

THE RELATIONSHIP BETWEEN DIFFERENTIAL THERMAL ANALYSIS DATA AND THE DETONATION CHARACTERISTICS OF POLY-NITROAROMATIC COMPOUNDS

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ABSTRACT

The thermal stabilities of 37 polynitroaromatic compounds are specified by means of non-isothermal DTA. The initial temperatures of the exotherms T_D , as well as the Piloyan decomposition activation energies, E , of the compounds are determined.

A relationship is derived between ET_D^{-1} and the detonation characteristics of the compounds being measured. It is shown that allocation of the measured compounds to separate forms of the determined relationship is, in addition to thermochemical factors, also determined by the electron configuration and steric conditions in the reaction center of the given molecule.

INTRODUCTION

The detonation velocity, D , Chapman–Jouguet (C–J) pressure, P , and detonation energy, Q , are basic characteristics of the detonation of explosives [1–4]. These characteristics, particularly D , can either be specified experimentally, or obtained by calculation on the basis of the standard hydrodynamic theory [1–4]. This general theory of detonation does not, however, take into account the chemical nature and kinetics of the detonation process but is limited to the heat of explosion, the initial density of the explosive in question, and the structure of the detonation products as well as to their equation of state [1–12].

Approximate semiempirical methods [3–12] have been successfully and widely applied to the calculation of D , P , and Q within the realm of hydrodynamic theory: according to one recent paper [12], the density and chemical formula of the explosive provide sufficient information for the calculation. These semiempirical calculation methods have, however, so far been applied only to the C–H–N–O [3–9] and C–H–N–O–F [12] type of explosives.

Recently, a simple, empirical, linear relationship between the detonation velocity at theoretical maximum density and a factor, F , that is dependent solely upon the chemical composition and structure was postulated for a range of ideal explosives of the C–H–N–O type [13].

A quantitative description of the detonation process, from the point of view of chemical kinetics, has so far not been suggested; the basic problem

in this realm of knowledge is the dependence of the "constant" values of the Arrhenius equation upon pressure and temperature [2,4,14]. An attempt at precision for this explosive change within the kinetics reaction can be found in papers by Bernard [15-17].

Difficulties of interpretation of the detonation process, from the point of view of chemical kinetics, can be accounted for by the absence of a relationship between the characteristics of detonation in organic polynitrocompounds (and explosives in general) on the one hand, and kinetic parameters exhibited by their slow, low-temperature decomposition, on the other. The values of kinetic data for the thermolysis of low-temperature explosives are, however, in their turn, dependent upon the physical conditions of the corresponding measurements. In this connection, it is appropriate to refer to the papers by Robertson [18] and Cook and Abegg [19] who claim that, with increasing polynitro compound thermolysis temperature, there is also an increase in the values of the activation energies and pre-exponential factors, accounted for by the above authors as being due to autocatalysis. Cook, however, is of the opinion [1] that under extreme temperatures, i.e. under conditions of detonation, autocatalysis ceases to exercise any influence, which, in Robertson's opinion [18], leads to a decrease of activation entropy. The ideas of Cook and Abegg [1,19] and Robertson [18] have been confirmed by the results of Pastine [14], who studied the influence exercised by the pressure and volume of the system upon the values of kinetic data obtained from reactions occurring in explosives.

It follows from the preceding discussion, that only such "low-temperature" data can be extrapolated to the conditions of explosion that have been obtained by following the thermal decomposition of the explosive in question without autocatalysis [1,19,20].

For the study of the thermal decomposition of aromatic polynitro compounds within the framework of the present paper, as well as within the framework refs. 21-31, non-isothermal DTA in its simple form was used [23]. As evidenced by the results of the experiments [22-31], the applied conditions of DTA measurements allowed that part of the exothermic decomposition of the examined compounds where autocatalysis had not yet begun to be recorded [22,27-29]. This finding has become the basis of the present paper for investigating the relationship between the data obtained from DTA [21-26,31], on the one hand, and the detonation characteristics of the compounds being measured, on the other. As in previous papers [21-31], the ET_D^{-1} term is taken as the data from DTA, where T_D is the value of the initial exothermic decomposition temperature and E is the Piloyan decomposition activation energy (see ref. 32) within the temperature range immediately following the beginning of the exotherm [21-31]. From among the detonation characteristics, the C-J pressure, P , is given preference in the present paper. As a supplement to the knowledge contained in ref. 30, some molecular-structural aspects of the thermal stability of the studied compounds are mentioned.

EXPERIMENTAL

Apparatus

All measurements were carried out on a DTA apparatus [33] with the rate of temperature increase $6^{\circ}\text{C min}^{-1}$. Measurements were made under atmospheric pressure with the sample and Al_2O_3 reference standard in direct contact with air.

Some of the measurements were carried using Fe—Co thermocouples enclosed in Type 19112e No. 36-1 stainless steel injection needles produced by Chirana Stará Turá, ČSSR; these measurements are labelled as method A. Method B, on the other hand, involved measurements using Fe—Co thermocouples enclosed in capillaries made of Simax glass or Rasotherm glass.

For recording temperature differences, an EZ-11 recorder (Laboratorní přístroje, Prague) was used. During measurements, the recorder worked within a range of 0.5 mV over the whole scale, i.e. 0 up to 355°C and the paper speed was 20 mm min^{-1} . A more detailed description of the apparatus is contained in ref. 23.

Samples

The origin and purity of most compounds measured are described in refs. 23–26 and 31. To be specific, the following substances were involved: 1,3,5-trinitrobenzene (TNB) [6], 2,4-dinitrotoluene (2,4-DNT) [31], 2,6-dinitrotoluene (2,6-DNT) [31], 2,4,6-trinitrotoluene (TNT) [23], 1,3-dimethyl-2,4,6-trinitrobenzene (TNX) [23], 1,3,5-trimethyl-2,4,6-trinitrobenzene (TNMs) [23], 1-chloro-2,4,6-trinitrobenzene (CTB) [23], 1,3-dichloro-2,4,6-trinitrobenzene (DCTB) [23], 1-hydroxy-2,4,6-trinitrobenzene (PA) [24], 3-methyl-1-hydroxy-2,4,6-trinitrobenzene (TNCr) [24], 1,3-dihydroxy-2,4,6-trinitrobenzene (TNR) [24], 1-amino-2,4,6-trinitrobenzene (PAM) [24], 1,3-diamino-2,4,6-trinitrobenzene (DATB) [24], 1,3-bis(methylamino)-2,4,6-trinitrobenzene (DMDATB) [30], 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) [24], 2,2',4,4',6,6'-hexanitrobiphenyl (HNB) [25,26], 3,3'-dimethyl-2,2',4,4',6,6'-hexanitrobiphenyl (DMHNB) [25], 2,2',2'',4,4',4'',6,6',6''-nonanitroterphenyl (NONA) [26], 2,4,6-tris(2,4,6-trinitrophenyl)-1,3,5-triazine (TPT) [26], 2,4,6-tris(2,4,6-trinitrophenylamino)-1,3,5-triazine (TPM) [25], 2,4,6-tris(3-methyl-2,4,6-trinitrophenylamino)-1,3,5-triazine (TMPM) [25], 2,2',4,4',6,6'-hexanitrodiphenylamine (DPA) [25], potassium 2,2',4,4',6,6'-hexanitrodiphenylamine (KDPA) [25], 2,2',4,4',6,6'-hexanitrooxanilide (HNO) [24], 2,2',4,4',6,6'-hexanitroazobenzene (HNAB) [25], 2,2',4,4',6,6'-hexanitrodiphenylmethane (DPM) [25], α , β -bis(2,4,6-trinitrophenyl)ethane (DPE) [25], 2,2',4,4',6,6'-hexanitrostilbene (HNS) [25], 2,2',4,4',6,6'-hexanitrodiphenylsulfide (DIPS) [25], 2,2',4,4',6,6'-hexanitrodiphenylsulfone (DIPSO) [25], 1,5-dinitronaphthalene (1,5-DNN) [31], 1,8-dinitronaphthalene (1,8-DNN) [31], 1,4,5-trinitronaphthalene (TNN) [31], 1,4,5,8-tetranitronaphthalene (TENN) [26].

In addition to the above compounds, the following samples were also used in the present study: 1,3,7,9-tetranitrophenothiazine-5,5-dioxide

(TNPTD), which was obtained [21] from the oxidation of 1,3,7,9-tetra-nitrophenothiazine-5-oxide with CrO_3 in nitric acid and purified by multiple crystallization from dimethylsulfoxide-ethanol mixture, 1,3,7,9-tetra-nitrophenoxazine (TNPO), which was obtained by the nitration of the 1,3-dinitro derivative by nitric acid in glacial acetic acid [21] and purified by crystallization from acetone and then from dimethylformamide, 1,3-bis-(methylnitramino)-2,4,6-trinitrobenzene (DITETRYL), which was obtained by nitration of DMDATB [34] and purified by multiple crystallization from an acetone-ethanol mixture.

Procedure

The conclusions reached in the present paper have been arrived at by considering the DTA measurements of pure substances [21–26,31] with sample weights within the range 77–156 mg. A more detailed description of the procedure is contained in ref. 23.

RESULTS AND DISCUSSION

The average values of the Piloyan activation energies, E , and the initial exothermic decomposition temperatures, T_D , from DTA measurements [21–26,31] are contained in Table 1. The values for compounds 32 and 33 are each the average of two measurements [21] and for compound 37 are the average of three measurements [22,35]. For C–H–N–O type substances, D and P values are given in this survey as calculated according to the method of Kamlet and Jacobs [5]. For some compounds containing further hetero-atoms within the molecule, i.e. for compounds 7, 24, 30 and 31, the C–J pressure was calculated from the published D values at the given densities, ρ , using the relationship [36]

$$P \text{ (GPa)} = 0.2562 D^2 \rho \quad (1)$$

The values in Table 1 which are given to three decimal places are values taken from the literature; the densities quoted to two decimal places are values assumed on the basis of molecular structural analogy and according to Tarver [37].

The difference in DTA results obtained by method A, on the one hand, and method B, on the other, had already been discussed [22–30] and it has been suggested that the difference is due to the influence exercised by the construction material upon the kinetics of the thermolysis of the compounds studied.

A detailed analysis of the results in Table 1 revealed that the relationship between ET_D^{-1} and P , or $P\rho^{-1}$ can best be described by the equation

$$\log\left(\frac{E}{T_D}\right) = b \frac{P}{\rho} + a \quad (2)$$

Equation (2) exhibits, for the compounds being measured, a number of concrete forms whose coefficients were specified on the basis of linear

TABLE 1

Survey of results

Sub- stance no;	Substance	Differential thermal analysis data						Crystal density, ρ (g cm^{-3})	Characteristics of detonation		Ref.
		Method A			Method B				D (km s^{-1})	P (GPa)	
		Initial of exo- therm, T_D (K)	Temp. range (K)	E (kJ mole^{-1})	Initial of exo- therm, T_D (K)	Temp. range (K)	E (kJ mole^{-1})				
1	TNB	579.1		565.78 ^a	587.2		403.70 ^a	1.688	7.27	22.9	5,8
2	2,4-DNT				515.4	516-529	233.27 \pm 11.07	1.495	5.93	13.8	b
3	2,6-DNT				497.7	499-510	181.56 \pm 14.97	1.560	6.14	15.3	b
4	TNT	526.2	529-541	344.53 \pm 1.42	512.7	513-527	212.20 \pm 10.35	1.654	7.02	20.7	65
5	TNX	521.3	523-535	252.31 \pm 22.61	493.1	495-505	146.84 \pm 13.35	1.615	6.76	19.1	b
6	TNMs	487.6	491-501	115.84 \pm 1.09	464.1	465-476	76.25 \pm 10.73	1.480	6.23	15.3	b
7	CTB	569.3	571-585	436.79 \pm 62.99	564.1	565-575	375.33 \pm 48.62	1.797	7.20	24.0	c
8	DCTB	570.2	575-591	263.13 \pm 46.85				1.860			
9	PA	497.6	498-523	216.18 \pm 0.65	504.8	505-517	217.06 \pm 22.30	1.760	7.37	24.7	5
10	TNCr				475.0	477-487	215.79 \pm 2.02	1.680	7.42	23.4	b
11	TNR	447.2		196.53 ^d				1.830	7.71	26.6	b
12	PAM	514.4	516-524	292.16 \pm 3.81	520.8	521-535	225.82 \pm 29.32	1.770	7.54	25.0	b
13	DATB	526.8	531-541	132.42 \pm 10.13	526.2	529-540	228.21 \pm 18.40	1.837	7.71	26.7	65
14	DMDATB				493.7	495-506	242.38 \pm 9.45	1.70			
15	TATB	561.2	563-587	209.77 \pm 0.44	572.1	576-593	238.41 \pm 29.04	1.938	7.95	29.3	65
16	HNB	534.3	538-553	363.21 \pm 27.10	548.0	549-565	319.76 \pm 12.24	1.740	7.50	24.4	65
17	DMHNB	486.6	491-496	257.56 \pm 19.94				1.68			
18	NONA	577.8	586-596	350.46 \pm 5.44	570.6	572-581	316.28 \pm 11.75	1.780	7.61	25.5	65
19	TENN	578.8	583-605	289.70 \pm 11.60	571.3	572-595	283.08 \pm 23.10	1.800	7.30	23.6	65
20	TPT				592.8	595-607	258.46 \pm 20.72	1.670	7.08	21.2	65
21	TPM	550.0	558-568	402.98 \pm 32.80	538.7	539-551	325.32 \pm 31.97	1.750	7.42	24.9	67
22	TPPM	505.3	507-515	227.00 \pm 10.38				1.67			
23	DPA	506.6			503.7	506-515	261.77 \pm 22.93	1.640	7.23	21.95	b
24	KDPA				496.9	498-509	183.92 \pm 13.71	1.850	6.92	21.26	e

TABLE 1 (continued)

Sub- stance no;	Differential thermal analysis data						Crystal density, ρ (g cm^{-3})	Characteristics of detonation		
	Method A			Method B				D (km s^{-1})	P (GPa)	Ref.
	Initial of exo- therm, T_D (K)	Temp. range (K)	E (kJ mole^{-1})	Initial of exo- therm, T_D (K)	Temp. range (K)	E (kJ mole^{-1})				
25	HNO	549.7	553-561	150.67 ± 4.31	543.6	545-555	1.74	7.31	23.17	f
26	HNAB	515.0	519-539	217.32 ± 27.67	518.2	519-532	1.775	7.73	26.30	65
27	DPM	461.2	462-473	180.42 ± 1.65			1.66	7.14	21.53	g
28	DPE	514.5	518-528	362.62 ± 12.20			1.69			
29	HNS	544.2	550-560	306.10 ± 5.13	545.2	547-561	1.740	7.27	23.00	65
30	DIPS	525.5	529-541	398.44 ± 12.26	526.0	528-541	1.660	7.15	21.91	h
31	DIPSO	530.3	537-561	222.04 ± 9.42	526.7	529-549	1.840	5.21	12.89	i
32	TNPTD	491.7	493-509	252.16 ± 13.90			1.70			
33	TNPO	504.7	506-519	230.54 ± 17.44			1.70			
34	1,5-DNN				569.1	570-585	1.578	5.52	12.46	b
35	1,8-DNN				558.3	561-571	1.510	5.38	11.48	b
36	1,4,5-TNN				549.0	541-565	1.60	6.27	16.21	b
37	DITETRYL				436.8	439-448	1.70	7.93	26.97	b

^a Calculated from the ET_D^{-1} value obtained from form I of eqn. (2) (Tables 2 and 3).

^b Calculated according to the method of Kamlet and Jacobs [5].

^c Value of P calculated by means of eqn. (1) from the experimental D value [66].

^d Calculated from ET_D^{-1} value obtained from form II₁ of eqn. (2) (Table 2).

^e Value of P calculated by means of eqn. (1) from the experimental D value [68] for density 1.72 g cm^{-3} .

^f $\Delta H_f = -200.7 \text{ kJ mole}^{-1}$ [35] was used for the calculation according to the method of Kamlet and Jacobs [5].

^g $\Delta H_f = 11.3 \text{ kJ mole}^{-1}$ [35] was used for the calculation according to the method of Kamlet and Jacobs [5].

^h Value of P calculated by means of eqn. (1) from the experimental D value [69] for density 1.66 g cm^{-3} .

ⁱ Value of P calculated by means of eqn. (1) from the experimental D value [59] for density 1.84 g cm^{-3} .

regression analysis and are summed up, together with the standard errors of estimation, in Tables 2 and 3.

The coefficients of eqn. (2) for the group of compounds labelled I (see Tables 2 and 3) were specified using the data for compounds 4-7. To this group, 1,3,5-trinitrobenzene (i.e. compound 1) was also added.

The boiling point of compound 1 is within its decomposition range and the corresponding Piloyan activation energies could, therefore, not be determined [21,22,26]. The values of the ET_D^{-1} terms for this substance were consequently subtracted using form I of eqn. (2) and the C-J pressure and density for compound 1: for DTA measurements, ET_D^{-1} was determined as 0.9770 kJ mole⁻¹ K⁻¹ according to method A and 0.6875 kJ mole⁻¹ K⁻¹ according to method B. As the values of ET_D^{-1} for compound 1 are, from eqn. (2), in logical relationship with the data for compounds 16 and 18 (the group III compounds, see Tables 2 and 3), this procedure may be regarded as justified.

From the calculated ET_D^{-1} values as well as from the experimental values T_D for compound 1, corresponding values of the Piloyan activation energies were obtained. These values of E, as compared with Piloyan activation energies of the other measured compounds containing trinitrophenyl groups within the molecule, are in agreement with the conclusions arrived at earlier [30]. Any hydrogen substitution in trinitrobenzene will lead to a decreased chemical thermal stability of the resulting derivative.

To the most extensive group within the framework of the present paper belong the compounds correlated to form II of the eqn. (2). The substances in question are 9, 10, 12, 13, 15, 23, 25, 26, 29 and 37. What is the common feature of these compounds?

In the nitrogen and oxygen compounds containing free electron pairs, there is an incomplete sp^3 hybridization on the central atoms [38]. On the amine nitrogen of *p*-nitroaniline, however, the electron density is, due to the -K effect of the *p*-nitro group, delocalized towards the benzene nucleus so that it is sp^2 hybridization [39]. By introducing further nitrogroups into the *p*-nitroaniline molecule, the hybridization will be preserved, or even more pronounced (for aspects of conformation of polynitropolyaminobenzenes,

TABLE 2

Coefficients of the individual forms of eqn. (2) for DTA measurements according to method A

Form of eqn. (2) (group)	Structure of group ^a	Value of coefficient			Standard error of estimate
		<i>b</i>	<i>a</i>	<i>r</i>	
I	4, 5, 6, 7 and 1	0.1782	-2.4271	0.9946	0.0304
II ₁	9, 12, 15, 26, 29	-0.0893	0.9420	0.8222	0.0529
II ₂	13, 25, 27	-0.0956	0.7714	0.8524	0.0752
III	1, 16, 18	-0.2782	3.7538	0.9853	0.0261
IV	20, 21, 22	-1.8078	0.1175		

^a Compounds numbered as in Table 1.

TABLE 3

Coefficients of the individual forms of eqn. (2) for DTA measurements according to method B

Form of eqn. (2) (group)	Structure of group ^a	Value of coefficient			Standard error of estimate
		<i>b</i>	<i>a</i>	<i>r</i>	
I	4, 5, 6, 7 and 1	0.1893	-2.7306	0.9972	0.0230
II	9, 10, 12, 13, 15, 23, 25, 26, 29, 37	-0.0629	0.5452	0.9572	0.0172
III	1, 16, 18	-0.1257	1.5385	0.9851	0.0118
V	34, 35, 36	0.1533	-1.7135	0.9928	0.0362

^a Compounds numbered as in Table 1

see refs. 40-48). It is therefore logical to expect sp^2 hybridization to exist on the nitrogen of the amine functions in compounds 12, 13, 15, 23, 25 and 37 (here, the -K effect of the *N*-nitrogroup makes itself felt) and probably also on the nitrogen atoms of the azo bridge in compound 26 (here, however, the length of the corresponding bonds [49] does not confirm the accepted idea too convincingly). Therefore, the idea of sp^2 hybridization on the hydroxyl oxygen atom can be formulated in compounds 9 and 10. sp^2 hybridization does also exist on the carbon atoms of the vinyl bridge in compound 29.

It is a well-known fact that amino [24,50-52], hydroxy [24,50,51] and azo groups [25,53], as well as the vinyl bridge [25,30,54] share directly in the primary step of the thermolysis mechanism of the corresponding polynitro compounds. Analogously to the primary thermolytic process going on in tetryl [55], it is possible to locate the process in compound 37 in the *N*-methylnitramine group.

Results obtained by DTA measurements, according to the method A, however, permit division of the compounds mentioned above into two groups: substances 9, 12, 15, 26 and 29, which are thermolysed mainly in the liquid state [form II₁ of eqn. (2)] and substances 13, 25 and 27, which are thermolysed only in the solid state (form II₂ of eqn. (2)). This is due to the influence of the different interaction intensities with the surface of the stainless steel needle in the liquid and solid states of the compounds being measured (see refs. 25 and 26).

As stated earlier [24], the Piloyan method cannot be used for compound 11. The value of ET_D^{-1} for this compound may therefore be subtracted using the II₁ form of the eqn. (2) and the corresponding detonation data. From this ET_D^{-1} term and the experimentally determined value of T_D , the Piloyan activation energy, *E*, for compound 11 was calculated (see Table 1). From the molecular structural point of view, the value of *E* obtained in this way was related to the value for compound 9 in the way expected.

The II₂ form of the eqn. (2) is well correlated with the DTA data for compound 33. The value of *D* for this compound, calculated by means of this form of eqn. (2) and eqn. (1), is in good agreement with the value obtained according to the method of Rothstein and Petersen [13] (see Table 4). The

II_2 form of eqn. (2) was also applied to the determination of P for compound 32 (see Table 4).

It follows from the preceding discussion that one of the possible explanations as to why the compounds belong to separate forms of eqn. (2) might be electron configuration on the reaction centre in the molecules of the compounds being examined.

Form I of eqn. (2) is well correlated with the data for characterizing compounds 24 and 30. Intramolecular electron interactions going on in their respective molecules can best be assessed if the knowledge obtained in this field from studies of compounds such as $Ph-X-Ph$ (where Ph is phenyl and X is NH, S, Se and O) [56,57] is considered: the non-bonding electron pair of the heteroatom is oriented approximately in a parallel direction towards the π -system of only one aromatic nucleus, none of the nuclei being preferred. The $Ph^-=X^+$ group then interacts with the second nucleus through an induction mechanism [56]. Sulfur atoms can also conjugate, with its vacant d orbitals, with the π -electron system of the nucleus [57]. In this sense, this interaction makes itself particularly apparent in compound 24. As follows from the study of the crystal structure of guanidinium dipicrylamine [58], the benzene nuclei in hexanitrodiphenylamine anion are not equal to one another. This might, among other things, account for the fact that compounds 24 and 23 belong to different forms of eqn. (2).

With regard to the value of the C—J pressure, P , which was calculated from experimental data [59], compound 31 was assigned to form I of eqn. (2). Unlike compounds 24 and 30, this compound contains a polar bridge group, $-SO_2-$, within the molecule which exhibits a strong negatively induced effect. The spatial arrangement of the sulfur atom in sulfones is very similar to a tetrahedron [60]. This configuration ensures a higher rigidity of the molecule of compound 31 compared with compound 30. Together with the cumulation of electronegative substituents in positions 1,1',2,2',6,6', it is the reason for the higher thermal reactivity of the former compound in solution [30].

The methyl group, as well as substituents of the type $Pi-CH_2-$ (where Pi is trinitrophenyl) derived from it, has sp^3 hybridization on its carbon atom and interacts with the aromatic π -system by hyperconjugation. Compound 27, however, has in the molecule an activated methylene group, i.e. it easily forms an anion (sp^2 hybridization on the carbon atom of the methylene group). This fact is the reason why compound 27 belongs to II_2 form of eqn. (2).

The structure of the group of compounds belonging to the form I of eqn. (2) reveals that steric factors in the reaction center of the molecule may be of considerable importance in assigning them to this group. From this point of view, it may be of some interest to compare the increasing volatility of polychloro-2,4,6-trinitrobenzenes [61] and, to some extent, polymethyl-2,4,6-trinitrobenzenes [62,63] with the increasing number of chlorine atoms or methyl groups in the molecule on the one hand, and the decreased C—J pressure, P , on the other. The increased volatility due to multiple substitution is here linked with the deformation of the molecules accompanying the substitution, i.e. with the increasing distances between the centers of the

TABLE 4
Survey of P and D values obtained by means of eqn. (2) and eqn. (1), respectively

Substance	Crystal density (g cm^{-3})	Calculation on basis of DTA data				Calculated detonation characteristics			
		Form of eqn. (2) ^e	Method A		Method B		According to ref. 5		According to ref. 13 D (km s^{-1})
			P (GPa)	D (km s^{-1})	P (GPa)	D (km s^{-1})	P (GPa)	D (km s^{-1})	
DCTB	1.860	I	21.82	6.74					6.62 ^a
DMDATB	1.70	II			23.00	7.25			6.76
DMHNB	1.68	I	20.27	6.83					6.76
DPE	1.69	I	21.56	7.03			21.68 ^b	7.12 ^b	6.99
TMPM	1.67	IV	20.71	6.93			20.02 ^c	6.87 ^c	7.04
DIPSO	1.840	I	21.15	6.67	21.80	6.77			6.75
TNPTD	1.70	II ₂	18.87	6.50					6.60
TNPO	1.70	II ₂	19.76	6.70			18.55 ^d	6.58 ^d	

^a For compound 5, for example, a value for D of 6.12 km s^{-1} is obtained.

^b $\Delta H_f = -29.1 \text{ kJ mole}^{-1}$ [35] was used for the calculation.

^c $\Delta H_f = -37.1 \text{ kJ mole}^{-1}$ [35] was used for the calculation.

^d $\Delta H_f = -62.0 \text{ kJ mole}^{-1}$ [35] was used for the calculation.

^e Form of eqn. (2) numbered as in Tables 2 and 3.

local intermolecular non-bonding interaction (in general, see, for example, Bondi [64]).

An individual position in the $\log(ET_D^{-1})-P\rho^{-1}$ plots is shown by compound 19. As suggested by the knowledge mentioned above, its position may be linked with the form of eqn. (2) for tetranitronaphthalenes. The lower nitrated naphthalenes, i.e. compounds 34–36, do not exhibit, in the sense of eqn. (2), any sign of a relationship towards compound 19, thus constituting an independent group [see form V of eqn. (2) in Table 3]. Similarly, in the case of compounds 2 and 3, another form of eqn. (2) is indicated, also without any relation to compound 4. From what has been said, it follows that, together with the electronic configuration and steric conditions in the reaction center of the molecule, the classification of the compounds into different forms of eqn. (2) is also determined by thermochemical factors.

Taking into account the knowledge of the thermal reactivity of 1,3,5-triazine derivatives [25,30], the existence of one form of eqn. (2) for compounds 20–22 can be assumed. For technical reasons, compound 20 was not measured according to method A and, in its turn, compound 22 was not measured according to method B. To specify the assumed form of eqn. (2), an analysis based on similarity was applied in ref. 22. By comparing the positions of compounds 16, 18, 19–21 and 29 in the $\log(ET_D^{-1})-P\rho^{-1}$ plots for DTA measurements according to method A, on the one hand, and according to method B, on the other, a value for ET_D^{-1} of $0.4798 \text{ kJ mole}^{-1} \text{ K}^{-1}$ was obtained for compound 20 and DTA measurement according to method A. Using the value of ET_D^{-1} found in this way, the corresponding coefficients of eqn. (2) were calculated for the DTA measurements according to method A [see form IV of eqn. (2) in Table 2]. This procedure may be taken as justified, because values of P and D obtained in this way for compound 22 are in good agreement with those later calculated [35] according to the method of Kamlet and Jacobs [5] as well as with the value of D obtained according to the method of Rothstein and Petersen [13] (see Table 4).

Using the derived forms of eqn. (2), values of the C–J pressure, P , were calculated, and then, using eqn. (1), values of D were obtained for compounds 8, 14, 17, 22, 28 and 31–33. The results are contained in Table 4.

So far, attention has been directed towards the relationship of the type shown by eqn. (2). It follows, however, from eqn. (1) that the $P\rho^{-1}$ term is proportional to D^2 . Equation (2) thus represents a relationship between ET_D^{-1} and D^2 .

For an approximate calculation of the detonation energy, Q , the equation

$$Q = 0.3136D^2 \quad (3)$$

can be used [36] where Q is expressed in J g^{-1} . Equation (2) is thought of as also representing a relationship between ET_D^{-1} and Q .

CONCLUSIONS

If the non-isothermal DTA of polynitroaromatic compounds is performed in such a way that part of their exothermic decomposition can be recorded

without being influenced by autocatalysis, then a relationship can be derived between the resulting thermal analysis data and the detonation characteristics of the given compounds. In the present paper, the ET_D^{-1} term is applied as data from non-isothermal DTA in its simple form as well as with contact of the measured compounds with atmospheric air, E being the Piloyan decomposition activation energy in the temperature region immediately after the beginning of the exotherm, T_D .

The relationships found are represented, in the most general form, by the equation

$$\log\left(\frac{E}{T_D}\right) = bX + a$$

where X may be $P\rho^{-1}$ (P is the C-J pressure and ρ is the density of the explosive) the square of detonation velocity, D^2 , or the detonation energy, Q .

It follows from the analysis of the allocation of the measured compounds to separate concrete forms of the given relationship, that in addition to thermochemical factors, decisive roles are played by the electronic configuration and steric conditions within the reaction center of the molecule, which is that part of the molecule where primary fission processes are at work during low-temperature thermolysis.

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