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THERMAL BEHAVIOR OF SOME COMPOUNDS OF METHANESULFONIC ACID WITH TRANSITION METALS

F. CHARBONNIER *

Laboratoire de Synthèse Minérale, Université Claude Bernard (Lyon I), 69621-Villeurbanne (France)

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ABSTRACT

The following compounds of methanesulfonic acid, CH_3SO_3H, have been prepared: $Cu(CH_3SO_3)_2 \cdot 4\ H_2O$; $Zn(CH_3SO_3)_2 \cdot 4\ H_2O$; $Mn(CH_3SO_3)_2 \cdot 2\ H_2O$; $Cd(CH_3SO_3)_2 \cdot 2\ H_2O$ and $Ag(CH_3SO_3)$. Their thermal behavior has been studied using TG and DTA, together with X-ray analysis of the solid products formed during the heating. The water of hydration is evolved in one step (Mn, Cd) or in two step (Cu, Zn). The intermediate hydrates and the anhydrous salts are crystallized. The anhydrous Zn, Ag and Cd compounds melt, the anhydrous Cd salt undergoing a polymorphic transition before melting. They then begin to decompose in the temperature range 325—440°C. Under an inert atmosphere, the decomposition yields well-crystallized residues of various composition: Cu + Cu_2S; Ag + Ag_2S (the sulfides being in very minute amounts); MnS; CdS; ZnO + ZnS.

INTRODUCTION

The alkanesulfonic acids, of general formula RSO_3H ($R = C_nH_{2n+1}$), are strong organic acids, which form well-defined compounds with inorganic and organic bases [1]. Many of them have considerable commercial importance as detergents in the form of their sodium salts. A bibliographic study showed that the physico-chemical properties of most of the metallic alkanesulfonates were unknown; particularly no investigations have been made pertaining to their thermal stability. A number of our works on the sulfonates of lithium, sodium, potassium [2], calcium [3] and cobalt [4] have been previously published.

Accordingly, the aim of this paper is to study and compare the thermal behavior of the Mn(II), Cu(II), Zn(II), Ag(I) and Cd(II) methanesulfonates as determined by TG and DTA; interest has mainly centered on the nature of the solid products formed under heating. X-ray diffraction was therefore used in order to detect and characterize the encountered phases in the course and at the end of the TG and DTA experiments.

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* Present address: Laboratoire de Chimie Analytique 2, Université Claude Bernard (Lyon I), 69621-Villeurbanne, France.

EXPERIMENTAL

Preparation and characterization of compounds

The methanesulfonic acid used was a Merck product of highest purity. The other chemicals employed were all of reagent grade quality.

The Mn(II), Zn(II), Cu(II) and Cd(II) methanesulfonates were obtained from metathesis of barium methanesulfonate and corresponding sulfate solutions. The Ag salt was obtained by the action of methanesulfonic acid on Ag_2O carefully prepared in the laboratory.

The compounds were analyzed for sulfur content by a gravimetric method previously described [4] and for metal content (except Ag) by a volumetric method (EDTA titration). The Ag content was determined by gravimetric analysis (AgCl). Drying in an oven and thermogravimetry were used to determine water of hydration.

Analytical results, given in Table 1, point to the following formulae for the isolated compounds: $Mn(CH_3SO_3)_2 \cdot 2\,H_2O$; $Cu(CH_3SO_3)_2 \cdot 4\,H_2O$; $Zn(CH_3SO_3)_2 \cdot 4\,H_2O$; $Cd(CH_3SO_3)_2 \cdot 2\,H_2O$ and $Ag(CH_3SO_3)$. These hydrates are new; for the Cu compound, the literature gives a pentahydrate [5,6].

Apparatus

Thermogravimetry. An Adamel-Chevenard thermobalance with graphical recording was used. A Pt—PtRh 10% thermocouple placed under the sample holder was employed. The mass of samples was 150 mg and the heating rate 2 or 5°C min^{-1}. The controlled atmosphere consisted of dry deoxygenated nitrogen ("U" from l'Air Liquide) passing over the sample at the rate of 30 ml min^{-1}.

Differential thermal analysis. A differential thermal microanalyzer "Bureau de Liaison-Setaram" with hollow thermocouples and open crucibles was employed. The curves $\Delta T = f(T)$ were plotted on a Sefram recorder of the X—Y Luxytrace type after amplification of the differential temperatures by an

TABLE 1

Results of the chemical analysis

Compound	Wt. % obtained by analysis			Theoretical wt. % for given formula		
	M	S	H_2O	M	S	H_2O
$Mn(CH_3SO_3)_2 \cdot 2\,H_2O$	19.46	22.70	12.9	19.53	22.83	12.83
$Cu(CH_3SO_3)_2 \cdot 4\,H_2O$	19.47	19.51	22.0	19.50	19.69	22.11
$Zn(CH_3SO_3)_2 \cdot 4\,H_2O$	20.11	19.44	21.9	19.96	19.57	22.00
$Ag(CH_3SO_3)$	52.96	15.61	0	53.14	15.79	0
$Cd(CH_3SO_3)_2 \cdot 2\,H_2O$	33.21	18.80	10.6	33.19	18.94	10.64

Amplispot Agt Sefram (10 μV cm^{-1}, i.e. 0.25°C cm^{-1}).

After grinding in a mortar and pestle, no more than 5 mg of sample were used in each run. The controlled atmosphere was as in the TG study. A heating rate of 2 or 5°C min^{-1} was employed. No reference material was necessary.

X-ray analysis

The X-ray patterns were obtained from powdered samples with filtered CuK_α radiation. Apparatus and techniques employed for determining space groups were previously described [7].

RESULTS AND DISCUSSION

Crystallographical study

Table 2 summarizes the crystal data of the studied compounds. Further details may be obtained by consulting the papers reported in ref. 7.

Thermal behavior

In Table 3 are collected the results of the thermal studies. In all cases, the shape of the TG curves clearly shows that the compounds undertake two separate mass losses corresponding with first the dehydration, then the decomposition; the DTA curves reveal transition or melting points for some compounds. Figures 1 and 2 present, respectively, the TG curves for Mn and Cu compounds and the DTA curves for Cd and Ag compounds, given as examples.

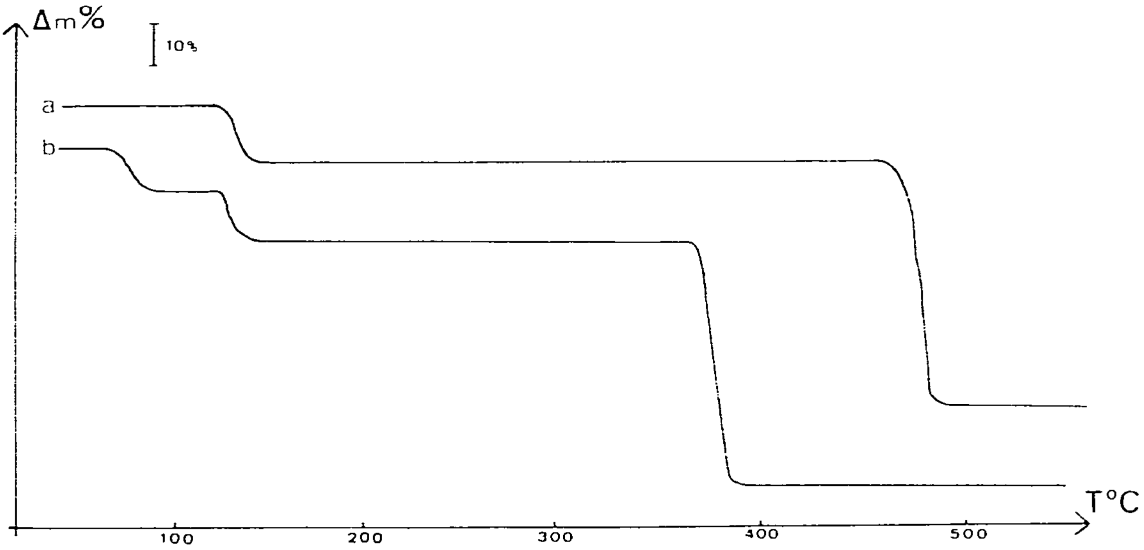

Fig. 1. TG curves of (a) $Mn(CH_3SO_3)_2 \cdot 2\,H_2O$ and (b) $Cu(CH_3SO_3)_2 \cdot 4\,H_2O$ (dry dynamic nitrogen atmosphere; 5°C min^{-1}).

TABLE 2

Results of the crystallographical study

Z is the number of "molecules" per unit cell, ρ_m and ρ_x are the measured and calculated densities, respectively.

Compound	Space group	a (Å)	b (Å)	c (Å)	α	β	γ	Z	ρ_m (g cm^{-3})	ρ_x (g cm^{-3})
$Mn(CH_3SO_3)_2 \cdot 2\ H_2O$	1 or $\bar{1}$	5.146 ± 0.008	5.675 ± 0.012	9.20 ± 0.03	114°83 ± 0.18	103°21 ± 0.20	90°93 ± 0.20	1	2.00	1.98
$Cu(CH_3SO_3)_2 \cdot 4\ H_2O$	$P\ 2_1/c$	9.32 ± 0.02	9.636 ± 0.005	7.31 ± 0.01	90°	122°2 ± 0.1	90°	2	1.93	1.95
$Zn(CH_3SO_3)_2 \cdot 4\ H_2O$	$P\ 2_1/c$	9.47 ± 0.02	9.907 ± 0.007	7.21 ± 0.02	90°	124°6 ± 0.1	90°	2	1.91	1.95
$Ag(CH_3SO_3)$	$P\ 2_1/c$	8.70 ± 0.01	5.772 ± 0.004	8.260 ± 0.006	90°	100°2 ± 0.1	90°	4	3.32	3.30
$Cd(CH_3SO_3)_2 \cdot 2\ H_2O$	1 or $\bar{1}$	4.773 ± 0.003	6.08 ± 0.01	9.965 ± 0.019	124°63 ± 0.12	91°94 ± 0.12	94°34 ± 0.12	1	2.31	2.38

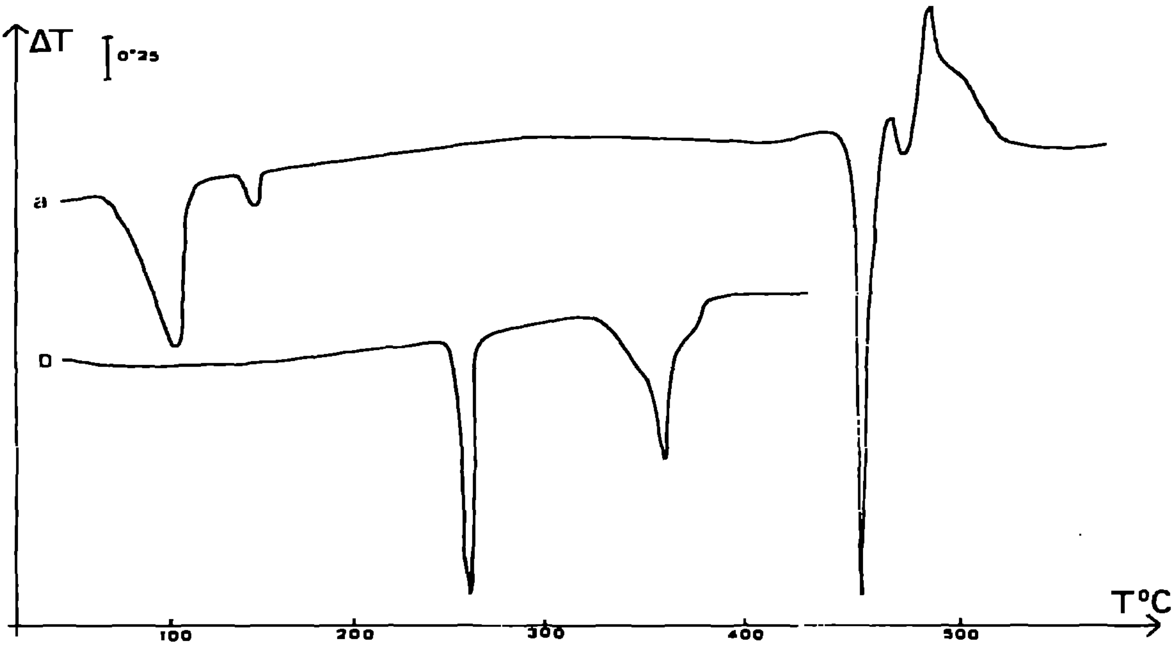

Fig. 2. DTA curves of (a) $Cd(CH_3SO_3)_2 \cdot 2\ H_2O$ and (b) $Ag(CH_3SO_3)$ (dry dynamic nitrogen atmosphere; 5°C min^{-1}).

TABLE 3

Results concerned with the thermal behaviour of the methanesulfonates from TG and DTA curves

Heating rate = 5°C min^{-1}, under nitrogen atmosphere

Compound	Dehydration (°C)	Start of the decomposition (°C)	Other observations
$Mn(CH_3SO_3)_2 \cdot 2\ H_2O$ (see Fig. 1)	124—161 (2 → 0)	462	No melting before decomposition
$Cu(CH_3SO_3)_2 \cdot 4\ H_2O$ (see Fig. 1)	68— 97 (4 → 2) 121—136 (2 → 0)	370	No melting before decomposition
$Zn(CH_3SO_3)_2 \cdot 4\ H_2O$	50— 84 (4 → 2) 122—151 (2 → 0)	340	Simultaneous melting and decomposition
$Ag(CH_3SO_3)$ (see Fig. 2)		325	Melting at 259°C
$Cd(CH_3SO_3)_2 \cdot 2\ H_2O$ (see Fig. 2)	63—110 (2 → 0)	440	Polymorphic transformation at 146°C; simultaneous melting and decomposition

The TG curves show an initial mass loss corresponding to the dehydration in one or two stages (see Table 3), first a plateau, the length of which indicates the stability range of the anhydrous compound, then they slope sharply during the decomposition (which occurs in a temperature range of 10—20°C) to lead to a second plateau, heating being stopped at 500°C.

On the DTA curves, the loss of water of crystallization results in one or two irreversible endotherms, in agreement with the TG results. The melting or transition points are evidenced by characteristic endotherms, reversible to cooling and the decomposition corresponds with the final endotherm. In the case of the Cd compound, the last endotherm is immediately followed by an exotherm, the significance of which will be explained in the course of the discussion.

For all the metals, the hydrated and anhydrous salts are well-crystallized, their X-ray patterns differing. As an example, Table 4 lists the first 20 diffraction lines for the different Cu methanesulfonates isolated. The residual solid products are also well-crystallized and their composition depends on the nature of the metal.

In the case of the Mn and Cd methanesulfonates, the residues are only the sulfides MnS or CdS.

The Cu and Ag methanesulfonates decompose to Cu_2S + Cu and Ag_2S + Ag mixtures, respectively. The sulfides are in very minute amounts; their

TABLE 4

Diffraction lines of copper methanesulfonates

Tetrahydrate		Dihydrate		Anhydrous	
d (Å)	*I* [a]	*d* (Å)	*I* [a]	*d* (Å)	*I* [a]
7.86	vs	8.48	vs	9.28	vs
6.09	w	7.94	w	7.07	s
5.852	w	5.639	m	6.31	w
5.202	w	4.896	vs	4.828	m
4.802	vs	4.657	w	4.676	w
4.153	vs	4.409	m	4.148	m
4.106	m	4.206	w	4.011	s
3.940	m	3.760	m	3.360	s
3.794	w	3.636	s	3.273	m
3.654	vs	3.536	m	3.159	m
3.598	vs	3.450	s	3.001	vs
3.376	w	3.345	vs	2.724	m
3.336	w	3.236	m	2.624	w
3.091	s	3.124	s	2.438	w
3.045	w	2.864	s	2.189	m
2.936	m	2.816	m	2.075	w
2.919	m	2.594	m	2.004	m
2.886	s	2.476	s	1.916	w
2.849	m	2.368	m	1.855	w
2.637	s	2.295	s	1.817	m

[a] Visually estimated intensity *I*: vs = very strong; s = strong; m = medium; w = weak.

presence, along with the metal, has been evidenced by X-ray diffraction only for Cu_2S (lines of low intensity) while no diffraction lines corresponding with Ag_2S appeared on the patterns. The presence of Ag_2S with Ag has been proved by DTA study of the decomposition residue of $Ag(CH_3SO_3)$: between 163 and 173°C, the curve exhibits an exothermic peak reversible to cooling, corresponding to the polymorphic transition Ag_2S (monoclinic) $\rightleftharpoons$ Ag_2S (cubic) (the above temperatures agree with those reported in ref. 8 dealing with this transition).

The Zn methanesulfonate undergoes thermal decomposition to yield the ZnO + ZnS mixture, easily identified by X-ray analysis (ZnS being the β-form or sphalerite).

Attempts were made to determine the volatile decomposition products (of very unpleasant odour) using chemical analysis, but the exact composition of the evolved gases could not be determined due to the difficulty in identifying the diverse compounds. However, there is neither hydrogen sulfide nor sulfur dioxide in the gaseous phase.

DISCUSSION

It seems interesting, while commenting on the previous experimental results, to compare them with those obtained on the corresponding acetates, the $CH_3SO_3^-$ methanesulfonate anion appearing to be derived from the $CH_3CO_2^-$ acetate anion with the carboxylic group replaced by the sulfonic group.

Thermal behavior until the start of decomposition

The dihydrated Mn and Cd salts loose their water of crystallization in one step; the tetrahydrated Cu and Zn salts loose their water of crystallization in two steps, the dihydrates being the only intermediate compounds (it has not been possible to evidence other intermediate hydrates by reducing the heating rate). As shown in Table 3, the thermal stability range of these hydrates is rather wide.

In all cases, at the end of the dehydration reactions, the compounds obtained are anhydrous and, what is noteworthy, they are well-crystallized, whereas the anhydrous acetates are amorphous to X-rays.

The anhydrous Ag methanesulfonate melts congruently at 259°C while the Ag acetate decomposes before melting [9].

As with the corresponding acetates [9,10], Zn and Cd anhydrous methanesulfonates melt and decompose simultaneously while the Cu and Mn salts do not undergo melting before decomposition.

Among the anhydrous methanesulfonates studied here, that of Cd is the only one which presents a phase transition (at 146°C) (the literature gives no phase transition for the Mn, Cu, Ag, Zn and Cd acetates).

Decomposition reactions

The methanesulfonates sharply and rapidly decompose to yield well-defined residues. In the case of the Cu(II) compound, there is no formation of the Cu(I) compound in the course of the decomposition, whereas that of cuprous acetate from cupric acetate has been clearly proved by numerous authors, particularly Judd et al. [9]. This result is not surprising since CH_3SO_3H is a strong acid: now, the formation of cuprous compounds during the decomposition of cupric salts has only been observed in the case of salts of weak carboxylic acids (as the formic, acetic, propionic, benzoic acids) [11].

The sulfides are of well-defined stoichiometry (MS or M_2S); that was not the case [4] with other transition metals such as Ni and Co.

The problem is to explain why sulfides form. The case of the Ag methanesulfonate can be exemplary. The crystal structure of this compound, determined by Charbonnier et al. [12], shows that there is no distinct molecule within the crystal: the methanesulfonato groups act as pentacoordinating ligands through the medium of their three oxygen atoms, two being bonded to two different Ag atoms and the third to three other Ag atoms; each Ag is surrounded by five oxygen atoms forming a distorted trigonal bipyramid; the Ag—O distances are the longest within the crystal (average Ag—O bond length: 2.47 Å). It can be thought that there is breakage of all the Ag—O bonds upon heating, the metal being liberated.

It has been thought that in the case of the Cu and Ag compounds, the gas issued could be different from those obtained for the Mn, Zn and Cd compounds, explaining why Cu and Ag are very little sulfurized. Now after heating of mixtures of anhydrous Ag and Cd methanesulfonates or Cu and Cd methanesulfonates, the residues obtained were CdS + Ag and CdS + Cu, respectively, Ag and Cu metals not being sulfurized.

The results concerning the very poor sulfurization of Cu and Ag are surprising when it is known how easily these metals are sulfurized by the action of hydrogen sulfide (and, on the other hand, how Mn, Zn and Cd are sulfurized with more difficulty). This confirms that there is no hydrogen sulfide evolved during the decomposition.

On the DTA curve of the Cd methanesulfonate (see Fig. 2), the sulfurization of the metal is evidenced by the exotherm which immediately follows the endotherm corresponding to the simultaneous fusion and decomposition. The presence of zinc oxide, ZnO, as well as the sulfide, ZnS, is unexpected. Bernard and Busnot [10] found that the decomposition of the Zn acetate under an inert atmosphere also yielded the oxide without the metal. On the other hand, under the same conditions, the decomposition of the Ag, Cu and Cd anhydrous acetates leads to the metal [9,10], involving breakage of all the metal—oxygen bonds, as for the corresponding methanesulfonates.

CONCLUSIONS

This study on the thermal behavior of Mn, Cu, Zn, Ag and Cd methanesulfonates contributes to the knowledge of the physico-chemical properties of the metallic methanesulfonates. Since a certain correlation may be established between the methanesulfonic and acetic acids, the thermal behavior of the preceding methanesulfonates has been compared with that of the corresponding acetates previously investigated by numerous workers. The discussion has shown that there were notable differences concerning the thermal behavior of salts of these two "parent" organic acids.

The well-crystallized MnS and CdS obtained from the thermal decomposition of the corresponding methanesulfonates seem noteworthy.

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