

THE THERMAL DECOMPOSITION OF ALKALINE EARTH METAL SALICYLATES

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The thermal decompositions of the salicylates of magnesium, calcium, strontium and barium were investigated using thermogravimetry and differential thermal analysis, together with the analysis of intermediate products formed during the decomposition processes. One intermediate product was isolated and identified during the decomposition of the magnesium salt, and two for each of the remaining metal salts.

Both salicylic acid and its derivatives have been extensively used in medicine as antiseptic, antipyretic and analgesic agents. The thermal decomposition of salicylic acid has been known to be largely averted owing to the ease of its sublimation. Upon gentle heating it has been reported to sublime undecomposed, whilst with an increasing heating rate it undergoes decarboxylation to give phenol [1].

This report deals with the thermal decomposition of alkaline earth metal salicylates. It has been anticipated that there is a correlation between the decomposition mechanism and the basicity or atomic radii of the metal cations of the salts, which should become evident when various heating rates are used.

Experimental

Materials

Magnesium and calcium salicylates were obtained by reacting salicylic acid with the stoichiometric quantity of the appropriate metal oxide in aqueous solution at reflux temperature. The strontium salt was obtained similarly, strontium carbonate being used in place of the oxide. The barium salt was obtained by neutralization of barium hydroxide with salicylic acid. All of the salts were isolated after evaporation of water. Crude products were recrystallized from 95% ethanol and dried to constant weight at ambient temperature in vacuo (10 mm Hg). In this way the salts were obtained whose formulae are reported in Table 1.

Methods

Elemental analyses of both metal salicylates and their decomposition products were made using a flash-combustion method developed by Kozłowski et al. [2]. Infrared absorption spectra were recorded on a Perkin Elmer 357 spectrophotometer, using KBr discs. Results of elemental analyses are shown in Table 1.

Table 1
Elemental analyses of alkaline earth metal salicylates

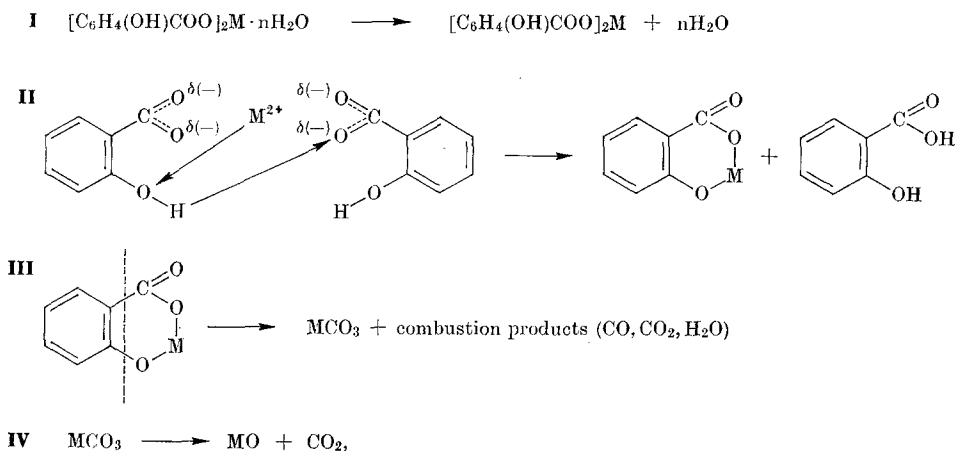
Formula	Calc.		Found	
	%C	%H	%C	%H
$[\text{C}_6\text{H}_4(\text{OH})\text{COO}]_2\text{Mg}$	56.32	3.38	56.38	3.39
$[\text{C}_6\text{H}_4(\text{OH})\text{COO}]_2\text{Ca} \cdot 2\text{H}_2\text{O}$	48.00	4.03	48.04	4.18
$[\text{C}_6\text{H}_4(\text{OH})\text{COO}]_2\text{Sr} \cdot 1.5\text{H}_2\text{O}$	43.24	3.37	42.92	3.47
$[\text{C}_6\text{H}_4(\text{OH})\text{COO}]_2\text{Ba} \cdot 2\text{H}_2\text{O}$	37.57	3.15	37.50	3.17

The thermal analysis of the salts was performed in air using a Paulik – Paulik – Erdey (MOM) Derivatograph [3, 4] and platinum crucibles. Sample weights ranged from 100 to 200 mg. The salicylates of magnesium, calcium, strontium and barium were heated up to 700°, 900°, 750° and 650° respectively, at heating rates of 1.5, 3, 5, 7, 9 and 13°/min. Alumina was employed as reference material.

Results and discussion

The results are listed in Table 2 and presented in Figs 1–4.

In general, the thermal decompositions of the salts considered were shown to occur via the following stages:



where M is Mg, Ca, Sr or Ba.

In stages I, II and IV, large weight losses occurred which were accompanied by endothermic effects.

Stage III is likewise characterized by a weight loss, but its overall heat effect is exothermic. In this case, an endothermic effect due to volatilization of gaseous

Table 2
Thermal behaviours of alkaline earth metal salicylates (heating rate 5°/min in air)

Compound	Decomp. stage	Temp. range, °C	Formula	Calc.		Found			
				Wt. loss, %	%C	%H	Wt. loss, %	%C	%H
Mg salicylate	I	250—350	undiscernible [C ₆ H ₄ (O)COO]Mg undiscernible MgO	46.3	52.41	2.51	46.0	52.57	2.22
	II								
	III								
	IV								
Ca salicylate	I	150—200	[C ₆ H ₄ (OH)COO] ₂ Ca	10.1	53.50	3.21	10.0	53.60	3.28
	II								
	III								
	IV								
Sr salicylate	I	180—220	[C ₆ H ₄ (OH)COO] ₂ Sr	7.0	46.47	2.79	6.5	45.88	2.82
	II								
	III								
	IV								
Ba salicylate	I	200—230	[C ₆ H ₄ (OH)COO] ₂ Ba · H ₂ O	3.0	39.24	2.82	4.1	38.74	2.71
	II								
	III								
	IV								

products is outweighed by an exothermic one due to partial combustion of the salicylate moiety.

To isolate intermediate products of decomposition, samples were withdrawn from the furnace at appropriate temperatures and analyzed. Three analyses were made for each stage, which gave the mean results presented in Table 2.

An increase of heating rate over the range $1.5-13^{\circ}/\text{min}$ was found to shift the individual stages of decomposition proportionately towards higher temperatures. At the same time, the DTA peaks became narrower and higher.

Characterization of the thermal behaviour of individual salts

1. Magnesium salicylate

Stages II and IV only could be distinguished during the thermal decomposition of this salt (Fig. 1). The salt isolated in stage II, $[\text{C}_6\text{H}_4(\text{O})\text{COO}]\text{Mg}$, is a pale-yellow solid, sparingly soluble in water and almost insoluble in methanol, ethanol, chloroform, carbon tetrachloride and dimethyl sulphoxide. In the infrared spec-

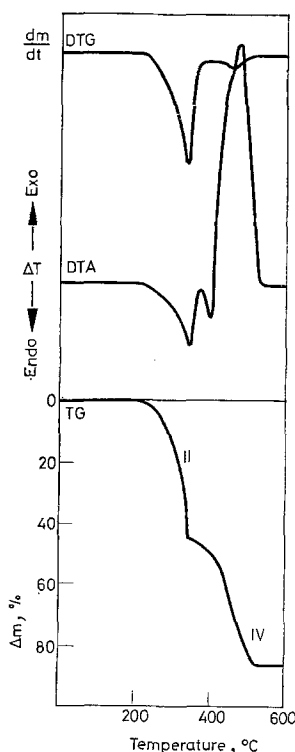


Fig. 1. TG, DTG and DTA curves of magnesium salicylate, $[\text{C}_6\text{H}_4(\text{OH})\text{COO}]_2\text{Mg}$ (heating rate $5^{\circ}/\text{min}$)

trum of this salt, bands at 1660, 3500–3200 and 3250 cm^{-1} , due to the C=O stretch [5], the O . . . H–O stretch [5] and the uncombined OH stretch of the phenolic group [8, 9], respectively were missing, and new ones appeared due to stretching vibrations of the carboxylate ions: symmetric ones at 1605 and 1555 cm^{-1} , and antisymmetric ones at 1415 and 1300 cm^{-1} [10].

2. Calcium salicylate

The decomposition of this salt proceeded in four steps (Table 2 and Fig. 2). The compound isolated in stage II is a yellowish-green solid, practically insoluble

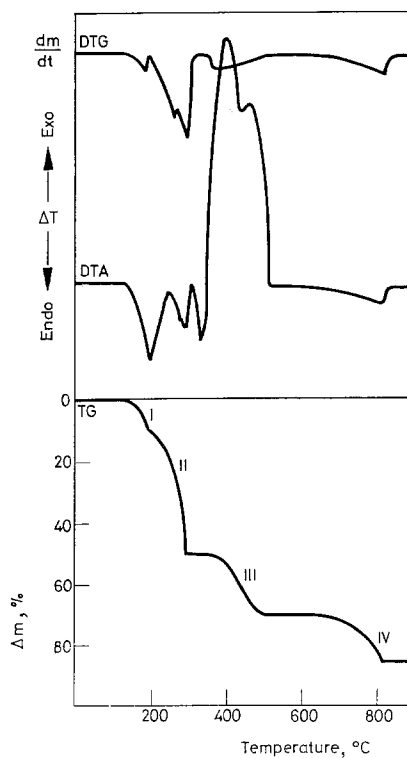


Fig. 2. TG, DTG and DTA curves of calcium salicylate, $[\text{C}_6\text{H}_4(\text{OH})\text{COO}]_2\text{Ca} \cdot 2\text{H}_2\text{O}$ (heating rate $5^\circ/\text{min}$)

in organic solvents. In its infrared spectrum, absorption bands due to the OH group were missing and those due to the carboxylate ion occurred at 1610 and 1560 cm^{-1} (asym. stretch) and at 1415 and 1310 cm^{-1} (sym. stretch) [5–10].

3. Strontium salicylate

The decomposition of this salt occurred in three steps (Fig. 3). The isolation of the substance decomposed in stage I was difficult due to the lack of a well-defined horizontal in the TG trace. The dark-yellow solid isolated in stage II was identified as $[\text{C}_6\text{H}_4(\text{O})\text{COO}]\text{Sr}$. Its solubility behaviour was similar to that of its magnesium and calcium congeners. Results of analyses of products isolated in the individual stages are shown in Table 2.

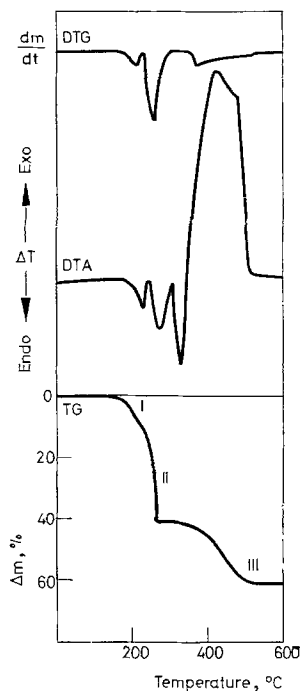


Fig. 3. TG, DTG and DTA curves of strontium salicylate, $[\text{C}_6\text{H}_4(\text{OH})\text{COO}]_2\text{Sr} \cdot 1.5\text{H}_2\text{O}$ (heating rate $5^\circ/\text{min}$)

4. Barium salicylate

Three decomposition stages were discernible during the thermal decomposition of this salt. In stage I the loss of one molecule of water occurred, whilst in stage II the rest of the water was lost along with one molecule of salicylic acid, to give $[\text{C}_6\text{H}_4(\text{O})\text{COO}]\text{Ba}$. The final product was contaminated with carbon. The results are shown in Table 2 and Fig. 4.

The data listed in Table 2 show that the stability of the individual metal carbonates increases as the ionic radius of the metal increases. Further evidence support-

ing this view is provided by the failure of an attempt to isolate MgCO_3 in the case of magnesium salicylate on one hand, and the ease of isolation of the carbonates of the remaining metals on the other. This finding may also be explained in terms

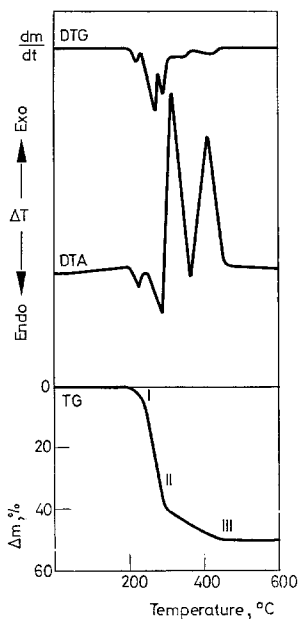


Fig. 4. TG, DTG and DTA curves of barium salicylate, $[\text{C}_6\text{H}_4(\text{OH})\text{COO}]_2\text{Ba} \cdot 2\text{H}_2\text{O}$ (heating rate $5^\circ/\text{min}$)

of the percentage of the metal cation in the salt, which ranges between 8% and 30% from magnesium to barium salicylate.

The surface areas of the DTA peaks were found to decrease with increasing ionic radius and specific gravity of the metal.

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RÉSUMÉ — On a étudié par thermogravimétrie et analyse thermique différentielle la décomposition thermique des salicylates de magnésium, calcium, strontium et baryum et l'on a analysé les produits intermédiaires qui se forment pendant la décomposition. C'est ainsi que l'on a isolé et identifié un produit intermédiaire au cours de la décomposition du sel de magnésium et deux pour chacun des autres sels.

ZUSAMMENFASSUNG — Die thermische Zersetzung der Salicylate von Magnesium, Calcium, Strontium und Barium sowie die Analyse der während des Vorganges gebildeten Zwischenprodukte wurden durch die thermogravimetrische und Differential-Thermal-Analyse untersucht. Im Verlaufe der Zersetzung des Magnesiumsalzes wurde ein Zwischenprodukt isoliert und identifiziert, bei den übrigen Metallsalzen je zwei.

Резюме — Исследовано термическое разложение салицилатов магния, кальция, стронция и бария, используя термогравиметрию и дифференциальный термический анализ, совместно с анализом промежуточных продуктов, образующихся в процессе разложения. При разложении магниевой соли был выделен и идентифицирован один промежуточный продукт, в то время как для оставшихся солей — два продукта.