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THERMAL DECOMPOSITION REACTIONS OF METAL CARBOXYLATO COMPLEXES IN THE SOLID STATE. I. THERMOGRAPHIC AND DIFFERENTIAL THERMAL STUDIES OF METAL OXALATO, MALONATO AND SUCCINATO COMPLEXES

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ABSTRACT

Thermal investigation of metal carboxylato complexes of the first transition metals, Mn(II), Fe(II), Fe(III), Co(II), Ni(II) and Cu(II) and non-transition metals like Zn(II) and Cd(II) in the solid state has been carried out under non-isothermal conditions in nitrogen atmosphere by simultaneous TG and DTA. TG and DTA curves inferred that the thermal stability of the complex decreased approximately with the increase of the standard potential of the central metal ion. The thermal parameters like activation energy, $E_a^\star$, enthalpy change, ΔH, and entropy change, ΔS, corresponding to the dehydration and decomposition of the complexes are determined from TG and DTA curves by standard methods. A linear correlation is found between ΔH and ΔS and $E_a^\star$ and ΔS in dehydration and decomposition processes. DTA curves show an irreversible phase transition for $Na_2[Mn(mal)_2]$, $Na_2[Cu(mal)_2]$ and $Na_2[Co(suc)_2]$ complexes. The residual products in these decomposition processes being a mixture of two oxides, of oxide and carbonate or a mixture of two carbonates.

INTRODUCTION

Thermal investigations of metal oxalato complexes of the solid state under non-isothermal conditions have been carried out by several researchers [1–7], but studies on transition metal malonato and succinato complexes are very scanty [8]. Complexes prepared were of the type: $Na_2[ML_2] \cdot nH_2O$ and $Na_3[FeL_3] \cdot nH_2O$, where M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II); L = oxalate, malonate and succinate ligands and $n = 1$–7. The present paper reports the characterization of the complexes by elemental analysis and results of thermal investigation under non-isothermal conditions. Thermal decomposition of the complex, e.g. $Na_3[FeL_3] \rightarrow Na_2[FeL_2]$, was initiated by electron transfer from the coordinated ligand ion to the central metal ion. An attempt has been made to draw some useful conclusions from the thermodynamic parameters.

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EXPERIMENTAL

Complexes of the type $Na_2[ML_2]\cdot nH_2O$ and $Na_3[FeL_3]\cdot nH_2O$ were prepared according to the literature [1,2]. Certain modifications were made in the cases of malonato complexes due to their high solubilities in aqueous media. The chemicals used were obtained from B.D.H., and the complexes were characterized by elemental analysis (Table 1) and, in certain cases, by IR spectral measurements. The thermogravimetric (TG) and differential thermal analysis (DTA) curves were recorded by a Shimadzu DT-30 (Japan) thermal analyser in a constant flow of nitrogen with a platinum crucible using α-Al_2O_3 as standard. About 10–20 mg powdered sample was taken maintaining the heating rate at 10°C min^{-1} for each run. The enthalpy change (ΔH) was calculated from the DTA peak area using indium metal as calibrant. IR spectra were recorded in KBr medium with a Perkin Elmer 783 IR spectrometer.

TABLE 1

Analytical data for metal oxalato (ox), malonato (mal) and succinato (suc) complexes

Compound	Elemental analysis (%) [a]	
	Central metal	Carbon
$Na_2[Mn(ox)_2]\cdot 3H_2O$	16.52(16.60)	14.10(14.50)
$Na_2[Fe(ox)_2]\cdot 3H_2O$	16.46(16.82)	14.02(14.46)
$Na_3[Fe(ox)_3]\cdot 3H_2O$	12.11(12.61)	15.95(16.25)
$Na_2[Co(ox)_2]\cdot 3H_2O$	17.23(17.59)	14.61(14.33)
$Na_2[Ni(ox)_2]\cdot 3H_2O$	17.59(17.54)	14.54(14.34)
$Na_2[Cu(ox)_2]\cdot 1.5H_2O$	20.01(20.33)	15.29(15.36)
$Na_2[Zn(ox)_2]\cdot 3H_2O$	18.98(19.15)	14.01(14.06)
$Na_2[Cd(ox)_2]\cdot 4H_2O$	27.21(27.66)	11.65(11.81)
$Na_2[Mn(mal)_2]\cdot 3H_2O$	15.20(15.31)	19.89(20.06)
$Na_2[Fe(mal)_2]\cdot 3H_2O$	15.30(15.52)	19.91(20.01)
$Na_3[Fe(mal)_3]$	12.43(12.96)	25.34(25.07)
$Na_2[Co(mal)_2]\cdot 2H_2O$	16.98(17.08)	19.99(20.87)
$Na_2[Ni(mal)_2]\cdot 3H_2O$	16.20(16.19)	19.75(19.85)
$Na_2[Cu(mal)_2]\cdot 2H_2O$	17.97(18.18)	20.00(20.60)
$Na_2[Zn(mal)_2]\cdot 2H_2O$	18.29(18.61)	17.00(17.29)
$Na_2[Cd(mal)_2]\cdot 3H_2O$	26.29(26.99)	17.40(17.29)
$Na_2[Mn(suc)_2]\cdot 7H_2O$	11.71(11.97)	20.01(20.91)
$Na_2[Fe(suc)_2]\cdot 7H_2O$	12.00(12.14)	20.17(20.88)
$Na_3[Fe(suc)_3]\cdot 7H_2O$	9.00(9.33)	23.89(24.05)
$Na_2[Co(suc)_2]\cdot 7H_2O$	12.11(12.73)	20.69(20.74)
$Na_2[Ni(suc)_2]\cdot 7H_2O$	12.01(12.69)	20.09(20.75)
$Na_2[Cu(suc)_2]\cdot 3.5H_2O$	16.00(15.71)	23.19(23.73)
$Na_2[Zn(suc)_2]\cdot 7H_2O$	13.71(13.93)	20.04(20.45)
$Na_2[Cd(suc)_2]\cdot 7H_2O$	21.76(21.77)	18.07(18.59)

[a] Figures in parentheses are calculated values.

RESULTS AND DISCUSSION

TG and DTA studies

TG and DTA curves of some metal oxalato, malonato and succinato complexes are shown in Figs. 1 and 2. The dehydration temperature ranges are 40–245, 30–270 and 30–265°C for oxalato, malonato and succinato complexes (shown in Tables 2, 3 and 4, respectively). From TG curves it was found that the complexes lost water molecules before decomposition, except $Na_2[Zn(suc)_2] \cdot 7H_2O$, where dehydration and decomposition took place simultaneously in a single step (Fig. 1). The oxalato and malonato complexes have three and seven molecules of water, respectively, except

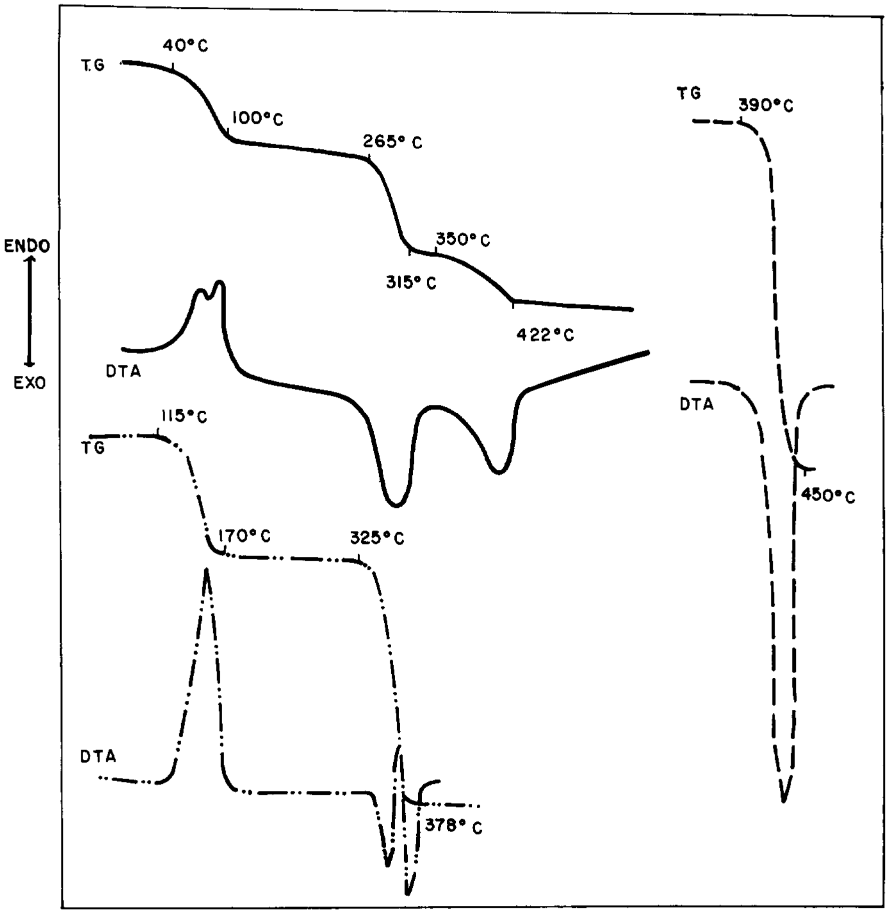

Fig. 1. Thermal curves of: $Na_3[Fe(ox)_3] \cdot 3H_2O$, sample mass 10.5 mg (———); $Na_2[Zn(ox)_2] \cdot 3H_2O$, sample mass 14.0 mg (··—··—··); and $Na_2[Zn(suc)_2] \cdot 7H_2O$, sample mass 14.5 mg (— — —).

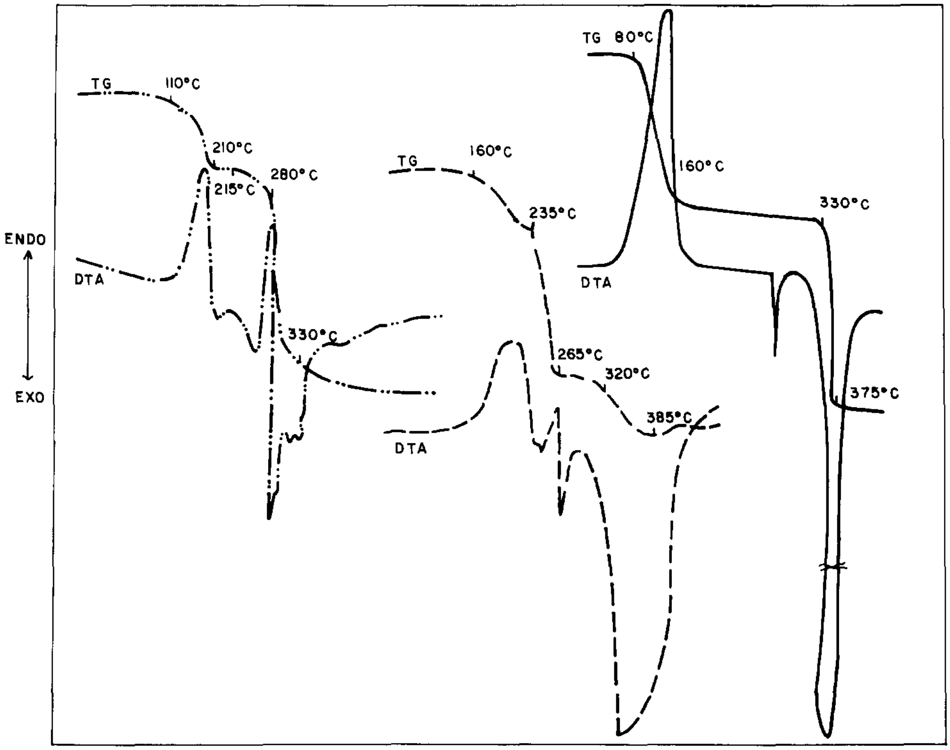

Fig. 2. Thermal curves of: $Na_2[Mn(mal)_2]\cdot 3H_2O$ sample mass 14.2 mg (··–··–··); $Na_2[Cu(mal)_2]\cdot 2H_2O$ sample mass 12.8 mg (— — —); and $Na_2[Co(suc)_2]\cdot 7H_2O$ sample mass 12.2 mg (———).

$Na_2[Cu(ox)_2]\cdot 1.5H_2O$, $Na_2[Cd(ox)_2]\cdot 4H_2O$, $Na_2[Co(mal)_2]\cdot 2H_2O$, $Na_2[Cu(mal)_2]\cdot 2H_2O$, $Na_2[Zn(mal)_2]\cdot 2H_2O$ and $Na_2[Cu(suc)_2]\cdot 3.5H_2O$. $Na_3[Fe(mal)_3]$ has no water molecule (Tables 2–4). The dehydration occurred in a single step having one endothermic peak, except for $Na_2[Fe(mal)_2]\cdot 3H_2O$ and $Na_2[Cd(mal)_2]\cdot 3H_2O$, where dehydration in the TG curve was observed in two steps (Table 3). The temperature ranges and peak temperatures of dehydration are shown in Tables 2–4.

The TG curves of oxalato complexes show a single-step decomposition (Table 2). A similar phenomenon is also reflected in DTA curves, except for Co(II) and Cd(II) complexes where two peaks were observed. In the Zn(II) complex, an exotherm followed by an endotherm and finally an exotherm were noticed (Fig. 1). From the nature of these DTA peaks, it may be assumed that some kind of structural arrangement might be occurring during the decomposition of $Na_2[Zn(ox)_2]$ complex. The $Na_3[Fe(ox)_3]$ and $Na_3[Fe(mal)_3]$ complexes show two-stage decomposition in their TG curves while a single-step decomposition was found for $Na_3[Fe(suc)_3]$. In DTA curves multiple peaks were observed for $Na_3[Fe(ox)_3]$, $Na_3[Fe(mal)_3]$ and Na_3[Fe-

TABLE 2

Dehydration and decomposition reactions of metal oxalato complexes

No.	Decomposition reaction	Temperature range (°C)	DTA peak temperature (°C)		E_a^* (kJ mol^{-1})		ΔH (kJ mol^{-1})	ΔS (J K^{-1} mol^{-1})
			Endo	Exo	TG	DTA		
1	$Na_2[Mn(C_2O_4)_2]\cdot 3H_2O \rightarrow Na_2[Mn(C_2O_4)_2]$	116–150	140		126.4	115.9	257.0	622.3
	$Na_2[Mn(C_2O_4)_2] \rightarrow Na_2O, MnO_2$	278–355		325	106.3	110.5	218.7	362.5
2	$Na_2[Fe(C_2O_4)_2]\cdot 3H_2O \rightarrow Na_2[Fe(C_2O_4)_2]$	145–200	190		92.0	72.0	128.5	277.5
	$Na_2[Fe(C_2O_4)_2] \rightarrow Na_2O, FeO$	200–300		265	70.5	85.4	233.1	433.3
3	$Na_3[Fe(C_2O_4)_3]\cdot 3H_2O \rightarrow Na_3[Fe(C_2O_4)_3]$	40–100	75, 90		85.7	–	128.1	–
	$Na_3[Fe(C_2O_4)_3] \rightarrow Na_2[Fe(C_2O_4)_2]$	265–315		290	113.5	142.5	151.4	268.9
	$Na_2[Fe(C_2O_4)_2] \rightarrow Na_2O, FeO$	350–422		410	293.4, 96.6 [a]	128.9	85.1	124.7
4	$Na_2[Co(C_2O_4)_2]\cdot 3H_2O \rightarrow Na_2[Co(C_2O_4)_2]$	100–175	165		116.9	138.0	103.0	235.6
	$Na_2[Co(C_2O_4)_2] \rightarrow Na_2O, CoO$	332–462		335, 395	134.5	241.5	225.8	–
5	$Na_2[Ni(C_2O_4)_2]\cdot 3H_2O \rightarrow Na_2[Ni(C_2O_4)_2]$	85–245	230		65.0	138.0	140.7	238.0
	$Na_2[Ni(C_2O_4)_2] \rightarrow Na_2O, NiO$	320–362		350	246.1	300.6	179.6	288.0
6	$Na_2[Cu(C_2O_4)_2]\cdot 1.5H_2O \rightarrow Na_2[Cu(C_2O_4)_2]$	130–150	140		174.8	–	87.4	211.6
	$Na_2[Cu(C_2O_4)_2] \rightarrow Na_2O, CuO$	262–355		320	168.3	120.0	205.2	346.0
7	$Na_2[Zn(C_2O_4)_2]\cdot 3H_2O \rightarrow Na_2[Zn(C_2O_4)_2]$	115–170	155		101.2	110.5	168.8	394.5
	$Na_2[Zn(C_2O_4)_2] \rightarrow Na_2O, ZnO$	325–378	360	350, 370	400.5	–	–	–
8	$Na_2[Cd(C_2O_4)_2]\cdot 4H_2O \rightarrow Na_2[Cd(C_2O_4)_2]$	55–130	115		71.0	72.8	181.4	467.6
	$Na_2[Cd(C_2O_4)_2] \rightarrow Na_2O, CdO$	302–390		345, 375	97.2	–	108.8	–

[a] Calculated by the Coats and Redfern method [11].

TABLE 3

Dehydration and decomposition reactions of metal malonato complexes

No.	Decomposition reaction	Temperature range (°C)	DTA peak temperature (°C)		E_a^* (kJ mol^{-1})		ΔH (kJ mol^{-1})	ΔS (J K^{-1} mol^{-1})
			Endo	Exo	TG	DTA		
1	$Na_2[Mn(C_3H_2O_4)_2]\cdot 3H_2O \rightarrow Na_2[Mn(C_3H_2O_4)_2]$	110–210	200		92.4	108.7	152.7	322.7
	$Na_2[Mn(C_3H_2O_4)_2] \xrightarrow[\text{change}]{\text{phase}} Na_2[Mn(C_3H_2O_4)_2]$	215–270	230		–	–	17.9	35.5
	$Na_2[Mn(C_3H_2O_4)_2] \rightarrow Na_2CO_3, MnO_2$	280–330	285	290, 310, 320	165.8	–	289.0	–
2	$Na_2[Fe(C_3H_2O_4)_2]\cdot 3H_2O \rightarrow Na_2[Fe(C_3H_2O_4)_2]\cdot 2.5H_2O$	160–250	180		177.2	–	142.2	–
	$Na_2[Fe(C_3H_2O_4)_2]\cdot 2.5H_2O \rightarrow Na_2[Fe(C_3H_2O_4)_2]$	250–270	[a]	–	–	–	–	–
	$Na_2[Fe(C_3H_2O_4)_2] \rightarrow Na_2CO_3$, FeO	270–350		270, 320	84.8	–	683.6	–
3	$Na_3[Fe(C_3H_2O_4)_3] \rightarrow 2Na_2[Fe(C_3H_2O_4)_2]$	270–295		280, 290	274.4	–	–	–
	$2Na_2[Fe(C_3H_2O_4)_2] \rightarrow 2Na_2CO_3$, 2FeO	295–460		330	–	–	–	–
4	$Na_2[Co(C_3H_2O_4)_2]\cdot 2H_2O \rightarrow Na_2[Co(C_3H_2O_4)_2]$	135–210	200		99.9	118.9	79.2	172.5
	$Na_2[Co(C_3H_2O_4)_2] \rightarrow Na_2CO_3$, CoO	260–345	292	340	265.4	–	–	–
5	$Na_2[Ni(C_3H_2O_4)_2]\cdot 3H_2O \rightarrow Na_2[Ni(C_3H_2O_4)_2]$	120–180	160		58.4	84.5	116.2	269.0
	$Na_2[Ni(C_3H_2O_4)_2] \rightarrow Na_2[Ni(C_3H_2O_4)_{1/2}]$	305–330	328		–	–	19.0	31.5
	$Na_2[Ni(C_3H_2O_4)_{1/2}] \rightarrow Na_2CO_3$, NiO	330–410		390, 405	418.0	–	–	–
6	$Na_2[Cu(C_3H_2O_4)_2]\cdot 2H_2O \rightarrow Na_2[Cu(C_3H_2O_4)_2]$	160–235	185		78.7	61.8	122.5	270.4
	$Na_2[Cu(C_3H_2O_4)_2] \rightarrow Na_2[Cu(C_3H_2O_4)_{1/2}]$	235–265	260		–	–	16.2	30.4
	$Na_2[Cu(C_3H_2O_4)_{1/2}] \xrightarrow[\text{change}]{\text{phase}} Na_2[Cu(C_3H_2O_4)_{1/2}]$	265–290		285	–	–	12.2	22.4
	$Na_2[Cu(C_3H_2O_4)_{1/2}] \rightarrow Na_2CO_3$, CuO	320–385		350	191.3	173.9	226.9	366.3
7	$Na_2[Zn(C_3H_2O_4)_2]\cdot 2H_2O \rightarrow Na_2[Zn(C_3H_2O_4)_2]$	145–205	195		220.1	173.9	104.6	221.1
8	$Na_2[Cd(C_3H_2O_4)_2]\cdot 3H_2O \rightarrow Na_2[Cd(C_3H_2O_4)_2]\cdot 1.5H_2O$	30– 62	55		96.4	112.7	45.8	138.4
	$Na_2[Cd(C_3H_2O_4)_2]\cdot 1.5H_2O \rightarrow Na_2[Cd(C_3H_2O_4)_2]$	120–178	140		51.0	64.4	74.6	180.6
	$Na_2[Cd(C_3H_2O_4)_2] \rightarrow Na_2CO_3$, CdO	285–355		350	218.0	257.6	246.9	396.3

[a] Endothermic peak merges with the exothermic peak of decomposition.

TABLE 4

Dehydration and decomposition reactions of metal succinato complexes

No.	Decomposition reaction	Temperature range (°C)	DTA peak temperature (°C)		E_a^* (kJ mol^{-1})		ΔH (kJ mol^{-1})	ΔS (J K^{-1} mol^{-1})
			Endo	Exo	TG	DTA		
1	$Na_2[Mn(C_4H_4O_4)_2]\cdot 7H_2O \rightarrow Na_2[Mn(C_4H_4O_4)_2]$	35–155	105		82.1	77.3	235.4	418.1
2	$Na_2[Fe(C_4H_4O_4)_2]\cdot 7H_2O \rightarrow Na_2[Fe(C_4H_4O_4)_2]$	45–175	120		63.7	64.4	260.7	698.9
	$Na_2[Fe(C_4H_4O_4)_2] \rightarrow Na_2O, FeO$	275–320		290	136.6	–	–	–
3	$Na_3[Fe(C_4H_4O_4)_3]\cdot 7H_2O \rightarrow Na_3[Fe(C_4H_4O_4)_3]$	30–265	65		44.0	63.0	274.7	812.7
	$Na_3[Fe(C_4H_4O_4)_3] \rightarrow Na_2O, FeO$	275–297		275, 290	252.2	–	–	–
4	$Na_2[Co(C_4H_4O_4)_2]\cdot 7H_2O \rightarrow Na_2[Co(C_4H_4O_4)_2]$	80–160	130		83.6	96.6	380.2	992.7
	$Na_2[Co(C_4H_4O_4)_2] \xrightarrow[\text{change}]{\text{phase}} Na_2[Co(C_4H_4O_4)_2]$	275–295		285	–	–	23.9	42.9
	$Na_2[Co(C_4H_4O_4)_2] \rightarrow Na_2O, CoO$	330–375		365	305.4	–	–	–
5	$Na_2[Ni(C_4H_4O_4)_2]\cdot 7H_2O \rightarrow Na_2[Ni(C_4H_4O_4)_2]$	100–180	155		73.0	96.6	209.6	492.0
	$Na_2[Ni(C_4H_4O_4)_2] \rightarrow Na_2O, NiO$	362–380		365, 375	338.7	–	–	–
6	$Na_2[Cu(C_4H_4O_4)_2]\cdot 3.5H_2O \rightarrow Na_2[Cu(C_4H_4O_4)_2]$	40–100	90		72.5	72.5	138.3	380.9
	$Na_2[Cu(C_4H_4O_4)_2] \rightarrow Na_2O, CuO$	295–370		320, 350, 360	243.9	–	461.8	–
7	$Na_2[Zn(C_4H_4O_4)_2]\cdot 7H_2O \rightarrow Na_2CO_3, ZnCO_3$	390–450		445	369.2	301.9	304.4	504.8
8	$Na_2[Cd(C_4H_4O_4)_2]\cdot 7H_2O \rightarrow Na_2[Cd(C_4H_4O_4)_2]$	30–158	60, 115		–	–	365.8	–
	$Na_2[Cd(C_4H_4O_4)_2] \rightarrow Na_2CO_3, CdO$	328–455		335, 390	–	–	–	–

(suc)$_3$]. For the tris-oxalato complex the results suggested the decomposition reaction to be

$$Na_3[Fe(C_2O_4)_3] \rightarrow Na_2[Fe(C_2O_4)_2] + 1/2Na_2C_2O_4 + CO_2$$

A similar two-step decomposition was also followed in malonato and succinato complexes. The evolution of CO_2 during decomposition lead to the conclusion that an electron transfer occurred from the coordinated ligand ion to the central metal ion [2].

The TG curves for most of the malonato complexes involve a single-step decomposition, except for $Na_2[Ni(mal)_2]$ and $Na_2[Cu(mal)_2]$ where a two-step decomposition occurred (Table 3). The thermal curves for $Na_2[Zn(mal)_2]$ could not be recorded due to its swelling after dehydration. $Na_2[Cd(mal)_2]$ showed a single-step decomposition in TG and DTA curves. $Na_2[Mn(mal)_2]$ and $Na_2[Cu(mal)_2]$ manifested first an endotherm followed by an exotherm in DTA curves. These features were not noticed in oxalato and succinato complexes.

For $Na_2[Mn(mal)_2]$ and $Na_2[Cu(mal)_2]$ no weight loss was found along their TG curves in the temperature ranges 215–270 and 265–290°C, respectively, while in DTA curves endothermic/exothermic peaks were obtained, suggesting some structural rearrangement. The decomposition of $Na_2[Mn(suc)_2]$ could not be recorded because of its tendency to expand. TG curves show single-step decomposition for succinato complexes. In $Na_2[Zn(suc)_2] \cdot 7H_2O$ dehydration and decomposition occurred simultaneously in a single step. A prominent phase transition was noticed in the DTA curve (Fig. 2) for $Na_2[Co(suc)_2]$ in the temperature range 275–295°C whereas in the TG curve no weight loss was found, indicating some sort of structural change. For $Na_2[Cd(suc)_2]$ two exothermic peaks appeared in the DTA curve; the first peak has a small area with respect to the second. In $Na_2[Ni(suc)_2]$ and $Na_2[Cu(suc)_2]$ a small hump was noticed before the exothermic peak begins to appear.

Dehydration with respect to DTA peak temperature in single-step, as well as in the first stage of two-step processes, is in the order Ni(II) > Fe(II) > Co(II) > Zn(II) > Mn(II) ≈ Cu(II) > Cd(II) for oxalato and succinato complexes. Malonato complexes have certain deviations as Co(II) ≈ Mn(II) > Zn(II) > Cu(II) > Fe(II) > Ni(II) > Cd(II). For oxalato complexes decomposition peak temperatures follow the order Ni(II) ≈ Zn(II) > Cd(II) > Co(II) > Mn(II) ≈ Cu(II) > Fe(III) > Fe(II) (see Table 2). The trends in malonato and succinato complexes are Cd(II) > Co(II) > Ni(II) > Mn(II) > Fe(II) > Cu(II) and Zn(II) > Ni(II) ≈ Co(II) > Cu(II) > Fe(II) > Fe(III), respectively (Tables 3 and 4). Decomposition peak temperatures of the complexes having the same metal in the outer coordination sphere (Na^+) and the same central metal ion with different ligands follow the approximate order ox > mal > suc, in the cases of Mn(II), Fe(III), Ni(II) and Cd(II), and is reversed for Fe(II), Co(II) and Cu(II). The order of stabilities may be

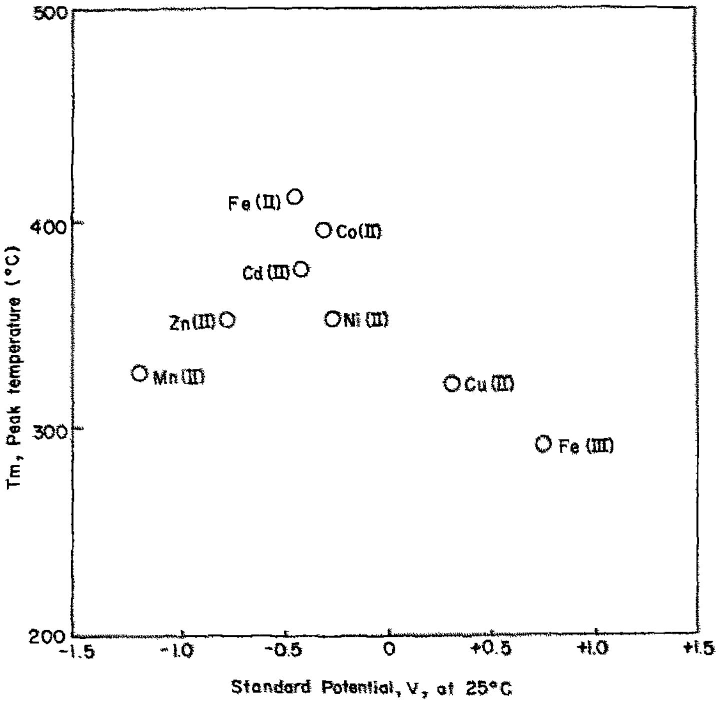

Fig. 3. Plots of peak temperature of decomposition, T_m (°C), for metal oxalato complexes vs. standard potential, V, of central metal ion at 25°C.

explained either on the basis of the tendency of the central metal ions to capture the electron from the respective ligand [2] or on the size of the chelate ring formed by the ligand to the central metal ion.

Activation energy ($E_{\text{a}}^{\star}$) values for dehydration and decomposition were computed from TG curves by the Horowitz and Metzger method [9] and from DTA curves using the Borchardt and Daniels equation [10], considering the order of reaction as unity; the values are given in Tables 2–4. In most cases the values are fairly close to each other, except the second decomposition step of $Na_3[Fe(ox)_3]$, where the Coats and Redfern equation [11] was applied.

For dehydration, activation energies ($E_{\text{a}}^{\star}$) obtained from DTA peaks for oxalato and succinato complexes are in the sequence: Co(II) ~ Ni(II) > Mn(II) > Zn(II) > Cu(II) > Cd(II) > Fe(III) and in malonato complexes Zn(II) > Co(II) > Cd(II) > Mn(II) > Ni(II) > Cu(II). The enthalpy changes (ΔH) of oxalato, malonato and succinato complexes are of the order: Mn(II) > Cd(II) > Zn(II) > Ni(II) > Fe(II) > Fe(III) > Co(II) > Cu(II), Mn(II) > Fe(II) > Cu(II) > Ni(II) > Zn(II) > Co(II) > Cd(II) and Co(II) > Cd(II) > Fe(III) > Fe(II) > Mn(II) > Ni(II) > Cu(II) respectively, and their respective entropy changes (ΔS) are in the following sequence: Mn(II) > Cd(II) > Zn(II) > Fe(II) > Ni(II) > Co(II) > Cu(II), Mn(II) > Cu(II) >

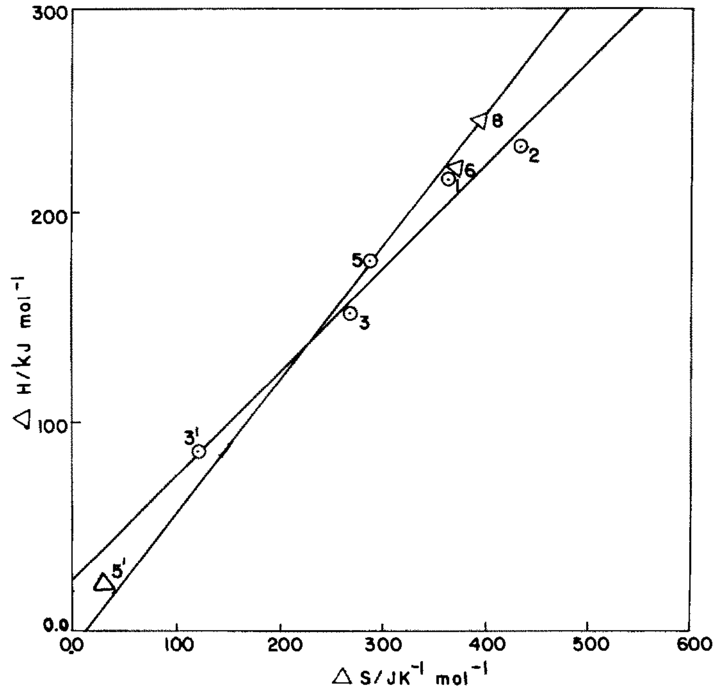

Fig. 4. Plots of ΔH vs. ΔS for the thermal decomposition of metal oxalato complexes (–⊙–⊙–): (1) Mn(II), (2) Fe(II), (3) Fe(III), (3′) Fe(II) (obtained from the reduction of Fe(III)), (5) Ni(II); and malonato complexes (–△–△–): (5′) Ni(II), (6) Cu(II) and (8) Cd(II).

Ni(II) > Zn(II) > Co(II) > Cd(II) and Co(II) > Fe(III) > Fe(II) > Ni(II) > Mn(II) > Cu(II).

Activation energies (E_a^*) of decomposition for oxalato complexes follow the order: Ni(II) > Co(II) > Fe(III) > Cu(II) > Mn(II) > Fe(II) and for succinato complexes * the sequence is Ni(II) > Co(II) > Fe(III) > Cu(II) > Fe(II). Malonato complexes * follow the same trend as succinato complexes, except the position of Co(II) and Fe(III) is reversed. Enthalpy changes (ΔH) for all ** complexes in decomposition processes are in the order: Fe(II) > Co(II) > Mn(II) > Cu(II) > Ni(II) > Fe(III) > Cd(II). Entropy changes (ΔS) for oxalato and malonato complexes are found in the order: Fe(II) > Mn(II) > Cu(II) > Ni(II) > Fe(III). By plotting DTA peak temperature of the oxalato complexes (Fig. 3) against the standard potential of the

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* From TG curves, as values from DTA peaks are not large enough to compare.

** In a few cases, for malonato and succinato complexes, the enthalpy changes (ΔH) were evaluated for excessive overlapping of the DTA peaks.

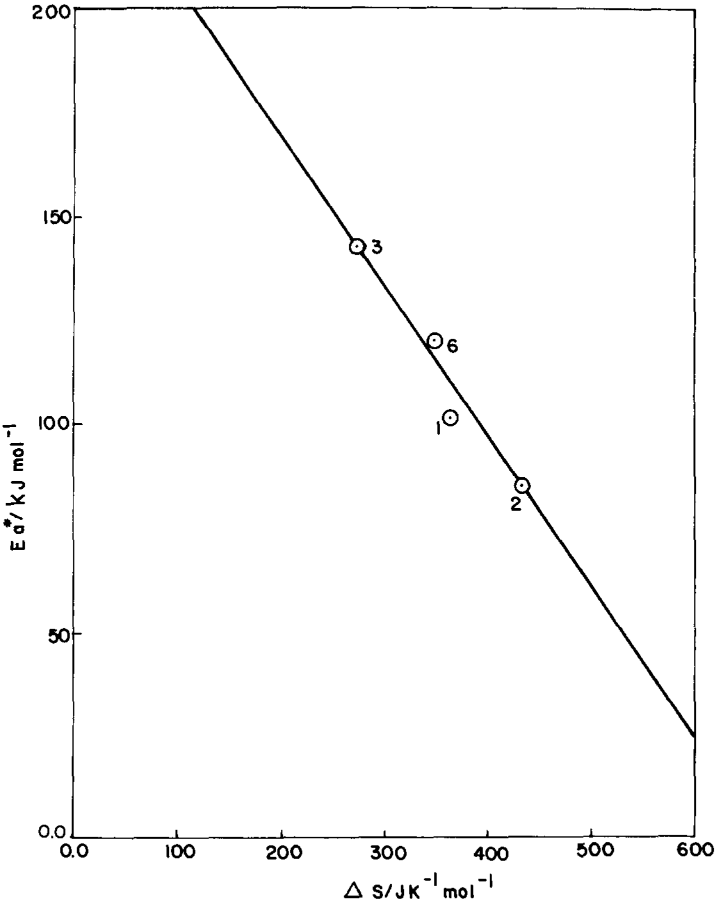

Fig. 5. Plots of E_a^* vs. ΔS for the thermal decomposition of metal oxalato complexes (1) Mn(II), (2) Fe(II), (3) Fe(III) and (6) Cu(II).

central metal ion *, it was found that the thermal stability of the complex decreases approximately with the increase of the tendency of the central metal ion to capture the electron from the ligand. Similar trends are also observed in the cases of malonato and succinato complexes. An attempt has been made to correlate a thermal parameter like enthalpy change with entropy change. The entropy change (ΔS) values are obtained by the relation [12]

$$\Delta S = \frac{\Delta H}{T_m}$$

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* The plots of DTA peak temperatures of the complexes versus the standard potential [13] of the central metal ion forming an aquo complex are given in Fig. 3. These potentials are considered to measure the tendency of the central metal ion to capture the electron from the ligand forming an oxalato complex, since the D_q value of H_2O is near to that of $C_2O_4^{2-}$.

where T_m is the peak temperature of decomposition in DTA curves. A linear correlation was found by plotting ΔH versus ΔS (Fig. 4). Similarly a plot of $E_a^\star$ versus ΔS also gives a linear relationship (Fig. 5).

It has been observed that a system having higher entropy change (ΔS) will require less activation energy ($E_a^\star$) for its decomposition. In the dehydration process a similar observation was also made.

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