*Journal of Thermal Analysis, Vol. 31 (1986) 667–670*

# THERMAL DECOMPOSITION OF BIS-(DL-VALINATO)COPPER(II) AND BIS-(DL-METHIONINATO)COPPER(II)*

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(Received August 28, 1985)

A kinetic study of the thermal decomposition of the complexes bis-(DL-valinato)copper(II) and bis-(DL-methioninato)copper(II) was carried out using thermogravimetry in a dynamic regime, following the theoretical model of Šatava and including the equation used by Johnson and Gallagher: $\frac{1}{1-\alpha} - 1 = kt$. Kinetic parameters were calculated and are compared with those obtained previously for the complex bis-(L-tryptophanato)copper(II). The sequence of thermal stability found is: $Cu(DL\text{–}Val)_2 < Cu(L\text{–}Trp)_2 < Cu(DL\text{–}Met)_2$.

Little has been published till now on the solid →solid + gas reactions of the bis-(aminoacidato)Cu(II) complexes. Olafson and Byran [1] studied the thermal decomposition of some bis-(aminoacidato)Cu(II) complexes by differential scanning calorimetry, and Gili and de la Fuente [2] described the thermal decomposition of the complex bis-(L-tryptophanato)copper(II) using thermogravimetry.

In this work we report for the first time a kinetic study of the thermal decomposition in the solid phase of the complexes bis-(DL-valinato)-copper(II) and bis-(DL-methioninato)copper(II) (abbreviated $Cu(DL\text{-}Val)_2$ and $Cu(DL\text{-}Met)_2$, respectively). This study has been carried out using thermogravimetry in a dynamic regime following the theoretical model of Šatava [3] and including the second-order equation $\frac{1}{1-\alpha} - 1 = kt$ used by Johnson and Gallagher [4].

* Presented at the 1985 World Conference on Thermal Analysis, Bad Hofgastein, Austria.



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*Akadémiai Kiadó, Budapest*

## Results and discussion

The curves of loss of mass against temperature and their derivatives indicate one stage in the thermal decompositions of the complexes $Cu(DL\text{-}Val)_2$ and $Cu(DL\text{-}Met)_2$.

Copper was obtained as final product at 873 K for $Cu(DL\text{-}Val)_2$. Similar behaviour was found for bis-(L-tryptophanato)copper(II) [2]. On the other hand, the final product of $Cu(DL\text{-}Met)_2$ at 800 K is not Cu [8].

The shapes of the curves obtained by plotting the degree of decomposition ($\alpha$) *vs.* $T$(K) are different for the two complexes. $Cu(DL\text{-}Val)_2$ presents a curve which reflects a large process of acceleration, followed by a short interval of deceleration. For $Cu(DL\text{-}Met)_2$ there is scarcely an acceleratory period.

The logarithms of the functions $g(\alpha)$ [3, 4] were plotted *vs.* $1/T$(K), it was found that the largest correlation factor in the adjustment to linearity by least squares corresponds to the equation $\alpha^2 = kt$ for $Cu(DL\text{-}Val)_2$, which gives a one-dimensional diffusion mechanism as the rate-determining process, and to the second-order equation $\frac{1}{1-\alpha} - 1 = kt$ for $Cu(DL\text{-}Met)_2$.

The activation energy for the thermal decomposition was calculated with the formulae:

$$E_1 = -\frac{449 + \tan\beta}{217} \tag{5}$$

$$E_2 = \{[8 \tan\beta \cdot T_m + (\tan\beta)^2]^{1/2} - \tan\beta\} \tag{3}$$

where $\tan\beta$ is the slope of the selected linear plot of $\log g(\alpha)$ *vs.* $1/T$ and $T_m$ is the mean temperature.

The results obtained are given in Table 1. For comparative purposes, only the first decomposition step for bis-(L-tryptophanato)copper(II) is included.

The initial temperatures of decomposition indicate that the sequence of thermal stability is:

$$Cu(DL\text{-}Val)_2 < Cu(L\text{-}Trp)_2 < Cu(DL\text{-}Met)_2$$

This sequence does not correspond to the formation constants of the complexes in solution [9].

The lower stability of $Cu(DL\text{-}Val)_2$ is probably due to the position of the methyl groups of the ligand. On the other hand, the linear chain of the methionine produces a higher thermal stabilization in the complex, with probable S—Cu interaction at higher temperatures. The decomposition of $Cu(L\text{-}Trp)_2$ is more complicated, due to the stability of the indole group.

**Table 1** $T_i$ (Initial Temperature); $T_f$ (Final Temperature); $E_a$ (Activation Energy) and $Z$ (pre exponential factor) for the thermal decomposition of the complexes

| Compound | $T_i$, K | $T_f$, K | $E_a$, kJ/mol | | $Z$, $s^{-1}$ | | Ref. |
|---|---|---|---|---|---|---|---|
| | | | $E_1$ | $E_2$ | $Z_1$ | $Z_2$ | |
| $Cu(DL\text{-}Val)_2$ | 493 | 551 | 494.0 | 490.1 | $2.58 \cdot 10^{45}$ | $1.13 \cdot 10^{45}$ | This work. |
| $Cu(DL\text{-}Met)_2$ | 523 | 563 | 600.7 | 595.8 | $1.28 \cdot 10^{56}$ | $4.12 \cdot 10^{55}$ | This work. |
| $Cu(L\text{-}Trp)_2$ | 498 | 541 | — | — | — | — | (2). |

## Experimental

$Cu(DL\text{-}Val)_2$ was obtained by mixing DL-valine in hot water with an aqueous solution of $Cu(AcO)_2 \cdot H_2O$ in the required amount. The resulting precipitate was filtered, washed several times with water and then recrystallized. Anal.: Calculated for $Cu(C_5H_{10}NO_2)_2$: Cu 21.48; C, 40.60; N, 9.47; H, 6.82. Found: Cu, 21.48; C, 40.50; N, 9.36; H, 6.90. $Cu(DL\text{-}Met)_2$ was prepared by the method described by Ou et al. [6]. Anal.: Calculated for $Cu(C_5H_{10}NO_2S)_2$: Cu, 17.65; C, 33.37; N, 7.78; H, 5.60. Found: Cu, 17.52; C, 33.40; N, 7,75; H, 5.62.

The infrared spectra of both complexes present bands at 3240 and 2910 $cm^{-1}$, corresponding to the $NH_2$ group of the ligands, and indicate the coordination of this group to the metal. The $NH_2$ deformation mode in both compounds was observed as a sharp band at 1580 $cm^{-1}$, located next to the intense stretching mode of the $-C\lesssim^{O}_{O}$-group at 1600 $cm^{-1}$. Other characteristic bands of the infrared spectra were found for both complexes in accordance with references [6, 7].

The thermogravimetric measurements were carried out on a Perkin–Elmer TGS–2 thermobalance with an FDC first derivative computer, in a nitrogen atmosphere. The heating rate was 5 deg/min. Each run was repeated twice and the experimental reproducibility was good for each mass used ($\simeq$ 4 mg).

## References


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**Zusammenfassung** — Die thermische Zersetzung der Komplexe Bis-(DL-valinato)kupfer(II) und Bis-(DL-methioninato)kupfer(II) wurde thermogravimetrisch im dynamischen Regime untersucht, indem von dem theoretischen Modell von Šatava Gebrauch gemacht und die von Johnson und Gallagher benutzte Gleichung $\frac{1}{1-\alpha} - 1 = kt$ einbezogen wurde. Kinetische Parameter wurden berechnet und mit den kürzlich für den Komplex Bis-(L-tryptophanato)kupfer(II) erhaltenen parametern verglichen. Die Stabilität der Komplexe nimmt in folgender Reihenfolge zu: $Cu(DL\text{-}Val)_2 < Cu(L\text{-}Trp)_2 < Cu(DL\text{-}Met)_2$.

**Резюме** — Кинетическое исследование термического разложения комплексов бис-(ДЛ-валинато)- и биз-(ДЛ-метионинато)меди(II) проведено методом термогравиметри в динамическом режиме, следуя теоретической модели Сатавы и включая уравнение Джонсона–Гэллэхера: $\frac{1}{1-\alpha} - 1 = kt$. Вычисленные кинетические параметры были сопоставлены с полученными ранее для комплекса бис-(L-триптофанато)меди(II). По термоустойчивости комплексы располагаются в ряд $Cu(DL\text{-}Val)_2 < Cu(L\text{-}Trp)_2 < Cu(DL\text{-}Met)_2$.