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APPLICATIONS OF THERMAL ANALYSIS IN SOME SOLID-STATE REACTIONS

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Abstract

TG–DTG–DTA has been used to characterize various isomers of $CoCl_2 \cdot 2(CH_3C_6H_4NH_2)$. Thermal analysis is further used to analyse the binary mixtures of these isomers. DTA recorded after different elapsed times follows the progress of reaction between cobalt chloride and benzocaine where progressively small endotherms are associated with starting materials. The application of thermal analysis to following the solid-solid reactions between metal acetates and 8-hydroxyquinoline was highlighted. The stoichiometry of such reactions was confirmed from the decrease in intensity of an endotherm as one increases the stoichiometry.

Keywords: solid-state reactions, thermal analysis

Introduction

The importance of comparative studies of thermal decomposition has been amply described [1, 2]. Many applications of thermal analysis have been reported by us during the last 15 years. Bassi *et al.* [3] studied the thermal stabilities of metal propionates. The thermal decomposition of copper and zinc carboxylates in which the anion permits two different positional isomeric structures were described [4]. A comparative study of metal maleate and fumarate has been reported [5]. TG-DTA have been successfully applied to study the stoichiometry of the reaction between 8-hydroxyquinoline and uranyl acetate [6]. DSC and TG have been shown to study the reaction between copper acetate and 8-hydroxyquinoline [7]. The participation of a liquid phase has been seen in this two-step reaction. The stoichiometry of this reaction has been ascertained from the thermal curves of the various ratios. The importance of thermal techniques in studying the mechanism of decomposition of metal carboxylato ferrates [8] and solid–solid reactions has been detailed [9].

The present work is a part of studies on the applications of thermal techniques. It reports on characterization of complex isomers i.e. copper chloride·2-ethylaminobenzonate (*o*-, *m*-, *p*-isomer). Thermal analysis has been used to determine the presence of the one isomer in a mixture of the other. The use of these techniques for studying the stoichiometry and extent of reactions in solid-state reactions is also reported. A particular interest in these reactions lies due to the practical use of materials such as – ethyl aminobenzoate as an anesthetic, 8-hydroxyquinoline as an analytical reagent, metal carboxylates as driers in paints and varnishes, etc.

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Experimental

Cobalt acetate (Apex, AR) was dried at 140°C for 6 h to get the anhydrous sample. Ethyl ester hydrochlorides of *o*-, *m*, and *p*-aminobenzoic acids were prepared by passing dry hydrogen chloride gas in solutions of respective aminobenzoic acids in dry ethanol and purified by recrystallization from ethanol. $CoCl_2{\cdot}2X$(X=ethyl-*o*-, *m*-, or *p*-aminobenzoate) were prepared by mixing saturated solutions of cobalt acetate and hydrochloride each in dry ethanol. The identity of these compounds was established by the percentages of metal determined volumetrically and of carbon, hydrogen and nitrogen by micro analysis. Cobalt chloride (GR, Sterling) was dried at 393–413 K. Benzocaine was prepared as given in literature [10]. Manganese acetate$\cdot 4H_2O$ (A.R) and cadmium acetate$\cdot 2H_2O$ were used after dehydrating for 6 h. The composition of anhydrous sample was checked for metal volumetrically with EDTA using xylenol orange as indicator. TG–DTA–DTG studies were carried on Stanton Redcroft (STA-780) using alumina as reference and in air.

Results and discussion

Thermal analysis of isomers of $CoCl_2{\cdot}2$-ethyl amino-benzoate and their mixtures

Figure 1 presents thermal curves of cobalt(II) chloride·2-ethyl-*o*-aminobenzoate. The DTA curve exhibits three small endotherms with maxima at 313, 356 and 406 K respectively followed immediately by a large exothermic region (609 to 679 K). The first two endotherms are due to the phase transition and the third one corresponds to melting. The TG curve corresponding to the first three DTA peaks, indicate only 0.15% of mass loss. The loss corresponding to the endothermic peak at 449 K is in accordance with the formation of cobalt(II) chloride·1/3-ethyl-*o*-aminobenzoate. The DTG–DTA–TG of cobalt chloride·2-ethyl-*m*-aminobenzoate shows

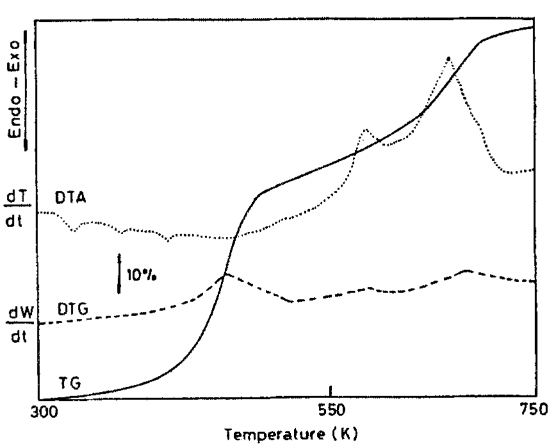

Fig. 1 Simultaneous TG–DTG–DTA curves of cobalt(II) chloride·2-ethyl-*o*-aminobenzoate at a heating rate of 10°C min^{-1} in air

an endothermic peak at 460 K and an exothermic region at 645 K (Fig. 2). The endotherm corresponds to melting and thus decomposition takes place in the molten state. The TG curve corresponding to the DTA endothermic step reveals a loss in weight equivalent to the loss of 1/3 of ethyl-*m*-aminobenzoate. The TG curve thus shows the formation of cobalt(II) chloride·1/3-ethyl-*m*-aminobenzoate at 716 K. DTA for cobalt(II) chloride·2-ethyl-*p*-aminobenzoate reveals an initial endothermic peak at 488 K due to decomposition followed by another endotherm at 499 K due to melting (observed under microscope). The second endotherm shows that decomposition ad melting are simultaneous. There are corresponding peaks in the DTG curve indicating that thermal effects are accompanied by weight loss. The TG curve corresponding to the two DTA steps reveals a loss in weight equivalent to 2/3 moles of ethyl-*p*-aminobenzoate loss. Finally there is an exothermic peak at 645 K when TG shows the formation of cobalt(II) chloride·1/3-ethyl-*p*-amino benzoate at 599 K. At higher temperatures the TG shows continuous loss.

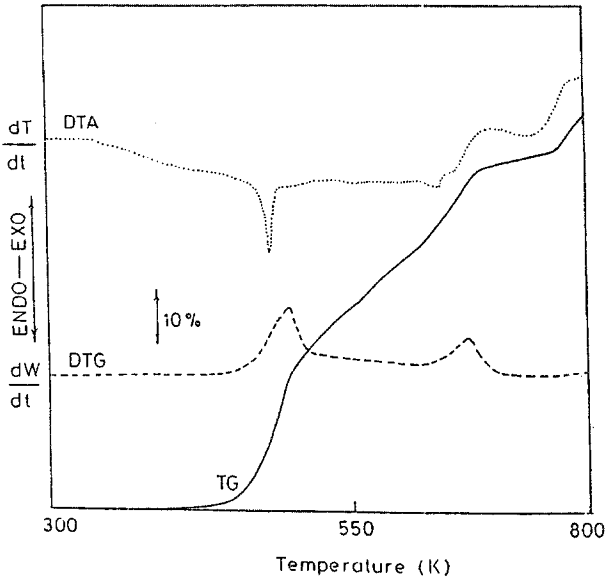

Fig. 2 Simultaneous TG–DTG–DTA curves of cobalt(II) chloride·2-ethyl-*o*-aminobenzoate at a heating rate of 10°C min^{-1} in air

A mixture of cobalt(II) chloride·2-ethyl-*p*-aminobenzoate and cobalt(II) chloride·2-ethyl-*m*-aminobenzoate in 1:1 ratio reveals an endothermic peak at 458 K due to cobalt(II) chloride·2-ethyl-*m*-amino benzoate followed by two endothermic peaks at 488 and 499 due to cobalt(II) chloride·2-ethyl-*p*-aminobenzoate. In Fig. 3 for a 1:1 mixture of $CoCl_2$·2-ethyl *o*-aminobenzoate and $CoCl_2$·2-ethyl-*m*-aminobenzoate there are endotherms at 313, 356 and 406 K due to the *o*-isomer followed by another endothermic peak at 458 K due to the *m*-isomer. DTA for a 1:1 mixture between cobalt(II) chloride·2-ethyl-*p*-aminobenzoate and cobalt(II) chloride·2-ethyl-*o*-aminobenzoate shows three endothermic peaks at 313, 353 and

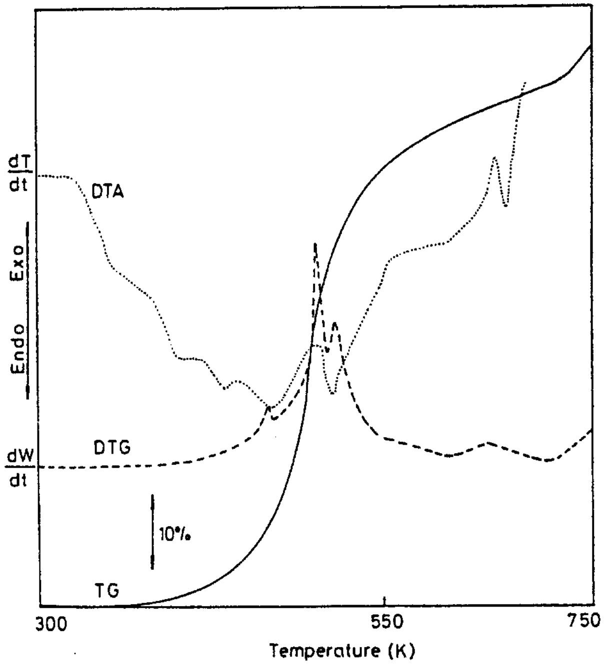

Fig. 3 Simultaneous TG–DTG–DTA curves of 1:1 mixtures of cobalt(II) chloride·2-ethyl-*o*-aminobenzoate and cobalt(II) chloride·2-ethyl-aminobenzoate at a heating rate of $10^{\circ}C\ min^{-1}$ in air

406 K due to $CoCl_2$·2-ethyl-*o*-aminobenzoate followed by two endotherms at 470 and 488 K due to $CoCl_2$·2-ethyl-*p*-aminobenzoate. Comparison of the T_i (temperature of initial mass loss) values for the decompositions indicate that para-substituted complex is more stable than the ortho-substituted complex as the *o*-isomer has a sterically hindered structure. The meta substituted complex is in between the *p*- and *o*-substituted complexes. These results show that the initial thermal effects of the isomers remain unchanged in their binary mixtures and can be used to identify the presence of one another in a binary mixture and also that simultaneous thermal analysis is a useful technique to detect the stability of complex isomers.

Progress of the reaction and stoichiometry

DTA provided a sensitive method of following the progress of the reaction with the advantage that the sample required no special preparation for analysis. Figure 4 shows DTA traces for the solid-state reaction between $CoCl_2$ and benzocaine. As the reaction takes place DTA shows a progressively small melting endotherm associated with one of the starting materials. The area under the DTA curve for the products obtained in the solid phase decreased with time, showing that the reaction is quantitative and goes to completion even in the solid-state.

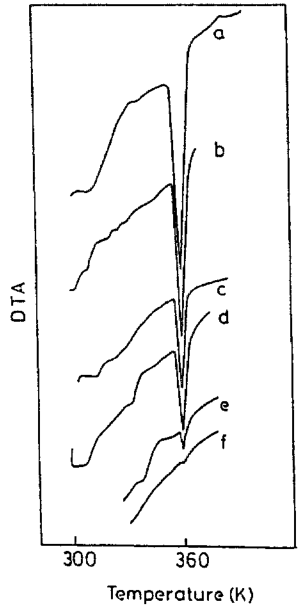

Fig. 4 DTA traces of the solid-state product of reaction between cobalt(II) chloride and benzocaine at a heating rate of 10°C min^{-1} in air a) freshly mixed, b) after 2 h, c) after 6 h, d) after 10 h, e) after 24 h, f) after 30 h

The solid–solid reaction of manganese acetate with 8-hydroxyquinoline occurs in 1:1 stoichiometry,

$$\underset{(s)}{Mn(CH_3COO)_2} + \underset{(s)}{C_9H_6NOH} = \underset{(s)}{Mn(CH_3COO)_2{\cdot}C_9H_6NOH}$$

No evidence was obtained for the evolution of acetic acid. DTA experiments using 8-hydroxyquinoline, manganese acetate (hydrated and anhydrous) and mixtures of 8-hydroxyquinoline and manganese acetate in the ratios of 1:1, 1:2 and 2:1 were run with variations of particle size and heating rate with equivalent amounts. 8-hydroxyquinoline show a sharp melting endotherm at 347 K while the TG shows a continuous weight loss due to sublimation of 8-hydroxyquinoline. Manganese acetate shows decomposition at 432 K. Thermal curves of fresh 1:1 stoichiometric mixtures (Fig. 5) show a succession of peaks 320–360 K due to the formation of an adduct between the reactants to give $MnAC_2{\cdot}HQ$ and/or because of melting of 8-hydroxyquinoline (if any) which remains unreacted.

In DTA curves of the samples obtained after different grinding intervals it was observed that intensity of these peaks decrease with increasing grinding time which shows that the adduct formation was completed during the grinding process itself. A continuously heated fresh mixture of 8-hydroxyquinoline and manganese acetate (1:1) examined under a microscope showed slight melting at ~338–348 K, while the stoichiometric mixture already ground for 10–15 min did not show any evidence of melting. TG also does not show any mass loss in this region. Thermal curves for a 1:2 stoichiometric mixture ground for 1/2 h and recorded at different time intervals always show the presence of melting peak which is, however, missing

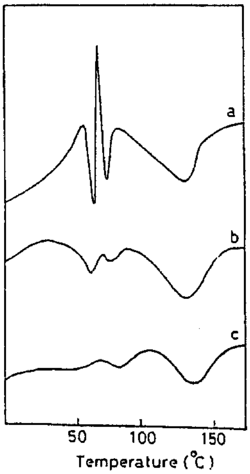

Fig. 5 DTA curve of fresh mixture of manganese acetate and 8 hydroxyquinoline (1:1) at different intervals showing absence of melting endotherm at a heating rate of 10°C min^{-1} in air

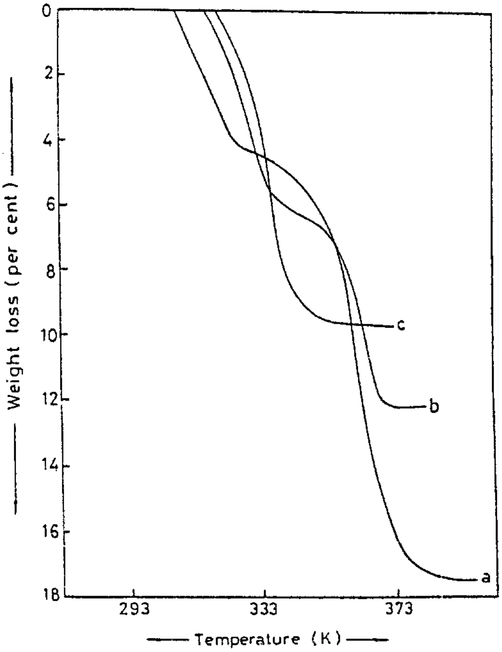

Fig. 6 TG plots of mixtures of $CuCl_2 \cdot 2H_2O$ and 4-toluidine a) 2:1, b) 1:1 and c) 2:1 stoichiometric ratio at a heating rate of 10°C min^{-1}

in 2:1 stoichiometric mixture as compared to in 1:1 stoichiometric mixture. Also the absence of this peak in 2:1 mixture suggests the presence of unreacted manganese acetate. The XRD powder pattern does not show any lines corresponding to either of reactants in 1:1 ratio, confirming the completion of reaction.

Stoichiometry

The solid–solid reaction of $CuCl_2\cdot 2H_2O$ with 4-toluidine involves the replacement of water with aniline. To establish the stoichiometry of the reaction, TG studies were carried out with mixtures of $CuCl_2\cdot 2H_2O$ and $C_6H_4NH_2CH_3$ prepared by mixing finely powdered reactants before each TG run. TG of copper(II) chloride shows a single step dehydration with a loss of 21.0%.

Figure 6 shows TG curves for the $CuCl_2\cdot 2H_2O$ and 4-toluidine system. The 2:1 mixture shows a two step loss; 5.0% in the first step and 12.0% in the second step. The first step corresponds to the solid-state reaction in which one of the amine molecules reacts with $CuCl_2\cdot 2H_2O$ as in Scheme I, where one mole of water is evolved. The remaining $CuCl_2\cdot 2H_2O$ dehydrates at its usual temperature when 3 moles of gaseous water are lost.

Scheme I

$$\underset{(s)}{\mathrm{2CuCl_2\cdot 2H_2O}} + \underset{(s)}{\mathrm{CH_3C_6H_4NH_2}} \rightarrow$$

$$\rightarrow \underset{(s)}{\mathrm{1/2CuCl_2\cdot 2(CH_3\cdot C_6H_4NH_2)}} + \underset{(g)}{\mathrm{H_2O}} + \underset{(s)}{\mathrm{3/2CuCl_2\cdot 2H_2O}}$$

$$\underset{(s)}{\mathrm{3/2CuCl_2\cdot 2H_2O}} \rightarrow \underset{(s)}{\mathrm{3/2CuCl_2}} + \underset{(g)}{\mathrm{3H_2O}}$$

The TG of a 1:1 mixture shows a two step loss. The first step, 6.0% (6.4 theor.) corresponds to the loss of one mole of water along with the solid-state reaction in which all of the amine reacts with the $CuCl_2\cdot 2H_2O$ according to Scheme II. In the second step the dehydration of unreacted $CuCl_2\cdot 2H_2O$ takes place with a loss of 7.0% (6.4).

Scheme II

$$\underset{(s)}{\mathrm{CuCl_2\cdot 2H_2O}} + \underset{(s)}{\mathrm{CH_3C_6H_4NH_2}} \rightarrow$$

$$\rightarrow \underset{(s)}{\mathrm{1/2CuCl_2\cdot 2(CH_3\cdot C_6H_4NH_2)}} + \underset{(g)}{\mathrm{H_2O}} + \underset{(s)}{\mathrm{1/2CuCl_2\cdot 2H_2O}}$$

$$\underset{(s)}{1/2CuCl_2{\cdot}2H_2O} \rightarrow \underset{(s)}{1/2CuCl_2} + \underset{(g)}{H_2O}$$

The TG for a 1:2 ratio shows a single step loss of water, i.e., 10% (9.3 theor.), which corresponds to the solid-state reaction in which both the reactants are completely consumed (Scheme III). The observed loss of water occurs at a temperature lower than for the dehydration of $CuCl_2{\cdot}2H_2O$ alone.

Scheme III

$$\underset{(s)}{CuCl_2{\cdot}2H_2O} + \underset{(s)}{2CH_3C_6H_4NH_2} \rightarrow \underset{(s)}{CuCl_2{\cdot}2(CH_3{\cdot}C_6H_4NH_2)} + \underset{(g)}{2H_2O}$$

All systems studied thus confirm that the solid–solid reaction between $CuCl_2{\cdot}2H_2O$ and 4-toluidine (an aniline) occurs in 1:2 molar ratio.

Conclusions

(i) Thermal effects may be used (a) to characterize even closely related complex isomers, (b) to determine relative stability and (c) to analyse their binary mixtures.

(ii) Progress of the reaction may be studied for the change in area and shape of the peaks.

(iii) Stoichiometry of a solid–solid reaction can be determined from the steps observed in TG and the nature of DTA.

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