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Thermogravimetric analysis of some nitramines, nitrosamines and nitroesters

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Abstract

Four nitrosamines, seven nitramines, three nitroesters and the explosives Semtex 10 and Composition B have been investigated. The thermal reactivity of the compounds was studied by thermogravimetric analysis (TGA). Linear dependence was confirmed between the position of the TGA onsets, as defined in the sense of Perkin-Elmer's TGA-7 Standard Program, and the samples weights. The slope of this dependence is closely related to the thermal reactivity and molecular structure. The intercept values of the dependence correlate with the autoignition temperatures and with the critical temperatures of the studied compounds, without any clear influence from their molecular structure in this case. The results obtained show that Semtex 10 exhibits approximately the same thermostability as its active component, PETN. The results also show that TGA data for Composition B do not correlate with analogous data for pure nitramines.

INTRODUCTION

In our recent paper [1] which deals with thermogravimetric analysis (TGA) of the urea–formaldehyde polycondensates, a dependence between the positions of the characteristic DTG peaks and the sample weights was established. In further communications, the dependence was extended to TGA onsets of commercial explosives [2] and of some aminoderivatives of 1,3,5-trinitrobenzene [3]. The said dependence is given by the equation [1–3]

$$P_t = A_t n + B_t \qquad (1)$$

where P_t is the position of a DTG peak (P_{peak}) or the TGA onset (P_{onset}) in °C (both TGA characteristics are defined according the program [4]) and n is the weight of sample in mg.

As has been shown [1–3], the values of the coefficients A_t are closely related to the thermal reactivity. With respect to the rate constants k_t of the

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non-autocatalysed thermolysis of the nitrocompounds using the Soviet manometric method (SMM) [12, 19], the relation is expressed by the equation [3]

$$A_t = a_t \ln k_t + b_t \quad (2)$$

In the case of the commercial explosives, a linear dependence between coefficients A_t and the explosion (detonation) temperatures of the explosives has also been found [2].

The coefficients B_t, however, correlate with values of the autoignition temperatures T_{expo} (temperatures of explosive points), i.e. with characteristics of the decomposition of the nitrocompounds, which are influenced by catalysis. The correlation is given by the general equation [2, 3]

$$10^3/T_x = c_x B_t + d_x \quad (3)$$

These conclusions, however, have not yet been applied to the study of the thermal reactivity of the technically attractive nitramines, nitrosamines and nitroesters. Therefore, the present paper addresses these problems.

EXPERIMENTAL

Data

A list of the substances studied, together with their numerical codes and abbreviations, is given in Table 1, which also includes published values of the Arrhenius parameters derived from data for the non-autocatalysed thermolysis of these substances. Table 1 also contains published values for the temperature of the explosive points, i.e. autoignition temperatures for an induction period of 5 s [7], and published values of the critical temperatures [5, 14] (in the sense of the Frank–Kamenetskii equation [14]).

Materials

The origin and purity of most of the substances measured, i.e. substances 1–5 and 7–14, are described in ref. 20; for a description of nitramine 6, see ref. 6. Hexolite 60/40 (Composition B) is a product of CHEMKO's Special Production Plant. Semtex 10 is a plastic explosive formulated from PETN, which is produced by VCHZ Synthesia (EXPLOSIA division), Pardubice, and which is used for special applications, e.g. destruction of steel constructions, underwater blasting, etc.

Apparatus

Thermogravimetric measurements were carried out using a Perkin-Elmer TGA-7 apparatus, with samples weighing up to 11 mg being thermolysed in a nitrogen atmosphere. A linear temperature increase of 20°C min^{-1} was used; examples of the corresponding TGA curves are shown in Figs. 1–16.

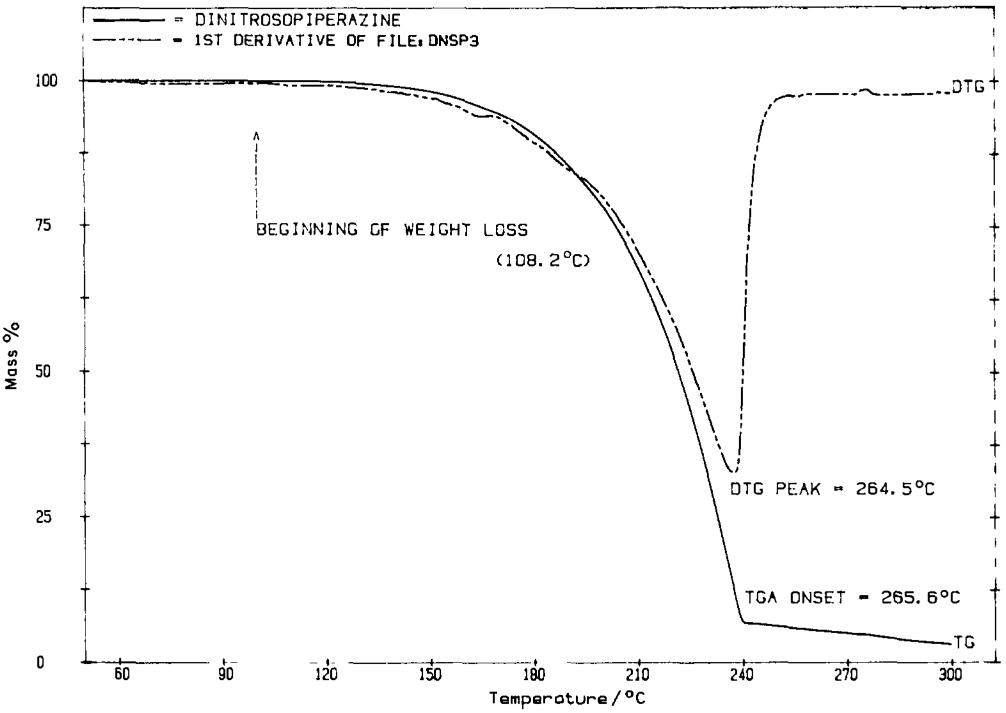

Fig. 1. TGA record of 1,4-dinitroso-1,4-diazacyclohexane (DNSDC).

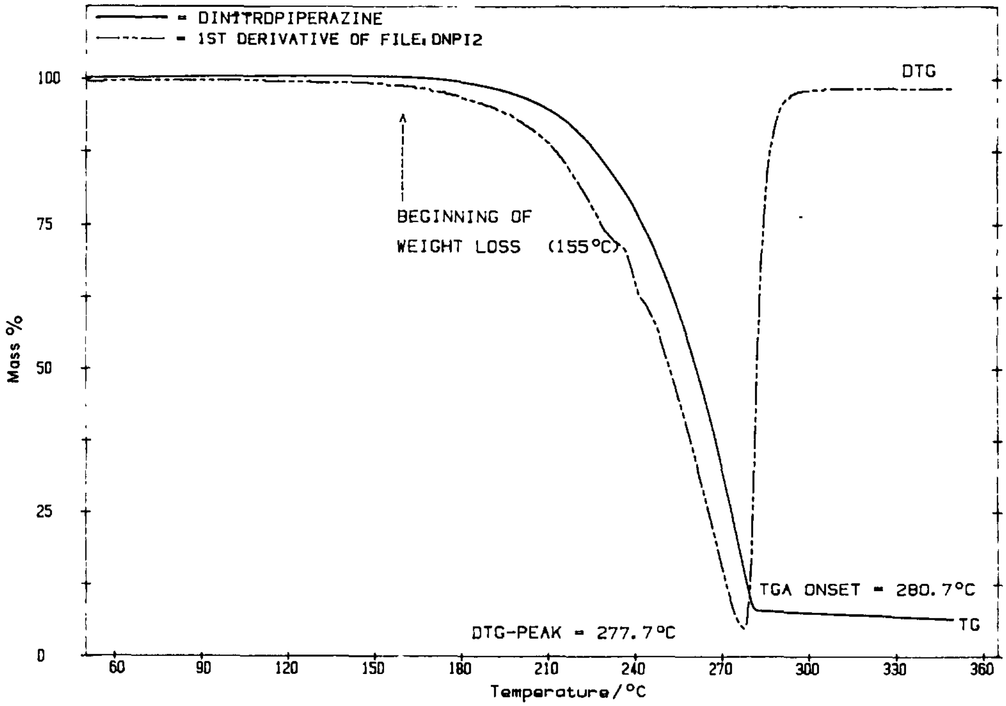

Fig. 2. TGA record of 1,4-dinitro-1,4-diazacyclohexane (DNDC).

TABLE 1

The substances studied, Arrhenius parameters of their non-autocatalysed thermolysis, and values of their autoignition and critical temperatures

Substance			Arrhenius parameters						Autoignition temp. [a] T_{expo} in (°C)	Critical temp. [b] T_{crit} in (°C)
No.	Chemical name	Abbreviation	Thermolysis method	State of thermal decomp.	Temp. range in (°C)	E (in kJ mol^{-1})	log A in (s^{-1})	Reference		
1	1,4-Dinitroso-1,4-diaza-cyclohexane	DNSDC	DSC	Liquid	217–237	143.9	14.0	10		
2	1,4,5,8-Tetranitroso-1,4,5,8-tetraazadecaline	TNSAD	DSC	Solid	187–207	149.1	15.5	10		
3	1,3,5-Trinitroso-1,3,5-triazacyclohexane	TMTA							220	
(3.1)		SMM		Liquid	110–150	144.3	13.1	9		
(3.2)		DSC		Liquid	182–197	146.9	15.5	10		
4	1,5-Methano-3,7-dinitroso-1,3,5,7-tetraazacyclooctane	DNPT	DSC	Solid	197–212	144.2	13.9	10		210 [h]
5	1,4-Dinitro-1,4-diaza-cyclohexane	DNDC	SMM	Liquid	216–234	198.5	17.3	15		
6	1,4,5,8-Tetranitro-1,4,5,8-tetraazadecaline	TNAD	DSC	Solid	204–234	210.0	18.9	16		
7	1,3,5-Trinitro-1,3,5-triazacyclohexane	RDX	DSC, TGA Manometric	Liquid	207–257	201 [c]	[c]	8	Decomp. 260	214
8	1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane	HMX	DSC, MS Manometric	Solid	257–317	211 [c]	19.1 [c]	8	327	258
9	1,5-Diacetyl-3,7-dinitro-1,3,5,7-tetraazacyclooctane	DADN	DSC	Solid	250–260	178 6	15.3	17, 10		
10	1,5-Methano-3,7-dinitro-1,3,5,7-tetraazacyclooctane	DPT								
(10.1)		Calc. [d]	Solid		195.1	15.4	8			
(10.2)		Calc. [d]	Liquid		167.8	15.4	8			

11	1,4-Dinitrotetrahydro-imidazo[4,5-d]imidazol-2,5(1H,3H)-dione	DINGU								
(11.1)			DSC	Solid	225–245	217.8	20.9	17		
(11.2)			Extrap.^{e}	Solid		209.0	18.6	18		
(11.3)			TGA	Solid	150–300	210.2	19.3	This paper		
12	Pentaerythritol tetranitrate	PETN	SMM	Liquid	80–140	163.2	15.6	11	Decomp. 225	197
13	Dipentaerythritol hexanitrate	DPEHN	Extrap.^{e}	Liquid		164.6	15.0	18	220^f	
14	1,1,1-Trimethylol-propane trinitrate	ETRYNIT	Extrap.^{e}	Liquid		165.3	14.9	18		
15	Hexolite 60/40	Composition B	DSC	Liquid	222–252	180.2	16.6	13	Decomp. 280	216
16	Semtex 10	Composition C							233^g	200^h

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[a] The autoignition temperature (temperature of the explosive point) for an induction period of 5 s; the values are taken from ref. 7. [b] The lowest temperature of the surface above which a thermal explosion is produced [5, 14]; the values are taken from ref. 5. [c] On the basis of the modified Evans–Polanyi–Semenov equation [18] and new relations from averaged values published in ref. 8, which result from significantly different thermolysis techniques; the values are taken from ref. 8. [d] Calculated using the relationship between the Arrhenius parameters of thermolysis and the ^{13}C- and ^{15}N-chemical shifts of nitramines [8]. [e] Extrapolated using the modified Evans–Polanyi–Semenov eqn. (18). [f] From ref. 21. [g] Calculated from eqn. (3) for the autoignition temperatures. [h] Calculated from eqn. (3) for the critical temperatures.

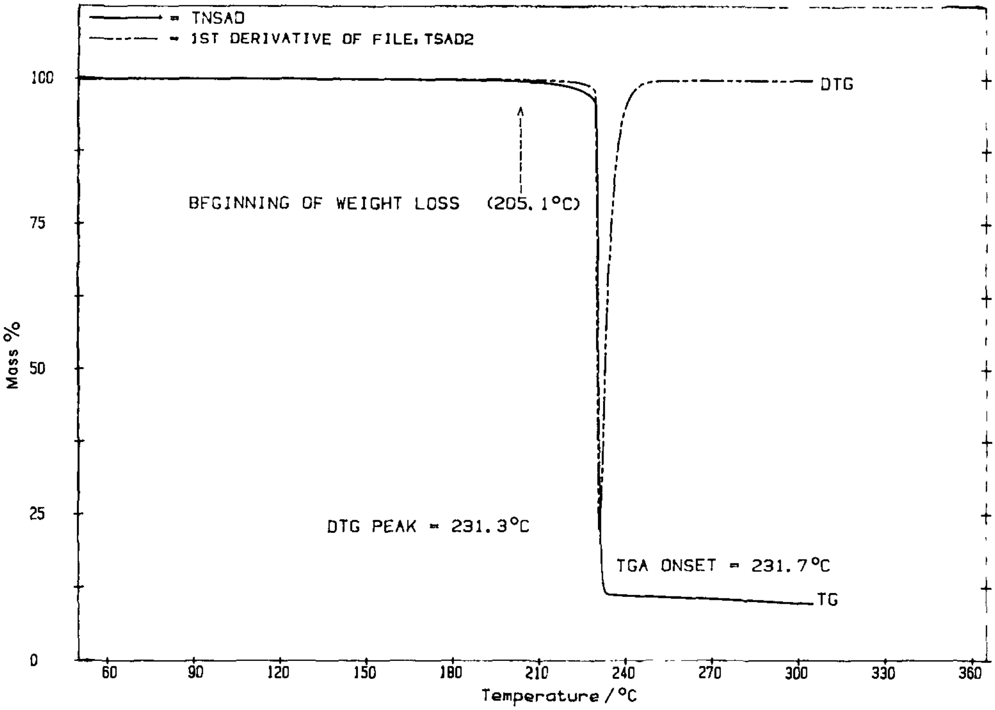

Fig. 3. TGA record of 1,4,5,8-tetranitroso-1,4,5,8-tetraazadecaline (TNSAD).

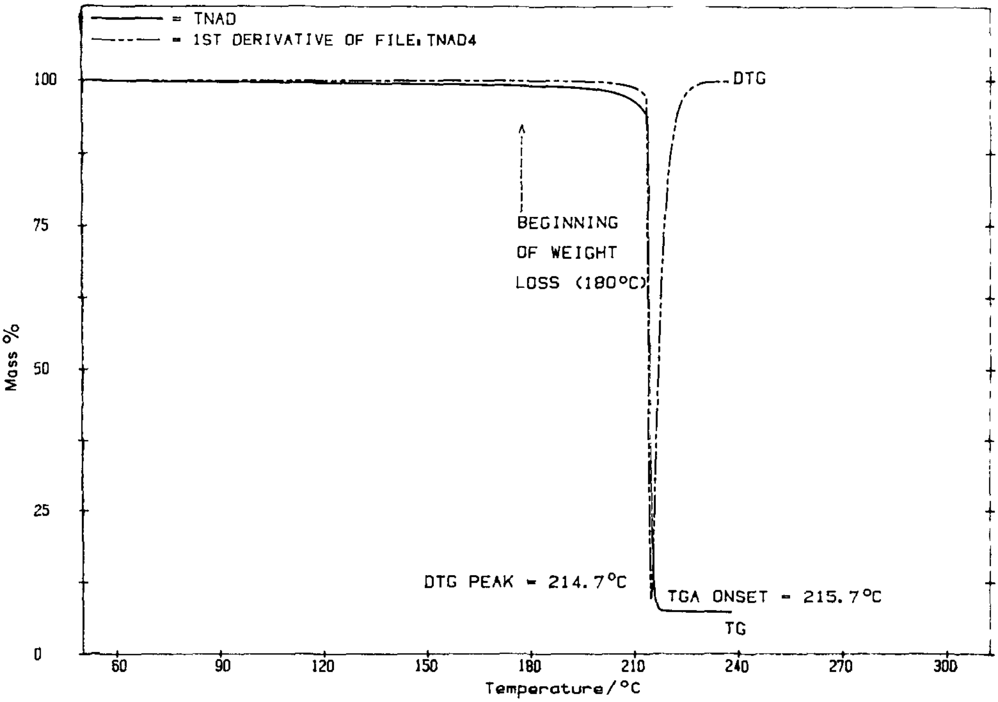

Fig. 4. TGA record of 1,4,5,8-tetranitro-1,4,5,8-tetraazadecaline (TNAD).

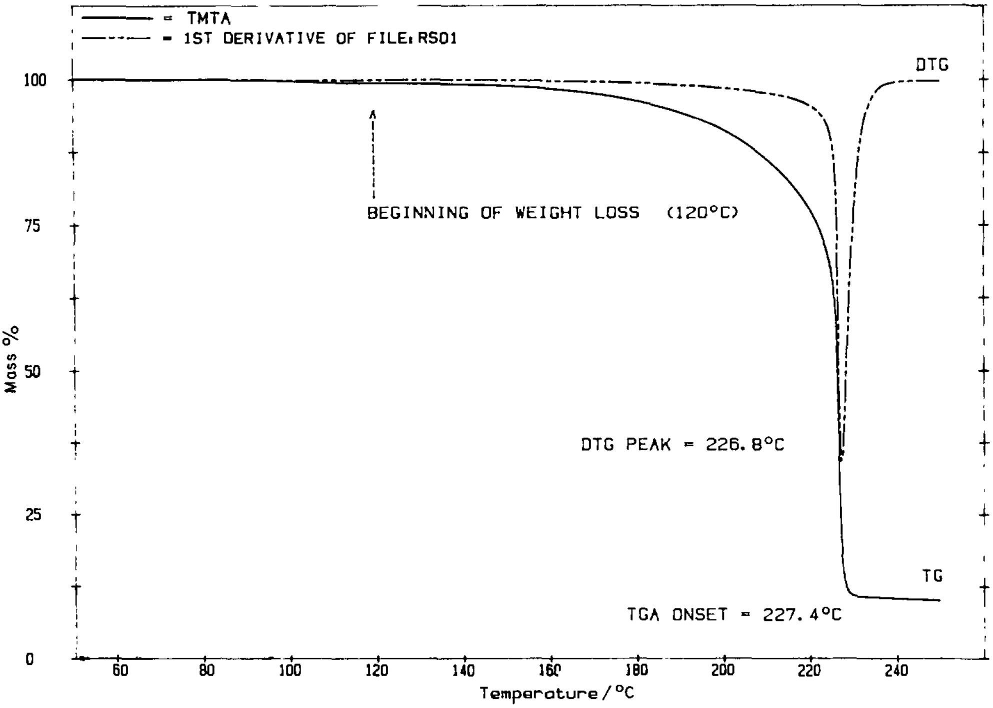

Fig. 5. TGA record of 1,3,5-trinitroso-1,3,5-triazacyclohexane (TMTA).

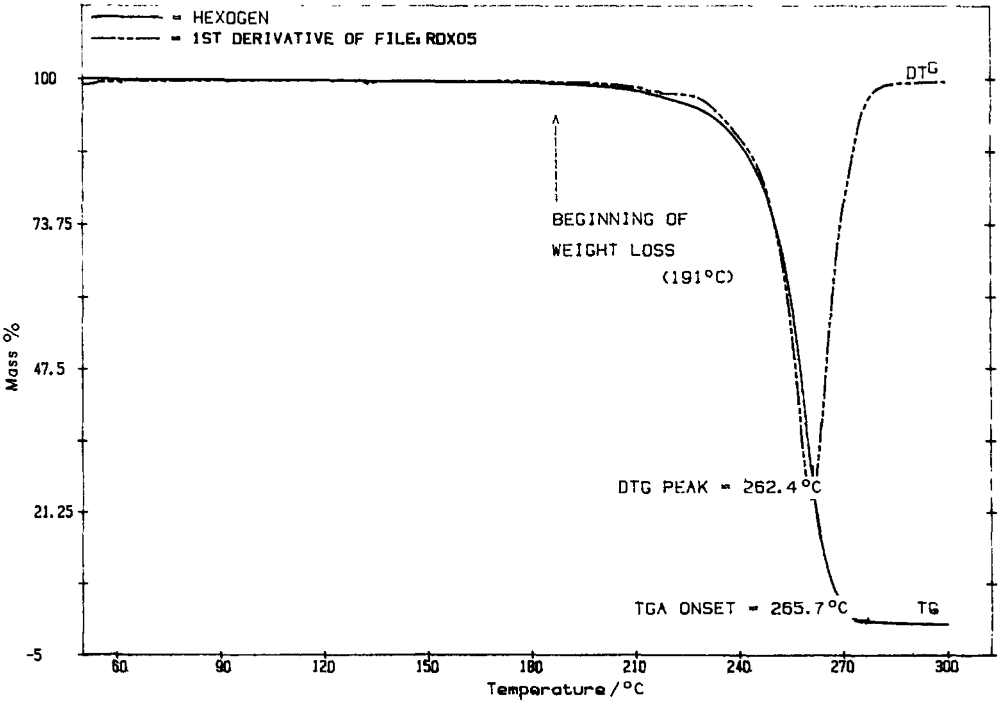

Fig. 6. TGA record of 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX).

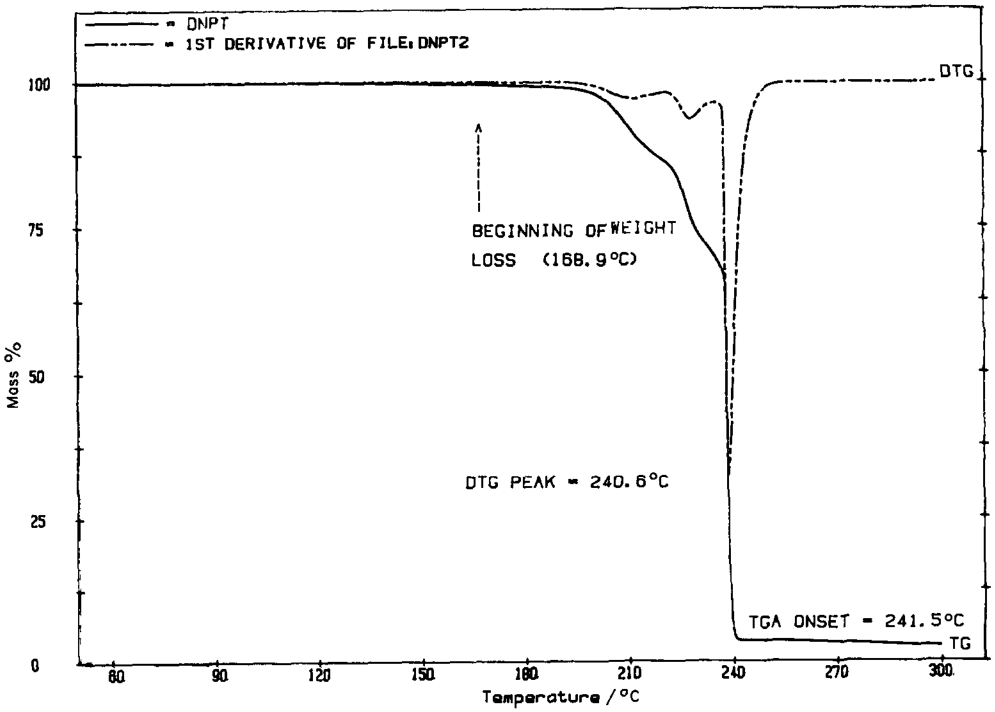

Fig. 7. TGA record of 1,5-methano-3,7-dinitroso-1,3,5,7-tetraazacyclooctane (DNPT).

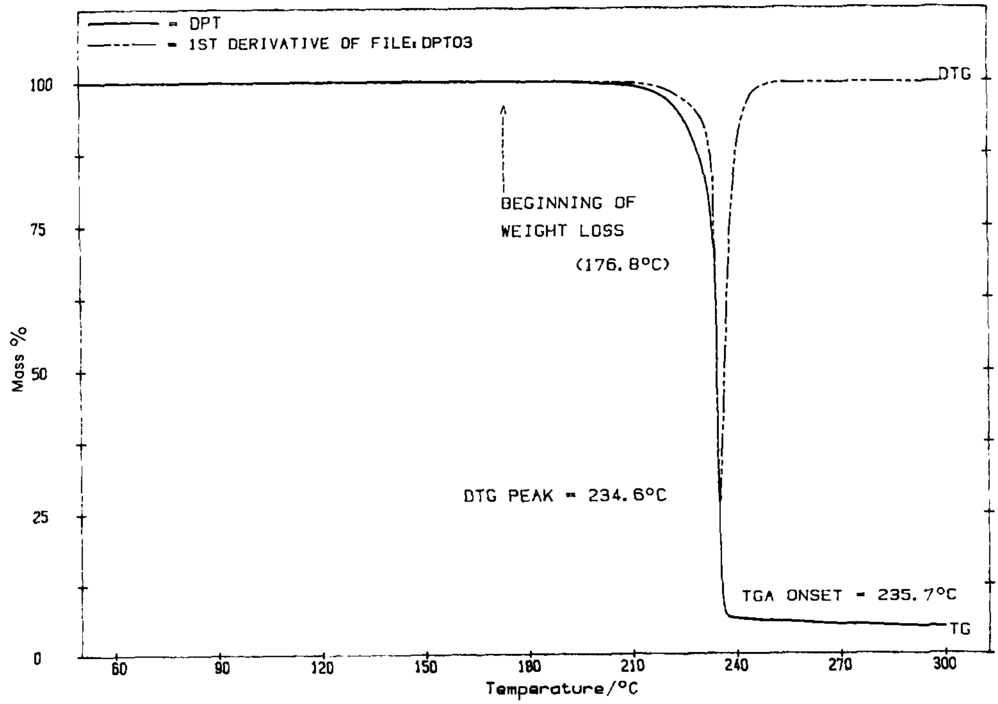

Fig. 8. TGA record of 1,5-methano-3,7-dinitro-1,3,5,7-tetraazacyclooctane (DPT).

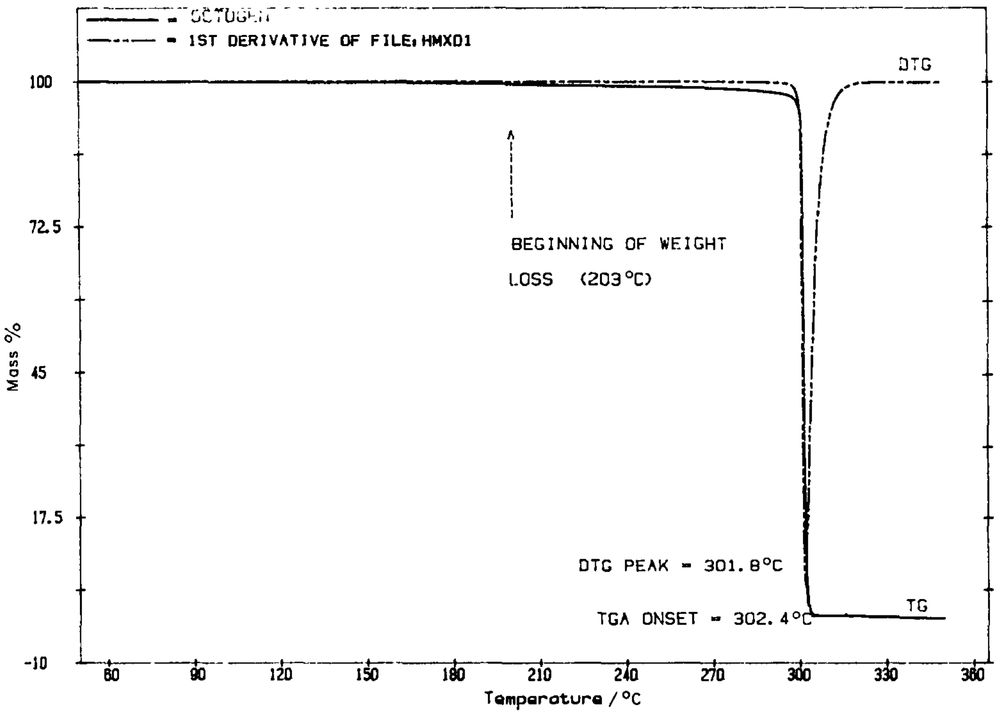

Fig. 9. TGA record of 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX).

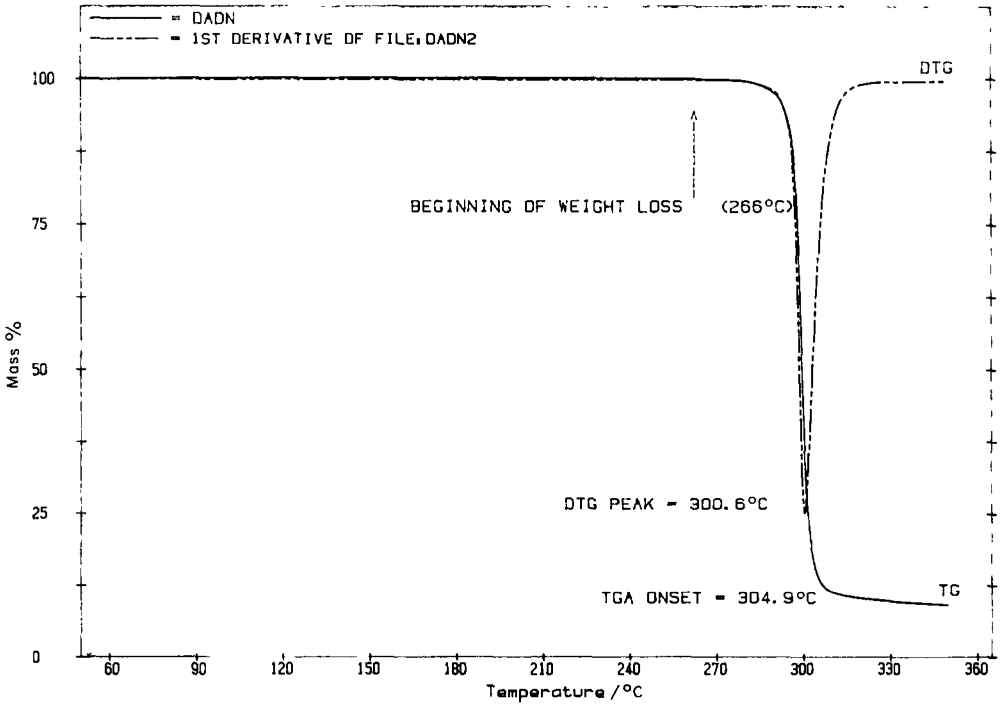

Fig. 10. TGA record of 1,5-diacetyl-3,7-dinitro-1,3,5,7-tetraazacyclooctane (DADN).

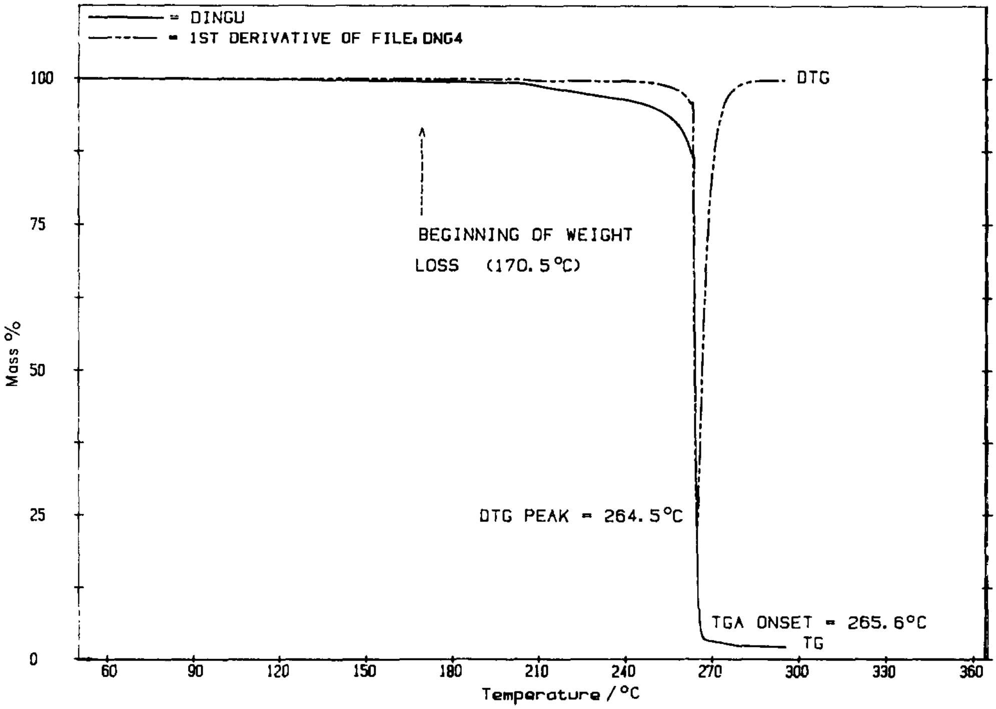

Fig. 11. TGA record of 1,4-tetrahydroimidazo[4,5-d]-imidazol-2,5(1H,3H)dione (DINGU).

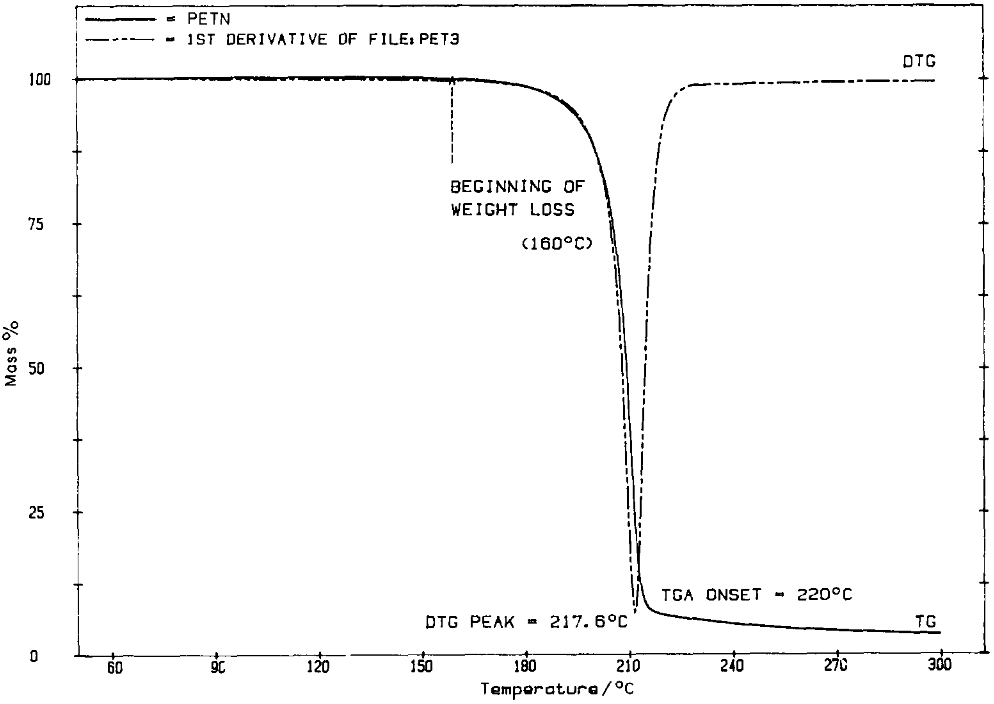

Fig. 12. TGA record of pentaerythritol tetranitrate (PETN).

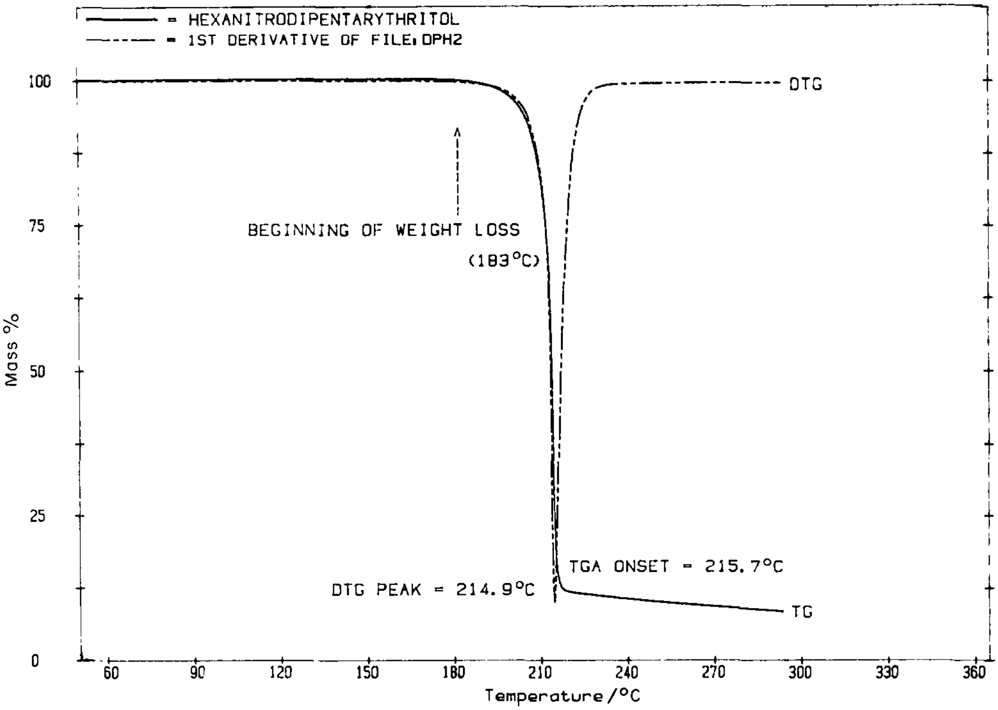

Fig. 13. TGA record of dipentaerythritol hexanitrate (DPEHN).

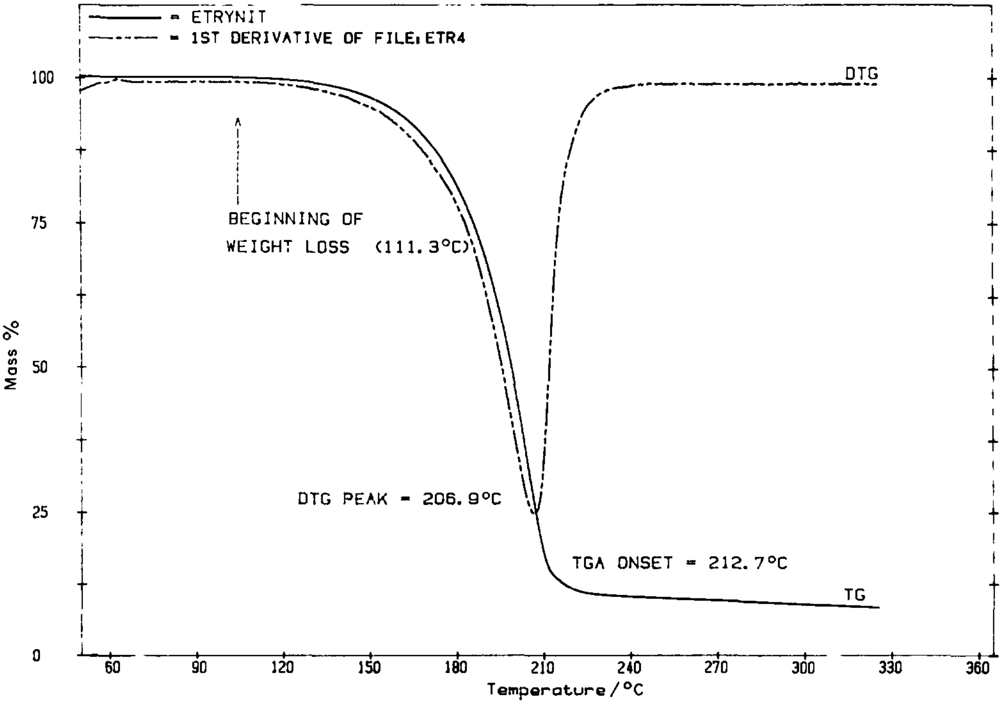

Fig. 14. TGA record of 1,1,1-trimethylolpropanetrinitrate (ETRYNIT).

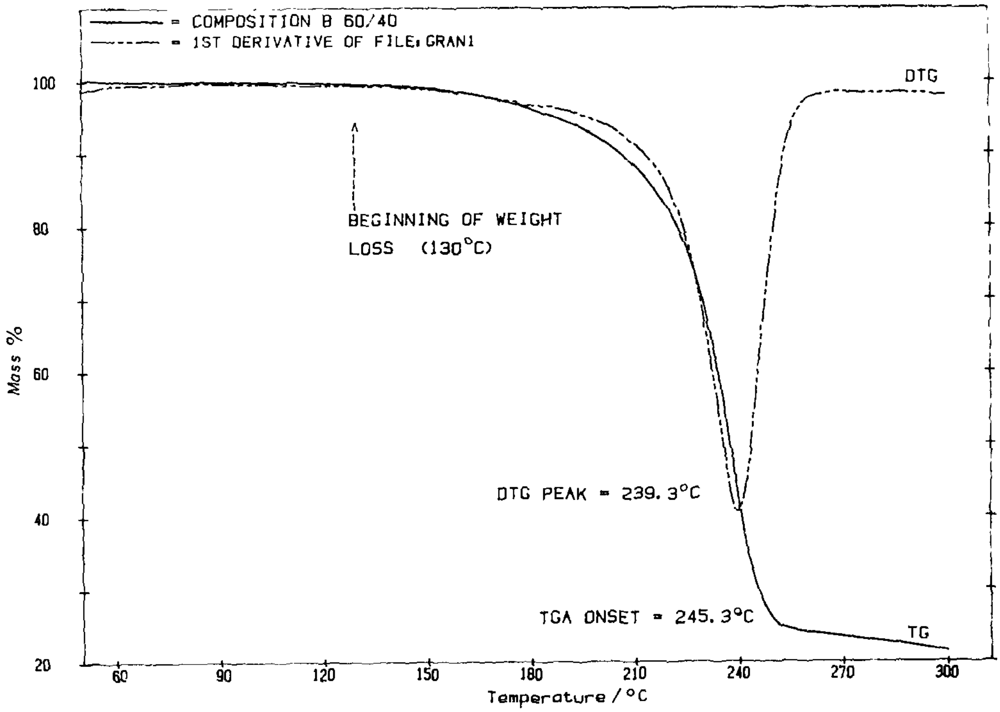

Fig. 15. TGA record of hexolite 60/40 (Composition B).

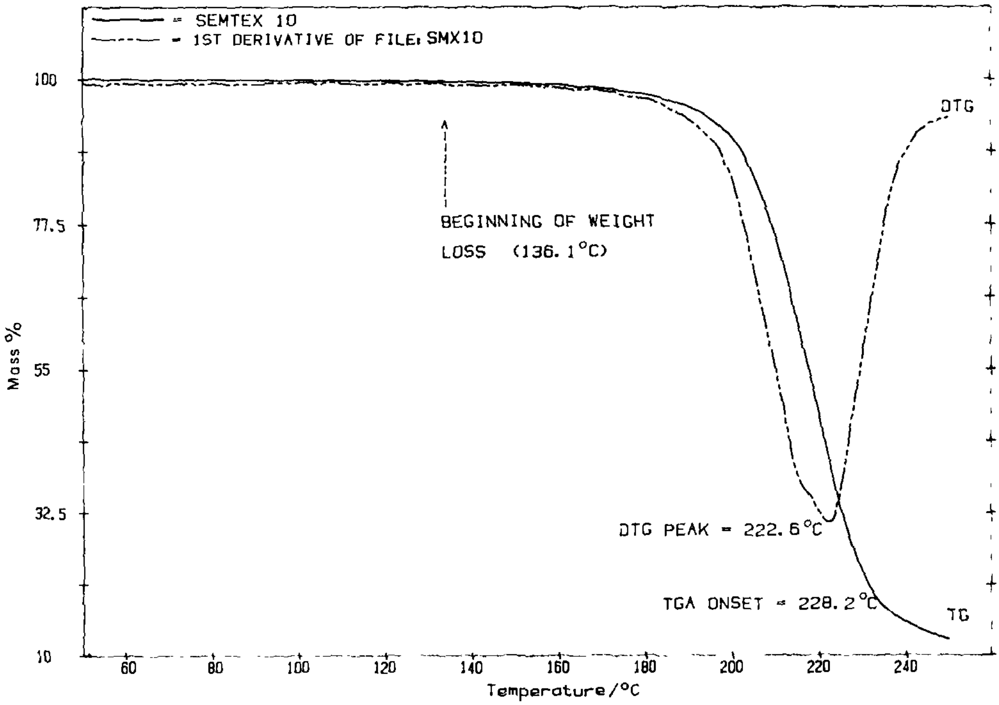

Fig. 16. TGA record of Semtex 10 (Composition C).

Treatment of TGA-7 results

TGA records were analysed by means of the TGA-7 Standard Program, which is licensed by Perkin-Elmer [4]. The observed end of the rapid weight loss portion of the TGA curve is, in the sense of the program, defined as "TGA onset" (see also Figs. 1–16).

RESULTS AND DISCUSSION

As shown in Table 2, eqn. (1) is also valid for the substances under investigation; in the framework of the present paper, TGA onsets are preferred over other TGA characteristics.

The validity of eqn. (2), however, is not unambiguous here (see Fig. 17): correlations for nitrosamines and nitroesters are only suggested, possibly because of a lack of data. In the case of nitrosamines, the slight dependence of their Arrhenius parameter values on molecular structure (see ref. 22) also has a considerable influence.

Comparing the A_{onset} value for explosive 16 with A_{onset} values and data positions for the nitroesters 12–14 in Fig. 17, it can be stated that the plastic binder in mixture 16 exhibits only a slight influence on the thermostability of PETN.

With respect to the nitramines, data for substances 5–8 and 11 do correlate in the sense of eqn. (2) (see Fig. 17); Table 3 presents the

TABLE 2

Coefficients of eqn. (1) for TGA onsets

Substance		A_{onset}	B_{onset}	Correlation coefficient
No.	Abbreviation			
1	DNSDC	15.12	210.47	0.9993
2	TNSAD	−0.95	233.75	−0.9578
3	TMTA	0.33	225.73	0.9958
4	DNPT	−2.06	251.06	−0.9613
5	DNDC	6.38	248.54	0.9484
6	TNAD	0.24	214.51	0.9986
7	RDX	−3.89	281.47	−0.9835
8	HMX	1.48	298.43	0.8566
9	DADN	−2.24	313.07	−0.9982
10	DPT	−1.18	243.60	−0.9191
11	DINGU	−2.26	274.38	−0.9862
12	PETN	−2.20	231.97	−0.9386
13	DPEHN	−2.34	225.87	−0.9922
14	ETRYNIT	4.06	206.09	0.8369
15	Composition B	−2.37	249.51	−0.9758
16	Composition C	−4.36	237.04	−0.9869

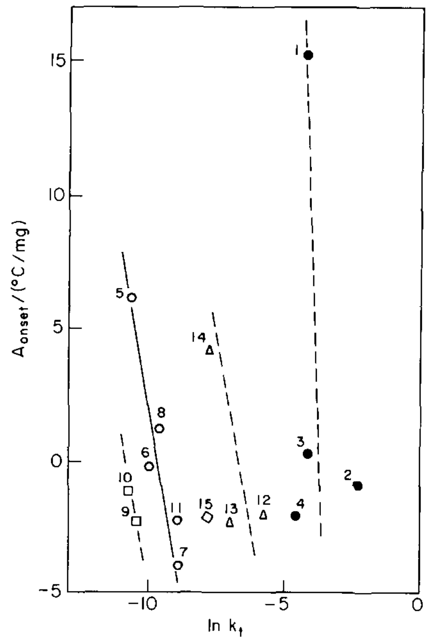

Fig. 17. Graphic representation of eqn. (2) for 200°C. Averaged k_t values were used in the case of substances 3, 10 and 11. Points: ●, nitrosamines; △, nitro-esters; ○, nitramines; □, 1,5-disubstituted derivatives of 3,5-dinitro-1,3,5,7-tetraazacyclooctane; ◇, Composition B. Thermal reactivity decreases in the order: nitrosamines, nitroesters, Composition B, polynitramines and 1,5-disubstituted derivatives of 3,5-dinitro-1,3,5,7-tetraazacyclooctane.

corresponding coefficients. Data for nitramines 9 and 10 do not correlate with the shapes of eqn. (2) (see Fig. 17). A substitution on the nitrogen heteroatoms in positions 1 and 5 in these substances could be the reason for this. Nor do the data correlate with eqn. (2) for mixture 15 which, from the point of view of its thermolysis, behaves as a solution of nitramine 7 in trinitrotoluene. It is known that the kinetic parameters of the thermolysis of nitrocompounds in solutions cannot be applied in the construction of molecular-structural correlations together with kinetic data for pure nitrocompounds (see refs. 18, 23, 24): many derived from solvents, mainly polynitroarenes, do not behave as inerts [23, 24].

TABLE 3

Coefficients of eqn. (2) for nitramines 5, 6, 7, 8 and 11

Coefficient	150°C	200°C	250°C	300°C
a_t	−4.92	−4.76	−4.29	−3.84
b_t	−77.82	−45.19	−18.95	−1.17
Correlation coeff.	−0.9269	−0.9593	−0.9463	−0.9201

TABLE 4

Coefficients of eqn. (3) for the autoignition temperatures T_{expo} and critical temperatures T_{crit}

Coefficient	T_{expo}	T_{crit}
c_x	-1.762×10^{-2}	-1.586×10^{-2}
d_x	8.4464	8.8477
Correlation coeff.	−0.8894	−0.89421

On the basis of the data in Table 3, the Arrhenius parameters for nitramine 11 were averaged; the values obtained in this way (see Table 1) are valid.

From the published values, autoignition temperatures T_{expo} or critical temperatures T_{crit} (see Table 1) specify the corresponding shapes of eqn. (3); their coefficients are presented in Table 4. As is shown, the molecular structure of the studied compounds do not have a significant influence on the correlation in the sense of eqn. (3). This reflects the dependence displayed by commerical explosives [2].

The values T_{expo} and T_{crit} for explosive 16 (see Table 1), which were calculated according to the shapes of eqn. (3), indicate approximately the same thermal stability for mixture 16 as for pure PETN. The T_{crit} value for nitrosamine 4 (see Table 1) obtained in an anologous manner, is in good conformity with the value of the so-called, decomposition temperatures (200–210°C) of the rubber blowing agents obtained from technical grade DNPT (Eiwa Chemical Ind. Co., Ltd.) [25].

CONCLUSIONS

A linear dependence exists between the position of the TGA onsets and the weight of the samples in nitramines, nitrosamines and nitroesters. There is a relationship between the intercept values of the above-mentioned dependence and the autoignition temperatures or critical temperatures of the compounds under study. In this case the relationship is not significantly influenced by molecular structure. The slope of this dependence is closely related to the thermal reactivity and to the molecular structure of the nitrogen compounds. On the basis of the derived relationships, it can be stated that the explosive Semtex 10 exhibits approximately the same thermal stability as its active component, i.e. pentaerythritol tetranitrate. As demonstrated by the mixture Composition B, the parameters of the thermolysis of nitrocompound solutions cannot be used to indicate molecular-structural correlations because many materials derived from solvents, mainly polynitroarenes, do not behave as inerts [18, 23, 24].

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