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Mössbauer Studies of the Thermal Decomposition of Iron(II) Pyridine and Picoline Complexes

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The thermal decomposition of tetrakispyridineiron(II) chloride, tetrakis(γ-picoline)iron(II) chloride, and tetrakispyridineiron(II) isothiocyanate has been studied in nitrogen. These complexes presumably decompose in the following sequences:

$Fe(py)_4Cl_2 \rightarrow Fe(py)_2Cl_2 \rightarrow Fe(py)Cl_2 \rightarrow Fe(py)_{2/3}Cl_2 \rightarrow FeCl_2$,
$Fe(\gamma\text{-pic})_4Cl_2 \rightarrow Fe(\gamma\text{-pic})Cl_2 \rightarrow FeCl_2$ and $Fe(py)_4(NCS)_2 \rightarrow Fe(py)_2(NCS)_2 \rightarrow Fe(NCS)_2$.

The Mössbauer spectra of these complexes and of their decomposition products have been studied in terms of the structural change about the iron atom during the thermal decomposition process.

The Mössbauer spectroscopy has become a useful technique to investigate the oxidation state and the electronic configuration of iron in iron compounds. Since the Mössbauer study of the radiolysis and photolysis of ferric oxalate[1] indicated that this new technique was useful for directly investigating the chemical changes induced in solids, we applied this method to the study of the thermal decomposition of tetrakispyridineiron(II) chloride.[2]

After our preliminary work had been submitted for publication, we learned of an earlier Mössbauer work on some complex oxalates of iron(III).[3] In those iron oxalates, the oxidation state of iron was found to fluctuate between +2 and +4 during the course of the thermal decomposition.

According to our work on the thermal decomposition behavior of the iron(II) pyridine complexes,[2] the oxidation state of iron remains unchanged during the process in nitrogen. The thermal decomposition of these complexes proceeds through the step-by-step formation of octahedral polymers. Therefore, the purpose of our present work is to study the change in the Mössbauer parameters at different phases of the thermal decomposition in terms of the structural change about the iron atom, or the growth of the polymer structure during the decomposition process.

In the present paper, we will give a more complete report on the system which was studied in our earlier work,[2] as well as new data on some other complexes which have been studied recently.

Experimental

Samples. Tetrakispyridineiron(II) chloride, tetrakis(γ-picoline)iron(II) chloride, and tetrakispyridineiron(II) isothiocyanate were prepared and used for the thermal decomposition studies.

(i) $Fe(py)_4Cl_2$. Tetrakispyridineiron(II) chloride was prepared as has been described in the literature.[4,5]

1) N. Saito, H. Sano, T. Tominaga and F. Ambe, This Bulletin, **38**, 681 (1965).

2) T. Tominaga, T. Morimoto, M. Takeda and N. Saito, *Inorg. Nucl. Chem. Lett.*, **2**, 193 (1966).

3) P. K. Gallagher and C. R. Kurkjian, *Inorg. Chem.*, **5**, 214 (1966).

4) R. Weinland, K. Effinger and V. Beck, *Arch. Pharm.*, **265**, 352 (1927).

5) H. S. Booth, "Inorganic Syntheses," Vol. 1, McGraw-Hill Book Co. Inc., New York (1939), p. 184.

Intense yellow crystals were obtained and dried in a vacuum desiccator containing pyridine vapor. Found: Fe, 12.6; Cl, 15.0%. Calcd for $Fe(py)_4Cl_2$: Fe, 12.6; Cl, 14.2%.

(ii) $Fe(\gamma\text{-pic})_4Cl_2$. This was prepared by a procedure similar to (i). To 20 m*l* of γ-picoline we added 5 m*l* of a saturated $FeCl_2$ solution. Yellow crystals of the complex were obtained. Found: Fe, 11.3: Cl, 16.5%. Calcd for $Fe(\gamma\text{-pic})_4Cl_2$: Fe, 11.2; Cl, 16.0%.

(iii) $Fe(py)_4(NCS)_2$. This compound was prepared by the method described in the literature.[6] The yellowish white crystals obtained were dried in a vacuum desiccator. Found: Fe, 11.5; C, 54.1; H, 4.28; N, 17.2%. Calcd for $Fe(py)_4(NCS)_2$: Fe, 11.5; C, 54.1; H, 4.14; N, 17.2%.

Thermal Decomposition. The thermal decomposition studies were carried out on a Shimadzu Thermal Balance at a rate of heating of 2°C/min. All the thermal decompositions were carried out in a nitrogen atmosphere.*1

The powder X-ray patterns of tetrakispyridineiron(II) chloride, isothiocyanate, and their thermal decomposition products were made using a Rigaku Denki Geigerflex and Fe*K*α radiation.

The infrared spectra of these compounds were measured by using Hitachi EPI-G2 and EPI-L Spectrophotometers and a Hitachi FIS-1 Far-infrared Spectrophotometer.

Mössbauer Measurements. The Mössbauer absorption spectra of the starting materials and of the thermal decomposition products were obtained at room temperature and at lower temperatures*2 (163°K or 100°K) by using a mechanical constant-velocity drive spectrometer with a source of ^{57}Co diffused into copper or platinum foil. The spectrometer was calibrated with sodium nitroprusside dihydrate powder.

Results and Discussion

Thermal Decomposition of the Iron(II) Pyridine and γ-Picoline Complexes. Although several studies have been made of the thermal decomposition of various metal complexes of pyridine and its derivatives,[7-11] the thermal decomposition of the iron pyridine complexes had never been reported before our preliminary work on $Fe(py)_4Cl_2$[2] was published.

As may be seen in Fig. 1, the thermal decomposition of $Fe(py)_4Cl_2$ in air produced no distinct intermediate phase other than $Fe(py)_2Cl_2$, presumably because of the oxidation taking place at about 100°C or higher temperatures. This was verified by the Mössbauer spectrum of the decomposition product obtained at 150°C (above the temperature for the formation of $Fe(py)_2Cl_2$), which indicated the presence of Fe(III) (δ ~0.5 mm/sec; ΔE_Q

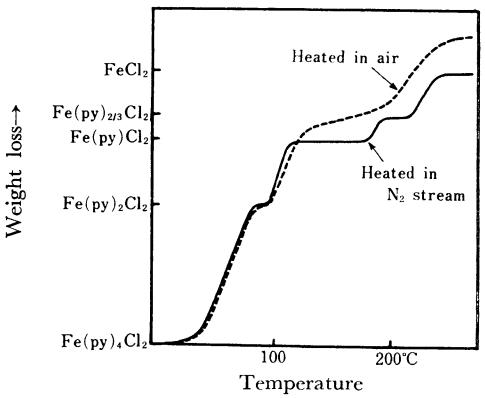

Fig. 1. Thermal decomposition of $Fe(py)_4Cl_2$.

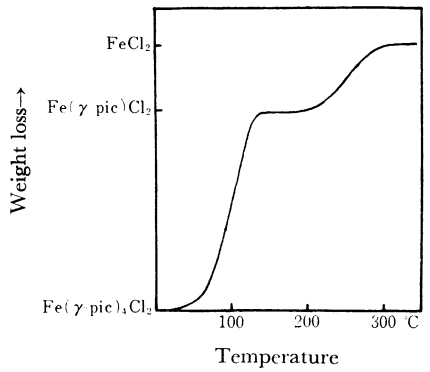

Fig. 2. Thermal decomposition of $Fe(\gamma\text{-pic})_4Cl_2$.

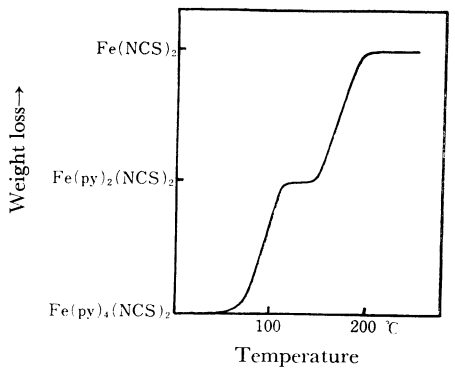

Fig. 3. Thermal decomposition of $Fe(py)_4(NCS)_2$.

6) Gmelins Handbuch der Anorganischen Chemie, Eisen, System-Nummer 59, Teil B.

*1 For purposes of comparison, the thermal decompositions of $Fe(py)_4Cl_2$ were also conducted in air.

*2 For the lower temperature measurements, samples were cooled by conduction through a thick copper plate dipping into liquid nitrogen in a styrofoam-insulated dewar.

7) L. R. Ocone, J. R. Soulen and B. P. Block, *J. Inorg. Nucl. Chem.*, **15**, 76 (1960).

8) D. H. Brown, R. H. Nuttall and D. W. A. Sharp, *ibid.*, **25**, 1067 (1963).

9) J. R. Allan, D. H. Brown, R. H. Nuttall and D. W. A. Sharp, *ibid.*, **26**, 1895 (1964); *ibid.*, **27**, 1529, 1865 (1965).

10) I. G. Murgulescu, E. Segal and D. Fatu, *ibid.*, **27**, 2677 (1965).

11) W. W. Wendlandt and S. I. Ali, *Z. Anorg. Allg. Chem.*, **337**, 6 (1965).

~0.5 mm/sec). Accordingly, all the thermal decompositions of the iron(II) complexes were carried out in a nitrogen atmosphere.

Figures 1 to 3 show the weight-loss curves of $Fe(py)_4Cl_2$, $Fe(\gamma\text{-pic})_4Cl_2$, and $Fe(py)_4(NCS)_2$, respectively. Four distinct phases can be observed during the thermal decomposition of $Fe(py)_4Cl_2$ in a nitrogen atmosphere (Fig. 1). These four phases correspond to the products which can be obtained by the successive loss of two, one, one-third and two-thirds molecules of pyridine from the starting material, $Fe(py)_4Cl_2$. The results of analyses for the iron and chlorine contents were in good agreement with the values calculated for the assumed products. The X-ray powder patterns and Mössbauer spectra confirmed that all of these phases are separate and distinct entities. Therefore, it may be concluded that the thermal decomposition of $Fe(py)_4Cl_2$ proceeds in a nitrogen atmosphere as follows:

$$Fe(py)_4Cl_2 \rightarrow Fe(py)_2Cl_2 \rightarrow Fe(py)Cl_2 \rightarrow Fe(py)_{2/3}Cl_2 \rightarrow FeCl_2.$$

Similarly, the thermal decompositions of $Fe(\gamma\text{-pic})_4Cl_2$ and $Fe(py)_4(NCS)_2$ were found to proceed according to the sequences:

$$Fe(\gamma\text{-pic})_4Cl_2 \rightarrow Fe(\gamma\text{-pic})Cl_2 \rightarrow FeCl_2,$$

and

$$Fe(py)_4(NCS)_2 \rightarrow Fe(py)_2(NCS)_2 \rightarrow Fe(NCS)_2.$$

In addition, it may be worthwhile mentioning that, according to our preliminary work,[12] $Fe(py)_4Br_2$ and $Fe(\gamma\text{-pic})_4Br_2$ decompose through the following steps:

$$Fe(py)_4Br \rightarrow Fe(py)Br_2 \rightarrow FeBr_2,$$

and

$$Fe(\gamma\text{-pic})_4Br_2 \rightarrow Fe(\gamma\text{-pic})Br_2 \rightarrow FeBr_2.$$

Structures of the Decomposition Products. No X-ray study of the structure of $Fe(py)_4Cl_2$ has been reported to date. However, the electronic spectra[13] suggest that $Fe(py)_4Cl_2$ has a trans-octahedral configuration about the iron atoms. We confirmed this conclusion, since the powder X-ray patterns of $Fe(py)_4Cl_2$ are quite similar to those of $Co(py)_4Cl_2$ and $Ni(py)_4Cl_2$, whose structures are known.[14,15] The X-ray powder photography[16] indicated that $Fe(py)_2Cl_2$ has a structure analogous to that of $\alpha\text{-}Co(py)_2Cl_2$, an octahedral polymer with bridging chloride ions.[17] This conclusion was also confirmed by our powder X-ray data. The electronic spectra[13] suggest that $Fe(py)Cl_2$ also has an octahedral polymeric structure. Our powder X-ray data indicate that $Fe(py)_{2/3}Cl_2$ is isomorphous with $Co(py)_{2/3}Cl_2$, which may, according to the electronic spectra,[18] be supposed to have an octahedral polymer structure. Therefore, the thermal decomposition of $Fe(py)_4Cl_2$ proceeds with the formation of the polymer structure: the successive removal of pyridine molecules from the complex gives single, double, and triplechain polymers, and finally the chains are converted to the infinite plane structure of $FeCl_2$.[19] The structural changes which might take place during the thermal decomposition of $Fe(py)_4Cl_2$ are shown in Fig. 4. The structure of

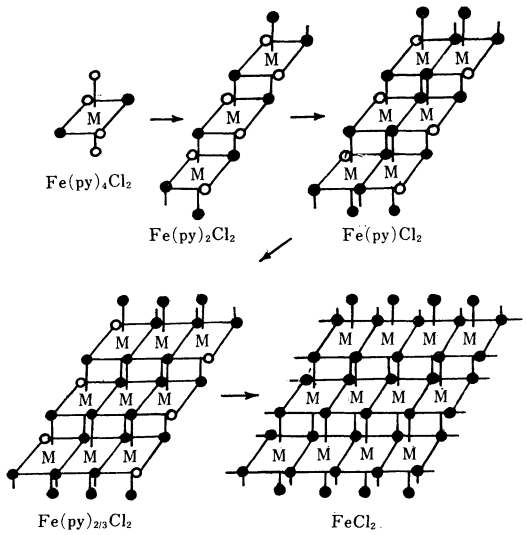

Fig. 4. Structures of $Fe(py)_xCl_2$.
M: Fe; O: py; ●: Cl.

$Fe(py)_4(NCS)_2$ was determined by the X-ray investigation.[20] It has a trans-octahedral arrangement about the iron atoms (nitrogen atoms are bonded to iron). Since the powder X-ray patterns of $Fe(py)_2(NCS)_2$ were found to be quite similar to those of $Co(py)_2(NCS)_2$, whose structure is known,[21] we assume that $Fe(py)_2(NCS)_2$ has an octahedral polymeric structure with bridging NCS ions (sulfur atoms occupy trans positions to iron). The comparison of the IR spectra of $Fe(py)_4(NCS)_2$ and

12) N. Saito, T. Tominaga, T. Morimoto and M. Takeda, Proc. 10th Intern. Conf. Coordination Chem. Nikko, Japan, p. 174 (1967).
13) D. M. L. Goodgame, M. Goodgame, M. A. Hitchman and M. J. Weeks, *Inorg. Chem.*, **5**, 635 (1966).
14) M. A. Porai-Koshits and A. S. Antsishkina, *Dokl. Akad. Nauk SSSR*, 333 (1953).
15) M. A. Porai-Koshits, L. M. Dickareva and E. K. Jukhnov, *Acta Crystallogr.*, **10**, 784 (1958).
16) N. S. Gill, R. S. Nyholm, G. A. Barclay, J. C. Christie and P. J. Pauling, *J. Inorg. Nucl. Chem.*, **18**, 88 (1961).
17) J. D. Dunitz, *Acta Crystallogr.*, **10**, 307 (1958).
18) J. R. Allan, D. H. Brown, R. H. Nuttall and D. W. A. Sharp, *J. Inorg. Nucl. Chem.*, **26**, 1895 (1964).
19) W. G. Wyckoff, "Crystal Structures," Vol. **1**, John Wiley & Sons, Inc. New York (1963), p. 272.
20) I. Søtofte and S. E. Rasmussen, *Acta Chem. Scand.*, **21**, 2028 (1967).
21) M.A. Porai-Koshits, *Kristallografiya*, **4**, 239 (1959).

$Fe(py)_2(NCS)_2$ also suggests the presence of bridging thiocyanate groups.

The Mössbauer Spectra of the Decomposition Products. The Mössbauer spectra (room temperature) of $Fe(py)_4Cl_2$, $Fe(\gamma\text{-pic})_4Cl_2$, $Fe(py)_4(NCS)_2$ and their decomposition products are represented in Figs. 5 to 7. All the Mössbauer spectra are composed of two absorption peaks. The isomer shifts and quadrupole splittings of these compounds obtained at various temperatures are summarized in Table I.

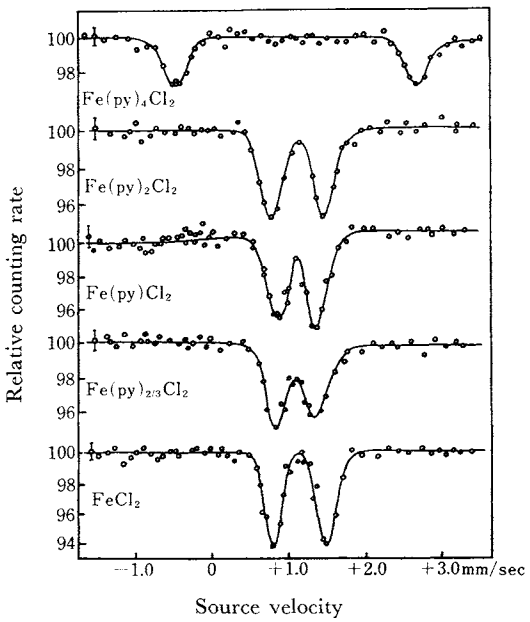

Fig. 5. Mössbauer spectra of $Fe(py)_xCl_2$.

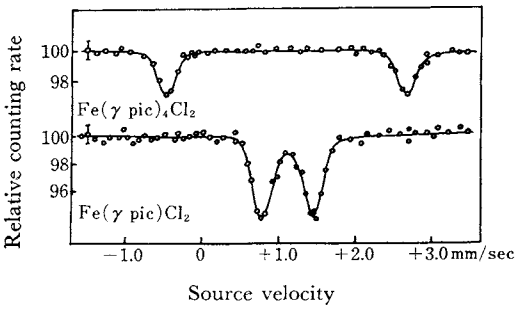

Fig. 6. Mössbauer spectra of $Fe(\gamma\text{-pic})_xCl_2$.

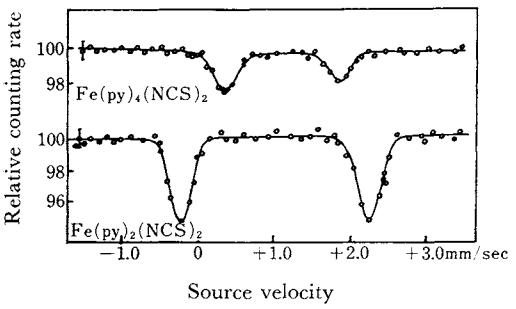

Fig. 7. Mössbauer spectra of $Fe(py)_x(NCS)_2$.

Table I. Mössbauer spectra of iron(II) pyridine and γ-picoline complexes and their decomposition products

Compound	Isomer shift* δ(mm/sec)		Quadrupole splitting ΔE_Q(mm/sec)	
	290°K	163°K	290°K	163°K
	(±0.03)		(±0.04)	
$Fe(py)_4Cl_2$	1.10	1.18**	2.94	3.44**
$Fe(py)_2Cl_2$	1.13	1.26**	0.56	1.26**
$Fe(py)Cl_2$	1.15	1.24	0.38	0.69
$Fe(py)_{2/3}Cl_2$	1.15	1.27	0.51	0.84
$FeCl_2$	1.16	1.29	0.75	0.88
$Fe(\gamma\text{-pic})_4Cl_2$	1.12	1.21**	2.94	3.43**
$Fe(\gamma\text{-pic})Cl_2$	1.14	1.18	0.64	0.90
$Fe(py)_4(NCS)_2$	1.11	1.24**	1.53	1.99**
$Fe(py)_2(NCS)_2$	1.07	1.20**	2.54	3.00**

* Vs. stainless steel (310SS) ** Obtained at 100°K

From the Mössbauer data on $Fe(py)_4Cl_2$ and its thermal decomposition products, we may draw the following conclusions:

(1) The isomer shifts (δ) of the different phases show only small variations during the thermal decomposition process in a nitrogen atmosphere. All the δ values fall within the range of δ values for a typical high-spin Fe(II) state. Thus, it is obvious that the oxidation state of iron in the starting material, $Fe(py)_4Cl_2$, remains unchanged throughout the decomposition process.

(2) The quadrupole splitting (ΔE_Q) is appreciably changed as the thermal decomposition proceeds; at room temperature, the quadrupole splitting of $Fe(py)_4Cl_2$ is 2.94 mm/sec, whereas the quadrupole splittings of the decomposition products are significantly decreased and fall within a range between 0.38 and 0.75 mm/sec. The changes in the quadrupole splitting may reflect the structural changes about the iron atoms.*3

(3) The intensities of absorption peaks are generally larger for the polymeric compounds than for the monomer, $Fe(py)_4Cl_2$. This may be due to the "polymer effect" suggested for organotin

*3 Since the quadrupole splitting of these high spin iron(II) compounds is closely related to the ligand-field splitting of d_ε orbitals, the temperature dependence of the quadrupole splittings of various iron pyridine complexes is now being studied in our laboratory. The results will be published elsewhere.

compounds[22-25] and α-$Co(py)_2Cl_2$[26]; the polymer structures may restrict the motion of the iron atoms and give higher recoilless fractions.

(4) In order to examine the mechanism of the primary step of decomposition, *i. e.*, $Fe(py)_4Cl_2 \rightarrow Fe(py)_2Cl_2$, the Mössbauer spectra were taken of the products obtained at intermediate stages before the $Fe(py)_2Cl_2$ phase was completely attained (Fig. 8). As may be seen in Fig. 8, only the absorption peaks of $Fe(py)_4Cl_2$ and $Fe(py)_2Cl_2$ are observed in the intermediate stages. The intensities of the $Fe(py)_4Cl_2$ peaks are decreased, whereas the intensities of the $Fe(py)_2Cl_2$ peaks are increased, as the decomposition proceeds. Therefore, it seems unlikely that any stable entity such as $Fe(py)_3Cl_2$ could exist as an intermediate phase for the $Fe(py)_4Cl_2 \rightarrow Fe(py)_2Cl_2$ transition. This suggests the possibility of the application of the Mössbauer spectroscopy to the study of the kinetics and the mechanism of solid-phase reactions.

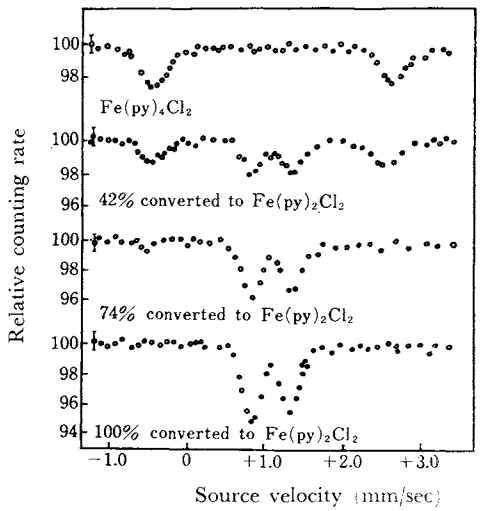

Fig. 8. Mössbauer spectra of the $Fe(py)_4Cl_2 \rightarrow Fe(py)_2Cl_2$ transition.

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23) H. A. Stöckler, H. Sano and R. H. Herber, *J. Chem. Phys.*, **47**, 1567 (1967).
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25) H. A. Stöckler and H. Sano, Proc. 2nd Materials Research Symposium on Molecular Dynamics and Structure of Solids (National Bureau of Standards, U. S. Department of Commerce, Washington, D. C., 1967).
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