

Thermochemical Properties and Non-isothermal Decomposition Reaction Kinetics of *N*-Guanylurea Dinitramide (GUDN)

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The constant-volume combustion energy, $\Delta_c U$ (GUDN, s, 298.15 K), enthalpy of solution in acetic ether, $\Delta_{\text{sol}} H_m^\ominus$ and kinetic behavior of the exothermic decomposition reaction of the title compound (GUDN) are determined by a precise rotating bomb calorimeter, a Calvet microcalorimeter and DSC, respectively. Its standard enthalpy of combustion, $\Delta_c H_m^\ominus$ (GUDN, s, 298.15 K), standard enthalpy of formation, $\Delta_f H_m^\ominus$ (GUDN, s, 298.15 K) and kinetic parameters of the exothermic main decomposition reaction in a temperature-programmed mode [the apparent activation energy (E_a) and pre-exponential factor (A)] are calculated. The values of $\Delta_c U$ (GUDN, s, 298.15 K), $\Delta_c H_m^\ominus$ (GUDN, s, 298.15 K), $\Delta_f H_m^\ominus$ (GUDN, s, 298.15 K) and $\Delta_{\text{sol}} H_m^\ominus$ of GUDN are $(-7068.64 \pm 2.37) \text{ J} \cdot \text{g}^{-1}$, $(-1467.66 \pm 0.50) \text{ kJ} \cdot \text{mol}^{-1}$, $(-319.76 \pm 0.58) \text{ kJ} \cdot \text{mol}^{-1}$ and $(165.737 \pm 0.013) \text{ kJ} \cdot \text{mol}^{-1}$, respectively. The kinetic model function in integral form and the value of E_a and A of the exothermic main decomposition reaction of GUDN are $220.20 \text{ kJ} \cdot \text{mol}^{-1}$ and $10^{21.18} \text{ s}^{-1}$, respectively. The critical temperature of thermal explosion of GUDN is $217.6 \text{ }^\circ\text{C}$

Keywords *N*-guanylurea dinitramide, combustion energy, standard enthalpy of formation, enthalpy of solution, thermal decomposition kinetics

Introduction

N-Guanylurea dinitramide (GUDN) is a new energetic oxidizer with higher energy and lower sensitivity. Its crystal density is $1.755 \text{ g} \cdot \text{cm}^{-3}$. The detonation velocity is about $8210 \text{ m} \cdot \text{s}^{-1}$. Its specific impulse and pressure exponent are 213.1 s and 0.73, respectively. It has the potential for possible use as an energy ingredient of propellants and explosives from the point of view of the above-mentioned high performance. Its preparation,¹ properties² and hygroscopicity² have been reported. In the present work, we report its combustion energy, standard combustion enthalpy, standard enthalpy of formation, enthalpy of solution in acetic ether, kinetic model function and kinetic parameters of the exothermic main decomposition reaction studied by using DSC. This is quite useful in the evaluation of its thermochemical properties and thermal stability under non-isothermal condition and in the study of its thermal changes at high temperature.

Experimental

Materials

According to the method reported in the literature¹

N-Guanylurea dinitramide was prepared. It is pale yellow crystal. m.p. $214 \text{ }^\circ\text{C}$ (dec.); UV-vis (H_2O) λ_{max} : 282.5, 212.0 nm; IR (KBr) ν : 1743 ($-\text{C}(\text{NH})-$), 1688 ($-\text{C}(\text{O})-$), 1523, 1444 ($-\text{NO}_2$). Anal. calcd for $\text{C}_2\text{H}_7\text{O}_5\text{N}_7$: C 11.48, H 3.34, N 46.89; found C 11.14, H 3.34, N 46.99. The analytical results show that it has the composition of $\text{C}_2\text{H}_7\text{O}_5\text{N}_7$. Acetic ether (A.R., Xi'an Chemical Com.) was used.

Apparatus and experimental conditions

The constant-volume combustion energy of GUDN was determined by a precise rotating bomb calorimeter (RBC-type II).³ The main experimental procedures were described previously.³ The initial temperature was regulated to $(25.0000 \pm 0.0005) \text{ }^\circ\text{C}$, and the initial oxygen pressure was 2.5 MPa.

The correct value of the heat exchange was calculated according to Linio-Pyfungdelel-Wsava formula.⁴

The calorimeter was calibrated with benzoic acid of 99.999% purity. It had an isothermal heat of combustion at $25 \text{ }^\circ\text{C}$ of $(-26434 \pm 3) \text{ J} \cdot \text{g}^{-1}$. The energy equivalent of calorimeter was determined to be $(17936.01 \pm 9.08) \text{ kJ} \cdot \text{K}^{-1}$. The precision of the measurements was 4.68×10^{-4} .

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The analytical methods for final products (gas, liquid and solid) were the same as those in Ref. 2. The analytical results of the final products show that the combustion reactions were complete. As a result, either carbon deposits or carbon monoxide formed during the combustion reactions and the amount of NO_x in the final gas phase were negligible.

The enthalpy of solution of GUND was determined by the RD496-III type microcalorimeter.⁵ The microcalorimeter was made in Engineering Physical Institute of China, which was equipped with two 15 mL vessels. The microcalorimeter was calibrated by Joule effect and its sensitivity was $(63.994 \pm 0.042) \mu\text{V} \cdot \text{mW}^{-1}$ at 298.15 K. The experimental precision and accuracy were checked by measurement of the enthalpy of solution of crystalline KCl with special purity in deionized water at 298.15 K. The molar ratio of H₂O to KCl was 2000. The experimental value of $\Delta_{\text{sol}}H_{\text{m}}^{\ominus}$ [$(17.238 \pm 0.048) \text{kJ} \cdot \text{mol}^{-1}$] was good agreement with that reported in the literature [$(17.241 \pm 0.018) \text{kJ} \cdot \text{mol}^{-1}$],⁶ indicating that the device used in this work was reliable. The precision of the measurements was 0.5%.

The thermal decomposition process of GUND under the condition of flowing N₂ gas was studied on a TG-DTG and DSC apparatus (TA, USA). The conditions of TG-DTG were as follows: sample mass, *ca.* 0.5 mg; heating rate, 10 °C · min⁻¹; atmosphere, a flowing rate of N₂ gas of 120 mL · min⁻¹; reference, α -Al₂O₃. The conditions of DSC were as follows: sample mass, *ca.* 1 mg; heating rates, 2.5, 5, 10 and 15 °C · min⁻¹, respectively; atmosphere, a flowing rate of N₂ gas of 60 mL · min⁻¹; reference, α -Al₂O₃.

Results and discussion

Combustion energy of GUND

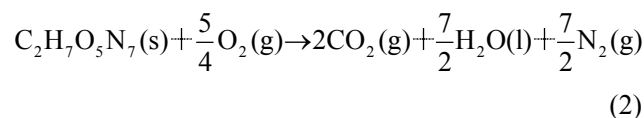
The determination method of combustion energy for GUND was the same as that for the calibration of the calorimeter with benzoic acid. The combustion energies of the samples were calculated by the formula

$$\Delta_{\text{c}}U(\text{GUNDN, s}) = \frac{W\Delta T - aG - 5.983b}{m} \quad (1)$$

where $\Delta_{\text{c}}U(\text{GUNDN, s})$ denotes the constant-volume combustion energy of the samples, W is the energy equivalent of the RBC-type II calorimeter (in J · K⁻¹), ΔT the correct value of the temperature rising, a the length of actual Ni-Cr wire consumed (in cm), G the combustion enthalpy of Ni-Cr wire for ignition ($0.9 \text{J} \cdot \text{cm}^{-1}$), 5.983 the formation enthalpy and solution enthalpy of nitric acid corresponding to 1 mL of 0.1000 mol · L⁻¹ NaOH (in J · mL⁻¹), b the volume in mL of consumed 0.1000 mol · L⁻¹ NaOH and m the mass in g of the sample. The results of the calculations were given in Table 1.

Standard combustion enthalpy of GUND

The standard combustion enthalpy of GUND, $\Delta_{\text{c}}H_{\text{m}}^{\ominus}(\text{GUNDN, s, 298.15 K})$, is referred to the combustion enthalpy change of the following ideal combustion reaction at 298.15 K and 100 kPa.



The standard combustion enthalpy of GUND calculated by the following equations:

$$\Delta_{\text{c}}H_{\text{m}}^{\ominus}(\text{GUNDN, s, 298.15 K}) = \Delta_{\text{c}}U(\text{GUNDN, s, 298.15 K}) + \Delta nRT \quad (3)$$

$$\Delta n = n_{\text{g}}(\text{products}) - n_{\text{g}}(\text{reactants}) \quad (4)$$

where n_{g} is the total amount in mole of gases present as products or as reactants, $R = 8.314 \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, $T = 298.15 \text{K}$. The result is $(-1467.66 \pm 0.50) \text{kJ} \cdot \text{mol}^{-1}$.

Standard enthalpy of formation of GUND

The standard enthalpy of formation of GUND, $\Delta_{\text{f}}H_{\text{m}}^{\ominus}(\text{GUNDN, s, 298.15 K})$, were calculated by Hess's law according to the above thermochemical equation (2):

$$\Delta_{\text{f}}H_{\text{m}}^{\ominus}[\text{GUNDN, s, 298.15 K}] = [2\Delta_{\text{f}}H_{\text{m}}^{\ominus}(\text{CO}_2, \text{g, 298.15 K}) + \frac{7}{2}\Delta_{\text{f}}H_{\text{m}}^{\ominus}(\text{H}_2\text{O, l, 298.15 K})] - \Delta_{\text{c}}H_{\text{m}}^{\ominus}(\text{GUNDN, s, 298.15 K})$$

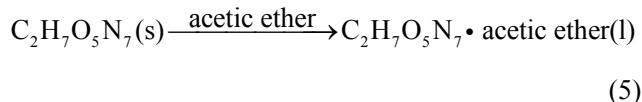
Table 1 Experimental results for the combustion energies of the samples

No.	Mass of sample <i>m</i> /g	Calibrated heat of combustion wire Q_{c}/J	Calibrated heat of acid Q_{N}/J	Calibrated $\Delta T/\text{K}$	Combustion energy of sample $-\Delta_{\text{c}}U/(\text{J} \cdot \text{g}^{-1})$
1	1.04582	12.60	38.77	0.4130	7059.46
2	1.04640	12.60	38.79	0.4138	7069.29
3	1.03725	11.70	38.45	0.4105	7075.58
4	1.03247	9.00	38.27	0.4082	7071.02
5	1.04535	12.60	38.75	0.4131	7064.37
6	1.04624	12.60	38.78	0.4139	7072.10
mean					7068.64 ± 2.37

when $\Delta_f H_m^\ominus(\text{CO}_2, \text{g}, 298.15 \text{ K}) = (-293.51 \pm 0.13) \text{ kJ} \cdot \text{mol}^{-1}$, $\Delta_f H_m^\ominus(\text{H}_2\text{O}, \text{l}, 298.15 \text{ K}) = (-285.83 \pm 0.042) \text{ kJ} \cdot \text{mol}^{-1}$.⁷ The result is $(-319.76 \pm 0.58) \text{ kJ} \cdot \text{mol}^{-1}$.

Enthalpy of solution of GUDN in acetic ether

The dissolution process of GUDN can be expressed as follows:



The experimental results of the enthalpy of solution of GUDN in acetic ether (1 : 5000) determined at 298.15 K were shown in Table 2. Obviously, the solution reaction is endothermic.

Table 2 Enthalpy of solution of GUDN in acetic ether (298.15 K)

No.	Mass <i>m</i> /g	Heat of solution <i>Q</i> /mJ	$\Delta_{\text{sol}} H_m^\ominus / (\text{kJ} \cdot \text{mol}^{-1})$
1	3.35	2710.056	169.174
2	3.47	2718.341	163.323
3	3.48	2720.022	163.345
4	3.42	2715.442	166.040
5	3.38	2712.782	167.841
6	3.45	2717.077	164.696
mean			165.737 ± 0.013

Kinetic parameters of the thermal decomposition reaction of GUDN

Typical TG-DTG and DSC curves of GUDN are shown in Figures 1 and 2. The TG curve consisted of two-stage mass loss process. The first-stage began at about 191 °C and completed at 239 °C accompanied with 64.36% mass loss, and the second-stage completed at about 510 °C accompanied with 34.49% mass loss. It indicates that the decomposition of GUDN is much more complete. DSC curve shows one exothermic peak before 250 °C.

In order to obtain the kinetic parameters [apparent activation energy (E_a) and pre-exponential factor (A)] of the exothermic decomposition reaction for GUDN, a multiple heating method⁸ (Kissinger's method) was employed. From the original data in Table 3, E_k was determined to be $237.7 \text{ kJ} \cdot \text{mol}^{-1}$ and $A 10^{23.43} \text{ s}^{-1}$. The linear correlation coefficient (r_k) is 0.9531. The values of

Table 3 Maximum peak temperature (T_p) of the exothermic decomposition reaction for GUDN determined by the DSC curves at various heating rates (β)

$\beta / (\text{°C} \cdot \text{min}^{-1})$	2.5	5	10	15
$T_p / \text{°C}$	209.06	217.86	219.17	223.61

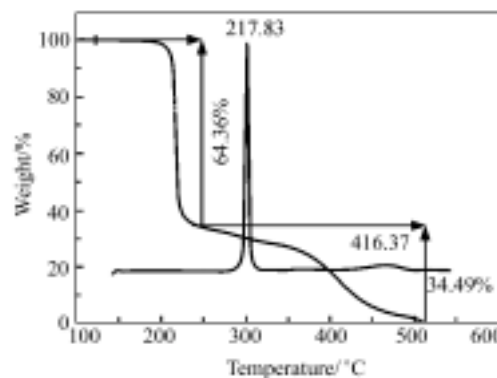


Figure 1 TG-DTG curve of GUDN at a heating rate of $10 \text{ °C} \cdot \text{min}^{-1}$.

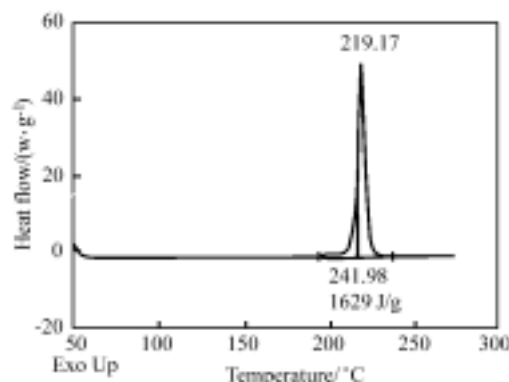


Figure 2 DSC curve of GUDN at a heating rate of $10 \text{ °C} \cdot \text{min}^{-1}$.

E_0 and r_0 obtained by Ozawa's method,⁹ are $233.8 \text{ kJ} \cdot \text{mol}^{-1}$ and 0.9559, respectively.

The integral Eqs. (6)—(8) are cited for the calculation of the values of E_a , A and the most probable kinetic model function [$f(\alpha)$] from a single non-isothermal DSC curve.¹⁰

$$\lg[G(\alpha)] = \lg\left(\frac{AE_a}{\beta R}\right) - 2.315 - 0.4567 \frac{E_a}{RT} \quad (6)$$

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

$$\lg[G(\alpha)] = \lg\left(\frac{AE_a}{\beta R}\right) - 0.4828 E_a^{0.4357} - \frac{0.449 + 0.217 E_a}{0.001 T} \quad (8)$$

where $G(\alpha)$ is the integral model function, respectively, R the gas constant, α the conversion degree ($\alpha = H_t/H_0$), dH_t/dt the exothermic heat flow at time t , H_0 the total heat effect (corresponding to the global area under the

DSC curve), H_t the reaction heat at a certain time (corresponding to the partial area under the DSC curve), T the temperature (K) at time t .

Forty-one types of kinetic model function¹¹ and the data in Tables (4)—(7) are put into Eqs. (6)—(8) for calculation, respectively. The values of E_a , A , linear correlation coefficient (r), standard mean square deviation (Q) and believable factor (d) [where $d=(1-\alpha)Q$] were obtained by the linear least-squares method.¹⁰

Table 4 Data of GUDN determined by DSC^a

Data point	T_i/K	α_i	$(dH_i/dt)_i / (mJ \cdot s^{-1})$	$(d\alpha/dT)_i \cdot 10^{-3} / K^{-1}$
1	455.15	0.0001	0.0103	0.2450
2	457.15	0.0004	0.0165	0.3924
3	459.15	0.0011	0.0289	0.6867
4	461.15	0.0022	0.0407	0.9646
5	463.15	0.0038	0.0558	1.320
6	465.15	0.0062	0.0765	1.810
7	467.15	0.0096	0.1075	2.550
8	469.15	0.0187	0.2239	5.310
9	471.15	0.0287	0.2453	5.820
10	473.15	0.0413	0.3583	8.500
11	475.15	0.0614	0.5836	13.85
12	477.15	0.0973	1.0866	25.78
13	479.15	0.1702	2.4101	57.19
14	481.15	0.3381	6.9782	165.6
15	483.15	0.7955	1.1493	158.7
16	485.15	0.9694	0.2232	27.27
17	487.15	0.9945	0.0834	5.300
18	489.15	0.9985	0.0641	1.980
19	491.15	0.9994	0.0593	1.520
20	493.15	0.9997	0.0001	1.410

^a $T_0=393.15$ K; $H_0=1011.4$ mJ; $\beta=0.04167$ °C · s⁻¹.

The probable kinetic model function of the integral methods selected by the logical choice method¹² 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) is $G(\alpha)=\alpha^{1/2}$, indicating that the reaction mechanism of the exothermic process of GUDN is according with the Mampel Power principle, and the mechanism function is No. 24, the Mampel Power equation with $n=1/2$. Substituting $f(\alpha)$ with $2\alpha^{1/2}$, E with 220.20 kJ · mol⁻¹, $\beta=0.1667$ K · s⁻¹ and A with $10^{21.18}$ s⁻¹ in Eq. (9),

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

we can now establish the kinetic equation of the exothermic decomposition process of GUDN as follows:

$$\frac{d\alpha}{dT} = 1.1998 \cdot 10^{22.18} \alpha^{1/2} e^{-2.648 \times 10^4 / T}$$

The corresponding kinetic parameters are summarized in Table 8.

The value (T_{p0}) of the peak temperature (T_p) corresponding to $\beta \rightarrow 0$ obtained by Eq. (10) taken from Ref. 11 is 205.1 °C.

$$T_{pi} = T_{p0} + b\beta_i + c\beta_i^2, \quad i=1, 2, 3, 4 \quad (10)$$

where b and c are coefficients.

The critical temperature of thermal explosion (T_b) obtained from Eq. (11) taken from Ref. 12 is 217.6 °C.

$$T_b = \frac{E_0 - \sqrt{E_0^2 - 4E_0RT_{p0}}}{2R} \quad (11)$$

where R is the gas constant (8.314 J · mol⁻¹ · K⁻¹), E_0 is the value of E obtained by Ozawa's method.

Table 5 Data of GUDN determined by DSC^a

Data point	T_i/K	α_i	$(dH_i/dt)_i / (mJ \cdot s^{-1})$	$(d\alpha/dT)_i \cdot 10^{-3} / K^{-1}$
1	459.15	0.0000	0.3659	0.0048
2	461.15	0.0003	0.3730	0.0049
3	463.15	0.0008	0.3872	0.0051
4	465.15	0.0016	0.4016	0.0053
5	467.15	0.0027	0.4196	0.0055
6	469.15	0.0047	0.4481	0.0059
7	471.15	0.0070	0.4857	0.0064
8	473.15	0.0108	0.5424	0.0071
9	475.15	0.0162	0.6340	0.0083
10	477.15	0.0251	0.8094	0.0106
11	479.15	0.0402	1.610	0.0152
12	471.15	0.0699	2.100	0.0275
13	483.15	0.1396	5.111	0.0668
14	485.15	0.2978	16.40	0.2144
15	487.15	0.7816	10.40	0.1359
16	489.15	0.9525	2.691	0.0352
17	491.15	0.9880	0.9829	0.0129
18	493.15	0.9966	0.5410	0.0071
19	495.15	0.9989	0.4326	0.0057
20	497.15	0.9996	0.4054	0.0053
21	499.15	0.9998	0.3959	0.0052
22	501.15	0.9999	0.3977	0.0052
23	503.15	1.0000	0.3951	0.0052

^a $T_0=443.15$ K; $H_0=917.76$ mJ; $\beta=0.08333$ °C · s⁻¹.

Table 6 Data of GUDN determined by DSC^a

Data point	T_i/K	α_i	$(dH_i/dt)_i /$ ($\text{mJ} \cdot \text{s}^{-1}$)	$(d\alpha/dT)_i \cdot 10^{-3} /$ K^{-1}
1	467.15	0.0000	0.0724	0.4457
2	469.15	0.0001	0.0867	0.5341
3	471.15	0.0004	0.1088	0.6704
4	473.15	0.0010	0.1417	0.8730
5	475.15	0.0021	0.1902	1.171
6	477.15	0.0037	0.2619	1.613
7	479.15	0.0066	0.3881	2.390
8	481.15	0.0117	0.6584	4.055
9	483.15	0.0216	1.250	7.698
10	485.15	0.0420	2.571	15.84
11	487.15	0.0837	5.280	32.52
12	489.15	0.1619	10.88	67.02
13	491.15	0.2916	24.60	151.5
14	493.15	0.6007	25.74	158.5
15	495.15	0.8867	8.086	49.80
16	497.15	0.9586	2.983	18.38
17	499.15	0.9829	1.256	7.737
18	501.15	0.9925	0.6080	3.745
19	503.15	0.9966	0.3419	2.106
20	505.15	0.9985	0.2296	1.414
21	507.15	0.9994	0.1788	1.101
22	509.15	0.9997	0.1573	0.9687
23	511.15	0.9999	0.1435	0.8840

^a $T_0=453.15 \text{ K}; H_0=974.14 \text{ mJ}; \beta=0.16667 \text{ } ^\circ\text{C} \cdot \text{s}^{-1}$.**Table 7** Data of GUDN determined by DSC^a

Data point	T_i/K	α_i	$(dH_i/dt)_i /$ ($\text{mJ} \cdot \text{s}^{-1}$)	$(d\alpha/dT)_i \cdot 10^{-3} /$ K^{-1}
1	473.15	0.0000	0.0156	0.0000
2	475.15	0.0001	0.0468	0.0002
3	477.15	0.0004	0.1127	0.0006
4	479.15	0.0011	0.2026	0.0010
5	481.15	0.0021	0.3248	0.0016
6	483.15	0.0038	0.4962	0.0024
7	485.15	0.0065	0.7827	0.0038
8	487.15	0.0108	1.346	0.0066
9	489.15	0.0190	2.739	0.0134
10	491.15	0.0374	7.049	0.0344
11	493.15	0.0827	22.40	0.1094
12	495.15	0.1837	61.74	0.3014
13	497.15	0.4256	76.77	0.3748
14	499.15	0.7838	37.53	0.1832
15	501.15	0.9239	14.48	0.0707
16	503.05	0.9714	5.937	0.0290
17	505.15	0.9893	2.400	0.0117
18	507.15	0.9962	0.9649	0.0047
19	509.15	0.9987	0.3943	0.0019
20	511.15	0.9996	0.1786	0.0009
21	513.15	0.9999	0.0989	0.0005
22	515.15	1.0000	0.0743	0.0004

^a $T_0=469.15 \text{ K}; H_0=819.37 \text{ mJ}; \beta=0.25 \text{ } ^\circ\text{C} \cdot \text{s}^{-1}$.**Table 8** Kinetic parameters obtained by the data in Table 2

No.	β	Equation	Function No. ^a	$E_a/(\text{kJ} \cdot \text{mol}^{-1})$	$\log(A/\text{s}^{-1})$	r	Q	$d \cdot 10^2$
1	2.5	(6)	24	212.46	20.46	0.9812	0.278	52.24
2		(7)	24	215.54	20.76	0.9798	1.478	2.99
3		(8)	24	216.36	20.83	0.9812	0.278	0.522
4	5	(6)	24	198.20	18.85	0.9663	0.638	2.149
5		(7)	24	200.43	19.08	0.9636	3.391	12.34
6		(8)	24	201.25	19.14	0.9663	0.638	2.149
7	10	(6)	24	222.74	21.48	0.9427	1.331	7.633
8		(7)	24	226.11	21.80	0.9387	7.074	42.35
9		(8)	24	227.27	21.91	0.9426	1.331	7.633
10	15	(6)	24	237.56	23.01	0.9534	1.016	4.739
11		(7)	24	241.60	23.37	0.9503	5.401	26.85
12		(8)	24	242.93	23.52	0.9534	1.016	4.739

mean: $E_a=220.20 \text{ kJ} \cdot \text{mol}^{-1}$ $\log(A/\text{s}^{-1})=21.18$ ^aFunction No. 24: $f(\alpha)=2\alpha^{1/2}$, $G(\alpha)=\alpha^{1/2}$.

Conclusions

The constant-volume combustion energy, standard enthalpy of combustion and enthalpy of solution in acetic ether of GUDN are determined by a precise rotating bomb calorimeter and Calvet microcalorimeter, respectively. They are $(-7068.64 \pm 0.50) \text{ J} \cdot \text{g}^{-1}$ and $(165.737 \pm 0.013) \text{ kJ} \cdot \text{mol}^{-1}$, respectively. The standard enthalpy of combustion and standard enthalpy of formation are calculated to be $(-1467.66 \pm 0.50) \text{ kJ} \cdot \text{mol}^{-1}$ and $(-319.76 \pm 0.58) \text{ kJ} \cdot \text{mol}^{-1}$. The kinetic model function in integral form, apparent activation energy and pre-exponential factor of the exothermic main decomposition reaction for GUDN are $a^{0.5}$, $220.20 \text{ kJ} \cdot \text{mol}^{-1}$ and $10^{21.18} \text{ s}^{-1}$, respectively. The critical temperature of thermal explosion of GUDN is $217.6 \text{ }^\circ\text{C}$.

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