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THERMAL DECOMPOSITION OF POTASSIUM COBALT HEXACYANOFERRATE(II)

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ABSTRACT

Potassium cobalt hexacyanoferrate(II), $K_2CoFe(CN)_6 \cdot 1.4H_2O$, loses its water when heated up to 170 °C, and the anhydrous compound begins to decompose above 230 °C. The cyanide groups are evaporated off in the temperature range 230–350 °C, and the solid products thus formed are K_2CO_3, Fe_2O_3, Co_3O_4 and $CoFe_2O_4$. In the range 550–900 °C, the cobalt-containing compounds become CoO, and K_2CO_3 probably partly decomposes to K_2O, so that the product mixture at 900 °C is K_2CO_3/K_2O, Fe_2O_3 and CoO. Above this temperature, K_2CO_3 decomposes to K_2O.

INTRODUCTION

A great number of transition metal hexacyanoferrate(II)s have been studied for their prospective use in the separation of radioactive cesium nuclides from nuclear-waste solutions [1–3]. One of the most promising cesium-selective hexacyanoferrate(II)s is potassium cobalt hexacyanoferrate(II), $K_2CoFe(CN)_6 \cdot xH_2O$ [4–8]. The thermal behaviour of this compound has been studied to only a limited extent. Ceranic [9] has reported on the formation of potassium carbonate together with undefined iron and cobalt oxides upon heating it up to 700 °C. The present paper gives a detailed report on the solid decomposition products and the temperature ranges of their formation. The gaseous products were not identified.

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EXPERIMENTAL

Potassium cobalt hexacyanoferrate(II) was prepared by adding 0.5 M $Co(NO_3)_2$ solution to an equal volume of 0.5 M $K_4Fe(CN)_6$ solution. After washing, the precipitate was dried at 110 ° C [8]. The composition of the product was determined by atomic absorption spectrophotometry from samples dissolved in boiling concentrated sulphuric acid. Determination of iron and cobalt gave the composition $K_{1.90}Co_{1.05}Fe(CN)_6 \cdot xH_2O$. The water content was calculated from the weight loss after heating a sample at 170 ° C, and it was found to be 7.0%. This corresponds to 1.4 moles of water per mole of $K_2CoFe(CN)_6$.

The thermograms (TG, DTG, DTA and EGD) were determined using a Netzsch STA 429 thermobalance. The determinations were carried out in air atmosphere and the heating rate was 1° C min^{-1}.

X-ray diffraction patterns of powder samples heated to different temperatures were determined with a Siemens Kristalloflex 4 and a Philips APD 1700 diffractometer using monochromatised Cu $K\alpha$ radiation. The samples were heated in a Naber 2084 oven and the temperature was determined with a chromel–alumel thermocouple. The annealings were carried out in porcelain ($\leqslant$ 650 ° C) and platinum (900 ° C) crucibles.

RESULTS AND DISCUSSION

The thermograms (Fig. 1) indicate four different weight-loss ranges: 20–170 ° C, 230–350 ° C, 550–900 ° C, and above 900 ° C. The first weight

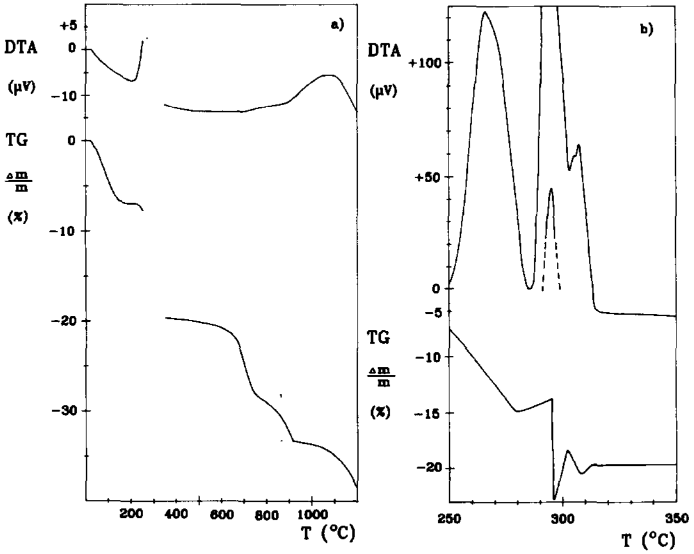

Fig. 1. Thermograms of $K_2CoFe(CN)_6 \cdot 1.4H_2O$: a, temperature range 20–1200 ° C; b, temperature range 250–350 ° C. Heating rate 1° C min^{-1}. Sample weight 50.2 mg.

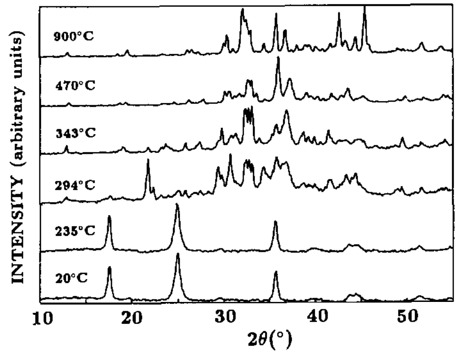

Fig. 2. X-ray diffraction patterns of solid products formed at different temperatures in the thermal decomposition of $K_2CoFe(CN)_6 \cdot 1.4H_2O$.

loss, occurring from ambient temperature (20 °C) to 170 °C, is due to release of water. The loss was 7.0%, which corresponds to 1.4 moles of water per mole of $K_2CoFe(CN)_6$. The water loss does not affect the crystal structure (FCC, $a = 1.006$ nm) [10]: the X-ray diffraction pattern of the anhydrous phase remains unchanged up to 230 °C (Fig. 2). The water loss is reversible; the anhydrous phase reabsorbs water when in contact with air. Decomposition of anhydrous $K_2CoFe(CN)_6$ begins above 230 °C: at about 300 °C its reflections have disappeared from the diffraction pattern, indicating that the $K_2CoFe(CN)_6$ has completely decomposed.

As seen from the thermograms the reactions become very complicated in the temperature range 230–350 °C. The cyanide groups are lost and gases are evolved. $K_3Fe(CN)_6$ and/or $K_3Co(CN)_6$ are formed as intermediate products, but being isomorphous these compounds cannot be distinguished from each other in the diffraction pattern. The other solid products formed in this temperature range are K_2CO_3, Fe_2O_3, Co_3O_4 and probably $CoFe_2O_4$.

Above about 350 °C, all the hexacyanoferrate(III) and hexacyanocobaltate(III) have decomposed and the products are K_2CO_3, Fe_2O_3, Co_3O_4 and $CoFe_2O_4$. For a sample annealed at 370 °C for one hour, the weight loss was 20.2%. The calculated weight loss would be 20.5% if the following decomposition had taken place

$$K_2CoFe(CN)_6 \cdot 1.4H_2O \rightarrow K_2CO_3 + \tfrac{1}{2}Fe_2O_3 + \tfrac{1}{3}Co_3O_4 \qquad (1)$$

Because the proportion of $CoFe_2O_4$ was not known, its presence has been ignored. However, this introduces only a minor error in the calculation.

The mixture of K_2CO_3, Fe_2O_3, Co_3O_4 and $CoFe_2O_4$ is more or less stable up to 550 °C. Above this temperature the cobalt compounds are converted to CoO, and K_2CO_3 probably partly decomposes to K_2O. At 900 °C the products are K_2CO_3/K_2O, Fe_2O_3 and CoO. For samples annealed at

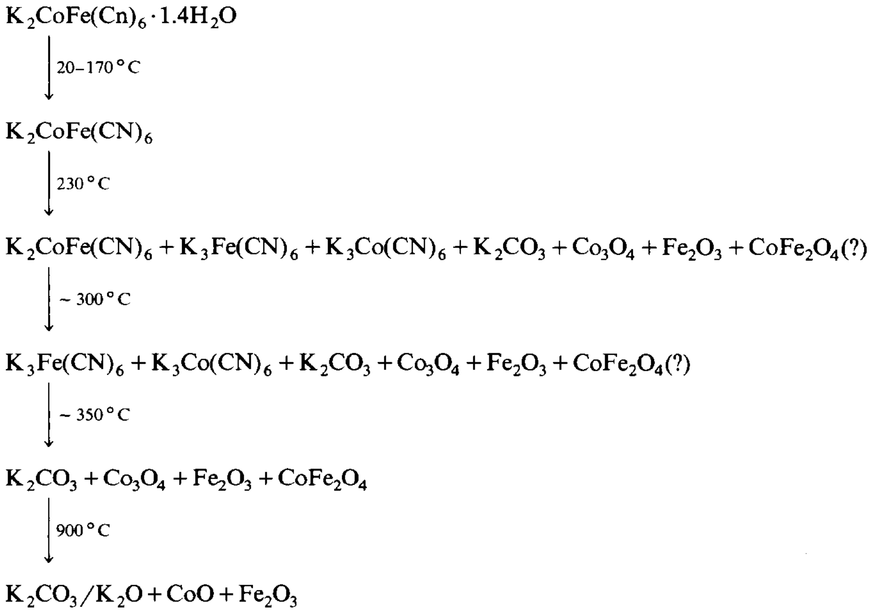

Fig. 3. Solid products formed in the thermal decomposition of $K_2CoFe(CN)_6 \cdot 1.4H_2O$.

900–930 °C for 15–60 minutes, the weight loss was 29.4%. For the decomposition reaction

$$K_2CoFe(CN)_6 \cdot 1.4H_2O \rightarrow K_2CO_3 + CoO + \tfrac{1}{2}Fe_2O_3 \qquad (2)$$

the weight loss would be only 22.0%, whereas for the reaction

$$K_2CoFe(CN)_6 \cdot 1.4H_2O \rightarrow K_2O + CoO + \tfrac{1}{2}Fe_2O_3 \qquad (3)$$

the weight loss would be 33.7%. According to the observed weight loss, the proportion of K_2O is fairly high. Above 900 °C, K_2CO_3 (m.p. 891 °C) decomposes to K_2O.

Figure 3 shows the decomposition process in a step-wise manner. Only solid decomposition products are shown, without molar coefficients.

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REFERENCES

1 V. Pekarek and V. Vesely, Talanta, 19 (1972) 1245.
2 H. Loewenschuss, Radioact. Waste Manag., 2 (1982) 327.

3 W.F. Hendrickson and G.K. Riel, Health Phys., 28 (1975) 17.
4 W.E. Prout, E.R. Russell and H.J. Groh, J. Inorg. Nucl. Chem., 27 (1965) 473.
5 J. Lehto and R. Harjula, Solvent Extraction and Ion Exchange, 5 (1987) 343.
6 R. Harjula, J. Lehto and J. Wallace, Proceedings of the Symposium on Waste Management, Tucson, AZ, 1–5 March 1987, Vol. 3, p. 93.
7 J. Lehto, R. Harjula and J. Wallace, J. Radioanal. Nucl. Chem. Articles, 111 (1987) 297.
8 J. Lehto, S. Haukka, R. Harjula and M. Blomberg, J. Chem. Soc., Dalton Trans., in press.
9 T.S. Ceranic, Documenta Chemica Yogoslavica, 39 (1974) 285.
10 T. Ceranic, Z. Naturforsch., 33b (1978) 1484.