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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 $3d$ 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 $[Fe_3(CH_3COO)_6 (OH)_2CH_3-COOH_2O]$, 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

Table 2.   *Heats of reaction.*

Material (kb)	H (ev)		
Acetyl acetonate	325°K		375°K
60	0.15		0.25
100	0.105		0.15
150	0.065		0.085
200	0.032		0.037
Basic acetate		398°K	
75		0.93	
100		0.60	
150		0.44	
Oxalate	315°K		360°K
25	0.19		0.34
70	0.23		0.39
100	0.26		0.42
150	0.29		—
Strontium ferric oxalate		333°K	
20		0.11	
50		0.15	
100		0.20	
200		0.24	

tures can probably be associated with thermal relaxation of the strains.   The heat of reaction decreases markedly with increasing pressure.

On the other hand, the oxalates exhibit a value of $B(P\Delta V/RT)$ and a heat of formation of the Fe(II) site which increases with pressure, i.e., the work to perform the reduction is greater at high than at low temperature.   It is known that oxalates tend to reduce photochemically,[12, 13] and when heated in the dark, they undergo a series of reactions; first reduction, then oxidation.[14]   In both cases CO_2 is evolved and the process is irreversible.

As indicated earlier, the high-pressure reduction is reversible and involves a lowering of energy of metal antibonding levels with respect to ligand nonbonding p-orbitals, so it is not necessary to postulate formation of CO_2 in the lattice. Nevertheless, the radical formed in the process quite possibly has a volume in the lattice that is rather temperature-dependent.   It is of interest to note that the slope B, and therefore the volume difference ($V^{III} - V^{II}$), is noticeably smaller for the strontium salt than for the ferric oxalate, although the number and gross symmetry of the ligands is apparently the same for both compounds.   This illustrates the important effect of the ability to redistribute the strain to next-nearest neighbors and beyond on the conversion equilibrium.

While the main interest in this study was the conversion of Fe(III) to Fe(II), isomer shift and quadrupole splitting data were obtained both for the Fe(III) and for the Fe(II) formed at high pressure.   These results appear in Tables 3 and 4.   Isomer shift data are shown only at room temperature, for it was necessary to change the source location slightly with increasing pressure, which caused a slight change in its temperature.   Peak locations established with changing amounts of Fe(III) and Fe(II) present are necessarily less accurate than those obtained in nonreacting systems, but one can comment on two trends of interest whose magnitude are well beyond any experimental error.
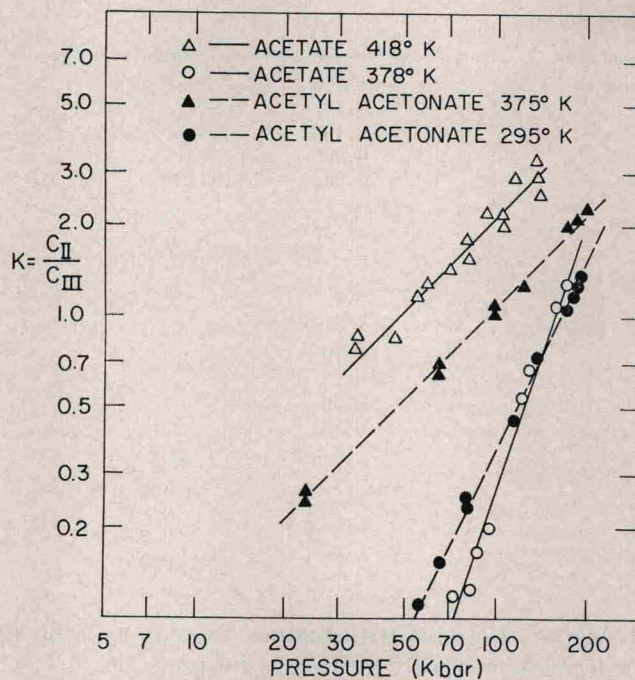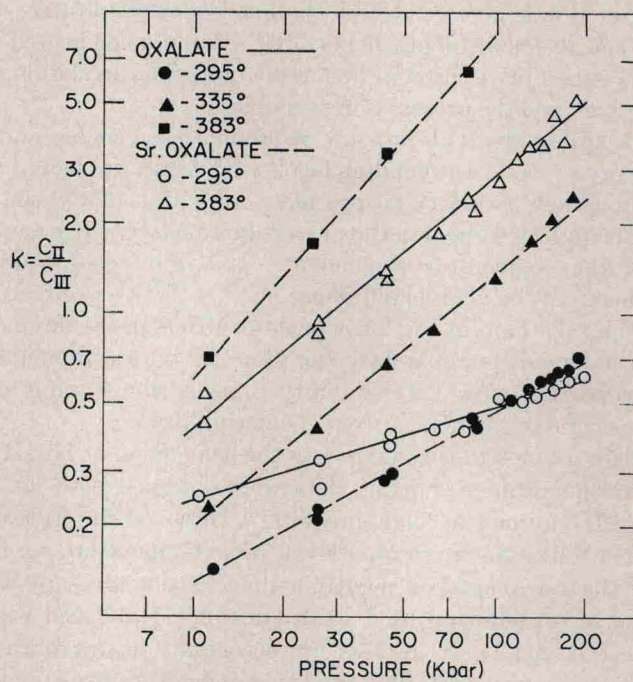
FIG. 1.—Ln K vs. ln P—acetate and acetyl acetonate.

FIG. 2.—Ln K vs. ln P—ferric oxalate and strontium ferric oxalate.

TABLE 3.   *Isomer shift versus pressure at 295°K.**

Pressure (kb)	Acetyl Acetonate Fe(III)	Acetyl Acetonate Fe(II)	Oxalate Fe(III)	Oxalate Fe(II)	Strontium Oxalate Fe(III)	Strontium Oxalate Fe(II)
0	0.35	—	0.45	—	0.41	—
25	0.38	1.28	0.44	1.24	0.40	1.27
50	0.40	1.20	0.43	1.26	0.39	1.29
75	0.39	1.16	0.43	1.29	0.385	1.31
100	0.38	1.14	0.42	1.31	0.38	1.33
125	0.36	1.12	0.41	1.34	0.375	1.36
150	0.33	1.11	0.40	1.36	0.37	1.38
175	0.33	1.10	0.39	1.38	0.365	1.40

* Mm/sec relative to iron metal at 1 atmosphere.

TABLE 4.   *Quadrupole splittings (mm/sec).*

(A) Ferric Ion

Pressure (kb)	Basic Acetate 378K°	Basic Acetate 418°K	Acetyl Acetonate 295°K	Acetyl Acetonate 375°K	Oxalate 295°K	Oxalate 335°K	Strontium Oxalate 295°K	Strontium Oxalate 382°K
0	—	—	0.46	0.70	0.59	0.54	0.50	0.72
25	—	—	0.76	1.00	0.82	0.77	0.68	0.88
50	—	0.85	0.80	1.10	0.95	0.92	0.78	1.00
75	0.82	0.90	0.92	1.15	1.02	1.00	0.90	1.10
100	0.90	0.95	1.03	1.17	1.08	1.07	1.02	1.18
125	0.96	1.02	1.14	1.20	1.13	1.12	1.12	1.25
150	1.02	1.06	1.22	1.23	1.20	1.16	1.16	1.32
175	1.08	1.10	1.28	1.26	1.26	1.20	1.20	1.38

(B) Ferrous Ion

Pressure (kb)	Basic Acetate 378°K	Basic Acetate 418°K	Acetyl Acetonate 295°K	Acetyl Acetonate 375°K	Oxalate 295°K	Oxalate 335°K	Strontium Oxalate 295°K	Strontium Oxalate 383°K
0	—	—	—	—	—	—	—	—
25	—	—	2.20	2.10	1.90	1.90	2.00	2.00
50	—	1.80	2.15	2.05	2.00	2.00	2.08	2.08
75	2.20	1.84	2.12	2.00	2.10	2.08	2.14	2.14
100	2.16	1.86	2.00	2.00	2.18	2.16	2.20	2.20
125	2.14	1.88	2.00	1.98	2.23	2.21	2.26	2.26
150	2.12	1.90	2.00	1.96	2.28	2.23	2.30	2.30
175	2.10	1.90	2.00	1.95	2.30	2.25	2.35	2.35

In both oxalates the isomer shift of the ferrous ion formed increased with pressure, i.e., the electron density at the iron nucleus decreased. This is in contrast to the behavior of all but a few other systems, and indeed to that of ordinary ferrous oxalate.[1] The bonding must be very strained and changes in occupation of the bonding orbitals with pressure apparently overwhelm the shielding and orbital compression effects.[5]

In the acetyl acetonate, there is a maximum in the isomer shift at about 40–50 kb, as shown in Figure 3. The apparent isomer shift at 102°C is plotted in the same figure to show that it also exhibits the maximum. In this case the changes in orbital occupation dominate in the low-pressure region, whereas the usual orbital distortion effects govern at high pressure. Figure 4 shows the quadrupole splitting for acetyl acetonate as a function of pressure. At room temperature there is a distinct leveling in the region of the isomer shift maximum, then a second rise at higher pressures. It is clear that the change in orbital occupation of the bonding orbitals affects the local asymmetry. At 102°C the change in quadrupole splitting with pressure is too small to determine whether the irregularity is
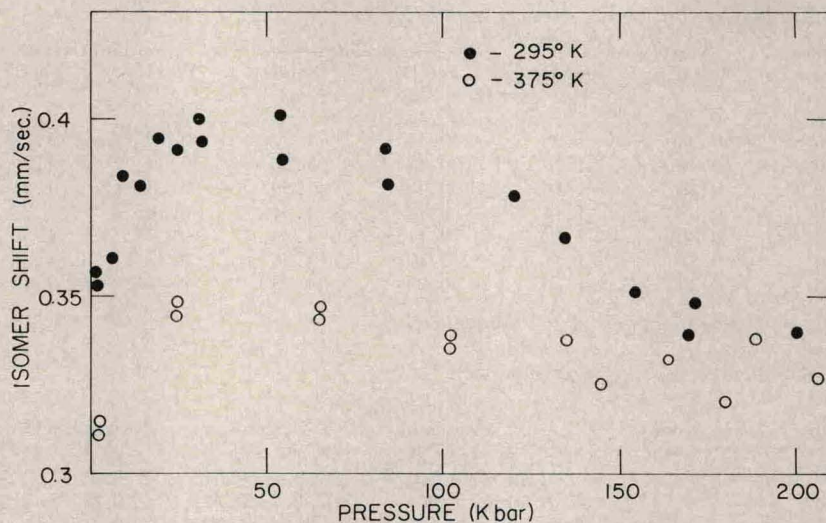
FIG. 3.—Isomer shift vs. pressure—ferric acetyl acetonate (Fe(III)).
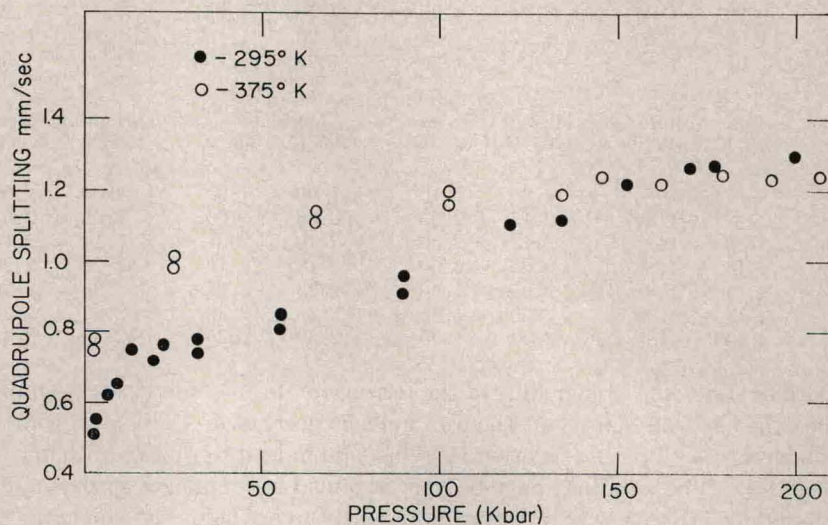

FIG. 4.—Quadrupole splitting vs. pressure—ferric acetyl acetonate (Fe(III)).

present. The increase in quadrupole splitting with increasing temperature in the low-pressure region is unusual. The anomalies in isomer shift and quadrupole splitting are not reflected in the conversion, which shows no irregularities with increasing pressure or temperature. This is not surprising as the conversion involves only nonbonding and antibonding orbitals.

Summary.—The effect of pressure on the oxidation state of ferric ion, in a site of essentially octahedral symmetry with six oxygen ligands, has been measured. Four compounds have been studied: basic ferric acetate, ferric acetyl acetonate, ferric oxalate, and strontium ferric oxalate. For all these

compounds the reduction followed the relationship $K = AP^B$ where K is the equilibrium constant C_{II}/C_{III}. For the acetate and acetyl acetonate, B decreased with increasing temperature, whereas both oxalates showed an increase in B with increasing temperature. These observations are discussed in terms of thermodynamic implications. The unusual behavior of the isomer shift and quadrupole splitting of the ferric ion in the acetyl acetonate is briefly discussed.

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