

MÖSSBAUER STUDY OF THE THERMAL DECOMPOSITION OF IRON(III) CITRATE PENTAHYDRATE

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The thermal decomposition of iron(III) citrate pentahydrate, $\text{Fe}(\text{C}_6\text{H}_5\text{O}_7) \cdot 5 \text{H}_2\text{O}$, has been investigated at different temperatures in air using Mössbauer spectroscopy, non-isothermal techniques (DTA–TG) and X-ray diffraction. The reduction of iron(III) to iron(II) takes place at 553 K. At higher temperature the formation of $\alpha\text{-Fe}_2\text{O}_3$ and $\gamma\text{-Fe}_2\text{O}_3$ as the ultimate thermal decomposition products has been confirmed.

Thermogravimetry or allied techniques in combination with other physico-chemical techniques (spectroscopic, microscopic, diffraction, etc.), provide extremely useful information about the decomposition of solids [1]. For complexes of iron, Mössbauer spectroscopy has recently been employed to identify the various intermediates and the change in oxidation state of the iron nucleus during thermal decomposition [2, 3]. In the thermal decomposition of iron(III) monocarboxylates and iron(III) dicarboxylates, an iron(II) species has been detected as an intermediate [2–5]. Gallagher and Kurkjian [2], using Mössbauer spectroscopy, reported the reduction of iron(III) to iron(II) at 473 K, and at higher temperature $\alpha\text{-Fe}_2\text{O}_3$ is formed as the end-product. In our earlier publications the formation of iron(II) in iron(III) monocarboxylates (propionate and butyrate) [3] and iron(III) dicarboxylates (adipate and succinate) [5] has been reported. However, the thermal decomposition behaviour of iron(III) tricarboxylates has not been described; the present work was therefore undertaken. The photo-decomposition of iron(III) citrate has been reported [6], but its thermal decomposition does not seem to have been investigated in the literature. The present work deals with the thermal decomposition of iron(III) citrate pentahydrate using DTA–TG and Mössbauer spectroscopic techniques.

Experimental

Material

Iron(III) citrate pentahydrate, $\text{Fe}(\text{C}_6\text{H}_5\text{O}_7) \cdot 5 \text{H}_2\text{O}$, was prepared by the method already reported [7]. The composition of this complex was established by chemical

analysis and infrared spectroscopy. Iron was estimated gravimetrically [8] and the carbon and hydrogen were determined by microanalysis. The estimated percentages of the elements are Fe = 16.8, C = 21.6, H = 4.6 (calcd. Fe = 16.7, C = 21.5, H = 4.5).

Methods

The infrared spectrum of iron(III) citrate pentahydrate was recorded on a Spectromom-2000 spectrophotometer (Hungarian Optical Works, Hungary). It showed a broad band in the region 3520–3400 cm^{-1} due to the (OH) stretching of the water molecules, a strong band in the region 1640–1610 cm^{-1} due to ν_{asym} (C=O) and a band at 1380 cm^{-1} due to ν_{sym} (C=O). These values indicate the presence of coordinated carboxylate groups [9].

Non-isothermal analysis was carried out by means of a Paulik–Paulik–Erdey MOM derivatograph (Hungary) with 200 mg of sample at 200 mg sensitivity at a heating rate of 10 deg min^{-1} in static air atmosphere.

A Mössbauer study was made of samples heated in a silica crucible at different temperatures for different periods in static air atmosphere.

A MBS-35 Mössbauer spectrometer (ECIL, India) coupled with an MCA-38B constant acceleration drive was employed to record the spectrum. A 5 mCi ^{57}Co (Rh) source was used. The isomer shift values are reported with respect to natural iron. All the spectra were recorded at 298 ± 2 K. A sample containing approximately 10 mg/cm^2 of natural iron was taken for each measurement. The isomer shift, quadrupole splitting and internal magnetic field values are reported with experimental errors of ± 0.04 mm/s , ± 0.04 mm/s and ± 5 KOE , respectively.

Results and discussion

The Mössbauer spectrum of iron(III) citrate pentahydrate, $\text{Fe}(\text{C}_6\text{H}_5\text{O}_7) \cdot 5 \text{H}_2\text{O}$, at room temperature consists of a doublet (Fig. 1a) with isomer shift and quadrupole splitting values of 0.40 and 0.57 mm/s , respectively. These values are in good agreement with those reported for iron(III) citrate pentahydrate [10]. The isomer shift shows this complex to be high spin, with the iron nucleus in the +3 oxidation state, while the quadrupole splitting indicates its distortion from cubic symmetry.

The Mössbauer spectrum of the sample heated at 553 K for 7 minutes exhibits two quadrupole doublets (Fig. 1b), one with isomer shift and quadrupole splitting values of 1.18 and 2.52 mm/s , respectively, indicating the formation of an iron(II) species, and the other doublet due to the presence of the parent complex. The isomer shift and quadrupole splitting values agree with the values for the iron(II) moiety obtained by the photolysis and gamma-radiolysis of iron(III) citrate pentahydrate [6, 11]. A complex nuclear Zeeman pattern is obtained for the sample heated at 673 K. The Mössbauer spectrum of the final residue obtained by heating the sample at 1073 K for one hour, exhibits a doublet (Fig. 1c) with isomer shift and quadrupole splitting values of 0.34 and 0.67 mm/s , respectively. These values are in agreement with those re-

ported for $\alpha\text{-Fe}_2\text{O}_3$ with a particle size < 10 nm [12]. The X-ray powder diffraction pattern also confirms the formation of $\alpha\text{-Fe}_2\text{O}_3$ (Table 1). The table shows that the end-product is not pure $\alpha\text{-Fe}_2\text{O}_3$, since certain lines cannot be exclusively assigned to $\alpha\text{-Fe}_2\text{O}_3$ [13]. A strong line at $d = 2.99$ Å is assigned to $\gamma\text{-Fe}_2\text{O}_3$ (literature value, $d = 2.95$ Å [14]). Thus, $\gamma\text{-Fe}_2\text{O}_3$ is also present in small amounts in the final product, along with $\alpha\text{-Fe}_2\text{O}_3$.

Thermal study of iron(III) citrate pentahydrate

Figure 2 shows the simultaneous DTA–TG curves of iron(III) citrate pentahydrate. There are four endothermic peaks, at 433, 513, 613 and 683 K, and three exothermic peaks, at 653, 743 and 1033 K. Dehydration of the compound starts from 353 K. The arrest in the TG curve corresponding to the DTA peak at 433 K shows a loss of 10.5%, indicating the loss of two water molecules of crystallization (calcd. loss = 10.7%). The dehydration continues, and is completed at 512 K. The observed loss in weight in

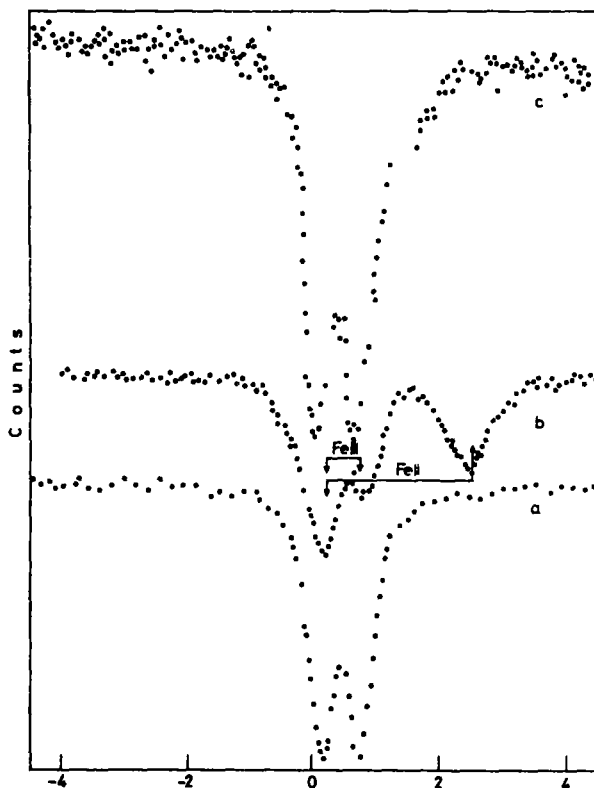


Fig. 1 Mössbauer spectra of Iron(III) citrate pentahydrate, a) at room temperature (298 ± 2 K), b) heated at 553 K for 7 minutes, c) heated at 1073 K for one hour. Abscissa: velocity, mm/s.

Table 1 X-ray diffraction data on the final thermal decomposition product

| 2θ | $d, \text{\AA}$ | Intensity |
|-----------|-----------------|-----------|
| 27.5 | 4.08 | W |
| 30.4 | 3.69 | MS |
| 37.8 | 2.99 | S |
| 40.6 | 2.79 | W |
| 42.0 | 2.70 | VVS |
| 45.2 | 2.52 | VS |
| 46.8 | 2.44 | W |
| 52.0 | 2.21 | MS |
| 55.5 | 2.08 | VW |
| 57.0 | 2.03 | W |
| 62.3 | 1.87 | W |
| 63.4 | 1.84 | S |
| 69.8 | 1.69 | S |
| 72.5 | 1.64 | VW |
| 74.5 | 1.60 | MS |
| 81.2 | 1.49 | S |
| 83.5 | 1.45 | S |

W = weak, M = medium, S = strong, V = very

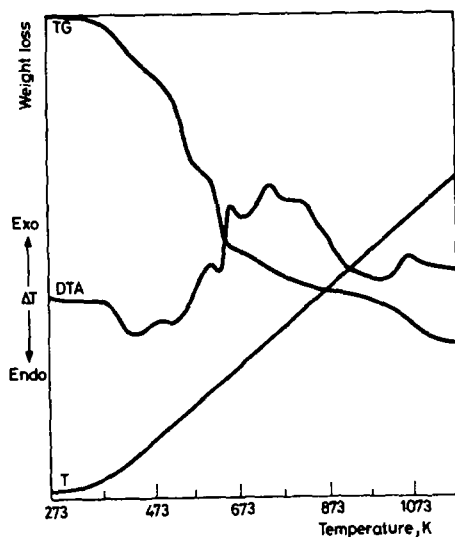


Fig. 2 Simultaneous DTA-TG curves of iron(III) citrate pentahydrate at a heating rate of 10 degree minute⁻¹

the TG curve corresponding to the endothermic DTA peak at 513 K is 26.6%, indicating the loss of five water molecules of crystallization (calcd. loss = 26.9%).

The loss in the TG curve corresponding to the DTA peak at 613 K is 41%. This weight loss indicates the formation of iron(II) acetonedicarboxylate, $\text{Fe}(\text{C}_5\text{H}_4\text{O}_5)$ (calcd. loss = 40.3%). The decomposition of citric acid into the acetonedicarboxylate ion, $(\text{C}_5\text{H}_4\text{O}_5)^{2-}$, with the evolution of carbon dioxide and water has been reported in the literature [15]. The existence of the Fe(II) species has also been detected by taking the Mössbauer spectrum of the compound heated at 553 K for 7 minutes. Further decomposition of this complex is a complicated multistep process. The TG shows a weight loss of 75% at 1033 K, indicating the formation of Fe_2O_3 (calcd. loss = 76.2%).

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References

- 1 H. G. Widemann and G. Bayer, cited in Topics in current chemistry – 77 Edited by M. J. S. Dewar et. al. (Springer-Verlag, Berlin–Heidelberg–New York) 1978, p. 67.
- 2 P. K. Gallagher and C. R. Kurkjian, Inorg. Chem., 5 (1966) 214.
- 3 P. S. Bassi, B. S. Randhawa and H. S. Jamwal, Thermochim. Acta, 62 (1983) 209.
- 4 D. Broadbent, D. Dollimore and J. Dollimore, J. Chem. Soc., A.(1967) 451.
- 5 P. S. Bassi, B. S. Randhawa and H. S. Jamwal, Thermochim. Acta, 65 (1983) 1.
- 6 D. N. E. Buchanan, J. Inorg. Nucl. Chem., 32 (1970) 3531.
- 7 G. G. Hawley (Ed.), The Condensed Chemical Dictionary, 8th Ed., Van Nostrand–Reinhold Company, New York, 1966, p. 384.
- 8 A. I. Vogel, Quantitative Inorganic Analysis, Longmans Green and Co., London, 1961, p. 533.
- 9 K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, 2nd Ed., Wiley Interscience, New York, 1970.
- 10 J. J. Bara, K. Krolas and T. Matlak, Applications of Mössbauer Effect, Akadémiai Kiadó, Budapest, 1971, p. 769.
- 11 N. Saito, T. Tominaga and T. Morimoto, J. Inorg. Nucl. Chem., 32 (1970) 2811.
- 12 W. Kundig, H. Bommel, G. Constabaris and R. H. Lindquist, Phys. Rev., 142 (1966) 327.
- 13 V. Kastalsky and M. F. Westcott, Australian J. Chem., 21 (1968) 1061.
- 14 R. Schrader and G. Buettner, Z. Anorg. Allgem. Chem., 320 (1963) 205.
- 15 O. Liesche, Z. Physik. Chem., 94 (1920) 663; Chem. Abs., 14 (1920) 2442.

Zusammenfassung – Die thermische Zersetzung des Pentahydrates von Eisen(III)-citrat in Luft wurde bei verschiedenen Temperaturen durch Mössbauer-Spektroskopie, nicht-isotherme Techniken (DTA, TG) und Röntgendiffraktometrie untersucht. Die Reduktion von Eisen(III) zu Eisen(II) erfolgt bei 553 K. Bei höheren Temperaturen entstehen $\alpha\text{-Fe}_2\text{O}_3$ und $\gamma\text{-Fe}_2\text{O}_3$ als Endprodukte der thermischen Zersetzung.

Резюме — Используя неізотермические методы (ДТА—ТГ), мёссбауэровскую спектроскопию и рентгено-дифракционный метод, было исследовано термическое разложение пятигидрата лимоннокислого железа (III) в атмосфере воздуха. При 553 К протекает восстановление трехвалентного железа до двухвалентного. Подтверждено, что при более высоких температурах имеет место совместное образование $\alpha\text{-Fe}_2\text{O}_3$ и $\gamma\text{-Fe}_2\text{O}_3$, как конечных продуктов термического разложения.