Synthesis, characterization and thermal behaviour of solid alkali metal mandelates in pyrolytic and oxidant atmosphere

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ABSTRACT

Characterization, thermal stability and thermal decomposition of alkali metal mandelates, $M(C_6H_5CH(OH)CO_2)nH_2O$ (where M represents Na, K, Rb and Cs and $n = 0.3$ (Na), 0.6 (K), 2 (Rb) and 1 (Cs)) were investigated employing simultaneous thermogravimetry and differential scanning calorimetry (TG-DSC), atomic absorption spectrophotometry (AA), X-ray diffractometry and TG-DSC coupled to infrared spectrophotometer (FTIR). For all the compounds, the mass loss occurs in the beginning of the TG-DSC curves. In the nitrogen atmosphere it was observed that the mass loss of the anhydrous compounds occurs in four or five steps and the mass loss is still observed up to 1000 °C, except for the anhydrous compounds under dynamic dry air atmosphere, after the first three steps occurs with the formation of the respective carbonate. The results also provided information concerning the thermal stability and decomposition as well as identification of the gaseous products evolved during the thermal decomposition of these compounds.

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1. Introduction

Mandelic acid is an aromatic alpha hydroxyl acid with the molecular formula $C_6H_5CH(OH)CO_2H$ and it has a long history as antibacterial, particularly in treatment of urinary tract infectious [1]. It has been reported in the literature some work about mandelic acid and their compounds, as shown: studies of some bivalent solid complexes of iron [2], infrared spectrum of mandelate complex of nickel II [3], the complexation of mandelates of lanthanide [4], magnesium bis[D(−)mandelate] anhydrous and other alkaline earth, alkali and zinc salts of mandelic acid [5], mixed-ligand complexes of copper (II) with α-hydroxycarboxylic acid and 1,10-phenanthroline [6], synthesis, structures and magnetic properties of layered bivalent metal mandelates [7] mononuclear, dinuclear and hidroxo-briged tetranuclear complexes from reactions of Cu (II) ions, mandelic acid diimina ligands [8] and synthesis, characterization and thermal study of solid-state alkaline earth mandelates, except beryllium and radium [9]. In this paper, the object of the present research was to prepare solid-state compounds of alkali metal mandelates (i.e. Na, K, Rb and Cs) and to investigate by means

of atomic absorption (AA), infrared spectroscopy (FTIR), simultaneous thermogravimetry and differential thermal analysis (TG-DTA) under air atmosphere, differential scanning calorimetry (DSC) and TG-DSC, under nitrogen atmosphere, coupled to FTIR.

2. Experimental

The mandelic acid, $C_6H_5CH(OH)CO_2H$ with 99% purity was obtained from Sigma and it was used as received.

Solid-state alkali metal mandelates were obtained by neutralization of sodium hydroxide 0.2 mol L^{-1} or potassium, rubidium and caesium carbonates 0.1 mol L^{-1} (100 mL) with mandelic acid solutions. Solutions were evaporated to near dryness in a water bath, dried at 50 °C in a forced circulation air oven (12 h) and kept in a desiccator over anhydrous calcium chloride.

In the solid-state, metal ions were determined by using atomic absorption spectrophotometer HR-CSF AAS, from Analytik Jena Contr AA 300.

Water content was determined from TG curves, and ligand lost was also determined from TG curves, based on the mass losses up to the temperature where the respective carbonates are formed.

X-ray powder patterns were obtained by using a Siemens D5000 X-ray diffractometer employing CuKα Radiation ($\lambda = 1.541$ Å) and setting of 40 kV and 20 mA.

Simultaneous TG-DSC curves were obtained by using TG-DSC STARe system, from Mettler Toledo.

The purge gas was an air and/or Nitrogen flow of $50\,mL\,min^{-1}$ and heating rate of $10\,°C\,min^{-1}$ was adopted with samples weighing about 12 mg. Platinum crucibles were used for recording the TG-DSC curves.

The monitoring of gaseous products were carried out using TG-DSC 1 Mettler Toledo coupled to FTIR spectrophotometer Nicolet with gas cell and DTG S KBr detector. The furnace and heated gas cell ($250\,°C$) were coupled through a heated ($200\,°C$) 120 cm stainless steel line transfer with diameter of 3 mm, both purged with dry air ($50\,mL\,min^{-1}$). The FTIR spectra were recorded with 16 scans per spectrum at a resolution of $4\,cm^{-1}$.

The morphology of sample holder was observed using a high resolution field-emission gun scanning electron microscopy FEG-SEM (Supra 35-VP, Carl Zeiss, Germany).

3. Results and discussion

The analytical and thermoanalytical (TG), under air atmosphere, results are shown in Table 1. From these data the stoichiometry of these compounds could be established, as shown in succession. For sodium compound, as example:

$$H_2O = 2.84\% \div 18.02^* = 0.158 \div 0.5592 = 0.3$$

$$^*H_2O = 18.02$$
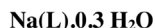
$$\Delta L = 67.86\% \div 121.145^{**} = 0.5602 \div 0.5592 = 1.00$$

$$^{**}\,NaL - 0.5\,Na_2CO_3 = 121.145$$

$$0.5\,Na_2O = 17.33\% \div 30.99^{***} = 0.5592 \rightarrow \boxed{1}$$

$$^{***}\,0.5\,Na_2O = 30.99$$

$$Na(L).0.3\,H_2O$$

Thus, the general formula of these compounds: $M(L)\cdot nH_2O$ where M represents Na, K, Rb and Cs; L is mandelate and $n = 0.3$ (Na), 0.6 (K), 2 (Rb) and 1 (Cs). All the compounds are hygroscopic, and the hygroscopicity of these compounds follows the order: Rb > Cs > K > Na.

The X-ray diffraction powder patterns in Fig. 1 shows that the sodium and potassium compounds have a crystalline structure, without evidence of formation of isomorphous ones. For rubidium and caesium the X-ray diffraction powder patterns was not obtained due to the high hygroscopicity of these compounds.

The TG-DSC curves of the compounds in dynamic dry air atmosphere are shown in Fig. 2. These curves show mass losses in five or six steps and thermal events corresponding to these losses or due to physical phenomenon. These curves also show that the mass loss due to dehydration occurs for all the compounds in the beginning of the TG-DSC curves ($40\,°C$), in spite of the compounds have been maintained at $50\,°C$ in a forced circulation air oven during 12 h and kept in a desiccator over anhydrous calcium chloride up to dryness. Thus the dehydration occurred in the beginning of the TG-DSC curves because these compounds are hygroscopic. For potassium and rubidium compounds the dehydration occurs in two consecutive steps and for sodium and caesium ones the dehydration occurs in a single step and through a slow process.

The thermal stability of the anhydrous compounds shown by TG-DSC curves depends on the nature of the metal ion and they follow the order:

K > Na > Rb > Cs
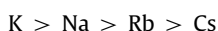
Only for caesium compounds the TG-DSC curves show that the final thermal decomposition occurs under to $950\,°C$, while for sodium, potassium and rubidium compounds these curves show that the mass losses are still being observed up to $1000\,°C$.
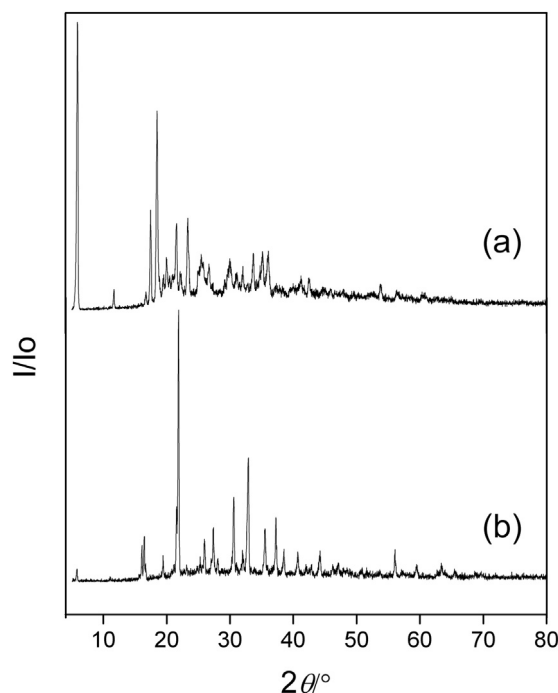

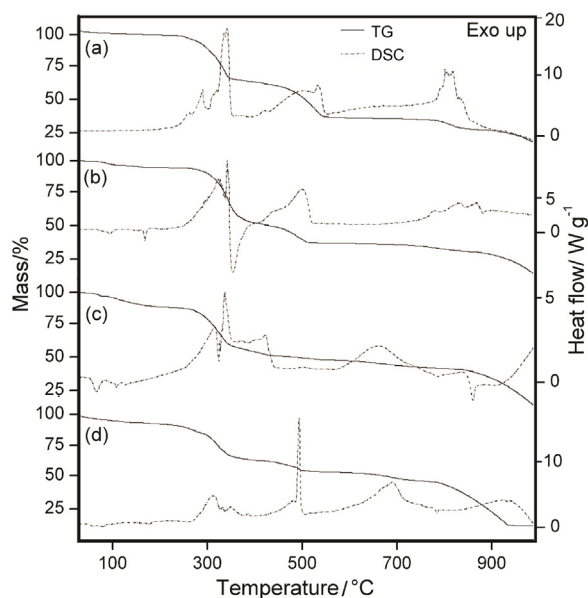Fig. 1. X-ray powder diffraction patterns of the compounds: (a) NaL and (b) KL (L = mandelate).

Fig. 2. Simultaneous TG-DSC curves of the compounds in dry air atmosphere: (a) NaL (m = 12.1800 mg), (b) KL (m = 12.0730 mg), (c) RbL (m = 12.1000 mg), (d) CsL (m = 12.0060 mg) under dry air atmosphere.

The percent of ligand and metals were determined by stoichiometry calculations, based on thermal analysis and atomic absorption, respectively.

The thermal behaviour of the compounds is also dependent on the nature of the metal ion and so the features of each of these compounds are discussed individually.

3.1. Sodium compound

The TG-DSC curves are shown in Fig. 2(a). The first mass loss between 40 and $190\,°C$ is attributed to dehydration with loss of