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## **THERMAL BEHAVIOUR STUDIES OF SOLID STATE COMPOUNDS OF CINNAMYLIDENEPYRUVATE WITH TRIVALENT LANTHANIDES AND YTTRIUM (III) IN AN ATMOSPHERE OF CO<sub>2</sub>**

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**ABSTRACT:** Solid state cinnamylidenepyruvate of trivalent lanthanides (except for promethium) and yttrium, were 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 behavior of these compounds in a dynamic CO<sub>2</sub> atmosphere. The results obtained showed significant differences on the thermal stability and thermal decomposition of these compounds, with regard to the thermal behavior study in a dynamic air atmosphere.

**KEYWORDS:** Lanthanides and yttrium, cinnamylidenepyruvate, CO<sub>2</sub> atmosphere, thermal behavior.

### **Introduction**

Studies involving complexes of benzylidenepyruvate, C<sub>6</sub>H<sub>5</sub>-(CH)<sub>2</sub>COCOO<sup>-</sup> (BP), cinnamylidenepyruvate, C<sub>6</sub>H<sub>5</sub>-(CH)<sub>4</sub>COCOO<sup>-</sup> (CP) and several phenyl-substituted of BP and CP, i.e. 4-dimethylamino-(DMBP), 2-chloro-4-dimethylamino-(2-Cl-DMBP), 4-methoxy-(4-MeO-BP), 2-chloro-(2-Cl-BP), 4-chlorobenzylidenepyruvate (4-Cl-BP) and 4-dimethylaminocinnamylidenepyruvate (DMCP) with several metallic ions have been carried out in

aqueous solutions<sup>2-5,12,15</sup>.

In the solid state, compounds of 4-MeO-BP, DMBP, CP and DMCP with various metallic ions have been prepared and investigated by using thermoanalytical techniques, X-ray powder diffractometry, elemental analysis and complexometry<sup>1-6,11,13,14</sup>. The establishment of the stoichiometry and the thermal behavior have been the main objective of these works. As an extension of the work of ref. 11, hydrated compounds of cinnamylidenepyruvate with trivalent lanthanides and yttrium (III), were prepared and investigated by using thermoanalytical techniques (TG, DTG, DSC) in a CO<sub>2</sub> atmosphere. The results of this study are discussed in connection with those found for previously study involving these compounds in an air atmosphere.

## Experimental

For the preparation of the solid state compounds of trivalent lanthanides and yttrium (III) with CP, as well as, for the determination of the hydration water, metallic ions and ligand contents, the same procedures previously described<sup>11</sup> were used.

TG, DTG and DSC curves were obtained using a Mettler TA-4000 thermal analysis system, with a CO<sub>2</sub> flow of about 90 mL min<sup>-1</sup>, a heating rate of 20°C min<sup>-1</sup> and samples of about 8 mg. A platinum crucible was used for the TG and DTG curves, and an aluminum 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 arrangements was adopted using CuK $\alpha$  radiation ( $\lambda = 1.541\text{\AA}$ ) and a setting of 38 kV and 20 mA.

## Results and discussion

[Table 1](#) presents the analytical and thermoanalytical (TG) results for the prepared compounds, from which the general formula Ln(CP)<sub>3</sub>.2H<sub>2</sub>O can be established, where Ln represents trivalent lanthanide or yttrium (III) and CP is cinnamylidenepyruvate.

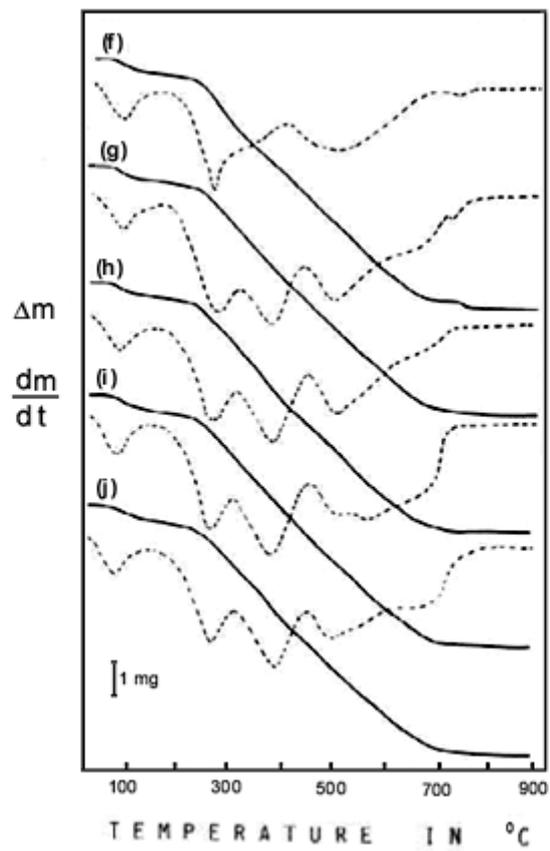
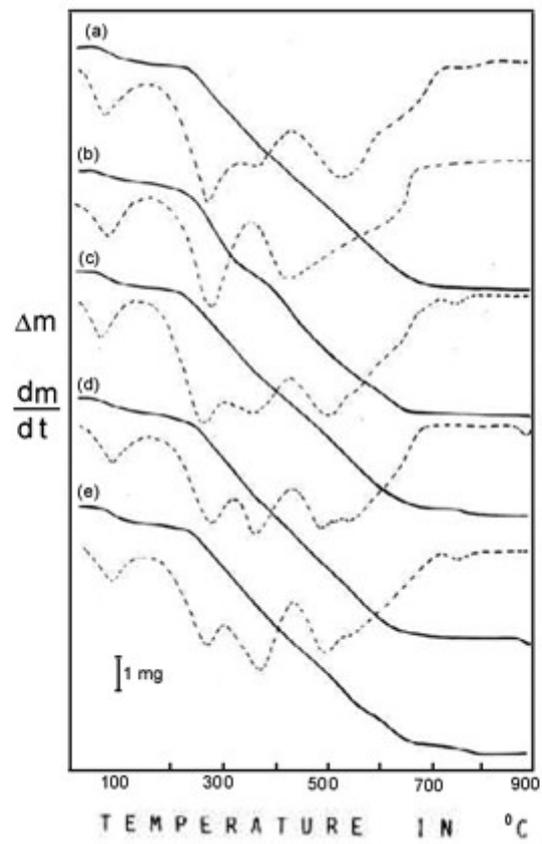
**Table 1.** Analytical and Thermoanalytical (TG) results.

Compound	Metal in %		CP* lost in %		Water in %		Residue	
	Calcd.	TG	EDTA	Calcd	TG	Calcd.		TG
La(CP) <sub>3</sub> .2H <sub>2</sub> O	17.84	17.77	18.19	71.62	71.60	4.63	4.75	La <sub>2</sub> O <sub>2</sub> CO <sub>3</sub>
Ce(CP) <sub>3</sub> .2H <sub>2</sub> O	17.97	17.88	18.00	73.31	73.32	4.62	4.71	CeO <sub>2</sub>
Pr(CP) <sub>3</sub> .2H <sub>2</sub> O	18.05	18.10	18.29	73.57	73.53	4.62	4.60	Pr <sub>6</sub> O <sub>11</sub>
Nd(CP) <sub>3</sub> .2H <sub>2</sub> O	18.40	18.52	18.59	73.94	73.64	4.60	4.69	Nd <sub>2</sub> O <sub>3</sub>
Sm(CP) <sub>3</sub> .2H <sub>2</sub> O	19.03	19.05	19.18	73.37	73.30	4.56	4.61	Sm <sub>2</sub> O <sub>3</sub>
Eu(CP) <sub>3</sub> .2H <sub>2</sub> O	19.20	19.33	19.26	73.22	73.13	4.55	4.50	Eu <sub>2</sub> O <sub>3</sub>
Gd(CP) <sub>3</sub> .2H <sub>2</sub> O	19.73	19.90	20.02	72.73	72.71	4.52	4.50	Gd <sub>2</sub> O <sub>3</sub>
Tb(CP) <sub>3</sub> .2H <sub>2</sub> O	19.90	19.99	20.25	72.08	72.03	4.49	4.53	Tb <sub>4</sub> O <sub>7</sub>
Dy(CP) <sub>3</sub> .2H <sub>2</sub> O	20.26	20.31	20.49	72.26	72.16	4.49	4.53	Dy <sub>2</sub> O <sub>3</sub>
Ho(CP) <sub>3</sub> .2H <sub>2</sub> O	20.50	20.51	20.43	72.04	72.01	4.48	4.50	Ho <sub>2</sub> O <sub>3</sub>
Er(CP) <sub>3</sub> .2H <sub>2</sub> O	20.73	20.69	20.91	71.83	71.94	4.47	4.40	Er <sub>2</sub> O <sub>3</sub>
Tm(CP) <sub>3</sub> .2H <sub>2</sub> O	20.89	20.80	20.82	71.68	71.75	4.46	4.50	Tm <sub>2</sub> O <sub>3</sub>
Yb(CP) <sub>3</sub> .2H <sub>2</sub> O	21.29	21.31	21.33	71.32	71.15	4.43	4.58	Yb <sub>2</sub> O <sub>3</sub>
Lu(CP) <sub>3</sub> .2H <sub>2</sub> O	21.43	21.46	21.72	71.20	71.73	4.43	4.26	Lu <sub>2</sub> O <sub>3</sub>
Y(CP) <sub>3</sub> .2H <sub>2</sub> O	12.20	12.17	12.31	79.56	79.71	4.95	4.84	Y <sub>2</sub> O <sub>3</sub>

\*CP is cinnamylidenebenzalpyruvate.

The X-ray powder patterns showed that all the compounds are amorphous. The amorphous state is undoubtedly related to the low solubility of these compounds, as already observed for the lanthanides and yttrium compounds with DMBP<sup>7</sup> and for the heavier lanthanides and yttrium with 4-MeO-BP<sup>8</sup>.

TG and DTG curves of the compounds are shown in [Fig. 1](#). These curves show mass losses beginning at 50°C and the first step up to 150°C is due to the dehydration, that occurs in one step and through a slow process with loss of 2H<sub>2</sub>O.



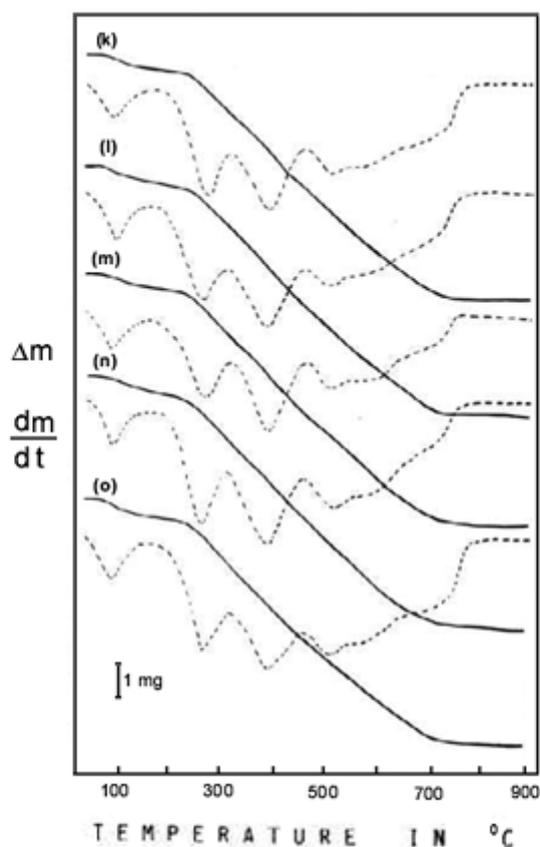


Figure 1. TG and DTG curves of the compounds: (a)  $\text{La}(\text{CP})_3 \cdot 2\text{H}_2\text{O}$  (8.043 mg); (b)  $\text{Ce}(\text{CP})_3 \cdot 2\text{H}_2\text{O}$  (7.894 mg); (c)  $\text{Pr}(\text{CP})_3 \cdot 2\text{H}_2\text{O}$  (8.057 mg); (d)  $\text{Nd}(\text{CP})_3 \cdot 2\text{H}_2\text{O}$  (8.252 mg); (e)  $\text{Sm}(\text{CP})_3 \cdot 2\text{H}_2\text{O}$  (8.140 mg); (f)  $\text{Eu}(\text{CP})_3 \cdot 2\text{H}_2\text{O}$  (8.227 mg); (g)  $\text{Gd}(\text{CP})_3 \cdot 2\text{H}_2\text{O}$  (8.172 mg); (h)  $\text{Tb}(\text{CP})_3 \cdot 2\text{H}_2\text{O}$  (8.070 mg); (i)  $\text{Dy}(\text{CP})_3 \cdot 2\text{H}_2\text{O}$  (7.997 mg); (j)  $\text{Ho}(\text{CP})_3 \cdot 2\text{H}_2\text{O}$  (8.225 mg); (k)  $\text{Er}(\text{CP})_3 \cdot 2\text{H}_2\text{O}$  (7.996 mg); (l)  $\text{Tm}(\text{CP})_3 \cdot 2\text{H}_2\text{O}$  (8.066 mg); (m)  $\text{Yb}(\text{CP})_3 \cdot 2\text{H}_2\text{O}$  (8.204 mg); (n)  $\text{Lu}(\text{CP})_3 \cdot 2\text{H}_2\text{O}$  (8.218 mg) and (o)  $\text{Y}(\text{CP})_3 \cdot 2\text{H}_2\text{O}$  (8.220 mg).

The resulting anhydrous compounds are stable up to  $200^\circ\text{C}$ , and above this temperature the DTG curves show that the thermal decomposition occurs with a large number of consecutive or simultaneous steps and through a more complex pathway, although the TG curves show mass losses continuously without possibility to suggest which part of the ligand is lost in the steps indicated by the DTG curves, except for the cerium compound, [Fig. 1\(b\)](#), that shows two steps. The patterns of the DTG curves, except for the cerium and europium compounds are similar, suggesting the same thermal decomposition mechanism. This behavior was also observed in the thermal decomposition of these compounds in an air atmosphere<sup>11</sup>.

For the lanthanum, praseodymium-europium compounds, [Fig. 1 \(a, c-f\)](#), the mass losses indicated by the TG curves up to  $700^\circ\text{C}$  (La),  $685^\circ\text{C}$  (Pr, Sm) and  $680^\circ\text{C}$  (Nd, Eu), are in agreement with the formation of lanthanide dioxycarbonate,  $\text{Ln}_2\text{O}_2\text{CO}_3$ , as intermediate: La, TG = 71.60%, calcd = 71.62%; Pr, TG = 71.50%, calcd = 71.44%; Nd, TG = 71.00, calcd = 71.13%; Sm, TG = 70.70%, calcd = 70.58%; Eu, TG = 70.46%, calcd = 70.44%. Tests with hydrochloric acid solution on samples heated up to the temperature of formation of the dioxycarbonate, as indicated by the TG

and DTG curves, confirmed the elimination of CO<sub>2</sub>.

Only in the lanthanum compound the intermediate is stable up to 900°C. In the other compounds the thermal decomposition of the intermediates occurs between 720-800°C (Pr), 840-900°C (Nd), 720-820°C (Sm) and 710-760°C (Eu), with the mass loss data in agreement with elimination of 0.5 CO<sub>2</sub> (Pr, TG = 2,03%, calcd = 2.14%; Nd, TG = 2,64%, calcd = 2.81%; Sm, TG = 2,60%, calcd = 2.79%; Eu, TG = 2.66%, calcd = 2.78%), with formation of the respective oxide, Pr<sub>6</sub>O<sub>11</sub>, LnO<sub>3</sub> (Ln = Nd, Sm, Eu), as a final residue.

The formation of dioxycarbonate as intermediate, was also observed in the thermal decomposition of these compounds and other phenyl-substituted derivatives of benzylidenepyruvate with lanthanides and yttrium in an air atmosphere<sup>1,7,8,11</sup>. The higher thermal stability of these intermediates in a CO<sub>2</sub> atmosphere than in an air atmosphere, is due to the increasing of the same gas evolved in the thermal decomposition of the dioxycarbonate, where the concentration of the ambient gas surrounding the sample increase, therefore the thermal stability increase.

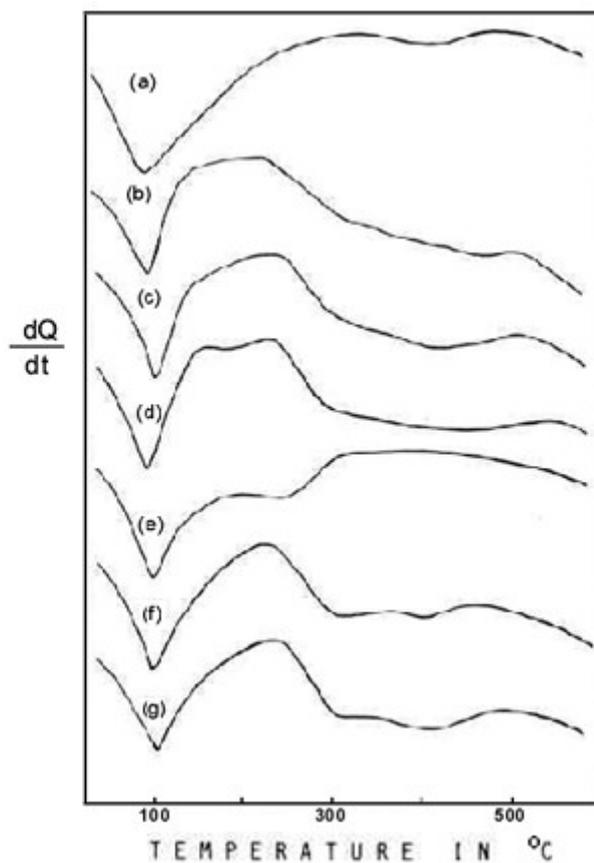
For the anhydrous cerium compound the TG and DTG curves show mass losses in two consecutive steps between 200-670°C, and the first step up to 360°C is in agreement with the loss of 3(C<sub>6</sub>H<sub>6</sub>), (TG = 29.33%, calcd = 29.60%). The following step which correspond to the final pyrolysis of the ligand, the mass loss is in agreement with formation of cerium oxide, CeO<sub>2</sub>, (TG = 43.99%, calcd = 43.71%). In the cerium compound, the dioxycarbonate is not formed probably due to the oxidation reaction of the cerium (III) to cerium (IV).

In the anhydrous gadolinium-lutetium and yttrium compounds, the TG and DTG curves, [Fig. 1 \(g – o\)](#), show mass losses that begin at 200°C, and above this temperature the thermal decomposition occurs slowly to give the respective oxide level, Tb<sub>4</sub>O<sub>7</sub> and Ln<sub>2</sub>O<sub>3</sub> (Ln = Gd, Dy-Lu, Y), beginning at 725°C (Gd, Dy), 740°C (Tb, Tm), 750°C (Ho), 760°C (Er, Y) and 780°C (Yb, Lu). For these compounds, the formation of dioxycarbonate is not observed, although this intermediate was identified in the thermal decomposition of these compounds in an air atmosphere, except for the terbium compound<sup>11</sup>.

In a dynamic gas atmosphere, compound that evolves the same gas during the thermal decomposition, the thermal stability is increased. However, for these compounds the intermediate is not observed, because the increasing thermal stability of the dioxycarbonate in a CO<sub>2</sub> atmosphere, probably is smaller than the increasing which is also observed in the final temperature of thermal decomposition. The increasing final temperature of about 200°C, when compared with an air atmosphere up to the temperature where the dioxycarbonate is formed, undoubtedly is due to the purge gas that is the same gas evolved in the pyrolysis of the organic matter. The ambient gas concentration surrounding the sample increases, decreasing in rate of the reaction.

In the terbium compound, the dioxycarbonate is not formed, probably due to the oxidation of Tb(III), that results in the formation of Tb<sub>4</sub>O<sub>7</sub>, as final residue.

The DSC curves of the compounds are shown in [Fig. 2](#). The endothermic peak at  $\gg 100^{\circ}\text{C}$ , observed in all compounds is due to the hydration water and in agreement with the first mass loss of the TG and DTG curves.



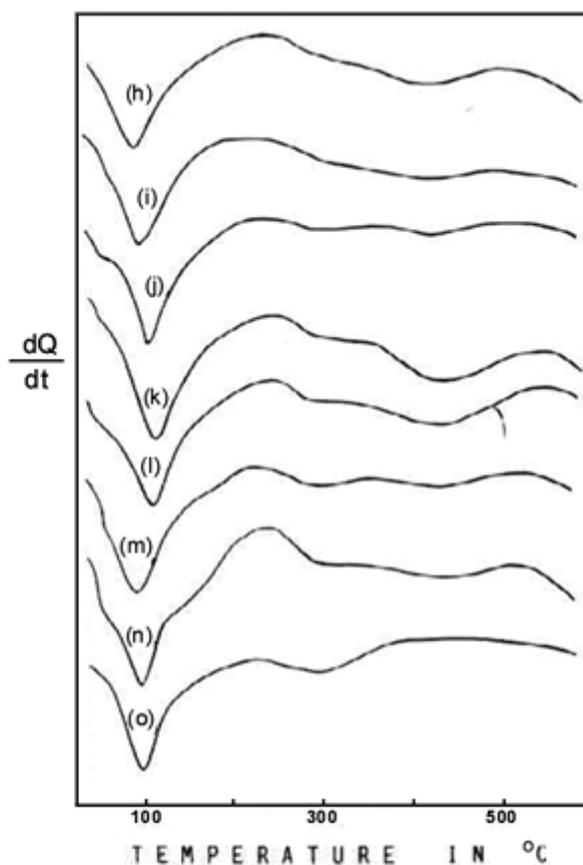


Fig. 2. DSC curves of the compounds: (a)  $\text{La}(\text{CP})_4 \cdot 2\text{H}_2\text{O}$ ; (b)  $\text{Ce}(\text{CP})_3 \cdot 2\text{H}_2\text{O}$ ; (c)  $\text{Pr}(\text{CP})_3 \cdot 2\text{H}_2\text{O}$ ; (d)  $\text{Nd}(\text{CP})_3 \cdot 2\text{H}_2\text{O}$ ; (e)  $\text{Sm}(\text{CP})_3 \cdot 2\text{H}_2\text{O}$ ; (f)  $\text{Eu}(\text{CP})_3 \cdot 2\text{H}_2\text{O}$ ; (g)  $\text{Gd}(\text{CP})_3 \cdot 2\text{H}_2\text{O}$ ; (h)  $\text{Tb}(\text{CP})_3 \cdot 2\text{H}_2\text{O}$ ; (i)  $\text{Dy}(\text{CP})_3 \cdot 2\text{H}_2\text{O}$ ; (j)  $\text{Ho}(\text{CP})_3 \cdot 2\text{H}_2\text{O}$ ; (k)  $\text{Er}(\text{CP})_3 \cdot 2\text{H}_2\text{O}$ ; (l)  $\text{Tm}(\text{CP})_3 \cdot 2\text{H}_2\text{O}$ ; (m)  $\text{Yb}(\text{CP})_3 \cdot 2\text{H}_2\text{O}$ ; (n)  $\text{Lu}(\text{CP})_3 \cdot 2\text{H}_2\text{O}$  and (o)  $\text{Y}(\text{CP})_3 \cdot 2\text{H}_2\text{O}$ .

The sequence of broad endothermic events verified after the dehydration, between  $200^\circ\text{C}$  and  $600^\circ\text{C}$ , are ascribed to the thermal decomposition of the anhydrous compounds, which take place in consecutive steps, in agreement with the DTG curves.

## Conclusion

Thermal decomposition of these compounds in an atmosphere of  $\text{CO}_2$  the dioxycarbonate as intermediate was observed only for the lanthanum, praseodymium – europium compounds, in disagreement with the thermal behaviour data in an air atmosphere, where this intermediate was observed for all the compounds, except for the cerium and terbium compounds.

The TG, DTG and DSC curves provided information about the influence of the  $\text{CO}_2$  as purge gas, in the thermal stability and thermal decomposition of these compounds.

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OLIVEIRA, J.D.S., FERTONANI, F.L., MELIOS, C.B., IONASHIRO, M. Estudo do comportamento térmico de compostos no estado sólido de cinamalpiruvatos de lantanídeos (III) e de ítrio (III) em atmosfera dinâmica de CO<sub>2</sub>. *Ecl. Quím. (São Paulo)*, v.27, p. , 2002.

**RESUMO:** Os cinamalpiruvatos de lantanídeos (III) (exceto promécio) e de ítrio (III), foram preparados no estado sólido. A termogravimetria, termogravimetria derivada (TG, DTG), calorimetria exploratória diferencial (DSC), difratometria de raios X e complexometria foram utilizadas para caracterizar e estudar o comportamento térmico desses compostos em atmosfera dinâmica de CO<sub>2</sub>. Os resultados obtidos mostraram diferenças significativas na estabilidade e na decomposição térmica desses compostos em relação ao estudo do comportamento térmico em atmosfera dinâmica de ar.

**PALAVRAS-CHAVE:** Lantanídios; ítrio; cinamalpiruvato; atmosfera de CO<sub>2</sub>; comportamento térmico.

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