with phenol were undertaken in various molar ratios (*i.e.*, 1:1, 1:2, and 1:3) in the presence of benzene. All the reactions were exothermic and resulted in instantaneous precipitation of sparingly soluble products during addition. The reaction mixtures were caused to reflux for about 3–4 hr and the liberated isopropyl alcohol was fractionated out. The presence of theoretically required isopropyl alcohol in the azeotrope in all the reactions confirm the completion of the reactions. The products were then isolated by stripping off the volatile solvent under vacuum and finally drying at 27–29° (0.1 mm). As the procedure was similar for all these reactions, they are, for brevity, summarized in Table IV.

Acknowledgments.—We are grateful to American Potash and Chemical Corp., New York, N. Y., for the gift of few lanthanon oxides. This work was supported by grants from Atomic Energy Establishment of India.

CONTRIBUTION FROM THE BELL TELEPHONE LABORATORIES, INC.,
MURRAY HILL, NEW JERSEY 07974

Further Studies of the Thermal Decomposition of Europium Hexacyanoferrate(III) and Ammonium Europium Hexacyanoferrate(II)

BY P. K. GALLAGHER* AND B. PRESCOTT

Received May 11, 1970

Mass spectrographic analysis of the evolved gases and infrared spectra of the solid residues are used to expand earlier studies concerning the thermal decomposition of $EuFe(CN)_6 \cdot 5H_2O$ and $NH_4EuFe(CN)_6 \cdot 4H_2O$. Under vacuum the decompositions are very complex. The chain of intermediates for iron is ($Fe(CN)_6{}^{3-}$ or $Fe(CN)_6{}^{4-}$)—$Fe(CN)_2$—Fe_3C—Fe. Similarly the europium is shown to proceed *via* a hydrolytic decomposition to EuOOH and finally to EuO after interaction with the free carbon at elevated temperatures.

Introduction

Rare earth hexacyanoferrates(III) and ammonium rare earth hexacyanoferrates(II) have been shown to be useful precursors for the production of rare earth orthoferrites.[1] The conversion to the desired compound is accomplished through their thermal decomposition in an oxidizing atmosphere. The decomposition under vacuum or in nitrogen is very complex and incompletely understood.[2] It is the purpose herein to present the results of evolved gas analysis and infrared spectroscopic examination of the solid residue for the europium compounds and to indicate how they contribute to a more complete understanding of the decomposition in an inert atmosphere.

Experimental Procedures and Results

Evolved Gas Analysis (ega).—Approximately 25 mg of the compound to be studied was suspended in a small platinum crucible from a platinum wire within a closed platinum furnace tube. This tube was connected to a Veeco SPI-10 residual gas analyzer and the pressure was maintained between 10^{-5} and 10^{-4} Torr. The furnace surrounding the platinum tube was programmed to rise at about 3°/min. The mass range of the analyzer was repeatedly scanned between 0 and 55 mμ and the output was recorded on pen one. The output from a Pt—Pt–10% Rh thermocouple in close proximity to the sample was simultaneous recorded on pen two of the Bristol recorder.

Figures 1 and 2 show the relative intensities of the pertinent mass peaks for the ega of $EuFe(CN)_6 \cdot 5H_2O$ and $NH_4EuFe(CN)_6 \cdot 4H_2O$, respectively.

Ir Spectra.—Infrared spectra of samples which had been heated to various temperatures for 0.5 hr under a low pressure of 10^{-5} Torr or in air were recorded on a Model 421 Perkin-Elmer spectrometer. The instrument was continuously purged with dry nitrogen. Samples were run from 4000 to 250 cm^{-1} using KBr pellet technique with an appropriate KBr pellet in the reference beam. Selected spectra are given in Figures 3–5 for samples of $EuFe(CN)_6 \cdot 5H_2O$ heated in air and under vacuum and of $NH_4EuFe(CN)_6 \cdot 4H_2O$ under vacuum. X-Ray diffraction patterns and Mössbauer spectra of these samples have been previously reported.[2]

Discussion

Previous work,[2] based primarily on the results of Mössbauer spectroscopy, had established that the hexacyanoferrate(III) and hexacyanoferrate(II) decomposed to $Fe(CN)_2$, then to Fe_3C, and finally to metallic iron. This is consistent with the results presented herein. The reduction of iron during the change from hexacyanoferrate(III) to $Fe(CN)_2$ is accomplished by the release of cyanogen, $(CN)_2$, which can be plainly seen around 370° in Figure 1. Such a reduction is not necessary for the decomposition of the hexacyanoferrate(II) species and no mass peak corresponding to cyanogen is observed in Figure 2.

The decomposition of the $Fe(CN)_2$ to form Fe_3C gives rise to the nitrogen peak at mass 28 around 600° in both Figures 1 and 2. The peak for this mass at higher temperature includes a large contribution from carbon monoxide as well as nitrogen. The origin of the carbon monoxide is discussed later.

Figure 4 shows the demise of the trivalent iron cyanide bands in accord with the reduction proposed earlier. The bands associated with divalent iron–cyanide interaction in Figures 4 and 5 gradually diminish and

---

* To whom correspondence should be addressed.

[1] P. K. Gallagher, *Mater. Res. Bull.*, **3**, 225 (1968).

[2] P. K. Gallagher and F. Schrey, "Thermal Analyses," Vol. 2, R. F. Schwenker, Jr., and P. D. Garn, Ed., Academic Press, New York, N. Y., 1969, p 929.

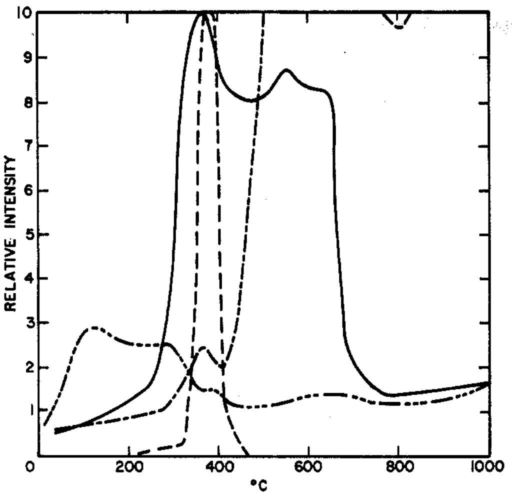

Figure 1.—Evolved gas analysis of $EuFe(CN)_6 \cdot 5H_2O$: mass 18, H_2O, —·—·—; mass 27, HCN, ——; mass 52, $(CN)_2$, - - -; mass 28, N_2 and CO, — — —.

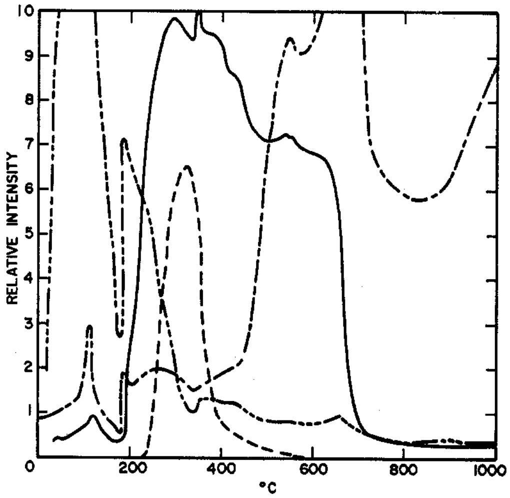

Figure 2.—Evolved gas analysis of $NH_4EuFe(CN)_6 \cdot 4H_2O$: mass 18, H_2O, —·—·—; mass 27, HCN, ——; mass 17, NH_3, - - -; mass 28, N_2 and CO, — — —.

disappear with the formation of iron carbide, Fe_3C, around 700°. The bands around 660 cm^{-1} are attributed to Fe_3C which is disassociated at higher temperatures to metal and carbon.

The disappearance of the ammonium band in Figure 5 correlates well with the evolution of ammonia shown in Figure 2. These two measurements clearly establish the decomposition temperature of the ammonium ion in this compound.

Figure 3 shows the infrared spectra of the residues obtained from the decomposition in an oxidizing atmosphere. It was established earlier[2] that these materials literally burn around 350° in flowing oxygen forming mixtures of the oxides Eu_2O_3 and α-Fe_2O_3. These react around 700–800° to form europium orthoferrite, $EuFeO_3$. The disappearance of the CN bands and the appearance of metal–oxygen bands shown in Figure 3 are compatible.

The main value of this work, however, lies in the interpretation of the europium intermediates during the

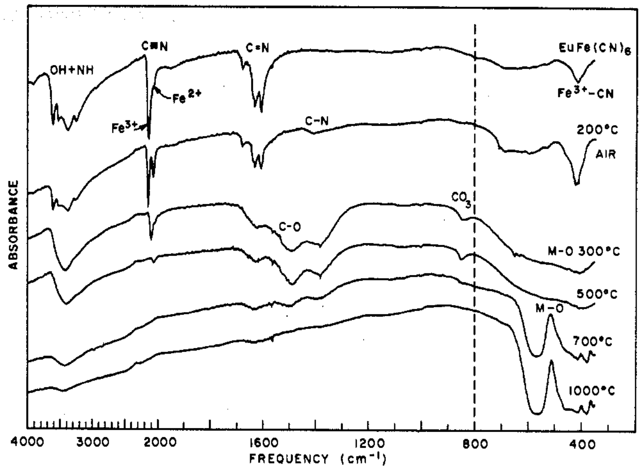

Figure 3.—Selected ir spectra of $EuFe(CN)_6 \cdot 5H_2O$ heated in air.

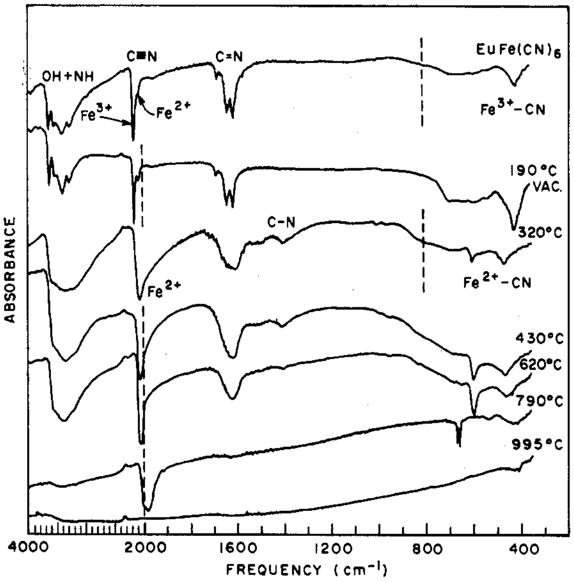

Figure 4.—Selected ir spectra of $EuFe(CN)_6 \cdot 5H_2O$ heated under vacuum.

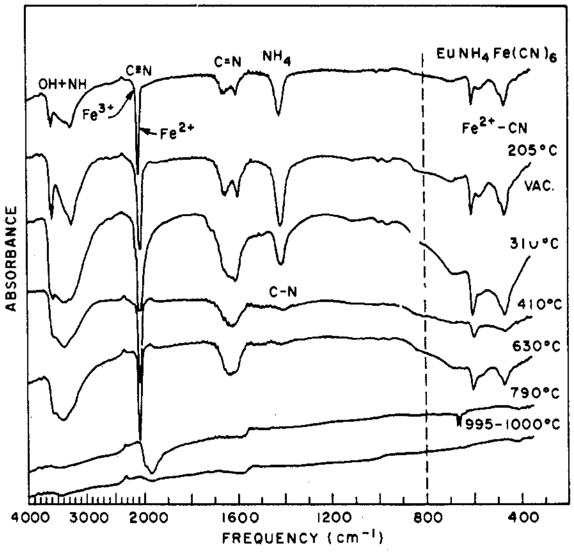

Figure 5.—Selected ir spectra of $NH_4EuFe(CN)_6 \cdot 4H_2O$ heated under vacuum.

decomposition under vacuum. The prior work on the samples of Figures 4 and 5 could only indicate that substantial quantities of divalent europium were formed with increasing temperature but the X-ray patterns and Mössbauer spectra did not correlate with any known carbide, nitride, or cyanide of europium. Figures 1 and 2, however, clearly show that the decomposition in a nonoxidizing atmosphere is hydrolytic in nature whereby the trivalent europium ion reacts with the water of crystallization during the decomposition of the complex in the overall manner

$$2EuFe(CN)_6 \cdot 5H_2O \longrightarrow 2EuOOH + 2Fe(CN)_2 + (CN)_2 + 6H_2O + 6HCN \quad (1)$$

$$NH_4EuFe(CN)_6 \cdot 4H_2O \longrightarrow EuOOH + Fe(CN)_2 + NH_3 + 2H_2O + 4HCN \quad (2)$$

The $Fe(CN)_2$ decomposes at higher temperatures to finally yield iron, carbon, and nitrogen as described previously. The EuOOH loses water over a fairly prolonged temperature range and the resulting oxide reacts with the carbon produced as indicated above to form the lower oxide of europium and carbon monoxide. The lines of EuO are clearly discernible in the X-ray patterns shown in Figures 6 and 7 of the earlier work.[2]

The infrared spectra in Figures 4 and 5 of this work also indicate the hydrolytic nature of the decomposition. The hydroxyl bands persist to around 650° consistent with the decomposition of EuOOH.[3]

Conclusions

The decomposition of $EuFe(CN)_6 \cdot 5H_2O$ and $NH_4EuFe(CN)_6 \cdot 4H_2O$ under vacuum has been shown to be hydrolytic in nature with respect to europium. The iron intermediates during the decomposition are $Fe(CN)_6 \rightarrow Fe_3C \rightarrow Fe$. Cyanogen is liberated during the reduction of hexacyanoferrate(III). The europium ion reacts with the water of hydration to form EuOOH and evolve HCN. This EuOOH then loses water and the resulting oxide reacts with the carbon present at elevated temperature under vacuum to form EuO.

[3] R. C. Rau and W. J. Glover, Jr., *J. Amer. Ceram. Soc.*, **47**, 382 (1964).

CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND PHYSICS,
TEXAS TECH UNIVERSITY, LUBBOCK, TEXAS 79409

The Prussian Blues[1]

BY R. E. WILDE,*[2a] SURENDRA NATH GHOSH,[2b] AND B. J. MARSHALL[2c]

Received March 20, 1970

Soluble and insoluble Prussian blues have been prepared and characterized by elemental analyses, magnetic susceptibility, infrared, and X-ray investigations. The magnetic susceptibility studies show that the Prussian blues obey a Curie–Weiss law with $\mu_{eff} = 6.29$ and 5.97 BM per Fe(III) for soluble and insoluble Prussian blue, respectively. Infrared spectra of the Prussian blues and Turnbull's blue were obtained in the region 70–4000 cm^{-1}. Analysis of the infrared spectra supports the cubic supercomplex structure and indicates that insoluble Prussian blue contains interstitial hydrated Fe(III). The infrared spectra of Turnbull's blue are identical with those of Prussian blue.

Introduction

There is gradually being acquired a large body of information on the "iron blues," as they were called by Holtzman.[3] The iron blues consist of "soluble" and "insoluble" Prussian blues[4] (ferric ferrocyanides) and Turnbull's blue (ferrous ferricyanide). Recent Mössbauer studies[5-9] have conclusviely shown that Prussian blue and Turnbull's blue are identical—namely, ferric ferrocyanides. In spite of a large number of powerful physical methods such as X-ray analysis,[10-12] visible–ultraviolet transmission and reflectance spectroscopy,[13,14] magnetic susceptibility studies,[15-16] and Mössbauer spectroscopy having been brought to bear on the structural problem of Prussian blue, there is still uncertainty as to the actual constitution of Prussian blue and the large number of Prussian blue analogs.

The accepted chemical formulas for the two Prussian blues date back to work by Muller and coworkers.[17] These formulas were arrived at indirectly, and all papers concerning the Prussian blues published since have been devoid of quantitative analytical data. With this in mind, we decided that it was necessary to establish

---

[1] (a) This research was supported by a grant from the Robert A. Welch Foundation. (b) Presented at the 159th National Meeting of the American Chemical Society, Houston, Texas, Feb 27, 1970.

[2] (a) Department of Chemistry; to whom correspondence should be addressed. (b) Department of Chemistry. (c) Department of Physics.

[3] H. Holtzman, *Ind. Eng. Chem.*, **37**, 855 (1945).

[4] "Soluble" and "insoluble" refer to the ease with which the Prussian blues are peptized. The Prussian blues are insoluble in water, but they do form sols.

[5] L. M. Epstein, *J. Chem. Phys.*, **36**, 2731 (1962).

[6] E. Fluck, W. Kerler, and W. Neuwirth, *Angew. Chem., Int. Ed. Engl.*, **2**, 277 (1963).

[7] J. F. Duncan and P. W. R. Wigley, *J. Chem. Soc.*, 1120 (1963).

[8] K. Maer, Jr., M. L. Beasley, R. L. Collins, and W. O. Milligan, *J. Amer. Chem. Soc.*, **90**, 3201 (1968).

[9] A. Ito, M. Suenaga, and K. Ono, *J. Chem. Phys.*, **48**, 3597 (1968).

[10] J. F. Keggin and F. D. Miles, *Nature (London)*, **137**, 577 (1936).

[11] A. K. Van Bever, *Recl. Trav. Chim. Pays-Bas*, **57**, 1259 (1938).

[12] H. B. Weiser, W. O. Milligan, and J. B. Bates, *J. Phys. Chem.*, **46**, 99 (1942).

[13] M. B. Robin, *Inorg. Chem.*, **1**, 337 (1962).

[14] P. S. Braterman, *J. Chem. Soc. A*, 1471 (1966).

[15] D. Davidson and L. A. Welo, *J. Phys. Chem.*, **32**, 1191 (1928).

[16] R. M. Bozorth, H. J. Williams, and D. E. Walsh, *Phys. Rev.*, **103**, 572 (1956).

[17] See the references and historic discussion in ref 3.