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Thermal Behavior and Nonisothermal Decomposition Reaction Kinetics of 4-Amino-1,2,4-triazole Copper Complex

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Abstract: Cu(4-ATz)₂Cl₂ · H₂O was synthesized with 4-amino-1,2,4-triazole (4-ATz) and copper chloride dihydrate, and was characterized by elemental analysis, IR and melting point determination. The thermal behaviors and nonisothermal decomposition reaction kinetics of the complex were studied by differential scanning calorimetry (DSC) and thermogravimetry and derivative thermogravimetry (TG-DTG) techniques. The results show that the mole ratio of metal to ligand is 1 : 2. The reaction mechanism of the main exothermic decomposition process of the complex is classified as chemical reaction and $f(\alpha) = \frac{3}{2}(1-\alpha)[-\ln(1-\alpha)]^{1/3}$, and the kinetic equation is obtained as: $d\alpha/dt = 10^{21.83} \times \frac{3}{2}(1-\alpha)[-\ln(1-\alpha)]^{1/3} \times \exp(-2.75 \times 10^4/T)$.

Key words: physical chemistry; copper complex; 4-amino-1,2,4-triazole; thermal decomposition mechanism; nonisothermal reaction kinetics

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1 Introduction

It is well known that the metal complexes with 1,2,4-triazole derivatives have potential advantage used in solid propellant formulations as a new generation of burning rate modifiers, because they have more particular properties, such as high nitrogen content, high enthalpy of formation and high densities^[1-5]. Recently, a great deal of interest in energetic materials based on the heterocyclic complexes such as triazole and tetrazole^[6-7]. These materials derive their energetic qualities from the large number of the heterocyclic ring systems in their molecule. The utilization of the 4-amino-1,2,4-triazole (4-ATz) derivatives, its perchlorate and nitrate, have been reported earlier^[8-9], but 4-amino-1,2,4-triazole copper ((4-ATz)Cu) complex and its thermal behaviors as well as nonisothermal decomposition reaction kinetics have not been reported in literatures^[10-11]. In order to provide deeper insight into the mechanism of inhibiting function and catalysis, it is essential to investigate its thermal decomposition behavior and kinetics. In this paper, (C₂N₄H₄)₂CuCl₂ · H₂O was prepared, and its structure was determined and the thermal behavior and nonisothermal decomposition reaction kinetics were studied.

2 Experimental

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2.1 Materials

(4-ATz)Cu used in this work was prepared according to the following method: an appropriate amount 4-ATz^[12] (0.0210 g, 0.25 mmol) was put into 10 mL of water, stirring at 60 °C for 30 min. CuCl₂ · 2H₂O (0.0213 g, 0.125 mmol) was dissolved in 10 mL ethanol and the solution was added into 4-ATz solution slowly and stirring at 60 °C for 120 min. Then, the blue precipitate was appeared. Finally, the precipitate was washed, filtrated and dried in vacuum at 80 °C, and then (C₂N₄H₄)₂CuCl₂ · H₂O was obtained. Yield: 70%. m. p.: 235 - 238 °C; IR (KBr)^[13] are: 3389, 3238, 3130, 1640, 1546, 1222, 1081, 1060, 977, 867, 615 cm⁻¹. Anal. Calc. for (C₂N₄H₄)₂CuCl₂ · H₂O (%): C 15.84, H 2.64, N 36.96. Found(%): C 15.08, H 2.508, N 34.89.

2.2 Equipment and conditions

DSC and TG-DTG curves for the complex under the condition of flowing nitrogen gas (purity, 99.999%, atmospheric pressure) were obtained by using a 204HP differential scanning calorimeter (Netzsch Co., Germany) and a SDT Q600 thermal analyzer (TA Co., USA), respectively. The conditions of DSC analyses were: sample mass is about 1 mg, and N₂ flowing rate is 50 cm³ · min⁻¹, and heating rate is 5, 10, 15, 20 K · min⁻¹, and furnace pressures is 0.1 MPa, and reference sample is α-Al₂O₃, and type of crucible is aluminum pan with a pierced lid. The conditions of TG-DTG were: sample mass, about 1 mg; N₂ flowing rate, 100 cm³ · min⁻¹; heating rate (β), 5, 10, 15, 20 K · min⁻¹.

3 Results and discussion

3.1 Decomposition processes analysis for (4-ATz)Cu

Typical DSC and TG-DTG curves for the complex are

shown in Figs. 1 and 2. The DSC curve indicates that the thermal decomposition of the complex was composed of two exothermic processes with the peak temperatures of 505.1 K and 899.3 K, respectively, corresponding to two mass-loss stages in TG curve and two peaks in DTG curve.

The first mass-loss stage in TG curve began at about 473.2 K and completed at 525.0 K with a mass loss of 34.6%. The second stage began from 592.2 K to 921.9 K, with a mass loss of 29.3%. The first stage is caused by the main exothermic decomposition reaction.

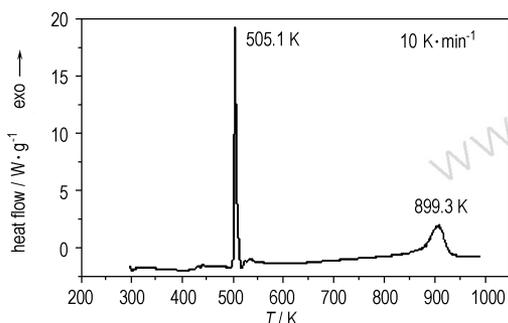


Fig. 1 DSC curve for the complex at a heating rate of $10 \text{ K} \cdot \text{min}^{-1}$

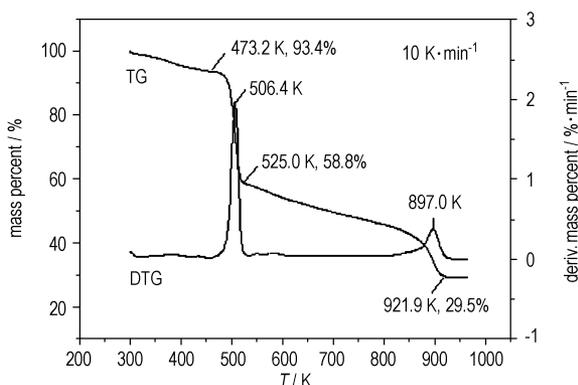


Fig. 2 TG-DTG curves for the complex at a heating rate of $10 \text{ K} \cdot \text{min}^{-1}$

3.2 Kinetic data analysis for (4-ATz) Cu

In order to obtain the kinetic parameters [the apparent activation energy (E_a) and pre-exponential constant (A)] of the main exothermic decomposition reaction of (4-ATz) Cu, and the most probable kinetic model function, the DTG curves at a heating rate of 5, 10, 15, and $20 \text{ K} \cdot \text{min}^{-1}$ were dealt with mathematic means, and five integral methods [Eqs. (1) –

(5)] and one differential method [Eq. (6)] in Table 1 are employed^[14–17].

In these equations, α is the conversion degree of the major exothermic reaction, T is the absolute temperature (K) at time of t , T_p is the peak temperature, A is the pre-exponential factor, R is the gas constant, β is the linear heating rate, E is the apparent activation energy. $f(\alpha)$ and $G(\alpha)$ are the differential model function and the integral model function, respectively, α is the conversion degree. The data needed for the equations of the integral and differential methods, i , α_i , β_i , T_i , T_e , T_p , $i=1, 2, 3, \dots, n$, are obtained from the DTG curves and summarized in Tables 2 and 3.

The values of E_a were obtained by Ozawa's method [Eq. (5)] with α changing 0 to 1, and the $E_a - \alpha$ relation curve is shown in Fig. 3. It indicates that the activation energy of the decomposition process changes greatly by diverse level with an increase in the conversion degree, except that for the section of $\alpha=0.10 - 0.90$, activation energy changes faintly, and it means that the decomposition mechanism of the process does not transfer in essence or the transference can be ignored. Therefore, it is feasible to research into the reaction mechanism and kinetics in the section of $\alpha=0.10 - 0.90$.

Forty-one types of kinetic model function in Ref. [16] and the original data tabulated in Table 2 are put into Eqs. (1) – (6) in Table 1 for calculation. The values of E_a , $\lg A$, linear correlation coefficient (r), and standard mean square deviation (Q) can be calculated with the linear least-squares method at various heating rates 5, 10, 15, $20 \text{ K} \cdot \text{min}^{-1}$, and they are listed in Table 3. The most probable mechanism function is selected by the better values of r , and Q taken from Ref. [16]. The results of satisfying the conditions mentioned above are also listed in Table 3.

The values of E_a , and $\lg A$ obtained from nonisothermal curve are in approximately 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 complex is classified as chemical reaction and $G(\alpha) = [-\ln(1-\alpha)]^{2/3}$.

Substituting $f(\alpha)$ with $\frac{3}{2}(1-\alpha)[- \ln(1-\alpha)]^{1/3}$, E with $228.89 \text{ kJ} \cdot \text{mol}^{-1}$ and A with $10^{21.83} \text{ s}^{-1}$ in Eq. (7):

$$d\alpha/dt = Af(\alpha)e^{-E/RT} \quad (7)$$

the kinetic equation of the exothermic decomposition reaction may be described as:

$$d\alpha/dt = 10^{21.83} \times \frac{3}{2}(1-\alpha)[- \ln(1-\alpha)]^{1/3} \times \exp(-2.75 \times 10^4/T).$$

Table 1 Kinetic analysis methods

method	equation	
ordinary-integral	$\ln[G(\alpha)/T^2] = \ln[AR/\beta E(1-2RT/E)] - E/RT$	(1)
Mac Callum-Tanner	$\lg[G(\alpha)] = \lg(AE/\beta R) - 0.4828E^{0.4357} - (0.449 + 0.217E)/(0.001T)$ (E in $\text{kcal} \cdot \text{mol}^{-1}$)	(2)
Šatava V, Šesták	$\lg[G(\alpha)] = \lg(A_s E_s/\beta R) - 2.315 - 0.4567E_s/RT$	(3)
Agrawal	$\ln[G(\alpha)/T^2] = \ln[AR/\beta E] \{ [1-2(RT/E)]/[1-5(RT/E)^2] \} - E/RT$	(4)
Flynn-Wall-Ozawa	$\lg \beta = \lg \{ AE/[RG(\alpha)] \} - 2.315 - 0.4567E/RT$	(5)
Kissinger	$\ln(\beta_i/T_{pi}^2) = \ln(A_k R/E_k) - E_k/RT_{pi}$, $i=1, 2, \dots, 4$	(6)

Table 2 Data for the decomposition process of the complex determined by DTG curve

α	T_5/K	T_{10}/K	T_{15}/K	T_{20}/K	α	T_5/K	T_{10}/K	T_{15}/K	T_{20}/K
0.00	468.1	473.2	477.2	480.6	0.52	498.2	505.5	508.8	512.7
0.02	479.6	487.2	490.2	494.6	0.54	498.6	505.9	509.2	513.1
0.04	483.2	490.6	493.7	497.9	0.56	498.9	506.2	509.5	513.5
0.06	485.2	492.8	495.9	499.8	0.58	499.3	506.5	509.8	513.8
0.08	486.7	494.3	497.4	501.2	0.60	499.6	506.9	510.2	514.2
0.10	487.9	495.5	498.6	502.3	0.62	500.0	507.2	510.5	514.6
0.12	488.9	496.4	499.6	503.2	0.64	500.3	507.5	510.9	515.0
0.14	489.7	497.3	500.4	504.0	0.66	500.6	507.9	511.2	515.4
0.16	490.4	498.0	501.1	504.6	0.68	501.0	508.2	511.6	515.8
0.18	491.1	498.6	501.8	505.3	0.70	501.4	508.6	512.0	516.2
0.2	491.7	499.2	502.3	505.8	0.72	501.7	509.0	512.4	516.7
0.22	492.2	499.7	502.9	506.4	0.74	502.1	509.3	512.8	517.1
0.24	492.7	500.2	503.4	506.9	0.76	502.5	509.7	513.2	517.6
0.26	493.2	500.6	503.9	507.3	0.78	502.8	510.2	513.6	518.0
0.28	493.6	501.1	504.3	507.8	0.80	503.2	510.6	514.0	518.5
0.30	494.0	501.5	504.7	508.3	0.82	503.7	511.1	514.5	519.0
0.32	494.5	501.9	505.2	508.7	0.84	504.1	511.6	515.0	519.6
0.34	494.9	502.3	505.6	509.1	0.86	504.6	512.1	515.5	520.2
0.36	495.3	502.7	505.9	509.5	0.88	505.1	512.7	516.1	520.9
0.38	495.6	503.1	506.3	510.0	0.90	505.7	513.3	516.8	521.6
0.40	496.0	503.4	506.7	510.4	0.92	506.3	514.0	517.5	522.5
0.42	496.4	503.8	507.1	510.8	0.94	507.1	514.9	518.4	523.6
0.44	496.8	504.2	507.4	511.2	0.96	508.3	516.0	519.5	524.9
0.46	497.1	504.5	507.8	511.5	0.98	510.3	517.7	521.1	526.8
0.48	497.5	504.8	508.1	511.9	1.00	518.5	525.0	526.6	533.3
0.50	497.9	505.2	508.5	512.3		499.7(T_p)	506.4(T_p)	509.1(T_p)	512.3(T_p)

Note: T with the subscript 5, 10, 15, and 20 is the temperature obtained at the heating rates of 5, 10, 15, and 20 $K \cdot \min^{-1}$, respectively.

Table 3 Calculated values of kinetic parameters of decomposition of the complex

method	$\beta/K \cdot \min^{-1}$	$E_a/kJ \cdot \text{mol}^{-1}$	$\lg(A/s^{-1})$	r	Q
ordinary-integral	5	226.83	21.65	0.9986	0.0317
	10	236.24	22.58	0.9976	0.0531
	15	234.66	22.43	0.9976	0.0549
	20	219.64	20.81	0.9951	0.1103
Mac Callum-Tanner	5	228.11	21.78	0.9987	0.0059
	10	237.71	22.74	0.9978	0.0099
	15	236.18	22.59	0.9977	0.0103
	20	221.12	20.95	0.9954	0.0207
Šatava V, Šesták	5	223.56	21.35	0.9986	0.0059
	10	232.62	22.26	0.9978	0.0099
	15	231.18	22.12	0.9977	0.0103
	20	216.96	20.56	0.9954	0.0207
Agrawal	5	226.83	21.65	0.9986	0.0317
	10	236.24	22.58	0.9976	0.0531
	15	234.66	22.43	0.9976	0.0549
	20	219.64	20.81	0.9951	0.1103
mean		228.89	21.83		
Flynn-Wall-Ozawa		226.62		0.9988	0.0005
Kissinger		229.90	21.99	0.9987	0.0026

Note: β is the heating rate; E_a is the apparent activation energy; A is the pre-exponential factor; r is the related coefficient; Q is the variance, respectively.

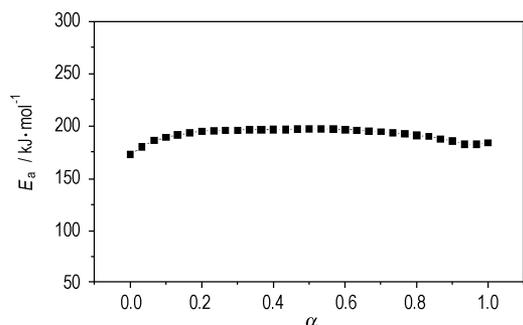


Fig. 3 E_a - α curve for the decomposition of the complex by Ozawa's method

4 Conclusions

(1) $\text{Cu}(4\text{-ATz})_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ was synthesized, its thermal decomposition processes have two mass-loss stages and the exothermic decomposition reaction occurred in the first stage.

(2) The decomposition reaction kinetics of the main decomposition process of $\text{Cu}(4\text{-ATz})_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ was investigated, and the kinetic model function, apparent activation energy, and pre-exponential constant of the reaction were obtained as $\frac{3}{2}(1-\alpha)[-\ln(1-\alpha)]^{1/3}$, $228.89 \text{ kJ} \cdot \text{mol}^{-1}$, $10^{21.83} \text{ s}^{-1}$, respectively.

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4-氨基-1,2,4-三唑铜配合物的热分解机理及非等温反应动力学

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摘要: 利用4-氨基-1,2,4-三唑(4-ATz)与二水氯化铜合成了标题化合物 $(\text{C}_2\text{N}_4\text{H}_4)_2\text{CuCl}_2 \cdot \text{H}_2\text{O}$, 采用元素分析和红外光谱分析对配合物进行了结构表征, 用 DSC 和 TG-DTG 研究了配合物的热行为及主放热分解阶段的动力学。结果表明, 金属离子与配体的化学计量比为 1:2。配合物的主要分解阶段由机理函数 $f(\alpha) = \frac{3}{2}(1-\alpha)[-\ln(1-\alpha)]^{1/3}$ 控制, 反应速率方程为:

$$d\alpha/dt = 10^{21.83} \times \frac{3}{2}(1-\alpha)[-\ln(1-\alpha)]^{1/3} \times \exp(-2.75 \times 10^4/T)$$

关键词: 物理化学; 铜配合物; 4-氨基-1,2,4-三唑; 热分解机理; 非等温反应动力学

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