Thermodynamic Data for the Decomposition of Some Copper Amino-acid Complexes as obtained by Differential Scanning Calorimetry

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THERMODYNAMIC data have been obtained for copper complexes of amino-acids in solution by titrimetric, polarographic, and calorimetric methods.[1] Variations in enthalpy values obtained for dissociation have been observed and have been attributed to varying degrees of solvolysis of the complexes. Since these solvent interactions would vary from one metal complex to another even under identical solvent conditions, it is desirable to develop a method for determining thermodynamic parameters in the absence of solvent.

We sought a method for determining the activation energy for thermal decomposition of the solid copper amino-acid complexes. The energies involved were obtained by use of differential scanning calorimetry. The complexes examined were allowed to assume their thermodynamically favoured forms by obtaining them from aqueous solutions in which the complexes of the metal ions are kinetically labile.

Aqueous solutions of the sodium salts of the amino-acids, prepared from exactly equivalent quantities of the free amino-acids and sodium hydrogen carbonate, were added to aqueous solutions of the equivalent quantity of copper(II) sulphate. The precipitated copper(II) complexes were crystallized (H_2O) and dried (P_2O_5) *in vacuo*. The decomposition temperature of each copper complex was measured over a series of constant temperature rates (1·25, 2·5, 5, 10, 20, 40, and 80°/min.), by use of a Perkin-Elmer DSC-IB Differential Scanning Calorimeter. Plots of log ϕ/T_m^2 against $1/T_m$ were obtained for each sample, where ϕ was the heating rate in degrees/min., and T_m the peak temperature (°K).

Activation energies for thermal decomposition of copper complexes of amino-acids were as follows: copper tryptophanate, 13·2; copper glycinate, 15·2; copper tryosinate, 25·2; copper glutamate, 28·4; copper glutaminate, 32·6; and copper alanate, 66·8 kcal.

Differential thermal analysis has been applied to various studies of chemical kinetics.[2] While Borchard and Daniels[3] applied this technique to the study of reaction kinetics in solutions, Murray and White[4,5] used it in the study of the kinetics of the decomposition of clay minerals. The latter[4] reported that the thermal decomposition of their material obeyed a first-order rate law, and developed an equation based on the assumption that the peak temperature occurs when the reaction rate is at a maximum:

$$\mathrm{d}(\ln\phi/T_m^2)/\mathrm{d}(1/T_m) = -E/R$$

where ϕ is the heating rate, T_m the peak temperature (°K), E the activation energy of the reaction, and R is the gas constant. Subsequent experimental data[6] verified the equation of Murray and White, and established its applicability to the determination of kinetic constants. Accurate values are only obtained from the equation, however, when instrumentation capable of providing linear heating over a series of different heating rates is available. Piloyan and his co-workers[7] circumvented this problem by developing a method for determining E from a single differential thermal analysis curve, recorded at a single heating rate.

The present work establishes the applicability of differential scanning calorimetry to the study of reaction kinetics of solid copper complexes of amino-acids.

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