

The High-Pressure Chemistry of Iron*

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The high-pressure chemistry of iron in the solid state is rich in new phenomena. Optical studies of the effect of pressure on the interelectronic repulsion parameters and the ligand-to-metal charge transfer peaks, as well as Mössbauer resonance measurements of the change of isomer shift with pressure, indicate that with increasing pressure the $3d$ orbitals lower in energy vis-à-vis the ligand orbitals. This has important effects on both the oxidation state and spin state of iron.

With increasing pressure Fe(III) reduces to Fe(II) in a wide variety of compounds. This process is analyzed in considerable detail. Examples of the reduction of Fe(IV) to Fe(III) and of Fe(VI) to Fe(IV) and Fe(III) are discussed briefly. The ferrocyanides are the classical low-spin iron compounds. The strong bonding is in part due to the back donation of iron $t_{2g}(\pi)$ electrons to the empty π^* orbitals of the cyanide. The increased affinity of iron for electrons at high pressure reduces this back donation and results in a partial conversion to high-spin Fe(II). The effect of pressure on the spin state of ferricyanides reduced at high pressure, and on substituted cyanides, especially nitroprussides, is also considered. Two cases of special interest, Prussian blue, $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$, and ferrous nitroprusside, $\text{Fe}[\text{Fe}(\text{CN})_5\text{NO}]$, are discussed at some length.

Introduction

Studies of the effect of pressure on electronic behavior in compounds of iron have revealed a number of new phenomena that have significance for many branches of science.

The tools used in these investigations have been primarily Mössbauer resonance, and, in lesser degree, optical absorption. It is useful to review briefly what can be observed with these tools and what is known about the effects of pressure on the electronic behavior of transition metal complexes.

Emission of a gamma ray occurs when a radioactive nucleus decays from an excited state to a lower level. The nuclear energy levels are measurably sensitive to electronic wave functions having non-zero amplitude at the nucleus (s wave functions). Thus, ^{57}Fe in a stainless steel source is not in resonance with ^{57}Fe in, say, a ferric chloride absorber. By moving the source with respect to the absorber, one can establish resonance, making use of the Doppler velocity. A Mössbauer spectrometer is a device for producing and measuring accurately the velocities necessary to establish resonance between

a source and absorber with different chemical environments. These energy differences are given in mm/sec; for ^{57}Fe , 1 mm/sec corresponds to a difference in energy of the order of 10^{-4} cal/mole.

The primary readout from Mössbauer resonance is the center of gravity of the spectrum, known as the isomer shift. In this work, we are interested in changes in isomer shift with changes in the environment. The $1s$ and $2s$ orbitals are strongly isolated from the environment. The $3s$ electrons do not interact directly with the ligands either, but the radial maximum of their orbitals is at about the same point as that of the $3d$ orbitals which, of course, interact strongly with the ligand orbitals. From changes in the isomer shift we can infer information concerning changes in the occupation and radial extent of the $3d$ orbitals, and thus about changes in the oxidation state and chemical bonding of iron.

The second readout of interest here is the quadrupole splitting—the interaction between the nuclear quadrupole moment and an electric field gradient at the nucleus. This interaction partially removes the degeneracy of the excited state of spin $3/2$, and gives two peaks in the spectrum instead of one. The possible sources of an electric field gradient include a noncubic arrangement of the ligands and an

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