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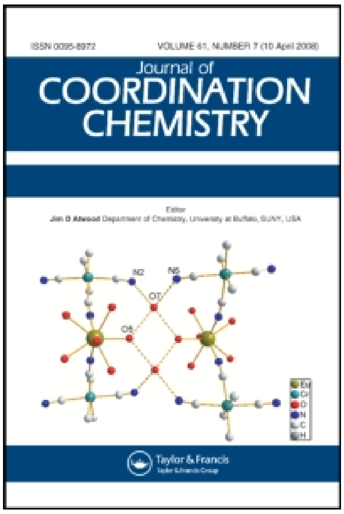

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SHORT COMMUNICATION
Ferrous Ferricyanide: Pyrolysis Preparation

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The previously reported synthesis of ferrous ferricyanide involved pyrolysis of Prussian Blue which contained both the soluble $KFeFe(CN)_6$ and the insoluble $Fe_4[Fe(CN)_6]_3$ forms. The soluble and insoluble Prussian Blues, and the ferrous ferricyanide compounds which derive from this vacuum pyrolysis at 300–500°C, have been examined by ^{57}Fe Mössbauer spectroscopy. The extra ferric ion present in the cages in insoluble P.B., which is replaced by potassium in soluble P.B., becomes ferrous on pyrolysis and gives a very small quadrupole splitting. Since it absorbs in an otherwise clear region of the spectrum its presence forms an analytical indicator for determining the soluble/insoluble ratio of P.B.'s. The spectra from the high and low spin irons overlap severely and isotopic enrichment was used to clarify the ferricyanide region. Unexpectedly, the isotopic enrichment was gradually lost on pyrolysis and reconstruction. This suggests that the cyanide ligands rotate readily above 300°C. It also suggests that ferrous ferricyanide prepared by pyrolysis is not simply an interchange of valency, but involves intermediate iron sites such as $Fe(CN)_x(NC)_{6-x}$.

INTRODUCTION

Prussian Blue (P.B.) can be made in an 'insoluble' form $Fe_4[Fe(CN)_6]_3$, or in a 'soluble' form, $KFeFe(CN)_6$.[1] The iron atoms in soluble P.B. differ in that the low-spin ferrous iron is tightly octahedrally coordinated to the carbon ends of six cyanide ligands, and the high-spin ferric iron is loosely octahedrally coordinated to the nitrogen end of six cyanide ligands. This face-centered cubic lattice is rather open, the distance between like irons $Fe^{II}{-}C{\equiv}N{-}{-}{-}Fe^{3+}{-}{-}{-}N{\equiv}C{-}Fe^{II}$ being 10.2 Å. These large cages normally contain lots of water (30–40% by weight) and also contain gegenions as needed.[2] In soluble P.B., the gegenion is potassium. In insoluble P.B., the gegenion is high-spin Fe^{3+}. The Fe^{3+} ions sitting in nitrogen holes are termed metal I(M I). The extra Fe^{3+} gegenions in insoluble P.B. are termed metal II(M II).[3]

Recent work[4,5] has shown that a mild vacuum pyrolysis at 300–530°C leads to a reversal of iron valencies, $Fe^{3+}Fe^{II} \rightarrow Fe^{2+}Fe^{III}$. This ferrous ferricyanide compound has been sought for a long time, and represents the intended (but not realized) 'Turnbull's Blue'. This pyrolysis does little damage to the P.B., since only small amounts of HCN, C_2N_2, and CO_2 are released. The major release is water, including adsorbed water and water trapped in cages. The face-centered cubic lattice of P.B. does not survive the pyrolysis. However, the P.B. can be reconstituted rapidly by contacting the ferrous ferricyanide with warm dilute HCl, or slowly reconstituted by contact with moist air. In these studies, the starting material was intermediate between soluble and insoluble P.B. Accordingly, it was thought necessary to examine separately the pyrolysis products of soluble and insoluble P.B. Further, isotopic enrichment was felt essential to clarify the overlapping ^{57}Fe Mössbauer spectra near zero velocity. The enrichment procedure with labelled iron goes much more easily with the high-spin iron.

Since the major difficulty is with the low-spin iron, ^{56}Fe labelling of the high-spin ferric iron in P.B. eliminated the interference.

SAMPLE PREPARATION

The soluble and insoluble preparations of P.B. began with the prescriptions of Bhattachara, et al.[6] They reported that soluble P.B. is formed by dropwise addition of aqueous $FeCl_3$ to aqueous $K_4Fe(CN)_6$, and that insoluble P.B. is formed by dropwise addition of aqueous $K_4Fe(CN)_6$ to aqueous $FeCl_3$. In each case, addition was continued to stoichiometry. We find the major controlling factor is pH. To get a

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very insoluble P.B., the aqueous $FeCl_3$ (3% by weight) was acidified by adding two drops concentrated HCl into 30 ml solution, followed by the dropwise addition of aqueous $K_4Fe(CN)_6$ (3% by weight) until 10% of stoichiometry was reached. The precipitate filtered readily, and was washed three times with water. Soluble P.B. was prepared by adding aqueous $FeCl_3$ dropwise to basic $K_4Fe(CN)_6$, where an adequate amount of KOH had been added to keep the pH at or slightly above that of the $K_4Fe(CN)_6$ alone. Again, the reaction was carried to only 10% of stoichiometry. Most of the product remained suspended, and any precipitate which settled on standing was discarded. Purification involved precipitation by adding 20% V/V ethanol, centrifugation, and washing by adding water. This was repeated three times.

The enrichment of insoluble P.B. commenced by dissolving $^{56}Fe_2O_3$ in excess concentrated HCl. As the ^{56}Fe is expensive, an equivalent amount (100% of stoichiometric) $K_4Fe(CN)_6$ was added slowly. The product was filtered and washed four times with distilled water.

Pyrolysis was carried out in Vycor in a tube furnace at a pressure of about 10^{-3} mm Hg. The temperature rise took 15–30 minutes. The temperature was maintained for 10 minutes, and the samples were allowed to cool under vacuum.

MÖSSBAUER APPARATUS

The Mössbauer data were collected with a constant acceleration spectrometer, and calibration of velocities was achieved via laser interferometry.[7]

DATA AND DISCUSSION

There are only subtle differences in the Mössbauer spectra of soluble and insoluble P.B. (Figures 1a, 2a, 3a and 4a.) Actually, it seems remarkable that they are so similar. The problem, basically, is that there is little difference between Mössbauer parameters of the high-spin M I and M II ferric irons. The intensities are anomalous, in that for soluble P.B. the Fe^{II}/Fe^{3+} ratio is expected to be 1/1 but we find at 77°K 1/1.68 and at 25°C 0.72/1.03. For insoluble P.B., where Fe^{II}/Fe^{+} is expected to be 1/1.33, the ratio at 77°K is 1/3.04 and at 25°C 0.93/1.48. The 'f' (intensity) factor reflects thermal motion, and this data confirms an intuitive notion that the dissimilar irons respond differently to temperature.

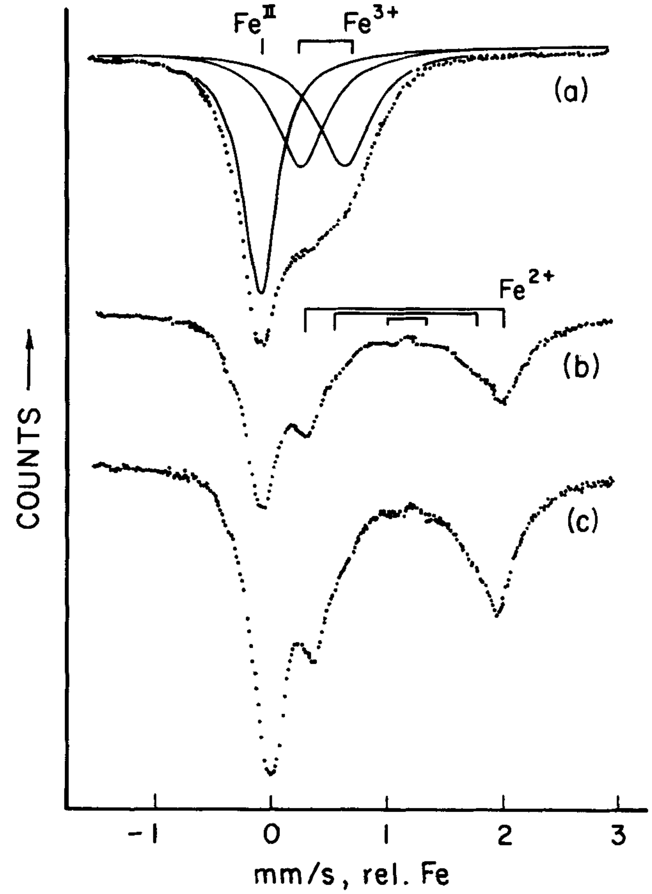

FIGURE 1 Mössbauer spectra of soluble Prussian Blue at room temperature, (a) before, (b) after pyrolysis at 300°, and (c) after pyrolysis 530°C.

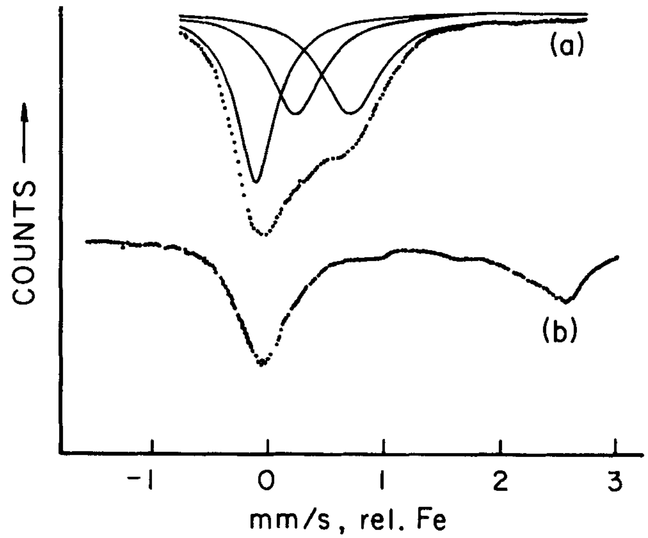

FIGURE 2 Mössbauer spectra of soluble Prussian Blue at 77°K, (a) before and (b) after pyrolysis at 300°C.

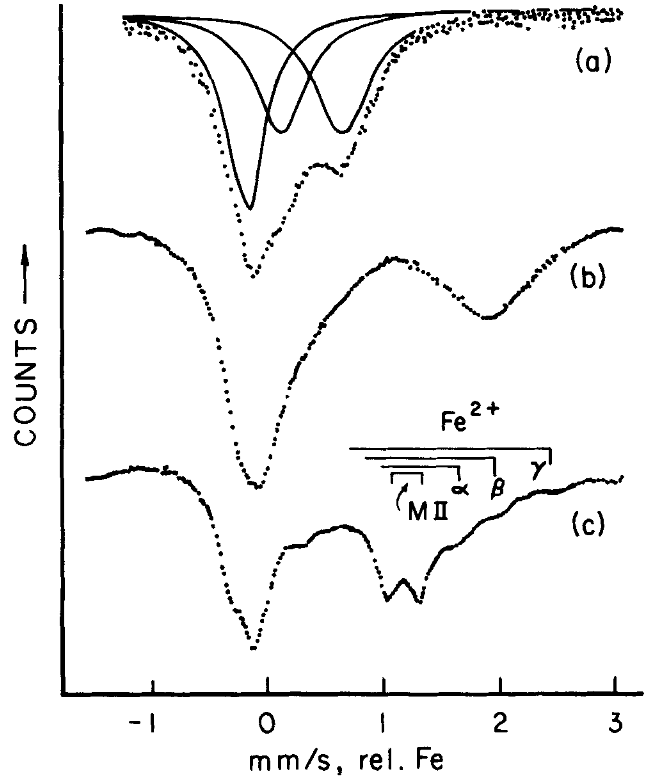

FIGURE 3 Mössbauer spectra of insoluble Prussian Blue at room temperature, before pyrolysis (a) and after pyrolysis at (b) 300°C and (c) 530°C.

However, on pyrolysis, the valency reversal causes the center of the high-spin iron (now 2+) to move into a clear area of the spectrum near +1 mm/s relative to iron metal. The left side of the quadrupole split doublet remains clouded by interference from the $\mathrm{Fe^{III}}$ cyanide, but the right side is free of interferences (Figure 1b, for example). The dominant $\mathrm{Fe^{2+}}$ site in soluble P.B. is the widely split pair centered at about +1.1 mm/s, although two other sites may be present. This dominant site is interpreted as M I $\mathrm{Fe^{2+}}$.

In soluble P.B., the larger mobility of the M II ferrous irons in the cages accounts for the narrow doublet (Figures 3c and 4c). Pyrolysis at 300°C reverses the valency, but does not remove sufficient water from the cages to permit the extensive thermal averaging (which reduces the quadrupole splitting) shown in Figures 3c and 4c. In other words, the M II irons rattle about in the now largely empty cage.

In addition to the M II iron, there are at least three other high-spin ferrous sites denoted α, β, and γ in Figure 3c. Of these, β appears to be the dominant site in the pyrolyzed soluble P.B. Identification of these sites awaits an x-ray structure analysis. A preliminary x-ray analysis indicates that the structure is no longer face-centered cubic.

A comparison of Figures 1c and 3c shows a basis for analysis of the ratio of soluble to insoluble P.B. Vacuum pyrolysis at 530°C moves all M II irons (insoluble P.B.) into a clear region of the spectrum.

The isotopic enrichment giving $^{56}\mathrm{Fe}_4[\mathrm{Fe(CN)}_6]_3$ (Figure 5a) shows clearly a ferrocyanide peak. This procedure was carried out to check on a query as to whether the ferricyanide spectrum was quadrupole split in ferrous ferricyanide. The result of a mild 300°C pyrolysis is startling (Figure 5b). Some of the $^{57}\mathrm{Fe}$ which had been tightly coordinated as ferrocyanide iron now appears as high-spin ferrous. Unfortunately, this precludes a definitive statement about the quadrupole splitting in ferricyanide, since the ferrous high-spin doublet interfered with the

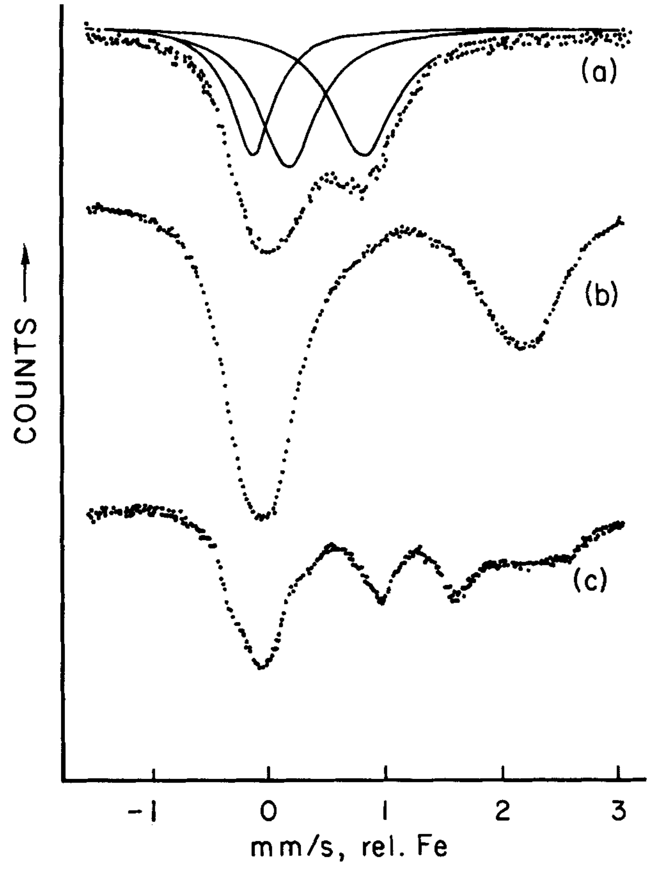

FIGURE 4 Mössbauer spectra of insoluble Prussian Blue at 77°K, before pyrolysis (a) and after pyrolysis at (b) 300°C and (c) 530°C.

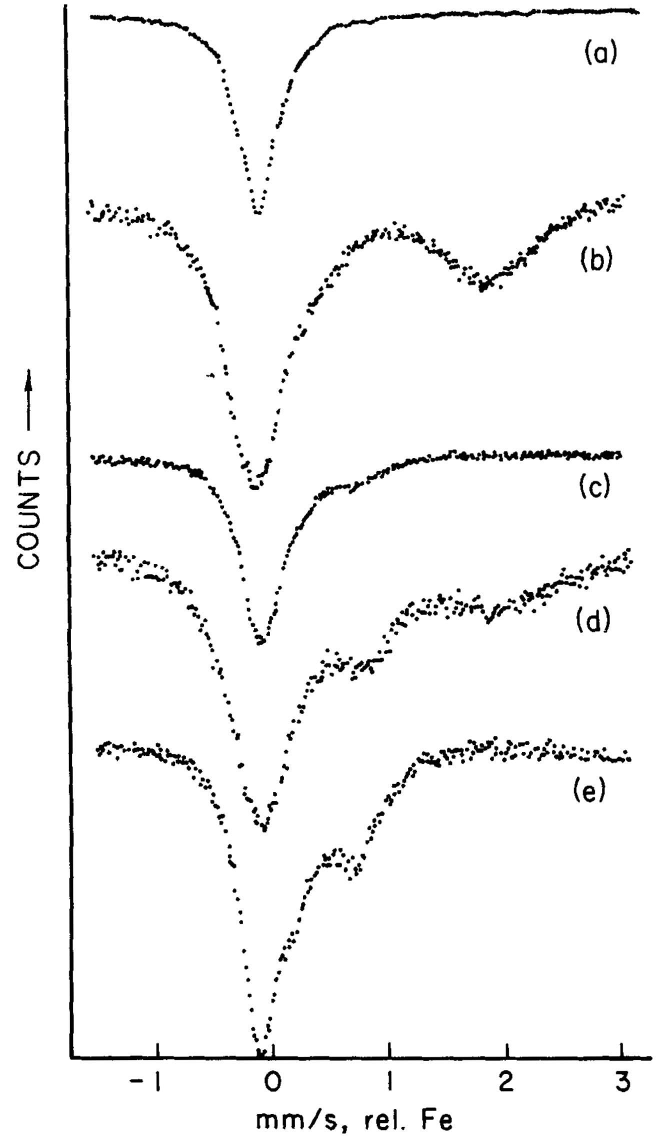

FIGURE 5 Mössbauer spectra of $^{56}FeCl_3 + K_4Fe(CN)_6$, room temperature. (a) as prepared. (b) pyrolyzed at 300°. (c) reconstituted. (d) again pyrolyzed at 300°. (e) again reconstituted.

region of interest. Reconstitution by treatment with warm dilute HCl confirmed (Figure 5c) that some of the original ferrocyanide iron was now high-spin ferric. Since the only ^{57}Fe (natural abundance) initially present was in carbon holes, and since some now appeared in nitrogen holes, this suggested that some of the cyanide ligands rotated during pyrolysis.

It is initially surprising that essentially no M II ferrous iron is present in the spectrum (Figure 6). This seems further evidence in support of the cyanide rotation, however, since this mechanism for valency reversal does not involve the M II irons in any way. They start as ^{56}Fe and remain ^{56}Fe, and are hence invisible.

If some but not all ligands rotate, there may occur a variety of lattice iron sites, i.e. $Fe(CN)_6$, $Fe(CN)_5(NC)$, $Fe(CN)_4(NC)_2$, $Fe(CN)_3(NC)_3$, $Fe(CN)_2(NC)_4$, $Fe(CN)(NC)_5$, and $Fe(NC)_6$. Only the first and the last are considered normal for P.B. Six cyanides certainly cause iron to be low-spin, and six N≡C ligands certainly cause iron to be high-spin. It remains to be seen where the change occurs from low-spin to high-spin. The bis Fe^{2+} phenanthroline halogen complexes are high-spin, and these have four fairly strong ligands. The cyanide is a much stronger ligand, and one might guess that three or more will cause the iron to become low spin. Considering only the $(CN)_2$, the $(CN)_1$, and the $(CN)_0$ ferrous high-spin cases, with (NC) ligands filling out the remainder of an assumed octahedral configuration, these lead to

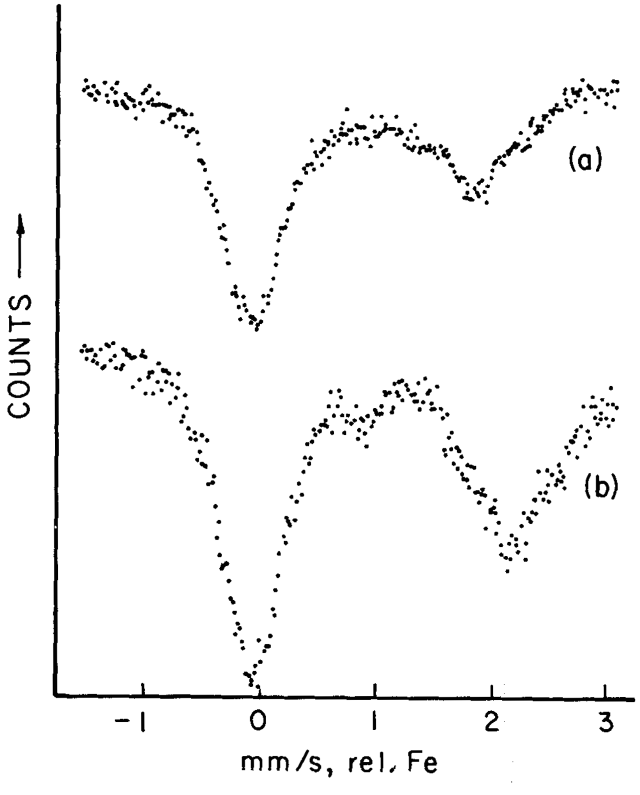

FIGURE 6 Mössbauer spectra of $^{56}FeCl_3 + K_4Fe(CN)_6$, room temperature. (a) pyrolyzed at 410°. (b) pyrolyzed at 530°.

four sites since the (CN) can be *cis* or *trans*. These four sites may be increased according to the angular relation between the odd 3d electron and the ligand direction, unless the configuration of that odd 3d electron moves in response to the ligand configuration. A careful examination of Figures 1 and 3 indicates that there are least four Fe^{2+} sites in addition to M II. If the left sides of the Fe^{2+} doublets were observable, the isomer shifts would help in assigning the number of CN ligands to each iron site. Unfortunately, this region is obscured by the low-spin iron spectra and, in view of the rotation of CN ligands on pyrolysis, cannot be resolved by isotopic enrichment procedures.

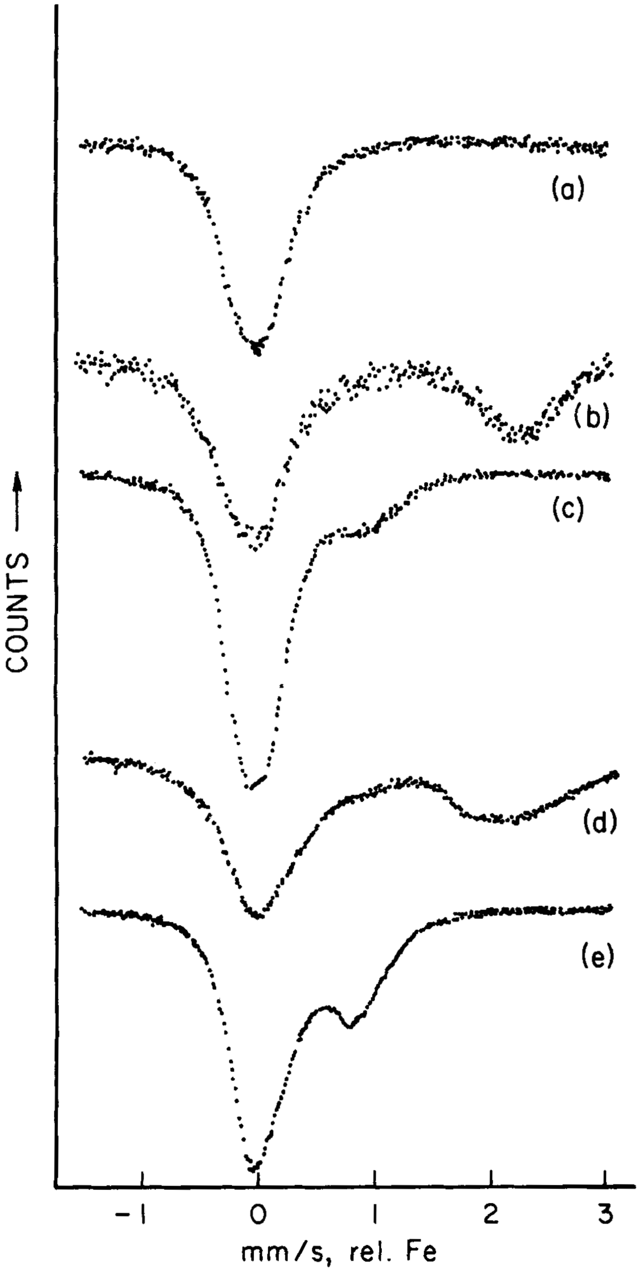

FIGURE 7 Mössbauer spectra of $^{56}FeCl_3 + K_4Fe(CN)_6$, 77°K. (a) as prepared. (b) pyrolyzed at 300°. (c) reconstituted. (d) again pyrolyzed at 300°. (e) again reconstituted.

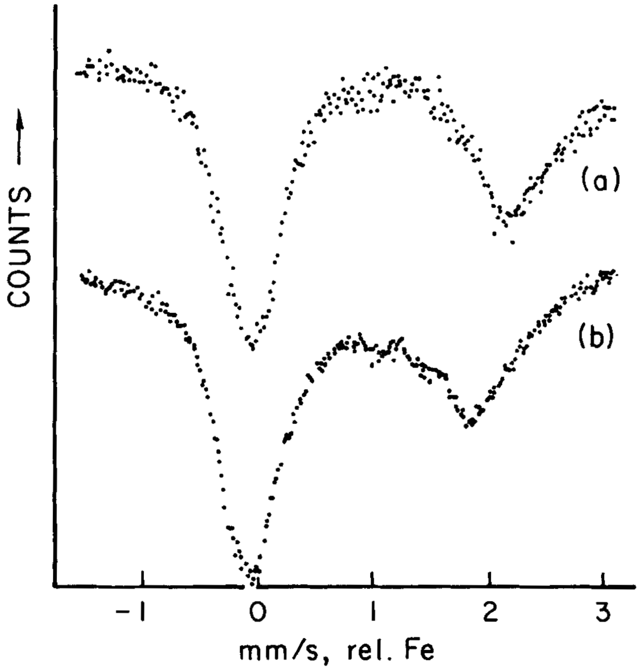

FIGURE 8 Mössbauer spectra of $^{56}FeCl_3 + K_4Fe(CN)_6$, 77°K. (a) pyrolyzed at 410°. (b) pyrolyzed at 530°.

CONCLUSION

The pyrolysis products of soluble and insoluble P.B.'s are confirmed as ferrous ferricyanides, but with a richer structure than previously supposed. The strong signature of M II ferrous iron after pyrolysis furnishes a basis for the analysis of relative amounts of soluble and insoluble P.B.'s. The dominant mode of valency reversal on pyrolysis appears to be cyanide rotation above 300°C. This distribution of ligands about a given iron, $Fe(CN)_x(NC)_{6-x}$, is frozen into place at room temperature. In the presence of warm dilute HCl (or, over a longer time, moist air), the P.B. configuration is reconstituted. This suggests that cyanide rotation occurs at room temperature under reconstitution conditions. The failure of M II irons to participate in the isotopic exchange further supports the proposed valency exchange mechanism of cyanide rotation. The final structure of ferrous ferricyanide prepared by pyrolysis of P.B., then, is the result of freezing in the random results of cyanide rotation. Those sites having few cyanide ligands become high-spin ferrous and those having many cyanide ligands become low-spin ferric. We guess that two or less cyanides lead to high-spin ferrous, and three or more lead to low-spin ferric. It remains unclear why the high-spin sites become ferrous and the low-spin sites ferric, unlike P.B., but this may reflect the anhydrous lattice of ferrous ferricyanide *vs.* the water-filled lattice of P.B.

ACKNOWLEDGMENT

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