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STUDIES ON SOLID STATE KINETICS OF SOME METAL CHELATES OF MACRO ORGANIC LIGANDS

S. K. BHARTIYA* and JAMADAR ROY[a]

Department of Physics, Inter College, B. M. P. –7, KATIHAR – 854105 (Bihar) INDIA
[a]Department of Chemistry, S. T. College, KATIHAR – 854105 (Bihar) INDIA

ABSTRACT

Thermogravimetric analysis was used to determine kinetic parameters such as order of reaction, activation energy, frequency factor etc. of some metal complexes based on the method of Freeman and Carroll.

Key words: Metal chelates, Macro-organic ligands, Kinetics, Solid state.

INTRODUCTION

Thermogravimetric analysis involves change in weight of system under examination with increase in temperature at a linear rate of solid-state reaction. The simple weight drops slowly as pyrolysis begins and then, it drops precipitously over a narrow temperature range and finally turns back to a zero slope as the reactant is exhausted. The shape of the curve is determined by the kinetic parameters of the pyrolysis such as reaction order, frequency factor and energy of activation etc. The most widely used method to determine the kinetic parameter is by Freeman and Carroll for the following pyrolysis process, which is based on equation –

$$\frac{d\alpha}{dt} = \left(\frac{-z}{a}\right) e^{\frac{-E^*}{RT}} F(\alpha) \qquad \ldots(1)$$

$$A\ (Solid) \rightarrow B\ (Solid) + C\ (Gas)$$

where $F(\alpha) = -X^n$

Here X is mole fraction or amount of reactant A and n is order of the reaction. The rate expression for disappearance of reactant A from the mixture can be written as –

* Author for correspondence

$$-\frac{dx}{dt} = ze^{\frac{-E^*}{RT}}X^n \qquad \ldots(2)$$

Where, X and T are evaluated on rearranging equation and differentiating its logarithmic form with respect to , the rate expression may be given in terms of amount of reactant as follows –

$$\frac{-(\frac{E^*}{R})\,\Delta(\frac{1}{T})}{\Delta \log n_a} = -x + \frac{\Delta \log(\frac{-dn_a}{dt})}{\Delta \log n_a} \qquad \ldots(3)$$

where n_a is the number of mole of A at time t. Relating number of moles of reactant to weight –

$$\frac{dn_a}{dt} = \frac{n_0}{W_0}\frac{dw}{dt} \qquad \ldots(4)$$

$$\text{and } W_r = W_o - w \qquad \ldots(5)$$

Where n_o = Initial number of moles of A and W = Total weight loss up to time t. Then the above equation (3) becomes –

$$\frac{\frac{-E^*}{2.3\,R}\,\Delta(\frac{1}{T})}{\log W_r} = -x + \frac{\Delta \log(\frac{-dw}{dt})}{\Delta \log W_r} \qquad \ldots(7)$$

Thus, by plotting $\frac{\log(\frac{dw}{dt})}{\log W_r}$ versus $\frac{\Delta T^{-1}}{\log W_r}\Delta T^{-1} / \log W_r$

A particular stage of reaction, the intercept gives the order of reaction and 2.3 R x slope gives E*, the activation energy by the stage, dw and W_r can be read directly from the T.G. curve. Kinetic parameters such as reaction order, activation energy and the pre-exponential factor were calculated from thermogravimetric curve and different procedures applied to data were compared.

Material and methods

Complex of some metals e.g. Ni^{2+}, Co2+, Zn^{2+}, Hg^{2+} and Pb^{2+} with 1, 5-bis (3-hydroxy-4-methoxy benzaldehyde thiocarbohydrazone were prepared by usual methods

and ligand by condensation of thiocarbohydrazone with 3, 4 – dihydroxy benzaldehyde and 3-hydroxy-4-methoxy benzaldehyde, respectively in aqueous ethanol.

Freeman and Carroll method

The existing percentage weight of the complex at equal temperature intervals i.e. 10^0C were noted directly from T.G. curves for a particular stage of thermal decomposition. A plot of log /log W_r versus T^{-1} A/ log W_r x 10^{-3} was drawn in each case where,

$W_r = W_c - w$,

W_c = Total weight loss at completion of reaction

W = Total weight loss upto time t.

The straight line obtained is suggestive of the order of reaction from their intercept of Y-axis and the activation energy = 2.3 x slope. Freeman and Carroll suggested that a good straight line is obtained but in the present work, however, a number of remarkable deviations have been found possibly on account of experimental factors compactness, particle size etc., which could not be controlled.

RESULTS AND DISCUSSION

Themogravimetric curves were drawn for individual compound on the electro–balance with an automatic recorder for recording the thermogram. In case of complex of nickel, where L stands for ligands, the elemental analysis suggests that the of molecular formula and molecular weight of the complex are ($Ni.L.Py_2Cl_2$) and 597.21, respectively.

The kinetic parameters in the present case are for the 2^{nd} stage of decomposition using primarily the Freeman and Carroll Method. The values were finally corroborated by Doyle's method as modified by Zsako. The data were substantiated for different weights taken for calculating δ and activation energy. Similar method were applied for calculation of activation energy and order of reaction for other complexes.

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