Thermal Behavior and Decomposition Kinetics of the Complexes of CuX₂ (X＝NO₃, Br, Cl and ClO₄) with 3,3'-Dimethyl-1-(1*H*-1,2,4-triazol-1-yl)-2-butanone

LU, Zhen-Rong*,[a](陆振荣)　　DING, Yuan-Chen[a](丁元晨)　　XU, Ying[a](徐颖)
LI, Bao-Long[b](李宝龙)　　ZHANG, Yong[b](张勇)

[a] *Testing and Analysis Cernter, Suzhou University, Suzhou, Jiangsu 215006, China*
[b] *Department of Chemistry and Chemical Engineering, Suzhou University, Suzhou, Jiangsu 215006, China*

The thermal behaviors of the complexes of Cu(DMTZB)₄X₂ (DMTZB＝3,3'-dimethyl-1-(1*H*-1,2,4-triazol-1-yl)-2-butanone, X＝NO₃ or ClO₄) and Cu(DMTZB)₂X₂ (X = Br or Cl) in a nitrogen atmosphere were studied under the non-isothermal conditions by simultaneous TG-DTG-DSC, EDS and elemental analysis techniques. The results showed that their decomposition proceeded in three different ways mainly depending on the anions in the molecules. The heat effect associated with the decomposition step of DMTZB molecules was also different. The decomposition mechanisms and the kinetic parameters of DMTZB were determined and calculated by jointly using four methods, which showed that its pyrolysis was controlled by D3 mechanism but with different activation energies and pre-exponential factors for different complexes.

Keywords　　copper complex, triazole and its derivative, TG-GTG-DSC, TA, decomposition kinetics

Introduction

N-1-Alkyl-substituted 1,2,4-triazole compounds, like some other heterocyclic derivatives containing nitrogen, have recently been the subjects of numerous studies due to their fungicidal action[1] and plant growth regulation.[2] Among them, the complexes with a sort of triazole as ligand are of considerable interest because of their broad-spectrum bioactivity, coordination and photochemical properties, as well as many potential applications in various fields.[3,4]

In our previous papers,[5,6] we prepared a series of the complexes, CuX₂ (X＝NO₃, Br, Cl and ClO₄) with 3,3'-dimethyl-1-(1*H*-1,2,4-triazol-1-yl)-2-butanone, cultivated two single crystals of [Cu(DMTZB)₄]X₂ (X＝ClO₄, NO₃) and reported their crystals and molecular structures. As an extension of our previous work, herein the thermal decomposition of Cu[(DMTZB)₄](ClO₄)₂, Cu-[(DMTZB)₄](NO₃)₂, Cu[(DMTZB)₂]Cl₂ and Cu[(DMTZB)₂]Br₂ has been investigated in detail, and the kinetic parameters evaluated using four non-isothermal methods.

Experimental

Sample

The ligand, 3,3'-dimethyl-1-(1*H*-1,2,4-triazol-1-yl)-2-butanone, was prepared as the procedures described in Ref. 7, while the title complexes were synthesized in the same route as reported in our previous work.[5,6]

Experimental equipment and conditions

Thermal analysis was carried out using a TA Instruments SDTA-2960 apparatus, which allows TG and DSC measurements to be taken simultaneously. The instrument was previously calibrated against standard substances provided by TA Instruments. The rate of heating was 5, 10, 15, 20 K•min⁻¹, respectively, and the mass of solid specimen was 3—5 mg which was gently crushed with a pestle and mortar before measurement. The experiments were performed in a current of N₂ flowing at a rate of 80 cm³•min⁻¹.

A Carlo-Erba model 1110 elemental analyzer and the energy-dispersive spectrometer (EDS), EDAX PV9900 were employed to check the composition for both intermediates and residues.

Kinetic methodology

There has been growing and convincing evidence that the processes involved in solid-state reactions are generally complicated.[8-11] Taking it into account, four widely used thermal analysis kinetic (TAK) methods were jointly employed to determine the decomposition mechanisms and to calculate the Arrhenius parameters for the compounds studied. These methods are as follows:

Differential methods　　Achar-Brindley-Sharp (A-B-S) equation:

$$\ln\left[\frac{1}{f(\alpha)}\frac{d\alpha}{dt}\right]=\ln A-\frac{E}{RT} \tag{1}$$

Kissinger equation:

$$\ln\frac{\beta}{T_p^2}=\ln\frac{AR}{E}-\frac{E}{RT_p} \tag{2}$$

Integral methods   Coats-Redfern (C-R) equation:

$$\ln\frac{g(\alpha)}{T^2}=\ln\left[\left(\frac{AE}{\beta R}\right)\left(1-\frac{2RT}{E}\right)\right]-\frac{E}{RT} \tag{3}$$

Flynn-Wall-Ozawa (F-W-O) equation:

$$\lg\beta=\lg\left(\frac{AE}{Rg(\alpha)}\right)-2.315-0.4567\frac{E}{RT} \tag{4}$$

where α is the reaction fraction, $f(\alpha)$ and $g(\alpha)$ are the kinetic model function in differential and integral form, respectively, E is the activation energy, A is the pre-exponential factor, β is the heating rate, R is the gas constant, and T and T_p are the temperature and the peak temperature of DTG curve in K, respectively.

As the two multiple scanning methods, *i.e.* Kissinger and Flynn-Wall-Ozawa equations, are model-free iso-coversional methods and allow the activation energy to be independently obtained, the E values calculated using them were used to check the constancy and validity of activation energy by the other methods.[12,13]

Results and discussion

Thermal behavior

Figures 1—3 show the TG-DTG-DSC curves of the title complexes recorded at a heating rate of 5 K•min^{-1} (as the decomposition patterns of Cu[(DMTZB)$_2$]Cl$_2$ and Cu[(DMT ZB)$_2$]Br$_2$ are very similar, only the former is presented as an example). It is interesting to note that the decomposition of the complexes studied proceeds in three different ways.

For complex Cu[(DMTZB)$_4$](ClO$_4$)$_2$, the whole decomposition is completed so quickly that its initial and final temperatures are very close (T_i = 242 °C, T_f = 250 °C), exhibiting an extremely steep and almost a vertical curve (Figure 1). This may be attributed to the fact that the perchloride is a sort of strong oxidant and usually shows explosivity. The instant decomposition of ClO$_4^-$ thus led to a simultaneous pyrolysis of DMTZB.

While for complex Cu[(DMTZB)$_4$](NO$_3$)$_2$, it decomposes in a two-step mode (Figure 2): mass loss percentage suggests that the first step (98—145 °C) is the release of two NO$_3$, then immediately followed by the next step of decomposition (145—511 °C) quantitatively corresponding to that of four DMTZB molecules.
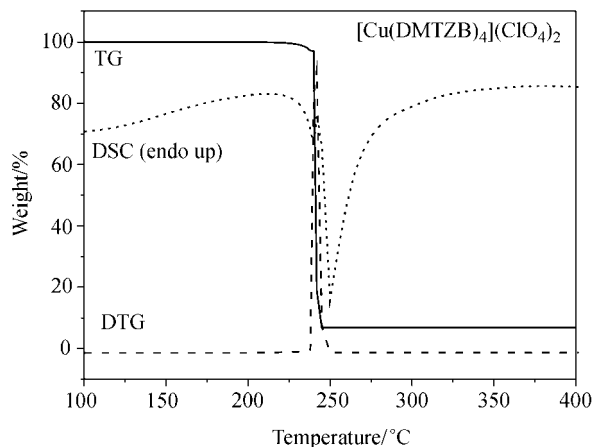

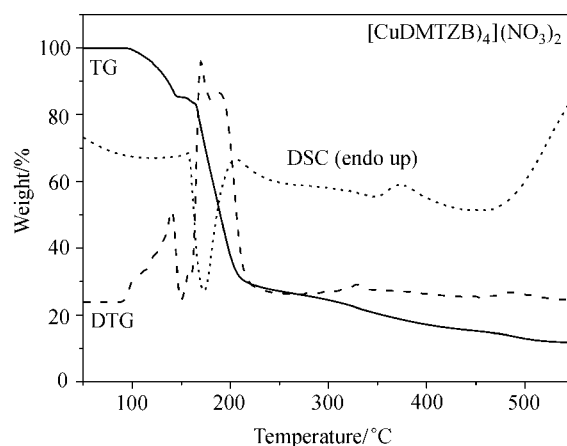**Figure 1**   TG-DTG-DSC curves of Cu[(DMTZB)$_4$](ClO$_4$)$_2$.

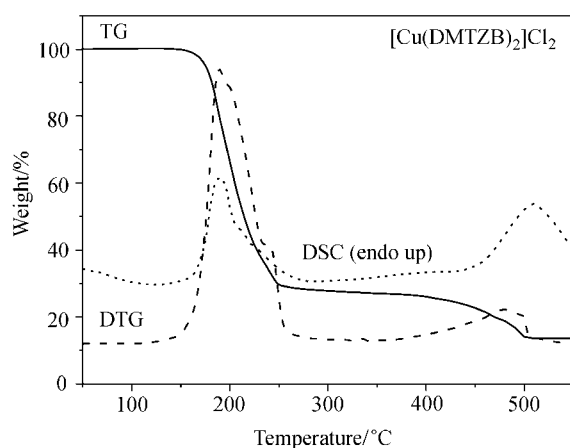
Figure 2   TG-DTG-DSC curves of Cu[(DMTZB)$_4$](NO$_3$)$_2$.

Figure 3   TG-DTG-DSC curves of Cu[(DMTZB)$_2$]Cl$_2$.

This seems to be chemically reasonable because of the difference between the bond strength of Cu—N from DMTZB and Cu—O from NO$_3^-$. As to be reported in our recent study on the molecular structure of single crystal sample of Cu[(DMTZB)$_4$](NO$_3$)$_2$, the bond length of Cu—O is 0.2431 nm, while Cu—N 0.2001 nm and the former is much longer, and then weaker, than the latter. Another reason why the evolution of NO$_3^-$ takes place before that of DMTZB is that nitrate is gen-

erally a kind of easily decomposed compound, while every DMTZB molecule is coordinated to Cu atom in form of relatively strong chelate ring via two N atoms.

As to $Cu[(DMTZB)_2]Cl_2$ and $Cu[(DMTZB)_2]Br_2$, both complexes released two DMTZB molecules first, leaving a relatively stable intermediate product $CuCl_2$ or $CuBr_2$ which started to decompose when temperature reached up to about 350 ℃ for Cl complex or 331 ℃ for Br complex. Their decomposition was ended at about 510 ℃ (Figure 3).

The mass loss and the elemental analysis using EDS indicate the final residue at the end of decomposition for all the complexes studied is powdery metal copper. Figure 4 shows the result for $Cu[(DMTZB)_4](NO_3)_2$.
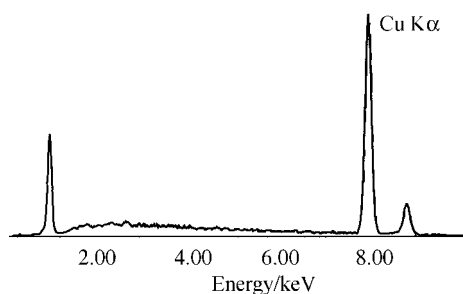

Figure 4 EDS analysis for the residue of $Cu[(DMTZB)_4]$-$(NO_3)_2$.

The DSC curves also show different patterns. For both $Cu[(DMTZB)_4](ClO_4)_2$ and $Cu[(DMTZB)_4](NO_3)_2$, the decomposition stage of DMTZB is associated with an exothermic process, while for $Cu[(DMTZB)_2]Cl_2$ and $Cu[(DMTZB)_2]Br_2$, endothermic. We think that the decomposition of DMTZB is actually accompanied with endothermic effect, but for the formers, this stage is either close to the pyrolysis of NO_3^- or simultaneous with that of ClO_4^- which is a strong exothermic process with a great amount of oxygen releasing, bringing to some oxidation of component in the expelled DMTZB molecules. As to the evolution of Cl or Br, DSC shows a quite weak endothermic process.

Decomposition kinetics

Thermogravimetric data for the decomposition step of DMTZB (except that of $Cu[(DMTZB)_4](ClO_4)_2$), the temperature of maximum decomposition rate T_p obtained under various linear heating rate β, are summarized in Table 1 which were used to calculate the activation energy E by Kissinger and F-W-O methods. Using the other data, α, T and $d\alpha/dT$ from TG-DTG curves and 43 commonly used kinetic mechanism functions of $f(\alpha)$ and $g(\alpha)$,[14] the kinetic parameters E, lg A and appropriate linear coefficients γ and standard deviation value were calculated by both A-B-S and C-R equations with the linear least square method. The most probable mechanism for this decomposition stage was determined following the commonly employed method. The values of E and lg A obtained by the two methods must not only be approximately equal and but also correspond to a higher linear correlation coefficient and a lower standard deviation, meanwhile, the E value calculated using both Kissinger and F-W-O equations were used for checking their reasonableness.

Table 1 Peak temperature T_p of DTG curves at various heating rates β for the decomposition step of DMTZB

Complex[a]	$\beta/(K \cdot min^{-1})$ $(T_p/℃)$			
$Cu[(DMTZB)_4](NO_3)_2$	5 (174)	10 (183)	15 (189)	20 (192)
$Cu[(DMTZB)_2]Cl_2$	5 (195)	10 (203)	15 (208)	20 (211)
$Cu[(DMTZB)_2]Br_2$	5 (188)	10 (196)	15 (201)	20 (204)

[a] DMTZB: 3,3'-dimethyl-1-(1*H*-1,2,4-triazol-1-yl)-2-butanane.

The kinetic parameters, E and lg A together with their appropriate linear correlation coefficient r and standard deviation, S.D., obtained by jointly employing four methods for the decomposition stage of DMTZB in all complexes except for $Cu[(DMTZB)_4](ClO_4)_2$, are presented in Table 2. The most probable mechanism of its decomposition reaction is D3, *i.e.* three-dimensional diffusion, $3(1-\alpha)^{2/3}/2[1-(1-\alpha)^{1/3}]$.

Table 2 Kinetic parameters of thermal decomposition for DMTZB

Complex[a]	Method[b]	$E/(kJ \cdot mol^{-1})$	lg A	r[c]	S.D.[d]
$Cu[(DMTZB)_4](NO_3)_2$	Kissinger	123.1	12.17	0.9988	0.03453
	F-W-O	124.3	—	0.9989	0.01504
	A-B-S	128.6	12.88	0.9977	0.03643
	C-R	129.5	12.93	0.9987	0.03204
$Cu[(DMTZB)_2]Cl_2$	Kissinger	153.9	15.01	0.9996	0.01877
	F-W-O	153.8	—	0.9997	0.008194
	A-B-S	155.6	15.35	0.9985	0.02431
	C-R	156.3	15.66	0.9975	0.03105
$Cu[(DMTZB)_2]Br_2$	Kissinger	149.2	14.75	0.9996	0.01883
	F-W-O	149.3	—	0.9997	0.00822
	A-B-S	151.6	14.82	0.9967	0.03421
	C-R	153.2	15.12	0.9976	0.03104

[a] The same as the notes to Table 1. [b] F-W-O, Flynn-Wall-Ozawa; A-B-S, Achar-Brindley-Sharp; C-R, Coats-Redfern. [c] Linear coefficient. [d] Standard deviation.

1090 *Chin. J. Chem.*, 2004, Vol. 22, No. 10

LU *et al.*

As shown in Table 2, the activation energy corresponding to the decomposition step of DMTZB for $Cu[(DMTZB)_4](NO_3)_2$ is lower than that of $Cu[(DMTZB)_2]Cl_2$ or $Cu[(DMTZB)_2]Br_2$, again indicating that the evolution of NO_3^- makes it more easily for DMTZB to be expelled.

For complex $Cu[(DMTZB)_4](ClO_4)_2$, as its four BMTZB molecules and two ClO_4^- ions decompose simultaneously and instantly with a TG curve of slope tending an infinite, it can be thus deduced that its reaction rate also tends an infinite, corresponding to a very small activation energy value according to a widely used general kinetic equation.

References

1　Lin, B. D. *Pesticide* **1983**, *1*, 31 (in Chinese).

2　McDaniel, G. L. *HortScience* **1983**, *18*, 199.

3　Ferrer, S.; Haasnoot, J. G.; Reedijk, J.; Muller, E.; Biagin-Cingi, M.; Manotti-Lanfredi, A. M.; Ugozzoki, F.; Foglia, C. *J. Chem. Soc., Dalton Trans.* **1992**, 3029.

4　Wang, C. F.; Yang, G. M.; Xu, J. Y.; Zhao, W. J.; Liu, Q. T.; Huang, X. Y.; Chen, C. N. *J. Struct. Chem.* **1996**, *15*, 159 (in Chinese).

5　Li, B. L.; Bian, G. Q.; Gu, J. S. *J. Suzhou Univ.* **1997**, *13,* 57 (in Chinese).

6　Gu, J. S.; Li, B. L.; Bian, G. Q.; Yu, K. B. *Chem. Res. Appl.* **1997**, *9*, 294 (in Chinese).

7　Zhang, H. K.; Liao, L. A.; Guo, Q. Z. *Chin. J. Org. Chem.* **1986**, *2*, 108 (in Chinese).

8　Vyazovkin, S. *Int. Rev. Phys. Chem.* **2000**, *19*, 45.

9　Sestak, J.; Malek, J. *Solid State Ionics* **1993**, *63—65*, 245.

10　Flynn, J. H. *Thermochim. Acta* **1997**, *300*, 83.

11　Lu, Z. R. *Chin. J. Inorg. Chem.* **1998**, *14*, 119 (in Chinese).

12　Lu, Z. R.; Ding, Y. C.; Xu, Y.; Yao, Z. G.; Liu, Q; Lang, J. P. *J. Therm. Anal. Cal.* **2002**, *70*, 985.

13　Lu, Z. R.; Ding, Y. C.; Xu,Y.; Dai, J. *Chin. J. Inorg. Chem.* **2003**, *19*, 920 (in Chinese).

14　Hu, R. Z.; Shi, Q. Z. *Thermal Analysis Kinetics*, Science Press, Beijing, **2001**, pp. 127—131 (in Chinese).