

Effect of Pressure on the Electronic Structure of Ferric Hydroxamates and Ferrichrome A

D. C. GRENOBLE AND H. G. DRICKAMER

School of Chemical Sciences and Materials Research Laboratory, University of Illinois, Urbana, Ill. 61801

Communicated December 24, 1970

ABSTRACT The effect of pressure up to 175 kilobars on the electronic structure of three ferric hydroxamates and on ferrichrome A has been studied by optical absorption and Mössbauer resonance. The ferric ion was reduced to ferrous ion with pressure, as has been previously observed for various compounds. For the hydroxamates, the amount of reduction correlated very well with the location and shift of the metal-to-ligand charge transfer peak. This is entirely consistent with a previously presented theory. The results for ferrichrome A did not fit quantitatively into the series. Since the shape of the potential well is almost certainly different for this compound, this result is not surprising.

Hydroxamic acids have received wide attention among analytical chemists because of their ability to form highly colored ferric coordination compounds. The chemical formula of a primary hydroxamic acid is $R-CO-NH(OH)$, where R can represent various chemical groups. Coordination to the ferric ion is through the $-CO-N(OH)-$ group after removal of the proton. There is renewed biochemical interest in hydroxamic acids as a result of finding this characteristic group in natural products from such organisms as aerobic microbial cells. The biological function of hydroxamates is to transfer iron through metabolic channels, and present it for incorporation into the porphyrins and other iron-containing enzymes and proteins. The biological transfer of iron is accomplished by a reduction of the ferric iron, which is bound tightly by the hydroxamic acid groups, to ferrous iron, which is only weakly bound and can easily be removed from the compound. Neilands (1-4) has written a review article and several papers concerning the chemical and biological aspects of hydroxamic acids.

In this study, three model compounds for the biological compounds and one biological hydroxamate, ferrichrome A, were studied under different pressures. The model compounds are tris(acetohydroxamato)iron(III), tris(benzohydroxamato)iron(III), and tris(salicylhydroxamato)iron(III). For brevity, these compounds are referred to as $Fe(AHA)_3$, $Fe(BHA)_3$, and $Fe(SHA)_3$, respectively. The iron atom in these compounds is octahedrally coordinated to six oxygen atoms (5), and thus requires three hydroxamic acid moieties for coordination to the iron. In contrast, ferrichrome A is a hexadentate iron compound. The crystal structure of this compound has also been determined (6).

Abbreviations: AHA, tris(acetohydroxamato); BHA, tris(benzohydroxamato); SHA, tris(salicylhydroxamato).

METHODS

The hydroxamates were prepared by methods available in the literature (7, 8), using iron enriched to 90% in ^{57}Fe , and gave appropriate analyses. The unenriched iron in the ferrichrome A was replaced by enriched iron by the method of Neilands (3). The techniques used in the high-pressure studies, Mössbauer resonance and optical absorption, have been described (9-11).

STUDIES WITH MODEL COMPOUNDS

The optical absorption of $Fe(AHA)_3$ in the visible region is shown in Fig. 1 as a function of pressure. The optical transition is a ligand-to-metal charge transfer. The initial charge transfer energy in $Fe(AHA)_3$ is at 23.25 kK (kiloKayser). The optical spectra were normalized to 1.0 at the peak maximum for each pressure. The shift to lower energy at 50% of the peak maximum is 1.19 kK (0.175 eV) in 140 kbar. Still further out on the tail, at about 25% of the peak maximum, the shift is 1.9 kK in 140 kbar. In contrast the peak maximum shows only a modest shift (less than 0.2 kK at 90% of the maximum absorption). The optical spectra of $Fe(BHA)_3$ and $Fe(SHA)_3$ are similar to $Fe(AHA)_3$, although the initial energies of the charge transfer bands are different. At 1 atm, the peak maxima for $Fe(AHA)_3$, $Fe(BHA)_3$, and $Fe(SHA)_3$ are, respectively, 23.25, 22.22, and 21.95 kK; and the energies at 50% of maximum absorption are 19.8, 18.9, and 18.55 kK, respectively. The shifts to lower energy at 50% of peak maximum in 140 kbar for $Fe(AHA)_3$, $Fe(BHA)_3$, and $Fe(SHA)_3$ are 1.19, 1.25, and 1.25 kK, respectively, so that the changes in optical spectra with pressure for these three compounds are very similar.

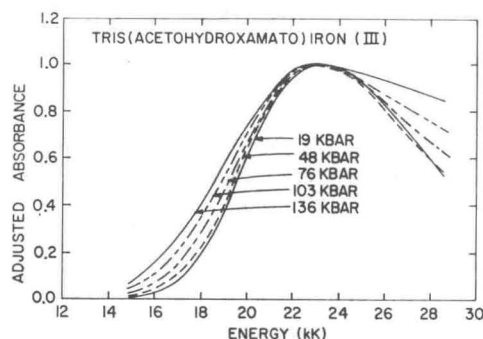
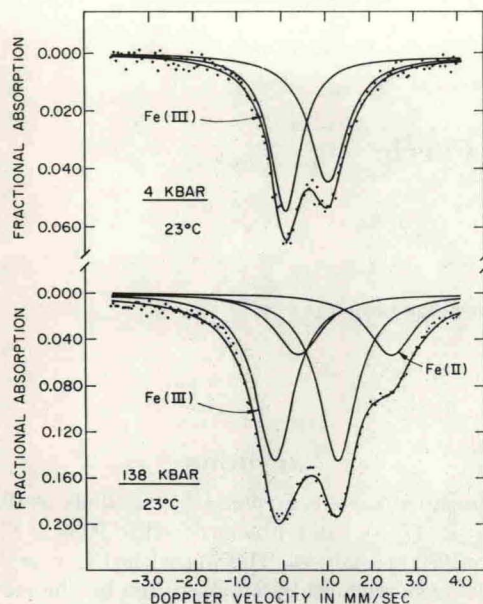
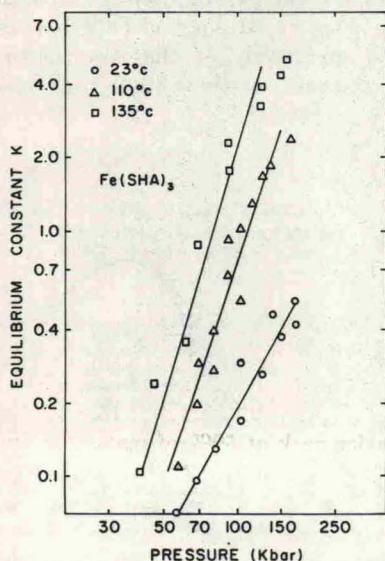
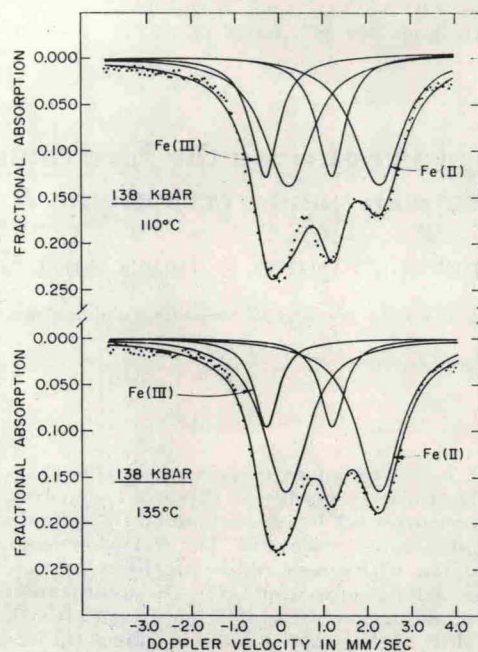


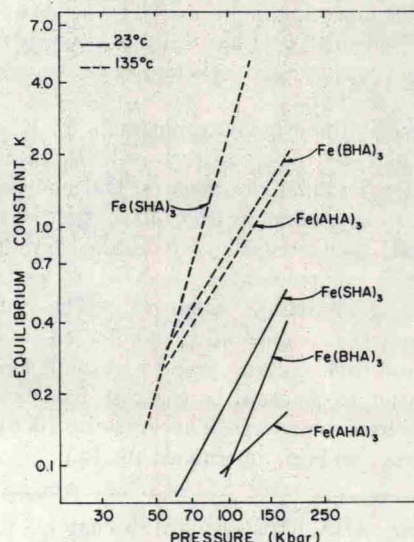
Fig. 1. Optical absorption spectra vs. pressure for $Fe(AHA)_3$.

Fig. 2. (a) Mössbauer spectra of $\text{Fe}(\text{SHA})_3$.

The Mössbauer spectra of $\text{Fe}(\text{SHA})_3$ at 4 kbar and 23°C , and at 138 kbar and 23, 110, and 135°C are shown in Figs. 2a and b. At low pressure the ferric peaks are asymmetric, indicating the presence of a spin-spin relaxation effect. This is similar to the spin-spin relaxation observed in hemin, which has been treated theoretically by Blume (12). The ratio of peak widths at 4 kbar is about 1.25; by 60 kbar, the ratio has decreased to 1.05. At higher pressures the peaks appeared to be symmetric. At high pressure the ferric iron reduces to ferrous iron; with increasing temperature the conversion increases significantly. The equilibrium constant K , defined as $K = C_{\text{II}}/C_{\text{III}}$, where C_{II} and C_{III} are the fraction of ferrous and ferric sites, is shown in Fig. 3 as a function of pressure for $\text{Fe}(\text{SHA})_3$. Fig. 4 shows a comparison of the conversions for the three hydroxamates at 23 and 135°C . Note that for all three compounds there is a marked increase in conversion

Fig. 3. $\text{Ln}K$ vs. $\text{Ln}P$ for $\text{Fe}(\text{SHA})_3$.Fig. 2. (b) Mössbauer spectra of $\text{Fe}(\text{SHA})_3$ (contd.).

with increased temperature. The isomer shifts and quadrupole splittings of the ferric and ferrous iron in the three compounds are given in Table 1. The Fe(III) in these compounds is in the high-spin configuration, with typical values of about 0.4 mm/sec for isomer shift. The quadrupole splittings, ranging from 0.70 to 0.94 mm/sec at 4 kbar, are somewhat high for high-spin Fe(III) in octahedral symmetry, but reflect the inequivalence of the oxygen atoms coordinating to the iron, since each hydroxamic acid group contributes one negative oxygen ion and one covalent oxygen atom to the octahedral coordination sphere. The Fe(III) isomer shift decreases by about 0.035 mm/sec in 175 kbar in $\text{Fe}(\text{AHA})_3$ and $\text{Fe}(\text{SHA})_3$, but in $\text{Fe}(\text{BHA})_3$ the isomer shift first increases by about 0.05 mm/sec in the first 25 kbar, and then decreases by about 0.03 mm/sec in the next 150 kbar. It should be noted, as

Fig. 4. $\text{Ln}K$ vs. $\text{Ln}P$ for ferric hydroxamates.