

Eclética Química

Print version ISSN 0100-4670 *On-line version* ISSN 1678-4618

Eclet. Quím. vol.23 São Paulo 1998

<http://dx.doi.org/10.1590/S0100-46701998000100008>

Preparation and thermal decomposition of solid state cinnamates of alkali earth metals, except beryllium and radium

Ana Glauce ZAINA CHIARETTO*

Marco Aurélio da Silva CARVALHO FILHO*

Nedja Suely FERNANDES*

Massao IONASHIRO*

ABSTRACT: Solid state compounds of general formula $ML_2 \cdot nH_2O$ [where M is Mg, Ca, Sr or Ba; L is cinnamate ($C_6H_5-CH=CH-COO-$) and $n = 2, 4, 0.8, 3$ respectively] have been synthesized. Thermogravimetry (TG), derivative thermogravimetry (DTG), differential scanning calorimetry (DSC) and X-ray diffraction powder patterns have been used to characterize and to study the thermal stability and thermal decomposition of these compounds. **KEYWORDS:** Alkali earth metals; cinnamate; thermal decomposition.

Introduction

Solid state compounds of 4-dimethylaminobenzylidenepyruvate and 4-methoxybenzylidenepyruvate with several metals ions, have been prepared and studied by complexometry, TG, DTG, DSC, DTA and X-ray powder diffractometry.²⁻⁵ Cinnamate of cobalt, nickel and copper, have also been prepared and characterized by analyses, magnetic moments, vibrational and electronic spectra, as well as, the thermal behaviour by thermogravimetry and differential thermal analyses (DTA)¹.

This work is concerned with the thermal behaviour of magnesium, calcium, strontium and barium cinnamates. The dehydration and thermal decomposition were studied by means of TG, DTG and DSC.

Experimental

The alkali earth metals cinnamates (except Be and Ra) were prepared by neutralizing the corresponding aqueous suspensions of metals carbonates with slight excess of cinnamic acid. The aqueous suspensions were heated to ebullition until effervescence ceased, and filtered in Whatman n° 42 filter papers. The solutions were dried in a water bath, washed with ethanol until elimination of the cinnamic acid in excess and kept in a desiccator over anhydrous calcium chloride.

The metal contents of the compounds were determined by complexometric titrations with standard EDTA solution, after samples of the compounds had been ignited to the metal oxide or carbonate and dissolved in hydrochloric acid solutions. The water and cinnamate contents were determined from the TG curves.

The TG and DTG curves were recorded on a Perkin-Elmer TGS-2 thermogravimetric system; samples of about 7 mg were used, in platinum crucibles, heated at a rate of 20°C min⁻¹ in flowing air (» 5 mL min⁻¹) at ambient pressure.

The DSC curves were obtained using a Mettler TA-4000 thermoanalyser system with air flowing at a rate of about 150 mL min⁻¹, heating rate of 20°C min⁻¹ and aluminium crucibles with perforated covers.

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 CoK α ($\lambda = 1.7889 \text{ \AA}$) and a setting of 38 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 ML₂.nH₂O can be established, where M represents Mg, Ca, Sr or Ba, L is cinnamate and n = 2, 4, 0.8, 3 respectively.

Table 1 - Analytical and thermoanalytical (TG) results.

Compound	Metal in %			ΔL^* in %		Water in %	
	Theor.	TG	EDTA	Theor.	TG	Theor.	TG
MgL ₂ .2H ₂ O	6.85	6.94	7.19	82.98	83.1	10.16	10.1
CaL ₂ .4H ₂ O	9.86	9.98	9.90	72.41	72.1	17.73	18.1
SrL ₂ .0.8H ₂ O	22.11	22.6	21.66	74.26	74.3	3.64	3.6
BaL ₂ .3H ₂ O	28.28	28.1	28.27	60.59	60.4	11.13	11.3

* L = cinnamate

The X-ray diffraction powder patterns, [Figure 1](#), show that the strontium and barium compounds are isomorphous. All the compounds have crystalline structure.

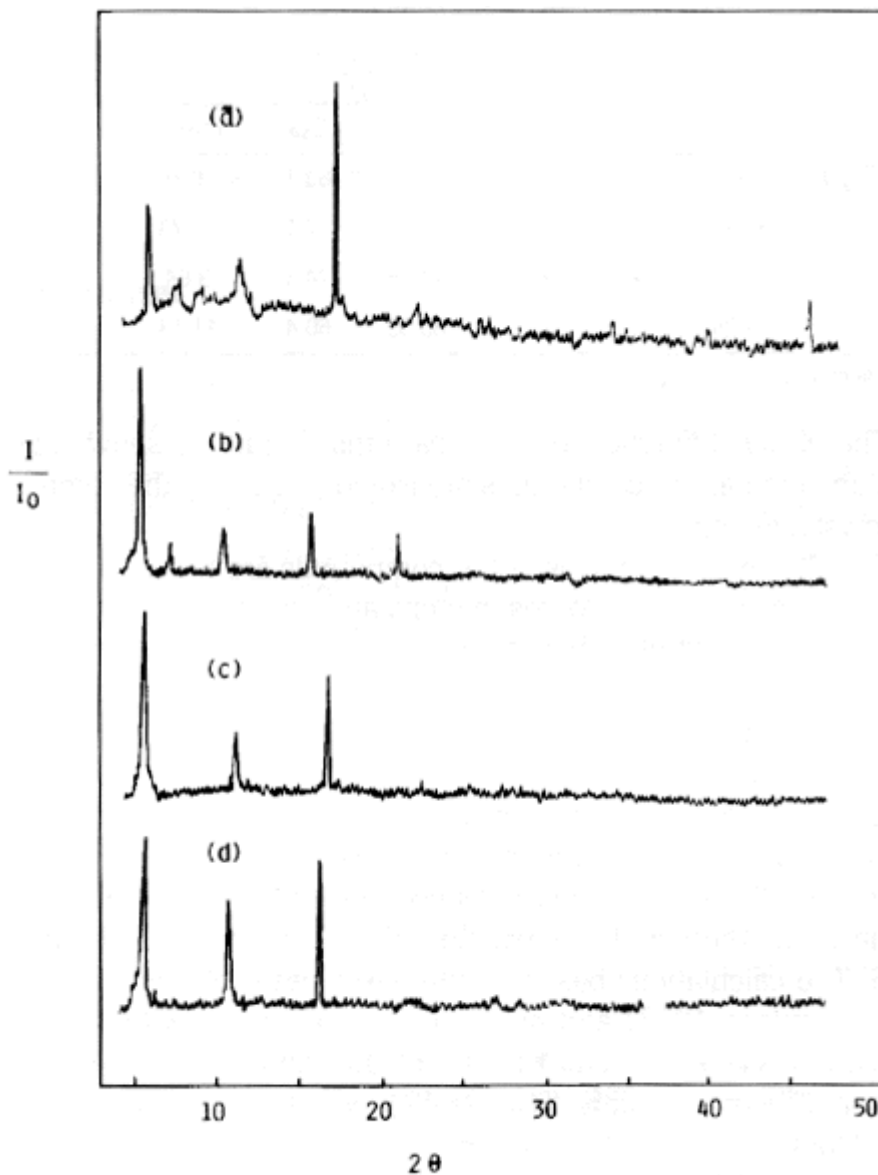


FIGURE 1 - X-ray powder diffraction patterns of hydrated cinnamates of: (a) Mg, (b) Ca; (c) Sr and (d) Ba.

The TG and DTG curves of the compounds are shown in [Figure 2](#). These curves show mass losses in steps and only for magnesium compound the formation of carbonate as intermediate is not observed, probably due to the low thermal stability of the magnesium carbonate.

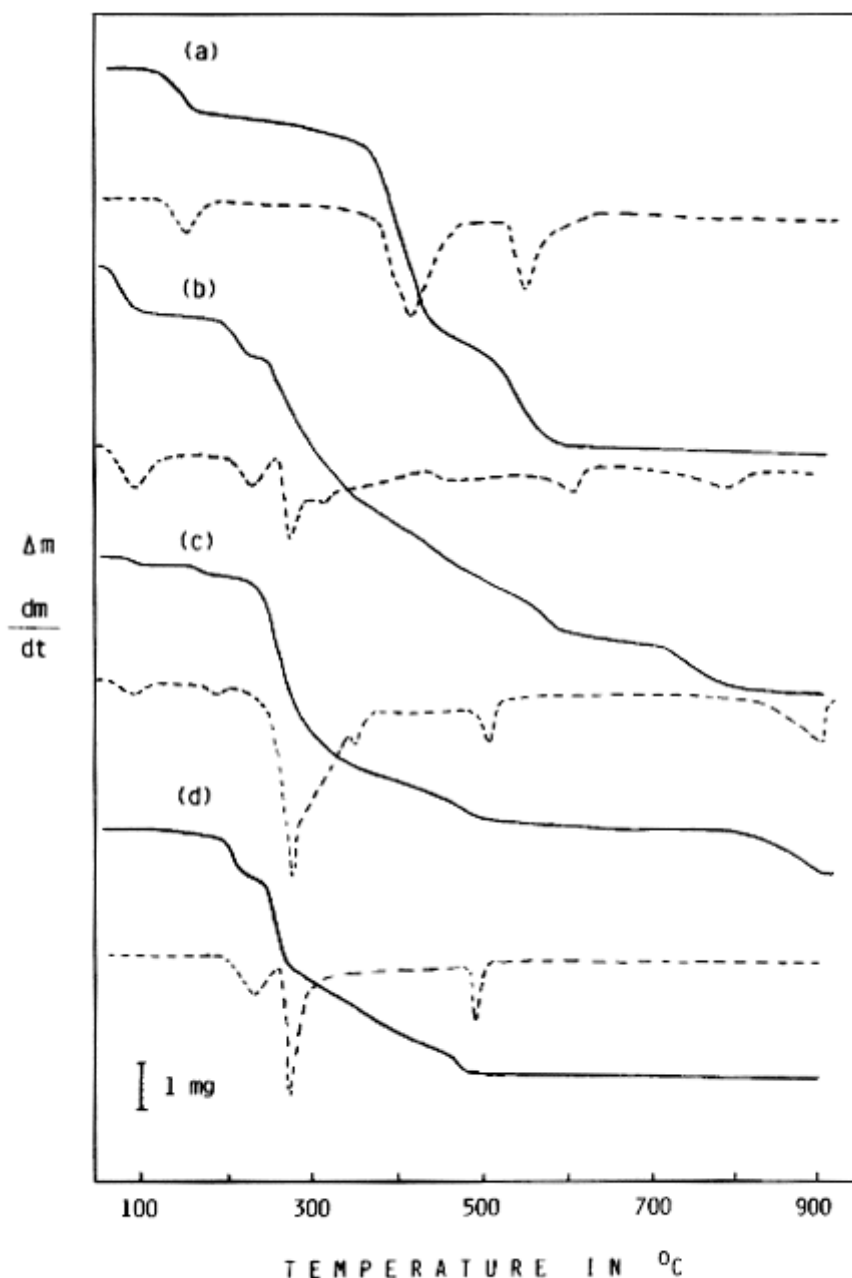


FIGURE 2 - TG and DTG curves of hydrated cinnamates. Heating rate $20^{\circ}\text{C min}^{-1}$, air flux $\approx 5 \text{ mL min}^{-1}$; (a) Mg; (b) Ca; (c) Sr and (d) Ba.

For the magnesium compound, [Figure 2\(a\)](#), the TG and DTG curves show mass losses in three steps, between 90°C and 580°C . The first step observed up to 200°C that begins with a fast process followed by a slow process is due to the dehydration with losses of $2\text{H}_2\text{O}$ (Theor.= 10.16%; TG = 10.1%). The second and third steps that occur in consecutive steps are due to the thermal decomposition of the resulting anhydrous compound. The calculations based on the mass losses observed in the TG curves, between 180°C and 450°C are in agreement with the loss of $2(\text{C}_6\text{H}_5)$; 2CH (Theor.= 50.82%; TG = 51.0%), and the rest of the ligand (last step) (Theor.= 27.65%; TG = 27.4%), with formation of magnesium oxide, MgO .

For the calcium compound, the TG and DTG curves [Figure 2\(b\)](#) show that the dehydration occurs

in two steps, with losses of 2.2 H₂O between 55°C and 110°C (Theor.= 9.75%; TG = 10.0%) and 1.8 H₂O between 175°C and 230°C (Theor.= 7.98%; TG = 8.1%). The thermal decomposition of the resulting anhydrous compound occurs with a slow process between 240°C and 600°C, with formation of calcium carbonate as intermediate accompanied of small quantity of carbonaceous residue (Theor.= 57.64%; TG = 56.73%). The last step observed between 600°C and 820°C, the mass loss that begins with a slow process up to 700°C followed by a fast process is ascribed to the pyrolysis of carbonaceous residue and the thermal decomposition of the carbonate to the calcium oxide CaO (Theor.= 10.83%; TG = 11.22%).

For the strontium compound, the TG and DTG curves [Figure 2\(c\)](#) show that the dehydration also occurs in two steps between 60°C - 100°C and 140°C - 180°C with losses of 0.4 H₂O in each step (Theor.= 1.82%; TG = 1.8%). The thermal decomposition of the resulting anhydrous compound occurs between 200°C and 500°C and begins with a fast process followed by a slow process with formation of strontium carbonate (Theor.= 59.12%; TG = 59.03%). The last step observed between 780°C and 900°C is due to the thermal decomposition of the carbonate to the strontium oxide, SrO (Theor.= 11,10%; TG = 10.67%).

For the barium compound, the TG and DTG curves [Figure 2\(d\)](#) show that the dehydration occurs in one step between 130°C and 230°C with losses of 3 H₂O (Theor.= 11.13%; TG = 11.3%). The thermal decomposition of the anhydrous compound that occurs between 230°C and 500°C, also begins with a fast process followed by a slow process with formation of barium carbonate, as residue (Theor.= 48.24%; TG = 48.37%).

The DSC curves of the Mg, Ca, Sr and Ba compounds are shown in [Figure 3 \(a\)-\(d\)](#). In all the curves the endothermic peaks at 175°C (Mg), 135°C and 225°C (Ca), 120°C and 205°C (Sr) and 215°C (Ba) are attributed to dehydration in agreement with the mass losses observed in the TG and DTG curves.

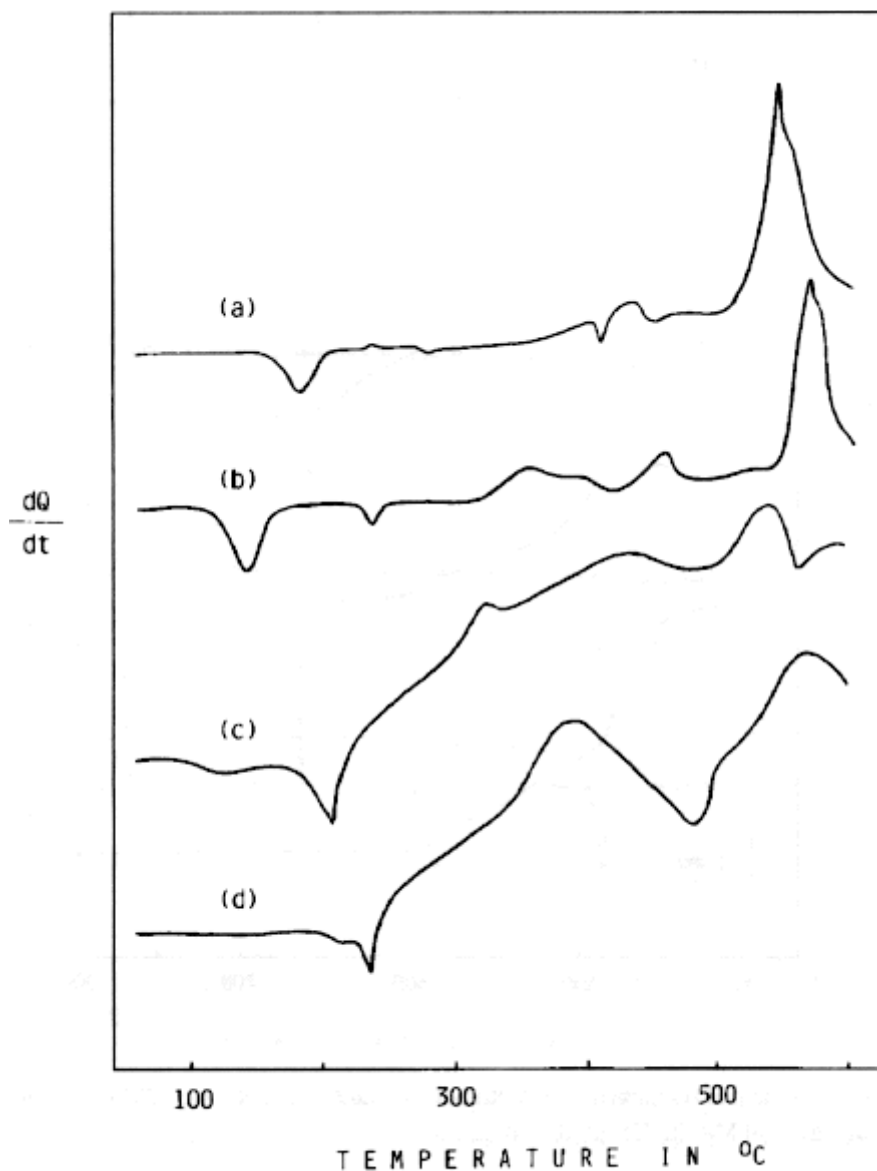


FIGURE 3 - DSC curves of hydrated cinnamates. Heating rate $20^{\circ}\text{C min}^{-1}$, air flux $\approx 150 \text{ mL min}^{-1}$; (a) Mg; (b) Ca; (c) Sr and (d) Ba.

For the magnesium compound, the small exothermic peak at 230°C suggest a recrystallization process; the small endothermic peak and the sequence of exothermic and endothermic peaks between 350°C and 460°C are attributed to the partial thermal decomposition of the anhydrous compound in correspondence with the second mass loss of the TG and DTG curves. The broad exothermic peak at 530°C is ascribed to the final pyrolysis of the compound.

For the other compounds, the exothermic peaks at 350°C , 450°C and 550°C (Ca); the broad exotherm in the ranges 250°C - 600°C (Sr) and (Ba) are attributed to the thermal decomposition of the anhydrous compounds, where the oxidation of the organic matter takes place in consecutive steps.

Conclusion

The X-ray powder patterns verified that the alkali earth metal compounds studied in this work have a crystalline structure.

The TG, DTG and DSC curves established the stoichiometry of the compounds in the solid state and provided information about the thermal stabilities and thermal decomposition. These curves also show that the thermal decomposition depend on the identity of the metal ion present.

Acknowledgements

The authors acknowledge the Fapesp (Proc. 90/2932-4), CNPq and PAE-UNESP for financial support and Isilda Marie Aparecida Ogata for aid in the preparation of this compuscript.

ZAINA CHIARETTO, A.G. et al. Preparação e decomposição térmica de cinamatos de metais alcalino terrosos, exceto berílio e rádio no estado sólido. *Ecl. Quím. (São Paulo)*, v.23, p.91-98, 1998.

RESUMO: Foram preparados compostos de fórmula geral $ML_2.nH_2O$, onde M é Mg, Ca, Sr e Ba; L é o cinamato ($C_6H_5-CH=CH-COO^-$) e n = 2; 4; 0,8; 3, respectivamente. A termogravimetria (TG), termogravimetria derivada (DTG), calorimetria exploratória diferencial (DSC) e difratometria de raios-X foram utilizados na caracterização, na verificação da estabilidade térmica e estudo da decomposição térmica desses compostos.

PALAVRAS-CHAVE: Metais alcalino-terrosos; cinamato; decomposição térmica.

References

1 ALLAM, J. R. et al. Thermal, spectral and magnetic studies of some compounds of cobalt(II), nickel(II) and copper(II) with cinnamic acid. *Thermochim. Acta*, v.154, p.315-22, 1989.

2 MIYANO, M. H. et al. The preparation and thermal decomposition of solid state compounds of 4-dimethylaminobenzylidenepyruvate and trivalent lanthanides and yttrium. *Thermochim. Acta*, v.221, p.53-62, 1993.

3 OLIVEIRA, L. C. S. et al. Preparation and thermal decomposition of solid state compounds of 4-methoxybenzylidenepyruvate and trivalent lanthanides and yttrium. *Thermochim. Acta*, v.219, p.215-24, 1993.

4 _____. Preparation and thermal decomposition of solid state compounds of 4-methoxybenzylidenepyruvate with alkali earth metals, except beryllium and radium. *Thermochim. Acta*, v.275, p.269-78, 1996.

5 RASERA, D. E. et al. The preparation and thermal decomposition of some metal compounds of 4-dimethylaminobenzylidenepyruvate in the solid state. *Thermochim. Acta*, v.250, p.151-63, 1995.

Recebido em 19.1.1998.

Aceito em 26.3.1998.

* Departamento de Química Analítica - Instituto de Química - UNESP - 14800-900 - Araraquara - SP - Brazil.