Full Paper

Propellants, Explosives, Pyrotechnics

DOI: 10.1002/prep.201700125

Thermal Behavior and Specific Heat Capacity of 1-*t*-Butyl-3,3-dinitroazetidinium Perchlorate

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Abstract: 1-*t*-Butyl-3,3-dinitroazetidinium perchlorate (TDNAZ·$HClO_4$) was synthesized, DSC and TG/DTG methods were used to study the thermal behavior of TDNAZ·$HClO_4$ under a non–isothermal condition. The intense exothermic decomposition process of DSC curves were analyzed to obtain its kinetic parameters. Continuous specific heat capacity (C_p) mode of micro–calorimeter was used to determine its C_p, its specific molar heat capacity ($C_{p,m}$) was 365.70 J mol^{-1} K^{-1} at 298.15 K. The self-accelerating decomposition temperature (T_{SADT}), thermal ignition temperature (T_{TIT}), and critical temperature of thermal explosion (T_b) were obtained to evaluate its thermal stability and safety. The above results of TDNAZ·$HClO_4$ were compared with those of 3,3-dinitroazetidinium perchlorate (DNAZ·$HClO_4$), and the effect of tert-butyl group on them was discussed.

Keywords: 1-*t*-Butyl-3,3-dinitroazetidinium perchlorate (TDNAZ·$HClO_4$) · Thermal behavior · Thermal safety · Specific heat capacity

1 Introduction

Perchloric acid is a strong acid with strong oxidizing properties, many perchlorates can be used in pyrotechnic composition, explosive or propellant. For example, NH_4ClO_4 is used in solid fuel propellant [1]. 3,3-dinitroazetidinium perchlorate (DNAZ·$HClO_4$) has good performance for energetic materials, its critical temperature of thermal explosion (T_b) is 461.50 K [2], its nitrogen content and oxygen-balance are 16.97 % and 3.23 %, respectively, its detonation velocity and detonation pressure are 8326.42 ± 5.23 m s^{-1} and 32.30 ± 0.05 GPa, respectively [3].

1-*t*-butyl-3,3-dinitroazetidinium perchlorate (TDNAZ·$HClO_4$) can be obtained from DNAZ·$HClO_4$, which secondary amine hydrogen is replaced by tert-butyl. How tert-butyl group affects the thermal decomposition processes, thermal safety and specific heat capacity of these compounds? In this paper, TDNAZ·$HClO_4$ was synthesized, and its thermal behavior was studied under a non-isothermal condition by differential scanning calorimetric (DSC) and thermogravimetric/differential thermogravimetric (TG/DTG) methods. Specific heat capacity (C_p) of TDNAZ·$HClO_4$ was determined with a continuous C_p mode of microcalorimeter. Base on the above results, the effect of tert-butyl group on these compounds was discussed.

2 Experimental Section

2.1 Materials and Analytic Instrument

1-*t*-butyl-3,3-dinitroazetidine (TDNAZ) was synthesized and purified by a reported method [4]. Other chemicals and reagents used in the synthesis of TDNAZ·$HClO_4$ were analytical pure and without further purification. Elemental analysis was performed on a PE-2400 (Perkin-Elmer, USA) elemental analyzer. The ^{1}H spectrum in CD_3OD was obtained using an INOVA-400 NMR (VARIAN, USA) spectrometer. The DSC and TG/DTG analyses for TDNAZ·$HClO_4$ were conducted using a Q600SDT (TA, USA) instrument at atmospheric pressure in a nitrogen atmosphere at a flow rate of 100 mL min^{-1}, the heating rates were 2.5, 5.0 and 10.0 K min^{-1}, the sample mass was about 1.115 mg. The specific heat capacity (C_p) of TDNAZ·$HClO_4$ was determined by a continuous C_p mode from 283.15 K to 353.15 K at a heating rate of 0.15 K min^{-1} on a Micro-DSCIII (Setaram, France) instrument with the sample mass of 262.08 mg at atmospheric pressure.

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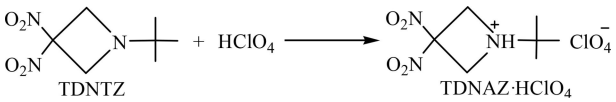
Supporting information for this article is available on the WWW under https://doi.org/10.1002/prep.201700125

2.2 Synthesis

TDNAZ·$HClO_4$ used in this work was prepared according to the following method (Scheme 1): TDNAZ (0.62 g, 3 mmol) was dissolved in dichloromethane (20 mL), then 70% $HClO_4$ (2.5 mL) was added dropwise to the solution at room temperature, stirred for 2 h. The white precipitate was collected by filtration. The colourless crystal of TDNAZ·$HClO_4$ was obtained by recrystallization from absolute ethyl alcohol, washed with absolute ethyl alcohol and dried in air (yield: 90% based on TDNAZ). Elem. anal. Calcd (%) for $C_7H_{14}O_8N_3Cl$ (303.66): C 27.69%, H 4.647%, N 13.84%. Found: C 27.53%, H 4.655%, N 13.95%. ^1H NMR(CD_3OD) (δ /ppm): 5.366(s, 4H), 1.391(s, 9H).



Scheme 1. Synthesis route of TDNAZ·$HClO_4$.

3 Results and Discussion

3.1 Thermal Behavior

Figures 1 and 2 are the DSC and TG/DTG curves of TDNAZ·$HClO_4$ at a heating rate of 10.0 K min^{-1}. The DSC curve shows that its thermal decomposition can be divided into four stages. The first stage is a crystal phase transformation process, the extrapolated onset temperature (T_e) and peak temperature (T_p) are 443.62 K and 445.24 K, respectively. DNAZ·$HClO_4$ has no this stage. The second stage is a melting and decomposition process, the T_e (melting point) and T_p are 473.25 K and 476.20 K, respectively, the TG curves show that this stage with a mass loss of 9.93%. But

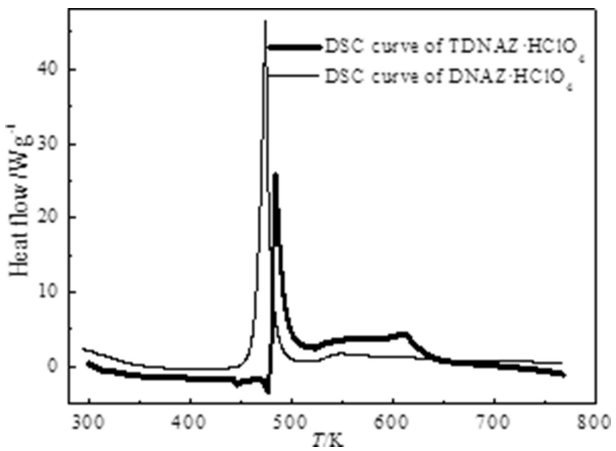


Figure 1. DSC curves of TDNAZ·$HClO_4$ and DNAZ·$HClO_4$ at a heating rate of 10.0 K min^{-1}.

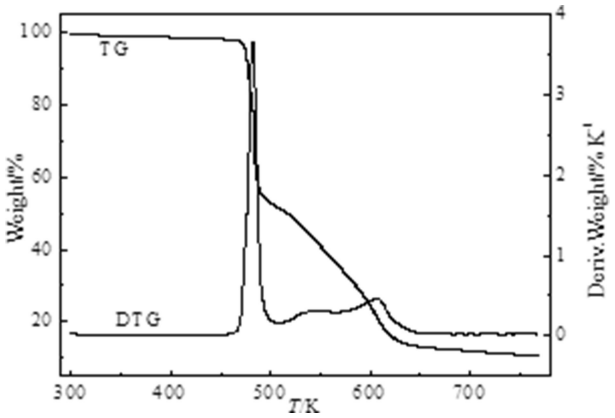


Figure 2. TG/DTG curves of TDNAZ·$HClO_4$ at a heating rate of 10.0 K min^{-1}.

there is no melting process for DNAZ·$HClO_4$, it shows that the lattice energy of DNAZ·$HClO_4$ is higher than that of TDNAZ·$HClO_4$, tert-butyl group leads to the decrease of lattice energy of compound. The third stage is an intense exothermic decomposition process, the T_e and T_p are 481.08 K and 484.31 K, respectively, they are all higher than those of DNAZ·$HClO_4$ (465.24 and 473.99 K) [2], which indicates that TDNAZ·$HClO_4$ has better thermal stability than DNAZ·$HClO_4$, and the molecular structure analysis shows that tert-butyl group improved the thermal stability of compound. The decomposition heat of TDNAZ·$HClO_4$ is −1348 J g^{-1}, it is lower than that of DNAZ·$HClO_4$ (−2937 J g^{-1}) [2]. The TG curves show that this stage with a mass loss of 37.33%, it is lower than that of DNAZ·$HClO_4$ (79.33%) [2], which indicates that the thermal decomposition of compound is difficult in the presence of tert-butyl group at low temperature. The fourth stage is a moderate exothermic decomposition process, the T_e and T_p are 523.36 K and 610.69 K, respectively, the TG curves show that this stage with a mass loss of 35.84%, it is higher than that of DNAZ·$HClO_4$ (18.59%) [2], the tert-butyl group has a significant contribution to this result. The temperature data on DSC of its intense exothermic decomposition process are listed in Table 1.

Table 1. The values of T_e, T_p, and ΔH_d of the intense exothermic decomposition process for TDNAZ·$HClO_4$ determined from the DSC curves at various heating rates (β).

β/ K min^{-1}	T_e/K	T_p/K	ΔH_d /J g^{-1}
2.5	465.50	467.85	−1258
5.0	473.21	476.28	−1306
10.0	481.08	484.31	−1348

3.2 Non-isothermal Reaction Kinetics

To explore the reaction mechanism of the intense exothermic decomposition process of TDNAZ·$HClO_4$ and obtain the corresponding kinetic parameters [apparent activation energy (E_a) and pre-exponential constant (A)] and the most probable kinetic model function, the DSC curves at the heating rates of 2.5, 5.0 and 10.0 K min^{-1} were dealt with the mathematic means, and the temperature data corresponding to the conversion degrees (α) were found. Six integral methods (MacCallum-Tanner, Šatava-Šesták, Agrawal, General integral, Universal integral and Flynn-Wall-Ozawa) and one differential method (Kissinger) were employed [5–9]. The corresponding temperature data of DSC curves at the heating rates of 2.5, 5.0 and 10.0 K min^{-1} to the conversion degrees (α) were found and listed in Table S1, the α-t curves at the heating rates of 2.5, 5.0 and 10.0 K min^{-1} were shown in Figure S1. The values of E_a were obtained by Flynn-Wall-Ozawa's method from the iso-conversional DSC curves at the heating rates of 2.5, 5.0 and 10.0 K min^{-1}, and the E_a-α relation was shown in Figure 3. One can see that the activation energy slightly changes in the range of 0.025–0.70 (α), and this range was selected to calculate the non-isothermal reaction kinetics in Figure 3.

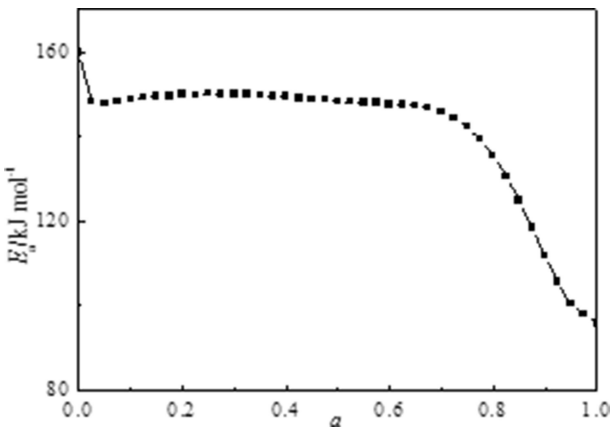


Figure 3. E_a vs α curve of TDNAZ·$HClO_4$ by Flynn-Wall-Ozawa's method.

Forty-one types of kinetic model functions (Table S2) and the basic data were put into the integral equations for calculation. The kinetic parameters and the probable kinetic model function were selected by the logical choice method and satisfying the ordinary range of the thermal decomposition kinetic parameters for energetic materials (E_a = 80−250 kJ mol^{-1} and $\log(A/s^{-1})$ = 7−30). These values together with their appropriate values of linear correlation coefficient (r) standard mean square deviation (Q) and believable factor (d, where $d=(1-r)Q$) were presented in Table 2. The values of E_a and log$A$ obtained from a single non-isothermal DSC curve are in good agreement with the calculated values obtained by the methods of Kissinger and Flynn-Wall-Ozawa. Therefore, we concluded that the reaction mechanism of the intense exothermic decomposition process of TDNAZ·$HClO_4$ was classified as two-thirds order $G(\alpha)=(1-\alpha)^{-1/2}$ and $f(\alpha)=2(1-\alpha)^{3/2}$. Substituting $f(\alpha)=2(1-\alpha)^{3/2}$, E = 155.01 kJ mol^{-1} and $A=10^{14.64}$ s^{-1} in Equation (1),

$$\frac{d\alpha}{dT}=\frac{A}{\beta}f(\alpha)e^{-E/RT} \quad (1)$$

the kinetic equation of the intense exothermic decomposition reaction of TDNAZ·$HClO_4$ was described as $d\alpha/dT=10^{14.64}(1-\alpha)^2\exp(-1.864\times10^4/T)/\beta$.

3.3 Thermal Safety Studies

The T_{e0} and T_{p0}, which are T_e and T_p corresponding to $\beta\rightarrow0$, were obtained from Equation (2), and its self-accelerating decomposition temperature (T_{SADT}) was obtained from Equation (3) [5–13]. The values of T_{SADT} and T_{p0} are 455.27 K and 456.48 K, respectively.

$$T_{e(or\ p)}=T_{e0(or\ p0)}+a\beta+b\beta^2+c\beta^3 \quad (2)$$

Where a, b and c are equation coefficients.

$$T_{SADT}=T_{e0} \quad (3)$$

Its thermal ignition temperature (T_{be0} or T_{TIT}) was obtained by substituting E_{eO} and T_{e0} into Equation (4) [5–13], and its critical temperature of thermal explosion (T_{bp0} or T_b) was obtained by substituting E_{pO} and T_{p0} into Equation (4) [5–13]. The T_{TIT} and T_b are 466.77 K and 468.59 K, respectively.

$$T_{be0(orbp0)}=\frac{E_{eO(orpO)}-\sqrt{E_{eO(orpO)}^2-4E_{eO(orpO)}RT_{e0(orp0)}}}{2R} \quad (4)$$

The T_{SADT}, T_{p0}, T_{TIT} and T_b of DNAZ·$HClO_4$ are 438.62 K, 450.02 K, 448.81 K and 461.50 K, respectively [2], which indicates that tert-butyl group leads TDNAZ·$HClO_4$ has better thermal stability and safety than DNAZ·$HClO_4$.

3.4 Specific Heat Capacity

The $C_{p,m}$ of TDNAZ·$HClO_4$ is showed in Figure 4. Its $C_{p,m}$ presents a good quadratic equation relationship with temperature from 283.15 K to 353.15 K, and the $C_{p,m}$ equation is shown as:

$$C_{p,m}(\text{TDNAZ}\cdot HClO_4)(\text{J mol}^{-1}\text{ K}^{-1})= -9.89179\times10^1+2.11574T-1.86950\times10^{-3}T^2 \quad (5)$$

Table 2. Kinetic parameters for the intense exothermic decomposition process of TDNAZ·$HClO_4$.

Method	β/K min^{-1}	E_a/kJ mol^{-1}	log(A/s^{-1})	r	Q	d
	2.5	131.21	12.13	0.9969	9.62×10^{-4}	2.99×10^{-6}
MacCallum-Tanner	5	200.17	19.94	0.9897	3.18×10^{-3}	3.28×10^{-5}
	10	135.39	12.67	0.9984	5.02×10^{-4}	8.11×10^{-7}
	2.5	132.06	12.28	0.9969	9.62×10^{-4}	2.99×10^{-6}
Šatava-Šesták	5	197.18	19.66	0.9897	3.18×10^{-3}	3.28×10^{-5}
	10	136.01	12.78	0.9984	5.02×10^{-4}	8.11×10^{-7}
	2.5	131.05	12.17	0.9965	5.10×10^{-3}	1.78×10^{-5}
Agrawal	5	200.33	19.99	0.9921	7.88×10^{-3}	6.23×10^{-5}
	10	134.92	12.67	0.9982	2.66×10^{-3}	4.84×10^{-6}
	2.5	131.05	12.17	0.9965	5.10×10^{-3}	1.78×10^{-5}
General integral	5	199.41	19.89	0.9889	1.68×10^{-2}	1.88×10^{-4}
	10	134.92	12.67	0.9982	2.66×10^{-3}	4.84×10^{-6}
	2.5	129.55	10.84	0.9964	5.10×10^{-3}	1.82×10^{-5}
Universal integral	5	198.07	18.40	0.9887	1.69×10^{-2}	1.90×10^{-4}
	10	133.80	11.36	0.9982	2.66×10^{-3}	4.91×10^{-6}
Mean		155.01	14.64			
Flynn-Wall-Ozawa	E_{eO}[a]	157.55		1.0000	2.32×10^{-6}	1.39×10^{-11}
	E_{pO}[b]	150.80		0.9997	1.04×10^{-4}	3.00×10^{-8}
Kissinger	E_K[c]	150.66	14.35	0.9997	5.42×10^{-4}	1.69×10^{-7}
Mean(E_{eO},E_{pO}, E_K)		153.00				

[a]E_{eO} is the E_a obtained from the T_e by Flynn-Wall-Ozawa's method. [b]E_{pO} is the E_a obtained from the T_p by Flynn-Wall-Ozawa's method. [c]E_K is the E_a obtained from the T_p by Kissinger's method.

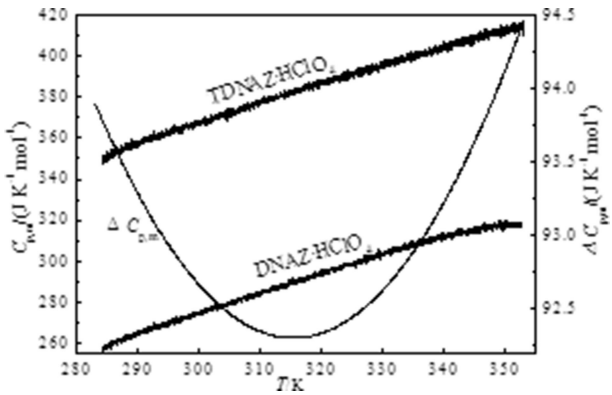


Figure 4. Determination results of the continuous $C_{p,m}$ of TDNAZ·$HClO_4$ and DNAZ·$HClO_4$.

$$C_{p,m}(\mathrm{DNAZ\cdot HClO_4})(\mathrm{J\,mol^{-1}\,K^{-1}}) = -3.42573\times10^{2} + 3.07544T - 3.39083\times10^{-3}T^{2} \quad (6)$$

$$\Delta C_{p,m}(\mathrm{J\,mol^{-1}\,K^{-1}}) = C_{p,m}(\mathrm{TDNAZ\cdot HClO_4}) - C_{p,m}(\mathrm{DNAZ\cdot HClO_4}) = 2.43656\times10^{2} - 9.59695\times10^{-1}T + 1.52133\times10^{-3}T^{2} \quad (7)$$

The correlation coefficients of the fitting (R^2) and the standard deviation (SD) results are 0.9968 and 0.9278, respectively. The $C_{p,m}$ of DNAZ·$HClO_4$ [2] and $\Delta C_{p,m}$ are also listed. The $C_{p,m}$ value of TDNAZ·$HClO_4$ was higher than that of DNAZ·$HClO_4$ at temperature from 283.15 K to 353.15 K, and the $\Delta C_{p,m}$ value decreased with the temperature increasing at temperature from 283.15 K to 315.41 K, when temperature from 315.41 K to 353.15 K, the $\Delta C_{p,m}$ value increased with the increase of temperature. The $C_{p,m}$ value of TDNAZ·$HClO_4$ and DNAZ·$HClO_4$ at 298.15 K are 365.70 J mol^{-1} K^{-1} and 272.93 J mol^{-1} K^{-1}, respectively. The $\Delta C_{p,m}$ value of TDNAZ·$HClO_4$ and DNAZ·$HClO_4$ at 298.15 K is 92.77 J mol^{-1} K^{-1}. The $C_{p,m}$ value of a compound can be influenced by many factors, such as substituent position, component elements, formula weight and molecular structure, ect. TDNAZ·$HClO_4$ is more than DNAZ·$HClO_4$ a tert-butyl group, the $\Delta C_{p,m}$ value of isobutene (96.65 J mol^{-1} K^{-1}, gas) [14] and hydrogen (28.80 J mol^{-1} K^{-1}, gas) [15] at 298.15 K was 67.85 J mol^{-1} K^{-1}, the results showed that tert-butyl group had remarkable contribution to $\Delta C_{p,m}$.

4 Conclusions

DSC and TG/DTG methods were used to study the thermal behavior of TDNAZ·$HClO_4$ under a non-isothermal condition. The E_a and A of the intense exothermic decomposition process are 155.01 kJ mol^{-1} and $10^{14.64}$ s^{-1}, respectively. The reaction mechanism of the intense exothermic decomposition process is classified as two-thirds order $G(\alpha)=(1-\alpha)^{-1/2}$, $f(\alpha)=2(1-\alpha)^{3/2}$. The T_{SADT}, T_{TIT}, and T_b are 455.27 K, 466.77 K and 468.59 K, respectively. The analysis showed that the tert-butyl group improved the thermal stability and safety of compound, it makes the decomposition heat and lattice energy of compound reduce. The specific molar heat capacity equation of TDNAZ·$HClO_4$ is $C_{p,m}(\mathrm{J\,mol^{-1}\,K^{-1}}) = -9.89179\times10^{1} + 2.11574\ T - 1.86950\times$

10^{-3} T^2 and the $C_{p,m}$ is 365.70 J mol^{-1} K^{-1} at 298.15 K. The $C_{p,m}$ value of TDNAZ·$HClO_4$ was higher than that of DNAZ·$HClO_4$ at temperature from 283.15 to 353.15 K, and the results showed that the tert-butyl group had remarkable contribution to $\Delta C_{p,m}$.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Nos. 21373161 and 21543016), the China Postdoctoral Science Foundation (No. 2017 M613191), the Provincial Natural Science Foundation of Shaanxi (No. 2014JQ2068), and the Startup Foundation for Advanced Talents of Yulin University (No. 14GK28).

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Received: May 5, 2017
Revised: August 25, 2017
Published online: ■■ ▮▮, 0000

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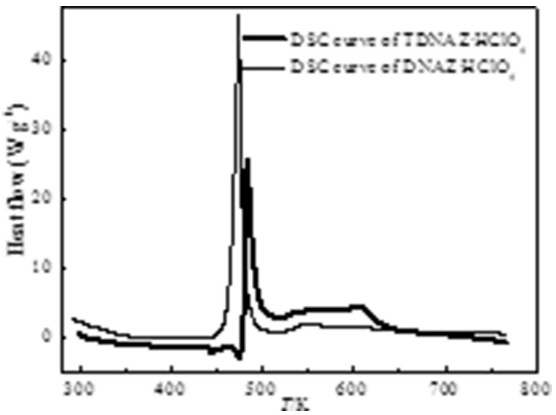

B. Yan, H. Li, Y. Guan, H. Ma*, J. Song, F. Zhao**

DSC and TG/DTG methods were used to study the thermal behavior of TDNAZ·$HClO_4$. The analysis showed that the tert-butyl group improved the thermal stability and safety of compound, and reduced the decomposition heat and lattice energy of compound. The $C_{p,m}$ of TDNAZ·$HClO_4$ is 365.70 J mol^{-1} K^{-1} at 298.15 K. The results showed that tert-butyl group had remarkable contribution to $\Delta C_{p,m}$.