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Kinetic Parameters from TG Analysis of Cobalt(II) Complex of the Schiff base Derived from Salicylaldehyde and Thiocarbohydrazide

U.N. VERMA
Department of Chemistry
Magadh University, Bodh-Gaya-824 234, India

Cobalt(II) chloride forms a 1:1 complex with Schiff base of salicyldehyde and thiocarbohydrazide. Kinetic parameters like apparent activation energy, frequency factor, activation entropy and apparent order of reaction of complex have been determined employing Freeman-Carroll, Fuoss *et al.*, Coats-Redfern, Karkhanawala-Dharwadker and Doyle methods as modified by Zsako using non-isothermal TG curves. These values are in good agreement with each other. The complex decomposes regularly without any distinguishable rest with random nucleation mechanism.

INTRODUCTION

The several factors associated with the complexation of central metal atom with ligand-like different solvent and solid conditions, temperature etc. make the study of stability of metallic complexes more complicated. While determining kinetic stability, it is often difficult to choose a suitable equation to explain the kinetics of thermal decomposition specially where rate is governed by one or more rate determining steps. The process takes place in several stages such as the chemical act of breaking of bonds, destruction of the initial crystal lattice, formation of crystal lattice of the solid products consisting of the formation of crystallisation centres and the growth of these centres and adsorption and desorption of gaseous product, diffusion of gas and heat transfer[1].

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 to the fraction reacted $-d\alpha/dt = k\alpha^n$ where n is the order of reaction and K the specific rate constant. The latter depends upon temperature by the expression $K = A \cdot e^{-E/RT}$. A is the pre-exponential factor, E the activation energy and R the gas constant.

Kinetics of thermal decomposition of the 1:1 (metal-ligand) complex of cobalt(II) chloride with Schiff base of salicylaldehye and thiocarbohydrazide has been investigated and the kinetic parameters computed using Freeman-Carroll[2], Fuoss *et al.*,[3] Coats-Redfern[4], Karkhanawala and Dharwadkar[5] and Doyle's method[6] as modified by Zsako[7].

EXPERIMENTAL

An electrobalance "Stanton-Red Craft TG 750" was used for recording thermogram. About 6–10 mg of complex was taken for analysis on TGA over a temperature range of 298–1273 K with heating rate 10 K/min, chart speed 120 mm/h and water flow rate 10 L/h. Calculations were carried out from a single TG curve for the first stage of decomposition of the complex around 413 K.

Preparation of sample: The Schiff base (ligand) was prepared by refluxing thiocarbohydrazide with salicylaldehyde in aqueous ethanol and the complex was obtained by mixing the hydrated cobalt(II) chloride (0.01 M in 60 mL 90% ethanol) and ligand (0.01 M) in quinoline ethanol mixture (50 mL of 30% quinoline). The reddish brown mixure was allowed to stand for $\frac{1}{2}$ h and then diluted with excess water to isolate the precipitate.

RESULTS AND DISCUSSION

On the basis of elemental analysis, the complex contains Co, 11.68; C, 57.48; H, 3.75; N, 13.90; S, 6.30% having formula Co(L)Q; Q stands for base quinoline.

The TG curve thus obtained has been analysed for the kinetic parameters for the first stage of decomposition of the complex using the following methods:

Freeman and Carroll[2] graphical method was primarily employed to evaluate the order of reaction and activation energy. The existing weights of the complex at equal temperature intervals 10°C were noted from the TG curve. The plot of

$$\frac{\Delta \log dw/dt}{\Delta \log Wr} \quad vs. \quad \frac{\Delta T^{-1} \times 10^3}{\Delta \log Wr} \quad \text{(Table-1)}$$

gave a straight line with an intercept at 0.1 suggesting the order of the reaction 0.1 and applying E = 2.303R, the slope gave the values of activation energy to be equal to 11.7241 kcal mole^{-1}. Here $W_r = W_c - W$, where W_c is weight loss at completion of reaction and W is total weight loss upto time t.

TABLE-1

S.No.	Temp. (K)	Weight (mg)	Wr	$\frac{\Delta \log dw/dt}{\Delta \log Wr}$	$\frac{\Delta T^{-1} \times 10^3}{\Delta \log Wr}$
1.	423	5.00	1.00	—	—
2.	433	4.95	0.95	9.51728	2.45172
3.	443	4.87	0.87	–5.34205	1.36430
4.	453	4.80	0.80	–5.01234	1.08574
5.	463	4.69	0.69	–3.05572	0.74221
6.	473	4.60	0.60	1.43598	0.75234
7.	483	4.46	0.46	–1.66273	0.37928
8.	493	4.41	0.41	8.94856	0.84050
9.	503	4.20	0.20	–0.51325	0.12933
10.	513	4.08	0.08	0.61072	0.09704

Initial weight at 413 K = 5.10 mg. Final weight at 523 K = 4.00 mg.

In the Fuoss *et al.* method[3] the energy of activation values were obtained directly from TG trace through determination of inflexion point corresponding to weight 4.00 mg at 523 K.

$$E = (-RT_i^2/W_i)(dW/dT)_i$$

$$Z = -(q/W_t)(dW/dT)_i\ e^{-E/RT_i}$$

T_i = temperature at the point of inflexion

W_i = amount remaining unreacted at temperature T_i

dW/dT = rate of weight loss with respect to temperature

The values of E and Z were found 9.0318 kcal $mole^{-1}$ and 19.8000 sec^{-1} respectively.

In the Coats and Refern[4] method log $[f(\alpha)/T^2]$ was calculated for different reaction orders (Table-2) and plotted against 1/T. The most linear plot was found for zero order having slope 2.08. The values of collision frequency and activation energy were calculated by the equations

$$Z = \text{antilog (intercept)}Eq/R$$

$$\text{slope} = E/2.303R$$

The values of E and Z were found 9.5900 kcal $mole^{-1}$ and 14.2114 sec^{-1} respectively.

TABLE-2

S.No.	$T^{-1} \times 10^3$	b = 0 log $[f(\alpha)/T^2]$	b = 1 log $[f(\alpha)/T^2]$	b = 2 log $[f(\alpha)/T^2]$
1.	2.36401	–6.29413	–6.27365	–6.25274
2.	2.30940	–6.13831	–6.10695	–6.07461
3.	2.25734	–5.97253	–5.92251	–5.87060
4.	2.20751	–5.87652	–5.80923	–5.73821
5.	2.15981	–5.75981	–5.66253	–5.55732
6.	2.11420	–5.69213	–5.56711	5.42896
7.	2.07045	–5.60318	–5.42746	–5.22453
8.	2.02830	–5.58821	–5.39143	–5.15963
9.	1.98801	–5.49031	–5.17142	–4.74992
10.	1.94930	–5.45301	–5.00170	–4.31471

In the Karkhanawala-Dharwadkér method[5] α and $T_0 + \Phi'$ were plotted at different temperatures between a stage of decomposition (413–523 K) (Table-3). Here T_0 is the inception temperature which is practically insensitive to experimental variables and Φ' is the percentage of the total span of temperature covered for a given value of α. The energy of activation was calculated at inflexion point and found to be 13.2544 kcal $mole^{-1}$. Other parameters were calculated accordingly.

In the Doyle's[6] method modified by Zsako[7], the weights of the compounds at different temperatures are noted from the TG curve and $f(\alpha)$ values are calculated (Table-4).

$$\alpha = \frac{W_o - W}{W_o - W_f}$$

where W_o = initial weight, W_f = final weight, W = actual weight.

TABLE-3

S.No.	Temp. (K)	α	$T_0 + \Phi'$
1.	423	0.09091	422.0913
2.	433	0.13636	431.1821
3.	443	0.20909	440.2731
4.	453	0.27272	449.3640
5.	463	0.37272	458.4551
6.	473	0.45454	467.5450
7.	483	0.58181	476.6360
8.	493	0.62727	485.7271
9.	503	0.81818	494.8180
10.	513	0.92727	503.9093

TABLE-4

S.No.	Temp. (K)	Weight (mg)	α	$\log \alpha$	$\log\left(\ln \frac{1}{1-\alpha}\right)$	$\log \frac{\alpha}{1-\alpha}$
1.	423	5.00	0.09091	–1.04139	–1.02086	–1.00000
2.	433	4.95	0.13636	–1.86530	–0.83385	–0.80163
3.	443	4.87	0.20909	–0.67966	–0.62972	–0.57779
4.	453	4.80	0.27272	–0.56427	–0.49695	–0.42596
5.	463	4.69	0.37272	–0.42860	–0.33126	–0.22606
6.	473	4.60	0.45454	–0.34242	–0.21743	–0.07918
7.	483	4.46	0.58181	–0.23521	–0.05956	0.14342
8.	493	4.41	0.62727	–0.20254	–0.00572	0.22606
9.	503	4.20	0.81818	–0.08715	0.23166	0.65321
10.	513	4.08	0.92727	–0.03279	0.41847	1.10551

Initial weight at 413 k = 5.10 mg. Final weight at 523 K = 4.00 mg.

The B_i values for different orders of reaction were calculated by the following equations:

$$B_0 = \log \alpha - \log p(x)$$

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

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

The values of $-\log p(x)$ were noted from Zsako[7] table. Thereafter, the values of minimum deviation were calculated by the relation

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

where r is the number of experimental data for the calculation of $\overline{B}$. The values of δ and E corresponding to B_0, B_1 and B_2 are given in Table-5.

TABLE-5

B_0		B_1		B_2	
E kcal/mole	δ_0	E kcal/mole	δ_1	E kcal/mole	δ_2
10	0.04093	12	0.05402	18	0.13932
12	0.09178	14	0.04476	20	0.13674
14	0.14606	16	0.08822	22	0.15728

A comparison of the δ_{min} value evidently indicated the least value 0.04093 corresponding to activation energy 10 kcal $mole^{-1}$ and $\overline{B} = 6.38333$.

The apparent frequency factor and the apparent entropy of activation were calculated using

$$\log Z = \overline{B} + \log Rq - \log E \quad \text{and} \quad \Delta S^{\#} = E \ln (Zh/KT)$$

The values obtained for the order of reaction, activation entropy for the first stage of decomposition of complex are in good agreement with each other which can be seen in Table-6.

TABLE-6

Kinetic parameters	Freeman Carroll	Fuoss *et al.*	Coats-Redfern	Karkhanawala-Dharwadker	Zsako
b	0.1000	—	0.0000	—	0.0000
E	13.9900	9.0318	9.5900	13.2544	10.0000
Z	12.2345	19.8000	14.2114	—	68.0000
$S^{\#}$	-27.4194	-26.9315	-27.2696	-21.2131	-25.5000

As standard deviation δ is a measure of precision between the experimental data and the presumed kinetic equation, these values can be considered more reliable and thus may be utilised in the study of solid state reaction mechanism.

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