THERMAL STUDIES ON SOLID COMPOUNDS OF 4-CHLOROBENZYLIDENEPYRUVATE OF SOME ALKALI EARTH METALS

N. S. Fernandes[1]*, M. A. S. Carvalho Filho*[2]*, R. A. Mendes*[3]*, C. B. Melios*[3] *and M. Ionashiro*[3]*

[1]Fundação Universidade Federal de Tocantins, UFT, Palmas – TO CEP 77020-210, Brazil
[2]Centro Universitário Positivo-UnicenP, Campo Comprido, Curitiba – PR CEP 81280-330, Brazil
[3]Instituto de Química, Unesp, C.P. 355, CEP 14801-970 Araraquara, SP, Brazil

Abstract

Solid-state M-4-Cl-BP compounds, where *M* stands for bivalent Mg, Ca, Sr, Ba and 4-Cl-BP is 4-chlorobenzylidenepyruvate, have been synthesized. Simultaneous thermogravimetry-differential thermal analysis (TG-DTA), differential scanning calorimetry (DSC), infrared spectroscopy, elemental analysis and complexometry were used to characterize and to study the thermal behaviour of these compounds. The results led to informations about the composition, dehydration, thermal stability and thermal decomposition of the isolated complexes.

Introduction

Synthesis of benzylidenepyruvic acid (HBP), as well as of phenyl-substituted derivatives of HBP, have been reported [1, 2]. These acids are of continuing interest as intermediates in pharmacological, industrial and chemical syntheses, in the development of enzyme inhibitors and drugs, as model substrates of enzymes, and in other ways [2–7].

Preparation and investigation of several metal-ion complexes of phenyl-substituted derivatives of BP, have been carried out in aqueous solutions [8–11], and in the solid-state [12–23]. In aqueous solutions these works reported mainly the thermodynamic stability (β_1) and spectroscopic parameters (ε_{1max}, λ_{max}), associated with 1:1 complex species, analytical applications of the ligands, e.g., in gravimetric analysis and as metallochromic indicators, while in the solid-state, the establishment of the stoichiometry and detailed knowledge of the thermal behaviour of the ligands and their metal ion compounds have been the main purposes of these studies.

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*   Author for correspondence: E-mail: massaoi@iq.unesp.br

In the present paper, solid-state compounds of magnesium, calcium strontium and barium with 4-chlorobenzylidenepyruvate, $4\text{-Cl–}C_6H_4\text{–CH=CH–COCOO}^-$, were prepared. The compounds were investigated by complexometry, elemental analysis, infrared spectroscopy, simultaneous thermogravimetry-differential thermal analysis (TG-DTA) and differential scanning calorimetry (DSC). The data obtained allowed us to acquire information concerning these compounds in the solid-state, including their thermal stability and thermal decomposition.

Experimental

The sodium salt of 4-chlorobenzylidenepyruvic acid (4-Cl-BP) was prepared from 4-chlorobenzaldehyde and sodium pyruvate, in the presence of an alkaline catalyst as described in [24].

The solid-state compounds were prepared by adding slowly, with continuous stirring, the ligand solution to the respective metal-chlorides solutions, until total precipitation of the metal-ions.

The precipitates were washed until elimination of chloride ions, filtered through and dried on Whatman n° 42 filter paper and kept in a desiccator over anhydrous calcium chloride, under reduced pressure (10^3 Pa), to constant mass.

In the solid-state compounds, metal ions, water and 4-Cl-BP contents, were determined from the TG curves. The metal ions, were also determined by complexometry with standard EDTA solution [25], after igniting the compounds to the respective oxides or carbonate and their dissolution in hydrochloric acid solution.

Simultaneous TG-DTA and DSC curves were obtained by using two thermal analysis systems, models SDT 2960, DSC 2010, respectively, both from TA Instruments. The purge gas was an air flow of 150 mL min^{-1}. A heating rate of 20°C min^{-1} was adopted, with samples weighing about 7–8 mg. Alumina and aluminium crucibles, the latter with perforated covers, were used for recording TG-DTA and DSC curves, respectively.

Carbon and hydrogen contents were determined by microanalytical procedures, by using an EA1110 CHNS-0 Elemental Analyser from CE Instruments.

Infrared spectra for 4-Cl-BP (sodium salt) as well as for its metal ion compounds, were run on a Nicolet mod. Impact 400 FT-IR instrument, within the 4000–400 cm^{-1} range. The solid samples were pressed into KBr pellets.

Results and discussion

The analytical and thermoanalytical (TG) data are shown in Table 1. These results allowed to establish the stoichiometry of these compounds, which are in agreement with the general formula: $M(4\text{-Cl-BP})_2 \cdot nH_2O$, where M represents Mg, Ca, Sr or Ba, 4-Cl-BP is 4-chlorobenzylidenepyruvate and n=1, 2 or 3.

Infrared spectroscopic data on 4-chlorobenzylidenepyruvate and its compounds with the metal ions considered in this work are shown in Table 2. The investigations

Table 1 Analytical data for the $ML_2 \cdot nH_2O$ compounds

	$M/\%$			$L(\text{lost})/\%$			$H_2O/\%$			$C/\%$		$H/\%$		Final residue
	calcd.	EDTA	TG	calcd.	TG		calcd.	TG		calcd.	EA	calcd.	EA	
$MgL_2 \cdot 2H_2O$	5.07	4.85	5.00	84.08	84.00		7.52	7.49		50.08	49.53	3.37	3.78	MgO
$CaL_2 \cdot H_2O$	8.40	8.07	8.27	84.48	84.64		3.78	3.85		30.32	50.50	2.96	3.61	CaO
$SrL_2 \cdot 3H_2O$	15.62	15.75	15.93	71.89	71.48		9.64	9.48		42.82	38.83	4.32	4.38	SrO
$BaL_2 \cdot H_2O$	23.90	23.56	23.87	70.18	69.30		3.14	3.25		41.80	38.27	2.46	2.86	BaO

Key: M – metal; L – 4-chlorobenzylidenepyruvate

were focussed mainly within the 1700–1400 cm^{-1} range because it is the region that is potentially most informative in attempting to assign coordination sites for the presently studied compounds.

Table 2 Spectroscopic data for sodium 4-methylbenzylidenepyruvate (4-MeBP) and for its compounds with some bivalent metal ions

Compound	$\gamma_{as}^{a}(COO^-)/$ cm^{-1}	$\Delta\gamma_{as}^{b}(COO^-)/$ cm^{-1}	$\gamma_{sym}^{a}(COO^-)/$ cm^{-1}	$\gamma^{c}(C=O)/$ cm^{-1}	$\Delta\gamma^{a}(C=O)$
4-Cl-BP-Na·0.5H$_2$O	1622s	–	1403m	1675s	–
Mg(4Cl-BP)$_2$·2H$_2$O	1617s	5	1395m	1657s	18
Ca(4Cl-BP)$_2$·H$_2$O	1595s	27	1405m	1638s	37
Sr(4Cl-BP)$_2$·3H$_2$O	1597s	25	1406m	1627s	48
Ba(4Cl-BP)$_2$·H$_2$O	1606s	16	1406m	1667s	8

s=strong, m=medium, sh=shoulder
a – $\gamma_{sym}(COO^-)$ and $\gamma_{as}(COO^-)$=symmetrical and anti-symmetrical vibrations of the COO^- group,
b – $\Delta\gamma_{as}(COO^-)$=$\gamma_{as}(COO^-)$ (Na salt) – $\gamma_{as}(COO^-)$ (metal complex), c – $\gamma(C=O)$=ketonic carbonyl stretching frequency, d – $\Delta\gamma(C=O)$=$\gamma(C=O)$ (Na salt) – $\gamma(C=O)$ (metal complex)

In 4-Cl-BP (sodium salt), strong band at 1622 and a medium intensity band located at 1403 cm^{-1} are attributed to the anti-symmetrical and symmetrical frequencies of the carboxylate groups, respectively [26, 27]. The band centered at 1675 cm^{-1} is typical of a conjugated ketonic carbonyl group [26–28]. This is in line with the observed carbonyl streching frequency for s-*trans*-benzylidene acetone (i.e., 1674 cm^{-1}) [27].

For the synthesized compounds the anti-symmetrical stretching carboxylate frequency as well as that assigned to the ketonic carbonyl are shifted to lower values relative to the corresponding frequencies in 4-Cl-BP itself (sodium salt); this behaviour indicates that both aforementioned groups act as coordination centres in the metal compounds [28, 29]. The data displayed in Table 2 show that the magnitude of the shifts are dependent on the metal ions.

Simultaneous TG-DTA and DSC curves of the compounds are shown in Figs 1–3. The TG-DTA curves show mass losses in five or six steps, corresponding to endothermic peaks due to dehydration and exothermic peaks attributed to thermal decomposition. The DSC curves (Fig. 3) also show endothermic and exothermic peaks, corresponding to the mass losses displayed by the TG curves. Small differences observed concerning the peak temperatures obtained by TG-DTA and DSC for the endothermic peaks are undoubtedly due to the perforated cover used to obtain the DSC curves, while the TG-DTA ones are obtained without cover.

The thermal stability of the anhydrous compounds (I), as well as the temperature where the oxide level begins (II) as shown by the TG-DTA curves, depend on the nature of the metal ion, and they follow the order:
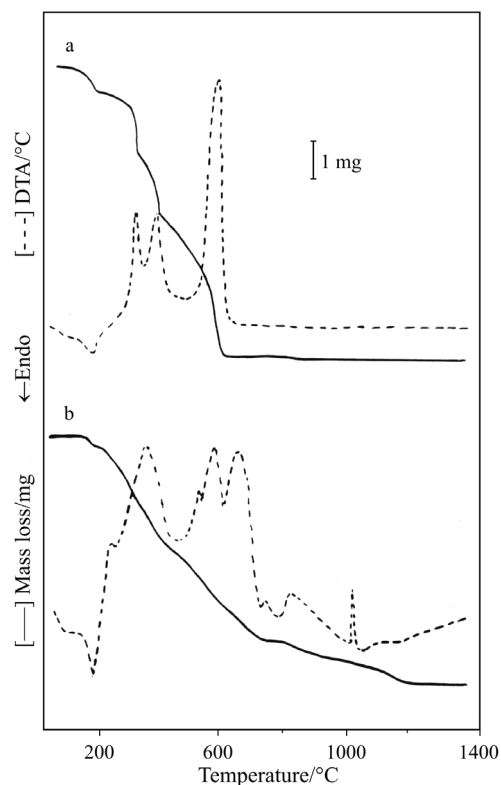
$$(I) \; Mg \approx Ca > Sr \approx Ba$$

$$(II) \; Ba > Sr > Ca > Mg$$

Fig. 1 TG-DTA curves of a – Mg(4-Cl-BP)$_2$·2H$_2$O, (*m*=7.354 mg),
        b – Ca(4-Cl-BP)$_2$·H$_2$O (*m*=7.215 mg)

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

Magnesium compound

The simultaneous TG-DTA curves and the DSC curve as well are shown in Fig. 1a and 3a, respectively. The first mass loss observed between 100 and 160°C (TG), corresponding to an endothermic peak at 150°C (DTA) and 170°C (DSC) is due to hydration water; it reflects the loss of 2H$_2$O (calcd.=7.52%, TG=7.49%). The thermal decomposition of the anhydrous compound occurs in three overlapping steps, between 200 and 310°C, 310 and 395°C, 395 and 586°C with losses of 19.00, 19.00 and 43.90%, respectively, corresponding to exothermic peaks at 304, 378 and 586°C (DTA) or exothermic ones at 300, 385 and 538°C (DSC), which are attributed to oxidation of the organic matter, with formation of intermediate: mixture of magnesium oxide and chloride or oxychloride. Test with AgNO$_3$ solution on sample
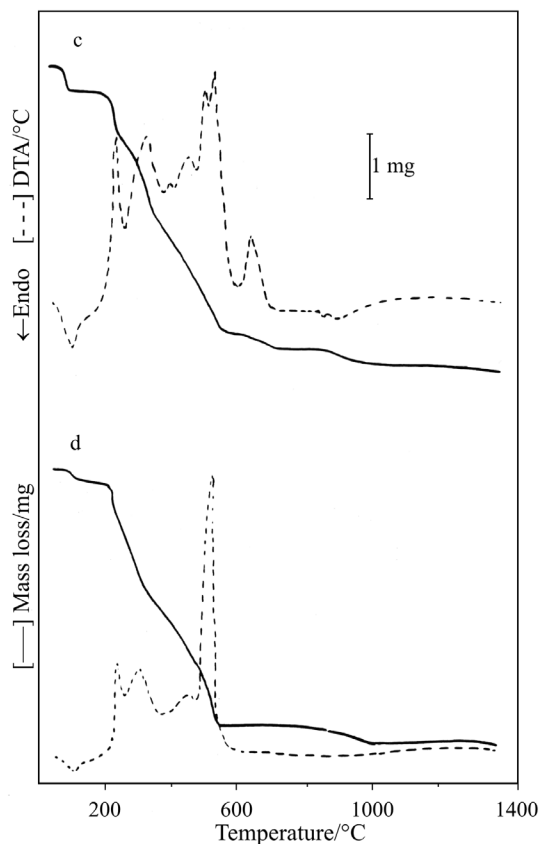
Fig. 2 TG-DTA curves of c – Sr(4-Cl-BP)$_2$·3H$_2$O (m=7.534 mg) and
d – Ba(4-Cl-BP)$_2$·H$_2$O (m=7.484 mg)

heated up to 620°C, after dissolution in nitric acid solution confirmed their presence of chloride ions.

The last step observed between 760 and 820°C with mass loss of 2.10% is ascribed to the thermal decomposition of the intermediate to the magnesium oxide.

Calcium compound

Simultaneous TG-DTA and DSC curves are shown in Figs 1b and 3b, respectively. The first mass loss observed between 110 and 160°C (TG), corresponding to endothermic peak at 155°C (DTA) and 150°C (DSC) is due to dehydration with loss of H$_2$O (calcd.=3.78%, TG=3.85%). After dehydration, between 200 and 750°C, the thermal decomposition of the anhydrous compound occurs in three overlapping steps with total loss of 68.48%, corresponding to exothermic peaks at 348, 586, 660 and 747°C, with shoulder at 230 and 529°C (DTA) and 170, 332 and 548°C with shoulder at 538°C, attributed to oxidation of organic matter with the formation of a mixture of calcium carbonate and chloride or
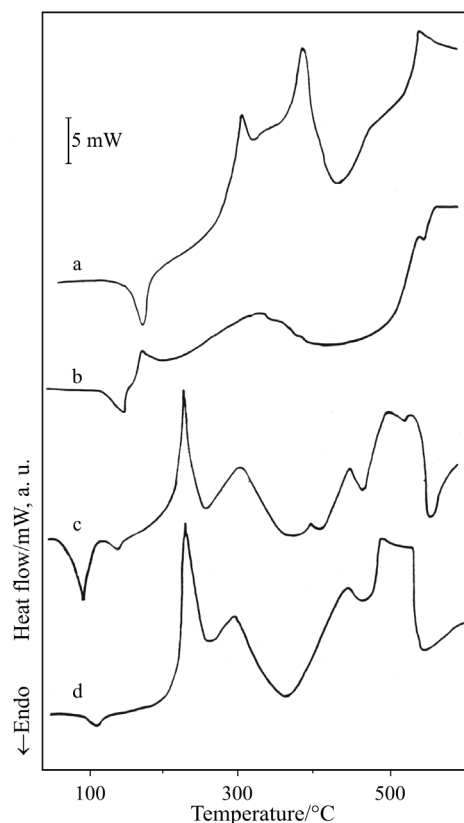
Fig. 3 DSC curves of a – Mg(4-Cl-BP)$_2$·2H$_2$O, (m=7.728 mg), b – Ca(4-Cl-BP)$_2$·H$_2$O
(m=7.637 mg), c – Sr(4-Cl-BP)$_2$·3H$_2$O (m=7.655 mg) and
d – Ba(4-Cl-BP)$_2$·H$_2$O (m=7.393 mg)

oxychloride in no simple stoichiometric relation, accompanied by small amount of carbonaceous residue. A test with AgNO$_3$ solution on sample heated up to 750°C, after dissolution in nitric acid solution confirmed the evolution of CO$_2$ and the presence of chloride ions and carbonaceous residue.

The last step between 800 and 1200°C the mass loss occurs through a slow process with loss of 16.16%, corresponding to exothermic peak at 927°C (DTA), attributed to the oxidation of carbonaceous residue and thermal decomposition of the mixtures of calcium carbonate and chloride or oxychloride to calcium oxide. No endothermic peak is observed due to the thermal decomposition of that mixture in the DTA curve; this is probably due to the small amount of heat absorbed in the thermal decomposition which is not enough to produce endothermic peak. The sharp endothermic peak at 1014°C, characteristic of physical phenomenon, is ascribed to the crystalline transition of calcium chloride or oxychloride.

Strontium compound

Simultaneous TG-DTA and DSC curves are shown in Figs 2c and 3c, respectively. The first mass loss between 60 and 88°C (TG), corresponding to the endothermic peak 80°C (DTA) is due to the dehydration with loss of $3H_2O$ (calcd.=9.64%, TG=9.48%). In the DSC curve the endothermic peak at 90°C is due to dehydration and in agreement with TG-DTA curves. For the second endothermic peak at 135°C, no mass loss is observed in the TG curve. However, DSC curve obtained with crucible without cover, only the endothermic peak at 90°C is observed, suggesting that during the dehydration occurs the condensation of the water evolved in the empty space of the crucible with perforate cover, and with the increase of the temperature the condensate water is evaporated, which justify the second endothermic peak.

After dehydration, between 176 and 720°C the mass loss occurs in four overlapping and consecutive steps with loss of 66.12%, corresponding to the exothermic peaks at 234, 324, 451, 496, 526 and 640°C (DTA) and 230, 300, 397, 447 and 494°C (DSC), ascribed to the oxidation of organic matter with formation of a mixture of strontium carbonate and chloride or oxychloride, in no simple stoichiometric relation. The presence of carbonate and chloride ions were also confirmed by qualitative tests.

The last two mass losses between 820–1100°C and 1100–1390°C are attributed to the thermal decomposition of strontium chloride or oxychloride and strontium carbonate to strontium oxide, with losses of 3.22 and 2.14%, respectively. The endothermic peaks at 857 and 893°C are ascribed to the fusion and thermal decomposition of strontium chloride or oxychloride, respectively.

Barium compound

Simultaneous TG-DTA and DSC curves are shown in Figs 2d and 3d, respectively. The first mass loss between 80 and 100°C, corresponding to endothermic peak at 90°C (DTA) or 110°C (DSC), is due to dehydration, with loss of $1H_2O$ (calcd.=3.14%, TG=3.25%). After the dehydration, the mass loss between 178 and 550°C occurs in three overlapping steps with total mass loss of 64.35%, corresponding to exothermic peaks at 24, 303, 444 and 525°C (DTA) and 230, 294, 445 and 492°C (DSC), attributed to the oxidation of organic matter with formation of a mixture of barium carbonate and chloride or oxychloride in no simple stoichiometric relation.

The two last mass losses (4.95%), between 800–1030 and 1220–1390°C are ascribed to the thermal decomposition of barium chloride or oxychloride and barium carbonate to barium oxide, respectively.

The dehydration enthalpies found for magnesium, calcium, strontium and barium compounds were: 212.0, 110.1, 168.3 and 36.5 J mol^{-1}, respectively.

Conclusions

From TG, complexometry and elemental analysis data, a general formula could be established for the binary compounds involving some alkali earth metals ions and 4-Cl-BP.

The infrared spectroscopic data suggest that 4-Cl-BP acts as a bidentate ligand towards the metal ions considered in this work.

The TG-DTA and DSC curves, provided previously unreported information about the thermal stability and thermal decomposition of these compounds.

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