

THERMOLYSIS OF COMPLEX CYANIDES, XV.*

DECOMPOSITION OF $[\text{Fe}(\text{CN})_4\text{BIPY}]^{n-}$ AND $[\text{Fe}(\text{CN})_4\text{PHEN}]^{n-}$ COMPLEXES

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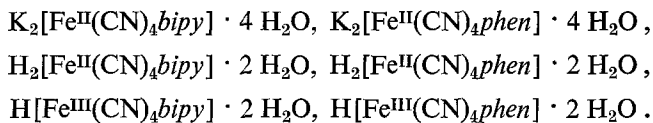
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The thermal decompositions of $\text{K}_2[\text{Fe}(\text{CN})_4\text{L}] \cdot 4 \text{H}_2\text{O}$, $\text{H}_2[\text{Fe}(\text{CN})_4\text{L}]$ and $\text{H}[\text{Fe}(\text{CN})\text{L}]$ ($\text{L} = 1,1'$ -bipyridine, of 1,10-phenanthroline) were studied. The experimental results showed that the protonated ferrous complexes decompose with formation of HCN at lower temperature than the corresponding potassium salts. The decomposition of $\text{K}_2[\text{Fe}(\text{CN})_4\text{L}]$ starts by removal of the ligand L. HCN elimination is followed by a redox reaction with formation of cyanogen in the case of $\text{H}[\text{Fe}^{\text{III}}(\text{CN})_4\text{L}]$.

Experimental

The following compounds were used for derivatographic studies:



These complexes were prepared by Schilt's method [1].

The thermal studies were made with a MOM 3427/SK derivatograph, in a Pt crucible with $\alpha\text{-Al}_2\text{O}_3$ as reference material and N_2 as inert gas. Other operating conditions: T_{max} : 1000° ; heating rate: $10^\circ/\text{min}$; The sample weight was 100–300 mg. The weight losses observed in the TG curves were referred to 1 mole of investigated complex.

The evolved HCN was determined quantitatively by evolved gas analysis [2]. It was absorbed in NH_4OH solution and was titrated continuously potentiometrically (using a CN-selective electrode) with AgNO_3 solution.

The complexes and their solid thermal residues were investigated by IR and Mössbauer spectroscopy. The IR spectra were recorded on a double-beam Carl Zeiss UR-10 spectrophotometer in KBr. For the Mössbauer measurements a ^{57}Co source diffused into Pt was used. The absorbent was cooled with liquid nitrogen.

$\text{H}_2[\text{Fe}(\text{CN})_4\text{bipy}] \cdot 2 \text{H}_2\text{O}$ and $\text{H}[\text{Fe}(\text{CN})_4\text{bipy}] \cdot 2 \text{H}_2\text{O}$ were decomposed directly in a Varian Mat 111 mass-spectrometer too at different temperatures.

* XIV. A. Hantshmann, J. Salvetter, H. Hennig and B. Mohai, *Thermochim. Acta.* 25 (1978) 341

Results and discussion

Thermal decomposition of $K_2[Fe^{II}(CN)_4L] \cdot 4 H_2O$

The thermal curves of $K_2[Fe(CN)_4bipy] \cdot 4 H_2O$ and $K_2[Fe(CN)_4phen] \cdot 4 H_2O$ are given in Fig. 1. In the first step the crystal water is lost at 130 and 140°, respectively. Thermal decomposition of the complexes starts with elimination of the aromatic ligand. The peak temperature of this process is 275° for the bipyridine complex, and 380° for the phenanthroline complex. The decomposition temperatures of these compounds are lower than those of $K_4[Fe(CN)_6]$, $[Fe(CN)_2bipy_2]$ and $[Fe(CN)_2phen_2]$ [3]. This shows that the substitution of two cyanide ligands

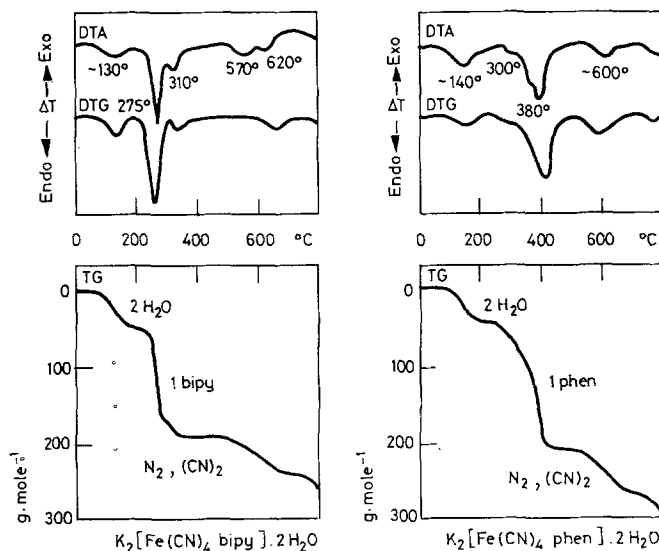


Fig. 1. TG, DTG, DTA curves of $K_2[Fe(CN)_4L]$

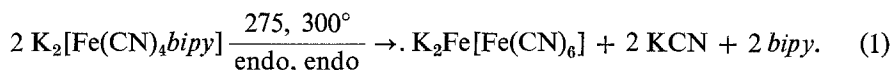
of $K_4[Fe(CN)_6]$ by one bipyridine or one phenanthroline produces a compound which has a lower thermal stability than that of $[Fe(CN)_2bipy_2]$, $[Fe(CN)_2phen_2]$ or $K_4[Fe(CN)_6]$ (Table 1).

Table 1

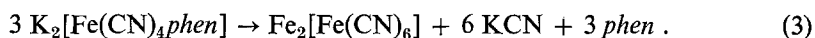
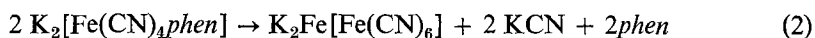
Peak temperature of splitting-off of first ligand at thermolysis of $K_4[Fe(CN)_6]$, $K_2[Fe(CN)_4L]$ and $[Fe(CN)_2L_2]$

Complex	T, °C	Ligand split off	Ref.
$K_4[Fe(CN)_6]$	600	CN	[3]
$K_2[Fe(CN)_4phen]$	300, 380	phen	
$K_2[Fe(CN)_4bipy]$	275	bipy	
$[Fe(CN)_2phen_2]$	440	phen	[3]
$[Fe(CN)_2bipy_2]$	315	bipy	[3]

It can be observed in the TG and DTG curves of $K_2[Fe(CN)_4bipy]$ that the reaction is accelerated in the final stage of bipyridine loss, while an endothermic effect appears in the DTA curve. This can be attributed to a structural transformation which helps the leaving of the bipyridine (300°). The reaction may be represented by the following equation:



The thermal curves of $K_2[Fe(CN)_4phen]$ show that the loss of the phenanthroline ligand occurs in two reactions. It can be assumed that these reactions are the following:



$K_2Fe[Fe(CN)_6]$ decomposes to KCN and $Fe_2[Fe(CN)_6]$ above 500° . The final stages in the TG and DTA curves of the complexes correspond to the decomposition of $Fe_2[Fe(CN)_6]$ and KCN [4].

Thermal decomposition of $H_2[Fe^{II}(CN)_4L] \cdot 2 H_2O$

The two hydrogen-tetracyanoferrate(II) complexes decompose with hydrogen cyanide formation in endothermic reactions. The complex with bipyridine gives off HCN in one step at 140° , while that with phenanthroline evolves HCN in two steps, at 130 and 160° (Fig. 2). The relatively stable decomposition intermediate

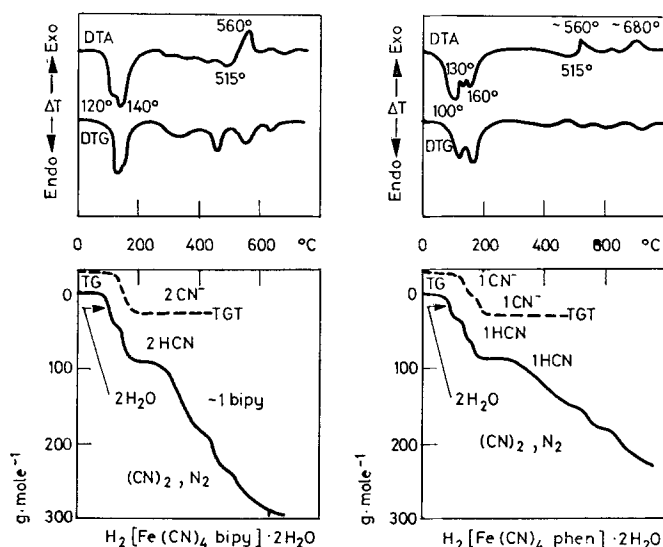


Fig. 2. TG, DTG and DTA curves of $H_2[Fe(CN)_4L]$

of $\text{H}_2[\text{Fe}(\text{CN})_4\text{phen}]$ is formally a coordinatively non-saturated complex, " $\text{H}[\text{Fe}(\text{CN})_3\text{phen}]$ "; but IR and Mössbauer spectroscopic data show that the central atom is six-coordinated. In the IR spectra of $\text{H}_2[\text{Fe}(\text{CN})_4\text{phen}]$ ν_{CN} can be observed at 2085 cm^{-1} , while " $\text{H}[\text{Fe}(\text{CN})_3\text{phen}]$ " has a wide ν_{CN} band at 2095 cm^{-1} . This indicates that there is a bridging cyanide ligand in the intermediate. The Mössbauer parameters of these compounds are not essentially different: $\Delta E_{\text{QA}} = 0.61$, $\Delta E_{\text{QB}} = 0.75$, $\delta_{\text{A}} = -0.25$, $\delta_{\text{B}} = -0.2$ ($\text{A} = \text{H}_2[\text{Fe}(\text{CN})_4\text{phen}]$, $\text{B} = \text{H}[\text{Fe}(\text{CN})_3\text{phen}]$). This also shows that the central atom is coordinatively saturated in " $\text{H}[\text{Fe}(\text{CN})_3\text{phen}]$ ".

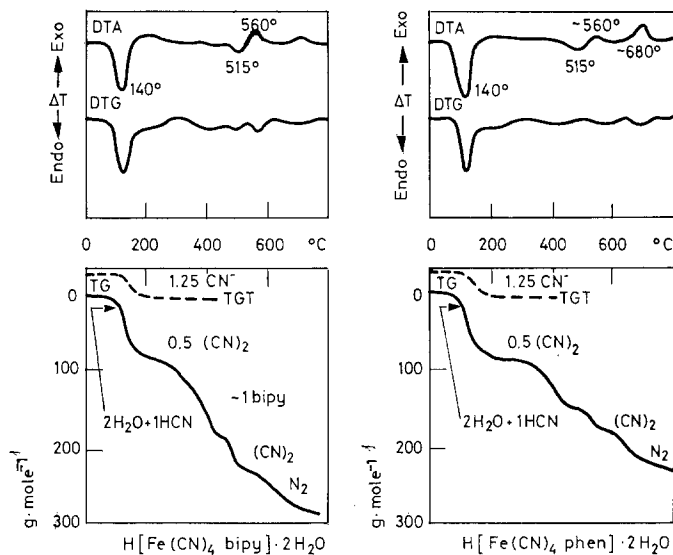
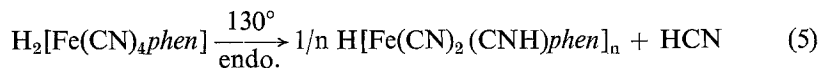
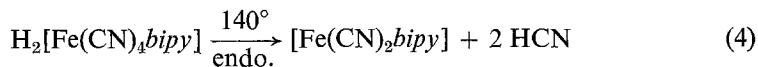


Fig. 3. TG, DTG and DTA curves of $\text{H}[\text{Fe}(\text{CN})_4\text{L}]$

The decomposition reactions of the compounds are as follows:



Thermal decomposition of $\text{H}[\text{Fe}^{\text{III}}(\text{CN})_4\text{L}] \cdot 2\text{H}_2\text{O}$.

The first endothermic reaction can be observed at 140° in the thermal curves of these complexes (Fig. 3). The weight change corresponds to the loss of crystal water, and one mole of HCN or half a mole of $(\text{CN})_2$. This process is followed by

a slow reaction at 160–200°, the weight loss again corresponding to the formation of HCN or 0.5 (CN)₂. The fact that cyanogen is formed in the second step has been proved by the following arguments:

a) The ν_{CN} of intermediate *C* (*C* is the solid residue of $\text{H}[\text{Fe}^{\text{III}}(\text{CN})_4\text{bipy}]$ heated to 160°) can be observed at 2130, 2065 and 2025 cm^{-1} , but IR spectra of intermediate *D* (the solid residue of $\text{H}[\text{Fe}^{\text{III}}(\text{CN})_4\text{bipy}]$ heated to 260°) showed ν_{CN} only at 2070 and 2030 cm^{-1} . This suggested that the reduction of ferrate(III) to ferrate(II) proceeded between 160 and 260°.

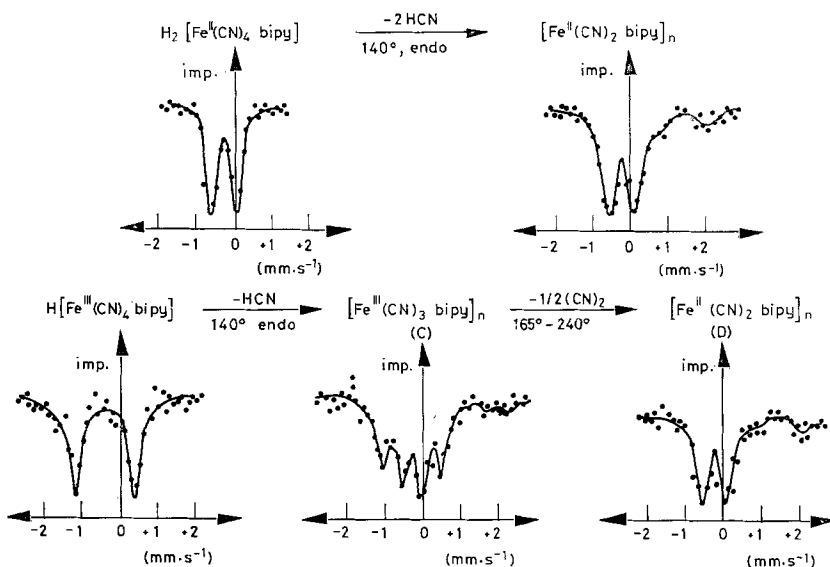


Fig. 4. Mössbauer spectra of $\text{H}_2[\text{Fe}^{\text{II}}(\text{CN})_4\text{bipy}]$ and $\text{H}[\text{Fe}^{\text{III}}(\text{CN})_4\text{bipy}]$ and their solid thermal residues

b) The Mössbauer spectra of intermediate *C* showed the signals of iron(III), while only iron(II) could be observed in the spectra of *D* (Fig. 4).

c) Strong HCN and weak (CN)₂ lines could be observed in the mass spectra of $\text{H}[\text{Fe}(\text{CN})_4\text{bipy}] \cdot 2\text{H}_2\text{O}$ at 155°, while the (CN)₂ lines were more intensive than those of HCN at 165°.

d) HCN formation is always endothermic in the thermal decomposition of any of the studied cyanoferrate acids; at the same time, if the thermal decomposition of paramagnetic cyano complexes which have one unpaired electron starts by cyanogen formation, the reaction is always exothermic [5].

e) The fact that the thermal curves of $\text{H}[\text{Fe}^{\text{III}}(\text{CN})_4\text{L}]$ correspond to the TG, DTG and DTA curves of $\text{H}_2[\text{Fe}^{\text{II}}(\text{CN})_4\text{L}]$ only after the slow reaction, is circumstantial evidence.

$\text{Fe}(\text{CN})_2\text{bipy}$ decomposes above 300° with formation of *bipy* and $\text{Fe}_2[\text{Fe}(\text{CN})_6]$. The endothermic (515°) and exothermic (560°) peaks in the DTA curves indicate the decomposition of $\text{Fe}_2[\text{Fe}(\text{CN})_6]$ [4].

The weight loss is smaller than one mole phenanthroline in the case of decomposition of $\text{Fe}(\text{CN})_2\text{phen}$. This shows that the bonds between the central atom and the phenanthroline ligand are very strong, and instead of the splitting-off of the ligand it is cracked. The relatively strong exothermic effect at 680° can be attributed to the decomposition of an iron–nitrile complex.

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References

1. A. A. SCHILT, J. Am. Chem. Soc., 82 (1960) 3000.
2. J. PAULIK and F. PAULIK, J. Thermal Anal., 3 (1971) 63.
3. E. Cs. PORZSOLT, B. MOHAI and M. T. BECK, Magyar Kémiai Folyóirat, 80 (1974) 254.
4. B. MOHAI, Acta Chim. Acad. Sci. Hung., 62 (1969) 217.
5. B. MOHAI, Magy. Tud. Akad. Kém. Tud. Oszt. Közl., 46 (1976) 163.

ZUSAMMENFASSUNG — Die thermische Zersetzung von $\text{K}_2[\text{Fe}(\text{CN})_4L] \cdot 4\text{H}_2\text{O}$, $\text{H}_2[\text{Fe}(\text{CN})_4L]$ und $\text{H}[\text{Fe}(\text{CN})_4L]$ ($L = 1,1'$ -Dipyridin, 1,10-Phenanthrolin) wurde untersucht. Die Versuchsergebnisse zeigten, dass die protonierten Ferrokomplexe unter Bildung von HCN bei niedrigeren Temperaturen zersetzt werden, als die entsprechenden Kaliumsalze. Die Zersetzung von $\text{K}_2[\text{Fe}(\text{CN})_4L]$ beginnt durch die Abspaltung des Liganden L . Nach Eliminierung des HCN folgt eine Redox-Reaktion unter Bildung von Dizyan im Falle von $\text{H}[\text{Fe}^{\text{III}}(\text{CN})_4L]$.

Резюме — Изучено термическое разложение $\text{K}_2[\text{Fe}(\text{CN})_4L] \cdot 4\text{H}_2\text{O}$, $\text{H}_2[\text{Fe}(\text{CN})_4L]$ и $\text{H}[\text{Fe}(\text{CN})_4L]$ где $L = 1,1'$ -бипиридин и 1.10-фенантролин. Экспериментальные результаты показали, что протонированные комплексы двухвалентного железа разлагаются при более низкой температуре, чем соответствующие калиевые соли. Разложение $\text{K}_2[\text{Fe}(\text{CN})_4L]$ начинается с отщепления лиганда L . В случае $\text{H}[\text{Fe}^{\text{III}}(\text{CN})_4L]$ выделение HCN сопровождается окислительно-восстановительной реакцией с образованием циана.