CHAPTER 7

SUMMARY

The present work describes the kinetics and mechanism of thermal decomposition of cobalt ammine complexes in air. The complexes studied include:

(i) Hexammine cobalt (III) chloride; HCC
(ii) Hexammine cobalt (III) bromide; HCBr
(iii) Hexammine cobalt (III) iodide; HCI
(iv) Hexammine cobalt (III) oxalate tetrahydrate; HCOX
(v) Hexammine cobalt (III) trioxalato cobalt (III); HCTOX.

In addition to these complexes cobalt (II) - chloride - bromide - oxalate dihydrates were also investigated to understand the effect of complexation on decomposition characteristics. Thermal decompositional studies of these compounds have been carried out using:

(i) dynamic TGA methods,
(ii) isothermal TGA methods,
(iii) compositional analysis methods, and
(iv) DTA methods.

Of the above mentioned compounds, HCTOX has not been investigated in the literature for thermal decomposition properties. This compound was therefore characterised by physical methods such as spectroscopy and XRD (Fig. 7.1 to 7.3).
Table 7.1

Electronic spectral transition* \( \mathbf{1}_{\text{Ag}} \rightarrow \mathbf{1}_{\text{Tlg}} \)

<table>
<thead>
<tr>
<th>Compound</th>
<th>HCC</th>
<th>HCl</th>
<th>HClO</th>
<th>HClOX</th>
<th>HCTOX</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \bar{\nu} ), cm(^{-1})</td>
<td>21200</td>
<td>21160</td>
<td>21160</td>
<td>21000</td>
<td>23640 and 16660</td>
</tr>
</tbody>
</table>

Characteristic I.R. vibrations of the compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>I.R. vibrational modes** cm(^{-1}).</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Associated with Co-NH(_3) Oxalate</td>
</tr>
<tr>
<td>HCC</td>
<td>820(s) 710(m) 500(w) 499(w) 476(w)</td>
</tr>
<tr>
<td>HClBr</td>
<td>830(s) 720(m) 520(w) 450(w) 440(w)</td>
</tr>
<tr>
<td>HCl</td>
<td>795(s) 715(m) 520(w) 470(w) -</td>
</tr>
<tr>
<td>HClO</td>
<td>840(s) 720(m) - 480(w) 450(w)</td>
</tr>
<tr>
<td>HClOX</td>
<td>1660(s) 875(s) 740(s)</td>
</tr>
<tr>
<td>HCTOX</td>
<td>1730(s) 1700(s) 850(s) 820(s) 620(m) 560(s)</td>
</tr>
</tbody>
</table>


Fig. 7.1: Infrared spectra of (a) HCC, (b) HCB, (c) HCl, (d) HCOX, (e) HCTOX.
FIG. 7.2: INFRARED SPECTRA OF (a) Co$_3$O$_4$ FROM HCC
(b) Co$_3$O$_4$ FROM CoCl$_2$·2H$_2$O.
Fig. 7.2: Electronic spectra of
a - HCC
b - HCOX
c - HCTOX
Table 7.2

XRD Data of Important lines

<table>
<thead>
<tr>
<th>Compound</th>
<th>HCOX</th>
<th>HCTOX</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Intensity $I/I_0$ experimental</td>
<td>2 $\theta$</td>
<td>d values experimental</td>
<td>Intensity $I/I_0$ experimental</td>
</tr>
<tr>
<td>100</td>
<td>27.5</td>
<td>4.0747</td>
<td>100</td>
</tr>
<tr>
<td>92.95</td>
<td>23.0</td>
<td>4.8582</td>
<td>48.32</td>
</tr>
<tr>
<td>80.37</td>
<td>27.8</td>
<td>4.037</td>
<td>21.26</td>
</tr>
<tr>
<td>42.99</td>
<td>16.8</td>
<td>6.631</td>
<td>10.63</td>
</tr>
<tr>
<td>33.64</td>
<td>28.6</td>
<td>3.921</td>
<td>16.60</td>
</tr>
<tr>
<td>28.04</td>
<td>42.5</td>
<td>2.6724</td>
<td>9.665</td>
</tr>
<tr>
<td>26.17</td>
<td>36.2</td>
<td>3.1176</td>
<td>9.610</td>
</tr>
<tr>
<td>23.74</td>
<td>42.8</td>
<td>2.6545</td>
<td>6.765</td>
</tr>
</tbody>
</table>
Fig. 7.3: X-ray diffraction of HCOX and HCTOX.
Table 7.3

\( \Delta H^* \) from DTA curve

<table>
<thead>
<tr>
<th>Compound</th>
<th>Atmosphere</th>
<th>Peak temp. ( ^0\text{C} )</th>
<th>Area ( \text{mm}^2 )</th>
<th>Instrument constant Cal/( \text{mm}^2 )</th>
<th>( \Delta H^* ) ( \text{kJ mole}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>COOX</td>
<td>air</td>
<td>310*</td>
<td>404</td>
<td>0.032</td>
<td>22.91</td>
</tr>
<tr>
<td>HCCOX</td>
<td>air</td>
<td>320*</td>
<td>384</td>
<td>0.034</td>
<td>23.13</td>
</tr>
<tr>
<td>HCTOX</td>
<td>air</td>
<td>350*</td>
<td>618</td>
<td>0.038</td>
<td>21.01</td>
</tr>
<tr>
<td>COX</td>
<td>PAA</td>
<td>450*</td>
<td>96</td>
<td>0.062</td>
<td>-15.24</td>
</tr>
<tr>
<td>HCOX</td>
<td>PAA</td>
<td>350*</td>
<td>70</td>
<td>0.038</td>
<td>-15.48</td>
</tr>
<tr>
<td>HCTOX</td>
<td>PAA</td>
<td>425*</td>
<td>524</td>
<td>0.054</td>
<td>-18.34</td>
</tr>
</tbody>
</table>

* \( \text{Co}_3\text{O}_4 \) as final residue

+ \( \text{Co metal} \) as final residue

‡ PAA - Pseudo Ambient Atmosphere
Electronic spectra of HCC, HCEr, HCl, HCOX are characterized by an absorption band due to $^1A_{1g} \rightarrow ^1T_{1g}$ transition at about 21000 cm$^{-1}$ (Table 7.1) of $[\text{Co(NH}_3)_6]^{3+}$ ion. This transition showed a small high frequency shift of about 2500 cm$^{-1}$ in the complex HCTOX. A new strong band appeared at 16660 cm$^{-1}$ which, then, could be confidently assigned to the $^1A_{1g} \rightarrow ^1T_{1g}$ transition of $[\text{Co(C}_2\text{O}_4)_3]^{-3}$ ion. The high frequency shift could be associated with the lowering of $t_{2g}$ levels of $[\text{Co(NH}_3)_6]^{3+}$ through inter-state mixing of the $[\text{Co(C}_2\text{O}_4)_3]^{-3}$ specie.

Similarly normal vibrational modes for the coordinated and non coordinated oxalato groups for HCTOX and HCOX are observed in the infrared spectra similar to other oxalate complexes. The pertinent vibrations are listed as Table 7.1. XRD of these two complexes are distinctly different and important $d$ values are listed in Table 7.2.

DTA of COX, HCOX and HCTOX has been studied in air and pseudo ambient atmospheres (CHAPTER 6). The important difference is a large reduction of endothermic peak area (for the decomposition of cobalt oxalate) in pseudo ambient atmosphere as compared to that studied in air atmosphere. TGA suggested the formation of cobalt metal. This was proved by expulsion of hydrogen from the decomposed oxalate.

Table 7.3 contains the heat of reactions for the endothermic
and exothermic peaks. For the three compounds, COX, HCOX and HCTOX heat of reaction for the endothermic peak for the conversion into Co₃O₄, was calculated to be about 22 kJ mole⁻¹ and, that for the conversion into cobalt metal was around 16 kJ mole⁻¹. It seems appropriate from the concurrence among these values for the three compounds that the formation of either Co₃O₄ or cobalt metal follows the same mechanism irrespective of the difference in the starting compounds.

For the first time isothermal DTA has been used in the present work to show the occurrence of oscillatory solid state reaction,

$$\text{CoBr}_2 \xrightarrow{\text{O}_2} \text{CoOBr} \xrightarrow{\text{O}_2} \text{Co}_3\text{O}_4$$

A periodic change in composition is, thus, responsible for a periodic change in differential temperature, and hence DTA can form a useful method for studying the periodic solid state reactions.

To summarize the results on thermal decomposition of HCC, HCBr, HCl, HCOX and HCTOX, the following points could be stated:

1. Hexammine cobalt (III) ion decomposes, regardless of atmosphere, by the following mechanism:
$$[\text{Co(NH}_3\text{)}_6]^{+3} \rightarrow [\text{Co} \ldots \text{NH}_2 \ldots \text{H}^+]$$

$$\text{Co}^{+2} + 4.66 \text{NH}_3 \uparrow + \frac{1}{6} \text{N}_2 \uparrow$$

Co$^{+2}$ ion forms the salt with the anion present in the molecule; thus, for HCC, CoCl$_2$ is formed, for HCBR, CoBr$_2$ for HCOX, CoC$_2$O$_4$ is formed, and so on. CoI$_2$ is thermally decomposed to CoO. Similarly, CoC$_2$O$_4$ decomposes to CoO.

2. CoX$_2$, (where $X = \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{C}_2\text{O}_4^{2-}$) decomposes in free supply of air to Co$_3$O$_4$ through CoO:

$$\text{CoX}_2 \xrightarrow{k_1} \text{CoO} \xrightarrow{k_2} \text{Co}_3\text{O}_4$$

However, this conversion could be kinetically studied only for HCC and HCBR. CoX$_2$ from HCl, HCOX and HCTOX is so labile that the rate of conversion of CoX$_2$ $\xrightarrow{k_1} \text{CoO}$ could not be studied. CoO has been chemically verified from the decomposition products of HCl, HCOX and HCTOX.

3. Isothermal TGA in the temperature region of 200 to 290 $^\circ$C of HCl, HCOX and HCTOX showed that the final decomposition product is Co$_2$O$_3$, since it is stable below 320 $^\circ$C. The final product from HCC, HCBR is Co$_3$O$_4$ since these decompositions need the temperatures above 500 $^\circ$C. However, it is noted that the physical state of Co$_3$O$_4$ derived from HCC, HCBR is of uniform particle size (0.3 to 0.8 microns) with neat crystalline structure, while that derived from CoCl$_2$ and CoBr$_2$, is amorphous.
and of particle size ranging from 0.3 to 3 microns. The origin of CoX₂ (X = Cl⁻, Br⁻) is an important factor in deciding the physical state of the oxide.

4. Kinetic expressions used for solid state reactions have some relevance to those used for solution reactions. This was verified in the present work. Thermal decomposition of CoCl₂ to Co₃O₄ is a two step reaction as:

\[
\text{CoCl₂} + \frac{1}{2} \text{O₂} \xrightarrow{k₁} \text{CoO} + \text{Cl₂} + \frac{1}{6} \text{O₂} \xrightarrow{k₂} \frac{1}{3} \text{Co₃O₄}
\]

Study of the kinetics using component chemical analysis method showed that the plots of fractions, (α), versus time for this solid state reaction are concurrent to similar irreversible solution reaction of order one. The rate constants were determined using least squares fitting method. (CHAPTER 2, 3 and 4).

Activation energy determined by dynamic rate expressions for a decomposition process was, usually, found to be higher in magnitude than that calculated from isothermal kinetic data.

5. Many of the decomposition processes for these complexes are diffusion controlled reactions. Such reactions are characterized by low activation energy and low magnitudes of reaction rates.
6. This study of the formation of $\text{Co}_3\text{O}_4$ from different cobalt compounds is of interest in the preparation of catalytic quality cobalt oxides. More elaborate studies on the architecture of these solids are needed.

7. 'The last and the most important observation from this work is the non-monotonous behaviour in solid-gas reaction,

$$\text{CoBr}_2(s) + \text{O}_2(g) \rightleftharpoons \frac{1}{3}\text{Co}_3\text{O}_4(s) + \text{Br}_2(g)$$

There are very few solid state oscillatory reactions. Thermodynamic consideration of a kinetic reaction predicts the presence of multiple steady states if the reaction is far from equilibrium. Such a stage could arrive in a reaction if autocatalytic species are generated which are responsible for branching mechanism.

When about $95\%$ of $\text{CoBr}_2$ has changed into $\text{Co}_3\text{O}_4$, covered by a thick layer of bromine gas oscillations set in with respect to composition of the system, $\text{CoBr}_2 + \text{O}_2$ (TGA of HCB, CHAPTER 4). The range of oscillations, as repeatedly observed, in terms of weight change is $2\%$ only. This indicates that the reaction responsible for oscillations is,

$$\text{Co}_3\text{O}_4 + \text{Br}_2 \rightleftharpoons \text{CoOBr} (?) + \text{CoO} + \frac{1}{2}\text{CoBr}_2$$

In presence of free supply of air, oscillatory behaviour was found to be quenched. To confirm this and non-monotonous
behaviour a series of experiments were conducted:

(i) Reaction of CoBr$_2$(s) with O$_2$(g) + Br$_2$(g) mixtures

(ii) Reaction of CoO(s) with O$_2$(g) + Br$_2$(g) mixtures

(iii) Reaction between Co$_3$O$_4$(s) + CoBr$_2$(s) (1:1 mole) for different time intervals.

These experiments (CHAPTER 4, Fig. 4.4.2a,b) showed a definite and clean break in the plots suggested by Edelstein as a diagnostic test for the nonmonotonous behaviour of a reaction.

On the basis of compositional and DTA studies the period of oscillations was found to be about 10 and 20 minutes respectively. A large number of reactions are proposed as under for this behaviour:

\[
\begin{align*}
\text{CoBr}_2 + \frac{1}{2} \text{O}_2 & \rightarrow \text{CoO} + \text{Br}_2 \\
\text{CoO} + \frac{1}{6} \text{O}_2 & \rightarrow \frac{1}{3} \text{Co}_3\text{O}_4 \\
\text{CoO} + \text{Br}_2 & \leftrightarrow \text{CoOBr} + \frac{1}{2} \text{Br}_2 \\
\text{Co}_3\text{O}_4 + \text{Br}_2 & \rightarrow \text{CoBr}_2 + \text{CoO} + \frac{3}{2} \text{O}_2 \\
\text{or} & \\
& \rightarrow \text{CoOBr} + \frac{1}{2} \text{CoBr}_2 + \frac{3}{2} \text{CoO} + \frac{3}{4} \text{O}_2 \\
\text{CoOBr} + \frac{1}{6} \text{O}_2 & \rightarrow \frac{1}{3} \text{Co}_3\text{O}_4 + \frac{1}{2} \text{Br}_2
\end{align*}
\]
The specie, CoOBr, is proposed to be responsible for autocatalytic behaviour. Reactions (1) and (2) are assumed to be irreversible. Reactions (3), (5) and (6) are reversible and the reaction (4) is taken as the main reaction which keeps itself far from equilibrium.

Further, it was found that the amplitude and period of oscillations diminished rapidly, under the present experimental conditions. (CHAPTER 2 and 4). This ascertains the hypothesis that partial pressures of bromine and oxygen are deciding factors in this system.

8. In CHAPTER 3, similar nonmonotonous behaviour for the reaction,

\[
\text{CoCl}_2 + \frac{1}{6} \text{O}_2 \rightleftharpoons \frac{1}{2} \text{Co}_3\text{O}_4 + \text{Cl}_2
\]

was predicted. A sharp break in the range 70 to 80 % V/V chlorine in oxygen (CHAPTER 3, Fig. 3.4.5) was clearly indicative of oscillatory behaviour. However, such a high chlorine concentration was impossible to obtain under the present experimental conditions (CHAPTER 2, and 3).

In general it could be said here that under the critically controlled reaction conditions, a given solid-gas reaction could be made non-monotonous if intermediates involving variable oxidation states (or electron transfer reactions) could be sought.

These are the salient features of the present investigations.