

## THERMAL DECOMPOSITION OF $\text{Cu(II)(C}_4\text{H}_4\text{O}_6) \cdot 3\text{H}_2\text{O}$ AND $\text{Co(II)(C}_4\text{H}_4\text{O}_6) \cdot 2.5\text{H}_2\text{O}$ . DETERMINATION OF MECHANISM BY MEANS OF SIMULTANEOUS THERMAL ANALYSIS AND MASS SPECTROMETRY

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### ABSTRACT

The correct thermal decomposition mechanism of  $\text{Cu(C}_4\text{H}_4\text{O}_6) \cdot 3\text{H}_2\text{O}$  and  $\text{Co(C}_4\text{H}_4\text{O}_6) \cdot 2.5\text{H}_2\text{O}$  was established using simultaneous thermal analysis (TG, DTG, DTA) and mass spectrometry (MS) under inert gas atmosphere (Ar). The reaction mechanism was found to be endothermic and radical in nature for the  $\text{M(C}_4\text{H}_4\text{O}_6)$  decomposition. Mass spectrometry proved the primary gaseous decomposition products to be  $\text{H}_2\text{O}$  and  $\text{C}_4\text{H}_4\text{O}_6^{2-}$ , the tartrate diradical. This diradical itself showed a characteristic degradation scheme towards smaller and more stable molecules like  $\text{H}_2\text{O}$ ,  $\text{CO}_2$  and  $\text{CO}$ . The formation of the metals Cu and Co could be proved by X-ray and TG experiments.

### INTRODUCTION

Thermal analysis—thermogravimetry (TG), differential thermogravimetry (DTG), and differential thermoanalysis (DTA)—and mass spectrometry (MS) are widespread and helpful instruments in the hands of the chemist to reveal the energetics of phase transitions and chemical reactions, the thermal stabilities of educts and products as well as the nature and consistency of gaseous reaction products. Of itself thermal analysis provides only weak clues pertaining to reaction mechanisms, especially for the gaseous reaction products of thermal decomposition reactions. This is the principal shortcoming of the method but can be overcome by the use of a combined TA and MS thermoanalyzer, which allows combined and simultaneous monitoring of discrete TG, DTG, DTA and MS signals and curves and their correlation with temperature.

In this paper we will report on simultaneous TA and MS experiments made on two *d*-element ( $\text{M}^{2+}$ ) tartrate hydrate salts,  $\text{Cu(C}_4\text{H}_4\text{O}_6) \cdot 3\text{H}_2\text{O}$  and  $\text{Co(C}_4\text{H}_4\text{O}_6) \cdot 2.5\text{H}_2\text{O}$ . The thermal behaviour of these and similar compounds has been reported repeatedly [1–7]. The experimental results published by these authors always contained the statement that the decom-

position mechanism was a two-step mechanism, the first step being an endothermic dehydration reaction, whereas the second step was an exothermic reaction yielding the transition metal oxides. This type of reaction mechanism, for the second step, was not found to be true. We repeatedly found, under the standard condition of an inert gas atmosphere (in this case Ar), that the second step was endothermic, yielding the metals, especially for the copper salt reaction, which we examined first in the course of our hydrogen bonding and hydrate water reactivity programme. To confirm the reproducibility of this reaction scheme we also proved it for the Co compound, which was found to be analogous. In both cases the metallic character of the residue was pointed out by weight loss and X-ray analysis. These experiments will be continued for other *d*-element ( $M^{2+}$ ) tartrate hydrate salts. Efforts are also made to prepare these compounds in the form of single crystals, as only such crystals guarantee a sufficient exclusion of impurities and homogeneous material.

By this, the endothermic tartrate decomposition and the metallic residue, we decided to confirm the decomposition mechanism by means of mass spectrometry. This method in fact enabled us to monitor reproducibly the  $C_4H_4O_6$  particle, most probably the diradical, to be the first particle to be eliminated from the tartrate in the course of the endothermic reaction down to the metal, a type of metal formation by means of a dicarboxylic acid salt decomposition, which could be proved for Ni oxalate by Dollimore [8]. Discrete fragments of the tartrate diradical apparently appearing synchronously and monitored by simultaneous MS confirmed the reaction mechanism, which will be discussed later.

A reference search pertaining to the instrumentation of previous workers [9] confirmed that these authors either worked in air or in an "inert gas" atmosphere not pure enough to exclude oxidation of the metal formed in the course of the tartrate decomposition reaction.

## EXPERIMENTAL

The compounds in question,  $Cu(C_4H_4O_6) \cdot 3 H_2O$  and  $Co(C_4H_4O_6) \cdot 2.5 H_2O$ , were prepared in the form of single crystals, ca. 2 mm in diameter, by the gel-growth method in U-tubes. The sodium silicate gel used was prepared from a commercial sodium silicate solution with a  $Na_2O:SiO_2$  ratio of 1:2.85, having a  $H_2O$  content of 63% (wt. %). The gel was precipitated by acetic acid.

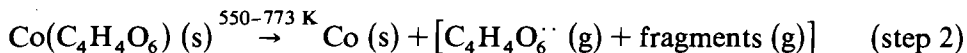
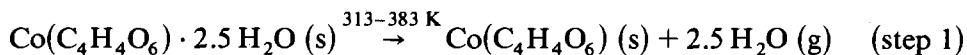
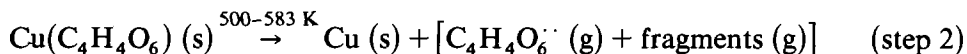
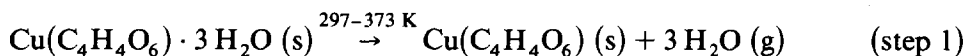
The TG, DTG- and DTA thermoanalytic experiments were carried out on a Netzsch STA 429 thermoanalyzer. The mass spectrometric results were obtained simultaneously with the TA results employing a Balzers QMG 511 quadrupole mass spectrometer. A constant molecular beam directed into the high vacuum of the mass spectrometer of  $10^{-6}$  mbar was kept upright by the

use of a heated Pt capillary tube with an inner diameter of 0.15 mm and a length of 120 mm, and an input orifice of 0.1 mm. The capillary tube was situated directly above the sample, as an integrated part of a special furnace for combined TA and MS experiments. As the instrumentation of our mass spectrometer allows monitoring either a mass scan up to  $m/e = 511$  or a continuous scan of the maxima of 12 selected masses ( $m/e$ ), both attempts were made to secure the mechanism. The 12 masses represent the most intensive masses recorded in the course of the overall scan. The instrumentation of our mass spectrometer is similar to that described by Eppler and Selhofer [10] and Yuen et al. [11].

The accompanying X-ray experiments were carried out on a Guinier-heating camera ( $\lambda = \text{Cu}K_{\alpha 1}$ ) and a Guinier camera system 621 (Huber/Rimsting) ( $\lambda = \text{Cu}K_{\alpha 1}$ ). The heating camera was built for open-system experiments (air) so that on the heating photographs only the diffraction patterns of CuO and  $\text{Co}_3\text{O}_4$  showed up and not those of the metals Cu and Co. Due to their thermal instability with the loss of  $\text{H}_2\text{O}$  in normal air and in a dry inert gas atmosphere ( $T = 298 \text{ K}$ ), the compounds were not ground for thermoanalytical treatment in order to reduce their surface.

## RESULTS AND DISCUSSION

The results of the simultaneous TG, DTG, DTA and MS thermal decomposition experiments are shown in Figs. 1 and 2 for  $\text{Cu}(\text{C}_4\text{H}_4\text{O}_6) \cdot 3 \text{H}_2\text{O}$  and  $\text{Co}(\text{C}_4\text{H}_4\text{O}_6) \cdot 2.5 \text{H}_2\text{O}$ , respectively. The curves in Figs. 1a and 2a show the TA experimental results whereas Figs. 1b and 2b show the corresponding and simultaneous MS curves. The TG, DTG, and DTA curves in Figs. 1a and 2a show that the thermal decomposition reactions of both the Cu and the Co compounds take place in the two endothermic reaction steps as described below, i.e., under inert and pure Ar atmosphere conditions.



The curves in Figs. 1b and 2b show the simultaneously monitored ionic currents of the 12 most intensive masses, i.e.  $m/e$ . They are formed in the course of the thermal decomposition reactions of both tartrate hydrate salts and are:

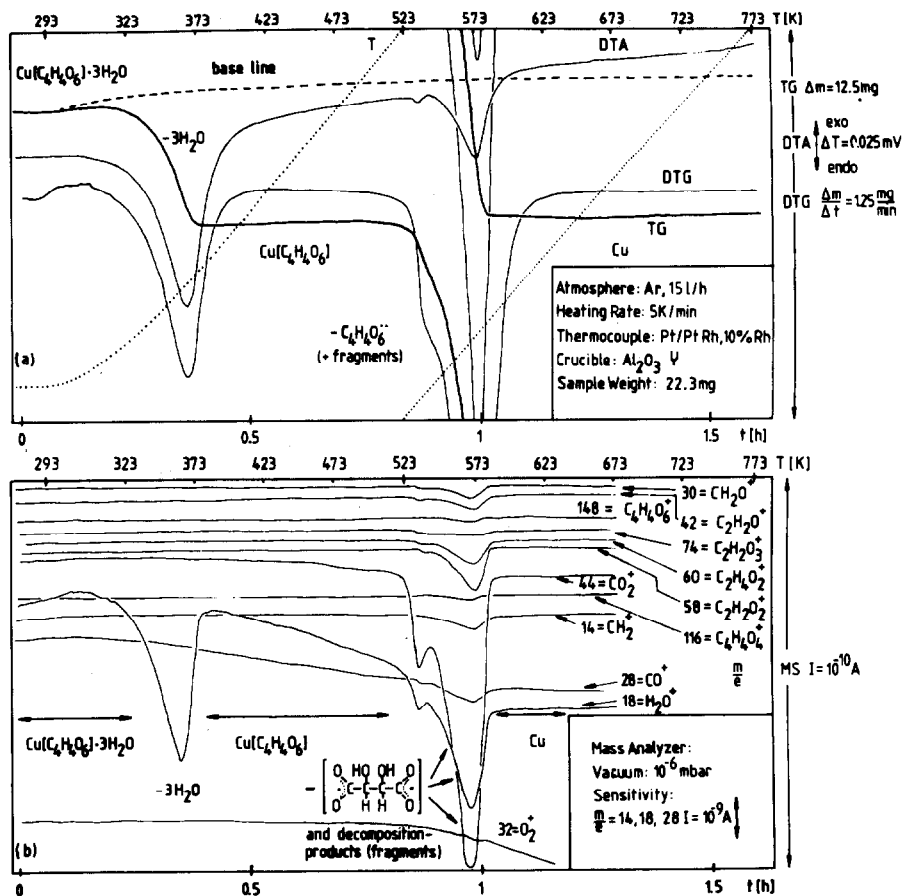
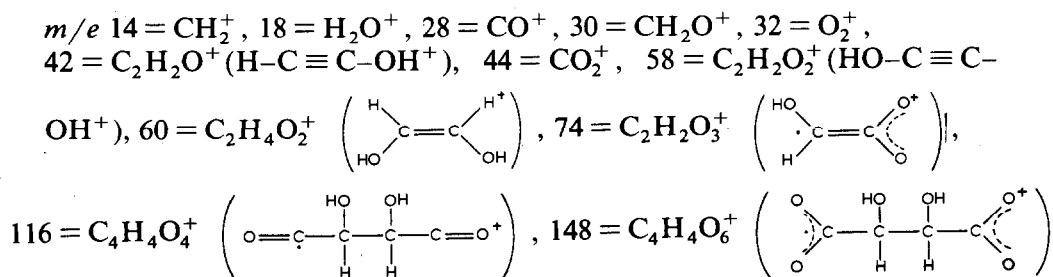


Fig. 1. Thermal analysis (TG, DTG, DTA) and MS curves for copper tartrate trihydrate,  $\text{Cu}(\text{C}_4\text{H}_4\text{O}_6) \cdot 3\text{H}_2\text{O}$ , studied under a purified Ar atmosphere. (a) Thermal analysis (TG, DTG and DTA) curves of the copper tartrate trihydrate decomposition reaction between 293 and 773 K, showing the decomposition steps down to Cu and the TG base line. (b) MS curves of the 12 most intensive mass signals of the copper tartrate trihydrate decomposition reaction between 293 and 773 K, showing the dehydration and tartrate decomposition reaction as well as the tartrate fragmentation.



The existence of a small tartrate peak in Figs. 1b and 2b ( $m/e = 148$ ),

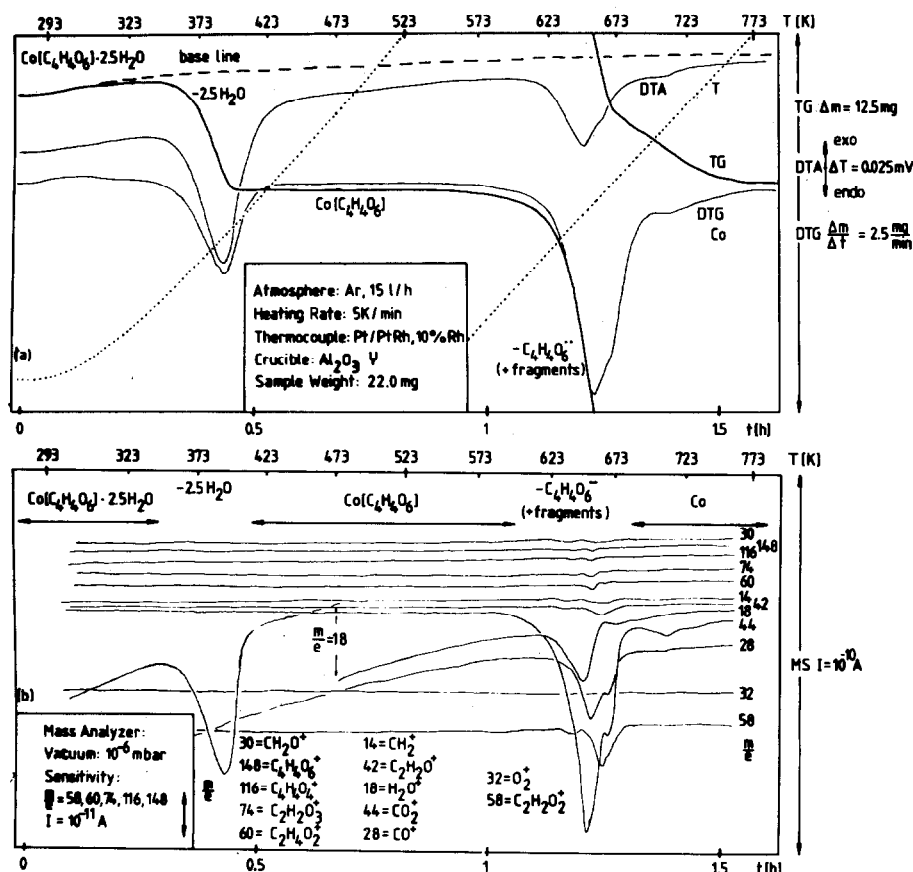
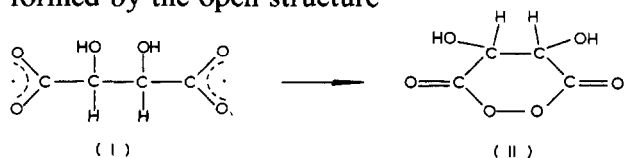


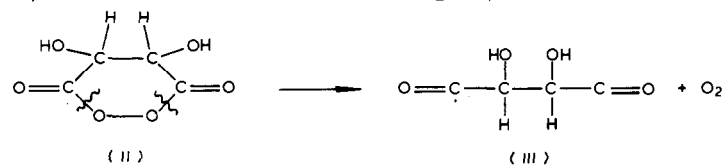
Fig. 2. Thermal analysis (TG, DTG, DTA) and MS curves for cobalt tartrate 2.5-hydrate,  $\text{Co}(\text{C}_4\text{H}_4\text{O}_6) \cdot 2.5 \text{H}_2\text{O}$ , studied under a purified Ar atmosphere. (a) Thermal analysis (TG, DTG and DTA) curves of the cobalt tartrate 2.5-hydrate decomposition reaction between 293 and 773 K, showing the decomposition steps down to Co and the TG base line. (b) MS curves of the 12 most intensive mass signals of the cobalt tartrate 2.5-hydrate decomposition reaction between 293 and 773 K, showing the dehydration and tartrate decomposition reaction as well as the tartrate fragmentation.

induced by the very unstable  $\text{C}_4\text{H}_4\text{O}_6^{\cdot\cdot}$  diradical formed in the course of the decomposition reaction of the anhydrous tartrate, shows that this reaction follows a radical electron-transfer mechanism. This fact is also indicated and proved by X-ray powder diffraction analysis of the TA residues, which always show the powder diffraction pattern of the metals. Other monitored masses, with the exception of  $\text{H}_2\text{O}$  ( $m/e = 18$ ), also being formed in the course of the dehydration reaction (first step), are fragmentation products of the unstable tartrate diradical. Unfortunately, especially for the copper compound reaction, we cannot definitely state that these fragments are formed exclusively in the furnace or in the ion source, a fact that could not even be clarified by changing the ionization voltage. Nevertheless, the results

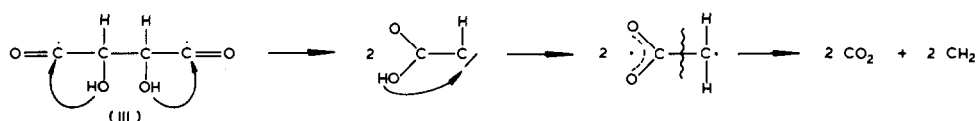
of the Co tartrate hydrate decomposition reaction, which will be discussed later, indicate that the fragments should have been formed in the furnace, i.e., in the sample. Also, we cannot clearly state, with our experimental data and methods, that the monitored tartrate peak ( $m/e = 148$ ) belongs to an open diradical species (I) or to a species built up of a six-membered ring (II) formed by the open structure



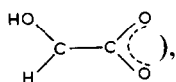
The existence of species (II) is indicated by its decay products  $C_4H_4O_2^{2-}$ ,  $m/e = 116$  [structure (III)], and  $O_2$ ,  $m/e = 32$ .



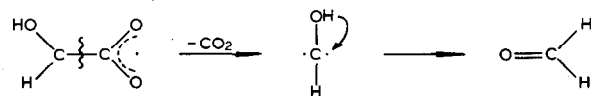
Furthermore, species (II) is also indicated by the appearance of the carbene  $CH_2$  ( $m/e = 14$ ), which can be seen in Figs. 1b and 2b and must have been formed by cleavage of species (III) and subsequent OH and H migration



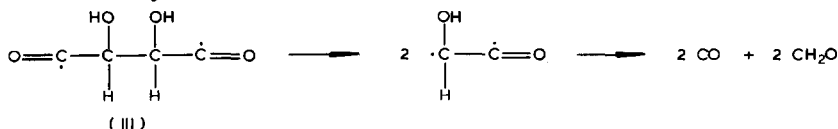
However, the low intensities of the corresponding peaks,  $m/e = 148$ , 116 and 32, make a more detailed discussion of the problem impossible if species (I) or (II) prevails.

Another interesting question comes from the peak  $m/e = 74$ . This peak may either result from the symmetrical half-fragment,  $C_2H_2O_3$  ()

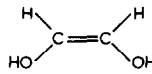
of the tartrate,  $m/e = 148$ , or may be an effect from the ion source, namely  $C_4H_4O_6^{2+}$ . However, this is not very probable because the half-fragment diradical is the most plausible source of  $CH_2O$ , the molecule producing  $CH_2O^+$ ,  $m/e = 30$



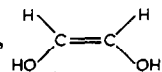
However, the aldehyde molecule may also have been formed in a similar way by a bisection reaction from species (III),  $m/e = 116$ , and a mechanism described by



The half-fragment of species (III),  $m/e = 58$ , has the same mass as the dihydroxyacetylene,  $\text{HO}-\text{C}\equiv\text{C}-\text{OH}$  and may be its source. This type of formation, by H migration, of that molecule seems to be more realistic than

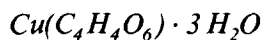
by  $\text{H}_2$  elimination from the ethylene,  ( $m/e = 60$ ), in the

furnace, especially as no hints could be found for an exclusive ion source formation of that molecule.

The dihydroxyethylene and monohydroxyacetylene molecules, 

and  $\text{H}-\text{C}\equiv\text{C}-\text{OH}$  ( $m/e = 60$  and  $42$ ), are either formed by  $\text{CO}_2$  elimination from the tartrate diradical [species (I)] or by  $\text{CO}$  elimination from species (II). Both reactions take place as both ( $\text{CO}_2$  and  $\text{CO}$ ) show up in Figs. 1b and 2b. Nevertheless, from the high intensity of the  $\text{CO}_2$  signal, clearly seen in Figs. 1b and 2b, one must suppose the  $\text{CO}_2$  elimination from the tartrate diradical to be more realistic. The acetylene,  $m/e = 42$ , is formed from the ethylene by  $\text{H}_2\text{O}$  elimination.

Although all masses observed in the course of the thermal decomposition reactions of both tartrate hydrates were identical, some characteristic differences do exist between their decomposition reactions, as shown by Figs. 1a and 2a. These results will be reported and discussed separately.



As indicated in Fig. 1, the copper compound,  $\text{Cu}(\text{C}_4\text{H}_4\text{O}_6) \cdot 3 \text{H}_2\text{O}$ , is a relatively unstable substance. This fact is clearly seen when comparing the TG curve with the TG base line. The superposition of both curves reveals a significant  $\text{H}_2\text{O}$  loss even at room temperature (298 K) which furthermore explains why the compound can only be stored for a longer period of time under closed system conditions and a  $\text{H}_2\text{O}$ -saturated atmosphere. The TG base line, which represents the changes in the buoyancy of a given sample, was obtained by heating an inert sample under the same experimental conditions as the sample in question.

The decomposition of the copper tartrate hydrate brings about  $\text{Cu}(\text{C}_4\text{H}_4\text{O}_6)$  at 297 K which exists up to 523 K, at which temperature it decomposes to  $\text{Cu}$  (s) and a couple of gaseous reaction products, which are formed as described. The decomposition of the Cu tartrate is characterized, as shown by the curves in Fig. 1a, by a two-step mechanism; this can also be observed from the MS curves in Fig. 2b. The reaction is endothermic and not exothermic, as described by previous authors [1-7]. Such an exothermic behaviour is an effect of oxidation in air or not sufficiently purified "inert atmosphere". This endothermic reaction shows a two-peak scheme on the DTA curve. The little precursor peak may be interpreted, as indicated by

slight changes in the diffraction pattern on the X-ray heating diagram, by a preceding solid–solid phase transition that initiates the decomposition reaction. This special behaviour is the subject of our present DSC and X-ray experiments on  $\text{Cu}(\text{C}_4\text{H}_4\text{O}_6)$  in the temperature region in question. It is furthermore interesting that all monitored masses show simultaneously that two-peak reaction scheme, in contrast to the Co compound.



As shown by the TG curve and the superposed TG base line in Fig. 2a, the Co compound is more stable than the copper compound. This fact is also described by Frei et al. [2,7]. It is therefore no longer necessary to take similar precautions for the long-time storage than for the Cu compound. Nevertheless, the ground material shows significant  $\text{H}_2\text{O}$  loss when stored in dry air and also when it is taken in the dry Ar atmosphere of the thermobalance even at room temperature. So, in order to avoid any false interpretation of the results, only the crystals were examined.

The hydrate salt decomposition, as shown in Fig. 2a, begins at about 313 K, some 15 K later than the copper compound. Exactly as in the case of  $\text{Cu}(\text{C}_4\text{H}_4\text{O}_6) \cdot 3 \text{H}_2\text{O}$ , the dehydration is a one-step reaction down to the tartrate,  $\text{Co}(\text{C}_4\text{H}_4\text{O}_6)$ . The tartrate itself is also more stable than the Cu tartrate, a fact which is clearly evident when comparing the TG, DTG and DTA curves of the corresponding reactions (see Figs. 1a and 2a). The onset of the tartrate decomposition is at about 613 K, at a heating rate of  $5 \text{ K min}^{-1}$ . As in the case of Cu tartrate, the ranges of the particular decomposition steps observed agree well with those formerly published [2,7]. Nevertheless, the tartrate decomposition is endothermic and not exothermic, as described by these authors.

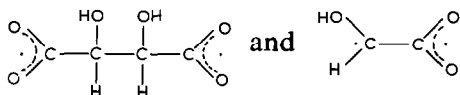
In contrast to the copper tartrate, the cobalt compound shows some peculiarities in the TG, DTG, DTA and MS curves, which indicate that the monitored masses are formed in the furnace or in the crucible during the reaction and not in the ion source of the mass spectrometer as one could also easily suppose. This is because of the non-synchronous reaction scheme and appearance of the tartrate fragments in the mass spectrum, which can be well correlated with the TG, DTG and DTA curves (see Fig. 2). The first masses to be monitored are  $m/e = 44$  ( $\text{CO}_2^+$ ) and 18 ( $\text{H}_2\text{O}^+$ ). Synchronously to these, mass ( $m/e$ ) 58 shows a small preceding peak. Mass 58 represents the acetylene,  $\text{HO}-\text{C}\equiv\text{C}-\text{OH}$ . Chronologically, the next mass to be monitored

is  $m/e = 28$  of CO, formed by CO elimination from  $\text{O}=\text{C}-\underset{\text{H}}{\overset{\text{HO}}{\text{C}}}-\underset{\text{H}}{\overset{\text{OH}}{\text{C}}}-\text{C}=\text{O}$ ,

$\text{C}_4\text{H}_4\text{O}_4$ ,  $m/e = 116$ . Both molecules, CO and  $\text{C}_4\text{H}_4\text{O}_4$ , appear synchronously on the mass spectrum in Fig. 2b.



Of further interest is the fact that the maxima of  $m/e = 58, 42$  and  $14$  coincide with significant minima in the very intensive curves of the masses ( $m/e = 44, 28$  and  $18$ ). This fact can be well correlated with shoulders and changes of the gradient of the TG, DTG and DTA curves, respectively (see Fig. 2a, b). This correlation shows clearly that the masses monitored in the mass spectrometer are formed as molecules in the furnace. In the same temperature range the decomposition reaction shows some acceleration by way of an additional formation of the acetylenes,  $\text{HO}-\text{C}\equiv\text{C}-\text{OH}$  and  $\text{H}-\text{C}\equiv\text{C}-\text{OH}$  ( $m/e = 58$  and  $42$ ), and the carbene,  $\text{CH}_2$  ( $m/e = 14$ ), whose formation has been described herein. In addition to this, the tartrate and its half-fragment



show up clearly and significantly in Fig. 2b, whereas the formaldehyde,  $\text{CH}_2\text{O}$  ( $m/e = 30$ ), is monitored more diffusely than in the course of the copper compound decomposition reaction.

Furthermore, it is interesting to note that the  $\text{CO}_2^+$  MS curve shows an additional peak at  $713\text{ K}$ , coinciding with significant DTA and DTG peaks in Fig. 2a, which is due to the  $\text{CO}_2$  elimination reaction, possibly from  $\text{CoCO}_3$ . The formation of the Co carbonate may be due to a partial oxidation of the Co metal by  $\text{O}_2$  from the six-membered ring tartrate. This explains why  $\text{O}_2^+$  ( $m/e = 32$ ) does not show up on the mass spectrum. In addition, this may also explain why the residue of the Co compound decomposition reaction shows only a rather diffuse X-ray powder diffraction pattern, as opposed to that of the copper compound. This process, i.e., the partial oxidation of the metal, the formation of the carbonate and its decomposition, which causes the low crystallinity of the residue, is a consequence of the less noble character of Co in comparison to Cu, a fact pointed out by Frei and Ederova [7].

In summary, we can say that a compilation of all available data—TG, DTG, DTA, MS and X-ray—shows unambiguously that both compounds follow the same radical decomposition mechanism of the tartrates resulting in the metals and not the oxides. Furthermore, in both cases the reaction is endothermic, provided that it is examined under an inert atmosphere, so that the reaction is not influenced and disturbed by oxidation. A further important fact is that the tartrate fragments are formed in the furnace and in the crucible, respectively, so that their appearance in the mass spectra confirms the mechanism.

#### ACKNOWLEDGEMENT

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