CHAPTER II

Thermogravimetric analyses of the complexes
Thermogravimetric analyses of complexes of Cobalt(II) and Copper(II) haloacetates with oxygen donor ligands

Thermogravimetry is a useful tool in studying the thermal stability of the complexes and to know the different stages in their thermal decomposition. The complexes of cobalt(II) and copper(II) haloacetates under investigation decompose on heating and, therefore, thermogravimetric analyses of some of the complexes has been carried out. The thermogravimetric (T.G.) and differential thermogravimetric (D.T.G.) curves have been plotted against temperature (°C) which reveal that at temperatures below 100°C, these complexes do not show any loss in weight. All these complexes produce metal oxides (tga is done in presence of air) as their final product of thermal decomposition which have been analysed quantitatively in each case. Different intermediates have been postulated merely on the basis of the weight changes noted from the T.G. and D.T.G. curves and the analytical evidence of their compositions could not be obtained because of their unstable nature. Thus, the formulations of the intermediates have not been ascertained unambiguously and the possibility of some different type of intermediates cannot be ruled out. The mode of thermal decomposition of the present complexes may depend upon the nature of metal haloacetate and that of the ligand attached. However, metal carbonate seems to be one of the most probable intermediates in some of the cases which further decomposes to give the oxide. The

† Thermograms of some of the complexes are shown in figures.
Thermogravimetry of each complex is being dealt with separately.

(i) Thermal decomposition of \( \text{Co(CH}_2\text{ClCO}_2 \text{)}_2 \cdot \text{B-pic-0} \) (where \text{B-pic-0} stands for B-picoline-N-oxide)

This complex is stable up to 110°C and starts decomposing intensively beyond 110°C. The weight corresponding to one ligand molecule is lost at 200°C, where the formation of pure copper(II) carboxylate has been postulated, which further loses more weight and changes into \( \text{Co}_3\text{O}_4 \) at 640°C.

(ii) Thermal decomposition of \( \text{Co(CHCl}_2\text{CO}_2 \text{)}_2 \cdot \text{B-pic-0} \) (where \text{B-pic-0} stands for B-picoline-N-oxide)

It is evident from the T.G. and D.T.G. curves that the complex is stable up to 120°C and the formation of pure carboxylate is indicated at 290°C. The latter decomposes immediately giving a stable oxide, viz., \( \text{Co}_3\text{O}_4 \) at 640°C.

(iii) Thermal decomposition of \( \text{Co(CCl}_3\text{CO}_2 \text{)}_2 \cdot \text{Y-pic-0} \) (where \text{Y-pic-0} is Y-picoline-N-oxide)

This complex remains stable up to 80°C and starts losing weight thereafter. At 250°C, there is a sudden loss in weight with the formation of an unstable intermediate bearing no definite composition. The decomposition continues and the D.T.G. curve reveals the formation of another intermediate at 570°C which decomposes immediately after its formation and the stable oxide, \( \text{Co}_3\text{O}_4 \) is obtained at 670°C.

(iv) Thermal decomposition of \( \text{Co(CF}_3\text{CO}_2 \text{)}_2 \cdot \text{2DMU} \) (where DMU stands for dimethylurea)

This complex starts losing weight at 110°C and from the
THERMAL DECOMPOSITION OF Co(CH₂ClCO₂)₂ β-pic-O.
weight loss an intermediate, CoCO$_3$, is predicted at 215°C which remains nearly stable up to 320°C. At 320°C, CoCO$_3$ starts losing weight and a constant weight is obtained beyond 400°C which corresponds to the compound Co$_3$O$_4$.

(v) Thermal decomposition of Cu(CH$_2$ClCO$_2$)$_2$·TPPO (where TPPO stands for triphenylphosphine oxide)

This complex appears to be comparatively more stable and its thermal decomposition starts at 200°C. A highly unstable intermediate with the possible formula as Cu(CH$_2$Cl)$_2$·TPPO appears to have been formed at 275°C which changes into another unstable intermediate, the composition of which could not be postulated. At 560°C, another unstable compound, Cu(CH$_2$Cl)$_2$ appears to have been formed which changes into the stable oxide, CuO at 750°C.

(vi) Thermal decomposition of Cu(CHCl$_2$CO$_2$)$_2$.2DMA (where DMA stands for dimethylacetamide)

The complex is stable up to 120°C and loses weight at 185°C corresponding to one ligand molecule with the formation of an unstable intermediate, Cu(CHCl$_2$CO$_2$)$_2$.DMA. The latter forms the end product, CuO, at 750°C.

(vii) Thermal decomposition of Cu(CHCl$_2$CO$_2$)$_2$.2$\beta$-pic-0 (where $\beta$-pic-0 is $\beta$-picoline-N-oxide)

The T.G. and D.T.G curves reveal that it starts decomposition at 170°C and the weight corresponding to one ligand molecule occurs at 236°C where the formation of an unstable compound, Cu(CHCl$_2$CO$_2$)$_2$.$\beta$-pic-0 is depicted. The latter changes into another highly unstable intermediate, Cu(CHCl$_2$)$_2$ at 246°C which
THERMAL DECOMPOSITION OF Co(CF₃CO₂)₂.2DMU
THERMAL DECOMPOSITION OF Cu(CHCl₂CO₂)₂·2DMA.

![Graph showing thermal decomposition of Cu(CHCl₂CO₂)₂·2DMA.](image-url)
forms the stable oxide at 520°C through the formation of CuCO$_3$ at 280°C.

(viii) Thermal decomposition of Cu(CCl$_3$CO$_2$)$_2$.2DMU (where DMU stands for dimethylurea)

The T.G. and D.T.G. curves of this complex reveal that the complex is stable upto 100°C. In the temperature range 100-130°C, there is intensive loss in weight and the formation of the unstable compound Cu(CCl$_3$)$_2$ is predicted at 130°C. The compounds of the type M(CCl$_3$)$_2$ (where M = Hg) have already been isolated by decarboxylation reactions (123) which lend a support to the intermediate, Cu(CCl$_3$)$_2$ postulated in the present complex. An unsuccessful attempt has been made to isolate Cu(CCl$_3$)$_2$ by heating the complex at 130°C, which indicates that this intermediate is fairly unstable. The T.G. curve further indicates that Cu(CCl$_3$)$_2$ decomposes into CuCO$_3$ at 260°C which continues losing its weight and stable oxide CuO is obtained at 580°C.

(ix) Thermal decomposition of Cu(CF$_3$CO$_2$)$_2$.2DMA (where DMA is dimethylacetamide)

The T.G. and D.T.G. curves of this complex show that the complex starts decomposing at 120°C and an unstable intermediate, CuCO$_3$, is postulated at 315°C which forms stable cupric oxide (CuO) at 490°C.

(x) Thermal decomposition of Cu(CF$_3$CO$_2$)$_2$.2*pic-0 (where *pic-0 stands for *picoline-N-oxide)

As evident from the T.G. and D.T.G. curves, the complex remains stable upto 180°C and at 250°C the weight loss corresponds to one ligand molecule, where the formation of compound,
THERMAL DECOMPOSITION OF Cu(CCl₃CO₂)₂·2DMU.
Cu(CF_3CO_2)_2·α-pic-0 is postulated. The latter decomposes immediately and another labile intermediate appears to be formed at 285°C from the weight loss at a stage where the decomposition becomes nearly constant for some time, and in this case, the such intermediate is Cu(CF_3)_2. Such a compound could not be isolated even on heating the complex at the temperature where the constant weight occurs in T.G. graph because of the possibility of its instantaneous decomposition immediately after its formation. However, in the literature, there are some reports of the formation of the compounds M(CF_3)_2 (where M = Hg) (124) and M(CF_3)_2·L (where M = Hg, and L = bipyridyl) (125) which have been obtained by thermal decomposition of the compounds of the type Cu(CF_3CO_2)_2 and Cu(CF_3CO_2)_2·L, respectively, and these do support the present proposed unstable intermediate. The intermediate, Cu(CF_3)_2 forms the stable end product, CuO at 600°C.