

# Kinetics and Thermal Decomposition of Co(II) complex with Sulfamethazine

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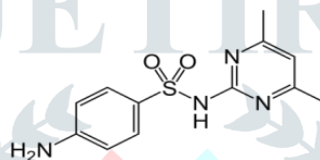
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**Abstract :** A metaldrug complex of Co(II) with Sulfamethazine  $[\text{Co}(\text{SZ})_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$  was isolated through microwave assisted synthesis. Kinetics of decomposition for the synthesized complex have been investigated through thermogravimetric analysis (TGA), derivative thermogravimetric analysis (DTG) and differential thermal analysis (DTA). Evaluation of kinetic and thermodynamic parameters has been done by using Coats and Redfern integral equations for all the stages of decomposition.

**IndexTerms -** Metaldrug, Sulfamethazine, Microwave assisted synthesis, Thermogravimetric Analysis.

## I. INTRODUCTION

Sulfonamides or Sulfa drugs are important antibiotic medicines to be administered in human systems for the very first time [1]. Sulfamethazine [4-amino-N-(4,6-dimethyl pyrimidin-2-yl) benzene sulfonamide] is also a significant member of sulfa drug family which is widely used as short acting antibacterial drug against urinary infections, prostatitis and respiratory tract infections caused by bacteria [2]. It is a dimethyl derivative of sulfadiazine with the following structure.



**Figure 1.** Sulfamethazine

The medicinal properties and pharmacodynamics of the drug molecules are known to be modified significantly upon chelation with metal ions [3]. The metal complexes of Sulfa drugs (Metallosulfa drugs) find wide application as antibacterials, antibiotics, antidiabetics, anticancer and antitumor agents [4]. Co(II) complexes of various sulfa drugs have been reported in the literature [5]-[7]. It is revealed that, thermal degradation studies of Co(II) complex of Sulfamethazine, synthesized through green microwave irradiation method have rarely been reported in the past. The present study involves kinetics and thermal decomposition studies of Co(II) complex of Sulfamethazine that has been synthesized by novel green microwave irradiation method [8]-[9]. Thermogravimetric analysis of this metal based sulfa drug is exclusively studied as an attempt to analyze the structural properties and its thermal stability.

## II. MATERIALS AND METHODS

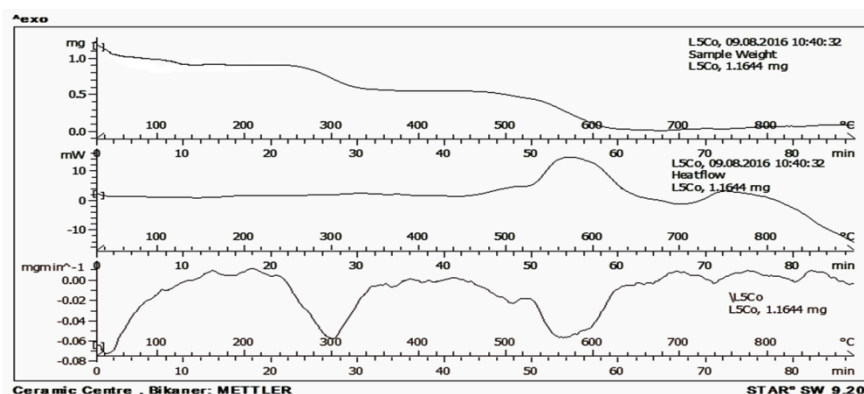
Solutions of metal halide,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (Himedia) (3mmol), and ligand Sulfamethazine (Himedia) (1mmol), were separately prepared by dissolving in acetone each and were finally mixed together to obtain the resultant reaction mixture. This final reaction mixture was then exposed to microwave irradiation in a domestic microwave oven reactor Model KENSTAR - OM20ACF, 2450MHz, at a medium power level of 600 W for about 4 to 5 minutes. The reaction products were monitored by thin layer chromatography (TLC) using silica gel. The complex finally precipitated down as amorphous solid and was filtered off, washed initially with distilled water and then with ethanol, and was then dried in desiccators. Thermogravimetric Analysis (TGA), Derivative Thermogravimetric Analysis (DTG) and Differential Thermal Analysis (DTA) of the complex was conducted at a constant heating rate of  $10^\circ\text{C}/\text{min}$ , using Mettler Toledo (TGA/ DSC/ IHT/ 546) STARE system, within a temperature range of  $30\text{-}900^\circ\text{C}$  using alumina crucible and in an inert nitrogen atmosphere. The kinetics of decomposition steps were investigated using non isothermal method of Coats and Redfern [10].

## III. RESULTS AND DISCUSSIONS

Thermal decomposition for Sulfamethazine complex of cobalt i.e.  $[\text{Co}(\text{SZ})_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$  has been investigated within a temperature range of  $30\text{-}900^\circ\text{C}$ . The thermogravimetric analysis (TGA), derivative thermogravimetric analysis (DTG) and differential thermal analysis (DTA) plots (thermograms) of synthesized metaldrug complex are presented in **Fig.2**.

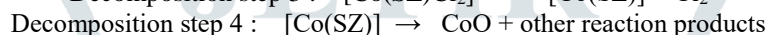
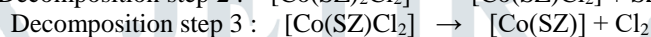
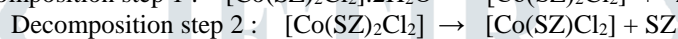
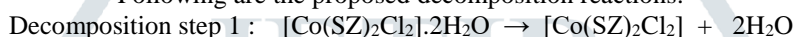
Thermal data clearly indicates that the complex exhibits a four stage decomposition process. An initial weight loss observed within a temperature range of  $30\text{-}90^\circ\text{C}$  for the complex  $[\text{Co}(\text{SZ})_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$  may be attributed to the loss of sorbed water. This desorption process was immediately followed by the phenomenon of dehydration that continued till  $140^\circ\text{C}$ . This dehydration step proceeded with a weight loss of 4.98% (obsd. 5.21%), corresponding to the loss of two molecules of water of hydration. TGA provides an excellent proof for distinguishing between the type of water molecules associated with a complex molecule. An early loss of water molecules before  $140^\circ\text{C}$  confirms the presence of non coordinated form of water in the synthesized Co(II) complex. TGA data hence serves as a very important analytical tool for evaluating the structural aspects of a complex molecule. A small endothermic peak shown near  $148^\circ\text{C}$  in the DTA plot marks the melting process of the solid complex, without any change of mass. This melting point corresponds to the experimental melting point of Co(II) complex observed at  $150^\circ\text{C}$ . Thereafter the complex slowly underwent the next step of decomposition within  $250\text{-}360^\circ\text{C}$ . This degradation is depicted as a small but broad endothermic peak in the DTG plot. An estimated weight loss of 43.50% (obsd. 42.71%) and  $\text{DTG}_{\text{max}}$  at  $300^\circ\text{C}$ , corresponded to loss of one

ligand molecule. The third stage of degradation defined a clear exothermic rise within 460-540°C. An estimated mass loss of 53.33% (obsd. 53.13%) for this step stage corresponds to the release of a chlorine molecule from the complex. The final decomposition step (540-610°C) followed a huge exothermic change and was observed along with a calculated mass loss of 89.63% (obsd. 89.58%). The final decomposition process of the complex, yielded a black coloured residue with a weight that corresponded that of CoO. This fraction remained constant till 700°C, after which it underwent further oxidation to yield Co<sub>3</sub>O<sub>4</sub> beyond 800°C. The final residue remained stable thereafter till 900°C [11]-[14].



**Figure 2.** Thermogravimetric analysis (TGA), Differential thermal analysis (DTA) and Derivative thermogravimetric (DTG) curves for [Co(SZ)<sub>2</sub>Cl<sub>2</sub>].2H<sub>2</sub>O

Following are the proposed decomposition reactions:



#### IV. EVALUATION OF KINETIC PARAMETERS

Determination of kinetic parameters from thermal data requires a careful selection of an appropriate reaction model. In the present work, a non-isothermal reaction model proposed by Coats and Redfern has been adopted for studying the kinetics of decomposition of all the four stages.

The kinetics of a heterogeneous solid state reaction occurring in non-isothermal conditions can be expressed by the following equation;

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-E/RT} \cdot f(\alpha) \quad (1)$$

where  $A$  is the pre exponential factor or the frequency factor,  $E$  is the activation energy of the reaction,  $\beta$  is the linear heating rate in °C/min,  $T$  is the temperature,  $R$  is the universal gas constant,  $f(\alpha)$  is the conversion function dependent on reaction mechanism and  $\alpha$  is the extent of reaction which can be calculated from TGA/DTA data as;

$$\alpha = \frac{m_o - m_t}{m_o - m_f} \quad (2)$$

where  $m_o$ , is the mass of sample at beginning of the reaction,  $m_t$  is the mass of sample at a particular temperature and  $m_f$  is the mass of sample at the end of reaction.

Coats and Redfern integral equations can be expressed as;

$$\ln \left[ \frac{-\ln(1-\alpha)}{T^2} \right] = \ln \left[ \frac{AR}{\beta E} \left( 1 - \frac{2RT}{E} \right) \right] - \frac{E}{RT} \quad (3)$$

for  $n = 1$  and

$$\ln \left[ \frac{1 - (1-\alpha)^{1-n}}{T^2(1-n)} \right] = \ln \left[ \frac{AR}{\beta E} \left( 1 - \frac{2RT}{E} \right) \right] - \frac{E}{RT} \quad (4)$$

for  $n \neq 1$ .

where  $n$  represents the order of reaction.

The heating rate  $\beta$ , in the present studies is taken to be 10°C/min.

A plot of  $\ln \left[ \frac{-\ln(1-\alpha)}{T^2} \right]$  vs  $1/T$  for  $n=1$  and  $\ln \left[ \frac{1-(1-\alpha)^{1-n}}{T^2(1-n)} \right]$  versus  $1/T$  for  $n \neq 1$ , gives the value of activation energy  $E$  from the slope and also the value of frequency factor  $A$  from the intercept. Upon application of different values of  $n$ , the Equations (1) and (2) were plotted as mentioned above for Sulfamethazine complex of Co(II) [15]. The resultant linear plots having best correlation coefficient were then selected to get the value of  $n$ , for all the four steps of decomposition and are presented in Fig.3.

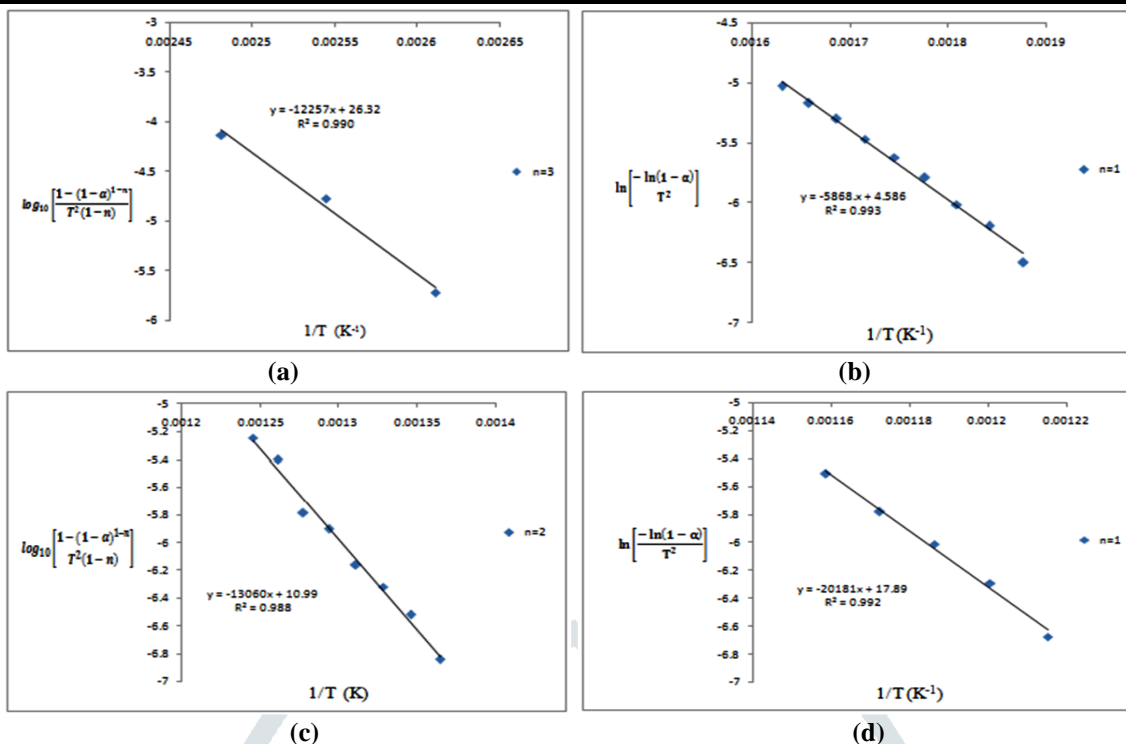


Figure 3. Coats Redfern plots for all four stages of decomposition respectively.

Table.1: Thermoanalytic Data and Kinetic Parameters of Co(II)-Sulfamethazine complex

Complex	Decomp. Steps	Temp. Range (°C)	Loss in weight per step (%) calcd (obsd)	DTG <sub>max</sub> (°C)	Reaction Order (n)	Activation Energy (kJ/mol) E	Frequency Factor (sec <sup>-1</sup> ) A	Correlation Coefficient R <sup>2</sup>
[Co(SZ) <sub>2</sub> Cl <sub>2</sub> ].2H <sub>2</sub> O	Decomp. Stage 1	100-140	4.98 (5.21)	120	3	234.69	1.02 x 10 <sup>30</sup>	0.990
	Decomp. Stage 2	250-360	43.50 (42.71)	300	1	112.36	9.51 x 10 <sup>7</sup>	0.993
	Decomp. Stage 3	460-540	53.33 (53.13)	510	2	250.06	5.20 x 10 <sup>24</sup>	0.988
	Decomp. Stage 4	540-600	89.63 (89.58)	565	1	386.41	6.28 x 10 <sup>21</sup>	0.992

IV. EVALUATION OF THERMODYNAMIC PARAMETERS

Entropy of activation, ΔS was calculated using;

$$\Delta S = R \ln \left[ \frac{Ah}{kT_{max}} \right] \tag{5}$$

where  $T_{max}$  is the DTG peak temperature,  $h$  is Planck's constant and  $k$  is Boltzmann's constant. Standard thermodynamic relations were used to derive enthalpy of reaction ΔH and Gibbs free energy ΔG, that are as follows:

$$\Delta H = E - RT \tag{6}$$

$$\Delta G = \Delta H - T\Delta S \tag{7}$$

The calculated thermodynamic parameters are enlisted in Table.2.

Table. 2: Thermodynamic Parameters of Co(II)-Sulfamethazine complex

Complex	Decomp. Steps	Temp. Range (°C)	Entropy of Activation (J/Kmol) $\Delta S$	Enthalpy of Activation (kJ/mol) $\Delta H$	Gibb's Free Energy (kJ/mol) $\Delta G$
[Co(SZ) <sub>2</sub> Cl <sub>2</sub> ].2H <sub>2</sub> O	Decomp. Stage1	100-140	327.33	231.42	102.78
	Decomp. Stage 2	250-360	-97.63	107.60	163.54
	Decomp. Stage 3	460-540	220.26	243.55	71.09
	Decomp. Stage 4	540-600	163.82	379.44	242.16

## V. CONCLUSIONS

The experimental data suggests that decomposition of Sulfamethazine complex of Co(II) occurred in four stages. The complex underwent melting only after the process of dehydration. Thereafter decomposition proceeded in next three steps of degradation. The relatively higher activation energy (E) for first step (dehydration) as compared to the second step indicates that the hydrated form involved much stable and stronger bonding interactions. The higher activation energy (E) for last degradation stage may be attributed to the decomposition of ligand group. A similar trend was observed for the frequency factor (A) and enthalpy of activation ( $\Delta H$ ) in all the steps of thermal degradation. The negative value of entropy of activation ( $\Delta S$ ) for the second step of degradation suggests that the four coordinated geometry obtained after the removal of first ligand molecule involves higher ordered structure than the six coordinated complex. The positive values of Gibbs free energy ( $\Delta G$ ), indicated that the complex is highly stable at room temperature and the process of dehydration and thermal decomposition are non spontaneous under normal temperature conditions.

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