FIGURE 8. Characteristics of substituted acetylacetonates.

of technique to minimize effects of shear and of other experimental artifacts. The compounds used, listed in Figure 8, provided a systematic variation of electronic properties which could be correlated with the conversion.

The substituted acetylacetonates form a series of rather covalent complexes with ferric iron. (The Racah parameter B is of the order 500 cm^{-1} compared with a free ion value of 900 cm^{-1}.) They provide a useful basis for studying the relationships between the electronic structure of the ligands, covalency, σ and π overlap, and pressure. These are discussed in some detail in the original paper. We introduce this discussion here only to the extent it bears directly on the conversion as a function of pressure. We shall therefore discuss the properties only in the region 40–180 kbar.

The essential feature is the correlation of electron donor ability of the ligand with degree of conversion. Data were available for a number of the ligands (or for their complexes with copper) on such measures of donor ability as pK_a (acid dissociation constant), polarographic half-wave potential, appearance potential from mass spectrometric studies, and Hammett σ, all evaluated at 1 atm, of course. These correlated quite well with the ferric isomer shift at 1 atm, i.e. a smaller isomer shift corresponds to greater probability of transfer of an electron from the ligand. As discussed in the original

paper there is a reasonable correlation between conversion and isomer shift for a group of six of the compounds which are all poor π acceptors.

The isomer shift depends in a complex way on both σ and π orbital overlaps, while the reduction of Fe(III) depends on the ability of the ligand π orbitals to transfer an electron to the metal d_π orbitals. In general the $\pi_L \rightarrow d_\pi$ orbital energy difference decreases with increasing pressure and thus reduction proceeds. Among a series of related compounds it is to be expected that the relative increase in conversion with pressure will depend on the relative change of the electron donor ability as measured by the ferric isomer shift. In Figure 9 we plot the increase of conversion with pressure between 60–160 kbar versus the change in isomer shift over the same range. We see that the correlation holds quite well, i.e. those compounds which show a relatively large increase in donor ability, as measured by a large decrease in isomer shift, show a large increase in conversion, while those complexes which exhibit a relative decrease in donor ability (increase in isomer shift) show a relatively small increase in conversion.

Optical absorption peaks appear in the visible and near-uv spectra of these compounds which are assigned to charge transfer transitions. None of these is the $\pi \rightarrow t_{2g}$ transfer directly involved in the reduction. Nevertheless, the area under the charge transfer peak should reflect the concentration of ferric sites present. Indeed, the relative area under the charge transfer peaks decreases with increasing pressure, by an amount that closely parallels the conversion measured by Mössbauer resonance.
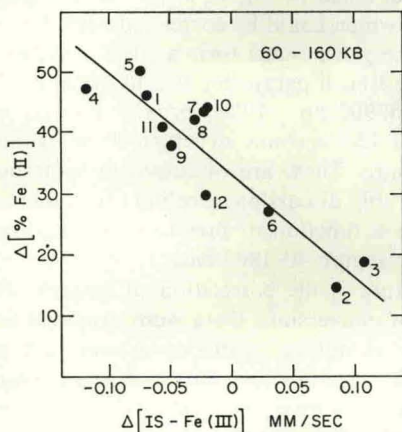

FIGURE 9. Change of ferric isomer shift vs change of conversion [Fe(III) → Fe(II)]. Twelve acetylacetonate derivatives.