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Thermal behavior and thermal safety on 3,3-dinitroazetidinium salt of perchloric acid

H. X. Ma · B. Yan · Y. H. Ren · Y. Hu · Y. L. Guan · F. Q. Zhao · J. R. Song · R. Z. Hu

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Abstract 3,3-Dinitroazetidinium (DNAZ) salt of perchloric acid (DNAZ·$HClO_4$) was prepared, it was characterized by the elemental analysis, IR, NMR, and a X-ray diffractometer. The thermal behavior and decomposition reaction kinetics of DNAZ·$HClO_4$ were investigated under a non-isothermal condition by DSC and TG/DTG techniques. The results show that the thermal decomposition process of DNAZ·$HClO_4$ has two mass loss stages. The kinetic model function in differential form, the value of apparent activation energy (E_a) and pre-exponential factor (A) of the exothermic decomposition reaction of DNAZ·$HClO_4$ are $f(\alpha) = (1-\alpha)^{-1}/2$, 156.47 kJ mol^{-1}, and $10^{15.12}$ s^{-1}, respectively. The critical temperature of thermal explosion is 188.5 °C. The values of $\Delta S^{\neq}$, $\Delta H^{\neq}$, and $\Delta G^{\neq}$ of this reaction are 42.26 J mol^{-1} K^{-1}, 154.44 kJ mol^{-1}, and 135.42 kJ mol^{-1}, respectively. The specific heat capacity of DNAZ·$HClO_4$ was determined with a continuous C_p mode of microcalorimeter. Using the relationship between C_p and T and the thermal decomposition parameters, the time of the thermal decomposition from initiation to thermal explosion (adiabatic time-to-explosion) was evaluated as 14.2 s.

Keywords 3,3-Dinitroazetidine (DNAZ) · $HClO_4$ · Thermal behavior · Thermal safety

Introduction

Highly nitrated small-ring heterocycles are good candidates for energetic materials (EMs) because of the increased performance from the additional energy release upon opening of the strained ring system during decomposition [1]. Azetidine-based explosives, such as 1,3,3-trinitroazetidine (TNAZ) [2, 3] demonstrate excellent performance partly because of the high strain associated with the four-membered ring. As one of the important derivates of TNAZ, 3,3-dinitroazetidine (DNAZ, $pK_b = 6.5$) [3, 4] can prepare a variety of solid energetic DNAZ salts with high oxygen-balance [3, 5–11]. In this study, the energetic salt of DNAZ with perchloric acid ($HClO_4$) was synthesized, its thermal behavior was studied by DSC and TG/DTG techniques, and the non-isothermal kinetics was determined by means of Kissinger method, Ozawa method, the differential method, and the integral method. The specific heat capacity was determined with a continuous C_p mode of microcalorimeter (Micro-DSCIII). The adiabatic time-to-explosion was also estimated for evaluating the safety performance of DNAZ·$HClO_4$.

H. X. Ma (✉) · B. Yan · Y. H. Ren · Y. Hu · Y. L. Guan · J. R. Song
School of Chemical Engineering/Shaanxi Key Laboratory of Physico-Inorganic Chemistry, Northwest University, Xi'an, Shaanxi 710069, China
e-mail: mahx@nwu.edu.cn

B. Yan
School of Chemistry and Chemical Engineering, Yulin University, Yulin, Shaanxi 719000, China

F. Q. Zhao · R. Z. Hu
Xi'an Modern Chemistry Research Institute, Xi'an 710065, China

J. R. Song
Department of Conservation Technology, The Palace Museum, 4 Jingshan Qianjie, Beijing 100009, China

Experimental

Materials

DNAZ·$HClO_4$ used in this study was prepared according to the following method: an appropriate amount of $HClO_4$ was put into methanol, which was then stirred and the same equimolar of DNAZ was added to the above solution at room temperature, stirred for 2 h. The white precipitate was collected by filtration. Single crystal suitable for X-ray measurement was obtained by slow evaporation in methanol for 15 days. The structure was characterized by elemental analyses, IR spectrometry and nuclear magnetic resonance spectrometry. Anal. Calcd (%): N 16.97, C 14.56, H 2.443, found (%): N 17.21, C 14.23, H 2.456. ^{1}HNMR (CD_3OD, TMS) (δ/ppm): 5.108(s, 4H), 3.320 (s, 2H). ^{13}CNMR (CD_3OD, TMS) (δ/ppm): 44.979(C-2,4), 97.653(C-3). IR(KBr, cm^{-1}): $\nu^{s}_{NH} = 3074.75$, $\nu^{\alpha s}_{CH_2} = 3006.07$, $\nu^{S}_{NH_2^+} = 2657.24–2409.56$, $\nu^{\alpha s}_{NO_2} = 1588.87$, $\nu^{s}_{NO_2} = 1339.22$, $\nu_{ClO_4^-} = 1071.12$. The sample was kept in a vacuum desiccator before use.

Experimental equipments and conditions

The elemental analysis was measured on a PE-2400 Elemental Analytical instrument (Perkin-Elmer, USA) and IR on a Nicolet 60 SXR FT-IR (Nicolet, USA) spectrometer in the 4,000–400 cm^{-1} region using KBr pellets. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on an INOVA-400 NMR (VARIAN, USA) spectrometer using CD_3OD as the solvent.

X-ray intensities were recorded at room temperature on Bruker SMART APEX CCD X-ray diffractometer using MoKα radiation ($\lambda = 0.071073$ nm) graphite monochromation. In the range of $2.76° < \theta < 25.10°$, $-8 < h < 9$, $-13 < k < 12$, $-12 < l < 15$, 1492 independent reflections were obtained. The final conventional R_1 is 0.1627 and ωR (unit weight) is 0.4199 for 892 observable independent reflections with reflection intensity $I > 2\sigma(I)$. The structure was solved by the direct methods (SHELXTL-97) and refined by the full-matrix-block least-squares method on F^2 with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were added according to the theoretical models.

The crystal structure is monoclinic with space group $P2(1)/n$. Crystal data: $a = 0.7779(4)$ nm, $b = 1.0925(6)$ nm, $c = 1.2663(5)$ nm, $\beta = 127.67(2)°$, $V = 0.8518(8)$ nm^3, $D_c = 1.930$ gcm^{-3}, $Z = 4$, $F(000) = 504$, $\mu = 0.486$ mm^{-1}. The analytical results indicate that the formula of the molecule is $C_3N_3O_4H_6{}^+ClO_4{}^-$, which is made up of a cation $C_3N_3O_4H_6{}^+$ (DNAZ$^+$) and an anion $ClO_4{}^-$. The molecular structure and atom labeling are shown in Fig. 1.

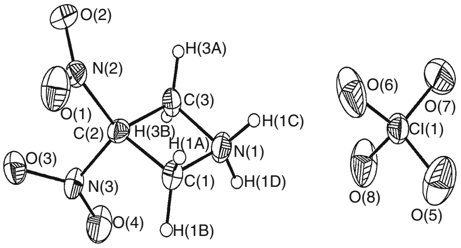

Fig. 1 Molecular structure of DNAZ·$HClO_4$

Thermal decomposition condition

The DSC and TG-DTG experiments for DNAZ·$HClO_4$ were performed using a model Q600SDT (TA, USA) under a nitrogen atmosphere, at a flow rate of 100 mL min^{-1} with the sample mass of about 0.935 mg. The heating rates used were 2.5, 5.0, 10.0, and 15.0 °C min^{-1} from ambient temperature to 500 °C. The temperature and heat were calibrated using pure indium and tin particles. The DSC and TG-DTG curves obtained under the same conditions overlap with each other, indicating that the reproducibility of tests was satisfactory.

The determination of the specific heat capacity

The specific heat capacity of DNAZ·$HClO_4$ was determined by a continuous C_p mode within 283–353 K at a heating rate of 0.15 K min^{-1} on Micro-DSCIII (Seteram, France) with the sample mass of 320.60 mg. The Microcalorimeter was calibrated with α-Al_2O_3 (calcined), its mathematical expression is C_p (Jg^{-1} K^{-1}) $= 0.1839 + 1.9966 \times 10^{-3}\,T$ within 283 to 353 K and the standard heat capacity $C^{\Theta}_{p,m}(\alpha - Al_2O_3)$at 298.15 K was determined as 79.44 J mol^{-1} K^{-1} which is in an excellent agreement with the value reported in the literature [12] (79.02 J mol^{-1} K^{-1}).

Results and discussion

Thermal behavior and analysis of kinetic data for the exothermic main decomposition reaction of DNAZ·$HClO_4$

Typical DSC and TG-DTG curves for DNAZ·$HClO_4$ are shown in Figs. 2 and 3. The DSC curve indicates that the thermal decomposition of DNAZ·$HClO_4$ is composed of one exothermic process with a peak temperature of 200.84 °C. However, the TG-DTG curves show two stages of mass loss processes. The first stage begins at about 165.81 °C and completes at 233.92 °C with a mass loss of 79.33% and the second stage begins at 233.92 °C and completes at 387.17 °C with a mass loss of 18.59%.

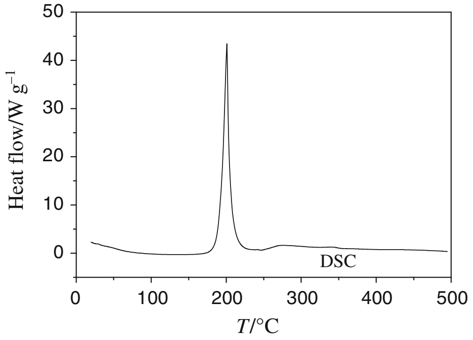

Fig. 2 DSC curve of DNAZ·HClO$_4$ at 10 °C/min

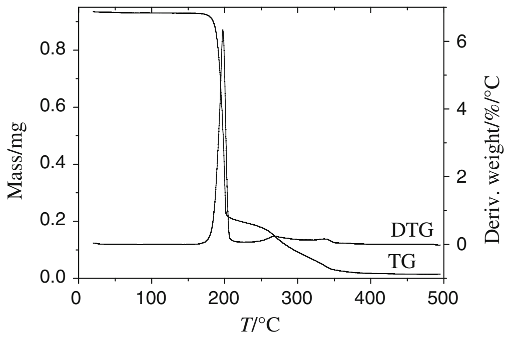

Fig. 3 TG/DTG curves of DNAZ·HClO$_4$ at 10 °C/min

In order to obtain the kinetic parameters [apparent activation energy (E_a) and pre-exponential factor (A)] of the exothermic main decomposition reaction for DNAZ·HClO$_4$, three model-free isoconversional methods (Eqs. 1–3) were employed. These methods are as follows.

Differential method

Kissinger equation [13]

$$\frac{\mathrm{d}\ln\frac{\beta}{T_p^2}}{\mathrm{d}\frac{1}{T_p}} = -\frac{E_\alpha}{R} \qquad (1)$$

Integral method

Flynn–Wall–Ozawa (F–W–O) equation [14]

$$\lg\beta + \frac{0.4567E_\alpha}{RT} = C \qquad (2)$$

integral isoconversional non-linear [NL-INT] equation [15]

$$\left|\sum_{i}^{n}\sum_{j\neq i}^{n}\frac{\beta_j I\left(E_\alpha, T_{\alpha,i}\right)}{\beta_i I\left(E_\alpha, T_{\alpha,j}\right)} - n(n-1)\right| = \min \qquad (3)$$

where α is the conversion degree, T is the absolute temperature, E_α is the apparent activation energy, β is the heating rate, R is the gas constant, T_p is the peak temperature of DSC curve, and A is the pre-exponential factor.

From the original data in Table 1, E_α obtained by the Kissinger [13] method is determined to be 154.44 kJ mol^{-1}. The pre-exponential constant (A) is $10^{15.12}$ s^{-1}. The linear correlation coefficient (r_k) is 0.9978. The value of E_α obtained by Ozawa's method [14] is 154.26 kJ mol^{-1} and the value of r_o is 0.9980. The value of E_{oe} obtained by T_{ei} vs. β_i relation is 164.32 kJ mol^{-1}. The value of r_{oe} is 0.9991.

By substituting the original data, β_i, T_{0i}, T_i, α_i, and $(\mathrm{d}\alpha/\mathrm{d}T)_i$, $i = 1,2,\ldots,n$, tabulated in Table 2 from TG-DTG curves into Eqs. 2 and 3, the values of E_α for any given value of α in Table 2 are obtained. The average value of E_α in the α range of 0.375–0.925 in Fig. 4 is in good agreement with the calculated values obtained by Kissinger's method and Ozawa's method. The E values calculated using Eqs. 2 and 3 were used to check the validity of activation energy by other methods.

The integral Eqs. 3–6 are cited to obtain the values of E, A, and the most probable kinetic model function $G(\alpha)$ from a single non-isothermal TG curve [16].

Mac Callum–Tanner equation

$$\lg[G(\alpha)] = \lg\left(\frac{AE}{\beta R}\right) - 0.4828E^{0.4357} - \frac{0.449 + 0.217E}{0.001}\frac{1}{T} \qquad (4)$$

Table 1 Values of the kinetic parameters for the exothermic decomposition reaction for DNAZ·HClO$_4$ calculated from the DSC curves at various heating rates and a flowing rate of N$_2$ gas of 100 ml/min

β/°C min^{-1}	T_e/°C	E_{oe}/kJ mol^{-1}	r_{oe}	T_p/°C	E_k/kJ mol^{-1}	log(A_k/s^{-1})	r_k	E_o/kJ mol^{-1}	r_o
2.5	177.90	164.32	0.9991	185.06	154.44	15.12	0.9978	154.26	0.9980
5.0	185.55	–	–	191.75	–	–	–	–	–
10.0	192.09	–	–	200.84	–	–	–	–	–
15.0	196.27	–	–	204.58	–	–	–	–	–
Mean: $E_o = (164.32 + 154.44 + 154.26)/3 = 157.67$ kJ mol^{-1}									

[α] β, heating rate; T_e, onset temperature in the DSC curve; T_p, maximum peak temperature; E, apparent activation energy; A, pre-exponential constant; r, linear correlation coefficient; subscript k, data obtained by Kissinger's method, subscript o, data obtained by Ozawa's method. E_{oe} means the activation energy obtained by T_e through Ozawa's method and r_{oe} is the corresponding linear correlation coefficient

Table 2 Data of DNAZ·$HClO_4$ determined by TG at different heating rates and apparent activation energies (E_a) of thermal decomposition obtained using isoconversional methods

Data point	α	$T_{2.5}$/K	T_5/K	T_{10}/K	T_{15}/K	$E_{\text{NL-INT}}$/kJ mol^{-1}	$E_{\text{F–W–O}}$/kJ mol^{-1}
1	1.000	470.44	484.97	507.11	488.20	69.26	73.16
2	0.975	459.13	469.05	482.30	478.66	123.54	124.65
3	0.950	458.83	466.14	475.01	477.66	158.88	158.26
4	0.925	458.72	465.58	474.36	477.30	161.50	160.83
5	0.900	458.59	465.26	474.09	477.03	162.33	161.62
6	0.875	458.46	465.02	473.86	476.80	162.62	162.23
7	0.850	458.31	464.80	473.64	476.58	163.41	162.64
8	0.825	458.15	464.61	473.43	476.38	163.68	162.90
9	0.800	457.97	464.42	473.21	476.18	163.84	163.04
10	0.775	457.79	464.23	472.98	475.98	164.05	163.24
11	0.750	457.60	464.04	472.75	475.77	164.23	163.41
12	0.725	457.40	463.85	472.52	475.55	164.39	163.56
13	0.700	457.19	463.66	472.27	475.33	164.57	163.72
14	0.675	456.97	463.47	472.01	475.10	164.76	163.90
15	0.650	456.75	463.27	471.75	474.86	164.99	164.11
16	0.625	456.53	463.06	471.48	474.62	165.23	164.34
17	0.600	456.3	462.85	471.20	474.37	165.49	164.59
18	0.575	456.06	462.63	470.91	474.10	165.81	164.89
19	0.550	455.82	462.40	470.60	473.82	166.27	165.31
20	0.525	455.57	462.17	470.29	473.51	166.82	165.84
21	0.500	455.32	461.93	469.97	473.20	167.40	166.38
22	0.475	455.05	461.69	469.62	472.89	167.94	166.89
23	0.450	454.78	461.43	469.27	472.56	168.55	167.47
24	0.425	454.5	461.16	468.89	472.19	169.47	168.34
25	0.400	454.21	460.88	468.5	471.77	170.65	169.46
26	0.375	453.91	460.59	468.10	471.35	171.78	170.53
27	0.350	453.60	460.27	467.70	470.90	172.94	171.63
28	0.325	453.26	459.95	467.29	470.38	174.37	172.98
29	0.300	452.91	459.6	466.86	469.82	176.02	174.54
30	0.275	452.54	459.22	466.40	469.31	177.19	175.65
31	0.250	452.14	458.80	465.90	468.78	178.31	176.71
32	0.225	451.70	458.35	465.37	468.20	179.46	177.80
33	0.200	451.22	457.84	464.80	467.58	180.55	178.82
34	0.175	450.67	457.27	464.18	466.90	181.42	179.65
35	0.150	450.06	456.59	463.48	466.12	182.55	180.71
36	0.125	449.32	455.79	462.67	465.19	183.64	181.74
37	0.100	448.42	454.76	461.70	464.08	184.56	182.59
38	0.075	447.25	453.46	460.45	462.63	185.84	183.80
39	0.050	445.57	451.54	458.62	460.52	187.96	185.78
40	0.025	442.73	448.20	455.31	456.75	194.49	191.96
Mean: 0.375–0.925							

T with the subscript 2.5, 5.0, 10.0, and 15.0 are the temperature obtained at the heating rates of 2.5, 5.0, 10.0, and 15.0 °C min^{-1}, respectively. E with the subscript F–W–O and NL-INT are the activation energy calculated by NL-INT and F–W–O equations

Satava–Sestak equation

$$\lg[G(\alpha)] = \lg\left(\frac{AE}{\beta R}\right) - 2.315 - 0.4567\frac{E}{RT} \tag{5}$$

Agrawal equation

$$\ln\left[\frac{G(\alpha)}{T^2}\right] = \ln\left\{\frac{AR}{\beta E}\left[\frac{1-2\left(\frac{RT}{E}\right)}{1-5\left(\frac{RT}{E}\right)}\right]\right\} - \frac{E}{RT} \tag{6}$$

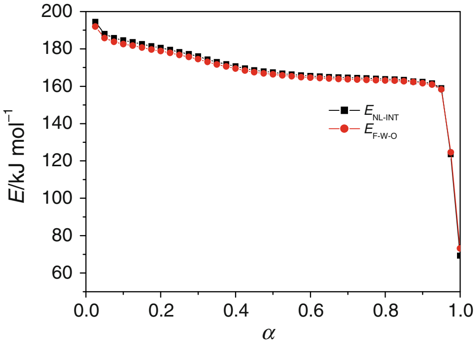

Fig. 4 E_a vs. α curve of DNAZ·$HClO_4$ by NL-INT and Flynn–Wall–Ozawa's methods

The Universal Integral equation

$$\ln\left[\frac{G(\alpha)}{T-T_0}\right]=\ln\left(\frac{A}{\beta}\right)-\frac{E}{RT} \tag{7}$$

The General Integral equation

$$\ln\left[\frac{G(\alpha)}{T^2\left(1-\frac{2RT}{E}\right)}\right]=\ln\left(\frac{AR}{\beta E}\right)-\frac{E}{RT} \tag{8}$$

where $G(\alpha)$ is the integral model function, T is the temperature (K) at time t, α the conversion degree, R the gas constant.

Forty-one types of kinetic model functions in reference [17] and the original data tabulated in Table 2 are put into Eqs. 3–7 for calculation, respectively. The kinetic parameters and the probable kinetic model function was selected by the logical choice method and satisfying the ordinary range of the thermal decomposition kinetic parameters for energetic materials (E = 80–250 kJ mol^{-1}, log A = 7–30 s^{-1}). These data together with the appropriate values of linear correlation coefficient (r), standard mean square deviation (S), and believable factor (d, where $d = (1-r)S$), are presented in Table 3. The values of E are very close to each other. The values of E_a and A obtained from a single non-isothermal DSC curve are in good agreement with the calculated values obtained by Kissinger's method and Ozawa's method. Therefore, we conclude that the reaction mechanism of exothermic main decomposition process of the compound is classified as reaction order $f(\alpha) = (1-\alpha)^{-1}/2$. Substituting $f(\alpha)$ with $(1-\alpha)^{-1}/2$, E with 156.47 kJ mol^{-1} and A with $10^{15.12}$ s^{-1} to Eq. 9,

$$d\alpha/dT=\frac{A}{\beta}f(\alpha)e^{-E/RT} \tag{9}$$

where $f(\alpha)$ and $d\alpha/dT$ are the differential model function and the rate of conversion, respectively.

Table 3 Calculated values of kinetic parameters of decomposition reaction for DNAZ·$HClO_4$

β/K min^{-1}	Eq.	E/kJ mol^{-1}	log (A/s^{-1})	r	S	d
2.5	(4)	164.00	16.25	0.9856	2.68×10^{-3}	3.86×10^{-5}
	(5)	163.02	16.18	0.9856	2.68×10^{-3}	3.86×10^{-5}
	(6)	163.84	16.28	0.9843	1.42×10^{-2}	2.24×10^{-4}
	(7)	163.84	16.28	0.9843	1.42×10^{-2}	2.24×10^{-4}
	(8)	167.64	15.06	0.9850	1.42×10^{-2}	2.24×10^{-4}
5.0	(4)	171.48	17.14	0.9767	4.33×10^{-3}	1.01×10^{-4}
	(5)	170.09	17.02	0.9767	4.33×10^{-3}	1.01×10^{-4}
	(6)	171.16	17.15	0.9746	2.30×10^{-2}	5.82×10^{-4}
	(7)	175.01	15.92	0.9757	2.30×10^{-2}	5.57×10^{-4}
	(8)	171.16	17.15	0.9746	2.30×10^{-2}	5.82×10^{-4}
10.0	(4)	137.73	13.24	0.9860	2.62×10^{-3}	3.66×10^{-5}
	(5)	138.22	13.34	0.9860	2.62×10^{-3}	3.66×10^{-5}
	(6)	137.52	13.28	0.9844	1.39×10^{-2}	2.17×10^{-4}
	(7)	141.44	12.14	0.9852	1.39×10^{-2}	2.05×10^{-4}
	(8)	137.52	13.28	0.9844	1.39×10^{-2}	2.17×10^{-4}
15.0	(4)	150.61	14.77	0.9874	2.34×10^{-3}	2.94×10^{-5}
	(5)	150.38	14.78	0.9874	2.34×10^{-3}	2.94×10^{-5}
	(6)	150.25	14.78	0.9861	1.24×10^{-2}	1.73×10^{-4}
	(7)	154.19	13.61	0.9868	1.24×10^{-2}	1.64×10^{-4}
	(8)	150.25	14.78	0.9861	1.24×10^{-2}	1.73×10^{-4}
Mean		156.47	15.12			

Note: S means standard mean square deviation and d means believable factor [$d = (1-r)S$]

The kinetic equation of the exothermic decomposition reaction may be described as $d\alpha/dT = \frac{10^{15.12}}{2\beta}(1-\alpha)^{-1}\exp(-1.88 \times 10^4/T)$.

The values (T_{eo} and T_{po}) of the onset temperature (T_e) and peak temperature (T_p) corresponding to $\beta \to 0$ obtained by Eq. 10 taken from [16] are 171.17 and 177.09 °C, respectively.

$$T_{\mathrm{eorp}} = T_{\mathrm{eoorpo}} + a\beta_i + b\beta_i^2 \quad i = 1 \sim 4 \tag{10}$$

where a and b are coefficients.

The corresponding critical temperatures of thermal explosion (T_b) obtained from Eq. 11 taken from [18] is 188.5 °C.

$$T_b = \frac{E_o - \sqrt{E_o^2 - 4E_oRT_{po}}}{2R} \tag{11}$$

where R is the gas constant (8.314 J mol^{-1} K^{-1}), E_o is the value of E obtained by Ozawa's method.

The entropy of activation ($\Delta S^{\neq}$), enthalpy of activation ($\Delta H^{\neq}$), and free energy of activation ($\Delta G^{\neq}$) corresponding to $T = T_{pdo}$, $E_a = E_k$, and $A = A_k$ obtained by Eqs. 12, 13, and 14 are 42.26 J mol^{-1} K^{-1}, 154.44 kJ mol^{-1}, and 135.42 kJ mol^{-1}, respectively.

$$A = \frac{k_B T}{h} e^{\Delta S^{\neq}/R} \tag{12}$$

$$A\exp(-E_a/RT) = \frac{kT}{h}\exp\left(\frac{\Delta S^{\neq}}{R}\right)\exp\left(-\frac{\Delta H^{\neq}}{RT}\right) \tag{13}$$

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} \tag{14}$$

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

Determination of the specific heat capacity

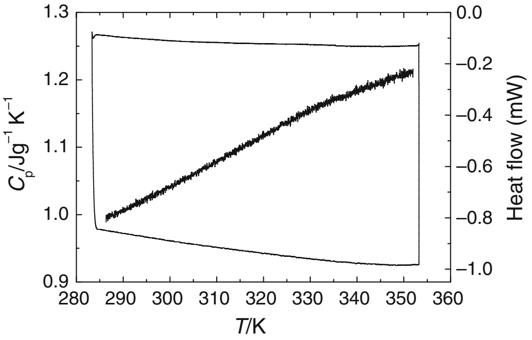

Fig. 5 Determination results of the continuous specific heat capacity of DNAZ·HClO$_4$

Figure 5 shows the determination results of DNAZ·HClO$_4$ using a continuous specific heat capacity mode of Micro-DSC apparatus. One can see that specific heat capacity of DNAZ·HClO$_4$ presents a good quadratic relationship with temperature in determining temperature range. Specific heat capacity equation is shown as:

$$C_p\left(\mathrm{Jg^{-1}\ K^{-1}}\right) = -1.3838 + 1.2423 \times 10^{-2}T - 1.3697 \times 10^{-5}T^2\ (283\ \mathrm{K} < T < 353\ \mathrm{K}) \tag{15}$$

The standard molar specific heat capacity of DNAZ·HClO$_4$ is 272.93 J mol^{-1} K^{-1} at 298.15 K.

Thermal safety

The adiabatic time-to-explosion (t, s) of energetic materials is the time of energetic material thermal decomposition transiting to explosion under the adiabatic conditions, and is an important parameter for assessing the thermal stability and the safety of energetic materials. The estimation formula of adiabatic time-to-explosion of energetic materials is showed as Eq. 17 taken from [18, 19], and t value obtained by the definite integral equation is 14.2 s, longer than that of TNAZ [20] and NTO DNAZ (3-nitro-1,2,4-triazol-5-one 3,3-dinitroazetidinium) [8], shorter than that of DNAZ 3,5-DNSA (3,3-dinitroazetidinium 3,5-dinitrosalicylate) [5].

$$C_p\frac{dT}{dt} = QA\exp(-E/RT)f(\alpha) \tag{16}$$

$$t = \frac{1}{QA}\int_{T_0}^{T}\frac{C_p\exp(E/RT)}{f(\alpha)}dT \tag{17}$$

where C_p as expressed by Eq. 15 in the temperature range of 283–353 K; $f(\alpha)$, differential mechanism function $f(\alpha) = (1-\alpha)^{-1}/2$; E is the activation energy, 156.47 kJ mol^{-1}; A is the pre-exponential constant, $A = 10^{15.12}$ s^{-1}; Q is the decomposition heat, 2938.25 Jg^{-1}; n is the decomposition reaction order, 2; R is the gas constant, 8.314 J mol^{-1} K^{-1}; α is the conversion degree, and

$$\alpha = \int_{T_0}^{T}\frac{C_p}{Q}dT \tag{18}$$

where the integral upper limit $T = T_{bp} = 461.65$ K and the lower limit $T_0 = T_{e0} = 438.55$ K. In the calculation process of adiabatic time-to-explosion, a little change in the activation energy located in the integral equation with exponential form can make a great difference in the result, and a small increase of the activation energy can induce adiabatic time-to-explosion to rise greatly.

Conclusions

(1) The thermal behavior of DNAZ·HClO$_4$ under the non-isothermal condition by DSC, TG/DTG methods was

studied. The apparent activation energy and pre-exponential factor of the exothermic decomposition reaction are 156.47 kJ mol^{-1} and $10^{15.12}$ s^{-1}, respectively.

(2) The specific heat capacity was determined with Micro-DSC method. The specific heat capacity equation is $C_p(\mathrm{J g^{-1} K^{-1}}) = -1.3838 + 1.2423 \times 10^{-2} T - 1.3697 \times 10^{-5} T^2$ $(283\ \mathrm{K} < T < 353\ \mathrm{K})$ and the standard molar specific heat capacity is 272.93 J mol^{-1} K^{-1} at 298.15 K.

(3) The adiabatic time-to-explosion was calculated to be 14.2 s.

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References

1. Frumkin AE, Churakov AM, Strelenko YA, Kachala VV, Tartakkovsky VA. Synthesis of 1,2,3,4-tetrazino[5,6-f]benzo-1,2,3,4-tetrazine 1,3,7,9-tetra-N-oxides. Org Lett. 1999;1:721–4.
2. Archibald TG, Gilardi R, Baum K, George C. Synthesis and X-ray crystal structure of 1,3,3-trinitroazetidine. J Org Chem. 1990;55:2920–4.
3. Hiskey MA, Coburn MD, Mitchell MA, Benicewicz BC. Synthesis of 3,3-dinitroazetidine from 1-t-butyl-3,3-dinitroazetidine. J Heterocycl Chem. 1992;29:1855–6.
4. Hiskey MA, Stincipher MM, Brown JE. Synthesis and initial characterization of some energetic salts of 3,3-dinitroazetidine. J Energy Mater. 1993;11:157–65.
5. Ma HX, Yan B, Li ZN, Song JR, Hu RZ. Synthesis, molecular structure, non-isothermal decomposition kinetics and adiabatic time to explosion of 3,3-dinitroazetidinium 3,5-dinitrosalicylate. J Therm Anal Calorim. 2009;95:437–44.
6. Gao R, Ma HX, Yan B, Song JR, Wang YH. Structure–property investigation on TDNAZ·HNO_3 and DNAZ·HCl. Chem J Chin U. 2009;30:577–82 (in Chinese).
7. Ma HX, Yan B, Song JR, Lü XQ, Wang LJ. Molecular structure and quantum chemical investigation of acyl derivatives of DNAZ. Chem J Chin U. 2009;30:377–81 (in Chinese).
8. Ma HX, Yan B, Li ZN, Guan YL, Song JR, Xu KZ, Hu RZ. Preparation, non-isothermal decomposition kinetics, heat capacity and adiabatic time-to-explosion of NTO·DNAZ. J Hazard Mater. 2009;169:1068–73.
9. Li ZN, Ma HX, Yan B, Guan YL, Song JR. Synthesis, crystal structure, theoretical calculation and thermal behavior of DNAZ·NTO. Chin J Chem. 2009;27:2284–90.
10. Yan B, Ma HX, Hu Y, Guan YL, Song JR. 1-(2,4-Dinitrophenyl)-3,3-dinitroazetidine. Acta Crystallogr E. 2009;65:o3215.
11. Yan B, Ma HX, Li JF, Guan YL, Song JR. 1-Benzoyl-3,3-dinitroazetidine. Acta Crystallogr E. 2010;66:o57.
12. Ditmars DA, Ishihara S, Chang SS, Bernstein G. Enthalpy and heat-capacity standard reference material: sapphire (a-Al_2O_3) from 10 to 2250 K. J Res Natl Bur Stand. 1982;87:159–63.
13. Kissinger HE. Reaction kinetics in differential thermal analysis. Anal Chem. 1957;29:1702–6.
14. Ozawa T. A new method of analyzing thermogravimetric data. Bull Chem Soc Jpn. 1965;38:1881–6.
15. Vyazovkin S, Dollimore D. Linear and nonlinear procedures in isoconversional computations of the activation energy of non-isothermal reactions in solids. J Chem Inf Comput Sci. 1996; 36:42–5.
16. Hu RZ, Yang ZQ, Liang YJ. The determination of the most probable mechanism function and three kinetic parameters of exothermic decomposition reaction of energetic materials by a single non-isothermal DSC curve. Thermochim Acta. 1988;123: 135–51.
17. Hu RZ, Shi QZ. Thermal analysis kinetics. 2nd ed. Beijing: Science Press; 2001 (in Chinese).
18. Zhang TL, Hu RZ, Xie Y, Li FP. The estimation of critical temperatures of thermal explosion for energetic materials using non-isothermal DSC. Thermochim Acta. 1994;244:171–6.
19. Smith LC. An approximate solution of the adiabatic explosion problem. Thermochim Acta. 1975;13:1–6.
20. Zhao HA, Hu RZ, Wang XJ, Zhao FQ, Gao HX, Zhang H, Zhang XL, Feng Y, Ma HX. Thermal safety of 1,3,3-trinitroazetidine (TNAZ). Acta Chim Sinica. 2009;67:2536–40 (in Chinese).