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Specific Heat Capacity of Sodium Salts of 2,4,6-Trinitro-1,3,5-trihydroxybenzene

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Abstract: The continuous specific heat capacities at constant pressure (C_p) of 2,4,6-trinitro-1,3,5-trihydroxybenzene (TNPG), mono-substituted sodium (Na_1TNPG), di-substituted (Na_2TNPG) and tri-substituted (Na_3TNPG) trinitrophloroglucinate were measured by differential scanning calorimeter (DSC) method. The change of enthalpy and entropy were calculated at an interval of 5 ℃ in the range from 50 ℃ to 100 ℃. The temperature dependence of C_p were determined from the experimental values as $C_p(J \cdot g^{-1} \cdot ℃^{-1}) = a + bT + cT^2 + dT^3$ with the exception $d = 0$ for the substituted sodium salts of TNPG. The deviation analysis indicates that DSC method is effective and can be used to measure the specific heat capacity of other energetic materials. The correlation coefficients that are close to 1 show that the C_p values of these compounds are well-regulated.

Key words: analytical chemistry; specific heat capacity; 2,4,6-trinitro-1,3,5-trihydroxybenzene (TNPG); sodium salt; differential scanning calorimeter (DSC)

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1 Introduction

2,4,6-Trinitro-1,3,5-trihydroxybenzene (trinitrophloroglucinol, TNPG) is a strong acidic organic compound with three nitro-groups and three phenolic hydroxyl groups conjugated with the ring. TNPG is an important nitrophenol explosive, and can react with many metallic compounds forming mono-, di- and tri-substituted metallic salts of TNPG, which have strong combustion and detonating properties and are used as primary explosive[1,2].

Specific heat capacity (C_p) is a fundamental quantity for evaluation of thermodynamic properties, closely related to the energetic structure and sensitive to the variations in other properties of substances[3,4], imaging the ability to endothermicity or exothermicity. The application and synthetic methods of TNPG and its alkali metal salts have been reported[5-7]. Up to now, no reports on specific heat capacity of them have been found. Therefore, we studied the low-temperature specific heat capacity of TNPG and its substituted sodium salts in the temperature range between 50 ℃ and the melting point with a differential scanning calorimeter (DSC), which as an effective thermal analysis tool has been widely applied in many fields[8]. Other thermodynamic data, such as molar differences of enthalpy and entropy, were calculated from C_p. We can ulteriorly explore the stability of TNPG and its related substances.

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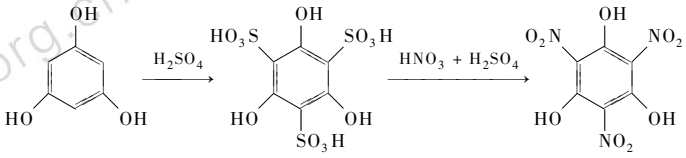
2 Experimental

2.1 Sample

TNPG is a yellow needle crystal. TNPG and its mono-, di- and tri-substituted sodium salts used for the present work have been prepared by CHEN Hong-yan (Beijing Institute of Technology)[7,9]. The preparation principle is as follows.



$$TNPG + NaHCO_3 \longrightarrow NaTNPG/Na_2TNPG/Na_3TNPG + CO_2 + H_2O$$

The structures of the products were characterized by IR, MS, TG and DSC. Furthermore, their melting points were determined to be about 150 ℃ with CDR-4P DSC and the purities were indicated larger than >99%.

2.2 Determination of specific heat capacity

The heat flow rate into the sample is proportional to its continuous specific heat capacity. By recording this heat flow rate as a function of temperature and comparing it with the heat flow into a standard material under the same conditions, the specific heat capacity of the sample is determined as a function of temperature . The ultimate

precision of this method is 0.3% or better, which approaches the precision of adiabatic calorimetry[10]. The experiment was carried out by Pyris 1 DSC (PERKIN-ELMER Inc.) in the temperature range between 50 ℃ and 100 ℃ under the linear heating rate of 10 ℃ · min^{-1}. The atmosphere was nitrogen gas with purity of 99.999% and a flow rate of 20 mL · min^{-1}. Baseline measurements (no sample) and reference measurements (synthetic sapphire) were made in the same temperature range as the sample measurements for calibrating the calorimeter. The mass of the sample loaded in an aluminum pan was accurately weighed before each heating, the standard substance 28.599 mg. The high-precision apparatus has an automatic data processing program and the procedure control software which can determine basic thermodynamic and kinetics functions.

3 Results and discussion

3.1 Examination of the precision

In order to examine the precision of this instrument, we measured the melting point and fusion heat of In and Zn shown in Table 1 and calibrated the temperature and heat flow of this instrument according to these values. It can be clearly seen that all the relative deviations are within 1% and the precision of the instrument is high.

Table 1　The melting point and fusion heat values of In and Zn by Pyris 1 DSC

materials	T_{ref} /K	$\triangle_{fus}H_{ref}$ /J · g^{-1}	T_{exp} /K	$\triangle_{fus}H_{exp}$ /J · g^{-1}	relative deviation	
					T	$\triangle_{fus}H$
In	429.75	28.45	429.7	28.38	0.03%	0.23%
Zn	692.62	108.37	692.82	107.27	0.05%	1%

3.2 Specific heat capacity of TNPG

Seven times parallel experiments were carried out, and the average results were obtained from the measured values. The low-temperature experimental C_p for TNPG are plotted in Fig. 1. It can be seen that the C_p of the compound increases with temperature and no phase change occurs in this temperature range. Furthermore, the $C_p - T$ curve shows that the C_p of TNPG has a sudden increase in the end. We infer that not system error but the crystal water causes this transition. The sample absorbs heat and then loses crystal water, which results in this sudden increase in specific heat capacity.

The following polynomial equation was obtained by the least square fitting by using the experimental C_p and temperature in the temperature range from 50 ℃ to 100 ℃. The correlation coefficient $R = 0.976$. The standard deviation $D_s = 0.085$.

$$C_p = -15.107 + 0.704T - 0.010\ T^2 + 4.832 \times 10^{-5} T^3$$

3.3 Specific heat capacity of sodium salts of TNPG

The low-temperature experimental C_p average values for seven times has been plotted in Fig. 2.

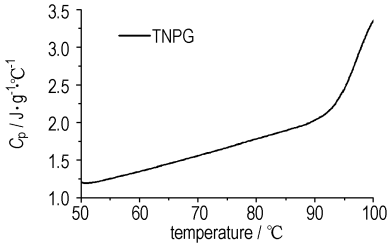


Fig. 1　Experimental curve for specific heat capacity of TNPG

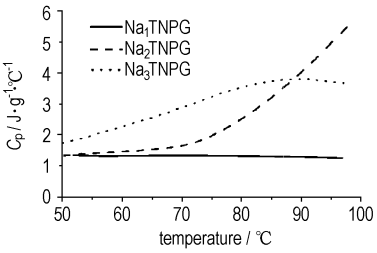


Fig. 2　Experimental curves for specific heat capacity of TNPG-salts

The tendency of the specific heat capacity of Na_1TNPG, Na_2TNPG and Na_3TNPG can be seen. On the whole, C_p of Na_1TNPG is basically invariable, C_p of Na_2TNPG and Na_3TNPG increases with the temperature, and occurs just a little change in the end.

The C_p of Na_1TNPG, Na_2TNPG and Na_3TNPG have been fitted to three following polynomials (Table 2) in experimental temperature by means of the least square fitting. From three equations, the C_p change of three sodium salts of TNPG accord with quadratic equation. And the correlation coefficients R of least square fitting are close to 1, D_s to 0. The C_p of Na_1TNPG, Na_2TNPG and Na_3TNPG change by rule. Furthermore, we calculate enthalpy ($\triangle H$) and entropy ($\triangle S$), respectively, based on the following thermodynamic relationships: $\triangle H = \int_{T_1}^{T_2} C_p \mathrm{d}T$ and $\triangle S = \int_{T_1}^{T_2} C_p / T \mathrm{d}T$ at an interval of 5 ℃ and list them in Table 3. Table 3 shows the differences of enthalpy and entropy: Na_2TNPG > Na_3TNPG > Na_1TNPG.

Table 2 Polynomial equation of Na_1TNPG, Na_2TNPG and Na_3TNPG

sample	temperature ranges/℃	equation	R	D_s
Na_1TNPG	50 – 100	$1.254+0.003T-3.455\times10^{-5}T^2$	0.973	0.015
Na_2TNPG	50 – 100	$10.942-0.325T+0.003T^2$	0.997	0.071
Na_3TNPG	50 – 100	$-4.941+0.171T-8.339\times10^{-4}T^2$	0.981	0.097

Table 3 $\triangle H$ and $\triangle S$ of Na_1TNPG, Na_2TNPG and Na_3TNPG

	Na_1TNPG		Na_2TNPG		Na_3TNPG	
T/℃	$\triangle H$ /J·g^{-1}	$\triangle S$ /J·g^{-1}·℃$^{-1}$	$\triangle H$ /J·g^{-1}	$\triangle S$ /J·g^{-1}·℃$^{-1}$	$\triangle H$ /J·g^{-1}	$\triangle S$ /J·g^{-1}·℃$^{-1}$
50	0	0	0	0	0	0
55	6.632	0.126	6.945	0.132	9.815	0.187
60	13.26	0.242	14.2	0.259	21.03	0.383
65	19.92	0.348	21.83	0.382	33.7	0.590
70	26.57	0.447	30.24	0.509	48	0.808
75	33.2	0.538	40.47	0.656	64	1.038
80	39.78	0.623	53.42	0.837	81.34	1.274
85	46.28	0.702	69.82	1.058	85.35	1.510
90	52.71	0.774	90.3	1.327	117.97	1.734
95	59.03	0.842	115.4	1.646	135.98	1.940

4 Conclusions

Differential scanning calorimetry is a quick and exact method of determining the continuous specific heat capacity of materials. The specific heat capacity values of energetic materials of TNPG, Na_1TNPG, Na_2TNPG, Na_3TNPG were measured by it. Their C_p-T relationships were obtained by the fitting of the experimental data. It was confirmed from the variation regularity of the C_p with T that the stability of Na_1TNPG is the best, secondly Na_2TNPG in the temperature range of 50 – 100 ℃. It is seen that the specific heat capacity value of sodium salts of TNPG is bigger than that of TNPG at normal temperature 50 ℃. The R-Squares (COD) of the results are all more than 0.97. The deviation analysis indicates that DSC method is effective and can be used to measure the specific heat capacity of other energetic materials.

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2,4,6-三硝基-1,3,5-苯三酚钠盐的比热容

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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(TNPG)、一取代(Na_1TNPG)、二取代(Na_2TNPG)、三取代钠盐(Na_3TNPG)定压下的连续比热容,计算了在50 ~ 100 ℃温度范围内每间隔5 ℃的焓差值和熵变值。从实验得出的比热容与温度的关系为: C_p(J·g^{-1}·℃$^{-1}$) $=a+bT+cT^2+dT^3$, TNPG取代钠盐例外 $d=0$。有关误差分析表明,该测试方法是有效的,并可用于其它含能材料的比热容的测量。另外,实验相关系数接近1,表明这些化合物的比热容呈现很好的规律性。

关键词: 分析化学; 比热容; 2,4,6-三硝基-1,3,5-苯三酚(TNPG); 钠盐; 差式扫描量热法(DSC)

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