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MÖSSBAUER STUDY OF THE THERMAL DECOMPOSITION OF POTASSIUM TRIS(MALONATO)FERRATE(III) TRIHYDRATE

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ABSTRACT

The thermal decomposition in air of potassium tris(malonato)ferrate(III) trihydrate was investigated up to 550°C using thermogravimetric techniques, X-ray diffraction, infrared spectrophotometry and mainly Mössbauer spectroscopy. It was found that the dehydration occurs between 80 and 110°C. The final products formed were α-Fe_2O_3 and K_2CO_3. The iron-containing intermediate products were identified as a high spin Fe(II) compound which converts into iron metal and Fe_3O_4. A particle size distribution for Fe_3O_4 was also observed, where the particle size increased with the heat treatment temperature. A comparison between the thermal decomposition of the potassium tris(malonato)ferrate(III) trihydrate and its similar potassium (oxalato)ferrate(III) trihydrate was also presented.

INTRODUCTION

Mössbauer effect studies on thermal decomposition of iron(III) dicarboxylates have been reported for compounds containing the ligand oxalate [1,2] ($C_2O_4^{2-}$) and the anion succinate [3] ($C_4H_4O_4^{2-}$) but not the ligand malonate ($C_3H_2O_4^{2-}$), although the thermal decomposition of iron(II) malonate has already been reported [4].

As the malonate has one more CH_2 group than the oxalate, it would be interesting to see how this increased carbon chain affects the electronic properties and the thermal behavior of the iron(III) complexes having dicarboxylates as ligands. In this sense, a comparative Mössbauer study between potassium tris(malonato)ferrate(III) trihydrate and potassium

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tris(oxalato)ferrate(III) trihydrate becomes suitable, once the latter has already been investigated [1,2].

Therefore, in this work Mössbauer spectroscopy has been associated with conventional thermal analysis, X-ray diffraction and infrared spectrophotometry to study the thermal decomposition in air of potassium tris(malonato)ferrate(III) trihydrate, hereafter denoted $K_3[Fe(C_3H_2O_4)_3] \cdot 3H_2O$.

EXPERIMENTAL

Complex preparation and heat treatment

The potassium tris(malonato)ferrate(III) trihydrate was prepared by adapting the method described previously for the preparation of potassium tris(oxalato)ferrate(III) trihydrate [5].

To a solution of ferric sulfate was added potassium malonate and barium malonate with an excess of about 3%. The pH was kept below 2.8 by means of malonic acid. The mixture was stirred for about 15 h on a steam bath and filtered. The filtrate was evaporated to crystallization. The light-green crystallites were dissolved in water and precipitated with ethanol.

The elemental analysis of the synthetized complex led to the following results (%): found: K, 21.12; Fe, 10.94; C, 19.60; H, 2.30; calc. for $K_3[Fe(C_3H_2O_4)_3] \cdot 3H_2O$: K, 21.99; Fe, 10.47; C, 20.27; H, 2.29.

For the thermal decomposition, samples were heated isothermally at different temperatures for 20 min under open atmosphere. Heat treatments up to 260°C were performed using an oil-bath with an accuracy of ± 0.5°C. Above this temperature a muffle furnace was used with an accuracy of ± 5°C.

Measurements

The thermogravimetric-type measurements were carried out in air at a heating rate of 10°C min^{-1} using a Rigaku Denki Co. Ltd. apparatus, which performs simultaneous TG and DTA as a function of temperature. Infrared absorption spectra were recorded on a Perkin-Elmer spectrophotometer (Model 621) and samples were in the form of KBr pellets. Powder X-ray diffractograms were obtained using a Rigaku Denki X-ray diffractometer, with Ni-filtered Cu$K\alpha$ radiation, for angles 2θ from 10 to 90°. Mössbauer data were taken on a conventional constant acceleration spectrometer against a ^{57}Co-Rh source at room temperature. Powdered samples were measured at room and liquid nitrogen temperatures. Mössbauer spectra were computer-fitted on the assumption of Lorentzian line shapes. All isomer shift values are referred to iron metal.

RESULTS AND DISCUSSION

Mössbauer spectra of potassium tris(malonato)ferrate(III) trihydrate measured at 295 K (Fig. 1A) and at 85 K (Fig. 2A) consist of a single broad absorption peak with non-Lorentzian line shape. The full line width at half-height increases from 1.40 to 1.90 mm s^{-1} when the temperature goes from 295 to 85 K. These features are due to electronic spin relaxation effects, which are under investigation and will be reported elsewhere. The same relaxation effect has already been observed for potassium tris(oxalato)ferrate(III) trihydrate [6].

The isomer shift ($\delta = 0.40$ mm s^{-1}) at 295 K is characteristic of Fe(III) in

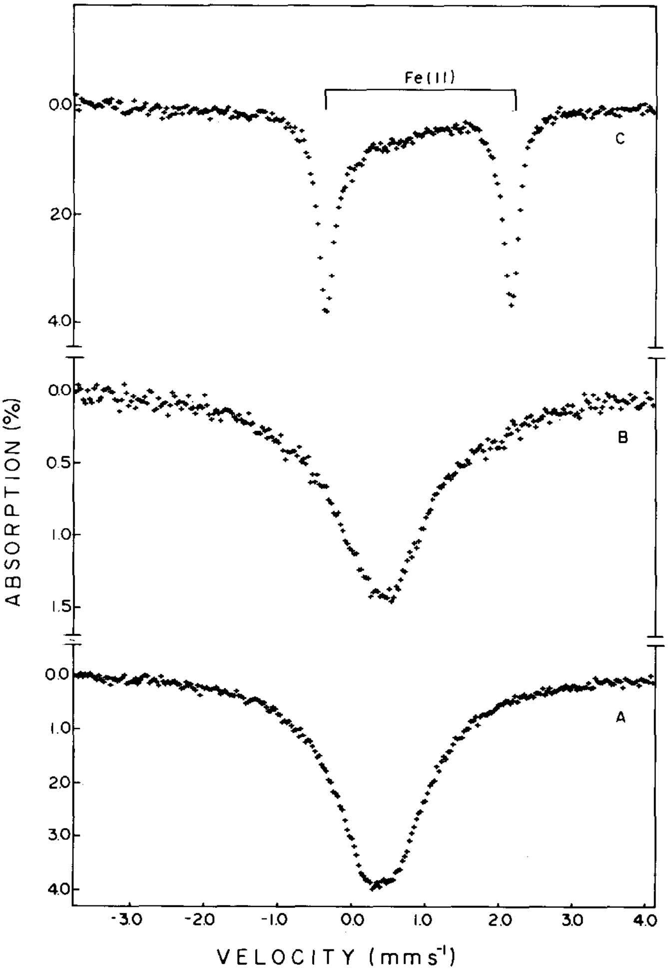

Fig. 1. Mössbauer spectra at 295 K for potassium tris(malonato)ferrate(III) trihydrate samples: (A) unheated; (B) heated at 230°C/20 min; (C) heated at 260°C/60 min.

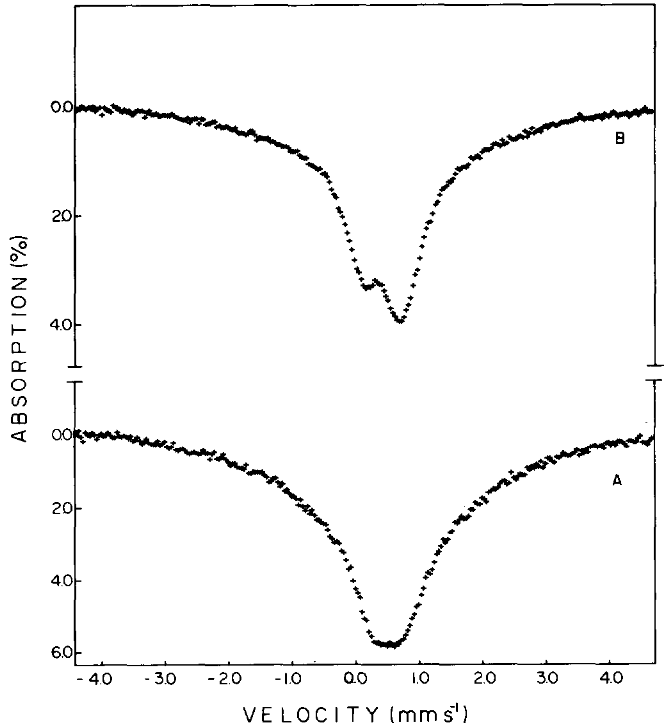

Fig. 2. Mössbauer spectra at 85 K for potassium tris(malonato)ferrate(III) trihydrate samples: (A) unheated; (B) heated at 230°C/20 min.

a high spin state. The higher value ($\delta = 0.40$ mm s^{-1}) for potassium tris(malonato)ferrate(III) trihydrate compared to $\delta = 0.33$ mm s^{-1} for potassium tris(oxalato)ferrate(III) trihydrate [1] indicates greater ionic bonding in Fe(III) malonato than in oxalato. This is in agreement with infrared results [7].

Figure 3 shows the simultaneous TG (——) and DTA (- - - -) plot of potassium tris(malonato)ferrate(III) trihydrate in air, at a heating rate of 10°C $\min^{-1}$.

An endothermic peak between approximately 80 and 110°C is observed in the DTA curve associated with a weight loss of about 10.7% in the TG curve (I). These results are consistent with the elimination of three water molecules of crystallization, which gives a calculated weight loss of 10.1%.

This first step of the thermal decomposition is also supported by a significant change observed in the powder X-ray diffractogram and in the Mössbauer spectra of a sample heated at 230°C for 20 min when compared to the unheated sample. Mössbauer spectra of this heated sample measured at 295 K (Fig. 1B) and at 85 K (Fig. 2B) show a broad, asymmetrical unresolved doublet which could not be fitted to any combination of two Lorentzian lines. The marked change observed in the asymmetry of the

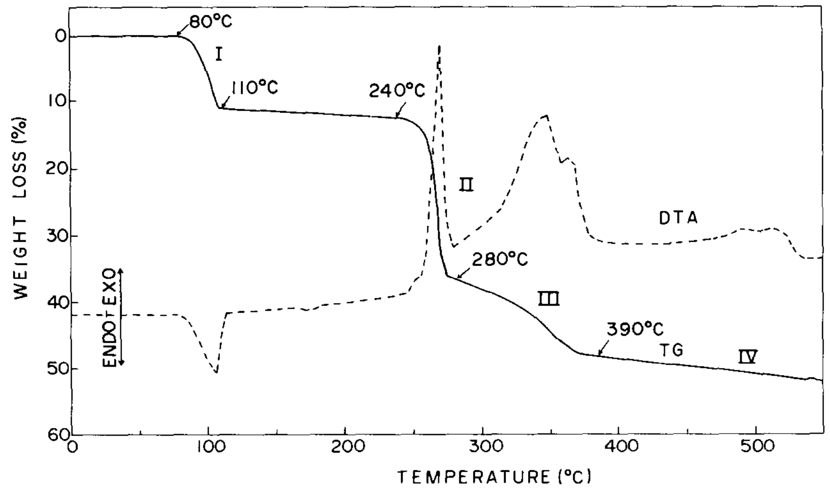

Fig. 3. Thermogravimetric curves of potassium tris(malonato)ferrate(III) trihydrate in air at heating rate of 10°C min^{-1}.

doublet when the temperature goes from 295 to 85 K strongly suggests that, as in the parent complex, an electronic spin relaxation effect is present.

The second step of the thermal decomposition occurs between approximately 240 and 280°C as evidenced by an exothermic peak in the DTA curve, associated with an abrupt weight loss of about 22% in the TG curve (II, Fig. 3).

It should be noticed that this second step is superimposed to the next one as shown by the broad and unresolved exothermic peak in the DTA curve and by a slow weight loss in the TG curve, right above 280°C.

The following proposed decomposition scheme gives a weight loss of 21.4% in excellent agreement with the observed value of 22%.

$$K_3[Fe(C_3H_2O_4)_3] \xrightarrow{240\text{–}280^\circ C} Fe(C_3H_2O_4) + \tfrac{3}{2}K_2CO_3 + \tfrac{3}{2}CO + CO_2 + C_2H_4$$

The loss of CO_2 was determined by a conventional reaction between the evolved gas and a solution of barium chloride. The carbonate ion was identified through infrared analysis of the precipitate formed by dissolving a sample heated at 270°C for 20 min (pH 1) to which $BaCl_2$ was added. The infrared spectrum of this precipitate shows bands characteristic of the CO_3^{2-} ion.

The formation of an Fe(II) compound was detected by the Mössbauer spectrum of a sample heated at 260°C for 60 min measured at 295 K (Fig. 1C). The doublet with isomer shift of 1.33 mm s^{-1} and quadrupole splitting of 2.71 mm s^{-1} is typical of high spin Fe(II), and was assigned to $Fe(C_3H_2O_4)$. The small absorption peak appearing around 0.5 mm s^{-1} corresponds to a small fraction of the undecomposed anhydrous malonato.

This fact was confirmed through Mössbauer spectra of samples heated at 260°C for different intervals of time, such as 20, 60 and 120 min. It was observed that the areas under Mössbauer curves corresponding to Fe(II) doublet increase as the heating intervals increase while the areas corresponding to Fe(III) decrease.

The possibility of the Fe(II) compound being the dimer $K_6[Fe_2(C_3H_2O_4)_5]$, similar to $K_6[Fe_2(C_2O_4)_5]$ formed in the thermal decomposition of the potassium tris(oxalato)ferrate(III) trihydrate [1], was discharged because this would give a weight loss of about 9.6%, much smaller than the observed value of 22%.

Above 280°C the thermal decomposition is a complicated multistep process as shown by a broad and unresolved exothermic peak in the DTA curve and by a slow weight loss in the TG curve (III and IV, Fig. 3). However, the final products were identified as being α-Fe_2O_3 and K_2CO_3, and the weight loss of 50.6% agrees well with the observed value of 52%. The presence of K_2CO_3 was confirmed by the infrared spectrum of a sample heated at 550°C for 20 min. The Mössbauer spectrum of this sample, measured at 295 K consists of a six-line pattern due to magnetic hyperfine interaction (Fig. 5A), with isomer shift, quadrupole splitting and internal magnetic field values of (0.35 ± 0.02) mm s^{-1}, (0.11 ± 0.02) mm s^{-1} and (514 ± 5) KOe respectively, indicating the formation of α-Fe_2O_3 with particle size no smaller than 1.54 μm [8]. The presence of α-Fe_2O_3 in the final products was also confirmed by X-ray diffractograms.

In order to investigate the intermediate products formed between 280 and 390°C (region III in the TG curve, Fig. 3) samples were heated at 300 and 350°C in air for 20 min each.

For these heated samples the infrared spectra show the absence of the band at about 945 cm^{-1} due to CH_2 rocking and the bands at about 975 and 990 cm^{-1} due to $\nu(C{-}C)_{sym}$, indicating that the malonate ion has disappeared. In addition, the presence of a broad and strong band at about 1660 cm^{-1} shows that carbonate ion was formed.

The Mössbauer spectrum of the sample heated at 300°C measured at 295 K (Fig. 4A) shows one central doublet with isomer shift $\delta = (0.35 \pm 0.02)$ mm s^{-1} and quadrupole splitting $\Delta = (0.66 \pm 0.02)$ mm s^{-1} along with three six-line magnetic hyperfine patterns with internal magnetic field values of $H_1 = (329 \pm 5)$ KOe, $H_2 = (449 \pm 5)$ KOe and $H_3 = (480 \pm 5)$ KOe. The corresponding values found at 85 K (Fig. 4B) are: $\delta = (0.41 \pm 0.02)$ mm s^{-1} and $\Delta = (0.69 \pm 0.02)$ mm s^{-1} for the central doublet and $H_1 = (337 \pm 5)$ KOe, $H_2 = (465 \pm 5)$ KOe and $H_3 = (493 \pm 5)$ KOe for the internal magnetic fields. The measured values for the central doublet are in close agreement with the values reported for α-Fe_2O_3 with particle size smaller than 10 nm [9].

The measured values for the internal magnetic field H_1 agree very well with the values we found for α-Fe foil used for velocity calibration, indicat-

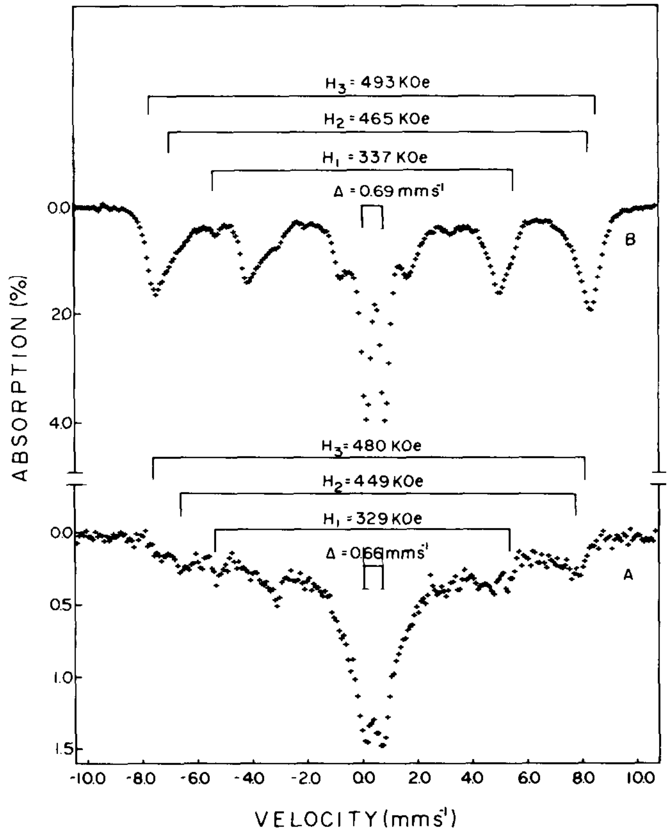

Fig. 4. Mössbauer spectra of potassium tris(malonato)ferrate(III) trihydrate samples heated at 300°C/20 min at: (A) 295 K; (B) 85 K.

ing the formation of iron metal. The measured values for the internal magnetic fields H_3 and H_2 were assigned to the tetrahedral and octahedral sites of Fe_3O_4, respectively. The slightly smaller values found for H_3 and H_2 when compared to earlier reported values [10] are consistent with a particle size distribution around 10 nm [11].

For some ferric oxides it has been observed that in general the internal magnetic field increases with the particle size [8,9,11,12]. It has been also observed that the particle size of some ferric oxides increases when either the heat treatment temperature increases isochronally [13–15] or the heating time increases isothermally [15].

Therefore, the presence of Fe_3O_4 in the sample heated at 300°C was confirmed by Mössbauer and X-ray diffraction measurements of a sample heated at 350°C. Mössbauer spectra of the latter sample measured at 295 K (Fig. 5B) and at 85 K (Fig. 5C) consist of only three six-line magnetic hyperfine patterns for each temperature. The internal magnetic field values, $H_1 = (326 \pm 5)$ KOe at 295 K and $H_1 = (337 \pm 5)$ KOe at 85 K, support the

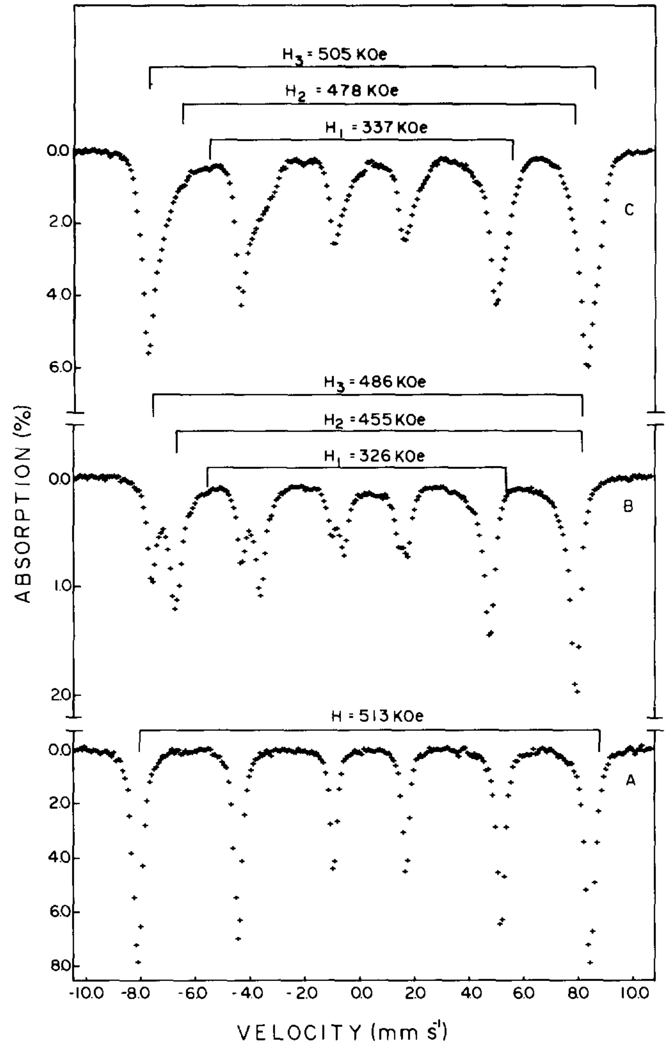

Fig. 5. Mössbauer spectra of potassium tris(malonato)ferrate(III) trihydrate samples: (A) heated at 550°C/20 min measured at 295 K; and heated at 350°C/20 min measured at (B) 295 K and (C) 85 K.

presence of iron metal. The values for the internal magnetic field, $H_2 = (455 \pm 5)$ KOe and $H_3 = (486 \pm 5)$ KOe at 295 K and $H_2 = (478 \pm 5)$ KOe and $H_3 = (505 \pm 5)$ KOe at 85 K, are in excellent agreement with the reported values [10] for the tetrahedral and octahedral sites of Fe_3O_4 at 295 and 85 K, respectively. The presence of Fe_3O_4 was also confirmed by the X-ray diffractogram.

The absence of the central doublet and the higher values of the internal magnetic fields for the sample heated at 350°C when compared to those found for the sample heated at 300°C show that the particle size of Fe_3O_4 increases with the heat treatment temperature.

On the other hand, the presence of iron metal in the air decomposition is surprising. For a similar complex oxalato, iron metal is only formed in the vacuum decomposition [1].

In summary, the main steps of the thermal decomposition in air of the potassium tris(malonato)ferrate(III) trihydrate can be written as

$$\text{(I)}\quad K_3[Fe(C_3H_2O_4)_3]\cdot 3H_2O \xrightarrow{80-110°C} K_3[Fe(C_3H_2O_4)] + 3\ H_2O$$

$$\text{(II)}\quad K_3[Fe(C_3H_2O_4)_3] \xrightarrow{240-280°C} Fe(C_3H_2O_4) + \tfrac{3}{2}\ K_2CO_3$$

$$+ CO_2 + \tfrac{3}{2}\ CO + C_2H_4$$

$$\text{(III)}\quad Fe(C_3H_2O_4) + \tfrac{3}{2}\ K_2CO_3 \xrightarrow{>390°C} \tfrac{1}{2}\ Fe_2O_3 + \tfrac{3}{2}\ K_2CO_3$$

$$+ \tfrac{1}{2}\ CO_2 + \tfrac{3}{2}\ CO + \tfrac{1}{2}\ C_2H_4$$

And for the intermediate step (III) Fe_3O_4 and iron metal are formed as already mentioned for the samples heated at 300 and 350°C.

CONCLUSIONS

The following conclusions can be draw for the thermal decomposition in air of the tris(malonato)ferrate(III) trihydrate compared to its similar tris(oxalato)ferrate(III) trihydrate.

(1) The initial step (dehydration process) and the final step (formation of Fe_2O_3) are identical for both complexes.

(2) In the intermediate step the ferrous malonate formed was not a dimer as happened for the ferrous oxalate.

(3) While Fe_3O_4 was found in the intermediate products for both complexes, iron metal was detected only for the malonato.

(4) It was observed that the malonate ligand lead to a system that during the process of the decomposition has more reducing power than the oxalate ligand.

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