

Short communication

Thermochemical properties and non-isothermal decomposition reaction kinetics of 3,4-dinitrofurazanfuroxan (DNTF)

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Abstract

The constant-volume combustion energy, $\Delta_c U$ (DNTF, s, 298.15 K) and kinetic behavior of the exothermic decomposition reaction of the title compound (DNTF) are determined by a precise rotating bomb calorimeter and DSC, respectively. Its standard enthalpy of combustion, $\Delta_c H_m^\theta$ (DNTF, s, 298.15 K), standard enthalpy of formation, $\Delta_f H_m^\theta$ (DNTF, s, 298.15 K) and kinetic parameters of the major exothermic decomposition reaction in a temperature-programmed mode [the apparent activation energy (E_a) and pre-exponential factor (A)] are calculated. The values of $\Delta_c U$ (DNTF, s, 298.15 K), $\Delta_c H_m^\theta$ (DNTF, s, 298.15 K), and $\Delta_f H_m^\theta$ (DNTF, s, 298.15 K) of DNTF are $-9733.96 \pm 8.59 \text{ J g}^{-1}$, $-3018.29 \pm 2.68 \text{ kJ mol}^{-1}$, and $657.23 \pm 2.70 \text{ kJ mol}^{-1}$, respectively. The kinetic model function in integral form and the value of E_a and A of the major exothermic decomposition reaction of DNTF are $1 - (1 - \alpha)^{1/3}$, $177.03 \text{ kJ mol}^{-1}$ and $10^{13.68} \text{ s}^{-1}$, respectively. The critical temperature of thermal explosion of DNTF is 240.6°C .

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Keywords: DNTF; Combustion energy; Standard enthalpy of formation; Thermal decomposition; Kinetics

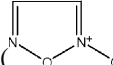
1. Introduction

3,4-dinitrofurazanfuroxan (DNTF) is a new energetic oxidizer with higher energy and lower sensitivity. Its crystal density is 1.937 g cm^{-3} . The detonation velocity corresponding to $\rho = 1.937 \text{ g cm}^{-3}$ is about 9250 m s^{-1} . Therefore, it has the potential for possible use as an energetic ingredient of propellants and explosives from the point of view of the above-mentioned high performance. Its preparation [1] and properties [2] have been reported. In the present work, we report its combustion energy, standard combustion enthalpy, standard enthalpy of formation, and kinetic model function and kinetic parameters of the major exothermic decomposi-

tion reaction studied with 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.

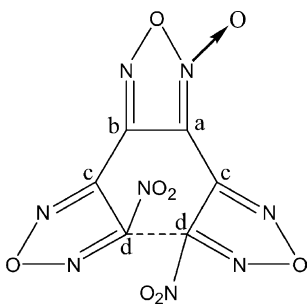
2. Experimental

2.1. Materials

DNTF was prepared according to the reported method [1]. The compound was purified by crystallization from acetone for analysis. IR (KBr): $1641, 11515, 1447, 1586, 1564, 1447, 1411$ () $1523, 1355$ ($-\text{C}(\text{NO}_2)$), 880 ($\text{C}-\text{N}$) cm^{-1} . ^{13}C NMR ($\text{DM}-\text{COd}_6$, 400 MHz): $\delta_{\text{ca}}=104.411 \text{ ppm}$; $\delta_{\text{cb}}=138.073 \text{ ppm}$;

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Scheme 1. Structure of DNTF.

$\delta_{cd}=143.748$ ppm; $m/z = 312$. Anal. called for $C_6N_8O_8$: C 23.08, N 35.90; found C 23.29, N 36.11. Its structure is shown in Scheme 1. The sample was kept in vacuum desiccator before use.

2.2. Experimental and apparatus conditions

The constant-volume combustion energy of DNTF 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 $(25.0000 \pm 0.0005)^\circ\text{C}$ and the initial oxygen pressure was 2.5 MPa.

The correct value of the heat exchange was calculated according to Linio–Pyfengdelel–Wsava formula [4].

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

The analytical methods for final products (gas, liquid and solid) were the same as those in Ref. [3]. The analytical results of the final products showed 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 thermal decomposition process of DNTF was studied on a DSC apparatus (TA, USA). The conditions of DSC were as follows: sample mass, ca. 1 mg; heating rates, 2, 10, 15 and 20 K min^{-1} ; atmosphere, N_2 gas, 1 MPa; reference sample, $\alpha\text{-Al}_2\text{O}_3$.

3. Results and discussion

3.1. Combustion energy of DNTF

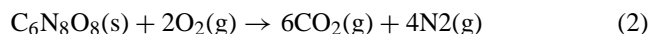
The determination method of combustion energy for DNTF was the same as that for the calibration of the calorimeter with benzoic acid. The combustion energies of the samples were calculated by the formula

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

where $\Delta_c U(\text{DNTF, s})$ 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 J cm^{-1}); 5.983 the formation enthalpy and solution enthalpy of nitric acid corresponding to 1 mL of 0.1000 mol L^{-1} solution of NaOH (in J mL^{-1}); b , the volume in mL of consumed 0.1000 mol L^{-1} solution of NaOH, and; m , the mass in g of the sample. The results of the calculations were given in Table 1.

3.2. Standard combustion enthalpy of DNTF

The standard combustion enthalpy of DNTF, $\Delta_c H_m^\theta$ (DNTF, s, 298.15K), referred to the combustion enthalpy change of the following ideal combustion reaction at 298.15 K and 100 kPa.



The standard combustion enthalpies of DNTF calculated by the following equations: $(3)\Delta_c H_m^\theta(\text{DNTF, s, 298.15 K}) = \Delta_c U(\text{DNTF, s, 298.15 K}) + \Delta nRT$

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

where n_g is the total amount in mole of gases present as products or as reactants, $R = 8.314\text{ J K}^{-1}\text{ mol}^{-1}$, $T = 298.15\text{ K}$. The result is $-3018.29 \pm 2.68\text{ kJ mol}^{-1}$.

3.3. Standard enthalpy of formation of DNTF

The standard enthalpies of formation of DNTF, $\Delta_f H_m^\theta$ (DNTF, s, 298.15 K), were calculated by Hess's law according to the above thermochemical Eq. (2):

$$\Delta_f H_m^\theta(\text{DNTF, s, 298.15 K}) = 6 \Delta_f H_m^\theta(\text{CO}_2, \text{g, 298.15 K}) - \Delta_f H_m^\theta(\text{DNTF, s, 298.15 K})$$

when $\Delta_f H_m^\theta(\text{CO}_2, \text{g, 298.15 K}) = -393.51 \pm 0.13\text{ kJ mol}^{-1}$ [5]. The result is $657.23 \pm 2.70\text{ kJ mol}^{-1}$.

3.4. Thermodynamic data for the melting process of DNTF

A typical DSC curve of the melting process of DNTF is shown in Fig. 1. The extrapolated onset temperature (T_e), peak temperature (T_m), melting enthalpy (ΔH_m) and melting entropy (ΔS_m) obtained by five measurements are $106.39 \pm 0.10^\circ\text{C}$, $108.66 \pm 0.10^\circ\text{C}$, $93.83 \pm 0.30\text{ kJ mol}^{-1}$, and $247.22 \pm 0.30\text{ J K}^{-1}\text{ mol}^{-1}$. The final temperature of melting (T_f) is obtained by the calculated formula presented in Fig. 1. The average value of five measurements is $106.47 \pm 0.10^\circ\text{C}$. Thus, the temperature range of melting for DNTF, $T_e\text{--}T_f$ is from 106.39°C to 106.47°C .

Table 1
Experimental results for the combustion energies of the samples

Number	Mass of sample, m (g)	Calibrated heat of combustion wire, Q_c (J)	Calibrated heat of acid Q_N , (J)	Calibrated, ΔT (K)	Combustion energy of sample, $\Delta_c U$ (J g ⁻¹)
1	1.23501	12.60	86.91	0.6834	9755.46
2	1.12325	12.60	78.95	0.6195	9721.89
3	1.20260	12.60	84.53	0.6658	9760.12
4	1.21236	11.70	85.21	0.6688	9725.72
5	1.22323	12.60	85.98	0.6734	9704.77
6	1.20033	12.60	84.37	0.6628	9735.77
Mean					9733.96 ± 8.59

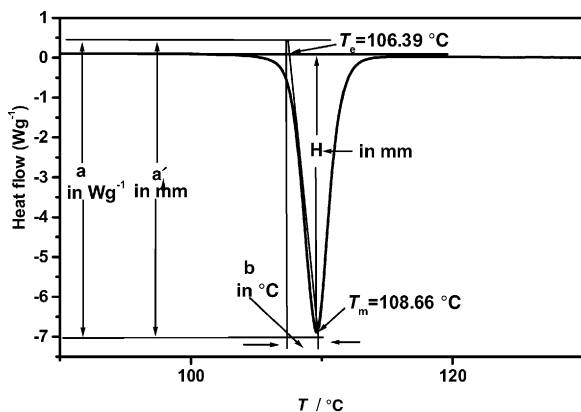


Fig. 1. DSC curve of the melting process of for DNTF at a heating rate of 10 °C min⁻¹. $T_t = T_m - T_{td} = T_m - SHR_0 = T_m - (Hb)/a'$, where $T_{td} = SHR_0 = (Hb)/a'$ is the thermal delay temperature in °C; $S = a/a'$, sensitivity in W g⁻¹ cm⁻¹; H , peak high in mm, and; R_0b/a , thermal resistance, in °C (W⁻¹ g⁻¹).

3.5. Thermal behavior

Typical DSC curve for DNTF as shown in Fig. 2. The DSC curve shows an endothermic peak begins at its melting point (108.96 °C) with summit peak at 111.63 °C. A major exothermic peak at 292.41 °C is due to decomposition of DNTF in molten state. Two exothermic processes at temperature higher than 310 °C are caused by the further decomposition of the decomposition products in coacervate phase.

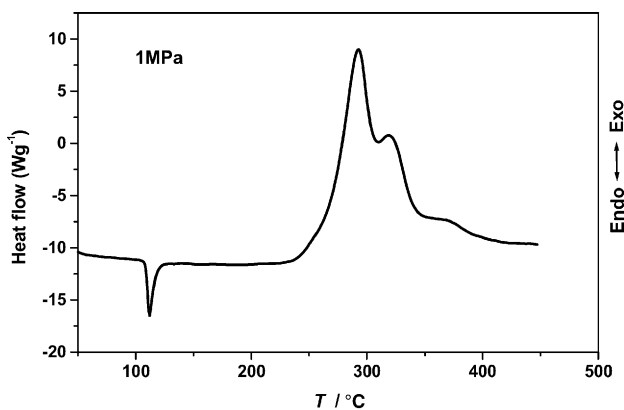


Fig. 2. DSC curve for DNTF at a heating rate of 20 °C min⁻¹.

3.6. Analysis of kinetic data of the thermal decomposition reaction of DNTF

In order to obtain the kinetic parameters [apparent activation energy (E_a) and pre-exponential factor (A)] of the major exothermic decomposition reaction for DNTF, a multiple heating method [6] (Kissinger's method) was employed. From the original data in Table 2, E_k is determined to be 150.7 kJ mol⁻¹ and A , 10^{12.2} s⁻¹. The linear correlation coefficient (r_k) is 0.9995. The values of E_0 and r_0 obtained by Ozawa's method [7] are 152.0 and 0.9996 kJ mol⁻¹, respectively. The values of E_0 and r_0 obtained from the relationship of β_i versus T_e^{-1} are 148.10 and 0.9830 kJ mol⁻¹, respectively. Average value of E_0 is 150.05 kJ mol⁻¹.

The integral Eqs. (5), (6) and differential Eq. (7) are cited to obtain the values of E_a , A and the most probable kinetic model function [$f(\alpha)$] from a single non-isothermal DSC curve [8].

$$G(\alpha)f(\alpha) = \frac{RT^2}{E} \frac{d\alpha}{dT} \quad (5)$$

$$\ln \left[\frac{G(\alpha)}{T - T_0} \right] = \ln \left(\frac{A}{\beta} \right) - \frac{E_a}{RT} \quad (6)$$

$$\ln \left[\frac{d\alpha/dT}{f(\alpha) [E_a(T - T_0)/RT^2 + 1]} \right] = \ln \left(\frac{A}{\beta} \right) - \frac{E_a}{RT} \quad (7)$$

where $f(\alpha)$ and $G(\alpha)$ are the differential and integral model functions, respectively; T_0 , the initial point at which DSC curve deviates from the baseline; R , the gas constant; α , 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 , temperature (K) at time t , $d\alpha/dT = (1/H_0\beta)(dH/dt)$.

Forty-one types of kinetic model functions [9] and the data in Tables 3 and 4 are put into Eqs. (5)–(7) for calculation, respectively. The values of E_a , A , linear correlation coefficient

Table 2
Maximum peak temperature (T_p) and onset temperature (T_e) of the major exothermic decomposition reaction for DNTF determined by the DSC curves at various heating rates (β) and 1 MPa

β (°C, min ⁻¹)	2	10	15	20
T_p (°C)	256.60	280.35	287.99	292.41
T_e (°C)	230.63	248.84	255.95	265.07

Table 3
Data of DNTF determined by DSC^a

Data point	T_i (°C)	α_1	$(dH_i/dt)_i$ (mJ s ⁻¹)	$d\alpha/dT$, 10 ³ (K ⁻¹)
1	225	0.0010	0.0890	0.0001
2	226	0.0013	0.1068	0.0002
3	227	0.0016	0.1602	0.0003
4	228	0.0021	0.1958	0.0003
5	229	0.0026	0.2492	0.0004
6	230	0.0033	0.3204	0.0005
7	231	0.0041	0.3738	0.0006
8	232	0.0049	0.4450	0.0007
9	233	0.0060	0.5162	0.0008
10	234	0.0071	0.6052	0.0010
11	235	0.0084	0.6764	0.0011
12	236	0.0099	0.7654	0.0013
13	237	0.0115	0.8366	0.0014
14	238	0.0132	0.9256	0.0015
15	239	0.0151	1.0324	0.0017
16	240	0.0173	1.1570	0.0019
17	241	0.0196	1.2816	0.0021
18	242	0.0222	1.4062	0.0023
19	243	0.0249	1.5308	0.0025
20	244	0.0280	1.6732	0.0027
21	245	0.0312	1.8156	0.0030
22	246	0.0347	1.9758	0.0032
23	247	0.0384	2.1538	0.0035
24	248	0.0425	2.3318	0.0038
25	249	0.0469	2.5507	0.0042
26	250	0.0516	2.7768	0.0045
27	251	0.0567	2.9975	0.0049
28	252	0.0622	3.1559	0.0052
29	253	0.0678	3.2627	0.0053
30	254	0.0733	3.3838	0.0055
31	255	0.0790	3.5831	0.0059
32	256	0.0851	3.8911	0.0064
33	257	0.0920	4.3201	0.0071
34	258	0.0998	4.7775	0.0078
35	259	0.1083	5.2225	0.0085
36	260	0.1176	5.6319	0.0092
37	261	0.1274	6.0022	0.0098
38	262	0.1378	6.3653	0.0104
39	263	0.1488	6.7533	0.0110
40	264	0.1603	7.1859	0.0117
41	265	0.1728	7.6576	0.0125
42	266	0.1862	8.1506	0.0133
43	267	0.2005	8.6134	0.0141
44	268	0.2154	8.9659	0.0146
45	269	0.2269	9.2880	0.0152
46	270	0.2354	9.6049	0.0157
47	271	0.2517	9.9128	0.0162
48	272	0.2687	10.2848	0.0168
49	273	0.2862	10.6622	0.0174
50	274	0.3043	11.0200	0.0180
51	275	0.3230	11.3386	0.0185
52	276	0.3423	11.6163	0.0190
53	277	0.3619	11.8370	0.0193
54	278	0.3820	11.9990	0.0196
55	279	0.4025	12.0951	0.0198
56	280	0.4232	12.1289	0.0198

^a $T_0=217.20$ °C; $H_0=3673.90$ mJ; $\beta=0.1666$ °C s⁻¹.

Table 4
Data of DNTF determined by DSC^a

Data point	T_i (°C)	α_1	$(dH_i/dt)_I$ (mJ s ⁻¹)	$d\alpha/dT$, 10 ³ (K ⁻¹)
1	231	0.0005	0.2601	0.0002
2	232	0.0007	0.3167	0.0003
3	233	0.0009	0.3779	0.0004
4	234	0.0012	0.4406	0.0004
5	235	0.0015	0.5049	0.0005
6	236	0.0019	0.5783	0.0005
7	237	0.0023	0.6640	0.0006
8	238	0.0028	0.7681	0.0007
9	239	0.0034	0.8996	0.0008
10	240	0.0041	1.0419	0.0010
11	241	0.0049	1.1888	0.0011
12	242	0.0059	1.3372	0.0013
13	243	0.0070	1.4948	0.0014
14	244	0.0082	1.6616	0.0016
15	245	0.0095	1.8268	0.0017
16	246	0.0110	2.0150	0.0019
17	247	0.0127	2.2323	0.0021
18	248	0.0145	2.4679	0.0023
19	249	0.0165	2.7234	0.0026
20	250	0.0188	3.0003	0.0028
21	251	0.0213	3.2895	0.0031
22	252	0.0241	3.6047	0.0034
23	253	0.0271	3.9229	0.0037
24	254	0.0304	4.2412	0.0040
25	255	0.0340	4.5456	0.0043
26	256	0.0379	4.8134	0.0045
27	257	0.0419	5.0827	0.0048
28	258	0.0461	5.3718	0.0051
29	259	0.0506	5.6870	0.0054
30	260	0.0555	6.0282	0.0057
31	261	0.0605	6.3801	0.0060
32	262	0.0660	6.7580	0.0064
33	263	0.0717	7.1558	0.0067
34	264	0.0777	7.5766	0.0071
35	265	0.0842	8.0294	0.0076
36	266	0.0910	8.5083	0.0080
37	267	0.0982	9.0163	0.0085
38	268	0.1059	9.5594	0.0090
39	269	0.1140	10.1194	0.0095
40	270	0.1226	10.7054	0.0101
41	271	0.1316	11.3082	0.0107
42	272	0.1412	11.9401	0.0113
43	273	0.1512	12.6087	0.0119
44	274	0.1619	13.3278	0.0126
45	275	0.1732	14.0469	0.0132
46	276	0.1852	14.7966	0.0140
47	277	0.1976	15.5157	0.0146
48	278	0.2108	16.2501	0.0153
49	279	0.2245	16.9386	0.0160
50	280	0.2389	17.5965	0.0166
51	281	0.2537	18.2697	0.0172
52	282	0.2692	18.9123	0.0178
53	283	0.2853	19.4937	0.0184
54	284	0.3019	20.0292	0.0189
55	285	0.3191	20.5035	0.0193
56	286	0.3368	20.8860	0.0197
57	287	0.3550	21.1308	0.0199

^a $T_0 = 223.0$ °C; $H_0 = 4242.16$ mJ; $\beta = 0.2500$ °C s⁻¹.

Table 5
Kinetic parameters obtained by the data in Table 2

Number	β	Equation	Function number ^a	E_a (kJ mol ⁻¹)	log(A/s ⁻¹)	r	Q	$d \times 10^2$
1	10	(5)	29	161.38	–	0.9942	0.0078	0.0045
2		(6)	29	180.65	13.87	0.9786	5.580	11.93
3		(7)	29	177.62	13.48	0.9660	8.738	0.2970
4	15	(5)	29	182.16	–	0.9953	0.0048	0.0023
5		(6)	29	199.49	15.53	0.9811	6.307	11.94
6		(7)	29	160.90	11.83	0.9746	5.556	0.140

Mean: $E_a=177.03$ kJ mol⁻¹ log(A/s⁻¹) = 13.68

^a Function number 29: $f(\alpha) = 3(1 - \alpha)^{2/3}$, $G(\alpha) = 1 - (1 - \alpha)^{1/3}$.

(r), standard mean square deviation (Q) and believable factor (d) [where $d = (1 - \alpha) Q$] were obtained by the linear least-squares and iterative methods [8].

The probable kinetic model functions of the integral and differential methods selected by the logical choice method [10] and satisfying the ordinary range of the thermal decomposition kinetic parameters for energetic materials ($E = 80$ – 250 kJ mol⁻¹; log $A = 7$ – 30 , A in s⁻¹) are $f(\alpha) = 3(1 - \alpha)^{2/3}$ and $G(\alpha) = 1 - (1 - \alpha)^{1/3}$, indicating that the reaction mechanism of the exothermic process of DNTF is classified as phase reaction R_3 with spherical symmetry. Substituting $f(\alpha)$ with $3(1 - \alpha)^{2/3}$, E with 177.03 kJ mol⁻¹, β with 0.1667 K s⁻¹ and A with $10^{13.68}$ s⁻¹ in Eq. (8),

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

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

$$\frac{d\alpha}{dT} = 10^{14.94} (1 - \alpha)^{\frac{2}{3}} e^{-2.129 \times 10^4 / T}$$

The corresponding kinetic parameters are summarized in Table 5.

The value (T_{e0}) of the peak temperature (T_e) corresponding to $\beta \rightarrow 0$ obtained by Eq. (9) taken from Ref. [9] is 226.0 °C.

$$T_{pi} = T_{po} + b\beta_i + c\beta^2, \quad i = 1-4 \quad (9)$$

where b and c are coefficients.

The critical temperature of thermal explosion (T_b) obtained from Eq. (10) taken from [10] is 240.6 °C.

$$T_b = \frac{E_0 - \sqrt{E_0^2 - 4E_0RT_{e0}}}{2R} \quad (10)$$

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

4. Conclusions

1. The constant-volume combustion energy, standard enthalpy of combustion, and standard enthalpy of formation

of DNTF are -9733.96 ± 8.59 J g⁻¹, -3018.29 ± 2.68 kJ mol⁻¹, and 657.23 ± 2.70 kJ mol⁻¹, respectively.

- The extrapolated onset temperature (T_e), peak temperature (T_m), melting enthalpy (ΔH_m) and melting entropy (ΔS_m) are 106.39 ± 0.10 °C, 108.66 ± 0.10 °C, 93.83 ± 0.30 kJ mol⁻¹, and 247.22 ± 0.30 J K⁻¹ mol⁻¹, respectively.
- The kinetic model function in integral form, apparent activation energy and pre-exponential factor of the major exothermic decomposition reaction for DNTF at 1 MPa are $1 - (1 - \alpha)^{1/3}$, 177.03 kJ mol⁻¹ and $10^{13.68}$ s⁻¹, respectively.
- The critical temperature of thermal explosion of DNTF is 240.6 °C.

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