Part II
Thermoanalytical studies

Chapter 3

Nimmy Kuriakose “Physicochemical, thermoanalytical, electrochemical and antitumour studies of transition metal complexes of schiff bases derived from heterocyclic carbonyl compounds” Thesis. Department of Chemistry, St. Thomas College, University of Calicut, 2015
CHAPTER 3

THERMAL DECOMPOSITION KINETICS OF Cr(III) COMPLEXES OF T2YMABA, PHMT2YBA, CTHMT2YBA AND CTHMF2YBA

Cr(III) complexes of four novel potential Schiff bases, (E)-3-[thiophen-2-ylmethyleneamino]benzoic acid (T2YMABA), (E)-4-(5-[(2-phenylhydrazono)methyl]thiophen-2-yl)benzoic acid (PHMT2YBA), (E)-4-(5-[(2-carbamothioylhydrazono)methyl]thiophen-2-yl)benzoic acid (CTHMT2YBA) and (E)-4-(5-[(2-carbamothioylhydrazono)methyl]furan-2-yl)benzoic acid (CTHMF2YBA) were synthesized and characterized by different analytical techniques. The details are well explained in Part 1. The thermal behavior of these Cr(III) complexes were studied using thermogravimetry and differential thermal analysis. Using Coats-Redfern method and nine mechanistic equations, the thermodynamic and kinetic parameters like activation energy, change in entropy and Arrhenius frequency factor were calculated. Non-isothermal methods were employed for the evaluation of reaction mechanism using the nine mechanistic equations given by Sestak and Berggren and Satava. The thermal behaviors of all these complexes are described in detail here.

Figures 2.1 to 2.4 represent the structures and instrumental TGA/DTA curves of Cr(III) complexes with four different ligands. The thermal decomposition data of these compounds are given in Tables 2.2 and 2.3.

Thermogravimetric curves of [CrL1Ac2(H2O)]2 (where L1=T2YMABA) gave a four stage decomposition pattern, in which the second stage comprises of two substages. The first stage of the curve represents the loss of two water molecules from the sample moiety in the temperature range of 60-140°C. This confirmed the presence of coordinated
water molecules in the complex. The loss of two non-bridged acetate groups and two CO$_2$ molecules from the ligands are exhibited in second stage, i.e. IIa and IIb respectively. The third stage represents the loss of the rest of both the ligands and the removal of two bridged acetate groups is depicted in the fourth stage of decomposition. The overall mass loss according to the TG curve is 81.53% and the theoretical mass loss for the conversion of the complex into Cr$_2$O$_3$ is 81.82%. The mass loss according to the pyrolytic data was also found to be in agreement with these results (81.10%).

The complex [CrL$_2$Ac$_3$(H$_2$O)$_2$] (where L$^2$=PHMT2YBA) has three stages of decomposition reaction. The first one is due to the removal of two coordinated water molecules from the complex. The second stage decomposition corresponds to the loss of one acetate group at around 290$^\circ$C and the in the last stage, the ligand and two acetate groups are removed from the complex molecule at 700$^\circ$C. The overall mass loss according to the TG curve is 87.37% and the theoretical mass loss for the conversion of the complex into metal oxide is 87.05%. The mass loss according to the pyrolytic data was found to be 86.54%.

The decomposition of Cr(III) complex of CTHMT2YBA, [CrL$_3$Ac$_2$(H$_2$O)$_2$] also resulted with a definite three stage pattern. The first stage (60-150$^\circ$C) is assigned to the loss of two water molecules. Two non-bridged acetate groups and two CO$_2$ molecules from the ligand are removed in the second stage. The third stage of decomposition corresponds to the loss of rest of both the ligands and two bridged acetates. The percentage mass loss according to the TG curve is 84.82% which is in good agreement with the theoretical value (84.35%). The mass loss from the pyrolysis is found to be 83.94%.
Cr(III) complex of the ligand CTHMF2YBA, [CrL\(^4\)Ac\(_2\)(H\(_2\)O)]\(_2\) underwent a four stage decomposition pattern. Loss of two water molecules are observed in the temperature interval 62-137\(^0\)C in the initial stage. The second stage consists of three substages in the temperature range 137-288\(^0\)C. Two amino groups, two CO\(_2\) molecules and two acetate groups are lost subsequently in each of these substages. Then in the third stage, two bridged acetate groups are removed and in fourth stage, the rest of both the ligands are lost. Overall mass loss of 83.70% is observed from the thermogravimetric curves. The theoretical and pyrolytic mass loss percentages are 84.03% and 82.95% respectively, which also confirms the probable assignments suggested for the decomposition stages.

**Kinetics of decomposition**

The mechanism of decomposition reaction of a chelate can be assigned by selecting the appropriate mechanistic equation which has a high degree of correlation coefficient\(^{49-51}\). The corresponding function \(g(\alpha)\) is chosen from which the kinetic parameters \(E\), \(A\) and \(\Delta S\) were calculated which are in good agreement with those obtained by the integral method.

From the kinetic parameters derived, it is assigned that the first stage decomposition, the first substage of second decomposition step and the third decomposition stage of the chelate [CrL\(^4\)Ac\(_2\)(H\(_2\)O)]\(_2\) follows first order kinetics. Since the parameters \(E\), \(A\) and \(\Delta S\) values obtained from the Coats-Redfern method with \(n=1\) are in close agreement with those obtained from the Mampel equation, it can be inferred that the rate controlling process of the reaction is random nucleation with the formation of one nucleus in each particle and is independent of thermal techniques used. For the substage
IIb and fourth stage of decomposition of Cr(III) complex, \( R_3 \) mechanism with order of the reaction \( 2/3 \) can be assigned which is evident from the comparison of kinetic parameters from mechanistic and non-mechanistic Coats-Redfern equation. The \( R_3 \) mechanism is based on phase boundary reaction, spherical symmetry and gives the maximum correlation for these decomposition stages.

For the Cr(III) complex of (E)-4-(5-[(2-phenylhydrazono)methyl]thiophen-2-yl)benzoic acid (PHMT2YBA) and (E)-4-(5-[(2-carbamothioylhydrazono)methyl]thiophen-2-yl)benzoic acid (CTHMT2YBA), all the different stages of decomposition process are assigned first order kinetics since the kinetic parameters calculated from the Coats-Redfern equation with \( n=1 \) are in good agreement with those obtained for the \( F_1 \) mechanism based on Mampel equation. This indicates that the rate controlling process is random nucleation.

In the case of first stage decomposition of the Cr(III) complex of (E)-4-(5-[(2-carbamothioylhydrazono)methyl]furan-2-yl)benzoic acid (CTHMF2YBA), the kinetic parameters derived using the non-mechanistic equation with \( n=1/3 \) are in good agreement with those values obtained from the equation VIII of mechanistic equations. It is therefore concluded that the decomposition process where two coordinated water molecules are removed from the complex, follows \( R_2 \) mechanism based on phase boundary reaction with cylindrical symmetry. For all other stages of decomposition, first order kinetics is assigned. The rate controlling process is random nucleation which follows \( F_1 \) mechanism based on Mampel equation.

The kinetic parameters such as energy of activation \( E \), pre-exponential factor \( A \) and entropy of activation \( \Delta S \) calculated for the various stages of decomposition of the
complexes using mechanistic and non mechanistic kinetic equations are summarized in Tables 2.4 to 2.8. The mechanisms of decomposition of various stages as well as the order of decomposition of all the various stages of the complexes are given in Tables 2.9 to 2.11. It can be noted that the larger the activation energy for the decomposition, greater the thermal stability of the compound. The relative thermal stabilities of these chelates can be given as $[\text{CrL}_3\text{Ac}_2(\text{H}_2\text{O})_2]<[\text{CrL}_4\text{Ac}_2(\text{H}_2\text{O})_2]<[\text{CrL}_1\text{Ac}_2(\text{H}_2\text{O})_2]<[\text{CrL}_2\text{Ac}_3(\text{H}_2\text{O})_2]$. From the thermal studies it is quite evident that the monomeric structure is more stable to heat than the dimeric structure.

![Fig. 2.1 Structure, TGA and DTA curves of [CrL\textsuperscript{1}Ac\textsubscript{2}(H\textsubscript{2}O)]\textsubscript{2}](image-url)
**Fig. 2.2** Structure, TGA and DTA curves of $[\text{CrL}_2\text{Ac}_3(\text{H}_2\text{O})_2]$.

**Fig. 2.3** Structure, TGA and DTA curves of $[\text{CrL}_3\text{Ac}_2(\text{H}_2\text{O})_2]$.
Fig. 2.4 Structure, TGA and DTA curves of \([\text{CrL}^4\text{Ac}_2(\text{H}_2\text{O})]_2\)
Table 2.2 Thermal decomposition data of Cr(III) complexes of (E)-3-[thiophen-2-ylmethyleneamino]benzoic acid (T2YMABA) and (E)-4-(5-[(2-phenylhydrazono)methyl]thiophen-2-yl)benzoic acid (PHMT2YBA)

<table>
<thead>
<tr>
<th>Complex</th>
<th>Stage</th>
<th>Temp range in TG (^0\text{C})</th>
<th>Peak temp in TG (^0\text{C})</th>
<th>Peak temp in DTA (^0\text{C})</th>
<th>Loss of mass %</th>
<th>Probable assignment</th>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>From TG</td>
<td>Cald.</td>
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<tr>
<td>[CrL(^1)\Ac(_2)(H(_2)O)(_2)](_2)</td>
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<td>60-140</td>
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<td>84</td>
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<td>4.31</td>
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<tr>
<td></td>
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<tr>
<td></td>
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\(L^1 = \text{T2YMABA}, \; L^2 = \text{PHMT2YBA}\)
Table 2.3 Thermal decomposition data of Cr(III) complexes of (E)-4-(5-[(2-carbamothioylhydrazono)methyl]thiophen-2-yl)benzoic acid (CTHMT2YBA) and (E)-4-(5-[(2-carbamothioylhydrazono)methyl]furan-2-yl)benzoic acid(CTHMF2YBA)

<table>
<thead>
<tr>
<th>Complex</th>
<th>Stage</th>
<th>Temp range in TG (°C)</th>
<th>Peak temp in TG (°C)</th>
<th>Peak temp in DTA (°C)</th>
<th>Loss of mass %</th>
<th>Probable assignment</th>
</tr>
</thead>
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<td></td>
<td></td>
<td>From TG</td>
<td>Calcd.</td>
</tr>
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L³ = CTHMT2YBA, L⁴ = CTHMF2YBA
Table 2.4 Kinetic parameters of the decomposition of Cr(III) complex of (E)-3-[thiophen-2-ylmethyleneamino]benzoic acid (T2YMABA) from TG using mechanistic equations

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<th>6</th>
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<th>8</th>
<th>9</th>
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<tbody>
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<td>[CrL1Ac2(H2O)]2</td>
<td></td>
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<td></td>
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<td>1.89 x10</td>
<td>4.1 x10</td>
<td>^ 32.424</td>
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<td>23 x10</td>
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<tr>
<td></td>
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<tr>
<td></td>
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<td>188.16</td>
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*E in kJmol⁻¹; A in s⁻¹, ΔS in JK⁻¹mol⁻¹
Table 2.5 Kinetic parameters of the decomposition of Cr(III) complexes of (E)-3-[thiophen-2-ylmethyleneamino]benzoic acid (T2YMABA) and (E)-4-(5-[(2-phenylhydrazono)methyl]thiophen-2-yl)benzoic acid (PHMT2YBA) from TG using mechanistic equations

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*E in kJmol⁻¹; A in s⁻¹, ∆S in JK⁻¹mol⁻¹
Table 2.6 Kinetic parameters of the decomposition of Cr(III) complex of (E)-4-(5-[(2-carbamothioylhydrazono)methyl]thiophen-2-yl)benzoic acid (CTHMT2YBA) from TG using mechanistic equations

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<td>[CrL³Ac₂(H₂O)]₂ Stage I</td>
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<td>110.79</td>
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<tr>
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<td>A</td>
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<td>4.92 x10¹⁰</td>
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<tr>
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<td>0.9473</td>
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*E in kJ mol⁻¹; A in s⁻¹; ΔS in JK⁻¹ mol⁻¹
Table 2.7 Kinetic parameters of the decomposition of Cr(III) complex of (E)-4-(5-[(2-carbamothioylhydrazono)methyl]furan-2-yl)benzoic acid (CTHMF2YBA) from TG using mechanistic equations

<table>
<thead>
<tr>
<th>Complex</th>
<th>Parameter*</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
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<tbody>
<tr>
<td></td>
<td>E</td>
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<td>64.98</td>
<td>65.12</td>
<td>29.39</td>
<td>17.49</td>
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</tr>
<tr>
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<tr>
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<tr>
<td>Stage I</td>
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</tr>
<tr>
<td></td>
<td>E</td>
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</tr>
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<td>0.9534</td>
<td>0.9494</td>
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</tr>
</tbody>
</table>

*E in kJmol⁻¹; A in s⁻¹, ΔS in JK⁻¹mol⁻¹
Table 2.8 Kinetic parameters of the decomposition of Cr(III) complex of (E)-4-(5-[(2-carbamothioylhydrazono)methyl]furan-2-yl)benzoic acid (CTHMF2YBA) from TG using mechanistic equations

<table>
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<tr>
<th>Complex</th>
<th>Mechanistic equations</th>
</tr>
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<tr>
<td></td>
<td>Parameter* 1 2 3 4 5 6 7 8 9</td>
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<tr>
<td>$[\text{CrL}_4\text{Ac}_2(\text{H}_2\text{O})]_2$</td>
<td>E 317.26 360.19 419.59 379.51 238.57 114.82 73.57 190.72 205.33</td>
</tr>
<tr>
<td>Stage IIc</td>
<td>A 2.82 x10^8 3.2 x10^{32} 7.15 x10^{37} 6.37 x10^{33} 1.89 x10^{21} 9.93 x10^8 6.54 x10^4 1.26 x10^{16} 2.6 x10^{17}</td>
</tr>
<tr>
<td></td>
<td>$\Delta S$ 294.95 372.57 474.98 397.45 157.65 -77.46 -157.4 958.50 83.69</td>
</tr>
<tr>
<td></td>
<td>r 0.8887 0.9097 0.9351 0.9187 0.9544 0.9515 0.9483 0.9210 0.9329</td>
</tr>
<tr>
<td>Stage III</td>
<td>E 294.48 323.44 363.28 336.34 199.29 94.73 59.88 166.89 176.73</td>
</tr>
<tr>
<td></td>
<td>A 2.31 x10^{23} 5.9 x10^{25} 6.55 x10^{28} 2.06 x10^{26} 2.5 x10^{15} 9.51 x10^5 552.29 1.18 x10^{12} 6.61 x10^{12}</td>
</tr>
<tr>
<td></td>
<td>$\Delta S$ 196.68 242.71 301.05 253.15 44.47 -136.15 -198.10 -19.52 -5.17</td>
</tr>
<tr>
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</tr>
<tr>
<td>Stage IV</td>
<td>E 223.27 242.91 269.53 251.53 143.89 66.07 40.14 122.32 128.89</td>
</tr>
<tr>
<td></td>
<td>A 2.59 x10^{13} 4.95 x10^{14} 1.47 x10^{16} 5.39 x10^{14} 1.1 x10^{18} 134.68 1.134 9 x10^5 2.21 x10^6</td>
</tr>
<tr>
<td></td>
<td>$\Delta S$ 4.385 28.90 57.12 29.61 -98.44 -211.64 -251.36 -137.81 -130.91</td>
</tr>
<tr>
<td></td>
<td>r 0.9114 0.9293 0.9485 0.9363 0.9591 0.9518 0.9424 0.9345 0.9439</td>
</tr>
</tbody>
</table>

*E in kJmol^{-1}; A in s^{-1}, $\Delta S$ in JK^{-1}mol^{-1}
Table 2.9 Kinetic parameters of the decomposition of Cr(III) complex of (E)-3-[thiophen-2-ylmethyleneamino]benzoic acid (T2YMABA) from TG using non mechanistic equation (Coats-Redfern) and its correlation with mechanistic equation

<table>
<thead>
<tr>
<th>Complex (stage)</th>
<th>Non-mechanistic/mechanistic equation</th>
<th>Kinetic parameters*</th>
<th>Order of reaction (n)</th>
<th>Mechanism of decomposition</th>
</tr>
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<tbody>
<tr>
<td></td>
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<td>E</td>
<td>A</td>
<td>ΔS</td>
</tr>
<tr>
<td>[CrL¹Ac₂(H₂O)]₂</td>
<td>Coats-Redfern</td>
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<td>4.1x10⁶</td>
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<tr>
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<td>Equation V</td>
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<td>4.1x10⁶</td>
<td>-119.69</td>
</tr>
<tr>
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<td></td>
<td>109.47</td>
<td>5.3x10¹⁰</td>
<td>-44.38</td>
</tr>
<tr>
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<td>Equation V</td>
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<td>5.3x10¹⁰</td>
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<tr>
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</tr>
<tr>
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</tr>
<tr>
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<td>Equation V</td>
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<td>Coats-Redfern</td>
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<td>2.04x10⁹</td>
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<td>6.83x10⁹</td>
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*E in kJmol⁻¹; A in s⁻¹, ΔS in JK⁻¹mol⁻¹
Table 2.10 Kinetic parameters of the decomposition of Cr(III) complexes of (E)-4-(5-[(2-phenylhydrazono)methyl]thiophen-2-yl)benzoic acid (PHMT2YBA) and (E)-4-(5-[(2-carbamothioylhydrazono)methyl]thiophen-2-yl)benzoic acid (CTHMT2YBA) from TG using non-mechanistic equation (Coats-Redfern) and its correlation with mechanistic equation

<table>
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<tr>
<th>Complex (stage)</th>
<th>Non-mechanistic/mechanistic equation</th>
<th>Kinetic parameters*</th>
<th>Order of reaction (n)</th>
<th>Mechanism of decomposition</th>
</tr>
</thead>
<tbody>
<tr>
<td>[CrL$_2$Ac$_3$(H$_2$O)$_2$]</td>
<td>Coats-Redfern</td>
<td>E: 61.91, A: 6.46x10$^6$, ΔS: -115.9, r: 0.9289</td>
<td>1</td>
<td>F$_1$ mechanism. Mampel equation. Random nucleation. One nucleus at each particle</td>
</tr>
<tr>
<td>Stage I</td>
<td>Equation V</td>
<td>E: 61.91, A: 6.46x10$^6$, ΔS: -115.9, r: 0.9289</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>Coats-Redfern</td>
<td>E: 65.05, A: 2.67x10$^4$, ΔS: -165.58, r: 0.9916</td>
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<td>F$_1$ mechanism. Mampel equation. Random nucleation. One nucleus at each particle</td>
</tr>
<tr>
<td></td>
<td>Equation V</td>
<td>E: 65.05, A: 2.67x10$^4$, ΔS: -165.58, r: 0.9916</td>
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<tr>
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<td>Coats-Redfern</td>
<td>E: 72.50, A: 1.5x10$^5$, ΔS: -37.18, r: 0.9953</td>
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<td>F$_1$ mechanism. Mampel equation. Random nucleation. One nucleus at each particle</td>
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<tr>
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<td>Equation V</td>
<td>E: 72.50, A: 1.5x10$^5$, ΔS: -37.18, r: 0.9953</td>
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<tr>
<td>[CrL$_3$Ac$_2$(H$_2$O)]$_2$</td>
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<tr>
<td>Stage I</td>
<td>Equation V</td>
<td>E: 61.910, A: 6.46x10$^6$, ΔS: -115.57, r: 0.9289</td>
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<td>Coats-Redfern</td>
<td>E: 75.24, A: 2.49x10$^5$, ΔS: -148.99, r: 0.9681</td>
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<td>Equation V</td>
<td>E: 75.24, A: 2.49x10$^5$, ΔS: -148.99, r: 0.9681</td>
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<td>Coats-Redfern</td>
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<td>F$_1$ mechanism. Mampel equation. Random nucleation. One nucleus at each particle</td>
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<td>Equation V</td>
<td>E: 135.46, A: 4.92x10$^7$, ΔS: -105.05, r: 0.9629</td>
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</table>

*E in kJmol$^{-1}$; A in s$^{-1}$, ΔS in JK$^{-1}$mol$^{-1}$
### Table 2.11 Kinetic parameters of the decomposition of Cr(III) complex of (E)-4-(5-[(2-carbamothioylhydrazono)methyl]furan-2-yl)benzoic acid (CTHMF2YBA) from TG using non mechanistic equation (Coats-Redfern) and its correlation with mechanistic equation

<table>
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<tr>
<th>Complex (stage)</th>
<th>Non-mechanistic/mechanistic equation</th>
<th>Kinetic parameters*</th>
<th>Order of reaction (n)</th>
<th>Mechanism of decomposition</th>
</tr>
</thead>
<tbody>
<tr>
<td>[CrL₄Ac₂(H₂O)]₂</td>
<td>Coats-Redfern Equation VIII</td>
<td>E 25.88  A 12.13  ΔS -225.51  r 0.9949</td>
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</tr>
<tr>
<td>Stage I</td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>Stage IIa</td>
<td>Coats-Redfern Equation V</td>
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<tr>
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<td>Coats-Redfern Equation V</td>
<td>E 200.13  A 1.01x10¹⁰  ΔS -16.06  r 0.9569</td>
<td>1  F₁ mechanism. Mampel equation. Random nucleation. One nucleus at each particle</td>
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<tr>
<td>Stage III</td>
<td>Coats-Redfern Equation V</td>
<td>E 199.29  A 2.59x10¹⁵  ΔS -44.47  r 0.9462</td>
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<td>Coats-Redfern Equation V</td>
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*E in kJmol⁻¹; A in s⁻¹, ΔS in JK⁻¹mol⁻¹