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Dynamic pressure thermal analysis of double-base propellants containing RDX

Research Article

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Abstract: The thermal decomposition of five double-base propellants modified with RDX was studied by dynamic pressure thermal analysis to determine the effect of RDX content (20-60 wt.%) on performance. All have good stability. Both stability and activation energy increase as RDX increases from 20% to 50% then decrease; 50% RDX performs best. The decomposition mechanism is affected by RDX content and temperature. Increasing temperature induces autocatalysis and accelerates decomposition.

Keywords: *Modified double-base propellant • Thermal decomposition • Kinetics • Thermal stability • DPTA • RDX*

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1. Introduction

Solid propellants are the heart of a solid rocket motor. They deflagrate steadily and vigorously, producing gases and releasing energy to push the rocket [1-3]. They are widely used in military, aerospace, and other areas and are important in the domestic economy, national defense, science, and technology [4]. With the growing demand for strong propulsion development of high-energy and high-impulse propellants has become a hot topic. Although the research is hazardous, there has been recent progress in new propellants [5-7].

Propellant performance measures include a tolerable flame temperature to minimize barrel erosion, reduced impact sensitivity, high density, good mechanical properties at extreme temperatures, and environmental friendliness. To improve their properties traditional double-base propellants (nitrocellulose (NC) plus nitroglycerine (NG)) also contain high-energy explosives such as RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine), HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) or CL-20 (hexanitrohexaazaisowurtzitane) [8-12]; oxidants (NH_4ClO_4 or NH_4NO_3) [13-15] and/or metallic catalysts (Al or Fe) [16-18]. These modified propellants give increased performance, reduced sensitivity to external stimuli and enhanced chemical and thermal stability. They have been suggested as replacement gun propellants [19-21]. RDX offers improved performance (high energy content and high impetus), thermal stability (low sensitivity), environmental friendliness and cost efficiency [22-24].

The most important properties of a propellant are thermal stability and the chemical compatibility of its ingredients. Good thermal stability is essential for reliability and storage security [25]. It can be characterized by the differential scanning calorimetry (DSC) initial decomposition temperature, the thermogravimetric analysis (TG) initial mass loss temperature, and the vacuum stability test (VST) amount of decomposition gas [26-29]. VST measures the thermal decomposition gas pressure at constant volume, low pressure, and low temperature [30] and is the best method for determining energetic materials' thermal stability and shelf life [31]. It is used to evaluate spontaneous decomposition in a real storage environment.

Dynamic pressure thermal analysis (DPTA), formerly known as the dynamic vacuum stability test (DVST), is based on the VST [29-35]. The analyzer monitors changes of evolved gas pressure and temperature during thermal decomposition. DPTA includes two stages: an initial heating at constant rate (<3°C min^{-1}) and an isothermal stage at comparatively low temperature (<200°C). The

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Table 1. Volume of gas produced from total process and isothermal stage.

T/°C	CP-1		CP-2		CP-3		CP-4		CP-5	
	V_t/mL	V_i/mL	V_t/mL	V_i/mL	V_t/mL	V_i/mL	V_t/mL	V_i/mL	V_t/mL	V_i/mL
60	0.104	0.039	0.083	0.030	0.065	0.023	0.048	0.012	0.056	0.016
70	0.156	0.051	0.139	0.039	0.116	0.033	0.093	0.023	0.105	0.029
80	0.213	0.085	0.194	0.075	0.162	0.065	0.126	0.054	0.141	0.060
90	0.396	0.238	0.360	0.215	0.315	0.207	0.286	0.186	0.295	0.191
100	0.885	0.460	0.810	0.423	0.743	0.394	0.641	0.334	0.688	0.359

kinetic parameters for non-isothermal and isothermal decomposition are calculated from the gas pressure - time relationship. The thermal stability and components' compatibility are judged from the results.

In this work, five double-base propellants modified with different RDX contents were tested by DPTA and the decomposition kinetic parameters and thermal stability were determined. The effects of RDX content were evaluated to optimize the propellant composition.

2. Experimental procedure

2.1. Materials

WARNING! Propellants are hazardous energetic materials and must be handled in small quantities with proper precautions.

The propellants contain NC, NG, RDX, combustion catalyst and other reagents. Each was prepared by slurry mixing, rolling, and extrusion. The propellant containing about 20 wt.% RDX is labeled CP-1, 30% RDX is CP-2, 40% RDX is CP-3, 50% RDX is CP-4, and 60% RDX is CP-5. To avoid the effects of adsorbed gaseous impurities the propellants were vacuum-dried at 40 ºC for 24 h and stored in a desiccator below room temperature until use.

2.2. Instruments and methods

DPTA examined the initial thermal decomposition from 25ºC to 200ºC. All operations were in strict accordance with current National Military Standards [39,40]. Sample (1.0000±0.0010 g) was loaded into an explosion-proof glass tube. The tube was evacuated bellow 0.1 kPa, sealed, and placed in the thermostat. It was heated from room temperature to the target temperature at <3ºC min^{-1} then held at the target temperature for 48 h. The target temperatures ranged from 60ºC to 100ºC with 20ºC increments. The temperature accuracy is ± 0.1ºC and the temperature differences among six simultaneously tested tubes were <0.1ºC. Samples were tested at least thrice.

3. Results and discussion

3.1. Thermal decomposition and stability

DPTA records the apparent evolved gas pressure over time. Errors due to thermal expansion and sensor drift/lag were corrected by standardization to obtain the net pressure.

The net pressure and temperature time dependences of five propellants are shown in Fig. 1. Their trends agree substantially. The pressure increases in approximately parabolic fashion with heating time. The curves consist of two parts: a rapid pressure rise while heating to the target temperature followed by slow pressure growth at constant temperature. Rising temperature causes a larger decomposition rate and more gas production. As shown in Fig. 2, the gas increases exponentially with temperature. At the same temperature the gas pressure decreases as RDX increases from 20% to 50% then increases (CP-1 > CP-2 > CP-3 > CP-5 > CP-4). This is because the double-base ingredients NC and NG decompose and release gas more easily than RDX [8-9]. As the RDX increases NC and NG decrease, as does their decomposition gas. However, when RDX is >50% interactions between RDX and the double-base ingredients promote RDX decomposition, producing more gas.

The thermal stability of energetic materials is evaluated by the amount of gas released in the isothermal stage; less gas signifies greater stability. The net gas pressure (p) is converted to the net gas volume (V) at the standard state (1.0 g sample, 101.325 kPa, and 273.15 K) in Table 1. Good thermal stability requires that this be <2.00 mL g^{-1} at 100ºC.

Although all have excellent thermal stability, it increases with increasing RDX content up to 50% then decreases (CP-1 < CP-2 < CP-3 < CP-5 < CP-4). This suggests that complex interactions between RDX and the double-base ingredients affect the thermal stability in nonlinear ways. Thus, empirical determination of the optimum composition is necessary.

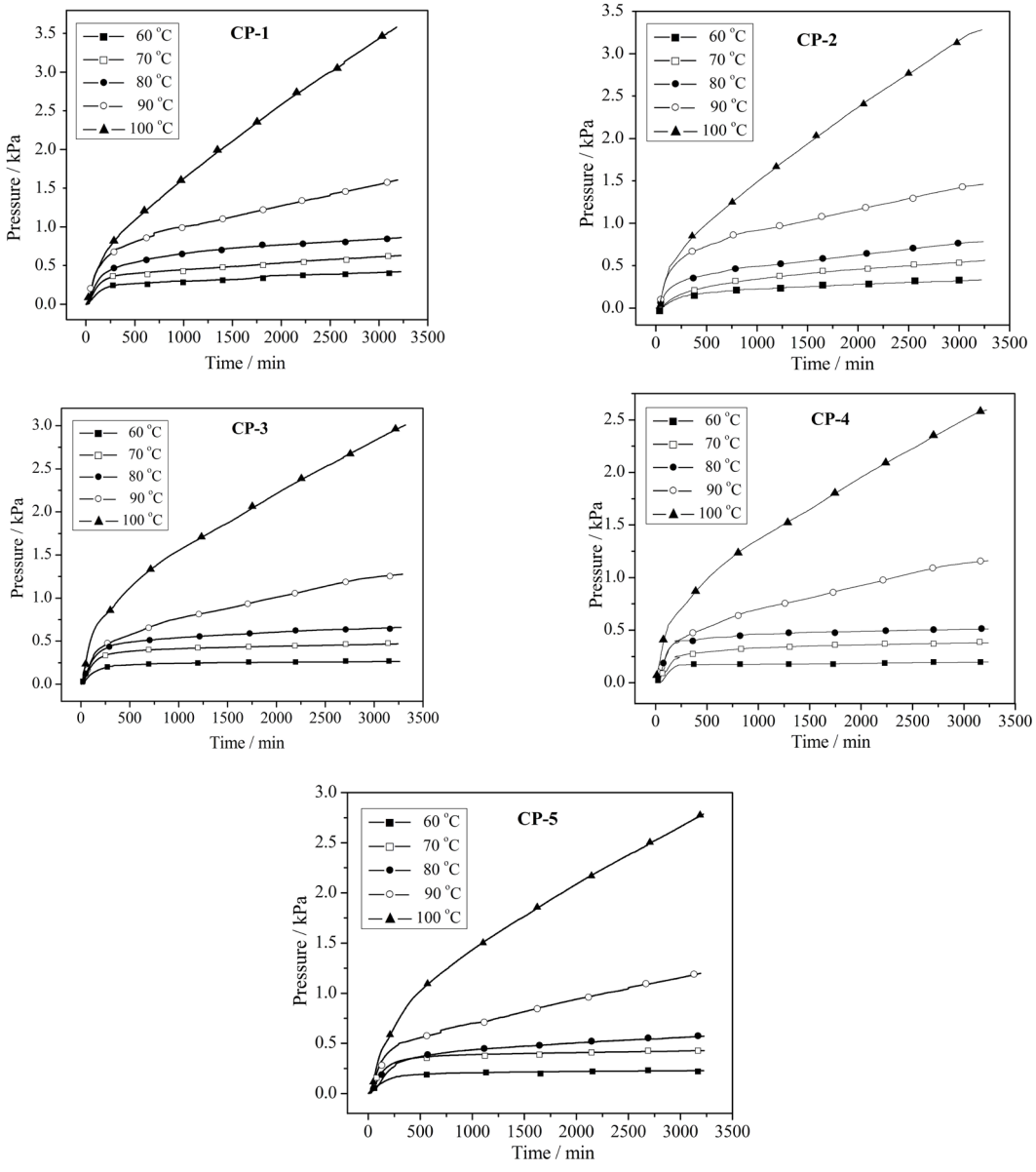

Figure 1. DPTA curves of the composite modified double-base propellants.

3.2. Thermal decomposition kinetics

The effects of RDX on the thermal decomposition kinetics were investigated. The non-isothermal kinetic parameters A and E_a were calculated using the universal integral method (UIM) and the differential equation method (DEM) [41].

$$\text{UIM:}\quad \ln\left[\frac{G(\alpha)}{T-T_0}\right]=\ln\frac{A}{\beta}-\frac{E_a}{RT} \tag{1}$$

$$\text{DEM:}\quad \ln\left\{\frac{\mathrm{d}\alpha/\mathrm{d}T}{f(\alpha)\left[E_a(T-T_0)/\left(RT^2\right)+1\right]}\right\}=\ln\frac{A}{\beta}-\frac{E_a}{RT} \tag{2}$$

where $G(\alpha)$ and $f(\alpha)$ are the reaction rates in integral and differential form, T_0 and T are the initial and test temperatures (K), E_a is the apparent activation energy (J mol^{-1}), A is the pre-exponential factor (s^{-1}), β is the heating rate (K min^{-1}), α is the reaction extent, and R is the gas constant (8.314 J mol^{-1} K^{-1}). Both methods gave approximately the same kinetic parameters, so their averages are listed in Table 2.

For each propellant, the apparent E_a decreases with temperature increase; the reduced energy barrier at high temperature promotes decomposition. The variation of E_a with T suggests that more than one step is involved

Table 2. Non-isothermal kinetic parameters of the composite propellants at different temperatures.

T/°C	CP-1			CP-2			CP-3			CP-4			CP-5		
	E_a / kJmol^{-1}	lg (A/s^{-1})	r	E_a / kJmol^{-1}	lg(A/s^{-1})	r	E_a / kJmol^{-1}	lg (A/s^{-1})	r	E_a / kJmol^{-1}	lg (A/s^{-1})	r	E_a / kJmol^{-1}	lg (A/s^{-1})	r
60	121.92±5.24	13.72±0.59	0.9875	135.75±5.82	15.88±0.58	0.9759	167.06±7.20	20.80±1.02	0.9989	222.40±9.58	29.47±1.36	0.9776	197.71±8.45	25.60±0.82	0.9853
70	110.34±4.74	11.45±0.52	0.9956	126.78±5.40	13.95±0.49	0.9868	165.76±7.12	19.88±0.92	0.9942	210.96±9.02	26.76±1.17	0.9879	190.59±8.12	23.66±0.74	0.9891
80	102.64±4.41	9.88±0.46	0.9898	115.93±4.97	11.84±0.42	0.9897	146.62±6.30	16.38±0.69	0.9912	188.34±8.03	22.55±0.94	0.9964	176.82±7.52	20.85±0.63	0.9738
90	95.97±4.12	8.54±0.39	0.9942	112.12±4.82	10.86±0.38	0.9948	136.75±5.86	14.41±0.63	0.9869	163.65±7.01	18.28±0.82	0.9998	150.26±6.45	16.35±0.51	0.9964
100	95.68±4.11	8.17±0.35	0.9968	110.55±4.75	10.25±0.36	0.9956	122.83±5.28	11.97±0.59	0.9828	154.08±6.61	16.34±0.62	0.9928	139.06±5.83	14.24±0.38	0.9922

Table 3. Isothermal kinetic parameters of the composite propellants at different temperatures.

T/°C	CP-1			CP-2			CP-3			CP-4			CP-5		
	G(α)	(k×10^6) /s^{-1}	r	G(α)	(k×10^6) /s^{-1}	r	G(α)	(k×10^6) /s^{-1}	r	G(α)	(k×10^6) k/s^{-1}	r	G(α)	(k×10^6) /s^{-1}	r
60	5*	4.42±0.15	0.9914	5	3.96±0.14	0.9953	5	1.68±0.07	0.9962	9	1.65±0.08	0.9889	7	2.84±0.12	0.9883
70	25	5.04±0.17	0.9878	25	4.63±0.16	0.9985	5	2.88±0.12	0.9963	9	2.74±0.13	0.9981	31	3.87±0.17	0.9828
80	25	5.14±0.17	0.9985	25	4.70±0.17	0.9882	5	3.86±0.16	0.9967	8	3.56±0.17	0.9938	8	4.05±0.18	0.9955
90	25	5.53±0.18	0.9997	25	5.15±0.18	0.9985	25	4.34±0.18	0.9974	8	4.12±0.20	0.9955	8	4.66±0.20	0.9821
100	8	5.83±0.20	0.9987	8	5.36±0.20	0.9977	25	5.02±0.21	0.9974	8	4.81±0.24	0.9995	8	5.08±0.22	0.9846

Refer to Supplementary data for more details about the mechanism functions.

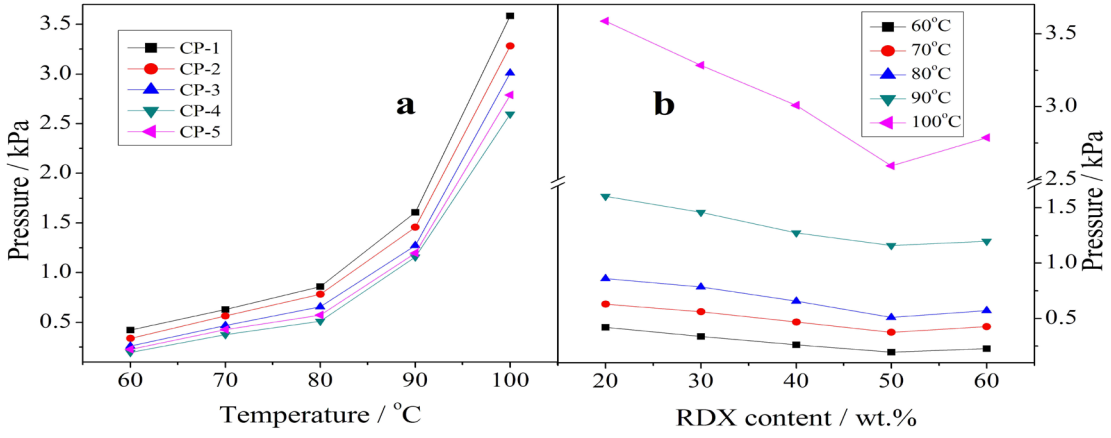

Figure 2. Curves of thermal decomposition gas pressure vs. temperature (a) and RDX content (b).

and E_a is a composite of the individual barriers. The positive correlation between E_a and A shows kinetic compensation. The decompositions include the same dominant and rate-determining reaction step [42-45], making single-step kinetics an adequate treatment. E_a increases in the same order as the thermal stability: 20% RDX < 30% RDX < 40% RDX < 60% RDX < 50% RDX (CP-1 < CP-2 < CP-3 < CP-5 < CP-4).

The isothermal data were least-squares fitted to 41 common rate laws [41]. The best fit was to

$$G(\alpha) = kt \quad (3)$$

where k is the rate constant (s^{-1}) and t is reaction time. The rate constants at different temperatures are listed in Table 3.

Thermal decomposition is a multi-step reaction. RDX affects the decomposition mechanism as well as the rate constant. Each ingredient in the mixture of RDX, NG, NC and other additives decomposes and interacts with the others. Therefore, different mixtures react differently. Even so, the single-step rate equation represents the multi-step process with a single rate-determining step adequately [46]. Moreover, increasing temperature changes the mechanism and further

promotes decomposition. The growth rate of *k* for 50% RDX (CP-4) is largest giving this mixture optimum performance (Fig. 3). This amount of RDX induces more autocatalysis, accelerating decomposition.

4. Conclusions

The thermal decomposition of five double-base propellants modified with varying amounts of RDX was studied by DPTA. The volume of decomposition gas *vs.* time gave the decomposition kinetic parameters. The thermal stability and E_a increase 20% RDX < 30% RDX < 40% RDX < 60% RDX < 50% RDX. As the RDX increases up to 50% the thermal stability improves, but with further increase its interactions with the double-base ingredients reduce thermal stability. Increasing temperature reduces E_a and further promotes thermal decomposition. The decomposition mechanism is affected by both RDX content and temperature; high temperature induces autocatalytic thermal decomposition. The thermal decomposition is a multi-step reaction but is dominated by a single step and can be described by simple kinetics. Finally, 50 wt.% RDX is the best performing propellant because it has excellent thermal stability and outstanding thermal response.

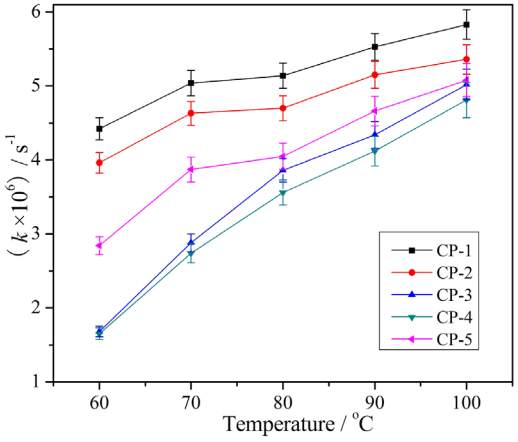

Figure 3. Curves of reaction rate constant vs. temperature.

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