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NOTE

Kinetic Parameters of Thiolactic Anilide Copper(II) Complex Using TG Analysis

U.N. VERMA*, S.N. PRASAD and KUNAL KUMAR
Department of Chemistry, Magadh University Bodh-Gaya-824 234, India

Copper(II) sulphate forms a 1 : 2 complex with thiolactic anilide. Kinetic parameters like apparent activation energy, frequency factor, activation entropy and apparent order of reaction of second stage of decomposition of complex have been determined employing the graphical method of Freeman and Carroll, Coat-Redfern and Doyle method as modified by Zsako using non-isothermal TG curves.

Key Words: Kinetic, TG analysis, Cu(II) complex, Thiolactic Anilide.

Thermogravimetric analysis is a continuous non-isothermal method which has many advantages over currently used isothermal methods. The advantages are that a single experimental curve is sufficient to obtain an estimate of the apparent heat of activation and that the kinetics can be probed over an entire temperature range in a continuous manner without any gap.

Kinetic constants of the complex cited have been investigated from thermal analysis procedures, *e.g.*, Freeman and Carroll[1], Coat-Redfern[2] and Doyle's method[3] as modified by Zsako[4] and it is found that the data obtained are in good agreement.

Single thermogravimetric curve was drawn on an electrobalance "Stanton Red Craft TG 750" with a recorder, operating on 1 mV full scale. The heating rate $10° \text{ min}^{-1}$ with chart speed 120 mm h^{-1} and water flow rate 10 L h^{-1} were maintained while recording the thermogram. Calculations were carried out from a single TG curve for the second stage of decomposition of the complex around 443 K.

Ligand thiolactic anilide (TLA) was prepared in a manner analogous to the preparation of thioglycoanilides[5, 6]. Aqueous solution of hydrated copper sulphate maintained at pH of 5.89 by addition of sodium acetate-acetic acid buffer and ethanolic solution of ligand (1 : 2) were added. Precipitate obtained was filtered after digestion.

Elemental analysis data reveal that the complex contains Cu (13.83%); C (46.95%); H (5.27%); N (6.11%); S (13.97%). Cu $(TLA)_2 \cdot 2H_2O$ requires Cu (13.82%); C (46.97%); H (5.26%); N (6.12%); S (13.95%).

The TG graph for this complex shows three stages of decomposition. In first stage loss of water molecule takes place up to 363 K. Further heating does not change the weight of the complex till 443 K. The second stage of decomposition starts from 443 K and ends at 553 K. There is no sharp weight loss till 713 K.

The second stage of decomposition of metal complex was selected to evaluate the kinetic parameters. The evaluated data employing Freeman and Carroll method are given in Table-1.

TABLE-1

S. No.	Temp. (°C)	Wt. of complex (mg)	$W_r = W_c - W$ (mg)	$\frac{\Delta \log (dw/dt)}{\Delta \log w_r}$	$\frac{\Delta T^{-1} \times 10^{-3}}{\Delta \log w_r}$
1.	170	1.74	—	—	—
2.	180	1.73	0.73	—	—
3.	190	1.69	0.69	–24.60401	1.94851
4.	200	1.65	0.65	0.00000	1.76060
5.	210	1.61	0.61	0.00000	1.58702
6.	220	1.56	0.56	–2.60932	1.13059
7.	230	1.48	0.48	–3.04884	0.60239
8.	240	1.37	0.37	–1.22346	0.34280
9.	250	1.28	0.28	0.72001	0.30791
10.	260	1.15	0.15	0.58915	0.13236
11.	270	1.07	0.07	0.63701	0.10438
12.	280	1.00	0.00	—	—

$$W_c = W_0 - W_f = 1.74 - 1.00 = 0.74$$

where, W_c = Weight loss at the completion of reaction, W = Total weight loss up to time t, W_0 = Initial weight of the sample, W_f = Final weight of the sample.

A plot of $\frac{\Delta \log \frac{dw}{dt}}{\Delta \log w_r}$ *vs.* $\frac{\Delta T^{-1} \times 10^{-3}}{\Delta \log w_r}$ was drawn which cuts the intercept at 1.00 and a slope 6.725.

These values, in turn, were suggestive of the order of reaction 1.00 and the activation energy 30.97535 kcal/mol for the stage of reaction under consideration.

In Coat-Redfern method, $\log \frac{F(\alpha)}{T^2}$ was calculated for b = 0, b = 1, b = 2, and $\log \frac{F(\alpha)}{T^2}$ *vs.* $\frac{1}{T}$ was plotted for different orders of reaction. As almost linear plot was found for b = 1 showing the order of reaction one and activation energy 20.198726 kcal/mol.

The same value of weights taken at different temperatures was employed in Zsako method[4] to calculate the required parameters. The values of log F(α) (Table-2) were used to evaluate the values of B_0, B_1 and B_2 for different activation

energies at all the temperatures. The calculated values of $\overline{B}$ were ultimately used to get the δ_{min} values for all the three presumed orders of reaction. The minimum value of δ_{min} corresponds to the order of reaction one and activation energy 22 kcal/mol. The value of frequency factor and apparent activation entropy were calculated using $\log Z = \overline{B} + R \log Rq - \log E$ and $\Delta S^{\neq} = 2.303R \log \frac{Zh}{kT}$ respectively. These are 1.21747×10^{10} sec^{-1} and –13.55592 e.u.

TABLE-2

S. No.	Temp. (°C)	Wt. (mg)	$\alpha = \frac{w_0 - w_t}{w_0 - w_f}$	$\log \alpha$	$\log\left[\ln \frac{1}{1-\alpha}\right]$	$\log \frac{\alpha}{1-\alpha}$
1.	170	1.74	—	—	—	—
2.	180	1.73	0.01351	–1.86923	–1.86628	–1.86332
3.	190	1.69	0.06757	–1.17026	–1.15516	–1.13988
4.	200	1.65	0.12162	–0.91499	–0.88713	–0.85867
5.	210	1.61	0.17568	–0.75529	–0.71401	–0.67139
6.	220	1.56	0.24324	–0.61396	–0.55484	–0.49292
7.	230	1.48	0.35135	–0.45426	–0.36365	–0.26627
8.	240	1.37	0.50000	–0.30103	–0.15917	0.0000
9.	250	1.28	0.62162	–0.20647	–0.01240	0.21560
10.	260	1.15	0.79730	–0.09838	0.20304	0.59476
11.	270	1.07	0.90541	–0.04316	0.37257	0.98098
12.	280	1.00	1.00000	—	—	—

$W_0 - W_f = 0.74$ mg

The values obtained for the order of reaction, activation energy, entropy of activation and frequency factor are in good agreement with each other.

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