*Chinese Journal of Chemistry*, **2004**, *22*, 1078—1082 **Article**

# Thermal Decomposition Kinetics of Triethylene Glycol Dinitrate

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The thermal behavior and kinetic parameters of the decomposition reaction of triethylene glycol dinitrate (TEGDN) in a temperature-programmed mode at different pressures (0.1, 2, 4 and 6 MPa) have been investigated by means of DSC and TG-DTG. The results show that the properties of the thermal decomposition of TEGDN are affected by the change of pressure, and the kinetic model function, the apparent activation energy $E_a$ and pre-exponential factor $A$ of this reaction are $2(1-\alpha)\left[-\ln(1-\alpha)\right]^{\frac{1}{2}}$, 106.54 kJ•mol$^{-1}$ and $10^{9.17}$ s$^{-1}$ at 0.1 MPa, and 120.82 kJ•mol$^{-1}$ and $10^{10.56}$ s$^{-1}$ at 2 MPa, respectively. The critical temperature of thermal explosion of TEGDN obtained by the values $T_{eo}$ and $T_{po}$ of the onset temperature $T_e$ and the peak temperature $T_P$ when the heating rate tends to zero are 191.05, 209.86 ℃ at 0.1 MPa, 207.59 and 221.65 ℃ at 2 MPa, respectively.

**Keywords** triethylene glycol dinitrate, DSC, non-isothermal kinetics, TG-DTG, thermal decomposition

## Introduction

Triethylene glycol dinitrate (TEGDN) is a novel energetic material containing two groups of —$NO_2$, which can be used as an energetic plasticizer ingredient in propellants because of its excellent proformance.[1] It exhibits lower impact sensitivity, better thermostability, weaker poisonousness and volatility, and stronger effectiveness of plasticizing cellulose nitrate than nitroglycerine (NG). As a new plasticizer TEGDN has good application prospects in the near future. Thermal behavior is one of the most important aspect of TEGDN in practical application. However, its thermal behavior and kinetic parameters of thermal decomposition have never been reported before. The aim of this work is to study its thermal behavior and kinetic parameters of the thermal decomposition reaction at different pressures (0.1, 2, 4 and 6 MPa) by DSC and TG-DTG. This is quite useful in the evaluation of its thermal stability under non-isothermal condition and in the study of its thermal changes at high temperature and different pressures.

## Experimental

### Material

TEGDN was prepared by Xi'an Modern Chemistry Research Institute, and its purity is more than 99.5%. The sample was kept in a vacuum desiccator before use. Its structure was characterized by IR and MS. IR (KBr) $\nu$: 1631, 1282, 1131, 1029 cm$^{-1}$; MS (70 eV) $m/z$: 46 ($NO_2^+$), 73($CH_2\overset{+}{O}CH_2CHO$).

### Equipment and conditions

The thermal decomposition experiment was carried out by a model DSC190S differential scanning calorimeter made in American TA Company. The conditions of DSC were as follows: sample mass, less than 2.00 mg; heating rate, 5, 10, 20, 30 and 40 ℃•min$^{-1}$; atmosphere, static nitrogen; reference sample, aluminum oxide. The TG/DTG curve was obtained using a model TGA2950 thermobalance. The conditions of TG were as follows: sample mass, less than 1.00 mg; heating rate, 10 ℃•min$^{-1}$; atmosphere, flowing $N_2$ gas, 50 mL•min$^{-1}$.

## Results and discussion

### Properties of the thermal decomposition of TEGDN at different pressures

The typical TG-DTG and DSC curves for the thermal decomposition of TEGDN at different pressures (0.1, 2, 4 and 6 MPa) are shown in Figures 1 and 2. From Figure 1 it can be seen that, there is only one mass loss stage between 80 and 200 ℃. After 200 ℃ the percent of the residue mass is close to zero (0.267%) and there is no change with temperature rising, showing that the decomposition of TEGDN is more completed. In Figure 2, in the scope of pressure 0.1—6 MPa, all the four DSC curves of TEGDN consist of one exothermic decomposition peak between 150 and 250 ℃. But the temperature of the peak and the enthalpy of the exothermic decomposition reaction ($\Delta H_{dec}$) are related to the pressure. At atmosphere pressure, the peak temperature $T_p$ and the onset temperature $T_e$ are 215.3

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Received March 9, 2004; revised and accepted June 22, 2004
Project supported by the Science and Technology Foundation of the National Defense Key Laboratory of Propellant and Explosive Combustion of China (No. 51455030101ZS3505).

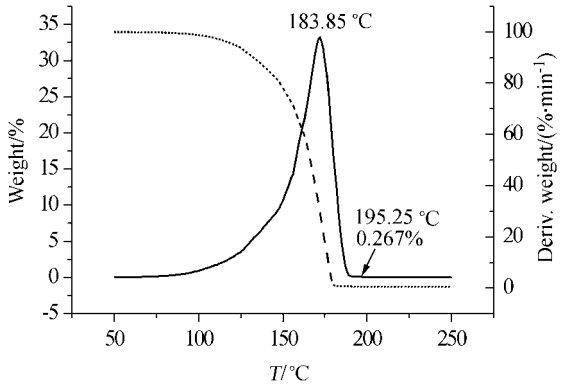


**Figure 1** TG and DTG curves for TEGDN at a heating rate of 10 ℃•min$^{-1}$.

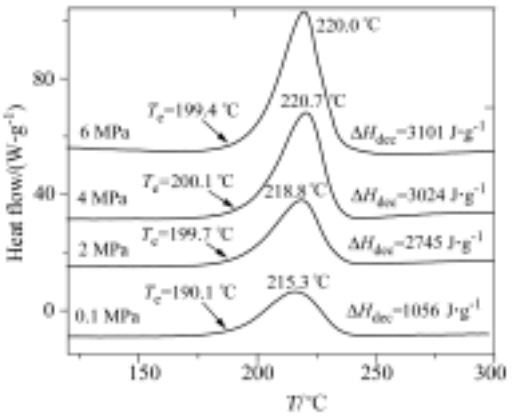


**Figure 2** DSC curves for TEGDN at a heating rate of 10 ℃•min$^{-1}$.

and 190.1 ℃, respectively, and the enthalpy of the exothermic decomposition ($\Delta H_{dec}$) is 1056 J•g$^{-1}$. When the pressure rises from 0.1 to 2 MPa, $T_P$ shifts 3.5 ℃ upwards and $\Delta H_{dec}$ increases 1689 J•g$^{-1}$ sharply. Once the pressure increases again, $T_P$ has little change and remains within the scope of 219—221 ℃, and the values of $\Delta H_{dec}$ at 2, 4 and 6 MPa are close with each other basically.

## Analysis of kinetic data

In order to obtain the kinetic parameters at 0.1 and 2 MPa [apparent activation energy ($E_a$) and pre-exponential constant ($A$)] of the exothermic decomposition reaction for TEGDN, a multiple heating method[2] (Kissinger's method) and Ozawa's method[3] were employed. From Table 1, it can been seen that, at 0.1 MPa, $E_o$ is very close to $E_k$, they are 112.69 and 113.98 kJ•mol$^{-1}$, respectively. At 2 MPa, the values of both are 122.99 and 120.54 kJ•mol$^{-1}$, respectively.

The integral Eqs. (1)[4] and (2),[5] differential Eq. (3)[6] 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 for TEGDN at 0.1 and 2 MPa.

$$\lg[G(\alpha)]=\lg\left(\frac{AE_a}{\beta R}\right)-2.315-0.4567\frac{E_a}{RT} \qquad (1)$$

**Table 1** Calculated values of the kinetic parameters for the exothermic decomposition reaction of TEGDN determined from the DSC curves at various heating rates [a]

| $\beta$/(℃•min$^{-1}$) | $T_e$/℃ | $E_o$/(kJ•mol$^{-1}$) | $r_o$ | $T_p$/℃ | $E_k$/(kJ•mol$^{-1}$) | log $A_k$ ($A_k$ in s$^{-1}$) | $r_k$ | $E_o$ /(kJ•mol$^{-1}$) | $r_o$ | $T_{eo}$/℃ | $T_b$[b]/℃ | $T_{po}$/℃ | $T_b$[c]/℃ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.1 MPa | | | | | | | | | | | | | |
| 10.0 | 189.78 | 109.09 | 0.9887 | 215.34 | 113.98 | 10.17 | 0.9889 | 116.29 | 0.9903 | 174.28 | 191.05 | 192.84 | 209.86 |
| 20.0 | 199.91 | | | 228.38 | | | | | | | | | |
| 30.0 | 204.67 | | | 231.96 | | | | | | | | | |
| 40.0 | 212.99 | | | 239.55 | | | | | | | | | |
| Mean: $E_o$=(109.09+116.29)/2=112.69 kJ•mol$^{-1}$ | | | | | | | | | | | | | |
| 2 MPa | | | | | | | | | | | | | |
| 5.0 | 190.15 | 123.44 | 0.9969 | 210.87 | 120.54 | 10.74 | 0.9985 | 122.54 | 0.9987 | 191.82 | 207.59 | 204.76 | 221.65 |
| 10.0 | 199.64 | | | 220.01 | | | | | | | | | |
| 20.0 | 207.77 | | | 231.38 | | | | | | | | | |
| 30.0 | 216.21 | | | 238.87 | | | | | | | | | |
| 40.0 | 220.65 | | | 244.18 | | | | | | | | | |
| Mean: $E_o$=(123.44+122.54)/2=122.99 kJ•mol$^{-1}$ | | | | | | | | | | | | | |

[a] $\beta$, heating rate; $T_e$, onset temperature in the DSC curve; $T_p$, maximum peak temperature; $T_{e0}$, the value of the onset temperature ($T_e$) corresponding to $\beta\rightarrow 0$ obtained by Eq. (4); $T_b$, critical temperature of thermal explosion; $E$, apparent activation energy; $A$, pre-exponential constant; $r$, linear correlation coefficient; subscript $k$ for data obtained by Kissinger's method; subscript o for data obtained by Ozawa's method. [b] The value of $T_b$ obtained by the value of $T_{e0}$ in Eq. (5). [c] The value of $T_b$ obtained by the value of $T_{p0}$ in Eq. (5).

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

$$\ln\frac{dH}{dt}=\ln\left\{AH_0 f(\alpha)\left[1+\frac{E_a}{RT}\left(1-\frac{T_0}{T}\right)\right]\right\}-\frac{E_a}{RT} \quad (3)$$

where $f(\alpha)$ and $G(\alpha)$ are the differential and integral model function, respectively, $T_0$ the initial point at which DSC curve deviates from the baseline, $R$ the gas constant, $\alpha$ the conversion degree ($\alpha=H_t/H_0$), $H_0$ 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 at time $t$, $\frac{d\alpha}{dT}=\frac{1}{H_0\beta}\frac{dH}{dt}=\frac{1}{\beta}\frac{d\alpha}{dt}$. Forty-one types of kinetic model function[7] and DSC data with different heating rate of 2, 5, 10 and 20 ℃•min$^{-1}$ at 0.1 and 2 MPa such as DSC data listed in Tables 2 and 3, respectively, were put into Eqs. (1), (2) and (3) for calculation, respectively. The values of $E_a$, $A$, correlation coefficient $r$, 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 results are listed in Table 4. The probable kinetic model function of three methods selected by the better values of $r$, $Q$ and $d$ and satisfying ordinary range of the thermal decomposition kinetic parameters for energetic materials ($E$=80—250 kJ•mol$^{-1}$ and log $A$=7—30) are $G(\alpha)=[-\ln(1-\alpha)]^{\frac{1}{2}}$ and $f(\alpha)=2(1-\alpha)\cdot[-\ln(1-\alpha)]^{\frac{1}{2}}$, respectively, which indicates that the reaction mechanism of the exothermic decomposition processes of TEGDN at 0.1 and 2 MPa is classified as nucleation and growth, and the mechanism function is the Avrami-Erofeev equation with $n$=1/2.

Under the condition of 0.1 MPa, the values ($T_{e0}$ and $T_{p0}$) of the onset temperature $T_e$ and the peak temperature $T_p$ corresponding to $\beta\to0$ obtained by Eq. (4) taken from Ref. 8 using the data of $T_e$, $T_p$ and $\beta$ in Table 1 are 174.28 and 192.84 ℃, respectively. At 2 MPa, $T_{eo}$ and $T_{po}$ are 191.82 and 204.76 ℃, respectively.

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

where $b$ and $c$ are coefficients.

At 0.1 MPa, the values of the critical temperature of thermal explosion ($T_b$) obtained from Eq. (5) taken from Ref. 8 using the above-mentioned values of $T_{e0}$ and $T_{p0}$, and the value of $E_o$ in Table 1 are 190.68 ℃ and 209.49 ℃, respectively. At 2 MPa, they are 224.25 ℃ and 239.48 ℃, respectively.

**Table 2** Basic data of the exothermic decomposition process of TEGDN determined by DSC[a] at 0.1 MPa [a]

| Data point | $T_i$/K | $\alpha_i$ | $(dH/dt)_i$/(mJ•s$^{-1}$) | $(d\alpha/dT)_i$ ×10$^3$/K$^{-1}$ |
|---|---|---|---|---|
| 1 | 433.15 | 0.0002 | 0.066 | 0.16 |
| 2 | 435.15 | 0.0005 | 0.097 | 0.24 |
| 3 | 437.15 | 0.0009 | 0.127 | 0.31 |
| 4 | 439.15 | 0.0014 | 0.174 | 0.43 |
| 5 | 441.15 | 0.0023 | 0.312 | 0.78 |
| 6 | 443.15 | 0.0037 | 0.353 | 0.87 |
| 7 | 445.15 | 0.0050 | 0.348 | 0.86 |
| 8 | 447.15 | 0.0063 | 0.382 | 0.94 |
| 9 | 449.15 | 0.0079 | 0.500 | 1.23 |
| 10 | 451.15 | 0.0102 | 0.687 | 1.70 |
| 11 | 453.15 | 0.0136 | 0.954 | 2.36 |
| 12 | 455.15 | 0.0182 | 1.182 | 2.92 |
| 13 | 457.15 | 0.0242 | 1.498 | 3.70 |
| 14 | 459.15 | 0.0316 | 1.765 | 4.36 |
| 15 | 461.15 | 0.0400 | 2.036 | 5.03 |
| 16 | 463.15 | 0.0494 | 2.323 | 5.74 |
| 17 | 465.15 | 0.0606 | 2.900 | 7.17 |
| 18 | 467.15 | 0.0749 | 3.654 | 9.03 |
| 19 | 469.15 | 0.0932 | 4.554 | 11.26 |
| 20 | 471.15 | 0.1160 | 5.605 | 13.85 |
| 21 | 473.15 | 0.1442 | 6.776 | 16.75 |
| 22 | 475.15 | 0.1783 | 8.039 | 19.87 |
| 23 | 477.15 | 0.2185 | 9.361 | 23.14 |
| 24 | 479.15 | 0.2644 | 10.539 | 26.05 |
| 25 | 481.15 | 0.3155 | 11.650 | 28.80 |
| 26 | 483.15 | 0.3713 | 12.769 | 31.56 |
| 27 | 485.15 | 0.4333 | 13.716 | 33.91 |
| 28 | 487.15 | 0.4996 | 14.306 | 35.36 |
| 29 | 489.15 | 0.5691 | 14.453 | 35.73 |
| 30 | 491.15 | 0.6389 | 14.127 | 34.92 |
| 31 | 493.15 | 0.7072 | 13.287 | 32.84 |
| 32 | 495.15 | 0.7717 | 12.066 | 29.83 |
| 33 | 497.15 | 0.8288 | 10.586 | 26.17 |
| 34 | 499.15 | 0.8785 | 8.946 | 22.11 |
| 35 | 501.15 | 0.9190 | 7.163 | 17.71 |
| 36 | 503.15 | 0.9498 | 5.336 | 13.19 |
| 37 | 505.15 | 0.9714 | 3.736 | 9.23 |
| 38 | 507.15 | 0.9851 | 2.502 | 6.18 |
| 39 | 509.15 | 0.9931 | 1.602 | 3.96 |
| 40 | 511.15 | 0.9972 | 1.051 | 2.6.0 |
| 41 | 513.15 | 0.9991 | 0.766 | 1.89 |
| 42 | 515.15 | 0.9998 | 0.599 | 1.48 |

[a] $T_0$=433.2 K; $H_0$=2427.24 mJ; $\beta$=0.1667 K•s$^{-1}$.

**Table 3** Basic data of the exothermic decomposition process of TEGDN determined by DSC[a] at 2 MPa [a]

| Data point | $T_i$/K | $\alpha_i$ | $(dH/dt)_i$/(mJ•s$^{-1}$) | $(d\alpha/dT)_i$ ×10$^3$/K$^{-1}$ |
|---|---|---|---|---|
| 1 | 456.15 | 0.00004 | 0.492 | 0.2337 |
| 2 | 458.15 | 0.00005 | 0.663 | 0.3150 |
| 3 | 460.15 | 0.0002 | 0.899 | 0.4268 |
| 4 | 462.15 | 0.0004 | 1.156 | 0.5488 |
| 5 | 464.15 | 0.0008 | 1.477 | 0.7012 |
| 6 | 466.15 | 0.0014 | 1.862 | 0.8842 |
| 7 | 468.15 | 0.0024 | 2.354 | 1.1179 |
| 8 | 470.15 | 0.0037 | 2.975 | 1.4126 |
| 9 | 472.15 | 0.0055 | 3.702 | 1.7581 |
| 10 | 474.15 | 0.0080 | 4.558 | 2.1646 |
| 11 | 476.15 | 0.0112 | 5.607 | 2.6626 |
| 12 | 478.15 | 0.0152 | 6.902 | 3.2774 |
| 13 | 480.15 | 0.0204 | 8.511 | 4.0417 |
| 14 | 482.15 | 0.0271 | 10.518 | 4.9949 |
| 15 | 484.15 | 0.0353 | 13.000 | 6.1687 |
| 16 | 486.15 | 0.0456 | 16.037 | 7.6159 |
| 17 | 488.15 | 0.0581 | 19.765 | 9.3862 |
| 18 | 490.15 | 0.0732 | 24.302 | 11.5407 |
| 19 | 492.15 | 0.0913 | 29.789 | 14.1463 |
| 20 | 494.15 | 0.1125 | 36.297 | 17.2368 |
| 21 | 496.15 | 0.1370 | 43.898 | 20.8465 |
| 22 | 498.15 | 0.1652 | 52.623 | 24.9898 |
| 23 | 500.15 | 0.1969 | 62.338 | 29.6037 |
| 24 | 502.15 | 0.2324 | 72.910 | 34.6240 |
| 25 | 504.15 | 0.2720 | 83.995 | 39.8882 |
| 26 | 506.15 | 0.3168 | 95.358 | 45.2846 |
| 27 | 508.15 | 0.3680 | 106.23 | 50.4472 |
| 28 | 510.15 | 0.4297 | 115.45 | 54.8272 |
| 29 | 512.15 | 0.5122 | 119.81 | 56.9004 |
| 30 | 514.15 | 0.6661 | 103.64 | 49.2175 |
| 31 | 516.15 | 0.8812 | 42.565 | 20.2134 |
| 32 | 518.15 | 0.9305 | 26.519 | 12.5934 |
| 33 | 520.15 | 0.9544 | 18.971 | 9.0092 |
| 34 | 522.15 | 0.9689 | 14.537 | 6.9035 |
| 35 | 524.15 | 0.9784 | 11.828 | 5.6169 |
| 36 | 526.15 | 0.985 | 10.052 | 4.7734 |
| 37 | 528.15 | 0.9898 | 8.765 | 4.1626 |
| 38 | 530.15 | 0.9933 | 7.811 | 3.7094 |
| 39 | 532.15 | 0.9958 | 7.101 | 3.3720 |
| 40 | 534.15 | 0.9976 | 6.563 | 3.1169 |
| 41 | 536.15 | 0.9988 | 6.163 | 2.9268 |
| 42 | 538.15 | 0.9995 | 5.885 | 2.7947 |
| 43 | 540.15 | 0.9999 | 5.692 | 2.7033 |

[a] $T_0$=423.2 K; $H_0$=3415.06 mJ; $\beta$ =0.3333 K•s$^{-1}$.

$$T_b=\frac{E_o-\sqrt{E_o^2-4E_oRT_{e0\text{ or }p0}}}{2R} \quad (5)$$

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.

At 0.1 and 2 MPa, substituting $f(\alpha)$ with $2(1-\alpha)\cdot[-\ln(1-\alpha)]^{\frac{1}{2}}$, $E_a$ with 106.54 and 120.82 kJ•mol$^{-1}$, $\beta$ with 0.1667 K•s$^{-1}$ and $A$ with $10^{9.17}$ and $10^{10.56}$ s$^{-1}$ in Eq. (6)

$$\frac{d\alpha}{dT}=\frac{A}{\beta}f(\alpha)\exp(-E_a/RT) \quad (6)$$

we can establish the kinetic equation of the exothermic decomposition process of TEGDN as follows

at 0.1 MPa,

$$\frac{d\alpha}{dT}=10^{10.25}(1-\alpha)[-\ln(1-\alpha)]^{\frac{1}{2}}e^{-1.281\times10^4/T}$$

at 2 MPa,

$$\frac{d\alpha}{dT}=10^{11.64}(1-\alpha)[-\ln(1-\alpha)]^{\frac{1}{2}}e^{-1.453\times10^4/T}$$

## Conclusions

The kinetic equations of the exothermic decomposition processes of TEGDN at 0.1 and 2 MPa can be expressed respectively as

at 0.1 MPa,

$$\frac{d\alpha}{dT}=10^{10.25}(1-\alpha)[-\ln(1-\alpha)]^{\frac{1}{2}}e^{-1.281\times10^4/T}$$

at 2 MPa,

$$\frac{d\alpha}{dT}=10^{11.64}(1-\alpha)[-\ln(1-\alpha)]^{\frac{1}{2}}e^{-1.453\times10^4/T}$$

The apparent activation energy and pre-exponential constant of the exothermic decomposition reaction of TEGDN are 106.54 kJ•mol$^{-1}$ and $10^{9.17}$ s$^{-1}$ at 0.1 MPa, and 120.82 kJ•mol$^{-1}$ and $10^{10.56}$ s$^{-1}$ at 2 MPa, respectively. The corresponding critical temperatures of thermal explosion are 191.05 and 209.86 ℃ at 0.1 MPa, 207.59 and 221.65 ℃ at 2 MPa, respectively.

**Table 4** Calculated values of kinetic parameters of the exothermic decomposition reaction of TEGDN

| $\beta$/℃ | $G(\alpha)$ | $f(\alpha)$ | Eq. (1) | | Eq. (2) | | Eq. (3) | |
|---|---|---|---|---|---|---|---|---|
| | | | $E_a$/ (kJ•mol$^{-1}$) | log$A$ ($A$ in s$^{-1}$) | $E_a$/ (kJ•mol$^{-1}$) | log$A$ ($A$ in s$^{-1}$) | $E_a$/ (kJ•mol$^{-1}$) | Log $A$ ($A$ in s$^{-1}$) |
| 0.1 MPa | | | | | | | | |
| 10 | $[-\ln(1-\alpha)]^{\frac{1}{2}}$ | $2(1-\alpha)[-\ln(1-\alpha)]^{\frac{1}{2}}$ | 103.52[a] | 9.02[a] | 101.01[b] | 8.70[b] | 117.94[c] | 10.00[c] |
| 20 | $[-\ln(1-\alpha)]^{\frac{1}{2}}$ | $2(1-\alpha)[-\ln(1-\alpha)]^{\frac{1}{2}}$ | 117.95[d] | 10.51[d] | 115.88[e] | 10.27[e] | 111.72[f] | 9.49[f] |
| 30 | $[-\ln(1-\alpha)]^{\frac{1}{2}}$ | $2(1-\alpha)[-\ln(1-\alpha)]^{\frac{1}{2}}$ | 118.90[g] | 10.64[g] | 116.71[h] | 10.39[h] | 72.41[i] | 5.45[i] |
| 40 | $[-\ln(1-\alpha)]^{\frac{1}{2}}$ | $2(1-\alpha)[-\ln(1-\alpha)]^{\frac{1}{2}}$ | 114.10[j] | 10.12[j] | 111.61[k] | 9.83[k] | 88.69[l] | 6.99[l] |
| Mean | $E_a$=106.54 kJ•mol$^{-1}$, log $A$=9.17 | | | | | | | |
| 2 MPa | | | | | | | | |
| 10 | $[-\ln(1-\alpha)]^{\frac{1}{2}}$ | $2(1-\alpha)[-\ln(1-\alpha)]^{\frac{1}{2}}$ | 116.55[m] | 10.34[m] | 114.57[n] | 10.11[n] | 111.72[o] | 9.49[o] |
| 20 | $[-\ln(1-\alpha)]^{\frac{1}{2}}$ | $2(1-\alpha)[-\ln(1-\alpha)]^{\frac{1}{2}}$ | 118.12[p] | 10.50[p] | 116.17[q] | 10.28[q] | 117.38[r] | 9.65[r] |
| 30 | $[-\ln(1-\alpha)]^{\frac{1}{2}}$ | $2(1-\alpha)[-\ln(1-\alpha)]^{\frac{1}{2}}$ | 134.91[s] | 12.23[s] | 133.62[t] | 12.10[t] | 118.58[u] | 9.97[u] |
| 40 | $[-\ln(1-\alpha)]^{\frac{1}{2}}$ | $2(1-\alpha)[-\ln(1-\alpha)]^{\frac{1}{2}}$ | 125.43[v] | 11.20[v] | 123.48[w] | 10.99[w] | 118.64[x] | 10.19[x] |
| Mean | $E_a$=120.82 kJ•mol$^{-1}$, log $A$=10.56 | | | | | | | |

[a] $r$=0.9942, $Q$=0.1874, $d$=0.0011; [b] $r$=0.9931, $Q$=1.0185, $d$=0.0070; [c] $r$=0.9899, $Q$=2.0466; $d$=0.0207;
[d] $r$=0.9820, $Q$=0.5705, $d$=0.0103; [e] $r$=0.9792, $Q$=3.0635, $d$=0.0638; [f] $r$=0.9635, $Q$=4.0622, $d$=0.1484;
[g] $r$=0.9668, $Q$=0.6169, $d$=0.0205; [h] $r$=0.9620, $Q$=3.2941, $d$=0.1253; [i] $r$=0.9456, $Q$=1.860, $d$=0.1012;
[j] $r$=0.9878, $Q$=0.2993, $d$=0.0037; [k] $r$=0.9858, $Q$=1.6103, $d$=0.0230; [l] $r$=0.9575, $Q$=3.1587, $d$=0.1342;
[m] $r$=0.9992, $Q$=0.0133, $d$=0.00001; [n] $r$=0.9991, $Q$=0.0716, $d$=0.00006; [o] $r$=0.9857, $Q$=1.0745, $d$=0.0154;
[p] $r$=0.9992, $Q$=0.0085, $d$=0.000006; [q] $r$=0.9991, $Q$=0.0716, $d$=0.00007; [r] $r$=0.9857, $Q$=1.0745, $d$=0.0154;
[s] $r$=0.9692, $Q$=1.5432, $d$=0.0476; [t] $r$=0.9652, $Q$=8.2448, $d$=0.2869; [u] $r$=0.9686, $Q$=6.2406, $d$=0.1960;
[v] $r$=0.9823, $Q$=0.5169, $d$=0.0092; [w] $r$=0.9796, $Q$=2.7679, $d$=0.0563; [x] $r$=0.9463, $Q$=7.2418, $d$=0.3542.

## References


1 Gerard, D. *J. Propul. Power* **1995**, *11*, 872.
2 Kissinger, H. E. *Anal. Chem.* **1957**, *29*, 1702.
3 Ozawa, T. *Bull. Chem. Soc. Jpn.* **1965**, *38*,1881.
4 Satava, V.; Sestak, J. *J. Therm. Anal.* **1975**, *8*, 477.
5 Coats, A. W.; Redfern, J. P. *Nature* **1964**, *201*(4914), 68.
6 Hu, R.-Z.; Yang, Z.-Q.; Ling, Y.-J. *Thermochim. Acta* **1988**, *123*, 135.
7 Hu, R.-Z.; Shi, Q.-Z. In *Thermal Analysis Kinetics*, Science Press, Beijing, **2001**, p. 127 (in Chinese).
8 Zhang, T.-L.; Hu, R.-Z.; Xie, Y.; Li, F.-P. *Thermochim. Acta* **1994**, *244*, 171.


(E0403092 ZHAO, X. J.)