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THERMAL DECOMPOSITIONS OF SULPHOSALICYLATES OF Mg(II), Ca(II) and Zn(II)

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The thermal decompositions of the sulphosalicylates of Mg(II), Ca(II) and Zn(II) have been investigated by means of TG and DTA. The preparation and analysis of these compounds are included. The possible decomposition reactions in the various stages and the final decomposition products are discussed.

Salicylic acid and its derivatives comprise an important class of ligands which form stable complexes with many elements. Their derivatives and the complexes find many applications in industry [1, 2] medicine [3] and analytical chemistry [4]. Only scanty data [5] are available on the thermal decompositions of salicylates, and particularly of salts of sulphosalicylic acid (SSA). As the use of SSA is more advantageous than that of salicylic acid and its other derivatives from the point of view of stability, a steady replacement of these metal salicylates by the SSA salts is in order. In view of this, the present work on the thermal decompositions of the SSA salts of Mg(II), Ca(II) and Zn(II) has been carried out by means of TG and DTA.

Experimental

All the chemicals used were of 'AnalaR' grade. For the preparation of the magnesium and calcium complexes, a saturated solution of SSA was reacted with the respective carbonate, and the complex was allowed to crystallize from the solution. For the zinc complex, freshly prepared zinc hydroxide was used in place of the carbonate. To ascertain the stoichiometry and the purity, the complexes were analysed for the respective metals, sulphur, carbon and hydrogen by the conventional methods [4]. The water content was determined by Karl Fischer titration using a dead-stop end-point method.

The experimental set-ups for TG and DTA were reported earlier [8, 9]. For TG, 5 to 11 mg of the complex was taken. The sensitivity was 0.04 mg per division and a

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heating rate of 10 deg min^{-1} was maintained in all experiments. For DTA, a heating rate of 6 deg min^{-1} was applied and 50 mg of sample mixed with 150 mg of calcined alumina was used against a reference of 200 mg of calcined alumina. All the TG and DTA experiments were conducted in static air, and the final products obtained were analysed for composition. The TG and DTA curves of SSA were also recorded for comparison.

Results and discussion

The complexes have the compositions $MgC_7H_4SO_6 \cdot 4H_2O$, $CaC_7H_4SO_6 \cdot 2H_2O$ and $ZnC_7H_4SO_6 \cdot 4H_2O$. The TG curves for the ligand and the complexes are given in Fig. 1, and their DTA curves in Fig. 2. Table 1 lists the information available from the TG data, together with relevant theoretical values.

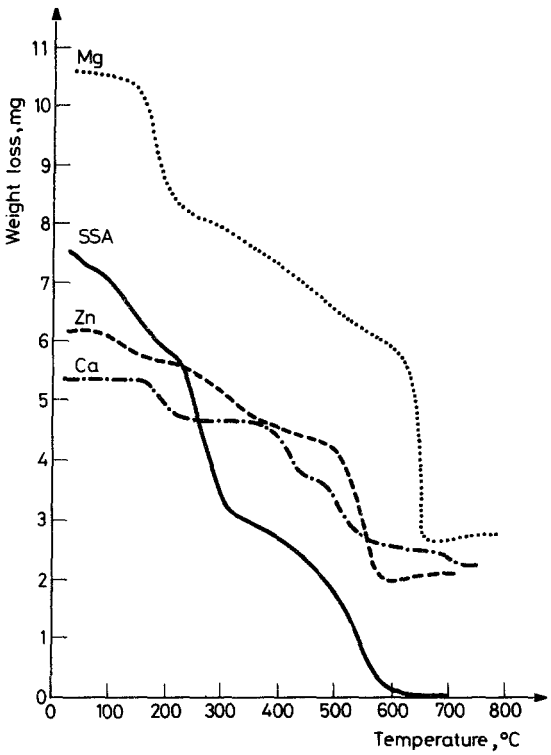

Fig. 1. TG curves of the compounds

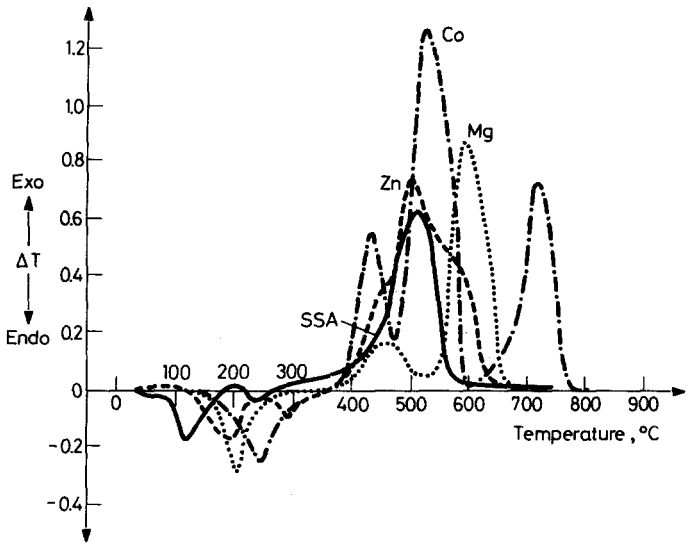

Fig. 2. DTA curves of the compounds

As can be seen from the Table and the Figures, all the compounds exhibit an endothermic section at the beginning of their DTA curves. The range for this reaction for all the compounds is within 120–300°. For SSA, which contains 2 molecules of water, the peak temperature of dehydration is 120°, which is the lowest for this set of experiments, while for the zinc complex it is 300°, which is the highest. The increase in the temperature of dehydration of the complexes evidently points to the coordination and the subsequent difference in the nature of the bonding of the water molecules to the metal atoms. One additional endothermic peak for the zinc complex perhaps shows that water is released in two stages, at least part of it being bonded more strongly than that released at the lower temperature. A comparison with the TG curves of the salts substantiates that the peaks correspond to the loss of water molecules, as the percentage weight loss for the water occurs in the temperature range of the DTA peaks. However, in the case of SSA the decomposition reaction starts simultaneously with the second stage of the dehydration.

The final decomposition peak for SSA is at 515°, which is close to the value for the zinc complex, 500°. This indicates that the decomposition of SSA is closely similar to that of the zinc complex. For SSA, the total weight loss from the TG curve was found to be nearly 100%, indicating that the substance decomposes without a residue. Evidently, in this case the sulphate group must have been decomposed to oxides of sulphur, while the final products of decomposition of the complexes are expected to be oxide, sulphide or sulphate, or a mixture of these. It was also

Table 1. TG data of the complexes

Compound	Data from TG analysis				Theoretical wt. loss in %		Conclusion
	Temp. range, °C	Wt. loss, %	Total wt. loss, %	Due to water	For sulphate formation	For oxide formation	
SSA, $2H_2O$	35–75	3.98					
	75–210	18.59		14.21			$-2H_2O$
	210–330	36.52					
	330–615	40.50	100				Complete decomposition
Mg SSA,	110–305	24.06		23.06			$-4H_2O$
$4H_2O$	305–520	15.09			61.7	87.2	* Oxide–sulphate
	520–650	35.38	78.3				formation
Ca SSA,	150–235	12.04					
$2H_2O$	335–475	19.44		12.37			$-2H_2O$
	475–570	19.44			53.6	80.9	* About 95% sulphate
	625–725	6.48	56.7				formation
Zn SSA,	100–195	6.62					$-4H_2O$
$4H_2O$	195–415	13.94		20.34	54.5	77.1	* Oxide–sulphate
	415–590	30.91	65.7				formation

* No sulphide was detected in the final residue.

expected that the final temperature of decomposition would be higher. This is not so, at least, in the case of the magnesium complex.

The decomposition temperatures of the complexes are a measure of their thermal stabilities. The decomposition temperatures of SSA, MgSSA, CaSSA and ZnSSA are 210°, 305°, 335° and 415°, respectively. In the case of SSA the decomposition and dehydration take place simultaneously, and thus it is difficult to get a clear picture of the thermal stability. The most probable sequence is as follows:

$$SSA < MgSSA < CaSSA < ZnSSA.$$

Table 1 gives the experimental total percentage weight losses, and the calculated percentage weight losses for final products of oxides, sulphides or sulphates. The final product from the calcium complex is $CaSO_4$. This indicates that the oxide formed in the decomposition reaction reacts immediately with the oxides of sulphur to form $CaSO_4$. This is possible only if the formation of the oxide precedes the decomposition of the sulphur group. For the magnesium and zinc complexes, the comparison points to the formation of a mixture of oxides and sulphates. These conclusions were confirmed by the chemical analyses of the final residues.

The marginal weight gain observed in the cases of the magnesium and zinc complexes can be attributed to the buoyancy change due to the sudden decomposition of the complexes and the resultant evolution of large amounts of gases.

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Zusammenfassung – Mittels TG und DTA wurde die thermische Zersetzung der Sulfosalizylate von Mg(II), Ca(II) und Zn(II) untersucht. Die Darstellung und Analyse dieser Verbindungen wird ebenfalls beschrieben. Die möglichen Zersetzungsreaktionen der einzelnen Schritte und die Zersetzungsprodukte werden diskutiert.

Резюме — Методом ТГ и ДТА изучено термическое разложение сульфосалицилатов магния, кальция и цинка. Приведен также метод получения этих соединений и их анализ. Обсужден возможный механизм реакций их разложения на различных стадиях, а также конечные продукты их разложения.