

THERMAL DEHYDRATION AND DECOMPOSITION OF $M[M(C_2O_4)_2] \cdot xH_2O$ ($x=3$ FOR $M=Sr(II)$ AND $x=6$ FOR $M=Hg(II)$)

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Abstract

Strontium(II) bis (oxalato) strontium(II) trihydrate, $Sr[Sr(C_2O_4)_2] \cdot 3H_2O$ and mercury(II) bis (oxalato) mercurate(II) hexahydrate, $Hg[Hg(C_2O_4)_2] \cdot 6H_2O$ have been synthesized and characterized by elemental analysis, reflectance and IR spectral studies. Thermal decomposition studies (TG, DTG and DTA) in air showed $SrCO_3$ was formed at ca. $500^\circ C$ through the formation of transient intermediate of a mixture of $SrCO_3$ and SrC_2O_4 around $455^\circ C$. Sharp phase transition from γ - $SrCO_3$ to β - $SrCO_3$ indicated by a distinct endothermic peak at $900^\circ C$ in DTA. Mercury(II) bis (oxalato) mercurate(II) hexahydrate showed an inclined slope followed by surprisingly steep slope in TG at $178^\circ C$ and finally 98.66% of weight loss at $300^\circ C$. The activation energies (E^*) of the dehydration and decomposition steps have been calculated by Freeman and Carroll and Flynn and Wall's method and compared with the values found by DSC in nitrogen. A tentative reaction mechanism for the thermal decomposition of $Sr[Sr(C_2O_4)_2] \cdot 3H_2O$ has been proposed.

Keywords: activation energy, complexes, kinetics, oxalato complexes, thermal decomposition

Introduction

Although, much of the work on oxalato complexes of transition and non-transition metals of various types have been reviewed [1] and the thermal decomposition of several complexes have been extensively studied by Wendlandt *et al.* [2-5], complexes of the type $Sr[Sr(C_2O_4)_2] \cdot xH_2O$ and $Hg[Hg(C_2O_4)_2] \cdot xH_2O$ are still unknown. Derouane *et al.* [6] studied the thermal decomposition of strontium(II) oxalate by the TG and mass spectroscopy and reported that it decomposed with dismutation of carbon monoxide. Simultaneously Nagase *et*

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al. [7] reported that SrCO_3 was formed at 403°C followed by the phase transition from $\gamma\text{-SrCO}_3$ to $\beta\text{-SrCO}_3$ at 875°C . Usha *et al.* [8] studied the compound $\text{NH}_4\text{Sr}[\text{Co}(\text{C}_2\text{O}_4)_3] \cdot n\text{H}_2\text{O}$ which was decomposed in a complex manner and the final product was affected by the surrounding atmosphere. Mössbauer study of the decomposition of $\text{Sr}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot n\text{H}_2\text{O}$ showed [9] at 700°C $\text{SrFe}^{\text{IV}}\text{O}_4$ was formed as final product. Awasthi *et al.* studied the complex $\text{Sr}_2\text{U}(\text{C}_2\text{O}_4)_4 \cdot n\text{H}_2\text{O}$ [10] and a dichelate oxalato complex of ammonium salt of the type $(\text{NH}_4)_2[\text{Hg}(\text{C}_2\text{O}_4)_2] \cdot 2\text{H}_2\text{O}$ has been reported [11]. Graddon [12] studied the possibility of covalently and ionically bound oxalato group in complexes of mercury along with other alkaline earth and transition metal. In continuation of our work [13–20] on bimetallic bivalent oxalato complexes of the type $\text{M}[\text{M}(\text{C}_2\text{O}_4)_2] \cdot x\text{H}_2\text{O}$ (where M = same metals), we report here the synthesis, characterization and thermal decomposition of hitherto unknown $\text{Sr}[\text{Sr}(\text{C}_2\text{O}_4)_2] \cdot 3\text{H}_2\text{O}$ and $\text{Hg}[\text{Hg}(\text{C}_2\text{O}_4)_2] \cdot 6\text{H}_2\text{O}$. We also report the kinetic parameters of the dehydration and decomposition and a tentative mechanism has been contemplated.

Experimental

The synthesis of the compounds were carried out by the method described [13–19] earlier from the respective metal chlorides.

Infrared spectra ($4000\text{--}200\text{ cm}^{-1}$), far infrared, diffuse reflectance spectra were recorded as described earlier [13–20]. The IR spectra of the gases evolved during decomposition were recorded as described earlier [21].

TG, DTG and DTA were carried out at a heating rate of $10\text{ deg}\cdot\text{min}^{-1}$ in static air up to 1000°C in case of strontium compound and up to 500°C for mercury complex. DSC was carried out in nitrogen using Perkin-Elmer DSC-7 at a heating rate of 5, 10 and $20\text{ deg}\cdot\text{min}^{-1}$. The kinetic parameters of the phase transformation process in DSC were evaluated by the method described by Wendlandt [22].

The water content was determined thermogravimetrically and gravimetrically as described earlier [21]. The strontium and mercury were estimated gravimetrically by precipitating as SrSO_4 and HgS respectively. Carbon and hydrogen contents were analysed (Table 1) using a Thomas CH analyzer.

Results and discussion

The white compounds are insoluble in water or in common organic solvents and decomposed in the presence of strong acid or alkali.

The water analysis revealed that the strontium and mercury compound should contain three and six molecules of water respectively per molecule of the compound. The estimated metal content and microanalytical results show good agreement for the proposed formula $\text{Sr}[\text{Sr}(\text{C}_2\text{O}_4)_2] \cdot 3\text{H}_2\text{O}$ and $\text{Hg}[\text{Hg}(\text{C}_2\text{O}_4)_2] \cdot 6\text{H}_2\text{O}$.

Table 1 Microanalytical and kinetic data evaluated by the methods: (a) Freeman and Carroll and (b) Flynn and Wall

Compound	Weight of sample examined/mg	Element	%		Step	Method	E^* / $\text{kJ}\cdot\text{mol}^{-1}$	Reaction
			Found	(Calcd.)				
$\text{Sr}[\text{Sr}(\text{C}_2\text{O}_4)_2]\cdot 3\text{H}_2\text{O}$	50	Sr	42.76	(43.24)	1	(a)	19	Dehydration
		C	12.32	(11.84)		(b)	24	Dehydration
		H	1.53	(1.48)	2	(a)	48.4	Decomposition
		H_2O	13.46	(13.32)		(b)	61.8	Decomposition
$\text{Hg}[\text{Hg}(\text{C}_2\text{O}_4)_2]\cdot 6\text{H}_2\text{O}$	15	Hg	57.24	(58.55)	1	(a)	28.7	Dehydration
		C	6.91	(7.01)		(b)	26.6	Dehydration
		H	1.82	(1.75)	2	(a)	-	-
		H_2O	16.17	(15.76)		(b)	-	-

Table 2 Selected bands in the IR spectrum of the complex Sr [Sr (C₂O₄)₂].3H₂O

IR bands ^a / cm ⁻¹	Assignments
3000–3750b	$\nu_{\text{sy}}(\text{O-H}) + \nu_{\text{asy}}(\text{O-H})$ or hydrogen bonding
1630s	$\delta_{\text{sy}}(\text{H-O-H})$
1500–1800b	$\nu_{\text{asy}}(\text{C=O})$
~1325, 1390sh	$\nu_{\text{sy}}(\text{C-O})$ and/or $\delta(\text{O-C=O})$
870m	$\nu_{\text{sy}}(\text{C-O})$ and/or $\delta(\text{O-C=O})$
790s	$\nu(\text{Sr-O})$ and/or $\delta(\text{O-C=O})$ or co-ordinated water
765mb	Co-ordinated water
610mb	Water of crystallization
525m	$\nu(\text{Sr-O})$ and/or $\nu(\text{C-C})$ $\delta(\text{O-C=O})$ and/or ring deformation
430m	$\nu(\text{Sr-O})$ and/or ring deformation
365m	$\delta(\text{O-C=O})$
230–340b	Out-of-plane bending
(Split into 290)	
197ms	$\nu(\text{Sr-Sr})$

^am, medium; s, strong; b, broad; sh, shoulder

Table 3 Selected bands in the IR spectrum of the complex Hg [Hg (C₂O₄)₂].6H₂O

IR bands ^a / cm ⁻¹	Assignments
2900–3700b	$\nu_{\text{sy}}(\text{O-H}) + \nu_{\text{asy}}(\text{O[-H]})$ or hydrogen bonding
1630s	$\delta_{\text{sy}}(\text{H-O-H})$
1500–1750b	$\nu_{\text{asy}}(\text{C=O})$
1420m	$\nu_{\text{sy}}(\text{C-O})$ and/or $\nu(\text{C-C})$
~1325s, ~1280sh	$\nu_{\text{sy}}(\text{C-O})$ and/or $\delta(\text{O-C=O})$
~795s	$\nu(\text{Hg-O})$ and/or $\delta(\text{O-C=O})$ or co-ordinated water
735b	Co-ordinated water
650mb, 630m	Water of crystallization
540s	$\nu(\text{Hg-O})$ and/or $\nu(\text{C-C})$
420m	$\nu(\text{Hg-O})$ and/or ring deformation
370b	$\delta(\text{O-C=O})$
260–350b	Out-of-plane bending
184ms	$\nu(\text{Hg-Hg})$

^asame as Table 2

The chelating character of the oxalato group as well as the presence of crystal and coordinated water were calculated from the IR spectral data (Tables 2 and 3). The bands were assigned on the basis of earlier studies [13–21, 23, 26]. From the observation of the removal of water molecule at higher temperature [24] the possibility of association of some of the water molecules with coordinated oxalato groups through hydrogen bonding cannot be ruled out like reported earlier [15, 17]. The insolubility of the compounds and the presence of medium sharp band at 197 and 184 cm^{-1} in the far IR spectra of respective strontium and mercury compounds indicated [25] the presence of metal–metal bond. Similar observations were reported [20] earlier. In the electronic spectra of the solid sample, the bands in the UV region were due to intraligand $\pi \rightarrow \pi^*$ transitions [15, 16].

In the thermal studies of $\text{Sr}[\text{Sr}(\text{C}_2\text{O}_4)_2] \cdot 3\text{H}_2\text{O}$ the water loss started from 30°C as indicated by TG curve (Fig. 2) and steep slope up to 170°C corresponding to the weight loss of 12.98% (calcd. 13.32%) indicated the removal of all the three molecules of water. A distinct broad change in around 30–65°C in DTA curve (Fig. 1) as well as a change in DTG indicated the removal of first molecule of water of crystallization. A strong endothermic change between 110–175°C in DTA having two overlapping peaks with ΔT_{min} of 135 and 155°C

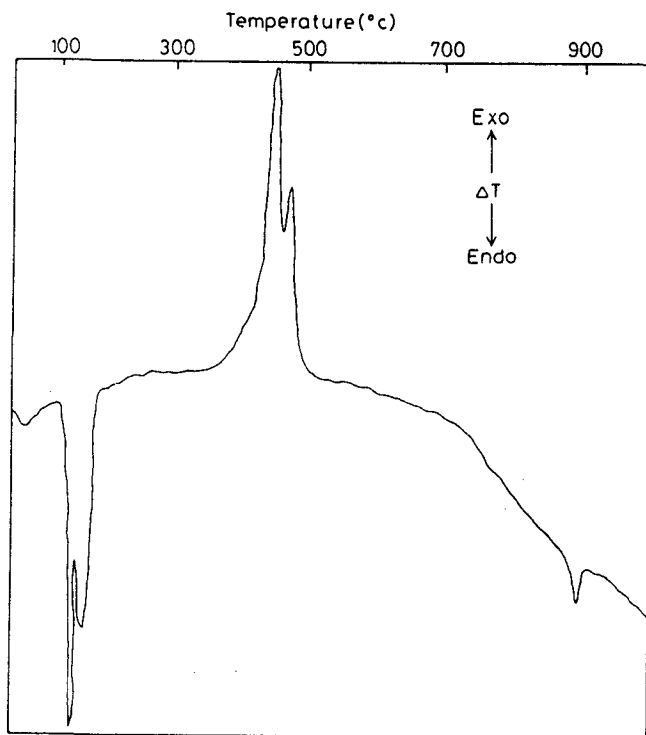


Fig. 1 DTA curve of $\text{Sr}[\text{Sr}(\text{C}_2\text{O}_4)_2] \cdot 3\text{H}_2\text{O}$ at $10 \text{ deg} \cdot \text{min}^{-1}$ in air

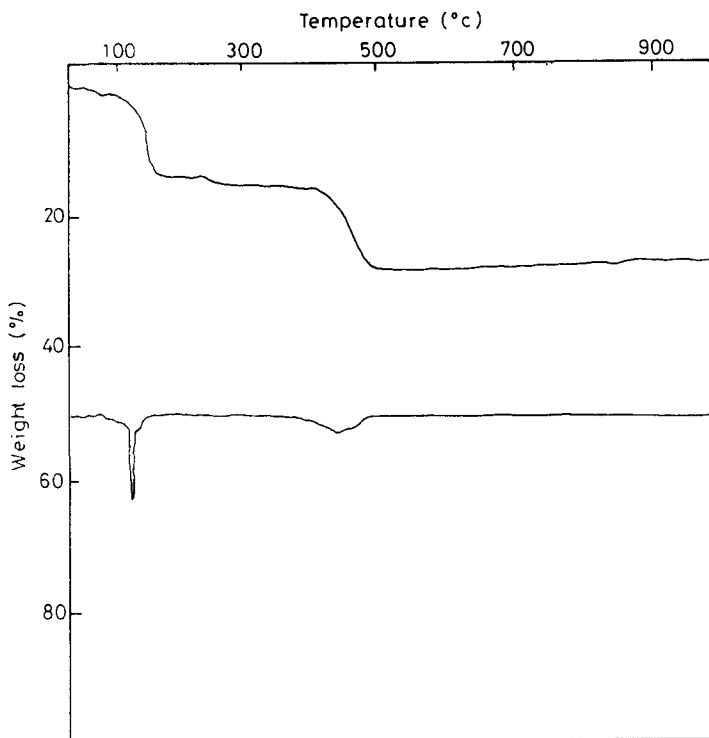


Fig. 2 TG and DTG curves of $\text{Sr}[\text{Sr}(\text{C}_2\text{O}_4)_2] \cdot 3\text{H}_2\text{O}$ at $10 \text{ deg}\cdot\text{min}^{-1}$ in air

suggested the removal of water takes place one after another. Corresponding to this, two respective DTA peaks temperature there occurred 4.36% (calcd. 4.44%) and 8.62% (calcd. 8.88%) weight loss in TG indicated the removal of first and second molecule of water. The compound formed at 170°C was stable up to 240°C in TG and the sudden weight loss of 2.2% and overall weight loss of 14% at ca. 255°C and finally stable up to 385°C suggested the high stability of anhydrous compound. The temperature arrest technique was used to isolate the anhydrous compound and the retention of the chelating character of oxalato group was confirmed [15] from the IR spectrum. The weight loss observed after independent pyrolysis in air up to 350°C is in good agreement with the calculated value. The removal of water molecule started at 93°C in TG of simple strontium oxalate as reported by Nagase *et al.* [7]. In the TG curve (Fig. 4) of $\text{Hg}[\text{Hg}(\text{C}_2\text{O}_4)_2] \cdot 6\text{H}_2\text{O}$ the weight loss started at 70°C and an inclined slope up to 276°C with a weight loss of 16.28% (calcd. 15.76%) indicated the loss of all six molecules of water. Corresponding to the dehydration stage in TG (Fig. 3) two small exothermic peaks at 120 and 200°C were observed. The relevant portion of the TG curve was chosen for the kinetic study and the activation energies calculated by the respective methods of Freeman and Carroll [27] and Flynn and Wall [28] for strontium and mercury compounds are tabulated in Table 1.

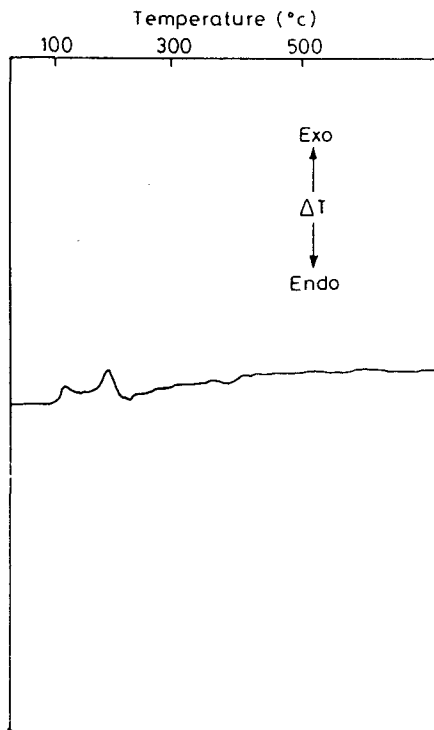


Fig. 3 DTA curve of $\text{Hg}[\text{Hg}(\text{C}_2\text{O}_4)_2] \cdot 6\text{H}_2\text{O}$ at $10 \text{ deg} \cdot \text{min}^{-1}$ in air

Corresponding to the dehydration step in DSC ($5 \text{ deg} \cdot \text{min}^{-1}$) in nitrogen an endothermic peak ranged between $129\text{--}175^\circ\text{C}$ ($\Delta T_{\text{min}} = 163.6^\circ\text{C}$) was observed. The activation energy (E^*), the logarithm of pre-exponential factor ($\ln k_0$), enthalpy change (ΔH) and the order of reaction at a heating rate of 5, 10 and $20 \text{ deg} \cdot \text{min}^{-1}$ for the dehydration and decomposition steps of strontium compound and at 5 and $20 \text{ deg} \cdot \text{min}^{-1}$ for the mercury compound are tabulated in Table 4. At 5°C for $\text{Hg}[\text{Hg}(\text{C}_2\text{O}_4)_2] \cdot 6\text{H}_2\text{O}$ exotherms for the decomposition could not be observed as it is scanned up to 480°C . Large variation of the kinetic parameters are observed in the values calculated by the methods [27, 28] applied on TG and DSC like reported earlier [20]. Due to the inherent peculiarities of high volatility associated with mercury, the anhydrous compound could not be isolated by the temperature arrest technique in TG and independent pyrolysis in air as well. From the TG curve (Fig. 4) it could be guessed that decomposition of the compound starts during the removal of last water molecule as there is surprisingly a very steep slope in TG with a weight loss of 93.59% within 176°C to 201°C . The high values of the kinetic parameters obtained by DSC in nitrogen with an overall weight loss of 93.59% in TG suggested the decomposition of the compound of mercury is violent and extremely rapid. Within the range of $201\text{--}298^\circ\text{C}$ the steep TG slope changed to inclined pattern with two visible

Table 4 The DSC data of $\text{Sr}[\text{Sr}(\text{C}_2\text{O}_4)_2] \cdot 3\text{H}_2\text{O}$ and $\text{Hg}[\text{Hg}(\text{C}_2\text{O}_4)_2] \cdot 6\text{H}_2\text{O}$ in nitrogen

Heating rate/ $\text{deg}\cdot\text{min}^{-1}$	Weight of sample $\text{examd.}/\text{mg}$	Compound	Step	$T/^\circ\text{C}$	Peak temp.	$\ln k_0$	$E^*/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta H/\text{J}\cdot\text{gm}^{-1}$	Order of reaction	Reaction
5	3.69		1	129-175 (endo)	163.6	53.9 ± 1.4	206 ± 5	198.6	1.1 ± 0.02	Dehydration
10	3.22	$\text{Sr}[\text{Sr}(\text{C}_2\text{O}_4)_2] \cdot 3\text{H}_2\text{O}$	2	-	-	-	-	-	-	-
			1	130-185 (endo)	166.5	54 ± 1.2	211 ± 4.6	213	1.14 ± 0.02	Dehydration
			2	452-656 (exo)	520	34 ± 0.8	283 ± 4.7	2168	0.98 ± 0.01	Decomposition
20	3.61		1	132-210 (endo)	181	56.4 ± 1.4	217 ± 4.8	265	1.30 ± 0.02	Dehydration
			2	466-610 (exo)	536	42 ± 0.9	317 ± 6.9	3068	1.40 ± 0.03	Decomposition

Table 4 Continued

Heating rate/ deg·min ⁻¹	Weight of sample examd./mg	Compound	Step	Temp. range/ °C	Peak temp.	lnk ₀	E*/ kJ·mol ⁻¹	ΔH/ J·gm ⁻¹	Order of reaction	Reaction
5	4.34		1	119–185 (exo)	153	13.2±0.3	68±1.5	52	0.6±0.01	Dehydration
			2	226–234 (exo)	227	535±8.6	558±12	178	4.2±0.13	Decomposition
10	4.70	Hg[Hg(C ₂ O ₄) ₂ ·6H ₂ O]	1	134–188 (exo)	157	67±1.7	98±2.1	79	1.4±0.02	Dehydration
			2	232–250 (exo)	234	547±12	616±13	183	4.8±0.10	Decomposition

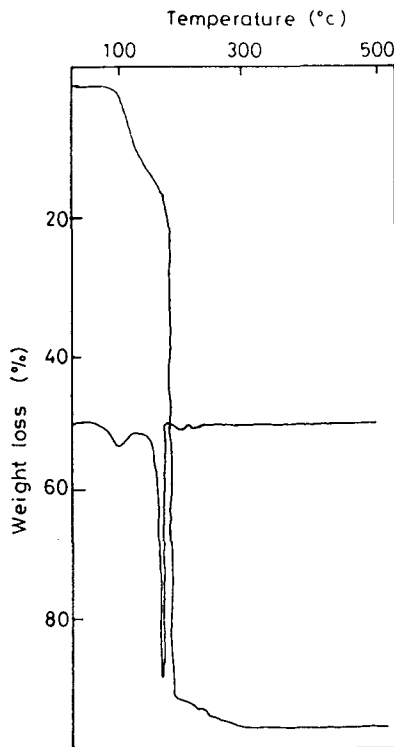


Fig. 4 TG and DTG curves of $\text{Hg}[\text{Hg}(\text{C}_2\text{O}_4)_2] \cdot 6\text{H}_2\text{O}$ at $10 \text{ deg} \cdot \text{min}^{-1}$ in air

break at 235 and 265°C with respective weight loss of 95.64% and 96.64% which might be ascribed due to volatilization and some phase changes from the end product. The DTA curve (Fig. 3) showed a slight exothermic behaviour up to 1000°C for the corresponding changes in TG. DTG curve also showed two small peaks for the above changes and finally TG and DTG curves were almost stable up to 520°C.

In TG (Fig. 2) the breakdown of $\text{Sr}[\text{Sr}(\text{C}_2\text{O}_4)_2]$ takes place beyond 385°C and slope up to 500°C with a weight loss of 28% (calcd. 27.16%) indicated the formation of 2SrCO_3 . Corresponds to this decomposition there occurred an exothermic change between 380–510°C in DTA with two sharp peak with ΔT_{max} of 455 and 490°C indicated the breakdown takes place via two stages. Corresponding to the exothermic peak at 455°C in DTA (Fig. 1) the weight loss of 20% in TG attributed the intermediate compound might be a mixture of SrCO_3 and SrC_2O_4 . The formation of the intermediates were supported by the presence of two distinct changes at 446 and 470°C in the range of 380–500°C in DTG curve. As SrC_2O_4 started to decompose beyond 455°C, in our study it could be concluded that the stability of SrC_2O_4 was enhanced by the presence of SrCO_3 . The initial weight loss temperature of decomposition of SrC_2O_4 was 403°C reported by Nagase *et al.* [7] compared with 455°C in our study. Unlike our ear-

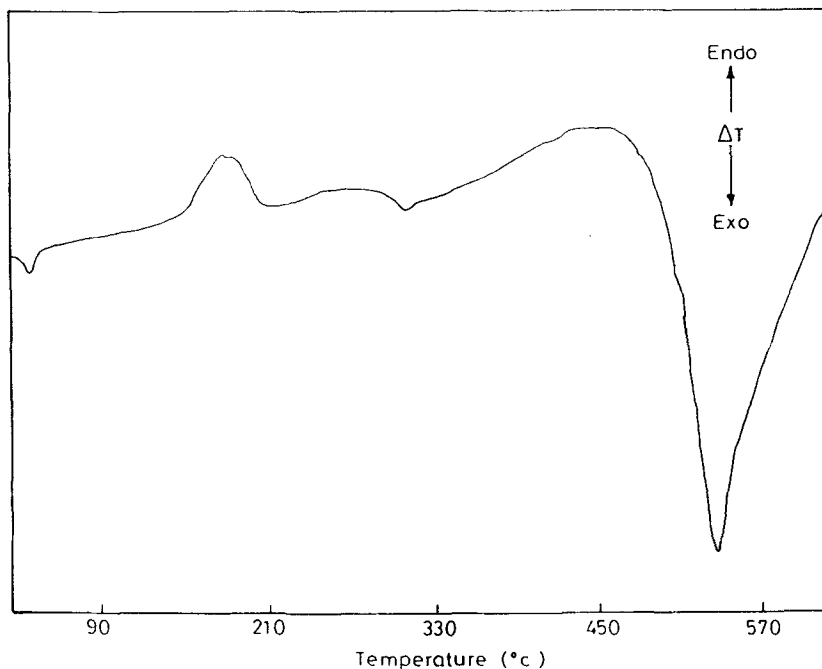


Fig. 5 DSC curve of $\text{Sr}[\text{Sr}(\text{C}_2\text{O}_4)_2] \cdot 3\text{H}_2\text{O}$ at $20 \text{ deg} \cdot \text{min}^{-1}$ in nitrogen

lier studies in the present case it can be suggested that presence of SrCO_3 increases the stability of SrC_2O_4 [19] instead of accelerating effect on the rapid decomposition of MC_2O_4 by metal oxide. Unlike other complexes SrC_2O_4 decomposed to SrCO_3 instead of strontium oxide. However, strontium oxide formed [29] above 1350°C . We carefully isolated the intermediate mixture by independent pyrolysis up to 450°C in air and separated SrC_2O_4 from SrCO_3 with difficulty by hot water. Similar separation was done in the mixture of NiO and NiC_2O_4 earlier [19]. SrC_2O_4 has been characterized by analytical, spectral and thermal techniques and the data were found identical with that of strontium oxalate reported by Nagase *et al.* [7]. The estimated strontium content in the insoluble product gives credence it to be SrCO_3 . The end product SrCO_3 formed around 500°C was almost stable and did not decompose further. The slight upward trend of the TG curve from 500 to 1000°C with a slight gain in weight of 1.5% and ultimate weight loss of 26% at 1000°C might be accounted for phase transformation of $\gamma\text{-SrCO}_3$ to $\beta\text{-SrCO}_3$. Corresponds to the phase transition or change in the crystalline structure of SrCO_3 there occurred a downward trend of DTA curve with a small sharp endothermic peak at 900°C . Similar observation was reported [7] at 875°C for $\gamma\text{-SrCO}_3$ to $\beta\text{-SrCO}_3$ phase transition. There was no any changes observed in DTG curve for this phase transition. The kinetic parameters evaluated from TG and DSC (at 10 and $20 \text{ deg} \cdot \text{min}^{-1}$) for the decom-

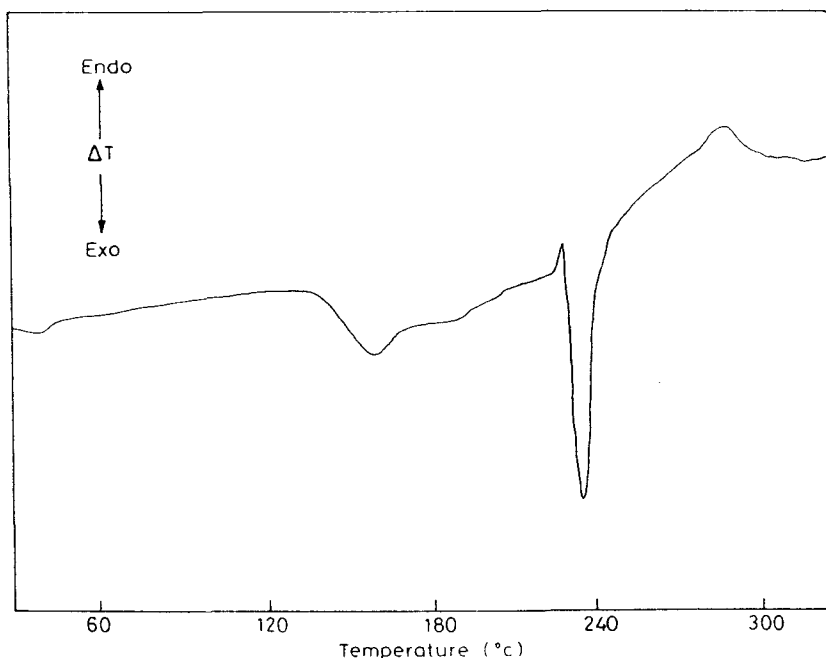
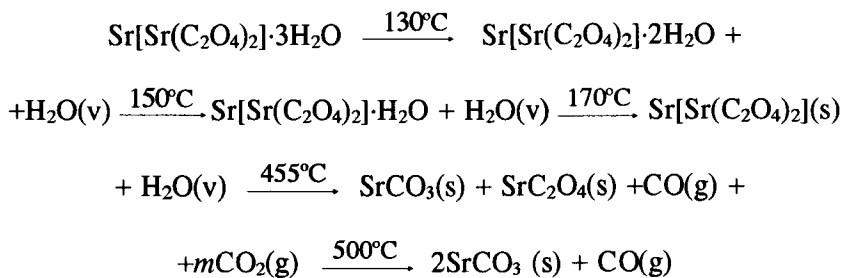


Fig. 6 DSC curve of $\text{Hg}[\text{Hg}(\text{C}_2\text{O}_4)_2] \cdot 6\text{H}_2\text{O}$ at $20 \text{ deg} \cdot \text{min}^{-1}$ in nitrogen

position steps are included in Table 4. The kinetic parameters for the decomposition step also increased with increase in heating rate like our earlier reported [15] complex.

The water vapour, carbon monoxide and carbon dioxide evolved during decomposition were identified by IR spectroscopy [23].

Above results supported the tentative mechanism,



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Zusammenfassung — Strontium(II)-bis(oxalato)-strontium(II)trihydrat $\text{Sr}[\text{Sr}(\text{C}_2\text{O}_4)_2] \cdot 3\text{H}_2\text{O}$ und Quecksilber(II)-bis(oxalato)-mercurat(II)hexahydrat $\text{Hg}[\text{Hg}(\text{C}_2\text{O}_4)_2] \cdot 6\text{H}_2\text{O}$ wurden hergestellt und mittels Elementaranalyse, Reflexionsvermögen und IR-Spektraluntersuchungen charakterisiert. Thermische Zersetzungsuntersuchungen (TG, DTG und DTA) in Luft zeigten die Bildung von SrCO_3 bei etwa 500°C , nachdem zuvor bei etwa 445°C als Zwischenprodukt ein Gemisch aus SrCO_3 und SrC_2O_4 gebildet wurde. Ein deutlicher endothermer Peak im DTA bei 900°C weist auf eine scharfe Phasenumwandlung von $\gamma\text{-SrCO}_3$ zu $\beta\text{-SrCO}_3$ hin. Quecksilber(II)-bis(oxalato)-mercurat(II)hexahydrat zeigt einen schrägen Anstieg, gefolgt von einem überraschend steilen Anstieg im TG bei 178°C und letztlich einen Massenverlust von 98.66% bei 300°C . Mittels der Methode von Freeman und Carroll und Flynn und Wall wurden die Aktivierungsenergien (E^*) der Dehydratation und Zersetzung berechnet und mit den in Stickstoff mittels DSC gefundenen Werten verglichen. Für die thermische Zersetzung von $\text{Sr}[\text{Sr}(\text{C}_2\text{O}_4)_2] \cdot 3\text{H}_2\text{O}$ wurde ein vorläufiger Reaktionsmechanismus vorgeschlagen.