

## THE MECHANISM OF THERMAL DECOMPOSITION OF $\text{Co}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$

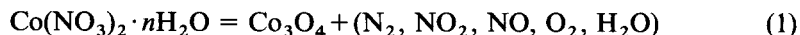
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The mechanism of thermal decomposition of  $\text{Co}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  was found to involve stages in which  $\text{Co}(\text{NO}_3)_3$  and  $\text{Co}_2\text{O}_3 \cdot \text{H}_2\text{O}$  are formed both of which decompose to  $\text{Co}_3\text{O}_4$ . During the process, the total cobalt enters the +3 oxidation state, which is consistent with the results reported by Mehandjiev [2].

The thermal decomposition of  $\text{Co}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  is a characteristic heterogeneous reaction of the type: solid  $\rightarrow$  solid + gas, which can be written as



The formulae in brackets on the right-hand side of this equation merely specify the gases evolved, without any details concerning their quantities. Their relative proportions in the gaseous products of decomposition depend on the conditions under which the reaction is carried out. A detailed thermal decomposition mechanism for  $\text{Co}(\text{NO}_3)_2$  and its hydrates has not yet been reported. It is generally assumed that the decomposition of  $\text{Co}(\text{NO}_3)_2$  hydrates involves a dehydration stage, followed by decomposition of an anhydrous compound to  $\text{Co}_3\text{O}_4$ . It has also been found that the decomposition of anhydrous  $\text{Co}(\text{NO}_3)_2$  proceeds in stages. Thermogravimetric studies have shown that the dehydration of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  proceeds in stages through the tetrahydrate, bihydrate and monohydrate, and leads to the anhydrous salt [1].

While measuring the effective magnetic moment ( $\mu$ ) of the  $\text{Co}^{2+}$  ions during the process of decomposition, Mehandjiev [2] found a minimum in  $\mu$  at a degree of decomposition equal to 0.9 (Fig. 1). This means that the content of  $\text{Co}^{2+}$  ions in the sample at this moment is lower than that in  $\text{Co}_3\text{O}_4$ , which is the final product of decomposition. This result suggests the formation of intermediate phases during

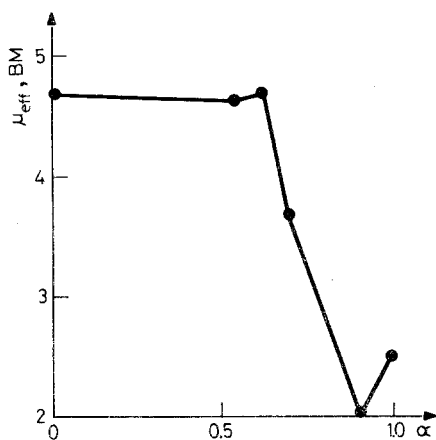


Fig. 1 Changes in the effective magnetic moment of the Co-ion for different decomposition degrees of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  [1]

the decomposition. In the present paper, an attempt is made to explain the mechanism of thermal decomposition of  $\text{Co}(\text{NO}_3)_2$ , the decomposition stages and intermediate phases are identified and chemical equations consistent with the findings are proposed.

### Experimental

$\text{Co}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  obtained by drying  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (pure for analysis) under reduced pressure (130 Pa) at 400 K was used in the investigations. Thermogravimetric analysis showed that the obtained substance had the composition  $\text{Co}(\text{NO}_3)_2 \cdot (2 \pm 0.05)\text{H}_2\text{O}$ . The following experimental methods were used: differential thermal analysis (DTA), chemical analysis of the solid products of decomposition, and mass spectral analysis of the gaseous products of decomposition. The DTA measurements were carried out on a derivatograph at different heating rates (0.06–10 deg/min) in air at atmospheric pressure.

Measurements at ca. 1 Pa were also made. Contents of  $\text{Co}^{2+}$ ,  $\text{Co}^{3+}$  and  $\text{NO}_3^-$  ions were analyzed in a number of specimens after different reaction degrees from 0.2 to 0.8. Mass spectral analysis was performed with an LKB 9000 S mass spectrometer coupled with a gas chromatograph.

## Results and discussion

Preliminary studies revealed that the true thermal decomposition of  $\text{Co}(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$  for  $n > 2$  is analogous to that of  $\text{Co}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ , the only differences relating to dehydration processes which do not lead to  $\text{Co}(\text{NO}_3)_2$  destruction. This facilitates a comparison between our results and those obtained by Mehandjiev for  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ . Further, it was found that the thermal decomposition of  $\text{Co}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  proceeds in stages. Figure 2 presents as an example DTA lines for the thermal decomposition at heating rates of 1.25 and 2.5 deg/min in air. Figure 3 presents the DTA and TG curves for  $\text{Co}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  decomposition in air at a heating rate of 2.5 deg/min. It can be seen that the stages of thermal decomposition of  $\text{Co}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  are not distinctly separated, and the shapes of the DTA curves depend on the rate of heating. This last phenomenon is conditioned by the differences in the kinetics of the intermediate reactions. The DTA curves for decomposition at ca. 1 Pa (Fig. 4) show a slightly better resolution and are independent of the heating rate. Therefore, a number of chemical analyses were performed to determine the chemical compositions of samples after different degrees of decomposition. Chemical analysis of the sample after decomposition corresponding to the first endothermic peak in the DTA curve showed that the dehydration and degradation of  $\text{Co}(\text{NO}_3)_2$  proceed simultaneously. In this stage of decomposition, the sample consists of two phases: a water-soluble one and a black

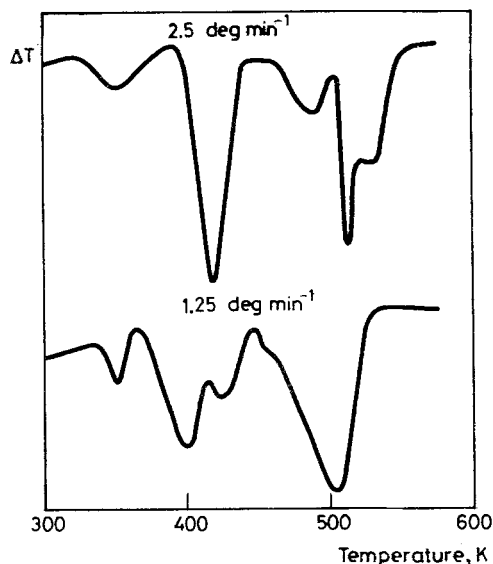


Fig. 2 DTA curves for thermal decomposition of  $\text{Co}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  in air at different rates of heating

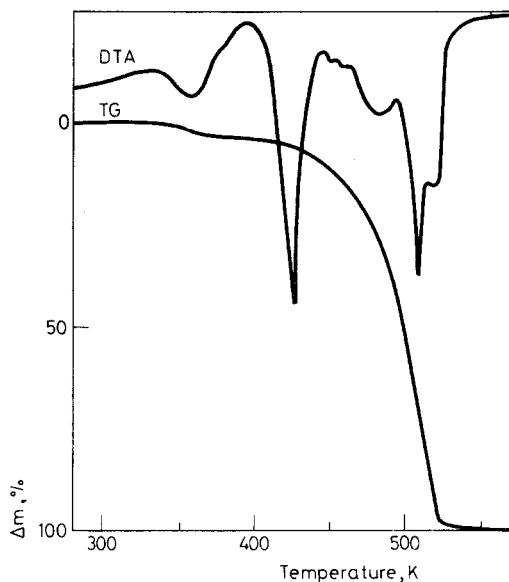


Fig. 3 DTA and TG curves for  $\text{Co}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  decomposition in air at 2.5 deg/min rate of heating

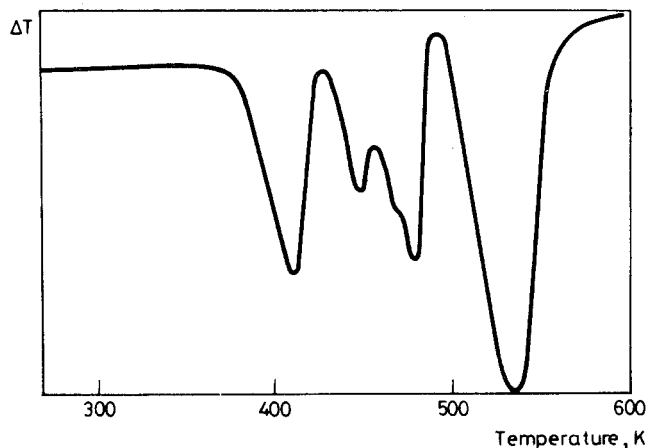


Fig. 4 Vacuum DTA curve of  $\text{Co}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  decomposition

powder insoluble in water. The analysis of  $\text{NO}_3^-$ ,  $\text{Co}^{2+}$  and  $\text{Co}^{3+}$  ions in the water-soluble part clearly showed that  $\text{Co}(\text{NO}_3)_3$  has been formed, and was soluble together with undecomposed  $\text{Co}(\text{NO}_3)_2$ . The black powder insoluble in water was identified as  $\text{Co}_2\text{O}_3 \cdot \text{H}_2\text{O}$ . With the advance of the reaction, an accumulation of  $\text{Co}_2\text{O}_3 \cdot \text{H}_2\text{O}$  was observed, with the persistent presence of  $\text{Co}(\text{NO}_3)_3$ . Ther-

mogravimetric analysis of the thermal decomposition of pure  $\text{Co}_2\text{O}_3 \cdot \text{H}_2\text{O}$  revealed that this compound decomposes to  $\text{Co}_3\text{O}_4$  at the temperature corresponding to the last endothermic peak in the DTA curve of  $\text{Co}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  decomposition. However, the presence of  $\text{Co}_3\text{O}_4$  in the decomposition products can be observed at lower temperatures. This indicates that  $\text{Co}_3\text{O}_4$ , the final product of  $\text{Co}(\text{NO}_3)_2$  decomposition, is not only formed through the decomposition of  $\text{Co}_2\text{O}_3 \cdot \text{H}_2\text{O}$ .

Apart from the chemical analysis of the solid products of decomposition mass spectrometric analysis of the gaseous products of decomposition was also carried out. These analyses were performed under polythermal conditions of decomposition, at a heating rate of 3 deg/min in vacuum, to avoid any contact with oxygen. Figure 5 presents the composition of the gaseous mixture above the decomposing sample as a function of temperature. It can be seen that,  $\text{H}_2\text{O}$ ,  $\text{NO}$  and  $\text{NO}_2$  are evolved in the initial stage (up to 440 K). In the next stage,  $\text{NO}_2$  disappears and the thermal decomposition of  $\text{NO}_3^-$  groups proceeds with the evolution of nitrogen and  $\text{NO}$  only. This means that the mechanism of decomposition of  $\text{NO}_3^-$  groups changes in this stage.

Hence, the following reaction can be proposed for the first stage of thermal decomposition of  $\text{Co}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ :

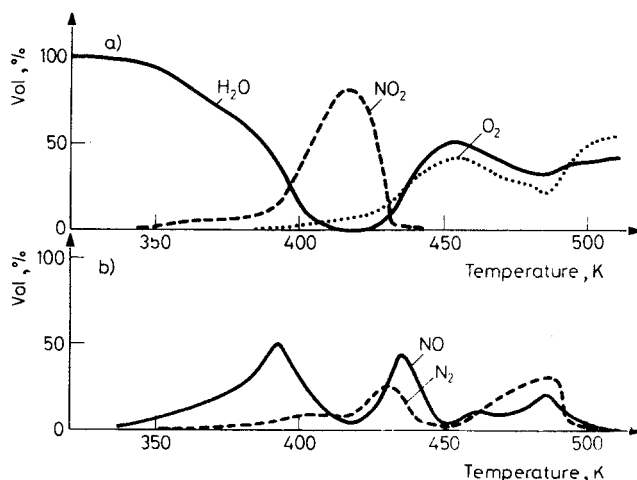
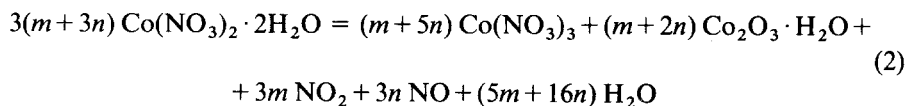
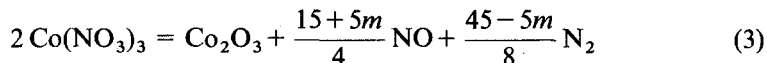
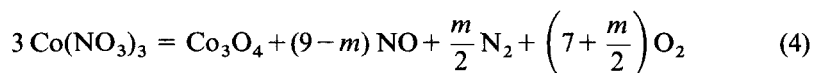


Fig. 5 The composition of gaseous mixture above decomposing  $\text{Co}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  as a function of temperature. a) —  $\text{H}_2\text{O}$ , ---  $\text{NO}_2$ , .....  $\text{O}_2$ ; b) —  $\text{NO}$ , ---  $\text{N}_2$

The change in the mechanism of decomposition of the  $\text{NO}_3^-$  groups in the second stage is related to the decomposition of  $\text{Co}(\text{NO}_3)_3$ , which has been found as an intermediate.  $\text{Co}(\text{NO}_3)_3$  can decompose according to the following equations:

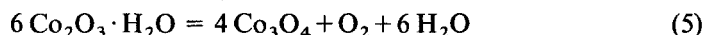


or



A detailed explanation of the mechanism of thermal decomposition of  $\text{Co}(\text{NO}_3)_3$  was impossible, due to our inability to obtain a pure compound. On the basis of our results, therefore it can be stated that either or both of the above reactions take place.

The formation of  $\text{Co}_2\text{O}_3 \cdot \text{H}_2\text{O}$  in the first stage is confirmed by chemical analysis of the solid products of decomposition, and also by analysis of the gaseous products. It is seen in Fig. 5 that the content of water in the gaseous products of decomposition first decreases to zero, as a function of temperature, and next increases, with a simultaneous rise in the oxygen content. This corresponds to the last stage of the decomposition reaction, which proceeds according to the following equation:



To summarize:

—  $\text{Co}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  decomposition proceeds in stages, through the formation of  $\text{Co}(\text{NO}_3)_3$  and  $\text{Co}_2\text{O}_3 \cdot \text{H}_2\text{O}$ .

—  $\text{Co}_3\text{O}_4$  formation is mainly a result of  $\text{Co}_2\text{O}_3 \cdot \text{H}_2\text{O}$  decomposition but we can not exclude the possibility that some of it is formed in  $\text{Co}(\text{NO}_3)_3$  decomposition.

— The results indicate that  $\text{Co}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  decomposition proceeds in stages, in which the total cobalt enters the +3 oxidation state, the average oxidation number of the cobalt present during the process being higher than that in  $\text{Co}_3\text{O}_4$ . This is consistent with the results of magnetic studies reported by Mehandjiev [2].

## References

- 1 D. Weigel, Bull. Soc. Chim., 4 (1964) 836.
- 2 D. Mehandjiev, E. Zhecheva and S. Angelov, Proc. 9th Int. Symp. Reactivity of solids, Cracow, 1980.

**Zusammenfassung** — Es wurde gefunden, daß der Zersetzungsmechanismus von  $\text{Co}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  Schritte umfaßt, bei denen  $\text{Co}(\text{NO}_3)_3$  sowie  $\text{Co}_2\text{O}_3 \cdot \text{H}_2\text{O}$  gebildet werden, beides weiterzerfallend zu  $\text{Co}_3\text{O}_4$ . Während des Vorganges erreicht das Gesamtkobalt die Oxidationsstufe +3, was mit Ergebnissen von Mehandjiev übereinstimmt [2].

**Резюме** — Установлено, что механизм термического разложения дигидрата нитрата кобальта включает стадии образования безводного нитрата трехвалентного кобальта и моногидрата оксида трехвалентного кобальта, которые разлагаются до  $\text{Co}_3\text{O}_4$ . Во время этого процесса весь кобальт находится в трехвалентном состоянии, что согласается с ранее приведенными в литературе данными.