USE OF D.C. ELECTRICAL CONDUCTIVITY AS A SUPPLEMENTARY TECHNIQUE IN THERMAL ANALYSIS

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D. C. electrical conductivity instrument is used as a supplementary technique in thermal analysis, especially to understand the behaviour of thermal dehydration and decomposition of some iron(II) carboxylates. This paper deals with the thermal studies on iron(II) maleate trihydrate under static air, dynamic nitrogen and dynamic air. The intermediates obtained during the decomposition are characterised by XRD pattern, infrared spectral studies and micro elemental analysis.

The study of thermal dehydration and decomposition of any material has been generally carried out by simultaneous TG, DTA, DTG. In the study of thermal decomposition of some iron(II) carboxylates thermal analysis has limitations, as the oxidative decomposition on DTA gives rise to a very broad and strong exothermic peak and continuous weight loss in TG. These curves do not reveal the various types of metastable intermediates formed during the oxidative decomposition. Hence it is desirable to have a technique which can distinguish the metastable intermediates formed in the thermal decomposition of ferrous carboxylates. The parent compound and the metastable intermediates formed in their decomposition have varying electrical properties [1]. These changes in electrical behaviour of the sample can be studied by direct current electrical conductivity (d. c. e. c.) instrument, which measures the electrical conductivity (σ ohm^{-1}cm^{-1}) of a sample as a function of temperature. The measurement can be carried out under different atmosphere. The d. c. e. c. results can be compared with the TA data and thus the general behaviour of thermal dehydration and decomposition can be better understood.

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In our earlier work this method was successfully applied to some ferrous carboxylates such as ferrous oxalate dihydrate [2], iron(II) succinate tetrahydrate [3], iron(II) fumarate half hydrate [4], iron(II) malonate dihydrate [5}, and iron(II) tartrate two and half hydrate [6].

Experimental

Preparation of iron(II) maleate trihydrate (FeC₄H₂O₄.3H₂O):

Preparation of iron(II) maleate trihydrate ($FeC_4H_2O_4.3H_2O$):

An equimolar solution of ferrous sulphate heptahydrate (AR grade) and barium maleate (AR grade) were mixed and stirred at 60° for 0.5 h. Barium sulphate precipitated out, the resulting filtrate was concentrated and then cooled to get orange yellow crystals of iron(II) maleate trihydrate. The whole procedure was carried out under dry dynamic nitrogen atmosphere. The elemental analysis for C, H and Fe gave C, 21.00 (21.40), H, 4.00 (3.60) and Fe, 25.00 (24.8) wherein the values in parenthesis are calculated ones, the magnetic moment of this sample was found to be 4.83 B.M.

The i.r. spectra was recorded in the region 4000-300 cm^{-1} on Beckman spectrophotometer and Perkin Elmer 337 spectrophotometer using nujol. TG/DTA/DTG were carried out under static air (heating rate 10 deg per min), dynamic dry nitrogen and dynamic air (flow rate 100 ml per minute and heating rate of 5 deg per min). The sample mass taken was 25.10 mg (under static air atmosphere) and 21.50 mg (under dynamic air and nitrogen). The sample was in powder form with polycrystalline in nature. The sample holder was cylindrical type, platinum crucible mounted on one of 2 mm alumina rods of the sample carrier covering the Pt/Pt-10% Rh differential thermocouple which can measure the sample temperature simultaneously and the reference materials was air. The thermal analysis measurements were recorded on A Netzch STA 409 differential thermal analyser. The procedure for measuring d. c. electrical conductivity and magnetic parameters are reported in our earlier work [2]. The XRD pattern was obtained on Philips PW/730 diffractometer using Mo$k\alpha$ radiation (λ = 0.709A, Zn filter) with 2θ values ranging from 5° to 90°. The gases obtained by thermal decomposition under nitrogen atmosphere of ferrous maleate trihydrate were analysed by using Shimadju RIA and Hewlett Packard No. 5790 GLC instruments, with nitrogen as carrier gas.

Results and discussion

Static air atmosphere

The two step dehydration process of iron(II) maleate trihydrate shown in Fig. 1(a) could be detected on DTA curve by a sharp endothermic peak at 134° with a hump at 114°. A peak and hump at these temperatures were also observed on DTG curve. The TG curve showed a continuous weight loss up-to 178° with loss of one water molecule at 110° and loss of two water molecules at 170°.
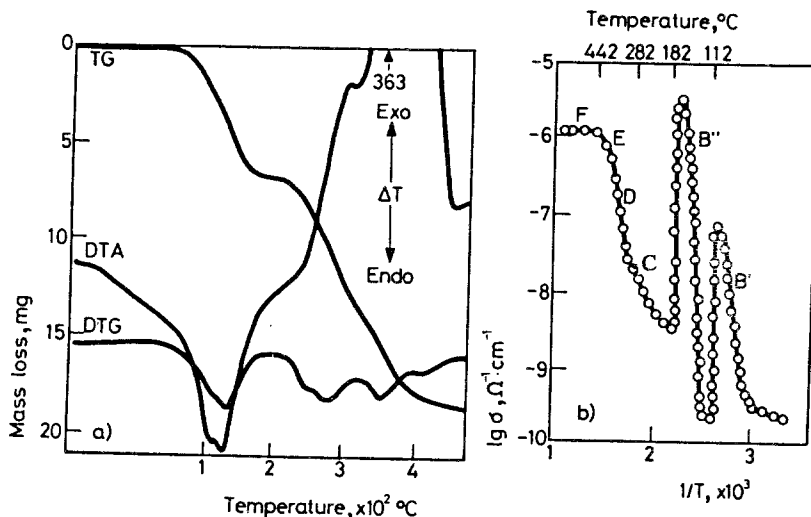

Fig. 1 Static air atmosphere (a) TG/DTA/DTG curves; (b) Plot of log σ vs. 1/T (o) during heating

The oxidative decomposition of this sample was indicated by a broad exothermic peak at 363° and hump at 278° on the DTA curve. The TG curve showed a continuous weight loss 208 to 420°. Hence DTA/TG experiments alone could not reveal the behaviour of oxidative decomposition. However the DTG curve was resolved with peaks at 271° and 363° apart from humps at 248° and 420°. Electrical conductivity measurement vide Fig. 1(b), shows two peaks B′ and B″ in the temperature region corresponding to dehydration process. The presence of two peaks B′ and B″in this region is indicative of two step dehydration process as evidenced by DTA/DTG curve in Fig. 1(a).

After dehydration the σ value increased with rise in temperature (208° to 320°) corresponding to region C, in Fig. 1(b). After reaching 320° the σ value showed a steep rise upto 400° (region D) above 400° there was slower rise in σ value upto 422° (region E) and finally the region F (transition to α-Fe_2O_3).

This plot of log σ vs. T^{-1} (Fig. 1(b) showed that the decomposition of ferrous maleate trihydrate proceeds, with the formation of different intermediates having different regions of σ values, whereas in conventional thermal analysis, the TG curve showed no clear plateau and the DTA curve showed only the broad exothermic peak corresponding to oxidative decomposition. The qualitative analysis of the plot using different experimental techniques followed is as shown below.

Table 1 Predicted intermediates and final products obtained from $FeC_4H_2O_4.3H_2O$ under different atmospheres by d.c.e.c. measurements

Atmosphere	Steps	Temp. range, $^\circ$C	Predicted intermediates and final products
Static air	B'	45-114	$FeC_4H_2O_4.2H_2O$
	B''	114-208	$FeC_4H_2O_4$
	C	208-320	$FeC_4H_2O_4 + FeO$
	D	320-400	Fe_3O_4
	E	400-422	γ-Fe_2O_3
	F	above 422	α-Fe_2O_3
Dynamic dry	B'	80-141	$FeC_4H_2O_4.2H_2O$
nitrogen	B''	141-200	$FeC_4H_2O_4$
	C	200-320	$FeC_4H_2O_4 + FeO$
	D	320-440	$FeC_4H_2O_4 + Fe_3O_4$
Dynamic	B'	45-100	$FeC_4H_2O_4.2H_2O$
air	B''	100-180	$FeC_4H_2O_4$
	C	180-290	$FeC_4H_2O_4 + FeO$
	D	290-440	Fe_3O_4
	F	above 440	α-Fe_2O_3

The i.r. spectrum of the sample heated at 180° for a few minutes, showed sharp peaks for the maleate group frequencies but the H-OH band intensity was found to be considerably reduced. The XRD pattern obtained was generally broad with no significant changes in the intensity ratios and interplanar spacings. The elemental analysis corresponded to anhydrous ferrous maleate ($FeC_4H_2O_4$).

The i.r. spectrum of the sample heated to 320° showed decrease in intensities of coordinated carboxylate band frequencies. Band at 550(s), 390(s) and 360(m) cm^{-1} indicated the formation of metal oxide in the region C. The XRD pattern of this heated sample was polycrystalline in nature and the peak characteristic of both FeO and anhydrous ferrous maleate, were present.

When the sample was heated to temperature corresponding to region D, the carboxylate band disappeared but the intensities of the metal oxide bands increased. The XRD pattern revealed that the intermediate obtained There is mainly Fe_3O_4. A sample in region E was probably a mixture of Fe_3O_4 & γ - Fe_2O_3; the XRD pattern of this sample was biphasic and generally broad. The sample obtained above 425° (region F) was found to be exclusively α - Fe_2O_3. Measurements when supplemented with i.r. spectral data, XRD pattern and microelemental analysis gave a detailed behaviour of thermal dehydration and decomposition of $FeC_4H_2O_4.4H_2O$.
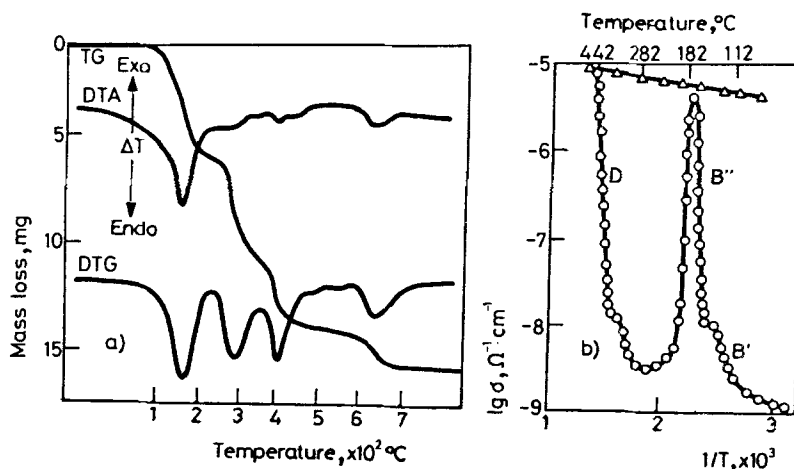

Fig. 2 Dynamic nitrogen atmosphere (a) TG/DTA/DTG curves; (b) Plot of log σ vs. $1/T$: (o) during heating (Δ) during cooling

Dynamic dry nitrogen atmosphere

The two step dehydration process shown in Fig. 2(a) could be detected on DTA curve by a sharp endothermic peak at 178° and a hump at 121°. A peak and hump at the same temperature were also observed on DTG curve.

The TG curve showed a continuous weight loss upto 220°, with loss of one water molecule at 120° and a further loss of two water molecules at 220°.

The decomposition process showed two endothermic peaks one at 450° and the other at 632° in DTA. The DTG curve showed peaks at 298°, 405° and 646°. The TG curve had three regions of weight loss, the first one was from 248° to 320°, the second one from 320° to 615° and the third from 625° to 666°. However these regions of weight loss do not correspond to the formation of single intermediate, and the final product of decomposition was α - Fe_2O_3.

D. c. e. c. measurement shown in Fig. 2(b) did not show the well defined peaks for dehydration process, however, there was a strong peak (B'') 181° with a hump at a 120° (B'). The σ value then decreased upto 200° indicating the completion of dehydration process at this temperature. The value σ than gradually increased upto 440° (region D). The cooling curve of this sample from 440° upto room temperature showed a slight decrease in σ value.

The i.r. spectrum of sample heated to 200° had no δ_{H-OH} band frequencies, the XRD showed it to be polycrystalline in nature with slight decrease in interplanar spacings. Elemental analysis agreed with the anhydrous formula. Hence the dehydration process is complete at this stage.

For sample at 300°, stretching frequencies due to Fe-O increased in intensity and that due to coordinated carboxylate bands decreased in intensity. The XRD pattern was similar to that of sample at 300° under static air atmosphere, indicating that the sample obtained was a mixture of FeO and some amount of anhydrous ferrous maleate. The cooling curve of the sample showed that there was no complete formation of Fe_3O_4 (metallic semiconductor at 440°, region D). The decrease in σ value in the cooling curve suggested the presence of some other compound along with Fe_3O_4. When the sample of ferrous maleate trihydrated was heated to 440° there were weak coordinated carboxylate band frequencies and strong Fe-O stretching frequencies in the i.r. spectrum. The XRD pattern corresponded to Fe_3O_4 with some ferrous maleate. Further the elemental analysis indicated some percentage of C and H. Hence although the intermediate formed at this temperature (440°) was mainly Fe_3O_4;the presence of some amount of anhydrous ferrous maleate showed the decrease in σ value [2-5]. Comparison of the behaviour of solid state thermal decomposition of ferrous maleate trihydrate in normal air and in dynamic dry nitrogen atmosphere showed some differences:

(1) The two step dehydration process was more resolved under static air atmosphere.

(2) The presence of some amount of anhydrous ferrous maleate along with Fe_3O_4 was observed under nitrogen atmosphere, whereas no such step was observed under static air.

(3) The region E, corresponding to the formation of γ-Fe_2O_3 could not be identified with nitrogen atmosphere whereas the same was observed under static air.

Since it is seen that the solid state dehydration and decomposition is influenced by the composition of atmosphere, therefore similar measurements in other controlled atmosphere were undertaken.

Dynamic air atmosphere

The TG curve showed a continuous weight loss upto 190° and then a further loss upto 420° Fig. 3(a). The DTA curve had a strong endothermic peak at 140° with a hump at 105°, and then a strong exothermic peak at 374° with hump at 312° corresponding to oxidative decomposition. The DTG curve had peaks at 153°, 304° and 358°. The weight loss measurements showed that dehydration process is completed at 190° and might be a two step one as observed in DTA curve.
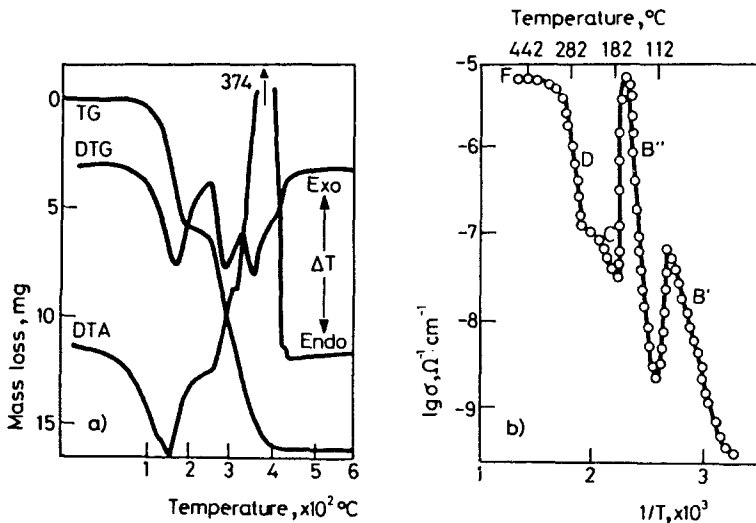

Fig. 3 Dynamic air atmosphere (a) TG/DTA/DTG curves; (b) Plot of log σ vs. $1/T$: (o) during heating

The plot of log σ vs. $1/T$ in Fig 3(b) showed that dehydration process was a two step one as indicated by the presence of two peaks B' and B''. The i.r.

spectrum, XRD data and elemental analysis of the intermediate obtained on ferrous maleate trihydrate heated to 180° confirmed the formation of anhydrous carboxylate at this temperature.

A rise in σ value was observed from 185° to 290°, a steep rise in σ value from 290 to 350° and then a slow increase in σ value upto 440°. The isothermal decomposition studies of ferrous maleate trihydrate at 360° indicated FeO alongwith some anhydrous carboxylate and at 440° Fe_3O_4. Above 440° the sample obtained was only α-Fe_2O_3. The decomposition behaviour is almost similar to Fig. 1(a,b) with slight change in the temperatures of formation and stabilities of the intermediates.

The gases obtained by thermally decomposing iron(II) maleate trihydrate under dynamic dry nitrogen atmosphere were fed to GLC. The chromatograms showed the presence of both types of gases i.e., polar (viz. CO) and non polar gases (viz. CO_2, H_2, CH_4, C_2H_6, etc.). The CO, CO_2 and H_2 gases were observed using TCD and column was Sperocarb where as CH_4, C_2H_6 etc. gases were observed using FID and column was Porpak Q.

Conclusions

The present study brings out the following important aspects in the solid state dehydration and decomposition of ferrous maleate trihydrate

(1) The nature of thermal dehydration and the behaviour of thermal decomposition could be clearly understood by analysing the plots of log σ vs. $1/T$ graph that is by measurements of d. c. e. c. with temperature under different atmospheres.

(2) The dehydration process under all atmospheres was a two step one with loss of one water molecule in the first stage and further loss of two water molecules in the second stage.

(3) The oxidative decomposition always followed dehydration.

(4) The final product of decomposition under all atmospheres was found to be α - Fe_2O_3.

(5) On the above basis it can be stated that use of d. c. e. c. measurement as a supplimentary technique in thermal analysis is beneficial to understand the nature and behaviour of thermal dehydration and decomposition of some ferrous carboxylates.

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References

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Zusammenfassung — Insbesondere zum besseren Verständnis des thermischen Dehydratationsverhaltens und der Zusammensetzung einiger Eisen(II)-carboxylate wurde als Ergänzung der Thermoanalyse ein DC elektrisches Leitfähigkeitsmeßgerät eingesetzt. Vorliegende Arbeit beschäftigt sich mit thermischen Untersuchungen an Eisen(II)-maleat-trihydrat in statischer bzw. dynamischer Luftatmosphäre und in dynamischer Stickstoffatmosphäre. Die während der Zersetzung erhaltenen Zwischenprodukte wurden durch XRD-Aufnahmen, IR-Spektren und Mikroelementaranalyse beschrieben.