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Nonisothermal Decomposition Kinetics and Computational Studies on the Properties of 2,4,6,8-Tetranitro-2,4,6,8-tetraazabicyclo[3,3,1]onan-3,7-dione (TNPDU)

Hai-Xia Ma,*[†,‡] Ji-Rong Song,*[‡,§] Feng-Qi Zhao,[⊥] Rong-Zu Hu,[⊥] and He-Ming Xiao[‡]

College of Chemical Engineering/Shaanxi Key Laboratory of Physico-Inorganic Chemistry, Northwest University, Xi'an, Shaanxi, 710069, People's Republic of China, Department of Chemistry, Nanjing University of Science and Technology, Nanjing, 210094, People's Republic of China, Conservation Technology Department, The Palace Museum, 4 Jingshan Qianjie Beijing, 100009, People's Republic of China, and Xi'an Modern Chemistry Research Institute, Xi'an, 710065, People's Republic of China

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The thermal decomposition and the nonisothermal kinetics of the thermal decomposition reaction of 2,4,6,8-tetranitro-2,4,6,8-tetraazabicyclo[3,3,1]onan-3,7-dione (TNPDU) were studied under the nonisothermal condition by differential scanning calorimetry (DSC) and thermogravimetry−derivative thermogravimetry (TG−DTG) methods. The kinetic model function in differential form and the value of E_a and A of the decomposition reaction of TNPDU are $f(\alpha) = 3(1 - \alpha)[-\ln(1 - \alpha)]^{2/3}$, 141.72 kJ mol^{-1}, and $10^{11.99}$ s^{-1}, respectively. The critical temperature of thermal explosion of the title compound is 232.58 °C. The values of $\Delta S^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta G^{\ddagger}$ of this reaction are −15.50 J mol^{-1} K^{-1}, 147.65 kJ mol^{-1}, and 155.26 kJ mol^{-1}, respectively. The theoretical investigation on the title compound as a structure unit was carried out by the DFT-B3LYP/6-311++G** method. The IR frequencies and NMR chemical shift were performed and compared with the experimental results. The heat of formation (HOF) for TNPDU was evaluated by designing isodesmic reactions. The detonation velocity (D) and detonation pressure (P) were estimated by using the well-known Kamlet−Jacobs equation, based on the theoretical densities and HOF. The calculation on bond dissociation energy suggests that the N−N bond should be the trigger bond during the pyrolysis initiation process.

1. Introduction

2,4,6,8-Tetranitro-2,4,6,8-tetraazabicyclo[3,3,1]onan-3,7-dione (TNPDU) is a new nitrogen-rich material with four $-NO_2$ groups. The detonation velocity is about 9034 m s^{-1} corresponding to the compressed density of 1.93 g cm^{-3}. It is a good candidate 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] properties,[1] and hydrolytic behavior[2] have been reported. Its kinetic parameters of thermal decomposition were reported which were obtained in a cell of aluminum with a rolled-up cell in static air by differential scanning calorimetry (DSC) curves.[3] Here, we report its kinetic model function and kinetic parameters of the decomposition reaction studied with thermogravimetry−derivative thermogravimetry (TG−DTG) and DSC in nitrogen atmosphere at a flow rate of 100 mL min^{-1} with open ceramic cells. This is quite useful in the evaluation of its thermal stability under nonisothermal condition and in the analysis of compatibility of energetic materials. The theoretical calculation was also performed for further studying the relationship between the structure and properties of this material. The performance of TNPDU as an energetic material, including heat of formation (HOF), the density (ρ), the detonation velocity (D), detonation pressure (P), and the thermal stability, are investigated.

2. Experimental Section

2.1. Sample. The title compound used in this work was prepared according to the reported method in literature.[1] The sample we used was purified by recrystallization from nitromethane and kept in a vacuum drying oven before use. Anal. Calcd (%) for $C_5H_4N_8O_{10}$: C, 17.84; N, 33.33; H, 1.17. Found (%): C, 18.02; N, 33.77; H, 1.17. IR (KBr): $\nu^{s}_{C=O} = 1700$, $\nu^{as}_{C-NO_2} = 1620$, $\nu^{s}_{C-NO_2} = 1290$, and $\nu^{s}_{C-H} = 3000$ cm^{-1}. ^{1}H NMR (solvent, acetone, 400 MHz) δ: 7.81 (>CH−, 2H), 3.57 ($-CH_2-$, 2H).

2.2. 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, 5.0, 10.0, 15.0, and 20.0 °C min^{-1} from ambient temperature to 400 °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 is satisfactory.

2.3. Quantum Chemical Investigation. Many studies[4−6] have shown that the density functional theory (DFT) methods, especially the B3LYP hybrid model,[7,8] in combination with the basis set 6-311++G**[9−11] can produce reliable geometries, energies, and infrared vibrational frequencies. The initial geometry of TNPDU generated from Chem3D software was fully optimized at the DFT-B3LYP level by the Berny method[12,13] with the 6-311++G** basis set. The NMR chemical shift calculations were performed using Hartree−Fock NMR[5,6] calculations with the 6-311+G (2d, p) basis set at geometries

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* To whom correspondence should be addressed. E-mail: mahx@nwu.edu.cn (H.-X.M.); songji@nwu.edu.cn (J.-R.S.).

[†] Northwest University.

[‡] Nanjing University of Science and Technology.

[§] The Palace Museum.

[⊥] Xi'an Modern Chemistry Research Institute.

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optimized with the B3LYP method and the 6-311++G** basis set. The scaled IR frequencies were calibrated by multiplying 0.96.[14] All calculations were carried out on a IBM P4 computer with the Gaussian 03W[15] program.

The method of isodesmic reaction has been employed very successfully to calculate HOF from total energies obtained from ab initio calculations.[16] The isodesmic reaction process, in which the number of each kind of formal bond is conserved, is used with application of the bond separation reaction rules. Therefore, the HOF of TNPDU is evaluated by eq 2 for the isodesmic reaction 1:

$$C_5O_2H_4N_4(NO_2)_4 + 8NH_3 + 5CH_4 \rightarrow 2HCONHNO_2 + 2NH_2NO_2 + 8CH_3NH_2 \quad (1)$$

$$\Delta H^0_{298} = \Delta E_0 + \Delta ZPE + \Delta H^0_T = \sum \Delta H_{f,P} - \sum \Delta H_{f,R} \quad (2)$$

where ΔH^0_{298} is the enthalpy change of the reaction at 298 K, ΔE_0 is the change in the total energy, ΔZPE is the zero-point energy, and ΔH^0_T is the enthalpy change from 0 to 298 K, respectively. $\sum \Delta H_{f,P}$ and $\sum \Delta H_{f,R}$ are the sums of the HOFs of the products and reactants, respectively. In addition, as to the reference compound $HCONHNO_2$, its HOF is evaluated by G3 theory, based on the atomization energies being used by Curtiss et al.[17]

The empirical Kamlet−Jacobs (K−J) equation is widely applied to estimate the values of *D* and *P* for the explosives containing C, H, O, and N as follows:

$$D = 0.7062(NM^{1/2}Q^{1/2})^{1/2}(1 + 1.30\rho) \quad (3)$$

$$P = (7.167 \times 10^8)NM^{1/2}Q^{1/2}\rho^2 \quad (4)$$

where each term in eqs 3 and 4 is defined as follows: *D*, detonation velocity (km s^{-1}); *P*, detonation pressure (GPa); *N*, moles of gases detonation products per gram of explosive; *M*, average molecular weight of gaseous products; *Q*, chemical energy of detonation (J g^{-1}); ρ, density of explosives (g cm^{-3}). Here, the theoretical density of the title compound was obtained from the molecular weight divided by the average molecular volume. The average mole volume of the compound was obtained from the statistical average value of 100 molar volumes. The mole volume of each molecule, defined as the volume inside a contour of 0.001 e/$bohr^3$ density,[18] was calculated by the Monte Carlo method in the Gaussian 03W program package.[15] Our group has ever validated this method by comparing the experimental density with the calculated values for 45 energetic compounds.[19] Most of these compounds are nitramines ($N-NO_2$-based), and the total average value of ρ_{cald}/ρ_{exptl} is more than 1.003.

The thermal stability of the title compound is evaluated by calculating the bond dissociation energy. Each of the bond breaks leads to an intermediate with a triplet ground state, and spin-unrestricted wave functions were employed for the obtained intermediates.

All calculations were performed on an IBM personal computer, and the default convergence criteria given in the programs were used throughout the computation.

3. Result and Discussion

3.1. Thermodynamic Data for the Melting Process of the Compound. Typical DSC, TG−DTG, and *T* versus α curves for the title compound are shown in Figures 2−4. The DSC curve indicates that the thermal decomposition of the title compound is composed of one exothermic process with a peak temperature of 249.50 °C. The TG−DTG curves also show a stage of mass loss process. The stage begins at about 210.85

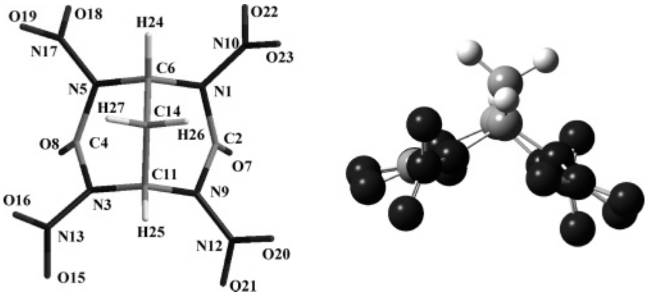

Figure 1. Optimized structure and atomic numbering of the title compound.

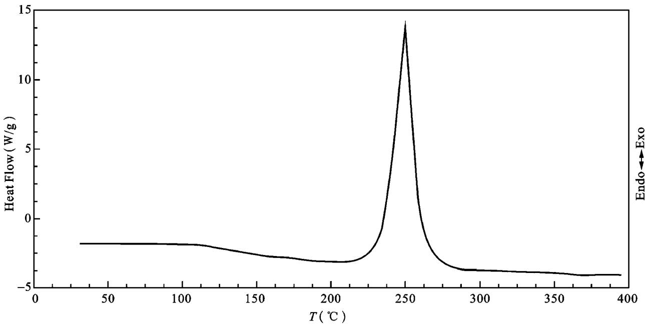

Figure 2. DSC curve for the title compound at a heating rate of 10 °C min^{-1}.

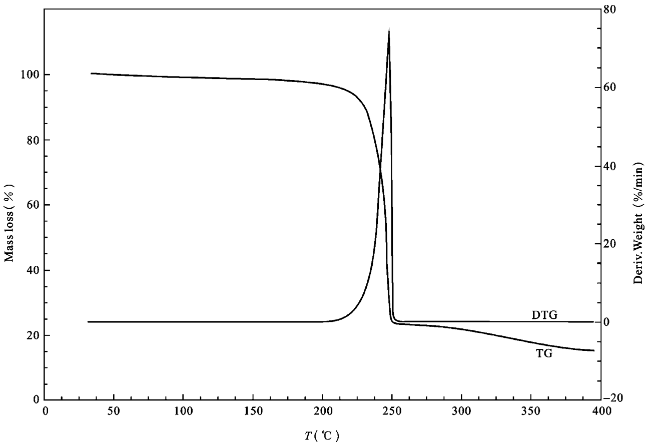

Figure 3. TG−DTG curves for the title compound at a heating rate of 10 °C min^{-1}.

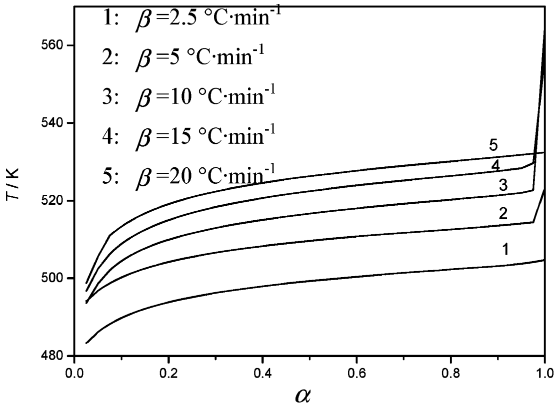

Figure 4. *T* vs α curves for the decomposition of TNPDU at different heating rates.

TABLE 1: Calculated Values of the Kinetic Parameters for the Exothermic Decomposition Reaction for the Title Compound Determined from the DSC Curves at Various Heating Rates and a Flowing Rate of N_2 Gas of 100 mL min^{-1} [a]

β (°C min^{-1})	T_e (°C)	E_{0e} (kJ mol^{-1})	r_{0e}	T_p (°C)	E_k (kJ mol^{-1})	log(A_k/s^{-1})	r_k	E_0 (kJ mol^{-1})	r_0
2.5	218.66	152.79	0.9954	230.20	142.16	12.20	0.9982	143.39	0.9985
5.0	229.38			240.98					
10.0	235.90			249.50					
15.0	241.89			256.41					
20.0	247.22			261.71					

mean: $E_0 = (152.79 + 142.16 + 143.39)/3 = 146.11$ kJ mol^{-1}

[a] 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.

°C and completes at 291.57 °C with a mass loss of 87.68% which indicates that the decomposition of TNPDU is much more complete.

3.2. Analysis of Kinetic Data for the Exothermic Main Decomposition Reaction of the Compound. In order to obtain the kinetic parameters (the apparent activation energy (E_a) and pre-exponential constant (A)) of the exothermic main decomposition reaction for the title compound, three isoconversional methods [eqs 5−7] were employed.

Differential methods.

Kissinger eq:[20]

$$\ln \frac{\beta}{T_p^2} = \ln \frac{AR}{E} - \frac{E}{RT_p} \qquad (5)$$

Integral methods.

Ozawa eq:[21]

$$\lg \beta + \frac{0.4567E}{RT} = C \qquad (6)$$

Integral isoconversional nonlinear [NL−INT] eq:[22]

$$\left| \sum_{i}^{n} \sum_{j \neq i}^{n} \frac{\beta_j I(E_\alpha, T_{\alpha,i})}{\beta_i I(E_\alpha, T_{\alpha,j})} - n(n-1) \right| = \min \qquad (7)$$

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

From the original data in Table 1, E_a obtained by the Kissinger[20] method is determined to be 142.16 kJ mol^{-1}. The pre-exponential constant (A) is $10^{12.20}$ s^{-1}. The linear correlation coefficient (r_k) is 0.9982. The value of E_o obtained by Ozawa's method[21] is 143.39 kJ mol^{-1}. The value of r_0 is 0.9985, and the value of E_{eo} obtained by T_{ei} versus β_i relation is 152.79 kJ mol^{-1}. The value of r_{eo} is 0.9954.

By substituting the original data, β_i, T_i, and α_i, $i = 1, 2, ..., n$, tabulated in Table 2 from TG−DTG curves into eq 7, the values of E_α for any given value of α were obtained in Table 2. The average value of E_α in the α range of 0.125−0.900 in Figure 5 is in good agreement with the calculated values obtained by Kissinger's method and Ozawa's method. The E values calculated using eq 7 are used to check the validity of activation energy by the other methods.

The integral eqs 8−11 and differential eq 12 are cited to obtain the values of E, A, and the most probable kinetic model function [f(α)] from a single nonisothermal TG curve.[23]

MacCallum−Tanner eq:

$$\lg[G(\alpha)] = \lg\left(\frac{AE}{\beta R}\right) - 0.4828E^{0.4357} - \frac{0.449 + 0.217E}{0.001}\frac{1}{T} \qquad (8)$$

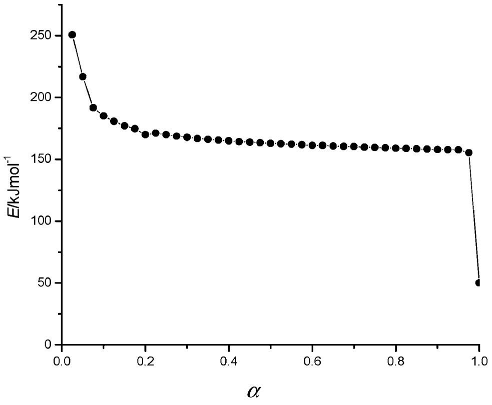

Figure 5. E_α vs α curve for the decomposition of TNPDU by NL−INT.

Satava−Sestak eq:

$$\lg[G(\alpha)] = \lg\left(\frac{A_s E_s}{\beta R}\right) - 2.315 - 0.4567\frac{E_s}{RT} \qquad (9)$$

Agrawal eq:

$$\ln\left[\frac{G(\alpha)}{T^2}\right] = \ln\left\{\frac{AR}{\beta E}\left[\frac{1 - 2\left(\frac{RT}{E}\right)}{1 - 5\left(\frac{RT}{E}\right)}\right]\right\} - \frac{E}{RT} \qquad (10)$$

The General Integral eq:

$$\ln\left[\frac{G(\alpha)}{T^2\left(1 - \frac{2RT}{E}\right)}\right] = \ln\left(\frac{AR}{\beta E}\right) - \frac{E}{RT} \qquad (11)$$

Achar−Brindley−Sharp eq:

$$\ln\left[\frac{d\alpha}{f(\alpha)dT}\right] = \ln\left(\frac{A}{\beta}\right) - \frac{E}{RT}\left(\frac{d\alpha}{dt} = \beta\frac{d\alpha}{dT}\right) \qquad (12)$$

where f(α) and G(α) are the differential model function, respectively, dα/dt is the rate of conversion, T is the temperature (K) at time t, α is the conversion degree, and R is the gas constant.

Forty-one types of kinetic model functions in ref 24 and the original data tabulated in Table 3 were put into eqs 8−12 for calculation, respectively. The kinetic parameters and the probable kinetic model function, 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}), together with their appropriate values of linear correlation coefficient (r), standard mean square deviation (Q), and believable factor (d, where $d = (1 - r)Q$), are presented in Table 4. Their values of E are very close to each other. The values of E_a and A obtained from

TABLE 2: Data of TNPDU Determined by TG at Different Heating Rates and Apparent Activation Energies (E_a) of Thermal Decomposition Obtained Using Isoconversional Methods[a]

α	$T_{2.5}$/K	T_5/K	T_{10}/K	T_{15}/K	T_{20}/K	E_α/kJ mol^{-1}
1.000	504.71	523.19	564.65	557.65	532.45	50.000
0.975	504.13	514.45	522.65	529.70	532.11	155.25
0.950	503.74	514.08	522.03	528.32	531.80	157.68
0.925	503.44	513.79	521.65	527.91	531.52	157.77
0.900	503.18	513.52	521.34	527.58	531.24	157.87
0.875	502.95	513.29	521.06	527.28	530.96	158.12
0.850	502.74	513.05	520.79	526.99	530.68	158.43
0.825	502.52	512.83	520.53	526.70	530.40	158.72
0.800	502.29	512.61	520.27	526.40	530.13	158.93
0.775	502.07	512.39	520.01	526.11	529.84	159.26
0.750	501.85	512.16	519.74	525.81	529.56	159.56
0.725	501.62	511.94	519.47	525.51	529.27	159.86
0.700	501.39	511.70	519.19	525.20	528.97	160.19
0.675	501.14	511.47	518.91	524.90	528.68	160.36
0.650	500.91	511.23	518.62	524.58	528.37	160.77
0.625	500.66	510.99	518.32	524.25	528.05	161.13
0.600	500.4	510.73	518.02	523.92	527.73	161.14
0.575	500.14	510.47	517.70	523.58	527.39	161.78
0.550	499.86	510.20	517.37	523.21	527.04	162.15
0.525	499.58	509.91	517.03	522.85	526.68	162.51
0.500	499.29	509.62	516.68	522.46	526.31	162.94
0.475	498.98	509.32	516.31	522.05	525.91	163.40
0.450	498.65	508.99	515.91	521.61	525.50	163.84
0.425	498.31	508.65	515.49	521.16	525.06	164.35
0.400	497.95	508.29	515.05	520.68	524.59	164.93
0.375	497.57	507.91	514.59	520.17	524.10	165.52
0.350	497.15	507.50	514.09	519.61	523.57	166.13
0.325	496.71	507.06	513.55	519.02	523.00	166.83
0.300	496.24	506.59	512.97	518.37	522.37	167.74
0.275	495.72	506.07	512.33	517.66	521.68	168.70
0.250	495.16	505.51	511.62	516.88	520.92	169.87
0.225	494.53	504.88	510.84	516.00	520.08	171.14
0.200	493.84	504.19	509.95	514.99	519.13	169.87
0.175	493.04	503.41	508.90	513.85	518.04	174.71
0.150	492.13	502.51	507.71	512.51	516.77	177.14
0.125	491.08	501.47	506.27	510.90	515.21	180.69
0.100	489.79	500.23	504.44	508.87	513.36	184.99
0.075	488.19	498.72	502.05	506.20	510.92	191.66
0.050	486.16	496.78	498.68	502.50	505.61	216.70
0.025	483.29	494.11	493.62	496.74	498.75	250.69

mean in the range of 0.125−0.900 164.33 kJ mol^{-1}

[a] T with the subscript 2.5, 5, 10, 15, 20 were the temperatures obtained at the heating rates of 2.5, 5, 10, 15, 20 °C min^{-1}, respectively.

a single nonisothermal 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 Avrami−Erofeev equation $f(\alpha) = 3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$. Substituting $f(\alpha)$ with $3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$, E with 141.72 kJ mol^{-1}, and A with $10^{11.99}$ s^{-1} in eq 13, the kinetic equation of the exothermic

$$d\alpha/dT = \frac{A}{\beta} f(\alpha) e^{-E/RT} \qquad (13)$$

decomposition reaction may be described as $d\alpha/dT = (10^{12.47}/\beta)(1-\alpha)[-\ln(1-\alpha)]^{2/3} \exp(-1.704 \times 10^4/T)$.

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 14 taken from ref 23 are 206.29 and 217.75 °C, respectively.

$$T_{\text{e or p}} = T_{\text{eo or po}} + a\beta_i + b\beta_i^2 + c\beta_i^3, \quad i = 1\sim5 \qquad (14)$$

where a, b, and c are coefficients.

The corresponding critical temperatures of thermal explosion (T_b) obtained from eq 15 taken from ref 25 are 219.54 and 232.58 °C, respectively.

$$T_b = \frac{E_o - \sqrt{E_o^2 - 4E_oRT_{\text{eo or po}}}}{2R} \qquad (15)$$

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

The entropy of activation ($\Delta S^\ddagger$), enthalpy of activation ($\Delta H^\ddagger$), and free energy of activation ($\Delta G^\ddagger$) corresponding to $T = T_{pdo}$, $E_a = E_k$, and $A = A_k$ obtained by eqs 16−18 are −15.50 J mol^{-1} K^{-1}, 147.65 kJ mol^{-1}, and 155.26 kJ mol^{-1}, respectively.

$$A = \frac{k_BT}{h} e^{\Delta S^\ddagger/R} \qquad (16)$$

$$A \exp(-E_a/RT) = \frac{kT}{h} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \exp\left(-\frac{\Delta H^\ddagger}{RT}\right) \qquad (17)$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \qquad (18)$$

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

3.3. IR Frequencies and NMR Chemical Shifts. Vibrational frequencies were calculated after stationary points were located in order to ascertain that the structure obtained corresponds to a minimum on the potential energy surface. In the result of frequency calculation, there is no imaginary frequency which indicates that our optimized geometry is the stable one. To verify the suitability of the basis set we used, single-point calculations were further carried out with the aug-cc-pvdz basis set. The total energy calculated with the 6-311++G** basis set is −1383.08218 hartree and that with the aug-cc-pvdz basis set is

TABLE 3: Data of the Title Compound Determined by TG−DTG

data point	T_i/K	α	dα/dT/× 10^3 K^{-1}	data point	T_i/K	α	dα/dT/× 10^3 K^{-1}
$\beta = 2.5$ °C min^{-1}; $T_o = 478.96$ K							
1	491.08	0.125	2.068	17	499.58	0.525	7.431
2	492.13	0.150	2.454	18	499.86	0.550	7.518
3	493.04	0.175	2.849	19	500.14	0.575	7.562
4	493.84	0.200	3.251	20	500.4	0.600	7.587
5	494.53	0.225	3.630	21	500.66	0.625	7.568
6	495.16	0.250	4.055	22	500.91	0.650	7.527
7	495.72	0.275	4.440	23	501.14	0.675	7.439
8	496.24	0.300	4.803	24	501.39	0.700	7.342
9	496.71	0.325	5.191	25	501.62	0.725	7.203
10	497.15	0.350	5.547	26	501.85	0.750	7.063
11	497.57	0.375	5.890	27	502.07	0.775	6.918
12	497.95	0.400	6.197	28	502.29	0.800	6.748
13	498.31	0.425	6.519	29	502.52	0.825	6.527
14	498.65	0.450	6.804	30	502.74	0.850	6.324
15	498.98	0.475	7.048	31	502.95	0.875	6.102
16	499.29	0.500	7.248	32	503.18	0.900	5.864
$\beta = 5$ °C min^{-1}; $T_o = 490.05$ K							
1	501.47	0.125	2.332	17	509.91	0.525	8.096
2	502.51	0.150	2.731	18	510.20	0.550	8.205
3	503.41	0.175	3.159	19	510.47	0.575	8.259
4	504.19	0.200	3.581	20	510.73	0.600	8.274
5	504.88	0.225	4.022	21	510.99	0.625	8.236
6	505.51	0.250	4.45	22	511.23	0.650	8.181
7	506.07	0.275	4.855	23	511.47	0.675	8.121
8	506.59	0.300	5.307	24	511.70	0.700	7.977
9	507.06	0.325	5.679	25	511.94	0.725	7.854
10	507.50	0.350	6.117	26	512.16	0.750	7.697
11	507.91	0.375	6.495	27	512.39	0.775	7.504
12	508.29	0.400	6.843	28	512.61	0.800	7.333
13	508.65	0.425	7.168	29	512.83	0.825	7.076
14	508.99	0.450	7.459	30	513.05	0.850	6.906
15	509.32	0.475	7.714	31	513.29	0.875	6.619
16	509.62	0.500	7.924	32	513.52	0.900	6.356
$\beta = 10$ °C min^{-1}; $T_o = 484.0$ K							
1	506.27	0.125	1.204	17	517.03	0.525	5.2
2	507.71	0.150	1.473	18	517.37	0.550	5.327
3	508.90	0.175	1.751	19	517.70	0.575	5.424
4	509.95	0.200	2.035	20	518.02	0.600	5.472
5	510.84	0.225	2.332	21	518.32	0.625	5.492
6	511.62	0.250	2.587	22	518.62	0.650	5.465
7	512.33	0.275	2.867	23	518.91	0.675	5.42
8	512.97	0.300	3.15	24	519.19	0.700	5.341
9	513.55	0.325	3.42	25	519.47	0.725	5.244
10	514.09	0.350	3.667	26	519.74	0.750	5.108
11	514.59	0.375	3.927	27	520.01	0.775	4.993
12	515.05	0.400	4.179	28	520.27	0.800	4.836
13	515.49	0.425	4.397	29	520.53	0.825	4.676
14	515.91	0.450	4.626	30	520.79	0.850	4.503
15	516.31	0.475	4.847	31	521.06	0.875	4.301
16	516.68	0.500	5.025	32	521.34	0.900	4.086
$\beta = 15$ °C min^{-1}; $T_o = 485.5$ K							
1	510.90	0.125	1.381	17	522.85	0.525	6.08
2	512.51	0.150	1.676	18	523.21	0.550	6.264
3	513.85	0.175	1.992	19	523.58	0.575	6.459
4	514.99	0.200	2.316	20	523.92	0.600	6.549
5	516.00	0.225	2.644	21	524.25	0.625	6.593
6	516.88	0.250	2.973	22	524.58	0.650	6.594
7	517.66	0.275	3.321	23	524.90	0.675	6.557
8	518.37	0.300	3.645	24	525.20	0.700	6.468
9	519.02	0.325	3.932	25	525.51	0.725	6.326
10	519.61	0.350	4.246	26	525.81	0.750	6.189
11	520.17	0.375	4.551	27	526.11	0.775	6.027
12	520.68	0.400	4.843	28	526.40	0.800	5.821
13	521.16	0.425	5.12	29	526.70	0.825	5.576
14	521.61	0.450	5.382	30	526.99	0.850	5.354
15	522.05	0.475	5.632	31	527.28	0.875	5.112
16	522.46	0.500	5.867	32	527.58	0.900	4.778

TABLE 3 (Continued)

data point	T_i/K	α	dα/dT/× 10^3 K^{-1}	data point	T_i/K	α	dα/dT/× 10^3 K^{-1}
			$\beta = 20$ °C min^{-1}; $T_o = 480.97$ K				
1	515.21	0.125	1.433	17	526.31	0.525	5.970
2	516.77	0.150	1.749	18	526.68	0.550	6.187
3	518.04	0.175	2.066	19	527.04	0.575	6.385
4	519.13	0.200	2.366	20	527.39	0.600	6.562
5	520.08	0.225	2.690	21	527.73	0.625	6.709
6	520.92	0.250	3.019	22	528.05	0.650	6.822
7	521.68	0.275	3.350	23	528.37	0.675	6.898
8	522.37	0.300	3.675	24	528.68	0.700	6.937
9	523.00	0.325	3.995	25	528.97	0.725	6.940
10	523.57	0.350	4.344	26	529.27	0.750	6.905
11	524.10	0.375	4.648	27	529.56	0.775	6.840
12	524.59	0.400	4.938	28	529.84	0.800	6.687
13	525.06	0.425	5.218	29	530.13	0.825	6.549
14	525.50	0.450	5.483	30	530.40	0.850	6.399
15	525.91	0.475	5.733	31	530.68	0.875	6.225
16	515.21	0.500	1.433	32	530.96	0.900	6.033

TABLE 4: Calculated Values of Kinetic Parameters of Decomposition Reaction for the Title Compound

β/°C min^{-1}	eq	mech funct no.	E/kJ mol^{-1}	log(A/s^{-1})	r	Q	d
2.5	8	11	151.09	13.22	0.99314	5.45×10^{-3}	3.74×10^{-5}
	9	11	150.84	13.23	0.99314	5.45×10^{-3}	3.74×10^{-5}
	10	11	150.35	13.19	0.992393	2.88×10^{-2}	2.19×10^{-4}
	11	11	150.35	13.19	0.992393	2.88×10^{-2}	2.19×10^{-4}
	12	11	141.20	10.81	0.969575	0.105269	3.20×10^{-3}
5	8	11	158.68	13.98	0.993289	5.33×10^{-3}	3.58×10^{-5}
	9	11	158.00	13.95	0.993289	5.33×10^{-3}	3.58×10^{-5}
	10	11	157.70	13.93	0.992579	2.82×10^{-2}	2.09×10^{-4}
	11	11	157.70	13.93	0.992579	2.82×10^{-2}	2.09×10^{-4}
	12	11	158.45	12.48	0.974323	0.101252	2.60×10^{-3}
10	8	11	129.92	11.06	0.990992	7.15×10^{-3}	6.44×10^{-5}
	9	11	130.85	11.21	0.990992	7.15×10^{-3}	6.44×10^{-5}
	10	11	129.04	11.02	0.989813	3.78×10^{-2}	3.85×10^{-4}
	11	11	129.04	11.02	0.989813	3.78×10^{-2}	3.85×10^{-4}
	12	11	159.85	12.49	0.988219	6.72×10^{-2}	7.91×10^{-4}
15	8	11	119.44	10.00	0.990486	7.55×10^{-3}	7.18×10^{-5}
	9	11	120.95	10.23	0.990486	7.55×10^{-3}	7.18×10^{-5}
	10	11	118.55	9.96	0.989116	3.98×10^{-2}	4.34×10^{-4}
	11	11	118.55	9.96	0.989116	3.98×10^{-2}	4.34×10^{-4}
	12	11	157.31	12.28	0.990102	6.37×10^{-2}	6.31×10^{-4}
20	8	11	126.45	10.75	0.990739	7.35×10^{-3}	6.81×10^{-5}
	9	11	127.57	10.93	0.990739	7.35×10^{-3}	6.81×10^{-5}
	10	11	125.44	10.70	0.989468	3.88×10^{-3}	4.09×10^{-4}
	11	11	125.44	10.70	0.989468	3.88×10^{-3}	4.09×10^{-4}
	12	11	190.17	15.45	0.977462	0.194435	4.38×10^{-3}
	mean		141.72	11.99			

−1382.8956738 hatree which indicates that the results are not greatly affected by basis set size.

From the Table 5 and the optimized geometry (Figure 1), one can conclude that the whole molecules are not coplanar but rotationally symmetric about the atom of C14. However, N1, C2, O7, N9, C11 and N3, C4, O8, N17, C6 are almost coplanar.

On the basis of the simple harmonic oscillator analysis, $3N - 6$ (the number of atom is 27) frequencies and intensities of 75 frequencies were obtained; only those larger than 400 cm^{-1} are listed in Table 6. The scaled IR frequencies were calibrated by multiplying 0.96. For the complexity of vibrational mode, it is difficult to assign all bands, so we have only analyzed some typical vibrational modes comparing with those of the experimental. The theoretical value at 2966 and 3023 cm^{-1} caused by the C−H stretching vibration is in agreement with that of the experimental (3000 cm^{-1}). The asymmetric characteristic absorption peaks of $C-NO_2$ are found to be at 1610, 1613 cm^{-1}, relevant to those of the experimental of 1620 cm^{-1}. The symmetric stretching vibration of $-NO_2$ is found to be at 1243 cm^{-1} which is consistent with the experimental value of 1290 cm^{-1}. The experimental stretching vibrations of the carbonyl are at 1700 cm^{-1} which are found to be 1644 and 1764 cm^{-1} in the theoretical calculation.

Through the NMR calculation, we got four data of chemical shifts of ^1H, which are listed in Table 7. In comparison with the corresponding experimental values, the calculated results derivate slightly because the theoretical properties were calculated based on the gas phase.

3.4. Heat of Formation and Detonation Properties. The HOF of $HCONHNO_2$ and NH_2NO_2 calculated by G3 theory are −114.99 and 6.22 kJ mol^{-1}, respectively. On the basis of the energy properties of the reference compounds listed in Table 8 and the isodesmic reaction 1, the HOF of TNPDU obtained with the B3LYP/6-311++G** method is 91.56 kJ mol^{-1}.

The calculated density (ρ) of the title compound was 1.999 g cm^{-3} which is consistent with the experimental value of 1.98 g cm^{-3}.[27] Therefore, the calculated detonation velocities (D) and detonation pressure (P) are 9355 m s^{-1} and 38.81Gpa, respectively. The experimental detonation velocity correspond-

TABLE 5: Calculated Non-Hydrogen Bond Lengths (in Å), Bond Angles (in Deg), and Dihedrals (in Deg)

bonds	length/Å	bonds	length/Å
N1−C2	1.413	N3−C4	1.413
N1−C6	1.464	N3−C11	1.464
N1−N10	1.484	N3−N13	1.484
C2−O7	1.193	C4−O8	1.193
C2−N9	1.425	C4−N5	1.425
C6−C14	1.519	C11−C14	1.519
N9−C11	1.469	N5−C6	1.469
N9−N12	1.451	N5−N17	1.451
N10−O22	1.210	N13−O15	1.210
N10−O23	1.196	N13−O16	1.196
N17−O18	1.218	N12−O21	1.218
N17−O19	1.199	N12−O20	1.199

bonds	bond angles/deg	bonds	bond angles/deg
C2−N1−C6	126.7	C4−N3−C11	126.7
C2−N1−N10	114.4	C4−N3−N13	114.4
C6−N1−N10	115.8	C11−N3−N13	115.8
N1−C2−O7	123.5	N3−C4−O8	123.5
N1−C2−N9	111.5	N3−C4−N5	111.5
O7−C2−N9	125.0	N5−C4−O8	125.0
N1−C6−N5	112.8	N3−C11−N9	112.8
C4−N5−C6	123.7	C2−N9−C11	123.7
C2−N9−N12	119.1	C4−N5−N17	119.0
N1−C6−C14	109.3	N3−C11−C14	109.3
N9−N12−O21	113.7	C5−N17−O18	113.7
N5−C6−C14	106.9	N9−C11−C14	106.9
O18−N17−O19	128.2	O20−N12−O21	128.2
N9−N12−O20	118.0	C5−N17−O19	118.0
O22−N10−O23	129.5	O15−N13−O16	129.5
N1−N10−O23	115.9	N3−N13−O15	114.6
C6−N5−N17	115.6	C11−N9−N12	115.6
N1−N10−O22	114.6	N3−N13−O16	115.9
C6−C14−C11	105.5		

bonds	dihedrals/ deg	bonds	dihedrals/ deg
C6−N1−C2−O7	−169.0	C11−N3−C4−O8	−169.0
C6−N1−C2−O9	10.7	C11−N3−C4−N5	10.7
N10−N1−C2−O7	−9.9	N13−N3−C4−O8	−9.9
N10−N1−C2−O9	169.7	N13−N3−C4−N5	169.7
C2−N1−C6−N5	−100.1	C4−N3−C11−O9	−100.1
C2−N1−C6−C14	18.6	C4−N3−C11−C14	18.6
N10−N1−C6−N5	101.1	N13−N3−C11−O9	101.1
N10−N1−C6−C14	−140.1	N13−N3−C11−C14	−140.1
C2−N1−N10−O22	−120.0	C4−N3−N13−O15	−120.0
C2−N1−N10−O23	60.4	C4−N3−N13−O16	60.4
C6−N1−N10−O22	41.4	C11−N3−N13−O15	41.4
C6−N1−N10−O23	−138.1	C11−N3−N13−O16	−138.1
N1−C2−O9−C11	0.9	N3−C4−N5−C6	0.9
N1−C2−O9−N12	165.9	N3−C4−N5−N17	165.9
O7−C2−O9−C11	−179.5	O8−C4−N5−C6	−179.4
O7−C2−O9−N12	−14.4	O8−C4−N5−N17	−14.4
C4−N5−C6−N1	80.5	C2−O9−C11−N3	80.5
C4−N5−N17−O18	−151.2	C2−O9−N12−O21	−151.2
C4−N5−C6−C14	−39.7	C2−O9−C11−C14	−39.7
C4−N5−N17−O19	30.7	C2−O9−N12−O20	30.6
C6−N5−N17−O18	15.0	C11−O9−N12−O21	15.0
C6−N5−N17−O19	−163.2	C11−O9−N12−O20	−163.2
N17−N5−C6−C14	154.9	N12−O9−C11−C14	154.9
N1−C6−C14−C11	−56.4	N3−C11−C14−C6	−56.4
N5−C6−C14−C11	66.0	O9−C11−C14−C6	66.0
N17−N5−C6−N1	−85.0	N12−O9−C11−N3	−85.0

ing to ρ =1.93 g cm^{-3} is 9034 m s^{-1}. This indicates that the K−J formula is suitable for evaluation the detonation properties of this kind of material.

3.5. Pyrolysis Mechanism. The dissociation energy (E) for each possible trigger bond is often a key factor in investigating the pyrolysis mechanism for an energetic compound. Generally, the smaller the E for breaking a bond is, the more easily the bond is broken. To break the bond will be the initial step during the thermolysis process. To elucidate the pyrolysis mechanism and thermal stability of TNPDU, we calculated the dissociation energies for three possible initial steps in the pyrolysis route: (1) breaking the N−N bond, (2) breaking the C−C bond, and (3) breaking the ring C−N bond on the skeleton (Table 9).

TABLE 6: Scaled IR Frequencies (cm^{-1}) for the Title Compound

υ/cm^{-1}	I/km mol^{-1}	exptl/cm^{-1}	υ/cm^{-1}	I/km mol^{-1}	exptl/cm^{-1}
425	31.3		1043	1.0	
439	9.4		1062	25.9	
448			1068	706.7	
511	1.9		1139	132.1	
527	3.9		1162	306.4	
563	7.9		1191	7.4	
606	0.2		1201	4.5	
613	11.4		1243	906.5	1290
635	5.3		1253	12.9	
665	63. 5		1261	69.4	
681	52.2		1273	0.1	
690	17.0		1311	21.6	
703	91.2		1317	9.6	
717	1.7		1337	14.0	
726	15.9		1353	1.4	
735	33.8		1373		
738	26.9		1427	12.5	
780	2.4		1610	5.0	1620
803	60.5		1613	421.8	1620
806	3.6		1644	470.4	1700
834	21.5		1644	56.8	
843	618.7		1764	830.2	1700
905	159.3		1773	242.7	
942	9.5		2966	0.8	3000
994	372.4		3018	1.2	
1010	11.7		3021	19.6	
1022	0.2		3023	0.1	3000

TABLE 7: ^{1}HNMR Chemical Shifts (ppm)

NMR chemical shifts	calcd/ppm	exptl/ppm
$\delta_{(H24)}$	7.09	7.81
$\delta_{(H25)}$	7.10	7.81
$\delta_{(H26)}$	2.48	3.57
$\delta_{(H27)}$	2.48	3.57

TABLE 8: Total Energies (E_0), Zero-Point Energies (ZPE), Thermal Corrections(H_T^0), and HOFs for the Compounds at the B3LYP/6-311++G Level**

compd	E_0 (au)	ZPE (au)	H_T^0 (au)	HOF/kJ mol^{-1}
CH_4	−40.533956	0.044544	0.048357	−74.4
$HCONHNO_2$	−374.4829221	0.047888	0.054531	−114.99
NH_3	−56.5827214	0.034257	0.038075	−45.94
CH_3NH_2	−95.8938887	0.063793	0.068176	−22.529[a]
NH_2NO_2	−261.1249351	0.039188	0.043829	6.22
TNPDU	−1383.0821805	0.156697	0.176835	91.56

[a] Ref 26.

TABLE 9: Dissociation Energies for TNDPU at the B3LYP/6-31G Level (kJ mol^{-1})

compd	E_{C-N}	E_{N-N}	E_{C-N}
TNPDU	318.61	163.68	346.78

Comparing E_{C-N} with E_{N-N} and E_{C-C}, we found that E_{N-N} is the smallest, which predicts that the N−N bond should be the trigger bond during the thermolysis initiation process. The dissociation energy for N−N is 163.68 kJ mol^{-1}, a little larger than that of the apparent activation energy (141.72 kJ mol^{-1}) calculated from the nonisothermal investigation on the decomposition.

4. Conclusion

(1) The kinetics of the exothermic decomposition reaction kinetics of the title compound has been investigated, and the kinetic model function in differential form, apparent activation energy, and pre-exponential constant of this reaction are $f(\alpha)$

$= 3(1 - \alpha)[-\ln(1 - \alpha)]^{2/3}$, 141.72 kJ mol^{-1}, and $10^{11.99}$ s^{-1}, respectively.

(2) The calculated HOF of TNPDU is 91.56 kJ mol^{-1}, and the calculated detonation velocities (D) and detonation pressure (P) are 9355 m s^{-1} and 38.81 GPa, respectively.

(3) The calculations on bond dissociation energies suggested that the N−N bond is the trigger bond during the thermolysis initiation process.

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