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Study of initiation reactivity of some plastic explosives by vacuum stability test and non-isothermal differential thermal analysis

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Abstract

On the basis of measurements of 18 high explosives by means of the Czech Vacuum Stability Test (VST) STABIL, a relationship has been specified between the results of this test and those of Russian manometric method. The said relationship was used to predict the Arrhenius parameters (E_a and $\log A$ values) of four plastic explosives based on RDX and one high explosive based on PETN (Semtex). The slopes E_aR^{-1} of Kissinger's equation were specified by means of non-isothermal differential thermal analysis (DTA) and evaluation of the measurement results by means of the Kissinger method. The role played by binders and plasticizers in thermal decomposition of nitramines was pointed out on the basis of relationship between the E_a values obtained from VST and the E_aR^{-1} values obtained from DTA, both for plastic explosives, eight nitramines, Composition B and PETN. The relationships between the E_aR^{-1} values and thermostability threshold was specified for the given group of explosives. The relationship classify some of the studied plastic explosives as belonging to nitramines with steric hindrance in the molecule (CPX, TNAZ and HNIW). The relationship between E_aR^{-1} values and drop energies, E_{dr}, sharply differentiates between plastic explosives and individual nitramines. From the relationship between the E_{dr} and D^2 values it was found that the increasing performance of the studied nitramines and plastic explosives is connected with the decrease in their impact sensitivity. Also specified are the approximate linear dependences between the peak temperatures of exothermic decomposition of all the explosives studied and their ignition temperatures, T_{ig}, or critical temperatures, T_c; these dependences were applied to prediction of T_{ig} and T_c of both the studied plastic explosives and some of the nitramines.

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Keywords: DTA; Explosives; Nitramines; Thermal decomposition; Impact sensitivity; Vacuum stability test

1. Introduction

An important starting point for developing safer energetic materials and methods for specifying their risk properties consists in studies of relationships between molecular structure of these materials and their impact sensitivities, shock sensitivities, sensitivities to electric spark and to heat. In the case of energetic materials based on polynitro compounds, the key role in the mentioned sensitivities is played by the groupings C–NO$_2$, N–NO$_2$ and O–NO$_2$ [1–8]. Therefore, it is not surprising to find out that the primary chemical mechanism of initiation of detonation of these compounds by action of impact, shock, electric spark and heat is the same [4–6]. That is why it is also possible to specify mutual relationships between the parameters of individual sensitivities (see Refs. [4–6] and references herein).

So far, the studies of these mutual relationships between sensitivities have preferred the data of individual polynitro compounds [4–8]. From among thermoanalytical methods, we mostly used the simple non-isothermal differential thermal analysis (DTA), whose results used to be evaluated by means of modified Piloyan method [7,9] in the past. Recently, we have used the method by Kissinger [10] in the studies of chemical micro-mechanism of initiation of energetic materials by means of DTA [5–8]. Lately, this study has been extended to technologically significant explosive mixtures based on ammonium nitrate [11,12] and on 1,3,5-trinitroso-1,3,5-triazinane [13].

In former Czechoslovakia, a manometric method was developed [14], which is known under the name STABIL: it can be considered – to a certain extent – to be an automated variant

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of the American vacuum test [15]. Originally, this method was designed for technological checking of quality in production of explosives. However, several – not yet very numerous – reports (e.g., see paper [16]) document that it should also be used for studies of kinetics and mechanism of not only thermolysis but also of detonation of energetic materials [16]. Thus, a relation was found between the reaction rate of low-temperature thermolysis and the chemical process taking place in the reaction zone of detonation wave [16].

The application of both the methods, i.e. the mentioned vacuum stability test STABIL (VST) and DTA to studies of initiation of important explosives with plastic consistency has not been sufficiently investigated yet. This present paper deals with this problem with the aim of specifying the relationships between outputs of both the methods, and the relationships of outputs of DTA and the impact and detonation reactivity of the explosives mentioned.

2. Experimental

2.1. Substances and data

A survey of the polynitro compounds, military plastic explosives studied, and Arrhenius parameters, E_a and $\log A$, of their low-temperature thermal decomposition are presented in Table 1. The parameters correspond to the results of the Russian isothermal manometric method (SMM; for its principle and layout, see Refs. [17–19], see also Section 2.11). By means of Arrhenius relationship the rate constants k were calculated for individual compounds and Comp. B for temperatures at which their isothermal measurement in system STABIL were carried out. The military explosives RDX, HMX, C-4, CHa, CHc, CHe and Comp. B are products of the Slovak Company Chemko Ltd. The explosives HNIW, PETN, TNAZ and Semtex 1A are products of the Explosia Ltd., Pardubice. DINA, TNT, HNS and TETRYL were of foreign provenance. The other substances listed in Table 1 were prepared in our laboratories.

2.2. Vacuum stability test STABIL

We used a modernized apparatus STABIL 16-Ex [20] (manufactured by OZM Research; the original apparatus is described in Ref. [14]). The amount of measured samples was 2 g. Tests were performed for 20 h, in some cases for 10 h. Temperatures of the isothermal measurements were chosen from within the 125–160 °C range (depending on the known thermal reactivity of the given sample). The dried samples in evacuated glass test tubes were placed into the heating block and heated to the desired temperature. Pressure transducers continuously estimated the pressure increase in the glass tubes. The results were in the form of time dependence of the gas volume evolved from 1 g sample per second (i.e. w values in $\mathrm{cm^3\,g^{-1}\,s^{-1}}$) and corrected to standard conditions. The results of all the tests are presented in Table 1 (here the w values are detached to the real time of measurements, i.e. to the 20 or 10 h).

2.3. Differential thermal analysis (DTA)

We used a DTA 550 Ex apparatus [20] 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 aluminium oxide. We used linear rates of temperature increase, *viz.* 5, 10, and 15 $^\circ\mathrm{C\,min^{-1}}$. The raw data were treated by means of the software delivered with the DTA apparatus and the values obtained were processed by the Kissinger method [10]; the results are presented in Figs. 3 and 4. The values of E_aR^{-1} (i.e. slopes of Kissinger relationship [10]) thus obtained were taken as characteristics of thermal reactivity of the studied substances. A survey of these slopes of studied explosives is given in Table 3.

2.4. Determination of heat of decomposition

The determination of heats of decomposition of plastic explosives was realized by means of DSC Pyris 1 (Perkin-Elmer). The apparatus was calibrated for indium and lead. During the measurement, nitrogen was introduced into the furnace of the DSC and the heating rate was 10 $^\circ\mathrm{C\,min^{-1}}$. Weighed amounts (0.90–1.50 mg) of explosive were placed in aluminium pans (Perkin-Elmer, Part No. BO14-3016) fitted with covers (Perkin-Elmer, Part No. BO14-3040) which were perforated. The resulting DSC records were analysed by means of the Pyris series thermal analysis software (Perkin-Elmer, Part No. N557-0600), which is licensed by Perkin-Elmer. The results of measurements are summarised in Table 2.

2.5. Determination of thermal conductivity

The thermal conductivity λ was measured in Institute of polymers, Slovak Academy of Sciences, Bratislava by means of impulse method using a probe with built-in thermocouples and heat source. In a pre-programmed way, both the probe and the sample measured were heated by electric impulses. The thermal conductivity coefficient was the higher, the more heat was withdrawn from the probe surface through the sample measured. The chosen parameter α (diameter of sphere, cylinder or thickness of layer) was 0.8 mm (taken from Ref. [43]), the chosen factor δ was 0.88 (as for a plate of infinite dimensions). The results are summarised in Table 2.

2.6. Impact sensitivity

The impact sensitivity, expressed as drop energy E_{dr}, was specified by means of standard Cast apparatus according to the procedure given in Ref. [21]. The E_{dr} values of some materials were calculated from published drop heights $h_{50\%}$ [22,23]. A survey of the results is presented in Table 3.

Table 1
Survey of the samples measured, Arrhenius parameters of their thermal decomposition and outputs of VST STABIL

Name of sample	Code design	Arrhenius parameters			STABIL outputs		
		Temperature range (°C)	E_a (kJ/mol)	log A (s^{-1})	Ref.	w (ml/g/20 h)	For T (°C)
2,4,6-Trinitrotoluene	TNT	190–250	144.4	9.3	[26]	0.0582	140
	TNT					0.1210 (10 h)[a]	150
2,4,6-Trinitrophenol	PA	183–273	161.2	11.7	[17]	0.2685	160
1,3,5-Trinitro-2-[(*E*)-2-(2,4,6-trinitrophenyl) vinyl]-benzene	HNS	260–300	183.8	12.0	[28]	0.3539	160
2,4- Diamino-1,3,5-trinitro benzene	DATB	[b]	193.7	15.1	[29]	0.0797	160
1,3,5-Trinitro-2-[(2,4,6-trinitrophenyl)thio] benzene	$\text{DIPS}_{(1)}$	235–255	131.8	7.4	[30]	0.1620	160
1,4-Dinitro-l,4-diazabutane	EDNA	70–95	186.2	18.0	[31]	2.2376	140
1,3,3-Trinitroazetidine	TNAZ	230–260	161.3	13.9	[42]		
1,4-Dinitropiperazine	DNDC	216–234	198.5	17.3	[32]	0.2028	140
	DNDC					0.1294 (10 h)[c]	140
1,3-Dinitroirnidazolidine	CPX	150–200	149.5	13.5	[32]	0.4690 (10 h)[c]	120
l,3,5-Trinitro-l,3,5-triazmane	RDX	150–197	217.6	19.1	[33]	0.1333	160
	RDX	150–197	213.5	18.6	[17]		
l,3,5,7-Tetranitro-l,3,5,7-tetrazocane	HMX	271–314	220.5	19.5	[34]	0.1707	160
	HMX					0.1210 (10 h)[c]	150
Mixture of 65% RDX, 43% TNT and of 1% wax	Comp. B	[b]	180.2	16.6	[35]	1.80	140
N-methyl-*N*-nitro-2,4,6-trinitro aniline	$\text{TETRYL}_{(s)}$	[b]	190.4	14.6	[36]	0.0045 (10 h)[a]	120
	$\text{TETRYL}_{(1)}$	130–165	156.9	14.5			
l,4-Dinitrotetrahydroimidazo-[4,5-d]imidazol-2,5(1H,3H)dione	DINGU	225–245	217.8	20.9	[37]	0.0470 (10 h)[a]	120
N,*N*-*bis* (2-nitroxyethyl) nitramine	DINA	100–160	173.7	16.5	[38]	2.6692	140
Pentaerythritol tetranitrate	PETN	[b]	173.6	15.2	[39]	0.1652	110
2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaaza-isowurtzitane	HNIW	160–180	172.00	13.8	[40]	0.2940	170
4,10-Dinitro-2,6,8,12-tetraoxa-4,10-diazaisowurtzitane	TEX		196.80	15.4	[41]	0.0425	170
Plastic explosive with 91% RDX (contains mixture of dioctyl sebacate with mineral oil)	C-4	130–160	268.0	26.5	[c]	0.080	130
						0.260	140
						1.830	160
Plastic explosive with 88% RDX (contains mineral oil)	CHa	130–160	232.3	21.4	[c]	0.042	130
						0.140	140
						0.650	160
Plastic explosive with 84% RDX (contains SiO_2 and mineral oil)	CHc	120–160	346.2	38.1	[c]	0.048	120
						1.900	140
						34.00	160
Plastic explosive with 80% RDX (aluminized with content of dioctyl phthalate)	CHe	120–140	380.7	40.0	[c]	0.0047	120
						0.0128	130
						0.1115	140
Plastic explosive with 87% PETN (contains mineral oil)	Semtex 1A	100–125	223.2	24.0	[c]	0.320	100
						0.570	110
						3.860	125

Note: [a]The value calculated from VST results for 10 h measurement; [b]the data are not presented in original paper; [c]the values calculated from the VST results in this paper by means of relationships in Fig. 2.

Table 2
Survey of the thermal conductivity and DSC measurements (the Q_{dec} values)

Explosive	Thermal conductivity, λ		Heat of decomposition, Q_{dec}		
	$W\,m^{-1}\,K^{-1}$	$cal\,cm^{-1}\,s^{-1}\,K^{-1} \times 10^{-4}$	Temperature range (°C)	$J\,g^{-1}$	$cal\,g^{-1}$
Semtex 1A	0.27723	6.626	166.4–225.1	2319.1	554.47
Comp. C-4	0.27622	6.602	199.3–214.1	2047.3	489.32
Comp. CHa	0.21020	5.024	201.5–211.4	1906.2	455.58
Comp. CHc	0.29727	7.105	202.3–222.7	1879.5	449.20
Comp. CHe	0.35564	8.500	200.0–210.6	1489.54	356.00
RDX	0.106[a]	2.5[a]	204.4–214.9	2167.32	518.00

Note: [a]The value taken from Ref. [43].

2.7. *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} [21] until the point of ignition of the sample was reached. The corresponding results are presented in Table 3.

2.8. *Calculation of critical temperature*

The calculation for the plastic explosives studied was carried out using the well-known Frank–Kamenetskii equation [29,43]

$$\frac{E_a}{T_c} = R \ln \frac{\alpha^2 \rho Q_{dec} A E_a}{T_c^2 \lambda \delta R} \quad (1)$$

where T_c is critical temperature in K, E_a the activation energy, R the universal gas constant, α the diameter of sphere or cylinder or thickness of layer, ρ the density, Q_{dec} the decomposition heat, A the pre-exponential factor of the monomolecular decomposition, λ the thermal conductivity, and δ is the shape factor (0.88, 2.00 and 3.22 for infinite plate, cylinder and sphere, respectively). The input data for the calculation were taken from Tables 1 and 3. The results are summarised in Table 3.

2.9. *Thermostability threshold*

The thermostability threshold is the maximum temperature that can be applied to the given explosive for a period of 6 h without destroying its functionality (this roughly corresponds to a chemical change of max. 2% of the explosive) [49,50]. The calculation of this threshold starts from the Arrhenius equation in the form:

$$T_{max} = \frac{E}{2.303 R(\log A - \log k)} \quad (2)$$

Semi-empirically it was found that at the condition mentioned the rate constant k is 10^{-6} [49] and $10^{-6.5}$ [50] for polynitro arenes and polynitramines, respectively. The results are presented in Table 3.

2.10. *Detonation velocities*

We used the maximum values of experimentally determined values of detonation velocities, D, given by the manufacturers. Some of the D values were taken from literature; for TEX, HNIW and CPX they were calculated according to Kamlet and Jcobs [24] for 91% of theoretical density of crystal. The D values are presented in Table 3.

2.11. *Russian manometric method*

The basic problem of defining the kinetics and mechanism of the thermal decomposition of energetic materials lies in the strong dependence of the corresponding kinetic parameters on temperature, pressure, and construction materials in contact with the sample decomposed (see Refs. [4] and [58] and references therein). Hence, the mutual compatibility of results obtained from thermal analyses of energetic materials using different methods and/or different types of apparatus of different origin is very rare (see Ref. [4] and references therein). So far the most reliable results in this area are both theoretical and practical findings obtained by Russian scientists on the basis of their manometric method (see Refs. [4,5,58] and quotations herein). The data obtained by this method are known to correspond to the non-autocatalysed stage of thermal decomposition of the given material (i.e. to molecular structure [4,5,58]), and also to the absolute values of corresponding Arrhenius parameters. Therefore, the outputs of the given method (E_a and $\log A$ values) were used as comparison standards in this paper, too, and they are presented in Table 1.

3. Discussion

The basic principles of Russian manometric method (SMM) [17–19] and the Czech system STABIL [14,20] are the same, i.e. those of the vacuum stability test (VST). This is reflected in Fig. 1, in which the values of logarithm of rate constant, $\ln k$, are calculated from the Arrhenius parameters of SMM for the temperatures used in the isothermic exposure of the respective polynitro compounds in STABIL test. The $\ln w$ values correspond to logarithm of the decomposition velocities determined in this test related to 1 second (the reaction velocity of evolution of gaseous products here corresponds to a zero-order reaction [16] and, therefore, w represents the rate constant). The closeness of said mutual relationship of rate characteristics in Fig. 1 is connected with the difference between conducting the measurement proper in the two methods. The Russian method mostly works with starting pressures of 10^{-8} to 10^{-10} Pa; the final pressures are given here by the character of the sample measured and the purposes of measurement [19]. In the STABIL test, the starting pressure value of ca 100 Pa can increase up to 4000 Pa

Table 3

A survey of characteristics of the thermal reactivity, detonation velocities and impact sensitivities of the studied explosives

Explosive	DTA results		Ignition temperature, T_{ig} (°C)	Thermal stability threshold for 6 h (°C)	Critical temperature, T_c (°C)			Detonation velocity			Impact sensitivity	
	T_m (°C)	E_aR^{-1} (K)			Experimental	Ref.	From DTA	ρ (cm^3 g^{-1})	D (km s^{-1})	Ref.	E_{dr} (J)	Ref.
Semtex 1A	188.5	31045	180–182	109.4	188	[a]	191.8	1.50	7.418	[b]	21.1	[b]
Comp. C-4	211.8	29099	211	151.4	213	[a]	212.9	1.58	8.108	[c]	24.0	[c]
Comp. CHa	211.8	21358	208	162.0	234	[a]	212.9	1.58	8.186	[c]	44.0	[c]
Comp. CHc	212.8	24536	212–217	132.6	173	[a]	213.8	1.58	7.973	[c]	30.0	[c]
Comp. CHe	212.2	19603	206–208	154.8	195	[a]	212.7	1.63	7.442	[c]	21.0	[c]
Comp. B	214.1	19365	207	134.6	216	[29,43]	215.0	1.72	7.900	[c]	14.5	[45]
TNT	277.7	12474	276–278	220.1	286	[29,43]	272.7	1.59	6.950	[b]	39.2	[46]
HNS	330.6	61507	326	266.6	320	[29,43]	320.8	1.60	6.800	[43]	11.5	[46]
TETRTL	184.2	30964	183	115.5			187.8	1.51	7.150	[43]	7.8	[46]
HMX	273.7	47397	254[e]	170.1	258	[29,43]	269.1	1.89	9.110	[43]	6.4	[46]
RDX	215.3	44175	221	171.5	214	[29,43]	216.1	1.60	8.250	[43]	5.9	[46]
TEX	296.9	69779	−300	196.6			290.2	1.81	7.773	[d]	24.2	[49]
α-HNIW	204.2	30621	220				206.0	1.82	8.770	[d]	10.2	[47]
ε-HNIW	223.4	23226	225	169.7			223.4	1.88	9.100	[d]	11.9	[47]
CPX	193.5	14273	192	117.6			195.8	1.55	7.540	[d]	16.1	[e]
TNAZ	244.5	18639	−232	140.1	238	[45]	242.0	1.78	8.620	[25]	6.9–7.1	[48]
PETN	186.6	39185	178[e]	136.0	197	[29,43]	190.0	1.60	7.900	[34]	2.9	[46]

Notes: [a]This paper; [b]the values of the Company Explosia, Ltd.; [c]the values of the Company Chemko, Ltd.; [d]the values calculated by Kamlet and Jacobs method [24] for 91% of the theoretical crystal density; [e]the value of the Inst. of Energetic Materials.

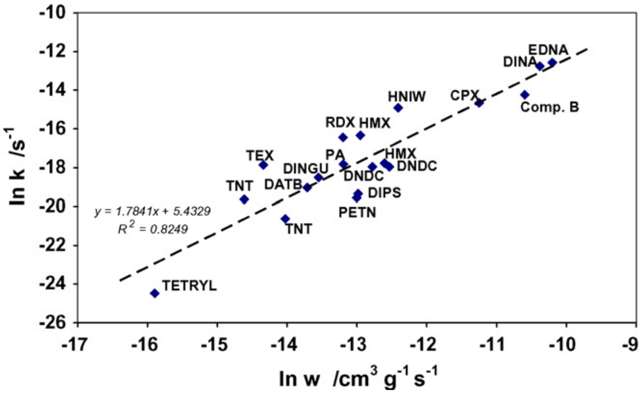

Fig. 1. Relationship between the logarithm of rate constants, ln k, calculated from Arrhenius parameters of the Russian manometric method for the compounds measured, and the logarithm of zero order rate, ln w, from measurements by means of the VTS STABIL.

after 20-h measurement. The evolution of gaseous products in SMM is detected by means of a Bourdon manometer [17–19]. In the STABIL system, the pressure change in the apparatus containing 2 g sample is detected by means of a pressure sensor [14,20]. Another factor influencing the closeness of the correlation in Fig. 1 is the way of obtaining (calculating) the ln k values. These were calculated for the lower temperature range, than the temperature ranges corresponding to the specification of the used Arrhenius parameters (see Table 1).

From the calibration curve in Fig. 1 were read the ln k values of plastic explosives Semtex 1A, CHa, CHe, CHc and C-4, from which the corresponding Arrhenius parameters were derived in the sense of Fig. 2. The calibration curve (Fig. 1) has been constructed on the basis of data of monomolecular decomposition of pure polynitro compounds. However, interactions of binders with active components of studied explosives in their thermal decomposition can have a significant effect upon the mechanism and kinetics of their decomposition: Smilowitz et al. [64] show for example that plasticizer is responsible for decreasing the nucleation energy at the HMX crystal surface (a formation of potential reaction centres). This is reflected in the values of corresponding Arrhenius parameters of plastic explosives containing a liquid plasticizer (see Table 1), which is usual in mixtures of this type [51,52]: e.g., for plastic bonded explosives (PBX) based on HMX and RDX, the E_a values vary from 187 to 615 kJ mol^{-1}, and the log A values from 17.5 to 56.0 [51]. For PBX with PETN content, namely the explosive Detasheet C, was found the value of $E_a = 246$ kJ mol^{-1} [52], whereas for mixtures of PETN with nitrocelulose and without liquid plasticizer, this value varied in the limits of 135–205 kJ mol^{-1} [52]. Application of thus predicted Arrhenius parameters of thermal decomposition of studied plastic explosives to calculation of their critical temperatures, T_c, gave non-realistic values for explosives CHa and CHc (see Table 3).

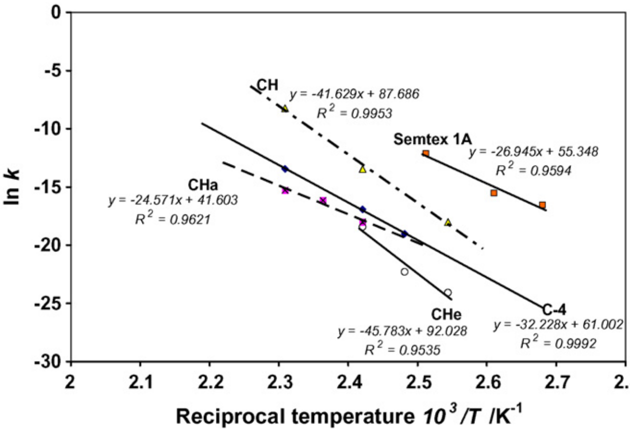

Fig. 2. Arrhenius relationships for the thermal decomposition of the studied plastic explosives by means of the VST STABIL—the corresponding ln k values were obtained by subtraction from Fig. 1 on the basis of experimentally obtained ln w values.

The studied mixtures C-4, CHe and Comp. B contain a solvent of RDX (dioctyl sebacate, dioctyl phthalate and TNT, respectively) in the binder. Mineral oils are used to plasticize mixtures CHa and CHc. Organic additives (particularly plasticizers and polymers) added to individual energetic materials affect the initiation reactivity of resulting mixtures also through their interactions with surface molecules of crystal (especially at the defect spots of surface). With the use of RDX it was proved [33] that a film of inert liquid inhibits the thermal decomposition of RDX, while an additive of solvent type accelerates this decomposition. From this finding it follows that these additives interfere with intermolecular interactions in crystals of the given explosive. The said interactions are a significant factor in impact reactivity, shock reactivity, and electric spark reactivity of polynitro compounds [4,5], being also dominant in the thermolysis kinetics of the given compounds in condensed state (see Refs. [4,5,59]). It appears that many additives of the type of solvents of RDX cannot be considered as inert because they can change the chemism of thermal decomposition of nitramines [61]. Binding, plasticizing and phlegmatizing (desensitizing) additives contribute to sensitivities of the respective mixtures also through their specific physico-chemical properties, such as specific heat (see Ref. [53]), capability of generating radicals by action of impact and shock, etc. [27,62,63]. It must also be stated that efficiency of action of desensitizing agent upon the sensitivity of EMs to mechanical stimuli is connected with not only the change in physical and mechanical properties of desensitized EMs (as compared with the original ones) but also the ability of desensitizing agent to trap active products of decomposition of the given EM and inhibit this decomposition [44].

The evaluation of records of differential thermal analysis by Kissinger method [10] shows (see Figs. 3 and 4) that the effect of additives in explosives C-4, CHa, CHe and CHc upon thermal stability of RDX is not very distinct. This also agrees with the values of ignition temperatures and critical temperatures in Table 3. Thermal reactivity of Semtex 1A is somewhat lower than that of pure PETN (Fig. 3), which is also documented by the respective data in Table 3. However, from the standpoint of longer-term thermal exposition of these plastic explosives they exhibit a more distinct drop in thermal stability as compared with pure RDX and PETN, which is documented by values of thermostability threshold for 6-h thermal exposition (see Table 3).

Fig. 5 compares values of activation energies, E_a, with values of slopes in the Kissinger relationship. In this sense, individual

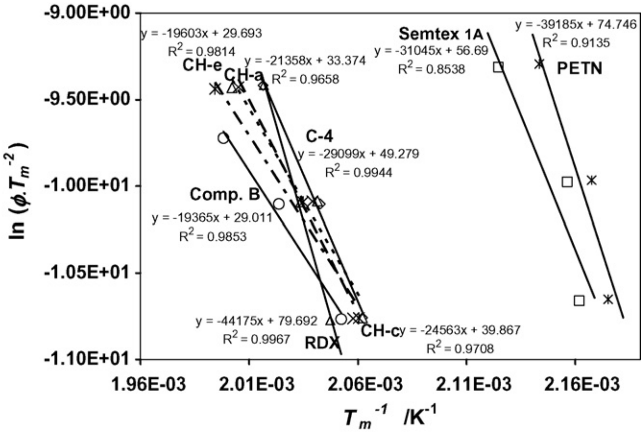

Fig. 3. Evaluation of the DTA measurements with the studied plastic explosives by Kissinger method—thermal stability is increasing from the right- to left-hand side. Here, T_m is a peak temperature of exothermic decomposition and ϕ is a linear rate of temperature increase.

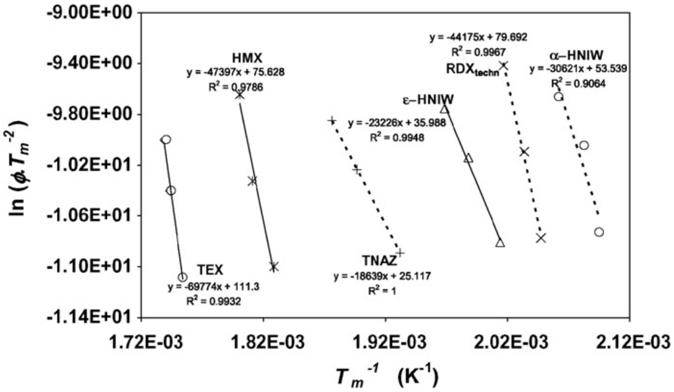

Fig. 4. Evaluation of the DTA measurements with the studied nitramines by Kissinger method—thermal stability is increasing from the right- to left-hand side. Here, T_m is a peak temperature of exothermic decomposition and ϕ is a linear rate of temperature increase.

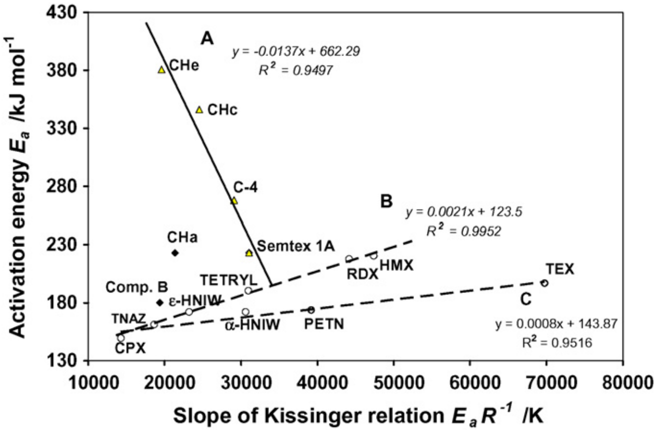

Fig. 5. Relationship between the activation energies, E_a, from the application of Russian manometric method and slopes of Kissinger relation, E_aR^{-1}, for the studied plastic explosives, nitramines, PETN and Composition B.

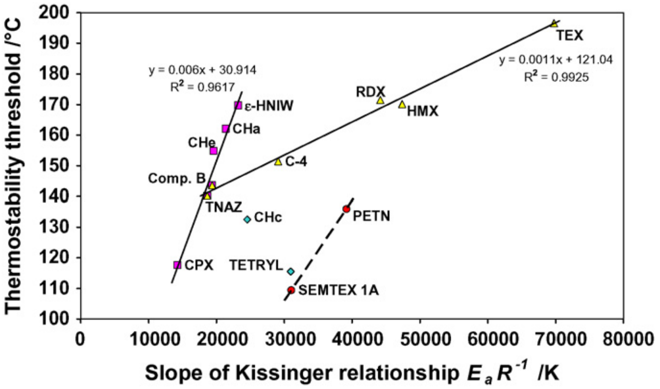

Fig. 6. Relationship between the thermostability thresholds for 6 h thermal exposure and the slopes of Kissinger relation, E_aR^{-1}, for the studied plastic explosives, nitramines, PETN and Composition B.

nitramines are classified as less and more reactive (lines *B* and *C*, respectively); e.g., α-HNIW is more reactive than ε-HNIW—see the data of their thermal and impact reactivity in Table 3. The data of Comp. B approach line B; its published value of E_a was determined with a sample of different provenance from that of the sample used in DTA measurement. The considerably differing course of dependence *A* found for plastic explosives supports the view of afore-said participation of components of mixture in the decomposition of RDX and PETN.

The relationship between thermostability threshold and slope of Kissinger relationship (in Fig. 6) was described for the first time in the case of thermally stable polynitro arenes [54]. The said relationship is connected with the mechanism of primary splitting of the molecule. It is sharply delimited by structure of the reaction centre of molecule and can also reflect intermolecular force effects [54]. Also for this reason, this relationship (Fig. 6) separates substances with sterically hindered molecules from the nitramine group (CPX, TNAZ and HNIW); the data of plastic explosives CHa, CHe and Comp. B correlate with this group. The explosive CHc contains SiO_2, which can affect its thermostability threshold (SiO_2 particles acting as hot spots). The data of Tetryl and PETN do not correlate due to their molecular structure.

In the paper Ref. [55] it was stated that some relationship exists between vibrational excitation by impact, on the one hand, and thermal activation of the molecules of energetic materials, on the other. Therewith connected is also the relationship between the slopes of Kissinger relationship (E_aR^{-1}) and drop energies (E_{dr}) (the impact sensitivity detected by sound) of the explosives studied, which is documented by Fig. 7. The data of the explosive CHe do not correlate with any of the dependences given in Fig. 7—this explosive contains only 80% RDX (the reason can lie in thermochemical effects on the impact sensitivity).

The linear relation between drop energies, E_{dr}, and heats of explosion, *Q*, was found in the case of highly thermostable polynitro arenes [56]. Between the *Q* values and squares of detonation velocities, D^2, there exists a relationship [57] of the following form:

$$Q = \frac{D^2}{2(\gamma^2 - 1)} \tag{3}$$

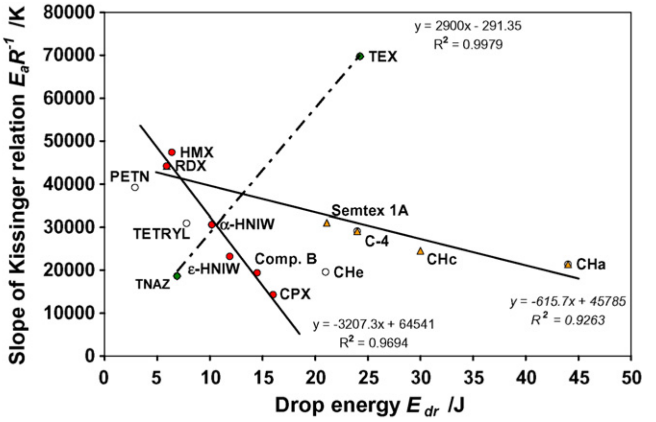

Fig. 7. Relationship between the slopes of Kissinger relation, E_aR^{-1}, and drop energies, E_{dr} (impact sensitivities) for the studied plastic explosives, nitramines, PETN and Composition B.

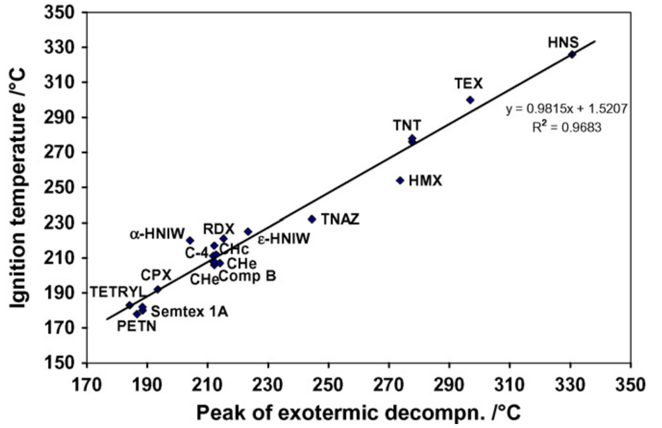

Fig. 9. Relationship between the ignition temperatures and the peak temperatures of exothermic decomposition (from DTA) for the polynitro compounds from Table 1—the peak corresponds to the linear temperature increase of 5 °C min^{-1}.

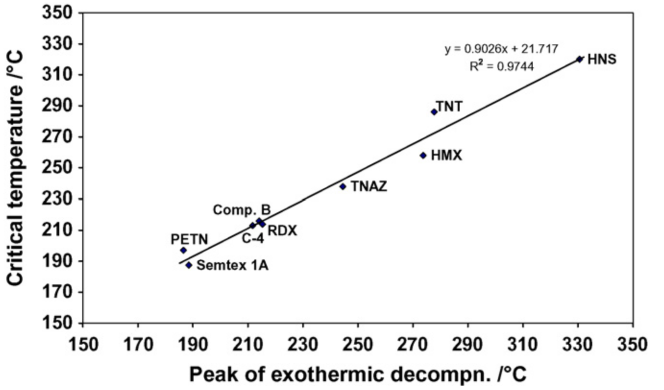

Fig. 10. Approximate relationship between the critical temperatures and the peak temperatures of exothermic decomposition (from DTA) for the explosives from Table 1—the peak corresponds to the linear temperature increase of 5 °C min^{-1}.

where γ is the coefficient of polytropy. Thus, Fig. 8 also documents validity of the relationship for the explosives studied. In contrast to the polynitro arenes mentioned, the dependences given in this figure show that the increasing energy content (i.e. performance) of the explosives studied is associated with decrease in their impact sensitivity. This trend is the opposite to that generally associated with energetic materials, *viz.* the view that a high performance is usually accompanied by an enhanced sensitivity and that an insensitive explosive will not exhibit a top performance [60].

The simplest logical relationship between the DTA outputs (peak temperatures T_m of exothermic curves) and the ignition temperatures is presented in Fig. 9, which was constructed from the results of measurements of various military explosives. Also logical is the approximate relationship between the values of critical temperatures (calculated on the basis of Frank–Kamenetskii relationship (1) [29,43] or experimentally determined [29,43]) and the values of DTA-peak temperatures of exothermic decomposition. This relationship is presented in Fig. 10, and the data given in Table 3 correspond with it. In both dependences the considered peak temperatures T_m of exothermic decomposition correspond to the linear temperature increase of 5 °C min^{-1}. For the given DTA apparatus (Section 2.3), Figs. 9 and 10 can be used to estimate the ignition and critical temperatures, respectively. Fig. 9 documents that the thermal stability of HNIW is approximately the same as in the case of RDX and inferred plastic explosives from it.

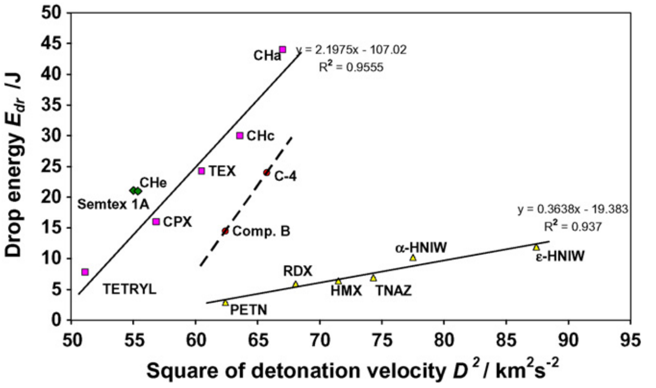

Fig. 8. Relationship between the drop energies, E_{dr} (impact sensitivities) and square detonation velocities, D^2, for the studied plastic explosives, nitramines, PETN and Composition B.

4. Conclusions

The velocities of evolution of gas products in the Czech vacuum stability test STABIL correlate relatively well with the rate constants derived from the outputs obtained from the Russian manometric method. With the use of pure individual energetic materials (EMs) it is thus possible to construct a calibration curve which allows estimates of kinetic parameters from measurement results of the STABIL system. In this way, the resulting values of Arrhenius parameters (E_a and $\log A$) for plastic explosives based on RDX and PETN with liquid plasticizer are as those usual for this type of EMs; these values are higher than those of pure RDX and PETN. The primary reason in this case lies in the application of the rules of monomolecular decomposition of pure EMs to complicated interaction of binder and especially plasticizer with the active component during decomposition of plastic explosives of the type investigated.

In practical realisation, easily accessible characteristics of thermal decomposition are slopes E_aR^{-1} of Kissinger's relationships resulting from the evaluation of outputs from non-isothermal differential thermal analysis (DTA) by means of the Kissinger method. The interrelationship of these characteristics with the E_a values of decomposition of the plastic explosives studied, on the one hand, and those of their pure active components, on the other hand, documents the already mentioned difference between the decomposition mechanisms and kinetics of both these EMs groups. The relationships between E_aR^{-1} values and thermostability thresholds classifies some of the plastic explosives investigated as belonging among the nitramines with steric hindrance in the molecule (TNAZ, CPX and HNIW); this group also includes the mixture of TNT with RDX (Comp. B). The given classification does not apply to the well-known explosive C-4. The logical relationship between the E_aR^{-1} values and drop energies (impact sensitivity) distinctly separates the mixed explosives studied from their active components.

A simple output obtained from the above-mentioned DTA method is the peak temperatures of exothermic decomposition of EMs. The linear relationships between these temperatures and the ignition temperatures or critical temperatures of the explosives studied can be used as a calibration curve for satisfactory estimate of both temperature values last mentioned. These relationships also show that the thermal stability of HNIW is approximately the same as in the case of RDX and inferred plastic explosives from it.

A specific feature of the nitramines studied and the explosives based on them is the decrease in their impact sensitivity connected with increase in performance. This is opposite to the general knowledge about EMs. The least sensitive EM studied (with nitramine content) is Composition CHa.

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