Thermochimica Acta, 130 (1988) 77–85
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMAL DECOMPOSITION OF $K_3Co(CN)_5L$ IN HYDROGEN ATMOSPHERE AND THE INFLUENCE OF REDUCED IRON POWDER

YUAN JINHUA, XIN XINQUAN and DAI ANBANG

Coordination Chemistry Institute, Nanjing University, Nanjing, People's Republic of China

(Received 1 October 1987)

ABSTRACT

The thermal decomposition of $K_3Co(CN)_5L$ ($L = CN^-$, NO_2^-, N_3^-, NO) in a hydrogen atmosphere has been studied by gas chromatography. The first stage of thermal decomposition of these complexes is to release crystal water if contained, and the second stage is to dissociate the ligand at very high speed, with a large amount of heat being released when $L = N_3^-$. Thirdly, the residual cyano-cobalt complex is further decomposed to form HCN, $(CN)_2$ and N_2, and a little NH_3 and CH_4. In the presence of iron powder, the evolution of NH_3 is increased greatly, whereas HCN disappeared entirely. The influence of reduced iron powder upon the decomposition is also studied.

INTRODUCTION

Cyano-cobalt complexes have been widely studied as a redox catalyst [1,2], but few studies have been made on their thermal behaviour [3]. Because of the similarity of the molecular orbitals of CN^- and N_2, it is natural that the information about the cleavage and the hydrogenation of CN^- and the catalyst effects of iron can be a help in nitrogen fixation research. In this study, a series of $K_3Co(CN)_5L$ complexes ($L = CN^-$, NO_2^-, N_3^-, NO) were prepared, and the thermal decomposition of these complexes was studied in a hydrogen atmosphere mainly by gas chromatograph. The influence of reduced iron powder upon the thermal decomposition was also observed.

EXPERIMENTAL

Materials

$K_3Co(CN)_6$ was synthesized by the reaction of $CoCl_2 \cdot 6H_2O$ with KCN [4]. Each of $K_3Co(CN)_5NO_2$, $K_3Co(CN)_5N_3 \cdot 2H_2O$ and $K_3Co(CN)_5NO \cdot$

0040-6031/88/$03.50

$2H_2O$ was synthesized separately by the reaction of $Co(NH_3)_5LCl_2$ with KCN according to the methods given in literature [5,6]. Recrystallization was performed to insure high purity of the products, which were confirmed pure by IR. Samples of size between 100 and 160 mesh were used in this study.

Reduced iron powder of Analytic Grade is purchased from Reagent Supplier Inc. of China, Bejing.

Apparatus

The apparatus used was constructed in this laboratory [7,8]. It consists of a furnace, a sample temperature recorder and a Suchua Model SC-6 gas chromatograph operated at carrier gas (H_2) flow rate 60 ml min^{-1}, column temperature 120 °C, TCD 150 °C, 150 mA.

Procedure

A 200-mg sample was placed in the reaction Pyrex tube located in the furnace and the air in the system was then swept out by hydrogen which flowed continuously through the tube and carried the evolved gaseous products from the sample into a six-way stop-cock. At intervals of 20 °C the six-way stop-cock was adjusted so that the evolved gaseous product from the sample was fed into the separation column for detection. The peaks appearing on the gas chromatograms were identified by the retention times of various pure substances which may be expected to be formed during the thermal decomposition of the sample. From the peak areas the amount of the decomposition products could be ascertained, and when plotted as a function of temperature the evolved gaseous products (EG) curves of the sample were obtained. The column used was 2 m Porapark QS plus 1 m Chromsorb 104, the chromatographic patterns for various pure substances

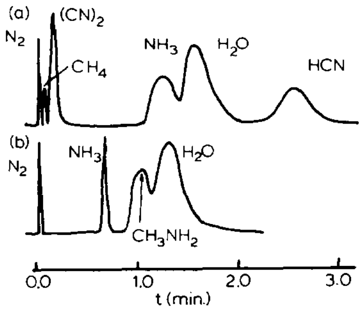


Fig. 1. Gas chromatograms of various substances. (a) 2 m Porapark QS + 1 m Chromsorb 104. (b) 1 m Chromsorb 103. The carrier gas is hydrogen.

are shown in Fig. 1a. However, the retention time of both CH_3NH_2 and H_2O are equal on the column used. For their separation a 1-m stainless steel column packed with chromsorb 103 was used: the chromatogram is shown in Fig. 1b. In this study, no CH_3NH_2 was found in the evolved gaseous product.

IR spectra

Infrared spectra were recorded using a Nicolet-FT-IR 170 Sx.

XRD

X-ray diffractograms were obtained using a Shimadazu Model XD-3A X-ray diffractometer with a copper target.

RESULTS AND DISCUSSION

Thermal decomposition of $K_3Co(CN)_5L$ in hydrogen

Figure 2 gives the EG curves of $K_3Co(CN)_5L$ complexes in the range 60–600 °C in a hydrogen atmosphere. It can be seen that the first stage of

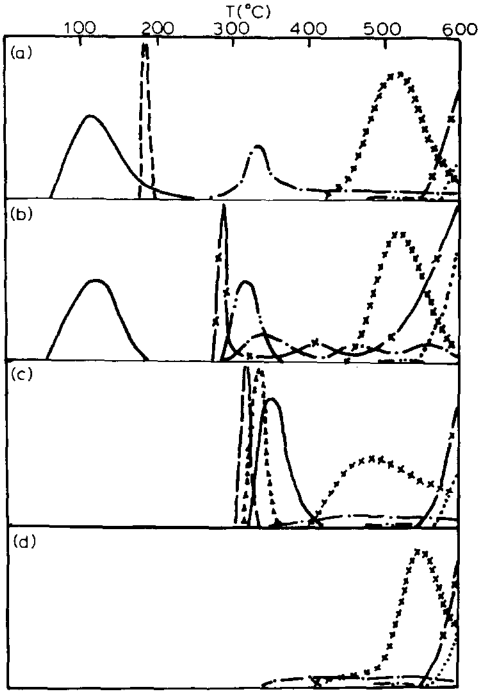


Fig. 2. EG curves of cyano-cobalt complexes in a hydrogen atmosphere. (a) $K_3Co(CN)_5NO \cdot 2H_2O$. (b) $K_3Co(CN)_5N_3 \cdot 2H_2O$. (c) $K_3Co(CN)_5NO_2$. (d) $K_3Co(CN)_6$. ——, H_2O; - - - - - -, NO: ▲▲▲▲▲▲, NO_2; ·–·–·, $(CN)_2$; × × × × × × ×, HCN; × – – – – – ×, N_2; · · · · · ·, CH_4; · · – · · –, NH_3.

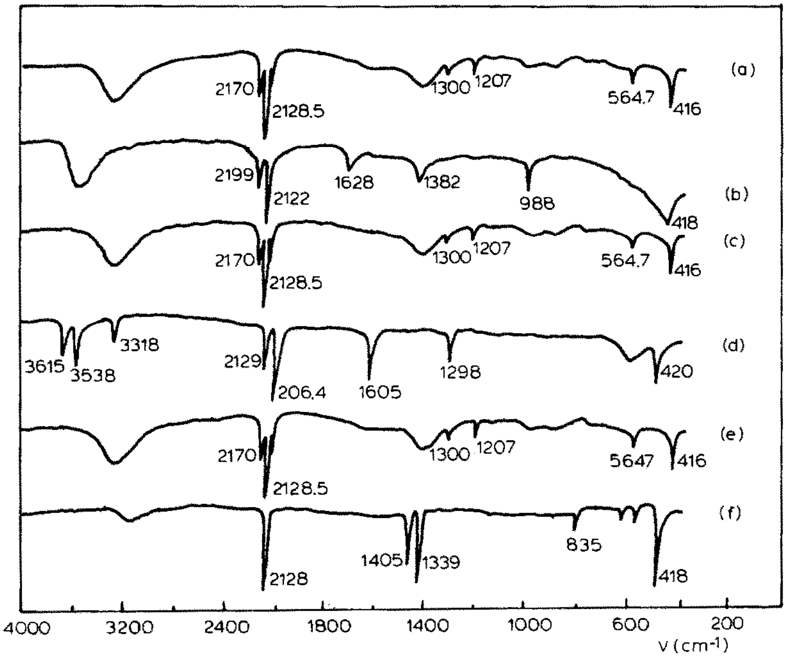


Fig. 3. IR spectra of $K_3Co(CN)_5L$ and the solid products after dissociating L in a hydrogen atmosphere. (a) 220 °C, $K_3Co(CN)_5NO \cdot 2H_2O$. (b) $K_3Co(CN)_5NO \cdot 2H_2O$. (c) 300 °C, $K_3Co(CN)_5N_3 \cdot 2H_2O$. (d) $K_3Co(CN)_5N_3 \cdot 2H_2O$. (e) 320 °C, $K_3Co(CN)_5NO_2$. (f) $K_3Co(CN)_5NO_2$.

thermal decomposition of these coordination compounds is the loss of water of crystallization, and the second stage is dissociation of L from the cobalt coordination sphere, forming corresponding gaseous products. The temperatures of the dissociation of L (T_L) increase in the sequence $T_{NO} < T_{N_3^-} < T_{NO_2^-} < T_{CN^-}$, the order being consistent with the coordination ability of L as a ligand.

Figure 3 is the IR spectra of $K_3Co(CN)_5L$ and the solid products after dissociating L. It can be clearly seen that the characteristic vibration bands

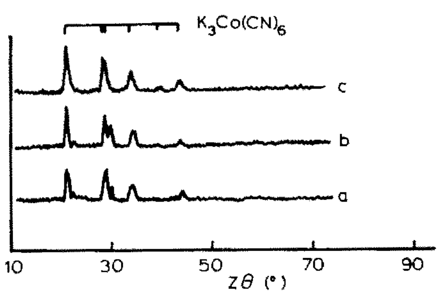


Fig. 4. XRD results of the thermal decomposition products of $K_3Co(CN)_5L$ in a hydrogen atmosphere. (a) 220 °C, $K_3Co(CN)_5NO \cdot 2H_2O$. (b) 280 °C, $K_3Co(CN)_5N_3 \cdot 2H_2O$. (c) 320 °C, $K_3Co(CN)_5NO_2$.

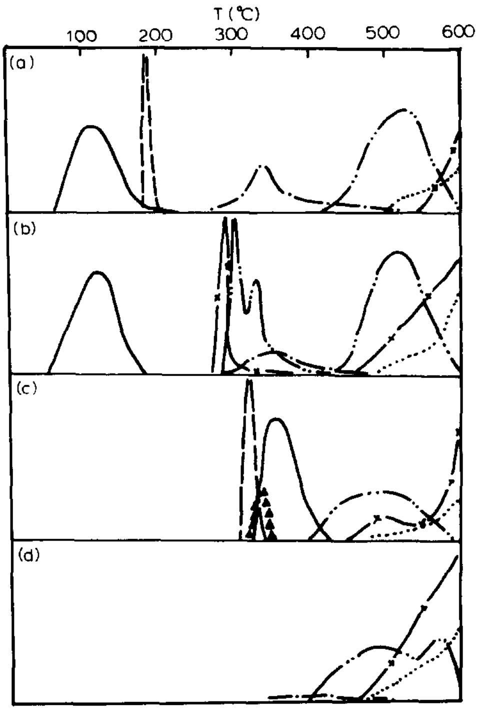


Fig. 5. EG curves of $K_3Co(CN)_5L$ with reduced iron powder in a 1 : 6 mole ratio in a hydrogen atmosphere. (a) $K_3Co(CN)_5NO \cdot 2H_2O$. (b) $K_3Co(CN)_5N_3 \cdot 2H_2O$. (c) $K_3Co(CN)_5NO_2$. (d) $K_3Co(CN)_6$. ———, H_2O; ------, NO; ▲▲▲▲▲▲, NO_2; ·–·–·, $(CN)_2$; ×-----×, N_2; ······, CH_4; ··–··–, NH_3.

of NO, NO_2^- and N_3^- disappeared. It is interesting to note that the IR spectra of the solid products of $K_3Co(CN)_5L$ after dissociating L are all the same (Fig. 3a,c,e). The sharp peaks at 2128.5, 564.7 and 416 cm^{-1} all show the existence of $K_3Co(CN)_6$ while the band at 2170 cm^{-1} indicates the existence of bridge CN^- [9].

Figure 4 shows the XRD results of the solid products of $K_3Co(CN)_5L$ after thermal decomposition in hydrogen. Although the intensity of the diffraction peak is rather weak due to the incomplete crystallization of the products, it still can be seen clearly that the diffraction patterns of the products in Fig. 4 are the same, and the corresponding substance is $K_3Co(CN)_6$. This also reinforces the conclusion obtained by IR.

Figure 5 shows the EG curves of $K_3Co(CN)_5L$ with reduced iron powder in 1 : 6 mole ratio in a hydrogen atmosphere. Comparing Fig. 5 with Fig. 2, it can be seen that the presence of iron powder did not affect the dissociation of the ligand, but when the temperature was further raised, the composition of the evolved gaseous products changed and the amount of NH_3 increased while HCN disappeared entirely. A small amount of CH_4 is also formed above 500 ° C.

Thermal decomposition mechanism of $K_3Co(CN)_5L$ in hydrogen

$K_3Co(CN)_6$

This compound is very stable to heating. Thermal decomposition begins at 350 °C at a very slow rate, releasing a small amount of $(CN)_2$. After 400 °C the gas–solid reaction takes place forming HCN, and at 550 °C a large amount of HCN is evolved. Nitrogen and a small amount of NH_3 and CH_4 are also evolved, implying the breaking of the triple bond of CN^-. The thermal decomposition of $K_3Co(CN)_6$ can be represented as

$$10K_3Co(CN)_6 \xrightarrow{>350\,°C} 2Co_3[Co(CN)_6]_2 + 30KCN + 3(CN)_2 \quad (1)$$

$$10K_3Co(CN)_6 + 3H_2 \xrightarrow{>400\,°C} 2Co_3[Co(CN)_6]_2 + 30KCN + 6HCN \quad (2)$$

$$3Co_3[Co(CN)_6]_2 + 20H_2 \xrightarrow{>500\,°C} 5Co_3C + 31HCN + 3NH_3 + N_2 \quad (3)$$

$$Co_3C + 2H_2 \xrightarrow{>550\,°C} 3Co + CH_4 \quad (4)$$

The formation of KCN and Co_3C can be demonstrated by XRD (Fig. 6).

According to this mechanism, the amount of HCN evolved should be more than that of NH_3, and this is the case (Fig. 2)

$K_3Co(CN)_5NO \cdot 2H_2O$

This complex is different from other cobalt complexes; the valence of the NO ligand is +1. The dissociation of NO from $K_3Co(CN)_5NO$ is an oxidation step, which renders the compound less stable thermally. The first step of its thermal decomposition is the loss of water of crystallization around 120 °C, and the second step is the dissociation of NO from the cobalt coordination sphere, forming NO gas. One of the solid products at

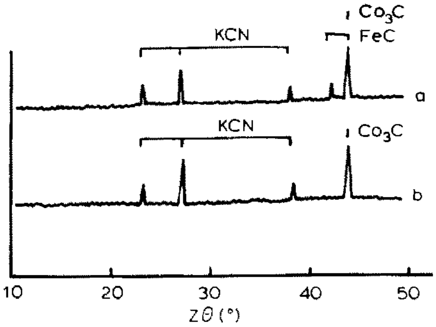


Fig. 6. XRD results of the thermal decomposition products of $K_3Co(CN)_6$ at 600 °C in a hydrogen atmosphere. (a) 1 : 6 mole ratio $K_3Co(CN)_6$ and iron powder. (b) $K_3Co(CN)_6$.

this stage is $K_3Co(CN)_6$ which implies the rearrangement of the CN^- ligand. It is also interesting to note that no diffraction peak of $K_3Co(CN)_5$ appears on the XRD, i.e. $K_3Co(CN)_5$ is not formed in the thermal decomposition of $K_3Co(CN)_5NO$ [10]. The mechanism of its reaction is

$$K_3Co(CN)_5NO \cdot 2H_2O \xrightarrow{120\,^\circ C} K_3Co(CN)_5NO + 2H_2O \tag{5}$$

$$5K_3Co(CN)_5NO \xrightarrow{180\,^\circ C} K_3Co(CN)_6 + \text{pseudo-Prussian blue} + 5NO \tag{6}$$

The formation of $K_3Co(CN)_6$ is demonstrated by XRD and IR spectra; the existance of pseudo-Prussian blue can be inferred from IR spectra (2170 cm^{-1}). When the temperature is further raised, cyano-cobalt complexes decompose further

$$\text{pseudo-Prussian blue} \xrightarrow{>400\,^\circ C} KCN + Co_3C + HCN + (CN)_2 + NH_3 \tag{7}$$

$$10K_3Co(CN)_6 + 3H_2 \xrightarrow{>400\,^\circ C} 2Co_3[Co(CN)_6]_2 + 30KCN + 6HCN \tag{8}$$

$$3Co_3[Co(CN)_6]_2 + 20H_2 \xrightarrow{>500\,^\circ C} 5Co_3C + 31HCN + 3NH_3 + N_2 \tag{9}$$

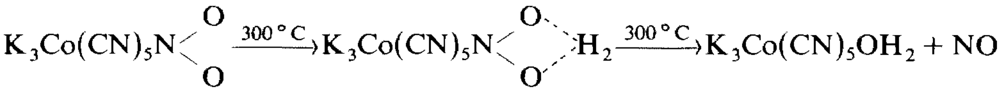
$$Co_3C + 2H_2 \xrightarrow{>550\,^\circ C} 3Co + CH_4 \tag{10}$$

$K_3Co(CN)_5NO_2$

This compound does not contain water of crystallization. The first step of the thermal decomposition is the dissociation of NO_2, releasing NO and NO_2, and also H_2O in a hydrogen atmosphere

$$5K_3Co(CN)_5NO_2 + 3H_2 \xrightarrow{>300\,^\circ C} K_3Co(CN)_6 + \text{pseudo-Prussian blue} + 3NO + 2NO_2 + 3H_2O \tag{11}$$

The gas first evolved is NO, then NO_2, with H_2O following NO and NO_2, implying that NO is not formed by the reduction of NO_2 in gaseous phase, otherwise they should have evolved simultaneously. The following mechanism is more probable



$$K_3Co(CN)_5N\!\begin{smallmatrix}O\\O\end{smallmatrix} \xrightarrow{300\,^\circ C} K_3Co(CN)_5N\!\begin{smallmatrix}O\\O\end{smallmatrix}\!\cdot\!\cdot H_2 \xrightarrow{300\,^\circ C} K_3Co(CN)_5OH_2 + NO \xrightarrow{>310\,^\circ C} K_3Co(CN)_6 + \text{pseudo-Prussian blue} + H_2O \tag{12}$$

The further decomposition reaction is similar to that of $K_3Co(CN)_5NO$.

$K_3Co(CN)_5N_3 \cdot 2H_2O$

The first step is deaquation, releasing water of crystallization at 120 °C. At 280 °C, $K_3Co(CN)_5N_3$ explosively decomposed and, like many N_3^-

compounds, N_2 and NH_3 were evolved; meanwhile a large amount of heat is released. The final temperature is about 360 °C when the dissociation of the N_3^- ligand is complete

$$K_3Co(CN)_5N_3 \cdot 2H_2O \xrightarrow{120\,^\circ C} K_3Co(CN)_5N_3 + 2H_2O \tag{13}$$

$$2K_3Co(CN)_5N_3 + 3H_2 \xrightarrow{280\,^\circ C} K_3Co(CN)_6 + \text{pseudo-Prussian blue} + 2N_2 + 2NH_3 \tag{14}$$

Because of the high activity of the N_3^- ligand, a part of N_3^- is hydrogenated, forming NH_3.

The sequence of the temperature of dissociation of the ligand, i.e. $T_{NO} < T_{N_3^-} < T_{NO_2^-} < T_{CN^-}$ is basically consistent with the results obtained by Yatsimiskii et al. [11] who studied a series $K_3Co(CN)_5L$ ($L = NO$, NO_2^-, N_2, N_3^-, CN^-) using X-ray photoelectron spectroscopy. By analysis of the spectra of the 1*s*-electrons of N and O atoms and also the 2*p*-electrons of Co and K atoms of the compounds, they obtained the sequence $NO < NO_2^- < N_3^- < CN^-$ for the effect of a ligand on the value of the binding energy of the 1*s*-electron of cyanide N atoms, as well as on the binding energy of the ${}^2P_{5/2}$ electron of the Co atoms. The difference of the position in this sequence compared with the sequence of dissociation temperatures of N_3^- and NO_2^- may explain the peculiar explosive property of N_3^- on heating.

When iron powder was present, HCN gas did not appear in the evolved gaseous products; instead a considerable amount of NH_3 was produced, while a little CH_4 is formed in contrast with NH_3. This excludes the simple catalytic action of iron on CN^-, since the amounts of NH_3 and CH_4 are not equal. According to the frontier molecular orbital theroy, the H_2 molecule is difficult to react with CN^- directly because of the symmetry prohibition. However, the reaction could be catalyzed by a transition metal which is capable of back-donating *d*-electrons to the anti-bonding orbital σ_{1s}^a of H_2 molecule; thus the rupture of the H–H bond is facilitated, while HCN is adsorbed on iron and reacts with iron to form a cyano-iron complex, with the terminal C coordinated to iron (Fig. 7).

The H atoms readily react with CN^- and the triple bond breaks down. However, from the large difference in amounts of NH_3 and CH_4, it is logical to infer that the hydrogenation takes place at the N end of the cyano

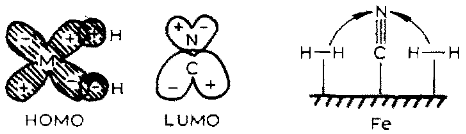


Fig. 7. Mechanism of the catalytic hydrogenation of CN^- by iron powder.

group, to which H atoms are transferred by iron, forming NH_3, with the C end still attached to iron, forming FeC (which is demonstrated by XRD (Fig. 6a). Although CN^- and N_2 have similar molecular orbitals, due to their great difference in coordination ability, hydrogenation of the cyanide group is quite different from that of dinitrogen.

CONCLUSION

Thermal decomposition of $K_3Co(CN)_5L$ may be divided into three steps. The first step is the loss of water of crystallization, the second is the dissociation of the L ligand and the third is the entire decomposition of the cyano complexes. Presence of iron facilitates the hydrogenation of CN^-, and in this capacity iron is more effective than cobalt.

REFERENCES

1 M. Morioka, Y. Takeuchi, H. Mizuno and M. Suzuki, Nippon Kagaku Kaishi, 8 (1980) 1300.
2 T. Funabiki, Y. Yasuyuki and T. Kimio, J. Chem. Soc. Chem. Commun., 2 (1978) 63.
3 J.S. Yoo, E. Griswold and J. Kleinberg, Inorg. Chem., 4 (1965) 365.
4 H.S. Booth, (Ed.), Inorganic Syntheses, Vol. II, McGraw-Hill, New York, 1976, p. 225.
5 R. Nast and M. Rohner, Z. Anorg. Allg. Chem., 285 (1956) 278.
6 J. Fujita and Y. Shimura, Bull. Chem. Soc. Jpn., 36 (1963) 1281.
7 C.H. Yuan, X.Q. Xin and A.B. Dai, Inorg. Chem. Chin., 2 (1988).
8 J.N. Niu, X.Q. Xin and A.B. Dai, Acta Chimica Sinica, 4 (1986) 335.
9 J.C. Bailar, Jr. H.T. Emelens, R. Nyholm and A.F. Trotman-Dickenson, Comprehensive Inorganic Chemistry, Vol. 4, Pergamon, 1973, p. 105.
10 W.P. Griffith and A.J. Wickham, J. Chem. Soc. A, (1969) 834.
11 K.B. Yatsimirskii, V.V. Nemoshkalenko, Yu. P. Nazarenko, V.V. Zhilinskaya, V.G. Aleshin and G.A. Kozlov. Teor. Eksp. Khim., 14 (1978) 391; Chem. Abstr., $93{:}196829_q$, $89{:}171141_p$.