The Nonisothermal Decomposition Kinetics of Copper(II) Complexes with Phthalanilic Acids and Amino Acids

LI-PING REN,[1] WEI-LIN DAI,[1] YONG CAO,[1] HE-XING LI,[2] XIAO-HUI ZHENG,[3]
KANGNIAN FAN[1]

[1] *Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Department of Chemistry, Fudan University, Shanghai 200433, People's Republic of China*
[2] *Department of Chemistry, Shanghai Normal University, Shanghai 200234, People's Republic of China*
[3] *Pharmaceutical College of Xi'an JiaoTong University, Xi'an 710061, People's Republic of China*

Received 6 November 2002; accepted 28 July 2003

DOI 10.1002/kin.10161

ABSTRACT: Fifteen new kinds of mixed ligand complexes Cu(x-P)A [P = 2-(COO)C_6H_4CONH-C_6H_4; x = H, 2-Cl, 2-CH_3, 2-OCH_3, 4-OCH_2CH_3; A = dehydronium Met, Leu, Phen] were synthesized. The thermal decomposition behavior of each complex is studied by TG. Coats–Redfern, MacCallum–Tammer, and Zsako methods are adopted to estimate the values of the apparent activation energy E_a, the activation entropy $\Delta S^{\neq}$, the reaction order n, and the frequency factor A. The results showed that the reaction order is 2/3 for each of the complex. Studies on the mechanism of the thermal decomposition reactions suggested that these reactions all fit the kinetic equation $1 - (1 - \alpha)^{1/3} = kt$. © 2003 Wiley Periodicals, Inc. Int J Chem Kinet 35: 623–628, 2003

INTRODUCTION

Phthalanilic acid compounds have prominent biological activity and are widely used as plant growth stimulants, herbicides, insecticides, drugs, etc. [1–3]. Their biological activity has been found to increase with the formation of their transition-metal complexes [4]. We have had 3 years of field experiments for winter wheat at XiNing (a city in the west of China) with the transition-metal complex of phthalanilic acid, and have achieved remarkable increments (15%) in biological activity, and have also found strong biological effects on tomato [5]. It is well-known that the complexes of copper(II) with amino acids are mostly used as important components in many drugs [6,7]. However, little has been reported on the studies of synthesis and properties of the same series compounds with

---

Correspondence to: Wei-Lin Dai; e-mail: wldai@fudan.edu.cn.

Contract grant sponsor: NSFC.
Contract grant number: Project 20073009.
Contract grant sponsor: Natural Science Foundation of Shanghai Science and Technology Committee.
Contract grant number: 02DJ14021.
Contract grant sponsor: Committee of the Shanghai Education.
Contract grant number: 02SG04.

mixed ligands. In the present work, the mixed ligands of Cu(II)–phthalanilic acid complexes have been synthesized for the first time, which can be potentially used as new kinds of plant growth regulators and/or drugs. The thermal decomposition of these complexes was also studied. The values of the apparent activation energy E_a, the activation entropy $\Delta S^{\neq}$, the reaction order n, and the frequency factor A were calculated by theoretical methods and the kinetic equation of this decomposition reaction was also reported.

EXPERIMENTAL DETAILS

Synthesis of the Ligands

Phthalanilic acid compounds were prepared by the method reported in Ref. [8]. The products were purified by recrystallization with glacial acetic acid once and 95% ethanol twice. Three types of amino acids, methionine (Met), leucine (Leu), and phenylalanine (Phen) were used as purchased without further purification.

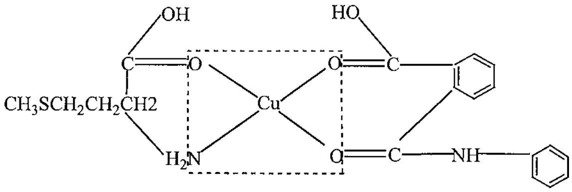
Preparation of the Complex

Ten milliliters of 0.01 M phthalanilic acid and 10 mL of 0.01 M sodium hydroxide were mixed in 50 mL ethanol and heated to produce a clear sodium salt solution of phthalanilic acid. Then the sodium salt solution of the amino acid was prepared by mixing 10 mL of 0.01 M amino acid and 10 mL of 0.01 M sodium hydroxide. Finally, the copper salt solution was obtained by dissolving 10 mg copper acetate in 40 mL distilled water, followed by filtration to remove the solid impurity.

The two sodium salt solutions with different ligands were mixed and placed into a 50–60°C water bath with stirring. During this process, a large quantity of precipitate was obtained. After further stirring and reaction for 30 min, the as-obtained blue powder was filtrated and then washed with hot ethanol and chloroform. The final product was dried in a desiccator containing phosphorus pentoxide.

Characterization of the Complex

On the basis of elemental analysis, infrared, and ultraviolet spectra, the molecular composition of these complexes were determined as Cu(x-P)A (x = H, 2-Cl, 2-CH_3, 2-OCH_3, 4-OCH_2CH_3; P = 2-(COO)C_6H_4-$CONHC_6H_4$; A = dehydronium Met, Leu, Phen). The results indicated that coordination occurs through the carboxylate oxygen, the oxygen of the amido group in 2-[(substituted phenylamino)-carbonyl]benzoic acid and carboxylate oxygen, and the nitrogen of the amino group in the amino acid. The stereoconfiguration of these molecules was planar square. As a typical example, the structure of the complex Cu(Met)(H–P) is given in Scheme 1.



Scheme 1 Representative molecular structure of the Cu(II) complex(Cu(Met)(H–P)).

The TG analysis was carried out on the DuPont 9900 TG analyzer under N_2 atmosphere with a heating rate of 10 K/min, and the sample amount was 5 mg.

THEORETICAL DETAILS

Coats and Redfern (C&R) Equation [9]

The equation derived by Coats and Redfern is

$$\log\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \log\left[\frac{ART^2}{\beta E_a}\left(1-\frac{2RT}{E_a}\right)\right] - \frac{E_a}{2.3RT} \quad (n \neq 1) \qquad (1)$$

$$\log\left[-\frac{\ln(1-\alpha)}{T^2}\right] = \log\left[\frac{ART^2}{\beta E_a}\left(1-\frac{2RT}{E_a}\right)\right] - \frac{E_a}{2.3RT} \quad (n = 1) \qquad (2)$$

where α is the fraction decomposed, n presents the reaction order, and β is the heating rate (and T is the temperature in Kelvin).

MacCallum and Tammer (M&T) Equation [10]

The equation is

$$\log F(\alpha) = \log\frac{AE_a}{\beta R} - 0.01209E_a^{0.44} - (0.45 + 5.255 \times 10^{-5}\, E_a)/T \times 10^{-3} \qquad (3)$$

When drawing a line with the left side of the Eqs. (1), (2), and (3) versus the reciprocal of the absolute temperature ($1/T$), the correlation value for n is obtained according to the best linearity. The activation energy E_a and frequency factor A can also be calculated.

Zsako Equation [11]

The equation derived by Zsako is

$$\log \frac{AE_a}{\beta R} = \log F(\alpha) - \log p(x) = B \qquad (4)$$

In Eqs. (3) and (4), six kinds of calculation formula for $F(\alpha)$ from $f(\alpha) = (1-\alpha)^n$ was given in Ref. [11].

The value for $p(x)$ can be calculated from the following formula:

$$p(x) = \frac{e^x}{x^2}\left(1 + \frac{2!}{x} + \frac{3!}{x^2} + \cdots\right) \quad (x = -E/RT) \qquad (5)$$

In this work, the value of $p(x)$ was calculated by the values of the first five terms on the right side of Eq. (5). The exact values of E_a and n, and the values of B_i under different temperatures can also be calculated according to Eq. (4). The standard deviation δ for the individual B_i values from their arithmetical mean $\bar{B}$ can be defined as

$$\delta = \sqrt{\frac{\sum (B_i - \bar{B})^2}{r}} \qquad (6)$$

where r is the number of experimental data used for the calculation of $\bar{B}$. A series of δ, denoted as $\delta_1, \delta_2, \delta_3 \ldots$, can be obtained with change of E_a and the $\delta_{\min}$ can be obtained. In the same way, a series of $\delta_{\min}$ can also be obtained with change of n. Then the minimum $\delta_{\min}$ can be selected, which was corresponded to the best E_a and n values.

RESULTS AND DISCUSSION

Thermal Decomposition of the Complex

The TG curve for the complex is a standard Z-shaped curve (rate of weight loss is about 30%), which is linked by another Z-shaped curve (rate of weight loss is about 55%). The residual is about 15%. Figure 1 presents a typical TG curve for the complex of Cu(Met)(H—P). The IR spectra for the intermediate and the metal complex with phthalanilic acid are identical by and large. The complex is decomposed in a two-step way according to the TG curves. From an analysis of the weight loss data, we proposed that the complex is first decomposed to Cu(x-P)$_2$·CuO, and subsequently to CuO in the first step. The second step was studied more carefully in this paper. Detailed decomposition temperature and weight loss data of all the complexes are shown in Table I.

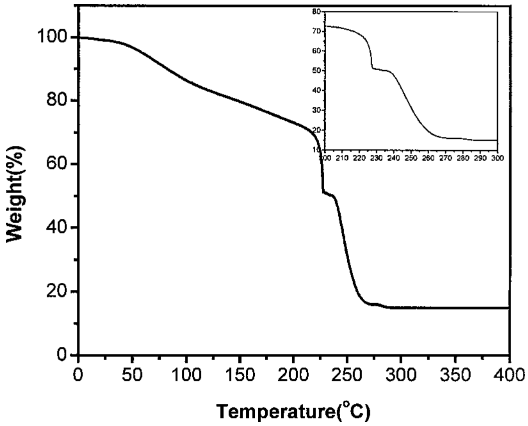


Figure 1 TG curve for the complex of Cu(Met)(H—P).

Kinetic Study of the Complex

The Reaction Mechanism. Using a computer program, the reaction mechanism was ranked according to the usual nine types of reaction mechanism equation [12]. It was found that the linearity of the R_3 mechanism was the best, whose correlation coefficient is above 0.9977, indicating that the rate-controlling processes for the thermal decomposition reaction for all the complexes are phase boundary reactions with spherical symmetry (R_3). All the reactions fit the kinetic equation $1 - (1-\alpha)^{1/3} = kt$. The reaction orders are all

Table I Thermal Decomposition Process

Compound No.	Complex	Decomposition Temperature (°C)	Weight Loss (%) (Calculated)
1	Cu(Met)(H—P)	226–240–298	50.03 (51.38)
2	Cu(Met)(Cl—P)	216–228–235	51.39 (54.81)
3	Cu(Met)(Me—P)	222–241–248	50.81 (52.82)
4	Cu(Met)(OMe—P)	217–228–241	53.50 (54.40)
5	Cu(Met)(OEt—P)	225–238–255	52.49 (55.67)
6	Cu(Leu)(H—P)	222–247–261	51.08 (53.53)
7	Cu(Leu)(Cl—P)	218–232–272	52.86 (56.93)
8	Cu(Leu)(Me—P)	208–255–267	50.83 (54.97)
9	Cu(Leu)(OMe—P)	217–247–275	54.60 (56.52)
10	Cu(Leu)(OEt—P)	218–250–258	53.54 (57.75)
11	Cu(Phen)(H—P)	211–219–236	46.08 (49.66)
12	Cu(Phen)(Cl—P)	209–221–229	50.73 (53.09)
13	Cu(Phen)(Me—P)	206–236–249	49.52 (51.11)
14	Cu(Phen)(OMe—P)	209–225–239	51.08 (52.73)
15	Cu(Phen)(OEt—P)	211–221–231	51.56 (53.97)

Table II The $f(\alpha)$ Data for the Complex of Cu(Met)(H—P)

α	$f(\alpha)$
0.01	0.9933
0.15	0.8973
0.20	0.8618
0.30	0.7884
0.48	0.6466
0.50	0.6300
0.70	0.4481
0.82	0.3188
0.84	0.2947
0.85	0.2823

2/3. Table II gives the $f(\alpha)$ data of compound **1** according to the reaction order.

M&T and C&R Methods. Six kinds of expressions reported in the literature [11] were helpful for seeking the thermal decomposition reaction order. Six groups of reaction orders can be calculated by the trial and error method. The results show that the reaction orders are all 2/3. The kinetic parameters calculated based on the two methods are given in Table III. Figure 2 clearly shows the trial and error process with each reaction order and the C&R method corresponding to compound **1**, suggesting that the reaction order for compound **1** is 2/3 because of its best linearity. From the slope of the line as mentioned above we can also get the value of E_a, which is equal to 51.19 kJ/mol.

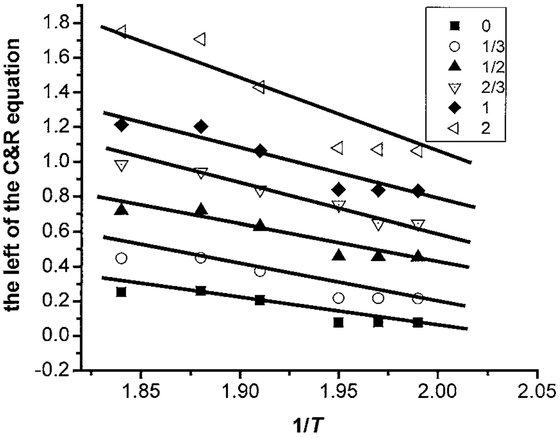


Figure 2 The curve for the left of the C&R equation vs. $1/T$ for the complex of Cu(Met)(H—P).

Then using the M&T method, the relationship between $\log F(\alpha)$ and $1/T$ could be obtained. Thus, the value of A and E_a can also be derived easily. Figure 3 gives the curve of $\log F(\alpha)$ vs. $1/T$ with good correlation for the complex of Cu(Met)(H—P) as an example.

Zsako Method. Using the improved Zsako method program, the values for $\delta_{\min}$ corresponding to all the reaction orders of the complexes were also calculated and are listed in Table IV. Obviously, the reaction orders of all the thermal decomposition reactions were found to be 2/3. It coincides well with the results obtained from

Table III Kinetic Parameters of the Complexes Calculated with M&T and C&R Methods

Compound No.[a]	Activation Energy E_a (kJ mol^{-1})	log A	Activation Entropy $\Delta S^{\neq}$ (J mol^{-1} K^{-1})	Correlation Coefficient r[b]
1	53.34 (53.27)	4.78 (4.78)	−161.33 (−161.27)	−0.9999 (−0.9998)
2	67.33 (67.49)	6.62 (6.67)	−125.89 (−124.79)	−0.9984 (−0.9980)
3	73.75 (72.87)	6.81 (6.77)	−122.84 (−123.60)	−0.9994 (−0.9993)
4	76.36 (75.81)	7.30 (7.30)	−113.13 (−113.17)	−0.9981 (−0.9978)
5	85.72 (85.39)	8.51 (8.54)	−89.86 (−89.32)	−0.9977 (−0.9974)
6	94.46 (94.21)	9.26 (9.24)	−75.72 (−76.20)	−0.9976 (−0.9972)
7	96.89 (95.93)	9.66 (9.70)	−67.83 (−67.07)	−0.9995 (−0.9994)
8	100.88 (100.38)	10.17 (10.19)	−58.14 (−57.77)	−0.9995 (−0.9994)
9	112.31 (111.26)	10.83 (10.79)	−45.85 (−46.51)	−0.9998 (−0.9998)
10	134.06 (133.01)	12.30 (12.30)	−4.07 (−4.66)	−0.9999 (−0.9999)
11	134.57 (133.60)	13.06 (13.02)	−2.96 (−3.69)	−0.9987 (−0.9985)
12	143.14 (142.00)	13.93 (13.84)	13.44 (11.67)	−0.9999 (−0.9999)
13	146.92 (145.87)	14.16 (14.11)	18.08 (17.06)	−0.9999 (−0.9998)
14	148.72 (147.17)	14.73 (14.69)	29.10 (28.23)	−0.9999 (−0.9999)
15	158.00 (156.49)	15.18 (15.08)	37.39 (35.53)	−0.9996 (−0.9995)

[a] See Table I.

[b] The data in brackets are calculated with C&R method.

Table IV The $\delta_{\min}$ Calculated with Zsako Method

Compound No.[a]	$n = 0$	$n = 1/3$	$n = 1/2$	$n = 2/3$	$n = 1$	$n = 2$
1	0.00419	0.00304	0.00167	0.00037	0.00156	0.00644
2	0.00472	0.00434	0.00522	0.00404	0.00567	0.00786
3	0.00798	0.00377	0.00383	0.00229	0.00805	0.03649
4	0.01849	0.01413	0.01158	0.00846	0.01812	0.06524
5	0.00492	0.00477	0.00532	0.00391	0.00776	0.02221
6	0.01307	0.00917	0.00718	0.00417	0.00549	0.03404
7	0.01014	0.00879	0.00860	0.00835	0.01228	0.04369
8	0.01530	0.01349	0.01364	0.01318	0.01796	0.05248
9	0.00927	0.00493	0.00284	0.00140	0.00979	0.04994
10	0.01324	0.00767	0.00668	0.00646	0.00801	0.02199
11	0.01015	0.00990	0.00998	0.00363	0.01120	0.01616
12	0.02310	0.01539	0.01019	0.00452	0.01860	0.12435
13	0.01628	0.01097	0.00748	0.00365	0.00665	0.05014
14	0.02584	0.02255	0.02177	0.01203	0.02792	0.07318
15	0.02082	0.01305	0.00777	0.00163	0.01470	0.09649

[a] See Table I.

the kinetic mechanism equation as mentioned earlier. The corresponding kinetic parameters are displayed in Table V.

Discussion

The order of the thermal decomposition activation energy for these complexes is Phen complex > Leu complex > Met complex, which is mainly due to the two following reasons. Firstly, as the Leu ligand has two methyl groups and the Phen ligand has a benzyl group (all of which are electron donors), the bond energy between carboxyl oxygen of Phen/Leu and Cu(II) is greatly enhanced and the activation energy for the breaking of Cu—O bond (carboxylate oxygen of the amino group in the amino acid) was increased. Secondly, the Phen and Leu ligands have stronger space hindrance. They therefore need relatively more energy for the breaking of Cu—O bond. The order of magnitude for A and $\Delta S^{\neq}$ is also Phen complex > Leu complex > Met complex. This is mainly because the complicated molecule could, during the collided activation process, get many kinds of energies, which can be accumulated on every interior

Table V The Kinetic Parameter Corresponding to $\delta_{\min}$

Compound No.[a]	$\delta_{\min}$	Order of Reactions n	Activation Energy E_a (kJ mol^{-1})	log A	Activation Entropy $\Delta S^{\neq}$ (J mol^{-1} K^{-1})
1	0.00037	2/3	53.76	4.70	−159.114
2	0.00404	2/3	67.20	6.53	−123.801
3	0.00229	2/3	71.40	6.38	−127.597
4	0.00846	2/3	76.86	7.22	−111.143
5	0.00391	2/3	84.00	8.24	−91.424
6	0.00417	2/3	92.40	9.34	−70.176
7	0.00835	2/3	96.60	9.11	−75.211
8	0.01318	2/3	100.80	10.07	−56.444
9	0.00140	2/3	113.40	10.82	−42.379
10	0.00646	2/3	133.56	12.96	−1.240
11	0.00363	2/3	134.40	12.97	−0.950
12	0.00452	2/3	142.38	13.97	17.945
13	0.00365	2/3	146.14	14.56	29.482
14	0.01203	2/3	147.00	13.69	12.316
15	0.00163	2/3	156.66	14.94	36.258

[a] See Table I.

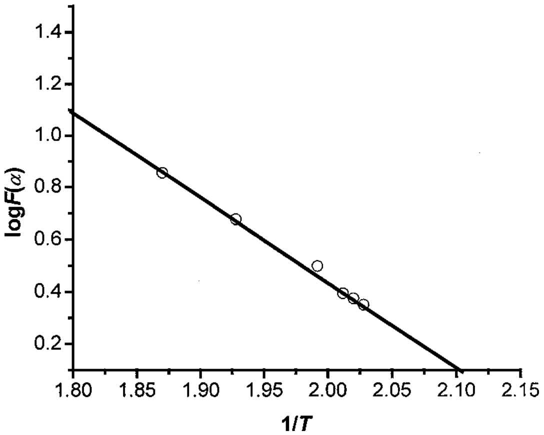


Figure 3 The curve of log $F(\alpha)$ vs. $1/T$ for the complex of Cu(Met)(H–P).

degree of freedom of the molecule to provide enough E_a energy. The activation energy of the complicated molecule obtained in this way is certainly larger than the simple one, i.e. the active concentration of the complicated molecules is greater than the simple ones in the total molecular group.

BIBLIOGRAPHY

1. Lee, S. H.; Do, U. H. Sikmul Poho 1969, 8, 11.
2. Cahn, J.; Wermuth, C. G. Fr Demande 2,102,170, 1972.
3. Yabutani, K.; Kishikawa, J. Japan Kokai 75 30, 868, 1975.
4. Besan, J.; Kovas, M.; Pfeifer, G. Hungary 25, 924, 1983.
5. Shi, J. Ch.; Yang, B. Q.; Ma, H. R. Xibei Daxue Xuebao 1992, 22, 46.
6. Ackermann, H.; Lexow, B.; Krueger, S. Ger (East) DD 46,247, 1987.
7. Horsak, I.; Balaz, V.; Kotoucek, M. Czech CS 264,410, 1989.
8. Malcolm, D. H. J Chem Soc, Perkin Trans 2 1976, 6, 642.
9. Coats, A. W.; Redfern, J. P. Nature 1964, 201, 68.
10. MacCallum, J. R.; Tammer, J. Eur Polym J 1970, 6, 1033.
11. Zsako, J. J Phys Chem 1968, 72, 2406.
12. Nair, C. G. R.; Madhusudanan, P. M. Thermochim Acta 1976, 14, 373.