

THERMAL DECOMPOSITIONS OF SOME TRANSITION METAL SALICYLATES

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The thermal decompositions of divalent cobalt, cadmium, nickel and copper salicylates and intermediates formed during the decomposition processes were investigated by means of thermogravimetry. Two intermediates were identified in each case, except for copper(II) salicylate.

The thermal behaviour of salicylic acid, H_2SA , and its alkali metal and alkaline earth metal salts has already been studied [1]. The thermal decomposition of sodium salicylate, $NaHSA$, involves transformation into the disodium salt, Na_2SA , with the loss of phenol and carbon dioxide. From the potassium salt, $KHSA$, not only the dipotassium salt, K_2SA , but also dipotassium *p*-hydroxybenzoate is formed [2]. The thermal decompositions of alkaline earth metal salicylates have been shown to occur via four stages: water loss, formation of an internal salt through the loss of salicylic acid, decomposition of this salt into the carbonate, and dissociation of the carbonate into the oxide [3].

In the present paper the thermal decompositions of divalent nickel, cobalt, cadmium and copper salicylates have been investigated by means of thermogravimetry.

Experimental

Materials

Divalent nickel, cobalt, cadmium and copper salicylates were obtained by reacting salicylic acid, in slight excess, with the appropriate carbonates in aqueous solution at reflux temperature. All of the salts were isolated after the evaporation of water, and were recrystallized from the same solvent. The products obtained were dried to constant weight at 50° . The results and the formulas of the salts thus obtained are shown in Table 1.

Table 1 Elemental analyses of Ni^{II}, Co^{II}, Cd^{II} and Cu^{II} salicylates

| Formula | Calc. | | Found | |
|--|-------|------|-------|------|
| | C, % | H, % | C, % | H, % |
| (C ₆ H ₄ (OH)COO) ₂ Ni · 4 H ₂ O | 41.5 | 4.4 | 41.8 | 4.4 |
| (C ₆ H ₄ (OH)COO) ₂ Co · 3 H ₂ O | 43.4 | 4.1 | 43.0 | 4.2 |
| (C ₆ H ₄ (OH)COO) ₂ Cd · 2 H ₂ O | 39.8 | 3.3 | 40.1 | 3.3 |
| (C ₆ H ₄ (OH)COO) ₂ Cu · H ₂ O | 47.2 | 3.4 | 47.5 | 3.3 |

Methods

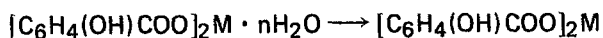
Elemental analyses of both the salicylates and their decomposition products were performed with a Carlo Erba 1106 analyzer. Infrared absorption spectra were recorded on a Perkin-Elmer 1430 spectrophotometer, using potassium bromide discs. Elemental analysis results are shown in Tables 1 and 2.

The thermal analyses (TG-DTG) of the salts were performed with a Perkin-Elmer TGS-2 thermobalance at a heating rate of 10 degree/min, from ambient temperature up to 500°, with an air purge of 30 ml/min. Sample weight ranged from 4 to 7 mg.

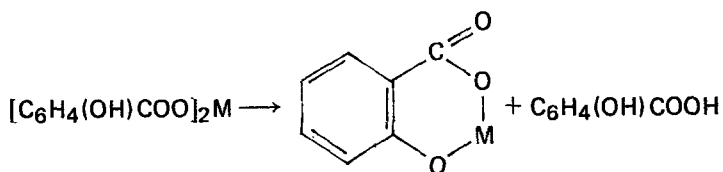
Results and discussion

The results are listed in Table 2 and Figs 1-4. In general, the thermal decomposition of the salts considered occur via the following stages:

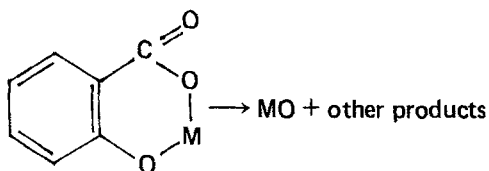
I. Dehydration:



II Formation of an internal salt through the loss of salicylic acid:



III. Oxide formation:



(M = Ni, Co, Cd and Cu).

Table 2 Thermal behaviours of Ni^{II}, Co^{II}, Cd^{II} and Cu^{II} salicylates (heating rate 10 deg./min, in air)

| Compound | Decomp. stage | T, °C range | Formula | Calc. | | Found | |
|------------------------------|---------------|-------------|---|-------------|------|-------------|------|
| | | | | Wt. loss, % | C, % | Wt. loss, % | C, % |
| Ni ^{II} -salicylate | I | 70-140 | [C ₆ H ₄ (OH)COO] ₂ Ni | 17.8 | 50.5 | 18.1 | 50.2 |
| | II | 140-300 | [C ₆ H ₄ (O)COO]Ni | 51.9 | 43.1 | 50.0 | 43.5 |
| | III | 300-380 | NiO | 81.5 | — | 82.0 | — |
| Co ^{II} -salicylate | I | 70-120 | [C ₆ H ₄ (OH)COO] ₂ Co | 14.0 | 50.5 | 15.4 | 50.4 |
| | II | 120-320 | [C ₆ H ₄ (O)COO]Co | 50.4 | 43.1 | 50.5 | 43.6 |
| | III | 320-390 | CoO | 80.6 | — | 80.5 | — |
| Cd ^{II} -salicylate | I | 90-160 | [C ₆ H ₄ (OH)COO] ₂ Cd | 8.5 | 43.5 | 9.1 | 43.3 |
| | II | 160-250 | [C ₆ H ₄ (O)COO]Cd | 41.2 | 33.8 | 40.7 | 34.1 |
| | III | 350-400 | CdO | 69.6 | — | 69.6 | — |
| Cu ^{II} -salicylate | I | — | undiscernible | — | — | — | — |
| | II | — | undiscernible | — | — | — | — |
| | III | 250-300 | CuO | 77.6 | — | 77.9 | — |

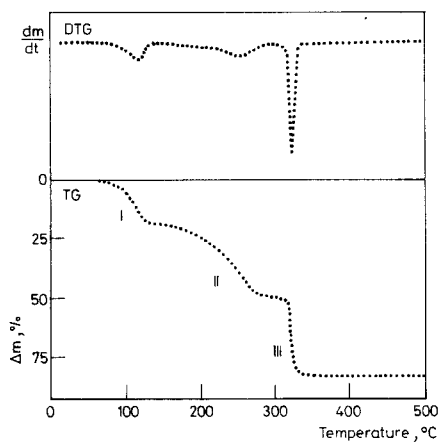


Fig. 1 TG and DTG curves of nickel salicylate, $[\text{C}_6\text{H}_4(\text{OH})\text{COO}]_2\text{Ni} \cdot 4 \text{H}_2\text{O}$. Heating rate $10^\circ/\text{min}$, Wt: 4.180 mg

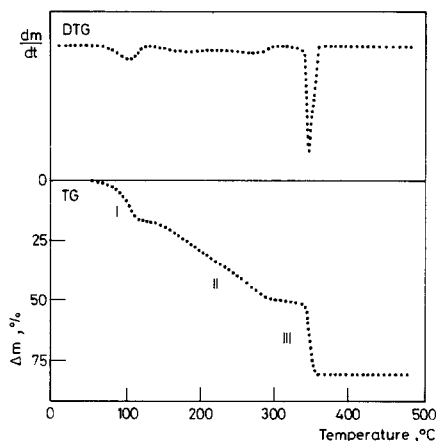


Fig. 2 TG and DTG curves of cobalt salicylate, $[\text{C}_6\text{H}_4(\text{OH})\text{COO}]_2\text{Co} \cdot 3 \text{H}_2\text{O}$. Heating rate $10^\circ/\text{min}$, Wt: 6.518 mg

To study the intermediates in the decompositions, samples of the obtained salicylates were heated in an oven at appropriate temperatures (Ni^{II} -salicylate: 120 and 280° ; Co^{II} -salicylate: 110 and 260° ; Cd^{II} -salicylate: 150 and 300° ; Cu^{II} -salicylate: 140 and 260°) and analysed. Results are shown in Table 2.

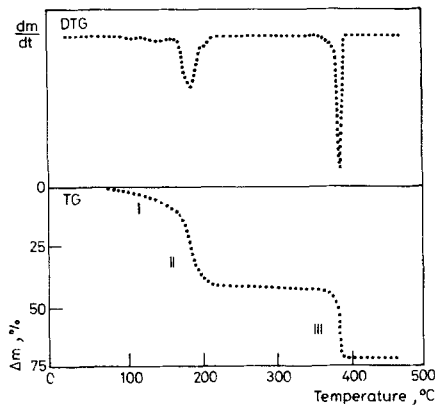


Fig. 3 TG and DTG curves of cadmium salicylate, $[\text{C}_6\text{H}_4(\text{OH})\text{COO}]_2\text{Cd} \cdot 2\text{H}_2\text{O}$. Heating rate $10^\circ/\text{min}$, Wt: 7.071 mg

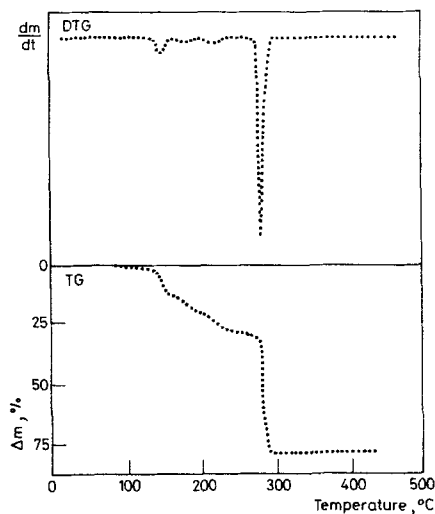


Fig. 4 TG and DTG curves of copper salicylate, $[\text{C}_6\text{H}_4(\text{OH})\text{COO}]_2\text{Cu} \cdot \text{H}_2\text{O}$. Heating rate $10^\circ/\text{min}$, Wt: 4.755 mg

Nickel(II), cobalt(II) and cadmium(II) salicylates

In the thermal decompositions of divalent nickel, cobalt and cadmium salicylates, three distinct stages (I–III) can be observed (Figs 1–3).

In the infrared spectra of the intermediates of composition $[\text{C}_6\text{H}_4(\text{O})\text{COO}]_M$, besides other differences, the band at about 3250 cm^{-1} , due to the OH stretch of the phenolic group [4], is missing. The absorption between 3500 and 3200 cm^{-1} , due to the $\text{O} \dots \text{H}-\text{O}$ stretch, appears only in the spectra of the hydrated salts.

Copper(II) salicylates

In the thermal decomposition of copper(II) salicylate (Fig. 4), the stages listed above for the other salicylates investigated here cannot be distinguished. In order to obtain more evidence about the transformations that occur in copper(II) salicylate between 90 and 300°, samples were heated up to 140 and 260°, the infrared absorption spectra were recorded and elemental analyses were made. In the case of the sample heated up to 140°, the results are in accordance with those calculated for the dehydrated salt (calc. for $C_{14}H_{10}O_6Cu$: C, 49.8, H, 3.0; found: C, 49.5, H, 3.0%). For the sample heated to higher temperature, the elemental analysis data seem to indicate total dehydration and a partial loss of salicylic acid (calc. for $[C_6H_4(O)COO]Cu$. $[C_6H_4(OH)COO]_2Cu$: C, 46.9, H, 2.6; found: C, 46.2, H, 2.8%). The infrared spectrum of the latter sample shows the quasi-complete loss of the absorption corresponding to the OH stretch of the phenolic group at 3250 cm^{-1} , which is intense in the spectra of both the hydrated salt and the sample heated to lower temperature.

In another test, copper(II) salicylate was heated in air up to 250°, and a sublimate and a blackish residue were isolated. The sublimate, m.p. 155–160°, proved to be salicylic acid, identified via its m.p. [5] and its infrared spectrum. The blackish residue was treated with conc. hydrochloric acid and was shaken with ethyl ether. The ether extract gave a white solid, m.p. 156–160°, identified as salicylic acid via its m.p. and infrared spectrum.

It is probable that copper(II) salicylate undergoes thermal decomposition in the same way as the other salicylates investigated here and similarly to the alkaline earth metal salicylates. However, the intermediates, which could be isolated in the other cases, may not be stable under the given experimental conditions. This is the reason why the stages listed above cannot be distinguished.

* * *

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References

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Zusammenfassung — Die thermische Zersetzung von divalentem Kobalt-, Cadmium-, Nickel- und Kupfersalicylat und von während der Zersetzungsprozesse gebildeten Zwischenprodukten wurde thermogravimetrisch untersucht. Mit Ausnahme von Kupfer(II)-salicylat konnten in jedem Falle zwei intermediäre Produkte identifiziert werden.

Резюме — С помощью термогравиметрии исследовано термическое разложение салицилатов двухвалентных кобальта, кадмия, никеля и меди, а также промежуточных продуктов, образующихся в процессах разложения. В каждом случае, за исключением салицилата меди, были идентифицированы два промежуточных продукта.