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Thermodynamic Properties of Potassium Salts of Trinitrophenol

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Abstract: The continuous specific heat capacities at constant pressure (C_p) of energetic materials of mono-substituted potassium (K_1 TNPG), di-substituted (K_2 TNPG) and tri-substituted (K_3 TNPG) trinitrophenolate were measured by differential scanning calorimeter (DSC) method. The change of enthalpy and entropy were calculated at an interval of 5 °C in the range of 50 – 100 °C. The least square method is applied to treat experimental data. The temperature dependence of C_p was determined as quadratic equation: $C_p = a + bT + cT^2$. The correlation coefficients (R) of measured results of K_1 TNPG, K_2 TNPG and K_3 TNPG are 0.987, 0.999 and 0.993, respectively. The deviation analysis indicates that DSC method is effective and can be used to measure the specific heat capacity of other energetic materials.

Key words: analytical chemistry; specific heat capacity; trinitrophenolate; potassium salts; differential scanning calorimeter

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1 Introduction

Specific heat capacity is one of the most fundamental thermodynamic properties of substances, which depend on microstructure of substance and micro movements of substance particles^[1-4]. In 1966, M J O'NEILL^[5] described that specific heat capacity of materials can be measured by differential scanning calorimeter (DSC), and the ultimate precision of the method is 0.3% or better, which approaches the precision of adiabatic calorimeter. In 1997, the corresponding military standard is based on determining specific heat capacity of propellants and explosives to analysis heat of detonation, heat of combustion and critical temperature etc. At the same time, some thermodynamic properties, such as enthalpy, free energy, and entropy etc, are calculated basing on the specific heat capacity^[6].

2,4,6-trinitro-1,3,5-trihydroxybenzene (trinitrophenol, TNPG) is a strong acidic organic compound with yellow needle crystal structure. There are three nitro-groups and three phenolic hydroxyl groups conjugated with benzene ring, so it is an important nitrophenol explosive. TNPG can react with metallic compounds forming three type metallic salts easily, which have strong combustion and detonating properties^[7]. The crystal structures of mono-, di-, and tri-

substituted potassium salts of trinitrophenol (K_1 TNPG, K_2 TNPG, K_3 TNPG) have been reported^[8]. However, no reference on specific heat capacity of these compounds has been found up to now.

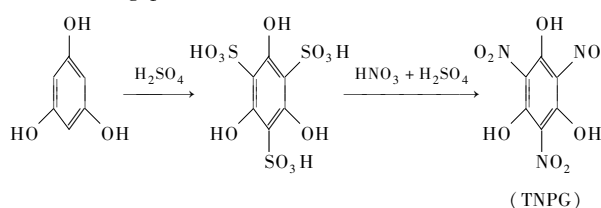
In this paper, we mainly study on thermodynamic properties of three potassium salts of TNPG between 50 °C and 100 °C. The aim of this work is to provide a basis for further researches on invariability for TNPG salts to expand their potential applications in the fields of national defense industry and gas generating reagents. These data are quite useful in evaluation of thermal stability.

2 Experimental

2.1 Sample preparation

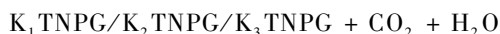
Synthetic sapphire (diameter: 3 mm; thickness: 1 mm; mass: 28.599 mg) provided by Perkin-Elmer Inc. was used to the experiments as reference materials for calibration of specific heat capacity.

Potassium salts of trinitrophenol used for the present calorimetric study were provided by Chen hongyan (Beijing Institute of Technology) and synthesized by the following procedure^[9].



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2.2 Differential scanning calorimeter (DSC)

The heat-capacity measurements were carried out by means of a differential scanning calorimeter in the range of 50 – 100 °C. This is a new instrumental method for the direct measurement of specific heat capacity. In differential scanning calorimetry (DSC), the sample material is subjected to a linear temperature program, and the heat flow rate into the sample is continuously measured; this heat flow rate is proportional to the instantaneous specific heat capacity of the sample. The procedure to measure the specific heat capacity as a function of the temperature is programmed as shown in Fig. 1. To establish a base line, the program is carried out with no sample present. However, empty aluminum foil sample containers are placed in the sample holders. Isothermally, the baseline indicates the differential losses of the two samples holders at the initial temperature. When the program begins, there may be a small offset from the isothermal base line, caused by the thermal capacity mismatch between the two sample holders and their contents. When the temperature program ends, baseline curve C reappears. Similarly, weighed sapphire and sample are placed in aluminum foil sample containers, the procedure is then repeated, and curve A and B are obtained.

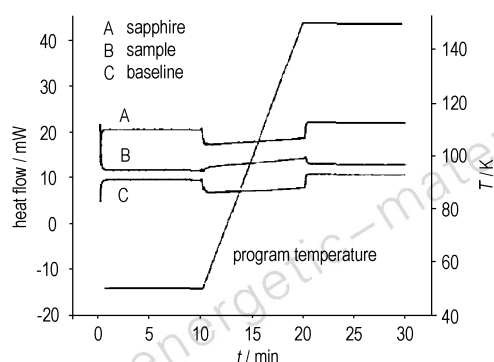


Fig. 1 DSC curves of sample, Sapphire and baseline determined

Therefore the heat flow rate into the sample is given by reference^[10].

$$dH/dt = mC_p dT/dt \quad (1)$$

Where dH/dt is the heat flow rate in milliwatt, m is the sample mass in milligram, C_p is the specific heat capacity in $\text{J} \cdot \text{g}^{-1} \cdot \text{°C}^{-1}$, and dT/dt is the program rate in

$\text{°C} \cdot \text{min}^{-1}$. From Equation (1), we can get

$$C_p / C_p' = m' \Delta Y / m \Delta Y' \quad (2)$$

Where $\Delta Y'$ and ΔY are the ordinate deflections due to the standard and the sample, C_p' and C_p are the specific heat capacity of the standard and sample, m' and m are the mass of standard and sample, respectively.

Furthermore, to confirm the validity of this apparatus, we measured the heat capacity of Sn with the same heating pattern. From Table 1, it can be found that the repeatability of the measurements is good, and the relative deviation is little. This shows that this method is quite satisfactory in the measurement precision and the specific heat capacity of the energetic compounds can be measured by this method.

Table 1 The specific heat capacity of Sn at 125 °C

times	mass /mg	C_p / $\text{J} \cdot \text{g}^{-1} \cdot \text{°C}^{-1}$	average of C_p reference ^[11] / $\text{J} \cdot \text{g}^{-1} \cdot \text{°C}^{-1}$	relative deviation/%
1	9.79	0.245		
2	9.39	0.229		
3	6.25	0.246	0.239	1.64
4	11.97	0.239		
5	10.89	0.237		

2.3 Thermal analysis

Thermal analysis was performed using a Pyris 1 DSC instrument produced by American Perkin-Elmer Corporation. A Pyris 1 Thermal Analysis System loaded with the program for data processing can calculate specific heat capacity. The measurement was made under high purity nitrogen atmosphere at a heating rate of $10 \text{ °C} \cdot \text{min}^{-1}$ with a flow rate of $20 \text{ mL} \cdot \text{min}^{-1}$. The mass of the sample used for DSC analysis was less than 4 mg for K_1TNPG , K_2TNPG and K_3TNPG .

3 Results and discussion

3.1 Specific heat capacity of potassium salts of TNPG

The C_p values of three energetic compounds were measured by DSC. Seven parallel experiments were carried out, and the average results were obtained from the measured values and plotted in Fig. 2. It can be seen that the specific heat capacity values of K_1TNPG , K_2TNPG , and K_3TNPG is very close. This shows that their endothermicity values are approximately same in condition of heating. The variation regularity of the C_p

with T is basically consistent. Specific heat capacities of the compound increase with temperature, and no especial change happen in the experimental range.

The specific heat capacities of K_1 TNPG, K_2 TNPG and K_3 TNPG have been fitted to three following polynomials (Table 2) in experimental temperature by means of the least square fitting. The fitted results are very compatible with the relationships. From three equations, the C_p change of three potassium salts of TNPG accord with quadratic equation. And the correlation coefficients (R) of least square fitting for K_2 TNPG and K_3 TNPG are 0.99, the standard deviations (SD) are 0.1. The relationship for K_2 TNPG are fitted best, secondly K_3 TNPG.

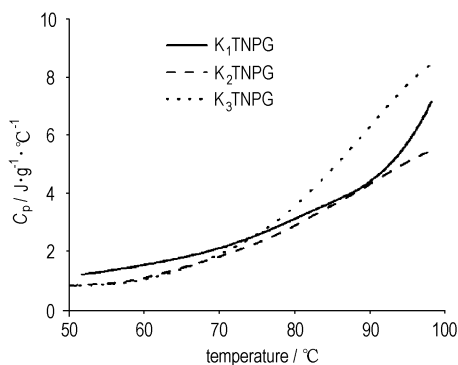


Fig. 2 C_p vs T for K_1 TNPG, K_2 TNPG and K_3 TNPG

3.2 Other thermodynamic properties

We calculated ΔH and ΔS , respectively, based on the following thermodynamic relationships: $\Delta H = \int_{T_1}^{T_2} C_p dT$ and $\Delta S = \int_{T_1}^{T_2} C_p/T dT$ at an interval of 5 °C and listed them in Table 3. It shows that ΔH and ΔS of K_1 TNPG only change irregularly, the rest gradually increase. The results are compatible as shown Fig. 2.

4 Conclusion

Differential scanning calorimetry is a quick and exact method of determining the continuous specific heat capacity of material. The specific heat capacity values of K_1 TNPG, K_2 TNPG and K_3 TNPG were measured by DSC. Their C_p vs T relationships were obtained. The correlation coefficients (R) of results are close to 0.99, providing important information for calculating characteristic parameters. In the temperature range of 50 – 100 °C, the specific heat capacities of energetic material of K_1 TNPG, K_2 TNPG and K_3 TNPG change by rule. It is confirmed that thermodynamic property of potassium salts of trinitrophenol is similar. The thermal stability of them is preferable, and the structures are stable. The deviation analysis indicates that DSC method is effective and can be used to measure the specific heat capacity of other energetic materials.

Table 2 Polynomial equation of K_1 TNPG, K_2 TNPG and K_3 TNPG

sample	temperature range	equation	R	SD
K_1 TNPG	50 – 100 °C	$C_p = 8.082 - 0.256T + 0.002T^2$	0.987	0.173
K_2 TNPG	50 – 100 °C	$C_p = 3.987 - 0.148T + 0.002T^2$	0.999	0.047
K_3 TNPG	50 – 100 °C	$C_p = 11.978 - 0.420T + 0.004T^2$	0.993	0.197

Table 3 ΔH and ΔS of K_1 TNPG, K_2 TNPG and K_3 TNPG

$T/^\circ\text{C}$	K_1 TNPG		K_2 TNPG		K_3 TNPG	
	$\Delta H/\text{J} \cdot \text{g}^{-1}$	$\Delta S/\text{J} \cdot \text{g}^{-1} \cdot ^\circ\text{C}^{-1}$	$\Delta H/\text{J} \cdot \text{g}^{-1}$	$\Delta S/\text{J} \cdot \text{g}^{-1} \cdot ^\circ\text{C}^{-1}$	$\Delta H/\text{J} \cdot \text{g}^{-1}$	$\Delta S/\text{J} \cdot \text{g}^{-1} \cdot ^\circ\text{C}^{-1}$
50	0	0	0	0	0	0
55	0.793	0.0153	8.668	0.165	4.807	0.0916
60	-0.107	-0.00177	10.468	0.182	5.307	0.0922
65	-0.507	-0.00809	12.768	0.204	6.807	0.109
70	-0.407	-0.00606	15.568	0.23	9.307	0.138
75	0.193	0.00260	18.868	0.26	12.807	0.176
80	1.293	0.0166	22.668	0.292	17.307	0.223
85	2.893	0.035	26.968	0.327	22.807	0.276
90	4.993	0.057	31.768	0.363	29.307	0.335
95	7.593	0.082	37.068	0.401	36.807	0.398

Influence of Humidity on Thermal Decomposition Behavior of Single-base Propellant

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Abstract: The thermal decomposition behaviors of single-base propellants stored with different humidity were studied by using microcalorimetry with sealed and open glass test-tube. The experimental results show that under the same humidity condition, the temperature of initial accelerating thermal decomposition of single-base propellant under the sealed condition, T_0 , is larger than that under the open condition. The temperature corresponding to maximum decomposition rate of single-base propellant under the sealed condition, T_{p2} , reduces obviously with humidity increasing, but that under the open condition does not. The process and reaction accelerating extent of the decomposition reaction of single-base propellant under the sealed condition are greater than those under the open condition.

Key words: physical chemistry; single-base propellant; thermal decomposition; relative humidity

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三硝基均苯三酚钾盐的热力学研究

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摘要: 用差示扫描量热法(DSC)测定了含能材料 2,4,6-三硝基-1,3,5-苯三酚一取代(K_1 TNPG), 二取代(K_2 TNPG)及三取代钾盐(K_3 TNPG)定压下的连续比热容, 计算了在 50 ~ 100 °C 温度范围内每间隔 5 °C 的焓差值和熵变值。用最小二乘法进行数据处理, 得出的比热容(C_p)与温度(T)的关系为: $C_p = a + bT + cT^2$, K_1 TNPG, K_2 TNPG and K_3 TNPG 的线性相关系数分别为 0.987, 0.999 和 0.993。

关键词: 分析化学; 比热容; 三硝基均苯三酚; 钾盐; 差示扫描量热法

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