THE EFFECT OF PRESSURE ON THE OXIDATION STATE OF IRON, II. OXYGEN LIGANDS*

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In a series of papers from this laboratory[1-4] we have discussed the effect of pressure on the oxidation state of iron, on the isomer shift (s-electron density at the nucleus), and on the quadrupole splitting (splitting of the nuclear level of spin 3/2 due to interaction with an electric field gradient at the nucleus) for a variety of iron compounds. Since high-spin ferrous ions exhibit a relatively low electron density at the nucleus (isomer shift ~ 1.2–1.4 mm/sec relative to metallic iron) and large quadrupole splitting (2–3 mm/sec), whereas high-spin ferric compounds show a distinctly lower isomer shift (0.3–0.5 mm/sec) and relatively small quadrupole splitting (0.3–0.6 mm/sec), it is easy to identify one phase in the presence of the other.

The observations can be summarized as follows:[5]

(1) With increasing pressure, Fe(III) ion reduces to the Fe(II) state (reversibly) in a wide variety of compounds including halides, phosphate, sulfate, citrate, ferricyanide, etc. The conversion as a function of pressure is of the form:

$$K = AP^B, \tag{1}$$

where $K = C_{II}/C_{III}$, with C_{II} and C_{III} the nominal concentrations of Fe^{II} and Fe^{III} measured from peak areas, and A and B are constants. From thermodynamic arguments[1, 5] one can write:

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

The fractional increase in conversion per fractional increase in pressure is thus proportional to the concentration of sites available for conversion: the proportionality coefficient is the work to convert a site measured in thermal units, and is independent of pressure. For typical ionic materials $B \sim 0.5$. The reaction is endothermic with a heat of reaction which increases with temperature and is independent of pressure for compounds like the halides.

The electron transfer is from ligand nonbonding to metal antibonding orbital $(t_{2u} \rightarrow t_{2g}$ in octahedral symmetry). The reduction of the energy difference between these two sets of orbitals with increasing pressure is associated with a spreading of the 3d metal orbitals observed optically and probably also with a relative increase in pi bonding that stabilizes the t_{2g} orbitals.[1, 5]

(2) With increasing pressure, the isomer shift decreases (the electron density at the nucleus increases) for most compounds. This can be discussed in terms of decreased shielding of the 3s-electrons by the 3d, due to the spreading of the 3d orbitals mentioned above, and of deformation of the s orbitals.[5]

(3) For high-spin ferric ions there is generally a significant increase in quadrupole splitting with pressure. Since the ground state is an *s* state, the splitting is due to lack of cubic symmetry in the surroundings, and the electric field gradient is very sensitive to compression of the lattice. The much larger quadrupole splitting of high-spin ferrous ions, primarily caused by the aspherical 3*d* shell, tends to increase or decrease by modest amounts with increasing pressure.

In this paper we present high-pressure Mössbauer resonance data for ferric acetyl acetonate $[Fe(C_5H_7O_2)_3]$, basic ferric acetate $[Fe_3(CH_3COO)_6(OH)_2CH_3COOH_2O]$, ferric oxalate $[Fe(C_2O_4)_3 \cdot 5H_2O]$, and strontium trisoxalatoferrate (III) $[Sr_3(Fe(C_2O_4)_3)_2 \cdot 2H_2O]$. The compounds were synthesized from iron enriched to 85 per cent in Fe^{57}. The basic acetate and the acetyl acetonate were made as described in reference 1; the ferric oxalate was made by the procedure of Weinland and Rein,[6] and the strontium salt was synthesized by the technique utilized by Gallagher.[7] The oxalates were handled in the dark or by red light to prevent photoreduction. All compounds gave the correct chemical analyses and exclusively ferric Mössbauer spectra at one atmosphere.

All four compounds have in common the fact that the ligands are bidentate and the iron is surrounded by six oxygen atoms (or ions) in essentially octahedral symmetry.[7–10] Early data on the acetate and acetyl acetonate indicated some conversion of Fe(III) to Fe(II) with increasing pressure at room temperature,[1] but the results were not quantitative. The high-pressure Mössbauer techniques have been described elsewhere.[11]

We shall be primarily concerned with the conversion of Fe(III) to Fe(II) as a function of pressure and temperature. The experimental results are exhibited in Figures 1 and 2. As can be seen, they follow the relationship of equation (1), but $B \neq 0.5$ and is a distinct function of temperature, in contrast to the behavior of compounds previously discussed. Values of A and B are listed in Table 1 and heats of formation in Table 2.

Consider first the acetate and acetyl acetonate. The work $P\Delta V$ to form Fe(II) from Fe(III) is considerably larger at a given temperature and pressure for these complexes than for the simpler ionic crystals. The volume change $V^{III} - V^{II}$ amounts to several cubic centimeters at 10 kilobars (kb). One can understand that for these bidentate ligands it would be more difficult to distribute the strain involved in the charge transfer and formation of ion radicals than it would be for $FeCl_3$ or $FeBr_3$. The smaller value of B (and of ΔV) at higher tempera-

TABLE 1. *Constants A and B for $K = AP^B$.*

Material	Temperature (°K)	A	B
Acetyl acetonate	295	1.24×10^{-5}	2.23
	375	0.96×10^{-2}	1.013
Basic acetate	378	0.22×10^{-6}	3.05
	418	2.21×10^{-2}	0.983
Oxalate	295	0.041	0.51
	335	0.029	0.833
	383	0.043	1.146
Strontium oxalate	295	0.115	0.301
	383	0.058	0.844