

## **THERMOANALYTICAL INVESTIGATIONS ON THE DECOMPOSITION OF TRANSITION METAL OXALATE COMPLEXES USING SELECTIVE CO, CO<sub>2</sub> AND H<sub>2</sub>O MONITORS**

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Simultaneous TG, DTG, DTA measurements along with the continuous and selective monitoring of carbon monoxide, carbon dioxide and water evolved were carried out on  $K_3[M(C_2O_4)_3] \cdot 3H_2O$ -type transition metal complexes (where  $M = Cr, Fe$  and  $Co$ ). Based on the comparison of the recorded curves a detailed description of the decomposition mechanism was possible. In the case of the cobalt complex an exothermic process corresponding to modification of electron configuration is superimposed on the endothermic dehydration reaction.

The reduction of the cobalt central atom - dissimilarly to that of chromium and iron - takes place in two steps.

The carbon monoxide detector developed recently proved to be an important tool in the study of the decomposition of these complexes.

Considering the differences in redox properties of the central atoms in  $K_3[M(C_2O_4)_3] \cdot 3H_2O$ -type complexes (where  $M = Cr, Fe$ , and  $Co$ ), different decomposition mechanisms can be anticipated. In the case of oxidizing central atoms (iron and cobalt) the formation of carbon dioxide is expected, while the decomposition of the chromium(III) compound - similarly to that of potassium or calcium oxalate - will certainly give carbon monoxide and carbon dioxide in separate steps.

The UV light induced redox reactions of these complexes have also been studied [1]. It was pointed out that the excitation promotes the transfer of an electron from the oxalate ligand to the metal in iron(III) and cobalt(III) complexes [2]. The decomposition takes place via the formation of an intermediate product,  $K_2[M(C_2O_4)_2]$ , when  $M = Co$ , leading to the immediate

formation of  $MC_2O_4$  if  $M = Fe$ . The difference is attributed to the instability of  $K_2[Fe(C_2O_4)_2]$  [3].

The goal of this work was the elucidation of the thermal decomposition mechanism of  $K_3[M(C_2O_4)_3] \cdot 3H_2O$ -type complexes as well as the demonstration of the advantages of the carbon monoxide detector developed recently [4].

## Experimental

### *Materials used*

The complexes studied were prepared according to established procedures [5]. The stoichiometric composition of the samples was checked by elemental analysis.

### *Instrument*

Thermoanalytical investigations were carried out by means of a Derivatograph C-type complex thermoanalytical instrument (Hungarian Optical Works, Budapest, Hungary). In order to carry out simultaneous carbon monoxide monitoring, the CO detector was connected to the Derivatograph. Dehydration was also followed by the water detector developed earlier [6], while the formation of carbon dioxide was detected by means of a  $CO_2$  monitor under development [7].

Magnetic susceptibility measurements were made by the use of a Sartorius microbalance equipped with a Bruker electromagnet.

A Philips PW 1730/10-type X-ray diffractometer was used to study the composition of the solid residues.

The chemical composition of the freshly prepared complexes was confirmed by a Perkin-Elmer 240 type elemental analyzer.

### *Procedure used*

Thermoanalytical investigations were carried out in nitrogen atmosphere at a heating rate of 5 deg/min. The signals of the carbon monoxide, carbon dioxide, and water detectors were recorded simultaneously along with the TG, DTG, and DTA curves.

Magnetic susceptibility measurements were carried out under vacuum in a quartz crucible. The heating rate was 5 deg/min, reading of the mass and temperature values was made in every two minutes.

## Results and discussion

### Thermal decomposition of $K_3[Cr(C_2O_4)_3] \cdot 3H_2O$

The thermal decomposition curves of 64.08 mg  $K_3[Cr(C_2O_4)_3] \cdot 3H_2O$  and the signals of the carbon monoxide and carbon dioxide detectors are shown in Fig. 1. The thermal decomposition of the complex starts with the removal of crystal water at 102°:

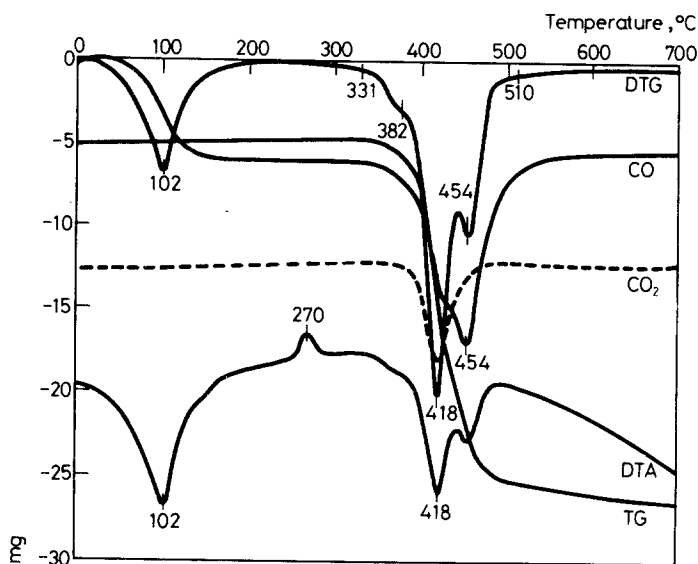
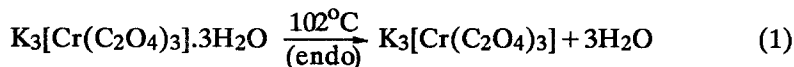
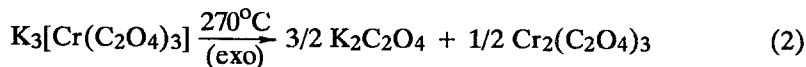
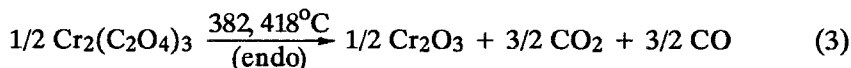


Fig. 1 Thermoanalytical curves of  $K_3[Cr(C_2O_4)_3] \cdot 3H_2O$  and the signals of the CO and CO<sub>2</sub> detectors

After the release of water the mass of the sample remains unchanged within a temperature interval of about 200°. At 270°, however, a sharp exothermic peak is observed which can be due to the formation of chromium(III) oxalate and potassium oxalate mixed crystals:

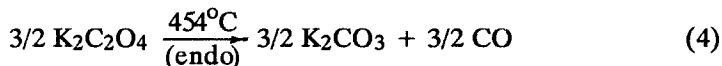


The decomposition of the chromium(III) oxalate component of the sample starts at 331° and is carried out at 382° and 418° according to the following reaction (based on the TG-curve):

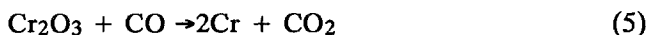


The reaction starts with the liberation of carbon monoxide, but due to the instability of chromium(III) carbonate at this temperature the formation of CO is immediately followed by the liberation of carbon dioxide as well, as indicated by the signal by the carbon dioxide detector.

The decomposition of potassium oxalate takes place at 454° closely overlapped with that of chromium(III) oxalate:



The temperature of the decomposition reaction is some 100° lower than in the case of the crystalline potassium oxalate. This deviation can be explained by structural differences. It is interesting to note that the mass loss observed in reaction (4) is some 15% higher than the theoretical value. Considering the fact that chromium metal was identified by X-ray diffraction in the solid residue it can be stated that chromium(III) oxide is partially reduced by carbon monoxide formed in the reaction:



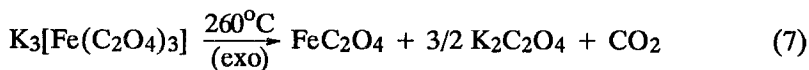
#### *Thermal decomposition of $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_2] \cdot 3\text{H}_2\text{O}$*

The thermoanalytical curves of 57.64 mg  $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$  and the traces of the carbon monoxide and carbon dioxide detectors are shown in Fig. 2. The first decomposition step at 101° belongs to the release of crystal water:



After deaquation the mass of the sample remains unchanged within a temperature interval of more than 100°. At 260° a sharp decomposition stage is observed with no indication of CO formation. Carbon dioxide, how-

ever, is formed in the reaction as indicated by the trace of the carbon dioxide detector accompanied with the reduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$ . Due to the instability of the iron(II) oxalato complex, a structural change (mixed crystal formation) is carried out along the redox reaction indicated by the exothermic peak in the DTA curve:



The separation of iron(II) oxalate and potassium oxalate is further supported by the fact that the decomposition of the two components - dissimilarly to that of the chromium complex - takes place in two separate stages. The melting of iron(II) oxalate is observed at  $381^\circ$  followed by its decomposition to iron(II) oxide at  $406^\circ$  accompanied by the liberation of CO and  $\text{CO}_2$ .

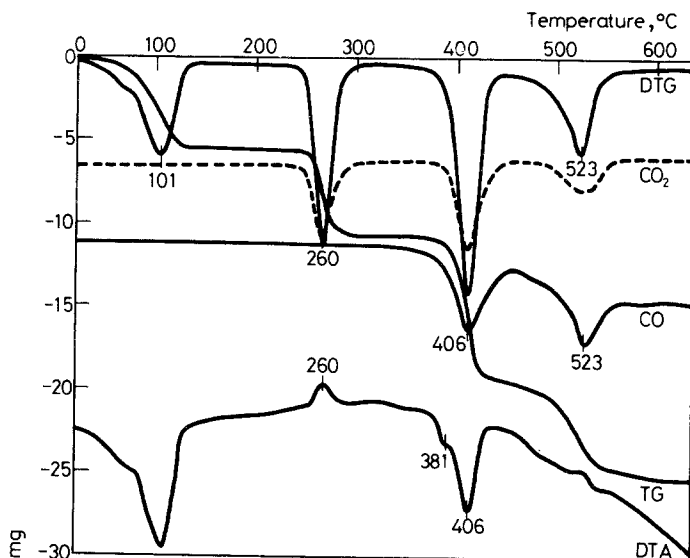
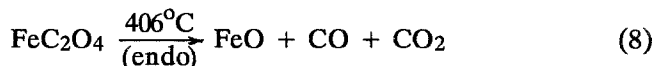


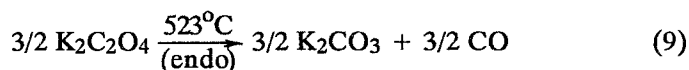
Fig. 2 Thermoanalytical curves of  $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$  including the signal curves of the CO and  $\text{CO}_2$  detectors

The reaction starts with CO formation as indicated by the signal curve of the carbon monoxide detector followed immediately by the decomposition

of the unstable iron(II) carbonate as in the case of the chromium(II) complex:



In the fourth, well-separated decomposition step carbon monoxide is formed:



However, it is interesting to note that the carbon dioxide detector indicates the formation of  $\text{CO}_2$  as well. At the same time the mass loss indicated by the TG curve is some 20% higher than the theoretical values, and the height of the CO-peak recorded by the carbon monoxide detector is lower than expected. Based on these findings it can be concluded that carbon monoxide formed in the decomposition reaction can partially reduce iron(II) oxide resulting in the formation of iron metal:



Beside iron(II) oxide and potassium carbonate, X-ray diffraction measurements clearly showed the presence of iron metal in the decomposition residue further supporting the validity of the proposed reaction mechanism.

#### *Thermal decomposition of $\text{K}_3[\text{Co}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$*

The thermoanalytical curves of 60.25 mg  $\text{K}_3[\text{Co}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$  and the traces of the carbon monoxide, carbon dioxide, and water detectors are shown in Fig. 3. The first decomposition step belongs to the liberation of three moles of crystal water as shown by the signal of the water detector. The DTA curve indicates an endothermic reaction ( $103^\circ$ ) which suddenly turns to an exothermic one at  $123^\circ$ . It can be stated that an exothermic process accompanied with no mass change is superimposed on the endothermic dehydration reaction giving rise to the DTA peak. Since the colour and the magnetic momentum of the heated sample are significantly changed (from deep green to pink and from diamagnetic to strongly paramagnetic, respectively) in this process, it is logical to suppose that a high spin cobalt(III) complex is formed from a low spin one during the deaquation reaction. This process can be due to the increase of temperature and the

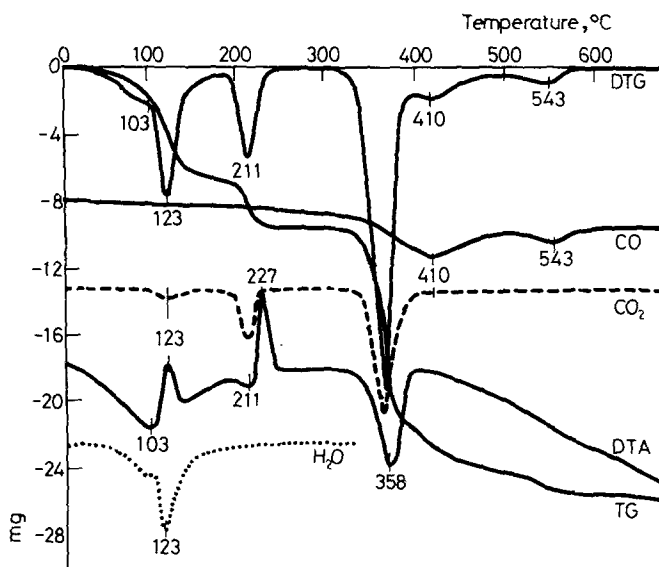


Fig. 3 Thermoanalytical curves of  $K_3[Co(C_2O_4)_3] \cdot 3H_2O$  and the signals of the CO, CO<sub>2</sub> and H<sub>2</sub>O detectors

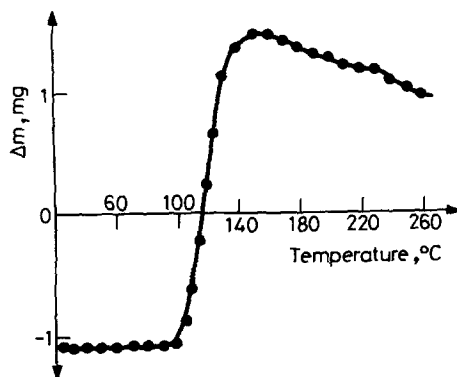
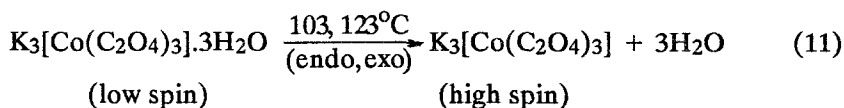


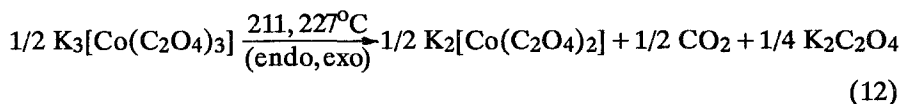
Fig. 4 The change in magnetic behaviour of the  $K_3[Co(C_2O_4)_3] \cdot 3H_2O$  complex in the function of temperature in a constant magnetic field

structural rearrangement of the complex which is less hindered (or not hindered at all) after the removal of water:



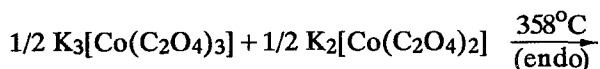
The change in magnetic behaviour of the sample was proved by thermogravimetric measurements carried out in a constant magnetic field. The mass change due to the diamagnetic to paramagnetic transition of the sample is shown in Fig. 4. It is interesting to note that a small amount of carbon dioxide (see the  $\text{CO}_2$  curve) is also formed in the dehydration reaction. This phenomena was first reported by Wendlandt *et al.* [8]. Considering the small amount of carbon dioxide released (about 0.1 mole) it is assumed that its liberation can be due to the substantial amount of heat formed in the sample as well as to the structural change taking place during dehydration.

The second mass loss observed at  $211^\circ$  belongs to the release of half a mole of carbon dioxide as indicated by the signal of the carbon dioxide detector:



The initial endothermic process turns to an exothermic one at  $227^\circ$  indicating that a significant structural change occurs along with the partial reduction of the cobalt(III) complex. A slight decrease in magnetic momentum ( $5.092\mu_B \rightarrow 4.995\mu_B$ ) supports this supposition (see Fig. 4). As a result of the relatively high spin-orbit coupling the magnetic momentum of the stable (tetragonal)  $\text{K}_2[\text{Co}(\text{C}_2\text{O}_4)_2]$  complex - typically of complexes having similar structures - can be expected to be in the 4.6 to 4.8  $\mu_B$  range. The partial reduction results in a decrease of some 0.1 to 0.25  $\mu_B$  in the magnetic momentum which is in conformance with the measured change. In contrast to the earlier proposal [8] no water formation was found in this step of the reaction which supports the validity of the proposed decomposition mechanism.

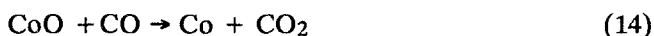
The third step of the TG curve at  $358^\circ$  is the result of the simultaneous decomposition of the cobalt(III) and cobalt(II) complexes:







Surprisingly enough, the signal of the CO-detector reveals the formation of a small amount of CO only, strongly overlapped with the next decomposition step at 410°. In addition, the area under the CO<sub>2</sub> peak as well as the height of the TG step are somewhat higher than expected. Therefore, it can be concluded that cobalt(II) oxide formed is partially reduced by the carbon monoxide released:



The presence of a significant amount of cobalt metal in the solid residue was confirmed by X-ray diffraction measurements.

About one third of potassium oxalate formed in the second and third stages of decomposition is in crystalline state, while the rest is amorphous. The latter one decomposes to potassium carbonate at 410° (CO is released), while the decomposition of the crystalline part is carried out at 543°. This temperature is very close to the literature value [9].

## Conclusions

1. The deaquation of the three transition metal trioxalato complexes takes place practically at the same temperature. In the case of the cobalt complex, however, an exothermic process without mass change - modification in electron configuration - is superimposed on the endothermic dehydration reaction.

2. The deaquated chromium(III) complex undergoes a structural change in an exothermic process without mass loss resulting in the formation of chromium(III) oxalate-potassium oxalate mixed crystals. In the case of the other two compounds decomposition and structural rearrangement start with the intramolecular redox reaction of the complex anion having 6-fold coordination and D<sub>3d</sub> symmetry.

3. The reduction of the trioxalatoferrate(III) complex is complete in one step. Since the Fe<sup>2+</sup> ion cannot form a stable coordination compound with the oxalate anion, FeC<sub>2</sub>O<sub>4</sub> and K<sub>2</sub>C<sub>2</sub>O<sub>4</sub> are formed.

4. As to the first redox reaction of the cobalt(III) complex every other Co<sup>3+</sup>-ion is reduced leading to the formation of tetragonal dioxalato cobaltate. In the next step the simultaneous decomposition of the cobalt(III) and cobalt(II) complexes takes place.

5. About one third of potassium oxalate formed is in crystalline state, while the rest is amorphous resulting in two separate decomposition stages at 410° and 543°.

6. Significant amount of metal was found in the solid residue in all the three cases. This is due to the high temperature reduction of oxides by carbon monoxide.

7. The use of the carbon monoxide detector connected to thermoanalytical equipment can contribute to the better understanding of thermal decomposition processes. In the case of the above complexes the interpretation of the TG, DTG, and DTA curves would hardly be possible without the simultaneously recorded CO, CO<sub>2</sub> and H<sub>2</sub>O curves. In figuring out the decomposition mechanism both the qualitative and the semi-quantitative features of the devices are essentially needed.

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**Zusammenfassung** — Unter gleichzeitiger kontinuierlicher Bestimmung des freigesetzten Kohlenmonoxides, Kohlendioxides und Wassers wurden an Übergangsmetallkomplexen des Types  $K_3[M(C_2O_4)_3] \cdot 3H_2O$  (mit  $M = Cr, Fe$  und  $Co$ ) simultane TG-, DTG- und DTA-Messungen durchgeführt. Der Vergleich der aufgezeichneten Kurven ermöglichte eine ausführliche Beschreibung des Zersetzungsmechanismus. Im Falle des Kobaltkomplexes wird die endotherme Dehydratationsreaktion durch einen exothermen Vorgang (Änderung der Elektronenkonfiguration) überlagert.

Die Reduktion des zentralen Kobaltatoms verläuft im Unterschied zu der von Chrom und Eisen in zwei Schritten.

Der zuvor entwickelte Kohlenmonoxid-detektor erwies sich als ein wichtiges Instrument bei der Untersuchung der Zersetzung dieser Komplexe.