A Relationship between ^{15}N NMR Chemical Shifts and Detonation Characteristics of Polynitro Derivatives of Arenes and Polyazaarenes [1, 2]

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Abstract: The ^{15}N NMR chemical shifts of eighteen polynitro arenes have been determined. The relationships were found and discussed between the characteristics of detonation and thermal decomposition, on the one hand, and ^{15}N NMR chemical shifts of nitrogen atoms of the primarily split off nitro groups, on the other hand. Also the relationships are specified between the ^{15}N NMR chemical shifts in the solid state of some polynitro derivatives of aminopyridines and aminopyrimidines, on the one hand, and squares of their detonation velocities, on the other. It has been stated that the chemical micromechanisms of primary fission processes of molecules of the studied compounds in the initiation by shock should be the same as in the case of their low-temperature thermal decomposition. Also mentioned is relevance of the modified Evans-Polanyi-Semenov relationship. On the basis of the findings presented it also has been stated that the detonation transformation itself of these polynitro compounds should be preceded by an induction period.

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Introduction

At present it is a generally accepted idea that nitro groups represent the primary cause of initiation reactivity of 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 nitramine groupings of nitramines and the Arrhenius parameters of their thermolysis [2-4, 8], impact sensitivity [1, 2, 5, 8], electric spark sensitivity [1, 6, 8] and their detonation characteristics [1, 7, 8].

An application of such approach to studies of chemical micromechanism of initiation of detonation of polynitro arenes was hindered by a serious problem – the unavailability of ^{15}N NMR spectra of most of them. An analogous application of the easily available ^{13}C NMR chemical shifts of "the bearers" of the most reactive nitro groups in their molecules is limited [1]. In the case of unsubstituted polynitro arenes this application does not provide any useful relationships (the primary fission should consist in the homolysis of $C–NO_2$ bond) [1]. However, for derivatives of the said compounds it is possible to find reliable relationships if the nitro group in the reaction centre of molecule stands in perfect mesomeric interaction with the π-electron system of nucleus at the moment of formation of the transition state [1]. This paper tries to eliminate the said shortness by determination of ^{15}N NMR chemical shifts, δ_N, of nitrogen atoms of nitro groups in some polynitro arenes and some of their aza-derivatives and subsequently by specification and interpretation of relationships between the δ_N values and detonation characteristics of the studied compounds. For comparison, we also present a relationship of the said type for polynitro derivatives of aminopyridines and aminopyrimidines, whose ^{15}N NMR spectra were measured in solid state [9]. With the aim of verification of chemical micromechanism of primary splitting, attention is also given to mutual relationship between the δ_N values and activation energies of thermal decomposition of some of the compounds studied.

Experimental

Substances

The polynitro arenes used were synthesized in the framework of earlier research activities at IEM. Their purity was checked by thin-layer

chromatography using Silufol UV 254 with acetone-cyclohexane as the mobile phase. Their survey is presented in Table 1. Besides these compounds, attention is also given to 3,5-dinitropyridine-2,4,6-triamine (I), 3,5-dinitropyridine-2,4,6-triamine 1-oxide (II), 3,5-dinitropyridine-2,4,6-diamine (III), 3,5-dinitropyridine-2,6-diamine 1-oxide (IV), 5-nitropyrimidine-2,4,6-triamine (V), 5-nitropyrimidine-2,4,6-triamine 1-oxide (VI), and 5-nitropyrimidine-2,4,6-triamine 1,3-dioxide (VII), whose data were taken from Ref. [9].

^{15}N NMR Spectroscopy of the substances in solution

The ^{15}N NMR spectra were measured with a Bruker AMX 360 instrument equipped with a 5-mm broadband probe at the frequency of 36.50 MHz (^{15}N), at 25 °C, and in dimethyl sulphoxide (DMSO-d_6) as the solvent. These spectra were calibrated using external neat liquid ^{15}N-nitromethane ($\delta = 0.0$ ppm) placed in coaxial capillary. The chemical shifts of nitrogen atoms were measured by direct detection. The results are presented in Table 1.

^{15}N NMR Chemical shifts of the substances in solid state

The ^{15}N NMR chemical shifts of nitrogen atoms in primarily leaving nitro groups of aminopyridine molecules (*i.e.* substances I-IV) and aminopyrimidines (*i.e.* substances V-VII) were taken from Ref. [9]. The relationships derived on the basis of these data are presented in Figure 3.

Detonation parameters

The values of detonation velocities, D, of a larger part of the arene derivatives studied were calculated using the known relationships of Kamlet & Jacobs [10] for the maximum theoretical densities of crystals (TMD, *i.e.* for a single crystal). The D value for DCTB was taken from Ref. [11], that for CTB from Ref. [12]. The D values for derivatives of aminopyridines and aminopyrimidines were calculated according to semiempirical method of Rothstein & Peterson [13]; this modified method was also used for estimation of the D value for DMDIPS.

The heats of detonation, Q_{real}, were calculated for single crystals by means of semiempirical relationships devised by Pepekin *et al.* [14]. These values correspond to the experimentally determined heats of detonation in the calorimetric bomb [14]. The Q_{real} values for polynitro compounds with Cl and S heteroatoms in their molecules were obtained by means of prediction methods (see Ref. [15] and the references herein). Table 1 presents both the kinds of data for the studied compounds.

Table 1. Survey of the measured polynitro arenes and polynitro azaarenes, their calculated characteristics of detonation and ^{15}N NMR chemical shifts

Polynitro arenes and polynitro azaarenes (Chemical name)	Code design.	Characteristics of detonation for TMD		^{15}N NMR Chemical shifts (ppm) at the position of the molecule			Note
		D (km s^{-1})	Q_{real} (MJ kg^{-1})	2	4	6	
1,3,5-Trinitrobenzene	TNB	7.27	4.754	-19.31	-19.31	-19.31	
2,2′,4,4′,6,6′-Hexanitrobiphenyl	HNB	7.50	4.689	-20.21	-21.76	-20.21	
5,7-Dinitro-1-(2,4,6-trinitrophenyl)-1*H*-1,2,3-benzotriazole	BTX	7.36	4.364	-20.10	-22.46	-20.10	at benzotriazole ring: 5 has -18.0 ppm; 7 has -21.65 ppm
4,6-Dinitro-2-(2,4,6-trinitrophenyl)-2*H*-1,2,3-benzotriazole 1-oxide	PDNBTO	7.41	4.110	-21.01	-23.63	-21.01	at benzotriazole ring: 6 has -18.63 ppm; 4 has -23.68 ppm
4,6-Dinitro-2,1,3-benzoxadiazole 1-oxide	DNBF	7.86	4.364	-	-22.18	-19.94	at benzoxadiazole ring: 1 has -17.81 ppm; 3 has -6.09 ppm
5,7-Dinitro-2,1,3-benzoxadiazol-4-amine 3-oxide	MADNBF	8.18	4.850	-	-19.69	-23.60	at benzoxadiazole ring: 3 has -14.81 ppm; 1 has -23.60 ppm; -272.2 ppm (NH$_2$)
2-Methyl-1,3,5-trinitrobenzene	TNT	7.02	4.277	-14.44	-20.07	-14.44	
1,1′-Methylenebis(2,4,6-trinitrobenzene)	DPM	7.14	4.560	-16.27	-21.21	-16.27	
3,3′-Dimethyl-2,2′,4,4′,6,6′-hexanitrobiphenyl	BITNT	7.10	4.468	-16.19	-16.87	-20.62	
1,1′-Thiobis(3-methyl-2,4,6-trinitrobenzene)	DMDIPS	6.90^a	3.900^b	-16.49	-21.28	-25.10	
2-Chloro-1,3,5-trinitrobenzene	CTB	7.20^c	4.479^d	-20.90	-22.10	-20.90	
2,4-Dichloro-1,3,5-trinitrobenzene	DCTB	6.80^e	4.040^d	-17.32	-13.98	-12.55	
2,4,6-Trinitroaniline	PAM	7.43	4.263	-14.42	-16.80	-14.41	-286.4 ppm (NH$_2$)
2,4,6-Trinitrophenol	PA	7.57	4.372	-13.51	-16.3	-11.80	
2,4,6-Trinitrobenzene-1,3-diol	TNR	7.53	3.771	-14.90	-15.17	-15.17	
3-Methyl-2,4,6-trinitrophenol	TNCr	7.42	4.056	-8.51	-14.59	-13.21	
2-Methoxy-1,3,5-trinitrobenzene	TNA	7.05	4.249	-18.03	-18.91	-18.02	
2,4,6-Trinitrobenzoic acid	TNBA	7.24	4.809	-18.30	-20.02	-18.30	

Notes to Table 1: **a)** the value calculated according to Ref. 13 (sulfur atom was taken as carbon one); **b)** the value predicted on the basis of results of ^{13}C NMR spectroscopy by means method according to Ref. 36; **c)** the value taken from Ref. 12; **d)** the value taken from Ref. 17; **e)** the value taken from Ref. 11.

Activation energies of thermal decomposition

The data obtained by the Russian manometric method (called SMM [15, 16]) are known to correspond to the primary non-autocatalyzed stage of thermal decomposition of the energetic materials (see Refs. [15, 16] and the references herein). The activation energies, E_a, resulting from the method were used for construction of the relationships in Figure 3. Their survey, together with corresponding references, is published in Ref. [16]. However, the E_a value used here for BTX was obtained for its decomposition in solid state by prediction on the basis of modified Evans-Polanyi-Semenov equation [17].

Results and Discussion

The relationship between detonation characteristics and ^{15}N NMR chemical shifts, d_N, of nitrogen atoms in primarily leaving nitro groups was described and interpreted for the first time in the case of nitramines [7]:

$$X = a \cdot \delta_N + b \ . \tag{1}$$

This relationship divided the nitramines studied into several groups, whose composition was the same as that applying to the squares of detonation velocities ($X = D^2$) as well as to heats of explosion ($X = Q_{real}$) [7]. However, compared with the nitramines, we might expect main complications in the case of polynitro arenes. This especially relates to the influence of mesomeric effect, which in arenes affects the whole molecule and influences its reaction centre. In the molecules of nitramines, on the other hand, this effect is restricted to the nitramino group; the reaction centres in their molecules are then affected by inductive and sterical effects only. Detonation products of nitramines are rich in nitrogen and do not contain solid fractions. However, detonation products of polynitro arenes often contain solid carbon. From the standpoint of molecular structure, this means that the relationship between the detonation velocities and detonation heats [18]

$$D = \sqrt{2\left(\gamma^2 - 1\right)Q} \tag{2}$$

cannot be so universally valid for polynitro arenes as it is for high explosives based on nitramines (the value of coefficient of polytropy, γ, also depends upon the amount of solid portions in the detonation products). The above-said fact is reflected in the comparison between Figures 1 and 2.
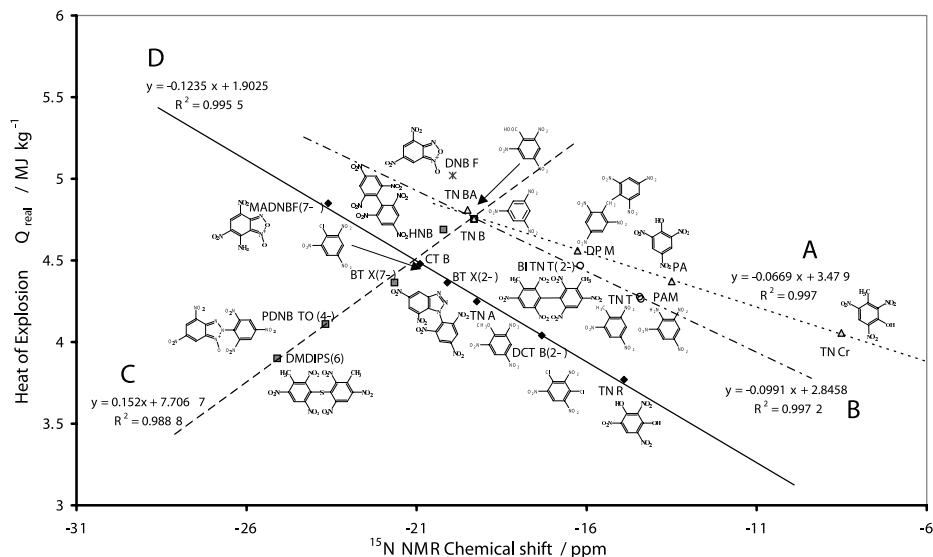
Figure 1. Graphic representation of relationship (1) for $X = Q_{real}$ (the numbers in parenthesis denote the position in molecule).

Figure 1 represents the shapes of Eq. (1) for $X = Q_{real}$. The substances in it are grouped on the basis of the chemical mechanism of primary splitting. Thus the groups A and B represent substances exhibiting the "trinitrotoluene mechanism" of this splitting (the primary fission of polynitro arenes derivatives which have hydrogen atom in the γ-position towards the nitro group – see scheme in Figure 4). The δ_N values of nitrogen atoms in the reaction centre of their molecules are affected by intramolecular hydrogen bonds in group A. Group C represents substances with primary homolysis of C–NO$_2$ bond, and C–S bond in the case of DMDIPS (with participation of nitro group at its 6-position [1, 19]). Group D includes polynitro derivatives characterized besides a more distinct steric effect probably also by the interaction between the *ortho*-standing nitro group and this substituent (mediated by the electron pair at oxygen atom) as the primary chemical process of thermolysis. This can be deduced from the mutual similarity between thermal decompositions of polychloro and polymethyl derivatives of trinitrobenzene [20], or from the results of splitting of *o*-nitroanisole [21]. The BTX data correlate both with the straight line of group C (through the ^{15}N shift of nitro group at 7-position of benzotriazole system) and with the straight line of group D (nitro group at 2-position of trinitrophenyl group). This means that BTX possesses two potential reaction centres of initiation reactivity. Similarly, also in the DMDIPS

molecule there are two such centres [19]: the centre represented by the nitro group at 2-position and the methyl group, and the centre being formed by interaction of oxygen atom of 6-nitro group and the bridge heteroatom of sulphur. As far back as the study [19] and later on also this present paper clearly document the exclusive preference of the second initiation centre mentioned in the DMDIPS molecule. Also the polynitro azaarene PDNBTO correlates only by ^{15}N shift of nitrogen atom of its nitro group at position 4 of benzotriazole system.
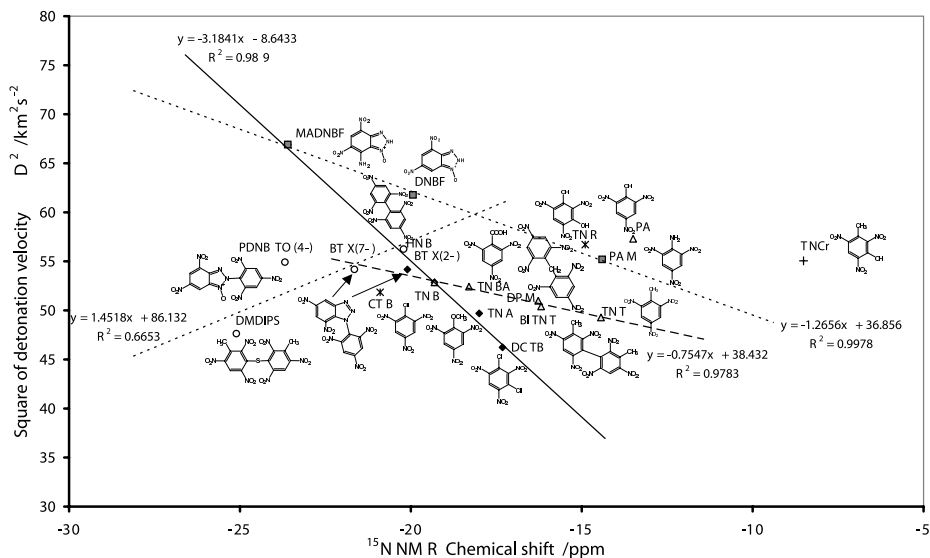

Figure 2. Graphic representation of relationship (1) for $X = D^2$ (the numbers in parenthesis denote the position in molecule).

Replacement of X in Eq. (1) by the square of detonation velocity, D^2, results in Figure 2. As already stated, in contrast to nitramines, there occurs a certain reorganisation of substances in the polynitro arene series: a somewhat larger stress is put here on the similarity of molecular structure (in contrast to Figure 1, a new logical group is created: PAM-DNBF-MADNBF), but the similarity of mechanism of primary splitting is predominating. Groups A and C were practically decomposed, while groups B and D mostly remained maintained.

Figure 3 is analogous to Figure 2, only the δ_N values being derived from NMR measurements of the samples in solid state. These values seem to be less sensitive to the details of molecular structure as compared with the δ_N values determined with the substances in solution.

Similarly to nitramines [2, 4], also in the polynitro arene series there exists a relationship between δ_N values of nitrogen atoms of primarily reacting nitro groups and the activation energies of thermal decomposition. This relationship is documented in Figure 4.
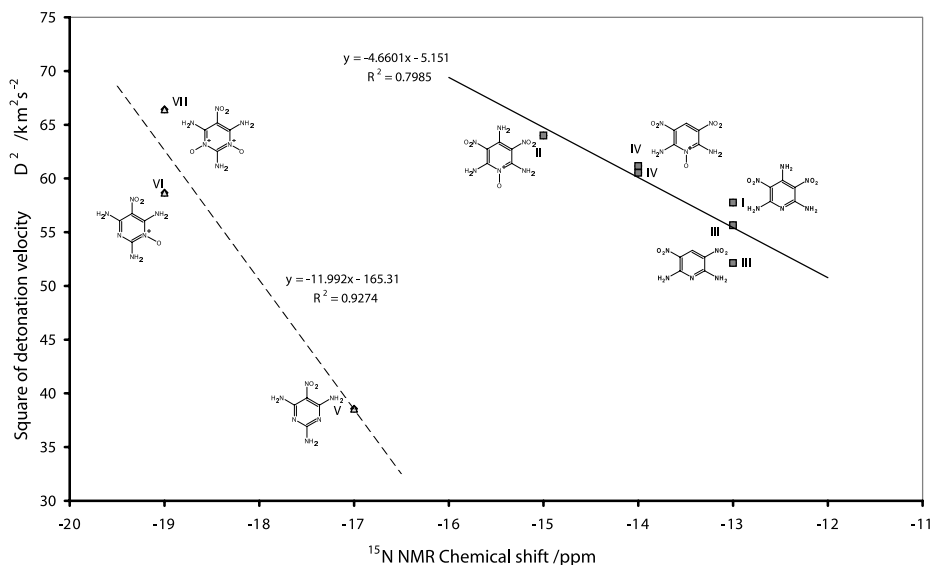

Figure 3. Graphic representation of relationship (1) for $X = D^2$ and for nitroderivatives of aminopyridine and aminopyrimidine:
- the D values were calculated from molecular structure according to Ref. 13 and for substnaces III and IV also by means of Kamlet & Jacobs method [10];
- the values of ^{15}N chemical shifts in solid state were taken from Ref. 9.

In Figure 4 the E_a value of DNBF thermal decomposition in solid state (149.8 kJ mol^{-1} [22] from SMM) might correlate with data of CTB and DCTB. However, the E_a value of its thermolysis in liquid sate (104.0 kJ mol^{-1} [22]) correlates with the group of substances, possesses the trinitrotoluene mechanism of primary step of their decomposition. In both the cases nitro group at the position 4 of DNBF might participate on the first step of benzofurazane system fission through an interaction of this group (mediated by the electron pair at oxygen atom) with aza-atom at position 3.
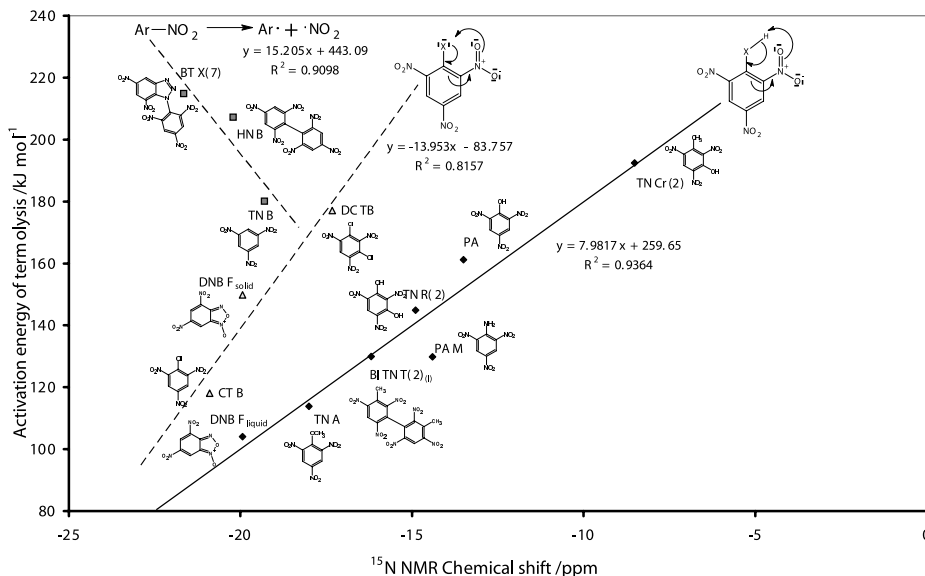
Figure 4. Graphic representation of relationship between activation energies, E_a, of low-temperature thermal decomposition and ^{15}N NMR chemical shifts of the studied compounds (the numbers in parenthesis denote the position in molecule):

- the E_a, values, resulting from Russian isothermal manometric method, were taken from survey [16], for BTX from paper [17] and for DNBF from [22];
- a general scheme of primary step of chemical decomposition is presented in closeness of each line.

The studies of above-mentioned kind have the drawback in that the values of ^{15}N NMR chemical shifts of energetic materials are still available to a very limited extent. However, the results obtained so far in the series of nitramines as well as polynitro arenes and polynitro azaarenes lead to quite identical conclusions. The common result is not only the specification of reaction centre of initiation reactions in the given molecule, but also the confirming of existence of the relationship between the activation energies of low-temperature decomposition and heats of detonation of energetic materials. Comparison of the relationships given in Figures 1-4, and taking into account relationship (2), leads to the following equation

$$E = a \cdot Q + \beta \qquad\qquad (3)$$

which is a modified Evans-Polanyi-Semenov (E-P-S) equation [15] for energetic materials. The original E-P-S equation describes a relationship between activation energies E of most substitution reactions of free radicals and corresponding heats of reaction, ΔH, of narrow sets of substance structures [23]. The equation documents that the strength of bond being split is a decisive factor in the given reaction. A motive stimulus for study of modified E-P-S relationship was the homolytic character of primary fission in an initiation of both the detonation and low-temperature thermal decompositions of energetic materials [15] including explosive mixtures (see *e.g.* Ref. [24]).

The validity of Eq. (3) was also successfully verified for the thermal decomposition of inorganic azides [25] and fulminates [26]. For azides the literature gives activation energy values, E_a, for thermal decomposition within various temperature ranges. In the sense of Eq. (3), however, only those E_a values correlate that correspond to the lowest experimental temperature ranges [15, 25].

All the above-mentioned facts mean that the effect of temperature (*i.e.* thermal decomposition) in classical sense has no application in the process of detonation initiation by shock or impact. Many recent papers have dealt with this and related problems (for example [27-30]). An idea about the initiation of detonation which could be nearest to these facts reads as follows: the excitation of crystal lattice vibration (phonons) after receiving impact or shock [27, 31, 32] is converted into bond stretching frequencies (vibrons) with subsequent spontaneous localisation of vibrational energy in the nitro (explosophore) groupings [28, 29]. Similar, but more detailed, description of this initiation is presented in another idea about electronic excitations facilitated by edge dislocations in explosive solids, which was obtained from application of physics of the solid state aspect to the study of pre-explosion state of heavy metal azides [33, 34].

The correlation of activation energies of low-temperature thermal decomposition (*i.e.* in the range up to 600 K) of energetic materials (in general [1, 2, 4]) in the sense of E-P-S equation thus means that the primary fission processes in this decomposition should be identical with those in the detonation transformation of these polynitro compounds [1, 8]. That also means that the detonation transformation itself of the given substance should proceed at milder conditions than those present at the front of detonation wave or in its reaction zone and should have an induction period [35]. From the point of view of physics of explosion, the necessity of such induction period was also postulated by Dremin [37, 38].

Conclusions

The primary fission processes of polynitro arene molecules in the low-temperature thermal decomposition should be identical with those in the shock initiation. The dominant factor in the initiation should be the electron structure and close neighbourhood of nitrogen atom of the primarily leaving nitro group.

The key atoms in the centres of initiation reactivity in molecules of these compounds can be advantageously determined by means of NMR spectroscopy. From the point of view of physics of explosion, the centres can be taken as "hot spots".

The more complex molecular structure of polynitro arenes makes the problem of their primary fission somewhat complicated, too. If a molecule of these compounds contains several types of substituents, it can contain several potential reaction centres (*e.g.* the BTX, DMDIPS or PDNBTO).

The relationships presented here, namely the modified Evans-Polanyi-Semenov equation, lead to a premise that the primary fragmentation of the studied polynitro compounds in their detonation transformation proceeds at milder conditions than those present at the front of detonation wave or in its reaction zone. That means that the detonation transformation itself of the given substances should be preceded by an induction period.

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