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Note

THERMAL DECOMPOSITION OF HEXAHYDRATO THORIUM(IV) FERROCYANIDE

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Seifer and Makarova [1—3] have studied the thermal decomposition of ferrocyanides using thermal and chemical analysis techniques. We have reported the thermal decomposition of tin ferrocyanide [4] and zirconium ferrocyanide [5] using thermogravimetric analysis, differential thermal analysis, magnetic susceptibility, infrared and Mössbauer spectroscopy. In continuation of this work, we now report on the thermal decomposition of hexahydrato thorium (IV) ferrocyanide using the above techniques. Our interest is to study the effect of the thorium (IV) cation on the thermal decomposition, and the products formed. Ferrites formed at higher temperature are widely employed in industry as catalysts and ferromagnetic materials.

MATERIALS AND METHODS

The compound $[Th(H_2O)_6][Fe(CN)_6]$ was prepared by adding an aqueous solution of 1 M $Th(NO_3)_4 \cdot 6\,H_2O$ to a 1 M aqueous solution of $K_4[Fe(CN)_6] \cdot 3\,H_2O$. The precipitate was filtered, washed, and dried at room temperature. Thorium ferrocyanide was heated at 100, 150, 200, 250 and 300°C for 3 h.

A Mössbauer spectrometer MBS-35 (ECIL) attached to a multichannel analyser MCA-38B with constant acceleration drive was used. The Mössbauer source was 5 mCi ^{57}Co. The velocity was calibrated with the six-line spectrum of natural iron and isomer shift values had been reported with respect to sodium nitroprusside as the reference. All the spectra were recorded at room temperature (20°C). The error in isomer shift and quadrupole splitting is ± 0.03 mm sec^{-1}.

The thermogravimetric analysis was carried out at TGA (FCIL, India). Differential thermal analysis was studied on a DTA-02-Universal (Veb Laborelektronik Hall, GDR) instrument at a heating rate of 10°C min^{-1}. Infrared spectra were obtained from KBr discs containing 2% sample using a MOM-

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2000 (MOM, Budapest, Hungary) infrared spectrophotometer. The magnetic susceptibility measurements were carried out on a Gouy's balance.

RESULTS AND DISCUSSION

Hexahydrato thorium (IV) ferrocyanide samples were heated at different temperatures and were labelled I (at room temperature), II (100° C), III (150° C), IV (200° C), V (300° C) and VI (400° C). In the case of sample I, the isomer shift was 0.15 mm sec^{-1} and there was no quadrupole splitting, as shown in Fig. 1(a). This shows that the ferrocyanide has cubic symmetry. The value of the isomer shift is comparable with ferrocyanides reported in the literature [6]. The infrared spectrum of sample I shows a broad absorption band at 3200—3550 cm^{-1} due to water molecules. The other absorption band, at 2075 cm^{-1}, is due to the cyanide group. Sample I is diamagnetic, as expected. The number of water molecules has been calculated from thermogravimetric analysis. On the basis of Mössbauer spectroscopy, infrared spectroscopy and magnetic susceptibility, it has been argued that $[Th(H_2O)_6][Fe(CN)_6]$ is formed.

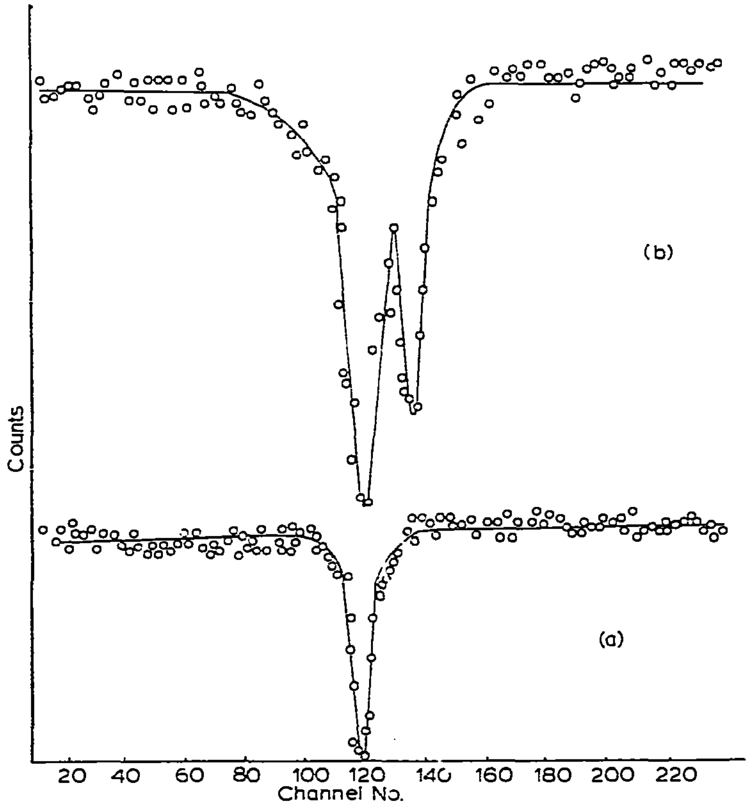

Fig. 1. Mössbauer spectra of the hexahydrato thorium (IV) ferrocyanide at (a) room temperature, and (b) 300°C.

Sample II was obtained by heating sample I at 100° C. There is no change in its Mössbauer spectrum isomer shift and its structure remains unchanged. Sample II is again diamagnetic and the loss of weight at 100° C is 1.5% due to the loss of uncoordinated water molecules. It is concluded from the observations that there is no decomposition of thorium ferrocyanide at 100° C.

The Mössbauer spectrum of sample III, obtained at 150° C, shows a slight change in the shape of the absorption band but the isomer shift does not change. This indicates that decomposition has started. Thermogravimetric analysis indicates the loss of two water molecules. Differential thermal analysis shows an endothermic peak at 150° C which is due to the loss of coordinated water molecules. There is no change in the infrared spectrum of the sample III. From these facts, it can be concluded that at 150° C thorium ferrocyanide has just started decomposing. The slight change in the shape of the absorption band in the Mössbauer spectrum may be due to loss of water molecules, which causes slight asymmetry in the ferrocyanide moiety.

The Mössbauer spectrum of the sample IV, obtained at 200° C, is different from I, II and III. In this case, along with the original peak of isomer shift 0.15 mm sec^{-1}, another doublet having an isomer shift of 0.72 mm sec^{-1} and quadrupole splitting of 0.96 mm sec^{-1} appeared. One of the peaks of the doublet overlaps the previous peak. The infrared spectrum shows the presence of the cyanide group. The doublet in the Mössbauer spectrum is due to the formation of $ThFe_2O_4$. The sample heated at 200° C contains a mixture of thorium ferrocyanide and $ThFe_2O_4$, which indicates decomposition of the ferrocyanide.

The Mössbauer spectra of samples V and VI are similar, having a doublet with an isomer shift of 0.72 mm sec^{-1} and quadrupole splitting of 0.96 mm sec^{-1} [Fig. 1(b).] The infrared spectra of these samples show no evidence of the presence of a cyanide group. These studies show that $ThFe_2O_4$ is formed at 300° C. It has an inverse spinel structure $Fe^{2+}[Fe^{2+}\ Th^{4+}]\ O_4$ and shows a quadrupole splitting similar to Ti(IV) Fe_2O_4 as reported in the literature [7].

The sample heated at 500° C does not give a Mössbauer spectrum at room temperature, which shows that the crystal structure of the ferrites has been changed above 500° C. The infrared spectrum does not show any absorption band in the 4000—700 cm^{-1} region.

It has been observed that the temperature of decomposition of thorium ferrocyanide in air is lower than the Group I ferrocyanides [1,8]. This may be due to the large number of water molecules, the polarity of thorium or the size of the thorium ion. Thorium ferrocyanide starts decomposing to $ThFe_2O_4$ at 200° C and decomposition to $ThFe_2O_4$ is complete at 300° C. In the case of the decomposition of tin(IV) ferrocyanide [4], the formation of tin dioxide starts at 150° C and at 200° C ferric ferrocyanide is formed. The mixed oxides are formed at higher temperatures. Zirconium ferrocyanide [5] decomposes to ZrO_2 and α-Fe_2O_3 at 300° C without giving intermediates such as mixed oxides. The decomposition temperature seems to be influenced by the outer cation. The outermost cation is converted to oxide because of weak bonding with the ferrocyanide. The oxides formed may further act as catalysts for the decomposition of ferrocyanide. The decomposition temperatures of Group I metals (Na, K, Rb, Cs) are higher than those of thorium, tin and zirconium ferrocyanides, which gives some evidence that the oxides of sodium, potassium, etc. are not good catalysts.

Although the actual mechanism of the solid state decomposition of thorium ferrocyanide may be complex, on the basis of thermogravimetric analysis, differential thermal analysis, infrared and Mössbauer spectroscopic studies, the following decomposition path is suggested.

$$[Th(H_2O)_6][Fe(CN)_6] \xrightarrow{150^\circ C} [Th(H_2O)_4][Fe(CN)_6] + 2\,H_2O$$

$$2[Th(H_2O)_4][Fe(CN)_6] \xrightarrow{200-400^\circ C} ThFe_2O_4 + 6(CN)_2 + 8\,H_2O + ThO_2$$

The samples were heated at the above temperatures for 3 h and the weight loss from TGA was slightly less than that calculated from the above series of reactions. This may be due to the decomposition of the ferrocyanides on prolonged heating.

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