

KINETICS OF THERMAL DECOMPOSITION OF IRON(III) DICARBOXYLATE COMPLEXES

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Tris(dicarboxylate) complexes of iron(III) with oxalate, maleate, malonate and phthalate viz. $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ (**1**), $K_3[Fe(OOCCH_2COO)_3] \cdot 3H_2O$ (**2**), $K_3[Fe(OOCCH=CHCOO)_3] \cdot 3H_2O$ (**3**), $K_3[Fe(OOC-1,2-(C_6H_4)-COO)_3] \cdot 3H_2O$ (**4**) have been synthesized and characterized using a combination of physicochemical techniques. The thermal decomposition behaviour of these complexes have been investigated under dynamic air atmosphere upto 800 K. All these complexes undergo a three-step dehydration/decomposition process for which the kinetic parameters have been calculated using Freeman–Carroll model as well as using different mechanistic models of the solid-state reactions. The trisoxalato and trismalonato ferrate(III) complexes undergo rapid dehydration at lower temperature below 470 K. At moderately higher temperatures (i.e. >600 and 500 K, respectively) they formed bis chelate iron(III) complexes. The trismalonato and trismaleato complexes dehydrate with almost equal ease but the latter is much less stable to decomposition and yields $FeCO_3$ below 760 K. The *cis*-dicarboxylate complexes particularly with maleate(2-) and phthalate(2-) ligands are highly prone to the loss of cyclic anhydrides at moderately raised temperatures. The thermal decomposition of the tris(dicarboxylato)iron(III) to iron oxide was not observed in the investigated temperature range up to 800 K. The dehydration processes generally followed the first or second order mechanism while the third decomposition steps followed either three-dimensional diffusion or contracting volume mechanism.

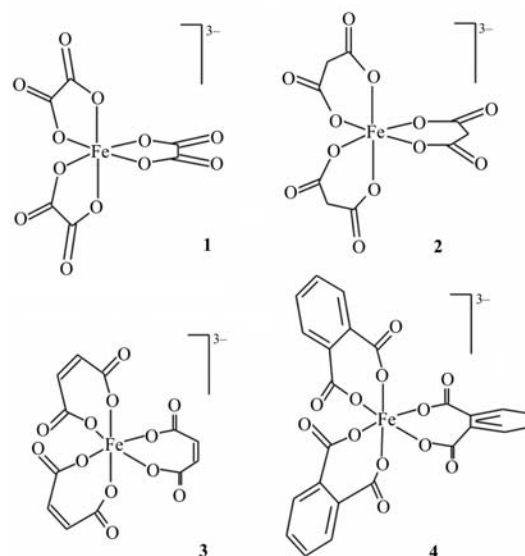
Keywords: iron(III), maleate, malonate, oxalate, phthalate, thermal decomposition

Introduction

The metal carboxylates are potential precursors for the manufacture of new inorganic materials and catalysts e.g., the iron(III) oxalate salts are being used in the synthesis of nanocrystalline metallic oxides [1–3] and molecular magnetic materials [4–7]. Besides, the ferric oxalate salt undergoes interesting photochemical redox reaction at ambient temperature, which forms the basis of chemical actinometry [8]. A similar behavior is expected in its other dicarboxylates. The iron(III) metal ion forms tris-chelate complex with dicarboxylate anions like oxalate ions which crystallizes as trihydrate salt. The trioxalato ferrate salts are also found in nature in minguzitte mineral.

The knowledge of the formation of thermal decomposition products from various precursors is very important in the materials synthesis. Thermal analysis techniques are important tool in such investigations. Therefore, it would be interesting to investigate the thermal behavior of the iron(III) dicarboxylate complexes having different structures. The thermal decomposition kinetics of metal carboxylate salts shows that the unimolecular decomposition processes are generally assisted by electron releasing substituents [9]. However, the thermal decomposition behaviors of metal dicarboxylate complexes are relatively less explored.

Therefore, we herein report synthesis and characterization as well as the kinetics of dehydration and thermal decomposition of tris(dicarboxylato)iron(III) complexes. We have chosen four structurally different dicarboxylates viz., oxalate, malonate, maleate and phthalate dianions that form hydrated anionic trischelate complexes with iron(III) as shown in Scheme 1.



Scheme 1

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Experimental

AR grade dicarboxylic acids viz., oxalic acid, malonic acid, maleic acid, phthalic acid, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and BaCl_2 salt were used. The solutions for metal estimation were prepared by NaOH-NaNO_3 fusion method. C, H analyses were carried out on Elementar Vario-III. The IR spectra were recorded on a Perkin-Elmer 1600 FTIR spectrophotometer with KBr pellets, electronic spectra were recorded on a Shimadzu 1601 spectrophotometer in aqueous solutions. Magnetic susceptibility were measured on a PARC-155 vibrating sample magnetometer at 300 K. Thermogravimetry/differential thermal analysis (TG/DTA) experiments were carried out on a Stanton Redcroft Thermobalance Model STA-780 under a dynamic air atmosphere.

Preparation of barium salts of the dicarboxylic acids

2.9 g (0.023 mol) were prepared by the neutralization of dicarboxylic acids with (5 N) NaOH solution and were added to the aqueous solution of barium chloride 5.0 g (0.02 mol) with constant stirring at room temperature. The reaction mixture was left for half an hour. The barium salts of dicarboxylates, that separated out were collected by filtration.

Preparation of iron(III) complexes

All iron(III) complexes were prepared by adopting the literature method for the preparation of potassium trioxalatoferate(III) [10]. The $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (2.7 g, 10 mmol), barium dicarboxylate (4.5–6.0 g, 20 mmol) and potassium salt of corresponding dicarboxylic acid (3.3 g, 20 mmol) (prepared by neutralizing acid with 5 M KOH) were taken in 60 mL distilled water. The reaction mixture was digested on water bath for one hour and was filtered in hot. The volume of the filtrate was reduced by slow evaporation at reduced pressure to ca. 10 mL. The light yellowish green crystals were obtained which were collected by filtration, washed with cold water and were recrystallized from water-ethanol mixture. Compounds were dried over CaCl_2 . (Yield ca. 3.4–5.0 g, 70%.)

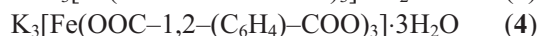
Thermal studies

The TG/DTA experiments were carried out under dynamic air environment for which the air flow rate was maintained at 50 mL min^{-1} . Programmed temperature regime with a heating rate of 10 K min^{-1} was applied. In all TG/DTA runs 10 mg of microcrystalline complexes were taken in alumina boats. Alumina was also used as reference material for the DTA scans. The sample temperature traces are straight lines, suggest-

ing negligible effect of self-heating due to exothermic processes. IR spectra of the residue after heating upto 800 K were recorded in KBr. The kinetic parameters were calculated using a series of BASIC programs.

Results and discussion

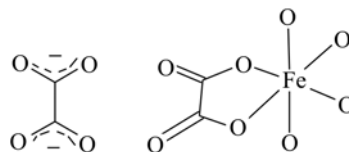
The tris-chelate complexes:



were prepared by the reaction of the barium and potassium salts of the dicarboxylates with aqueous $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. The direct reaction between the potassium dicarboxylate or the dicarboxylic acids with ferric chloride do not proceed well and instead gives their simple ferric salts. However the chelation is facilitated by the presence of Ba^{2+} ions although the mechanism is not certain. All these complexes crystallize as trihydrate salts as seen from their elemental analyses. Their spectral and magnetic susceptibility data are summarized in Table 1.

IR spectra

All these complexes exhibit a strong band between $1600\text{--}1700 \text{ cm}^{-1}$ characteristic of the COO^- group. Compared to corresponding barium or potassium salts this band, in complexes 1–4, is observed shifted ($\sim 70 \text{ cm}^{-1}$) towards higher frequency which is indicative of formation the coordination complexes. In the barium and potassium salts the two C–O bonds in a $-\text{COO}^-$ group are equivalent. Thus they give rise to $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{sym}}(\text{COO}^-)$ vibrations whose frequencies lie close to ca. 1600 cm^{-1} . But upon η^1 -coordination the equivalence of the two C–O bonds is lost. Thus they get decoupled upon coordination. The resulting $\nu_{\text{str}}(\text{C}=\text{O})$ in the η^1 -O-coordinated $-\text{COO}^-$ groups (Str. I) appear at higher frequency [11, 12]. In all these complexes the band at ca. 1400 cm^{-1} gains intensity upon complexation and a new strong band appears around 1100 cm^{-1} , while the band around 1350 cm^{-1} simultaneously diminishes in intensity and generally disappears. The appearance of these strong bands is suggestive of the coupling of



Str. I

Table 1 Physical and analytical data

Complex	IR, ν/cm^{-1}	UV-Vis, $\lambda_{\text{max}}/\text{nm}$ in H_2O	Analysis/%, obsd. (calcd.)			$\mu_{\text{eff}}^{289}/\text{B.M.}$
			C	H	Fe	
$\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]\cdot\text{H}_2\text{O}$ (1)	3510vs, 1676vs, 1405vs, 1273s, 900s, 801vs, 535s, 484s	267	14.4 (14.7)	1.5 (1.2)	11.3 (11.4)	3.45
$\text{K}_3[\text{Fe}(\text{OOCCH}_2\text{COO})_3]\cdot 3\text{H}_2\text{O}$ (2)	3500vs, 3100w, 1682m, 1571vs, 1400w, 1355m, 1245w, 1174w, 925m, 819w, 690s, 620sm, 590m	271	20.5 (20.3)	2.7 (2.3)	10.8 (10.5)	5.41
$\text{K}_3[\text{Fe}(\text{OOCCH}=\text{CHCOO})_3]\cdot 3\text{H}_2\text{O}$ (3)	3474vs, 1694w, 1620vs, 1500m, 1469m, 1369s, 1210s, 1113s, 899w, 864s, 711w, 657m, 561m, 519m	268	25.0 (25.3)	2.7 (2.1)	9.4 (9.8)	2.72
$\text{K}_3[\text{Fe}(\text{OOC}-1,2-(\text{C}_6\text{H}_4)-\text{COO})_3]\cdot 3\text{H}_2\text{O}$ (4)	3439vs, 3179m, 2638w, 2514m, 1698s, 1557vs, 1395s, 1271vs, 1146w, 1013m, 814m, 753m, 701m, 526s, 418s	281	39.7 (40.1)	3.0 (2.5)	7.6 (7.8)	3.53

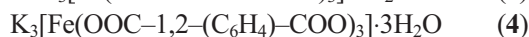
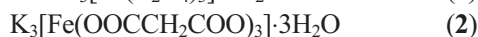
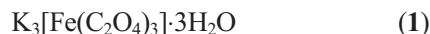
$\nu(\text{C}-\text{O})$ and $\nu(\text{C}-\text{C})$ vibrations upon coordination of the carboxylate unit.

Electronic spectra

The UV-Visible absorption spectra of iron(III) complexes with carboxylic acid exhibit characteristic bands in the region 260–290 nm having tails in the visible region. Band may be identified with the coordinatively bound carboxylate groups that arises from $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions in the COO^- groups. The presence of the low intensity bands in ultraviolet absorption spectrum in aqueous solution is the characteristics of a coordinatively bonded carboxylate groups.

Thermal studies

The TG/DTA plots of complexes:



are shown in Fig. 1 and their important characteristics are summarized in Table 2. All complexes undergo a

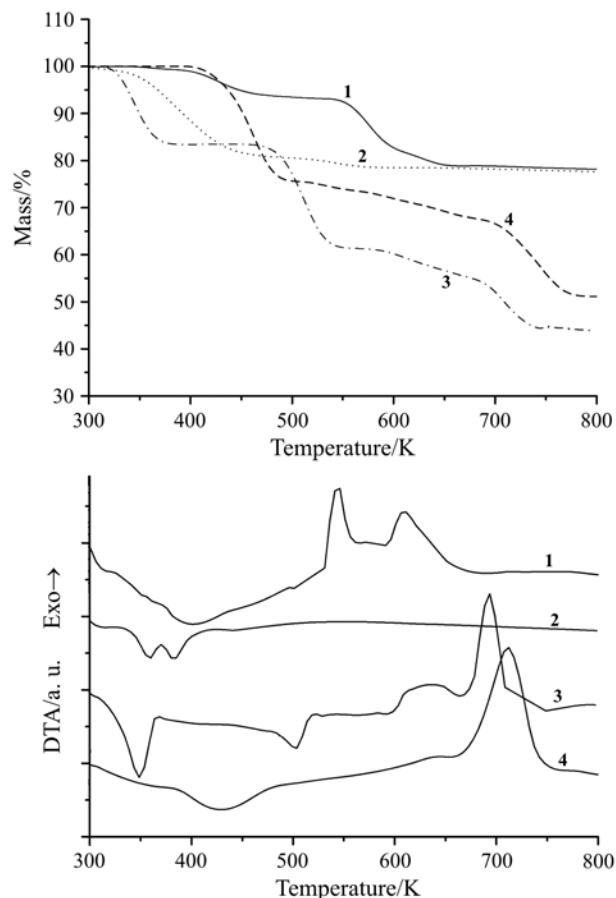


Fig. 1 TG and DTA plots of compounds 1–4

three-step dehydration/decomposition. The oxalate and malonate complexes, **1** and **2**, respectively, seem to follow similar pathway wherein initial dehydration step is followed by the loss of a CO_2 molecule in the second step. In the third step the malonate complex undergoes bimolecular decomposition leading to simultaneous removal of a CO and CO_2 molecules. The decomposition processes in maleate and phthalate complexes, **3** and **4**, follow altogether different pathways than that in complex **1** and **2**. The maleate complex **3** loses a CO_2 molecule along with three water molecules in the very first step. In the subsequent second and third steps, it loses two maleic anhydride molecules along with the loss of oxygen and biacetylene. Patron *et al.* reported the decomposition of malic acid complex $(\text{NH}_4)[\text{Fe}(\text{C}_4\text{H}_4\text{O}_5)(\text{OH})_2] \cdot 0.5\text{H}_2\text{O}$ from 273–873 K under static air [2, 13]. They have also observed a three-step decomposition with formation of anhydrous maleates, malonates and oxoacetates. The phthalate complex, **4** undergoes dehydration at higher temperature than complexes **1–3**. The loss of two water molecules is accompanied with simultaneous removal of a phthalic anhydride molecule. This complex subsequently loses the third water molecule and another phthalic anhydride gradually over 503–673 K, which is accelerated between 673–790 K. The IR spectra of the residues formed by heating upto 800 K, when recorded in KBr after cooling, showed strong carboxylate bands between $1650\text{--}1700\text{ cm}^{-1}$ in case of **1** and **2** while that of **3** and **4** showed a strong CO_3^{2-} band at 1060 cm^{-1} . Carp *et al.* have reported formation of iron oxide in the thermal decomposition of iron(II)/copper(II) oxalate mixed salts precipitate in this temperature range [14]. It is likely that copper ions present in the sample have catalyzed the process. The tris-chelate complexes seem to be more stable than simple iron(II) carboxylate salts.

DTA of all four complexes are shown in Fig. 1. The initial dehydration processes are seen as endothermic troughs. The step-3, redox decompositions to bischelate complexes (in case of **1** and **2**) or removal of anhydrides (in case of **3** and **4**) are observed as exothermic peaks. These are in agreement with the energetic nature of the assigned processes.

The Freeman and Carrol method [15] was used to evaluate the kinetic parameters. The steep parts of the TG curves were used for these calculations. The temperature regions used for the calculations of kinetic parameters for different steps are given in Table 3. The plots of $\Delta \ln(dw/dt)/\Delta \ln(w_r)$ vs. $\Delta(1/T)/\Delta \ln(w_r)$ (where $\Delta \ln(dw/dt) = \ln(dw/dt)_T - \ln(dw/dt)_{T_0}$; $\Delta(1/T) = (1/T) - (1/T_0)$; $\Delta \ln(w_r) = \ln(w_r)_T - \ln(w_r)_{T_0}$) for different stages of thermal decompositions are given in Fig. 2. The frequency factors ($\ln A$) for the decomposition processes were calculated using following relationship.

Table 2 TG and DTG characteristics of complexes

Complex	Step	Dec. temperature/K		Product expected		Residue	Mass remain/ ^o % obsd. (calcd.)
		T _i	T _f	Nature	Nature		
1	1-1	387	480	2H ₂ O		K ₃ [Fe(C ₂ O ₄) ₃]·H ₂ O	92.1 (92.7)
	1-2	542	607	CO ₂		K ₃ [Fe(C ₂ O ₄) ₂]·H ₂ O+HCOOK	84.3 (83.7)
	1-3	607	663	H ₂ O		K ₃ [Fe(C ₂ O ₄) ₂] + HCOOK	78.9 (80.0)
2	2-1	333	390	3H ₂ O		K ₃ [Fe(CH ₂ C ₂ O ₄) ₃]	90.5 (89.9)
	2-2	390	441	CO ₂		K ₂ [Fe(CH ₂ C ₂ O ₄) ₂] + CH ₃ COOK	81.7 (81.7)
	2-3	506	687	1/2CO+1/2CO ₂		K ₂ [Fe(CH ₂ C ₂ O ₄) ₂] + 1/2K ₂ O	78.2 (76.4)
3	3-1	311	392	3H ₂ O+CO ₂		K ₃ [Fe(C ₂ H ₂ C ₂ O ₄) ₂ (HCC-COO)]	82.3 (83.8)
	3-2	453	552	C ₄ H ₂ O ₃ *+1/2O ₂		K ₃ [Fe(C ₂ H ₂ C ₂ O ₄)(HCC-COO)]	60.9 (62.6)
	3-3	678	761	C ₄ H ₂ O ₃ *+3/2O ₂ +1/2HCC-CCH		3/2K ₂ O+FeCO ₃	44.2 (45.4)
4	4-1	400	437	C ₈ H ₄ O ₃ *+2H ₂ O		K ₃ [Fe(C ₆ H ₄ C ₂ O ₄) ₂ (C ₆ H ₅ C-COO)]·H ₂ O	75.8 (74.5)
	4-2	437	500				
	4-3	680	790	C ₈ H ₄ O ₃ +H ₂ O		3/2K ₂ O+FeCO ₃	50.6 (51.3)

*Anhydride

Table 3 Data obtained from TG, DTG analysis: Characteristic temperatures, fraction decomposed at highest decomposition rate, maximum rate of decomposition, half width of DTG curve and kinetic parameters^a

Step	Temperature/K			α_{max}	$d\alpha/dT_{max} \cdot 10^2$	Half width	Freeman-Carroll parameters			Mechanistic parameters ^c			
	T_{10}	T_{90}	T_p				Order	$E_a/kJ\ mol^{-1}$	$\ln A^b/s$	Model	$E_a/kJ\ mol^{-1}$	$\ln A/s$	Covariance (correl. coeff.)
1-1	409	458	425	0.393	2.19	42	2.3	154	22.7	F ₂	280	68.7	-3.71·10 ⁻⁵ (-0.997)
1-2	560	592	575	0.497	2.99	32	2.2	388	52.4	F ₁	479	89.4	-1.09·10 ⁻⁵ (-0.989)
1-3	605	642	627	0.506	2.77	26	1.0	242	28.4	D ₃	909.4	161.3	-1.80·10 ⁻⁵ (-0.997)
2-1	355	385	372	0.53	3.29	28	0.7	93	14.5	F ₁	221.7	158.0	-2.33·10 ⁻⁵ (-0.998)
2-2	395	427	410	0.49	2.99	25	0.9	73	9.8	F ₁	190.0	61.4	-1.19·10 ⁻⁵ (-0.998)
2-3	527	556	544	0.60	3.09	41	1.1	178	21.5	R ₃	308.5	45.0	-5.20·10 ⁻⁵ (-0.998)
3-1	331	362	344	0.45	3.33	28	2.4	174	31.6	F ₂	309.6	54.8	-6.00·10 ⁻⁵ (-0.999)
3-2	488	529	511	0.52	2.64	32	1.8	215	30.9	F ₁	324.1	65.2	-2.94·10 ⁻⁵ (-0.993)
3-3	696	730	709	0.44	2.97	37	1.3	328	37.5	F ₂	977	65.0	-0.63·10 ⁻⁵ (-0.999)
4-1	412	433	-	-	-	-	2.0	255.9	69.1	F ₁	363	93.0	-0.84·10 ⁻⁵ (-0.999)
4-2	443	478	462	0.66	2.20	40	0.9	98	20.8	R ₃	175	31.6	-0.93·10 ⁻⁵ (-0.991)
4-3	708	761	749	0.69	1.74	61	2.0	336	50.4	R ₃	349	42.0	-0.71·10 ⁻⁵ (-0.983)

^a T_p : temperature at which (d α /d t) is maximum; ^bCalculated from $\ln(d\alpha/dt)/(1-\alpha)^n$ vs. (1/ T) plot; ^cMechanistic models: D₃=three dimensional diffusion, F₁=first order, F₂=second order and R₃=contracting volume; (Conversion function, $f(\alpha)$ in the equation $(d\alpha/dt)=f(\alpha)$ is $(3/2)(1-\alpha)^{3/2}/[1-(1-\alpha)^{1/3}]$ for D₃, $(1-\alpha)$ for F₁, $(1-\alpha)^2$ for F₂ and $3(1-\alpha)^{2/3}$ for R₃ mechanisms)

$$\ln[(d\alpha/dt)/(1-\alpha)^n] = \ln A - E_a/RT \quad (1)$$

where $d\alpha/dt = (d\alpha/dT) \cdot \phi$; α is fraction decomposed, ϕ the heating rate. n is the order of decomposition reaction whose values were obtained from plots in Fig. 2.

The T_i , T_{10} , T_f and T_p (initial temperature, temperature for 10% mass loss, temperature for maximum mass loss for the step and temperature for maximum rate of mass loss respectively, Fig. 3) have been used as the main criteria to indicate the thermal stability of the complexes. All the three water molecules in malonate complex **2** are lost more readily in a single step. While in other complexes successive removal of one and then two water molecules takes place. Com-

plexes **1** and **2** undergo redox decomposition forming bis-chelate iron complexes. The process occurs more readily in **2** than in **1**. These reduced ferrous bis-chelates are thermally quite stable upto 800 K. The maleic and phthalic acid complexes **3** and **4** possess a very high tendency to remove cyclic anhydride. Complex **3** particularly decomposes to metal carbonate much readily below 800 K. While in phthalate complex the process occurs at much higher temperature (1015 K). The dehydrated oxalate complex, **1** (i.e. after step 1–2) is rather a stable product than corresponding dehydrated malonato complex, **2** (step 2–2) as the subsequent third step in **1** is observed at much higher temperature than in **2**.

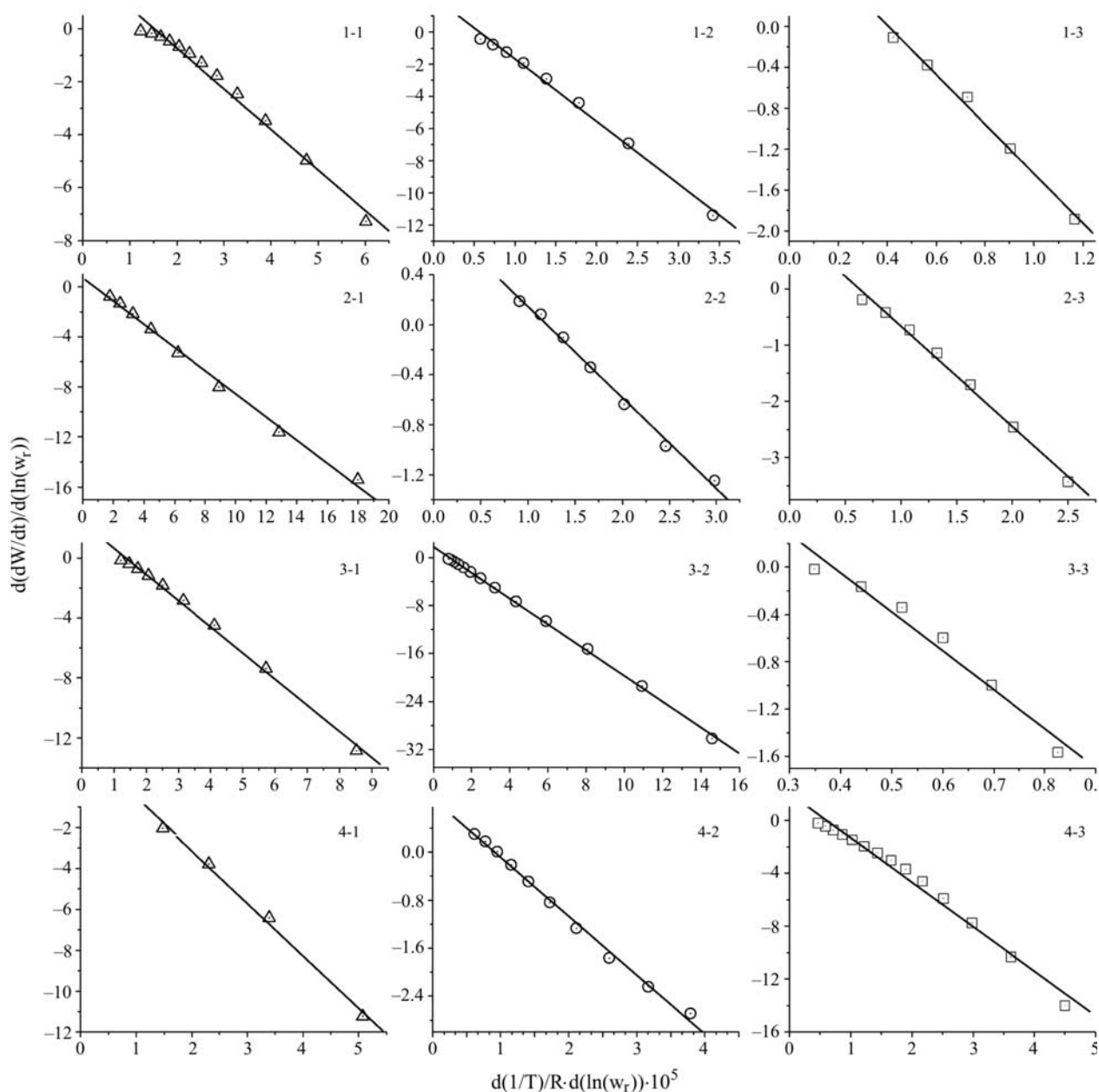


Fig. 2 Plots of $\Delta \ln(dw/dt)/\Delta \ln(w_r)$ vs. $\Delta(1/T)/\Delta \ln(w_r)$ for compounds 1–4

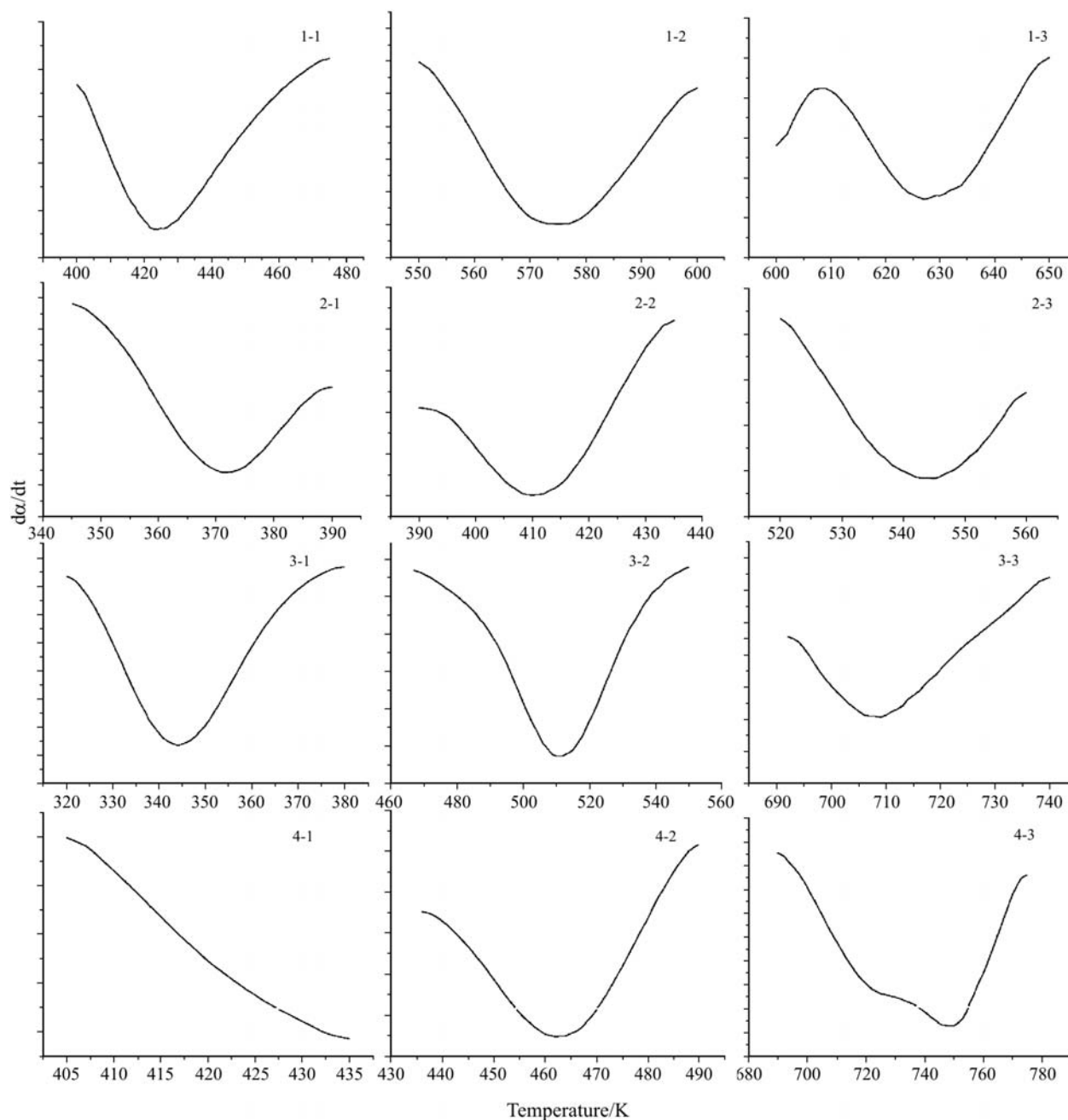


Fig. 3 Plots of $d\alpha/dt$ vs. T of complexes 1–4

The $d\alpha/dT$ vs. T plots all decomposition steps are shown in Fig. 3. These have been used for determining the mechanistic models of the thermal process [16]. The models that gave best linear fit for plots of $\ln[\phi(d(\alpha)/dT)/F(\alpha)]$ vs. $1/RT$ (Fig. 4) (where $F(\alpha)$ is such that $(d(\alpha)/dt)=k \cdot F(\alpha)$) are used to evaluate kinetic parameters. The model along with E_a and $\ln A$ are also given in Table 3. The assigned models show very high degree of correlation between $\ln[\phi(d(\alpha)/dT)/F(\alpha)]$ and $1/RT$, as reflected in the near unity values of their respective correlation coefficients (Table 3). The mechanistic models invariably gave higher values of E_a and

$\ln A$ than the Freeman and Carroll method [17]. It may be due to the differing perception of the course of the reaction in the two methods. While the mechanistic models are based on nucleation and growth of the reaction centers, the Freeman and Carroll method presumes that reaction occurs uniformly throughout the sample. The first two steps in all compounds generally follow F_1 or F_2 pathways. But the third step follows D_3 mechanism in **1** and R_3 in **2–4**. Iron maleate and phthalate salts also adopt similar mechanistic pathways [18].

The activation thermodynamic parameters namely enthalpy (H^\ddagger), entropy (S^\ddagger) and free energy (G^\ddagger) were

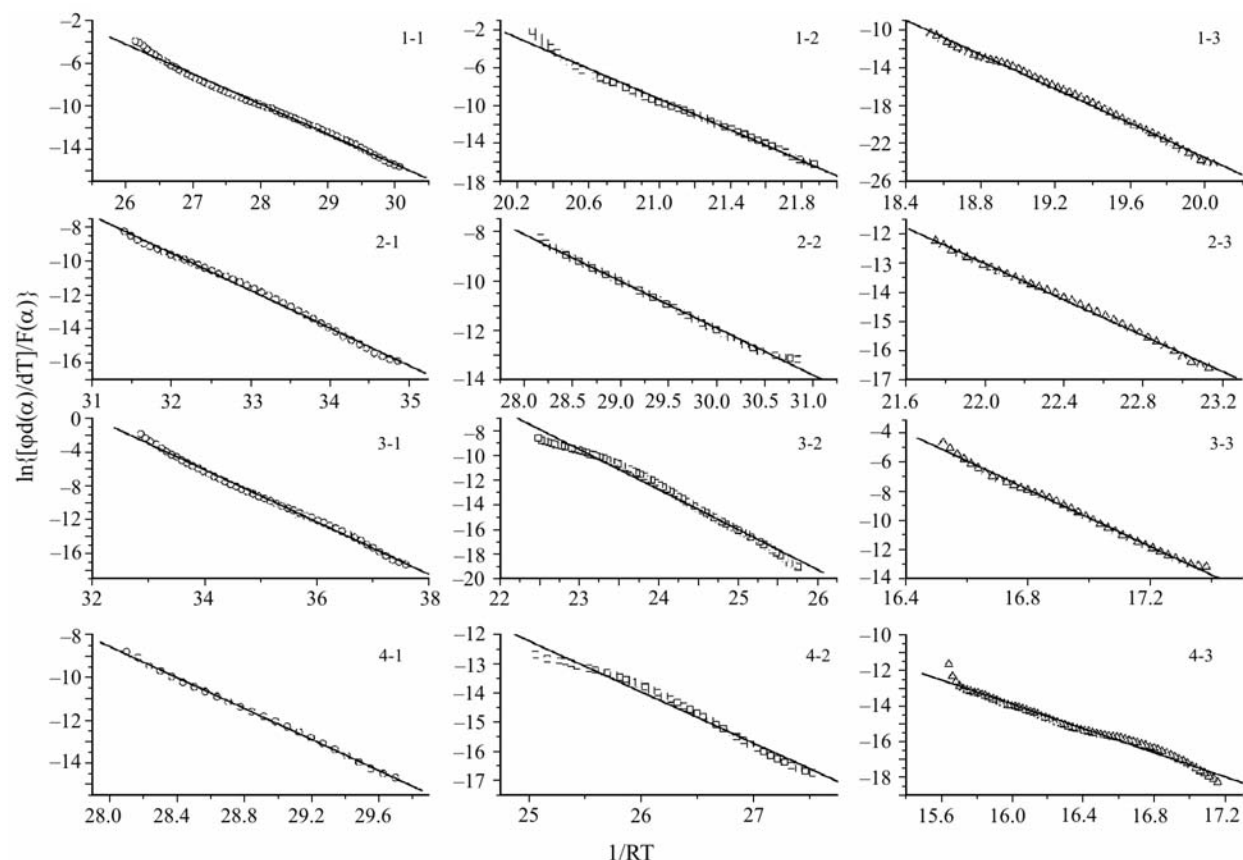


Fig. 4 Plots of $\ln\{\phi(d\alpha/dT)/F(\alpha)\}$ vs. $1/RT$ for the mechanistic models giving best linear fit for complexes 1–4

Table 4 Decomposition rate constant and thermodynamic parameters for the thermal decomposition process at T_p (i.e. temperature at highest rate of decomposition)

Complex	Step	T_p	$k \cdot 10^{-2}$	$\Delta H^\ddagger/\text{kJ mol}^{-1}$	$\Delta S^\ddagger/\text{J K}^{-1} \text{mol}^{-1}$	$\Delta G^\ddagger/\text{kJ mol}^{-1}$
1	1-1	425	1.150	145.2	56.59	121.1
	1-2	575	2.091	377.9	374.64	162.5
	1-3	627	0.935	236.7	87.53	181.8
2	2-1	372	0.930	90.5	-42.28	106.3
	2-2	410	0.913	69.7	-116.53	117.5
	2-3	544	1.411	172.7	32.16	155.2
3	3-1	344	2.330	167.4	209.36	95.4
	3-2	511	1.649	207.8	123.22	144.9
	3-3	709	1.052	320.8	163.19	205.3
4	4-1	415*	0.640	249.0	310.31	120.2
	4-2	462	0.876	94.6	-83.10	133.0
	4-3	749	3.103	323.3	150.24	210.8

*calculated for $T=415$ K

evaluated using standard equations and the values obtained are listed in Table 4.

Conclusions

In conclusion it could be said that tris-chelated oxalate and malonate complexes of iron(III) undergo rapid dehydration at lower temperature while at

higher temperature (above 540 K) they undergo dissociation forming bis chelate iron(III) complexes. The tris-chelated malonate and maleate complexes dehydrate with almost equal ease but the latter is much less stable to decomposition and yields FeCO_3 below 760 K. The *cis*-dicarboxylate complexes 3 and 4 are highly prone to loss of cyclic anhydrides. Iron oxides has not been formed with any of these tris(dicarboxylato)iron(III) precursors up to 800 K as

confirmed from the IR of the residues. The dehydration steps generally followed the first or second order pathways while the third decomposition steps followed either three dimensional diffusion or contracting volume pathways.

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