MASTER

C00-1198-777

RECEIVED BY DTIC JAN 21 1971

THE EFFECT OF PRESSURE ON THE ELECTRONIC STRUCTURE
OF FERRIC HYDROXAMATES AND FERRICHRONE A *

by

D. C. Grenoble and H. G. Drickamer

School of Chemical Sciences and Materials Research Laboratory

University of Illinois, Urbana, Illinois 61801

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

* This work was supported in part by the United States Atomic Energy Commission under Contract AT(1198).

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

ABSTRACT

The effect of pressure on the electronic structure of three ferric hydroxamates and on ferrichrome A has been studied to 175 kilobars, using optical absorption and Mössbauer resonance. The ferric ion reduced to ferrous ion with pressure as has been previously observed for a variety of 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 the theory previously presented. 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 a variety of chemical groups. The 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 as a function of pressure. 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/}

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

The optical absorption of $\text{Fe}(\text{AHA})_3$ in the visible region is shown in Figure 1 as a function of pressure. The optical transition is a ligand to metal charge transfer. The initial charge transfer energy in $\text{Fe}(\text{AHA})_3$ is at 23.25 kK. 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 $\text{Fe}(\text{BHA})_3$ and $\text{Fe}(\text{SHA})_3$ are similar to $\text{Fe}(\text{AHA})_3$, although the initial energies of the charge transfer bands are different. At one atmosphere the peak maxima for $\text{Fe}(\text{AHA})_3$, $\text{Fe}(\text{BHA})_3$, and $\text{Fe}(\text{SHA})_3$ 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 $\text{Fe}(\text{AHA})_3$, $\text{Fe}(\text{BHA})_3$, and $\text{Fe}(\text{SHA})_3$ are 1.19, 1.25,

and 1.25 kK respectively, also the changes in optical spectra with pressure for these three compounds are very similar.

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 Figures 2a and 2b. 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, and by 60 kbar the ratio has decreased to 1.05. At higher pressures the peaks appeared to be symmetric. It is seen that at high pressure the ferric iron reduces to ferrous iron, and 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, as a function of pressure, is shown in Figure 3 for $\text{Fe}(\text{SHA})_3$. Figure 4 shows a comparison of the conversions for the three hydroxamates at 23°C and 135°C . Note that for all three compounds there is a marked increase in conversion with increased temperature. The isomer shifts and quadrupole splittings of the ferric and ferrous iron in the three compounds are given in Table I. The $\text{Fe}(\text{III})$ 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 $\text{Fe}(\text{III})$ 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 Fe(AHA)_3 and Fe(SHA)_3 in 175 kbar, but in Fe(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 discussed below, that Fe(BHA)_3 showed markedly more asymmetric peaks than the other two model compounds, indicating some difference in its structure, which might account for the unusual behavior of its isomer shift. However, the fitting of such asymmetric peaks is difficult, and one cannot eliminate the possibility that the peculiar behavior in the low pressure region is in part an artifact of the fitting. The Fe(III) quadrupole splittings all increased by about 0.6 mm/sec in 175 kbar. The Fe(II) isomer shift of about 1.35 mm/sec and the large quadrupole splitting of about 2.20 mm/sec clearly indicates that the Fe(II) produced at high pressure is high spin.

As discussed above, Fe(SHA)_3 showed asymmetric peaks at low pressures, and with increasing pressure the asymmetry decreased. Fe(BHA)_3 showed even greater relaxation effects, and its ratio of peak widths was about 1.56 at 4 kbar, as compared to 1.25 for Fe(SHA)_3 . With increasing pressure, the relaxation effect in Fe(BHA)_3 also decreased, and by 70 kbar the ratio was down to 1.09. By 90 kbar the ratio appeared to be equal to one. Fe(AHA)_3 , in contrast to the other two compounds, showed only a small relaxation effect, so the peaks were fit as symmetric at all pressures. This relaxation effect was also observed in some ferric hydroxamates studied by Epstein et al.^{13/} They found that Fe(AHA)_3 and Fe(SHA)_3 showed

modest relaxation effects, while $\text{Fe}(\text{BHA})_3$ exhibited a much larger effect. The asymmetry is associated with the relative population of ground and excited nuclear states. As the distance between iron sites decreases with increasing pressure one would expect both an increase in splitting of the levels and a decrease in relaxation time. Both these factors would serve to decrease the asymmetry.

Ferrichrome A (FA) was also studied as a function of pressure both optically and with Mössbauer resonance. The optical visible spectrum is very much like the model compounds described above. The charge transfer peak is at 22.22 kK, and at 50% of maximum absorption the energy is 18.9 kK. The shift of the charge transfer peak at 50% of maximum absorption is 1.5 kK to lower energy, some 0.25 kK larger than the shifts in the model compounds.

The Mössbauer spectra of FA at 4 kbar and 138 kbar is shown in Figure 5. Note that the lower pressure spectrum is broadened considerably more than the model compound $\text{Fe}(\text{SHA})_3$ shown in Figure 2. In FA this broadening has been attributed by Wickman *et al.*^{14/} to the presence of a magnetic hyperfine structure. At room temperature the hyperfine interaction is produced by a field having a shorter relaxation time than at low temperatures, and the hyperfine interaction dissolves into the broad line shown. For comparison to the model compounds, the spectra were fit as a quadrupole split pair at low pressure. At high pressure FA also reduced, but in greater yields than in the model compounds as shown in Figure 6, where the conversion of FA at 23°C is compared to that of $\text{Fe}(\text{SHA})_3$.

FA was not run at higher temperatures because of the possibility of decomposition. The Fe(II) produced is also high spin, with an isomer shift of about 1.2 mm/sec. The isomer shift and quadrupole splitting of both Fe(III) and Fe(II) in FA are given in Table I, and the parameters A and B are given in Table II for all the ferric hydroxamates. One should consider the values of the parameters for FA as somewhat qualitative since the spectra were broadened by the hyperfine interaction.

The reduction of ferric iron to ferrous iron requires a transfer of an electron from the ligands to the metal. As previously mentioned, the charge transfer energies for Fe(AHA)₃, Fe(BHA)₃, and Fe(SHA)₃ are 23.25, 22.22, and 21.95 kK respectively. Referring back to Figure 4 it can be seen that this is also the order of increasing conversion, so there is a definite correlation between the energy of the charge transfer band and the amount of conversion observed in a series of closely similar compounds. This is entirely consistent with the theory presented previously.^{15,16/} There it was indicated that the reduction occurred because the excited state (the Fe(II) plus ligands with a hole) decreases in energy with respect to the ground state (Fe(III) ion plus normal ligands) with increasing pressure, until a thermal transfer of an electron becomes possible. As is shown in Figure 7, because of the Franck-Condon principle, the optical transfer of an electron occurs vertically on a configuration coordinate diagram, in contrast to the thermal process. Nevertheless, the correlation between optical and thermal processes might be expected as

long as the shapes of the potential wells are very similar from compound to compound. It is important that the compounds are similar since the ferrichrome A, with its charge transfer energy at 22.22 kK, is similar in the sense of being oxygen coordinated, but the structure is sufficiently different so that the potential well is modified and the conversion is not quantitatively consistent with those of the hydroxamates.

ACKNOWLEDGEMENTS

We are very grateful to J. B. Neilands for furnishing us with ferrichrome A and to L. P. Hager for helpful advice.

Table I
Mössbauer Parameters for Ferric Hydroxamates

Isomer Shift (mm/sec)*									
Pressure (kbar)	4	25	50	75	100	125	150	175	
Fe(SHA)₃									
Fe(III)	0.440	0.450	0.445	0.430	0.427	0.420	0.413	0.406	(23°C)
Fe(II)	-	-	-	1.36	1.35	1.34	1.33	1.32	
Fe(AHA)₃									
Fe(III)	0.415	0.414	0.414	0.411	0.410	0.403	0.393	0.381	(23°C)
Fe(II)	-	-	-	1.39	1.38	1.37	1.36	1.35	
Fe(BHA)₃									
Fe(III)	0.370	0.426	0.431	0.426	0.422	0.415	0.408	0.401	(23°C)
Fe(II)	-	-	-	-	1.35	1.31	1.27	1.23	
Ferrichrome A									
Fe(III)	0.195	0.265	0.390	0.410	0.394	0.370	0.350	0.335	(23°C)
Fe(II)	-	-	1.202	1.200	1.200	1.198	1.195	1.194	

Table I. (continued)

Quadrupole Splitting (mm/sec)

Pressure (kbar)	4	25	50	75	100	125	150	175	
Fe(SHA)₃									
Fe(III)	0.94	1.11	1.23	1.31	1.36	1.40	1.43	1.45	(23°C)
Fe(II)	-	-	-	2.29	2.20	2.17	2.15	2.14	
Fe(III)	-	-	1.26	1.30	1.42	1.47	1.51	1.53	(110°C)
Fe(II)	-	-	-	2.05	2.02	2.03	2.05	2.06	
Fe(III)	-	-	1.32	1.41	1.46	1.50	1.51	1.53	(135°C)
Fe(II)	-	-	2.08	2.04	2.06	2.09	2.12	2.14	
Fe(AHA)₃									
Fe(III)	0.70	0.99	1.13	1.21	1.25	1.28	1.30	1.33	(23°C)
Fe(II)	-	-	-	2.32	2.31	2.30	2.28	2.27	
Fe(III)	-	-	1.19	1.32	1.41	1.48	1.51	1.55	(135°C)
Fe(II)	-	-	-	1.97	1.98	2.00	2.01	2.03	

Table I (continued)

Quadrupole Splitting (mm/sec)

Pressure (kbar)	4	25	50	75	100	125	150	175	
Fe(BHA)₃									
Fe(III)	0.70	0.91	1.06	1.17	1.25	1.32	1.36	1.39	(23°C)
Fe(II)	-	-	-	-	2.31	2.25	2.19	2.14	
Fe(III)	-	1.06	1.18	1.27	1.36	1.42	1.47	1.48	(105°C)
Fe(II)	-	-	-	-	1.99	1.98	1.97	1.97	
Fe(III)	-	-	1.06	1.17	1.25	1.32	1.36	1.39	(135°C)
Fe(II)	-	-	1.86	1.86	1.85	1.85	1.84	1.84	
Ferrichrome A									
Fe(III)	0.37	0.59	1.01	1.20	1.32	1.39	1.46	1.50	(23°C)
Fe(II)	-	-	2.49	2.44	2.42	2.40	2.40	2.39	

*Relative to Iron Metal

Table II

Parameters A and B for $K = AP^B$

Compound	T(°C)	A	B	Pressure Range (kbar)
Fe(SHA) ₃	23	3.66×10^{-5}	1.86	60 - 170
	110	6.64×10^{-7}	3.03	50 - 150
	135	1.45×10^{-7}	3.62	40 - 110
Fe(BHA) ₃	23	8.08×10^{-7}	2.54	100 - 175
	105	2.35×10^{-5}	2.03	90 - 175
	135	3.96×10^{-4}	1.66	60 - 175
Fe(AHA) ₃	23	1.30×10^{-3}	0.94	100 - 175
	135	4.19×10^{-4}	1.60	55 - 175
Ferrichrome A	23	3.12×10^{-4}	1.67	40 - 175

REFERENCES

1. Nielsands, J. B., Structure and Bonding 1, 59 (1966).
2. Nielsands, J. B., Bact. Rev. 21, 101 (1957).
3. Emery, T. E., and J. B. Nielsands, J. A. C. S. 82, 3658 (1960).
4. Garibaldi, J. A. and J. B. Nielsands, J. A. C. S. 77, 2429 (1959).
5. Linder, H. J. and S. Göttlicher, Acta Cryst. B25, 832 (1969).
6. Zalkin, A., J. D. Forrester and D. H. Templeton, Science 146, 261 (1964).
7. Weinland, R. F. and G. Baier, Ber. 53B, 685 (1920).
8. Hantzsch, A., and C. H. Desch, Liebigs Ann. Chemie 323, 1 (1902).
9. Fitch, R. A., T. E. Slykhouse and H. G. Drickamer, J. Opt. Soc. Ann. 47, 1015 (1957).
10. Drickamer, H. G. and A. S. Balchou in "Modern Very High Pressure Techniques" R. Wentorf ed. Butterworths, London (1962).
11. Debrunner, P., R. W. Vaughan, A. R. Champion, J. Cohen, J. Moyzis and H. G. Drickamer, Rev. Sci. Inst. 37, 1310 (1966).
12. Blume, M., Phys. Rev. Letters 18, 305 (1967).
13. Epstein, L. M. and D. K. Straub, Inorg. Chem. 8, 453 (1969).
14. Wickman, H. H., M. P. Klein and D. A. Shirley, Phys. Rev. 152, 345 (1966).
15. Drickamer, H. G., G. K. Lewis and S. C. Furry, Science, 163, 885 (1969).
16. Drickamer, H. G., V. C. Bastron, D. C. Fisher and D. C. Grenoble, J. Sol. St. Chemistry, 2, 94 (1970).

LIST OF FIGURES

- Fig. 1 Optical Absorption Spectra vs. Pressure - Fe(AHA)_3 .
- Fig. 2a Mössbauer Spectra of Fe(SHA)_3 .
- Fig. 2b Mössbauer Spectra of Fe(SHA)_3 (contd.).
- Fig. 3 LnK vs. LmP - Fe(SHA)_3 .
- Fig. 4 LnK vs. LmP - Ferric Hydroxamates.
- Fig. 5 Mössbauer Spectra of Ferrichrome A.
- Fig. 6 LnK vs. LnP - Ferrichrome A.
- Fig. 7 Schematic Configuration Coordinate Diagram.

FIG.2a TRIS (SALICYLHYDROXAMATO) IRON (III)

FIG. 25 TRIS (SALICYLHYDROXAMATO) IRON (III) (CONT'D)

FIG. 3

FIG. 4

FIG. 5 FERRICHROME A

FIG. 7 SCHEMATIC CONFIGURATION
COORDINATE DIAGRAM.