Kinetic Parameters from TG Analysis of
Bis-{2-(*o*-hydroxyphenyl) Benzoxazolato} Nickel(II) Complex

A.K. SINGH,* A.P. SINHA and K.K. SINGH
Department of Chemistry
Magadh University, Bodh-Gaya-824 234, India

In the present work, the authors describe the calculation of some kinetic parameters from thermogavimetric analysis of bis-{2-(*o*-hydroxyphenyl) benzoxazolato} nickel(II) 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,

$$K = A \cdot e^{-E/RT}$$

where A is the preexponential factor, E the activation energy and R the gas constant.

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 $10°$ 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 $330°C$. The initial stage corresponded to the elimination of coordinated water.

Preparation of the sample: An aqueous solution of nickel(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 was 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 $NiL_2 \cdot 2H_2O$.

RESULTS AND DISCUSSION

The kinetic parameters of the complex have been calculated by both Freeman and Carroll method[1] and Zsako method[3].

Freeman and Carroll[1] suggested a linear relationship between $\dfrac{\log (dw/dt)}{\Delta \log W_r}$ and

$\dfrac{\Delta T^{-1}}{\Delta \log W_r}$ 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 activatioin E_a to $E_a/2.3R$. The reaction order and the activation energy of the compound have been evaluated as 2.5 and 44.005 Kcal mol^{-1} for the second transformation stage under consideration.

These values were compared with the method of Doyle[2] as modified by Zsako[3]. 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 and

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

where W, W_0 and W_1 are the actual, inititial 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 $b = 1$, $g_1(\alpha) = \ln\left(\dfrac{1}{1-\alpha}\right)$ and for $b = 2$, $g_2(\alpha) = \left(\dfrac{\alpha}{1-\alpha}\right)$.

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 constancy of the difference $\log (\alpha)$ 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 function $f(\alpha)$.

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

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

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

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

TABLE-1

Sl. No.	Temp. (°C)	W (mg)	$\log \alpha$	$\log\left(\dfrac{1}{1-\alpha}\right)$	$\log\left(\dfrac{\alpha}{1-\alpha}\right)$
1.	300	7.79	−2.5191	−2.5185	−2.5178
2.	310	7.77	−2.2181	−2.2168	−2.2155
3.	320	7.70	−1.7788	−1.7751	−1.7715
4.	330	7.55	−1.4052	−1.3965	−1.3878
5.	340	7.15	−1.0006	−0.9780	−0.9549
6.	350	6.86	−0.8424	−0.8092	−0.7750
7.	360	6.52	−0.7096	−0.6633	−0.6153
8.	370	6.00	−0.5625	−0.4948	−0.4235
9.	380	5.31	−0.4222	−0.3231	−0.2159
10.	390	4.70	−0.3274	−0.1966	−0.0513

$W_0 = 7.81$ mg, $W_t = 1.20$ mg

For quantitative evaluation of the value of E_a, the arithmetical mean of B_0, B_1 and B_2 have been calculated and the standard deviation δ for all the three pre-supposed order of reactions. δ is obtained from the relation

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

where B_1 is any value, B their arthmetical 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	0	E_a	1	E_a	2
38	0.1617	42	0.1413	44	0.1270
40	0.1553	44	0.1396	46	0.1238
42	0.1555	46	0.1477	48	0.1283

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 means, *i.e.*, it corresponds to 11.554.

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.[4]

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

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

The value 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.

ACKNOWLEDGEMENTS

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