



Relationship Between Electronic Charges at Nitrogen Atoms of Nitro Groups and Onsets of Thermal Decomposition of Polynitro Arenes

Svatopluk ZEMAN

*Department of Theory & Technology of Explosives,
University of Pardubice
CZ-532 10 Pardubice, Czech Republic
E-mail: svatopluk.zeman@upce.cz
Phone: +420 46 603 8023*

Zdeněk FRIEDL

*Faculty of Chemistry, Brno University of Technology
CZ-612 00 Brno, Czech Republic*

Abstract: Thermal stability of twenty-five polynitro arenes has been examined by means of non-isothermal differential thermal analysis (DTA), and it was expressed as an onset of thermal decomposition, T_D . Electronic charges, q^N , at nitrogen atoms of the polynitro arene molecules were calculated by means of the *ab initio* DFT B3LYP/6-31G** method. The relationship was confirmed between the onsets T_D and squares of the q^N values for the nitro groups that are primarily split off. In the sense of this relationship, the compounds studied fall into five groups. The reason of this diversification and principle of the relationship existence are discussed. It is stated that stabilising influence of the crystal lattice of the studied polynitro arenes can be evaluated by DTA of solutions of these compounds in 1,3,5-trinitrobenzene (TNB).

Keywords: DTA, *ab initio* DFT B3LYP/6-31G**, thermal decomposition, polynitro arenes

Introduction

It is well-known that nitro groups are centres of reactivity in organic polynitro compounds (see Ref. [1] and references herein). Therefore, it is logical that there exist relationships between the ^{15}N NMR chemical shifts δ_{N} of nitrogen atoms in nitro groups of nitramines and the Arrhenius parameters of their thermolysis [1-3], impact sensitivity [1, 2, 4], electric spark sensitivity [1, 5] and their detonation characteristics [1, 6]. The chemical shifts δ_{N} are connected with electron configurations at the respective nitrogen atoms and with steric conditions in the vicinity of the atom. The electronic configuration and steric conditions play decisive roles within the reaction centre of the molecule during its primary fission. Due to this fact, for instance, the thermal decomposition characteristics from differential thermal decomposition (DTA) of polynitro compounds should correlate with electronic charges at nitrogen atoms of the nitro groups primarily reacting in the initiation of the process. In the case of nitramines it was really possible to find a logical relationship between the Kissinger activation energies $E_a \cdot R^{-1}$ and the electron charges at nitrogen atoms of the primarily reacting nitro groups [7].

The ^{15}N NMR data of polynitro arenes have not been available in sufficient amount so far. However, by means of DTA it was possible to determine the thermal stabilities of a major set of these compounds: it was defined as the onset of their thermal decomposition, T_D [8, 9]. Therefore, this paper deals with the relationship between the T_D values and electron charges at nitrogen atoms of the most reactive nitro groups of polynitro arenes. In this respect, the present paper can be considered as an innovation of the previous paper [8].

Experimental

Non-isothermal differential thermal analysis

The measurements were carried out with a DTA apparatus described in more detail elsewhere [10]. The apparatus was constructed in CHEMKO Strážske (Slovakia) in 1971 [10]. Its furnace (an aluminium cylindrical block) was 150 mm in height and its diameter was 108 mm. In the upper part of this cylinder, there were openings for placing test tubes containing samples or

standard. The measurements were carried out under atmospheric pressure, with direct contact between the sample and the reference material (*i.e.* 100 mg Al_2O_3) in air. Open glass test tubes (outer diameter 6 mm, wall thickness 0.8 mm, length 74-76 mm) and the rate of temperature increase of $6\text{ }^\circ\text{C min}^{-1}$ were used. The weights of samples were 80-150 mg for pure polynitro arenes and 90-100 mg for their mixtures with TNB (the compounds given were mixed with TNB at suitable ratios and the mixtures were triturated in an agate mortar). The values of the onsets of exothermic decomposition, T_D , given in Table 1 were obtained using Fe-Co thermocouples enclosed in a stainless injection needle of 19112e No. 36-1 type (Chirana, Stará Turá, Slovakia). For recording temperature difference, an EZ-11 recorder was used (Laboratorní přístroje, Prague, 1970). In process of measurements the recorder worked within the range 0.5 mV on the whole scale, *i.e.* $0\text{ }^\circ\text{C}$ up to $355\text{ }^\circ\text{C}$, with paper speed of 20 mm min^{-1} . Examples of the DTA records of some polynitro arenes are presented in Figure 1.

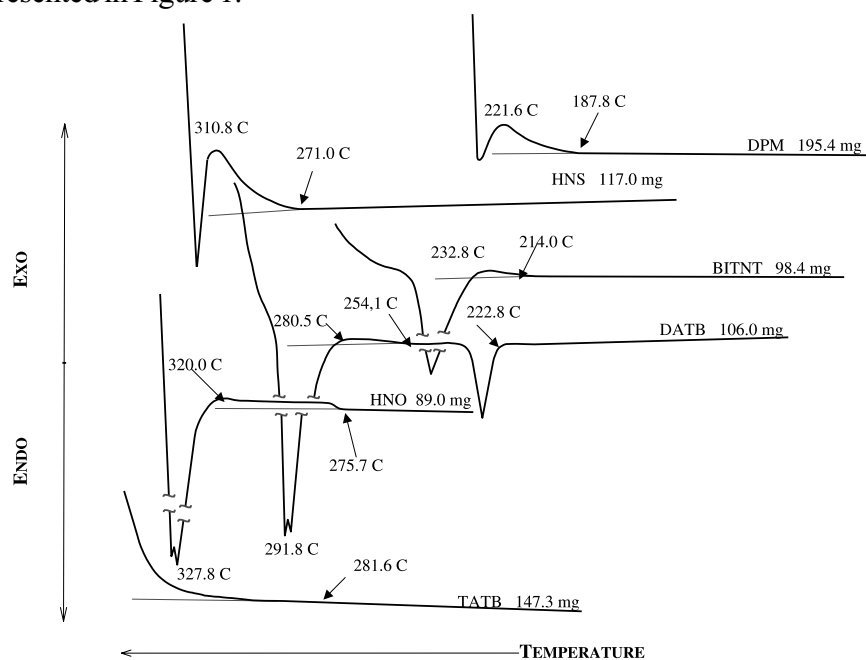


Figure 1. Examples of the DTA records of some studied polynitro arenes. Repainted from dissertation [27].

Electronic charges at nitrogen atoms

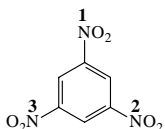
The calculation of electronic charges at nitrogen atoms of the polynitro arenes investigated was carried out by means of the Mulliken population analysis of electron densities, q^N , obtained by *ab initio* DFT B3LYP/6-31G** method [11]. The calculation has been provided the equilibrium geometry of an isolated molecule in the gas phase at 0 K.

A survey of the compounds studied, their codes and the results obtained are presented in Table 1.

Table 1. Survey of electronic charges, q , at nitrogen atoms and values of the onsets, T_D , of thermal decomposition (taken from Refs. [8, 9]) of the polynitro arenes studied:

TNB

1,3,5-Trinitrobenzene

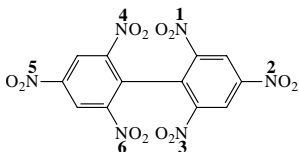


Mulliken charges q	
Nitrogen No	e
N1	0.4182
N2	0.4182
N3	0.4182

onset T_D : 579.1 K for pure substance in the liquid state [8, 9]

HNB

2,2',4,4',6,6'-Hexanitro-1,1'-biphenyl

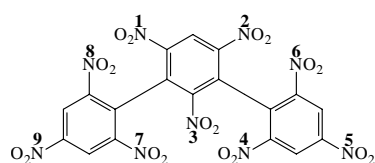


Mulliken charges q	
Nitrogen No	e
N1	0.4046
N2	0.4115
N3	0.4046
N4	0.4046
N5	0.4115
N6	0.4046

onset T_D : 534.3 K for pure substance in the liquid state [8, 9]

NONA

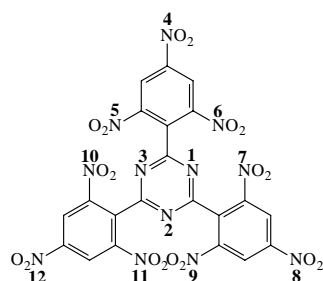
2,4,6,2',4',6',2'',4'',6''-Nonanitro[1,1',3',1'']terphenyl



Mulliken charges q	
Nitrogen No	e
N1	0.4066
N2	0.4081
N3	0.3993
N4	0.4277
N5	0.4124
N6	0.4082
N7	0.4070
N8	0.4266
N9	0.4121

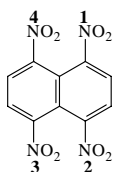
onset T_D : 577.8 K for pure substance in the solid state [8, 9]onset T_D : 489.9 K for 20.61% wt. solution in TNB [8]**TPT**

2,4,6-Tris(2,4,6-trinitrophenyl)-[1,3,5]triazine



Mulliken charges q	
Nitrogen No	e
N1	-0.4060
N2	-0.4076
N3	-0.3983
N4	0.4126
N5	0.4417
N6	0.4362
N7	0.4182
N8	0.4108
N9	0.4369
N10	0.4474
N11	0.4344
N12	0.4132

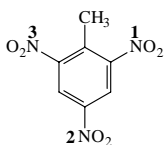
onset T_D : 598.0 K for pure substance in the solid state [8, 9]onset T_D : 449.3 K for 19.14% wt. solution in TNB [8]

TENN**1,4,5,8-Tetranitronaphthalene**

Mulliken charges q	
Nitrogen No	e
N1	0.4031
N2	0.4031
N3	0.4031
N4	0.4031

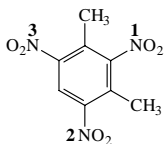
onset T_D : 578.8 K for pure substance in the solid state [8, 9]

onset T_D : 517.0 K for 21.04% wt. solution in TNB [8]

TNT**2,4,6-Trinitrotoluene**

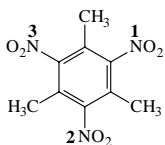
Mulliken charges q	
Nitrogen No	e
N1	0.3734
N2	0.4073
N3	0.3734

onset T_D : 526,2 K for pure substance in the liquid state [8, 9]

TNX**2,4-Dimethyl-1,3,5-trinitrobenzene**

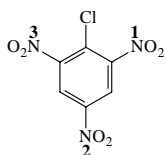
Mulliken charges q	
Nitrogen No	e
N1	0.3375
N2	0.3800
N3	0.3800

onset T_D : 521.3 K for pure substance in the liquid state [8,9]

TNMs**1,3,5-Trimethyl-2,4,6-trinitrobenzene**

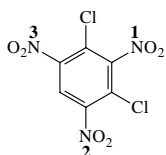
Mulliken charges q	
Nitrogen No	e
N1	0.3404
N2	0.3392
N3	0.3394

onset T_D : 487.6 K for pure substance in the solid state [8, 9]

CTB**2-Chloro-1,3,5-trinitrobenzene**

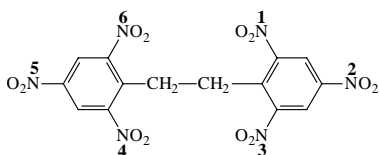
Mulliken charges q	
Nitrogen No	e
N1	0.4243
N2	0.4206
N3	0.4243

onset T_D : 569.3 K for pure substance in the liquid state [8, 9]

DCTB**2,4-Dichloro-1,3,5-trinitrobenzene**

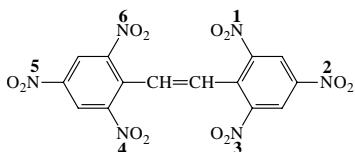
Mulliken charges q	
Nitrogen No	e
N1	0.4342
N2	0.4293
N3	0.4293

onset T_D : 570.2 K for pure substance in the liquid state [8, 9]

DPE**1,3,5-Trinitro-2-[2-(2,4,6-trinitrophenyl)ethyl]benzene**

Mulliken charges q	
Nitrogen No	e
N1	0.3845
N2	0.4078
N3	0.3776
N4	0.3879
N5	0.4107
N6	0.3940

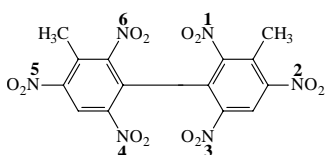
onset T_D : 514.5 K for pure substance in the liquid state [8, 9]

HNS1,3,5-Trinitro-2-[(*E*)-2-(2,4,6-trinitrophenyl)vinyl]benzene

Mulliken charges q	
Nitrogen No	e
N1	0.4054
N2	0.4090
N3	0.4054
N4	0.4054
N5	0.4090
N6	0.4054

onset T_D : 544.2 K for pure substance in the solid state [8, 9]onset T_D : 487.7 K for 9.03% wt. solution in TNB [8]**BITNT**

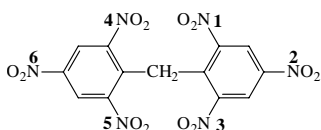
3,3'-Dimethyl-2,2',4,4',6,6'-hexanitro-1,1'-biphenyl



Mulliken charges q	
Nitrogen No	e
N1	0.3470
N2	0.3797
N3	0.4236
N4	0.4236
N5	0.3797
N6	0.3470

onset T_D : 486.6 K for pure substance in the solid state [8, 9]**DPM**

1,3,5-Trinitro-2-(2,4,6-trinitrobenzyl)benzene

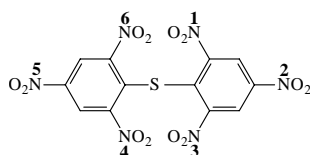


Mulliken charges q	
Nitrogen No	e
N1	0.3924
N2	0.4108
N3	0.3862
N4	0.3862
N5	0.3931
N6	0.4107

onset T_D : 461.2 K for pure substance in the solid state [8, 9]

DIPS

1,3,5-Trinitro-2-[(2,4,6-trinitrophenyl)thio]benzene

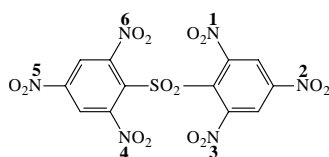


Mulliken charges q	
Nitrogen No	e
N1	0.3775
N2	0.4116
N3	0.3889
N4	0.3728
N5	0.4119
N6	0.3902

onset T_D : 486.6 K for pure substance in the liquid state [8, 9]

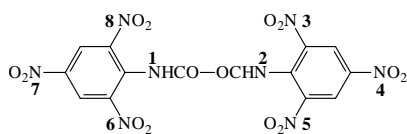
DIPSO

1,3,5-Trinitro-2-[(2,4,6-trinitrophenyl)sulfonyl]benzene



Mulliken charges q	
Nitrogen No	e
N1	0.3808
N2	0.4135
N3	0.3962
N4	0.4173
N5	0.4135
N6	0.4111

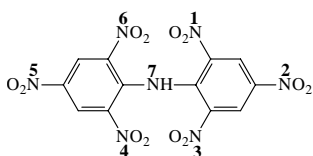
onset T_D : 530.3 K for pure substance in the solid state [8, 9]

HNO N,N' -Bis(2,4,6-trinitrophenyl)ethanediamide

Mulliken charges q	
Nitrogen No	e
N1	-0.5504
N2	-0.5537
N3	0.4271
N4	0.4120
N5	0.4141
N6	0.4278
N7	0.4115
N8	0.4148

onset T_D : 549.7 K for pure substance in the solid state [8, 9]

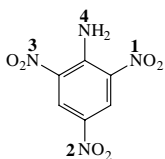
onset T_D : 512.2 K for 8.89% wt. solution in TNB [8]

DPA**2,4,6-Trinitro-*N*-(2,4,6-trinitrophenyl)aniline**

Mulliken charges q	
Nitrogen No	e
N1	0.3904
N2	0.4120
N3	0.4223
N4	0.3904
N5	0.4120
N6	0.4223
N7	-0.5147

onset T_D : 544.2 K for pure substance in the temperature region of its solid-liquid transition [8, 9]

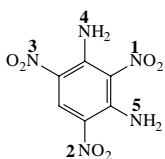
onset T_D : 477.5 K for 20.51% wt. solution in TNB [8]

PAM**2,4,6-Trinitroaniline**

Mulliken charges q	
Nitrogen No	e
N1	0.4218
N2	0.4076
N3	0.4218
N4	-0.5605

onset T_D : 514.4 K for pure substance in the liquid state [8, 9]

onset T_D : 520.6 K for 20.64% wt. solution in TNB [8]

DATB**2,4,6-Trinitrobenzene-1,3-diamine**

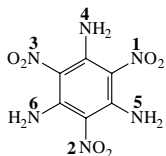
Mulliken charges q	
Nitrogen No	e
N1	0.3971
N2	0.3958
N3	0.3958
N4	-0.5952
N5	-0.5952

onset T_D : 526.8 K for pure substance in the solid state [8, 9]

onset T_D : 521.8 K for 22.92% wt. solution in TNB [8]

TATB

2,4,6-Trinitrobenzene-1,3,5-triamine



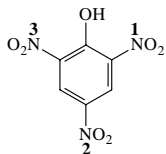
Mulliken charges q	
Nitrogen No	e
N1	0.3829
N2	0.3825
N3	0.3829
N4	-0.6055
N5	-0.6092
N6	-0.6060

onset T_D : 561.2 K for pure substance in the solid state [8, 9]

onset T_D : 507.2 K for 21.64% wt. solution in TNB [8]

PA

2,4,6-Trinitrophenol

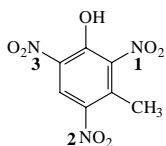


Mulliken charges q	
Nitrogen No	e
N1	0.3985
N2	0.4093
N3	0.3985

onset T_D : 497.6 K for pure substance in the liquid state [8, 9]

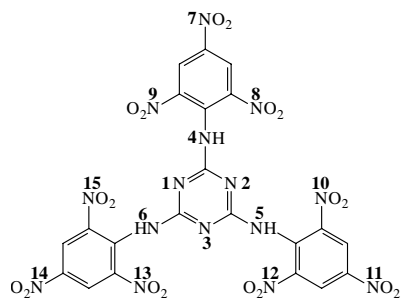
TNCr

3-Methyl-2,4,6-trinitrophenol

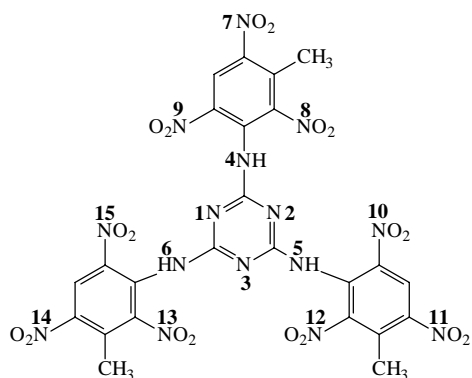


Mulliken charges q	
Nitrogen No	e
N1	0.3738
N2	0.3908
N3	0.4205

onset T_D : 466.0 K for pure substance in the liquid state

TPM*N,N',N''*-tris(2,4,6-trinitrophenyl)-1,3,5-triazine-2,4,6-triamine

Mulliken charges q	
Nitrogen No	e
N1	-0.5472
N2	-0.5621
N3	-0.5484
N4	-0.6163
N5	-0.5727
N6	-0.5883
N7	0.4072
N8	0.3960
N9	0.3727
N10	0.4261
N11	0.4105
N12	0.3940
N13	0.4004
N14	0.4077
N15	0.4390

onset T_D : 550.0 K for pure substance in the solid state [8, 9]**TMPM***N,N',N''*-tris(3-methyl-2,4,6-trinitrophenyl)-1,3,5-triazine-2,4,6-triamine

Mulliken charges q	
Nitrogen No	e
N1	-0.5596
N2	-0.5636
N3	-0.5625
N4	-0.6118
N5	-0.6083
N6	-0.6037
N7	0.3776
N8	0.3735
N9	0.3957
N10	0.3999
N11	0.3789
N12	0.3699
N13	0.3832
N14	0.3792
N15	0.4239

onset T_D : 505.3 K for pure substance in the solid state [8, 9]

Discussion

It is a generally known fact that chemical changes in thermolysis or in initiation of “genuine” polynitro arenes are primarily affected by nitro groups that are sterically hindered [1, 8, 12]. If the polynitro arene contains a functional group with a hydrogen atom attached to it, such as amino, hydroxy, alkyl or other groups, *i.e.* a hydrogen atom bound at the γ -position to the nitro group, then the primary splitting proceeds by the so-called “trinitrotoluene mechanism” [13]: the migration of this hydrogen atom to oxygen atom of *ortho*-nitro group is regarded to be the primary step of thermal decomposition of the corresponding molecules [13-17]. In the case of chloro derivatives, their primary thermal decomposition could perhaps be connected with the chemical interaction between chlorine atom and oxygen of *ortho*-standing nitro group (which is also indicated by negative values of the respective activation entropy ΔS^\ddagger [18]. An analogous interaction of this oxygen atom with sulphur atom in DIPS molecule could also start the decomposition of this substance (again the respective ΔS^\ddagger value is negative [18] – see also the scheme in Ref. [19]). The facts just mentioned specify the most reactive nitro groups in the molecules of the polynitro arenes studied [1]. The nitrogen atoms corresponding to such groups are given in boxes in Table 1. The above-mentioned facts correspond to knowledge of an initiation of the polynitro compounds in general [1]. It must again be stressed that in contrast to the T_D values, the q^N values correspond to equilibrium energy of isolated molecules at 0 K.

An approximate relationship between the q^N and T_D values is presented in Figure 2. In the sense of this relationship, the set of investigated polynitro arenes, both neat and in mixtures (solutions) with TNB, falls into five groups. Group A includes polynitro arenes containing a $-\text{CH}_2-$ linkage in the molecule and HNS (the trinitrotoluene mechanism of primary decomposition), the derivatives of diphenyl sulphide, mono- and dichloro derivatives of TNB (primary fragmentation through five-membered transition state). Among these substances, TNMs, BITNT, HNS and DIPSO begin their decomposition in solid state. The correlation of their data with those of this group indicates that their decomposition is connected with dissolution in the decomposition products, which eliminates the stabilising effect of crystal lattice; this effect can be demonstrated here

by comparing the T_D values of neat HNS with those of its solution in TNB.

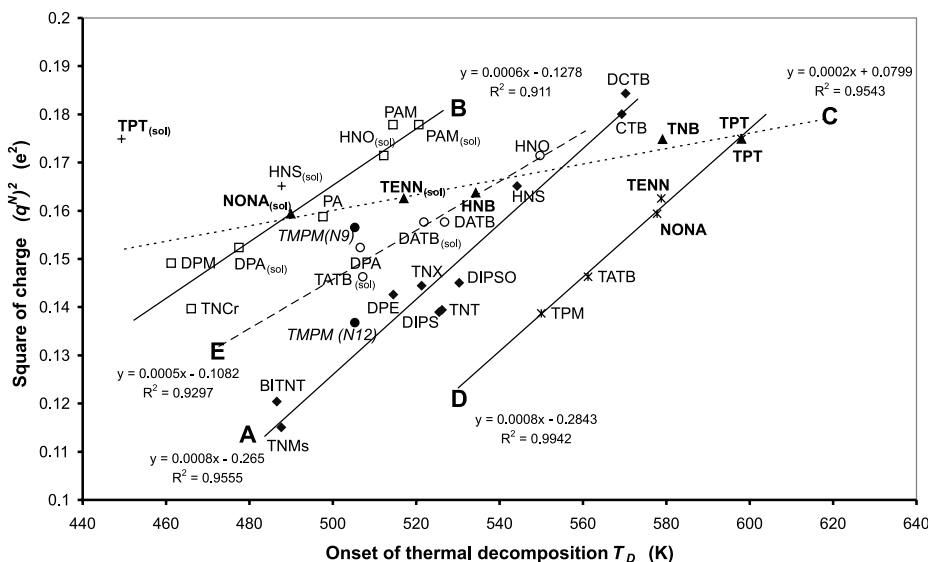


Figure 2. Relationship between the q^N and T_D values. Codes of the genuine polynitro arenes are written by bolted font.

Using the manometric method, Maksimov and co-workers [20] discovered a decrease in the reaction rates of thermal decomposition in the condensed state in the series TNT, TNX, and TNMs. The decrease of the reaction rates in this sense is correlated with the increase of the activation energy, E_a , values. An increase in the E_a values with increasing number of chlorine atoms in the molecule in polychlorotrinitrobenzenes was found by Andreev [20, 21]. Maksimov [20] came to the conclusion that the thermal stability in the condensed state increases with the number of methyl groups in the polymethyl-2,4,6-trinitrobenzene molecule. However, the results of the DTA measurements, *i.e.* trend of the T_D values, provide an opposite piece of evidence [8-10]. This evidence is practically confirmed also by trends in the relationship for group **A** in Figure 2, despite the difference between the stabilities of TNT and TNX is very small. However, the small stability increase is connected with the introduction of additional chlorine substituent in the CTB molecule (in contrast

to methyl group, chlorine substituent exhibits a combination of $-I$ and $+M$ effects).

The compounds in the group **B** also contain a hydrogen substituent γ -standing with respect to nitro group: this hydrogen is bound to nitrogen, oxygen or carbon (DPM with activated methylene group) with the ground-state hybridisation close to sp^2 . The data of HNS in TNB solution logically approach those of group **B** (the sp^2 hybridisation at the carbon atoms of vinyl bridge). The relatively highest scattering of data in this group of nitro compounds can be connected with the presence of hydrogen bonds in their molecules.

The homolysis of C–NO₂ bond should be the primary step of initiation of substances of group **C**, which is also indicated by positive values of the respective activation entropy ΔS^\ddagger [18]. The T_D values correspond to thermal decomposition of “genuine” polynitro arenes in liquid phase (TNB and HNB), in TNB solution (TENN and NONA) and in solid phase for TPT. The correlation of the data of TPT is probably due to the large steric crowding of nitro groups at the 2- and 6-positions of trinitrophenyl groups in its molecule (*i.e.* a striking decrease of the mesomeric interaction of these nitro groups with π -electronic system of the phenyl group). This crowding and the high symmetry of TPT molecule probably result in the highly distinct stabilising influence of its crystal lattice as documented by the extraordinary high difference of T_D values between solid TPT and its solution in TNB (Figure 2). The mentioned effect of crystal lattice somewhat compensates the difference in primary mechanisms of thermal decomposition of substances in the group **D** (here the members TATB and TPM structurally correspond to groups **E** and **B**).

The group **E** of the substances is a kind of analogue of group **B**. The correlation of data for TATB and DATB in solutions with the data of neat DPA, DATB and HNO indicates that the onset of decomposition of the last three substances mentioned could be connected with their dissolution in the decomposition products.

From the results in Ref. [1] it follows that a molecule of energetic material can contain more than one potential reaction centres of initiation. As an example, we can give TMPM with reaction centres in the vicinity of nitrogen atoms N9 and N12 [1]; the data of the second reaction centre mentioned approach those of substances of group **A**, which means that the primary splitting by heat should go by the classic trinitrotoluene mechanism (participation of the methyl group

and 2-NO₂ group in the formation of the activated complex of decomposition).

An attempt at interpretation of the principles underlying the relationships represented in Figure 2 could be based on the following considerations: substances containing strongly polar groups (*inter alia* nitro groups), particularly in crystalline state, are characterised by dominant direct electrostatic interactions and, as the case may be, hydrogen bonds. Let us presume the existence of electric micro-fields in the vicinity of “instantaneous point dipoles” in these molecules. It is known that the point-point (Coulombic) or point-dipole (field) electrostatic interactions can affect some properties of organic compounds [22]. The imposed electric field also lowers, *e.g.*, the energy barrier to migration of interstitials and vacancies in ionic crystals [23]. The electric conductivity, σ , is connected with the diffusion coefficient, F , of this migration through the Einstein-Nernst relationship [23]:

$$\sigma F^{-1} = n \cdot e^2 \cdot k_B^{-1} \cdot T^{-1} \quad , \quad (1)$$

where n is the number of defects, e is electronic charge, and k_B is the Boltzmann constant. If the charge q^N at the nitrogen atom of primarily reacting nitro group is considered as the representative of Coulombic electrostatic interaction during formation of the activated complex of thermal decomposition of the non-ionic polynitro arenes studied (interstitial could be replaced by the activation volume) then Eq. (1) can be rewritten in the following form:

$$(q^N)^2 = (k_B \cdot \sigma \cdot F^{-1} \cdot n^{-1}) T_D \quad , \quad (2)$$

which is similar to the dependences in Figure 2. With regard to the molecular-structure similarities of the substances and the cognate mechanisms of primary processes of their thermal decomposition in the individual groups of polynitro arenes, the term in brackets at the right-hand side of Eq. (2) could be roughly constant within a given group. The highly simplified approach to interpretation of relationships in Figure 2 mentioned above is the reason of their formal difference from Eq. (2). It is suitable to quote here a work of Mathieu *et al.* [25] which describes a relationship between the T_D values and calculated dissociation energies of the weakest X-NO₂ bonds in the isolated molecules of

some polynitro compounds (X can be O, N or C).

The above-mentioned direct Coulombic electrostatic interactions of “instantaneous point dipoles” (especially of a solvent with those of the dissolved compound) and, as the case may be, the subsequent electron transfer can significantly affect the kinetics of thermal decomposition of polynitro compounds dissolved in 1,3-dinitro- or 1,3,5-trinitrobenzene [8, 18, 24]; from an example in Ref. [26] it follows that TNB inhibits the thermal decomposition of 2,2',4,4',6,6'-hexanitroazobenzene. However, the application of TNB is satisfactory for evaluation of stabilising influence of crystal lattice of polynitro compounds.

Conclusions

The existence of the relationship between the charges, q^N , at nitrogen atom of primarily reacting nitro group and the onset of thermal decomposition, T_D , of polynitro arenes might be connected with the electrostatic interaction of “instantaneous point dipoles” at the reaction centre of their molecules. In the sense of this relationship, the compounds investigated can be divided into several groups according to the mechanism of primary splitting and, at the same time, their physical state at the beginning of decomposition; the physical state becomes dominant in the case of polynitro arenes exhibiting a very distinct stabilising influence of crystal lattice. For the purpose of evaluation of this influence in the compounds mentioned it is advantageous to apply the determination of T_D values of their solutions in 1,3,5-trinitrobenzene (TNB), even though TNB cannot be considered to be an inert solvent.

As for the trend of T_D values depending on molecular structure of the compounds studied it can be generally stated that any substitution in the nucleus of 1,3,5-trinitrobenzene is linked with a decrease in the stability of the resulting derivative. Molecular structural as well as intermolecular interaction factors, which are linked with this substitution, can in some cases suppress the thermal reactivity of the resulting polynitro arene to a considerable extent due to the stabilizing influence of the crystal lattice. It must be stressed that in contrast to the results of some other thermoanalytical methods, the facts mentioned above are valid also for polymethyl substitutions in the nucleus of 1,3,5-trinitrobenzene.

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