ELSEVIER Thermochimica Acta 247 (1994) 447–454

thermochimica
acta

Dependence on temperature of the results of the vacuum stability test for explosives

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Received 27 September 1993; accepted 14 March 1994

Abstract

The rates of isothermal decomposition at 110°C of fourteen explosives are specified by means of the Czech vacuum stability test STABIL. A dependence was found between these rates and the explosion (detonation) temperatures of the studied explosives. This dependence indicates that there may be some relationship between the rates of the processes in low-temperature thermolysis and the rate of the conversion in the reaction zone of the detonation of these explosives.

Keywords: Decomposition; Detonation; Explosive; Isothermal; Stability; Thermolysis; Vacuum stability test

1. Introduction

Sufficient stability is the basic property of explosives from the standpoint of their functional properties, safety in handling and long-term storage capacity. The most widely used methods that specify the chemical stability of explosives are manometric methods. For about a century, a variety of vacuum methods has been

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SSDI 0040-6031(94)01803-0

employed to this purpose (see Ref. 1 and references cited therein). Among the best known at present, are the isothermal manometric method in the Russian version [2,3] (for its short history, see Ref. 4) and the Amercian vacuum stability test [5–7]. The former method, which in Refs. 11–15 was named the Soviet manometric method (with code designation SMM), is used for the kinetics determination of the non-autocatalysed initial stage of explosives thermolysis [2–4]. The American vacuum stability test, however, is more suitable for the technical assessment of an explosive's stability [5–7]. The Czech system STABIL [8–10] can be considered as an automatic version of the American vacuum stability test.

Data, which are obtained from the study of the initial non-autocatalysed stage of thermal decomposition by means of SMM, correlate well with the characteristics of the detonation of the said compounds (see, for example, Refs. 11–13); the relationship to the impact sensitivity of explosives is also obvious [14,15].

The results obtained from the American vacuum stability test, however, appear to be part of the technical conditions of the explosives [16] or quality specifications in the corresponding tests. The same is valid in the STABIL system. The relationship between these results and the characteristics of explosion conversions has not yet been described. To rectify this, in this paper we apply the results of the thermal reactivity specification of commercial explosives using the STABIL system. Some of the commercial explosives studied come from the oldest Czecho-Slovak producer, the firm Istrochem, in Bratislava, which was established in October 1873 as a branch of the Dynamit Nobel Wien and, from 1953 to 1990, was known as CHZJD, Bratislava.

2. Experimental

2.1. Data and materials

The properties and necessary data of the applied commercial explosives are contained in Table 1: explosives 1–7 are produced by Istrochem, Bratislava; hydrophobized ammonium nitrate, sample 8, is a product of VCHZ Synthesia, Pardubice, whose commercial explosives division, Explosia, manufactures PETN plastic explosive, Semtex 10 (sample 9). RDX_{warmed} (hexogen, which was stabilized in boiling water) and Composition B (hexolite 60/40) are products of Chemko's Special Production Plant. TNT_{flake} (trinitrotoluene) is a foreign product, which corresponds to the NATO standard [23]. Pentolite was prepared in the laboratories of Chemko's Special Production Plants from TNT_{flake} and PETN (penterythritol tetranitrate, whose origin and purity are given in Ref. 24). Explosives 1–6 contain liquid nitroesters, i.e. liquid esters of nitric acid; explosive 7 is an amatol type, i.e. based on TNT–ammonium nitrate mixture. These explosives have a slightly positive oxygen balance. The other samples are high explosives with negative oxygen balances.

Table 1
Characteristics of the studied explosives

Sample no.	Explosive [a]	Liquid nitroesters content in wt%	Detonation temperature		Rate of thermolysis in $cm^3\ g^{-1}\ h^{-1}$
			T_E in K	Ref.	
1	Danubit 1	20.7	3263	17	0.2599
					0.3607
2	Danubit 2	22.5	3412	17	0.3371
					0.3334
3	Danubit Geofex 2	40.9	3750	17	2.2552
					2.3388
4	Carbodanubit	25.0	2758	17	0.4081
					0.3286
5	Harmonit AD	10.0	1808	17	0.0105
					0.0258
6	Slavit	10.0	2173	17	0.0265
					0.0387
7	Polonit V	0.0	3250	17	0.0367
					0.0284
8	Ammonium nitrate	–	1630	18	0.0198
			1818	17	0.0201
9	Semtex 10	–	4143	17	0.0334
					0.0349
10	TNT_{flake}	–	3600	19	0.0015
			3420	20	0.0016
11	PETN	–	4400	19	0.1011
			4540	20	0.0981
			4643	17	
12	RDX_{warmed}	–	3816	17	0.0078
			4300	19	0.0082
			3700	21	
13	Composition B	–	3633	22	0.0388
			3910	30	0.0297
14	Pentolite 75/25	–	4075	17	0.0785
					0.0799

[a] For information on the consistency and applicability of these explosives, see Ref. 22.

2.2. Apparatus

The vacuum stability test was carried out using the STABIL system (Metra, Blansko, Czech Republic). The system is a minicomputer-controlled automated apparatus, whose units are described in Refs. 8–10. To determine the thermal reactivity of the studied commercial explosives, the following operating conditions were selected: heating temperature, 110°C; heating period, 5 h; recording intervals (used for calculation), every 10 min; explosive weight, 1 g in each measuring device; evacuation of the measuring devices, 20 min under the laboratory temperature;

initial measuring delay, 10 min (after the evacuated devices were installed in the heating equipment). The results obtained are given in Table 1.

2.3. Treatment of the results

Examples of the decomposition curves of the explosives studied are given in Fig. 1. It can be seen that the curves are almost linear; therefore the assumption of a zero-order reaction for the formation of the gaseous products seems reasonable. Zero-order decomposition in the vacuum stability test of TNT, PETN and corresponding pentolites has already been found by Huang and Ger [1]. The decomposition rate v is calculated as the slope of the linear part of the curves in Fig. 1; the rate is expressed in cm^3 of gas released from 1 g of the sample over a 1 h period (see also Ref. 1). Most calculations are based on the line interval from the 20th to the 280th minute. This is different from the procedure described in Ref. 1, in which calculations of the thermolysis of pentolites are based on the time interval from the

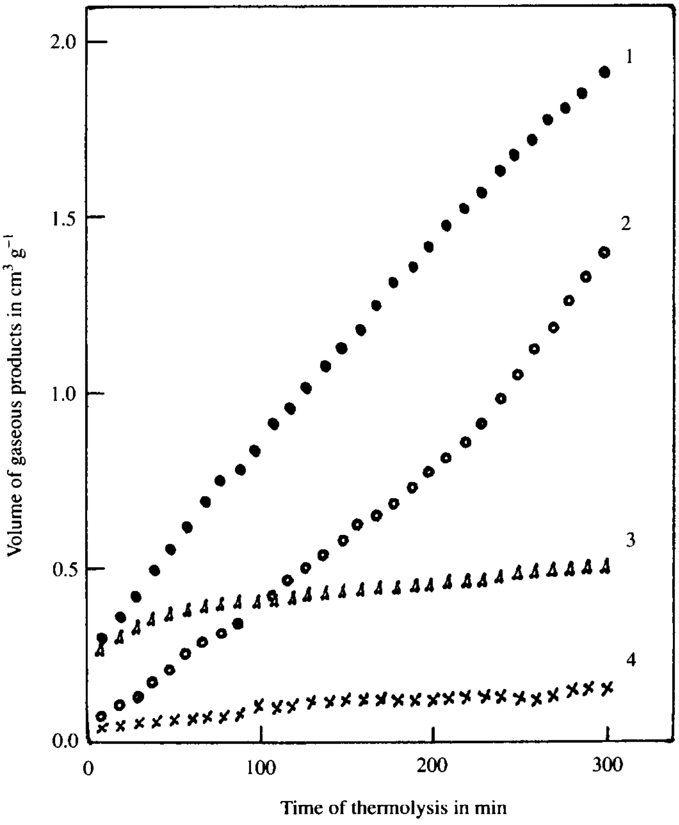

Fig. 1. Decomposition curves of the explosives: 1, Danubit 2; 2, Danubit 1; 3, Polonit V; 4, ammonium nitrate.

10th to the 40th hour. Because of this, the thermolysis rates of PETN in the present paper differ markedly from those determined in Ref. 1.

3. Results and discussion

The relationship between the thermolysis rate of the Istrochem explosives and their liquid nitroester content is illustrated in Fig. 2. The most important relationship, however, was found by comparing the obtained rate values v with the explosion (detonation) temperatures T_E of the explosives studied. This relationship is represented in Fig. 3 and by the general shape of the equation

$$\ln v = A \ln T_E - B \tag{1}$$

where A and B are coefficients which are characteristic for a given group of explosives examined (see Fig. 3). The detonation temperature may be the most important parameter in understanding the chemical kinetics in the reaction zone of the detonation wave and the thermodynamic state of the detonation products [19,20,25].

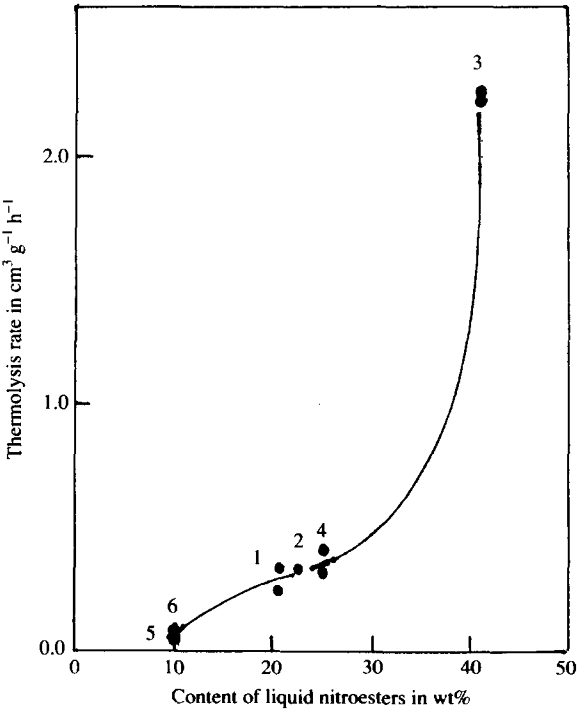

Fig. 2. Dependence of the thermolysis rate on the content of liquid nitroesters in the explosives studied; for key see Table 1.

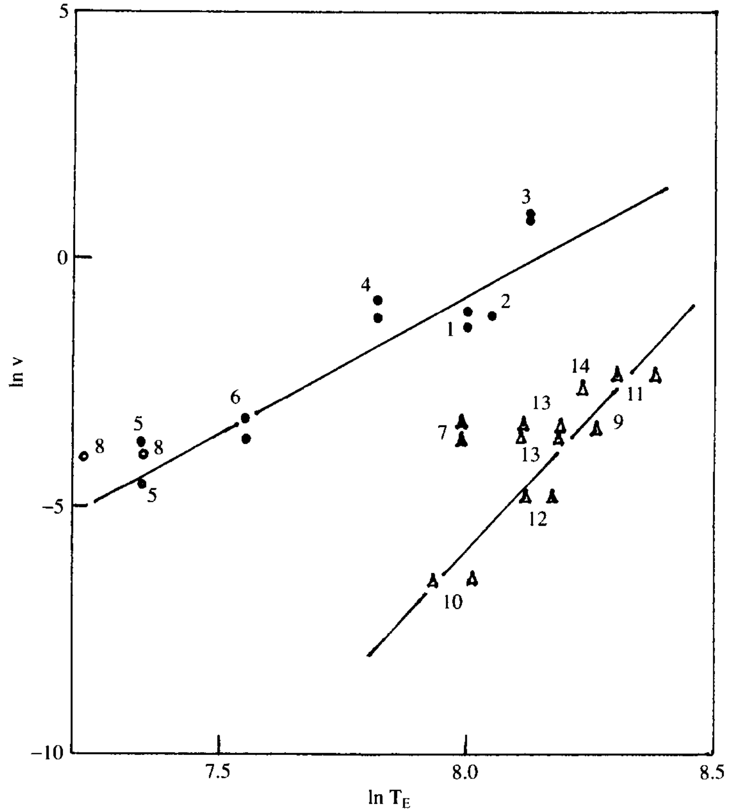

Fig. 3. Graphic representation of Eq. (1); for key see Table 1.

With reference to Eq. (1) and Fig. 3, the explosives examined can be divided into two categories.

(i) Istrochem products 1–6, which contain liquid nitroesters, ammonium and sodium salts, and which have a slightly positive oxygen balance. The data for ammonium nitrate (sample 8) also fall into this category.

(ii) High explosives 9–14, which have a negative oxygen balance and no solid salts in their detonation products. The data for amatol 7 (with a slightly negative oxygen balance) fall close to this category.

The significance of Eq. (1) might be interpreted as follows. As already mentioned, Fig. 1 implies that the formation of gaseous products may be a zero-order reaction. Thus the rate of the thermal decomposition is equal to the specific rate constant k_r of the reaction. If the rate constant is expressed by the Eyring equation

$$k_r = T(k/h)\exp-(\Delta G^{\neq}/RT) \qquad (2)$$

then Eq. (1) may be rewritten

$$[\ln T - (\Delta G^{\neq}/RT)] + \ln(k/h) = A[\ln T_E - B/A] \qquad (3)$$

where T is the medium temperature of the overall temperature range for the free energy of activation $\Delta G^{\neq}$, k is Boltzmann's constant and h is Planck's constant.

Eq. (3) may also be expressed as

$$\ln T - \Delta G^{\neq}/RT = A(\ln T_E - C) \quad (4)$$

where $C = (B + \ln k/h)/A$.

It is generally accepted that the molecular fragments (radicals) primarily formed by the shock compression of an explosive in the detonation front, initiate the chemical reaction in the reaction zone of the detonation wave. This reaction is a source of reaction heat, i.e. the heat of explosion, and the gaseous products of the detonation. The T_E values shown in Table 1 might be taken as the medium temperatures of the overall temperature range in the reaction zone of the detonation wave.

According to the present paper (and also to Ref. 1) the physical conditions of the thermolysis experiment can detect more complex decompositions in the explosives thermolysis, namely secondary reactions in the gaseous products released.

From what has been said so far (and on the basis of Eq. (4)), it follows that Eq. (1) might indicate the relationship between the reaction rates of the partial processes of the low-temperature decomposition of explosives and the reaction rates of processes in the reaction zone of their detonation conversion.

It is essential to add that relationships also exist between characteristics of the low-temperature secondary reactions involved in the thermolysis and characteristics of the detonation of explosives. During the last sixteen years, relationships between the heats of decomposition of explosives and their heats of explosion have been found from DSC measurements [26–29].

4. Conclusions

Using a modification of the American vacuum isothermal stability test, the Czech system STABIL [8–10], in the study of the thermal reactivity of explosives, pressure–time curves are often obtained which correspond to the zero-order reaction of gaseous products formation. Then, a dependence between the corresponding zero-order reaction velocities and explosion (detonation) temperatures of the explosives can be found. This dependence might indicate some relationship between the reaction rates of the processes of low-temperature thermolysis (with the occurrence of secondary reactions in the gaseous products formed) and the rate of conversion in the reaction zone of detonation of the given explosives.

Acknowledgements

The authors express their gratitude to Mrs. Marta Kriváková and Mrs. Jarmila Knapová from the Thermoanalytical Laboratory of Chemko's Special Production Plant for their precise measurements in the STABIL system.

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