Thermodynamics Investigation on 1, 2, 4-Triazole-5-one Copper Complex

LI Na, CHEN San-ping, GAO Sheng-li, HU Rong-zu

(Shaanxi Key Laboratory of Physico-Inorganic Chemistry, Department of Chemistry, Northwest University, Xi'an 710069, China)

Abstract：According to the synthesis process of $Cu(TO)_2Cl_2$ ($TO = 1, 2, 4$-triazole-5-one), a crystal growth kinetics model in mixed solvents was proposed. The thermodynamics parameters were obtained utilizing this kinetic model, as follows: $E_a = 45.37$ kJ · mol^{-1}, $\ln[A/s^{-1}] = 14.65$, $\Delta^{\neq}G_m = 82.11$ kJ · mol^{-1}, $\Delta^{\neq}H_m = 42.85$ kJ · mol^{-1}, $\Delta^{\neq}S_m = -131.58$ J · mol^{-1} · K^{-1}. Furthermore, the specific heat capacity of $Cu(TO)_2Cl_2$ at 298.15 K, and the standard enthalpies of formation of $[Cu(TO)_2]^{2+}$ (aq) and $Cu(TO)_2Cl_2$ (s) were determined using a microcalorimetry RD496-Ⅲ.

Key words：physical chemistry; microcalorimetry; crystallization kinetic; specific heat capacity; enthalpy of formation; $Cu(TO)_2Cl_2$

CLC number：TJ55; O64　　　　　　　　　**Document code**：A

1　Introduction

Certain triazolone derivatives are extensively studied in the field of energetic materials for their high-nitrogen compositions, high enthalpy of formation and high densities. In addition, their metal compounds due to high energy and low sensitivity may have potential applications as addictives in the explosives and propellants [1-6]. 1,2,4-triazole-5-one (abbreviated for TO), as one derivatives of triazolone, its lone electron pair of the nitrogen in the five-membered ring or oxygen atoms make it easy to coordinate with transition metal atoms to form complex which may have potential application as energetic materials. Many attentions have been paid to 1,2,4-triazole-5-one metal complexes and some single crystal structures are explored, especially by Zhang's research group [7-9].

In this paper, the new complex $Cu(TO)_2Cl_2$ was synthesized and according to the synthesis process, a crystal growth kinetic model was proposed, and thermodynamics parameters was obtained using a microcalorimetry RD496-Ⅲ [10] in order to provide theoretical data for the further exploration in the field of energetic materials. Moreover, the specific heat capacity and the enthalpy of formation of the complex $Cu(TO)_2Cl_2$ were also determined by the microcalorimeter.

2　Experimental

2.1　Materials

According to the literature method [11,12], formic acid (mass fraction 88%, Xi'an Chemical Co.) and semicarbazide hydrochloride (mass fraction 99%, Xi'an Chemical Co.) were used to synthesize 1, 2, 4-triazole-5-one (TO), DSC analysis shows its m. p. 234.0 ℃ which accorded with literatures [11,12].

$CuCl_2 · 2H_2O$ (AR) and nitric acid (≥98.2%) were derived from Xi'an Chemical Co. without further purification; KCl, benchmark benzoic acid and α-Al_2O_3 were spectrum grade made by Shanghai No. 1 Reagent Company.

2.2　Experimental equipments

C, H, N contents were determined on a Perkin-Elmer 2400 type elemental analyzer. IR spectrum was derived by a Nicolet 60 SXR FT-IR (Nicolet, USA) spectrometer in the 4000 – 400 cm^{-1} regions (KBr pellets).

The calorimetric experiment is performed using an RD496-Ⅲ [10] type microcalorimeter. The calorimetric constants at 298.15 K, 301.15 K, 304.15 K and 307.15 K are determined by Joule effect before experiment, which are (63.901 ±0.030) μV · mW^{-1}, (64.000 ±0.026) μV · mW^{-1}, (64.075 ±0.038) μV · mW^{-1}, (64.203 ±0.043) μV · mW^{-1}. The enthalpies of solution of KCl in deionized water (spectrum purity) were measured to be (17.238 ± 0.048) kJ · mol^{-1}, which was very close to (17.241 ±0.018) kJ · mol^{-1} in Refer-

-ence[13]. This indicates that the calorimetric system is reliable.

2.3 Synthesis

An appropriate amount of TO (2 mmol, 0.170 g) was dissolved in water (10 mL), which was mixed with an aqueous solution (10 mL) of $CuCl_2 \cdot 2H_2O$ (1 mmol, 0.170 g) with constant stirring for about 30 min. The resulting clear mixture was changed pH with diluted nitrate acid, and the green precipitations were immediately produced. The green precipitations were collected on a Buchner funnel (Whatman No. 5), and washed twice with 30 mL ethanol and dried in vacuum for 2 h to get the green power for analysis(0.238 g, 78.1%).

Cu^{2+} was titrated by iodimetry and determined as 20.62%. The elemental analysis result (C 15.96%, H 1.721%, N 27.52%), which shows the general formula of the complex is $Cu(TO)_2Cl_2$ compared with the calculation value (Cu 20.86%, C 15.77%, H 1.99% and N 27.59%).

IR spectrum analysis shows that ν_{NH}: 3242 cm^{-1}, 3164 cm^{-1}, $\nu_{=CH}$: 2856 cm^{-1}, the characteristic stretching vibration of C=O is found at 1745 cm^{-1}, which shifted 49 cm^{-1} to higher wave number compared with the ligand TO (1696 cm^{-1}), this should be ascribe the coordination interaction in the molecular.

3 Results and discussion

3.1 The crystallization kinetics investigation of $Cu(TO)_2Cl_2$

Due to the UV spectrum of the solution of the green power is consistent with the UV spectrum of the mixed solution of $CuCl_2$ and TO, the kinetic model in mixed solvents and Eqs. 1 and 2 were proposed.

$$Cu^{2+}(aq) + 2Cl^-(aq) + 2TO(aq) \xrightarrow{\Delta_r H_m^\theta(1)}$$
$$[Cu(TO)_2]^{2+}(aq) + 2Cl^-(aq) \quad (1)$$

$$[Cu(TO)_2](aq) + 2Cl^-(aq) \xrightarrow[HNO_3]{\Delta_r H_m^\theta(2)} Cu(TO)_2Cl_2(s) \quad (2)$$
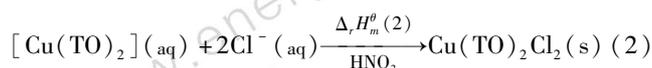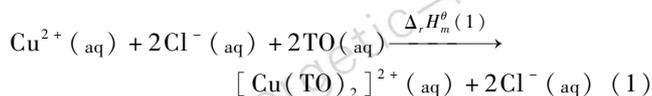
Furthermore, the optimum volume ratio of water to diluted HNO_3 in the calorimetric experiment was also determined by experimental methods. The maximum productivity of $Cu(TO)_2Cl_2$ was 73% when volume ratio of water to diluted HNO_3 was 30 : 7.

3.1.1 Derivation of the kinetic equation

In order to analyze the kinetics of the crystal growth process of the complexes of Cu^{2+} with TO, the following general form of the crystal growth process is used

$$A(aq) \rightarrow A(s) + heat \quad (3)$$

$t = 0$,	c_0	0	0
$t = t$,	c	m	Q
$t = \infty$,	c_∞	m_∞	Q_∞

Where c is the solute concentration in the solution at time t, m is the mass of solid deposited during a certain time, Q is the heat produced during a certain time. when $t = \infty$, $c = c_\infty$, $m = m_\infty$ and $Q = Q_\infty$. Q is the heat produced during a certain time.

From Equation (3), the rate equation was obtained.

$$\frac{dm}{dt} = k_1 m_\infty (c - c_\infty) \quad (4)$$

Where k_1 is the rate constant of crystal growth.

Eq. (4) may be expressed as:

$$\frac{dQ}{dt} = k_1 Q_\infty (c_0 - c_\infty)\left(1 - \frac{Q}{Q_\infty}\right) = k_2\left(1 - \frac{Q}{Q_\infty}\right) \quad (5)$$

Where $k_2 = k_1 Q_\infty (c_0 - c_\infty)$,

If $c_0 \gg c_\infty$, from Eq. (5), we have

$$\frac{dQ}{dt} = k_1 Q_\infty c_0\left(1 - \frac{Q}{Q_\infty}\right) = k_3\left(1 - \frac{Q}{Q_\infty}\right) \quad (6)$$

Where $k_3 = k_1 Q_\infty c_0$.

When $\left(\frac{dQ}{dt}\right)_i$ is plotted versus $\left(1 - \frac{Q}{Q_\infty}\right)_i$ by the least-squares method, this gives the value of k_3 or k_2 (slope) and a (intercept) in the Eqs. (7) and (8).

$$\frac{dQ}{dt} = k_3\left(1 - \frac{Q}{Q_\infty}\right) + a \quad (7)$$

or

$$\frac{dQ}{dt} = k_1 Q_\infty (c_0 - c_\infty)\left(1 - \frac{Q}{Q_\infty}\right) + a = k_2\left(1 - \frac{Q}{Q_\infty}\right) + a \quad (8)$$

Where

$$k_1 = \frac{k_2}{Q_\infty (c_0 - c_\infty)} \xrightarrow{c_0 \gg c_\infty} \frac{k_2}{Q_\infty c_0} \quad (9)$$

Eq. (10) is derived from Eqs. (7) and (8),

$$\frac{dm}{dt} = \left(\frac{m_\infty}{Q_\infty}\right)\frac{dQ}{dt} =$$

$$\frac{m_\infty}{Q_\infty}\left[k_1 Q_\infty (c_0 - c_\infty)\left(1 - \frac{Q}{Q_\infty}\right) + a\right] \quad (10)$$

Similarly, Eq. (9) can be written as

$$\frac{dm}{dt} = k_m_\infty (c - c_\infty) + b = \frac{m_\infty}{Q_\infty}[k_1 Q_\infty (c - c_\infty) + a] =$$

$$k_1 m_\infty (c - c_\infty) + \frac{am_\infty}{Q_\infty} \qquad (11)$$

Where b is the intercept of Eq. (11)

Comparing Eq. (10) with Eq. (11), a relationship of a and b is obtained

$$b = \frac{am_\infty}{Q_\infty} \qquad (12)$$

If the values of the constants a and b are small in comparison with those of k_2 and k_1, the kinetics of the crystal growth process can be expressed by Eqs. (4) and (5).

3.1.2 Dilution/crystallization kinetics

A typical schematic thermogram during the dilution and crystallization is depicted in Fig. 1. The original data obtained from the thermal kinetic(T_K) curve are shown in Table 1. Using the above data, the kinetic data during the dilution/crystallization process can be obtained from Eqs. (8), (9) and (12) (Table 2). Based on the experimental results, the kinetic parameters of the crystallization process were calculated by the Arrhenius Equation, and summarized in Table 3.
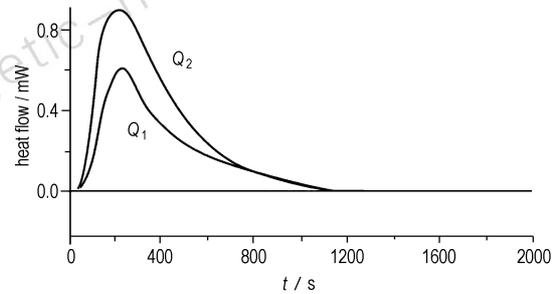
Fig. 1 Typical thermogram obtained during dilution/crystallization

Table 1 Thermokinetical data of the reaction at different temperatures[1)]

| T/K | t/s | total reaction process | | dilution process | | crystallization process | | $Q_{3i}/Q_{\infty 3}$ |
		Q_{1i} /mJ	$(dQ/dt)_{1i} \cdot 10^2$ /J·s^{-1}	Q_{2i} /mJ	$(dQ/dt)_{2i} \cdot 10^2$ /J·s^{-1}	Q_{3i} /mJ	$(dQ/dt)_{3i} \cdot 10^2$ /J·s^{-1}	
298.15	210	4886.65	2.86	1876.25	1.15	3010.40	1.72	0.2117
	220	5170.07	2.83	1990.32	1.30	3179.75	1.70	0.2237
	230	5449.48	2.78	2102.76	1.11	3346.72	1.67	0.2354
	240	5724.61	2.74	2213.44	1.09	3511.17	1.65	0.247
	250	5995.22	2.69	2322.26	1.08	3672.96	1.62	0.2583
	260	6261.16	2.65	2429.15	1.06	3832.00	1.59	0.2695
	270	6522.27	2.60	2534.06	1.04	3988.22	1.56	0.2805
	280	6778.32	2.55	2636.91	1.02	4141.41	1.53	0.2913
	290	7029.38	2.50	2737.62	0.994	4291.76	1.50	0.3019
	300	7275.39	2.45	2836.22	0.973	4439.17	1.47	0.3122
	310	7516.36	2.40	2932.70	0.952	4583.66	1.44	0.3224
	320	7752.27	2.35	3027.08	0.931	4725.19	1.41	0.3324
$Q_{1\infty} = -20534.885$ mJ, $Q_{2\infty} = -6317.540$ mJ, $Q_{3\infty} = -14217.345$ mJ								
301.15	170	4055.95	3.05	1470.40	1.10	2585.56	1.96	0.1709
	180	4325.53	3.01	1578.21	1.08	2747.32	1.93	0.1816
	190	4656.63	2.97	1684.37	1.07	2972.26	1.90	0.1964
	200	4949.77	2.91	1788.73	1.05	3161.05	1.87	0.2089
	210	5237.59	2.86	1891.16	1.03	3346.43	1.83	0.2212
	220	5519.81	2.80	1991.58	1.01	3528.24	1.79	0.2332
	230	5796.20	2.74	2089.93	0.987	3706.27	1.76	0.2450
	240	6066.61	2.68	2186.16	0.965	3880.50	1.72	0.2565
	250	6330.80	2.62	2280.15	0.944	4050.65	1.68	0.2677
	260	6588.77	2.56	2372.06	0.923	4216.72	1.63	0.2787
	270	6840.58	2.50	2461.82	0.901	4378.76	1.59	0.2894
	280	7086.22	2.43	2549.44	0.880	4536.78	1.55	0.2998
$Q_{1\infty} = -22725.625$ mJ, $Q_{2\infty} = -7595.439$ mJ, $Q_{3\infty} = -15130.186$ mJ								

(Table 1 continued)

T/K	t/s	total reaction process		dilution process		crystallization process		$Q_{3i}/Q_{\infty 3}$
		Q_{1i}	$(dQ/dt)_{1i} \cdot 10^2$	Q_{2i}	$(dQ/dt)_{2i} \cdot 10^2$	Q_{3i}	$(dQ/dt)_{3i} \cdot 10^2$	
		/mJ	/J$\cdot$s^{-1}	/mJ	/J$\cdot$s^{-1}	/mJ	/J$\cdot$s^{-1}	
304.15	300	9032.84	3.09	2763.68	0.886	6269.16	2.21	0.3751
	310	9338.84	3.03	2851.26	0.865	6487.57	2.16	0.3881
	320	9638.37	2.96	2936.82	0.845	6701.55	2.12	0.4009
	330	9931.42	2.90	3020.31	0.825	6911.10	2.07	0.4135
	340	10217.87	2.83	3101.83	0.805	7116.04	2.03	0.4257
	350	10497.94	2.77	3181.41	0.786	7316.53	1.98	0.4377
	360	10771.67	2.71	3259.09	0.767	7512.58	1.94	0.4494
	370	11039.15	2.64	3334.90	0.749	7704.25	1.89	0.4609
	380	11300.43	2.58	3408.88	0.730	7891.55	1.85	0.4721
	390	11555.60	2.52	3481.06	0.713	8074.54	1.81	0.4831
	400	11804.74	2.46	3551.46	0.695	8253.28	1.77	0.4938
	410	12047.77	2.40	3620.12	0.678	8427.65	1.72	0.5042

$Q_{1\infty} = -25468.586$ mJ, $Q_{2\infty} = -8753.365$ mJ, $Q_{3\infty} = -16715.221$ mJ

T/K	t/s	Q_{1i}	$(dQ/dt)_{1i} \cdot 10^2$	Q_{2i}	$(dQ/dt)_{2i} \cdot 10^2$	Q_{3i}	$(dQ/dt)_{3i} \cdot 10^2$	$Q_{3i}/Q_{\infty 3}$
317.15	300	11674.51	3.96	4080.34	1.37	7594.17	2.58	0.43133
	310	12066.188	3.88	4214.83	1.34	7851.35	2.53	0.44445
	320	12449.70	3.79	4346.50	1.32	8103.19	2.48	0.45730
	330	12825.08	3.71	4475.34	1.29	8349.74	2.42	0.46986
	340	13192.36	3.63	4601.27	1.26	8591.09	2.37	0.48214
	350	13551.39	3.55	4724.35	1.23	8827.04	2.32	0.49415
	360	13902.39	3.47	4844.59	1.20	9057.8	2.27	0.50590
	370	14245.49	3.39	4962.04	1.18	9283.46	2.21	0.51737
	380	14580.82	3.31	5076.75	1.15	9504.06	2.16	0.52859
	390	14908.46	3.24	5188.75	1.12	9719.71	2.12	0.53956
	400	15228.54	3.16	5298.05	1.10	9930.49	2.07	0.55027
	410	15541.16	3.09	5404.68	1.07	10136.5	2.02	0.56073

$Q_{1\infty} = -28529.895$ mJ, $Q_{2\infty} = -9743.265$ mJ, $Q_{3\infty} = -18786.63$ mJ

Note：1) $(dQ/dt)_{1i}$ is the total heat produce rate at t, which includes two parts：firstly, the heat produce rate $(dQ/dt)_{2i}$ from the mixing of the solution and diluent, secondly, the heat produce rate $(dQ/dt)_{3i}$ from crystallizing at t. Q_{1i}, Q_{2i} and Q_{3i} are the heat of the above three processes, respectively. The total heat produced during crystal growth process and the rate constant at different temperatures is shown in Table 2. Because the values of the constants a and b are small in comparison with those of k_2 and k_1, the kinetics of the crystal growth process can be expressed by Eqs. (4) and (5).

Table 2　The experimental results of the dilution/crystallization kinetics at different temperatures[1)]

T /K	solute /g	solvent /g	diluent /g	$-Q_\infty$ /J$\cdot$g^{-1}	$\dfrac{dQ}{dt} = k_2\left(1 - \dfrac{Q}{Q_\infty}\right) + a$			$\dfrac{dm}{dt} = k_1 m_\infty (c - c_\infty) + b$	
					$k_2 \cdot 10^2$ /J$\cdot$s^{-1}	$-a \cdot 10^3$ /J$\cdot$s^{-1}	r	$k_1 \cdot 10^3$ /s^{-1}	$-b \cdot 10^5$ /g$\cdot$s^{-1}
298.15	0.0609	2.789	0.1533	303.2	2.55	2.8	0.996	0.867	0.924
				306.4	2.53	2.5	0.999	0.860	0.825
				301.5	2.56	2.7	0.998	0.870	0.891
				302.7	2.54	2.9	0.994	0.863	0.957
				305.4	2.49	3.0	0.992	0.846	0.989
				304.6	2.58	2.6	0.996	0.877	0.858
			mean	304.0	2.54	2.8		0.863	0.907
301.15	0.0609	2.789	0.1533	322.7	3.14	6.2	0.992	1.00	1.92
				319.6	3.15	6.1	0.995	1.01	1.89
				324.4	3.12	5.0	0.998	0.996	1.55
				325.3	3.13	5.8	0.996	1.00	1.80
				320.7	3.16	5.4	0.997	1.01	1.67
				323.1	3.17	5.9	0.994	1.01	1.83
			mean	322.6	3.14	5.8		1.01	1.78

(Table 2 continued)

T /K	solute /g	solvent /g	diluent /g	$-Q_\infty$ /J·g⁻¹	$\dfrac{\mathrm{d}Q}{\mathrm{d}t} = k_2\left(1 - \dfrac{Q}{Q_\infty}\right) + a$			$\dfrac{\mathrm{d}m}{\mathrm{d}t} = k_1 m_\infty(c - c_\infty) + b$	
					$k_2 \cdot 10^2$ /J·s⁻¹	$-a \cdot 10^3$ /J·s⁻¹	r	$k_1 \cdot 10^3$ /s⁻¹	$-b \cdot 10^5$ /g·s⁻¹
304.15	0.0609	2.789	0.1533	356.5	3.75	1.3	0.999	1.08	0.365
				353.4	3.76	0.99	0.999	1.09	0.278
				359.2	3.70	1.5	0.998	1.07	0.421
				354.9	3.77	1.2	0.997	1.09	0.337
				356.7	3.69	0.97	0.998	1.07	0.272
				358.2	3.78	1.7	0.999	1.09	0.477
			mean	356.5	3.74	1.3		1.08	0.356
307.15	0.0609	2.789	0.1533	400.6	4.36	1.1	0.999	1.12	0.275
				404.3	4.32	1.5	0.998	1.11	0.374
				397.8	4.40	0.93	0.995	1.13	0.232
				402.3	4.38	0.96	0.999	1.13	0.240
				398.7	4.35	1.6	0.996	1.12	0.399
				396.9	4.37	0.99	0.998	1.12	0.247
			mean	400.1	4.36	1.18		1.12	0.295

Note: 1) Q_∞, Total heat produced, J·g⁻¹; dQ/dt, rate of heat production at time t, J·s⁻¹; k_2, rate constant of crystal growth, J·s⁻¹; Q, heat production at time t, J; a, constant, J·s⁻¹; dm/dt, rate of crystal growth at time t, g·s⁻¹; k_1, rate constant of crystal growth, s⁻¹; m_∞, total mass of solid deposited, g; c, solute concentration in the solution, (g/100 g solvent); c_∞, equilibrium saturation concentration, (g/100 g solvent); b, constant, g·s⁻¹.

Table 3　Kinetic, thermodynamical parameters for the reactions

T/K	k	$-\ln k$	r	$\Delta^{\neq} G_m$ /kJ·mol⁻¹
298.15	0.0255	3.669	0.996	82.11
301.15	0.0314	3.461	0.992	82.45
304.15	0.0375	3.283	0.999	82.84
307.15	0.0436	3.133	0.999	83.30

E_a /kJ·mol⁻¹	$\ln[A/s^{-1}]$	$\Delta^{\neq} H_m$ /kJ·mol⁻¹	$-\Delta^{\neq} S_m$ /J·mol⁻¹·K⁻¹
45.37	14.65	42.85	131.58

3.2　Measurement of the specific heat capacity of $Cu(TO)_2Cl_2$ at 298.15 K

3.2.1　Derivation of formula of specific heat capacity

The specific heat capacity of a substance can be determined according to the principle showed in Fig. 2.
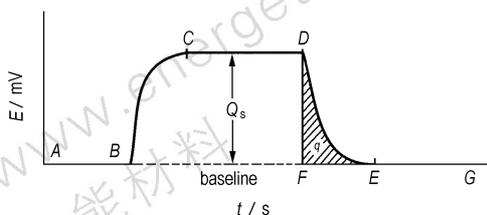
Fig.2　Schematic thermogram of the heat capacity of solid

In Fig. 2, AG is the baseline; at time B, the Peltier current is given to heat; at CD, a new homeostasis state forms (Q_s is the amount of heat flux under the steady-state condition); at the point D, the Peltier current is cut; at time E, the system comes back to the original state (that is baseline); q is the area integral of the shadow part in the figure representing the whole disequilibrium heat.

To measure the specific heat capacity capacities of the samples, the empty cell (system 1), the cell containing the test sample (system 2), the cell containing the first standard substance (system 3) and the cell containing the second standard substance (system 4) are heated by the same Peltier current with the microcalarimetry, then the endothermic equations are obtained:

to system 1： $q_0 = a\theta$　　　　　　　　　　(13)

to system 2： $q = (a + mc) \theta$　　　　　　(14)

to system 3： $q_1 = (a + m_1 c_1) \theta$　　　　(15)

to system 4： $q_2 = (a + m_2 c_2) \theta$　　　　(16)

where q_0、q、q_1、q_2 are the heats of thermal disequilibrium as the curve returns to baseline after the Peltier current of the above four systems are cut, respectively, J; a is the apparent heat capacity of the empty cell, J·K⁻¹; θ is the equilibrium temperature of calorimeter at homeostasis state, K; m、m_1、m_2 are the mass of the test sample,

the first standard substance and the second standard one, respectively, g; c、c_1、c_2 are the specific heat capacities of these samples, respectively, $J \cdot g^{-1} \cdot K^{-1}$.

Combining Eqs. (13) – (16), we have

$$c = \left[\frac{q - q_0}{2m} \right] \left[\frac{m_1 c_1}{q_1 - q_0} + \frac{m_2 c_2}{q_2 - q_0} \right] \quad (17)$$

Providing having the specific heat capacities c_1 and c_2 of the two standard substances, the specific heat capacity c,

calibrated by these standard substances, of the test sample can be calculated according to Eq. (17).

3.2.2   Specific heat capacities of the empty cell and the standard substances

RD-496 microcalorimeter is used to determine the specific capacity of $Cu(TO)_2Cl_2$. The specific heat capacities of the empty cell and the standard substances were determined according to the above method and listed in Table 4.

Table 4   Data of the heat and heat capability of the empty cell and the standard substances (298.15 K)

heats of disequilibrium and specific heat capacity	the empty cell	standard α-Al_2O_3	sublimed benzoic acid
m/g	32.46791	3.24294	2.80101
$q(1)/mJ^{1)}$	3689.151	3825.725	3909.248
$q(2)/mJ$	3686.060	3827.302	3912.491
$q(3)/mJ$	3687.238	3829.849	3911.858
$q(4)/mJ$	3690.008	3837.946	3908.362
$q(5)/mJ$	3683.045	3830.873	3912.998
$q(6)/mJ$	3691.994	3830.667	3914.650
$q(\text{mean} \pm SD^{2)})/mJ$	3687.916 ± 1.293	3828.727 ± 0.842	3911.601 ± 0.968
precision(RSD)$^{3)} \cdot 10^4$	3.506	2.200	2.476
specific heat capacity $c/(J \cdot mol^{-1} \cdot K^{-1})$		79.017 ± 1.647(79.03[14])	145.350 ± 1.201(145.327[15])

Note: 1) (1) – (6) is the sequence numbers of the experiments. 2) $SD = \sqrt{\dfrac{\sum (x_i - \bar{x})^2}{n-1}} \Big/ \sqrt{n}$; 3) $RSD = \dfrac{SD}{\bar{x}}$

3.2.3   Specific heat capacity of complex

The heat of disequilibrium for the complexes was measured by an RD-496 microcalorimeter, and their specific heat capacity was calculated from the data in Table 4 by Eq. 17 and presented in Table 5.

Table 5   Data of the specific heat capacities of the complexes $Cu(TO)_2Cl_2$ (298.15 K)

m /g	q /mJ	q (mean ± SD) /mJ	c (mean ± SD) /(J · mol^{-1} · K^{-1})
3.39969	3899.729		
3.39969	3901.281		
3.39969	3904.825		
3.39969	3899.954	3901.432 ± 0.973	114.301 ± 1.618
3.39969	3903.825		
3.39969	3898.976		

3.3   Calculation of the standard enthalpy of formation of $Cu(TO)_2Cl_2$

The enthalpy of solution of TO in deionized water at 298.15 K was determined by 6 experiments using an RD496-Ⅲ microcalorimeter according to the methods reported in literature[16], and $\Delta_{sol}H_m^\theta = (15.43 \pm 0.18)$ kJ · mol^{-1} was derived.

$$\Delta_f H_m^\theta (TO, aq) = \Delta_{sol}H_m^\theta + \Delta_f H_m^\theta (TO, cr) \quad (18)$$

Where $\Delta_f H_m^\theta (TO, cr) = (-142.4 \pm 0.70)$ kJ · mol$^{-1[17]}$, so $\Delta_f H_m^\theta (TO, aq) = (-126.97 \pm 0.72)$ kJ · mol^{-1}.

From the Eqs. (1) and (2), Eqs. (19) and (20) are derived:

$$\Delta_f H_m^\theta (Cu(TO)_2^{2+}, aq) =$$
$$\Delta_r H_m^\theta (1) + \Delta_f H_m^\theta (Cu^{2+}, aq) + 2\Delta_f H_m^\theta (TO, aq) \quad (19)$$
$$\Delta_f H_m^\theta (Cu(TO)_2Cl_2, s) =$$
$$\Delta_r H_m^\theta (2) + 2\Delta_f H_m^\theta (Cl^-, aq) + \Delta_f H_m^\theta (Cu(TO)_2^{2+}, aq) \quad (20)$$

Where $\Delta_r H_m^\theta (1) = (-1.25 \pm 0.02)$ kJ · mol^{-1}, $\Delta_r H_m^\theta (2) = (-71.09 \pm 0.43)$ kJ · mol^{-1}, ($\Delta_r H_m^\theta (1)$ and $\Delta_r H_m^\theta (2)$ are derived from 6 experiments using RD496-Ⅲ microcalorimeter according to the literature methods[18]), $\Delta_f H_m^\theta (Cu^{2+}, aq) = (65.69 \pm 0.80)$ kJ · mol$^{-1[19]}$, $\Delta_f H_m^\theta (Cl^-, aq) = (-167.08 \pm 0.09)$ kJ · mol$^{-1[19]}$, $\Delta_f H_m^\theta (TO, aq) = (-126.57 \pm 0.72)$ kJ · mol^{-1}, By substituting the above values to Equations 19 and 20, the enthalpies of formation of $Cu(TO)_2^{2+}(aq)$ and $Cu(TO)_2Cl_2(s)$ were obtained:

$$\Delta_f H_m^\theta [Cu(TO)_2^{2+}, aq] = (-189.50 \pm 1.65) \text{ kJ · mol}^{-1},$$
$$\Delta_f H_m^\theta [Cu(TO)_2Cl_2, s] = (-594.75 \pm 1.71) \text{ kJ · mol}^{-1}.$$

4   Conclusions

The new complex $Cu(TO)_2Cl_2$ was synthesized and characterized. According to the synthesis process of the complex, a crystal growth kinetics model in mixed sol-

vents was proposed，and the thermodynamics parameters were obtained utilizing this kinetic model. Furthermore，the enthalpy of formation and the specific heat capacity of the title complex was determined using the microcalimetry RD496-Ⅲ. These data provided theoretical foundation for the further exploration of metal complexes with 1,2,4-triazole-5-one in the field of energetic materials.

References：

［1］ MA Hai-xia，SONG Ji-rong，SUN Xiao-hong，et al. Preparation，crystal structure and thermodynamic properties of ［Mg（H₂O）₆］（NTO）₂ ·2H₂O［J］. *Thermochimica Acta*，2002，389：43 −47.

［2］ SONG Ji-rong，NING Bin-ke，HU Rong-zu，et al. Preparation，crystal structure and thermal decomposition process of ［Y（NTO）₂ NO₃（H₂O）₅］·2H₂O［J］. *Thermochimica Acta*，2000，352 −353：111 −115.

［3］ Jimmie C Oxley，James L Smith，ZHOU Zun-ling，et al. Thermal decomposition studies on NTO and NTO/TNT［J］. *J Phys Chem*，1995，99：10383 −10391.

［4］ ZHANG Jian-guo，ZHANG Tong-lai，ZHANG Zhi-gang，et al. Preparation and molecular structure of ｛［Ag（ATO）₂］ClO₄｝n［J］. *Acta Chimica Sinica*，2000，58（5）：533 −537.

［5］ Singh G，Prem Felix S. Studies on energetic compounds Part 36：Evaluation of transition metal salts of NTO as burning rate modifiers for HTPB-AN composite solid propellants［J］. *Combustion and Flame*，2003，135：145 −150.

［6］ ZHANG Tong-lai，HU Rong-zu，LI Fu-ping，et al. Preparation and crystal structure of di-（3-nitro-1，2，4-triazol-5-onate）-hexahydrate manganese（Ⅱ）with crystal water［J］. *Chinese Journal of Energetic Materials（Hanneng Cailiao）*，1993，1（1）：37 −42.

［7］ ZHANG Jian-guo，ZHANG Tong-lai，LU Zheng，et al. Preparation and crystal structure of ［Ag（TO）₂］ClO₄ ·H₂O［J］. *Acta Chimica Sinica*，1999，57：1233 −1238.

［8］ ZHANG Jian-guo，ZHANG Tong-lai，YANG Li，et al. Preparation and crystal structure of ［Cu（TO）₂（H₂O）₄］（PA）₂［J］. *Chin J Inorg Chem*，2002，18（3）：284 −288.

［9］ MA Gui-xia，ZHANG Tong-lai，ZHANG Jian-guo，et al. Structure and thermal stability of a novel 2D layered copper（Ⅱ）coordination polymer with the bidentate ligand 1，2，4-triazole-5-one［J］. *Anorg Allg Chem*，2004，630：423 −426.

［10］ JI Mian，LIU Ming-yan，GAO Sheng-li，et al. A new microcalorimeter for measuring thermal effects［J］. *Instrument Sci Technol*，2001，29：53 −57.

［11］ Boudakian M M，Fidler D A. Process for low chloride 1,2,4-triazol-5-one［P］. US Patent 1990，4,927,940.

［12］ LI Jia-rong，CHEN Bo-ren，OU Yu-xiang. Synthesis of 1,2,4-triazole-3-one derivatives［J］. *Chinese Journal of Energetic Materials（Hanneng Cailiao）*，1998，6（3）：107 −111.

［13］ Martha V K. The enthalpy of solution of SRM 1655（KCl）in H₂O［J］. *Res NBS*，1980，85：476 −481.

［14］ Ditmars D A，Ishihara S，Chang S S. Enthalpy and heat capacity standard reference material：Synthesis sapphire（α-Al₂O₃）from 10 to 2250 K［J］. *J Res Nat Bur Stand*，1982，87：159 −163.

［15］ Aaron R A，Eulogio O G. Thermochemistry of methyl-D-glucopyranosides and methyl-D-galactopyranosides［J］. *J Chem Thermody*，2000，32（6）：767 −775.

［16］ SONG Ji-rong，MA Hai-xia，HUANG Jie，et al. Preparation，crystal structure，thermal decomposition mechanism and thermodynamic properties of ［Co（H₂O）₆］（NTO）₂ ·2H₂O［J］. *Thermochimica Acta*，2004，416：43 −46.

［17］ Arthur Finch，P J Gardner，A J Head，et al. The enthalpy of formation of 1，2，4-triazole-5-one and 3-nitro-1，2，4-triazole-5-one［J］. *J Chem Thermodyn*，1991，23：1169 −1173.

［18］ CHEN San-ping，GAO Sheng-li，SHI Qi-zhen. Thermokinetic study on the complexation reaction of the first-row transition metal chlorides with histidine［J］. *Chin J Chem*，2004，22：1115 −1122.

［19］ Academic Press Inc.（London）Ltd. CODATA recommended key values for thermodynamics，1977 Report of the CODATA task group on key values for thermodynamics，1977［J］. *J Chem Thermodyn*，1978，10：903 −906.

$Cu(TO)_2Cl_2$ 的制备和热力学研究

李　娜，陈三平，高胜利，胡荣祖

（陕西省物理无机化学重点实验室，西北大学化学系，陕西 西安 710069）

摘要：根据制备过程，提出了配合物 $Cu(TO)_2Cl_2$ 在混合溶液中的晶体生长的动力学模型。通过这个动力学模型，测定了一系列的动力学参数：E_a = 45.37 kJ·mol^{-1}，$\ln(A/s^{-1})$ = 14.65，$\Delta^{\neq} G_m$ = 82.11 kJ·mol^{-1}，$\Delta^{\neq} H_m$ = 42.85 kJ·mol^{-1}，$\Delta^{\neq} S_m$ = 131.58 J·mol^{-1}·K^{-1}。另外，用 RD496-Ⅲ 型微量热计测定了该化合物在 298.15 K 时的比热容，并计算了 $[Cu(TO)_2]^{2+}$（aq）和 $Cu(TO)_2Cl_2$（s）的标准生成焓。

关键词：物理化学；微量热计；晶体生长的动力学；比热容；生成焓；$Cu(TO)_2Cl_2$

中图分类号：TJ55；O064　　　　　　　　　　　　　　　　　　　　**文献标识码**：A