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Depyridination Mechanism and Non-isothermal Kinetics of (μ-2-Nitrobenzoato-κ^{2}O:O′)*bis*-[(pyriden-κN)zinc(II)

HUA-QIONG LI and GUOLIANG ZHAO*
Zhejiang Key Laboratory for Reactive Chemistry on Solid Surfaces, Institute of Physical Chemistry, Zhejiang Normal University, Jinhua, Zhejiang 321004, P.R. China
Fax: (86)(579)82282595; Tel: (86)(579)83746733; E-mail: sky53@zjnu.cn

Thermal depyridination mechanism and the non-isothermal kinetics of (μ-2-nitrobenzoato-κ^{2}O:O')*bis*-[(pyriden-κN) zinc(II)] was studied by TG method. The decomposition residue of this complex was characterized by XRD. The data from non-isothermal experiments were analyzed by Achar and the improved Ozawa methods. It was found that the depyridination process is governed by three-dimensional diffusion (spherical symmetry, 2D3) and the kinetic equation is $3/2(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$.

Key Words: Depyridination mechanism, Non-isothermal kinetics, XRD.

INTRODUCTION

A lot of studies have been performed on the thermal decomposition of compounds, some of which focus on the kinetics of the reaction of general salt such as metal acetates[1] and the thermal stability of solid complexes[2]. Among those studies, there are many papers devoted to dehydration of inorganic salts as well as organic substances and metal complexes of organic ligands[3]. On the other hand, the kinetics of thermal deamination of some amino-complexes have been discussed and the activatation energy is obtained[4]. However, the determination of mechanism function and kinetic parameters of thermal depyridination of solid complexes formed by transition metal salt and pyridine have not been carried out. On the basis of the preparation and determination of the crystal structure of (μ-2-nitrobenzoato-κ^{2}O:O')*bis*-[(pyriden-κN)zinc(II)][5], we present our studies on its thermal depyridination procedure by TG techniques and the corresponding non-isothermal kinetics by means of Achar method[6] and improved Ozawa method[7], respectively.

†College of Chemistry and Life Science, Zhejiang Normal University, Jinhua, Zhejiang 321004, P.R. China.

EXPERIMENTAL

The (μ-2-nitrobenzoato-κ^{2}O:O')*bis*-[(pyriden-κN)zinc(II)] was prepared and its crystal structure was determined as described previously[4].

The thermal behaviour of the title compound was determined by using Mettler-Toledo TGA/SDTA 851^e simultaneous thermal analyzer in a temperature range from 30 to 900 ºC under air atmosphere. The heating rate was 5, 10, 15, 20 ºC/min and the sample weight was 2.0 ± 0.2 mg.

Calculation of kinetic parameters: In the present work, both the Achar method[6] and improved Ozawa method[7] have been applied to study the kinetics of the first decomposition process of the title compound.

The Achar method[6] has a differential equation:

$$\ln[(d\alpha/dt)/f(\alpha)] = \ln A - E/RT\ (d\alpha/dt - \beta d\alpha/dT) \quad (1)$$

where α = reaction of decomposition, dα/dt = rate of conversion, β = linear heating rate, T = absolute temperature, A = pre-exponential factor, R = gas constant, E = apparent activitation energy and f(α) = differential mechanism functions.

The improved Ozawa method[7], which is a integral way to analysis kinetics, contains two equation:

$$\beta_2/\beta_1 = (B-C)_{\beta 2}/(B-C)_{\beta 1} \quad (2)$$

$$\int_0^T \exp(-E/RT)dT \approx \frac{E}{R}\frac{e^{-u}}{u^2}\left(1 - \frac{2!}{u} + \frac{3!}{u^2} - \frac{4!}{u^3} + ...\right) \quad (3)$$

where u = E/RT. At first supposing a value of E, when the values of B and C are calculated by eqn. 3, the ratio of β/(B-C) can be obtained. If these ratios at different heating rate are not constant, we should change the value of E till the ratio is equal for two curves of β or the difference in these ratios is the minimum for a set of β curves. Then, the value of E is the exact value. According to the eqn. 2, two activation energies can be calculated by two different ways. One way is called Onset Way and its equation can be expressed as: $\beta_2/\beta_1 = (B_n - C_1)\beta_2/(B_n - C_1)\beta_1$, where n > 1. The other is called Point by Point Way and its eqn. is $\beta_2/\beta_1 = (B_n - C_{n-1})\beta_2/(B_n - C_{n-1})\beta_1$, where n > 1.

The thermal decomposition residue was tested by XRD. The Powder X-ray diffraction pattern was measured on a Philips PW3040/60 instrument, using CuK_α radiation.

RESULTS AND DISCUSSION

The TG curve of (μ-2-nitrobenzoato-κ^{2}O:O')*bis*-[(pyriden-κN)zinc(II)] (ZnL_2Py, HL = *o*-nitrobenzoic acid, Py = pyridine) at the heating rate of 5 ºC/min is shown in Fig. 1. The TG curve shows that ZnL_2Py exhibits two steps decomposition. The first stage is in the temperature range 149-188 ºC, with a mass loss of 16.11 % (calculated loss 16.66 %), which corresponds

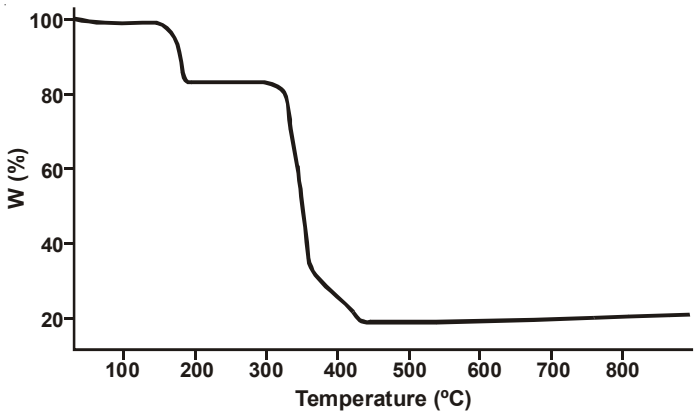

Fig. 1. TG curve of the title complex at the heating rate of 5 ºC/min

to the loss of one pyridine molecule. The second stage is in the temperature range 287-436 ºC, with a mass loss of 66.36 % (calculated loss 66.62 %), which is corresponding to the loss of two *o*-nitrobenzoic anions. After this, the mass of the thermal decomposition residue remains unchanged (found, 17.53 %; calculated, 17.14 %). The residue of decomposition is ZnO and its presence was confirmed by X-ray diffraction pattern of the residue (Fig. 2) and the PDF card number is 80-0075, which also shows the structure of ZnO is hexagonal. The probable thermal decomposition scheme can be described in the following manner:

$$ZnL_2Py \xrightarrow{-Py} ZnL_2 \xrightarrow[[O]]{-2L} ZnO$$

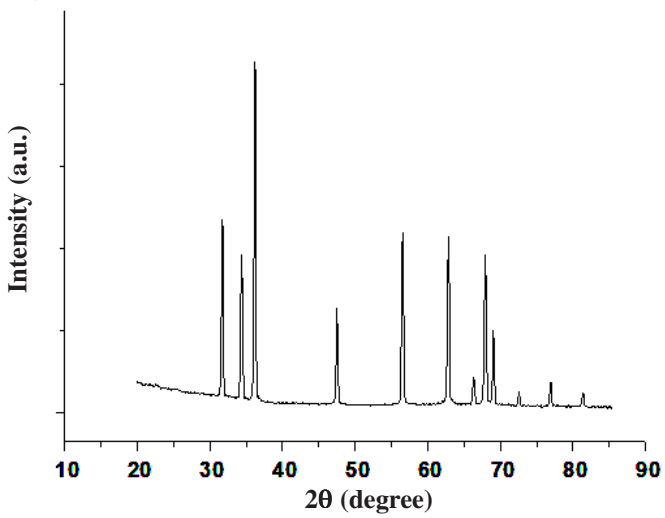

Fig. 2. XRD pattern of decomposition residue

Kinetic studies of non-isothermal decomposition: The basic parameters of α, T and $d\alpha/dT$ are listed in Table-1. The algebraic expression of differential $f(\alpha)$ functions for the most common mechanism[8] used in kinetics of solid-state decomposition tested in this work are listed in Table-2. On substitution of basic parameters in Table-1 and the 19 types of mechanism functions $f(\alpha)$ in Table-2 into eqn. 1, the values of E, ln A and the linear correlation coefficients r of different mechanism functions were calculated. The results are shown in Table-3.

TABLE-1
BASE DATA FOR THE TITLE COMPLEX OBTAINED FROM TG-DTG CURVE OF FIRST STAGE

T/K	α_i	$(d\alpha/dT)_i$	T/K	α_i	$(d\alpha/dT)_i$
433.49	0.09375	0.00168	449.10	0.46875	0.00711
437.40	0.12500	0.00244	453.01	0.68750	0.00976
441.31	0.21875	0.00352	456.94	0.93750	0.00726
445.21	0.31250	0.00498	–	–	–

TABLE-2
SOME DIFFERENTIAL COEFFICIENT KINETIC FUNCTIONS

Symbol	Different coefficient kinetic function	Mechanism
D1	$1/(2\alpha)$	One-dimensional diffusion
D2	$[-\ln(1-\alpha)]^{-1}$	Two-dimensional diffusion
1D3	$3/2[(1-\alpha)^{-1/3}-1]^{-1}$	Three-dimensional diffusion (cylindrical symmetry)
2D3	$3/2(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$	Three-dimensional diffusion(spherical symmetry)
3D3	$3/2(1+\alpha)^{2/3}[(1+\alpha)^{1/3}-1]^{-1}$	Three-dimensional diffusion
4D3	$3/2(1-\alpha)^{4/3}[1/(1-\alpha)^{1/3}-1]^{-1}$	Three-dimensional diffusion
A1	$(1-\alpha)$	Random nucleation and nuclei growth (n = 1)
A1.5	$3/2(1-\alpha)[-\ln(1-\alpha)]^{1/3}$	Random nucleation and nuclei growth (n = 1.5)
A2	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	Random nucleation and nuclei growth (n = 2)
A3	$3(1-\alpha)\ [-\ln(1-\alpha)]^{2/3}$	Random nucleation and nuclei growth (n = 3)
A4	$4(1-\alpha)\ [-\ln(1-\alpha)]^{3/4}$	Random nucleation and nuclei growth (n = 4)
R2	$2(1-\alpha)^{1/2}$	Contracting sphere (cylindrical symmetry)
R3	$3(1-\alpha)^{2/3}$	Contractingsphere (spherical symmetry)
P1	1	Exponential nucleation
P2	$2\alpha^{1/2}$	Exponential nucleation
P3	$3\alpha^{2/3}$	Exponential nucleation
P4	$4\alpha^{3/4}$	Exponential nucleation
C2	$(1-\alpha)^2$	Chemical reaction
C1.5	$2(1-\alpha)^{3/2}$	Chemical reaction

TABLE-3
FITTED DATA FOR FIRST STAGE OF THERMAL DECOMPOSITION OF THE TITLE COMPLEX

Differential kinetic functions f(α)							
No.	E(KJ/mol)	ln A	r	No.	E(KJ/mol)	ln A	r
D1	118.88190	30.8540	0.9072	A4	-64.00530	-18.0430	0.6287
D2	181.74400	47.4810	0.9959	R2	30.14573	7.0643	0.6492
1D3	209.57930	54.4470	0.9902	R3	56.20430	13.8300	0.6917
2D3	261.69980	67.9790	0.9613	P1	-48.02910	-13.7560	0.6637
3D3	77.09323	17.0380	0.7402	P2	-131.48600	-36.4080	0.9396
4D3	418.05290	111.0100	0.8817	P3	-159.30500	-44.1330	0.9583
A1	108.32310	29.2710	0.7030	P4	-173.21400	-48.0810	0.9645
A1.5	31.73121	8.4534	0.2147	C2	264.66790	72.2990	0.7050
A2	68.92472	17.6920	0.6274	C1.5	186.49960	50.0920	0.7048
A3	-44.85820	-12.6520	0.4323	–	–	–	–

In the constant condition of other parameters, the TG curves of ZnL_2Py at various heating rates (β = 5, 10, 15, 20 ºC/min) are shown in Fig. 3. According to the improved Ozawa method, the basic data of a and T collected from Fig. 3 are illustrated in Table-4 and the values of activation energy can be calculated by eqn. 2 with two ways. The average values of activation energy in Onset Way and activation energy in Point by Point Way are 287.19 and 285.69 KJ mol^{-1}, respectively.

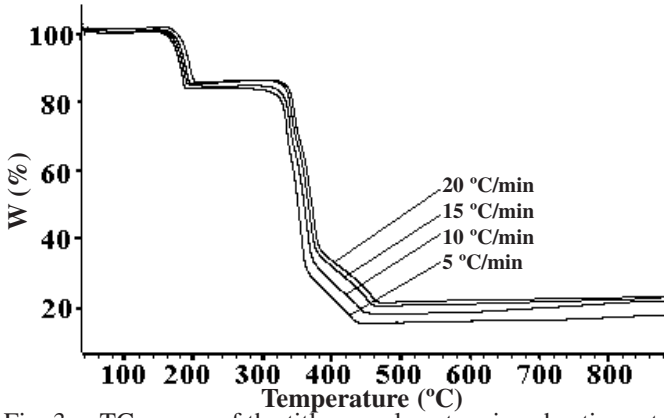

Fig. 3. TG curves of the title complex at various heating rates (β = 5, 10, 15, 20 ºC/min)

For the improved Ozawa method is a model-free method which plays an important role in kinetic analysis, it can distort error for the sake of choosing mechanism function improperly. The values of E obtained by two methods are approximately equal and the correlation coefficient is better, it can be concluded that the relevant function is the probable thermal decomposition mechanism of the complex. Then, it can be suggested that

the function of the possible mechanism is function No. 4 in Table-2 based on the data in Table-3. The decomposition reaction was governed by three-dimensional diffusion (spherical symmetry, 2D3). The kinetic equation of this process is $3/2(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$.

TABLE-4
BASIC DATA OF α AND T COLLECTED FROM FOUR TG CURVES

5 ºC/min		10 ºC/min		15 ºC/min		20 ºC/min	
α(%)	T (ºC)	α(%)	T (ºC)	α(%)	T (ºC)	α(%)	T (ºC)
10	165.75	10	170.17	10	173.50	10	177.34
20	171.75	20	175.67	20	179.00	20	182.45
30	175.58	30	179.33	30	182.50	30	185.52
40	178.50	40	182.00	40	185.25	40	187.37
50	180.83	50	184.17	50	187.24	50	190.17
60	182.75	60	186.00	60	189.26	60	193.84
70	184.42	70	187.61	70	190.74	70	195.68
80	185.92	80	189.17	80	192.25	80	198.39
90	187.42	90	191.00	90	194.27	90	201.42

Conclusion

The TG results indicate that thermal decomposition of ZnL_2Py occurs in two steps. The first stage is the loss of pyridine and the second stage is the loss of two *o*-nitrobenzoic anions. The depyridination process is governed by three-dimensional diffusion (spherical symmetry, 2D3) and the kinetic equation is $3/2(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$.

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