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THERMAL BEHAVIOR AND DECOMPOSITION KINETICS [1,1,1-trifluoro-3-(2-thenoyl)-acetonato]copper(II) and its adducts with some solvent molecules

Zhenrong Lu[1*], *Yuanchen Ding*[1], *Ying Xu*[1], *Shuhua Chen*[2] *and Yunpeng Yu*[2]

[1]Testing & Analysis Center, Suzhou University, Suzhou, Jiangsu, 215006, P. R. China
[2]Department of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang, 212003, Jiangsu, P.R. China

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Abstract

The thermal behaviors of [1,1,1-trifluoro-3-(2-thenoyl)-acetonato]copper(II) $Cu(TTA)_2$ and its adducts with pyridine $Cu(TTA)_2(Py)_2$, 2,2'-bipyridine $Cu(TTA)_2(Bpy)$, quinoline $Cu(TTA)_2(Ql)_2$, and dimethyl sulfoxide $Cu(TTA)_2(DMS)$ in a nitrogen atmosphere were studied under the non-isothermal conditions by simultaneous TG-DTG-DSC technique. The results showed that the evolution of the solvent molecules generally proceeded before the release of TTA in different ways according to their structures. The $Cu(TTA)_2(Bpy)$ exhibited a unique decomposition pattern due to its distinctive structure. The dependences of activation energy on extent of reaction for all the stage of each compound were determined by using an isoconversional method, Flynn-Wall-Ozawa equation, which show E values varied with reaction progress, indicating the complexity of these decomposition reactions. In addition, the values of activation energy E for TTA molecules evolution are generally higher than that for the solvent molecules release.

Keywords: adducts, copper complex, dimethyl sulfoxide, DSC, pyridine and its derivative, TG-DTG, 1,1,1 trifluoro-3-(2-thenoyl) acetone

Introduction

Complexes of β-diketones and their derivatives with transition metals have been extensively investigated due to their multiple uses: extracting agents, chemiluminescent materials and chemical shift agents [1]. Among them, the complexes of 1,1,1 trifluro-3-(2-thenoyl)acetone (TTA) with metals have become a subject of considerable attention for their variety of coordination configurations [2]. They can further react with some solvent molecules, such as pyridine and its derivatives, dimethyl sulfoxide, etc. to form adducts.

In our previous studies [3–7], we devoted attention to the preparation and the crystal structure of 1,1,1 trifluro-3-(2-thenoyl)acetonato copper(II) [4], $Cu(TTA)_2$ and its ad-

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[*] Author for correspondence: E-mail: zrlu@suda.edu.cn

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ducts with pyridine [5], $Cu(TTA)_2(Py)_2$; quinoline [6], $Cu(TTA)_2(Ql)_2$; 2,2'-bipyridine [7], $Cu(TTA)_2(Bpy)$ and dimethyl sulfoxide [3], $Cu(TTA)_2(DMS)$. In these compounds, except $Cu(TTA)_2(Bpy)$, the copper atom is square-planarly coordinated with four oxygen atoms of two TTA groups, showing a 'two-winged' chelates structure with solvent molecules added along axial direction; (Fig. 1, a, b, c, d); while in $Cu(TTA)_2(Bpy)$, one of the 'wings' is formed by coordinating to two nitrogen atoms of a 2,2'-bipyridine molecules, instead of a TTA molecule which, in this case, coordinates to copper atom through only one oxygen atom along the axial direction (Fig.1, e).

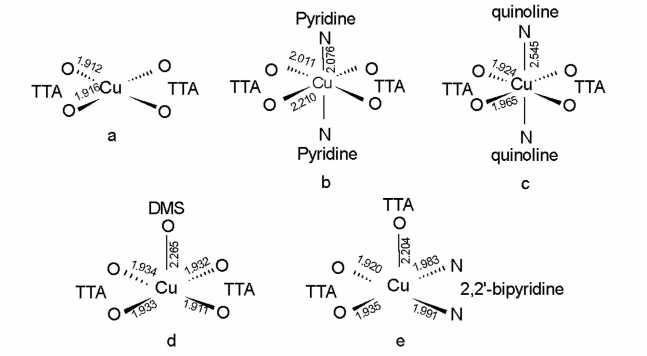


Fig. 1 The skeleton of molecular structure and important bond length value(Å) of the complexes a – $Cu(TTA)_2$, b – $Cu(TTA)_2(Py)_2$, c – $Cu(TTA)_2(Ql)_2$, d – $Cu(TTA)_2(DMS)$ and e – $Cu(TTA)_2(Bpy)$

Nowadays, TA has been playing an increasingly important role in solid study. As an extension of our previous work, we presented in this paper the thermal behavior of the above-mentioned complexes by simultaneous TG-DTG-DSC technique, together with the kinetic analysis results of their decomposition, specially the dependences of the activation energy on the extent of these decomposition reactions for all the stages. Meanwhile, we also discussed the relationship between their structure and thermal properties.

Experimental

Material

The compounds studied were synthesized by the method described in our previous papers [3–7]. All the chemicals used in the synthesis were Analar grade. Their compositions were confirmed by elemental analysis and the quality of sample for TA study was identified with that of the samples for single crystal XRD study.

Apparatus and methods

Thermal experiments were performed in an SDT 2960 DSC-TGA (TA Instruments). This apparatus allows TG and DSC measurements to be taken simultaneously. Crucibles were made from alumina. The instrument was previously calibrated against standard substances provided by TA Instruments. All the tests were carried out under non-isothermal conditions with different heating rate (β) of 5, 10, 15 and 20 K min^{-1} respectively, in flowing (100 ml min^{-1}) nitrogen of 99.99% using samples within the range 5–10 mg. Simultaneous TG-DTG-DSC curves were obtained in the range 35–650°C.

Kinetic methods

There has been growing and convincing evidence [8–13] that the expectation that the 'kinetic triplet', i.e., the Arrhenius parameters E, A and the reaction model f (α) or g (α), should be determined by a number of conventional model-fitting methods from a single heating rate experiment is actually unrealistic. Ignoring the complexity in solid-state reaction and based on an illusion that reaction mechanism and activation energy of reaction are independent of the temperature and reaction progress [8, 12], in these methods, kinetic triplet is usually estimated by fitting data to various reaction models. As reasonably analyzed by Vyazovkin *et al.* [8, 9, 14], because in a single non-isothermal experiment T and α are varied simultaneously, the model-fitting procedure allows error in the functional form of reaction model to be concealed by making compensating error in $k(T)$. As a result, almost any reaction model can satisfactorily fit data at the cost of estimating drastically different, but strongly correlated values of E and A. For this reason, the model-fitting methods tend to give rise to highly ambiguous kinetic information [8, 9],. This situation has also been demonstrated by a series report (Part A–E) on the ICTAC Kinetic Project [11–13, 15, 16]. In view of this fact, model-free iso-conversional methods have been strongly recommended [8, 12, 13–15] in thermal analysis kinetics although they are also being modified and developed [14, 17, 18].

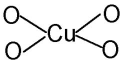
In the present work, Flynn-Wall-Ozawa (FWO) equations [19, 20] was used to process the TG-DTG data obtained from multiple heating rate experiments.

Results and discussion

Thermal behavior

The general information about the thermal behavior of the complexes, in terms of stability range, peak temperatures, and percentage mass loss and probable composition of the expelled groups corresponding to each decomposition stage is presented in Table 1

In order to make discussion clearer, it seems helpful to recollect both the main part of molecular structure and some useful crystal structure data of these complexes, which have been studied by XRD and reported in our previous papers [3–7], and now showed in Fig. 1.



As seen from Table 1, all adducts of $Cu(TTA)_2$ with solvent molecule, except $Cu(TTA)_2(Bpy)$, generally have a similar pattern of thermal decomposition: the evolution of the solvent molecule first, followed by the simultaneous removal of two TTA molecules. In the viewpoint of bond strength, this seems chemically reasonable [21]. According to the data in Fig. 1, either Cu–N or Cu_2O (the oxygen atom of DMS) distance is generally longer than any of four Cu–O bonds in, theoretically the former is less stable and easy to be broken down. This argument may also explain the decomposition mode of $Cu(TTA)_2(Bpy)$. Its mass loss suggests that the first stage is corresponding to the elimination of one TTA molecule instead of solvent molecule as in the case of the other adducts; while the next mass loss is due to the release of the solvent molecule, 2, 2'-bipyridine, then followed by the removal of the other TTA molecule. Taking into account the unique structure of $Cu(TTA)_2(Bpy)$ (Fig.1,e), its decomposition mode is expected: as legend, one of two TTA molecules is coordinated to the Cu atom through only one O atom with a longer bond length (2.204 Å); its bond energy is smaller than that of two chelate rings composed by a 2,2'-bipyridine molecule and the other TTA molecule respectively. As to the relative stability of the two chelate rings, is higher than due to the two facts: that the bond length of Cu–O is evidently shorter than that of Cu–N and that O atom is more electronegative than the N atom.

A close inspection of Table 1 demonstrates that the ways in which the solvent molecules decompose are also different. In the case of $Cu(TTA)_2(Py)_2$, one pyridine molecule evolves first, resulting in a quite stable intermediate within a wide temperature range, and then the other pyridine molecule and two TTA molecules are expelled simultaneously. For $Cu(TTA)_2(Ql)_2$, the two-quinoline molecules are released separately but continuously. The initial decomposition temperature of solvent molecules fall in the order Bip>DMS>Py>Ql, which indicates the corresponding bond length of Cu–N (or Cu–O for DMS).

It is interesting to note that a comparison of $Cu(TTA)_2$ as an original complex and $Cu(TTA)_2$ as an intermediate product of thermal decomposition of adducts shows that the releasing of two TTA molecules for the former covers a much wider temperature range

Table 1 Thermal decomposition data for complexes studied in dynamic nitrogen from TG-DTG-DSC analysis (measured at β=5 K min^{-1})

Complex[a]		DSC temp/°C	TG-DTG temp/°C			Mass loss / %		Probably expelled composition
		T_p	T_i	T_f	T_p	TG	Theory	
$Cu(TTA)_2$		261	211	552	296	87.48	87.43	2TTA
$Cu(TTA)_2(Py)_2$	I	116	105	151	117	12.02	11.91	Py
	II	241, 305	213	308	298	78.58	78.51	Py+2TTA
$Cu(TTA)_2(DMS)$	I	113	113	162	125	13.30	13.37	DMS
	II	247, 286	204	312	284	75.82	75.74	2TTA
$Cu(TTA)_2(Ql)_2$	I	123	87	130	119	16.82	16.89	Ql
	II	167	130	197	163	16.96	16.89	Ql
	III	241, 270	197	275	279	58.01	57.89	2TTA
$Cu(TTA)_2(Bpy)$	I	136	129	169	132	33.58	33.51	TTA
	II	229	169	258	236	23.59	23.65	Bpy
	III	275	258	322	284	33.55	33.51	TTA

[a] TTA=1,1,1-trifluro-3-(2-thenoyl)acetone; Py=pyridine; DMS=dimethyl sulfoxide; Ql=quinoline; Bpy=2,2'-bipyridine

and its TG curve exhibits long tailing, while for the latter, this process completes quickly. This phenomenon suggests that being an intermediate, the structure of $Cu(TTA)_2$ may be affected to a certain extent by the foregoing removal of solvent molecule.

The final residue at the end of decomposition for all the complexes studied is powdery metal copper. The DSC curves show that the all stages of decomposition are associated with endothermic process.

Figures 2–6 show some selected TG-DTG-DSC profiles of the complexes.

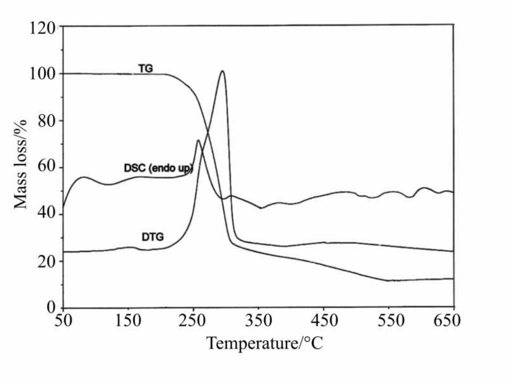


Fig. 2 TG-DTG-DSC curve of $Cu(TTA)_2$

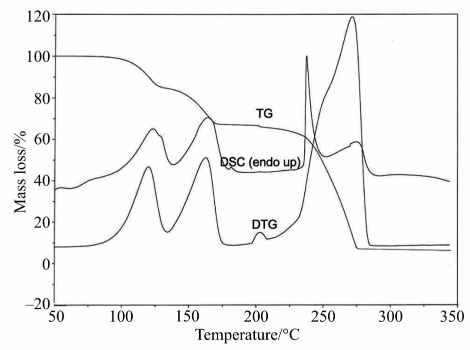


Fig. 3 TG-DTG-DSC curve of $Cu(TTA)_2(Ql)_2$

Thermal decomposition kinetics

Figures 7 and 8 present the dependences of the activation energy E on the reaction extent α of various solvent molecules evolution and TTA release determined by F-W-O method, respectively. As shown from them, the values of activation energy E for TTA molecules evolution are generally higher than that for the solvent molecules release. For all the decomposition stages, E value did not seem to keep constant in their corresponding overall process, but varied with the extent of conversion. The degree of variation in E value for the evolution of solvent molecules is about 30

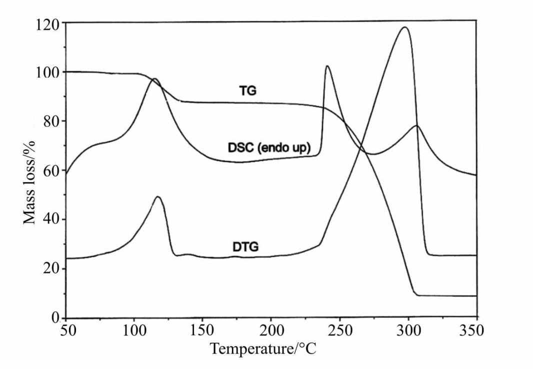


Fig. 4 TG-DTG-DSC curve of Cu(TTA)$_2$ (Py)$_2$

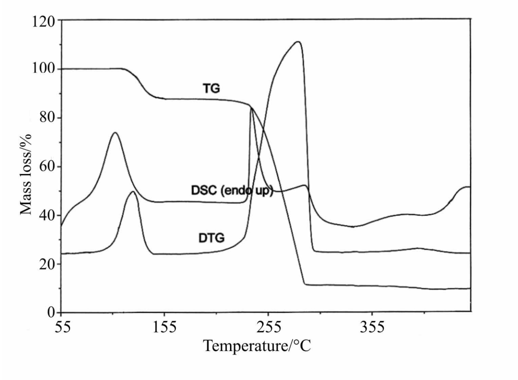


Fig. 5 TG-DTG-DSC curve of Cu(TTA)$_2$ (DMS)

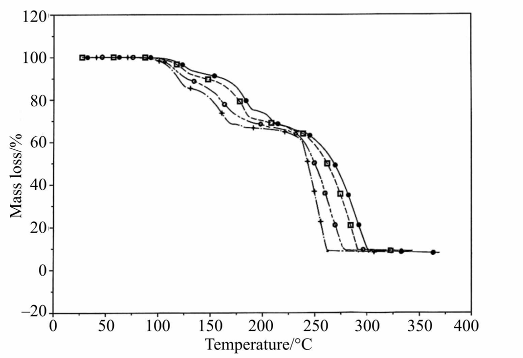


Fig. 6 TG curves at various heating rate for Cu(TTA)$_2$(Ql)$_2$
+ – 5K, ○ – 10K, □ – 15K and ● – 20 K min^{-1}

kJ mol^{-1}, while 50 kJ mol^{-1} for TTA molecule. As to the pattern of variation in E value, for the solvent evolution, E increased first and then decreased with α, while for TTA, the E generally decreased with α. (As the values of E and their variation with α

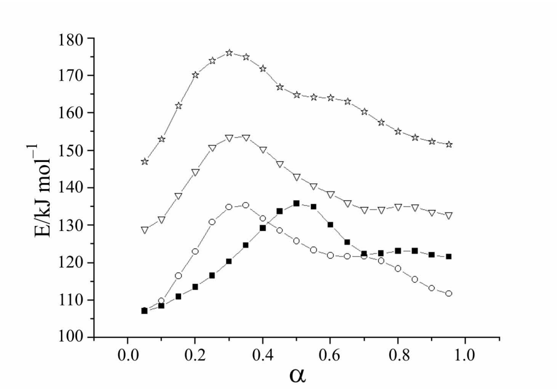


Fig. 7 Dependences of the activation on extent of solvent molecule evolutions ■ – $Cu(TTA)_2(Ql)_2$, ○ – $Cu(TTA)_2$ $(Py)_2$ ▽ – $Cu(TTA)_2(DMS)$ and ☆ – $Cu(TTA)_2(Bpy)$

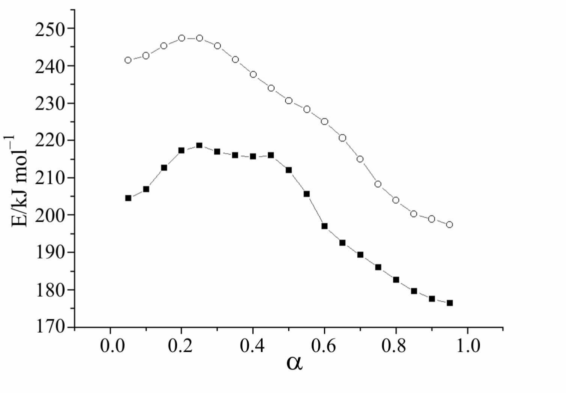


Fig. 8 Dependences of the activation on extent of TTA molecule evolutions ■ – $Cu(TTA)_2$ (Ql) 2 and ○ – $Cu(TTA)_2$

for TTA evolution of the other addicts are similar to that of $Cu(TTA)_2(Ql)_2$, they are omitted here to avoid making Fig. 8 unrecognizable.)

Variable activation energy usually indicates a multiple-step nature of solid-state reactions [8, 9], however, to properly interpret the *E*-dependences on α in this study by means of kinetic mechanism seems to be beyond our current knowledge. We only wish, therefore, that the results given in the present work could add a sample which, to a certain extent, shows that kinetics of reaction involved in solid state is far from being simple as we used to expect or are still expecting it to be.

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