# KINETICS OF THERMAL DECOMPOSITION OF ZN-HISTIDINE COMPLEX

## BY

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## ABSTRACT

L-Histidine forms 1:2 complex with Zn (II) and has been isolated in the solid state from aqueous solution. Thermogravimetry supports the probable formula of the complex, assigned on the basis of elemental analysis.

Various kinetic parameters such as activation energy, order of decomposition, frequency factor and activation entropy have been evaluated. The values of activation energy and order of decomposition calculated by two methods[2,3] are in reasonable agreement with each other.

**Experimental**

The thermogram of the complex was obtained on a Stanton HTD thermo balance with a heating rate of $9^0$c per minute in an inert atmosphere.

**Preparation of the complex**

The Zn-Histidine complex was prepared by mixing equimolar (0.1M) solutions of metal perchlorate and ligand. The pH of solution was raised with Na0H and the precipitate was filtered, washed and dried. The metal content in the complex was estimated by standard methods.

Experimental : $M = 9.04\%$ $C = 20.11\%$ $H = 6.06\%$ $N = 11.61\%$

Theoretical : $M = 9.09\%$ $C = 20.03\%$ $H = 6.12\%$ $N = 11.68\%$

## Results and Discussion

The equation for thermogravimetric curves given by Doyle[1] as modified by Zsako[2] employing standard deviations in the calculations is

$$g\ (\propto) = \frac{ZEa}{Rq}\ p\ (x), \qquad\qquad ..... (1)$$

Where Z= Frequency factor, Ea = Activation energy,

R = Gas constant and q = Heating rate.

The value g ($\propto$) is a certain function of $\propto$, and

$$(\propto) = \frac{w_o - w}{w_o - w_t} \qquad\qquad ..... (2)$$

Where w, $w_o$ and $w_t$ are the actual, initial and final weights of the sample respectively.

The value of p(x) depends essentially both on temperature and activation energy.

The g ($\propto$) may be calculated for various values of 'b' (order of decomposition)

$$\frac{d\propto}{dt} = k\ (1-\propto)^b \qquad\qquad ..... (3)$$

The values for b are considered as 0,1 and 2.

When b = 0, $g_o\ (\propto)\ = (\propto)$

Or $\qquad\qquad B_o = \log g_o\ (\propto)$ - log p (x) $\qquad\qquad ....(4)$

When $\qquad\qquad$ b = 1$g_1\ (\propto) = - \ln\ (1-\propto)$

Or $\qquad\qquad$ B1= log $g_1\ (\propto)$ – log p (x) $\qquad\qquad .....(5)$

When $\qquad\qquad$ b = 2, $g_2\ (\propto)\ = \frac{\propto}{1-\propto}$

Or $\qquad\qquad$ B2=log g2($\propto$) − logP(x) $\qquad\qquad .....(6)$

The average of the B value at different temperatures for the presumed order of reaction i.e., 0, 1 and 2 have been calculated and their '$\delta$' values have been determined employing the elations for standard deviation.

$$'\delta' = \sqrt{\frac{(B1 - \overline{B})^2}{r}}$$

Where $B_1$ is any value, $\bar{B}$ is the arithmetical mean, r is the number of values.

The '$\delta$' value at a particular temperature is minimum for a particular 'b' value i.e., the apparent reaction order. Using inter-polated – log p(x) at each temperature, the '$\delta$' values have been calculated for Ea values in a close range. The correct value for Ea gives minimum '$\delta$' value at particular 'b'.

The validity of this method has been supported by Coats and Redfern method[3]. Coats and Redfern deter-mined the order of reaction on the basis of TG data based on a plot of $\log 1-(1-\alpha)^{1-n}/ T^2 (1-n) = A$ VS $\frac{1}{T} x \ 10^3$, where $\alpha$ is the thermal decomposition rate calculated from thermogravimetric data of the sample.

The value of '$\alpha$' is calculated from eqn (2).

For assumed values of 'n' a number of relationships are plotted and the correct 'n' value gives a straight line. The energy of activation is calculated by using the equation.

E=2.303 mR

Where 'm' is the slops of the straight line and R is the gas constant.

Table 1- Sample weight and log ($\alpha$) data at different temperature

$W_o$ = 100mg

$W_t$ = 11mg

| Temp ($^o$c) | W (mg) | $\alpha$ | $\log \alpha$ | $\log (1n \frac{1}{1-\alpha})$ | $\log \frac{\alpha}{1-\alpha}$ |
|---|---|---|---|---|---|
| 250 | 3.0 | 0.0337 | -1.4722 | -1.4648 | -1.4574 |
| 260 | 4.0 | 0.0449 | -1.3473 | -1.3377 | -1.3278 |
| 270 | 5.0 | 0.0561 | -1.2504 | -1.2384 | -1.2259 |
| 280 | 6.0 | 0.0674 | -1.1712 | -1.1561 | -1.1410 |
| 290 | 10.0 | 0.1123 | -0.9493 | -0.9239 | -0.8978 |
| 300 | 16.0 | 0.1797 | -0.7552 | -0.7030 | -0.6594 |

Table 2- Activation energy and order of reaction

| Ea | b=0 | b=1 | b=2 |
|---|---|---|---|
| 12 | 0.01620 | 0.01988 | 0.02363 |
| 14 | 0.00645 | 0.01012 | 0.01388 |
| 16 | 0.00253 | 0.00114 | 0.00024 |
| 18 | 0.00522 | 0.00244 | 0.00040 |
| 20 | 0.00767 | 0.01036 | 0.00853 |

The value of '$\delta$' is minimum, if the apparent order of the reaction is taken as 2 i.e. second order of reaction. So from the tested 'b' value, b=2 is the best. '$\delta$' has minimum value for Ea = 16 KCals/Mole. For the corresponding Ea, $\overline{B2}$ is 7.6562. This value is in good agreement with the value for Ea calculated by Coats and Redfern method that is Ea = 15.61 Kcals/mole.

The frequency factor is calculated by the equation

Log z = $\bar{B}$ + log Rq – log Ea

And the apparent activation entropy as

S = 2.303 log $\frac{zh}{kT}$

The value for T is taken as the temperature (T1/2) at which the weight loss is half of the total weight loss during the considered step.

**Table 3** – Kinetic parameters of Zn $(Hist)_2.13H_2O$ complex.

| Ea | b | Log z | S* (eu) |
|---|---|---|---|
| 16 (15.6) | 2 | 7.7045 | - 12.83 |

The above data may be helpful in the understanding of the reaction mechanism in solid state and can be considered more reliable than any other method.

References

1. Dolye, J. Apple Polym. Sci., <u>5</u>(1961) 235.
2. Zsako, J. J. Phys. Chem.., 72 (1968) 2406.
3. Coats, A.W. <u>Nature</u> (London), <u>68</u>. (1964) 201.