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THERMAL DECOMPOSITION OF Co(II), Cu(II) AND Zn(II) METHANESULFONATES

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ABSTRACT

The thermal decomposition of Co(II), Cu(II) and Zn(II) tetrahydrated methanesulfonates has been studied in air, under vacuum and in N_2 flow. Dehydration enthalpies were measured from the DSC curves, and degradation products of anhydrate salts were identified by X-ray diffraction.

INTRODUCTION

Metallic salts of sulfonic acids are not well characterized. Although, recently they have been studied from the structural point of view, e.g. IR spectroscopy, crystal structure determination etc., there are few works on their thermal behavior, such as those from Charbonnier concerning alkaline [1] and calcium [2] alkanesulfonates and those from Meiser et al. [3] on transition metals benzenesulfonates.

Recently we have initiated a study of different metallic sulfonates. In this work the first results with Cu, Co and Zn methanesulfonates are presented. Throughout this paper the methanesulfonic group CH_3–SO_3– is represented as MS.

EXPERIMENTAL

The synthesis was effected in aqueous solution by the reaction between methanesulfonic acid and metallic basic carbonates. The solutions obtained

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were concentrated, filtered and allowed to crystallize in air at room temperature. The products were purified by successive recrystallizations.

Chemical analyses were carried out by EDTA complexometry, employing NET (for Zn) and murexide (for Co and Cu) as indicators. The anion determination was performed with acid cationic exchange resins, and titration of the eluted acid with NaOH.

X-ray diffraction was performed by the powder method in a Siemens K-810 diffractometer with a D-500 goniometer using Cu K_α radiation. Experiments were carried out under vacuum in an Anton Paar HTK10 high-temperature camera, with a Ta filament, attached to a Philips PW1310 diffractometer. Temperature measurements were made with a Pt–(Pt 13% Rh) thermocouple.

TG and DTA experiments were done in a Stanton 781 system, with a heating rate of 10 °C min^{-1} under air flow (50 ml min^{-1}) and N_2 flow (50 ml min^{-1}). Some experiments were performed in a Du Pont 951 thermobalance attached to a Du Pont 990 unit. DSC studies were carried out in a Perkin–Elmer DSC-2C, with a 3600 Perkin–Elmer data station at a heating rate of 5 °C min^{-1}.

RESULTS AND DISCUSSION

Decomposition in air

TG and DTA curves between 25 and 900 °C are presented in Figs. 1–3. Two major processes can be clearly identified: dehydration and anion decomposition.

Dehydration

In TG curves for Co (Fig. 2) and Zn (Fig. 3) two successive steps can be seen, each corresponding to the elimination of two water molecules. How-

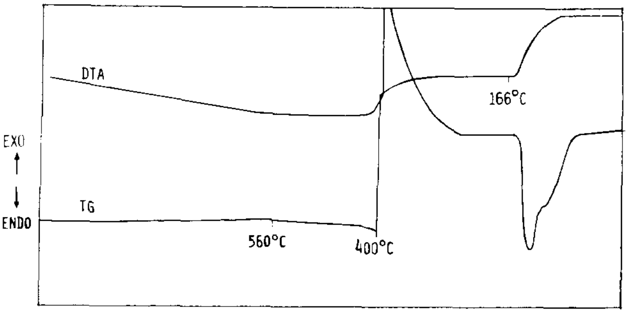

Fig. 1. TG and DTA curves for $Cu(MS)_2 \cdot 4H_2O$ in air flow.

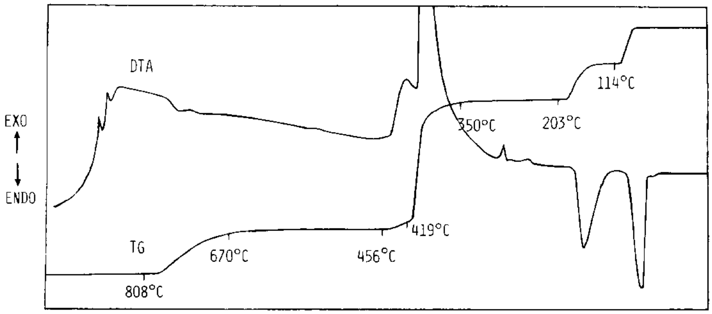

Fig. 2. TG and DTA curves for $Co(MS)_2 \cdot 4H_2O$ in air flow.

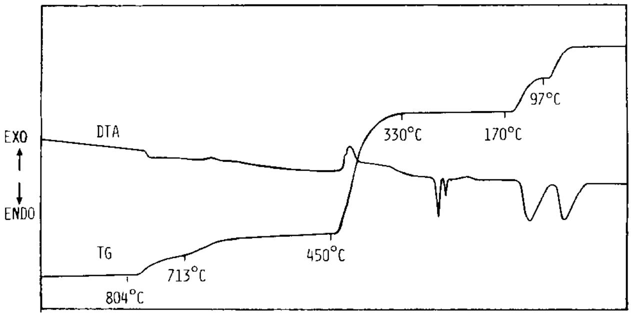

Fig. 3. TG and DTA curves for $Zn(MS)_2 \cdot 4H_2O$ in air flow.

TABLE 1

	First dehydration	*Second dehydration*
Co	$\Delta m_{exp} = 11.53\%$	$\Delta m_{exp} = 11.12\%$
	$\Delta m_{calc} = 11.22\%$	$\Delta m_{calc} = 11.22\%$
	$\Delta Q = 61.64$ kJ (mol $H_2O)^{-1}$	$\Delta Q = 85.45$ kJ (mol $H_2O)^{-1}$
	$\Delta T = 75.5$–114.54 °C	$\Delta T = 127.4$–203.42 °C
Zn	$\Delta m_{exp} = 10.64\%$	$\Delta m_{exp} = 10.90\%$
	$\Delta m_{calc} = 11.00\%$	$\Delta m_{calc} = 11.00\%$
	$\Delta Q = 55.73$ kJ (mol $H_2O)^{-1}$	$\Delta Q = 80.33$ kJ (mol $H_2O)^{-1}$
	$\Delta T = 45.33$–97.2 °C	$\Delta T = 100$–170.66 °C
	Global process	
Cu	$\Delta m_{exp} = 22.03\%$	
	$\Delta m_{calc} = 22.11\%$	
	$\Delta Q = 77.5$ kJ (mol $H_2O)^{-1}$	
	$\Delta T = 67.5$–166 °C	

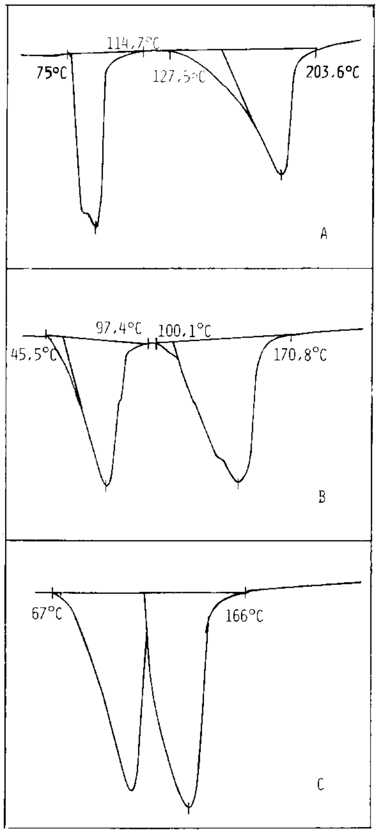

Fig. 4. DSC curves for (A) $Co(MS)_2 \cdot 4H_2O$; (B) $Zn(MS)_2 \cdot 4H_2O$; (C) $Cu(MS)_2 \cdot 4H_2O$.

ever, the copper salt shows a single step with a slight inflexion, corresponding to the loss of the four water molecules (Fig. 1). Therefore, H_2O is eliminated in two phases which, in the Cu salt, are practically overlapped. In Table 1 weight losses, experimental and calculated, and the temperature intervals are presented.

DTA curves show two endothermic effects which are also overlapped in the copper salt.

Figure 4 shows the DSC curves obtained for the three compounds in the temperature range corresponding to water elimination. Enthalpies calculated by integration are shown in Table 1. (For the copper salt, the value corresponds to the complete dehydration, due to the overlap of both peaks.)

Anhydrous salts obtained are pale blue (Cu), violet (Co) and white (Zn). Rehydration in air led to the original tetrahydrated compounds, as can be confirmed by X-ray diffraction.

TG curves show no decomposition up to 350 °C. Nevertheless, DTA of the cobalt salt shows several simultaneous processes, with an exothermic global effect, between 243 and 290 ° C. In DTA of the Zn salt two endothermic transformations, centered at 270 and 280 ° C, are observed.

Anion decomposition

For the copper salt (Fig. 1), anion decomposition that suddenly stops at 410 ° C is followed by a slight weight increase up to 560 ° C, which results from an oxidation process. At this temperature the solid is a mixture of $CuSO_4$ (ASTM: 15-775) and CuO (ASTM: 5-0661), resulting from the oxidation of Cu_2O (ASTM: 5-0667) whose formation has been detected in parallel thermal static treatments. $CuSO_4$ starts to decompose at 675 ° C, leading to CuO as the unique solid residue.

These anion degradation reactions could be formulated as

$$\mathrm{Cu(MS)_2} \xrightarrow{320\text{–}410\,^\circ\mathrm{C}} x\mathrm{Cu_2O} + y\mathrm{CuSO_4} \xrightarrow{440\text{–}560\,^\circ\mathrm{C}} 2x\mathrm{CuO}$$

$$+ y\mathrm{CuSO_4} \xrightarrow{675\,^\circ\mathrm{C}} \mathrm{CuO}$$

(weight loss calculated; 68.62%; experimental, 68.5%).

Cobalt salt decomposition starts at 350 ° C and finishes at 455 ° C, leading to a mixture of α-$CoSO_4$ (ASTM: 11-125), CoO (ASTM: 9-402) and Co_3O_4 (ASTM: 9-418) (Fig. 2).

Between 670 and 800 ° C, $CoSO_4$ decomposes and, finally, the residue obtained was identified as Co_3O_4. Thus, the decomposition reaction can be formulated

$$3\mathrm{Co(MS)_2} \xrightarrow{350\text{–}455\,^\circ\mathrm{C}} x\mathrm{CoSO_4} + y\mathrm{CoO} + z\mathrm{Co_3O_4} \xrightarrow{670\text{–}800\,^\circ\mathrm{C}} \mathrm{Co_3O_4}$$

(weight loss calculated; 67.75%; experimental, 66.4%).

Decomposition of the Zn compound takes place between 330 and 450 ° C; it leads to a mixture of $ZnSO_4$ (ASTM: 8-491) and $Zn_3O(SO_4)_2$ (ASTM: 32-1475), that was stable up to 623° C. At this temperature, $ZnSO_4$ decomposes to the oxosulfate, that gives ZnO (ASTM: 5-664) at 713° C, according to the reaction

$$3\mathrm{Zn(MS)_2} \xrightarrow{330\text{–}450\,^\circ\mathrm{C}} x\mathrm{ZnSO_4} + y\mathrm{Zn_3O(SO_4)_2} \xrightarrow{623\text{–}650\,^\circ\mathrm{C}} \mathrm{Zn_3O(SO_4)_2}$$

$$\xrightarrow{713\,^\circ\mathrm{C}} 3\mathrm{ZnO}$$

(weight loss calculated; 68.13%; experimental 68.2%).

In all cases DTA shows anion decomposition accompanied by exothermic effects. For the Zn compound the magnitude of exothermic effects is smaller, probably because of the oxosulfate formation that implies a lower stabilization of the system.

Decomposition in vacuo

In order to identify the intermediate compounds during thermal decomposition, experiments have been performed in a high-temperature X-ray diffraction camera. In the experimental conditions (4.5×10^{-3} mmHg), no significant differences in the thermal dehydration of these compounds have been observed, with respect to the experiments carried out in air flow.

For copper methanesulfonate both dehydrated and anhydrous salts are microcrystalline. Zinc salts are also crystalline, but $Zn(MS)_2$ becomes amorphous to X-ray diffraction analysis, without weight loss, on heating, probably due to melting, as can be observed in the DTA curve (endothermic effects centered at 270 and 280 ° C). Cobalt salts are amorphous to X-ray analysis, although $Co(MS)_2$ crystallizes when heating. This fact could explain the exothermic peaks observed in DTA between 243 and 290 ° C (Fig. 2).

In these conditions, the anion decomposition takes place in a different manner than that observed in air: $Cu(MS)_2$ decomposes at 550 ° C, leading to CuO. Degradation of $Co(MS)_2$ also takes place at lower temperatures, about 550 ° C, and the residue, identified by X-ray diffraction, was Co_9S_8 (ASTM: 19-364). When the temperature rises, Co (ASTM: 5-0727) appears. Thus, at 900 ° C, the final product of decomposition was Co with traces of Co_9S_8.

Zn salt decomposes at lower temperatures. The process begins slowly at 350 ° C and speeds up at 430 ° C, leading to a mixture of $Zn_3O(SO_4)_2$ and two different forms of ZnS (ASTM: 12-688 and 10-434). Between 630 and 700 ° C the oxosulfate gives ZnO, leaving the mixture of oxide and sulfides unchanged up to 950 ° C. These reactions could be formulated as

(a) $Cu(MS)_2 \xrightarrow{550\,^\circ C} CuO$

(weight loss calculated: 68.62%; experimental, 68.5%).

(b) $Co(MS)_2(\text{amorph.}) \xrightarrow{243\text{–}290\,^\circ C} Co(MS)_2(\text{cryst.})$

$\xrightarrow{500\,^\circ C} Co_9S_8 \xrightarrow{500\text{–}900\,^\circ C} Co$

($Co(MS)_2$ to Co_9S_8, weight loss calculated, 64.90%; experimental, 63.6%).

(c) $Zn(MS)_2(s) \xrightarrow{280\,^\circ C} Zn(MS)_2(l) \xrightarrow{350\text{–}430\,^\circ C} Zn_3O(SO_4)_2$

$+ ZnS \xrightarrow{630\text{–}700\,^\circ C} ZnO + ZnS$

(weight loss calculated, 66.56%; experimental, 65.1%).

Decomposition in N_2 flow

Figures 5–7 show the TG and DTA curves obtained under N_2 flow. Zinc and cobalt hydrated methanesulfonates exhibit similar behavior to that observed under vacuum, but the copper salt degradation occurs in a completely different way: $Cu(MS)_2$ decomposes between 360 and 400 ° C yielding metallic copper (weight loss calculated, 64.90%; experimental, 63.6%).

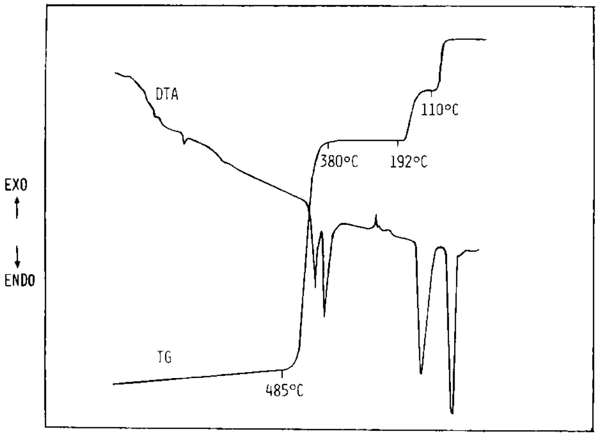

Fig. 5. TG and DTA curves for $Co(MS)_2 \cdot 4H_2O$ in N_2 flow.

The lowered decomposition temperatures for Cu and Co anhydrate salts under N_2 flow, offer us the possibility to record the melting of these compounds. Thus, the DTA curve for $Co(MS)_2$ shows a characteristic endotherm at 370 °C before the anion decomposition. In a similar way, the melting of $Cu(MS)_2$ is registered in DTA at 340 °C (Fig. 7).

The melting temperatures (280 °C for $Zn(MS)_2$, 340 °C for $Cu(MS)_2$ and 370 °C for $Co(MS)_2$) are in the same sequence as those registered for other salts of these cations, as chlorides or bromides [5].

As can be seen in the DTA curves, the anion degradation in the N_2 atmosphere shows, in the three cases, an endothermic effect, while in air, it is exothermic due to the oxidation reactions. The different behavior ob-

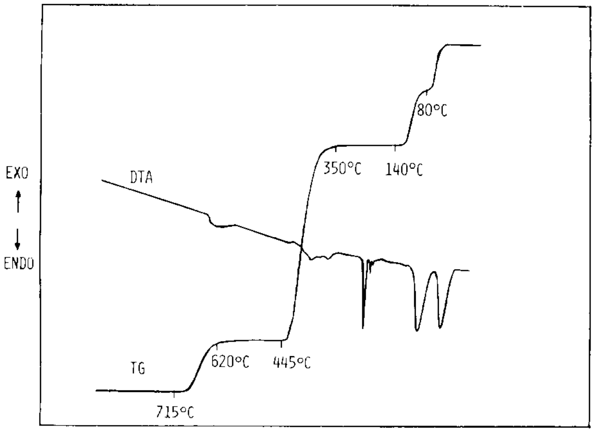

Fig. 6. TG and DTA curves for $Zn(MS)_2 \cdot 4H_2O$ in N_2 flow.

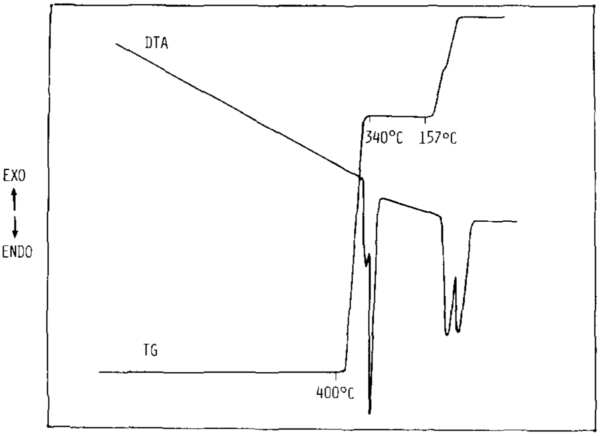

Fig. 7. TG and DTA curves for $Cu(MS)_2 \cdot 4H_2O$ in N_2 flow.

served for the Zn salt can be attributed to oxosulfate intermediate formation.

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