

also be stimulated by electron transfer between adjacent molecules (self complexing). For anthracene and tetracene the excited state may be too high initially to be sufficiently occupied at high pressure, or there may not be sufficient self-complexing action. Reaction does occur in molecules like hexacene and violanthrene with sufficiently low-lying π^* orbitals. This is, then, an example of an electronic transition with distinct chemical consequences. A number of aromatic hydrocarbons such as anthracene, pyrene, and perylene form electron donor acceptor complexes with electron acceptors like iodine, tetracyanoethylene, etc. These complexes typically have optical absorption peaks of energy 10–25 kK (1–3 eV) which decrease in energy with increasing pressure. Many of these complexes show irreversible electrical behavior at high pressure (64). The products have not yet been well characterized, but it is clear that sometimes both donors and acceptors have reacted and sometimes just the donors, so that the acceptor is recovered in its original condition. The prime purpose of the acceptor is to provide a low-lying excited state, so that its decrease in energy with pressure is sufficient to establish a new reactive ground state of the donor at high pressure. It would be very desirable to be able to characterize the products accurately, as it might be possible to design complexes with appropriate geometry and electronic structure to give desired products, and thus to establish a new solid state organic chemistry at high pressure.

CHEMISTRY OF IRON

The coordination chemistry of transition metal ions has been a very fruitful field of study. The splitting of the $3d$ orbital energies, the radial extent of these orbitals, and the spin state of the electrons in the orbitals depend on the symmetry and strength of the field due to the ligands and the degree of covalent bonding, which is a function of both the character of the ligand and the oxidation state of the metal ion. The behavior of iron is of considerable interest because of its importance in biology and geophysics as well as in chemistry and physics. The study of iron compounds at high pressure is significantly facilitated by the possibility of using Mössbauer resonance as well as optical absorption. With the latter technique one measures the difference in energy between a ground state and some excited state of an electron along a particular path. Changes in the optical excitation energy with pressure are helpful in understanding high pressure chemical processes. There are three types of excitations which are useful in connection with the high pressure chemistry of iron. Excitations from one state to another within the $3d$ shell measure the change in the field which the ligands impose on the metal $3d$ orbitals, and changes in the interelectronic repulsion (Racah) parameters. From changes in the energy associated with exciting an electron from one ligand state to another (usually $\pi \rightarrow \pi^*$ transitions) one can infer modifications of the ground state configuration of the ligands and, therefore, changes in bonding to the iron. From the energy of the ligand-to-metal charge transfer peaks one can infer the probability of electron transfer between ligand and metal, and thus

the change in oxidation state of the metal. The direction and magnitude of these optical shifts were discussed in the early part of the paper.

Mössbauer resonance is helpful in identifying the electronic ground state of the iron ion. Two parameters are important: the isomer shift and the quadrupole splitting. The isomer shift measures the s electron density at the iron nucleus; the quadrupole splitting measures the interaction of the nuclear quadrupole moment with an electric field gradient at the nucleus. These gradients arise, in the first order, from an asymmetric occupation of the $3d$ orbitals and, in the second order, from a noncubic arrangement of the ligands.

The factors determining the isomer shift have been summarized by Erickson (67). For high spin ions the major variable is the oxidation state, i.e. the number of $3d$ electrons which shield the $3s$ electrons from the nucleus. Typically, high spin ferric ions have isomer shifts in the range 0.25–0.50 mm/sec, while the values for the high spin ferrous ion lie in the range 0.9–1.4 mm/sec (both given relative to iron metal). Within each group the variation of isomer shift can be related to several factors, including the degree of spreading of the $3d$ orbitals (central field covalency), occupation of the $4s$ orbitals, overlap of metal $3s$ orbitals by ligand σ orbitals, and backdonation of metal $3d$ electrons into empty ligand π^* orbitals. This last phenomenon is especially important for Fe(II) ions. We shall discuss the effect of pressure on the isomer shift and quadrupole splitting only to the extent necessary to explain the various electronic transitions which occur.

The high spin ferrous ion can be distinguished from the high spin ferric ion not only by the difference in isomer shift but also by the difference in quadrupole splitting. The high spin Fe(II) exhibits a large quadrupole splitting (2.0–3.0 mm/sec) because of the asymmetric 5T_2 ground state, while high spin Fe(III), with a 6A_1 ground state, usually shows a splitting near 0.5–0.7 mm/sec. If the splitting due to the ligand field is large enough to overcome the spin pairing energy, one may obtain a low spin ground state. The low spin ferrous state is characterized by a relatively low isomer shift ~ 0.0 mm/sec relative to metallic iron, and little or no quadrupole splitting because of the 1A_1 symmetry. Thus, transitions from high spin Fe(III) to high spin Fe(II) and between the high spin Fe(II) and low spin Fe(II) are easy to identify. It is more difficult to obtain quantitative information on low spin Fe(III), as its isomer shift is very close to low spin Fe(II). As we shall mention later in the report, it may be possible to identify states of intermediate spin or mixed spin in molecules with lower symmetry. It seems desirable to analyze the possibilities and limitations involved in making quantitative high pressure Mössbauer resonance measurements.

For these experiments (68) the sample is made from iron enriched to 70–95% in ^{57}Fe , and the compounds are diluted (5/1 to 10/1) with boron and pressed into a hole 0.3 mm in diameter in a pellet of boron plus lithium hydride 2 mm in diameter (other diluents such as Al_2O_3 or graphite did not seem to affect the results). The pressure calibration is by X-ray diffraction. The problems in making quantitative measurements and in their interpretation fall into