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# Thermogravimetric Analysis of Copper(II) Thiourea Complex Derived from Sesame (*Sesamum indicum*) Oil

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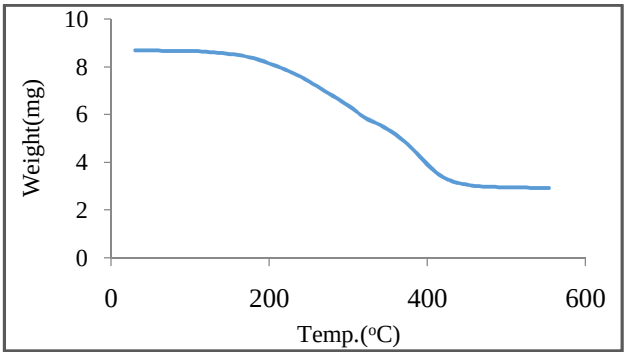
## ABSTRACT

*Copper (II) soap complex was synthesized with N and S containing ligand and characterized by elemental analysis, IR, NMR and ESR spectral techniques. TGA technique has been applied to Copper (II) sesame thiourea complex for its thermal analysis and evaluation of activation energy. Thermodynamic parameters such as heat of dissociation ΔH, change in free energy ΔG and entropy ΔS were evaluated for the different steps of degradation using the integral method of Coats- Redfern. The results of thermogravimetric analysis reveal that copper (II) thiourea complex undergo stepwise thermal degradation of saturated, unsaturated fatty acid components of edible oils. In the thermal decomposition of the copper (II) soap complex, the various steps involved have been analyzed by Coats-Redfern equation, Broido equation, Horowitz-Metzger equation and Piloyan-Novikova equation for evaluating kinetic parameters. It has been observed that for all the equations applied, the stepwise energy of activation follows the order –Step III>Step II > Step I. Thermodynamic parameters such as heat of dissociation ΔH, change in free energy ΔG and entropy ΔS were evaluated for the different steps of degradation using the integral method of Coats-Redfern and other equations.*

## Graphical Abstract




TGA of copper(II) sesame thiourea complex at 10 degree

**Keywords:** Copper(II) sesame thiourea complex, TGA, Energy of activation, Kinetic parameters, Thermodynamic parameters.

## INTRODUCTION

Oils consist of wide group compounds that are soluble in various organic solvents and insoluble in water. They have low density than water at normal room temperature range in consistency from solid to liquid, depending on their structure and composition [1-2]. Vegetable oil-based lubricants are slowly replacing the mineral oil due to their extraordinary biodegradability and many other specific properties [3-9]. Copper soaps derived from edible and non-edible oils play a very important role in various fields due to their surface-active properties [10-12]. Copper soaps have a tendency of complexation with 'nitrogen' and 'sulphur' containing ligands. Using thiourea as a ligand, complexation of synthesized Copper soaps has been done to obtain its thiourea complex [13-14]. This copper sesame thiourea complex was thermally analyzed by using TGA technique to study kinetic parameters like activation energy, rate constant, order of decomposition reaction [15-16]. The present study deals with the evaluation of kinetic as well as thermodynamic parameters for the degradation of several steps [17-18].

## MATERIALS AND METHODS

Copper sesame soap was prepared by direct metathesis of corresponding potassium soap with slight excess of required amount of copper sulphate at 50-55°C. After washing with hot distilled water and the alcohol, the sample was dried at 80-100°C and recrystallized with hot benzene at 50°C twice.

$$RCOOH \xrightarrow[EtOH]{KOH} RCOOK \xrightarrow{Cu^{+2}} (RCOO)_2Cu$$

**IR Spectral Analysis:** The complex was prepared by mixing the metal surfactants and ligand in the molar ratio of 1:1, dissolved in benzene and ethanol and mixture was reflux for about one and half hour. Purity of complex was checked by TLC. The complex was soluble in benzene but insoluble in water and highly stable at room temperature. The formation of the complex has been confirmed and characterized by elemental analysis, IR, NMR and ESR spectra. In order to study the structure of complexes, the Infrared spectra of complexes were obtained on a spectrophotometer (4000-200 $cm^{-1}$) from Dept. of chemistry, S.P.C. Govt. College Ajmer.

**Table 1.** IR Spectral data of copper (II) sesame thiourea complex

| Absorption Bands | CST ($cm^{-1}$) |
|---|---|
| **Corresponding to soap moiety** | |
| Olefinic =C-H stretching | 3000 |
| $CH_3$ and $CH_2$, C-H Anti symm. Stretching ($v_{as}$) | 2924 |
| $CH_3$ and $CH_2$, C-H symm. Stretching ($v_s$) | 2854 |
| >C=O stretching | 1744 |
| COO, C-O Antisymm. Streching | 1597 |
| Cu-O Streching | 602 |
| **Corresponding to ligand moiety** | |
| $NH_2$, N-H stretching | 3800-3500 |
| C-N stretching | 1458 |
| N-C-S stretching | 1273 |

**ESR Spectral Analysis:** The ESR spectra of complex were recorded at X-band with modulation frequency of 100 KHz at liquid nitrogen temperature (LNT) SAIF, IIT, POWAI, Mumbai. TCNE (g=2.00277) was used as a field marker (Fig. 2). For the complex of copper sesame soap, the values of ESR parameter $g_{\parallel}$, $g_{\perp}$ and $g_{av}$ are greater than the value of $g_o$ i.e.2.0027. This indicates that the

distortion from the regular octahedron has taken place in the shape of the complex. The higher values of $g_{\parallel}$ as compare to $g_{\perp}$ suggested that the presence of unpaired electron in $dx^2$-$y^2$ orbital.

**NMR Spectral Analysis:** $^1$H NMR Spectra was recorded at CDRI, SAIF, Lucknow using $C_6D_6$ as reference.

**Table 2.** $^1$H NMR spectral data of Copper (II) sesame thiourea complex (δ)

| Peak/Signal | Copper (II) sesame thiourea complex |
|---|---|
| -$CH_3$-$CH_2$-R | 0.910 |
| -$CH_2$-$CH_2$-R | 1.287 |
| -$CH_2$-C=C- | 2.115 |
| -C=C-H(vinylic proton) | 5.492 |
| -C=C-$CH_2$-C=C- | 2.889 |
| -$NH_2$(broadened peak) | 4.0-4.5 |

**Thermogravimetry:** Thermogravimetry has been employed to study the kinetics and thermodynamics of thermal decomposition of Copper sesame thiourea complex. The TGA curves were obtained by Perkin Elmer Thermal Analysis apparatus from SAIF, IIT- Powai, Mumbai. TGA was done on nitrogen atmosphere between 50-750°C at the rate of 5°C $min^{-1}$ and10°C $min^{-1}$. The results were obtained as plots of % weight loss v/s temperature and % weight loss v/s time.

## RESULTS AND DISCUSSION

Elemental Analysis has been done for Copper sesame soap and its thiourea complex for its metal content following standard procedures [**19**]. Molecular weights of Copper soap and its thiourea complex were determined from saponification value. The saponification equivalent or saponification value is a measure of the average length of the fatty acid that makes up a fat. The saponification equivalent (S.E.) is the amount of material saponified by one gram equivalent of potassium hydroxide and the saponification value (S.V.) is the number of mg of KOH required to hydrolyze one gram of fat, indicating the number of ester groups in the fat [**20**].

$$S.E. = 56100 / S.V. \qquad (1)$$

Thus equation (1) may be taken as average molecular weight of the oil. Value of S.E. is determined by experiment and from these values average molecular weight of copper sesame Soap and its thiourea complex have been calculated.

**Thermal Analysis:** Thermo-gravimetric method for kinetic analysis is reported here. Thermogravimetric analysis was carried out in range of 50°C-750°C on Perkin Elmer Thermal Analysis apparatus from SAIF, IIT- Powai, Mumbai in nitrogen atmosphere at two different heating rates(5°C and 10°C $min^{-1}$). This technique measures the weight change in a complex as a function of temperature and time, in a controlled environment [**20**]. This technique is very useful to investigate the thermal stability of a copper soaps and its thiourea complexes. The technique can be used in the examination of absorptive surfaces together with the nature and processes involved in the thermal decomposition [**21**] and oxidation process. As the heating rate is increased, the onset of decomposition is moved to higher temperatures. The results of thermogravimetric analysis usually reported in form of curves relating the mass lost from the sample against temperature as depicted in figure 1 and 2.

The results of thermogravimetric analysis indicate that stepwise thermal degradation in three steps of copper sesame thiourea complex corresponding to the decomposition of polyunsaturated, monounsaturated and saturated fatty acid components of their corresponding edible oil. On

observation of thermal decomposition steps, it was concluded that thermal degradation of Copper sesame thiourea complex at 10°C $min^{-1}$, first step is in the range of 423K to 523K(150-250°C). In the first step it may be suggest that decomposition of the unsaturated fatty acids begins. The long chain

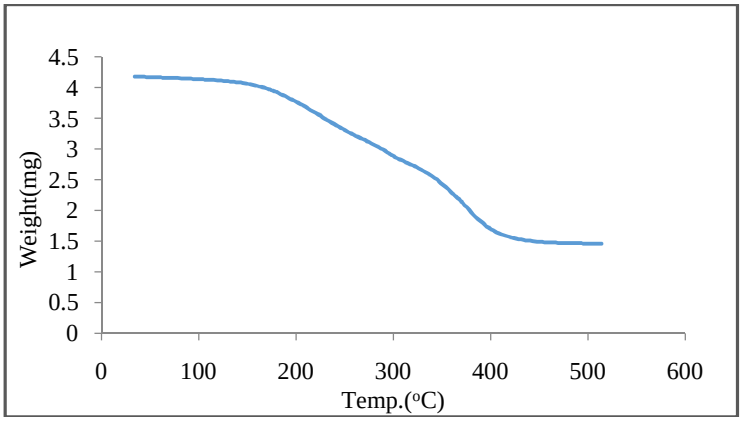



**Figure 1.** TGA of Copper(II) sesame thiourea complex at 5°C $min^{-1}$

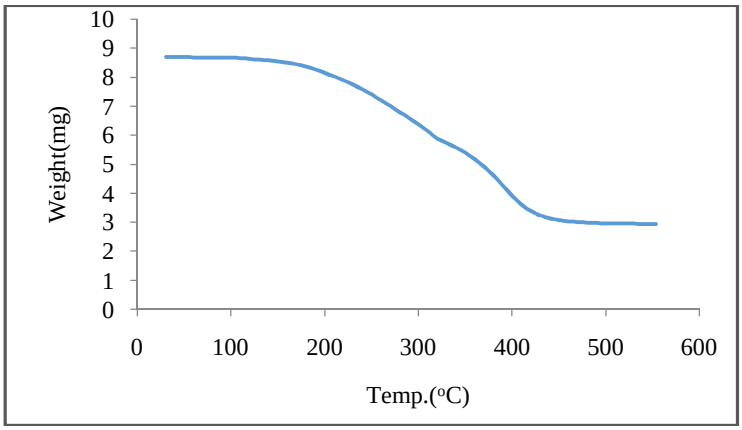



**Figure 2.** TGA of copper(II) sesame thiourea complex at 10°C $min^{-1}$

fatty acids produce volatile compounds, which are constantly removed by vapour generated during heating. Further, the second step of the thermal decomposition of complex was in the range of 523K to 623K (250-350°C). The second step corresponds to decomposition of monounsaturated fatty acids such as oleic acid. The double bonds are broken, causing the long chain fatty acid molecules in the edible vegetable oil to become saturated. The third step in the thermal decomposition occurs in the temperature range of 623K to 723K (350-450°C), which may correspond to the thermal decomposition of the saturated fatty acids such as palmitic acid. Thiourea complex of copper(II) sesame soap have higher thermal stability than its corresponding soaps. Thus, it can be suggested that thermal stability is influenced by the presence of the ligand.

The results of thermogravimetric analysis of thiourea complex of copper (II) sesame soap at 5°C $min^{-1}$ and 10°C $min^{-1}$ show that decomposition of complex is fairly rapid as temperature increases with time (Fig 3). The TGA curves plotted for thiourea complexes of copper (II) sesame soap at 5°C $min^{-1}$ depicted that decomposition of complex takes place in three steps, in temperature range 423K to 723K and at 10°C $min^{-1}$, decomposition of complex takes place in temperature range 433K to 683K. Thermal decomposition of copper(II) sesame thiourea complex occurred in three stages corresponding to the (i) decomposition of ligand moiety (ii)polyunsaturated and monounsaturated fatty acid components (iii) saturated fatty acid components respectively, at 10°C $min^{-1}$ decomposition of thiourea complexes of copper (II) sesame soap is quicker than 5°C $min^{-1}$.

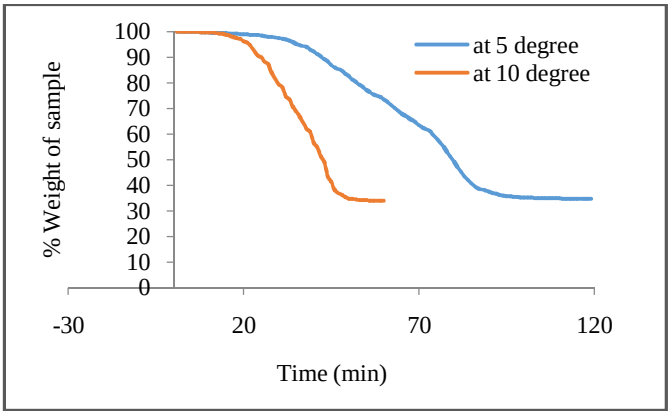



**Figure 3.** Plot of % weight of sample v/s time (min) depicting thermal degradation of copper(II) sesame thiourea complex at 5°C and 10°C

**Kinetic Parameters:** The results of thermogravimetric analysis have been applied in various equations like Coats-Redfern equation [22], Horowitz-Metzger equation [23], Broido equation [24] and Piloyan-Novikova method [25] and then evaluate the energy of activation (E) for thermal degradation of the various methods of kinetic analysis, Coats-Redfern equation has been found to be the most appropriate in calculating the energy of activation. For a first-order reaction process, Coats and Redfern provided an approximation. This is an integral form of the rate equation. The method follows the rate low mentioned as follows:

$$\log[-\log(1-\alpha)/T^2] = [\log AR/\beta E(1-2RT)/E\ ] - E/2.303RT \qquad (2)$$

Where 'α' stands for fraction of soap decomposed, 'K' for the rate constant, 'E' for the energy of activation of the reaction, β the heating rate, 'R' the gas constant (R = 8.317 $Jmol^{-1}$ $K^{-1}$) and 'A' for the exponential or frequency factor and is usually assigned to independent of absolute temperature 'T'.

The values of energy of activation using Coats- Redfern equation for the step have been evaluated from plots of 'log{[-log(1-α)]/$T^2$} V/S 1/T. The values of activation energies evaluated from the slope of these plots are recorded in table 4 and are observed to be in following order:

Step III> Step II > Step I.

To confirm the energy of activation Horowitz-Metzger equation has been used to evaluate the value of 'E'. The Horowitz-Metzger equation is as follows:

$$\ln[\ln(1-\alpha) - 1] = E/RTS^2 .\Theta \qquad (3)$$

Where 'α' is the fraction of soap decomposed at time't', $T_S$ is the temperature at which the rate of decomposition is maximum and Θ is equal to ($T-T_S$). The energy of activation is obtained from slope of the plot between 'ln[ln$(1-\alpha)^{-1}$] v/s Θ as depicted in fig 4. For Horowitz-Metzger equation the values of activation energy of each step are in the order-Step III >Step II > Step I. Broido has developed a model and the energy of activation associated with each step of decomposition was also evaluated by this method. The equation used for the calculation of activation energy (Ea) is:

$$\ln[\ln(1/y)] = E/R + C \qquad (4)$$

Where 'y' is fraction of weight at temperature 'T', 'E' is the activation energy and 'R' is the gas constant in Joule $mol^{-1}$ $K^{-1}$. The energy of activation for thiourea complex of copper(II) sesame soap is calculated from slope of plot between' ln[ln(1/y)] and (1/T)' as depicted in fig5.In Piloyan-Novikova method, the reaction order is not needed to be determined first. The rate of dissociation is given by the kinetic equation as follow:

$$log\,[\alpha/T] = log[ZR/E\beta] - E/2.303RT \qquad (5)$$

The activation energy has been calculated from the straight-line plot of log [$\alpha/T^2$] versus 1/*T*, for copper sesame thiourea complex.

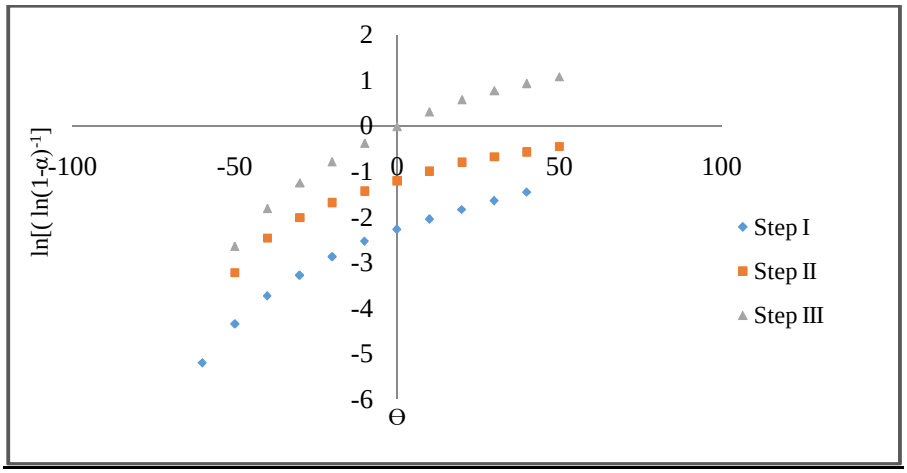



**Figure 4.** Horowitz-Metzger plot of copper(II) sesame thiourea complex for different steps at 10°C

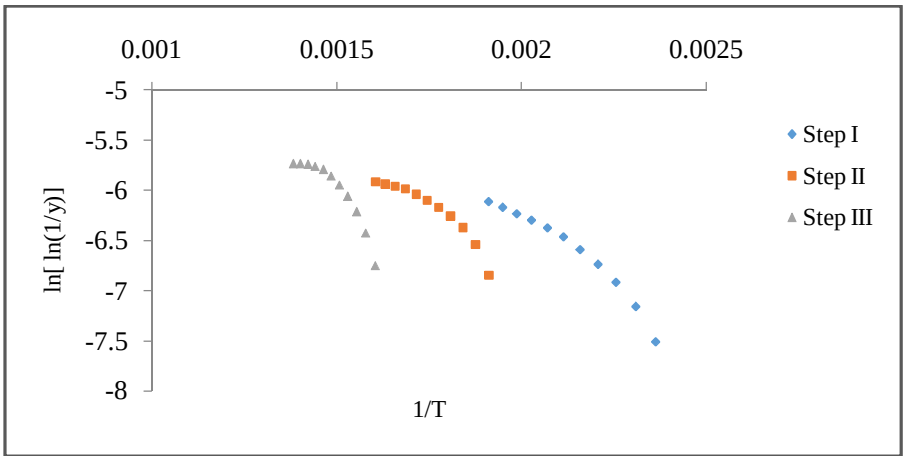



**Figure 5.** Broido plot of Copper(II) sesame thiourea complex for different steps at 10°C

A perusal of table 3 reveals that the value of activation energy is highest for the third step and smallest for the first step. There was a good correlation between the activation energies evaluated by various equations and approximation methods however the values obtained by the approximation methods were higher than the values obtained by integral methods which can be ascribed the different mathematical treatment of the methods. This may be concluded by the above studies that thiourea complex of copper(II) sesame soap may be easily degradable. The products prepared by natural edible and non-edible oils should be promoted and encouraged due to their significance applicability and degradability.

Table 3 shows the effect of different heating rate on activation energy for Coat-Redfern, Horowitz-Metzger, Broido and Piloyan-Novikova models. However, it concluded that, the use of multiple heating rate method represented more realistically. The verity of heating rate used for thermal degradation of Copper sesame thiourea complex because of the wide variation obtained when using various heating rates. It was found that by increasing the heating rate, the decomposition temperature of the Copper sesame thiourea complex was shifted to higher temperatures. This fact indicates that the values of activation energy decreases irregularly with increasing heating rate.

**Table 3.** Energy of activation of Copper(II) sesame thiourea complex at 5°C and 10°C

| Steps and Equations | Coats – Redfern | | | Horowitz- Metzger | | | Broido | | | Piloyan-Novikova | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | I | II | III | I | II | III | I | II | III | I | II | III |
| 5°C $min^{-1}$ | 61.89 | 64.55 | 125.15 | 74.67 | 78.56 | 138.84 | 69.60 | 78.88 | 135.54 | 59.09 | 61.41 | 91.87 |
| 10°C $min^{-1}$ | 57.25 | 59.67 | 123.55 | 67.60 | 69.14 | 134.67 | 65.05 | 69.14 | 134.67 | 48.28 | 51.88 | 79.72 |

**Thermodynamic Parameters:** The thermodynamic parameters of copper sesame thiourea complex were investigated in terms of according to Coats- Redfern (CR) integral formula [26]. The relation between heating rate (β) and energy of activation (E) is

$$\log[-\log(1-\alpha)/T^2] = [\log AR/\beta E(1-2RT)/E\,] - E/2.303RT \qquad (6)$$

Accordingly, the graph plotted between $\log\{[-\log(1-\alpha)]T^2\}$ against 1/T and best fitted straight line determines the operating mechanism. E and A values are calculated from slope and intercept respectively [27]. The entropy of activation (ΔS) was calculated by using relation-

$$\Delta S = 2.303 \times R \times \log[Zh/kT] \qquad (7)$$

Here, k is the Boltzmann constant, h the Plank constant, T the temperature and A is the frequency factor [27].

The enthalpy of activation was calculated by using the relation-

$$\Delta H = E - RT \qquad (8)$$

The Gibbs free energy of activation was estimated by using the relation-

$$\Delta G = \Delta H - T\Delta S \qquad (9)$$

By using the data of different methods various thermodynamic parameters are calculated for other equations and reported in table 4. The activation energy and the pre-exponential terms were calculated from slope and intercept respectively. The nonspontaneous nature of degradation process of the complex was supported by the positive value of ΔG in the degradation steps. The enthalpy was found to be positive value, and it was decreased with increased the temperature. The positive value of ΔH at a particular temperature indicated that the process was of endothermic nature [28-36].

The entropy of activation had negative values in all steps of degradation, which indicates that the decomposition reactions proceed with a lower rate than normal ones. Negative value of entropy also remarks the more ordered structure of Copper sesame complex of thiourea than the reactants. It is observed that the entropy of activation increases with the increase of activation energy. The negative values of the entropies of activation are compensated by the values of enthalpies of activation leading to almost the same values for the free energies of activation listed in table 4. The positive value of ΔG

shows that the reaction involved in the decomposition of copper sesame complex of thiourea is not spontaneous.

**Table 4.** A comparative thermodynamic parameter of copper (II) sesame thiourea complex

| Complex | Copper Sesame Thiourea at 5°C Per Minute | | | Copper Sesame Thiourea at 10°C Per Minute | | |
|---|---|---|---|---|---|---|
| **Degradation Steps** | **I** | **II** | **III** | **I** | **II** | **III** |
| Temperature Range(K) | 433-503 | 503-583 | 583-683 | 423-523 | 523-623 | 623-723 |
| Ea($kJmol^{-1}$) | | | | | | |
| Coats –Redfern | 61.89 | 64.55 | 125.15 | 57.25 | 59.67 | 123.55 |
| Horowitz-Metzger | 74.67 | 78.56 | 138.84 | 67.60 | 68.72 | 134.09 |
| Broido | 69.60 | 78.88 | 135.54 | 65.05 | 69.14 | 134.67 |
| Piloyan-Novikova | 59.09 | 61.41 | 91.87 | 48.28 | 51.88 | 79.72 |
| $Z(s^{-1})$ | | | | | | |
| Coats –Redfern | $5.00\times10^{4}$ | $1.52\times10^{4}$ | $2.74\times10^{8}$ | $1.59\times10^{3}$ | $3.13\times10^{3}$ | $2.04\times10^{8}$ |
| Horowitz-Metzger | $2.11\times10^{7}$ | $2.68\times10^{6}$ | $2.30\times10^{10}$ | $3.35\times10^{6}$ | $2.18\times10^{5}$ | $2.96\times10^{9}$ |
| Broido | $8.81\times10^{5}$ | $2.71\times10^{5}$ | $4.71\times10^{9}$ | $1.52\times10^{5}$ | $6.11\times10^{4}$ | $3.75\times10^{9}$ |
| Piloyan-Novikova | $7.22\times10^{3}$ | $8.09\times10^{3}$ | $1.52\times10^{6}$ | $1.67\times10^{3}$ | $1.04\times10^{3}$ | $7.08\times10^{5}$ |
| $\Delta S(Jk^{-1}mol^{-1})$ | | | | | | |
| Coats –Redfern | -159.00 | -170.19 | -89.91 | -187.48 | -183.47 | -92.61 |
| Horowitz-Metzger | -108.72 | -127.17 | -53.06 | -124.03 | -148.19 | -67.32 |
| Broido | -135.14 | -146.20 | -66.27 | -149.76 | -158.75 | -68.40 |
| Piloyan-Novikova | -175.08 | -151.19 | -133.11 | -187.26 | -192.62 | -158.86 |
| $\Delta H(kJmol^{-1})$ | | | | | | |
| Coats –Redfern | 57.88 | 59.87 | 119.71 | 53.24 | 54.91 | 117.95 |
| Horowitz-Metzger | 70.65 | 73.88 | 133.41 | 63.59 | 63.96 | 128.50 |
| Broido | 65.58 | 68.86 | 130.11 | 61.03 | 64.38 | 129.08 |
| Piloyan-Novikova | 55.07 | 56.73 | 86.44 | 44.27 | 47.11 | 74.13 |
| $\Delta G(kJmol^{-1})$ | | | | | | |
| Coats –Redfern | 134.70 | 155.71 | 178.43 | 143.82 | 160.06 | 180.29 |
| Horowitz-Metzger | 123.18 | 145.50 | 168.06 | 123.51 | 148.89 | 173.81 |
| Broido | 130.88 | 151.19 | 168.70 | 133.40 | 155.37 | 175.13 |
| Piloyan-Novikova | 139.66 | 155.51 | 173.39 | 134.74 | 157.51 | 181.06 |

## APPLICATION

Thermogravimetric methods have been used in characterization of oils and fats. This technique has been employed to study the kinetics by thermal decomposition of soaps and complexes derived from these oils. The present work will provide significant information towards green and safe chemistry because indiscriminate release of various pollutants such as surfactants in environment has created a new facet in environment pollution.

## CONCLUSION

The present study clearly demonstrates that the values of energy of activation 'E' reveal that for all the equations applied the stepwise energy of activation follow the order: Step III>Step II > Step I. It may be suggested that the increase of activation energy for different steps in thermal decomposition of the system studied, occurred due to the possible break in the molecular bonds of unsaturated fatty acids, which are less stable than the molecular bonds of stable saturated fatty acids requiring higher activation energy of degradation. The estimated thermodynamic parameters indicate the occurrence of an irreversible thermal decomposition through an endothermic process, and a better molecular orientation in the activated state.

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