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Thermochimica Acta 451 (2006) 105–114
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Molecular structure aspects of initiation of some highly thermostable polynitro arenes[☆]

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Received 4 July 2006; received in revised form 11 September 2006; accepted 15 September 2006

Abstract

The paper is focused on 2,4,6,4′,6′,2″4″6″-octanitro[l,1′,3′,1″]terphenyl (ONT), 2,2′,2″4,4′,4″6,6′,6″-nonanitro[l,l′,3′,1″]terphenyl (NONA), 2,4,6-tris(2,4,6-trinitrophenyl)-1,3,5-triazine (TPT), *N*,*N*-bis(2,4-dinitrophenyl)-2,4,6-trinitroaniline (NTFA), 1,3,7,9-tetranitro [l,2,3]benzotriazolo[2,l-*a*][l,2,3]benzotriazole-5,11-diium-6,12-diide (TACOT-Z), 2,2′,4,4′,6,6′-hexanitrobiphenyl (HNB), 1,3-dinitrobenzene (1,3-DNB), 1,3,5-trinitrobenzene (TNB) and 2,4,6-triamino-1,3,5-trinitrobenzene (TATB). The initiation reactivity of these substances has been studied by means of the data obtained from non-isothermal differential thermal analysis (DTA), their ignition temperatures, impact sensitivity, the data obtained from the Russian manometric method, the detonation characteristics, DFT B3LYP/6-31G(d,p) charges on the nitrogen atoms of nitro group $q^{\mathrm{N}}(\mathrm{NO_2})$ and net charges of these groups $Q(\mathrm{NO_2})$. For comparison, also the data published and calculated on 2,2′,2″,2‴,4,4′,4″,4‴,6,6′,6″,6‴-dodecanitro[l,3′,1′,1″]quaterphenyl (DODECA) have been included. The paper specifies and discusses the relationships between the results of various methods used, inclusive between their outputs and charges and net charges of the primarily reacting nitro groups in the initiations. Relations of these charges to the characteristics of thermal reactivity, detonation and impact sensitivity confirm presumption about the identity of primary chemical processes in the initiation by heat (low-temperature thermolysis), shock and impact. The technologically most attractive substances can be ordered in the sequence TACOT $\geq$ ONT $>$ TPT $>$ NONA $\gg$ NTFA $>$ TATB according to their decreasing thermal stability.

Keywords: Detonation; DFT B3LYP/6-31G(d,p); DTA; Explosives; Ignition; Impact sensitivity; Thermal reactivity; ONT; NONA; NTFA; TACOT-Z; TATB

1. Introduction

A number of high-energy heterocyclic and carbocyclic substances have been prepared and characterized [1,2] as potential substitutes for l,3,5,7-tetranitro-l,3,5,7-tetrazocane (HMX), 2,4,6-triamino-l,3,5-trinitrobenzene (TATB) and 2,2′,4,4′,6,6′-hexanitrostilbene (HNS) in weapon systems [1,2] and downhole well applications [3–5]. The previously developed 2,4,6,4′,6′,2″4″6″-octanitro[l,1′,3′,1″]terphenyl (ONT) [6,7] and 2,2′,2″4,4′,4″6,6′,6″-nonanitro[l,1′,3′,1″]terphenyl (NONA) [8,9], belong among them too. Earlier prepared 2,4,6-tris(2,4,6-trinitrophenyl)-l,3,5-triazine (TPT) [10,11] and ONT were registered for spacecraft applications [12]. All these “genuine” high thermally stable polynitro arenes continue to be still very attractive from the point of view of their use as an active part of perforators or detonators in downhole well applications [3–5,13].

We were engaged in a study of some molecular structure aspects of the initiation reactivity of these substances [14] and several new findings from this activity are presented in this and preceding paper [15]. For comparison, we have included into this materials also *N*,*N*-bis(2,4-dinitrophenyl)-2,4,6-trinitroaniline (NTFA) [16,17] which is a well-known Russian thermostable explosive for downhole well applications [13] and the most thermostable polynitro polyazaarenes l,3,7,9-tetranitro[l,2,3]benzotriazolo[2,l-*a*][l,2,3]benzotriazole-5,ll-diium-6,12-diide (TACOT-Z) [18] and TATB.

[☆] Presented in a part at the 3rd International Conference IPOEX 2006, Ustroń-Jaszowiec, 20–22 June 2006 (Poland).

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doi:10.1016/j.tca.2006.09.008

2. Experimental and data sources

2.1. Substances

A survey of the substances studied is given in Tables 1 and 4. Polynitro arenes ONT, NONA, TPT, TACOT-Z and TATB were prepared by known methods [7,8,10,18,19], and NTFA was obtained by nitration of triphenylamine in a mixture of anhydrous HNO_3 and H_2SO_4 [26]. As a reference we also used samples of 1,3-dinitrobenzene (1,3-DNB), 1,3,5-trinitrobenzene, 2,2′,4,4′,6,6′-hexanitrobiphenyl (HNB) and published data of 2,2′,2″2‴,4,4′,4″4‴,6,6′,6″6‴-dodecanitro[l,3′,1′,1″]quaterphenyl (DODECA) [20] as well. Purity of the substances studied, with exception of DODECA (the sample was not available), was specified by TLC in the systems hexane/acetone (3:1) and/or hexane/acetone/dichloroethane (8:3:1) [14]. According to the TLC analysis, the polynitro arenes examined were practically pure substances.

2.2. Kinetic parameters of the thermal decomposition

The data obtained from Russian manometric method (SMM) [24–26,29] have been the main source of the Arrhenius parameters (i.e. E_a and $\log A$) of thermal decomposition of the substances studied. Results of the thermo-gravimetric analysis (TGA) can be converted into compatible values by means of the calibration curves [34]. Also a prediction on the basis of modified Evans–Polanyi–Semenov equation was used [35]. Arrhenius parameters of the substances studied are presented in Table 1. Thermostability thresholds, i.e. the maximum theoretical temperature at which a sample of the given explosive can be heated for the period of 6 h without showing changes in its explosive characteristics, were calculated according to Maksimov–Shipitsyn semi-empirical method [36] adopting the Arrhenius parameters; the resulting values are given in Table 2.

2.3. Differential thermal analysis (DTA)

We used a DTA 550 Ex apparatus [24] specially modified in our institute for thermal analyses of explosives. The measurements were carried out at atmospheric pressure, the tested sample being in direct contact with the air atmosphere. The sample tested (0.05 g) was placed in a test tube made of Simax glass, 5 mm in diameter and 50 mm in length. The reference standard was 0.05 g aluminum oxide. We used linear rates of temperature increase, *viz.* 5, 10, and 15 °C min^{-1}. The results of these measurements were treated by means of the software delivered with the DTA apparatus. The results obtained were treated using the Kissinger method [25] which is presented by Fig. 1. The values E_aR^{-1} (i.e. slopes of Kissinger relationship [25], see in Fig. 1) thus obtained were taken as characteristics of thermal reactivity of the studied substances. A survey of onsets, T_D, of the thermal decomposition of studied polynitro arenes is given in Table 2.

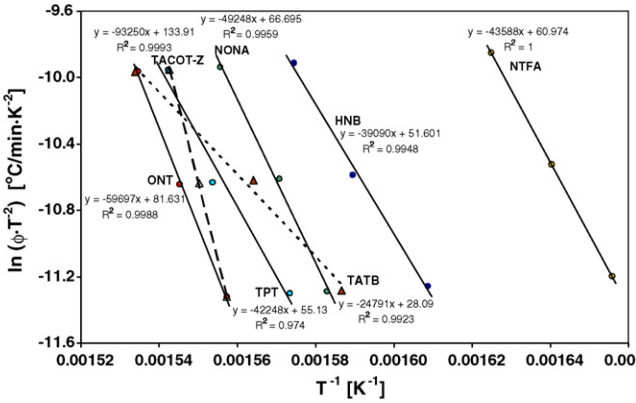


Fig. 1. Evaluation of the DTA outputs by Kissinger method – thermal stability is increasing from the right- to left-hand side (taken from Ref. [15] and completed by the data TATB and TACOT-Z).

2.4. Specification of ignition temperature

The ignition temperature was determined by heating of 100 mg sample of the given substance at a heating rate of 5 °C min^{-1} [27] until the point of ignition of the sample was reached. The corresponding results are presented in Table 2. It was not possible to determine the ignition temperatures of 1,3-DNB and TNB, because both these substances distilled at the experimental conditions. In the case of TPT, a non-violent decomposition took place within the temperature range of 350–360 °C.

2.5. Impact sensitivity

The impact sensitivity data (*the drop heights*) were taken from literature [28,29]. Most of them were measured at Los Alamos National Laboratory and/or Naval Surface Weapons Center, using the Bruceton method [28,29]. In this paper, the drop height data were converted into drop energies, E_{dr}. The impact sensitivity data of the studied compounds are presented in Table 2. The impact sensitivity of NTFA was determined in our laboratory.

2.6. Characteristics of detonation

The values of experimentally determined detonation velocities were taken from literature [13,37] and they are presented in Table 2. Theoretical detonation velocities, D, for theoretical maximum density (TMD) were calculated by means of Kamlet–Jacob method [38], and the maximum real heat of explosion, Q_{real}, was obtained by means of semi-empirical Pepekin et al. method [39]. The corresponding results are presented in Table 1.

2.7. Electronic charges at nitrogen atoms and net charges of the nitro groups

The charges at the nitrogen atoms of nitro groups, $q^N(NO_2)$, and the net charges of the nitro groups, $Q(NO_2)$, of the arenes investigated were obtained by means of Mulliken population

Table 1
A survey of the studied polynitro arenes, their calculated detonation parameters and Arrhenius thermolysis parameters

Data number	Chemical name	Code designation	Calculated[a] parameters of detonation for TMD		Arrhenius parameters of thermal decomposition by means of the Russian manometric method				
			D (km s^{-1})	Q_{real} (MJ kg^{-1})	State of decomposition	Temp. region (K)	E_a (kJ mol^{-1})	log A (s^{-1})	Reference
1	1,3-Dinitrobenzene	1,3-DNB	6.38	3871					
2	1,3,5-Trinitrobenzene	TNB	7.51	4540	Liquid	523–583	180.03	10.9	[30]
3	2,2′,4,4′,6,6′-Hexanitrobiphenyl	HNBB	7.48	4654	Liquid	513–573	207.24	16.1	[32]
4	2,4,6,4′,6′,2″,4″,6″-Octanitro[l,l′,3′,l″]-terphenyl	ONT	7.46	4550	Solid	573–623	281.58	19.5	[33]
5	2,2′,2″,4,4′,4″,6,6′,6″-Nonanitro[l,l′,3′,l″]-terphenyl	NONA	7.60	4751	Solid	523–623	236.30[b]	15.2[b]	[34]
6	2,2′,2″,2‴,4,4′,4″,4‴,6,6′,6″,6‴-Dodecanitro-[1,3′,1′,1″]quaterphenyl	DODECA	7.69	4802	Solid		217.48[c]	15.2[c]	[35]
7	2,4,6-Tris(2,4,6-trinitrophenyl)-[l,3,5]triazine	TPT	7.08	4324	Solid	573–623	269.45	18.2	[33]
		TPT				593–603	225.82[d]	15.2[d]	[30]
8	*N,N*-bis(2,4-Dinitrophenyl)-2,4,6-trinitroaniline	NTFA	7.19	3994	Solid		187.00	11.5	[36]
9	l,3,7,9-Tetranitro[l,2,3]benzotriazolo[2,l-*a*]-[l,2,3]benzotriazole-5,1 l-diium-6,12-diide	TACOT-Z	7.44	4374	Solid	583–623	234.30	15.4	[22]
10	2,4,6-Triamino-l,3,5-trinitrobenzene	TATB	7.92	3992	Solid	557–593	175.00	11.6	[22]
		TATB			Solid		250.62[e]	19.5[e]	[23]

[a] Calculated by means of the Kamlet–Jacobs method [38] for the D values and semi-empirical Pepekin et al. method [39] for the Q_{real} values.

[b] The value obtained by means by TGA [34].

[c] The value obtained on the basis of prediction [35].

[d] The value predicted on the basis of DTA measurements and it might correspond to the quasi-liquid state decomposition [30].

[e] The value obtained by means of DSC [23].

Table 2
A survey of initiation reactivities and detonation characteristics of the polynitro arenes studied

Data number	Polynitro arene code designation	Impact sensitivity (J)		Velocity of detonation D experimental ($\mathrm{km\,s^{-1}}$) for density p ($\mathrm{g\,cm^{-3}}$)			Onsets of exothermic decomposition from DTA		Ignition temperature (°C)	Threshold of thermal stability (°C)
		E_{dr}	Reference	D	ρ	Reference	In state	T_D (°C)		
1	1,3-DNB	39.00	[37]	6.10	1.47	[37]	Liquid	Distilled	Distilled	
2	TNB	24.64	[28,29]	7.30	1.71	[37]	Liquid	Distilled	347[a]	283
3	HNB	20.92	[29]	7.10	1.60	[13]	Liquid	282	354	245
4	ONT	15.73	[29]	7.20	1.72	[13]	Solid	334	370	290
5	NONA	9.10	[29]	7.30[b]			Solid	309	359	280
6	DODECA	9.85	[29]	7.40[b]						270
7	TPT	22.85	[29]	6.80[b]			Solid	340	350–360[c]	283
	TPT						Solid[d]	320[d]	359[e]	
8	NTFA	8.92	[f]	7.20	1.62	[13]	Solid	302	348	285
	NTFA			6.80	1.45	[13]				
9	TACOT-Z	69.00	[29]	7.25	1.64	[37]	Solid	368	374	300
10	TATB	114.33	[29]	7.35	1.80	[37]	Solid	356	355	245

[a] Calculated according to the relationship in Fig. 3 – published boiling point of TNB is 350 °C [41].

[b] The value calculated by means of Eq. (1).

[c] A value of 355 °C was taken for construction of relationships.

[d] This onset has been detected in the solid state at 319.6–320.4 °C by means of the more sensitive DTA method [30].

[e] The published value [40].

[f] Own unpublished results.

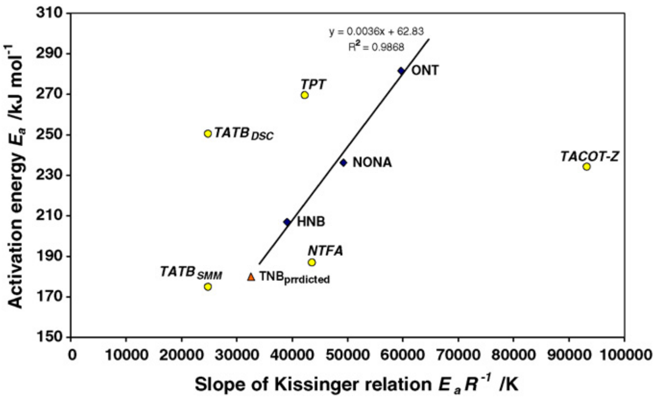


Fig. 2. Relationship between the activation energies E_a of thermal decomposition (that correspond to the SMM results) and the slopes of Kissinger relation, E_aR^{-1} (here the E_aR^{-1} value of 32500 K for TNB was predicted by means of its E_a value – taken from Ref. [15] and completed by the data TATB and TACOT-Z).

analysis of electron densities obtained at *ab initio* DFT level by B3LYP/6-31G(d,p) method under total geometry optimization and without subsequent frequency analysis [21]. The relevant charges are given in Table 3 and the structural formulas with nitrogen atoms numbering of the studied compounds are shown in Table 4. Summary of dihedral angles of twisted nitro/amino groups of non-planar polynitro arenes (mean absolute values in degrees) are present in Table 5.

3. Results and discussion

The thermal stability of the substances in Fig. 1 is increasing from the right- to left-hand side. This order does not correspond with that of the onsets of their decomposition, T_D (cf. Table 4) and with that of the long-term vacuum stability test at 200 °C [42] (in the latter case the thermal stability decreases in the order TPT > ONT > NONA > DODECA > HNB ⋙ TATB). It must be stated that with exception of TATB in the other studied compounds a homo lysis of C–NO_2 bond should be the first step of their initiation [44,45,47,49]. TATB, as a substance with hydrogen atom in γ-position towards to nitro group, primary decays by “trinitrotoluene mechanism” [31,51], i.e. with a transfer of the hydrogen atom through six-membered transition state to oxygen atom of the *ortho–nitvo* group with subsequent homolysis N–OH bond [31,51].

Fig. 2 presents the interrelationship between the activation energies E_a of thermal decomposition (which correspond to the SMM results) and the slopes of Kissinger relationship, E_aR^{-1}. Actually, this is an interrelationship between activation energy values obtained by two different methodologies; therefore, it a reason of very close molecular structure delimitation. Using this relationship, we estimated the value of $E_aR^{-1} = 32{,}500$ K for TNB, which distills at the DTA conditions.

From the point of view of molecular structure, the relationship between ignition temperatures and activation energies E_a (Fig. 3) is more universal. From the solution of the problem of thermal explosion during linear temperature increase it follows that the dependence of critical temperature on the activation energy of decomposition of given energetic material is virtually

Table 3
A survey of the electronic charges, q^N, at nitrogen atoms of nitro groups and net charges, $Q(NO_2)$, of these groups in the studied polynitro arenes (numbering of nitrogen atoms see in Table 4)

Compound	Nitrogen	q^N (NO_2) (e)	$Q(NO_2)$ (e)
1,3-DNB	Nl	0.4088	−0.3603
	N2	0.4088	−0.3603
TNB	Nl	0.4182	−0.3335
	N2	0.4182	−0.3335
	N3	0.4182	−0.3335
HNB	Nl	0.4046	−0.3433
	N2	0.4115	−0.3384
	N3	0.4046	−0.3433
	N4	0.4046	−0.3433
	N5	0.4115	−0.3384
	N6	0.4046	−0.3433
ONT	Nl	0.4015	−0.3333
	N2	0.3974	−0.3313
	N3	0.4098	−0.3390
	N4	0.3989	−0.3331
	N5	0.3958	−0.3322
	N6	0.4100	−0.3388
	N7	0.4306	−0.3423
	N8	0.4310	−0.3434
TPT	N4	0.4126	−0.3349
	N5	0.4417	−0.3072
	N6	0.4362	−0.3059
	N7	0.4182	−0.3113
	N8	0.4108	−0.3366
	N9	0.4369	−0.3083
TATB	Nl	0.3829	−0.5031
	N2	0.3825	−0.5037
	N3	0.3829	−0.5058
NONA	Nl	0.4066	−0.3513
	N2	0.4081	−0.3516
	N3	0.3992	−0.3407
	N4	0.4277	−0.3290
	N5	0.4124	−0.3361
	N6	0.4082	−0.3379
	N7	0.4070	−0.3371
	N8	0.4266	−0.3291
	N9	0.4121	−0.3362
DODECA	Nl	0.4048	−0.3352
	N2	0.4083	−0.3369
	N3	0.4084	−0.3388
	N4	0.4068	−0.3232
	N5	0.4148	−0.3367
	N6	0.4086	−0.3375
	N7	0.4164	−0.3417
	N8	0.3790	−0.3334
	N9	0.4147	−0.3427
	N10	0.4153	−0.3312
NTFA	Nl	0.3983	−0.2977
	N2	0.4064	−0.3400
	N3	0.3983	−0.2985
	N4	0.4109	−0.3560
	N5	0.3910	−0.3545
	N6	0.3907	−0.3540
	N7	0.4110	−0.3560
TACOT-Z	N5	0.4272	−0.3346
	N6	0.4036	−0.3599
	N7	0.4272	−0.3346
	N8	0.4036	−0.3599

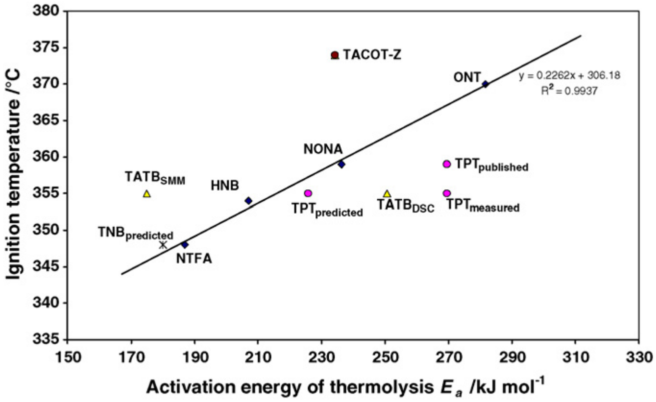


Fig. 3. Relationship between ignition temperatures and the activation energies E_a (that correspond to the SMM results): for a point TPT$_{predicted}$ the published value $E_a = 225.8\,kJ\,mol^{-1}$ [23] was used (taken from Ref. [15] and completed by the data TATB and TACOT-Z).

linear [43]. If in the first approximation the ignition temperature is considered as the critical temperature, then the dependence in Fig. 3 is logical. Almost the same can be stated also about the dependence in Fig. 4. Using this relationship, we estimated the ignition temperature of TNB (347 °C), which is practically identical with its boiling point of 350 °C [41]. The TPT$_{measured}$ data does not fit this correlation, because the E_a value used corresponds to its decomposition in the solid phase. The correlation would be complete if the predicted value $E_a = 225.8\,kJ\,mol^{-1}$ [30] was considered (TPT$_{predicted}$), which perhaps corresponds to its decomposition in the liquid phase. The decomposition of TPT during determination of its ignition temperature takes place in its liquid state (its melting point is 352–353 °C [40] and the published ignition temperature is 359 °C [40] – see the point TPT$_{pubiished}$ in Fig. 3). The DTA method which uses a more sensitive registration of temperature differences recorded the onset of exothermal decomposition of TPT in the solid state at 319.6–320.4 °C [30]. The thermal reactivity of TPT is strongly increased by the presence of substances having the character of a solvent of this polynitro arene [46,53] (in TNB solution, the decrease in the onset of its exothermic decomposition is 143 °C

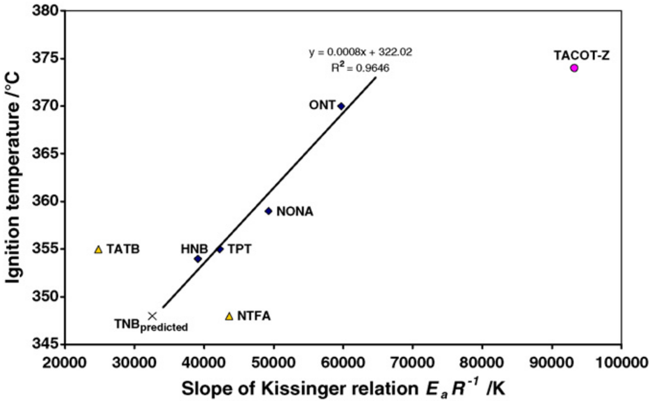
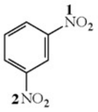
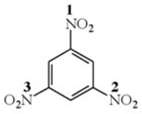


Fig. 4. Relationship between ignition temperatures and the slopes of Kissinger relationship, $E_a R^{-1}$ (here the ignition temperature of 347 °C for TNB was predicted – taken from Ref. [15] and completed by the data TATB and TACOT-Z).

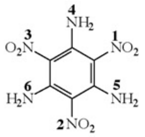
Table 4
A survey of structural formulas of the studied polynitro arenes (numbering of the nitrogen atoms corresponds to the data in Table 3)



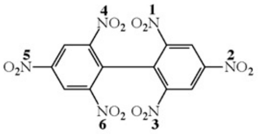
1,3-DNB



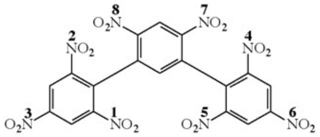
1,3,5-TNB



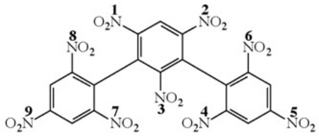
TATB



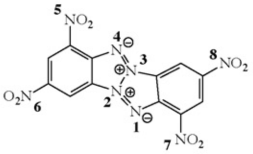
HNB



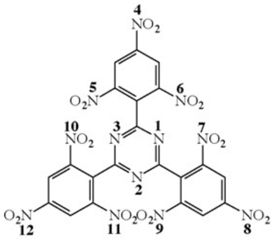
ONT



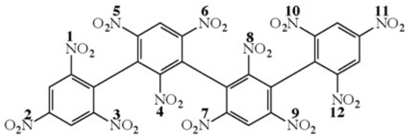
NONA



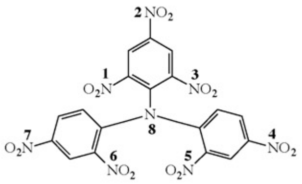
TACOT-Z



TPT



DODECA



NTFA

[53]). This substance has extremely strong stabilizing influence of its crystal lattice [46].

Fig. 5 shows a mutual comparison of the onsets of thermal decomposition and ignition temperatures of compounds studied. A very little difference of the magnitudes in the case of TATB and TACOT-Z is evident. If the onset for TNB is taken to be equivalent its predicted ignition temperature then a good correlation should be found with data of polynitro arenes discussed previously (see Fig. 5). From the point of chemical mechanism of the primary step of thermolysis the resulting group is inhomogeneous; this is typical for strong influence of intermolecular interactions in the given compounds [44,46]. Fig. 5 also shows difference between linearly condensed (HNB, NONA and ONT) and spatially condensed molecules (NTFA and TPT) of polynitro polyarenes. The molecules of TATB are bonded by strong hydrogen bonds into continuous planar gauzes [52] and thus recall the second mentioned kind of arenes.

From the standpoint of temperature threshold, the most stable of the polynitro arenes studied is TACOT-Z and smallest thermostability is characteristic for TATB (see also mentioned result

Table 5
Summary of dihedral angles of twisted nitro/amino groups of non-planar polynitro arenes (mean absolute values in degrees)

Data number	Code designation	C–C rings	Numbering of nitro or amino nitrogen atoms											
			1	2	3	4	5	6	7	8	9	10	11	12
3	HNB	82	20	1	20	20	1	20	–	–	–	–	–	–
4	ONT	86	28	36	2	28	36	2	12	12	–	–	–	–
5	NONA	85	19	19	41	25	2	16	25	16	2	25	2	25
6	DODECA	85	30	2	30	40	20	20	52	17	17	–	–	–
7	TPT	84	–	–	–	1	13	4	23	1	13	1	13	1
8	NTFA	66[a],49[b]	65	2	65	2	31	31	2	–	–	–	–	–
10	TATB	–	10	10	4	0	6	0	–	–	–	–	–	–

[a] Dihedral angle of trinitrophenyl ring C–N bond.
[b] Dihedral angle of dinitrophenyl ring C–N bond.

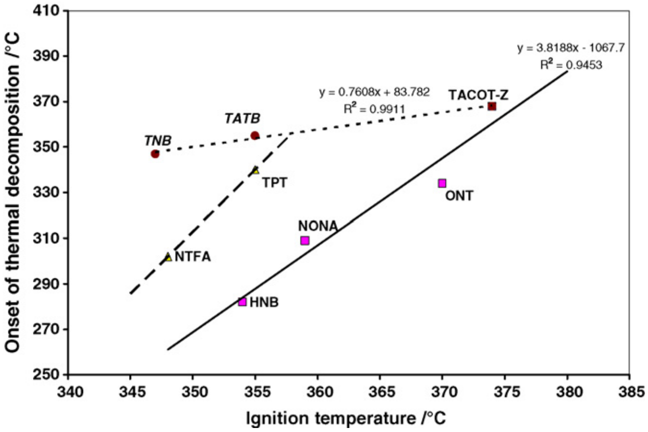


Fig. 5. Relationship between DTA onsets of thermal decomposition and ignition temperatures (presumed value of 347 °C was taken as an onset of thermal decomposition of TNB).

of vacuum stability test [42]). There is a relationship between these thresholds and the slopes, E_aR^{-1}, of Kissinger relation (Fig. 6). Both compared magnitudes are derived from experimental data and the influence of strong stabilizing effect of crystal lattice should detach the NONA and TPT [46] into a separate relationship in Fig. 6.

It is well known that presence of nitro group in molecule is usually a main reason of the initiation reactivity of given compound [44–47]. Also it was verified that the abilities of nitro groups of given molecule to participate in primary initiation processes are different [47–51]. Here is this fact documented by means of the electronic charges at nitrogen atoms of the nitro groups and net charges of the whole groups (see Table 3) and by means presented below relationships derived on their basis (Figs. 7–12). The used charges should correspond to primarily reacting nitro group in the given initiation step – in principle the same approach as postulated in previous papers [46,48,50,51].

Fig. 7 is an analogy of similar dependences in nitramines thermal reactivity [48]. Also in this case the resulting relations are tight. Strong intermolecular interaction in corresponding molecular crystals might be a reason for existence a group of “TATB, NTFA and TACOT-Z” which is inhomogeneous from the point of view of primary fission process. Fig. 8 presents analogous relationships for the net charges of nitro groups. Differences between these two plots can be explained in terms of mutually different parts of “instantaneous point dipoles” at the reaction centre [46] which correspond to the kind of charge applied.

The correlations in Fig. 9 are similar to previously found relationships for *m*-dinitrobenzopolyazaarenes [50]. Also here an influence of stabilizing effect of crystal lattice is observable (group containing TATB). Supplying the $q^N(NO_2)$ charges by

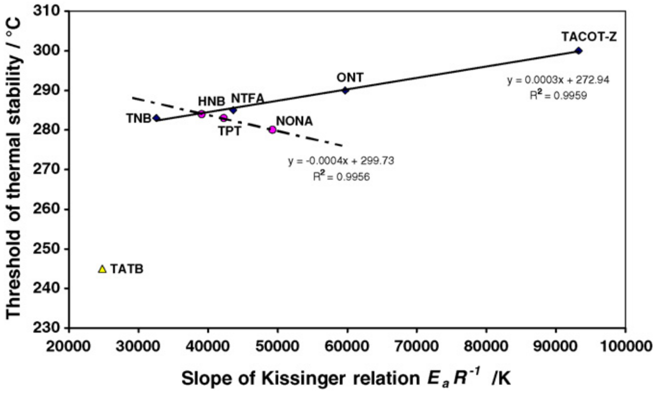


Fig. 6. Relationship between thresholds of thermal stabilities and slopes E_aR^{-1} of Kissinger relation – here an influence of stabilizing effect of crystal lattice manifests oneself in the case of TPT and NONA (see Ref. [46]).

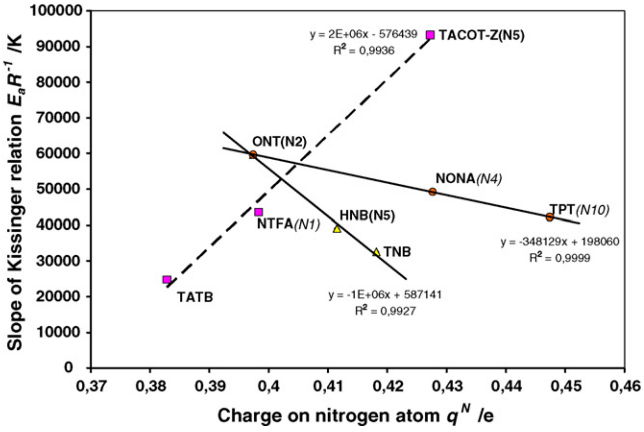


Fig. 7. Relationship between slopes E_aR^{-1} of Kissinger relation and charges on nitrogen atoms $q^N(NO_2)$ the primarily reacting nitro groups in initiation – here an influence of stabilizing effect of crystal lattice manifests oneself in the cases TATB (see Ref. [46]), NTFA and TACOT-Z (in parenthesis are given the respective numbers of nitrogen in the sense of Tables 3 and 4).

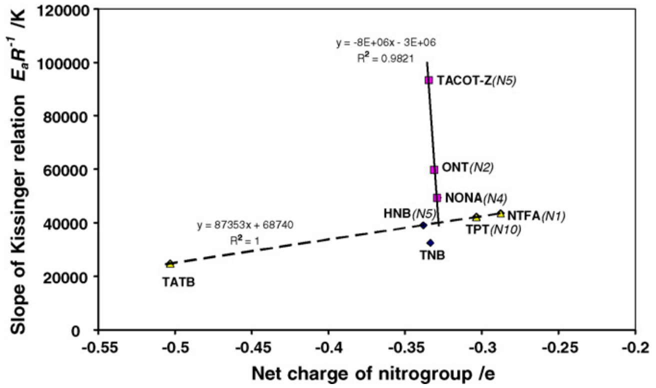


Fig. 8. Relationship between slopes E_aR^{-1} of Kissinger relation and net charges of nitro group $Q(NO_2)$ of the primarily reacting nitro groups in initiation – here an influence of stabilizing effect of crystal lattice manifests oneself in the cases of TATB, TPT (both see Ref. [46]) and NTFA (in parenthesis are given the respective numbers of nitrogen atoms in the sense of Tables 3 and 4).

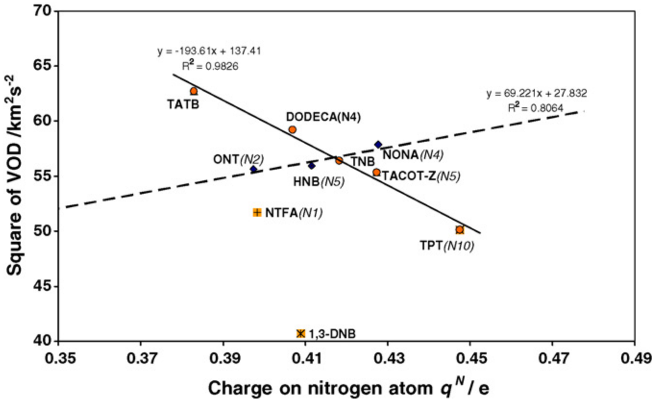


Fig. 9. Relationship between square of detonation velocity (VOD) and charges on nitrogen atoms $q^N(NO_2)$ of the primarily reacting nitro groups in initiation – here an influence of stabilizing effect of crystal lattice manifests oneself in the cases of TATB, TPT (both see Ref. [46]) and DODECA (in parenthesis are given the respective numbers of nitrogen atoms in the sense of Tables 3 and 4).

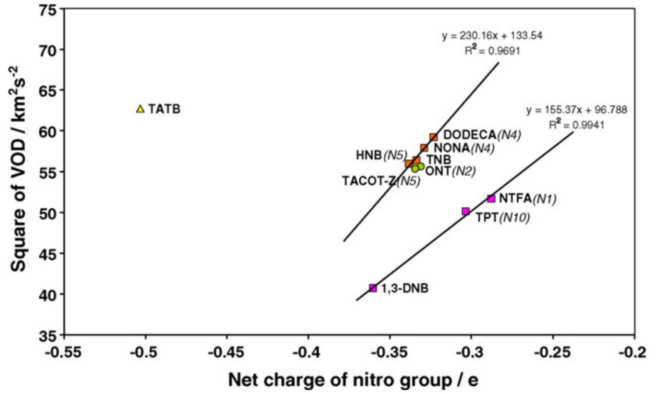


Fig. 10. Relationship between square of detonation velocity (VOD) and net charges of nitro groups $Q(NO_2)$ of the primarily reacting nitro groups in initiation (in parenthesis are given the respective numbers of nitrogen atoms in the sense of Tables 3 and 4).

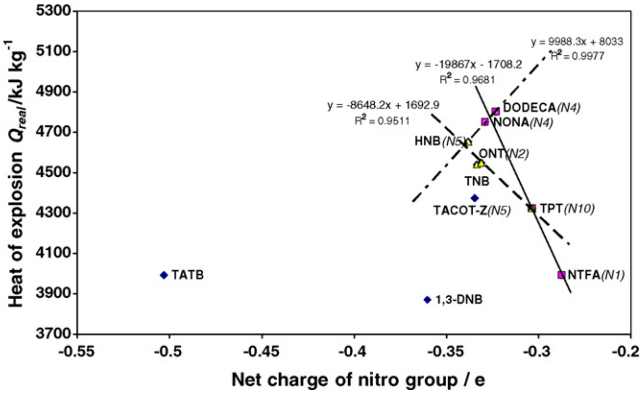


Fig. 11. Relationship between heat of explosion and net charges of nitro groups $Q(NO_2)$ of the primarily reacting nitro groups in initiation (in parenthesis are given the respective numbers of nitrogen atoms in the sense of Tables 3 and 4).

net charges of the nitro groups $Q(NO_2)$ the logical relationships are obtained (Fig. 10). These relationships are more defined from the point of view of molecular structure – they can be included into category of the modified Evans–Polanyi–Semenov relationships [44,45].

Substitution of square of detonation velocity D^2 in Fig. 10 by heat of explosion Q_{real} leads to the plots given in Fig. 11 where molecular structure plays even more important role: the group of NTFA-TPT-NONA gets off as 2-substituted 1,3,5-trintrobenzenes (primary homolysis of C–NO_2 bond in position 1 or 3 should take place in l,3,5-trinitrophenyl-2-group).

Fig. 12 represents very logical relationships: here linear condensed polynitro (poly)arenes are sharply separate from spatially condensed analogues (i.e. NTFA, TPT and TACOT-Z). Data of TATB do not correlate with both groups due to the above-mentioned singularity of primary fission of its molecule.

From what has been found so far it is shown that HNB correlates with calculated charges of its nitrogen atom or nitro group in the position 4. However, according to the correlations of ^{15}N NMR chemical shifts of nitro-nitrogen atoms in molecules of

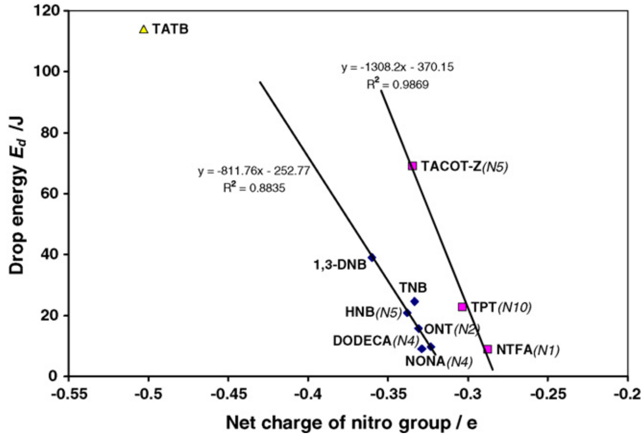


Fig. 12. Relationship between drip energies (impact sensitivity) and net charges of nitro groups $Q(NO_2)$ of the primarily reacting nitro groups in initiation (in parenthesis are given the respective numbers of nitrogen atoms in the sense of Tables 3 and 4).

polynitro arenes with characteristics of their thermal reactivity and detonation, the nitro group in the position 2 primarily reacts in the molecule of HNB [54]. Some attention should be paid to this difference. Nevertheless, the found relationships between electronic charges on the one hand, and the ER^{-1} values, detonation characteristics and drop energies (impact sensitivity) on the other hand confirm again known presumption of the identity of primary chemical processes in the initiation by heat (low-temperature thermolysis), shock and impact [44–48,51,54].

Literature often gives the so-called maximum values of experimentally determined detonation velocities of explosives without specifying the charge densities at which these velocities were determined. For TPT, NONA and DODECA, these velocities can be estimated on the basis of the relationship ($R^2 = 0.8589$) between the maximum theoretical values of detonation velocities, D_{theor}, from Table 1 and the maximum values published, D_{publ}, from Table 2:

$$D_{\text{publ}} = 0.870D_{\text{theor}} + 0.674 \tag{1}$$

4. Conclusions

The relative thermal reactivity of polynitro arenes studied depends upon the method of its specification. Interrelationships can be found between the results of individual methods of specification or evaluation of this reactivity. From the point of view of molecular structure, a clearly defined relationship exists for groups of substances between the activation energies, E_a, obtained from the Russian manometric (isothermal) method and slopes, ER^{-1}, of the Kissinger equation or ignition temperatures. The same is valid for relationship between the ER^{-1} values and ignition temperatures or between these temperatures and onsets of thermal decomposition of the studied compounds. Determining factor of these relationships, besides molecular structure, is also a mechanism of the primary fission of the given molecule in the initiation step. This mechanism is dominating in the relationships between thresholds of thermal stability and the ER^{-1} values.

Possible reaction centre in molecules of the studied compounds can be localized by means of electronic charges on the nitrogen atom of the primarily reacting nitro group or by net charges of such nitro groups. Relationships of these charges with the ER^{-1} values, detonation characteristics and drop energies (impact sensitivities) confirm an accepted presumption of the identity of primary chemical processes in the initiation by heat (low-temperature thermolysis), shock and impact [44–48,50,52,54].

The above-mentioned relationships also reflect the stabilizing effect of crystal lattice. A strong influence of this effect can erase an influence of difference in the primary chemical processes on the allocation of the studied compounds to the individual forms of the founded relationships.

Finally, the results presented in this paper and those published earlier allow arrange the most (technologically) attractive polynitro arenes in the order of their decreasing thermal stability: TACOT ≥ ONT > TPT > NONA > NTFA > TATB.

Acknowledgements

The work was carried partly out under the auspices of the Ministry of Industry & Trade of the Czech Republic as a part of its Research project TANDEM No. FT-TA/049 and partly out under support from the Ministry of Education, Youth & Sports of the Czech Republic as apart of its research project no. MSM 0021627501.

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