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Kinetic Parameters from TG Analysis of Bis-{2-(*o*-hydroxy phenyl) Benzimidazolato} Cobalt(II) Dihydrate Complex

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In the present paper we have reported some kinetic parameters from TGA of bis{2-(*o*-hydroxyphenyl) benzimidazolato} cobalt(II) dihydrate complex.

INTRODUCTION

The rate of thermal decomposition is determined by the rate of one or more of these stages. Sometimes the rate-determining stage at the beginning of the pyrolysis may lose its significance and later another stage can take its place.

The decomposition rate of a TG curve can be denoted as $d\alpha/dt$, where α stands for the fraction of the initial compound undergoing reaction. In isothermal conditions it may be presumed that the reaction rate is dependent only on the fraction reacted.

$$-d\alpha/dt = K\alpha^n$$

where n is the order of reaction and K the specific rate constant. The specific rate constant depends upon the temperature by the expression

$$K = Ae^{-E/RT}$$

where A is the pre-exponential factor, E the activation energy and R the gas constant. In the present work, some kinetic parameters from thermogravimetric analysis of bis-{2-*o*-hydroxy(phenyl) benzimidazolato} cobalt(II) dihydrate complex are presented.

EXPERIMENTAL

An electrobalance with a recorder operating at 1 mv full scale was used for obtaining the thermograms. A chromelalumel thermocouple placed 3–4 mm below the sample holder, the platinum boat (2 mm × 8 mm dia), was used for recording the sample temperature. A heating rate of 10°C min^{-1} was employed and chart speed was maintained at 600 mm h^{-1}. Calculations were carried out from a single TG curve for the second stage of decomposition of the complex around 330°. The initial stage corresponded to the elimination of coordinated water.

Preparation of the sample

An aqueous solution of cobalt(II) chloride (1.3 g in 10 mL) was diluted with

50 mL of ethanol and filtered. The clear filtrate was added to an ethanolic solution of the ligand (2 g in 50 mL) in 1 : 2 molar ratio with constant shaking. The little complex was precipitated as a rose crystalline precipitate. A few drops of ammonical ethanol were added to precipitate the complex completely. The complex was digested on a steam bath and filtered in hot. The complex was washed with ethanol and dried in air. The molecular formula of the complex corresponds to $CoL_2 \cdot 2H_2O$.

RESULTS AND DISCUSSION

The kinetic parameters of the complex have been calculated by both Freeman and Carroll method and Zsako method.

Freeman and Carroll[1] suggested a linear relationship between $\log \frac{dw/dt}{\Delta \log W_r}$ and $\frac{\Delta T^{-1}}{\Delta \log W_r}$, where $W_r = (W_c - W)$ and W_c is weight loss at completion of reaction, W the total weight-loss up to time t and T the absolute temperature. The intercept $-x$ of the straight line plotted from the evaluated values for the equation indicates the order of reaction and the slope indicates the energy of activation E_a to $E_a/2.3R$ The reaction order and the activation energy of the compound have been evaluated as 1.72 and 25.3897 kcal mol^{-1} respectively for the second transformation stage under consideration.

These values were compared with the method of Doyle[2] as modified by Zsako[2]. Doyle's equation for TG curve is

$$g(\alpha) = \frac{ZE_a}{Rq} p(x)$$

where Z is frequency factor, E_a the activation energy, R the gas constant and q the heating rate. The value $g(\alpha)$ is a certain function of α and

$$\alpha = \frac{W_0 - W}{W_0 - W_1}$$

where W, W_q and W_t are the actual, initial and final weights of the sample respectively. $g(\alpha)$ is calculated for various orders of decomposition from the equation

$$\frac{d\alpha}{dt} = K(1 - \alpha)^b$$

where b is the order of reaction. For $b = 0$ $g_0(\alpha) = \alpha$, for $b = 1$, $g_1(\alpha) = \ln\left(\frac{I}{1-\alpha}\right)$ and for $b = 2$, $g_2(\alpha) = \left(\frac{\alpha}{1-\alpha}\right)$.

The values of B_0, B_1 and B_2 have been calculated in the present case from the equations given herein with the help of the data for $g(\alpha)$ and $-\log p(x)$ at different temperatures. B_0, B_1 and B_2 are the constants of the difference $\log(\alpha) - \log p(x)$ for zero, first and second order reactions respectively, which provide information to suggest a quantitative method for determining the apparent activation energy consistent with a given a function $f(\alpha)$.

$$b = 0; \quad B_0 = \log \alpha - p(x)$$

$$b = 1; \quad B_1 = \log \left(\ln \frac{1}{1-\alpha} \right) - \log p(x)$$

$$b = 2; \quad B_2 = \log \left(\frac{\alpha}{1-\alpha} \right) - \log p(x)$$

and the values of $g(\alpha)$ are given in Table-1.

TABLE-1

S. No.	Temp. °C	W mg	$\log \alpha$	$\log\left(\frac{1}{1-\alpha}\right)$	$\log\left(\frac{\alpha}{1-\alpha}\right)$
1.	330	7.00	-2.5198	-2.5191	-2.5185
2.	340	6.97	-2.1218	-2.1202	-2.1185
3.	350	6.93	-1.8666	-1.8636	-1.8606
4.	360	8.86	-1.6167	-1.6114	-1.6061
5.	370	6.80	-1.4784	-1.4711	-1.4637
6.	380	6.72	-1.3437	-1.3337	-1.3235
7.	390	6.60	-1.1976	-1.1834	-1.1691
8.	400	6.49	-1.0965	-1.0785	-1.0603
9.	410	6.35	-0.9947	-0.9718	-0.9484
10.	420	6.20	-0.9070	-0.8786	-0.8496
11.	430	5.80	-0.7344	-0.6910	-0.6460

Initial weight = 7.02 mg, Final weight = 0.40 mg.

For quantitative evaluation of the value of E_a the arithmetical mean of B_0, B_1 and B_2 has been calculated and also the standard deviation δ for all the three pre-supposed orders of reaction. The value of δ is obtained from the relation

$$\delta = \frac{\sqrt{(B_1 - B)^2}}{r}$$

where B_1 is any value, B their arithmetical mean and r the number of values. The various values for the corresponding B_0, B_1 and B_2 are listed in Table-2.

TABLE-2

B_0		B_1		B_2	
E_a	o	E_a	1	E_a	2
26	0.1119	28	0.1011	28	0.1024
28	0.1014	30	0.0975	30	0.0946
30	0.1017	32	0.1032	32	0.0968

It is apparent from Table-2 that the standard deviations are minimum if the second order reaction is accepted and the value of δ is minimum for $E_a = 30$ kcal mol^{-1} and corresponds to 0.0946, the value of the arithmetical mean, *i.e.*, it corresponds to 11.412.

The frequency factor Z for the solid state kinetics is evaluated as log Z = 6.4536 by means of the relation

$$\log Z = B + \log Rq - \log E_a$$

where q is the heating rate and R the gas constant.

The apparent activation entropy $\Delta S^{\#}$ is calculated as –30.87 e.u. from the relation

$$\delta S^{\#2} = 2.303 \log (Zh/kT)$$

The values for T in this equation is the temperature T_1 at which the weight-loss is half the total loss during the step of transformation under consideration.

The values of E_a with order of reaction b = 2 by Freeman and Carroll and Zsako are 25.38 and 30.00 kcal $mole^{-1}$ respectively.

The values for E_a, b calculated by the procedures mentioned earlier seem to be in good agreement with each other and thus may be utilised in the study of solid state reaction mechanism.

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