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TGA and DTA studies on en and tmn complexes of Cu(II) chloride, nitrate, sulphate, acetate and oxalate

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Abstract

Dynamic thermogravimetric and differential thermal analysis (TGA and DTA) of ethylenediamine (en) and tetramethylethylenediamine (tmn) complexes of a number of Cu(II) salts (chloride, nitrate, sulphate, acetate and oxalate) have been carried out. The thermal decomposition of these complexes occurs in steps involving dehydration, deamination and deanionation processes. However, majority of the weight loss steps in TGA are found to be composite in nature involving simultaneous loss of the component moieties in varying proportions. The ΔH and E_a values for various steps are deduced and the observed trends are analysed in terms of the nature of the processes underlying the steps and the differences in the nature of co-ordination of the ligands and/or the stereochemistry exhibited by the counter anions about the Cu(II) ion in the complex.

Keywords: Thermogravimetric analysis (TGA); Differential thermal analysis (DTA); Ethylenediamine (en); Tetramethylethylenediamine (tmn)

1. Introduction

It is well-known that a reaction of Cu(II) with bidentate ligands such as ethylenediamine (en) and tetramethylethylenediamine (tmn) gives well-defined crystalline complexes. Attempts to measure the electrical conductivity of such complexes in solid state at higher temperatures exhibited a number of discontinuities, indicating structural phase changes on their heating. In order to understand the nature of the changes involved; thermogravimetric and differential thermal analysis (TGA and DTA) of a few Cu(II) and Ni(II) amine complexes had been carried out and the preliminary results reported in our earlier papers [1,2]. Since then a detailed study [3] of TGA and DTA of a variety of amine complexes of different Cu(II) salts was undertaken. The results on en and tmn complexes of Cu(II) nitrate, chloride, sulphate, acetate and oxalate are found to lead to an understanding of the roles of the ligand and the counter anion in determining the nature of thermal decomposition of such complexes and being reported here in view of general interest. Reports [4–6] on thermal analysis of some of the systems studied in the present work dealing with certain limited aspects are found in literature which are duly referred to at appropriate stages in the discussion part.

2. Experimental

2.1. Preparation

The various Cu(II)-amine complexes were prepared by treating the aqueous alcoholic solutions of

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CuX_2 [$X = Cl^-$, NO_3^-, $0.5(SO_4^{2-})$, CH_3COO^- and $0.5(COO^-)_2$] with those of en and tmn by following the standard procedures [7–19]. Commercially available AR grade ligands (en and tmn) and the Cu(II) salts (nitrate, chloride and sulphate) were used after distillation and recrystallisation from distilled water, respectively. The Cu(II) acetate and oxalate required were prepared from Cu(II) carbonate by treatment with the respective carboxylic acids. The resulting solid complexes were recrystallised from aqueous methanol, thoroughly dried and stored in a vacuum desiccator over P_2O_5.

2.2. Characterisation

The percentage weights of various elements (C, H, N and O) in all the complexes were first determined on the basis of elemental microanalysis (C and H), estimation of nitrogen as the total and amine nitrogens, chlorine as chloride and sulphur and oxygen as sulphate by following standard procedures [20]. for determining their empirical/molecular formulae. The complexes were further examined by their infrared and electronic absorption spectra (in the form of their nujol mulls and methanolic solutions) to understand the nature of co-ordination of the ligands and the stereochemistry about the central Cu(II) ion, respectively.

2.3. Thermal analysis

The TGA and DTA measurements were carried out on home-built equipments in air atmosphere at a constant heating rate of 3 °C/min over temperature range of 25–700 °C using 60–70 mg and ~100 mg of the samples for TGA and DTA, respectively in quartz or ceramic crucibles. The thermobalance was appropriately standardised by running a thermogram on an empty crucible so as to correct for the air buoyancy effect as well as by measurements on recrystallised samples of $CaC_2O_4 \cdot H_2O$ and $CuSO_4 \cdot 5H_2O$ which are recommended as the reference substances [21]. Similarly, the DTA equipment was standardised by first-blank measurements on finely powdered (200–250 mesh) AR grade MgO followed by measurements on several recommended samples [22], using the same MgO as the reference.

3. Results and discussion

3.1. Characterisation

The observed percentage weights of various elements were fitted with those calculated on the basis of different possible metal to ligand stochiometries (1:1; 1:2, etc.) together with probable numbers of water molecules of crystallisation (0, 0.5, 1, 2, etc.) for deducing the molecular/empirical formulae of the complexes. The molecular formulae so obtained (Tables 1 and 2) indicate that all of the present complexes exhibit 1:2 (metal:ligand) stoichiometry except the tmn complex of Cu(II) chloride which appears in dimeric form with 1:1 stoichiometry. The en complexes of Cu(II) nitrate and sulphate and tmn complexes of Cu(II) chloride and acetate are anhydrous while the remaining ones appear as hydrated to different extents. These features as well as the infrared and electronic spectral data on the complexes are in good agreement with the reported [24–27] ones on similar complexes and are indicative of a distorted octahedral symmetry of the complex cation with the four *N* atoms from two ligand molecules forming a square planar arrangement around the central Cu(II) ion.

3.2. Thermograms

The experimentally determined TGA and DTA curves for all the 10 complexes are presented in Figs. 1 and 2 and briefly described below. (cf. Tables 1 and 2).

The observed percentage weight losses corresponding to various steps in all the TGA curves were compared with those calculated on the assumption of possible compositions of the expelled groups [21,28,29], and those showing the best agreement with the former are incorporated in Table 1. These TGA patterns indicate that the thermal decomposition of these complexes broadly involves three stages; viz dehydration (in case of hydrated ones), deamination and deanionation. The dehydration process is generally found to spread over somewhat large temperature intervals resulting in broad steps; while the deamination steps in practically all the cases are quite steep ranging over an interval of only a few °C. In all the cases, the last steps comprising of deanionation with

Table 1
TGA data on the en and tmn complexes of various Cu(II) salts[a]

Complex	Step	Temperature range (°C)	Percentage weight loss observed (calculated)	Probable composition of expelled group/s	E_a (kJ/mol)[b]		Mechanism
					CR	HM	
$Cu(en)_2(NO_3)_2$	1	220–550	90.0 (74.3)	$en_2 + N_2O_5$	1438	1451	R_2
$Cu(en)_2Cl_2.H_2O$	1	90–180	6.5 (6.6)	H_2O	197	211	R_2
	2	190–275	21.5 (22.0)	en	133	158	R_2
	3	280–370	21.5 (22.0))	en	164	205	R_2
	4	375–580	28.5 (20.2	$Cl_2 - O^*$	95	128	R_2
$Cu(en)_2SO_4$	1	150–330	67.5 (67.0)	$2en + 0.70SO_4$	143	182	F_1
	2	350–600	3.0 (4.5)	$0.30SO_4$	169	188	R_2
$Cu(en)_2(CH_3COO)_2{\cdot}H_2O$	1	75–140	14.0 (14.1)	$H_2O + 0.4en$	117	127	R_2
	2	140–205	39.0 (38.3)	$1.6en + 0.5CH_3COO$	117	146	R_2
	3	205–450	25.5 (22.7)	$(1.5CH_3COO)-O^*$	36	59	D_3
$Cu(en)_2(COO)_2{\cdot}1.5H_2O$	1	160–260	65.0 (64.0)	$1.5H_2O + 2en + CO_2$	409	234	R_2
	2	270–700	9.0 (9.3)	CO	28		R_2
$Cu(tmn)_2(NO_3)_2{\cdot}3H_2O$	1	100–120	8.3 (8.5)	$2.25H_2O$	191	202	D_2
	2	150–360	64.0 (74.5)	$0.75H_2O + 2tmn + N_2O_5$	114	140	R_2
$[Cu(tmn)Cl_2]_2$	1	60–230	26.5 (26.6)	1.15tmn	54	63	F_1
	2	230–425	27.5 (26.8)	$0.85tmn + 0.5Cl_2$	79	98	R_2
	3	425–520	15.5 (14.9)	$(1.5Cl_2) - 2O^*$	386	406	R_2
$Cu(tmn)_2SO_4{\cdot}4H_2O$	1	50–210	28.5 (28.0)	$4H_2O + 0.5tmn$	41	62	R_2
	2	210–290	52.0 (52.0)	$1.5tmn + 0.70SO_4$	232	268	F_1
	3	290–420	9.5 (2.8)	$0.30SO_3$	159	179	D_4
$Cu(tmn)(CH_3COO)_2$	1	100–190	29.5 (29.3)	0.75tmn	94	118	D_3
	2	200–400	46.5 (44.0)	$(0.25tmn + 2CH_3COO) - O^*$	842	906	R_2
$Cu(tmn)(COO)_2{\cdot}0.5H_2O$	1	55–120	3.0 (3.25)	$0.5H_2O$	107	121	R_2
	2	120–370	70.0 (68.0)	$(tmn + 2CO_2) - O^*$	763	778	D_1

[a] Negative sign (−): gain in weight due to atmospheric oxidation of metallic Cu; CR: Coats and Redfern; HM: Horowitz and Metzager; D_1: one-dimensional diffusion; F_1: random nucleation; D_2: two-dimensional diffusion, cylindrical symmetry; F_2: random nucleation Avarmi Equation I ($n = 2$); D_3: three-dimensional diffusion, spherical symmetry Jander Equation; R_2: phase boundary reaction, contracting area cylindrical symmetry; D_4: three-dimensional diffusion spherical symmetry Ginstling and Brounstein Equation; R_3: phase boundary reaction contracting volume spherical symmetry; A_3: random nucleation Avarmi Equation II ($n = 3$).

[b] E_a (kJ/mol) refer to per mole of the complex decomposed.

simultaneous oxidation Cu to CuO are found to be very broad in nature. However, in majority of the cases, all these steps are not generally isolated but overlap to varying extents and frequently result in fractional losses of the constituent moieties. The DTA curves of all these complexes exhibit a weak and somewhat broad endothermic peak in the lower temperature region just prior to or accompanying the first weight loss step in the corresponding TGA curve. Since the latter corresponds to the loss of crystal water (in case of the hydrated complexes) or the ligand (in case of anhydrous complexes); the endothermic nature of these DTA peaks implies some kind of phase change associated with an absorption of the required latent heat. The DTA peaks corresponding to the dehydration steps in TGA are found endothermic and broad, while those for deamination, deanionation and conversion of metallic Cu to CuO processes are all exothermic in nature. However, there is no distinct peak corresponding to the last process of oxidation of metallic Cu to CuO since it occurs almost simultaneously with the deanionation process. The TGA steps corresponding to deamination involving sudden weight loss are accompanied by relatively sharp peaks in DTA. In case of the DTA peaks corresponding to the phase change of a complex prior to any actual dissociation, the TGA curves obviously exhibit no weight loss steps. In all the cases, the DTA peaks for the Cu to CuO process are rather weak and spread over a wide temperature range (~300–600 °C). The TGA plot of

Table 2
DTA data on the en and tmn complexes of various Cu(II) salts[a]

Complex	Peak	Temperature range (°C)	Peak temperature (°C)	Nature of peak	ΔH (kJ/mol)	E_a (kJ/mol)
$Cu(en)_2(NO_3)_2$	1	30–115	65	endo, br	173	10
	2	190–400	240 and 370	exo, br, s	328	206
$Cu(en)_2Cl_2 \cdot H_2O$	1	100–290	230	exo, br, s	149	143
	2	290–580	470	exo, br	158	20
$Cu(en)_2SO_4$	1	110–250	190	exo, br	90	37
	2	250–450	375	exo, br, s	795	83
$Cu(en)_2(CH_3COO)_2 \cdot H_2O$	1	30–150	125	endo, br	249	22
	2	150–550	210 and 400	exo, br	1550	50
$Cu(en)_2(COO)_2 \cdot 1.5H_2O$	1	150–450	240	exo, s	925	84
$Cu(tmn)_2(NO_3)_2 \cdot 3H_2O$	1	30–90	75	endo, br	656	30
	2	170–370	205	exo, br, s	1588	351
$[Cu(tmn)Cl_2]_2$	1	30–100	65	endo, br	115	30
	2	100–270	160	exo, br, s	693	64
	3	340–580	425	exo, br	822	44
$Cu(tmn)_2SO_4 \cdot 4H_2O$	1	30–120	115	endo, br, s	235	23
	2	150–500	290	exo, br	565	13
$Cu(tmn)(CH_3COO)_2$	1	180–190	185	endo, s	16	706
	2	190–470	220	exo, br, s	529	139
$Cu(tmn)(COO)_2 \cdot 0.5H_2O$	1	30–110	100	endo, br	72	26
	2	120–470	220 and 420	exo, s	893	83

[a] Exo: exothermic; endo: endothermic; br: broad; s: sharp.

the en complex of Cu(II) nitrate exhibits a steep step accompanied by sudden weight loss. This appears to be due to a chain type highly explosive reaction because of simultaneous presence of an oxidising group (NO_3) and a reducing group (en) in the same complex molecule. Similar explosive effect [30,31] is reported in the case of thermal decomposition of some amine complexes of Ni(II) nitrate. All these observations are in close agreement with those reported in literature [32].

3.3. Determination of thermodynamic parameters and probable mechanisms

A quantitative study of these thermograms was taken up to deduce the enthalpy change (ΔH) and activation energy (E_a) related to various decomposition steps. For this purpose, the observed degrees of decomposition (α) at various temperatures corresponding to each of the steps in the TGA curves were fitted to the Coats and Redfern (CR) [33] and Horowitz and Metzager (HM) [34] equations as described in standard texts [35,36]. The α values were calculated on the basis of molecular weights corresponding to monomeric forms of the complexes except that for the tmn complex of Cu(II) Chloride which appears in a dimeric form. The differential method [23], in which the data are collected from the medium steep part of the TGA curves, was employed for better accuracy. The values of the left hand sides of respective equations were plotted against $1/T$ for various assumed values of n; and the most appropriate value of n was chosen which corresponds to the graph giving the best straight line (correlation coefficient $r > 0.99$) and the respective slope was employed to obtain the E_a. Similar procedure for evaluation of kinetic parameters has been applied by a number of other workers [38].

The data on the fraction decomposed (i.e. the degree of dissociation α) at various temperatures (T) corresponding to a step in a TGA curve can be used to deduce the probable mechanism underlying the respective reaction by using different relations based on alternative reaction mechanisms [39]. The quantity $-\log(g(\alpha))$ appearing in various equations is plotted as a function of $1/T$ and the relation leading to the best linear fit is taken to correspond to the most probable mechanism [40]. As an illustration, such plots for the dehydration step of $Cu(en)_2Cl_2 \cdot H_2O$ based on several relationships are presented in Fig. 3. The mechanisms

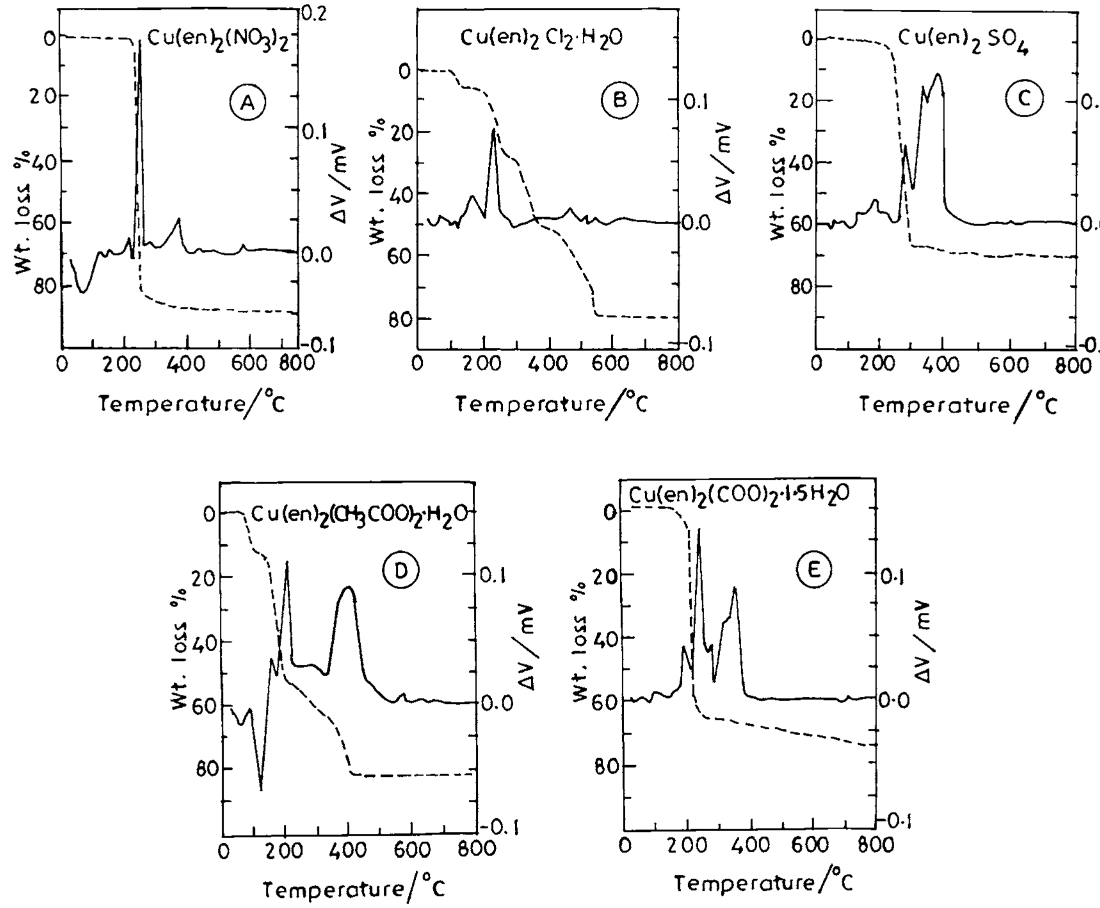

Fig. 1. Thermograms of en complexes of Cu(II) salts. TGA (- - -); DTA (—).

for thermal decomposition corresponding to the major steps in TGA curves for all the complexes so deduced are incorporated in Table 1 where the symbols A, D, F and R with subscripts 1,2 and 3 have usual meaning as explained in standard texts [35,36]. The calculations involved in all the above-referred fittings were carried out on the basis of computer programs suitably developed [38] in the Turbo Basic Advanced computer language.

DTA is also a convenient technique for estimating the E_a and ΔH involved in thermal decomposition reactions [37]. The ΔH for a particular process is given by the relation [41,42], $\Delta H = (k/m)A$, where $A(= \int \Delta T\,\mathrm{d}T)$, k and m are the area of the corresponding peak in a DTA curve; calibration constant and mass of the sample, respectively. The E_a is given by the equation [23] $\mathrm{d}\alpha/\mathrm{d}t = A(1-\alpha)^n\,\mathrm{e}^{-E/RT}$. The E_a and ΔH values corresponding to major peaks in DTA curves of all the complexes deduced by employing these relations are presented in Table 2.

The analysis of the observed thermograms and the ΔH and E_a associated with various steps leads to some generalisations as follows.

The thermal decomposition processes underlying the TGA and the nature of the steps observed in the DTA of these complexes can be schematically represented, respectively as

$$\mathrm{CuL_2X_2\cdot}n\mathrm{H_2O}\ \underset{\text{dehydration}}{\overset{-x\mathrm{H_2O}}{\longrightarrow}}\ \mathrm{CuL_2X_2}\ \underset{\text{deamination}}{\overset{-y\mathrm{L}}{\longrightarrow}}$$

$$\mathrm{CuX_2}\ \underset{\text{deanionation and oxidation}}{\overset{-z\mathrm{X}+\mathrm{O}}{\longrightarrow}}\ \mathrm{CuO}, \qquad (1)$$

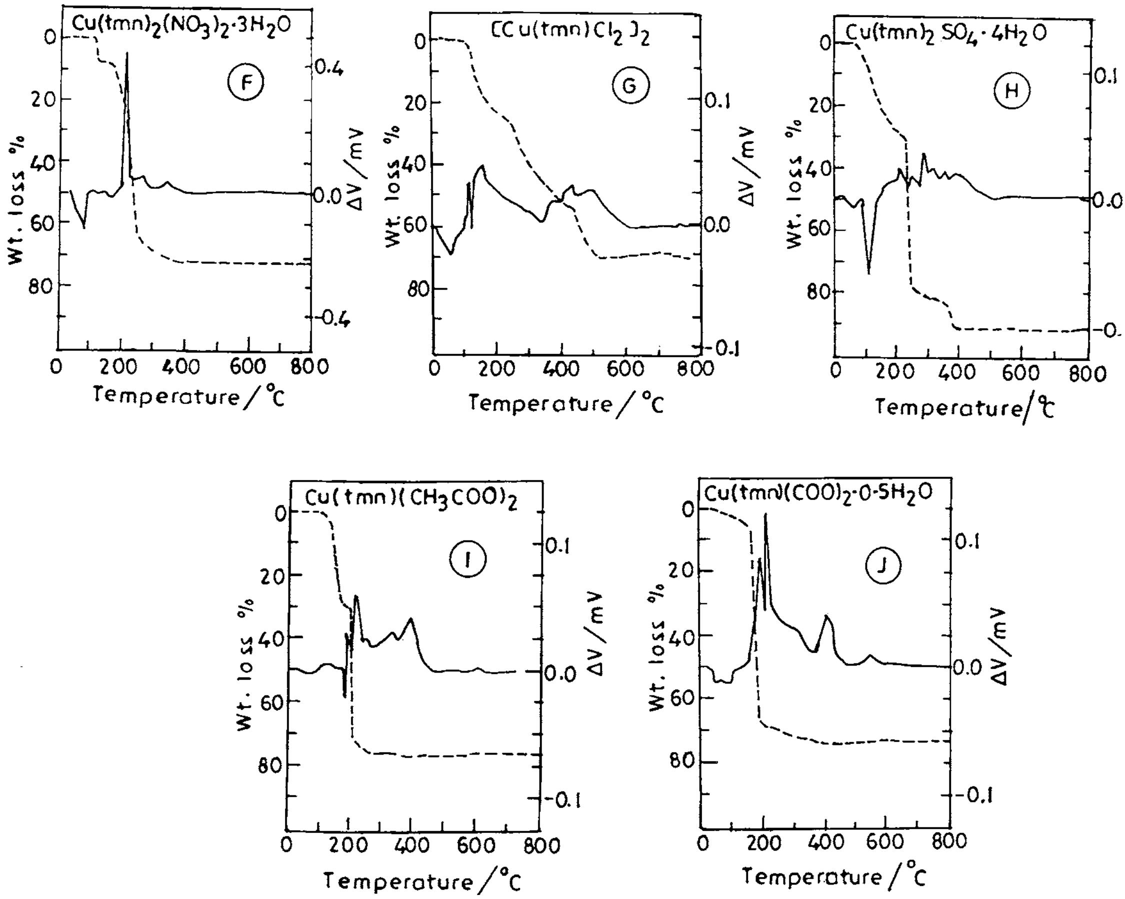

Fig. 2. Thermograms of tmn complexes of Cu(II) salts. TGA (- - -); DTA (—).

where x, y and z represent the appropriate numbers of respective species expelled in various decomposition steps; and

$$\underset{\text{(endothermic)}}{\text{Phase change}} \longrightarrow \underset{\text{(endothermic)}}{\text{Dehydration}} \longrightarrow \underset{\text{(exothermic)}}{\text{Deamination}}$$

$$\longrightarrow \underset{\text{(exothermic)}}{\text{Deanionation}} \longrightarrow \text{Cu} \xrightarrow{[\text{O}]} \text{CuO} \qquad (2)$$

However, for different complexes, the loss of crystal water, ligand moieties and anionic parts does not occur in the same relative proportions. The fitting procedure also implies the weight loss steps in TGA curves of various complexes to be composite in nature (i.e. involve simultaneous expulsion of more than one type of groups in the complex) and involving loss of various moieties in a fractional manner.

The kind of phase change corresponding to the first peak in DTA indicated above can be understood in terms of momentary separation of the crystal water and/or amine part from the molecular complex by sublimation followed by immediate condensation and dissolution of the remainder of the complex in the former. This mechanism could also explain why this particular DTA peak, though apparently endothermic, is rather weak and broad in appearance. This interpretation is verified from observation of actual liquefaction of the complexes at the corresponding temperatures when slowly heated in separate tubes outside the furnace. The endothermic and broad nature of the DTA peaks corresponding to the dehydration steps in TGA curves can also be understood in the same way. Similar observation about

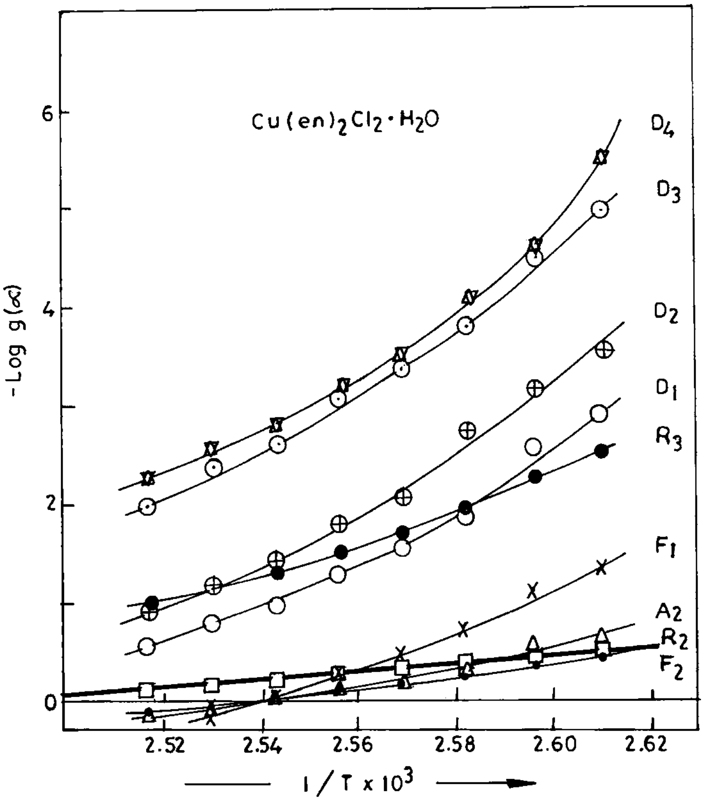

Fig. 3. Illustration for determining the probable reaction mechanism: plots of $-\log(g(\alpha))$ vs. $1/T$ for the dehydration step of $Cu(en)_2Cl_2{\cdot}H_2O$.

liquefaction has also been reported by some other workers [32].

The sequence of processes as represented in (i) above implies that, the crystal water in these complexes is held less strongly than the ligand moieties which in turn are bonded less strongly than the anionic moieties. The increasing trend of the decomposition temperatures corresponding to various steps (Table 1) and that of the ΔHs and E_as (Table 2) for the respective processes in the same order, would be consistent with this conclusion. The ΔHs and E_as for various decomposition processes in different complexes would be expected to exhibit certain general trends dependent on the strength of bonding of the ligand and anionic moieties, which in turn would be governed by their structure and type of co-ordination; provided the various processes can be observed independent of one another. However, due to the composite nature of various steps involving fractional loss of more than one moeities in varying proportions; the calculated activation energies and enthalpy changes are some kind of averages for the overall steps. Deducing exact quantitative correlations among the various ΔHs and E_as, therefore, does not appear possible. The observed trends, however, can be qualitatively understood as follows (The ΔHs and E_as referred to in the following discussion correspond to those deduced from the DTA and TGA studies, respectively).

3.4. Dehydration step

Of the various hydrated complexes; the dehydration steps of only the en complex of Cu(II) chloride and tmn complex of Cu(II) oxalate are found to be separate, while those of all others (e.g. tmn complexes of Cu(II) sulphate and nitrate) are overlapped by simultaneous expulsion of ligands and anionic moities to varying extents resulting in broad steps ($\Delta T \sim$ 20–160 °C) spreading over large temperature intervals (~50–210 °C). The present E_a value for the dehydration step of the en complex of Cu(II) chloride is of comparable order of magnitude as reported by Langfelderova et al. [5]. The ΔH and E_a for dehydration step of the en complex of Cu(II) oxalate are both larger than those for the en complex of Cu(II) acetate. This might be due to a larger fraction of ligand lost along with H_2O in the former. The activation energy for en complex of Cu(II) oxalate appears to be higher than that for en complex of any other salt, which can be due to the contribution from the simultaneous loss of ligand and anion parts of the complex.

3.5. Deamination

The ΔH for expulsion of en as well as that of tmn are both higher in case of complexes of Cu(II) oxalate than those of acetate indicating somewhat stronger co-ordination of both of these ligands to Cu(II) ion in case of oxalate as the counter ion than that in case of acetate. This is partly attributable to the chelating bidentate nature of co-ordination of an oxalate anion as against unidentate co-ordination of an acetate anion resulting in higher stability of the complex cation in the former. The higher values of ΔH in the former case could also be partly due to relatively larger fractional loss of oxalate anion along with the ligands as compared to that of acetate anion. Though the ΔH values for deamination step of both the en as well as tmn complexes of Cu(II) oxalate are higher than those of Cu(II) acetate; the E_a value for the expulsion step of tmn from its complex with Cu(II) oxalate is lower than that from its complex with Cu(II) acetate. This opposite trend may be partly due to the stronger co-ordination of the oxalate ion to Cu(II) due to its chelating bidentate nature as compared to the unidentate co-ordination by the acetate ion and the crowding at the N-sites in tmn resulting in weaker co-ordination by a tmn moiety to the Cu(II) in the oxalate salt than that in the acetate salt. Srivastava et al. [6] also have carried out thermal analysis studies on a number of amine complexes of Cu(II) salts including that on the en complex of Cu(II) oxalate. However, they have not reported any thermodynamic or kinetic parameters.

The ΔH values for the deamination step of the en complexes of inorganic salts of Cu(II) are found to vary in the order: $Cl^- < NO_3^- < SO_4^-$, which can be taken to imply the variation of the stability in the same order. The complexes of Cu(II) chloride are known to be axially compressed, while those of Cu(II) nitrate or sulphate are axially elongated. The co-ordination of a ligand in the former case could therefore be somewhat weaker, which can also partly explain the observed trends in the E_a and ΔH values associated with the loss of the ligands in these complexes. The E_a values for the deamination step of the complexes of Cu(II) sulphate are generally lower than those for the complexes of Cu(II) nitrate, which can be attributed to the stronger co-ordination of SO_4^{2-} with Cu(II) ion than that of NO_3^- and hence weaker co-ordination of the ligands to the Cu(II) ion in presence of SO_4^{2-} as the counter anion. Similarly, the lower activation energy and temperature corresponding to the loss of tmn from the complexes of Cu(II) nitrate, chloride and acetate than those for the loss of en from the corresponding complexes are attributable to crowding at N-sites and packing effects [23] of the coanions in these systems. The trends in the E_a and ΔH values for the deamination step are thus found to be largely determined by the nature of co-ordination and type of the counter anion in the Cu(II) salt. The higher values of ΔH in the case of en complexes of Cu(II) oxalate and acetate than those for the complexes of Cu(II) nitrate, chloride and sulphate could be possibly due to the simultaneous loss of ligand and anion in the composite steps in the former. Wendlandt [4] also has reported detailed studies on TGA and DTA of the bis-en complex of $Cu(II)SO_4$. His thermograms appear to differ somewhat from the present ones, which could be due to the differences in the atmosphere and heating rates employed. However, there are no other reports on the relevant ΔH and E_a values corresponding to thermal analysis so as to present any comparison with our present values.

3.6. Deanionation

The higher values of the E_a and ΔH for the decarboxylation step of en complex of Cu(II) oxalate than those for Cu(II) acetate are understandable in view of the oxalate group exhibiting chelating bidentate co-ordination with Cu(II) resulting in stronger bonding. However, the tmn complex of Cu(II) oxalate exhibits an opposite trend. This could be due to the crowding at the N-sites in the latter causing the oxalate anion in this complex to assume the bridging bidentate co-ordination to the Cu(II), which is likely to be weaker in strength as compared to that of the acetate grouping in the tmn complex of Cu(II) acetate. The temperature corresponding to the loss of the oxalate group from Cu(tmn)$(COO)_2\cdot 0.5H_2O$ is lower than that in Cu$(en)_2$-$(COO)_2\cdot 1.5H_2O$, both of which are lower than that for Cu(II) oxalate [43]**.** The lower decomposition temperatures in case of complexed Cu(II) oxalate than that for the uncomplexed one is attributable to weakening of the co-ordination of an oxalate anion in the former due to co-ordination by the ligands with the central metal ion. Similarly, in case of en complexes of Cu(II) salts of inorganic anions; the larger E_as for the steps corresponding to the loss of NO_3^- or SO_4^{2-} than that for the step involving the loss of Cl^- could be due to the contribution from the loss of en in the former cases.

4. Mechanisms

Since the mechanism of any reaction depends on a large number of factors, such as, e.g. temperature, exothermic or endothermic nature of the process, stoichiometry, crystal structure, packing, catalysing or other effect of accompanying species [23], etc. one cannot expect a unique mechanism to be applicable to all the decomposition steps or even to similar steps of different complexes. For the sake of completeness, the most probable mechanisms corresponding to the major decomposition steps of all the complexes deduced as explained earlier are indicated in Table 1 and some common trends observed are noted below.

The dehydration steps of majority of the complexes, viz. en complexes of Cu(II) chloride, nitrate, oxalate and acetate, and the tmn complexes of Cu(II) sulphate and oxalate, are found to fit more closely to the phase boundary reaction, contracting area cylindrical symmetry mechanism (R_2). The deamination step in the case of en complexes of Cu(II) chloride, nitrate, oxalate and acetate and tmn complex of Cu(II) nitrate fits closely to the phase boundary reaction, contracting area, cylindrical symmetry) (R_2) mechanism; and that in the case of tmn complexes of Cu(II) chloride and sulphate obey the random nucleation F_1 mechanism. The deanionation step in majority of the cases (viz. en complexes of Cu(II) chloride, nitrate, sulphate and oxalate, and tmn complexes of Cu(II) chloride and acetate) fits closely to the phase boundary reaction contracting area cylindrical symmetry R_2 mechanism.

5. Summary and conclusions

The present TGA and DTA studies, thus enable to understand the nature of thermal decomposition process in Cu(II) amine complexes. The trends in ΔH and E_a values corresponding to various steps for different complexes can be understood in a semi-quantitative manner in the light of the structure and co-ordinating nature of the ligands and the counter anions.

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