

THE EFFECT OF PRESSURE ON THE OXIDATION
STATE OF IRON. IV. THIOCYANATE AND
ISOTHIOCYANATE LIGANDS*

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Abstract and Summary.—The effect of pressure on the Mössbauer resonance spectra of Fe(III) with thiocyanate (M-SCN) and isothiocyanate (M-NCS) ligands has been studied. $\text{Fe}(\text{NCS})_2 \cdot 6\text{H}_2\text{O}$, which has the isothiocyanate structure, reduces with increasing pressure, reversibly, and with a pressure dependence for the conversion very similar to that shown by a wide variety of ionic ferric compounds. $\text{K}_2\text{Fe}(\text{SCN})_6$ has the thiocyanate structure. At low pressures, it exhibits a significantly larger reduction than the $\text{Fe}(\text{NCS})_2$. With increasing pressure the thiocyanate complexes isomerize, each complex apparently exhibiting about the same degree of conversion at a given pressure. At 150 kb the isomerization is essentially complete. The reduction of the Fe(III) to Fe(II) is reversible but the isomerization is not, and the sample, when powdered and reloaded in the high-pressure cell, exhibits the isomer shift, quadrupole splitting, and Fe(III) to Fe(II) conversion characteristic of an isothiocyanate. Heating the thiocyanate to 110°C at 5 kb yields a mixture of thiocyanate and isothiocyanate that converts with pressure completely to the isothiocyanate.

Mössbauer resonance has proved useful in studying the oxidation state, spin state, and chemical bonding in compounds of iron. The information is inferred from the isomer shift (the s electron density at the nucleus) and from the quadrupole splitting (the separation between the two peaks arising from the splitting of the nuclear state of spin 3/2 due to interaction of an electric field gradient with the nuclear quadrupole moment). Since resonance is obtained in a Mössbauer spectrometer by moving the source with respect to the absorber, these energies are characteristically expressed in mm/sec. In this paper, all isomer shifts are given relative to bec iron metal at one atmospheric pressure.

For typically ionic, high-spin ferrous compounds, the isomer shift lies in the range 1.2–1.4 mm/sec, which corresponds to a relatively low electron density at the nucleus. These compounds exhibit a large quadrupole splitting (2.0–3.0 mm/sec) that results from the aspheric distribution of electrons in the 3d shell. High-spin ferric compounds show isomer shifts in the range 0.3–0.5 mm/sec (i.e., the s electron density at the nucleus is much higher than for ferrous compounds) and small quadrupole splittings (0–0.6 mm/sec) caused entirely by a noncubic ligand field. There exist ostensibly ferrous compounds such as FeS, FeSe, and FeTe, whose binding has a large covalent component, that exhibit isomer shifts in the range 0.7–0.9 mm/sec.¹ They may also have quadrupole splittings of intermediate value.

It has been observed in this laboratory that ferric iron reduces to the ferrous

state in a wide variety of compounds including halides,² oxalates and acetate,³ phosphate, citrate and sulfate,⁴ ferriyanide and Prussian blue,⁵ and hemin and hematin.⁶ The process is reversible with some hysteresis. It follows the empirical relationship:

$$K = \frac{C_{\text{II}}}{C_{\text{III}}} = AP^B \quad (1)$$

where A and B are independent of pressure. From thermodynamic arguments, one obtains the equation:

$$\frac{\partial \ln C_{\text{II}}}{\partial \ln P} = \frac{P(V^{\text{III}} - V^{\text{II}})}{RT} (C_{\text{III}}) = B(C_{\text{III}}) \quad (2)$$

where V^{III} and V^{II} are the volumes of the ferric and ferrous ions with their associated ligands. There is both experimental and theoretical evidence that the antibonding metal orbitals decrease in energy vis-à-vis the nonbonding ligand orbitals with increasing pressure, and that it is this process which permits the thermal transfer of electrons.

In this paper, we discuss studies involving the thiocyanate ($-\text{SCN}$) and isothiocyanate ($-\text{NCS}$) ions. In the former case, the metal is bonded to the sulfur; in the latter case, to the nitrogen. There is a very extensive literature on the conditions for formation of thiocyanates and isothiocyanates.^{7–11} In general, the tendency is for first-row transition metal ions to form isothiocyanates and for second- and third-row ions to form thiocyanates. The bonding usually is established from small differences in the C-N stretching frequency or larger differences in the C-S stretching frequency. The latter peak is, however, very weak and not obtainable with small samples in solid-state mulls. Burmeister and Basolo¹⁰ have shown that one can obtain thiocyanate-isothiocyanate isomerization in the solid state, a fact which will be of considerable importance in the discussion below. The compounds studied were $\text{Fe}(\text{NCS})_2 \cdot 6\text{H}_2\text{O}$ and $\text{K}_2\text{Fe}(\text{SCN})_6$. Both compounds were synthesized with iron enriched to 85 per cent in Fe^{57} . The technique of Claus¹² was used for the $\text{Fe}(\text{NCS})_2 \cdot 6\text{H}_2\text{O}$, while the method of Krüss and Moraht¹³ was used for the $\text{K}_2\text{Fe}(\text{SCN})_6$. The compositions were checked by chemical analysis. The high-pressure Mössbauer operation has been described elsewhere.¹⁴

The $\text{Fe}(\text{NCS})_2 \cdot 6\text{H}_2\text{O}$ exhibited a broad intense peak at $\sim 2400 \text{ cm}^{-1}$, which is the usual location for the C-N stretching frequency in the isothiocyanate. At one atmosphere the Mössbauer spectrum showed a pair of symmetric peaks with isomer shift and quadrupole splitting typical of high-spin ferric compounds (see Tables 1 and 2). With increasing pressure, peaks appeared with location and intensity well within the usual range for high-spin ferrous compounds. The conversion is shown as a function of pressure in Figure 1 (solid triangles, dashed line). Ferric isomer shift and quadrupole splitting appear in Figures 2 and 3. The equilibrium constant follows equation (1) with a value of B typical of ionic ferric compounds (see Table 3). The process is reversible. The reaction is endothermic with a heat of reaction of 0.27 ev, essentially independent of pressure.