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THERMAL BEHAVIOR STUDIES OF SOLID STATE COMPOUNDS OF 4-DIMETHYLAMINOCINNAMYLIDENEPYRUVATE WITH ALKALI EARTH METALS, EXCEPT BERYLLIUM AND RADIUM

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ABSTRACT: Solid state compounds of general formula $M(DMCP)_2.nH_2O$, where M represents Mg, Ca, Sr, Ba, and DMCP is 4-dimethylaminocinnamylidenepyruvate, and n = 1, except for Ca, where n = 2.5, have been prepared. Thermogravimetry, derivative thermogravimetry (TG, DTG), differential scanning calorimetry (DSC), X-ray diffraction powder patterns and complexometry were used to characterize and to study the thermal decomposition of these compounds.
KEYWORDS: 4-Dimethylaminocinnamylidenepyruvate, Alkali earth metals, Thermal decomposition.

Introduction

Several binary metal-ion complexes of benzylidenepyruvate, C_6H_5-$(CH)_2$-COCOO- (BP) as well as those associated with phenyl substituted derivatives of BP, i.e., 4-methoxy(4-MeOBP); 4-dimethylamino(DMBP); 2 Chloro (2-Cl-BP); 4-Chloro (4-Cl-BP); 2Chloro-4-dimethylamino (2-Cl-DMBP) and 4-dimethylaminocinnamylidene- pyruvate ($(CH_3)_2N$-C_6H_5-$(CH)_4COCOO^-$) have been investigated in aqueous solution [3-6,14,18].

Solid state compounds of 4-MeOBP, DMBP, CP and DMCP with trivalent lanthanides (except promethium) and yttrium and other metals have also been prepared and investigated, using thermoanalytical techniques (TG, DTG, DTA, DSC), X-ray powder diffractometry, elemental analysis and complexometry [2,7,9-13,15-17]. The establishment of stoichiometry as well as the thermal behavior have been the main purposes of these studies.

In this work, solid state compounds of alkali earth metals, except Be and Ra, with DMCP were prepared and investigated by thermoanalytical techniques, X-ray powder diffractometry and complexometry. The data obtained allowed us to acquire informations concerning the thermal stability and termal decomposition of these compounds.

Experimental

The sodium salt of DMCP was prepared as described in the literature [2,14].

The solid state compounds of magnesium, calcium, strontium and barium with DMCP, were obtained by mixing aqueous solution of the respective metal nitrate with aqueous solution of the ligand. The precipitates were washed with distilled water until elimination of the nitrate ions, filtered, dried and kept in a desiccator over anhydrous calcium chloride.

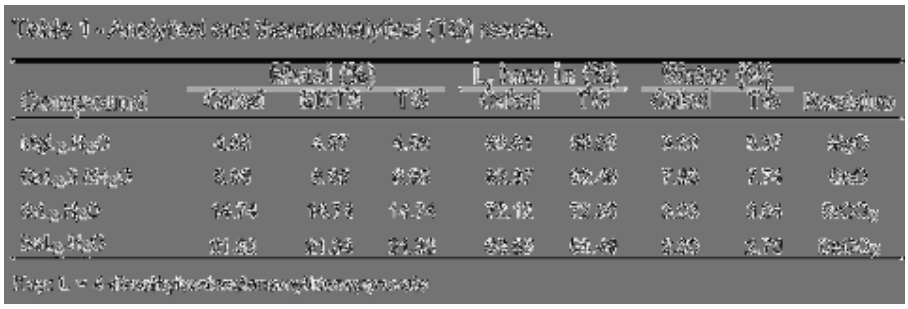
The metal contents of the compounds were determined by complexometry [1,8] after samples of the compounds had been ignited to the metal oxide or carbonate and dissolved in hidrochloric acid. Metal contents were also determined from the TG curves, as well as the water and ligand contents.

TG, DTG and DSC curves were obtained using a Mettler TA-4000 Thermal analysis system with an air flux of 150 mL min^{-1}, heating rate of 10^{o}C min^{-1} and samples weighing about 7 mg. An α-alumina crucible was used for the TG curves and an aluminium crucible with a perforated cover was used for the DSC curves.

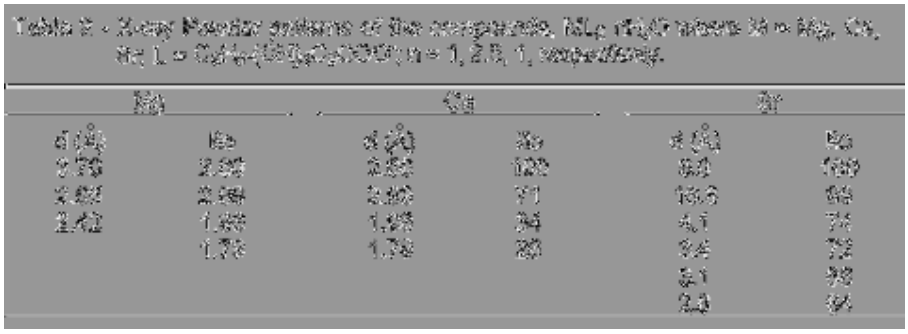
X-ray powder patterns were obtained with an HGZ 4/B horizontal diffractometer (GDR) equipped with a proportional counter and pulse height discriminator. The Bragg-Brentano arrangement was adopted using CuKα radiation (λ = 1.541 Å) and setting of 40 kV and 20 mA.

Results and Discussion

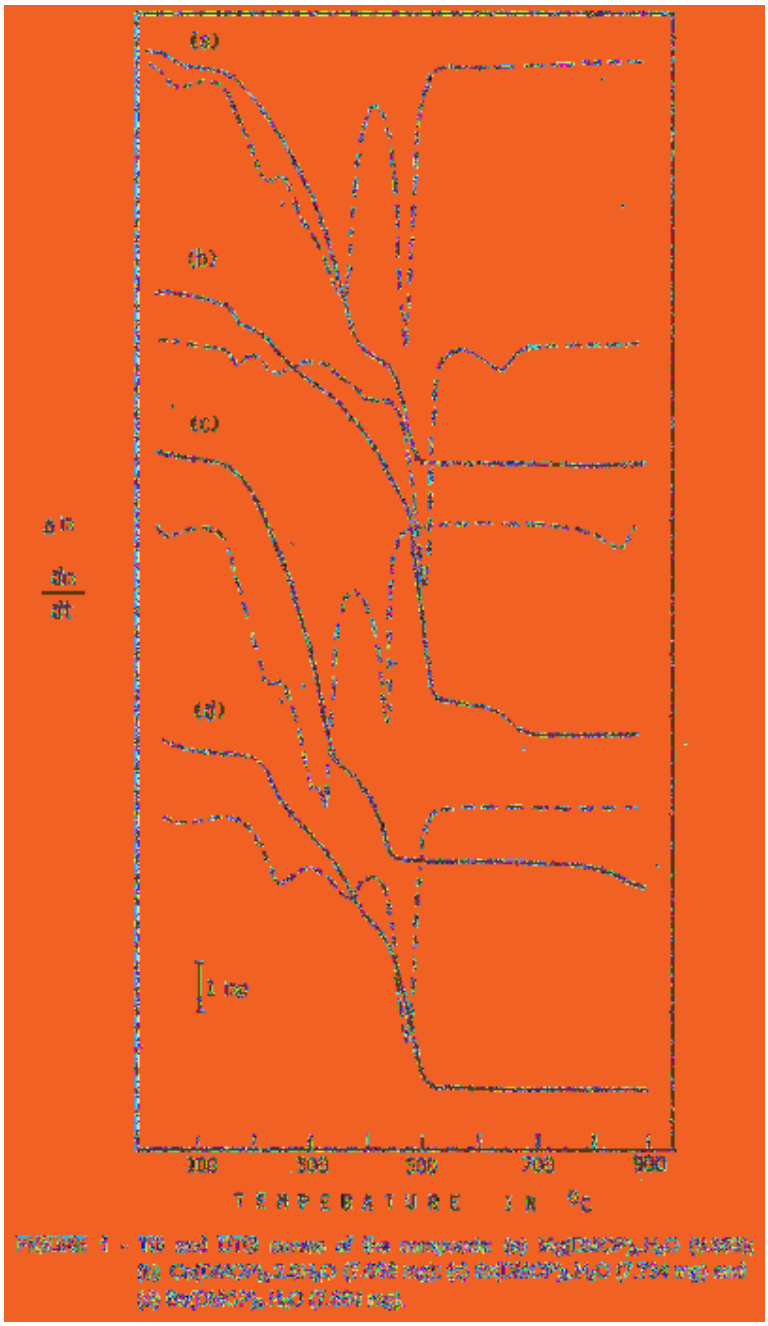
Table 1 presents the analytical and thermoanalytical (TG) data for the prepared compounds from which the general formula ML_2nH_2O can be established, where M represents Mg, Ca, Sr and Ba, L is 4-dimethylaminocinnamilidenepyruvate and n = 1 except for the calcium compound where n = 2.5.



The X-ray diffraction powder patterns show that the Mg, Ca and Sr compounds have crystalline structures, without evidence of an isomorphous series. The diffraction pattern of the barium compound, indicate an amorphous structure. The more characteristic lines obtained by the powder diffraction method are presented in Table 2.



The TG and DTG curves are shown in Figure 1. These curves show that the mass losses occurs in several steps and they are characteristic for each compound.



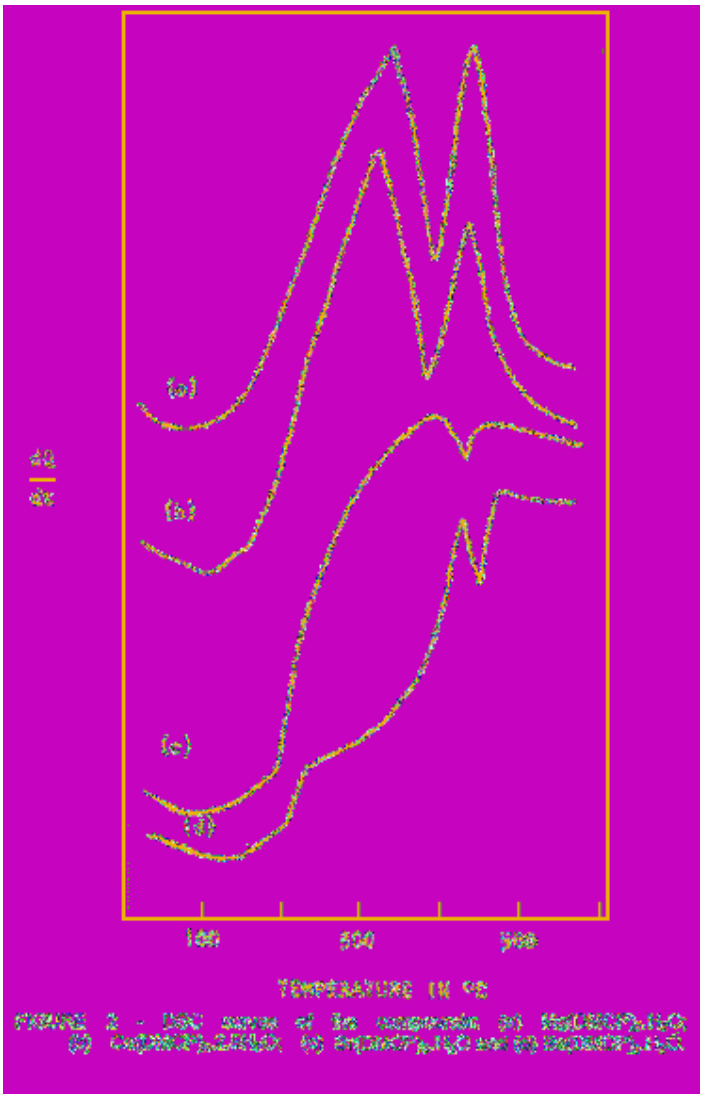
For the magnesium compound the TG curve Fig. 1(a) show mass losses in three steps, although the DTG curves indicate four steps. The first mass loss up to 104°C is due to the dehydration with loss of $1H_2O$ (Theor. = 4.58%; TG = 4.58%). The second and the third steps observed between 120°C and 510°C are ascribed to the thermal decomposition of the anhydrous compound to magnesium oxide, MgO, as final residue (Theor. = 7.60%; TG = 7.58%).

For the calcium compound, the TG and DTG curves, Figure 1(b) show mass losses between 40°C and 700°C. The first mass loss up to 200°C is due to the dehydration with losses of 2.5 H_2O (Theor. = 7;85%; TG = 7.74%). The mass loss between 200°C and 530°C, that begins with a slow process followed by a fast process is attributed to the thermal decomposition of the anhydrous compound, with formation of calcium carbonate as intermediate. The last step between 600°C and 700°C is due to the thermal decomposition of the carbonate to the calcium oxide, CaO, as final residue (Theor. = 9.78; TG = 9.77%).

For the strontium compound, the TG and DTG curves Figure 1(c), show mass losses in four steps. The first mass loss up to 100°C is due to the dehydration with loss of $1H_2O$ (Theor. = 3.03%; TG = 3.04%). The thermal decomposition of the anhydrous compound, that is similar to the magnesium compound, occurs in two consecutive steps between 120°C and 480°C, with formation of strontium carbonate (Theor. = 24.85%; TG = 24.60%). The last mass loss, between 800°C and 900°C is due to the partial thermal decomposition of the strontium carbonate, where the final residue is a mixture of carbonate and strontium oxide.

For the barium compound, the TG and DTG curves Figure 1(d), show mass losses in four steps between 30°C and 520°C. The first mass loss up to 100°C is due to the dehydration with loss of $1H_2O$ (Theor. = 2.80%; TG = 2.79%). The anhydrous compound is stable up to 190°C, and the thermal decomposition occurs in three consecutive steps with formation of barium carbonate, $BaCO_3$, stable up to 900°C (Theor. = 30.65%; TG = 30.72%).

The DSC curves are shown in Figure 2. For all the compounds the endotherm between 30°C and 120°C are due to the dehydration in correspondence with the first mass loss of the TG curves. The broad exotherms observed for all compounds, with two peaks between 120°C and > 600°C, are attributed to the thermal decomposition of the anhydrous compounds, where the oxidation of the organic matter takes place in two consecutive stages; this is in agreement with the TG curves.



The TG, DTG and DSC curves of these compounds show that the hydration degree, thermal stability as well as the thermal decomposition process depend on the metal present, as already observed in the thermal behavior study of the solid state compounds of lanthanides and yttrium with the same ligand [2]. The formation of carbonate, monoxycarbonate or dioxycarbonate that occur during the thermal decomposition of compounds containing carboxyl group, also depend on the metal present [9-11,14]. In the present study, the formation of calcium, strontium and barium carbonate as intermediate observed during the thermal decomposition of these compounds, are in agreement with the results obtained for the 4-methoxybenzalpyruvate of alkali earth metals [11]. These carbonates as intermediates are formed because the final step of thermal decomposition of these compounds occurs up to 530^{o}C, and up to this temperature these intermediates are thermally stable. In the magnesium compound, no intermediate is formed because the thermal stability of the

magnesium carbonate ~ 480°C is lower than the final temperature (510°C) of the thermal decomposition of this compound.

Conclusion

The X-ray powder patterns reveal that the Mg, Ca and Sr compounds tend towards a crystalline structure and that the barium compound presents an amorphous structure.

The analytical and thermoanalytical (TG) results established the stoichiometry of the compounds in the solid state and the TG, DTG and DSC curves provided information about the thermal stability and thermal decomposition.

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SCHNITZLER, E. et al. Estudo do comportamento térmico dos 4-dimetilaminocinamalpiruvato de metais alcalino terrosos, exceto berílio e rádio, no estado sólido. *Ecl. Quím (São Paulo),* v.25, p. 2000.

RESUMO: *Foram preparados no estado sólido, compostos de fórmula geral $M(DMCP)_2 nH_2O$, em que M representa Mg, Ca, Sr, Ba; DMCP é 4-dimetilaminocinamalpiruvato e n = 1, exceto para o Ca onde n = 2,5. Na caracterização, bem como no estudo da decomposição térmica desses compostos, foram utilizados a termogravimetria, termogravimetria derivada (TG, DTG), calorimetria exploratória diferencial (DSC), difração de raios-X pelo método do pó e complexometria.*

PALAVRAS-CHAVE: *4-dimetilaminocinamalpiruvato, Metais alcalino-terrosos, Decomposição térmica.*

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