TA groups were used as models:

TA1 TA2 TA3

Figure: 6

Here the first compound (trimethylamine) is the simplest tertiary amine without multiple and conjugated bonds, the second one is a compound with a double bond, and the third one is the closest model of **II**. The structure of the amine fragment of the isolated TA1 and TA2 molecules is tetrahedral and the nitrogen atom is in the sp^3 state. The structure of the TA3 molecule is flat, the N atom is in the sp^2 state and conjugation with the π-electrons of the triazine ring takes place.

In this work, we consider the complex formation of these model molecules and determine how the formation of TNM complexes with TA changes the strength of C–NO_2 bonds.

III. Realization Results

3.1 The TNM1-TA1 complex

The structure of the TNM1-TA1 complex is shown in Fig. 7. The TA1 molecule is symmetrical, so the strength of which C-NO_2 bond in TNM1 is considered in this complex does not matter. Only the structure of the final complex can affect the result.

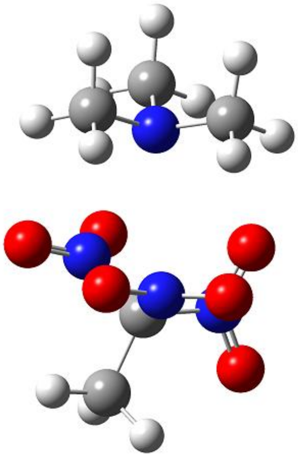


Figure: 7

The TNM1-TA1 complex.

As a result of the detachment of the NO_2 group from this complex, a product complex is formed in which the nitrogen atom of TA remains coordinated with carbon. Therefore, it does not matter which nitro group of the original TNM molecule was removed and the structure of the radical residue of the TNM molecule is the same in all cases:

Figure: 8

In other words, despite the fact that the original TNM1 molecule is asymmetric, due to the symmetry of the product the strengths of all three C–NO_2 bonds in TNM1 are equal. They are also equal to each other and in the complex with TA1, since the latter is initially symmetrical.

The TNM1-TA1 complex quite closely models the complex formation in the compound **II**, since the electronic structure of its constituent molecules containing trinitromethyl and tertiary amine groups is in many respects similar to the fragments of **II**. In this complex, there are no conjugated bonds and substituents that strongly change the electron density on the carbon-nitro group bonds. Only the TNM3-TA3 complex models the experimental conditions more accurately, but due to the large number of its constituent atoms, "heavy" quantum chemical methods cannot be applied. Therefore, in addition to purely research tasks (i.e. the calculation of the C–NO_2 binding energy in the complex), we use the small TNM1-TA1 complex to test how well the methods suitable for the TNM3-TA3 complex reproduce the results obtained at higher levels of calculation.

The results of calculations for the TNM1-TA1 complex are given in Table 1. As one can see, all calculation levels give similar results. The energy of complexation upon the removal of the NO_2 group increases, the complex of products being stronger than the initial one by 20 to 30 kJ·mol^{-1}, depending on the calculation method.

Table: 1 Enthalpies of the formation of the TNM1-TA1 complexes (ΔH_{Comp}) involving initial molecules and reaction products as well as energies of the C–NO$_2$ bond ($\Delta H_{\mathrm{C–NO2}}$) in the initial TNM1 molecule and TNM1-TA1 complex.

Computation method	ΔH_{Comp} (kJ·mol^{-1})		$\Delta H_{\mathrm{C\text{-}NO2}}$ (kJ·mol^{-1})	
	Initial molecules	Products	TNM1	TNM1-TA1
CCSD/cc-pVDZ	–32.5	–47.9	+189.6	+167.9
DLPNO-CCSD/aug-cc-pVDZ	–33.4	–52.4	+199.0	+173.7
DLPNO-CCSD(T)/aug-cc-pVDZ	–38.2	–60.6	+203.1	+174.3
DLPNO-CCSD(T)/aug-cc-pVTZ	–28.5	–49.7	+200.7	+173.1
CBS-QB3	–23.6	–58.0	+198.8	+164.4

The C–NO$_2$ binding energy in the initial molecule is about 200 kJ·mol^{-1}. Only the values obtained using the cc-pVDZ basis differ from the others by 10 kJ·mol^{-1}. Consequently, the size of this basis for this problem is not always sufficient. At the same time, the CBS, CCSD, and CCSD(T) methods in combination with the aug-cc-pVDZ and aug-cc-pVTZ basis sets almost equally estimate the strength of the bond under consideration. In the complex, the energy of this bond is lower and amounts to 165 – 174 kJ·mol^{-1} at all calculation levels. Thus, in the TNM1-TA1 complex, the enthalpy of abstraction of the nitro group is significantly (by 22 – 25 kJ·mol^{-1}) less than in a separate TNM1 molecule. Some difference in the results of various calculation methods is observed only in the estimation of the strengths of the complexes themselves, but it is not critical (within 10 kJ·mol^{-1}). Thus, for the problem under consideration, the calculation level CCSD/aug-cc-pVDZ is sufficient. To control the results we will additionally use the CCSD(T)/aug-cc-pVDZ calculation. There is no need to use a resource-intensive triple-zeta basis set.

3.2 The TNM1-TA2 complex

The structure of the TNM1-TA2 complex is shown in Fig. 9. In this complex, both TA2 and TNM1 molecules are non-symmetric. The substituents interact differently with the nitro groups of TNM1, so it can be expected that the strengths of the C–NO$_2$ bonds with different nitro groups should be different. Let us designate the nitro groups in this complex as NG1 to NG3. The results for them are presented below in Table. 2.

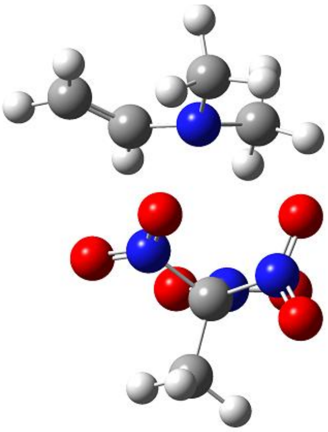


Figure: 9
The TNM1-TA2 complex.

Table: 2 Energy data for the TNM1-TA2 complex (for designations see Table 1).

Computation method	ΔH_{Comp}(kJ·mol^{-1})				$\Delta H_{\mathrm{C–NO2}}$ (kJ·mol^{-1})			
	Initial molecules	NG1	NG2	NG3	TNM1	NG1	NG2	NG3
CCSD/cc-pVDZ	–23.8	–34.3	–23.3	–15.5	189.6	186.7	197.4	205.4
DLPNO-CCSD /aug-cc-pVDZ	–28.8	–39.3	–30.3	–20.6	199.0	196.1	204.7	214.7

First, we note that the results of applying both calculation methods again, as for the first of the considered complexes, change symbatically. We also note that for this complex, the enthalpy of complex formation upon the detachment of the nitro group changes much less (within 10 kJ·mol^{-1}), for NG1 it is greater than the initial value, for NG2 it is the same, and for NG3 it is less. As a consequence, the bond strengths in this complex are different for the three nitro groups. They are equal to or greater than the corresponding value in the TNM1-TA1 complex, and in two cases out of three they significantly (by 15 kJ·mol^{-1}) exceed the ΔH_{C-NO2} value for the isolated TNM1 molecule. Thus, during the formation of the TNM-TA complex, the introduction of a double bond into the TA molecule leads to the strengthening of the C–NO$_2$ bond in the TNM molecule, a result that is directly opposite to the results for the TNM1-TA1 complex.

In TNM1-TA2, the weakest NG1 bond corresponds to the nitro group, which in the complex is closest to the TA2 double bond (on the left in Fig. 4). In this case, a complex of products is formed in which the methyl group of the former TNM1 is oriented to the TA double bond, and this complex is most stable (Table 2). Of the other two nitro groups, which are coordinated by TA methyl substituents, the weakest C–NO$_2$ bond is formed by the NG2 group, the plane of which is perpendicular to the C–C bond of the TNM molecule. The strongest C–N bond forms the NG3 nitro group, the plane of which is parallel to the C–C bond (on the right in Fig. 9).

3.3 The TNM2-TA2 complex

In each of the molecules that make up the TNM2-TA2 complex (Fig. 10), there are C=C bonds; the π-electrons of these bonds are delocalized. In fact, two π-systems interact with TA2 during the formation of the complex with TA2. The calculation results for such systems are shown in Table 3.

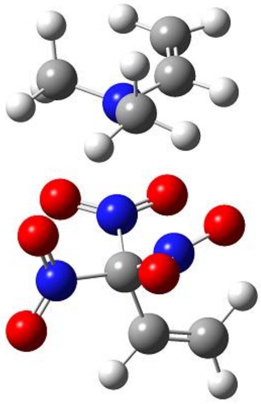


Figure: 10
The TNM2-TA2 complex.

Table: 3 Energy data for TNM2-TA2 complex (for designations see Table 1).

Computation method	ΔH_{Comp} (kJ·mol^{-1})				ΔH_{C-NO2} (kJ·mol^{-1})			
	Initial molecules	NG1	NG2	NG3	TNM2	NG1	NG2	NG3
CCSD/cc–pVDZ	–26.9	–24.1	–19.8	–15.5	143.3	139.2	143.2	148.4
DLPNO–CCSD /aug–cc–pVDZ	–25.3	–32.9	–27.8	–26.3	147.2	139.7	144.8	146.2

The results of calculations of the energy of complex formation of products and the energy of C–NO$_2$ bonding by the methods 1 and 2 change symbatically. Thus, both methods describe the features of these systems in the same way. Tables 1 to 3 show that in the TNM2 molecule, the C–NO$_2$ bond is 50 kJ·mol^{-1} weaker than in TNM1.

In the TNM2-TA2 complex, the energy of complexation is close to the two previous ones, but, in contrast to them, after the detachment of the nitro group, it changes insignificantly. The energies of all C–NO$_2$ bonds in TNM2-TA2 are close to each other. The minimum C–N bond energy was found for the nitro group interacting with the double bond (NG1, right in Fig. 5), and the maximum one for the nitro group, the plane of which is parallel to the C–C bond in the TNM2 molecule (NG3, left nitro group in Fig. 5). Consequently, the overall situation is the same as in the TNM1-TA2 complex, but the difference in bond strengths in this complex is only 6 kJ·mol^{-1}.

The main result that can be distinguished from these data is that the strengths of all C–NO$_2$ bonds in the TNM2-TA2 complex are close to each other and practically do not differ from the energy of this bond in an isolated TNM2 molecule. In other words, in the presence of double bonds in both molecules of the complex, intermolecular interaction does not affect the strengthы of the C–NO_2 bonds. More precisely, this effect is compensated by the redistribution of electron density in two interacting π-systems.

3.4 TNM3-TA3 complex

This complex is the most complete model of the complexes of the compound **II**. The structure of this complex is shown in Fig. 11.

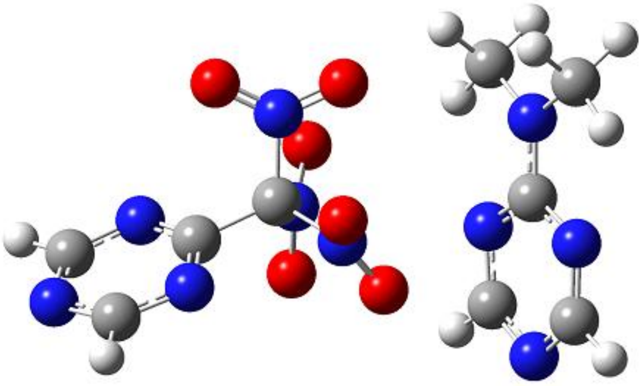


Figure: 11
The TNM3-TA3 complex.

As noted above, the TA3 molecule, in contrast to the other two tertiary amines, is planar and the nitrogen atom is in the sp^2 state. The calculated parameters of this complex are given in Table 4.

Table: 4 Energy data for the TNM3-TA2 complex (for designations see Table 1).

Computation method	ΔH_{Comp} (kJ·mol^{-1})				$\Delta H_{C–NO2}$ (kJ·mol^{-1})			
	Initial molecules	NG1	NG2	NG3	TNM3	NG1	NG2	NG3
CCSD/cc-pVDZ	–26.4	–44.3	–37.5	–37.5	166.5	143.6	150.4	150.3
DLPNO-CCSD /aug-cc-pVDZ	–36.7	–63.9	–50.8	–50.4	179.6	147.3	160.3	160.8
DLPNO-CCSD(T) /aug-cc-pVDZ	–38.5	–62.9	–49.1	–49.0	180.8	151.3	165.2	165.2

As for all other complexes, all calculation methods give similar results. When using the cc-pVDZ basis set, all enthalpy values are less than the corresponding values obtained with the aug-cc-pVDZ basis set. That is, in the first case, both the strengths of complexes and the strengths C–NO_2 bonds are somewhat underestimated, but, as in the cases of smaller modelling molecules (Table 1), this difference is not critical (about 10 kJ·mol^{-1}). In addition, as for the TNM1-TA1 complex, increasing the calculation level from CCSD to CCSD(T) has practically no effect on the results, which confirms the earlier conclusion that the CCSD/aug-cc-pVDZ level is sufficient for these tasks.

Here, as in the first TNM1-TA1 complex, the energy of complex formation upon the detachment of the nitro group increases significantly. For NG1, the final complex is the strongest, and for the detachment of the other two nitro groups, the binding energy of the final complex is practically the same and is lower by 14 kJ·mol^{-1}. Accordingly, the strength of the C C–NO_2 bond in NG1 is minimal, while in NG2 and NG3 the binding energies are equal and greater than in NG1. All C–NO_2 bonds in the complex are weaker than in the initial molecule by 23 and 16 (CCSD), by 33 and 20 (DLPNO-CCSD), and by 29 and 15 (DLPNO-CCSD(T)) kJ·mol^{-1}. Thus, due to the formation of the complex, the C–NO_2 bond energy decreases for all nitro groups.

Since the weakest interatomic bonds (and in this case, this is NG1) make the main contribution to the kinetics of the thermal decomposition of the compound **II**, it can be concluded that, in concentrated solutions, the activation energy of thermolysis due to complexation decreases by about 30 kJ·mol^{-1}. This result is also quantitatively consistent with the data for small aliphatic molecules: in the TNM1-TA1 complex, the decrease in the binding energy in the complex is 25 kJ·mol^{-1}.

Thus, in compounds with a trinitroalkyl group, the strength of the C–NO_2 bond (and hence their thermal stability) depends on the structure of the environment. For alkyl substituents, the C–NO_2 bond energy is equal to

200 kJ·mol$^{–1}$, for the triazine ring it is 180 kJ·mol$^{–1}$, and if the compound has a double bond, then the strength of this bond decreases to 150 kJ·mol$^{–1}$.

IV. Conclusion

- The results of this work show that the effect of a tertiary amine on the thermal stability of compounds containing trinitroalkyl groups can be different.
- First of all, we note that for compounds containing double bonds near the amino group, the formation of a complex with the trinitromethyl group either practically does not affect the strength of the C–NO_2 bond in the latter (if it has its own double bond), or even slightly increases the strength of this bond (for tertiary amines with alkyl substituents).
- A completely different situation occurs in the cases of tertiary amines with an alkyl or triazine substituent. For compounds containing trinitroalkyl groups, in complexes with such tertiary amines, the C–NO_2 bond strength is significantly (by 25–30 kJ·mol$^{–1}$) less than in isolated molecules. Accordingly, the thermal stability of these compounds in melts and concentrated solutions, where a significant part of the molecules form complexes, should be significantly lower than in dilute solutions and in the absence of tertiary amines. This result is in full agreement with the experimental data and explains them.

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REFERENCES

[1]. S. Dharavath, J. Zhang, G.H. Imler, D.A. Parrish, J.M. Shreeve, 5-(Dinitromethyl)-3-(trinitromethyl)-1,2,4-triazole and its derivatives: a new application of oxidative nitration towards gem-trinitro-based energetic materials, J. Materials Chem. A., 2017, 5, 4785.

[2]. Y. Xu, C. Shen, Q. Lin, P. Wang, C. Jiang, M. Lu, 1-Nitro-2-trinitromethyl substituted imidazoles: a new family of high performance energetic materials, J. Mater. Chem. A., 2016, 4, 17791.

[3]. R. Haiges, K.O. Christe, Energetic High-Nitrogen Compounds: 5-(Trinitromethyl)-2H-tetrazole and -tetrazolates, Preparation, Characterization, and Conversion into 5-(Dinitromethyl)tetrazoles, Inorg. Chem., 2013, 52, 7249.

[4]. Y. Wang, C. Qi, J.-W. Song, X.-Q. Zhao, C.-H. Sun, S.-P. Pang, Trinitromethyl/trinitroethyl substituted CL-20 derivatives: structurally interesting and remarkably high energy, J. Mol. Model., 2013, 19, 1079.

[5]. V.V. Zakharov, N.V. Chukanov, T.S. Larikova, G.V. Shilov, A.G. Korepin, A.N. Pivkina, K.A. Monogarov, B.L. Korsunskiy, D.V. Korchagin, S.M. Aldoshin, Effect of polymorphic phase transitions on stability of energetic compounds. Thermal transformations of 2,4,6-tris(2,2,2-trinitroethylnitramino)-1,3,5-triazine, Russian Chemical Bulletin, 2020, 69, 118.

[6]. B.L. Korsunskiy, T.S. Larikova, V.V. Zakharov, V.V. Nedel'ko, N.V. Chukanov, A.V. Shastin, Kinetics of Thermal Decomposition of 2,4-Bis(N,N-Dimethylamino)-6-Trinitromethyl-1,3,5-Triazine, Russian Journal of Physical Chemistry B, 2019, 13, 632.

[7]. V.V. Zakharov, N.V. Chukanov, G.V. Shilov, G.V. Malkov, A.V. Shastin, B.L. Korsunskiy, Thermal Conversions of 2,4-Bis(N,N-Dimethylamino)-6-Trinitromethyl-1,3,5-Triazine, Russian Journal of Physical Chemistry B, 2019, 13, 297.

[8]. G. M. Nazin, G. B. Manelis, Thermal decomposition of aliphatic nitro-compounds, Russian Chemical Reviews, 1994, 63, 313.

[9]. 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, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery, Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, Ö. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian 09. Revision C.01, Gaussian. Inc., Wallingford CT. 2009.

[10]. C. Adamo, V. Barone, Toward reliable density functional methods without adjustable parameters: The PBE0 model, J. Chem. Phys., 1999, 110, 6158.

[11]. B.E. Krisyuk, T.M. Sypko, New Thermolysis Routes of Diaminodinitroethylene (DADNE), Propellants, Explosives, Pyrotechnics, 2021, 46, 1079.

[12]. B.E. Krisyuk, D.A. Markin, T.M. Sypko, V.V. Zakharov, N.V. Chukanov, B.L. Korsunskiy, Mechanism of thermal decomposition of nitroguanidine, Chinese Journal of Explosives & Propellants, 2022, in press

[13]. F. Neese, The ORCA program system, Wiley Interdiscip. Rev.: Comput. Mol. Sci., 2012, 2, 73.

[14]. F. Neese, Software update: The ORCA program system—Version 5.0, Wiley Interdiscip. Rev.: Comput. Mol. Sci., 2022, in press.

[15]. S.K. Ignatov, http://qchem.unn.ru/moltran, http://github.com/skignatov/moltran [accessed May 27, 2022].