PART-A

CHAPTER-3

SECTION-III

Thermal studies of some N-(substitutedphenyl)-2-((5-(pyrazin-2-yl)-1,3,4-oxadiazol-2-yl)thio)acetamide derivatives.
SECTION-III: THERMAL STUDIES OF SOME N-(SUBSTITUTEDPHENYL)-2-((5-(PYRAZIN-2-YL)-1,3,4-OXADIAZOL-2-YL)THIO)ACETAMIDES.

INTRODUCTION

During last few years, the method of thermal analysis have been widely accepted in analytical chemistry to study industrially important products such as polymers, pharmaceuticals, metals, minerals, alloys, clays and various complex in inorganic chemistry. Several thermal methods have been recognized, which differ in the properties measured and temperature programs. This section of the thesis describes the thermal analysis of compound name.

Thermal analysis comprises of a group of techniques in which a physical property of a substance and/ or its reaction products is measured as a function of temperature while the substance is subjected to a controlled temperature program. The most frequently used techniques are thermogravimetry (TG), derivative thermogravimetry (DTG), differential scanning calorimetry (DSC), thermomechanical analysis (TMA) and dynamic mechanical thermal analysis (DMTA).

The International Confederation for Thermal Analysis and Calorimetry (ICTAC) defined thermal analysis as “a group of techniques in which a property of the sample is monitored against time or temperature while the temperature of the sample, in a specified atmosphere, is programmed”\(^1\). This definition was adopted by the International Union of Pure and Applied Chemistry (IUPAC) and the American Society for Testing and Materials (ASTM)\(^2\).

**Differential scanning calorimetry (DSC)**

Differential scanning calorimetry (DSC) involves measurement of the heat flow into or out of a sample compared with a reference as both are simultaneously subjected to a heating/cooling regime at pre-programmed rates that may include isothermal periods. Changes in the heat flow patterns correspond to various types of physical and chemical transformations including cure reactions. The benefit of the calorimeter over other calorimetry techniques is that it enables continuous measurement of thermal properties as temperature is varied in a single experiment rather than requiring several experiments at discrete temperatures. There are two types of DSC, heat flux and power compensation. In
both calorimeters a carrier gas is passed through the cells to ensure a constant atmosphere in the cells particularly in cases where volatile decomposition products may be produced. Typically either nitrogen or helium is used for the purpose.

In a heat flux calorimeter the sample and the reference are enclosed in a single cell. Thermal sensors measure the temperature difference between sample and reference to determine thermal properties.

In power compensation calorimeter the reference and sample are located in separately heated cells. The temperature of both cells is measured independently and the energy difference required to maintain the cells at identical temperature is used to determine thermal properties.

Normally the sample would be sealed in an inert pan although open pans may be utilized where reaction with a carrier gas is desired, for example oxidation. Commonly an identical empty pan is used as a reference and this allows heat capacity of the sample to be determined. In the case of reactions the heat flow due to the reaction is superimposed upon the heat flow due to heat capacity and any other physical transformation. For thermosetting resins there is generally a change in the heat capacity as the reaction progresses. This change in heat capacity is approximated in calculations of thermal properties. A drawback of the technique is that a number of assumptions which may not necessarily be correct need to be made in these thermal calculations. For example, the change in heat capacity could be assumed to be linear, sigmoidal, or some other non-linear curve. A further assumption is the presence or absence of physical transitions and their magnitudes, particularly in the case of composite samples.

Two considerations in DSC are instrument sensitivity and resolution. A limitation of DSC is that the sample must be small enough to minimize any temperature difference within the sample. The thermal conductivity of the sample limits its size. However this also limits the magnitude of the heat fluctuation. The sensitivity of the instrument is the response to these fluctuations separating the heat from the inevitable background electronic noise. Resolution is the ability of the instrument to distinguish between close thermal events. Minimizing the thermal lag in the instrument response is a necessity for overlapping events.
The response from an instrument can be improved in a scanning experiment by increasing the heating rate. However this has the detrimental effect of reducing the resolution. Getting an appropriate balance depends on the aim of the experiment.

Both isothermal and dynamic methods can be adopted to determine the kinetic parameters with DSC. For the isothermal method, the sample is quickly heated to the preset temperature. The system is kept at that temperature and the instrument records the change of heat flux as a function of time. For the dynamic method, the heat flux is recorded when the sample is scanned at a constant heating rate from low temperature to high temperature. The area under the heat flux curve and above baseline is calculated as the heat of reaction.

Various methods may be used in the analysis of the DSC curves to evaluate the reaction progress. All kinetic studies start with the basic rate equation:

$$\frac{d\alpha}{dt} = kf(\alpha)$$  \hspace{1cm} 1.1

where $k$ is the rate constant, $\alpha$ is the degree of conversion and $f(\alpha)$ is the function of the degree of conversion. In general, $k$ is dependent on temperature through an Arrhenius-type equation.

Thus, the rate equation can be written as:

$$\frac{d\alpha}{dt} = f(\alpha)A\exp\left(\frac{-E_a}{RT}\right)$$  \hspace{1cm} 1.2

where $A$ is the pre-exponential factor (s$^{-1}$) and relates to the amount of collisions that need to occur in a unit time to carry out the reaction, $E_a$ (J$\text{mol}^{-1}$) is the activation energy at a given degree of conversion, $R$ is the universal gas constant (8.314 J$\text{mol}^{-1}\text{K}$), and $T$ is the absolute temperature (K).

The DSC exotherm is used to measure the two basic parameters of the reaction, namely, the fraction reacted $\alpha$ and the reaction rate $d\alpha/dt$. At a sufficiently high enough temperature, the cross-linking reaction begins to proceed and the onset of curing is observed as an exothermic event.
The basic assumptions in applying the DSC to curing reaction kinetics are:

- The liberation of heat accompanying the curing reaction can be measured directly with the DSC and the rate of enthalpy change \( (dH/dt) \) with respect to temperature is recorded directly.
- Enthalpy change, \( \Delta H \), up to any temperature \( T \) is proportional to the number of moles of reactants consumed.
- The total area under the exotherm corresponds to the total enthalpy of curing reaction, \( \Delta H_{\text{Total}} \), and the partial area up to a certain temperature \( T \), corresponds to the enthalpy, \( \Delta H \), up to that temperature.
- The rate of enthalpy change, \( (dH/dt) \), relative to the instrumental baseline is directly proportional to the reaction rate.

From the above assumptions, the reaction rate \( da/dt \) at any point along the reaction exotherm temperature axis is obtained by dividing the peak height \( dH/dt \) at temperature \( T \) by the total peak area \( \Delta H_{\text{Total}} \), while the fraction reacted \( \alpha \) is obtained by measuring the ratio of the partial area \( \Delta H \) at temperature \( T \) to the total peak area \( \Delta H_{\text{Total}} \) (equation 1.3).

\[
\alpha = \left( \frac{\Delta H}{\Delta H_{\text{Total}}} \right) \quad 1.3
\]

\[
(1-\alpha) = \left( \frac{\Delta H_{\text{Total}}-\Delta H}{\Delta H_{\text{Total}}} \right) \quad 1.4
\]

where \( \alpha \) is the conversion or extent of reaction, \( \Delta H \) is the enthalpy change up to a certain temperature and \( \Delta H_{\text{Total}} \) is the total enthalpy change with the basic assumption that complete conversion of the reactants is achieved, and:

\[
\gamma = \left( \frac{da}{dt} \right) = \left( \frac{dH}{dt} \right) \left( \frac{\Delta H_{\text{Total}}}{A} \right) \quad 1.5
\]

where \( r \ (s^{-1}) \), is the rate of reaction, \( dH/dt \ (mJg^{-1}s^{-1}) \) is the ordinate of a DSC trace, and \( A \ (mJ) \), is the total area under the curve and corresponds to the total enthalpy of reaction \( \Delta H_{\text{Total}} \ (mJg^{-1}) \).
Various kinetic methods widely used to study dynamic kinetic are as follows:

1. **Kissinger method**

Kissinger method\(^3\) is based on a linear relationship between the logarithm of \(\frac{\beta}{T^2}\) with the inverse of the peak temperature of the exothermic curing reaction:

\[
\ln \frac{\beta}{T^2} = \ln \frac{Q_p AR}{E - E_a} \tag{1.6}
\]

where \(Q_p = -\frac{df(\alpha)}{d\alpha} = \alpha_p\)

The graphic representation of Eq. 1.6 allows us to examine both the activation energy and the pre-exponential factor of curing kinetics.

2. **Ozawa method**

Ozawa method\(^4\) relates the logarithm of the heating rate and the inverse of the exothermic peak temperature.

\[
\ln \beta = \ln \frac{AE^\alpha}{R} - \ln f(\alpha) - 5.331 - 1.052 \frac{E^\alpha}{RT} \tag{1.7}
\]

\[
F(\alpha) = \int_0^\alpha \frac{d(\alpha)}{f(\alpha)} \tag{1.8}
\]

where \(F(\alpha)\) is a constant function.

3. **Malek method**

The Malek method\(^5\) allows the calculation of the kinetic exponent’s \(m\) and \(n\) and of the logarithm of the pre-exponential factor (\(\ln A\)), but requires the previous determination of the activation energy by another method. Generally, the Kissinger method is used for this determination, but we can also use the Ozawa or Friedman method. The function that best describes the mechanism can be chosen from the shape of the plot of the standardized curve.

4. **Friedman method**

The Friedman method\(^6\) is used to determine a kinetic model of the curing process. The method is based on Eqs. (1.9) and (1.10) that leads to:

\[
\ln \frac{d\alpha}{dt} = \ln \beta \frac{d\alpha}{dt} = \ln \left[ Af(\alpha) \right] - \frac{E^\alpha}{RT} \tag{1.9}
\]
In case of the \( n \)-th-order reaction:

\[
f(\alpha) = (1-\alpha)^n
\]

From Eqs. (1.1), (1.2), and (1.10)

\[
\ln[Af(\alpha)] = \ln \left[ \int \frac{d\alpha}{dt} \right] + \frac{E_a}{RT} = \ln A + n \ln(1-\alpha)
\]

The value of \( \ln[Af(\alpha)] \) can be obtained from the known values of \( \ln[\text{d}\alpha/\text{d}t] \) and \( E_a/RT \). Therefore, the plot of \( \ln[Af(\alpha)] \) and \( \ln(1-\alpha) \) yields a straight line while the slope providing the reaction order. The intercept is the natural logarithm of the frequency factor if the reaction mechanism is of the \( n \)-th-order kinetics.

5. **Flynn–Wall–Ozawa method**

The isoconversional integral method was also proposed independently by Flynn, Wall, and Ozawa\(^7\) using Doyle’s approximation of the temperature integral.

\[
\ln \beta = \ln \frac{AE_a}{R} - \ln g(\alpha) - 5.331 - 1.052 \frac{E_a}{RT}
\]

\[
g(\alpha) = \int_0^\alpha \frac{d(\alpha)}{f(\alpha)}
\]

where \( g(\alpha) \) is the integral conversion function.

Thus, for a constant \( \alpha \), the plot of \( \ln \beta \) versus \( 1/T \) obtained from DSC thermograms using various heating rates should render a straight line where the slope allows the determination of the apparent activation energy. The apparent activation energy received from the Flynn–Wall–Ozawa analysis is reported to be more reliable than that from the Friedman analysis. Moreover, the Flynn–Wall–Ozawa method, owing to its integrating character, exhibits less sensitivity to noise than the Friedman method. The latter, however, provides a better visual separation of more reaction steps as well as information concerning the existence of an auto catalytically activated process\(^8\).

6. **Kissinger-Akahira-Sunose Method**
The Kissinger-Akahira-Sunose method is valid at any given conversion, but is derived using an approximation for \( p(x) \), \( p(x) = e^{-x^2/2} \) \((20 \leq x \leq 50)\). Under this assumption, Eq. (1.14) is obtained as follows:

\[
\ln \frac{\beta}{T^2} = \ln \frac{AR}{E_a} - \ln g(\alpha) - \frac{E_a}{RT}
\]  

All the isoconversional methods (Friedman, Ozawa, Ozawa corrected and Kissinger-Akahira-Sunose methods) will be applied for \( \alpha = 50\% \) and for the overall conversion interval.

**Thermo gravimetric analysis (TGA)**

In pharmaceutical sciences thermal methods of analysis have found important applications. TGA, in which the change in mass of a sample heated at constant rate is recorded and plotted vs. temperature, is an effective method for studying thermal stability and determination the kinetic parameters of the decomposition of drugs. TGA is an analytical, quantitative and comparative method capable of producing fast and reproducible results. It can be used in the quality control of drugs with a view to improvement of the final product and for the determination of drug quality via the technological parameters. There are three types of thermogravimetry namely:

1. Static or isothermal thermogravimetry,
2. Quasistatic thermogravimetry and
3. Dynamic thermogravimetry

Most of the studies of chemical substance are generally carried out with dynamic thermogravimetry. Normally the sample starts losing weight at a very slow rate up to a particular temperature and thereafter, the rate of loss becomes large over a narrow range of temperature. After this temperature, the loss in weight levels off. TGA curves are characteristic for a given substance because of unique sequence of physico-chemical reactions, which occur over definite temperature ranges. The change in weight is a result of the rupture and/or formation of various physical and chemical bonds at elevated temperatures that lead to evaluation of volatile products in the formation of heavier reaction products. The weight of the sample decreases slowly as reaction begins and then decreases rapidly over a comparatively narrow range of temperature and finally levels off.
as the reaction is completed. The shape of the curve depends on the kinetic parameters: reaction order n, frequency factor A and activation energy Ea. The values of these parameters have been shown to be of major importance to elucidate the mechanism of degradation reaction\(^{11}\).

For the estimation of kinetic parameters from TG traces, several so-called exact methods have been proposed. All these methods involve the two assumptions that thermal and diffusion barriers are negligible and that Arrhenius equation is valid. Since small quantities of materials are employed in TG studies, thermal and diffusion barriers would be negligible. Since the shape of any TG curve is dependent on the nature of apparatus and the way in which it is used. Most kinetic treatments are based on relationship of the type.

\[
\frac{dc}{dt} = kf(C) \tag{1.15}
\]

where \( C \) = degree of conversion, \( t \) = time, \( k \) = rate constant and \( f(C) \) = temperature independent function of \( C \).

The constant \( k \) is generally assumed to have the Arrhenius form

\[
k = Ae^{-\frac{E_a}{RT}} \tag{1.16}
\]

\( C \) is defined as the conversion with respect to initial material

\[
C = 1 - \frac{W}{W_o} \tag{1.17}
\]

Where, \( W_0 \) = initial weight of the material and \( W \) = weight of the material at any time

The residual weight fraction is given by

\[
\frac{W}{W_o} = (1 - C)
\]

and the rate of conversion is given by

\[
\frac{dC}{dt} = -\left(\frac{1}{W_o}\right)\frac{dW}{dt} \tag{1.18}
\]

For homogeneous kinetics, the conversion would be assumed to have the form
\[ f(C) = (1 - C)^n \quad \text{(1.19)} \]

where \( n \) = order of the reaction

Upon substituting Eqns. 1.16 and 1.19 into Eqn. 1.15

\[ \frac{dC}{dt} = Ae^{-E_a/RT} (1 - C)^n \]

OR

\[ \frac{dC}{dt} = \left( \frac{A}{\beta} \right) \left( e^{-E_a/RT} \right) (1 - C)^n \quad \text{(1.20)} \]

where \( \beta \) = Rate of heating

Methods of single heating rate

1. **Freeman-Carroll**\(^\text{12} \) and **Anderson-Freeman methods**\(^\text{13} \)

Freeman-Carroll developed the following relation to analyze TGA data at single heating rate:

\[
\frac{\Delta \ln (dC/dt)}{\Delta \ln (1 - C)} = n - \frac{E_a}{R} \left[ \frac{\Delta (1/T)}{\Delta \ln (1 - C)} \right]
\]

\[ \text{(1.21)} \]

A plot of L.H.S. against \( \Delta (1/T) / \Delta \ln (1-C) \) would yield a straight line with slope equal to \(-\frac{E_a}{R}\) and the intercept equal to \( n \). Using Eqn. 1.21 Anderson- Freeman derived the Eqn. 1.22

\[
\Delta \ln \left( \frac{dC}{dt} \right) = n \Delta \ln (1 - C) - \frac{E_a}{R} \Delta \left( \frac{1}{T} \right)
\]

\[ \text{(1.22)} \]

According to Eqn. (1.22), the plot of \( \Delta \ln (dC/dt) \) against \( \Delta \ln (1-C) \) for equal interval of \( \Delta (1/T) \) would be a straight line with slope equal to \( n \) and the intercept equal to \(-E_a/R \Delta (1/T)\).

2. **Sharp-Wentworth method**\(^\text{14} \)

For a first order process (\( n=1 \)), Sharp-Wentworth derived the following relation to analyze TGA data.

\[
\log \left[ \frac{dC/dt}{1 - C} \right] = \log \left( \frac{A}{\beta} \right) - \frac{E_a}{2.303RT} \frac{1}{T}
\]

\[ \text{(1.23)} \]
where $C =$ fraction of polymer decomposed at temperature $T$, $\beta =$ rate of heating, $A =$ Frequency factor and $E_a =$ the activation energy of the process. The plot of $\log \left[ \frac{dC}{dt} / (1-C) \right]$ against $1/T$ would be a straight line with slope equal to $-(E_a/2.303 \, \text{R})$ and the intercept equal to $\log (A/\beta)$.

3. **Chatterjee method**

Chatterjee has developed the following relation for the determination of $n$ from TG curves based on weight units.

$$n = \frac{\log \left( \frac{dW}{dt} \right)_1 - \log \left( \frac{dW}{dt} \right)_2}{\log W_1 - \log W_2} \quad 1.24$$

where $W_1$ and $W_2$ are the sample weights.

4. **Horowitz – Metzger method**

The value of $E_a$ can be determined from a single TG curve according to Horowitz – Metzger method.

$$\ln \left[ \ln \left( 1 - C \right)^{-1} \right] = \frac{E_a}{RT^2} \theta \quad 1.25$$

where, $C =$ fraction of the compound decomposed at time $t$, $E_a =$ activation energy, $T_s =$ Temperature at which the rate of decomposition is maximum and $\theta =$ $T$-$T_s$.

The frequency factor $A$ and entropy change $\Delta S$ can be determined respectively according to Eqns. 1.26 and 1.27.

$$\ln E_a - \ln \left( RT^2 \right) = \ln A - \ln \beta - \frac{E_a}{RT^2} \quad 1.26$$

$$A = \frac{k_b T e^{\Delta S/R}}{h} \quad 1.27$$

where $k_b$ is Boltzmann constant

**EXPERIMENTAL**

Differential scanning calorimetric (DSC) thermograms of the compounds were recorded on a Shimadzu DSC60 calorimeter in nitrogen atmosphere with flow rate 50 mL min$^{-1}$. About 2-3 mg samples were accurately measured, enclosed in an aluminium DSC crucible using crimper, and immediately subjected to a temperature scan from 25 to 250 $^0C$ with an empty aluminium crucible as the reference. Thermogravimetric (TG) thermograms of the compounds were recorded on a Shimadzu DTG-60H in nitrogen
atmosphere with flow rate 50 mL min\(^{-1}\). About 3-6 mg samples were put into open alumina pan and subjected to a temperature scan from room temperature to 800\(^{0}\)C with an empty alumina pan as the reference. The heating rate for all these experiments was fixed at 10 \(^{0}\)C min\(^{-1}\). Indium and Zinc metals (99.9\%) were used for calibration of instruments.

**Note: Synthetic scheme is described in chapter-3, section-II**

**General Structure of N-substituted-2-((5-(pyrazin-2-yl)-1,3,4-oxadiazol-2-yl)thio)acetamides.**

![General Structure of N-substituted-2-((5-(pyrazin-2-yl)-1,3,4-oxadiazol-2-yl)thio)acetamides.](image)

**Fig.1** TG curves of thioacetamide derivatives at 10 \(^{0}\)C heating rate in nitrogen atmosphere
Fig. 2 DSC curves of 2,5-dimethyl OXDS(1) at 10 °C heating rate in nitrogen atmosphere

Fig. 3 DSC curves of 4-fluoroOXDS (2) at 10 °C heating rate in nitrogen atmosphere

Fig. 4 DSC curves of 3,4-dichloro OXDS(1) at 10 °C heating rate in nitrogen atmosphere
Fig. 5 The Freeman-Anderson plots of compound-1

**Compound-3,4-dichoro OXDS(1) (Step-I)**

- Linear equation: $y = 0.6174x - 0.0605$
- $R^2 = 0.9818$

**Compound-3,4-dichoro OXDS(1) (Step-II)**

- Linear equation: $y = 0.9244x - 0.0881$
- $R^2 = 0.9678$
The Freeman-Anderson plots of compound 2 and 3

4-fluoro OXDS (2) single step

2,5-dimethyl OXDS (3) single step
Table 1  DSC data of selected N-substituted-2-((5-(pyrazin-2-yl)-1,3,4-oxadiazol-2-yl)thio)acetamides.

<table>
<thead>
<tr>
<th>Sr.No.</th>
<th>Compounds</th>
<th>Melting transitions ($T_m$) $^\circ$C (Endo)</th>
<th>Heat of fusion $\Delta H$, J/g</th>
<th>$\Delta H$, kJmol$^{-1}$</th>
<th>Entropy of transition $\Delta S$, JK$^{-1}$mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2,5-di Me OXDS</td>
<td>213.45</td>
<td>-22066.8032</td>
<td>-22.07</td>
<td>-45.35</td>
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<tr>
<td>2</td>
<td>4-F OXDS</td>
<td>162.07</td>
<td>-34882.4504</td>
<td>-34.88</td>
<td>-80.15</td>
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<tr>
<td>3</td>
<td>3,4-di Cl OXDS</td>
<td>196.26</td>
<td>-26598.6898</td>
<td>-26.60</td>
<td>-56.66</td>
</tr>
</tbody>
</table>

Table 2  TGA data of selected N-substituted-2-((5-(pyrazin-2-yl)-1,3,4-oxadiazol-2-yl)thio)acetamide

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Compounds</th>
<th>$T_0$ $^\circ$C</th>
<th>$T_{max}$ $^\circ$C</th>
<th>Decom. Range $^\circ$C</th>
<th>% Weight loss</th>
<th>% Residue At 500 $^\circ$C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2,5-di Me</td>
<td>325</td>
<td>320.32</td>
<td>265-355</td>
<td>69</td>
<td>16.8</td>
</tr>
<tr>
<td>2</td>
<td>4-F</td>
<td>325</td>
<td>310.56</td>
<td>240-350</td>
<td>71.9</td>
<td>15.76</td>
</tr>
<tr>
<td>3</td>
<td>3,4-di Cl</td>
<td>255</td>
<td>187.7</td>
<td>165-200</td>
<td>5.28</td>
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</tr>
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</table>

Table 3  The kinetic parameters of selected N-substituted-2-((5-(pyrazin-2-yl)-1,3,4-oxadiazol-2-yl)thio)acetamide derived according to Anderson-Freeman method

<table>
<thead>
<tr>
<th>Sr.No.</th>
<th>Compounds</th>
<th>$n$</th>
<th>$E_a$, Jmol$^{-1}$</th>
<th>$A$, S$^{-1}$</th>
<th>$\Delta S^*$, JK$^{-1}$mol$^{-1}$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2,5-di Me</td>
<td>0.49</td>
<td>84470.2</td>
<td>$1.31 \times 10^5$</td>
<td>-152.7</td>
<td>0.972</td>
</tr>
<tr>
<td>2</td>
<td>4-F</td>
<td>1.33</td>
<td>180413.8</td>
<td>$2.74 \times 10^{14}$</td>
<td>26.02</td>
<td>0.976</td>
</tr>
<tr>
<td>3</td>
<td>3,4-di Cl</td>
<td>0.58</td>
<td>99768</td>
<td>$1.92 \times 10^{9}$</td>
<td>-70.82</td>
<td>0.981</td>
</tr>
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<td></td>
<td></td>
<td>0.92</td>
<td>146326.4</td>
<td>$2.14 \times 10^{11}$</td>
<td>-33.42</td>
<td>0.967</td>
</tr>
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</table>
RESULTS AND DISCUSSION

TGA thermograms of 2,5-di Me OXDS, 4-F OXDS and 3,4-diCl OXDS at 10 °C min⁻¹ heating rate under nitrogen atmosphere are presented in Fig 1. From these figures it is observed that thioacetamide derivatives are thermally stable up to about 240-265 °C and followed either single step decomposition (2,5-di Me OXDS, 4-F OXDS) or two step decomposition (3,4-diCl OXDS). Various characteristic temperature such as initial decomposition temperature \( T_0 \), temperature of maximum weight loss \( T_{\text{max}} \), % weight loss involved in each step and % residue left at the end of the decomposition reaction are reported in Table 2. 2,5-di Me OXDS (265 °C) showed higher thermal stability than that of 4-F OXDS (240 °C). The associated kinetic parameters namely energy of activation \( (E_a) \), frequency factor \( (A) \), order of the reaction \( (n) \) and entropy change \( (\Delta S^*) \) at corresponding \( T_{\text{max}} \) were derived according to Freeman-Anderson method and reported in table 3.

DSC thermograms of 2,5-di Me OXDS, 4-F OXDS and 3,4-di Cl OXDS at 10 °C min⁻¹ heating rate under nitrogen atmosphere are presented in Figs 2, 3 and 4, respectively. The melting transitions \( (T_m) \) along with heat of fusion \( (\Delta H) \) and entropy of transitions \( (\Delta S) \) are listed in table 1. 2,5-di Me OXDS showed comparatively high \( T_m \). The entropy of the compound strongly depends upon heat of fusion and melting point. The ultimate magnitude of \( \Delta S \) is decide on the basis of the magnitudes of \( \Delta H \) and \( T_m \).

The Freeman-Anderson plots are presented in Fig.5. The least-squares values of the above mentioned parameters along with regression coefficients \( (R^2) \) are reported in table no. 3. The \( \Delta S^* \) values for compound-2 was found to be positive and large in magnitudes, which implied that the transition states were less in orderly state while in compound 1 and 2 the values are negative which indicates that the transition states were more orderly.
REFERENCES