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Effect of Pressure on the Electronic Structure of Twelve Ferric β -Diketone Complexes*

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The effect of pressure to 180 kbars on the electronic structure of 12 ferric β -diketone complexes has been measured by means of Mössbauer resonance and optical absorption. The systematic variation of the electron donor and acceptor properties of the ligands permits a more detailed interpretation of the results than in previous studies. These properties are correlated with the isomer shift of the Fe(III), and that of the Fe(II) produced under pressure, and with the change of the isomer shifts with pressure. The degree of conversion of Fe(III) to Fe(II) correlates well with the change of isomer shift with pressure, and thus with changes of the electronic properties of the ligands. Optical absorption studies as a function of pressure were made on both the charge transfer and intraligand $\pi \rightarrow \pi^*$ transitions of several complexes. The decrease in area under the CT peaks correlates very well with the amount of reduction of Fe(III) as obtained from the Mössbauer resonance studies. The shifts of both the CT peaks and $\pi \rightarrow \pi^*$ transitions are recorded and discussed briefly.

In this paper, we discuss the effect of pressure to 180 kbars on the electronic state of iron in a series of complexes with β -diketones. The experimental techniques used were Mössbauer resonance and optical absorption. These have been described previously.¹⁻³

A series of studies since 1967 has revealed changes of both spin state and oxidation state of iron with increasing pressure.⁴⁻⁹ Ferric iron tends to reduce to the ferrous state; for ferrous iron one observes either conversion from high spin to low spin or from low spin to high spin with pressure for various materials in different pressure ranges.

While the reduction of ferric iron has been observed in a wide variety of compounds, there has been no study where the electron donor properties of the ligand have been varied in a systematic way, nor have the Mössbauer resonance studies generally been accompanied by appropriate optical absorption measurements. We present such a systematic study here.

The previous measurements of the reduction of Fe(III) at high pressure have, however, revealed a number of general characteristics. The reduction takes place over a range of pressure, and does not go to completion within the limits of available pressure, at least at 25°C. Over a considerable range of pressure the conversion can frequently be approximated by the expression

$$K = C_{II}/C_{III} = AP^M,$$

where C_{II} and C_{III} are the fractions of ferrous and ferric sites; P is the pressure; and A and M are constants. The process is endothermic. It is reversible, but with considerable hysteresis. These characteristics are accounted for in a thermodynamic analysis presented by Slichter and Drickamer¹⁰ which is analogous to a molecular field theory of magnetism or to the regular solution theory of nonideal mixtures.

From an electronic viewpoint, the process involves transfer of an electron from nonbonding or weakly bonding ligand orbitals to the nonbonding or slightly antibonding metal $d_{\pi}(t_{2g})$ orbitals. A number of observations are consistent with a decrease in the energy

difference between the ligand π and metal d_{π} orbitals. The interelectronic repulsion (Racah) parameters generally decrease with increasing pressure. This is associated with a spreading of the $3d$ orbitals due to increasing central field covalency. The fact that the isomer shift (center of the Mössbauer spectrum measured with respect to *bcc* iron) decreases with pressure indicates that there is a higher electron density at the iron nucleus because of the decreased shielding of the $3s$ orbital by the $3d$ electrons. It is very difficult to find optical absorption peaks which are unequivocally assigned to the $\pi \rightarrow t_{2g}$ transition. However, peaks with substantial charge transfer character shift to lower energy and broaden with increasing pressure. These peaks typically lie in the range 2-4 eV and shift by several tenths of an electron volt in 100 kbars.

A large difference between optical and thermal transition energies is not unusual. Color centers, which have absorption peaks in the range 2-4 eV, can be bleached thermally at moderate temperatures, sometimes as low as 100°K. Redox reactions in solution, where the thermal energy difference between states is essentially zero, absorb in the visible region of the spectrum. Analyses by Marcus^{11,12} and by Hush^{13,14} can be modified to indicate a first approximation to the difference in thermal energy between initial and final states at 25°C:

$$E_{th} = h\nu_{max} - 3.6(\Delta\nu_{1/2})^2(\omega/\omega')^2,$$

where ν_{max} is the optical absorption maximum, $\Delta\nu_{1/2}$ is the halfwidth of the charge transfer peak in eV, and ω and ω' are the force constants for the ground and excited state potential wells. Both the observed red shift and broadening thus contribute to the change of ground state with pressure.

There are a number of factors which make the difference between thermal and optical energies reasonable. In the first place, the Franck-Condon principle requires optical transitions to occur vertically on a configuration coordinate diagram, while thermal processes are not so restricted. In the second place, the optical processes are subject to selection rules, while

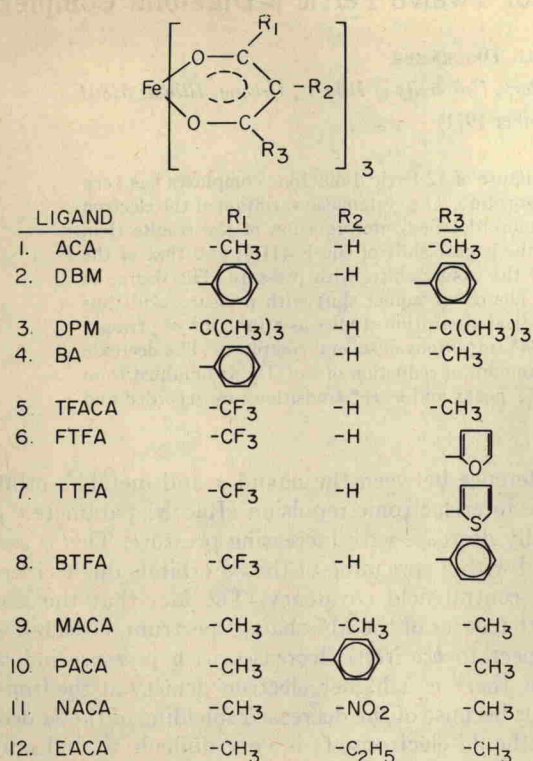


FIG. 1. Compounds studied.

the thermal processes occur over sufficient time that their selection rules are relaxed. In the third place, there will almost certainly be strong configuration interaction in the solid state which can increase the difference between thermal and optical energy requirements. Finally, the pressure selects the volume as a configuration coordinate, whereas optical processes may involve other configuration coordinates; this may further increase the energy difference for the two processes.

The reduction process has thus been characterized and justified in a general way. To relate the reduction in a systematic way to the electron donor characteristics of the ligand, we have studied the 12 β -diketone complexes shown in Fig. 1.

All except one of the derivatives were prepared by the ferric acetate procedure as described by Hantzsch and Desch,¹⁵ with some modifications. In order to obtain satisfactory Mössbauer spectra it was necessary to use ⁵⁷Fe enriched iron in the syntheses of the compounds. The enriched iron used in these preparations was purchased from Oak Ridge National Laboratory, Oak Ridge, Tennessee, in the form of α -Fe₂O₃ containing 77% ⁵⁷Fe. Metallic iron was prepared by reducing the α -Fe₂O₃ at 480°C in a hydrogen atmosphere over a period of 3 hrs. Each synthesis of an enriched compound was done on a microscale, yielding approximately 20 mg of product.

For each enriched synthesis, the iron powder was

dissolved in 0.4N HCl and then oxidized with chlorine gas to give a yellow solution. Molecular chlorine was removed by purging with a nitrogen stream and the pH was adjusted to about 5 by means of solid sodium acetate. An ethanolic solution of the β -diketone ligand, 20% in excess, was then added to the iron solution. Generally 2 ml of ethanol were mixed with the liquid β -diketones; considerably more was required for the solid ligands. Usually the chelate precipitated immediately. In some cases, however, it was necessary to let the solution sit in a refrigerator for three or four hours. The precipitate was then washed with water or a 50-50 ethanol-water solution and dried under vacuum.

Generally the chelates were prepared with commercially available substituted β -diketones. Since the nitro substituted ligand could not be so obtained, the procedure of Sen and Thankarajan¹⁶ was used to nitrate ferric acetylacetonate. In all cases the synthesis procedure was first checked using unenriched iron. The enriched material was prepared only after a satisfactory microanalysis had been obtained.

The samples prepared for optical work were made in considerably larger quantities. Here is proved simpler first to dissolve FeCl₃ in water and remove the undissolved material by filtration. The remainder of the procedure was identical.

DISCUSSION

In the following sections we discuss first the Mössbauer resonance results, the interpretation of the change of isomer shift with pressure, and then the conversion of ferric to ferrous iron with pressure. The second section discusses the optical absorption measurements, the assignment of the peaks in the visible and uv, the change in area under the charge transfer peaks with pressure, and, briefly, the shift of the peak locations with pressure.

Mössbauer Resonance

A minimum of two complete pressure runs was made on each compound. The samples were diluted at least 8/1 with boron to eliminate any effect of sample thickness. Considerable care was taken in the loading procedure to minimize shear. Typical Mössbauer spectra are shown in Figs. 2(a) and 2(b). The data were fit to Lorentzian peaks using a least squares fitting program. The locations of these peaks give the isomer shifts (presented here with respect to metallic iron) and the quadrupole splittings.

The relative areas under the ferrous and ferric peaks give the relative conversion. (It is necessary to assume equal *f* number at ferrous and ferric sites.) Fits at low pressure were particularly difficult because of the low peak intensity and the asymmetric nature of the ferric peaks due to spin-spin coupling.¹⁷ It can be seen from Fig. 2 that conversion increases continuously with pressure. After release of pressure and some effort to re-