

Fig. 2.—Isomer shift vs. pressure, Fe(II) ion.

about 1.3–1.4 mm/sec with a quadrupole splitting of 2–2.1 mm/sec. With increasing pressure and increasing conversion the inner pair of peaks moved out and merged with the outer pair. Heating the sample at low pressure apparently completely converted some complexes to the isothiocyanate and left others unconverted. As far as we could determine, the distribution was independent of time. At 10 kb and 110°C there was an approximately equal concentration of isothiocyanate and thiocyanate ferrous complexes. We could not determine the distribution of ferric complexes. Rapid cooling to 25°C at 10 kb reduced the amount of ferrous ion but it quenched in a mixture of thiocyanate and isothiocyanate complexes. With increasing pressure, the total amount of ferrous ion (thiocyanate plus isothiocyanate) increased, and the thiocyanate complexes

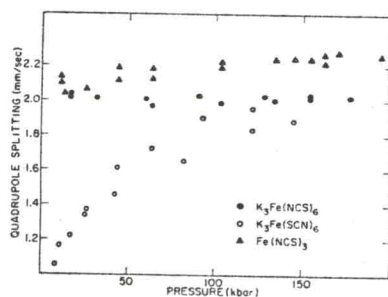


Fig. 3.—Quadrupole splitting vs. pressure, Fe(III) ion.

isomerized as had the original material. A sample ground thoroughly in a mortar and pestle and then subjected to pressure sometimes showed a mixture of thiocyanate and isothiocyanate ferrous complexes much like a heated sample.

In summary, ferric iron reduces reversibly to the ferrous state with both thiocyanate and isothiocyanate ligands, but the electron transfer occurs more easily in the former case than in the latter. The thiocyanate complex isomerizes irreversibly to the isothiocyanate with increasing pressure.

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