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EFFECT OF PRESSURES ON DECOMPOSITION REACTION KINETICS OF DOUBLE-BASE PROPELLANT CATALYZED WITH CERIUM CITRATE

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The decomposition reaction kinetics of the double-base (DB) propellant (No. TG0701) composed of the mixed ester of triethyleneglycol dinitrate (TEGDN) and nitroglycerin (NG) and nitrocellulose (NC) with cerium(III) citrate (CIT-Ce) as a combustion catalyst was investigated by high-pressure differential scanning calorimetry (PDSC) under flowing nitrogen gas conditions.

The results show that pressure (2 MPa) can decrease the peak temperature and increase the decomposition heat, and also can change the mechanism function of the exothermal decomposition reaction of the DB gun propellant under 0.1 MPa; CIT-Ce can decrease the apparent activation energy of the DB gun propellant by about 35 kJ mol^{-1} under low pressure, but it can not display the effect under high pressure; CIT-Ce can not change the decomposition reaction mechanism function under a pressure.

Keywords: *cerium citrate, combustion catalyst, double-base propellant, nitroglycerin, non-isothermal kinetics, triethyleneglycol dinitrate*

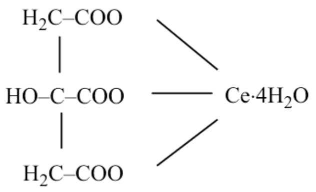
Introduction

Lead compounds are very important combustion catalysts used commonly in solid propellant formulations, and they can improve the propellant burning rate and reduce the pressure exponent [1]. But in recent years, much attention has been paid to its toxicity, and the scientific researches on the lead-free combustion catalysts and eco-friendly propellants become one of the main points in rocket and missile ordnance systems [2–6]. Cerium dioxide (CeO_2) and other rare earth compounds had been used in double-base (DB) formulations, the combustion experiment showed that it has a high burning catalytic efficiency and plateau or mesa effect in a broad pressure range [7]. In the paper, the decomposition reaction kinetics of the DB propellant, which consists of the mixed ester of triethyleneglycol dinitrate (TEGDN) and nitroglycerin (NG) and nitrocellulose (NC) with cerium(III) citrate (CIT-Ce) as a combustion catalyst was investigated by the non-isothermal method under different pressures to explore the effect of the pressure on its decomposition reaction mechanism and kinetics, and the research results have not been reported in literatures. The study on the thermal decomposition reaction of a DB gun propellant composed of TEGDN and NG under the high pressure, can provide the valuable data for the combustion property of the gun propellant used in the high-chamber-pressure guns.

Experimental

Materials

CIT-Ce used in the DB propellant formulation was prepared according to the previous method [8], as lanthanum(III) citrate (CIT-La) had been done [9]. Elemental anal. (%), calcd. for $C_6H_5O_7Ce\cdot 4H_2O$: C 17.94, H 3.24, Ce 34.92; found: C 17.74, H 3.33, Ce 36.20; IR (KBr), σ/cm^{-1}: 1732 ($\nu_{-C=O}$) and 2700–2500 (ν_{OH}) vanish, 1573 ($\nu^{as}_{(-COO-)}$) and 1405 ($\nu^{s}_{(-COO-)}$) appear, 3400 (ν_{OH}, associated) and 1070 (ν_{C-O}) do not shift. The scheme of CIT-Ce is shown in Scheme 1.



Scheme 1 Structure of CIT-Ce

The sample (No. TG0701) used in the experiment is a DB propellant composed of 60% (mass fraction) of NC, 37.5% of TEGDN/NG mixed ester (mass ratio, 9.5:28), and 2.5% of some additives, etc. The strand sample composed of 500 g ingredients and an amount of CIT-Ce ($C_6H_5O_7Ce\cdot 4H_2O$) as combustion catalyst was prepared by a solventless DB propellant extrusion technique. The control DB propellant (No. TG0601) without any combustion catalysts was also prepared by the same method for the comparison with the sample [10].

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Equipment and conditions

DSC curves were obtained by using a 204HP differential scanning calorimeter (Netzsch Co., Germany), and the conditions were: nitrogen gas purity, 99.999%; flowing rate, 50 cm^3 min^{-1}; pressure, 0.1 and 2 MPa; sample mass, about 1 mg; heating rate (β), 5, 10, 15 and 20 K min^{-1}; reference sample, α-Al_2O_3.

Results and discussion

The thermal decomposition behaviors of the DB propellant catalyzed with CIT-Ce

The DSC curves for the sample TG0701 at the heating rates of 5, 10, 15 and 20 K min^{-1} under 0.1 and 2 MPa are shown in Figs 1 and 2, respectively, and that of the control DB propellant (No. TG0601) [10] are shown in Figs 3 and 4, respectively. The corresponding decomposition heats were listed in Table 1.

From Figs 1–4 and Table 1, one can see that there is only one visible exothermic peak to appear in each DSC curve for TG0701 at different pressures, and the peak temperature (T_p/K) of DSC curve decreases with the increase in furnace pressure at a heating rate, but the decomposition heat rises, especially at the heating rate of 10 K min^{-1}. Comparing with TG0601, TG0701 makes an unobvious decrease in T_p and an irregular increase in the decomposition heat at a heating rate. The reason is that the high pressure can restrain the volatilization and accelerate the decomposition of the mixed ester, and participates in the rec-

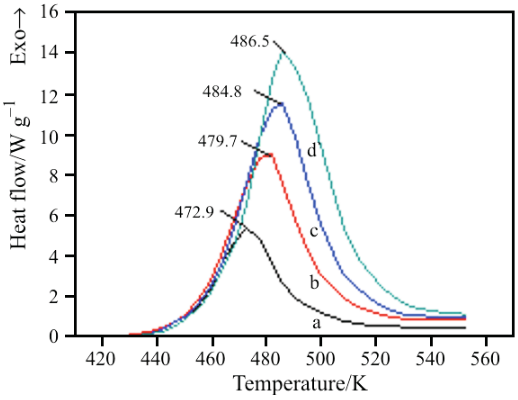

Fig. 1 DSC curves for TG0701 under 0.1 MPa, heating rate: a – 5, b – 10, c – 15 and d – 20 K min^{-1}

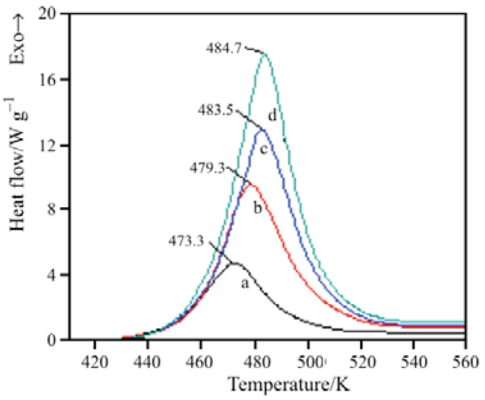

Fig. 3 DSC curves for TG0601 under 0.1 MPa, heating rate: a – 5, b – 10, c – 15 and d – 20 K min^{-1}

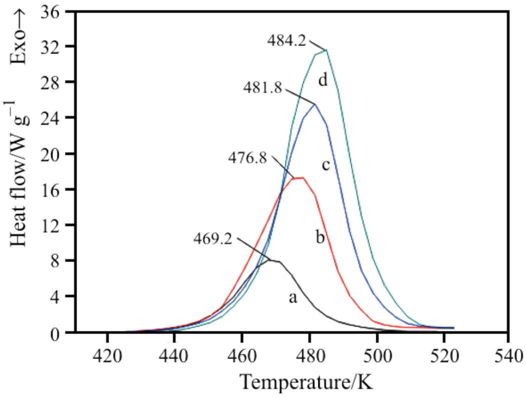

Fig. 2 DSC curves for TG0701 under 2 MPa, heating rate: a – 5, b – 10, c – 15 and d – 20 K min^{-1}

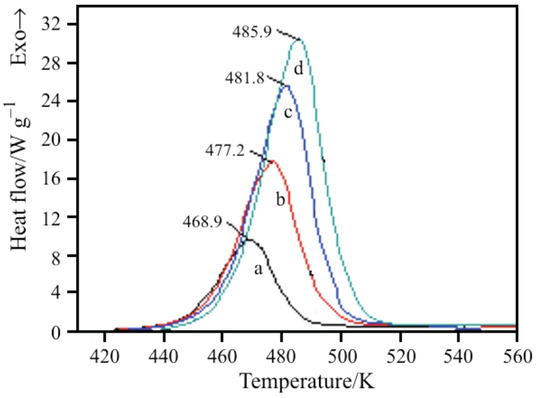

Fig. 4 DSC curves for TG0601 under 2 MPa, heating rate: a – 5, b – 10, c – 15 and d – 20 K min^{-1}

Table 1 The decomposition heats of the DB propellant TG0701 and TG0601

Sample No.	Decomposition heat/J g^{-1}							
	0.1 MPa				2 MPa			
	5 K min^{-1}	10 K min^{-1}	15 K min^{-1}	20 K min^{-1}	5 K min^{-1}	10 K min^{-1}	15 K min^{-1}	20 K min^{-1}
TG0701	1840	1721	1516	1459	2460	2703	2494	2401
TG0601	1661	1622	1466	1419	2657	2651	2468	2323

iprocity of the decomposition products of NC and C_2, which makes the system release more decomposition heat than that at low pressure. It can be concluded that the combustion catalyst CIT-Ce can make TG0701 show an irregular increase in the decomposition heat comparing with TG0601 with the increase in furnace pressure at the heating rates.

Calculation of non-isothermal reaction kinetics

To explore the thermal decomposition mechanism of the exothermic reaction of the sample TG0701 under 0.1 and 2 MPa, and obtain the corresponding kinetic parameters [apparent activation energy (E_a/kJ mol^{-1}), pre-exponential constant (A/s^{-1})] and the most probable kinetic model function, the DSC curves at heating rates of 5, 10, 15 and 20 K min^{-1} were dealt with the five integral methods [Eqs (1)–(5)] and one differential method [Eq. (6)] listed in Table 2 [11–19].

In those equations, α is the conversion degree of the major exothermic reaction, $\alpha=H_t/H_0$; H_0, the total heat effect (corresponding to the global area under the DSC curves); H_t, the reaction heat at a certain time (corresponding to the partial area under the DSC curves); T, the temperature (K) at time of t; R, the gas constant; $G(\alpha)$ is the integral model function, E_k, the value of apparent activation energy obtained by Kissinger's method, and the means of E_a, A, β and T_p have been mentioned earlier.

The values of E_a were obtained by Ozawa's method [Eq. (5)] with α changing from 0.02 to 1.00, and the two E_a–α curves are shown in Figs 5 and 6. From the figures, one can see that activation energy changes significantly with the increase in conversion degree except for the section of 0.06–0.84(α). In this section, activation energy changes faintly, which means that the decomposition mechanism of the process does not transfer in essence or the transference could be ignored. So, it is feasible to study the reaction mechanism and kinetics of in this section.

Forty-one types of kinetic model functions in [19–21] and the original data tabulated in Tables 3 and 4 are put into Eqs (1)–(6), respectively for calculations. The values of E_a, lg$A$, linear correlation coefficient (r) and standard mean square deviation (Q) can be calculated by the computer with the linear least-squares method at various heating rates of 5, 10, 15 and 20 K min^{-1}. The most probable mechanism function is selected by the better values of r and Q taken from [20–22]. The results satisfying the above-mentioned conditions at the same time are the final results as listed in Table 3, and the relevant function is the reaction mechanism function of the exothermic decomposition process of TG0701.

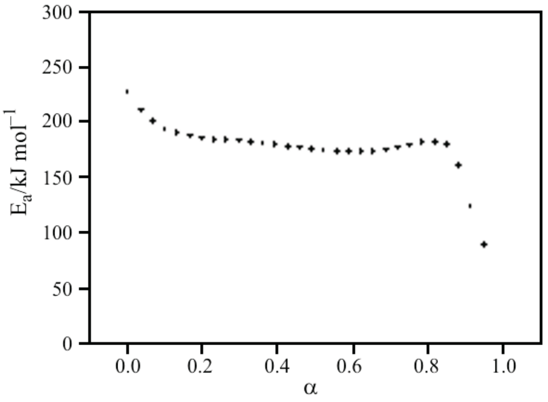

Fig. 5 E_a–α curve of TG0701 under 0.1 MPa obtained by Ozawa's method

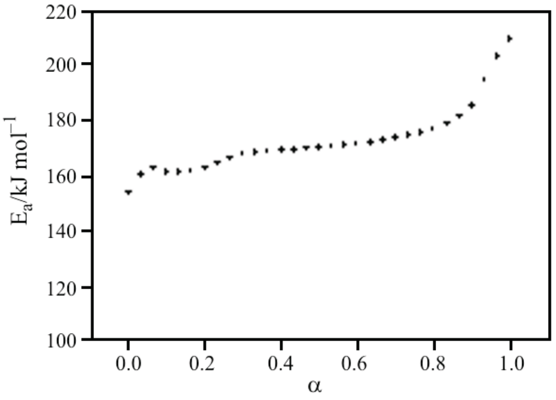

Fig. 6 E_a–α curve of TG0701 under 2 MPa obtained by Ozawa's method

From Table 3, one can find that the values of E_a and lg$A$ obtained from the non-isothermal DSC curves are in approximately good agreement with the values calculated by Kissinger's method and Ozawa's

Table 2 Kinetic analysis methods

Method	Equation	
Coats–Redfern	$\ln[G(\alpha)/T^2]=\ln[(AR/\beta E_a)(1-2RT/E_a)]-E_a/RT$	(1)
MacCallum–Tanner	$\lg[G(\alpha)]=\lg(AE_a/\beta R)-0.4828E_a^{0.4357}-(0.449+0.217E_a)/(0.001T)$ (E_a in kcal mol^{-1})	(2)
Šatava–Šesták	$\lg[G(\alpha)]=\lg(AE_a/\beta R)-2.315-0.4567E_a/RT$	(3)
Agrawal	$\ln[G(\alpha)/T^2]=\ln\{(AR/\beta E_a)[1-2(RT/E_a)]/[1-5(RT/E_a)^2]\}-E_a/RT$	(4)
Flynn–Wall–Ozawa	$\lg\beta=\lg\{AE_a/[RG(\alpha)]\}-2.315-0.4567E_a/RT$	(5)
Kissinger	$\ln(\beta_i/T_{p_i}^2)=\ln(A_kR/E_k)-E_k/RT_{p_i}$, i=1,2,...,4	(6)

Table 3 Kinetic parameters obtained for the decomposition process of TG0701 under 0.1 and 2 MPa

Eq.	β/K min^{-1}	0.1 MPa				2 MPa			
		E/kJ mol^{-1}	lg(A/s^{-1})	r	Q	E/kJ mol^{-1}	lg(A/s^{-1})	r	Q
(1)	5	179.2	17.5	0.9884	1.0980	155.1	15.0	0.9976	0.0761
	10	180.4	17.7	0.9955	0.4295	149.3	14.4	0.9980	0.0624
	15	188.2	18.6	0.9982	0.1688	154.6	15.0	0.9992	0.0265
	20	176.0	17.2	0.9951	0.4592	145.6	14.1	0.9970	0.0732
(2)	5	179.8	17.5	0.9894	0.2055	155.3	15.0	0.9978	0.0142
	10	181.1	17.8	0.9959	0.0801	149.6	14.4	0.9982	0.0116
	15	188.9	18.6	0.9984	0.0313	155.0	14.8	0.9993	0.0049
	20	176.8	17.2	0.9956	0.0855	146.0	14.1	0.9973	0.0137
(3)	5	177.9	17.4	0.9894	0.2055	154.8	15.0	0.9978	0.0142
	10	179.1	17.6	0.9959	0.0801	149.4	14.4	0.9982	0.0116
	15	186.6	18.4	0.9984	0.0313	154.5	15.0	0.9992	0.0049
	20	175.1	17.1	0.9956	0.0855	164.3	16.1	0.9973	0.0173
(4)	5	179.2	17.5	0.9884	1.0980	155.1	15.0	0.9976	0.0761
	10	180.4	17.7	0.9955	0.4295	149.3	14.4	0.9980	0.0624
	15	188.2	18.6	0.9982	0.1688	154.6	15.0	0.9992	0.0265
	20	176.0	17.2	0.9951	0.4592	164.8	16.2	0.9970	0.0926
Mean		180.8	17.7			153.6	14.9		
(5)		178.5		0.9961	0.0016	162.8		0.9985	0.0006
(6)		179.7	17.8	0.9958	0.0084	163.3	16.0	0.9983	0.0033

Table 4 Mechanism functions, apparent activation energies and kinetic equations of TG0701 and TG0601

Sample (pressure)	Reaction mechanism, mechanism function, $G(\alpha)$	Mech. funct. no. [19]	E_a/ kJ mol^{-1}	Kinetic equation	
TG0701 (0.1 MPa)	chemical reaction, $(1-\alpha)^{-1}-1$	37	180.8	$d\alpha/dt=10^{17.7}(1-\alpha)^2e^{-2.2\cdot10^4/T}$	(8)
TG0701 (2 MPa)	Avrami–Erofeev equation, (n=3/4), $[-\ln(1-\alpha)]^{3/4}$	15	153.6	$d\alpha/dt=10^{14.8}(1-\alpha)[-\ln(1-\alpha)]^{1/4}e^{-1.9\cdot10^4/T}$	(9)
TG0601 (0.1 MPa)	chemical reaction, $(1-\alpha)^{-1}-1$	37	216.2	$d\alpha/dt=10^{21.6}(1-\alpha)^2e^{-2.6\cdot10^4/T}$	(10)
TG0601 (2 MPa)	Avrami–Erofeev equation, (n=3/4), $[-\ln(1-\alpha)]^{3/4}$	15	145.3	$d\alpha/dt=10^{13.8}(1-\alpha)[-\ln(1-\alpha)]^{1/4}e^{-1.8\cdot10^4/T}$	(11)

method. The decomposition reaction mechanism functions of the sample (TG0701) and the control propellant (TG0601) under different pressures are listed in Table 4. Respectively substitute $f(\alpha)$, and the values of E_a/kJ mol^{-1} and A/s^{-1} into Eq. (7):

$$d\alpha/dt=Af(\alpha)e^{-E/RT} \qquad (7)$$

where α, conversion degree of the major exothermic reaction; d, abbreviation of differential; A, pre-exponential constant; $f(\alpha)$, differential model function; E, apparent activation energy; e, base of the natural system of logarithms, having a numerical value of approximately 2.7183; R, gas constant; T, temperature (K) at time of t.

And the corresponding kinetic equations of the decomposition reaction of TG0701 and TG0601 under 0.1 and 2 MPa are obtained and shown in Table 4.

From Table 4, one can find that the decomposition reaction mechanism function, the kinetic parameters and kinetics of the DB gun propellant under 0.1 MPa can be changed by the high pressure. Comparing with the control propellant (TG0601), one can conclude that CIT-Ce can decrease the apparent activation energy of the DB gun propellant by about 35 kJ mol^{-1} under low pressure, showing its catalytic effect on the thermal decomposition process of the DB gun propellant, but it can not display the effect under high pressure; CIT-Ce cannot change the decomposition reaction mechanism function under a pressure.

Conclusions

Pressure can decrease the peak temperature and increase the decomposition heat, and also can change the mechanism function of the exothermal decomposition reaction of the DB gun propellant.

The mechanism function of the sample under 0.1 MPa is: $G(\alpha)_{0.1\ \mathrm{MPa}}=(1-\alpha)^{-1}-1$, the mechanism obeys chemical reaction, the apparent activation energy $E_{0.1\ \mathrm{MPa}}$=180.8 kJ mol^{-1}, and the kinetic equation can be described as: $(\mathrm{d}\alpha/\mathrm{d}t)_{0.1\ \mathrm{MPa}}=10^{17.7}(1-\alpha)^2\mathrm{e}^{-2.2\cdot10^4/\mathrm{T}}$. Whereas the mechanism function of the sample under 2 MPa is: $G(\alpha)_{2\ \mathrm{MPa}}=[-\ln(1-\alpha)]^{3/4}$, the mechanism obeys Avrami–Erofeev equation (n=3/4), the apparent activation energy $E_{2\ \mathrm{MPa}}$=153.6 kJ mol^{-1}, and the kinetic equation can be expressed as: $(\mathrm{d}\alpha/\mathrm{d}t)_{2\ \mathrm{MPa}}=10^{14.8}(1-\alpha)[-\ln(1-\alpha)]^{1/4}\mathrm{e}^{-1.9\cdot10^4/\mathrm{T}}$.

CIT-Ce makes the DB gun propellant show an irregular increase in the decomposition heat comparing with the control propellant with the increase in furnace pressure at the heating rates; CIT-Ce can decrease the apparent activation energy of the DB gun propellant by about 35 kJ mol^{-1} under low pressure, but it can not display the effect under high pressure; CIT-Ce can not change the decomposition reaction mechanism function under a pressure.

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