

SYNTHESIS, MOLECULAR STRUCTURE, NON-ISOTHERMAL DECOMPOSITION KINETICS AND ADIABATIC TIME TO EXPLOSION OF 3,3-DINITROAZETIDINIUM 3,5-DINITROSALICYLATE

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The title compound 3,3-dinitroazetidinium (DNAZ) 3,5-dinitrosalicylate (3,5-DNSA) was prepared and the crystal structure has been determined by a four-circle X-ray diffractometer. The thermal behavior of the title compound was studied under a non-isothermal condition by DSC and TG/DTG techniques. The kinetic parameters were obtained from analysis of the TG curves by Kissinger method, Ozawa method, the differential method and the integral method. The kinetic model function in differential form and the value of E_a and A of the decomposition reaction of the title compound are $f(\alpha)=4\alpha^{3/4}$, $130.83 \text{ kJ mol}^{-1}$ and $10^{13.80} \text{ s}^{-1}$, respectively. The critical temperature of thermal explosion of the title compound is $147.55 \text{ }^\circ\text{C}$. The values of ΔS^\ddagger , ΔH^\ddagger and ΔG^\ddagger of this reaction are $-1.35 \text{ J mol}^{-1} \text{ K}^{-1}$, 122.42 and $122.97 \text{ kJ mol}^{-1}$, respectively. The specific heat capacity of the title compound 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 obtained.

Keywords: adiabatic time to explosion, 3,3-dinitroazetidinium 3,5-dinitrosalicylate (DNAZ)·(3,5-DNSA), kinetics, molecular structure, specific heat capacity

Introduction

Highly nitrated small-ring heterocycles are good candidates of energetic materials 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 derivatives 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]. In this work, we prepared the salt of DNAZ with 3,5-dinitrosalicyl acid (3,5-DNSA), its thermal behavior by DSC and TG/DTG techniques, the specific heat capacity of DNAZ·3,5-DNSA determined with continuous C_p mode of microcalorimeter (Micro-DSCIII) and studied the non-isothermal kinetics by means of Kissinger method, Ozawa method, the differential method and the integral method. The adiabatic time to explosion was also estimated for evaluating the safety performance of DNAZ·3,5-DNSA.

Experimental

Material

DNAZ·3,5-DNSA used in this work was prepared according to the following method: an appropriate amount of 3,5-DNSA was put into methanol, then stirred and the same equimolar of DNAZ was added to the above solution at room temperature. The yellow precipitate was collected by filtration. Single crystals suitable for X-ray measurement were obtained by recrystallization with methanol. A yellow crystal with cross-dimensions of $0.25 \times 0.30 \times 0.40 \text{ mm}^3$ was chosen for X-ray determination.

Methods

Apparatus and determination of crystal structure

X-ray intensities were recorded at room temperature on Bruker SMART APEX CCD X-ray diffractometer using MoK_α radiation ($\lambda=0.071073 \text{ nm}$) graphite monochromation. In the range of $1.33^\circ < \theta < 27.84^\circ$, $-8 < h < 8$, $-15 < k < 18$, $-10 < l < 20$, 6129 independent reflections were obtained. The final conventional R_1 is 0.0691 and ωR (unit mass) is 0.1764 for 1243 observable independent reflections with reflection intensity $I > 2\sigma(I)$. The C, N, O atoms were obtained

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by direct method and the hydrogen atoms were obtained by geometric calculation after their existences were approved by difference Fourier synthesis, the structure of the compound was refined by full-matrix least-squares on F^2 .

Thermal decomposition condition

The DSC and TG-DTG experiments for the title compound were performed using a model Q600SDT (TA, USA) under a nitrogen atmosphere, at a flow rate of 100 mL min^{-1} . The sample mass was about 0.6 mg. The heating rates used were 2.5, 5, 10 and $15^\circ\text{C min}^{-1}$ 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 the title compound was determined by a continuous C_p mode within 283–353 K at a heating rate of 0.15 K min^{-1} on Micro-DSC III (Setaram, France) with the sample mass of 117.6 mg. The Micro-calorimeter was calibrated with $\alpha\text{-Al}_2\text{O}_3$ (calcined), its mathematical expression was $C_p/\text{J g}^{-1} \text{ K}^{-1} = 0.1839 + 1.9966 \cdot 10^{-3} T$ within 283 and 353 K and the standard heat capacity at $C_{p,m}^\ominus(\alpha\text{-Al}_2\text{O}_3)$ at 298.15 K was determined as $79.44 \text{ J mol}^{-1} \text{ K}^{-1}$ which is in an excellent agreement with the value reported in the literature [5] ($79.02 \text{ J mol}^{-1} \text{ K}^{-1}$).

Result and discussion

Crystal structure

The bond lengths and bond angles are summarized in Tables 1 and 2. The molecular structure and atom

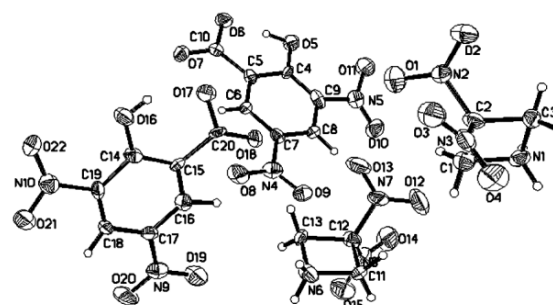


Fig. 1 Molecular structure of DNAZ·3,5-DNSA

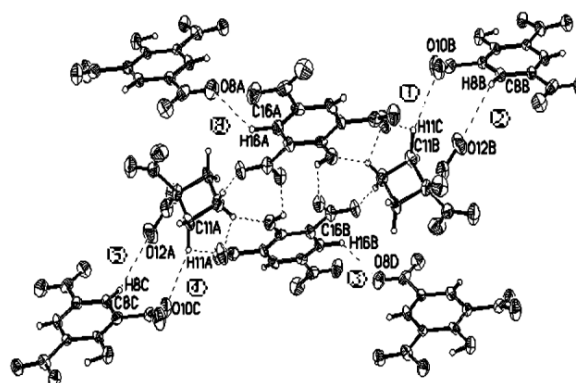


Fig. 2 Two-dimensional structure of DNAZ·3,5-DNSA

labeling are shown in Fig. 1, two-dimension monolayer structure and the packing of the molecules in the crystal lattice are shown in Figs 2 and 3.

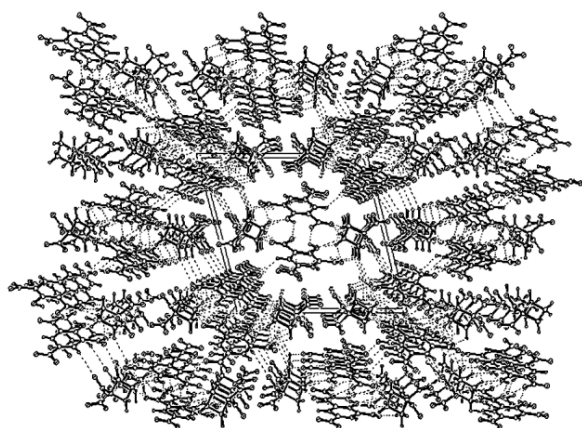
The analytical results indicate that the molecule is made up of a cation $\text{C}_3\text{N}_3\text{O}_4\text{H}_6^+$ (DNAZ⁺) and an anion $\text{C}_7\text{N}_2\text{O}_7\text{H}_3^-$. There are two DNAZ·3,5-DNSA molecules as the basic cells in the crystal, we defined A molecule with the tab of C from 1 to 10 and B from 11 to 19. The atoms of C(1), C(2), C(3) and N(1) in the four-member ring are nearly in a plane. The atom of C(2) is almost coplanar with the plane of the nitro group of $-\text{N}(2)\text{O}_2$, $-\text{N}(3)\text{O}_2$ and N in DNAZ, respectively. The planes of the two nitro groups on DNAZ⁺ are almost vertical. The carboxylic, nitro

Table 1 Selected bond distances (nm) of DNAZ·3,5-DNSA

Bonds	Lengths	Bonds	Lengths	Bonds	Lengths
C1-C2	0.1534(10)	C6-C7	0.1374(10)	C13-N6	0.1537(9)
C1-N1	0.1497(9)	C7-C8	0.1377(9)	C14-C15	0.1413(10)
C2-C3	0.1523(10)	C7-N4	0.1460(9)	C14-C19	0.1441(10)
C2-N2	0.1496(10)	C8-C9	0.1412(10)	C15-C16	0.1347(9)
C2-N3	0.1542(10)	C9-N5	0.1479(10)	C15-C20	0.1511(10)
C3-N1	0.1519(8)	C11-C12	0.1546(11)	C16-C17	0.1370(10)
C4-C5	0.1423(10)	C11-N6	0.1473(9)	C17-C18	0.1390(10)
C4-C9	0.1365(10)	C12-C13	0.1522(10)	C17-N9	0.1452(9)
C5-C6	0.1376(9)	C12-N7	0.1501(10)	C18-C19	0.1317(9)
C5-C10	0.1460(10)	C11-N8	0.1473(10)	C19-N10	0.1477(9)

Table 2 Selected bond angles ($^{\circ}$) and dihedrals ($^{\circ}$) of DNAZ·3,5-DNSA

Bond angles					
Bonds	Angles	Bonds	Angles	Bonds	Angles
C2-C1-N1	90.0(6)	C6-C7-C8	120.6(7)	C11-N6-C13	91.9(5)
C1-C2-C3	89.4(6)	C7-C8-C9	118.2(7)	C15-C14-C19	115.1(7)
N2-C2-C3	106.9(7)	C4-C9-C8	121.9(7)	C14-C15-C16	120.2(7)
N1-C3-C2	89.6(5)	C12-C11-N6	89.7(6)	C15-C16-C17	121.7(8)
C1-N1-C3	91.0(5)	C11-C12-C13	89.8(6)	C16-C17-C18	120.7(7)
C5-C4-C9	118.5(7)	N7-C12-N8	108.2(6)	C17-C18-C19	117.9(7)
C4-C5-C6	119.2(7)	N6-C13-C12	88.2(5)	C14-C19-C18	124.3(8)
C5-C6-C7	121.4(8)				
Bond dihedrals					
Bonds	Dihedrals	Bonds	Dihedrals	Bonds	Dihedrals
O1-N2-O2-C2	-178.1	C8-C9-N5-O11	-159.1(7)	C16-C15-C20-O17	174.3(7)
O3-N3-O4-C2	-179.1	C9-C4-C5-C10	-176.5(7)	C16-C17-N9-O20	-175.9(7)
N2-C2-N3-N1	177.7	C9-C8-C7-N4	-177.4(6)	C17-C16-C15-C20	175.7(7)
C4-C5-C10-O7	174.9(7)	O6-C10-O7-C5	-179.5	C17-C18-C19-N10	-179.2(7)
C4-C9-N5-O10	-157.5(8)	O8-N4-O9-C7	-178.4	C18-C19-C14-O16	179.8(7)
C5-C4-C9-N5	177.1(7)	O10-N5-O11-C9	-178.6	C18-C17-N9-O19	-176.1(7)
C5-C6-C7-N4	179.6(7)	O12-N7-O13-C12	175.8	C18-C19-N10-O22	-156.6(8)
C6-C5-C4-O5	-178.9(6)	O14-N8-O15-C12	-178.2	C19-C14-C15-C20	-176.8(6)
C6-C5-C10-O6	176.0(7)	N7-C12-N8-N6	175.3	C19-C18-C17-N9	-176.0(7)
C6-C7-N4-O9	-177.1(7)	C14-C15-C20-O18	176.0(7)	O17-C20-O18-C15	-176.9
C7-C6-C5-C10	176.9(7)	C14-C19-N7-O21	-155.2(7)	O19-N9-O20-C17	175.0
C7-C8-C9-N5	179.9(6)	C15-C14-C19-N10	178.6(6)	O21-N10-O22-C19	179.3
C-8-C9-C4-O5	-178.8(7)	C15-C16-C17-N9	177.6(7)		
C8-C7-N4-O8	-177.7(7)	C16-C15-C14-O16	-178.3(7)		

**Fig. 3** Packing diagram of DNAZ·3,5-DNSA

group of N(5)O(10)O(11), oxygen atom O(5) that connected with the benzene ring are almost coplanar with the plane of the Benzene C atoms. From the experimental results on bond lengths and bond angles in Tables 1 and 2, the bond length of C(2)-N(3) is 0.1542(10) nm, it is longer than the conventional C-N

bonds (0.147–0.150 nm) [6], and it is the longest one in A molecule, suggesting that the nitro group connected with C(2) will be firstly lost when DNAZ·3,5-DNSA is heated. Due to the repulsion effect between the electric charge of the O atom and nitro group in benzene ring, the bond lengths of C(4)-C(5) are longer than those of others in the benzene ring. The B molecule have a similar construction with A.

From Fig. 2, one can see that each basic cell in one-dimensional chain of B is crossed connected with four A through six hydrogen bonds to form an interlaced three-dimensional structure (Fig. 3).

Thermal behavior and analysis of kinetic data for the exothermic main decomposition reaction of the compound

Typical DSC and TG-DTG curves for the title compound are shown in Figs 4 and 5. The DSC curve indicates that the thermal decomposition of the title compound is composed of one exothermic process

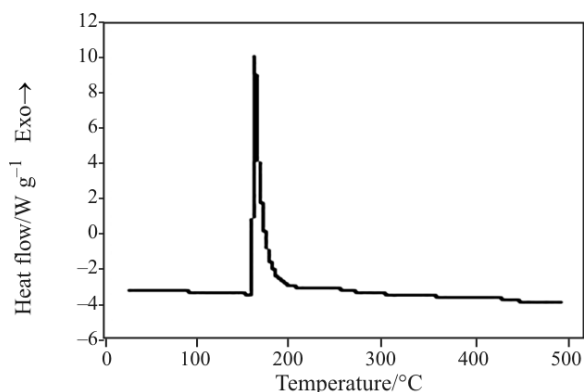


Fig. 4 DSC curve for the title compound at a heating rate of $10^{\circ}\text{C min}^{-1}$

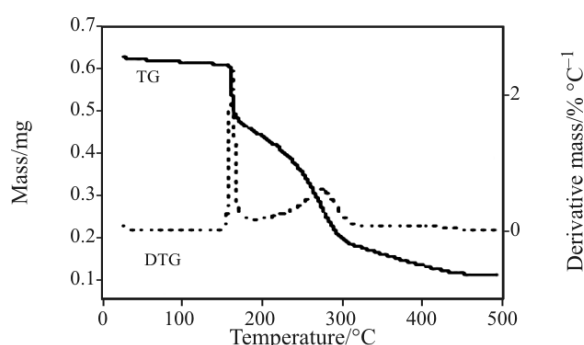


Fig. 5 TG-DTG curves for the title compound at a heating rate of $10^{\circ}\text{C min}^{-1}$

with a peak temperature of 161.78°C . However the TG-DTG curves show two stages of mass loss process. The first stage begins at about 160.02°C and completes at 189.14°C with a mass loss of 28.27% and the second stage begins at 189.14°C and completes at 400°C with a mass loss of 54.23%.

In order to obtain the kinetic parameters [apparent activation energy (E_a) and pre-exponential factor (A)] of the decomposition reaction for the title compound, the three model-free isoconversional

methods [Eqs (1)–(3)] were employed. These methods are as follows:

- Differential methods

Kissinger equation [7]

$$\ln \frac{\beta}{T_p^2} = \ln \frac{AR}{E} - \frac{E}{RT_p} \quad (1)$$

- Integral methods

Flynn–Wall–Ozawa (F–W–O) equation [8]

$$\lg \beta = \lg \left(\frac{AE}{RG(\alpha)} \right) - 2.315 - 0.4567 \frac{E}{RT} \quad (2)$$

Integral isoconversional non-linear [NL-INT] equation [9]

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

Here α is the conversion degree, T is the absolute temperature, T_0 is the initial point at which DTG curve deviates from the baseline, E_α is the apparent activation energy, β is the heating rate, R is the gas constant, T_p is the peak temperature of DTG curve, E is the apparent activation energy, A is the pre-exponential factor, $G(\alpha)$ is the integral mechanism function, I is integral and n is the experimental times.

From the original data in Table 3, E_a obtained by the Kissinger [7] method is determined to be $122.42 \text{ kJ mol}^{-1}$. The pre-exponential constant (A) is $10^{12.86} \text{ s}^{-1}$. The linear correlation coefficient (r_k) is 0.9956. The value of E_a obtained by Ozawa's method is $123.18 \text{ kJ mol}^{-1}$. The value of r_o is 0.9960.

By substituting the original data, β_i , T_{0i} , T_i , α_i and $(d\alpha/dT)_i$, $i=1,2,\dots,n$, tabulated in Table 4 from TG-DTG curves into Eqs (2) and (3), the values of E for any given value of α in Table 4 are obtained. The average value of E in the α range of 0.150 to 0.700 in Fig. 6 is in good agreement with the calculated values obtained by Kissinger's method and Ozawa's method. The E values calculated using

Table 3 Values of the kinetic parameters for the exothermic decomposition reaction for the title compound calculated from the DSC curves at various heating rates and a flowing rate of N_2 gas of 100 mL min^{-1}

$\beta /$ $^{\circ}\text{C min}^{-1}$	$T_c /$ $^{\circ}\text{C}$	$E_{oc} /$ kJ mol^{-1}	r_{oc}	$T_p /$ $^{\circ}\text{C}$	$E_k /$ kJ mol^{-1}	$\log(A_k / \text{s}^{-1})$	r_k	$E_o /$ kJ mol^{-1}	r_o
2.5	141.98			144.67					
5.0	148.43			151.95					
10.0	158.83	121.51	0.9941	161.78	122.42	12.86	0.9956	123.18	0.9960
15.0	161.88			164.81					
Mean: $E_0 = (121.51 + 122.42 + 123.18) / 3 = 122.37 \text{ kJ mol}^{-1}$									

β : heating rate; T_c : 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_{oc} : activation energy obtained by T_c through Ozawa's method; r_{oc} : the corresponding linear correlation coefficient

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Table 4 Data of DNAZ-3,5-DNSA determined by TG at different heating rates and apparent activation energies (E_a) of thermal decomposition obtained using isoconversional methods

Data	α	$T_{2.5}/K$	T_5/K	T_{10}/K	T_{15}/K	$E_o/kJ\ mol^{-1}$	$E_N/kJ\ mol^{-1}$
1	1.000	440.83	445.27	462.27	473.70	82.69	79.66
2	0.975	436.13	442.77	458.38	470.18	81.63	78.61
3	0.950	432.55	440.21	454.59	466.73	81.62	78.65
4	0.925	429.30	437.84	451.11	463.49	81.64	78.72
5	0.900	426.77	435.79	447.98	460.58	82.37	79.52
6	0.875	424.61	434.12	445.43	457.02	85.56	82.91
7	0.850	422.75	432.68	442.93	453.87	88.82	86.37
8	0.825	421.43	431.50	440.95	450.99	93.04	90.83
9	0.800	420.45	430.55	439.20	448.52	97.55	95.59
10	0.775	419.86	429.71	437.73	446.49	102.39	100.69
11	0.750	419.56	429.03	436.62	444.78	107.64	106.21
12	0.725	419.34	428.48	435.99	443.41	112.10	110.91
13	0.700	419.17	428.07	435.64	442.43	115.30	114.28
14	0.675	419.01	427.76	435.41	441.80	117.12	116.19
15	0.650	418.86	427.52	435.23	441.43	117.91	117.03
16	0.625	418.73	427.32	435.08	441.18	118.30	117.44
17	0.600	418.59	427.15	434.94	440.98	118.44	117.60
18	0.575	418.46	426.99	434.82	440.80	118.53	117.69
19	0.550	418.33	426.85	434.70	440.65	118.52	117.68
20	0.525	418.20	426.72	434.59	440.51	118.45	117.61
21	0.500	418.08	426.59	434.48	440.37	118.44	117.60
22	0.475	417.95	426.47	434.37	440.24	118.35	117.50
23	0.450	417.81	426.36	434.25	440.11	118.23	117.38
24	0.425	417.67	426.25	434.13	439.97	115.15	117.30
25	0.400	417.53	426.14	433.99	439.83	118.11	117.26
26	0.375	417.38	426.02	433.85	439.69	118.00	117.15
27	0.350	417.22	425.91	433.70	439.52	118.00	117.15
28	0.325	417.04	425.77	433.52	439.35	117.90	117.05
29	0.300	416.85	425.63	433.31	439.16	117.89	117.04
30	0.275	416.64	425.48	433.08	438.95	117.87	117.02
31	0.250	416.41	425.31	432.81	438.71	117.91	117.07
32	0.225	416.16	425.12	432.51	438.42	118.08	117.26
33	0.200	415.87	424.90	432.15	438.08	118.31	117.50
34	0.175	415.51	424.66	431.74	437.68	118.46	117.67
35	0.150	415.02	424.37	431.24	437.21	118.27	117.47
36	0.125	413.55	423.97	430.46	436.61	113.46	112.44
37	0.100	391.36	423.24	424.96	435.72	50.66	46.76
38	0.075	360.26	422.58	391.29	430.90	21.73	16.65
39	0.050	334.23	421.29	350.73	390.90	8.31	4.06
40	0.025	312.31	368.40	316.33	343.46	6.20	2.96

T with the subscript 2.5, 5, 10, 15 are the temperature obtained at the heating rates of 2.5, 5, 10, 15°C min⁻¹ respectively. E with the subscript o and N are the activation and N are the activation energy by F–W–O and NL–INT equations, respectively

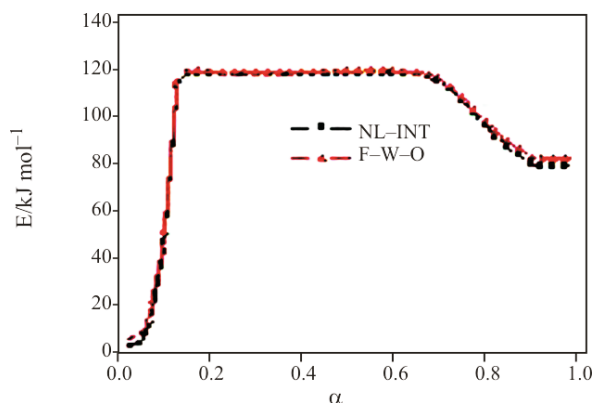


Fig. 6 $E_a \sim \alpha$ curves for the decomposition of DNAZ-3,5-DNSA by F-W-O and NL-INT method

Eqs (2) [8] and (3) [9] were used to check the validity of activation energy by the other methods.

The Eqs (4)–(7) 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 [10]. Mac Callum–Tanner Eq.

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

Satava–Sestak Eq.

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

Agrawal Eq.

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

The General Integral Eq.

$$\ln\left[\frac{G(\alpha)}{T^2 \left(1 - \frac{2RT}{E}\right)}\right] = \ln\left(\frac{AR}{\beta E}\right) - \frac{E}{RT} \quad (7)$$

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

Forty-one types of kinetic model functions in [11] and the original data tabulated in Table 4 are put into Eqs (4)–(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 their 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 5. 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

Table 5 Calculated values of kinetic parameters of decomposition reaction for the title compound

$\beta/^\circ\text{C min}^{-1}$	Equation	$E/\text{kJ mol}^{-1}$	$\log A/\text{s}^{-1}$	r	S	d
2.5	MacCallum–Tanner	120.18	12.45	0.9899	$1.48 \cdot 10^{-3}$	$1.52 \cdot 10^{-5}$
	Satava–Sestak	121.65	12.67	0.9898	$1.48 \cdot 10^{-3}$	$1.52 \cdot 10^{-5}$
$\alpha: 0.150\text{--}0.725$	Agrawal	120.99	12.60	0.9886	$7.86 \cdot 10^{-3}$	$8.95 \cdot 10^{-5}$
	The General Integral	120.99	12.60	0.9886	$7.86 \cdot 10^{-3}$	$8.95 \cdot 10^{-5}$
5	MacCallum–Tanner	152.63	16.49	0.9772	$3.30 \cdot 10^{-3}$	$7.53 \cdot 10^{-5}$
	Satava–Sestak	152.29	16.49	0.9772	$3.30 \cdot 10^{-3}$	$7.53 \cdot 10^{-5}$
	Agrawal	153.06	16.60	0.9751	$1.75 \cdot 10^{-2}$	$4.36 \cdot 10^{-4}$
	The General Integral	153.06	16.60	0.9751	$1.75 \cdot 10^{-2}$	$4.36 \cdot 10^{-4}$
10	MacCallum–Tanner	132.66	13.98	0.9948	$7.59 \cdot 10^{-4}$	$3.95 \cdot 10^{-6}$
	Satava–Sestak	133.43	14.12	0.9950	$7.59 \cdot 10^{-4}$	$3.95 \cdot 10^{-6}$
	Agrawal	133.11	14.10	0.9942	$4.02 \cdot 10^{-3}$	$2.33 \cdot 10^{-5}$
	The General Integral	133.11	14.10	0.9942	$4.02 \cdot 10^{-3}$	$2.33 \cdot 10^{-5}$
15	MacCallum–Tanner	115.87	11.88	0.9678	$4.64 \cdot 10^{-3}$	$1.50 \cdot 10^{-4}$
	Satava–Sestak	117.58	12.14	0.9678	$4.64 \cdot 10^{-3}$	$1.50 \cdot 10^{-4}$
	Agrawal	116.33	11.99	0.9638	$2.46 \cdot 10^{-2}$	$8.92 \cdot 10^{-4}$
	The General Integral	116.33	11.99	0.9638	$2.46 \cdot 10^{-2}$	$8.92 \cdot 10^{-4}$
	Mean	130.83	13.80		–	

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 Mampel power law $f(\alpha)=4\alpha^{3/4}$. Substituting $f(\alpha)$ with $4\alpha^{3/4}$, E with $130.83 \text{ kJ mol}^{-1}$ and A with $10^{13.80} \text{ s}^{-1}$ in Eq. (8),

$$d\alpha/dT = \frac{A}{\beta} f(\alpha) e^{-E/RT} \quad (8)$$

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

The kinetic equation of the exothermic decomposition reaction may be described as

$$d\alpha/dT = \frac{10^{14.40}}{\beta} \alpha^{3/4} \exp(-1.5710^4/T)$$

The values (T_{e0} and T_{p0}) of the onset temperature (T_e) and peak temperature (T_p) corresponding to $\beta \rightarrow 0$ obtained by Eq. (9) taken from [10] are 133.04 and 135.61°C , respectively.

$$T_{e \text{ or } p} = T_{e0 \text{ or } p0} + a\beta_i + b\beta_i^2, \quad i=1\sim 4 \quad (9)$$

where a and b are coefficients.

The corresponding critical temperatures of thermal explosion (T_b) obtained from Eq. (10) taken from reference [12] is 145.00 and 147.55°C , respectively.

$$T_b = \frac{E_o - \sqrt{E_o^2 - 4E_oRT_{e \text{ or } p0}}}{2R} \quad (10)$$

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

The entropy of activation (ΔS^\ddagger), enthalpy of activation (ΔH^\ddagger) and free energy of activation (ΔG^\ddagger) corresponding to $T=T_{p0}$, $E_a=E_k$ and $A=A_k$ obtained by Eqs (11), (12) and (13) are $-1.35 \text{ J mol}^{-1} \text{ K}^{-1}$, 122.42 and $122.97 \text{ kJ mol}^{-1}$, respectively.

$$A = \frac{k_B T}{h} e^{\Delta S^\ddagger/R} \quad (11)$$

$$A \exp(-E_a/RT) = \frac{kT}{h} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \exp\left(-\frac{\Delta H^\ddagger}{RT}\right) \quad (12)$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (13)$$

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

Determination of the specific heat capacity

Figure 7 shows the determination results of DNAZ·3,5-DNSA using a continuous specific heat capacity mode of Micro-DSC apparatus. We can see that specific heat capacity of DNAZ·3,5-DNSA presents a good quadratic relationship with temperature in

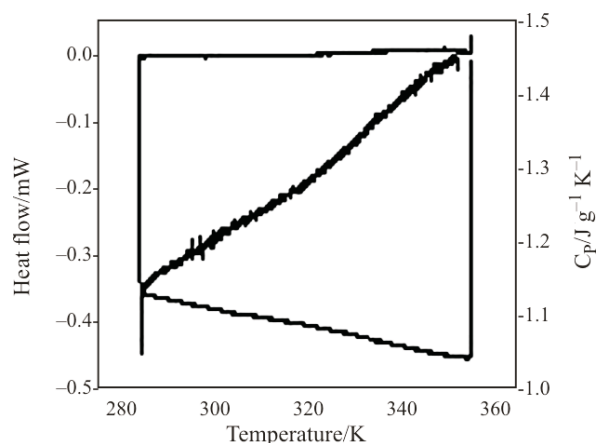


Fig. 7 Determination results of the continuous specific heat capacity of the title compound

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

$$C_p(\text{J g}^{-1} \text{ K}^{-1}) = 1.9702 - 8.9843 \cdot 10^{-3} T + 0.2143 \cdot 10^{-4} \cdot T^2 \quad (283\text{K} < T < 353\text{K}) \quad (14)$$

The standard molar specific heat capacity of the title compound is $447.69 \text{ J mol}^{-1} \text{ K}^{-1}$ at 298.15 K .

Estimation of the adiabatic time-to-explosion

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. (16) taken from [12, 13], and t value obtained by the definite integral equation is 56.54 s .

$$C_p \frac{dT}{dt} = QA \exp(-E/RT) f(\alpha) \quad (15)$$

$$t = \frac{1}{QA} \int_{T_0}^T \frac{C_p \exp(E/RT)}{f(\alpha)} dT \quad (16)$$

where C_p as expressed by Eq. (14) in the temperature range of $283\text{--}353 \text{ K}$; $f(\alpha)$, differential mechanism function $f(\alpha)=4\alpha^{3/4}$; E , activation energy, $130.83 \text{ kJ mol}^{-1}$; A , pre-exponential constant, $10^{13.80} \text{ s}^{-1}$; Q , decomposition heat, 1173.5 J g^{-1} ; n , decomposition reaction order, 0.75 ; R , the gas constant, $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$; α , the conversion degree, and

$$\alpha = \int_{T_0}^T \frac{C_p}{Q} dT \quad (17)$$

where the integral upper limit $T=T_{bp}=420.7$ K and the lower limit $T_0=T_{e0}=406.19$ 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

- The compound, DNAZ-3,5-DNSA was synthesized and its structure was determined by single-crystal X-ray diffraction, it is an ionic compound which is made up of a cation DNAZ⁺ and an anion C₇N₂O₇H₃⁻.
- The thermal behavior of the title compound 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 130.83 kJ mol⁻¹ and 10^{13.80} s⁻¹, respectively.
- The specific heat capacity was determined with Micro-DSC method. The specific heat capacity equation is $C_p(\text{J g}^{-1} \text{K}^{-1})=1.9702-8.9843\cdot 10^{-3}T+0.2143\cdot 10^{-4}\cdot T^2$ (283 K < T < 353 K) and the standard molar specific heat capacity is 447.69 J mol⁻¹ K⁻¹ at 298.15 K. The adiabatic time-to-explosion was calculated to be 56.54 s.

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