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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. $Fe(NCS)_3 \cdot 6H_2O$, 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. $K_3Fe(SCN)_6$ has the thiocyanate structure. At low pressures, it exhibits a significantly larger reduction than the $Fe(NCS)_3$. 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 bcc 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 acetonate,[3] phosphate, citrate and sulfate,[4] ferricyanide and Prussian blue,[5] and hemin and hematin.[6] The process is reversible with some hysteresis. It follows the empirical relationship:

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

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

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

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 (—SCN) and isothiocyanate (—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 Basolo[10] 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 $Fe(NCS)_3 \cdot 6H_2O$ and $K_2Fe(SCN)_6$. Both compounds were synthesized with iron enriched to 85 per cent in Fe^{57}. The technique of Claus[12] was used for the $Fe(NCS)_3 \cdot 6H_2O$, while the method of Krüss and Moraht[13] was used for the $K_3Fe(SCN)_6$. The compositions were checked by chemical analysis. The high-pressure Mössbauer operation has been described elsewhere.[14]

The $Fe(NCS)_3 \cdot 6H_2O$ exhibited a broad intense peak at ~2400 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*). Ferrous 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.

TABLE 1. *Isomer shift vs. pressure.**

Pressure (kb)	Fe(NCS)		$K_2Fe(NCS)_6$		$K_2Fe(SCN)_6$	
	Fe(III)	Fe(II)	Fe(III)	Fe(II)	Fe(III)	Fe(II)
0	0.40	—	0.39	—	0.36	0.88 (10)
25	0.36	1.34	0.37	1.33	0.34	0.94
50	0.33	1.31	0.36	1.31	0.325	1.05
75	0.31	1.29	0.35	1.30	0.315	1.13
100	0.295	1.28	0.34	1.29	0.310	1.16
125	0.28	1.27	0.33	1.28	0.300	1.18
150	0.27	1.26	0.325	1.275	—	—
175	0.26	1.25	0.32	1.27	—	—

* mm/sec relative to iron metal at one atmosphere.

TABLE 2. *Quadrupole splitting vs. pressure (mm/sec).*

Pressure (kb)	$Fe(NCS)_3$		$K_3Fe(NCS)_6$		$K_3Fe(SNC)_6$	
	Fe(III)	Fe(II)	Fe(III)	Fe(II)	Fe(III)	Fe(II)
0	0.58	—	0.82	—	0.82	1.15 (10)
25	0.88	2.08	0.92	2.02	0.92	1.35
50	1.05	2.14	0.99	2.00	0.99	1.60
75	1.14	2.17	1.04	2.00	1.04	1.74
100	1.19	2.20	1.09	2.00	1.09	1.84
125	1.22	2.22	1.12	2.00	1.12	1.90
150	1.24	2.24	1.15	-2.00	—	—
175	1.25	2.26	1.17	2.00	—	—

The infrared spectrum of $K_2Fe(SCN)_6$ exhibited a rather sharp peak near 2100 cm^{-1}, which would indicate the probability of thiocyanate bonding. The atmospheric Mössbauer spectrum showed a pair of asymmetric peaks at slightly lower isomer shift (slightly higher electron density) than the $Fe(NCS)_3 \cdot 6H_2O$. With the application of 10 kb pressure, a pair of new peaks appeared with an isomer shift of about 0.9 mm/sec and a quadrupole splitting of 1.1 mm/sec. This isomer shift is in the range observed for compounds like FeS, FeSe, and FeTe. The material was about half converted at 10 kb, and the conversion increased slowly with pressure (*open circles*, Fig. 1). Meanwhile, the isomer shift and quadrupole splitting of the new peaks increased rapidly with increasing pressure, as can be seen in Figures 2 and 3. The peaks did not broaden, so that apparently there was a single ferrous material, not a mixture. Above 100 kb the conversion actually decreased with increasing pressure, as can be seen in Figure 1. Upon release of pressure the conversion reversed, and we found only a pair of symmetric peaks much like those found for $Fe(NCS)_3 \cdot 6H_2O$. Since our samples were considerably diluted with boron, it was difficult to get a good optical spectrum after a pressure run, but it appeared that the C-N stretching peak was shifted to lower frequency, and probably broadened.

If a sample that had been at high pressure was powdered and reloaded, it exhibited two symmetric peaks at slightly higher isomer shift (lower electron density) than the original material but in the range of typical ferric compounds (see Table 1). As can be seen in Figure 1, the material converted to the ferrous state with increasing pressure (*solid circles*) but with a much smaller conversion at a given pressure, in the low-pressure region. However, by 140–160 kb, the

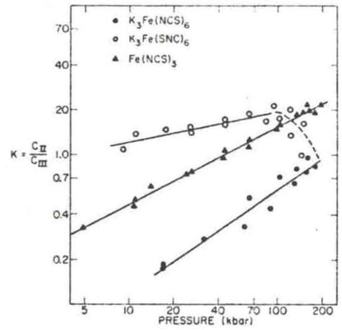

FIG. 1. Ln *K* vs. ln *P* vs. $Fe(NCS)_3 \cdot 6H_2O$, $K_2Fe(SCN)_6$, and $K_3Fe(NCS)_4$.

conversion was essentially the same as in the original material compressed to this pressure. Upon release of pressure the ferrous peaks disappeared, and the spectrum consisted of two symmetric ferric peaks again.

It appears that with pressure the thiocyanate isomerizes to the isothiocyanate. This is a continuous process, since the isomer shift and quadrupole splitting of the ferrous peaks continuously increase with pressure (Figs. 2 and 3). The peak widths were essentially independent of pressure, so that we apparently had primarily one species at any one pressure. That is to say that, at any given pressure, each ferrous ion has essentially the same distribution of thiocyanate and isothiocyanate ligands. The ferric ion spectrum became more symmetrical with increasing pressure, so that the ferric complexes were also isomerizing. However, we could get no quantitative measure of the amount, nor could we establish the degree to which isomerization preceeded or followed reduction.

The early portion of the conversion data for the thiocyanate (*open circles*) was fit with an equation of the usual form, but it is doubtful whether the constants *A* and *B* have physical significance, since the distribution of ligands varied with pressure.

If the starting material was heated to 110°C at 5 kb, the original asymmetric spectrum became more symmetric. As this heated material reduced under increasing pressure, two pairs of ferrous peaks appeared: one with an isomer shift of about 0.9 mm/sec and a quadrupole splitting of 1.1–1.2 mm/sec and one at

TABLE 3. *Constants A and B in equation $K = AP^B$.*

Compound	*A*	*B*
$Fe(NCS)_3$	0.136	0.528
$K_3Fe(NCS)_6$	0.0244	0.692
$K_3Fe(SCN)_6$	0.75	0.208

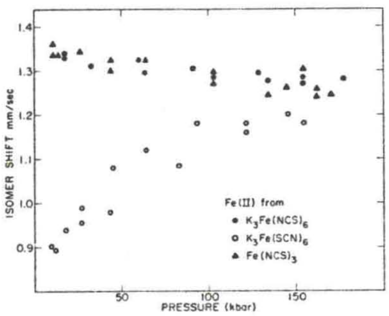

FIG. 2.—Isomer shift vs. pressure, Fe(II) ion.

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

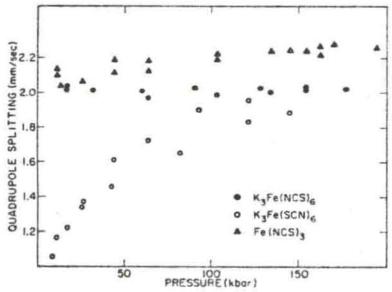

FIG. 3.—Quadrupole splitting vs. pressure, Fe(III) ion.

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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