Non-isothermal Kinetics of the Thermal Decomposition of 3-Nitro-1,2,4-triazol-5-one Magnesium Complex

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The thermal decomposition of 3-nitro-1,2,4-triazol-5-one magnesium complex and its kinetics were studied under the non-isothermal condition by DSC and TG/DTG methods. The kinetic parameters were obtained from analysis of the DSC and TG/DTG curves by the Kissinger method, the Ozawa method, the differential method and the integral method. The most probable mechanism functions for the thermal decomposition of the first stage, the second stage and the third stage were suggested by comparing the kinetic parameters. The entropy of activation ($\Delta S^{\neq}$), enthalpy of activation ($\Delta H^{\neq}$) and free energy of activation ($\Delta G^{\neq}$) at Tpdo are $-66.74\ J\cdot mol^{-1}\cdot K^{-1}$, 119.2 $kJ\cdot mol^{-1}$ and 152.44 $kJ\cdot mol^{-1}$, respectively.

Keywords 3-nitro-1, 2, 4-triazol-5-one magnesium complex, non-isothermal kinetics, thermal decomposition mechanism

Introduction

3-Nitro-1,2,4-triazol-5-one (NTO) metal complexes have many special structures and some potential uses in ammunition.[1-4] We previously prepared and determined the crystal structure of its magnesium complex,[5] and in this paper, we discussed its thermal behavior by DSC and TG/DTG techniques and studied its non-isothermal kinetics by the means of the Kissinger method, the Ozawa method, the differential method and the integral method.

Experimental

Sample

$[Mg(H_2O)_6](NTO)_2\cdot 2H_2O$ was prepared as follows: A calculated amount of $Mg(OH)_2\cdot 4MgCO_3\cdot 6H_2O$ was added gradually to the aqueous solution of NTO with stirring at 60 ℃. A yellow precipitate was collected by filtration, washed with water and dried in a vacuum drier.

DSC, TG *and* DTG *analysis*

The DSC and TG/DTG experiments for the title compound were performed using a NETZSCH STA 449C under a nitrogen atmosphere, at a flow rate of 30 $mL\cdot min^{-1}$. The heating rates used were 2, 5, 10 and 15 $℃\cdot min^{-1}$ from ambient temperature to 700 ℃.

Results and discussion

Thermogravimetric analysis data

DSC and TG/DTG curves are shown in Figs. 1 and 2 respectively. The results of thermal analysis indicate that the thermal decomposition of the title compound begins at 78 ℃ and ends at 695.2 ℃. The process can be divided into four stages as shown in the DTG curve, and the maximum mass loss was between 210.7 ℃ and 416.5 ℃. The first stage started from 78 ℃ to 143.8 ℃ with a mass loss of 17.83% corresponding to the loss of the 2 mol of crystalline H_2O and 2 mol of coordinated H_2O (theoretical mass loss is 16.89%). The dehydration can also be confirmed by the crystal structure data in Table 1. As shown in Fig. 3, The Mg atom is located at the symmetrical center. Six oxygen atoms of six water molecules are combined with a Mg atom to form $[Mg(H_2O)_6]^{2+}$. Two NTO anions and two crystalline water molecules are combined by hydrogen bonds. The bond distances of Mg—O(6) and Mg—O(6A) are much longer than those of the other four Mg—O bonds. Theoretically, the former bonds are easy to be broken down. The second endothermic process is between 143.8 ℃ and 210.7 ℃, the mass loss is 16.06%, which coincides with the calculated value of 16.89%, corresponding to the loss of 4 mol of water molecules.

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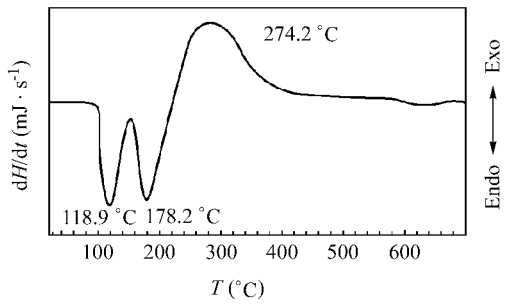

Fig. 1 DSC curve for the title compound at a heating rate of 15 ℃·min^{-1}.

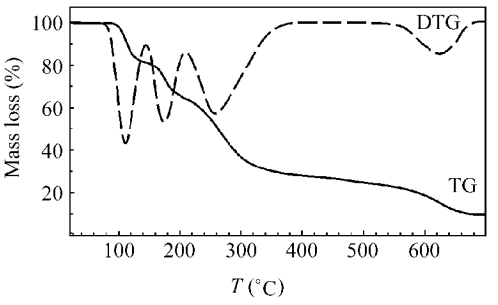

Fig. 2 TG/DTG curve for the title compound at a heating rate of 15 ℃·min^{-1}.

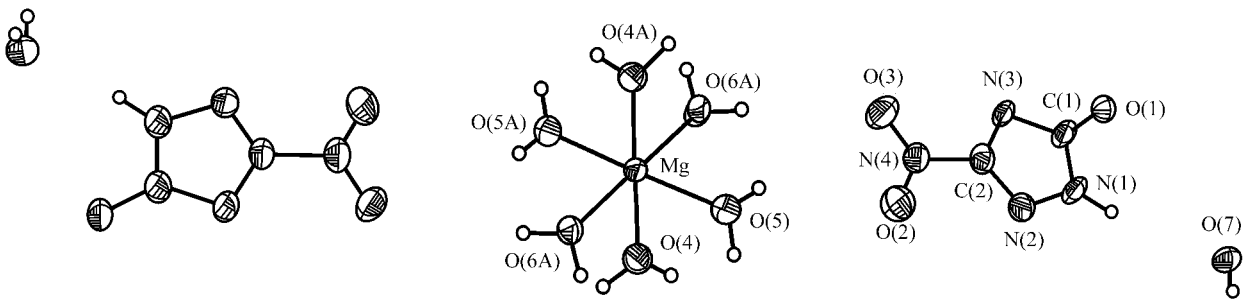

Fig. 3 Molecular structure of $[Mg(H_2O)_6](NTO)_2\cdot 2H_2O$.

Table 1 Selected bond lengths (nm)

Mg—O(4)	0.2057 (1)	Mg—O(4A)	0.2057 (1)
Mg—O(5)	0.2046 (1)	Mg—O(5A)	0.2046 (1)
Mg—O(6)	0.2087 (1)	Mg—O(6A)	0.2087(1)

Further decomposition of the complex occurs between 210.7 ℃ and 416.5 ℃ accompanied by 35.36% mass loss, corresponding to the thermal decomposition of $Mg(NTO)_2$. In this process, plenty of gas was emerged and the IR spectrum of the residue showed that the decomposition remains at 416.5 ℃ were a mixture. The characteristic absorp-tion peaks of $Mg(OCN)_2$ have formed at 2245 and 1188 cm^{-1}, the characteristic absorption peaks of $MgCO_3$ and polymers containing the —CO—NH— group have formed at 1457, 852 cm^{-1} and 3420, 1617, 1576 cm^{-1}, respectively. In the fourth-exothermal stage, the experimental value of the mass loss is about 17.10%. The characteristic absorption peak of MgO was found at 429 cm^{-1}. At the end of this stage, the residue amounted to 10.29%. This value is in good agreement with the calculated amount of 9.4%.

From the above analysis, the thermal decomposition of $[Mg(H_2O)_6](NTO)_2\cdot 2H_2O$ is postulated to proceed as follows:

$$[Mg(H_2O)_6](NTO)_2\cdot 2H_2O \rightarrow [Mg(H_2O)_4](NTO)_2 \rightarrow Mg(NTO)_2 \rightarrow MgCO_3 + Mg(OCN)_2 + \text{volatile substances} \rightarrow MgO$$

Non-isothermal decomposition kinetics

In the present work, the Kissinger method, the Ozawa method, the differential method and the integral method were applied to study the kinetics of the decomposition process of $[Mg(H_2O)_6](NTO)_2\cdot 2H_2O$. The Kissinger,[6] Ozawa,[7] differential and integral equations are as follows respectively:

$$\frac{\mathrm{d}\ln\dfrac{\beta}{T_P^2}}{\mathrm{d}\dfrac{1}{T_P}} = -\frac{E}{R} \tag{1}$$

$$\lg\beta + \frac{0.4567E}{RT} = C \tag{2}$$

$$\ln\left[\frac{\mathrm{d}\alpha/\mathrm{d}t}{f(\alpha)}\right] = \ln A - \frac{E}{RT} \quad \left(\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \beta\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right) \tag{3}$$

$$\ln\left[\frac{G(\alpha)}{T^2}\right] = \ln\frac{AR}{\beta E} - \frac{E}{RT} \tag{4}$$

where α is the fraction of conversion, $\mathrm{d}\alpha/\mathrm{d}t$ is the rate of conversion, T the absolute temperature, T_P the peak temperature, A the pre-exponential factor, R the gas constant, E the apparent activation energy, β the linear heating rate, $f(\alpha)$ and $G(\alpha)$ are the differential and integral mechanism functions respectively, C is a constant.

The values of E and A were obtained by the Kissinger method (with a subscript of k) and the Ozawa

method (with a subscript of o) with a multiple heating method. From the original data in Table 2, the apparent activation energy E_k and E_o, pre-exponential factor A_k and linear correction coefficient r_k and r_o were determined and shown in Table 3.

Table 2 The maximum peak temperature (T_P) of the decomposition reaction for the title compound determined by DSC curves at various heating rates (β)

β (℃·min^{-1})	T_{P1}(℃)	T_{P2}(℃)	T_{P3}(℃)
2	94.9	155.4	237.3
5	102.3	133.6	249.3
10	111.9	171.1	256.3
15	118.9	178.2	274.2

Table 3 The Kinetic parameters obtained by the data in Table 2

Stage	E_k	lg A_k	r_k	E_o	r_o
First	92.88	10.7	0.9875	94.33	0.9891
Second	136.3	14.17	0.9919	136.6	0.9927
Third	119.2	9.53	0.9801	121.8	0.9828

The values of α, T and $d\alpha/dt$ obtained from the TG-DTG curve in Fig. 2 are listed in Table 4. By substituting the values in Table 4 and 41 different mechanism functions $f(\alpha)$ and $G(\alpha)$ in Ref. 8 into Eqs. (5)—(11), the values of E, lg A and r were obtained and listed in Table 5.

Mac Callum-Tanner Eq.

$$\lg[G(\alpha)] = \lg\left(\frac{AE}{\beta R}\right) - 0.4828E^{0.4357} - \frac{0.449 + 0.217E}{0.001}\frac{1}{T} \quad (5)$$

Satava-Sestak Eq.

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

The Universal Integration Eq.

$$\ln\left[\frac{G(\alpha)}{T - T_0}\right] = \ln\left(\frac{A}{\beta}\right) - \frac{E}{RT} \quad (7)$$

The General Integral Eq.

$$\ln\left[\frac{G(\alpha)}{T^2\left(\left(1 - \frac{2RT}{E}\right)\right.}\right] = \ln\left(\frac{AR}{\beta E}\right) - \frac{E}{RT} \quad (8)$$

Agrawal Eq.

$$\ln\left\{\frac{G(\alpha)}{T^2\left[\frac{\left(1 - 2\left(\frac{RT}{E}\right)\right.}{1 - 5\left(\frac{RT}{E}\right)^2}\right]}\right\} = \ln\left(\frac{AR}{\beta E}\right) - \frac{E}{RT} \quad (9)$$

Achar-Brindley-Sharp Eq.

$$\ln\left[\frac{d\alpha}{f(\alpha)dT}\right] = \ln\left(\frac{A}{\beta}\right) - \frac{E}{RT} \quad (10)$$

The Exothermic Rate Eq.

$$\ln\left[\frac{dH_t}{dt}\right] = \ln\left\{AH_0 f(\alpha)\left[1 + \frac{E}{RT}\left(1 - \frac{T_0}{T}\right)\right]\right\} - \frac{E}{RT} \quad (11)$$

If all the following conditions are satisfied at the same time: (1) the values of E and lg A obtained by differential and integral method are approximately equal; (2) the linear correlation coefficient is better; (3) the values of E and lg A accord with the universal law (the value of E ranges from 80 to 250 kJ·mol^{-1}, lg A from 7 to 30)[9]; (4) The values of E obtained by the Ozawa method and the Kissinger method are also approximately identical with those obtained by Achar method and Mac Callum-Tanner method mentioned above, the relevant function under such conditions is the probable mechanism function of thermal decomposition of the complex.

By comparing E, lg A and r in Table 5 obtained by Eqs. (5)—(11), the probable mechanism function for the first stage is $f(\alpha) = (1 - \alpha)^{0.2174}$. The kinetic equation of this process is $\frac{d\alpha}{dt} = 10^{10.4}\exp\left(\frac{-91.43 \times 10^3}{RT}\right)(1 - \alpha)^{0.2174}$. By comparing E, lg A and r in Table 5 obtained by Eqs. (5)—(10), we can see that for the second stage, only the values obtained when the function is $f(\alpha) = (1 - \alpha)^{1.0076}$ can meet the four-mentioned conditions at the same time. So the probable mechanism function in the second stage is $f(\alpha) = (1 - \alpha)^{1.0076}$. The kinetic equation of this process is $\frac{d\alpha}{dt} = 10^{15.89}\exp\left(\frac{-145.2 \times 10^3}{RT}\right)(1 - \alpha)^{1.0076}$. The probable mechanism function in the third stage of decomposition of the title compound is $f(\alpha) = \frac{1}{2}(1 - \alpha)[-\ln(1 - \alpha)]^{-1}$, $G(\alpha) = [-\ln(1 - \alpha)]^2$, $n = 2$. Therefore, it can be decided that the reaction mechanism in the third stage is random nucleation and subsequent growth. The kinetic equation is $\frac{d\alpha}{dt} = \frac{1}{2} \times 10^{10.0}\exp\left(\frac{-129.4 \times 10^3}{RT}\right)(1 - \alpha)[\ln(1 - \alpha)]^{-1}$.

The value (T_{pdo}) of the peak temperature (T_p) corresponding to $\beta \to 0$ obtained by Eq. (12) taken from Ref. 10 is 224.9 ℃.

$$T_{pdi} = T_{pdo} + b\beta_i + c\beta_i^2 + d\beta_i^3 \quad i = 1, 2, 3, 4 \quad (12)$$

where b, c and d are coefficients.

The critical temperature of thermal explosion (T_b) obtained from Eq. (13) taken from Ref. 10 is 243.1 ℃.

$$T_b = \frac{E_o - \sqrt{E_o^2 - 4E_o RT_{pdo}}}{2R} \quad (13)$$

Table 4 Basic data for $[Mg(H_2O)_6](NTO)_2 \cdot 2H_2O$ determined by TG and DTG curves ($\beta = 2\ ^\circ C \cdot min^{-1}$)

No.	Stage 1 $T_0 = 333.15$ K, $H_0 = 4872.54$ mJ			Stage 2 $T_0 = 392.15$ K, $H_0 = 2594.56$ mJ			Stage 3 $T_0 = 440.15$ K, $H_0 = 7233.30$ mJ		
	T (K)	α	$d\alpha/dT \times 10^3$ (K^{-1})	T (K)	α	$d\alpha/dT \times 10^3$ (K^{-1})	T (K)	α	$d\alpha/dT \times 10^3$ (K^{-1})
1	348.15	0.0474	1.3221	406.15	0.0840	3.9903	472.15	0.1212	6.4210
2	358.15	0.0822	3.2008	411.05	0.1551	6.8468	488.15	0.2318	10.545
3	366.15	0.1507	8.0997	415.15	0.2231	10.079	504.15	0.3957	13.828
4	371.15	0.2334	12.386	420.15	0.3718	14.831	510.15	0.4630	13.749
5	376.15	0.3699	21.874	423.15	0.4790	18.248	522.15	0.5885	12.243
6	381.15	0.6012	32.650	427.15	0.6656	22.136	534.15	0.6967	10.102
7	383.15	0.7134	34.517	431.15	0.8151	18.798	546.15	0.7844	8.2042
8	386.15	0.8714	32.249	434.15	0.9328	7.8070	562.15	0.8714	5.8112

Table 5 The kinetic parameters obtained by the data in Table 4

No.[a]	Stage 1				Stage 2				Stage 3			
	$f(\alpha)$	E ($kJ \cdot mol^{-1}$)	lg A	r	$f(\alpha)$	E ($kJ \cdot mol^{-1}$)	lg A	r	$f(\alpha)$	E ($kJ \cdot mol^{-1}$)	lg A	r
1	$2(1-\alpha)^{1/2}$	94.64	9.8	0.9848	$2(1-\alpha)^{1/2}$	140.9	14.29	0.9988	18[b]	128.0	9.86	0.9921
2	$2(1-\alpha)^{1/2}$	97.54	10.2	0.9848	$2(1-\alpha)^{1/2}$	141.2	14.37	0.9988	18	129.1	10.00	0.9921
3	$2(1-\alpha)^{1/2}$	98.92	8.98	0.9837	$2(1-\alpha)^{1/2}$	143.6	13.20	0.9987	18	129.4	10.00	0.9924
4	$2(1-\alpha)^{1/2}$	96.47	10.1	0.9830	$2(1-\alpha)^{1/2}$	141.5	15.83	0.9995	18	127.5	9.86	0.9911
5	$2(1-\alpha)^{1/2}$	96.47	10.1	0.9830	$2(1-\alpha)^{1/2}$	143.6	17.98	0.9987	18	127.2	9.81	0.9911
6	$(1-\alpha)^0$	102.0	12.4	0.9926	$3(1-\alpha)^{2/3}$	141.5	15.09	0.9810	18	111.4	9.73	0.9850
7	$(1-\alpha)^{0.2174}$	91.43	10.4	—	$(1-\alpha)^{1.0076}$	145.23	15.89	—	—	—	—	—

[a] 1, Mac Callum-Tanner method; 2, Satava-Sestak method; 3, the universal integration method; 4, the general integral method; 5, Agrawal method; 6, Achar-Brindley-Sharp method; 7, the exothermic rate method; [b] $f(\alpha) = \frac{1}{2}(1-\alpha)[-\ln(1-\alpha)]^{-1}$.

where E_o is the apparent activation energy obtained by Ozawa's method; R is the gas constant.

The entropy of activation ($\Delta S^{\neq}$), enthalpy of activation ($\Delta H^{\neq}$) and free energy of activation ($\Delta G^{\neq}$) corresponding to $T = T_{pdo}$, $E_a = E_k$ and $A = A_k$ obtained by Eqs. (14), (15) and (16) are $-66.74\ J \cdot mol^{-1} \cdot K^{-1}$, $119.2\ kJ \cdot mol^{-1}$ and $152.44\ kJ \cdot mol^{-1}$, respectively.

$$A = \frac{k_B T}{h} e^{\Delta S^{\neq}/R} \tag{14}$$

$$A\exp(-E_a/RT) = \frac{kT}{h}\exp\left(\frac{\Delta S^{\neq}}{R}\right)\exp\left(-\frac{\Delta H^{\neq}}{RT}\right) \tag{15}$$

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} \tag{16}$$

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

Conclusion

The mechanism of the decomposition reaction for the title compound could be expressed by the reaction mechanism shown in the text. The kinetic equation for the first stage is $\frac{d\alpha}{dt} = 10^{10.4}\exp\left(\frac{-91.43 \times 10^3}{RT}\right)(1-\alpha)^{0.2174}$, for the second stage is $\frac{d\alpha}{dt} = 10^{15.89}\exp\left(\frac{-145.2 \times 10^3}{RT}\right)(1-\alpha)^{1.0076}$ and for the third stage is $\frac{d\alpha}{dt} = \frac{1}{2} \times 10^{10.0} \times \exp\left(\frac{-129.4 \times 10^3}{RT}\right)(1-\alpha)[-\ln(1-\alpha)]^{-1}$.

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