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THERMAL ANALYSIS OF SOME HYDRATED COBALT(II) ALKANESULFONATES

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ABSTRACT

The cobalt(II) salts of some alkanemono- and disulfonic acids have been prepared; all are new and most of them crystallized with six molecules of water. Their behaviour under heating has been studied by thermogravimetric analysis (TG) and differential thermal analysis (DTA). Most of them lose their water in several steps and some anhydrous salts melt; the decomposition begins at a temperature which depends upon the structure of the organic anion and it leads to residues, the composition of which depends on the surrounding atmosphere.

INTRODUCTION

The alkanesulfonic acids and their organic derivatives have been extensively investigated. On the other hand, few metallic salts are known. The works that have been published are concerned with the identification of some hydrated salts of barium, sodium, copper or lead[1], infrared spectrum studies of lithium and sodium methanedisulfonates[2] and research on the structure of potassium methanedisulfonate and sodium long-chain alkanesulfonates[3–5]. But no investigation has been made concerning thermal dehydration and decomposition reactions. Thus it seemed interesting to study the thermal stability of some alkanesulfonates. A number of our investigations on the sulfonates of copper, manganese, lithium, sodium, potassium and calcium have been published[6–9]. In the present investigation the thermal dehydration and decomposition reactions of some alkanemono- and disulfonates of cobalt were further investigated by thermogravimetric analysis (TG) and differential thermal analysis (DTA). After the complete decomposition the solid residues were identified by radiocrystallographic analysis and chemical analysis.

EXPERIMENTAL

Materials

All the compounds investigated were prepared in the laboratory. The acids are $R\text{–}SO_3H$ and $HSO_3\text{–}R'\text{–}SO_3H$ (R is C_nH_{2n-1} and R′ is $(CH_2)_n$ with $1 \leqslant n \leqslant 5$); the methods of preparation and purification have been published previously[8]. The salts were obtained from metathesis between the barium alkanesulfonates and cobalt(II) sulfate solutions, as follows:

$$Ba(RSO_3)_2 + CoSO_4 \rightarrow BaSO_4\downarrow + Co(RSO_3)_2$$

$$Ba[SO_3(CH_2)_nSO_3] + CoSO_4 \rightarrow BaSO_4\downarrow + Co[SO_3(CH_2)_nSO_3]$$

The cobalt salts are highly soluble. The solutions were slowly evaporated down at 50°C, and then kept at 3°C whereby the salts crystallized.

The compounds were analyzed for cobalt content by an electrolytic method as described previously[10] and for sulfur content by residue analysis (as $BaSO_4$), using a gravimetric method (the sulfonate reacted with Na_2O_2 in an IKA bomb, giving sulfate ions which were precipitated by $BaCl_2$). Coordinated water was determined by drying in an oven (set at 120°C or 150°C) and the results conformed with the mass-loss on the thermo-balance.

Thermogravimetry

The thermogravimetric studies were carried out using an Adamel–Chevenard thermobalance with graphical recording. A Pt–PtRh 10% thermocouple placed under the sample-holder was used. The samples ranged in mass from 100 to 300 mg and the heating rate was 2, 3 or 5°C/min. A dynamic atmosphere of either dry air or dry nitrogen was employed.

Differential thermal analysis

A "Bureau de Liaison" (C. Mazieres type) apparatus was used. It has been described previously by Harmelin[11]. The curves $\Delta T = f(T)$ were plotted on a SEFRAM recorder of the X–Y Luxytrace type after amplification of the differential temperature by an Amplispot AGT SEFRAM (10 μV/cm that is 0.25°C/cm). Samples of 2–5 mg were used and a heating rate of 2 or 5°C/min was employed.

Radiocrystallographical analysis

The residues formed after complete decomposition were studied by powder radiocrystallography. The patterns were obtained using a Philips photographic camera (114.6 mm in diameter), the cobalt Kα line (Philips generator PW 1320) and the Straumanis mounting technique. Aluminium was used as standard.

RESULTS AND DISCUSSION

Table 1 lists the hydrated salts obtained as described above. All are new. *n* is the number of coordinated water molecules.

TG results

A. Dehydration reactions

Most of the TG curves in a dry air atmosphere show some mass losses and thus reveal the formation of intermediate hydrates. But both the salts $Co(SO_3CH_2SO_3)\cdot$

$5H_2O$ and $Co[SO_3(CH_2)_4SO_3]\cdot 4H_2O$ lost their water molecules in one step to form the anhydrous compounds.

In Table 2 the intermediate hydrates obtained from the other salts are shown. As examples the TG curves of $Co(CH_3SO_3)_2\cdot 7H_2O$ and $Co[C_2H_5CH(CH_3)SO_3]_2\cdot 6H_2O$ are illustrated in Fig. 1. The temperatures at which the mass losses began to occur were always lower than 90°C (for a heating rate of 5°C/min).

TABLE 1

SALTS PREPARED

(n = number of water molecules)

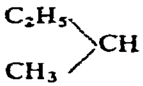
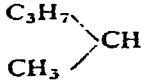
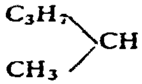
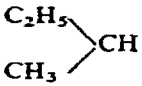
$Co(RSO_3)_2$		*$Co(RSO_3)_2$*		*$Co[R'(SO_3)_2]$*	
R	*n*	*R*	*n*	*R'*	*n*
CH_3	7	 $\begin{matrix}C_2H_5 & \\ & \rangle CH \\ CH_3 & \end{matrix}$	6	CH_2	5
CH_3CH_2	6	$CH_3(CH_2)_4$	6	$(CH_2)_2$	6
$CH_3(CH_2)_2$	6	 $\begin{matrix}C_3H_7 & \\ & \rangle CH \\ CH_3 & \end{matrix}$	6	$(CH_2)_3$	6
$(CH_3)_2CH$	6	$(C_2H_5)_2CH$	6	$(CH_2)_4$	4
$(CH_3)_2CHCH_2$	6	$(CH_3)_2CH(CH_2)_2$	4	$(CH_2)_5$	6

TABLE 2

INTERMEDIATE HYDRATES ISOLATED BY TG STUDY

$Co(RSO_3)_2$	*Intermediate hydrates*	*$Co(RSO_3)_2$ and $Co[R'(SO_3)_2]$*	*Intermediate hydrates*
$R = CH_3$	5–2	$R = CH_3(CH_2)_4$	4–2
CH_3CH_2	2	 $\begin{matrix}C_3H_7 & \\ & \rangle CH \\ CH_3 & \end{matrix}$	4
$CH_3(CH_2)_2$	2	$(C_2H_5)_2CH$	4
$(CH_3)_2CH$	4–2	$(CH_3)_2CH(CH_2)_2$	2
$CH_3(CH_2)_3$	2	$R' = (CH_2)_2$	4–2
$(CH_3)_2CHCH_2$	2	$(CH_2)_3$	4–2
 $\begin{matrix}C_2H_5 & \\ & \rangle CH \\ CH_3 & \end{matrix}$	4–2–1	$(CH_2)_5$	2

In most cases the 2-hydrate is an intermediate compound. Butane-2-sulfonate is interesting because it was the only compound that lost its six water molecules in four steps to form the 4-, 2-, and 1-hydrates; only in the case of this salt could we isolate the 1-hydrate. In each case the final product was the anhydrous salt.

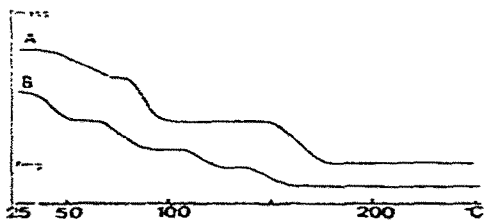


Fig. 1. TG curves of $Co(CH_3SO_3)_2 \cdot 7H_2O$ (A), and $Co[C_2H_5CH(CH_3)SO_3]_2 \cdot 6H_2O$ (B). Dry air; 2 °C/min.

B. Decomposition reactions

The temperatures at which decomposition started to occur were determined with a heating rate of 3 °C/min for each anhydrous compound. The results of investigations in a dry air atmosphere are presented in Fig. 2. The temperatures were about 30° higher in a dry nitrogen atmosphere.

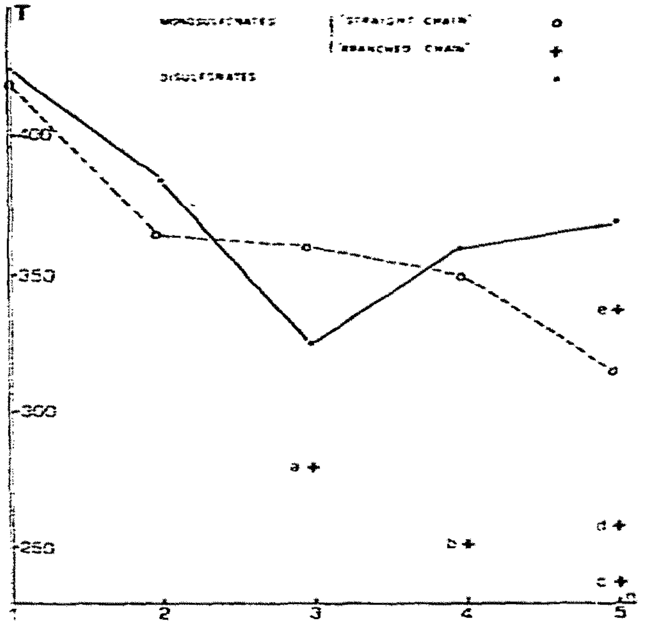


Fig. 2. Temperature at which decomposition starts (dry air; 3 °C/min). a: propane-2-sulfonate; b: butane-2-sulfonate; c: pentane-2-sulfonate; d: pentane-3-sulfonate; e: 3-methylbutane-1-sulfonate. n = number of carbon atoms.

The decomposition of the monosulfonates with a "straight chain" and of the disulfonates began at a temperature higher than 300 °C. Most of the monosulfonates with a "branched chain" decomposed at a temperature lower than those of the corresponding isomers with a "straight chain".

The nature of the final products after complete decomposition depends on the surrounding atmosphere. The residues were slowly cooled under this atmosphere before their composition was studied.

(a) In a dry air atmosphere the residues were in each case mixtures of often well crystallized cobalt oxides (CoO and Co_3O_4) and cobalt sulfate.

(b) In a dry nitrogen atmosphere the results obtained are more complex. The residues contained neither oxides nor sulfate but sulfides (with much more carbonaceous particles than in air); thus these residues were subjected to action by acids in the hot with evolution of hydrogen sulfide. The X ray patterns showed that the nature of the sulfides and their crystallization states seemed to depend on the ratio C/S, C and S being respectively the numbers of carbon and sulphur atoms in each sulfonate. (Note that in all the sulfonates studied here, S is equal to 2 and the ratio Co/S to 0.5.)

When the sulfide could be well identified, we thought that it was the non-stoechiometric compound Co_9S_8 previously described by Lundqvist and Westgren[12] rather than one of the other non-stoechiometric sulfides Co_6S_5[13] and Co_4S_3[14] (cubic form), the interplanar spacings of which are close to those of Co_9S_8.

In Table 3 some characteristic lines of these compounds are compared, which explains our choice of Co_9S_8. As example the well crystallized residue obtained from the decomposition of $Co(CH_3SO_3)_2$ (with C/S = 1) was selected.

TABLE 3

COMPARISON BETWEEN SOME INTERPLANAR SPACINGS

Residue from the pyrolysis of Co methanesulfonate.

Residue		*Co_9S_8*[15]		*Co_6S_5*[15]		*Co_4S_3 (cubic)*[15]	
d (Å)	*Intensity (visual)*	*d (Å)*	*I/I₁*	*d (Å)*	*I/I₁*	*d (Å)*	*I/I₁*
3.483	(w)	3.48	(40)	3.52	(25)	no line	
2.974	(vs)	2.97	(100)	3.00	(80)	2.99	(70)
2.851	(s)	2.85	(60)	2.87	(60)	2.87	(60)
1.905	(s or m)	1.91	(60)	1.91	(60)	1.91	(70)
1.575	(vw)	1.57	(20)	no line		no line	
1.749	(vs)	1.75	(100)	1.76	(100)	1.76	(100)

vs = very strong; s = strong; m = medium; w = weak; vw = very weak.

The sulfonates for which the C/S ratio was equal to 0.5, 1, 1.5, 2 or 2.5, led to residues containing Co_9S_8. Thus this sulfide was highly crystallized (narrow lines) when C/S = 1. When the C/S ratio became greater than 2.5, the X ray patterns of the imperfectly crystallized residues could not be interpreted because the lines did not correspond with those of previously known sulfides[15]. For example, in the case when C/S was equal to 5, the interplanar spacings corresponding to the strongest lines were as follows (listed with decreasing intensities): 1.750 Å; 3.104 Å; 2.815 Å; 1.905 Å. The first and fourth values are the only ones which are in line with those of Co_9S_8.

In any case, whatever the value of the ratio C/S may be, there were in the patterns some non-explained lines which corresponded with the interplanar spacings as follows: 3.29 Å (weak); 3.14–3.15 Å (weak); 2.57–2.58 Å (medium); 1.93–1.94 Å (medium).

The two last values would perhaps correspond to the strongest lines of Co_4S_3 hexagonal form[14]. On the other hand it is possible that non-stoechiometric sulfides $Co_{1-x}S$ are formed[16].

Thus, it appears that the X ray patterns of residues that are obtained from the pyrolysis of cobalt alkanesulfonates in a dry nitrogen atmosphere cannot be completely explained.

In a non-oxidizing atmosphere the pyrolysis of cobalt(II) alkanesulfonates leads to sulfide residues. It seems that sulfate and oxides which are formed in an air atmosphere proceed from an oxidation. A study of the thermolysis of copper(II) alkanesulfonates[6], manganese(II) alkanesulfonates[7] and nickel(II) alkanesulfonates (non-published work) led to the same results; but in the cases of copper and nickel salts the residue contained the metal (well crystallized) besides the sulfides.

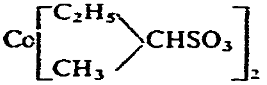
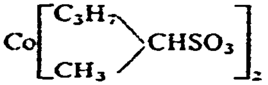
The mechanism of these decomposition reactions seems hard to explain. Certainly some bondbreakings occur, such as metal–oxygen in the "molecule" (as for some carboxylates of transition metals) and carbon–sulfur and sulfur–oxygen in the alkanesulfonate anions. Further work is in progress to determine the gaseous compounds resulting from the pyrolysis and to study the residual products after decomposition under vacuum.

DTA results

The DTA results confirm those obtained by TG. Thus the DTA curves show first several endothermic peaks the number of which equals that of the mass losses observed on the corresponding TG curves. All the peaks of the dehydration reactions were irreversible. After these peaks another endothermic peak was observed for some compounds and it corresponded to a melting of anhydrous salt. At the time of the decomposition, several exothermic peaks occurred in an air atmosphere, but there was only one large endothermic peak under dry nitrogen. The exothermic peaks can be explained by an oxidation of gases and solid residues.

TABLE 4

MELTING POINTS OF SOME COBALT ALKANEMONOSULPHONATES

Anhydrous salt	*Melting point (°C)*	*Start of the decomposition (see Fig. 2)*
$Co[(CH_3)_2CHSO_3]_2$	230	280 a
 $Co\left[\begin{matrix}C_2H_5\\CH_3\end{matrix}>CHSO_3\right]_2$	219	250 b
 $Co\left[\begin{matrix}C_3H_7\\CH_3\end{matrix}>CHSO_3\right]_2$	131	235 c
$Co[(C_2H_5)_2CHSO_3]_2$	227	255 d
$Co[(CH_3)_2CH(CH_2)_2SO_3]_2$	243	335 e

Five compounds with a "branched chain" melted. The melting points were measured in dry air atmosphere under ordinary pressure and they are listed in Table 4. There was no mass loss at these temperatures in the corresponding TG curves. For these salts it appears clear that the decomposition occurs after melting. In contrast, the monosulfonates with a "straight chain" and the α,ω-disulfonates decomposed before melting.

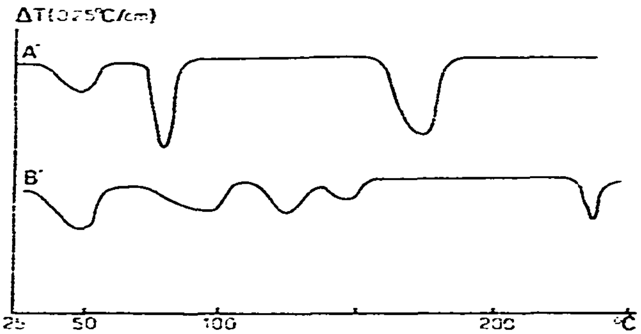


Fig. 3. DTA curves of $Co(CH_3SO_3)_2 \cdot 7H_2O$ (A'), and $Co[C_2H_5CH(CH_3)SO_3]_2 \cdot 6H_2O$ (B'). Dry air; 2°C/min.

As examples the DTA curves for $Co(CH_3SO_3)_2 \cdot 7H_2O$ and $Co[C_2H_5CH(CH_3)SO_3]_2 \cdot 6H_2O$ are illustrated in Fig. 3 (the peaks of decomposition are not shown). The three endothermic peaks in the curve for $Co(CH_3SO_3)_2 \cdot 7H_2O$ correspond to the loss of two, three and two water molecules at about 50°C, 80°C and 170°C respectively. For $Co[C_2H_5CH(CH_3)SO_3]_2 \cdot 6H_2O$four peaks canc learly be seen for the loss of the hydrated water (there were four mass losses in the TG curve, Fig. 1) corresponding to the intermediate hydrates listed in Table 2. At about 220°C the curve reveals an endothermic peak reversible on cooling, and this reaction corresponds to the phase transition solid → liquid.

CONCLUSION

This work makes a small contribution to the knowledge of the hitherto unknown physico-chemical properties of the cobalt alkanesulfonates. Much investigation must still be undertaken. Thus it would, for example, be interesting to study the effects of the presence of water vapor on the dehydration reactions, to determine the heats of dehydration and phase transition solid → liquid reactions and to find out by magnetochemical means how the cobalt(II) ions are coordinated. Comparisons could in particular be made between the properties of cobalt(II) methanesulfonate and those of cobalt(II) acetate previously studied by Wendlandt and fellow workers[17].

It is our intention to determine the crystal lattices of some of the salts that we have presented in this paper.

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