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

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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-Val)_2 < Cu(L-Trp)_2 < Cu(DL-Met)_2.


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-Val)_2 and Cu(DL-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].

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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-Val)$_2$ and Cu(DL-Met)$_2$.

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

The shapes of the curve obtained by plotting the degree of decomposition ($\alpha$) vs. $T$ (K) are different for the two complexes. Cu(DL-Val)$_2$ presents a curve which reflects a large process of acceleration, followed by a short interval of deceleration. For Cu(DL-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-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-Met)$_2$.

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

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

$$E_2 = \frac{8 \tan \beta \cdot T_m + (\tan \beta)^2}{(8 \tan \beta \cdot T_m + (\tan \beta)^2)^{1/2} - \tan \beta}$$

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:

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

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

The lower stability of Cu(DL-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-Trp)$_2$ is more complicated, due to the stability of the indole group.