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Review

THERMAL STABILITIES OF POLYNITROAROMATIC COMPOUNDS AND THEIR DERIVATIVES

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ABSTRACT

The thermal stabilities of 33 polynitroaromatic compounds and their derivatives were determined using non-isothermal differential thermal analysis (DTA). For twelve of these, the thermal stabilities of their mixtures with 1,3,5-trinitrobenzene was also determined. The results obtained are discussed from a molecular structural point of view.

The results obtained from DTA measurements are compared with the published data which were derived from the results of the application of the manometric method to the study of the thermal reactivity of polynitroaromatic compounds. The differences which exist between the conclusions reached on basis of DTA application, on the one hand, and those obtained on the basis of the application of the manometric method, on the other hand, are discussed.

Using the published relationship for the calculation of the temperature limit (T_{max}) for the use of polynitroaromatic compounds as secondary thermostable explosives, T_{max} values are calculated for the compounds being measured. A relationship is derived between T_{max} and T_D the initial exothermal decomposition temperature obtained from the DTA of the studied compounds.

INTRODUCTION

Supersonic aircraft, missile development and space exploration required the synthesis of new heat resistant explosives[1–6]. There is also analogous requirement for a number of specialized branches of industry, especially for crude oil and natural gas production[7–9].

Of the explosives which are thermally stable, the most promising seems to be a group of polynitroaromatic compounds[9] and their derivatives. This group is the best potential source of compounds possessing an optimum combination of explosive[2, 3, 8, 10] and thermostable[3, 8, 9, 11] features.

The important starting point for the choice and exploitation of thermally stable polynitrocompounds is the study of their thermal reactivity. In this area of knowledge, Soviet science occupies a dominant position. Russian authors use the manometric method equipped with a glass compensating manometer of the Bourdon type[12-15] to examine the kinetics of thermolysis in the compounds. In this way, kinetic thermolysis data have been obtained over the last twenty years characterizing a great number of organic polynitro compounds and, to a lesser degree, *N*-nitrosoamines. This is evidenced by the publication activities of K. K. Andreev and his co-workers, particularly of Yu. Ya. Maksimov, G. M. Nazin, G. B. Manelis, F. I. Dubovickii, B. L. Korsoonskii and others.

The kinetic data of thermal decomposition obtained from the study of the decomposition of polynitroaromatic compounds in this way were the starting point for Maksimov's calculation of the temperature limit, T_{max}, for the use of these compounds as secondary thermostable explosives[9]. Maksimov also considered experimental data on the thermal explosion of polynitroaromatic compounds and made use of the knowledge of the application of thermally stable explosives in the practical work[8]. By Maksimov and Shipicin's definition[9], T_{max} is the maximum temperature at which a charge of the given explosive can be heated for the period of six hours without showing changes in its explosive characteristics let alone causing autoignition. For calculating this temperature, the authors used the adapted Arrhenius relationship[9]

$$T_{max} = \frac{E_M}{19.133\,(\log A - \log k)} \tag{1}$$

where E_M is the activation energy of the thermal decomposition in J mole^{-1}, log A is the logarithm of the pre-exponent (the two Arrhenius parameters have been derived from the kinetic measurements on the basis of the manometric method), and k is the rate constant which Maksimov takes equal to 10^{-6} s^{-1}.

The thermal reactivity of organic polynitrocompounds, however, can also be studied using thermoanalytical methods[16-30]. The application of differential thermal analysis to the set of problems has also been dealt with recently, to a considerable extent, by a number of Japanese researchers[16, 20-27]. Interpretation of the DTA results, from the point of view of reaction kinetics, has not, however, become common in practical research work[31, 32] and, as far as it had been used in polynitro compounds in the past, it lay predominantly in using the Kissinger method[16, 20, 25].

Recently, the results obtained from the application of the Piloyan method for determining activation energies of decomposition[34, 35] by non-isothermal DTA of polynitroaromatic compounds[11, 35-39, 42, 43] and of polynitrosoamines[40, 41] have become available. The values of the activation energies, *E*, obtained in this way are in a certain relationship both to the degree of purity of the substances[11, 40, 41] and to the structure of its molecule[11, 42]. If the experimental conditions[11, 35] are conveniently selected, the very region of the thermal decomposition of organic polynitro compounds at which there is still no autocatalysis can be recorded. Also, a relationship was found between the initial stages of exothermal decomposition (initial of the exotherm T_D) of polynitroaromatic compounds and their molecular structures[11, 42].

The results of the experiments[11, 35–39, 42, 43] reveal that the most convenient datum following from the application of the Piloyan method in the DTA of polynitroaromatic compounds is the term ET_D^{-1}. The Piloyan activation energy, E, here belongs to the temperature range intermediately after the beginning of the T_D exotherm[11, 35–39, 42, 43].

It was found[39, 42, 43] that the term ET_D^{-1} has a definite relationship to the entropy of thermolysis activation, though, in itself, it cannot be considered to be entropy[39, 42, 43]. Also, the character of the relationship of this therm to the Arrhenius parameters E_M and log A was specified; the Arrhenius parameters have been derived by Andreev and Maksimov and their coworkers from the results obtained from the application of the manometric method to the study of the thermolysis of aromatic polynitrocompounds in condensed form. The equations found have the general form[36–39]

$$\frac{E}{T_D} = b\,E_M + a \tag{2}$$

$$\frac{E}{T_D} = b_1 \log A + a_1 \tag{3}$$

The results[36–39, 43] provide evidence that the relationship of individual polynitroaromatic compounds to the given shapes of eqns. (2) and (3) is conditioned by both the affinity of the primary thermolytic processes and the geometry of the molecule.

Using the DTA measurements[11, 35–39, 43] as well as eqns. (2) and (3), E_M values and log A values were obtained for aromatic polynitrocompounds whose kinetics of thermal decomposition had not been described in the existing literature[38, 39].

The DTA method is, in its simple form[11, 35], very feasible and readily available. It offers to the synthetical chemist, when selecting compounds which are thermally stable, the possibility of readily obtaining quick primary information on their thermostability by determining the initial of the exotherm T_D of the given substance.

From the point of view of technological practice, the meaning of eqn. (1), that is the value of T_{max}, is of paramount importance for the thermal stability of polynitroaromatic compounds. This is the reason why, in addition to the molecular structural aspects of the thermal stability in this group of substances, attention has been paid, in the present paper, to the specification of the relationship of these values to those of the initial stages T_D of the exotherm.

EXPERIMENTAL

Apparatus

All measurements were carried out on a Marcin design DTA apparatus[35] (Chemko Strážske, 1971). The rate of temperature increase used was 6°C min^{-1}.

Measurements were made in air under atmospheric pressure in direct contact with the sample and the comparison standard (Al_2O_3).

Part of the measurements was carried out using Fe–Co thermocouples enclosed in Type 19112e No. 36-1 stainless 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, a EZ-11 recorder (Laboratorní přistroje, 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. 35.

Samples

The origin and purity of most compounds measured are described in refs. 11, 36–39 and 43. To be specific, the following substances are involved: 1,3,5-trinitrobenzene (TNB)[39]; 2,4,6-trinitrotoluene (TNT)[36]; 1,3-dimethyl-2,4,6-trinitrobenzene (TNX)[36]; 1,3,5-trimethyl-2,4,6-trinitrobenzene (TNMs)[36]; 1-chloro-2,4,6-trinitrobenzene (picrylchloride, CTB)[36]; 1,3-dichloro-2,4,6-trinitrobenzene (DCTB)[36]; 1-amino-2,4,6-trinitrobenzene (picramide, PAM)[37]; 1,3-diamino-2,4,6-trinitrobenzene (DATB)[37]; 1,3,5-triamino-2,4,6-trinitrobenzene (TATB)[37]; 2,2',4,4',6,6'-hexanitrobiphenyl (HNB)[38, 39]; 3,3'-dimethyl-2,2',4,4',6,6'-hexanitrobiphenyl (DMHNB)[38]; 2,2',2'',4,4',4'',6,6',6''-nonanitroterphenyl (NONA)[39]; 1,4,5,8-tetranitronaphthalene (TENN)[39]; 2,4,6-tris-(2,4,6-trinitrophenyl)-1,3,5-triazine (tripicryltriazine, TPT)[39]; 2,4,6-tris(2,4,6-trinitrophenylamino)-1,3,5-triazine (tripicrylmelamine, TPM)[38]; 2,4,6-tris(3-methyl-2,4,6-trinitrophenylamino)-1,3,5-triazine (TMPM)[38]; 2,2',4,4'-6,6'-hexanitrodiphenylamine (dipicrylamine, hexyl, DPA[38]; potassium 2,2',4,4',6,6'-hexanitrodiphenylaminate (KDPA)[38]; 2,2',4,4',6,6'-hexanitrooxanilide (HNO)[37]; 2,2',4,4',6,6'-hexanitroazobenzene (HNAB)[38]; alpha, beta-bis(2,4,6-trinitrophenyl)-ethane (1,2-dipicrylethane, DPE)[38]; bis(2,4,6-trinitrophenyl)methane (dipicrylmethane, DPM)[38]; 2,2',4,4',6,6'-hexanitrostilbene (HNS)[38]; 2,2',4,4',6,6'-hexanitrodiphenylsulfide (dipicrylsulfide, DIPS)[38]; 2,2',4,4',6,6'-hexanitrodiphenylsulfone (dipicrylsulfone, DIPSO)[38]; 1-hydroxy-2,4,6-trinitrobenzene (picric acid, PA)[37]; 1,3-dihydroxy-2,4,6-trinitrobenzene (styphnic acid, TNR)[37]; 3-methyl-1-hydroxy-2,4,6-trinitrobenzene (trinitrocresol, TNCr)[37]; 1,3,7,9-tetranitrophenothiazine-5,5-dioxide (TNPTD)[11, 43]; 1,3,7,9-tetranitrophenoxazine (TNPO)[11, 43].

In addition to the above compounds, the following samples were also measured in the present study: 1,3-bis(methylamino)-2,4,6-trinitrobenzene (DMDATB) which was obtained from the reaction in ethyl alcohol of DCTB with methylamine and purified by crystallization from dimethylformamide–acetone mixture; 2,4- and 2,6-dinitrotoluenes (DNT) were obtained from technical products using repeated crystallization from ethyl alcohol.

Procedure

The conclusions reached in the present paper have been arrived at by considering the DTA measurements of pure substances[11, 36–39] with sample weights within the range 80–150 mg. A more detailed description of the procedure is contained in ref. 35.

In the modification of the samples by addition 1,3,5-trinitrobenzene (TNB), the given compound was mixed with TNB in suitable ratios and the mixture thus obtained was mulled in an agate dish. The weighed amounts of the sample used, in this case, ranged from 90 to 110 mg.

The values of the initial stages of the endothermal changes, subtracted from the thermograms of the pure substances being measured are, in the present paper, the average of two measurements[11, 43].

The given values of the initial of the exotherms (T_D) in the method A are the average of two measurements, the average of three or four measurements being used for method B. The T_D values for thermolysis in mixtures with TNB are the average of two measurements[11, 43].

RESULTS AND DISCUSSION

A survey of the results obtained from the DTA measurements with pure compounds are contained in Table 1 together with the Arrhenius parameters E_M and log A which were derived, for the substances being measured, by Andreev[14] and Maksimov and coworkers[9, 44–48]. In Table 1, the values of E_M and log A calculated from the results of DTA measurements using eqns. (2) and (3) are presented for some compounds, viz. nos. 10, 17, 18, 19, 20, 22, 23, 24, 27, 28, 32 and 33. Using eqn. (1), values of T_{max} were then calculated.

As be seen from the survey in Table 1, some of the examined substances were measured both by method A[11, 35–39] and method B[35–39, 43]. Comparison of the T_D values obtained for the given compound by each of the methods, reveals a marked influence of the material from which the thermocouple container is made on the thermal stability of the substances being measured[36–39]. There is also a positive influence exercised by the contact of compounds 1, 9, 12, 15, 16, 26, 29, and possibly also of 30, with the glass surface of the capillary (method B) on their thermal stability. For compounds 9, 12, and 15, these facts have been interpreted[37] as being due to non-binding interaction of hydrogen atoms of intra- and intermolecular hydrogen bonds of the molecules of these substances with protophilic centres on the surface of the glass capillary.

The reduced thermal stability of compounds 4, 5, and 6 during their contact with the glass surface can be interpreted by the catalytic effect of the alkaline components of the glass on the thermolysis of these substances[36].

During the DTA measurements according to the method B, reduced thermostability was also recorded in compounds 18, 19, 21, 23, 25, and 31. This is true of the compounds that possess a stabilizing influence of the crystal lattice.

The stabilizing influence of the crystal lattice[50] can be removed by dissolving

TABLE 1

SURVEY OF THE RESULTS FOR PURE COMPOUNDS

Substance no.	*Substance*	*Initial of endothermal changes (K)*		*Initial of exotherm, T_D (K)*		*Arrhenius parameters*			*T_{max} (K) calculated according to*	
		Polymorph. trans.	*Fusion*	*Method A*	*Method B*	*E_M (kJ mole^{-1})*	*log A (s^{-1})*	*Ref.*	*eqn. (1)*	*eqn. (4)*
1	TNB		394.4	579.1	587.2	180.03	10.9	14, 46	556.1	551.6
2	2,4-DNT	333.1	341.1		515.4	139.56	9.0	44	486.3	493.6
3	2,6-DNT		335.7		497.7	198.87	14.3	44	512.0	477.1
4	TNT	342.7	354.8	526.2	512.7	144.44	9.3	45	493.4	497.2
5	TNX		454.7	521.3	493.1	146.95	9.1	46	508.6	485.8
6	TNMs		511.9	487.6	464.1	185.05	12.3	46	528.5	455.9
7	CTB	340.8	355.3	569.3		118.07	5.7	44	527.4	540.3
8	DCTB		402.3	570.2		177.09	10.5	44	560.9	541.0
9	PA	369.0; 376.6	394.9	497.6	504.8	161.18	11.7	14	475.9	480.4
10	TNCr		376.2		475.0	87.20	5.5	37		455.2
11	TNR	421.9	445.1	447.2		144.86	11.2	14	440.6	426.9
12	PAM		460.1	514.4	520.8	129.79	7.1	14	517.8	495.5
13	DATB	492.8	552.7	526.8	526.2	196.77	13.2	9, 47, 48	535.6	503.6
14	DMDATB		> 520.0		493.7	212.45	17.7	Calculated according to ref. 37	468.5	473.3

15	TATB		> 600.0	561.2	572.1	175.00	11.6	9, 14, 48	520.9	538.1
16	HNB		508.8	534.3	548.0	207.24	16.1	14	490.1	516.4
17	DMHNB		505.6	486.6		148.18	10.02	38	483.4	466.5
18	NONA		> 600.0	577.8	570.6	214.11	14.1	39	556.7	544.3
19	TENN	542.9	> 600.0	578.8	571.3	223.05	15.0	39	555.8	545.0
20	TPT	414.1	621.5		592.8	225.82	15.2	39	556.7	559.3
21	TPM		575.7	550.0	538.7	257.06	19.0	48	537.4	519.2
22	TMPM		> 580.0	505.3		116.18	7.2	38	460.0	484.2
23	DPA		515.5	506.6	503.7	223.70	16.4	38	521.9	484.1
24	KDPA		> 530.0		496.9	107.57	5.2	38	502.0	476.4
25	HNO		588.6	549.7	543.6	215.62	16.0	9, 14, 48	512.2	521.2
26	HNAB		486.1	515.0	518.2	121.83	6.8	9, 48	497.5	494.6
27	DPM		493.2	461.2		92.95	5.2	38	433.8	441.3
28	DPE	409.4	493.3	514.5		209.03	15.3	38	510.5	492.7
29	HNS		583.7	544.2	545.2	183.80	12.0	9, 48	533.9	519.5
30	DIPS	434.4	504.3	525.5	526.0	178.77	12.0	9	519.1	502.9
31	DIPSO		> 600.0	530.3	526.7	106.76	5.6	9, 48	481.0	505.3
						200.96	11.7	48	593.4	471.4
32	TNPTD	555.8	572.3	491.7		143.79	8.5	Calculated according to ref. 37	518.9	
33	TNPO		539.9	504.7		158.55	10.0	Calculated according to ref. 37	517.9	483.7

TABLE 2

SURVEY OF THE RESULTS FOR MIXTURES OF PURE SUBSTANCES WITH TNB

Substance no.	*Substance*	*Amount of substance in mixture (wt. %)*	*Thermal stability of mixture*		*Values T_{max} calculated from eqn. (4)*
			Initial temp. of exotherm, T_D (K)	*Ref.*	
12	PAM	20.64	520.6	11	498.3
13	DATB	22.92	521.8	11	499.3
15	TATB	21.64	507.2	11	486.0
18	NONA	20.61	489.9	11	469.7
19	TENN	21.04	517.0	43	495.0
20	TPT	19.14	449.3	43	429.0
23	DPA	20.51	477.5	11	457.7
25	HNO	8.89	512.2	11	490.6
27	DPM	20.39	438.4	11	417.5
28	DPE	21.40	509.4	11	488.0
29	HNS	9.03	487.7	43	467.6
31	DIPSO	9.11	449.6	43	429.4

the substance. In an inert solvent and in a sufficient dilution, it would be theoretically possible to determine the thermal stability of the isolated molecule of a given compound.

For the study of molecular structural dependences in thermolysis of organic polynitrocompounds, some authors selected TNB as solvent[49, 51–53]. As follows from ref. 49, TNB inhibits the thermal decomposition of compound 26. In the study of the thermal decomposition of 1,3,5-trinitro-1,3,5-triazacyclohexane in TNB solution[53], formation of 2,4,6,3′,5′-pentanitrobiphenyl was proved in the static system at temperatures from 173 to 184°C. These facts are evidence that TNB cannot be considered to be an inert solvent.

In the framework of refs. 11 and 43, TNB was made use of as admixture solvent for judging the stabilizing influence of the crystal lattice in compounds 13, 15, 18, 19, 20, 23, 25, 27, 29, and 31. The mixture of pure substances with TNB were measured according to method B[11, 43]. The results thus obtained are presented in Table 2. For the sake of comparison, substances 12 and 28 were also measured. The amount of the substance being measured in the mixture with TNB was selected so as to bring about a reliable recording of the initial stages of the decomposition. For substances 25, 29, and 31, lower contents had to be used in mixture with TNB; due to their lower solubility in TNB, there was a considerable misrepresentation of the initial stage of exothermic changes because of the influence of endothermic changes of dissolution[11].

In ref. 11, thermal stability which had been specified by exclusion of the crystal lattice influence was defined as "chemical thermal stability". The chemical thermal stability of explosives is, in general as well as in relation to the molecular structure, a most complex problem, or set of problems. Thermal decomposition of organic explosives is very complicated due to a wide variability of its mechanism with the temperature. This is, in its turn, conditioned by the complexity of the molecular structure of organic compounds in general.

It follows from the analysis of the relation between the molecular structure and thermal reactivity of the aromatic hydrocarbons and their derivatives[11] that the thermal stability of the compounds is reduced by the substitution going on in the aromatic nucleus which enables particularly n-π^* transitions within the molecule or which causes the growth of the overall π-electron energy in the system or which causes deformation of the valence angles (i.e. steric effects). At the same time, thermal reactivity is here increased by the presence of intra- and intermolecular hydrogen bonds or by CT-complex formation[11]. Benzene can be considered as one of the most stable organic compounds[11]. Any substitution in its nucleus is linked with a decrease of thermal stability in the derivative formed[11, 54, 55]. The only exceptions are penta- and hexafluorination[54].

This item of general knowledge on the thermal reactivity of aromatic hydrocarbons can also be applied to polynitroaromatic compounds containing 2,4,6-trinitrophenyl groups in the molecule[11]. Among these, the most stable compound is TNB, and any hydrogen substitution in its nucleus leads to a decrease of thermal stability of the resulting derivative[11]. Using the data contained in Table 2, all that has been said can be evidenced by the results of the measurements in the present paper, excepting, of course, compounds 2, 3, 19, 32 and 33, which are not derived from TNB.

The thermal reactivity of TNB derivatives (and of polynitroaromatic compounds in general) is increased by multiple substitution in its nucleus. In the survey contained in Table 1, however, there is indication of a slight increase in thermal stability of compound 8 compared with compound 7; the same increase in thermal stability is indicated in the survey contained in Table 2, i.e. of compound 13 compared with compound 12.

Considering the values of Piloyan activation energies, E, for the first two mentioned compounds[11, 36], compound 7 exhibits a slightly decreased thermal stability compared with compound 8.

As far as compounds 12 and 13 are concerned, ref. 11 states that their chemical thermal stabilities are practically identical; introduction of the one amino group into the TNB molecule excercising roughly the same influence upon thermal stability as introduction of two amino groups. Trisubstitution by the amino group is, however, closely linked with a decrease of chemical thermal stability in compound 15 (see Table 2).

The negative influence of the increasing steric hindrance on chemical thermal stability can best be exemplified by the series of compounds 1, 16, 18, by the series 4, 28, 17, and by the series 4, 5, 6. The steric effect in the first of these series is, in the remaining two series, enhanced by the influence of the chemical entity of the alkyl substituents.

The influence of the chemical entity of the bridge bond in dipicryl- (generally, in polypicryl compounds) upon their thermal reactivity can, to a considerable degree, enhance steric influence. This is the case in compound 27, where the bridge bond is activated methylene, or in compound 23, in the presence of an intramolecular hydrogen bond.

The trend of chemical thermal stabilities in the series of compounds 4, 28, and 29 (Tables 1 and 2) is in agreement with the knowledge gained by Rosen and Dickinson[51]. A lower chemical thermal stability of compound 29 compared with compound 28 is, indubitably, caused by "more acidic hydrogen atoms" of the vinyl bridge (sp^2 hybridization on the carbon atoms of the bridge). This fact, no doubt, enables a cyclic activated thermolysis complex to be formed.

Analogously, in compound 20, the chemical reactivity of the 1,3,5-triazine nucleus has a negative influence on thermal stability of this substance in solution. 1,3,5-Triazine in itself is, from the chemical point of view, an unstable compound[56, 57]. The thermal stability of the derivatives of 1,3,5-triazine decreases with the increasing positive substitution in its nucleus[58]. In this connection, it is necessary to state that the picryl group is, in electrophilic substitution reactions, characterized by a positive induction effect[59, 60], a marked steric effect.

Steric factors can exercise a negative influence not only on chemical thermal stability, but also, at the same time, on the reaction rate of the thermolysis of aromatic polynitrocompounds. For example, Maksimov et al.[46] discovered a decrease in reaction rates of thermal decomposition in the condensed state in the series of compounds 4, 5 and 6. This decrease, the authors infer, are linked with the increasing deviation of nitrogroups from the plane of the benzene nucleus (see also ref. 36) in the given sequence of compounds.

Maksimov et al.[46] also found that the decrease of reaction rates in a sense is correlated by the increase of E_M values. The increase in E_M with increasing number of chlorine atoms in the molecule in TNB polychloroderivatives was found by Andreev[14]. Taking this knowledge into account, Maksimov et al.[46] arrived at the conclusion that the thermal stability of the polymethyl derivatives of TNB in the condensed state increases with the number of methyl groups in the molecule[46].

The results of DTA measurements[36], however, confirm the opposite fact, i.e. they are in agreement with the general knowledge of the thermal stability of TNB derivatives. As good correlations were also obtained, using eqns. (2) and (3), for the compounds 4, 5, 6, 7 and 8[36], this discrepancy must, above all, be attributed to mutually conflicting interpretations of the concept "thermal stability". In the conception of Maksimov[46] the concept involves more or less thermodynamic stability. From the application of non-isothermal DTA[35, 36], results are obtained on the thermal limit which, if exceeded (under given experimental conditions), causes chemical changes to take place within the given compound.

For a perfect specification of the thermal stability of organic polynitro- and polynitroso compounds, the selection of suitable procedures and experimental methods is of paramount importance[11, 36, 40]. The course of the thermal decomposition of these compounds is generally followed from its secondary phenomena[11], i.e. from the quantity or quality of the reaction products, or from the thermal effects of the reaction, respectively. In practice, preference of one of the mentioned decomposition phenomena should be determined by the character of the decomposition. For the substances whose thermal decomposition results mostly in products of low molecular weight and whose process in itself does not go through numerous intermediate stages (nitrosamines, nitramines, polynitroaliphatic compounds), the change in the amount of reaction products can be followed along with the reaction time and in relatively good agreement with the thermolysis kinetics.

In the polynitro compounds of the aromatic series, however, thermal decomposition of the molecule can take place via a whole series of relatively stable intermediates[52, 61–63], but its induction period need not necessarily be linked with a more pronounced evolution of gaseous products; this observation was confirmed, for example, by the decomposition of compound 4 at high temperatures[64].

Since is possible to register induction periods of the thermal decomposition in both types of thermolysis using thermoanalytical methods, particularly in DSC and DTA, their application gives a more realistic order of thermal stabilities of the compounds than would follow from measurements carried out by gasometric methods.

Regardless of differences in principles and the possible application of DTA on the one hand, and the manometric method on the other hand, quantitative relationships[36–39] were found between the results derived from the application of the two methods; the relationships are represented, as mentioned already, by eqns. (2) and (3). Also, T_{max} values can be considered, to a considerable extent, to be the derived result of the manometric method. By analyzing the mutual relationship of T_{max} values with those of T_D, a general equation was formulated as

$$T_{max} = b_2 \log T_D + a_2 \qquad (4)$$

On the basis of linear regression analysis, the coefficients of eqn. (4) obtained for separate DTA measurement methods (see Table 3). Both shapes of eqn. (4) for the DTA measurements according to method A and method B are fairly similar; also, mathematical treatment of the combined data of the two DTA methods was carried out. The shape of eqn. (4) obtained in this way was then applied to the calculation of T_{max} for individual compounds (Table 1) and also of mixtures containing TNB (Table 2). In ref. 39, eqn. (4), changed to the form

$$T_D = 180.28 \exp\left(\frac{T_{max}}{469.87}\right) \qquad (5)$$

was made use of as one of the criteria to judge the validity of E_M and log A values which had been calculated using eqns. (2) and (3) for compounds 18, 19 and 20.

From the mathematical treatment, within specification of the shape of eqn. (4), data for compound 10 were excluded; for this compound, due to a small number of calibration points in ref. 37 values of E_M and log A which were too low were obtained. Data for the compounds 3, 5, 6, 12, 13, 23, 24, 32 and 33 were also excluded from the calculation. Their T_{max} values, calculated using eqn. (1), exceeded the T_D values for pure substances. It was estimated for these compounds, using eqn. (4),

TABLE 3

SURVEY OF THE RESULTS OF THE LINEAR REGRESSION ANALYSIS OF THE MUTUAL RELATIONSHIP OF T_{max} VALUES WITH THOSE OF T_D — COEFFICIENTS OF EQN. (4)

DTA method	b_2	a_2	*Coefficient of correlation*	*Standard error of estimate*
A	1073.26	−2415.22	0.9291	14.40
B	1106.71	−2508.27	0.8781	15.45
A + B	1081.89	−2440.70	0.9003	15.42

that the rate constant k of their thermolysis, under conditions which Maksimov and Shipicin had supposed to be convenient in deriving the shape of eqn. (1)[9], should be of the order $10^{-7 \cdot 1}$ s^{-1}. Excepting the compounds 3, 5 and 6, the presence of an amine function in the molecule is typical of these compounds.

Particularly great is the difference between T_{max} and the determined value of T_D for compound 32. From the published values for E_M and log A for this compound[48] and the use of eqn. (1), the T_{max} value obtained exceeds the determined value of T_D by 100 K.

The published Arrhenius parameters for compound 32 do not correlate with the shapes of eqns. (2) and (3) derived for the compounds containing intra- and intermolecular hydrogen bonds in the molecule[37]. On the basis of the information published in refs. 36–39, it would mean that heterolysis with an acitautomer serving as intermedia[37] will probably not be the primary step in the thermolysis of compound 32 in the solid phase, but that some other fission reaction will be involved. Considering the analysis of the gaseous products obtained during the thermal decomposition of substance 32 in the solid phase, Maksimov and Kogut[48] suppose that there is a dominating homolysis in the C–NO_2 bond involved.

The published data on the application of the manometric method to the study of the kinetics of thermolysis of the substances containing 1,3-dinitrophenylene building units within the molecule[48] concern so far only the compound 32, TACOT-1 and TACOT-2. It is therefore premature to draw conclusions on the mutual relationship of the results of the manometric method, on the one hand, and DTA, on the other hand, for this category of compounds. This is why values of E_M and log A are presented in Table 1 for compounds 32 and 33 corresponding to heterolytic primary processes of thermolysis of polynitroaromatic compounds containing intra- and intermolecular hydrogen bonds within the molecule[37].

Another limiting condition on the use of polynitroaromatic compounds and their derivatives as thermostable explosives is their physical thermal stability[8, 9, 11]. In Table 1, this stability is characterized by the beginning endothermal changes which are linked with the fusion of the compounds measured.

The relationship of the molecular structure to the physical thermal stability of this group of compounds is subjected to a more detailed analysis in ref. 11. The relationship can be summarized as follows: separation of charges within the molecule, the increase of the molecule by total building units, the presence of intermolecular hydrogen bonds and, last but not least, the presence of intramolecular hydrogen bonds, in so far as they increase the rigidity of the molecule, are particularly favourable for the increase of physical thermal stability. These factors, in general, decrease the chemical thermal stability; by means of the stabilizing influence of the crystal lattice, they can, however, in some cases, also suppress the thermal reactivity. This is evidenced by the comparison of the data in Table 2 with those contained in Table 1. This is particularly true of the compounds 18, 20 and 31.

Equation (1) represents the calculation of the theoretical temperature limit T_{max}. The real temperature limit of the thermal stability of a given explosive, depending upon the hydrostatic pressure of the medium as well as upon the size of the explosive charge, can be lower by 50–80 K than the calculated value T_{max} (ref. 9). This conclusion was arrived at by Maksimov and Shipicin[9] considering practical knowledge gained from the realm of thermal explosion and from the application of thermally stable explosives[8].

CONCLUSIONS

As in benzene, any substitution in the nucleus of 1,3,5-trinitrobenzene is linked with a decrease in the thermal 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 1,3,5-trinitrobenzene derivative to a considerable extent, due to the stabilizing influence of the crystal lattice.

Also, in the DTA of polynitroaromatic compounds, the stabilizing influence of the crystal lattice can be assessed by using 1,3,5-trinitrobenzene as admixture solvent of the compound being examined. It must, however, be borne in mind that 1,3,5-trinitrobenzene cannot be regarded, in this sense, as an inert solvent.

The knowledge gained from this work confirms that, in the study of thermolysis of organic polynitrocompounds, it is possible to find a relationship between the results obtained from the applied manometric method, on the one hand, and the results of non-isothermal DTA in its simple execution, on the other hand. From the point of view of technological practice, the values (T_D) of the initial stages of the exothermal decomposition from the DTA-mentioned compounds gain a more concrete significance.

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