

**Table 1. Comparison of the energy (in eV) associated with thermal and optical excitations of the  $\pi-\pi^*$  transition in phenanthroline.**

P(kbar)	$h\nu_{\max}$	$\delta E_{\frac{1}{2}}$	$E_{\text{th}}$
0	4.6	0.95	+1.35
50	4.45	1.05	+0.45
100	4.30	1.14	-0.40
150	4.20	1.20	-0.98

can be completely removed from the recovered material. Its function is to provide a new ground state at high pressure to put the hydrocarbon into a reactive configuration, but it does not enter into the product. The hydrocarbons formed are soluble and can be fractionated by chromatography and characterized by nmr and by optical and mass spectroscopy. The major product from the perylene complex is a cage-like dimer of a type not previously seen. Its structure is shown in Fig. 5. The major product from pyrene is a tetramer of analogous structure. By establishing complexes of appropriate geometry and electronic structure it may be possible to develop a series of products and a new solid state chemistry of organic compounds.

Three electronic transitions which have been observed in the chemistry of iron compounds are  $\text{Fe(II)HS} \rightarrow \text{Fe(II)LS}$ ,  $\text{Fe(II)LS} \rightarrow \text{Fe(II)HS}$ , and  $\text{Fe(III)HS} \rightarrow \text{Fe(II)HS}$ . In addition to optical absorption measurements, one can utilize Mössbauer resonance to identify the states of iron. The latter is similar to nmr in that one measures the energy of a nuclear transition which is perturbed by electronic wave functions to infer information about the electronic structure. The perturbations take the form of changes in the energy of the transition (isomer shift) and of the splitting of the excited state (quadrupole splitting). To bring about resonance between a source and absorber in different chemical environments one is moved with respect to the other. The velocities necessary for resonance are correlated with energy perturbations characteristic of the various states. Figure 6 shows typical Mössbauer spectra for the high-spin ferrous, high-spin ferric and low-spin ferrous states.

The high-spin to low-spin conversion is easiest to understand. We know that the ligand field  $\Delta$  increases with pressure. If it becomes greater than the spin pairing energy a low-spin compound will result. One example is Fe(II) as a dilute substitutional impurity in  $\text{MnS}_2$  which is isomorphous with  $\text{FeS}_2$  (pyrites). In  $\text{FeS}_2$  iron is low spin, while in  $\text{MnS}_2$  it is high spin. This is not surprising since the lattice parameter of the latter is significantly larger than that of the former so that one can think of the Fe(II) as being under a negative pressure, relative to its situation in pyrites. At about 40 kilobars pressure some low spin appears in the spectrum; by 140 kilobars it is completely converted. The

**Table 2. Optical v. thermal excitation for ligand-metal charge transfer in ferric hydroxamates and ferrichrome A [for 10 per cent reduction of Fe(III)].**

Compound	Pressure	$h\nu_{\max}$	$\delta E_{\frac{1}{2}}$	$E_{\text{th}}$
Tris(acetohydroxamato) iron(III)	125	2.80	0.90	-0.11
Tris(benzohydroxamato) iron(III)	105	2.70	0.875	-0.06
Tris(salicyclohydroxamato) iron(III)	70	2.54	0.84	-0.02
Ferrichrome A	37	2.65	0.835	+0.11

process is reversible with some hysteresis.

Turn now to the inverse transformation, *i.e.* low-spin ferrous to high-spin ferrous, with increasing pressure. First, what is the evidence for this somewhat surprising transformation? Figure 7 shows Mössbauer spectra for a trisphenanthroline ferrous complex as a function of pressure. At one atmosphere, it has a typical low-spin spectrum. By 42 kilobars, there is a measurable amount of high-spin material and by 153 kilobars there is perhaps 30 per cent conversion. Some substituted phenanthrolines may give as high as 60 per cent high-spin at high pressure. Significant low-spin to high-spin conversions have been observed in heavy metal ferrocyanides at high pressure and temperatures above 110 °C, and phthalocyanine complexed with pyridine exhibits a low-spin to intermediate-spin transition at high pressure.

At first this transformation seems paradoxical on both thermodynamic and electronic grounds. From the thermodynamic viewpoint one must remember that it is the volume of the system as a whole which must decrease with increasing conversion. Changes in both bond length and intermolecular distance may be involved, so not every bond need shorten. All of the complexes which exhibit this phenomenon are extensively backbonded. Backbonding requires low lying available  $\pi^*$  orbitals on the ligands. It was shown earlier

**Fig. 8. Plot of  $\ln K$  against  $\ln P$  for the reduction of ferric acetylacetonate.  $K$  is the ratio of the fractions of ferrous and ferric ion.**

