Study of the Thermal Decomposition in Solid Phase of L-Tryptophanatocopper(II)

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Introduction

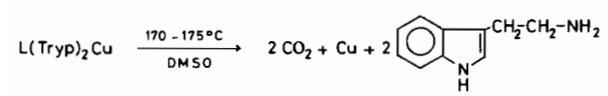
Numerous thermodynamic and kinetic studies of complexes of aminoacids of copper(II) in solution have been carried out, yet very little has been published on the solid → solid + gas reactions of these complexes.

The aim of this work is, on the one hand, to study the kinetics of the thermal decomposition of the solid complex $L(Tryp)_2Cu$ (L-tryptophanatocopper(II)) using a thermogravimetric method in dynamic regime and, on the other hand, to try to obtain tryptamine (an important compound in the synthesis of indole alkaloids which also shows pharmacological activity) more economically than through those methods previously reported starting from the decarboxylation of $L(Tryp)_2Cu$ in different solvents [1].

Results and Discussion

The curves of loss of mass against temperature indicate three stages in the thermal decomposition of the complex, and copper is obtained at 680 °C as a final product.

The IR spectra of the products isolated in the intermediate stages show that they are not tryptamine, which again was not obtained in isothermic regime at 175 °C. Therefore, in order to give tryptamine, the solvent must intervene actively in the thermal decomposition mechanism:



Curves with two differentiated periods are obtained from the representations of the degree of decomposition (α) *vs.* T K. A process of acceleration followed by one of deceleration, with a short interval of temperature, is observed in the three steps.

TABLE I. T_i (Initial Temperature), T_f (Final Temperature) and E_a (Activation Energy) for Three Decomposition Steps for the L-tryptophanate Copper(II).

	T_i (K)	T_f (K)	E_a (kJ mol^{-1})
1st step	298	541	–
2nd step	541	750	20.65
3rd step	750	953	45.73
			E_a (total) = 66.38

The logarithms of the Satava functions $F(\alpha)$ [2] have been calculated from the α values and have been represented *vs.* 1/T K. From the plot of these functions it is observed that a straight line is fitted in the last two steps by the equation:

$$(-\ln(1-\alpha))^{1/3} = kT$$

which gives a random nucleation mechanism as the rate-determining process. The behaviour observed for the first stage could not be explained by the Satava method.

The activation energy for the thermal decomposition has been calculated for each step and the results obtained are given in Table I.

The total value of the activation energy is in the same order as obtained by P. G. Olafsson and A. M. Byran [3], 55.23 kJ/mol, although our value is higher. In ref. [3] the authors use differential scanning calorimetry and do not specify what isomer of tryptophane was involved.

At the present time we are studying the thermal decomposition of complexes of Cu(II), Co(II) *etc.*, with aminoacids and other ligands such as terpyridine.

Experimental

The complex was obtained by mixing L-tryptophane, which had been previously dissolved in hot water, with an aqueous solution of copper(II) chloride in the required amount. The resulting precipitate was filtered and washed several times with hot water until no traces of chlorides remained. The complex was recrystallized (H_2O–DMSO) and dried ($CaCl_2$). *Anal.* Calculated for $(C_{11}H_{12}N_2O_2)_2Cu$: Cu, 13.52; C, 56.22; N, 11.92; H, 4.72%. Found: Cu, 13.52; C, 56.64; N, 11.82; H, 4.83%.

The characterization of the compound was based on its IR spectra, electronic absorption spectra and X-ray diffraction [4].

The thermogravimetric measurements were carried

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out on a thermobalance Perkin-Elmer TGS-1 with a UU-1 temperature programmer in nitrogen atmosphere. The calibration of temperatures was performed by means of ferroelectric standards and in mass by mass patterns. Heating rate 10 °C min^{-1}. Each run was repeated 2 or 3 times and the experimental reproducibility was good for each mass used.

References

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2 V. Satava, *Thermochim. Acta, 2,* 423 (1971).
3 P. G. Olafsson and A. M. Byran, *Chem. Commun., 23,* 1473 (1968).
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