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Synthesis, characterization and the thermal decomposition of calcium(II)bis(oxalato)calcium(II)dihydrate

N. Deb ^{a,*}, S.D. Baruah ^b, N.N. Dass ^c

^a *Department of Chemistry, North Eastern Regional Institute of Science and Technology,
Nirjuli 791 109, Arunachal Pradesh, India*

^b *Regional Research Laboratory, Jorhat 785 006, Assam, India*

^c *Department of Chemistry, Dibrugarh University, Dibrugarh 786 004, Assam, India*

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Abstract

Calcium(II)bis(oxalato)calcium(II)dihydrate, $\text{Ca}[\text{Ca}(\text{C}_2\text{O}_4)_2] \cdot 2\text{H}_2\text{O}$, has been synthesized and characterized by elemental analysis, and reflectance and IR spectral studies. Thermal decomposition studies (TG, DTG, and DTA) in air showed that the final end product was CaO at 865°C through the intermediate formation of a mixture of CaCO_3 and CaO at approx. 818°C. At around 424°C a mixture of CaO and $\text{Ca}(\text{C}_2\text{O}_4)_{1,2}$ is formed by partial decomposition of oxalate which is stable up to 670°C. DSC studies up to 700°C in nitrogen at 10°C min⁻¹ showed both endothermic and exothermic peaks with activation energies of 190 and 458 kJ mol⁻¹, respectively, and compared with values calculated from TG. Some of the decomposition products were identified by spectral, analytical and X-ray powder diffraction studies and a tentative mechanism for the decomposition is proposed.

Keywords: Thermal decomposition; Elemental analysis; Reflectance studies; IR studies

1. Introduction

There has been considerable interest in the study of oxalato complexes of transition and non-transition metals and much of the work has been periodically reviewed [1]. Although the oxalato complexes of alkaline earth metals of only simple types have been reported [2], complexes of the type $\text{M}[\text{M}(\text{C}_2\text{O}_4)_n] \cdot x\text{H}_2\text{O}$ are relatively unfamiliar. The thermogravimetric evaluation of the kinetics of the three-stage decomposition of

* Corresponding author.

calcium oxalate monohydrate was reported by Freeman and Carroll [3]. The effect of water vapour on the equilibrium and kinetics of dehydration of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ was studied [4] using a new controlled water vapour microsample DTA instrument. Usha et al. [5] studied the compound $\text{NH}_4\text{Ca}[\text{Co}(\text{C}_2\text{O}_4)_3] \cdot n\text{H}_2\text{O}$ which decomposed in a complex manner to yield metal carbonate or oxide and cobalt oxide as the final products, depending on the surrounding atmosphere. In continuation of our research [6–13] on bimetallic oxalato complexes of the type $\text{M}[\text{M}(\text{C}_2\text{O}_4)_n] \cdot x\text{H}_2\text{O}$ (where M is the same metal), we report here the characterization and thermal decomposition of the hitherto unknown $\text{Ca}[\text{Ca}(\text{C}_2\text{O}_4)_2] \cdot 2\text{H}_2\text{O}$ in air and nitrogen. The activation energies (E^*) of the dehydration and decomposition steps were evaluated by Freeman and Carroll's method [3] and the tentative mechanism of the decomposition is proposed. In addition, the nature of the intermediates was investigated by spectral and thermal techniques.

2. Experimental

Calcium hydroxide, prepared from calcium chloride, was made free from chloride. It was dissolved in glacial acetic acid and heated on a steam bath. A white compound was precipitated by dropwise addition of a saturated solution of oxalic acid in glacial acetic acid. The compound was filtered off, washed several times with distilled water and dried over calcium chloride. The water content was determined gravimetrically [14] and thermogravimetrically. The carbon and hydrogen contents were determined using a Thomas CH analyser. Found: C, 16.42; H, 1.43; Ca, 27.52; H_2O , 12.83%. Calcd. for $\text{C}_4\text{H}_4\text{O}_{10}\text{Ca}_2$: C, 16.44; H, 1.38; Ca, 27.43; H_2O , 12.33%.

IR spectra ($4000\text{--}600\text{ cm}^{-1}$) were recorded as nujol mulls using a Perkin–Elmer 781 spectrophotometer. Far-IR spectra were obtained using a Polytec FTIR-30 instrument. IR spectra of the gases evolved were recorded by the reported method [14]. Diffuse reflectance spectra were recorded with a Shimadzu UV-240 spectrophotometer using BaSO_4 as the reference material. DTA, TG and DTG were carried out in a Paulik–Erdy-type MOM derivatograph fabricated by the M/S Hungarian optical works, Budapest, operating at a heating rate of $8.5^\circ\text{C min}^{-1}$. $\alpha\text{-Al}_2\text{O}_3$ was used as the inert reference substance. The furnace atmosphere was static air. When necessary, intermediate products were obtained using the temperature arrest technique. DSC curves were recorded with a Perkin-Elmer DSC-7 in nitrogen at the heating rates of 5, 10 and $20^\circ\text{C min}^{-1}$. For intermediates, the samples were also heated in a tube as described earlier [14].

3. Results and discussion

The complex, $\text{Ca}[\text{Ca}(\text{C}_2\text{O}_4)_2] \cdot 2\text{H}_2\text{O}$, was obtained as a white powder compound which was insoluble in common organic solvents, but decomposed in strong acid or alkali.

Water analysis revealed that the compound should contain two molecules of water per molecule of the compound. The estimated metal content and microanalytical

Table 1
Selected bands in the IR spectrum of the complex $\text{Ca}[\text{Ca}(\text{C}_2\text{O}_4)_2] \cdot 2\text{H}_2\text{O}$

IR band/ cm^{-1}	Assignment
3000–3700b	$\nu_{\text{sym}}(\text{O}-\text{H}) + \nu_{\text{asym}}(\text{O}-\text{H})$ or hydrogen bonding
1620b	$\delta_{\text{sym}}(\text{H}-\text{O}-\text{H})$
1450–1800b	$\nu_{\text{asym}}(\text{C}=\text{O})$
ca. 1370m	$\nu_{\text{sym}}(\text{C}-\text{O})$ and/or $\nu(\text{C}-\text{C})$
ca. 1320s, Ca. 950s	$\nu_{\text{sym}}(\text{C}-\text{O})$ and/or $\delta(\text{O}-\text{C}=\text{O})$
890s	$\nu(\text{C}-\text{O})$ and/or $\delta(\text{O}-\text{C}=\text{O})$
790s	$\nu(\text{Ca}-\text{O})$ and/or $\delta(\text{O}-\text{C}=\text{O})$
660m	Water of crystallization.
520ms	$\nu_{\text{sym}}(\text{C}-\text{C})$ and/or ring deformation
200–320b (split into 230 and 270)	Out-of-plane bending
170 (sharp)	$\nu(\text{Ca}-\text{Ca})$

Key: b, broad; m, medium; and s, strong.

results suggested that the formula of the complex was $\text{Ca}[\text{Ca}(\text{C}_2\text{O}_4)_2] \cdot 2\text{H}_2\text{O}$. The IR peaks were assigned (Table 1) on the basis of earlier studies [6–13] and suggested the chelating nature of the oxalato group as well as the presence of coordinated water molecules [15]. The possibility of hydrogen bonding between coordinated water molecules and the oxalato group cannot be ruled out due to the presence of a broad band between 2800 and 3700 cm^{-1} in the IR spectrum. The removal of water starting at a higher temperature gives credence to this view. The extreme insolubility and the presence of a medium-sharp peak at 170 cm^{-1} in the far-IR spectrum indicated the presence of a metal–metal bond [8]. The bands observed in the UV region of the electronic spectrum of the solid compound are due to intraligand $\pi \rightarrow \pi^*$ transitions.

Water vapour, carbon monoxide and carbon dioxide were evolved during decomposition and identified by IR spectroscopy [15].

The DTA curve, see Fig. 1, recorded in air showed a sharp endothermic peak with a ΔT_{min} of 216°C. It was followed by a large exothermic peak with a ΔT_{max} of 424°C having a shoulder peak at approx. 400°C. After this, endothermic decomposition was observed in the DTA curve between 670 and 818°C.

Water loss started from 110°C as indicated by the TG curve, see Fig. 2, and the steep slope up to 216°C indicated the removal of two molecules of water. This corresponded well with the weight loss data (found, 12.4%; calcd., 12.33%). The dehydration stage was indicated by an endothermic peak at 216°C in the DTA and a peak ranged between 108 and 220°C with a ΔT_{max} of 215°C in the DTG curve. The anhydrous compound was isolated by the temperature arrest technique as it was stable up to 370°C, indicated by no change in the DTA, TG and DTG curves up to this temperature. The compound produced was studied by analytical and IR spectral methods which indicated that the chelating character of the oxalato group was retained. The removal of water at high temperatures was evidence [10] of metal–oxygen co-ordination to water. In simple

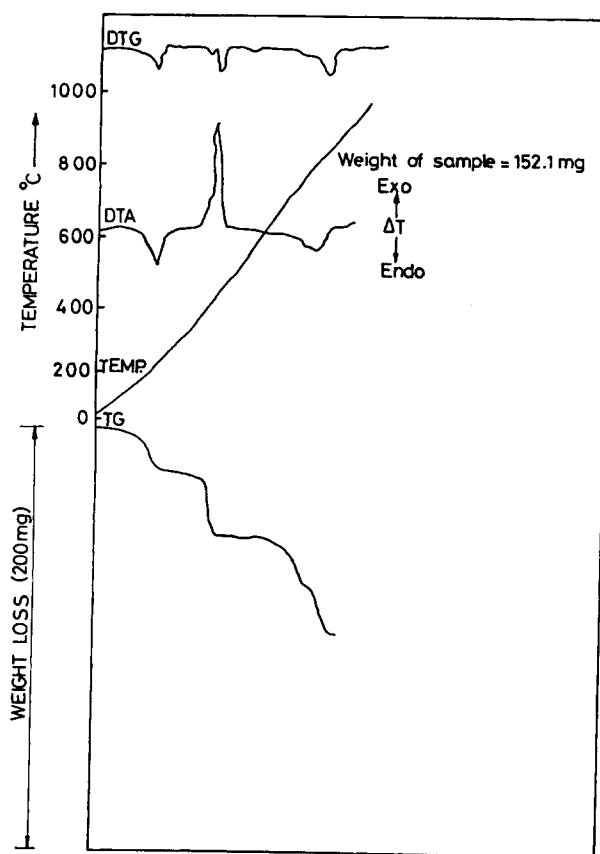


Fig. 1. DTA curve of $\text{Ca}[\text{Ca}(\text{C}_2\text{O}_4)_2] \cdot 2\text{H}_2\text{O}$ in air.

oxalate [16], the initial weight loss temperature of dehydration was 100°C ; this was also observed in a shifting of the peak near 840 cm^{-1} due to $\nu(\text{M}-\text{O})$ in the prepared anhydrous compound which was observed [12] at $\sim 790\text{ cm}^{-1}$ in the hydrated complex. The activation energy (E^*) of the dehydration step calculated from the TG slope by Freeman and Carroll's method [3] and was found to be 63.72 kJ mol^{-1} which is much lower than 92.05 kJ mol^{-1} calculated [3] for the simple oxalate. The order of reaction was calculated to be 0.9 in comparison to 1.0 in the case of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ [3]. The dehydration stage was evident in the DSC (nitrogen) curves by endothermic peaks at $133\text{--}203^\circ\text{C}$ ($\Delta T_{\min} = 190^\circ\text{C}$), $148\text{--}214^\circ\text{C}$ ($\Delta T_{\min} = 201^\circ\text{C}$) and $134\text{--}240^\circ\text{C}$ ($\Delta T_{\min} = 215^\circ\text{C}$) for heating rates of 5, 10 and $20^\circ\text{C min}^{-1}$, respectively. The activation energy (E^*), the logarithm of the pre-exponential factor ($\ln k_0$), the enthalpy change (ΔH) and the order of reaction are listed in Table 2.

Corresponding to the large exothermic peak at 424°C in DTA and a DTG peak between 368 and 427°C , there was a steep slope in the TG curves ranged between 370

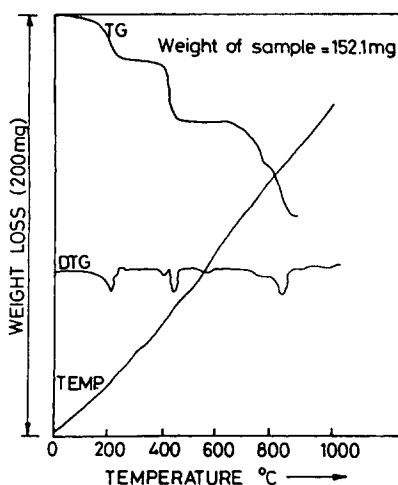


Fig. 2. TG and DTG curves of $\text{Ca}[\text{Ca}(\text{C}_2\text{O}_4)_2] \cdot 2\text{H}_2\text{O}$ in air.

and 424°C which corresponds to a weight loss of 32.07%. The weight loss data indicated that the compound might be a mixture of CaO and $\text{Ca}(\text{C}_2\text{O}_4)_{1.2}$ for which the calculated weight loss is 32.08%. The estimated calcium content (found, 38.65%; calcd., 39.73%) and microanalytical results of the compound preheated to 500°C , which was stable up to 670°C in the TG curve, partially suggested it to be a mixture of CaO and $\text{Ca}(\text{C}_2\text{O}_4)_{1.2}$. A similar partial decomposition of bimetallic oxalate was observed [10] around 358°C with the evolution of trace amounts of $\text{CO}_2(\text{g})$, without breaking the metal–metal bond. The trace amounts of gases evolved were identified by their IR spectrum, where a broad band due to $\text{CO}_2(\text{g})$ occurred at 664 cm^{-1} along with a weak band around $\sim 2445\text{ cm}^{-1}$, which might be due to $\delta(\text{O}-\text{C}-\text{O})$ and $\nu_{\text{asym}}(\text{O}-\text{C}=\text{O})$ respectively, whereas a weak band around $\sim 2096\text{ cm}^{-1}$ might be due to $\text{CO}(\text{g})$. The band of $\text{CO}(\text{g})$ was very weak, probably due to some oxidation of $\text{CO}(\text{g})$ to $\text{CO}_2(\text{g})$ in air, it might also be due to some disproportionation [17] of $\text{CO}(\text{g})$ to $\text{CO}_2(\text{g})$ and carbon. The product obtained around 500°C was separated by hot water with difficulty. The insoluble dirty white compound was identified analytically as CaO (Ca: found, 70.23%; calcd., 71.47%) and by a broad band around 330 cm^{-1} in the IR spectrum. The estimated metal content (found, 27.42%; calcd., 27.51%) of the white compound obtained from the soluble part, and the presence of bands around 1810, ~ 1360 , ~ 1325 and 950 cm^{-1} in the IR spectrum, indicated the presence of the oxalato group; the compound might be $\text{Ca}(\text{C}_2\text{O}_4)_{1.2}$. Moreover the presence of sharp bands at ~ 890 and $\sim 725\text{ cm}^{-1}$ strongly supports the presence of $\text{Ca}-\text{O}$, $\text{C}-\text{O}$ and $\delta(\text{O}-\text{C}=\text{O})$ groups. A shoulder at 400°C was observed in the exotherm of the DTA curve as well as at 420°C in DSC ($10^\circ\text{C min}^{-1}$); this may be due to the breakdown of the metal–metal bond. The E^* and order of the reaction were calculated to be 98.5 kJ mol^{-1} and 0.24 respectively. The formation of a mixture of CaO and $\text{Ca}(\text{C}_2\text{O}_4)_{1.2}$ indicated that the outer calcium in the complex formed calcium oxide and the inner

Table 2
DSC data of $\text{Ca}[\text{Ca}(\text{C}_2\text{O}_4)_2] \cdot 2\text{H}_2\text{O}$ in nitrogen

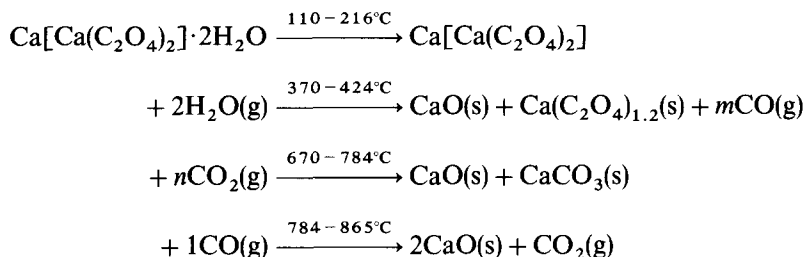
Heating rate/ $^{\circ}\text{C min}^{-1}$	Step	Temperature range/ $^{\circ}\text{C}$	Peak temperature/ $^{\circ}\text{C}$	Weight loss/%		$\ln k_0$	$E^*/\text{kJ mol}^{-1}$	$\Delta H/\text{J g}^{-1}$	Order of reaction	Reaction
				Found	Calcd.					
5	1	133.07–203.71	190.39	–	12.33	48 ± 1	201 ± 4.34	403.5 ± 0.02	1.03 ± 0.02	Dehydration
	2	427.73–479	459.44	31.06	32.08	111.14 ± 2.4	703.86 ± 15.2	837.7	1.22 ± 0.02	Decomposition
10	1	148.66–214.	201.33	–	12.33	44.61 ± 1.64	190.13 ± 4.1	388.3	0.98 ± 0.02	Dehydration
	2	419.06–495.7	473.04	30.69	32.08	69.75 ± 1.5	458.36 ± 9.9	1422.1	1.03 ± 0.02	Decomposition
20	1	134.19–240	215.89	–	12.33	24.59 ± 0.53	114.5 ± 2.47	499.2 ± 0.02	0.92 ± 0.02	Dehydration
	2	446.11–517.32	494.14	28.08	32.08	74.3 ± 1.61	494.85 ± 10.68	1327.3	1.08 ± 0.02	Decomposition

calcium formed $\text{Ca}(\text{C}_2\text{O}_4)_{1.2}$ with partial oxidation of the oxalato group. A distinction was observed for the present complex, compared with other complexes in which there is an accelerating effect by the metal oxide on the rapid decomposition of metal oxalate: it increased somewhat the stability of the metal oxalate to 670°C . The decomposition of CaC_2O_4 starts at 418°C , as reported by Nagase et al. [16]. The exothermic peaks in the range $427\text{--}479^\circ\text{C}$ ($\Delta T_{\text{max}} = 459^\circ\text{C}$) at 5°C min^{-1} , $419\text{--}495^\circ\text{C}$ ($\Delta T_{\text{max}} = 473^\circ\text{C}$) at $10^\circ\text{C min}^{-1}$, and $446\text{--}517^\circ\text{C}$ ($\Delta T_{\text{max}} = 494^\circ\text{C}$) at $20^\circ\text{C min}^{-1}$ heating rates in DSC, might account for this first-stage decomposition. Kinetic parameters are listed in Table 2. The weight losses of 31.06%, 30.69% and 28.08% for the annealed sample at the end of scanning at around 600°C at heating rates of 5, 10, and $20^\circ\text{C min}^{-1}$ respectively, were observed in the DSC scan. Scanning at different heating rates indicated that the higher the heating rate, the higher the temperature of decomposition. The values of the kinetic parameters (Table 2) decrease as the heating rates are increased, as reported earlier [7].

Weight loss started at 670°C and it continued to 865°C , as indicated by an inclined slope with a break at 784°C in the TG curve, suggesting that the further decomposition is a two-step process. The weight loss at the break of the TG curve (784°C) was found to be 46.02% and the product was assumed to be a mixture of CaCO_3 and CaO for which the calculated weight loss is 47.27%. The slight variation in weight loss from the calculated value might be due to the presence of carbon in the product formed due to disproportionation [17] of evolved $\text{CO}(\text{g})$ to $\text{CO}_2(\text{g})$. Corresponding to this overall decomposition, an endothermic change between 670 and 865°C in the DTA with a shoulder at around 780°C indicated that decomposition was accompanied by absorbed heat and confirmed the two-stage decomposition process reported earlier [12]. This was further substantiated by the presence of two overlapping DTG peaks between 650 and 875°C . The intermediate compound at 784°C was isolated by the temperature arrest technique and analysis of the intermediate chemical compounds supports the formation of a mixture of CaCO_3 and CaO . The weight loss observed during the independent pyrolysis in air up to 784°C is in excellent agreement with the calculated value and it can be postulated that the chance of disproportionation is less in an open vessel due to the rapid oxidation of carbon monoxide to carbon dioxide. The E^* and order of reaction of this step were calculated from the inclined nature of the TG curve up to 784°C and found to be 65 kJ mol^{-1} and 0.6 respectively. The order of reaction was reported to be 0.7 for the calcium oxalate decomposition [3, 18]. The inclined nature of the TG curve ended at 865°C with a weight loss of 62.72% (calcd., 62.13%) which might be accounted for by the formation of 2CaO . The X-ray powder diffraction pattern and the very broad band at 330 cm^{-1} in the IR spectrum are similar to those obtained for pure CaO [19, 20]. The estimated metal content of the end product (Ca, found, 70.82%; calcd., 71.47%) further confirms that the residue is CaO . The E^* and the order of reaction of this step were calculated to be $166.73 \text{ kJ mol}^{-1}$ and 0.4 respectively; the values were exactly the same as those calculated by Freeman et al. [3] for calcium carbonate decomposition to calcium oxide. The low value of E^* for the third step of our complex in comparison to a similar decomposition step of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ [16] is probably due to the presence of CaO as well as the exothermic nature of the decomposition which lowers the energy of activation.

The infrared spectroscopic analysis of the gaseous products of the different steps confirmed the evolution of both carbon monoxide and carbon dioxide.

On the basis of the above results, a tentative scheme of the thermal decomposition in air may be summarized as



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