

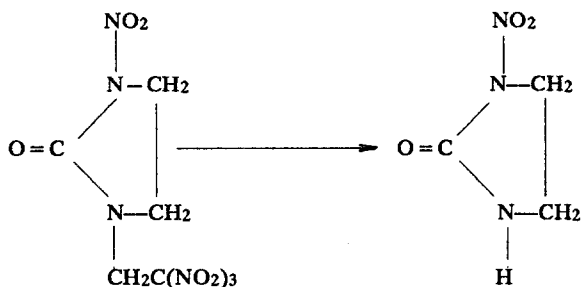
KINETICS AND MECHANISM OF THE EXOTHERMIC FIRST-STAGE DECOMPOSITION REACTION FOR 1-NITRO-3-(β,β,β -trinitroethyl)-2-IMIDAZOLIDINONE

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Under linear temperature increase condition the thermal behavior, mechanism and kinetic parameters of the exothermic first-stage decomposition reaction of the title compound have been studied by means of DSC, TG, DTA, IR and mass spectrometry. The mechanism of above-mentioned reaction could be expressed by the following scheme.



The apparent activation energy, pre-exponential constant and reaction order of this reaction are 112 kJ/mol, $10^{9.62}\text{sec}^{-1}$ and 0 respectively.

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1-nitro-3-(β,β,β - trinitroethyl)-2-imidazolidinone is a typical cyclourea nitramine which has a greater density and a higher detonation velocity. Its thermal behavior under condition of linear temperature increase has not been reported. In the present work, its kinetic parameters and mechanism of the exothermic first-stage decomposition reaction are studied by means of DSC, TG, DTG, IR and MS. 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.

Experimental

The purified 1-nitro-3-(β,β,β - trinitroethyl)-2-imidazolidinone was prepared by our Institute. Its purity was more than 99.5%. Sample was kept in a vacuum desiccator.

TG-DTG curve was obtained using a Perkin-Elmer's Model TGS-2 thermobalance. The heating rate was 5 deg/min. The flow rate of N₂ gas was 40 ml/min. DSC experiments were carried out with MODEL CDR-1 thermal analyzer made in the Shanghai Balance Instrument Factory, using Ni/Cr-Ni/Si thermocouple plate and working under static air condition with five different heating rates ranging from 1 to 20 deg/min. The α -Al₂O₃ was used as reference material in the DSC measurements. The infrared spectra and mass spectra of solid intermediate products were recorded using a Perkin-Elmer's Model 180 IR spectrophotometer and a MAT's Model MAT-312 mass spectrometer respectively.

Results and discussion

Thermal behavior and decomposition mechanism

Typical TG-DTG and DSC curves for the title compound with a heating rate of 10 deg/min were shown in Fig. 1. An endothermic peak began at its melting point (122°) with summit peak at 124°, and the exothermic peak at 142° was due to decomposition of the title compound in molten state. From the area of DSC peak, it is easy to find out the corresponding melting enthalpy of 20.3 kJ/mol. In the same way, the decomposition heat of 342 kJ/mol could also be obtained. The appearance of three peaks in the DTG curve suggested that thermal decomposition process of the title compound occurs

in different steps. The TG curve consisted of four-stage weight loss process (Data see Table 1).

Table 1 Mass loss and temperature for the title compound

Stage	Temperature range, °C	Mass loss, %
first-stage	158-212	56.5
second stage	212-241	15.3
third-stage	241-270	8.1
fourth-stage	270-553	16.6

The first-stage began at about 150° and completed at 212° accompanied with 56.5% mass loss. It is in agreement with the theoretical value of the mass loss of 55.4%, corresponding to the loss of the trinitroethyl group attached to nitrogen atom on one side of carbonyl to obtain 1-nitro-2-imidazolidinone. In order to understand the first-stage decomposition process of the title compound, decomposition-interruption tests were conducted

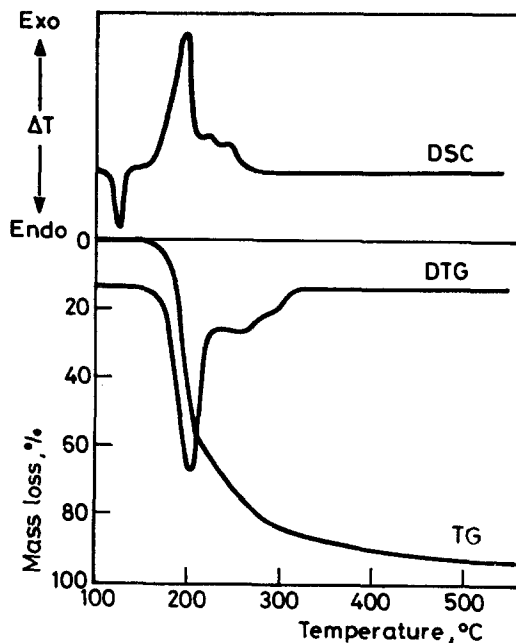


Fig. 1 DSC and TG-DTG curves for the title compound

with DSC experiments. Thermal degradation of the title compound was performed by heating the sample to a certain temperature in the first-stage decomposition and then cooling down to room temperature.

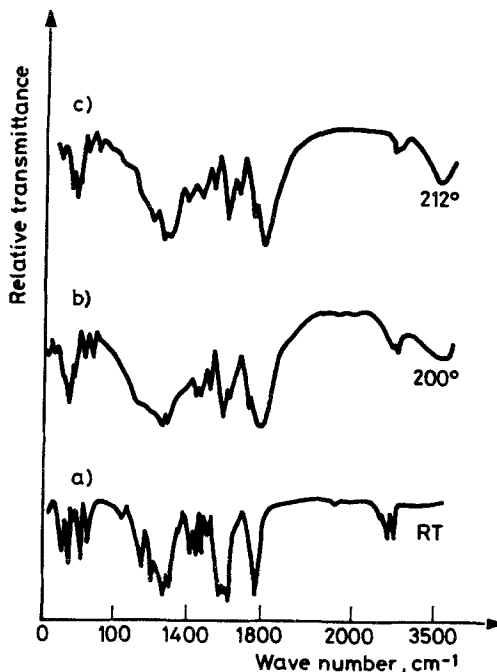


Fig. 2 The IR spectra of the title compound (a) and its decomposition products at 200°C (b) and 212°C (c)

The infrared and mass spectrum analyses of the title compound before and after thermaldecomposition were conducted. As shown in Fig. 2, the characteristic absorption peaks for trinitroethyl group of the title compound heated to 212° were disappeared at 1600 and 1300 cm^{-1} . However the characteristic absorption peaks for N-NO₂ group at 1560, 1580 and 1260 cm^{-1} did not disappear. The mass spectrum of the title compound after heated to 200° (Fig. 3) has a large peak of mass 131 (base peak) and the mass spectrum peak of mass 294 for the title compound disappeared.

On the basis of above-mentioned experiments and calculated result, the mechanism of the exothermic first-stage decomposition reaction for the title compound could be expressed by the scheme shown in the abstract.

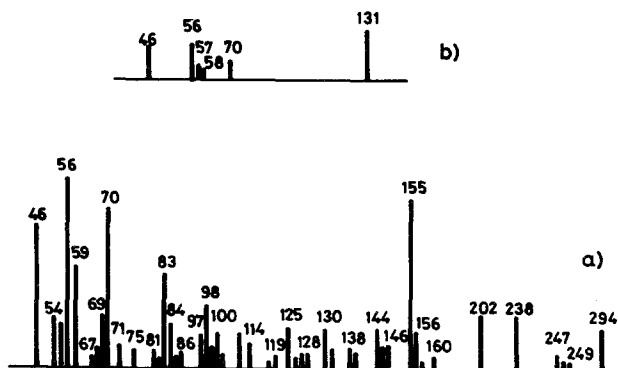


Fig. 3 Mass spectra of the title compound (a) and its decomposition product at 200°C (b)

The mass losses in the second-stage and the third-stage began at 212° and 241° respectively. Their mass losses were 15.3 and 8.1% respectively. In the fourth-stage, at the final decomposition temperature (553°), an additional mass loss of 16.1% was still observed in the TG curves. It should be noted that the fourth-stage reaction occurs without heat liberation.

Analysis of kinetic data

In order to obtain the kinetic parameters (the apparent activation energy (E) and pre-exponential constant (A)) of the exothermic first-stage decomposition reaction for the title compound, a multiple heating method (Kissinger's method) was employed. As shown in Fig. 4, the relationship of $\ln(\varphi / T_m^2)$ vs. T_m^{-1} indicates a straight line, where φ is the heating rate and T_m is the maximum peak temperature of the exothermic first-stage decomposition reaction in the DSC curves. From the original data in Table 2, the calculated apparent activation energy is determined to be 114 kJ/mol. The pre-exponential constant is $10^{10.4} \text{ sec}^{-1}$. The linear correlation coefficient is 0.99.

In order to obtain the values of E , A and reaction order (n) from a single non-isothermal DSC curve, the following equation was employed

$$\left(\frac{dH_t}{dt}\right)_i = AH_o \left\{ (1 - a_i)^n \left[1 + \frac{E}{RT_i} \left(1 - \frac{T_o}{T_i} \right) \right] \right\} \exp\left(-\frac{E}{RT_i}\right) \quad (1)$$

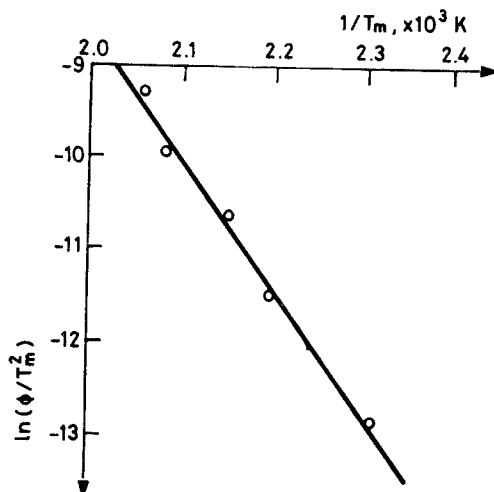


Fig. 4 Kissinger's plot of the exothermic first-stage peak temperature obtained by DSC experiments

where dH_t/dt is the exothermic rate at time t , H_0 is the total exothermicity of the substance (corresponding to the global area under the DSC curve); H_t is the reaction heat in a certain time (corresponding to the partial area under the DSC curve); T_i is the temperature (K) at time t ; α is the conversion degree ($\alpha = H_t/H_0$), T_0 is the initial point at which DSC curve deviates from the baseline; R is the gas constant, A is the pre-exponential constant; n is the reaction order and E is the apparent activation energy.

Table 2 The maximum peak temperature (T_m) of the exothermic first-stage decomposition reaction for the title compound determined by the DSC curves at various heating rates (φ)

φ , deg/min	T_m , K
0.5000	433.2
2.059	455.2
5.280	465.2
10.40	481.2
21.93	485.2

The logarithmic calculation of Eq.(1) gives the following relation

$$\ln\left(\frac{dH_t}{dt}\right)_i = \ln\left\{AH_0\left\{(1-\alpha_i)^n\left[1 + \frac{E}{RT_i}\left(1 - \frac{T_0}{T_i}\right)\right]\right\}\right\} - \frac{E}{RT_i} \quad (2)$$

Taking minimal values of evaluation functions (E , A and n)

$$\Omega = \sum_{i=1}^m \left\{ \ln \left(\frac{dH_t}{dt} \right)_i - \ln \left\{ AH_o (1 - \alpha_i)^n \left[1 + \frac{E}{RT_i} \left(1 - \frac{T_o}{T_i} \right) \right] \right\} + \frac{E}{RT_i} \right\}^2 \quad (3)$$

The following normal equation can be obtained from Eq.(3)

$$\begin{cases} \frac{\partial \Omega}{\partial A} = 0 & (4) \end{cases}$$

$$\begin{cases} \frac{\partial \Omega}{\partial n} = 0 & (5) \end{cases}$$

$$\begin{cases} \frac{\partial \Omega}{\partial E} = 0 & (6) \end{cases}$$

or

$$\begin{cases} m \cdot \ln A + a \cdot n = b + \frac{E_a}{R} c - m \ln H_o - d & (7) \end{cases}$$

$$\begin{cases} a \cdot \ln A + e \cdot n = f + \frac{E_a}{R} g - a \ln H_o - h & (8) \end{cases}$$

$$\begin{cases} p - (\ln A + \ln H_o) g - nr - S + \frac{E_a}{R} W = 0 & (9) \end{cases}$$

where

$$a = \sum_{i=1}^m \ln(1 - \alpha_i) \quad (10)$$

$$b = \sum_{i=1}^m \ln \left(\frac{dH_t}{dt} \right)_i \quad (11)$$

$$c = \sum_{i=1}^m \frac{1}{T_i} \quad (12)$$

$$d = \sum_{i=1}^m \ln \left[1 + \frac{E}{RT_i} \left(1 - \frac{T_o}{T_i} \right) \right] \quad (13)$$

$$e = \sum_{i=1}^m \ln^2(1 - \alpha_i) \quad (14)$$

$$f = \sum_{i=1}^m \ln \left(\frac{dH_t}{dt} \right)_i \ln(1 - \alpha_i) \quad (15)$$

$$g = \sum_{i=1}^m \frac{\ln(1 - \alpha_i)}{T_i} \quad (16)$$

$$h = \sum_{i=1}^m \left\{ \ln \left[1 + \frac{E_a}{RT_i} \left(1 - \frac{T_0}{T_i} \right) \right] \cdot \ln(1 - \alpha_i) \right\} \quad (17)$$

$$Q_i = \frac{1}{RT_i} - \frac{1 - \frac{T_0}{T_i}}{RT_i + E_a \left(1 - \frac{T_0}{T_i} \right)} \quad (18)$$

$$p = \sum_{i=1}^m Q_i \ln \left(\frac{dH_t}{dt} \right)_i \quad (19)$$

$$q = \sum_{i=1}^m Q_i \quad (20)$$

$$r = \sum_{i=1}^m Q_i \ln(1 - \alpha_i) \quad (21)$$

$$s = \sum_{i=1}^m Q_i \ln \left[1 + \frac{E_a}{RT_i} \left(1 - \frac{T_0}{T_i} \right) \right] \quad (22)$$

$$W = \sum_{i=1}^m \frac{Q_i}{T_i} \quad (23)$$

Solving Eqs (7) and (8) we obtain

$$\ln A = \frac{(b-d)e + (h-f)a + \frac{E_a}{R}(ce - ga)}{-(a^2 - me)} - \ln H_0 \quad (24)$$

and

$$n = \frac{(b-d)a + (h-f)m + \frac{E_a}{R}(ac - gm)}{a^2 - me} \quad (25)$$

The values of p , $\ln A$, q , n , r , s and w in Eq.(9) are correlated with the value of E . Once the value of E has been calculated from Eq.(9), the corresponding values of A and n can be obtained from Eqs (24) and (25).

Table 3 Data of the title compound determined by DSC*

Data point	T_i, K	α_i	$(dH_i/dt)_i, mJ/s$
1	447.2	0.1424	1.674
2	449.2	0.1765	2,008
3	453.2	0.2198	2.510
4	454.2	0.2446	2.761
5	457.2	0.3096	3.481
6	458.2	0.3375	3.983
7	459.2	0.3715	4.519
8	461.2	0.4180	5.104
9	463.2	0.4675	5.690
10	464.2	0.5139	6.318
11	466.2	0.5789	6.778
12	467.2	0.6409	7.364
13	468.2	0.7399	7.699

* $T_0 = 415.2 K$; $H_0 = 1622 mJ$; $\varphi = 5.28 \text{ deg/min}$

By substituting the original data tabulated in Table 3 into above-mentioned Eqs (10) - (23), the value of E of 112 kJ/mol is obtained by Eq.(9) and the values of A of $10^{9.62} \text{ sec}^{-1}$ and n of 0 are obtained by Eqs (24) and (25) respectively. These values of E and A obtained from a single non-isothermal DSC curve are in good agreement with the calculated values obtained by Kissinger's method.

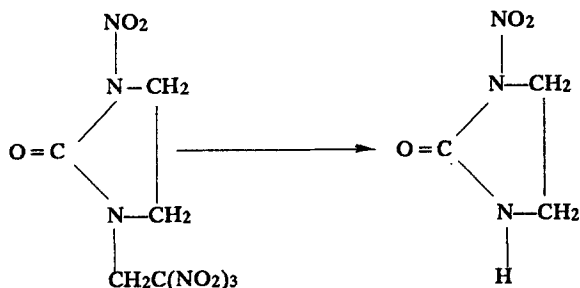
Conclusions

The mechanism of the exothermic first-stage decomposition reaction for the title compound could be expressed by the scheme shown in the abstract. The apparent activation energy, pre-exponential constant and reaction order of above-mentioned reaction are 112 kJ/mol, $10^{9.62} \text{ sec}^{-1}$ and 0 respectively.

References

- 1 H. E. Kissinger, *Anal. Chem.*, 29 (1957) 1702.
- 2 Hu Rongzu, Yang Zhengquan and Liang Yanjun, *Thermochim. Acta*, 123 (1988) 135.

Zusammenfassung — Bei linearem Temperaturanstieg wurde mittels DSC, TG, DTA IR und Massenspektrometrie das thermische Verhalten, der Mechanismus und die kinetischen Parameter der exothermen first-stage Zersetzungsreaktion der Titelverbindung untersucht. Der Mechanismus der obengenannten Reaktion kann mit folgendem Reaktionsschema veranschaulicht werden:



Die scheinbare Aktivierungsenergie, der präexponentielle Faktor und die Reaktionsordnung dieser Reaktion betragen 112 kJ/mol, $10^{9.62} \text{ s}^{-1}$ bzw. 0.