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THERMOGRAVIMETRIC ANALYSIS OF POLYNITRO ARENES

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Abstract

Attention was paid to seventeen samples of polynitro arenes. Stability of these nitrocompounds was specified by means of non-isothermal thermogravimetric analysis (TG). Linear relationships were specified between the positions of TG-onsets and the mass of the samples. The relation of slopes of the mentioned relationships to the rate constants of the thermal decomposition under condition of Russian manometric method (SMM) was confirmed and solved for studied polynitro arenes. These arene derivatives were classified into several groups in the sense of this relation. The classification was interpreted by dominating influence of intermolecular interaction factors on the corresponding TG-onsets positions. The found relations can be used for the TG results conversion to the parameters, which are comparable with SMM outputs.

Keywords: explosives, polynitro arenes, TG, thermal decomposition

Introduction

Recently, the new method of results interpretation of the thermogravimetric analysis (TG) of urea-formaldehyde polycondensates has been presented [1]. The method was already applied in TG [6] of commercial explosives [2], some aminoderivatives of 1,3,5-trinitrobenzene [3], nitramines and nitric esters [4] and, at the last time, military plastic explosives [5]. The method is based on the relationship [1–6]:

$$P_i=A_in+B_i \tag{1}$$

where P_i is a position of DTG-peak (P_{peak}) or TG-onset (P_{onset}) on the temperature scale (in °C) and n is a weighed amount given in mg.

A_i coefficients of Eq. (1) are linked up with the reactivity of measured compounds [1, 3, 4, 6]. In the case of one-component explosives the following relationship was found [3]:

$$A_i=a\ln k_i+b \tag{2}$$

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Table 1 Survey of the studied polynitro arenes, their code designation and Arrhenius parameters of their non-autocatalyzed thermal decomposition

Polynitro arene			Arrhenius parameters					
No.	Chemical name	Code designation	Method of decomp. study	For the state	Temperature region/K	E_a/ kJ mol^{-1}	log$A$/s^{-1}	Ref.
1	1-Amino-2,4,6-trinitrobenzene	PAM						
1.1			SMM	liquid	523–573	129.8	7.1	[7]
2	1,3-Diamino-2,4,6-trinitrobenzene	DATB						
2.1			SMM	solid	493–543	196.8	13.2	[8]
3	1,3,5-Triamino-2,4,6-trinitrobenzene	TATB						
3.1			DSC	solid	[a]	250.6	19.5	[9]
3.2			SMM	solid	557–593	175.0	11.6	[8]
4	2,2’,4,4’,6,6’-Hexanitrooxanilide	HNO	SMM	solid	503–568	215.6	16.0	[8]
4.1								
5	2,2’,4,4’,6,6’-Hexanitrodiphenylamine	DPA						
5.1			TG	solid–liquid	473–573	153.3	11.0	[3]
6	2,2’,4,4’,6,6’-Hexanitrostilbene	HNS						
6.1			DSC	liquid	590–628	126.7	9.2	[9]
6.2			SMM	solid	533–573	183.8	12.0	[8]
6.3			extrapol.	solid–liquid	523–623	140.9	10.3	[b]
7	2,4,6-Trinitrotoluene	TNT						
7.1			SMM	liquid	463–523	144.4	9.3	[11]
7.2			DSC	liquid	[a]	143.9	11.4	[9]
7.3			extrapol.	liquid	523–623	157.0	10.8	[b]

Table 1 Continued

Polynitro arene			Arrhenius parameters					
No.	Chemical name	Code designation	Method of decomp. study	For the state	Temperature region/K	E_a/ kJ mol^{-1}	log$A$/s^{-1}	Ref.
8	1,3,5-trinitrobenzene	TNB						
8.1			SMM	liquid	523–583	180.0	10.9	[11]
9	2,2’,4,4’,6,6’-Hexanitrobiphenyl	HNB						
9.1			SMM	liquid	513–573	207.2	16.1	[7]
10	2,2’,4,4’,6,6’-Hexanitrodiphenylsulfide	DIPS						
10.1			SMM	solid	473–493	178.8	12.0	[7]
10.2			SMM	liquid	508–528	131.8	7.4	[12]
10.3			extrapol.	liquid	523–623	162.2	9.9	[b]
11	2,2’,4,4’,6,6’-Hexanitrodiphenylsulfone	DIPSO						
11.1			SMM	solid	475–563	106.7	5.6	[13]
12	2,2’,2’’,4,4’,4’’,6,6’,6’’-Nonanitro-*m*-terphenyl	NONA						
12.1			DTA	solid	572–596	214.1	14.1	[14]
13	2,4,5-tris(2,4,6-Trinitrophenylamino)-1,3,5-triazine	TPM						
13.1			SMM	solid	523–563	257.0	19.0	[8]
14	2,4,6-tris(2,4,6-Trinitrophenyl)-1,3,5-triazine	TPT						
14.1			SMM	solid	573–623	269.4	18.1	[15]
15	1,4,5,8-Tetranitronaphthalene	TENN						
15.1			DTA	solid	572–595	214.1	14.1	[14]

Table 1 Continued

Polynitro arene			Arrhenius parameters					
No.	Chemical name	Code designation	Method of decomp. study	For the state	Temperature region/K	E_a/ kJ mol^{-1}	log$A$/s^{-1}	Ref.
16	1,3,7,9-Tetranitrophenothiazine-5,5-dioxide	TNPTD						
16.1			SMM	solid	523–573	200.9	11.7	[8]
16.2			SMM	solution[c]	483–603	259.8	17.4	[30]
16.3			extrapol.	solid–liquid	523–623	249.2	17.7	[b]
17	Trinitrotoluene (military) with 0.4 mass% of HNS	TNT/HNS						
17.1			extrapol.	liquid	523–623	152.8	10.8	[b]

[a] in the original paper is not presented; [b] extrapolated in this paper by means of Eq. (2) and data from Tables 2 and 3; [c] solution in hexachlorobenzene

where k_i is a rate constant of the thermal decomposition under conditions of the Russian manometric method (SMM – e.g. [7, 20]).

As the obtained results [1–6] are important from a practical point of view, the above-mentioned TG method is extended in this paper to the study of attractive polynitro arenes. The paper is a direct continuation of a work from [3].

Experimental

Data and substances

Survey of the studied polynitro arenes and their derivatives is given in Table 1. It also contains values of the Arrhenius parameters E_a and log$A$ of their non-autocatalyzed low-temperature thermal decomposition (also [20]). The parameters were obtained mainly by means of Russian manometric method (SMM.) and partially by differential scanning calorimetry (DSC – its outputs are comparable with SMM results in many cases). Several TG and DTA results were also applied after their conversion into parameters, comparable with SMM ones by means of calibration curves [3, 6, 14].

The origin and purity of the measured compounds are described in [23–26]. A sample of military TNT, modified by 0.4 mass% of HNS, is a product of CHEMKO’s Special Production Plant (Slovak Republic).

Apparatus

All of the measurements were performed using TGA-7 (Perkin Elmer) apparatus operating at a heating rate of 20°C min^{-1}, with weighed samples up to 11 mg, thermally

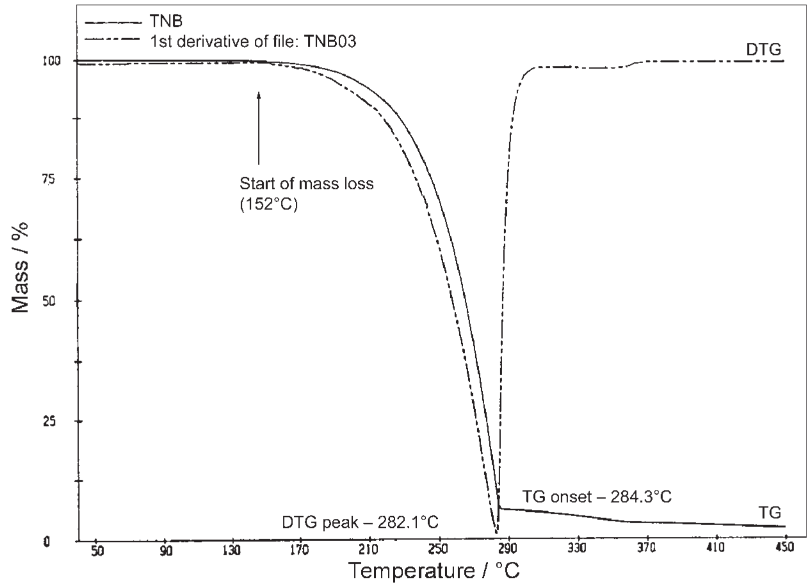

Fig. 1 TG record of 1,3,5-trinitrobenzene (TNB)

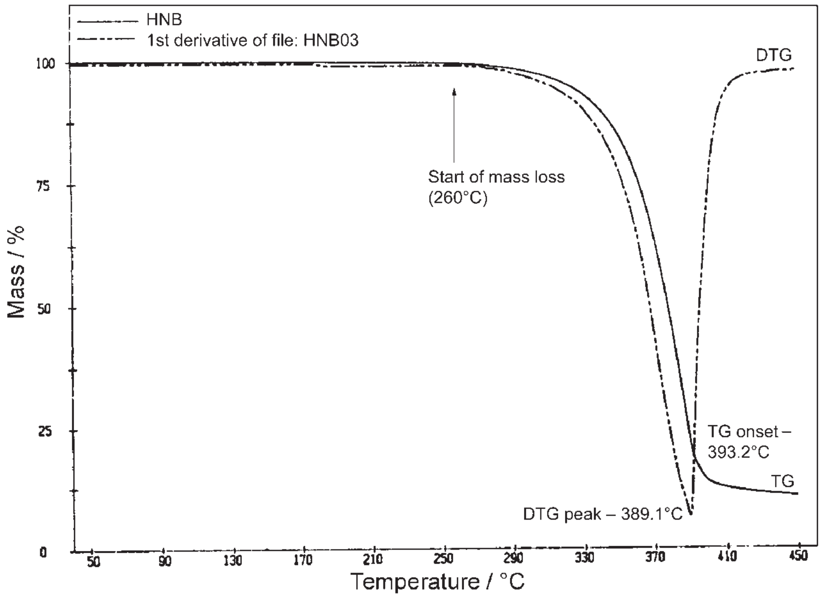

Fig. 2 TG record of 2,2',4,4',6,6'-hexanitrobiphenyl (HNB)

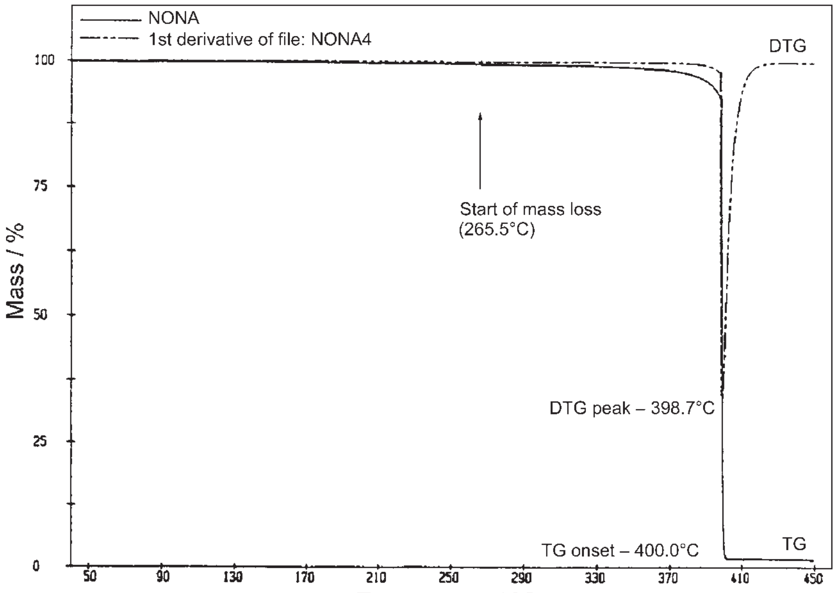

Fig. 3 TG record of 2,2',2'',4,4',4'',6,6',6''-nonanitro-*m*-terphenyl (NONA)

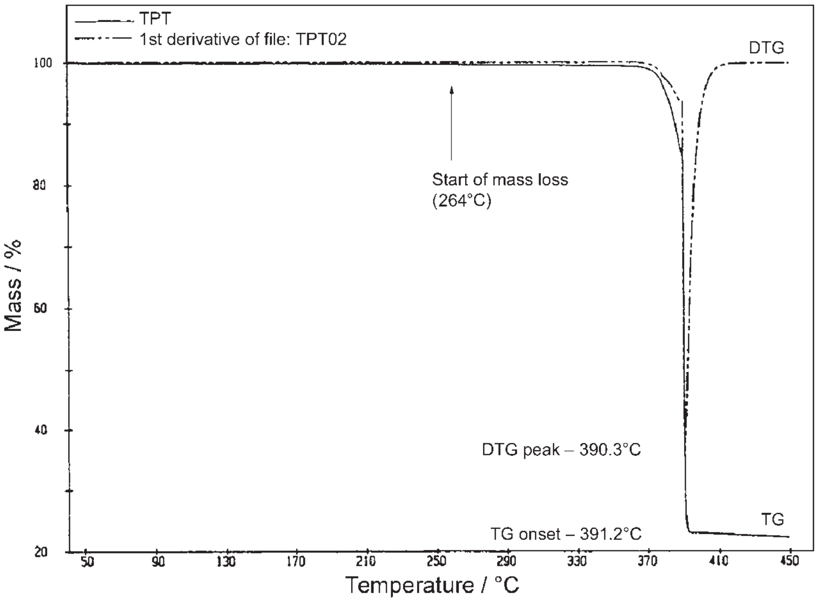

Fig. 4 TG record of 2,4,6-tris(2,4,6-trinitrophenyl)-1,35-triazine (TPT)

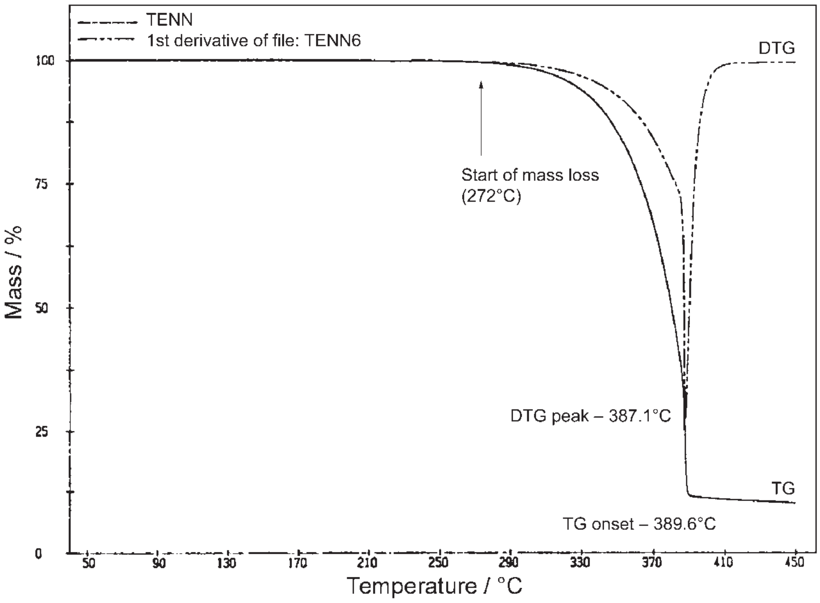

Fig. 5 TG record of 1,4,5,8-tetranitronaphtelane (TENN)

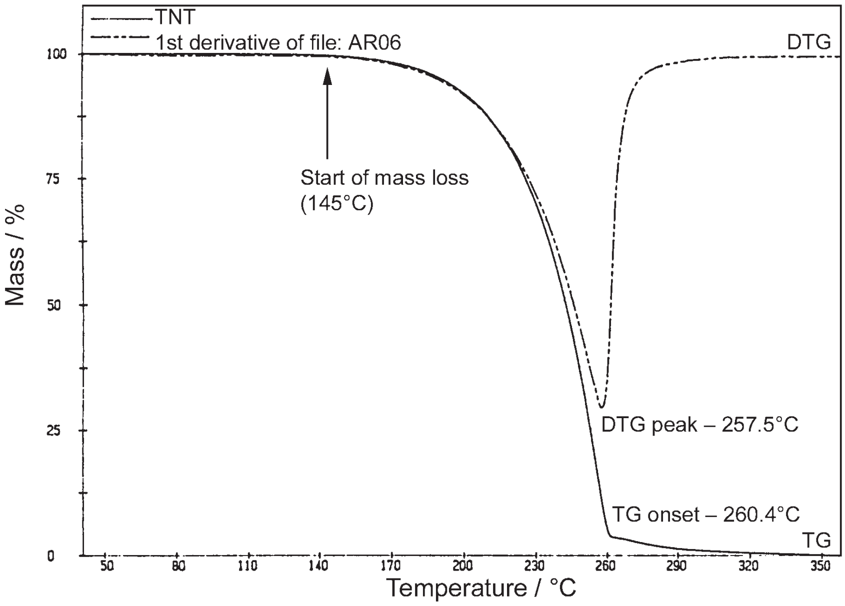

Fig. 6 TG record of 2,4,6-trinitrotoluene (TNT)

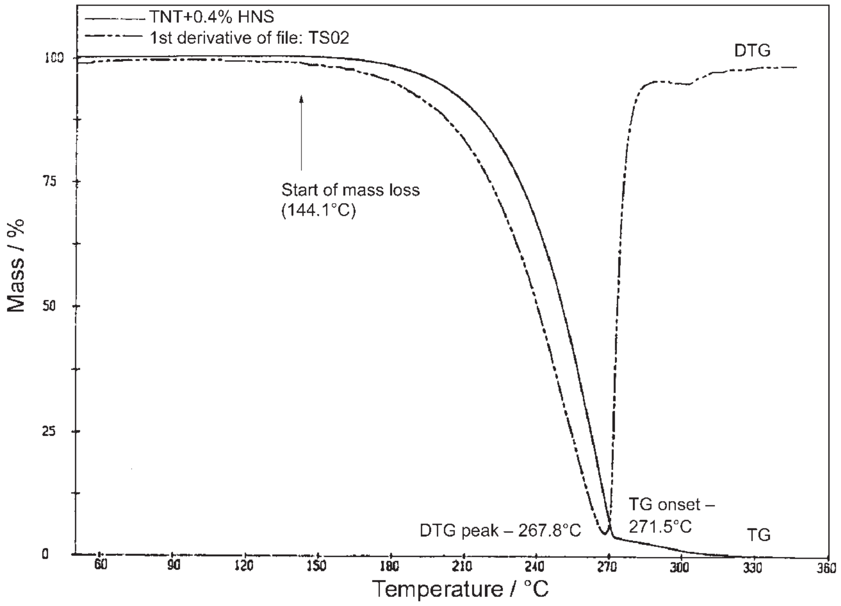

Fig. 7 TG record of 2,4,6-trinitrotoluene modified by 0.4 mass% of HNS (TNT/HNS)

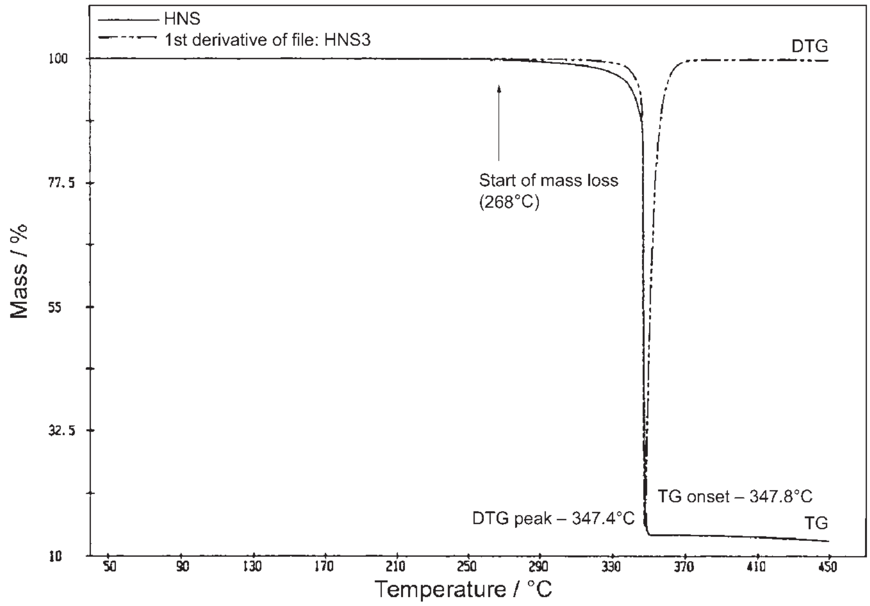

Fig. 8 TG record of 2,2',4,4',6,6'-hexanitrostilbene (HNS)

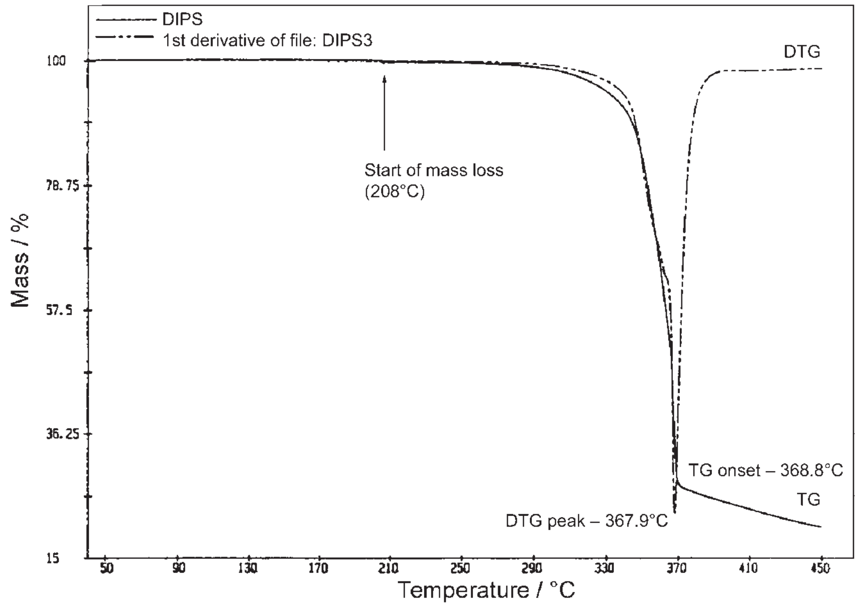

Fig. 9 TG record of 2,2',4,4',6,6'-hexanitrodiphenylsulfide (DIPS)

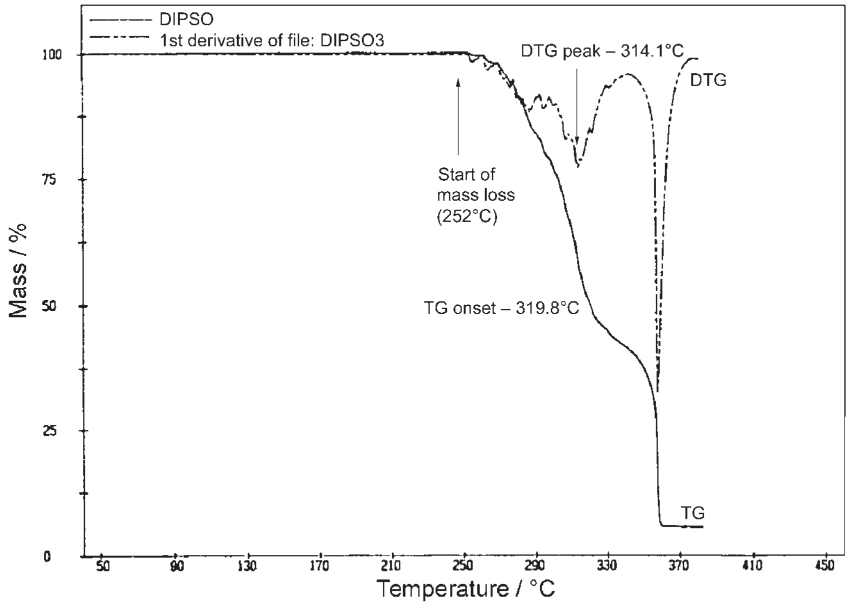

Fig. 10 TG record of 2,2',4,4',6,6'-hexanitrodiphenylsulfone (DIPSO)

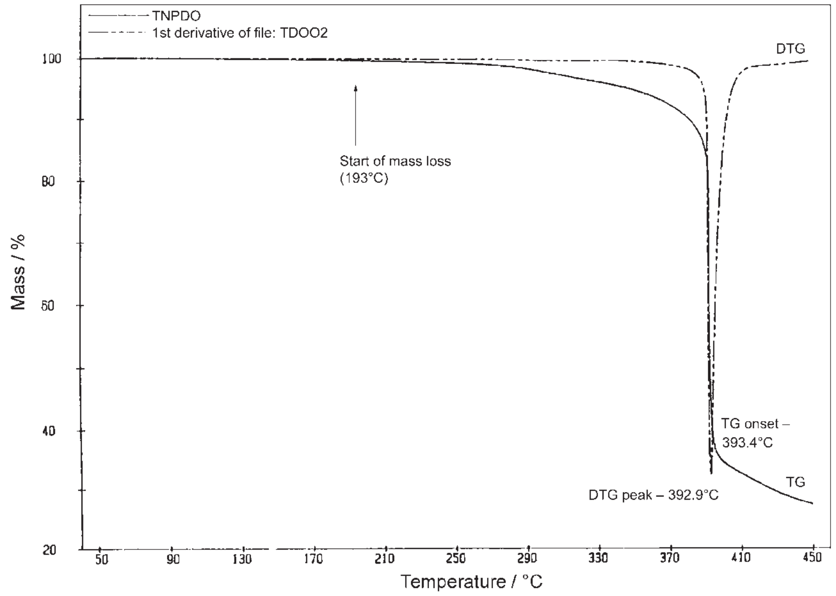

Fig. 11 TG record of 1,3,7,9-tetranitrophenothiazine-5,5-dioxide (TNPTD)

decomposed in a nitrogen atmosphere. TG onsets are defined according to a software of Perkin Elmer Corp. [16]: this definition is obvious from Figs 1–11 which present the TG records of the substances 6–12, and 14–17 (examples of TG records of substances 1–5 and 13 [3]).

Results and discussion

Similarly to TG analysis of urea-formaldehyde polycondensates [1] and explosives [2–6], the position of the characteristic changes in TG records of the studied compounds are influenced by the sample mass in the sense of Eq. (1). Coefficients of the equation for studied substances are given in Table 2.

Table 2 Coefficients of Eq. (1) for TG-onsets (*i.e.* P_{onset})

Polynitro arene		A_i/°C mg^{-1}	B_i/°C	Coefficient of correlation	Ref.
No.	Code designation				
1	PAM	33.42	230.17	0.9998	[3]
2	DATB	35.10	273.06	0.9999	[3]
3	TATB	22.02	366.65	0.9744	[3]
4	HNO	8.61	309.05	0.9906	[3]
5	DPA	3.88	254.82	0.9990	[3]
6	HNS	–5.31	392.31	–0.9294	this paper
7	TNT	5.81	250.01	0.9595	this paper
8	TNB	5.75	244.38	0.9447	this paper
9	HNB	3.12	367.73	0.9262	this paper
10	DIPS	–2.34	375.89	–0.9919	this paper
11	DIPSO	0.90	310.83	0.9555	this paper
12	NONA	–3.84	433.87	–0.9082	this paper
13	TPM	1.75	323.58	0.7838	[3]
14	TPT	–3.38	412.36	–0.9602	this paper
15	TENN	1.00	382.11	0.8980	this paper
16	TNPTD	0.67	396.08	0.95370	this paper
17	TNT/HNS	4.51	253.60	0.9973	this paper

In the case of energetic materials the physical meaning of Eq. (1) is close to the problem of thermal explosion during linear heating [17]. With respect to the fact that the balance of heat flow in the theory of thermal explosion involves also the rate constants of monomolecular decomposition [9, 17–19], the existence of Eq. (2) is comprehensible.

The obtained results testify the validity of Eq. (2) also for substances being measured (rate constants k_i values were calculated from Arrhenius parameters in Table 1).

Coefficients of Eq. (2) for temperatures 250, 300 and 350°C are presented in Table 3. In the sense of this equation, the set of the studied polynitro compounds is broken into three groups and 1,3,5-trinitrobenzene (Table 3) [6]:

Table 3 Coefficients of Eq. (2) – taken from [6].

Group of polynitro arenes			Coefficients			
No.	Code designation	Structure of data*	For temperature/°C	*a*	*b*	correlation
I	PAM, DATB, TATB, HNO, DPA, HNS	1.1, 2.1, 3.2, 4.1, 5.1, 6.1	250	–6.2	–59.56	0.9198
			300	–6.93	–44.28	0.9050
			350	–8.5	–35.64	0.9327
II	DPA, HNB, DIPS, DIPSO, NONA	5.1, 9.1, 10.1, 11.1, 12.1	250	1.21	15.16	0.9346
			300	1.56	15.11	0.8772
			350	1.15	7.41	0.8662
III	TPM, TPT, TENN	13.1, 14.1, 15.1	250	1.14	19.58	0.9869
			300	1.28	15.45	0.9148
			350	1.11	8.88	0.8599

*data numbered as in Table 1

I) polyamino-derivatives of 1,3,5-trinitrobenzene (PAM, DATB and data 3.2 of the TATB), hexanitrostilbene (HNS) and hexanitrodiphenylamine (DPA), *i.e.* nitrocompounds with dominating electron configuration near sp^2 or directly sp^2 of ground state at the atom which primarily interacts, through the hydrogen atom bound to it, during the thermal decomposition with the oxygen atom of *ortho*-standing nitro group [21, 22] – data of TNT excellently correlate with this shape of Eq. (2);

II) dipicryl-derivatives (HNB, DIPS, DIPSO), including NONA and also DPA, i.e. inhomogenous group of compounds from the point of view of primary fission processes of their thermal decomposition – dominating influence of intermolecular interaction (stabilizing influence of crystal lattice) on this fission might influence the position of corresponding TG-onsets;

III) derivatives of 1,3,5-triazine (TPM and TPT) and TENN, i.e. compounds with centrosymmetrical molecules and with very strong intermolecular interactions in corresponding crystals;

IV) 1,3,5-trinitrobenzene, the data of which correlate with neither of the shapes of Eq. (2) – probably due to distillation of the nitrocompound under experimental conditions.

Data 3.1 of the TATB do not correlate with shape of Eq. (2) for group I. With respect to the conclusions of paper [3], the instability of the liquid phase of TATB at atmospheric pressure (its sublimation at temperature around its hypothetical melting point [3]) can be the reason for this phenomenon. Facts verified the assumption [3] that kinetic parameters of the TATB thermal decomposition in vacuum (*i.e.* under conditions of SSM [8]) could be influenced by endothermic changes of this substances, especially by high vapor pressure over its crystals in the corresponding measurements.

The above-mentioned classification of the studied substances shows that only the constitution of the group *I* is determined by chemical mechanism of the primary fission in their thermal decomposition. The substances possess hydrogen bonding in their molecules (in the case of TATB [27]). Their primary thermal decomposition involves migration of the hydrogen atom from the mentioned bonding (through a six-membered transition state) to the oxygen of *ortho*-nitro group: this mechanism is also called 'trinitrotoluene mechanism' [28, 29]. Arrhenius parameters of the sample 16 (*i.e.* TNT modified by 0.4 mass% of HNS), HNS and also TNT (*i.e*. data 6.3 and 7.3) were calculated in this paper by means of Eq. (2) for this group (Table 1).

Intermolecular interactions in the crystals of the largest molecules in the groups II and III of the studied nitrocompounds cause a suppression of the influence of primary fission in the thermal decomposition on TG-onsets positions, *i.e.* upon these compounds classification according to primary mechanisms of their pyrolysis. This is a contrast to some differential thermal analysis [6, 14, 21–26] and differential scanning calorimetry studies (e.g. [6, 22]). It can be mentioned that a similar influence of the intermolecular interactions was recorded when the initiation of individual energetic materials by impact [31] and electric spark [32] was studied.

The above-mentioned difference between the applied TG method and both the DTA and DSC methods is not a restriction in use of Eqs (1) and (2) for conversion of TG results into parameters comparable with the SMM results. Thus taking shape of Eq. (2) for group II the data 10.3 result for thermal decomposition of DIPS in the liquid state which are near these data 10.1, however, for solid state decomposition: it might be caused by large temperature region of extrapolation. Likevise data 16.3 for TNPTD result by means of the shape of Eq. (2) for group III. The data are almost identical with ones 16.2 for TNPTD decomposition in hexachlorobenzene solution. The mutual correspondence of both data may be due to the dissolution of TNPTD in its decomposition products because its thermal decomposition starts in the solid state at about 492 K [33] and its liquidification begins at 572.3 K [33]. Nevertheless, the temperature region of the data 16.3 extrapolation is 523–623 K (Table 1).

Conclusions

As found in recent studies [2–6] and confirmed in the present paper, the positions of the onsets (defined according to the software [14]) in the non-isothermal TG of energetic materials are influenced by the sample mass: this interference is described by a linear relationship (1). The physical meaning of the relationship is close to the problem of thermal explosion during linear heating (about this explosion [17]). In the light of these facts the relation of slopes of Eq (1) to the rate constants of thermal decomposition of polynitro compounds under conditions of Russian manometric method (SMM), i.e. existence of Eq. (2), is comprehensible [6]. Studied polynitro arenes are classified into three groups in the sense of Eq. (2): it is caused by the dominating influence of intermolecular interactions in the nitrocompounds on the corresponding TG-onsets positions. If the mentioned interaction factors are dominantly conditioned by the hydrogen bondings, then the chemical mechanism of the primary fission in thermal decomposition apparently determines the structure of the given group of polynitro arenes. On the basis of both solved relations, the TG results can be converted to parameters, which are comparable with SMM outputs.

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