

配合物 $\text{Zn}(\text{Leu})\text{SO}_4 \cdot 0.5\text{H}_2\text{O}$ 的合成与热行为李焕勇¹ 郭鹏江² 胡荣祖¹ 高胜利^{*1} 史启祯¹⁽¹⁾ 西北大学化学系, 陕西省物理无机化学重点实验室, 西安 710069)⁽²⁾ 西北大学数学系, 西安 710069)

在水-丙酮溶液中制备了 $\text{Zn}(\text{Leu})\text{SO}_4 \cdot 0.5\text{H}_2\text{O}$ 的配合物。通过热重和红外分析, 研究了它的热分解机理, 可分为三步完成。第一阶段配合物的脱水过程在 60 ~ 180°C, 形成 $\text{Zn}(\text{Leu})\text{SO}_4$, 第二阶段, $\text{Zn}(\text{Leu})\text{SO}_4$ 进一步分解为 $\text{Zn}(\text{Leu})\text{SO}_4 \cdot 9\text{ZnSO}_4$, 随后其在 728°C 完全分解为 ZnO 。在不同线性升温 5.0, 10.0, 15.0, 20.0 $\text{K} \cdot \text{min}^{-1}$ 条件下, 用两种积分法和三种微分法研究了题目化合物失去配体过程的非等温动力学, 相应过程的表现活化能 E 为 $133.78\text{kJ} \cdot \text{mol}^{-1}$, 指前因子 A 为 $10^{8.19}\text{s}^{-1}$, 配体失去过程为三维扩散机理控制, 并建立了反应过程的动力学方程。

关键词: 动力学 机理 热分解 配合物 $\text{Zn}(\text{Leu})\text{SO}_4 \cdot 0.5\text{H}_2\text{O}$
分类号: O614.24*1

The Preparation and Thermal Behavior of $\text{Zn}(\text{Leu})\text{SO}_4 \cdot 0.5\text{H}_2\text{O}$ LI Huan-Yong¹ GUO Peng-Jiang² HU Rong-Zu¹ GAO Sheng-Li^{*1} SHI Qi-Zhen¹⁽¹⁾ Department of Chemistry, Key Laboratory of Physico-inorganic Chemistry of Shaanxi Provinces, Northwest University, Xi'an 710069)⁽²⁾ Department of Mathematics, Northwest University, Xi'an 710069)

The solid complex $\text{Zn}(\text{Leu})\text{SO}_4 \cdot 0.5\text{H}_2\text{O}$ was prepared in water-acetone system. The non-isothermal decomposition of $\text{Zn}(\text{Leu})\text{SO}_4 \cdot 0.5\text{H}_2\text{O}$ was studied at various heating rates of 5.0, 10.0, 15.0 and 20.0 $\text{K} \cdot \text{min}^{-1}$ by TG-DTG and IR. The thermal decomposition processes of the complex can be divided into three stages. For the first stage, the complex was dehydrated from 60 to 185°C and $\text{Zn}(\text{Leu})\text{SO}_4$ was formed. And for the second stage, anhydrous $\text{Zn}(\text{Leu})\text{SO}_4$ was decomposed into $\text{Zn}(\text{Leu})\text{SO}_4 \cdot 9\text{ZnSO}_4$ and finally $\text{Zn}(\text{Leu})\text{SO}_4 \cdot 9\text{ZnSO}_4$ was decomposed completely into ZnO at 728°C. The non-isothermal decomposition mechanism and kinetics parameters of the ligand-losed process were obtained from an analysis of the TG-DTG curves by two integral and three differential methods. The results showed that three dimension diffusion mechanism controlled the ligand-losed process and the apparent activation energy E was $133.78\text{kJ} \cdot \text{mol}^{-1}$ and the pre-exponential constant A was $10^{8.19}\text{s}^{-1}$. The empirical kinetics model equation was proposed in this paper.

Keywords: kinetics mechanism thermal decomposition the solid complex $\text{Zn}(\text{Leu})\text{SO}_4 \cdot 0.5\text{H}_2\text{O}$

0 Introduction

Recently, considerable interest has been focused

on the complexes of zinc with amino acids due to their additives in medicines, food-stuff and cosmetics^[1-5]. The investigations on thermal behavior and thermo-

收稿日期: 2002-04-22。收修改稿日期: 2002-07-19。

国家自然科学基金资助项目(No. 29871032, 20171036), 陕西省教育厅专项基金资助项目。

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chemistry of some zinc amino acids are important to their further application, which have been reported in literature^[4-8]. However, studies on the solid complex $\text{Zn}(\text{Leu})\text{SO}_4 \cdot 0.5 \text{H}_2\text{O}$ (Leu = Leucine) have not been reported, which can provide necessary data and be based to the practices process of medicine food and cosmetics because of high temperature in the heat treatment. Being the metal chelates comprised of the trace element zinc with *L*- α -Leucine(Leu), $\text{Zn}(\text{Leu})\text{SO}_4 \cdot 0.5\text{H}_2\text{O}$, shows higher chemical stability and chemocobiological stability, but these need a theoretical supporting. The studies of $\text{Zn}(\text{Leu})\text{SO}_4 \cdot 0.5\text{H}_2\text{O}$ on its thermo-stability and decomposition kinetics, especially the process of ligand-losed, can reveal what is intermediate and whether noxious substance is produced, which are a prerequisite to a excellent additives in medicine food and cosmetics.

In this paper, the solid complex $\text{Zn}(\text{Leu})\text{SO}_4 \cdot 0.5\text{H}_2\text{O}$ was prepared in water-acetone system. The kinetic behavior and process of thermal decomposition of $\text{Zn}(\text{Leu})\text{SO}_4 \cdot 0.5\text{H}_2\text{O}$ were investigated by two integral and three differential methods in our program system of thermoanalysis kinetics. The most probable mechanism for thermal decomposition was suggested by comparing with the kinetic parameters, and then the kinetic equation for the ligand-losed process was established.

1 Experiment

1.1 Reagents and Experimental Apparatus

$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (A. R.) was purchased from Xi' an chemical reagent Ltd. *L*- α -Leucine (B. R. purity > 99.99%) was recrystallized from water and analyzed, its purity was 99.99%. Other reagents were A. R.. The Infrared (IR) analysis of $\text{Zn}(\text{Leu})\text{SO}_4 \cdot 0.5\text{H}_2\text{O}$ were conducted on BRUKER EQ UINOX-550 spectrometer (KBr discs) at room temperature. The TG and DTG analyses for the title compound were conducted on NETZSCH STA 449 type thermal analyzer between 60°C and 780°C in flowing O_2 atmosphere. The sample was about $1.50 \pm 0.02\text{mg}$ and the heating rates were 5.0, 10.0, 15.0, 20.0 $\text{K} \cdot \text{min}^{-1}$, respectively.

1.2 Analytical Methods

Zn^{2+} was determined using complexometric titration with EDTA. Leucine was analyzed by the formalin method, and the Zn^{2+} was removed by precipitating with $\text{K}_2\text{C}_2\text{O}_4$ before it was titrated. Carbon, hydrogen and nitrogen analysis were carried out on a 2400-type (PE Ltd.) elemental analyzer.

1.3 Preparation and Composition of the Complexes

The phase equilibrium diagram of the ZnSO_4 -*L*- α -Leu- H_2O system at 25°C indicates that the solid complex $\text{Zn}(\text{Leu})\text{SO}_4 \cdot 0.5\text{H}_2\text{O}$ can not be prepared in water^[9]. According to previously reported procedures^[10] the solid complex $\text{Zn}(\text{Met})\text{SO}_4 \cdot \text{H}_2\text{O}$ was prepared, an appropriate amount of acetone was added into a water solution of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and Leucine with stirring after adjusting the volume ratio of acetone and water to lower than 1:30, and prolong the stirring time, a pale precipitate is separated by filtration, washed with a few amounts of acetone and finally dried in vacuum at 105°C until constant weight, yield 89.58%, so the solid complex, $\text{Zn}(\text{Leu})\text{SO}_4 \cdot 0.5\text{H}_2\text{O}$, a pale powder was obtained. The complex is insoluble in EtOH or acetone, but soluble in water. Results of chemical and elemental analysis of the complex are Zn, 21.78%; Leu, 43.17%; C, 23.5%; H, 4.59%; N, 4.61%. Analysis calcd. for $\text{Zn}(\text{Leu})\text{SO}_4 \cdot 0.5\text{H}_2\text{O}$: Zn, 21.68%; Leu, 43.49%; C, 23.89%; H, 4.43%; N, 4.46%. In the preparing process of $\text{Zn}(\text{Leu})\text{SO}_4 \cdot 0.5\text{H}_2\text{O}$, the experimental results of water and acetone with the various volume ratios are listed in Table 1.

Data of IR absorption for main groups of the complex and ligand are listed in Table 2. Non-existing the characteristic absorption bands of -COOH group at $1700 \sim 1750\text{cm}^{-1}$ for complex reveals that Leucine still keeps zwitter-ion structure; Larger displacement of $\nu_{(\text{NH}_3^+)}$ and $\delta_{(\text{NH}_3^+)}$ for complex contrasting with ligand indicates that the Leu coordinated Zn through N and O atom as bidentate ligand. The wide characteristic absorption band at 3444.2cm^{-1} is the contribution of asymmetric vibration of OH^{-1} radical reveals that the

Table 1 Experiment Results of Water and Acetone with the Various Volume Ratios

volume ratio	1:1	1:2	1:3	1:4	1:5	1:6	1:10	1:20
results	turbid	turbid	amounts of precipitate	precipitate	precipitate	precipitate	a few amounts of precipitate	a few amounts of precipitate
yield/%	—	—	63.0	80.0	89.0	80.0	67.0	50.0

Table 2 Data of IR Absorption for Main Group of Ligand and Complex (cm⁻¹)

compounds	$\nu(NH_2)$	$\nu(NH_2)$	$\delta(NH_2)$	$\delta(NH_2)$	$\nu(COO^-)$	$\nu(COO^-)$	$\nu(SO_4)$	$\nu(OH)$
L- α -Leu	453.8	2958.3	1613.4	1514.2	1583.3	1407.3	—	—
$Zn(Leu)SO_4 \cdot 0.5H_2O$	3489.7	2958.3	1582.6	1513.8	1555.1	1408.1	1108.3	3444.2

complex contains H_2O molecules.

2 Results and Discussion

2.1 Thermal Behavior

The TG and DTG curves of $Zn(Leu)SO_4 \cdot 0.5H_2O$ with $\beta = 5.0K \cdot min^{-1}$ are shown in Fig. 1. The thermo-analytical data are given in Table 3, including the peak temperatures, temperature ranges of DTG curve, the percentages of mass loss and probable compositions of expelled groups. The DTG curve of Fig. 1 shows that there were three peaks at temperatures higher than 60°C, indicating that the thermal decomposition process of the complex can be divided into three stages. In the first stage, between 60°C and 185°C, a mass loss of 3.03% is observed corresponding to the loss of 0.5 molecules for water. IR spectrum (Fig. 2) of the products obtained at 185°C shows that the wide characteristic absorption peaks for water molecules had been disappeared. In the second stage, the complex is decomposed at 185 ~ 439°C. The characteristic absorption peaks of the complex and $ZnSO_4$ emerge in the spectra of decomposition products, indicating that the step of the thermal decomposition process involved loss of Leu group. The theoretical mass loss corresponding to the formation of $ZnSO_4$ from $Zn(Leu)SO_4$ is 42.11%. The experimental mass loss is 42.00%. In the third stage, the IR spectrum of the final decomposition products coincides with the standard IR spectrum of ZnO , indicating that the interme-

diates further decompose to ZnO at 439 ~ 788°C. The formation of ZnO from the original complex should be accomplished with a theoretical overall mass loss of 26.98%. This value is in agreement with the experi-

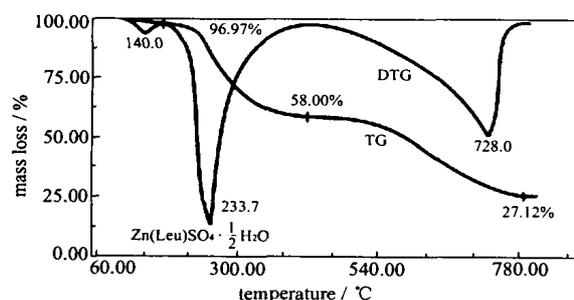


Fig. 1 TG-DTG curve of $Zn(Leu)SO_4 \cdot 0.5H_2O$ ($\beta = 5K \cdot min^{-1}$)

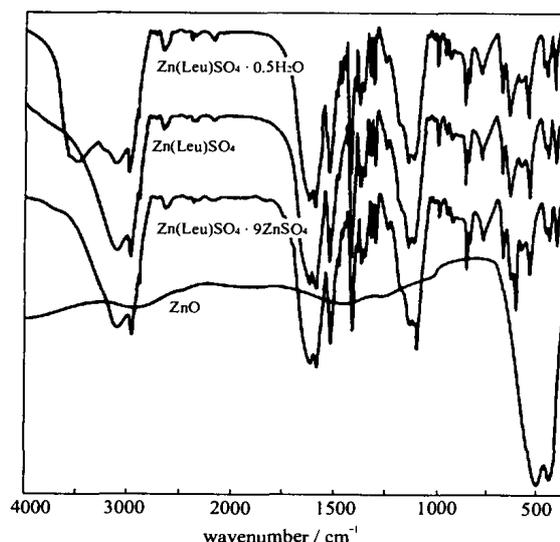
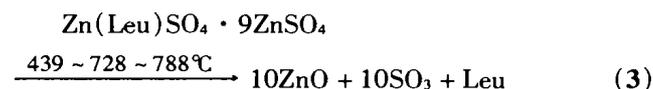
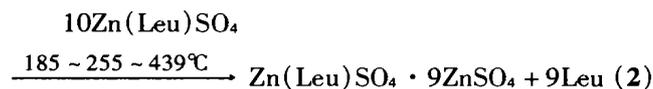
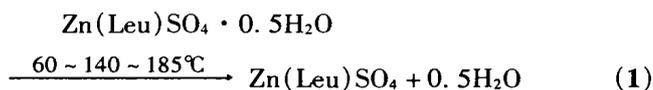


Fig. 2 IR spectra of $Zn(Leu)SO_4 \cdot 0.5H_2O$ and its decomposition products at different temperatures

Table 3 Thermal Decomposition Data for $Zn(Leu)SO_4 \cdot 0.5H_2O$ from TG and DTG Analyses ($\beta = 5^\circ C \cdot min^{-1}$)

stage	temp. range/°C	DTG peak temp. /°C	loss of mass/wt%		probable composition of expelled groups	intermediate
			TG	calcd.		
I	50 ~ 185	140.0	3.03	2.99	-0.5H ₂ O	$Zn(Leu)SO_4$
II	185 ~ 439	233.7	42.00	42.11	-Leu	$Zn(Leu)SO_4 \cdot 9ZnSO_4$
III	439 ~ 788	728.0	72.88	73.02	-SO ₃	ZnO

mental value of 27.12%. On the basis of above-mentioned experimental and calculated results, the thermal decomposition mechanism of $\text{Zn}(\text{Leu})\text{SO}_4 \cdot 0.5\text{H}_2\text{O}$ is postulated to be as follows:



2.2 Non-Isothermal Decomposition Kinetics

In order to obtain the most probable mechanism function and corresponding kinetics parameters for the ligand-losed decomposition process of the complex, the following two integral methods [eqns. (4), (5)] and three differential methods [eqns. (6) ~ (8)] are employed:

the universal integration equation^[11]

$$\ln \frac{G(\alpha)}{(T - T_0)} = \ln \frac{A}{\beta} - \frac{E}{RT} \quad (4)$$

the Flynn-Wall-Okazawa equation^[12,13]

$$\log \beta = \log \frac{AE}{RG(\alpha)} - 2.315 - \frac{0.456E}{RT} \quad (5)$$

the Kissinger equation^[14]

$$\ln \frac{\beta}{T_p^2} = \ln \frac{AR}{E} - \frac{E}{RT_p} \quad (6)$$

the Starink equation^[15]

$$\ln \frac{\beta}{T_p^{1.8}} = C_s - \frac{E}{RT} \quad (7)$$

the Achar-Brindley-Sharp-Wendworth equation^[16,17]

$$\ln \frac{d\alpha}{f(\alpha)dT} = \ln \frac{A}{\beta} - \frac{E}{RT} \quad (8)$$

where α is the fractional decomposition; T is the absolute temperature; T_0 is the initial point at which DTG curve deviates from the baseline, A is the pre-exponential factor, E is the apparent activation energy, β is the heating rate; $f(\alpha)$ and $G(\alpha)$ are the differential and integral mechanism function, respectively; T_p is the peak temperature of DTG curve, and C_s is the constant.

The data needed for the equations of the integral and differential methods, β , T_0 , T_i , α_i , $(d\alpha/dT)_i$, $i = 1, 2, 3 \dots, n$, are obtained from the TG and DTG curves and summarized in Table 4. By substituting T_0 and T_p in Table 4 into Eqn. (5) ~ (7), the apparent activation energy E and the pre-exponential constant A can be obtained as listed in Table 5. Then substituting the mechanism function forms^[17] of $f(\alpha)$ and $G(\alpha)$ and the original data in Table 4 into eqn. (4) and (8), the value of A and E can be calculated at various heating rates of 5.0, 10.0, 15.0 and 20.0 $\text{K} \cdot \text{min}^{-1}$, and corresponding the linear correlation coefficients (r) and the variances (Q) were obtained by the linear least-squares methods on the computer. All the calculated results from five different methods for the ligand-losed process with the β value equals to 5.0, 10.0, 15.0 and 20.0 $\text{K} \cdot \text{min}^{-1}$, respectively, are showed in Table 5.

The E , A , r and Q obtained by above methods are the reference foundation to choice the most probable mechanism function. Based on the following five con-

Table 4 Data for the Ligand-Losed Process of $\text{Zn}(\text{Leu})\text{SO}_4 \cdot 0.5\text{H}_2\text{O}$ at Different Heating Rates

$\beta / (\text{K} \cdot \text{min}^{-1}) = 5.0$			$\beta / (\text{K} \cdot \text{min}^{-1}) = 10.0$			$\beta / (\text{K} \cdot \text{min}^{-1}) = 15.0$			$\beta / (\text{K} \cdot \text{min}^{-1}) = 20.0$		
T/K	α_i	$\frac{d\alpha}{dT} \times 10^3 / \text{K}^{-1}$	T/K	α_i	$\frac{d\alpha}{dT} \times 10^3 / \text{K}^{-1}$	T/K	α_i	$\frac{d\alpha}{dT} \times 10^3 / \text{K}^{-1}$	T/K	α_i	$\frac{d\alpha}{dT} \times 10^3 / \text{K}^{-1}$
476.05	0.0197	0.1129	485.75	0.0233	0.1592	492.65	0.0201	0.1954	496.25	0.0251	0.1701
482.05	0.0239	0.1366	488.75	0.0287	0.1624	496.65	0.0241	0.2092	500.25	0.0312	0.1885
485.05	0.0288	0.1521	492.75	0.0326	0.1845	501.65	0.0328	0.2195	503.25	0.0398	0.1961
488.05	0.0345	0.1616	496.75	0.0381	0.1963	505.65	0.0425	0.2274	507.25	0.0507	0.2145
491.05	0.0405	0.1720	500.75	0.0496	0.2235	509.65	0.0545	0.2408	511.25	0.0729	0.2276
494.05	0.0465	0.1798	506.75	0.0637	0.2405	512.65	0.0608	0.2496	515.25	0.0925	0.2478
499.05	0.0530	0.1851	509.75	0.0692	0.2557	516.65	0.0787	0.2582	520.25	0.1002	0.2548
503.85	0.0643	0.2126	512.75	0.0916	0.2612	519.65	0.0914	0.2635	524.25	0.1325	0.2602
506.85	0.0892	0.2418	516.75	0.1112	0.2953	522.65	0.1067	0.2823	530.25	0.1708	0.2784
513.85	0.1210	0.2235	520.75	0.1374	0.2786	526.65	0.1402	0.2518	536.25	0.2135	0.2572
$T_0 = 458.75\text{K} \quad T_p = 506.85\text{K}$			$T_0 = 471.15\text{K} \quad T_p = 516.75\text{K}$			$T_0 = 485.15\text{K} \quad T_p = 522.65\text{K}$			$T_0 = 489.15\text{K} \quad T_p = 529.45\text{K}$		

Table 5 Kinetic Parameters Obtained from Five Methods for the Ligand-Losted Process of $Zn(Leu)SO_4 \cdot 0.5H_2O$ at Different Heating Rates

$\beta/(K \cdot \min^{-1})$	methods	$E/(kJ \cdot \text{mol}^{-1})$	$\log(A/s^{-1})$	r	Q	function No. *
5.0	kissinger	130.69	10.19	0.9950	0.0096	—
	flynn-wall-ozawa	132.46	—	0.9956	0.0018	—
	starink	130.64	—	0.9950	0.0096	—
10.0	universal-integral	131.13	7.59	0.9827	0.0910	No. 8
	achar-brindley-sharp-wendworth	130.08	6.90	0.9953	0.0496	No. 8
15.0	universal-integral	130.59	8.03	0.9812	0.1012	No. 8
	achar-brindley-sharp-wendworth	136.34	7.80	0.9982	0.0201	No. 8
20.0	universal-integral	138.60	8.74	0.9815	0.1805	No. 8
	achar-brindley-sharp-wendworth	136.63	7.82	0.9987	0.0121	No. 8
20.0	universal-integral	135.93	8.76	0.9885	0.1396	No. 8
	achar-brindley-sharp-wendworth	135.93	7.92	0.9843	0.0927	No. 8
	average values	133.78	8.19	—	—	—

*: The kinetic model function $f(\alpha)$ in differential form of No. 8^[19] is $\left\{\frac{3}{2}(1+\alpha)^{2/3}[(1+\alpha)^{1/3}-1]^{-1}\right\}$, and the function $G(\alpha)$ in integral form is $[(1+\alpha)^{1/3}-1]^2$.

ditions^[18, 19]: (a) the values of E and $\log A$ selected are in the ordinary range of the thermal decomposition kinetic parameters for solid materials ($E = 80 \sim 250 \text{ kJ} \cdot \text{mol}^{-1}$ and $\lg A = 7 \sim 30 \text{ s}^{-1}$); (b) the linear correlation coefficient (r) is great than 0.98; (c) the variance (Q) is less than 0.30; (d) the values of E and A obtained with the integral and differential methods are approximately the same; (e) The mechanism function selected must be in agreement with the tested sample state. The results of satisfying the above-mentioned conditions at the same time are the final result as listed in Table 5, and the relevant function is the reaction mechanism function of the ligand-losed process of $Zn(Leu)SO_4 \cdot 0.5H_2O$. The data in Table 5 indicate that the value of A and E from mechanism function No. 8. by Eqn. (4) and (8) are in good agreement with the calculated value obtained by Kissinger's method and Ozawa's method. So the only most probable mechanism is No. 8 (Table 5) and corresponding three-dimension diffusion mechanism controls the ligand-losed reaction.

Substituting $f(\alpha)$ with $\left\{\frac{3}{2}(1+\alpha)^{2/3}[(1+\alpha)^{1/3}-1]^{-1}\right\}$, E with $133.78 \text{ kJ} \cdot \text{mol}^{-1}$ and A with $10^{8.19} \text{ s}^{-1}$ in eqn. (9)

$$\frac{d\alpha}{dT} = Af(\alpha) \exp\left(-\frac{E}{RT}\right) \quad (9)$$

the kinetics equation (10) of the ligand-losed process

of $Zn(Leu)SO_4 \cdot 0.5H_2O$ is obtained:

$$\frac{d\alpha}{dT} = 10^{8.19} \cdot \left\{\frac{3}{2}(1+\alpha)^{2/3}[\ln(1+\alpha)^{1/3}-1]^{-1}\right\} \times \exp(-16090.9/T) \quad (10)$$

3 Conclusions

The solid complex $Zn(Leu)SO_4 \cdot 0.5H_2O$ was prepared in water-acetone system. The thermal decomposition processes of the complex can be divided into three stages. The non-isothermal decomposition of $Zn(Leu)SO_4 \cdot 0.5H_2O$ was studied at various heating rates of 5.0, 10.0, 15.0 and 20.0 $\text{K} \cdot \text{min}^{-1}$ by TG-DTG. The non-isothermal decomposition mechanism and kinetics parameters of the ligand-losed process were obtained from an analysis of the TG-DTG curves by two integral and three differential methods. The results show that three dimension diffusion mechanism controls the ligand-losed process and the apparent activation energy E is $133.78 \text{ kJ} \cdot \text{mol}^{-1}$ and the pre-exponential constant A is $10^{8.19} \text{ s}^{-1}$. The empirical kinetics model equation was proposed.

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