

Investigation of the Crystallization Kinetics of Zn(Met)(AcO)₂•H₂O in Mixed Solution of Water and Acetone by Microcalorimetry

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The crystal growth process of Zn(Met)(AcO)₂•H₂O from the mixed solution of water and acetone has been investigated using a Calvet microcalorimeter. The heat produced and the rate of heat production during the crystal growth process at 298.15, 301.15, 304.15, 307.15 and 310.15 K have been measured. On the basis of experimental and calculated results, the thermodynamics parameters (the apparent activation enthalpy, the activation entropy, and the activation free energy), the rate constant and the kinetic parameters (the activation energy, the pre-exponential factor) during the crystal growth process have been obtained. The results show that the crystal growth proceeds in accordance with the Burton-Cabrera-Frank dislocation theory.

Keywords zinc acetate, *L*-α-methionine, complex, crystallization kinetics, microcalorimetry

Introduction

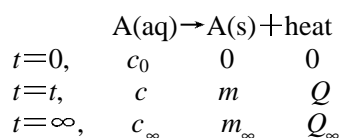
The complexes of zinc salts with α-amino acid as additive have a wide application in medicine, foodstuff and cosmetics.¹⁻³ The synthesis methods of the complexes of zinc salts with α-amino acid have been reviewed.⁴ The solubility of Zn(AcO)₂-Met-H₂O system at 298.15 K has ever been investigated by the semi-micro-phase equilibrium method.⁵ The phase diagram is a simple one, in which the solid complex of Zn(AcO)₂ and Met can not be obtained at 298.15 K. Zn(Met)²⁺ in solution was reported in Ref. 6. In order to obtain the solid complex, we intend to change the properties of solvent and thus decrease the solubility of the complex.

In this paper, the complex of Zn(Met)(AcO)₂•H₂O, which was not reported, was prepared by adding acetone into the reaction solution of Zn(AcO)₂ and Met with the optimum volume ratio of water : acetone of 1 : 25. The crystal growth processes of the complex at 298.15, 301.15, 304.15, 307.15 and 310.15 K were investigated by microcalorimetry. The experimental results showed that the process accorded with the Burton-Cabrera-Frank dislocation theory.⁷ This work was valuable for the preparation of the new complexes of zinc salts with α-amino acid.

Derivation of the kinetic equation of the crystal growth process⁷⁻⁹

In order to analyze the kinetics of the crystal growth process of the complexes of Zn²⁺ with amino acid, the

following general form of the crystal growth process was used



where c is the solute concentration in the solution at time t , m the mass of solid deposited during a certain time t , Q the heat produced during a certain time t . When $t=0$, $c=c_0$, $m=0$ and $Q=0$; when $t=\infty$, $c=c_\infty$, $m=m_\infty$, and $Q=Q_\infty$. The relationship between the energy change (*i.e.* the heat produced) of a reaction system and the extent (*i.e.* mass or concentration) of the reaction is given by

$$\frac{Q}{Q_\infty} = \frac{m}{m_\infty} = \frac{c_0 - c}{c_0 - c_\infty} \quad (1)$$

$$\text{and } \frac{c_\infty - c}{c_\infty - c_0} = \frac{m_\infty - m}{m_\infty} = \frac{Q_\infty - Q}{Q_\infty} \quad (2)$$

From Eq. (1), we have $\frac{m_\infty}{Q_\infty} \cdot Q = m$ and

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$$\frac{dm}{dt} = \left(\frac{m_\infty}{Q_\infty} \right) \frac{dQ}{dt} \quad (3)$$

and from Eq. (2), we obtain

$$c - c_\infty = (c_0 - c_\infty) \left(1 - \frac{Q}{Q_\infty} \right) \quad (4)$$

According to the Burton-Cabrera-Frank (BCF) dislocation theory, for relatively high supersaturations, the rate of crystal growth at time t (dm/dt) may be expressed as

$$\frac{dm}{dt} = k_1 m_\infty (c - c_\infty) \quad (5)$$

where k_1 is the rate constant of crystal growth.

The combination of Eq. (5) may be expressed as Eq. (6)

$$\frac{dQ}{dt} = k_1 Q_\infty (c_0 - c_\infty) \left(1 - \frac{Q}{Q_\infty} \right) = k_2 \left(1 - \frac{Q}{Q_\infty} \right) \quad (6)$$

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

If $c_0 \gg c_\infty$, from Eq. (6), we have

$$\frac{dQ}{dt} = k_1 Q_\infty c_0 \left(1 - \frac{Q}{Q_\infty} \right) = k_3 \left(1 - \frac{Q}{Q_\infty} \right) \quad (7)$$

where $k_3 = k_1 Q_\infty c_0$.

On plotting $\left(\frac{dQ}{dt} \right)_i$ versus $\left(1 - \frac{Q}{Q_\infty} \right)_i$ by the

least-squares method, k_3 or k_2 (slope) and a (intercept) are obtained, as shown in the Eqs. (8) and (9)

$$\frac{dQ}{dt} = k_3 \left(1 - \frac{Q}{Q_\infty} \right) + a \quad (8)$$

or

$$\frac{dQ}{dt} = k_1 Q_\infty (c_0 - c_\infty) \left(1 - \frac{Q}{Q_\infty} \right) + a = k_2 \left(1 - \frac{Q}{Q_\infty} \right) + a \quad (9)$$

where

$$k_1 = \frac{k_2}{Q_\infty (c_0 - c_\infty)} \quad \frac{c_0 \gg c_\infty}{\frac{k_2}{Q_\infty c_0}} \quad (10)$$

The combination of Eqs. (7) and (8) gives

$$\begin{aligned} \frac{dm}{dt} &= \left(\frac{m_\infty}{Q_\infty} \right) \frac{dQ}{dt} = \frac{m_\infty}{Q_\infty} \left[k_1 Q_\infty (c_0 - c_\infty) \left(1 - \frac{Q}{Q_\infty} \right) + a \right] \\ &= \frac{m_\infty}{Q_\infty} [k_1 Q_\infty (c - c_\infty) + a] = k_1 m_\infty (c - c_\infty) + \frac{a m_\infty}{Q_\infty} \end{aligned} \quad (11)$$

Similarly, Eq. (5) may be written as

$$\frac{dm}{dt} = k_1 m_\infty (c - c_\infty) + b \quad (12)$$

where b is the intercept of Eq. (12).

Combining Eqs. (11) and (12), Eq. (13) is obtained

$$b = \frac{a m_\infty}{Q_\infty} \quad (13)$$

If the constants a and b are small as compared with those of k_2 (or k_3) and k_1 , the kinetics of the crystal growth process can be expressed by Eqs. (5) and (6).

On the basis of experimental and calculated results, according to the Ref. 8, three thermodynamics parameters (the activation enthalpy, the activation entropy and the activation free energy), the rate constant, three kinetic parameters (the activation energy, the pre-exponential constant and the reaction order) were obtained at different temperatures.

Experimental

Materials

Zn(AcO)₂•2H₂O and acetone (A.R., Xi'an Chemical Co.), its density was 0.792 g•cm⁻³ at 298.15 K. *L*-α-Met (B.R., Shanghai Kangda Co.) with purity >99.9% was used. The conductivity of the deionized water was 5.48 × 10⁻⁸ S•cm⁻¹ and density was 0.99705 g•cm⁻³ at 298.15 K. The others were of A.R. grade.

Analysis method

Zn²⁺ was determined with EDTA by complexometric titration. Met was analyzed by the formalin method, before which Zn²⁺ was removed by precipitating with K₂C₂O₄. Carbon, hydrogen and nitrogen analyses were performed on a 2400 type elemental analyzer.

Experimental method

The calorimetric experiment was performed using a RD496-III type microcalorimeter.⁹ The microcalorimeter was calibrated by Joule effect before experiment, and the sensitivities were determined to be (63.994 ± 0.042), (64.190 ± 0.028), (64.299 ± 0.064), (64.399 ± 0.072) and (64.498 ± 0.057) μV•mW⁻¹ at 298.15, 301.15, 304.15, 307.15 and 310.15 K, respectively. The enthalpy of solution in deionized water of KCl (spectral purity) was measured to be (17.238 ± 0.048) kJ•mol⁻¹, which was very close to (17.241 ± 0.018) kJ•mol⁻¹.¹⁰ The accuracy

was 0.02% and the precision was 0.3%, which indicated that the calorimetric system was accurate and reliable. The reaction solution/solvent and the diluent were taken in a stainless steel sample cell (15 cm³) in Figure 1, separately. After equilibrium, the bottom of the sample and reference were pushed down simultaneously. As a result, the two liquids were mixed and the thermogram was recorded.

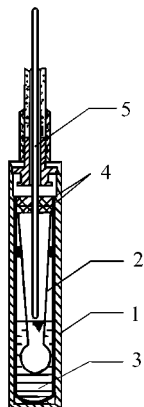


Figure 1 Sketch used for study of the formation reaction. 1—calorimetric cell; 2—solution of Zn(AcO)₂ with Met; 3—acetone; 4—silicone rubber cover; 5—glass rod.

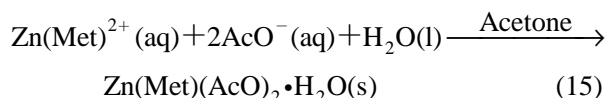
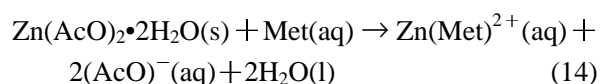
Results and discussion

Preparation of the complex

Zn(Met)²⁺(aq) was produced from the reaction of Zn(AcO)₂•2H₂O with Met in water (lg *K* is 4.40).⁶ The solubility was too high to obtain the solid complex. Addition of acetone decreased the solubility of the complex and the solution became a relatively high-supersaturated system. Based on the above consideration, with the volume ratio of water : acetone of 1 : 25, the white solid compound was obtained. After suction filtration for the mixed solution, followed by rinsing with a little acetone and drying to constant weight in vacuum, the white powder was obtained. The compound is soluble in water, but insoluble in alcohol, acetone and other organic solvents. The yield of the compound is 76%. The result of elemental analysis is Zn 18.82%, Met 42.17%, C 30.69%, H 5.88% and N 4.12%, which shows that the chemical formula of the compound is Zn(Met)(AcO)₂•H₂O compared with the theoretical value Zn 18.65%, Met 42.55%, C 30.82%, H 5.46% and N 3.99%. The experimental result on variable volume ratio of water to acetone is summarized in Table 1.

Dilution/crystallization kinetics

The crystal process is expressed in reactions (14) and (15).



A typical schematic thermogram during the dilution and crystallization is depicted in Figure 2. The original data obtained from the *T-K* curve are shown in Table 2. Using those data, the kinetic data during the dilution/crystallization process can be obtained from Eqs. (8), (9) and (12) (Table 2).

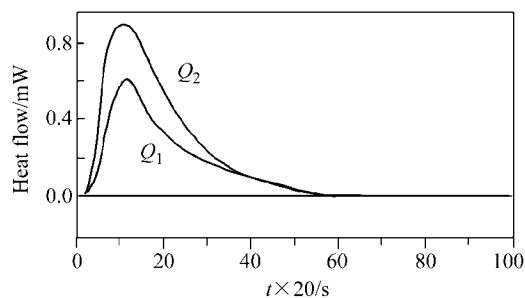


Figure 2 Typical thermogram of the dilution/crystallization process.

The experimental results in Table 3 were obtained based on the principle presented as a block diagram in Figure 3. In Figure 3, (d*Q*/d*t*)_{1*i*} is the rate of total heat production at time *t*, including (d*Q*/d*t*)_{2*i*}, the rate of the heat of mixing produced between solvent and diluent at time *t*, and (d*Q*/d*t*)_{3*i*}, the rate of the heat of crystallization of the crystal at time *t*; and *Q*_{1*i*} is the total heat produced during a certain time including *Q*_{2*i*}, *Q*_{2*i*} the heat of mixing produced between solvent and diluent during a certain time, *Q*_{3*i*} the heat of crystallization of the crystal during a certain time. The total heats produced during crystal growth process and the rate constants at different temperatures are shown in Table 3.

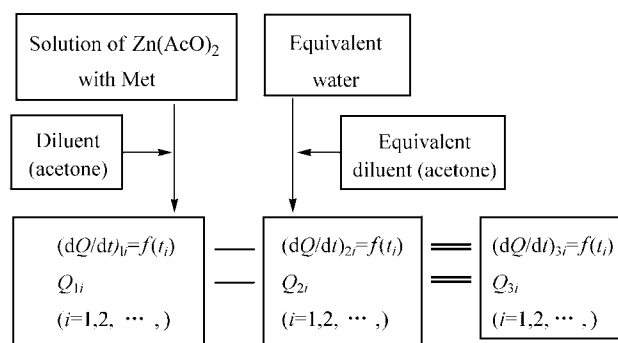


Figure 3 Block diagram of the process of studying dilution/crystallization kinetics.

Since 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 of Zn(Met)(AcO)₂•H₂O can be expressed by Eqs. (5) and (6). So, the crystal growth process of Zn(Met)(AcO)₂•H₂O accords with the BCF dislocation theory model. Finally, according to the Ref.

8, the kinetics parameters and the thermodynamics parameters during the crystal growth process were calculated, which are summarized in Table 4.

From Table 4, it is evident that the rate of reaction increases with increasing temperature and the reaction is

first order when the values of E and $\Delta^\ddagger H_m^\ominus$ are very low and $\Delta^\ddagger S_m^\ominus$ is high, which shows that the complexation reaction is spontaneous over the temperature range of 298.15—310.15 K.

Table 1 Experimental results of water and acetone with different volume ratio

Volume ratio	1 : 10	1 : 15	1 : 20	1 : 25	1 : 28	1 : 30	1 : 33
Phenomenon	turbid	turbid	precipitate	precipitate	precipitate decreasing gradually		
Yield/%	50	54	58	76	68	60	50

Table 2 Thermokinetical data of title reaction at different temperatures

<i>T/K</i>	<i>t/s</i>	Total reaction process		Dilution process		Crystallization process		$Q_{3i}/Q_{\infty 3}$
		Q_{1i}/mJ	$(dQ/dt)_{1i} \cdot 10^3 / (\text{J} \cdot \text{s}^{-1})$	Q_{2i}/mJ	$(dQ/dt)_{2i} \cdot 10^3 / (\text{J} \cdot \text{s}^{-1})$	$-Q_{3i}/\text{mJ}$	$-(dQ/dt)_{3i} \cdot 10^3 / (\text{J} \cdot \text{s}^{-1})$	
298.15	175	4348.27	26.8	4940.22	31.8	591.95	5.00	0.4399
	200	4992.98	24.9	5694.98	29.5	702.00	4.55	0.5217
	225	5589.90	23.0	6394.38	27.1	804.48	4.12	0.5978
	250	6140.19	21.2	7038.52	24.8	898.33	3.63	0.6675
	275	9947.48	19.5	7628.35	22.8	980.87	3.25	0.7289
	300	7114.68	17.9	8167.20	20.9	1052.52	2.91	0.7821
	325	7544.37	16.5	8659.49	19.0	1115.12	2.53	0.8286
	350	7939.69	15.2	9105.06	17.3	1165.37	2.14	0.8660
	375	8302.92	13.9	9511.09	15.9	1208.16	1.95	0.8978
	400	8635.84	12.8	9880.52	14.6	1244.68	1.83	0.9249
	425	8942.11	11.8	10216.5	13.4	1274.43	1.66	0.9470
450	9224.31	10.9	10522.4	12.4	1298.11	1.53	0.9646	
$Q_{1\infty} = 12672.31 \text{ mJ}, Q_{2\infty} = 14018.03 \text{ mJ}, Q_{3\infty} = -1345.72 \text{ mJ}$								
301.15	150	3463.18	29.5	3867.39	35.5	404.20	6.05	0.3204
	175	4180.24	28.2	4615.43	34.1	435.19	5.83	0.3450
	200	4862.93	26.7	5339.38	32.2	476.45	5.55	0.3777
	225	5504.39	25.0	6028.98	30.2	524.59	5.22	0.4158
	250	6102.58	23.2	6667.44	28.2	564.86	4.95	0.4478
	275	6658.53	21.5	7279.62	26.1	621.09	4.57	0.4923
	300	7172.64	19.9	7828.46	24.2	655.82	4.33	0.5198
	325	7646.44	18.3	8344.52	22.3	698.08	4.04	0.5533
350	8082.69	16.8	8817.34	20.6	734.64	3.79	0.5823	
$Q_{1\infty} = 13803.01 \text{ mJ}, Q_{2\infty} = 15064.57 \text{ mJ}, Q_{3\infty} = -1261.56 \text{ mJ}$								
304.15	200	7691.39	27.5	7900.54	37.5	209.15	9.94	0.1729
	250	8909.23	23.0	9292.29	31.4	383.06	8.35	0.3166
	300	9913.15	19.1	10434.5	26.1	521.38	7.08	0.4310
	350	10737.1	15.7	11355.9	21.9	618.84	6.18	0.5115
	400	11409.8	13.0	12090.9	18.6	681.05	5.61	0.5629
	450	11958.0	10.7	12675.0	16.0	716.99	5.29	0.5927
	500	12404.6	8.88	13163.0	13.8	758.34	4.90	0.6268
	550	12768.6	7.40	13530.7	12.2	762.00	4.81	0.6299

Continued

T/K	t/s	Total reaction process		Dilution process		Crystallization process		$Q_{3f}/Q_{\infty 3}$
		Q_{1f}/mJ	$(dQ/dt)_{1f} \cdot 10^3 / (\text{J} \cdot \text{s}^{-1})$	Q_{2f}/mJ	$(dQ/dt)_{2f} \cdot 10^3 / (\text{J} \cdot \text{s}^{-1})$	$-Q_{3f}/\text{mJ}$	$-(dQ/dt)_{3f} \cdot 10^3 / (\text{J} \cdot \text{s}^{-1})$	
	600	13065.8	6.19	13852.6	10.8	786.86	4.64	0.6504
	650	13308.8	5.22	14107.3	9.74	798.55	4.52	0.6608
	700	13507.9	4.44	14311.7	8.91	803.78	4.48	0.6644
		$Q_{1\infty} = 14562.85 \text{ mJ}, Q_{2\infty} = 15772.62 \text{ mJ}, Q_{3\infty} = -1209.78 \text{ mJ}$						
307.15	100	3264.61	32.5	3339.17	46.9	74.56	14.5	0.0637
	150	4835.61	30.4	5066.99	42.8	231.39	12.5	0.1977
	200	6270.77	27.1	6734.96	36.6	464.19	9.49	0.3967
	250	7535.95	23.7	8185.63	30.9	649.68	7.13	0.5552
	300	8636.93	20.6	9449.30	25.6	812.36	5.06	0.6942
	350	9586.79	17.7	10532.2	21.1	945.41	3.36	0.8079
	400	10401.9	15.2	11348.3	18.5	946.42	3.35	0.8087
	450	11098.9	13.0	12076.8	15.9	977.84	2.95	0.8356
	500	11693.2	11.1	12684.3	13.9	991.11	2.78	0.8470
		$Q_{1\infty} = 15136.83 \text{ mJ}, Q_{2\infty} = 16307.00 \text{ mJ}, Q_{3\infty} = -1170.17 \text{ mJ}$						
310.15	110	3237.63	41.3	3567.72	54.1	330.09	12.8	0.3268
	115	3433.62	41.3	3777.65	53.8	344.02	12.5	0.3405
	120	3635.76	41.2	3986.41	53.6	350.65	12.4	0.3471
	125	3835.77	41.0	4193.77	53.3	358.01	12.3	0.3544
	130	4031.78	40.9	4399.52	53.0	367.75	12.1	0.3640
	140	4423.94	40.4	4803.52	52.2	381.58	11.8	0.3777
		$Q_{1\infty} = 17247.44 \text{ mJ}, Q_{2\infty} = 18257.65 \text{ mJ}, Q_{3\infty} = -1010.20 \text{ mJ}$						

Table 3 The experimental results of the dilution/crystallization kinetics at different temperatures

T/K	Solute/g	Solvent/g	Diluent/g	$-Q_{\infty} / (\text{J} \cdot \text{g}^{-1})$	$\frac{dQ}{dt} = k_2 \left(1 - \frac{Q}{Q_{\infty}} \right) + a$			$\frac{dm}{dt} = k_1 (c - c_{\infty}) + b$	
					$k_2 \cdot 10^3 / (\text{J} \cdot \text{s}^{-1})$	$a \cdot 10^3 / (\text{J} \cdot \text{s}^{-1})$	r	$k_1 \cdot 10^2 / \text{s}^{-1}$	$b \cdot 10^6 / (\text{g} \cdot \text{s}^{-1})$
298.15	Zn(Met)(AcO) ₂ ·H ₂ O (0.00701)	H ₂ O (0.0997)	acetone (1.9800)	252.6	6.80	1.20	0.996	1.51	4.75
				256.1	6.75	2.80	0.992	1.47	10.9
				251.9	6.84	1.30	0.980	1.52	5.16
				255.0	6.81	4.50	0.999	1.49	17.6
				253.1	6.79	3.90	0.989	1.50	15.4
				248.2	6.83	1.10	0.986	1.54	4.43
				mean	252.8	6.80	2.47		1.51
301.15	Zn(Met)(AcO) ₂ ·H ₂ O (0.00701)	H ₂ O (0.0997)	acetone (1.9800)	236.8	8.60	2.00	0.999	2.03	8.45
				233.3	8.62	2.50	0.987	2.07	10.7
				238.4	8.55	1.80	0.999	2.01	7.55
				231.2	8.67	3.30	0.969	2.10	14.3
				240.9	8.59	1.60	0.990	1.99	6.64
				235.2	8.63	2.20	0.979	2.05	9.35
				mean	236.0	8.61	2.23		2.04

T/K	Solute/g	Solvent/g	Diluent/g	$-Q_{\infty}/$ (J•g ⁻¹)	$\frac{dQ}{dt} = k_2 \left(1 - \frac{Q}{Q_{\infty}}\right) + a$			$\frac{dm}{dt} = k_1 (c - c_{\infty}) + b$	
					$k_2 \cdot 10^3 / (\text{J} \cdot \text{s}^{-1})$	$a \cdot 10^3 / (\text{J} \cdot \text{s}^{-1})$	r	$k_1 \cdot 10^2 / \text{s}^{-1}$	$b \cdot 10^6 / (\text{g} \cdot \text{s}^{-1})$
304.15	Zn(Met)(AcO) ₂ •H ₂ O (0.00701)	H ₂ O	acetone	227.1	11.1	0.70	0.999	2.73	3.08
				227.6	10.9	1.00	0.987	2.68	4.39
				230.8	11.5	0.30	0.999	2.79	1.30
				224.9	10.8	1.20	0.969	2.69	5.34
				226.1	10.6	3.60	0.990	2.62	15.9
				226.3	11.8	0.90	0.979	2.92	3.98
				mean	227.1	11.1	1.28		2.74
307.15	Zn(Met)(AcO) ₂ •H ₂ O (0.00701)	H ₂ O	acetone	219.6	14.9	0.50	0.999	3.79	2.28
				220.3	15.0	1.30	0.987	3.81	5.90
				218.9	14.6	0.90	0.999	3.73	4.11
				216.0	15.2	0.10	0.969	3.94	0.46
				215.4	14.7	2.30	0.990	3.82	10.7
				222.8	15.4	1.40	0.979	3.87	6.28
				mean	218.8	14.9	1.08		3.83
310.15	Zn(Met)(AcO) ₂ •H ₂ O (0.00701)	H ₂ O	acetone	189.6	15.0	0.04	0.999	5.58	0.21
				190.5	14.6	0.01	0.987	5.61	0.05
				185.2	15.2	0.12	0.999	5.59	0.65
				191.6	14.7	0.32	0.969	5.43	1.67
				192.8	15.4	0.11	0.990	5.60	0.57
				187.3	14.9	0.03	0.979	5.68	0.16
				mean	189.5	18.9	0.11		5.58

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 of BCF (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 of BCF (g•s⁻¹).

Table 4 Kinetic and thermodynamical parameters of title reaction

T/K	$k \cdot 10^3 / \text{s}^{-1}$	r	$E / (\text{kJ} \cdot \text{mol}^{-1})$	$\ln A$ (A in s^{-1})	r	$\Delta^{\ddagger} G_{\text{m}}^{\ominus} / (\text{kJ} \cdot \text{mol}^{-1})$	$\Delta^{\ddagger} H_{\text{m}}^{\ominus} / (\text{kJ} \cdot \text{mol}^{-1})$	$\Delta^{\ddagger} S_{\text{m}}^{\ominus} / (\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$	r
298.15	6.80	0.996	66.46	21.8	0.998	-85.39	63.93	-72.12	0.998
301.15	8.60	0.999				-85.69			
304.15	11.1	0.999				-85.92			
307.15	14.9	0.999				-86.04			
310.15	18.9	0.998				-86.29			

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