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3,6-二胍基-1,2,4,5-四嗪的热行为、比热容及绝热至爆时间

徐抗震^{1,2} 赵凤起^{1,*} 任莹辉² 马海霞² 宋纪蓉^{2,3} 胡荣祖¹⁽¹⁾ 西安近代化学研究所, 西安 710065; ⁽²⁾ 西北大学化工学院, 西安 710069; ⁽³⁾ 故宫博物院文保科技部, 北京 100009

摘要: 利用差示扫描量热法(DSC)、热重-微商热重法(TG-DTG)研究了 3,6-二胍基-1,2,4,5-四嗪(DHT)的热行为, 其分解过程可分为两个放热的分解过程, 且热分解反应的表现活化能分别为 154.8 和 123.4 kJ·mol⁻¹, 指前因子分别为 10^{16.63} 和 10^{9.48} s⁻¹. DHT 热爆炸的临近温度为 426.10 K. 同时, 利用微量热法和理论计算方法研究了 DHT 的比热容, 298.15 K 时的标准摩尔比热容为 183.61 J·mol⁻¹·K⁻¹. 计算获得了 DHT 的绝热至爆时间为 263.84–297.58 s 之间的某一值.

关键词: 3,6-二胍基-1,2,4,5-四嗪; 热行为; 比热容; 绝热至爆时间

中图分类号: O642; O643

Thermal Behavior, Specific Heat Capacity and Adiabatic Time-to-Explosion of 3,6-Dihydrazino-1,2,4,5-tetrazine

XU Kang-Zhen^{1,2} ZHAO Feng-Qi^{1,*} REN Ying-Hui²MA Hai-Xia² SONG Ji-Rong^{2,3} HU Rong-Zu¹

(¹*Xi'an Modern Chemistry Research Institute, Xi'an 710065, P. R. China;* ²*College of Chemical Engineering, Northwest University, Xi'an 710069, P. R. China;* ³*Conservation Technology Department, the Palace Museum, Beijing 100009, P. R. China*)

Abstract: Thermal behavior of 3,6-dihydrazino-1,2,4,5-tetrazine (DHT) was studied by differential scanning calorimetry (DSC) and thermogravimetry-derivative thermogravimetry (TG-DTG), and the decomposition process can be divided into two exothermic decomposition stages. Values of the apparent activation energy (*E*) and pre-exponential constant (*A*) of the two exothermic decomposition stages are 154.8 and 123.4 kJ·mol⁻¹, 10^{16.63} and 10^{9.48} s⁻¹, respectively. The critical temperature of thermal explosion is 426.10 K. The specific heat capacity of DHT was determined by the micro-DSC method and theoretical calculation method. The standard molar specific heat capacity was found to be 183.61 J·mol⁻¹·K⁻¹ at 298.15 K. The adiabatic time-to-explosion of DHT was calculated to be a certain value between 263.84 s and 297.58 s.

Key Words: 3,6-Dihydrazino-1,2,4,5-tetrazine; Thermal behavior; Specific heat capacity; Adiabatic time-to-explosion

High nitrogen heterocycle compounds are becoming one of the important developing fields of energy materials because of their positive enthalpy of formation, high thermal stability, and low sensitivity to impact and friction^[1–8]. Moreover, high nitrogen content makes them present high density and easily obtain oxygen balance, and the main combustion product is clean gas—N₂. So, high nitrogen heterocycle compounds are being considered as green energy materials used in solid propellant, explo-

sive, and civil combustible-gas generator^[7,8]. 3,6-Dihydrazino-1,2,4,5-tetrazine (DHT) is an important high nitrogen heterocycle compound, whose nitrogen content, oxygen balance, enthalpy of formation, density, extrapolated onset temperature (*T*₀), theoretical specific impulse (*I*_{sp}), and characteristic velocity (*η*^{*}) are 78.84%, 78.8%, 535 kJ·mol⁻¹, 1.66 g·cm⁻³, 2212.0 K, 2308.5 N·s·kg⁻¹, and 1465.0 m·s⁻¹, respectively^[9–11]. Furthermore, DHT is an important intermediate to synthesize other high nitrogen heterocycle com-

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*Corresponding author. Email: npecc@163.com; Tel: +8629-88307755, +8629-88291663.

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pounds, such as 3,6-diazido-1,2,4,5-tetrazine (DAT). In this article, we studied DHT's thermal behavior, and reported its specific heat capacity and adiabatic time-to-explosion. As an important parameter, adiabatic time-to-explosion is easy and intuitionistic to evaluate the thermostability of energetic materials.

1 Experimental

1.1 Sample

DHT used in this research was prepared according to Ref. [11]. Found(%) for $C_2H_6N_8$: C 16.84, H 4.31, N 77.46; Anal. calcd.: C 16.90, H 4.25, N 78.84. IR (KBr) ν (cm^{-1}): 3290, 3221, 3020, 1644, 1550, 1050, 938.

1.2 Experimental equipments and conditions

The DSC and TG-DTG experiments for DHT were performed using a SDT-Q600 apparatus (TA, USA) under a nitrogen atmosphere at a flow rate of $100 mL \cdot min^{-1}$. The amount of used sample was about 1.3 mg. The heating rates used were 2.5, 5.0, 10.0, and $15.0 K \cdot min^{-1}$ from ambient temperature to 673.15 K.

The specific heat capacity of DHT was performed using a Micro-DSCIII apparatus (Setaram, France) and the amount of used sample was 102.84 mg. The heating rate was $0.10 K \cdot min^{-1}$ from 293.15 to 303.15 K, in which the precisions of temperature and heat flow were $1.0 \times 10^{-4} K$ and $0.2 \mu W$, respectively. The principle for measuring of the continuous specific heat capacity (C_p) is shown as:

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

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

1.3 Theoretical calculation of specific heat capacity

A molecular unit was selected as the initial structure, while HF method and B3LYP method with different basis sets in Gaussian 03 package^[12] were used to optimize the structure of DHT and compute its frequencies at different temperatures. A series of thermodynamic data of DHT based on the statistic thermodynamic theory were obtained. At the same time, vibration analysis shows that the optimized structure is in accord with the minimum points on the potential energy surfaces, which means

Fig.1 DSC curve for DHT at a heating rate of $15.0 K \cdot min^{-1}$

no virtual frequencies, proving that the optimized structure is stable and our calculation results are reliable. All the convergent precisions are the system default values, and all the calculations were carried out on the personal IBM computer.

2 Results and discussion

2.1 Thermal behavior

From the typical DSC and TG-DTG curves (Figs.1 and 2), we can see that DHT has no melting point, and its thermal behavior can be divided into two stages. The first stage is an intense exothermic decomposition process with a mass loss of about 52%, and the extrapolated onset temperature (T_o), peak temperature (T_p) and exothermic decomposition enthalpy (ΔH_d) at the heating rate of $15.0 K \cdot min^{-1}$ are 437.86 K, 443.21 K, and $157.57 kJ \cdot mol^{-1}$, respectively. The second stage is a slow exothermic decomposition process with a mass loss of about 26%, and the values of T_o , T_p , and ΔH_d at the heating rate of $15.0 K \cdot min^{-1}$ are 530.74 K, 557.85 K, and $21.57 kJ \cdot mol^{-1}$, respectively.

In order to obtain the kinetic parameters (the apparent activation energy (E) and pre-exponential factor (A)) of the exothermic decomposition reaction for DHT, multiple heating methods (Kissinger's method^[13] and Ozawa's method^[14]) were employed. The Kissinger and Ozawa equations are as follows:

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

$$\lg\beta + \frac{0.4567E_o}{RT} = C \quad (3)$$

where β is the linear heating rate, A is the pre-exponential constant, R is the gas constant, $E_{K(o)}$ is the apparent activation energy, and C is a constant.

The original values (the beginning temperature (T_o), extrapolated onset temperature (T_o), peak temperature (T_p), and exothermic decomposition enthalpy (ΔH_d)) of the two exothermic decomposition reactions were listed in Tables 1 and 2.

The values ($T_{(0)}, T_{(0)}$ and $T_{(p)}$) of T_o , T_e and T_p of the first decomposition stage corresponding to $\beta \rightarrow 0$ obtained by Eq.(4) were also listed in Table 1^[15].

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

where n and m are coefficients.

Fig.2 TG-DTG curves for DHT at a heating rate of $15.0 K \cdot min^{-1}$

Table 1 Values of T_b , T_c , T_p , ΔH_d , T_{00} , T_{c0} , and T_{p0} of the thermal decomposition determined by DSC curves at different heating rates (β) in the first stage

$\beta/(K \cdot \min^{-1})$	T_f/K	T_d/K	T_p/K
2.5	390.66	421.87	426.46
5.0	396.21	428.43	433.44
10.0	399.23	433.92	440.87
15.0	401.33	437.86	443.21
$\Delta H_d/(kJ \cdot mol^{-1})$	T_{00}/K	T_{c0}/K	T_{p0}/K
157.57	386.48	416.32	418.79

Table 2 Values of T_c , T_p , and ΔH_d of the thermal decomposition determined by DSC curves at different heating rates (β) in the second stage

$\beta/(K \cdot \min^{-1})$	T_f/K	T_p/K	$\Delta H_d/(kJ \cdot mol^{-1})$
2.5	494.75	525.28	
5.0	507.14	538.46	
10.0	518.46	552.32	
15.0	530.74	557.85	21.57

The above mentioned values (E and A) determined by Kissinger's method and Ozawa's method and the linear correlation coefficients (r) were shown in Table 3. From the results, we can see that the apparent activation energy obtained by Kissinger's method is in good accord with that obtained by Ozawa's method. The linear correlation coefficients (r) are all very close to 1. So, the results are credible. Moreover, we can see that the activation energy (E) of the exothermic reaction was quite low, indicating that DHT is easy to decompose at the temperature range of 388.15–453.15 K.

The corresponding critical temperature of thermal explosion (T_b) obtained by Eq.(5)^[6] is 426.10 K.

$$T_b = \frac{E_0 - \sqrt{E_0^2 - 4E_0RT_0}}{2R} \quad (5)$$

where E_0 is the value of E obtained by Ozawa's method.

The entropy of activation ($\Delta S^\ddagger$), enthalpy of activation ($\Delta H^\ddagger$), and free energy of activation ($\Delta G^\ddagger$) of the first thermal decomposition process corresponding to $T=T_{p0}$, $A=A_K$, and $E=E_K$ obtained by Eqs. (6–8) taken from Ref. [15] are $70.63 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, $155.20 \text{ kJ} \cdot \text{mol}^{-1}$, and $125.62 \text{ kJ} \cdot \text{mol}^{-1}$, 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.

2.2 Specific heat capacity

Fig.3 shows the determination results of specific heat capacity of DHT, using a continuous specific heat capacity mode of Micro-DSCIII apparatus. We can see that the specific heat capacity of DHT presents a good linear relationship with temperature in

Fig.3 Determination results of the continuous C_p of DHT

determined temperature range. Specific heat capacity equation is shown as:

$$C_p = 49.146 + 0.451T \quad (293.0 \text{ K} < T < 303.0 \text{ K}) \quad (9)$$

The standard molar specific heat capacity of DHT is $183.61 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ at 298.15 K. Although only 10 K range was taken in the determination process, the specific heat capacity equation obtained is a stable and continuous equation, which can provide a reference and some help for the wide temperature applications.

The calculation results of specific heat capacity of DHT at B3LYP/6-311+G*, B3LYP/6-311++G**, and HF/6-311++G** levels are 156.39, 157.52, and $142.86 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ at 298.15 K, respectively. We can see that the results by B3LYP method are bigger than that by HF method, and the influence of basis set on the calculation result of specific heat capacity is very small, but the influence of method is obvious. Table 4 shows the results of specific heat capacity obtained by theoretical calculation (B3LYP/6-311++G**) and experimental determination and their relative deviations at different temperatures. We can see that the calculated results are all less than the experimental results, and the relative deviations are comparatively great, from 15.24% to 16.67%. But, the deviation becomes smaller and smaller with the rise of temperature. The reason for the result is that only gas-phase molecule is used in theoretical calculation process, which is clearly different from actual solid phase molecule.

2.3 Thermodynamic properties

The enthalpy change, entropy change and Gibbs free energy change of DHT were calculated by Eqs.(10–12) at 278.0–388.0 K, from ambient temperature to thermal decomposition temperature, taking 298.15 K as the benchmark. The results were listed in Table 5.

$$H_T - H_{298.15} = \int_{298.15}^T C_p dT \quad (10)$$

$$S_T - S_{298.15} = \int_{298.15}^T C_p \cdot T^{-1} dT \quad (11)$$

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

Table 3 Kinetic parameters obtained from the data in Table 1 and Table 2

	$E_K/(kJ \cdot mol^{-1})$	$\lg(A_K/s^{-1})$	r_K	$E_O/(kJ \cdot mol^{-1})$	r_O	$\bar{E}/(kJ \cdot mol^{-1})$
the first decomposition stage	155.2	16.63	0.9954	154.4	0.9958	154.8
the second decomposition stage	122.1	9.48	0.9974	124.7	0.9978	123.4

Subscripts K and O, data obtained by Kissinger's method and Ozawa's method.

Table 4 Comparison of C_p by the theoretical calculation and experimental determination and their relative deviations at different temperatures

T/K	$C_p/(J \cdot mol^{-1} \cdot K^{-1})$		Relative deviation (%)
	theoretical calculation value	experimental value*	
293.0	155.38	181.29	16.67
298.0	157.52	183.54	16.52
303.0	159.51	185.80	16.48
313.0	163.64	190.31	16.30
323.0	167.77	194.82	16.12
353.0	180.17	208.35	15.64
383.0	192.54	221.88	15.24

*including extended temperatures

Table 5 Thermodynamic function data of DHT

T/K	$(H_T - H_{298.15})/(kJ \cdot mol^{-1})$	$(S_T - S_{298.15})/(J \cdot mol^{-1} \cdot K^{-1})$	$(G_T - G_{298.15})/(kJ \cdot mol^{-1})$
278.0	-3.61	-12.52	0.13
288.0	-1.84	-6.28	0.03
298.0	-0.03	-0.09	0.00
308.0	1.83	6.04	0.03
318.0	3.73	12.11	0.12
328.0	5.68	18.14	0.27
338.0	7.67	24.13	0.48
348.0	9.71	30.07	0.75
358.0	11.79	35.97	1.08
368.0	13.92	41.83	1.47
378.0	16.09	47.65	1.92
388.0	18.31	53.44	2.43

2.4 Adiabatic time-to-explosion

Energetic materials need time from the beginning thermal decomposition to thermal explosion in adiabatic condition. We called the time as the adiabatic time-to-explosion^[15,17-21]. Ordinarily, we use heating rate (dT/dt) and critical heating rate $(dT/dt)_b$ in thermal decomposition process to evaluate the thermostability of energetic materials. However, we can calculate the adiabatic time-to-explosion (t) by the following Eqs.(12-14)^[15,18-21] when we have obtained a series of experimental data. As an important parameter, it is very easy and intuitionistic to evaluate the thermostability of energetic materials according to the length of the adiabatic time-to-explosion.

$$C_p \frac{dT}{dt} = QA \exp(-E/RT) f(\alpha) \quad (13)$$

$$f(\alpha) = (1-\alpha)^n \quad (14)$$

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

where t is the adiabatic time-to-explosion, Q is the exothermic value, A is the pre-exponential factor, E is the apparent activation energy of the first exothermic stage, R is the gas constant, $f(\alpha)$ is the most probable kinetic model function, n is the rate order, and α is the fraction of conversion.

According to the above determined results of DHT, we use:

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

where a and b are coefficients.

The combination of Eqs.(13-16) gives the following equation:

$$t = \int_0^t dt = \int_{T_0}^{T_b} \frac{C_p \exp(E/RT)}{QA f(\alpha)} dT$$

$$= \frac{1}{QA} \int_{T_0}^{T_b} \frac{(a+bT) \exp(E/RT)}{(1-\alpha)^n} dT$$

$$= \frac{\int_{T_0}^{T_b} (a+bT) \exp(E/RT) dT}{QA \left\{ 1 - \frac{1}{Q} [a(T_b - T_0) + \frac{b}{2}(T_b^2 - T_0^2)] \right\}^n} \quad (17)$$

The limit of the temperature integration in Eq.(17) is from T_0 to T_b .

Presuming that the rate order (n) of the thermal explosion of DHT equals 0, 1, and 2, we can directly get $t_0=263.84$ s, $t_1=280.20$ s, and $t_2=297.58$ s from Eq.(17), according to the above experimental results. As a rule, the rate order (n) of energetic materials ranges from 0 to 2, so the adiabatic time-to-explosion of DHT is a certain value between 263.84 s and 297.58 s, a comparative long time, and it can be proved credible according to the change of DSC curve in the exothermic decomposition stage.

3 Conclusions

(1) The thermal behavior of DHT was studied with DSC and TG-DTG methods and can be divided into two exothermic decomposition stages. The values of the apparent activation energy (E) and pre-exponential constant (A) of the two exothermic decomposition reactions are 154.8 and 123.4 $kJ \cdot mol^{-1}$, $10^{16.63}$ and $10^{9.48} s^{-1}$, respectively. The critical temperature of thermal explosion is 426.10 K.

(2) The specific heat capacity of DHT was determined with Micro-DSC method and theoretical calculation method. Specific heat capacity equation is $C_p=49.146+0.451T$ ($293.0 K < T < 303.0 K$) and the standard molar specific heat capacity is 183.61 $J \cdot mol^{-1} \cdot K^{-1}$ at 298.15 K. The adiabatic time-to-explosion of DHT was calculated to be a certain value between 263.84 s and 297.58 s.

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