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THE THERMAL DECOMPOSITION OF TRIPLE-BASE PROPELLANTS

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Abstract

The thermal decompositions of a double-base propellant (DB), five triple-base propellants (TB) and nitroguanidine (NGV) were examined. The kinetic parameters were evaluated using the ASTM, Kissinger, Rogers-Morris, Freeman-Carroll and Borchardt-Daniels methods. The values of the orders of some of the chemical reactions (n), like some values of activation energies (E_a), do not have any physical meaning, but they represent the manner of propellant decomposition and prove that the mechanism of the reaction changes during the decomposition process. As a result of this fact, differences appear in the evaluated kinetic parameters between various methods.

Keywords: ASTM method, Borchardt-Daniels method, double-base propellant, Freeman-Carroll method, kinetic parameters, Kissinger method, nitroguanidine, Rogers-Morris method, triple-base propellant

Introduction

The thermal characterization of propellants not only has theoretical importance, but also practical application [1]. This work represents the continuation of our previous work dealing with the thermal analysis of propellant stability [2]. Understanding the mechanism of thermal decomposition processes is useful for the prediction of propellant behaviour during their use [3, 4], as well as for the prediction of propellant shelf life [2, 5] and their potential hazards [6]. Thermal characterization is performed after finalization of propellant production, after their artificial ageing, as well as for the characterization of their energetic raw materials [7–9]. The results, extrapolated to ambient storing conditions, are not always in agreement with the observed real changes in storehouses. This is probably because of insufficient knowledge of the kinetics and mechanism of the thermal degradation of energetic materials.

Some results of investigations of the thermal decomposition of NGV, activation energies (E_a) and frequency factors ($\log A$), are shown in Table 1.

The methods for determining Arrhenius parameters from nonisothermal curves are questionable [14–17] and in some cases give wrong results [18]. The E_a and $\log A$ values were determined on three instruments. Two of them gave high values of E_a, but the value determined in the first stage of decomposition was lower. The reason for this was a change in the mechanism of decomposition [13].

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Table 1 Kinetic parameters of NGV decomposition

Instrumentation	Range of temperature/°C	$\log A/\mathrm{s}^{-1}$	$E_a/\mathrm{kJ\ mol}^{-1}$	Reference
DSC	110–240	21.78	215.70	10
Flowing afterglow	160–180	30–50	293.02–460.46	11
Flowing afterglow	<160	5–7	104.65–146.51	11
DSC	200–204	7.5	87.49	12
ARC**	160–180	155±25	1297.66±209.30	13
ARC	160–180	150±20	1255.80±167.40	13
ARC	160–168		83.72±8.37	13

*The order of the reaction was assumed to be one, $n=1$.

**ARC=Accelerating rate calorimeter.

The E_a for the homolytic part of decomposition of DB ranged from 146.51 to 154.88 kJ mol^{-1}. The E_a for the autocatalytic part of the process ranged from 192.56 to 200.64 kJ mol^{-1} [19]. In the temperature range 120 to 160°C, the E_a for double base rocket propellants was determined by TG and found to have the value of 58.60 kJ mol^{-1} [19], and from 170 to 205°C, the value 376.74 kJ mol^{-1} [20]. The E_a for DB, with a heat of combustion from 2930.2 to 4562.7 J g^{-1}, was determined by differential thermal analysis, up to 220°C, to be equal to 142.32 kJ mol^{-1} [21]. Values for the kinetic parameters of triple base propellants were not available.

Experimental

The triple-base propellants were produced via a semi-solvent process by the addition of various quantities of NGV to a powder-paste. A double-base propellant was produced from the same powder-paste. Propellants and NGV were analyzed by DSC for the determination of the kinetic parameters and for obtaining knowledge of their thermal behaviour. The compositions of the examined double-base propellant and the triple-base propellants are given in Table 2 (nitrocellulose (NC) with 12.05 mass% of nitrogen, nitroglycerine (NG), dibutyl phthalate (DBP), centralite I (CI, diethylphenylamine), NGV). The propellant compositions were determined by classical methods of chemical analyses.

Samples of approximately 1 mg were hermetically sealed in Al pans and examined on a Perkin Elmer DSC-4, under a nitrogen flow of 50 ml min^{-1}. The temperature range was 30 to 300°C, at heating rates (β) of 10, 15, 20 and 30°C min^{-1}. The curves obtained at heating rates of 10, 15 and 20°C min^{-1} were used for evaluating the kinetic parameters using the ASTM and Kissinger methods. The curves obtained at heating rate of 15°C min^{-1} were excluded in further analyses (using other methods).

Table 2 Chemical compositions of the propellants

Chemical composition/ mass%	Propellant labelings					
	B_{00}	B_{10}	B_{20}	B_{30}	B_{40}	B_{50}
NC	57.04	50.58	44.45	36.38	30.75	24.69
NG	37.53	33.34	30.54	27.38	24.09	21.16
NGV		10.48	19.73	30.46	39.76	48.88
DBP	2.97	3.21	2.96	3.56	3.27	3.25
CI	2.26	2.18	2.16	2.06	2.00	1.95
H_2O	0.20	0.21	0.16	0.16	0.13	0.07

Results and discussion

The DSC curves of the propellants and NGV scanned at a heating rate of 20°C min^{-1} are shown in Fig. 1.

The mean values of at least three determinations of the T_{onset} of decomposition, the T_{max} of decomposition, and the change in enthalpy of decomposition (ΔH_{dec}) for the propellants and NGV are shown in Table 3. The DSC curves of NGV are characterized by two peaks, the first, endothermic peak of melting, overlaps with the second, exothermic peak of decomposition. The peaks do not separate upon increase or decrease of the heating rate. The ΔH values are calculated from the exotherm peaks.

The kinetic parameters, energy of activation and order of decomposition, were evaluated using the ASTM [6], Kissinger [22], Rogers-Morris [23], Freeman-Carroll [24] and Borchardt-Daniels [25] methods. The obtained values are shown in Table 4.

The kinetic of decomposition in terms of E_a, which varies from a few tenths to a few hundredth of a kJ mol^{-1}, either for one method with different heating rates, or

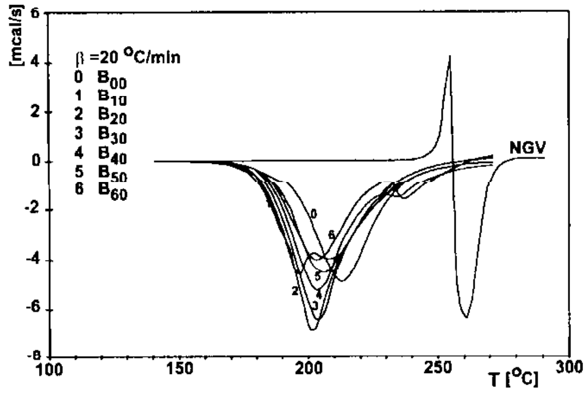

Fig. 1 DSC curves of the propellants and NGV scanned at heating rate of 20°C min^{-1}

Table 3 Decomposition parameters of the propellants and NGV

Decomposition parameters	β/ °C min^{-1}	Samples						
		B_{00}	B_{10}	B_{20}	B_{30}	B_{40}	B_{50}	NGV
T_{onset}/°C	10	182.7	171.2	170.0	171.9	173.8	178.2	247.1
	15	187.5	177.3	178.1	178.8	181.1	180.0	252.2
	20	189.7	177.2	182.1	181.9	183.0	184.5	251.8
	30	188.1	183.9	185.4	185.9	186.3	184.6	253.1
T_{max} of the peak/°C	10	203.2	188.6	189.4	195.6	197.2	199.0	248.7
	15	208.9	189.0	194.2	197.3	198.4	198.5	255.8
	20	211.6	195.8	200.3	203.0	205.1	204.1	260.7
	30	217.3	201.2	204.2	206.6	208.4	208.3	268.1
ΔH_{dec}/kJ g^{-1}	10	–1.57	–1.95	–1.95	–1.82	–1.77	–0.83	–0.70
	15	–1.57	–2.04	–2.10	–2.13	–2.11	–1.79	–1.04
	20	–1.77	–1.96	–2.14	–1.90	–1.76	–0.89	–0.75
	30	–1.51	–1.97	–1.92	–1.99	–1.71	–0.88	–0.82

for the different methods, shows the complexity of the process [26]. The differences in the energies of activations for DB are the lowest compared to TB and NGV. With increasing content of NGV in TB, the change in E_a becomes greater, and the highest changes of the E_a values are for NGV. With increasing heating rate, the onset temperature of the melting endotherm of NGV is shifted to the higher values. The endothermic peak is transferred directly into exothermic one. Hence, the shift in the endothermic peak with increasing heating rate, causes the exothermic peak to become distorted, and so an estimation of the activation energies becomes unreliable.

Furthermore, we considered the Rogers-Morris values of the activation energy of NGV, obtained from the first part of the curve, for the three heating rates. The values of E_a for the heating rates 10, 20 and 30°C min^{-1}, are 140.92, 325.05 and 329.24 kJ mol^{-1}, respectively. The literature value of the activation energy derived using the ASTM E698 method was 133.95 kJ mol^{-1} [17], while our value was 158.92 kJ mol^{-1}. The difference between these values originates from the various qualities of the analyzed NGV, and from the uncertainty in determining the decomposition peak limits.

The Freeman-Carroll and Borchardt-Daniels values for E_a and n, for the propellants, are erroneous. The activation energy of DB, sample B_{00}, has the value which is usually found in literature [19] (from 154.97 to 208.08 kJ mol^{-1}). The activation energies of the TB vary from 130 to 335.81 kJ mol^{-1}. There is a change in the decomposition mechanism in double-base propellant and in triple-base propellants, but the influence of NGV in TB (the crystal phase incorporated in the powder paste)

Table 4. Kinetic parameters for the decomposition processes of NGV and of the propellants with various contents of NGV 1 – Rogers-Morris, 2 – Freeman-Caroll, 3 – Borchard-Daniels, 4 – Kissinger

β/ °C min^{-1}	Method	B_{00}		B_{10}		B_{20}		B_{30}		B_{40}		B_{50}		NGV	
		E_a/ kJ mol^{-1}	n	E_a/ kJ mol^{-1}	n	E_a/ kJ mol^{-1}	n	E_a/ kJ mol^{-1}	n	E_a/ kJ mol^{-1}	n	E_a/ kJ mol^{-1}	n	E_a/ kJ mol^{-1}	n
	ASTM*	204.79		242.90		158.63		283.59		276.21		280.85		158.92	
	Kissinger	208.75		246.81		162.44		287.47		280.10		284.80		163.30	
10	1	164.63		245.23		130.92		216.34		223.50		177.82		140.92	
	2	175.45	0.55	201.72	3.61	335.81	4.56	297.53	4.56	328.44	3.64	285.82	3.01	1011.9	1.78
	3	192.25		261.87		174.74		251.26		252.63		214.42		628.19	
	4		1.30		2.28		2.36		2.36		1.35		2.51		2.12
20	1	167.37		238.10		220.08		200.05		217.08		206.99		325.05	
	2	179.31	0.78	188.74	4.87	276.24	1.28	322.56	1.28	334.92	3.65	275.37	2.39	1397.7	3.74
	3	187.34		253.98		249.42		238.02		250.12		235.80		590.16	
	4		1.31		2.31		1.44		1.44		1.37		2.69		1.73
30	1	154.97		238.34		205.32		215.13		207.09		218.89		329.24	
	2	208.08	3.72	266.77	2.26	320.42	3.51	323.22	3.51	312.44	3.19	335.07	4.40	936.74	3.12
	3	175.62		256.44		239.64		248.01		240.19		246.59		509.58	
	4		1.33		2.57		1.68		1.68		1.29		1.29		

*The ASTM method uses heating rates up to 20°C min^{-1}, and in this calculation heating rate of 10, 15 and 20°C min^{-1} were included must not be neglected. Also, the reaction products have a strong accelerating effect on the decomposition rate of NGV [12, 17].

Conclusions

Most of the methods assume that the decomposition follows the Arrhenius dependence on temperature, which means the same mechanism is operative from the beginning to the end of the process. The differences in the estimated E_a and n values originate from the different methods of taking out data for calculations, namely from the first part of the curve (Rogers-Morris), from the whole curve (Freeman-Carroll, Borchardt-Daniels), or considering only the temperature of the peak maximum obtained through various heating rates (ASTM, Kissinger). The differences in the estimated E_a, either from method to method or by changing the heating rates, point to changes in the decomposition mechanism, so that the E_a no longer represent a simple energetic barrier for breaking and forming chemical bonds. The differences point to the complexity of the exothermic reaction.

To determine the temperature where the mechanism of the reaction is changing, the mechanism of decomposition, and the real kinetic parameters, the process should be observed by different types of thermal analysis.

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