

Syntheses and Thermal Behaviors of Rb(FOX-7)·H₂O and Cs(FOX-7)·H₂OJinan Luo, Kangzhen Xu,* Min Wang, Jirong Song,[†] Xiaolei Ren, Yongshun Chen, and Fengqi Zhao[‡]

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Two new energetic organic alkali metal salts, 1,1-diamino-2,2-dinitroethylene rubidium salt [Rb(FOX-7)·H₂O] and 1,1-diamino-2,2-dinitroethylene cesium salt [Cs(FOX-7)·H₂O], were synthesized by reacting of 1,1-diamino-2,2-dinitroethylene (FOX-7) and rubidium chloride or cesium chloride in alkali methanol aqueous solution, respectively. The thermal behaviors of Rb(FOX-7)·H₂O and Cs(FOX-7)·H₂O were studied with DSC and TG methods. The critical temperatures of thermal explosion of the two compounds are 216.22 and 223.73 °C, respectively. Specific heat capacities of the two compounds were determined with a micro-DSC method, and the molar heat capacities are 217.46 and 199.47 J mol⁻¹ K⁻¹ at 298.15 K, respectively. The adiabatic times-to-explosion were also calculated to be a certain value of 5.81 - 6.36 s for Rb(FOX-7)·H₂O, and 9.92 - 10.54 s for Cs(FOX-7)·H₂O. After FOX-7 becoming alkali metal salts, thermal decomposition temperatures of the compounds heighten with the rise of element period, but thermal decomposition processes become intense.

Key Words: 1,1-Diamino-2,2-dinitroethylene (FOX-7), Rubidium salt, Cesium salt, Thermal behavior, Specific heat capacity, Adiabatic time-to-explosion

Introduction

1,1-Diamino-2,2-dinitroethylene (FOX-7) is a novel high-energy material with high thermal stability and low sensitivity to impact and friction. When first synthesized in 1998,^{1,2} FOX-7 received much attention and was deemed to the most important preferred component of propellant in future. Many researches have been carried out on the synthesis, mechanism, molecule structure, thermal behavior, explosive performance and application of FOX-7.³⁻²⁸

“Push-pull” nitro-enamine is a kind of compound with special construction, which possesses a highly polarized carbon-carbon double bond with positive and negative charges being stabilized by the amino group and nitro group respectively, and exists in manifold tautomers and resonances.²⁹ FOX-7 is a representative “push-pull” nitro-enamine compound and presents different structural forms within the pH range of 1-13.^{1,6,10,13} FOX-7 can react with many nucleophiles and strong alkalis to synthesize new energetic compounds. Our interest mainly consisted in modifying molecular structure of FOX-7 in order to obtain new high energetic compounds and study their structure-property relationship.³⁰⁻³⁷ Furthermore, we also prepared four salts of FOX-7: 1,1-diamino-2,2-dinitroethylene guanidine salt [G(FOX-7)],^{13,33} 1,1-diamino-2,2-dinitroethylene potassium salt [K(FOX-7)·H₂O],^{13,37} 1,1-diamino-2,2-dinitroethylene rubidium salt [Rb(FOX-7)·H₂O] and 1,1-diamino-2,2-dinitroethylene cesium salt [Cs(FOX-7)·H₂O]. However, we are unable to get lithium salt, sodium salt and other metal salts, because of the weak acidity of FOX-7. At the same time, we found that alkali metal salts of FOX-7 all have a coordinated water molecule, which can be confirmed by the crystal structure and thermal decomposition of K(FOX-7)·H₂O.³⁷ Moreover, the interaction of the coordinated water with anion-cation is strong after analysis of the crystal structure, so the coordinated water is quite

difficult to lose in thermal decomposition process.³⁷ However, there is no water molecule in G(FOX-7).^{13,33} After FOX-7 becoming alkali metal salts, thermal decomposition temperatures of the compounds heighten, and thermal decomposition processes become very intense. So, we expect to use them as energetic additives to increase combustion rate of propellant.

In this paper, we mainly reported the syntheses of Rb(FOX-7)·H₂O and Cs(FOX-7)·H₂O, studied their thermal behaviors with DSC and TG methods, determined special heat capacities with a micro-DSC method, and calculated adiabatic times-to-explosion for analyzing their structure-property relationship and further estimating thermal stabilities.

Experimental Section

Material. FOX-7 (0.015 mol, 2.22 g) was suspended in 10 mL of water and to it two solutions of NaOH (1.2 g in 5 mL of water) and RbCl (3.63 g in 5 mL of water) were added drop wise, respectively. After reaction at room temperature for 20 min, 50 mL of methanol were also added drop wise, and the resulting mixture was slowly cooled to 0 °C. Many faint yellow crystals of Rb(FOX-7)·H₂O were formed, which were filtered, washed with methanol and dried under vacuum, yielding 2.37 g (63%). Anal. Calcd. (%) for C₂H₅N₄O₅Rb: C 9.59, H 2.01, N 22.36; found: C 9.52, H 2.24, N 22.25. The characteristic peaks of IR (KBr) are: 3392, 3310, 3047, 1657, 1608, 1485, 1350, 1219, 1102, 794 cm⁻¹. The synthetic method of Cs(FOX-7)·H₂O (faint yellow) is same to that of Rb(FOX-7)·H₂O, yielding 2.99 g (67%). Anal. Calcd. (%) for C₂H₃N₄O₄Cs: C 8.06, H 1.69, N 18.80; found: C 8.11, H 2.01, N 18.26. The characteristic peaks of IR (KBr) are: 3389, 3300, 3028, 1654, 1608, 1481, 1346, 1216, 1104, 796 cm⁻¹.

Experimental equipments and conditions. The DSC experiments for Rb(FOX-7)·H₂O and Cs(FOX-7)·H₂O were performed

ed using a DSC-Q200 apparatus (TA, USA) under a nitrogen atmosphere at a flow rate of 50 mL min⁻¹ and the amount of used sample was about 0.6 mg. The heating rates used were 2.5, 5.0, 10.0 and 15.0 °C min⁻¹ from ambient temperature to 400.0 °C, respectively.

The TG experiments for Rb(FOX-7)·H₂O and Cs(FOX-7)·H₂O were performed using a SDT-Q600 apparatus (TA, USA) under a nitrogen atmosphere at a flow rate of 100 mL min⁻¹. The amount of used sample was about 0.6 mg. The heating rate used was 5.0 °C min⁻¹ from ambient temperature to 400.0 °C.

The specific heat capacities (C_p) of Rb(FOX-7)·H₂O and Cs(FOX-7)·H₂O were determined using a Micro-DSC III apparatus (SETARAM, France), the amounts of used samples were 437.93 and 608.81 mg, respectively. The heating rate used was 0.15 °C min⁻¹ (2.5×10^{-3} K s⁻¹) from 10.0 to 80.0 °C, in which the precisions of temperature and heat flow were 10⁻⁴ °C and 0.2 μW, respectively. The principle for measuring of the continuous specific heat capacity is shown as:

$$C_p = \frac{A_s - A_b}{m_s \times \beta} \quad (1)$$

where C_p is the specific heat capacity, A_s and A_b are the heat flows of the sample and blank, m_s is the amount of the sample, β is the heating rate.

Results and Discussion

Thermal behavior. The typical DSC and TG curves (Figures 1 and 2) indicate the thermal behaviors of Rb(FOX-7)·H₂O and Cs(FOX-7)·H₂O are similar to each other and all can be divided into two obvious decomposition stages. The first stages are endothermic processes, and occur at 200 - 212 °C with a mass loss of about 7% for Rb(FOX-7)·H₂O, and 210 - 224 °C with a mass loss of about 6% for Cs(FOX-7)·H₂O, which coincide with the theoretical values of 7.2% for Rb(FOX-7)·H₂O and 6.1% for Cs(FOX-7)·H₂O corresponding to the loss of 1 mol coordinated water molecule. Corresponding extrapolated onset temperatures and peak temperatures are 203.17 and 206.18 °C for Rb(FOX-7)·H₂O, 218.68 and 220.60 °C for Cs(FOX-7)·H₂O at the heating rate 5.0 °C min⁻¹, respectively. The second stages of the two

compounds are all very intense exothermic decomposition processes, and occur at 213 - 225 °C with a mass loss of about 42% for Rb(FOX-7)·H₂O and 225 - 230 °C with a mass loss of about 31% for Cs(FOX-7)·H₂O, respectively. From TG curves of the two compounds, we also can see that the intense exothermic decomposition can generate certain jet power to make thermo-balance shake up and down. The final residues for the two compounds are about 42% and 51% at 400 °C. All are consistent with that of K(FOX-7)·H₂O,³⁷ further confirming that there is a coordinated water molecule in all alkali metal salts of FOX-7, the interaction of the coordinated water with anion-cation is strong and the coordinated water was lost only at much high decomposition temperature. But, all are quite different to that of FOX-7, whose thermal behavior presents only two slow big exothermic decomposition processes.¹² After FOX-7 becoming alkali metal salts, thermal decomposition temperatures of the compounds heighten with the rise of element period, and thermal decomposition processes become intense. As energetic additives, they are very useful for the increment of combustion rate in propellant.

In order to obtain the kinetic parameters (the apparent activation energy (E) and pre-exponential constant (A)) of the exothermic decomposition reaction, a multiple heating method (Kissinger method³⁸ and Ozawa method³⁹) was employed. The Kissinger and Ozawa equations are as follows:

$$\ln \left(\frac{\beta}{T_p^2} \right) = \ln \frac{AR}{E} - \frac{E}{R} \frac{1}{T_p} \quad (2)$$

$$\log \beta + \frac{0.4567E}{RT_p} = C \quad (3)$$

where T_p is the peak temperature (K), β is the linear heating rate (K min⁻¹), E is the apparent activation energy (kJ mol⁻¹), A is the pre-exponential constant (s⁻¹), R is the gas constant (J mol⁻¹ K⁻¹) and C is a constant.

The measured values of the beginning temperature (T_0), extrapolated onset temperature (T_e), peak temperature (T_p) and enthalpy (ΔH_d) of the exothermic decomposition reaction for

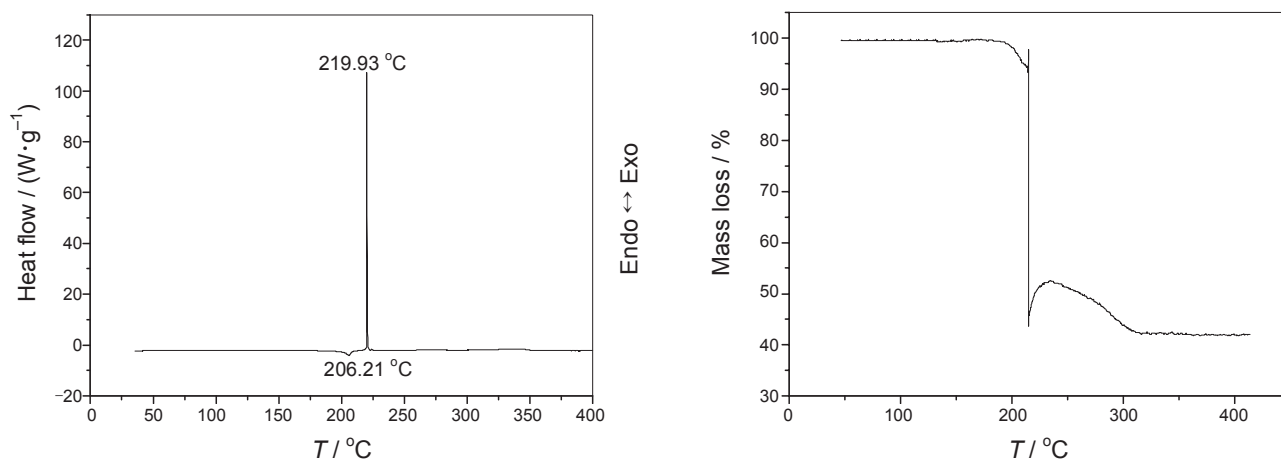


Figure 1. DSC and TG curves of Rb(FOX-7)·H₂O at a heating rate of 5.0 °C min⁻¹.

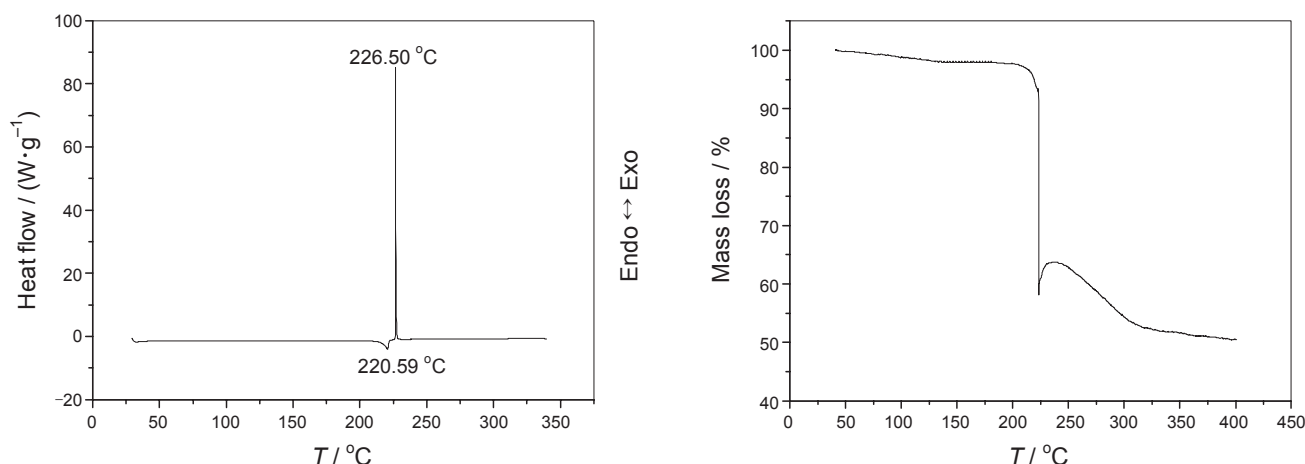


Figure 2. DSC and TG curves of Cs(FOX-7)·H₂O at a heating rate of 5.0 °C min⁻¹.

Table 1. The values of T_0 , T_e , T_p , ΔH_d , T_{00} , T_{e0} and T_{p0} of the first exothermic decomposition stages for Rb(FOX-7)·H₂O and Cs(FOX-7)·H₂O determined from the DSC curves at various heating rates (β)

	β / (°C min ⁻¹)	T_0 / °C	T_e / °C	T_p / °C	ΔH_d / (J g ⁻¹)	T_{00} / °C	T_{e0} / °C	T_{p0} / °C
Rb(FOX-7)·H ₂ O	2.5	205.28	211.21	211.31	518.9 ± 20.7	197.78	203.66	204.08
	5.0	216.30	219.08	219.93				
	10.0	221.74	227.58	227.58				
	15.0	227.01	233.07	233.58				
Cs(FOX-7)·H ₂ O	2.5	218.13	219.37	219.47	394.9 ± 15.7	211.40	212.01	212.50
	5.0	224.53	226.39	226.50				
	10.0	232.61	234.89	234.67				
	15.0	237.41	239.67	239.90				

Table 2. The kinetic parameters obtained by the data in Table 1^a

	E_k / (kJ mol ⁻¹)	$\log(A / s^{-1})$	r_k	E_o / (kJ mol ⁻¹)	r_o
Rb(FOX-7)·H ₂ O	158.5	14.61	0.9990	158.5	0.9991
Cs(FOX-7)·H ₂ O	175.7	16.20	0.9992	175.1	0.9993

^aSubscript k, data obtained by Kissinger's method; subscript o, data obtained by Ozawa's method.

Cs(FOX-7)·H₂O and Re(FOX-7)·H₂O were listed in Table 1. The values of T_{00} , T_{e0} and T_{p0} corresponding to $\beta \rightarrow 0$ obtained by Eq. (4) are also listed in Table 1.⁴⁰

$$T_{(0, e \text{ or } p)i} = T_{(00, e0 \text{ or } p0)} + n\beta_i + m\beta_i^2 \quad i = 1 \sim 4 \quad (4)$$

where n and m are coefficients.

The kinetic parameters obtained by the data in Table 1 were listed in Table 2. We can see that the apparent activation energies (E) obtained by Kissinger method for Cs(FOX-7)·H₂O and Re(FOX-7)·H₂O all agree well with that obtained by Ozawa method. Moreover, the linear correlation coefficients (r) are all very close to 1. So, the results are credible. Moreover, the apparent activation energies (E) for the two compounds were lower, indicating that the two compounds are much easy to decompose at higher temperature.

The critical temperatures of thermal explosion (T_b) of

Rb(FOX-7)·H₂O and Cs(FOX-7)·H₂O obtained by Eq. (5) were 216.22 and 223.73 °C.⁴⁰ The sequence of T_b for the series compounds is: Cs(FOX-7)·H₂O (223.73 °C) > Rb(FOX-7)·H₂O (216.22 °C) > K(FOX-7)·H₂O (212.02 °C) > FOX-7 (207.08 °C) > G(FOX-7) (201.72 °C).^{22,37,41} After FOX-7 became alkali metal salts, thermal stabilities of the compounds heighten with the rise of element period.

$$T_b = \frac{E_o - \sqrt{E_o^2 - 4E_o RT_{e0}}}{2R} \quad (5)$$

where E_o is the apparent activation energy obtained by Ozawa's method.

The entropies of activation (ΔS^\ddagger), enthalpies of activation (ΔH^\ddagger) and free energies of activation (ΔG^\ddagger) of the thermal decomposition process corresponding to $T = T_{p0}$, $A = A_k$ and $E = E_k$ obtained by Eqs. (6)–(8) taken from Ref. (40) for Rb(FOX-7)·

H₂O and Cs(FOX-7)·H₂O are 30.9 and 61.17 J mol⁻¹ K⁻¹, 158.5 and 175.5 kJ mol⁻¹, 143.8 and 160.7 kJ mol⁻¹, respectively.

$$A = \frac{k_B T}{h} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \quad (6)$$

$$A \exp\left(-\frac{E}{RT}\right) = \frac{k_B T}{h} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \exp\left(-\frac{\Delta H^\ddagger}{RT}\right) \quad (7)$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T \Delta S^\ddagger \quad (8)$$

where k_B is the Boltzman constant and h is the Plank constant.

Specific heat capacity. Figures 3 and 4 show the determination results of Rb(FOX-7)·H₂O and Cs(FOX-7)·H₂O, using a continuous specific heat capacity mode of Micro-DSC III. In determined temperature range, specific heat capacities all present good linear relationships with temperature. Specific heat capacity equations of Rb(FOX-7)·H₂O and Cs(FOX-7)·H₂O are as follows:

$$C_p(\text{J g}^{-1} \text{K}^{-1}) = 0.2245 + 2.1580 \times 10^{-3} T \quad (283.0 \text{ K} < T < 353.0 \text{ K}) \quad (9)$$

$$C_p(\text{J g}^{-1} \text{K}^{-1}) = 0.2353 + 1.4560 \times 10^{-3} T \quad (283.0 \text{ K} < T < 353.0 \text{ K}) \quad (10)$$

The molar heat capacities of Rb(FOX-7)·H₂O and Cs(FOX-7)·H₂O are 217.46 and 199.47 J mol⁻¹ K⁻¹ at 298.15 K, respectively. From the results, we can see that specific heat capacity (J g⁻¹ K⁻¹) decreased with the rise of element period. The sequence of specific heat capacity (J g⁻¹ K⁻¹) for the series compounds is: Cs(FOX-7)·H₂O < Rb(FOX-7)·H₂O < K(FOX-7)·H₂O < FOX-7 < G(FOX-7),^{22,37,41} which is just opposite to that of the critical temperature of thermal explosion. The reason for the result may be the content of metal in compounds, and the higher content of metal results in the lower specific heat capacity.

Thermodynamic properties. The enthalpy change, entropy change and Gibbs free energy change of Rb(FOX-7)·H₂O and Cs(FOX-7)·H₂O were calculated by Eqs. (11)–(13) at 283–353 K, from ambient temperature to thermal decomposition temperature, taking 298.15 K as the benchmark. The results were listed in Table 3.

$$H_T - H_{298.15} = \int_{298.15}^T C_p dT \quad (11)$$

$$S_T - S_{298.15} = \int_{298.15}^T C_p \cdot T^{-1} dT \quad (12)$$

$$G_T - G_{298.15} = \int_{298.15}^T C_p dT - T \int_{298.15}^T C_p \cdot T^{-1} dT \quad (13)$$

Estimation of adiabatic time-to-explosion. Energetic materials need a time from the beginning thermal decomposition to

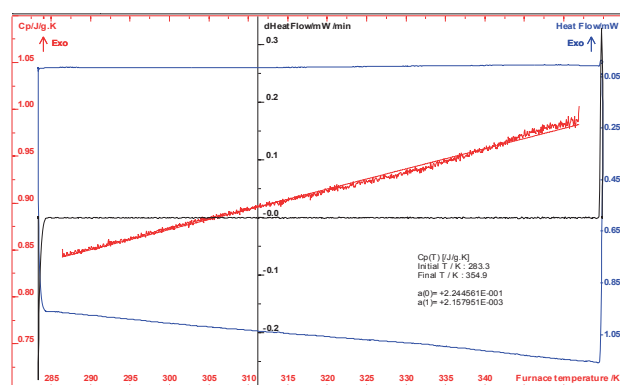


Figure 3. Determination results of the continuous specific heat capacity of Rb(FOX-7)·H₂O.

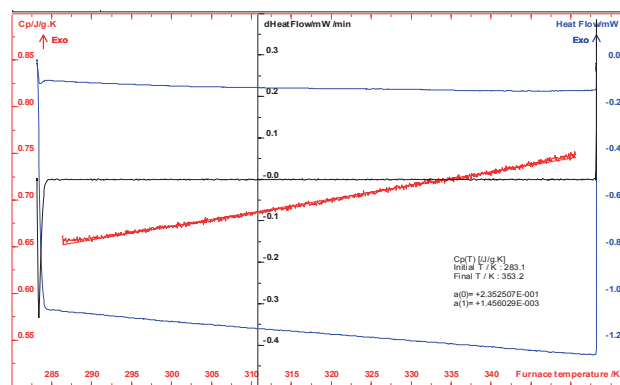


Figure 4. Determination results of the continuous specific heat capacity of Cs(FOX-7)·H₂O.

Table 3. Thermodynamic function data of Rb(FOX-7)·H₂O and Cs(FOX-7)·H₂O

T (K)	$H_T - H_{298.15}$ (kJ·mol ⁻¹)		$S_T - S_{298.15}$ (J·mol ⁻¹ ·K ⁻¹)		$G_T - G_{298.15}$ (kJ·mol ⁻¹)	
	Rb(FOX-7)·H ₂ O	Cs(FOX-7)·H ₂ O	Rb(FOX-7)·H ₂ O	Cs(FOX-7)·H ₂ O	Rb(FOX-7)·H ₂ O	Cs(FOX-7)·H ₂ O
283.0	-3.23	-2.97	-11.13	-10.23	-0.09	-0.07
293.0	-1.11	-1.02	-3.76	-3.46	-0.01	-0.01
303.0	1.06	0.97	3.53	3.24	-0.01	-0.01
313.0	3.29	3.0	10.76	9.86	-0.08	-0.07
323.0	5.57	5.09	17.94	16.39	-0.23	-0.20
333.0	7.91	7.22	25.06	22.87	-0.44	-0.40
343.0	10.30	9.39	32.13	29.28	-0.72	-0.66
353.0	12.74	11.59	39.16	35.63	-1.08	-0.99

thermal explosion in adiabatic condition. We called the time as the adiabatic time-to-explosion.^{22,36,40-45} Ordinarily, we use heating rate (dT/dt) and critical heating rate $(dT/dt)_b$ in thermal decomposition process to evaluate the thermal stability of energetic materials. However, we can calculate the adiabatic time-to-explosion (t) by the following Eqs. (14)-(15)^{22,36,40-44} when we have obtained a series of experimental data. Thereby, as an important parameter, it is very easy and intuitionistic to evaluate the thermal stability of energetic materials according to the length of the adiabatic time-to-explosion.

$$C_p \frac{dT}{dt} = QA \exp(-E/RT) f(\alpha) \quad (14)$$

$$\alpha = \int_{T_0}^T \frac{C_p}{Q} dT \quad (15)$$

where C_p is the specific heat capacity ($J \cdot mol^{-1} \cdot K^{-1}$), T is the absolute temperature (K), t is the adiabatic time-to-explosion (s), Q is the exothermic values ($J \cdot mol^{-1}$), A is the pre-exponential factor (s^{-1}), E is the apparent activation energy the thermal decomposition reaction ($J \cdot mol^{-1}$), R is the gas constant ($J \cdot mol^{-1} \cdot K^{-1}$), $f(\alpha)$ is the most probable kinetic model function and α is the fraction of conversion.

According to the above determining results of specific heat capacity, we use:

$$C_p = a + bT \quad (16)$$

where a and b are coefficients.

In fact, the conversion degree (α) of energetic materials from the beginning thermal decomposition to thermal explosion in the adiabatic conditions is very small, the most probable kinetic model function [$f(\alpha)$] at this beginning decomposition process is unimportant and almost has no influence on the result of the estimation of the adiabatic time-to-explosion. So, we used Eq. (17) and supposed that the rate order of the mechanism function (n) of Rb(FOX-7)·H₂O and Cs(FOX-7)·H₂O in the decomposition process equaled 0, 1 and 2.^{22,40,41}

$$f(\alpha) = (1 - \alpha)^n \quad (17)$$

The combination of Eqs. (14)-(17) gives the following adiabatic time-to-explosion equation:

$$\begin{aligned} t &= \int_0^t dt = \int_{T_0}^T \frac{C_p \exp(E/RT)}{QA f(\alpha)} dT \\ &= \frac{1}{QA} \int_{T_0}^T \frac{(a + bT) \exp(E/RT)}{(1 - \alpha)^n} dT \\ &= \frac{1}{QA \left\{ 1 - \frac{1}{Q} \left[a(T_b - T_{00}) + \frac{b}{2}(T_b^2 - T_{00}^2) \right] \right\}^n} \\ &\quad \int_{T_0}^T (a + bT) \exp(E/RT) dT \end{aligned} \quad (18)$$

The limit of the temperature integral in Eq. (18) is from T_{00} to T_b .

We can directly get $t_0 = 5.81$ s, $t_1 = 6.08$ s, $t_2 = 6.36$ s for Rb(FOX-7)·H₂O, and $t_0 = 9.92$ s, $t_1 = 10.23$ s, $t_2 = 10.54$ s for Cs(FOX-7)·H₂O from Eq. (18), according to the above obtained data and neglecting the effects of melting and other changes. As a rule, the rate order (n) of energetic materials ranges from 0 to 2, so the adiabatic time-to-explosion should be a certain value of 5.81 - 6.36 s for Rb(FOX-7)·H₂O and 9.92 - 10.54 s for Cs(FOX-7)·H₂O, respectively. The two times are very short, and can be proved credible according to the intense change of DSC curves in the exothermic decomposition. The two times are much shorter than that of FOX-7 as 78.94 - 88.93 s.²² All indicate that the alkali metal salts of FOX-7 are much easy to intensely decompose at the certain high temperature, despite heightening the thermal decomposition temperatures.

Conclusion

(1) Rb(FOX-7)·H₂O and Cs(FOX-7)·H₂O were prepared and their thermal behaviors were studied. The critical temperatures of thermal explosion for the two compounds are 216.22 and 223.73 °C, respectively. (2) Specific heat capacity equations of Rb(FOX-7)·H₂O and Cs(FOX-7)·H₂O are $C_p(J \cdot g^{-1} \cdot K^{-1}) = 0.2245 + 2.1580 \times 10^{-3} T$, $C_p(J \cdot g^{-1} \cdot K^{-1}) = 0.2353 + 1.4560 \times 10^{-3} T$ ($283.0 \text{ K} < T < 353.0 \text{ K}$), and the molar heat capacities are 217.46 and 199.47 $J \cdot mol^{-1} \cdot K^{-1}$ at 298.15 K, respectively. The adiabatic times-to-explosion were also calculated to be a certain value of 5.81 - 6.36 s for Rb(FOX-7)·H₂O, and 9.92 - 10.54 s for Cs(FOX-7)·H₂O. After FOX-7 becoming alkali metal salts, thermal decomposition temperatures of the compounds heighten with the rise of element period, but thermal decomposition processes become intense.

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