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Kinetic Parameters from TG Analysis of Chloroaquo-bis(3-Methyl-4-Amino-5-Mercapto-1,2,4-Triazole) Copper(I) Complex

ASHOK KUMAR†, BIJAY KUMAR SINHA†, GIRISH PRASAD†,
REWATI KANT* and SANJEEV KUMAR
P.G. Department of Chemistry
Magadh University, Bodh Gaya-824 234, India

In the present work, we describe the kinetic parameters from TG-analysis of a copper(I) 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 defined 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.

$$-\frac{d\alpha}{dt} = K\alpha^n$$

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 pre-exponential 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 was placed 3–4 mm below the sample holder. A platinum boat (2 mm × 8 mm dia) was used for recording the sample temperature. A heating rate of $10° \text{ min}^{-1}$ was employed and chart speed was maintained at 120 mmh^{-1}. Calculations were carried out from a single TG curve.

Synthesis of Complex: A methanolic solution of hydrated cupric chloride (0.01 M in 50 mL) was treated with hot methanolic solution of 3-methyl-4-amino-

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†P.G. Department of Chemistry, Gaya College, Gaya (Bihar)

5-mercapto-1,2,4-triazole ligand (0.025 M in 100 mL) and refluxed on a steam bath for 20 minutes, when a faint yellow complex separated out. The precipitate was filtered, washed several times with aqueous methanol to remove excess of reagents and dried in a desiccator over $CaCl_2$.

RESULTS AND DISCUSSION

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

Freeman and Carroll suggested a linear relationship between

$$\Delta \log \frac{dW}{dt} / \Delta \log W_r \quad \text{and} \quad \Delta T^{-1} / \Delta \log W_r,$$

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 1.0 and 13.88 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[3]. Doyle's equation for TG curve is

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

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

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

where W, W_0 and W_t are the actual, initial and final weights of the sample respectively. The g(α) 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 $b = 1$, $g_1(\alpha) = \ln\left(\frac{1}{1-\alpha}\right)$ 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(α) and –log p(x) at different temperatures. B_0, B_1 and B_2 are the constants of the difference log (α) – 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 function f(α).

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

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

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

and the values of g(α) are given in Table-1.

TABLE-1

S. No.	Temp. (°C)	W (mg)	$\log \alpha$	$\log\left(\mathrm{In}\frac{1}{1-\alpha}\right)$	$\log\left(\frac{\alpha}{1-\alpha}\right)$
1.	140	5.64	-1.32221	-1.31175	-1.30111
2.	150	5.59	-1.11136	-1.09400	-1.07639
3.	160	5.48	-0.84500	-0.81207	-0.77817
4.	170	5.42	-0.74818	-0.70617	-0.66276
5.	180	5.32	-0.62324	-0.56554	-0.50516
6.	190	5.15	-0.56940	-0.38255	-0.28945
7.	200	4.92	-0.32221	-0.18934	-0.04139
8.	210	4.74	-0.23408	-0.05776	0.14612
9.	220	4.57	-0.16461	-0.06207	0.33641
10.	230	4.28	-0.06694	0.28911	0.77814

$W_0 = 5.64$ mg. $W_t = 4.04$ mg

For quantitative evaluation of the value of E_a the arithmetical means of B_0, B_1 and B_2 have been calculated and also the standard deviation δ for all the three presupposed orders of reaction. δ is obtained from the relation,

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

where B_1 is any value, $\bar{B}$ the arithmetical mean and r the number of values. The 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 kcal/mol	δ_0	E_a kcal/mol	δ_1	E_a kcal/mol	δ_2
10	0.0630056	12	0.0831656	16	0.1187729
12	0.0527149	14	0.0382683	18	0.0917425
14	0.0944639	16	0.0594030	20	0.0998681

It is apparent from Table-2 that the standard deviations are minimum if the first order reaction is accepted, and the value for δ is minimum for $E_a = 14.0$ kcal mol^{-1} and corresponds to 0.0382683. The value of the arithmetical mean, *i.e.* $\bar{B}_1$, corresponds to 8.656100.

The frequency factor Z for the solid state kinetics is evaluated and found to be 1.0716×10^{4} sec^{-1} with the help of the equation

$$\log Z = \overline{B} + \log Rq - \log E_a$$

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

The apparent activation entropy, $\Delta S^{\neq}$ is calculated as −171.603 eu from relation $\Delta S^{\neq} = 2.303 \log (Zh/KT)$.

The value for T in this equation is the temperature $T_{1/2}$ at which the weight loss is half the total loss during the step of transformation under consideration.

The values for Ea with order of reaction b = 1 by Freeman & Carroll[1] and Zsako[3] are 13.88 and 14.00 kcal mol^{-1} respectively. The values for $E_{a,}$ and 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.

REFERENCES

1. E.S. Freeman and B. Carroll, *J. Phys. Chem.*, **62**, 394 (1958).
2. C.D. Doyle, *J. Appl. Polym. Sci.*, **5**, 285 (1961).
3. J. Zsako, *J. Phys. Chem.*, **72**, 2406 (1968).

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