Thermogravimetric and differential thermal analysis of bipyridyl, ortho-phenylenediamine and 1,10 phenanthroline complexes of some Cu(II) salts

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Dynamic TGA and DTA studies on thermal decomposition of coordination complexes of bipyridyl, ortho-phenylenediamine and 1,10 phenanthroline with Cu(II) chloride, nitrate, sulphate, acetate and oxalate reveal that the process occurs through the stages: liquefaction, dehydration, deamination, deamination and oxidation of Cu. All the steps are composite in nature consisting of simultaneous loss of the component moieties in varying proportions and the related ΔHs and Eas are significantly dependent on the nature of the co-anions and ligands.

The thermogravimetric and differential thermal analysis (TGA and DTA) study on co-ordination complexes of aliphatic bidentate amines [ethylene diamine (en) and tetramethyl-ethylenediamine (tmn)] with some Cu(II) and Ni(II) salts has shown their thermal decomposition process to depend on the type of co-anions. The results of further study on similar complexes of aromatic and heterocyclic amines [o-phenylene diamine (opd), 1,10-phenanthroline (phen) and bipyridyl (bpy)] with a number of Cu(II) salts with co-anions of inorganic type (chloride, nitrate and sulphate) as well as of organic type (acetate and oxalate), which have shown the thermal decomposition process to depend on the type of co-anions and that of the ligands, are presented herein.

Experimental
The desired complexes were prepared by treating various Cu(II) salts with opd, phen and bpy in aqueous alcoholic media as described earlier. Commercially available AR grade Cu(II) chloride, nitrate and sulphate were employed for preparing the complexes with inorganic co-anions, while the Cu(II) acetate and oxalate, first obtained by treating Cu(II) carbonate with acetic and oxalic acids as described earlier, were employed for those with organic co-anions.

The products were analysed for % weights of various elements by estimating C and H by microanalysis, N as the total and amine nitrogens, Cl as chloride, S as sulphate and Cu by iodometry. The molecular formulae were subsequently deduced by comparing the observed % weights with the respective ones calculated by assuming different possible metal-to-ligand ratios (1:1, 1:2, etc.) and probable numbers of crystal water molecules (0, 0.5, 1, 2, etc.). The electronic and infrared absorption spectra (in the form of methanolic solutions and nujol/HCB mulls) were examined to understand the geometry of the complex cations and the nature of co-ordination of the co-anions respectively.

The TGA and DTA measurements were performed on home-built equipment in air atmosphere over 25-800°C (heating rate 3°C/min) as described in the earlier work. In accordance with the normal practice, the steps in TGA curves were identified by finding the best fits of the observed % mass losses with those calculated on the assumed losses of probable moieties (cf. Table 1). Peaks in DTA curves were likewise ascribed to the probable processes in the respective temperature ranges (cf. Table 2). The activation energies (Ea) for the processes corresponding to the major steps in various TGA curves were estimated by fitting the degree of dissociation (α) over the respective temperature ranges to equations by Coats and Redfern, Horowitz and Metzger and Piloyan and Novikava. The related most probable mechanisms were deduced as illustrated in our earlier work. The enthalpy changes (ΔH) for various processes were estimated by employing the relation, ΔH = (k/m)A, where k, m and A refer to the instrument calibration constant, mass of the substance and the corresponding peak area (evaluated by graphical integration) in the DTA curve respectively.

Results and discussion
The results of elemental analysis indicate 1:1 metal-to-ligand ratio for the bpy complex of Cu(II) oxalate and bis nature (i.e. 1:2 ratio) for all the remaining ones. The opd and bpy complexes of Cu(II) nitrate and bpy complex of Cu(II) chloride are
Table 1—TGA data on the bpy, opd and phen complexes of Cu(II) salts

| Complex                        | Step | Temp. range/°C | % wt loss obs. (cal.) | Probable composition of expelled groups/s | E_i/(kJ/mol) | M
|--------------------------------|------|----------------|-----------------------|-------------------------------------------|--------------|-------
| [Cu(bpy)]_2(NO_3)_2             | 1    | 280-300        | 73.0 (73.2)           | 2 bpy + 0.5 N_2O_3                          | 1527         | R_2
| [Cu(bpy)]_2Cl_2                 | 2    | 320-410        | 8.0 (10.8)            | 0.5 N_2O_3                                 | 308          | R_2
| [Cu(bpy)]_2SO_4·2H_2O           | 1    | 75-210         | 16.3 (16.3)           | 2 bpy + 0.3 bpy                             | 85           | A_2
|                                | 2    | 250-550        | 68.7 (68.0)           | (1.7 bpy + SO_4)                           | 124          | D_3
| [Cu(bpy)]_2(ac)_3H_2O S         | 1    | 30-075         | 4.50 (4.9)            | 1.5 H_2O                                   | 148          | R_4
|                                | 2    | 80-300         | 67.5 (67.3)           | 1.5 H_2O + 2 bpy + 0.5 ac                  | 37           | F_1
|                                | 3    | 310-500        | 15.0 (13.2)           | (1.5 ac - O) #                             | 120          | D_3
| [Cu(bpy)]_2(ox)_2·0.5H_2O       | 1    | 150-250        | 75.0 (74.8)           | 0.5H_2O + bpy + CO_2 + CO                  | 387          | R_7
| [Cu(opd)]_2(NO_3)_2             | 1    | 190-210        | 51.0 (53.5)           | 2 opd                                      | 1031         | 670
|                                | 2    | 270-380        | 26.0 (26.7)           | N_2O_3                                     | 116          | 73
| [Cu(opd)]_2SO_4·H_2O            | 1    | 40-520         | 79.5 (79.8)           | 1H_2O + 2 opd + SO_3                      | 20           | 18
| [Cu(phen)]_2(NO_3)_2·2H_2O      | 1    | 80-210         | 62.5 (6.2)            | 2 H_2O                                     | 10           | 22
|                                | 2    | 210-400        | 79.8 (80.1)           | 2 phen + N_2O_3                           | 470          | 353
|                                | 3    | 400-750        | 35.5 (34.1)           | (0.7 phen + Cl_2) - 2 O #                  | 64           | 43

#: -ve sign for O lost = uptake of atmospheric O. $: ac = (CH_3COO)_2$, ox = (COO)_2.
$^*$: M = mechanisms: D_1: One-dimensional diffusion, D_2: Three-dimensional diffusion (spherical symmetry), R_2: Phase boundary reaction (contracting area, cylindrical symmetry), A_2: Random nucleation (Avrami eqn, n =2), F_1: Random nucleation (first order).
ligand and/or the metal sulphate moieties\(^{27}\). TGA curves for the bpy complexes of Cu(II) chloride and acetate, and phen complex of Cu(II) chloride exhibit a small hump (increase in weight) associated with oxidation of Cu by uptake of atmospheric oxygen\(^{28}\). The TGA curves for the complexes of Cu(II) nitrate and sulphate, however, do not exhibit such humps indicating the oxidation of Cu in the latter cases occurring by intrinsic oxygen available from decomposition of the respective co-aniions\(^{27}\).

Thermal decomposition of these complexes thus gives rise to TGA steps involving simultaneous loss of more than one type of moieties in nearly continuous manner and correspondingly, multiple peaks in DTA. These processes and their characteristics are summarised as:

- liquefaction \(\rightarrow\) dehydration\(^*\) \(\rightarrow\) deamination \(\rightarrow\) oxidation of Cu
- deamination \(\rightarrow\) dehydration

\(^*\): in case of hydrated complexes.

Due to composite nature of the processes; the \(E_a\), \(\Delta H\) and mechanisms deduced on the basis of TGA steps and DTA peaks (Tables 1 and 2) would be applicable only to the overall processes and not to any individual constituent. However, some generalisations are apparent as noted below:

In majority of the cases, the \(\alpha\)-values show reasonably good linear fit to Coats-Redfern\(^{11}\) equation with \(n = 2\), suggesting the underlying processes to be approximately of two dimensional in nature. The \(E_a\) based on Horowitz-Metzger\(^{12}\) equation are comparable within \(\pm 5\) to \(10\%\) with the former ones for similar values of \(n\). The \(E_a\) based on Piloyan-Novikava\(^{13}\) equation, which does not involve an assumption of the order of a reaction, are considerably smaller.

A physical phase change like liquefaction does not cause weight loss steps in TGA but is characterised by sharp, endothermic peaks in DTA. The dehydration process (usually accompanied by expulsion of some ligand and anionic moieties) is generally slow exhibiting broad and weak steps in TGA and endothermic peaks in DTA. The low temperatures and...
small $E_a$s for dehydration are indicative of loose binding of crystal water molecules ascribable to crowding at the central Cu(II) ion. The dehydration steps of bpy complexes of Cu(II) nitrate and oxalate, and phen complex of Cu(II) chloride fit to the phase boundary reaction (contracting area) cylindrical symmetry mechanism ($R_2$). The deamination process occurs over a short temperature interval resulting in steep steps in TGA. The higher temperature for the loss of bpy and phen ligands (~200°C) than that for opd (~300°C) is suggestive of stronger coordination of the former. Deamination of complexes containing organic co-anions occurs at considerably lower temperature (~200°C) than that of complexes with inorganic co-anions (~300°C). The $E_a$ and $\Delta H$ for the loss of bpy, phen and opd ligands are higher than those for the loss of en and tmn from similar complexes\(^1\), which is attributable to stronger coordination of the former type of ligands because of their planarity and rigidity. The deamination steps of opd and phen complexes of Cu(II) nitrate and bpy complexes of Cu(II) nitrate, chloride and oxalate fit to the phase boundary reaction cylindrical symmetry ($R_2$) mechanism. The deamination process, almost always accompanied by oxidation of the liberated Cu, is generally quite slow, resulting in considerably weak steps in TGA and broad peaks in DTA. The $E_a$ for the loss of nitrate ion is generally larger than that for chloride and sulphate ions. In case of complexes containing organic co-anions, the $E_a$ for loss of an oxalate ion is generally higher than that for acetate ion, attributable to stronger bonding of the former due to its chelating nature. The deamination process of the opd and bpy complexes of Cu(II) nitrate and bpy complex of Cu(II) chloride fit to the $R_2$ mechanism, while that of the bpy complex of Cu(II) acetate and phen complex of Cu(II) chloride fit to the three dimensional diffusion (spherical symmetry) mechanism ($D_3$). Because of the lack of distinct steps in TGA or peaks in DTA for the process of oxidation of Cu, the related $\Delta H$s, $E_a$s and mechanisms could not be deduced.

The present study confirms that, the course of thermal decomposition of coordination complexes and the related thermodynamic and kinetic parameters depend significantly on the nature of the co-anions as well as that of ligands. This can be attributed to their influence on the geometry of the complex cation and crystal packing in solids.

References