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transitions metal ions in dynamic N2 and CO2 atmospheres

THERMAL BEHAVIOUR OF SUCCINIC ACID, SODIUM SUCCINATE AND ITS COMPOUNDS WITH SOME BIVALENT TRANSITIONS METAL IONS IN DYNAMIC N$_2$ AND CO$_2$ ATMOSPHERES

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Abstract: Thermal stability and thermal decomposition of succinic acid, sodium succinate and its compounds with Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) were investigated employing simultaneous thermogravimetry and differential thermal analysis (TG-DTA) in nitrogen and carbon dioxide atmospheres and TG-FTIR in nitrogen atmosphere. On heating, in both atmospheres the succinic acid melt and evaporate, while for the sodium succinate the thermal decomposition occurs with the formation of sodium carbonate. For the transition metal succinates the final residue up to 1180 ºC in N$_2$ atmosphere was a mixture of metal and metal oxide in no simple stoichiometric relation, except for Zn compound, where the residue was a small quantity of carbonaceous residue. For the CO$_2$ atmosphere the final residue up to 980 ºC was: MnO, Fe$_3$O$_4$, CoO, ZnO and mixtures of Ni, NiO and Cu, Cu$_2$O.

Keywords: bivalent transitions metals, succinate, thermal behavior.

Introduction

Preparation and investigation on the thermal behaviour and thermal decomposition of several metal-ion succinates have been reported. These papers are concerned with the thermal decomposition of bivalent succinates in the solid state [1], the thermal, spectral and magnetic studies of succinic acid and compounds of some transition metal ions [2], thermal dehydration of manganese (II) dicarboxylate hydrates [3], synthesis, properties and thermal decomposition of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) succinates [4], a study of the thermal decomposition of Cu(II) and Zn(II) malonate, maleate and succinate complex [5] and a comparative study on the thermal decomposition of some transition metal carboxylates [6]. As continuation of our previous study on thermal behavior of

succinic acid, sodium succinate and its compounds with some bivalent transition metal ions in air atmosphere [7], this paper deals with the thermal behavior and thermal decomposition of these compounds in dynamic N$_2$ and CO$_2$ atmospheres.

Experimental

The succinic acid C$_4$H$_6$O$_4$, and its sodium salt Na$_2$C$_4$H$_4$O$_4$.6H$_2$O, both with 99% purity were obtained from Sigma.

Solid state Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) compounds were prepared by mixing the aqueous suspension of the corresponding metal carbonates in excess with 50.0 mL of succinic acid 0.10 mol L^{-1} solution, and heated slowly up to near

ebullition, until total neutralization of the acid. The carbonate in excess was removed by filtration and the aqueous solution of the respective metal succinates were evaporated to near dryness in a water bath, dried in air and kept in a desiccator over anhydrous calcium chloride. To avoid the oxidation of Fe(II), all the solutions, as well as in the evaporation of the solution in water bath were purged with nitrogen gas.

In the solid-state compounds, metal ions, hydration water and succinate contents were determined from TG curves. The metal ions were also determined by complexometry with standard EDTA solution, after igniting the compounds to the respective oxides and their dissolution in hydrochloric acid solution [8].

Carbon and hydrogen contents were determined by microanalytical procedures, with an EA 1110 CHNS-O Elemental Analyser from CE Instruments.

Simultaneous TG-DTA curves were obtained with the thermal analysis system, model SDT 2960 from TA Instruments. The purge gases were nitrogen and carbon dioxide flow of 100 mL min^{-1}. A heating rate of 20ºC min^{-1} was adopted, with sample weighing about 7 mg and alumina crucible was used for recording the TG-DTA curves.

The measurements of the gaseous products were carried out using a Thermogravimetric Analyzer Mettler TG-DTA coupled to a FTIR spectrophotometer Nicolet is10, with gas cell and DTGS KBr detector. The furnace and the heated gas cell (250ºC) were coupled through a heated (T = 200ºC) 120 cm stainless steel line transfer with diameter of 2 mm, both purged with dry nitrogen (50 mL min^{-1}). The FTIR spectra were recorded with 32 scans per spectrum at a resolution of 4 cm^{-1}.

Results and Discussion

Succinic acid

The TG-DTA curves and infrared spectrum of the released product during the heating of succinic acid in N$_2$ and CO$_2$ atmospheres are shown in Fig. 1. The TG-DTA curves, Fig 1a and 1b show mass loss in single step between 165 and 260ºC (N$_2$, CO$_2$) corresponding to the endothermic peaks at 194 and 247 ºC (N$_2$) or 194 and 250 ºC (CO$_2$), attributed to the fusion and evaporation of succinic acid, respectively. The product evaporated was monitored and identified mostly on base of their FTIR reference available on Nicolet libraries, as shown in Fig. 1c.
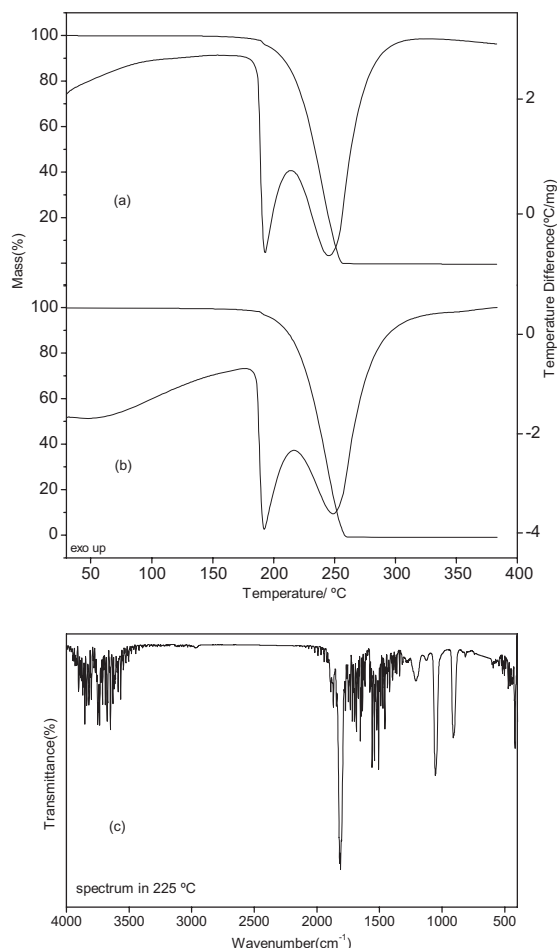
Figure 1. Simultaneous TG-DTA curves in dynamic (a) N$_2$ (m = 7.326 mg), (b) Co$_2$ (7.359 mg) atmospheres and (c) IR spectrum of the gases released during the decomposition of succinic acid in N$_2$ atmosphere.

Sodium Succinate hexahydrated

For the sodium succinate hexahydrated, the TG-DTA curves in N$_2$ and CO$_2$ atmospheres are shown in Fig. 2a and 2b, respectively. These curves show mass losses in two steps and thermal events corresponding to these losses or due to physical phenomenon. The first mass loss between 30 – 130ºC (N$_2$) and 30 – 150 ºC (CO$_2$), corresponding to an endothermic peak at 85 ºC (N$_2$, CO$_2$) is due to dehydration with loss of 6H2O (Calcd. 40.02 %, TG = 39.86 % (N$_2$), 40.20 %(CO$_2$)). The endothermic peak at 410 ºC (N$_2$, CO$_2$), without mass loss in TG curve is due to fusion of the compound. In
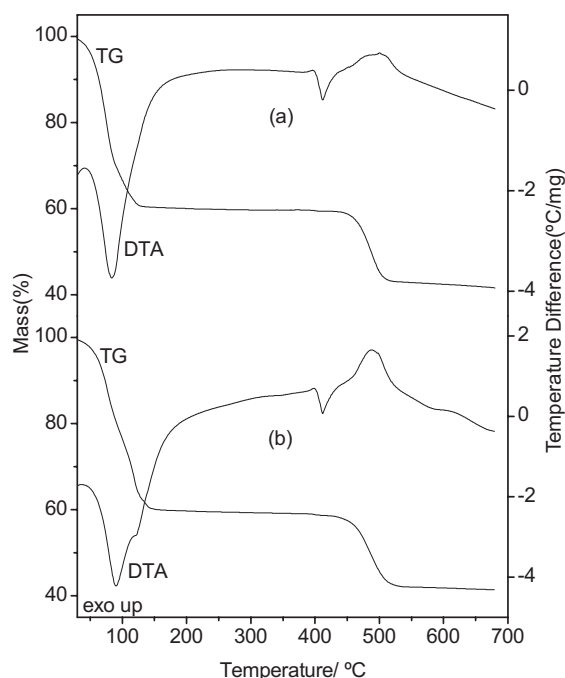
Figure 2. Simultaneous TG-DTA curves of the sodium succinate in (a) N_2 (3.726 mg) and (b) Co_2 (3.700 mg), atmospheres.

both atmospheres the anhydrous compound is stable up to 425ºC and above this temperature the mass loss occurs between 425 – 525 ºC (N_2) or 425 – 540 ºC (CO_2) with loss of 18.52 % (N_2) and 18.42 % (CO_2), corresponding to the exothermic peak at 490 ºC attributed to the decarboxylation with formation of sodium carbonate accompanied by carbonaceous residue.

Transition metal succinates

TG-DTA Curves

The analytical and thermoanalytical (TG) data for the synthesized compounds are shown in table 1. These results permitted to establish the stoichiometry of these compounds, which are in agreement with the general formula, $MC_4H_4O_4 \cdot nH_2O$, where M represents Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II), $C_4H_4O_4$ is succinate and n = O (Cu, Zn), 1 (Fe), 2 (Mn), 3 (Co) or 3.5 (Ni).

The simultaneous TG-DTA curves of these compounds obtained in N_2 and CO_2 atmospheres are shown in Fig. 3. These curves show mass losses or gain in two up to six steps, corresponding to endothermic peaks due to dehydration or pyrolysis of the anhydrous compounds and exothermic peaks attributed to physical phenomenon.

The thermal stability of the anhydrous compounds, in both atmospheres, as shown by the TG-DTA curves depend on the nature of the metal ion and they follow the order:

$$Zn > Co > Ni > Mn > Cu > Fe$$

For each compound a great similarity is observed concerning the TG-DTA profiles around 400ºC, in both atmospheres and above this temperature the thermal decomposition depend on the nature of the purge gas used and so the features of each of these compounds are discussed individually.

Manganese compound. The simultaneous TG-DTA curves in N_2 and CO_2 atmospheres are shown in Fig. 3a and 3a*, respectively. The first mass loss between 70 and 230 ºC, corresponding to an endothermic peak at 110 ºC in both atmospheres is due to the

Table 1. Analytical data for the $MC_4H_4O_4 \cdot nH_2O$ compounds.

Compound	Metal oxide (%)			L(lost) (%)		H_2O (%)		C (%)		H (%)		Final
	Calcd.	EDTA	TG*	Calcd.	TG*	Calcd.	TG*	Calcd.	E.A.	Calcd.	E.A.	Residue
MnL·2H$_2$O	36.84	36.86	36.81	45.75	45.59	17.41	17.60	23.20	23.48	3.90	3.71	Mn$_3$O$_4$
FeL·H$_2$O	42.04	41.91	41.73	48.47	48.97	9.49	9.30	25.29	25.56	3.19	3.10	Fe$_2$O$_3$
CoL·3H$_2$O	35.04	34.49	34.94	41.36	41.71	23.60	23.35	20.97	21.15	4.41	4.37	Co$_3$O$_4$
NiL·3H$_2$O	32.65	32.81	32.30	43.73	43.90	23.62	23.80	20.99	21.07	4.41	4.30	NiO
CuL	44.29	43.94	43.94	55.71	56.06	-	-	26.74	26.51	2.25	2.11	CuO
ZnL	44.84	45.13	44.65	55.16	55.35	-	-	26.48	26.67	2.23	2.35	ZnO

L=succinate
*TG = air atmosphere
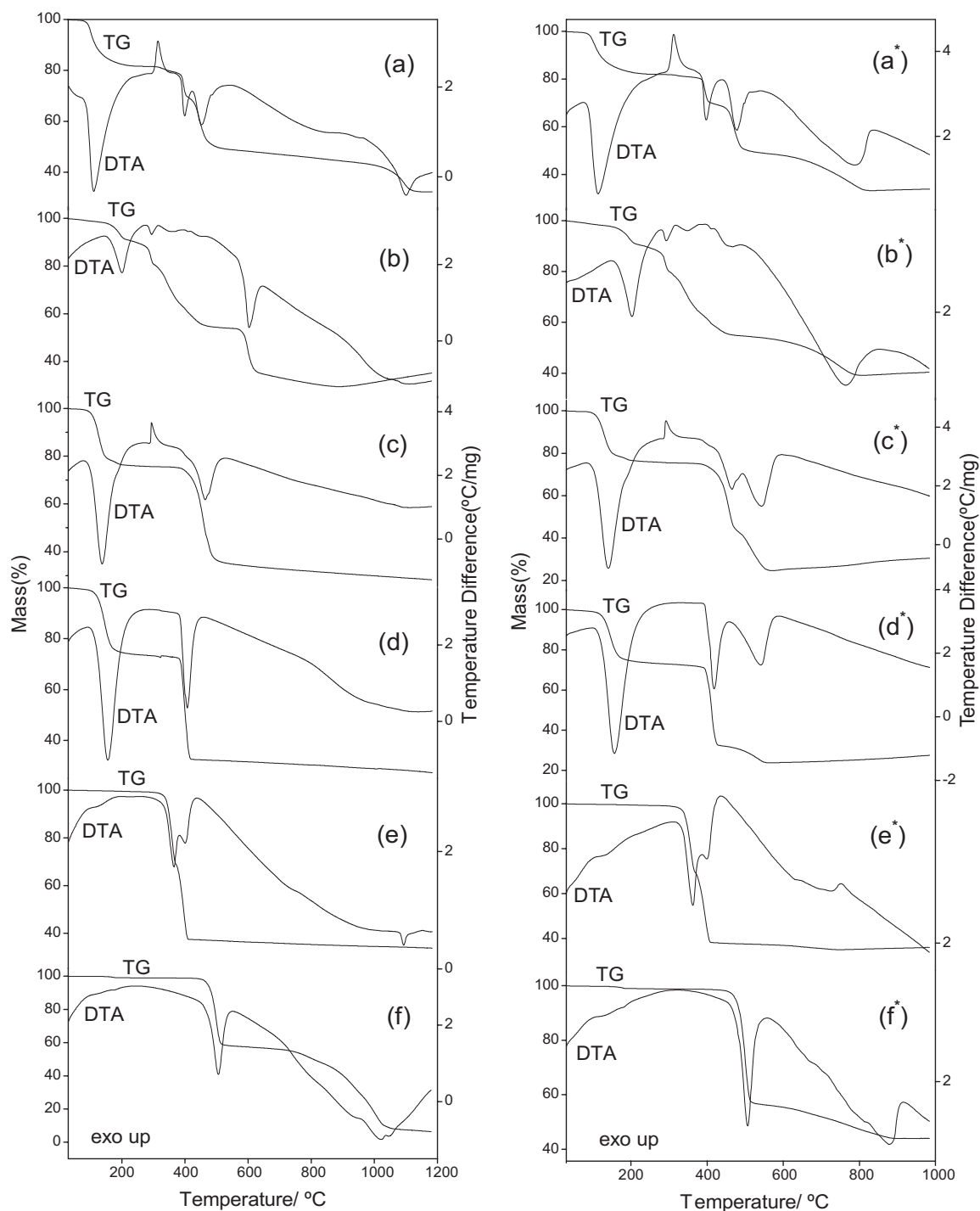
Figure 3. TG-DTA curves of the compounds in dynamic N_2 and CO_2* atmospheres: (a,a*) MnL.2H$_2$O (m = 7.174 mg; 7.044 mg *), (b,b*) FeL.1H$_2$O (m = 7.076 mg;7.030 mg*), (c,c*) CoL.3H$_2$O (m =7.066 mg; 7.135 mg*), (d,d*) NiL.3.5H2O (m = 7.155 mg; 7.076 mg*), (e,e*) CuL (m = 7.409 mg; 7.095 mg*) and (f,f*) ZnL (m = 7.261mg; 7.164 mg*). [L = succinate]

dehydration with loss of 2 H_2O (Calcd. 17.41 %, TG = 17.70 % (N2), 17.35 % (CO_2)). The exothermic peak at 315 ºC observed in both atmospheres is attributed to the crystallization process, as shown in Fig. 4.

The thermal decomposition of the anhydrous compound in N_2 atmospheres occurs in three steps between 320 – 410ºC, 410 – 510ºC and 510 – 1150ºC, with losses of 13.08% , 19.45 % and 17.50%, respectively, corresponding to the endothermic peaks at 400ºC, 455ºC and 1100ºC attributed to the thermal decomposition, with formation of a mixture of Mn and MnO in no simple stoichiometric relation.

For the CO_2 atmospheres, the thermal decomposition also occurs in three steps between 320 – 410ºC, 410 – 505ºC and 505 – 830ºC, with losses of 12.34%, 20.68% and 15.67%, corresponding to the endothermic peaks at 400ºC, 480ºC and 790ºC with formation of MnO as final residue (Calcd. = 65.74 %, TG = 66.04 %).

Iron Compound. The simultaneous TG-DTA curves in N_2 and CO_2 atmospheres are shown in Fig. 3b and 3b[*], respectively. The first mass loss between 70 – 215 ºC (N2) and 70 – 225 ºC (CO2), corresponding to the endothermic peak at 200 ºC (N_2) and 205 ºC (CO_2) is due to dehydration with loss of 1 H_2O (Calcd. = 9.49 %, TG = 9.24 % (N_2), 9.63 % (CO_2)).

The thermal decomposition of the anhydrous compound in N_2 atmosphere, occurs in four steps between 215 – 300 ºC, 300 – 480 ºC, 565 – 635 ºC and 635 – 900 ºC, corresponding to the endothermic peaks at 295 ºC and 605 ºC, with losses of 9.25 %, 26.78 %, 19.13 % and 6.06 %, respectively. Calculations based on the mass losses observed up to 900 ºC, are in agreement with the formation of Fe (Calcd. = 70.59 %, TG = 70.46 %). The mass gain (5.66 %) observed between 900 and 1180 ºC is attributed to the partial oxidation of Fe with formation a mixture of Fe and FeO. No thermal event is observed corresponding to the second and fourth mass losses, probably because endothermic and exothermic events must to occur simultaneously and the net heat or the small heat involved in these steps is insufficient to produce a thermal event.

For the CO_2 atmosphere, the thermal decomposition occurs in three steps between 225 – 300ºC, 300 – 480ºC and 500 – 800ºC, corresponding to the endothermic peaks at 295ºC, 355 ºC, 455ºC and 760ºC, with losses of 9.97 %, 25.78 % and 34.95 %, respectively. The mass losses up to 800 ºC, suggest the formation of a mixture of FeO and Fe_3O_4. The mass gain (1.12 %) observed between 800 and 980 ºC is attributed to the oxidation of FeO with the formation of Fe_3O_4, as final residue (Calcd. = 59.37 %, TG = 59.61 %).

Cobalt Conpound. The simultaneous TG-DTA curves in N_2 and CO_2 atmospheres are shown in Fig. 3c and 3c[*], respectively. The first mass loss between 70 and 200 ºC, corresponding to an endothermic peak at 140 ºC, in both atmospheres is due to dehydration with loss of 3 H_2O (Calcd. 23.60 %, TG = 23.45 % (N_2), 23.29 % (CO_2)). The exothermic peak at 290 ºC (N_2, CO_2) without mass loss in the TG curve is attributed to the irreversible solid phase transition, which was confirmed by X-ray powder, with sample before and after the exothermic peak.

The thermal decomposition of the anhydrous compound in N_2 occurs in two steps between 365 – 520 ºC, corresponding to the endothermic peak at 465 ºC and 520 – 1180 ºC, with losses of 41.40 % and 6.90 %, respectively. No thermal event corresponding to the second mass loss in observed in the DTA curve, probably because the small mass loss occurs so slowly that the heat involved in this step is not sufficient to produce a thermal event. Calculations based on the mass losses up to 510 ºC suggest the formation of Co_3O_4 (Calcd. = 64.69 %, TG = 64.32 %) and up to 1180 ºC a mixture of Co and CoO, in no simple stoichiometric relation.

For the CO_2 atmosphere the thermal decomposition occurs in two steps between 375 – 480 ºC and 480 – 575 ºC, corresponding to the endothermic peaks at 470 ºC and 545 ºC, with losses of 32.91 % and 19.17 %, respectively. The total mass loss up to 575 ºC is in agreement with the formation of Co as final residue (Calcd. = 74.27 %, TG = 74.57 %). The mass gain (5.07 %) observed between 575 – 980 ºC is attributed to the partial oxidation of Co with the formation of a mixture of Co and CoO.

Nickel Compound. The simultaneous TG-DTA curves in N_2 and CO_2 atmospheres are shown in Fig. 3d and 3d[*], respectively. The first mass loss between 70 – 250 ºC, corresponding to an endothermic peak at 155 ºC in both atmospheres is attributed to the dehydration with loss of 3.5 H_2O (Calcd. = 26.51 %, TG = 26.77 % (N_2), 26.76 % (CO_2)). The thermal decomposition of the anhydrous compound occurs in two steps between 360 – 430 ºC (N_2, CO_2) and 430 – 1180 ºC (N_2) or 430 – 560 ºC (CO_2), corresponding to endothermic peaks at 405 ºC (N_2) or 415 ºC and 540 ºC (CO_2), with losses of 41.40% and 6.90 % (N_2) or 40.80 % and 8.66 %, respectively. The total mass losses up to 1180 ºC (N_2) suggest the formation of a mixture of Ni and NiO and up to 560 ºC (CO_2) is in agreement with Ni (Calcd. = 75.32 %, TG = 75.22 %). The mass gain (2.72%) observed between 560 – 980 ºC (CO_2) is attributed to the partial oxidation of Ni to a mixture of Ni and NiO.

Copper Compound. The simultaneous TG-DTA curves in N_2 and CO_2 atmospheres are shown in Fig. 3e and 3e[*], respectively. These curves show that the anhydrous compound is stable up to 305 ºC, in both atmospheres and above this temperature the thermal decomposition occurs in three steps. These curves also show that the first two steps occur through fast processes and overlapping one between 305 – 375 ºC and 375 – 420 ºC, corresponding to the endothermic peaks at 365 ºC and 400 ºC (N_2, CO_2) with losses of 27.77 % and 31.80 % (N_2) or 30.60 % and 30.79 % (CO_2). Calculations based on the mass losses up to 420 ºC suggest the formation a mixture of Cu and CuO. The last step that occurs through a slow process between 420 – 1000 ºC (N_2) or 420 – 750 ºC (CO_2) with losses of 0.7 % and 3.15 %, respectively, is attributed to the reduction of the mixture (Cu, CuO) to Cu, as final residue (Calcd. = 64.22 %, TG = 64.48 % (N_2), 64.54 % (CO_2). The endothermic peak at 1090 ºC (N_2) is due to the fusion of Cu.

Zinc Compound. The simultaneous TG-DTA curves in N_2 and CO_2 atmospheres are shown in Fig. 3f and 3f[*], respectively. These curves show that the anhydrous compound is stable up to 430ºC and above this temperature the thermal decomposition occurs in two steps between 430 – 535 ºC and 535 - > 1080ºC (N_2) or 430 – 525ºC and 525 – 885 (CO_2), corresponding to the endothermic peaks at 505ºC, 1020ºC and 1050ºC (N2) or 505ºC and 885ºC (CO_2), with losses of 40.10 % and 51.95% (N_2) or 41.88 % and 13.08 % (CO_2).

For the CO_2 atmospheres the mass lost up to 885 ºC is in agreement with the formation of ZnO as final residue (Calcd. = 55.16 %, TG = 54.95 %). For the N_2 atmospheres in the last step occurs the reduction of Zn(II) to Zn followed by ebullition (boiling point = 907 ºC). The final residue (7.95 %) up to 1080 ºC is attributed to the carbonaceous residue, which was confirmed after to analysis the crucible residue.

The mass gain attributed to the oxidation reaction of Fe to FeO in N_2 atmosphere or Co to CoO and Ni to NiO in CO_2 atmosphere occurs, probably because the equipment is not hermetically sealed and/or a trace of oxygen in the N_2 or CO_2 which were used as purge gas.

Evolved gas analysis

The gaseous products evolved during the thermal decomposition in dynamic nitrogen atmosphere of the sodium and transition metal ion compounds studied in this work were monitored by FTIR and identified on basis of their FTIR references available on Nicolet libraries. For the sodium succinate the gaseous products evolved during a thermal decomposition were identified as methane, acetone, CO, and
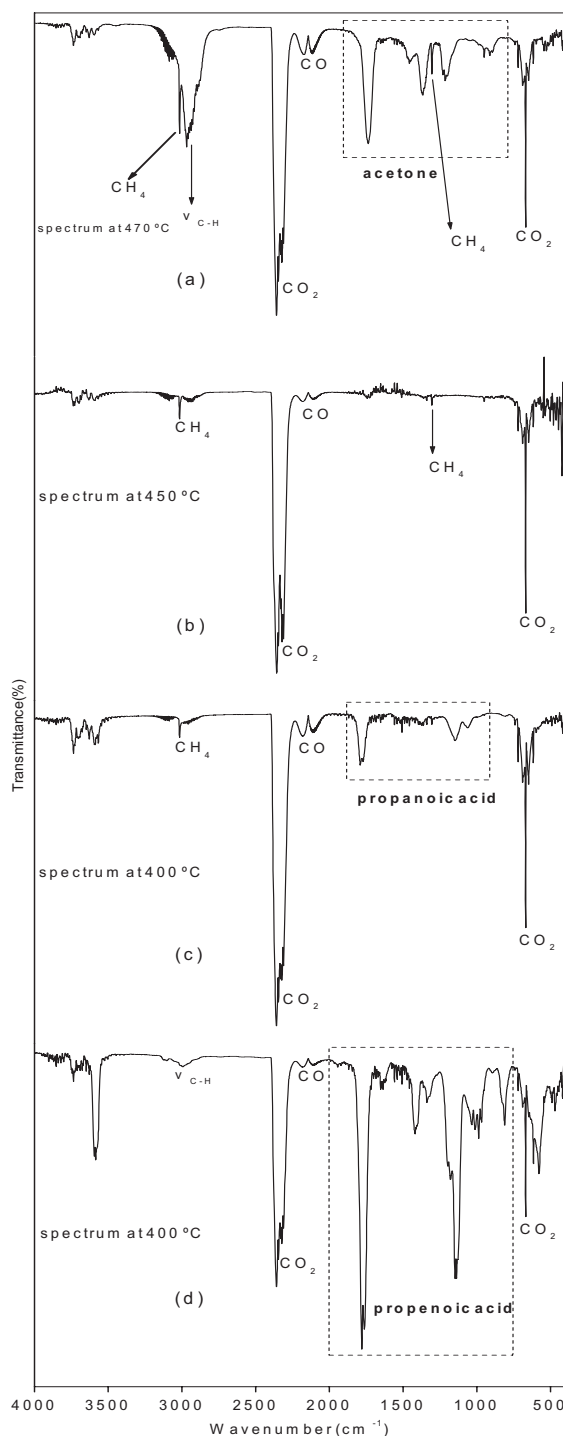
Figure 4. IR spectra of gaseous products evolved during the decomposition of the compounds in nitrogen atmosphere: (a) NaL.6H$_2$O, (b) MnL.2H$_2$O, (c) NiL.3.5H$_2$O and (d) CuL. [L = succinate]

CO_2; for the cobalt and nickel compounds were methane, propanoic acid, CO, and CO_2; for the copper compound were propenoic acid, CO, and CO_2 and for the manganese, iron, and zinc compounds were methane, CO and CO_2. The IR spectra of the gaseous products evolved during the thermal decomposition of sodium, manganese, nickel and copper as representative of other compounds, are shown in Fig. 4.

Conclusion

The present study showed that the succinic

acid melt and evaporate, without decomposition.

In the sodium and all the synthesized compounds, the evolved products during the thermal decomposition in nitrogen atmosphere was CO and CO_2, besides methane and acetone for sodium succinate, propanoic acid for cobalt and nickel compounds and propenoic acid for nickel compound.

Resumo: A estabilidade e a decomposição térmica do ácido succínico, succinatos de sódio, Mn(II), Fe(II), Co(II), Ni(II), Cu(II) e Zn(II) foram investigados empregando termogravimetria e análise térmica diferencial simultânea (TG-DTA) em atmosferas de nitrogênio e dióxido de carbono e TGFTIR em atmosfera de nitrogênio. Sobre aquecimento em ambas as atmosferas o ácido succínico funde e evapora, enquanto para o succinato de sódio a decomposição térmica ocorre com a formação de carbonato de sódio. Para os succinatos de metais de transição o resíduo final até 1180 ºC em atmosfera de N_2 foi uma mistura de metal e óxido de metal sem relação estequiométrica, exceto para o composto de zinco, onde o resíduo foi uma pequena quantidade de resíduo de carbono. Para a atmosfera de CO_2 o resíduo final até 980 ºC foi: MnO, Fe_3O_4, CoO, ZnO e misturas de Ni, NiO e Cu, Cu_2O.

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