

Fig. 6. $\ln K$ vs. $\ln P$ —Hemin

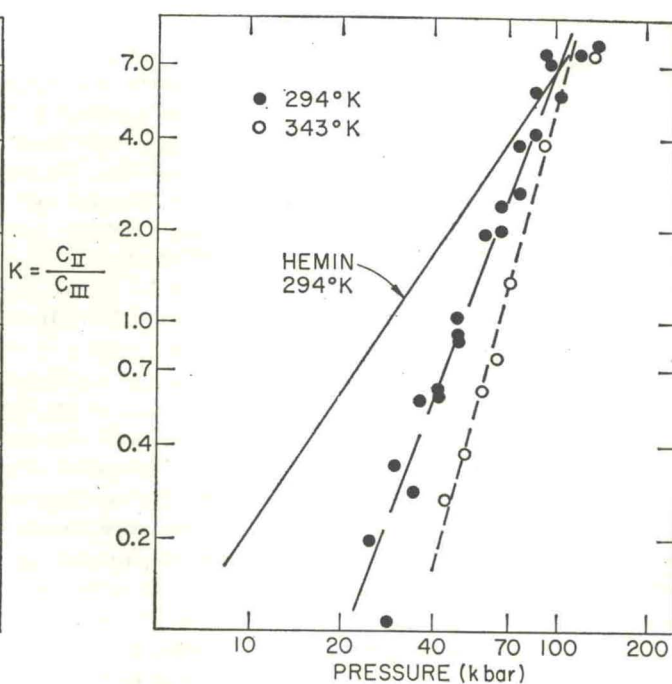


Fig. 7. $\ln K$ vs. $\ln P$ —Hematin

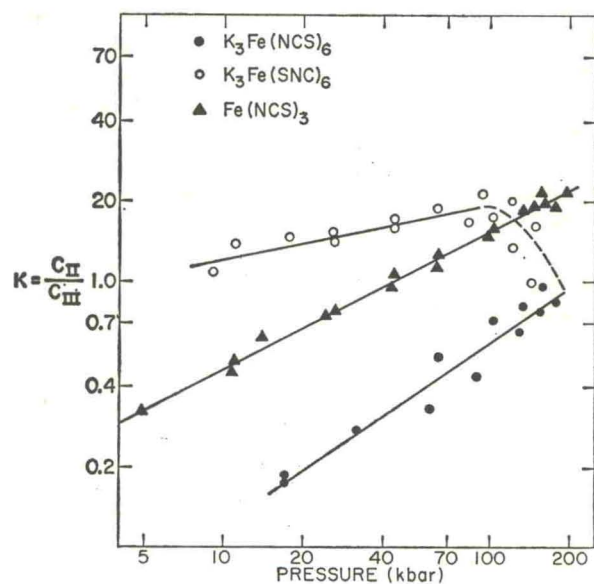


Fig. 8 (above left). $\ln K$ vs. $\ln P$ —Thiocyanate and isothiocyanate.

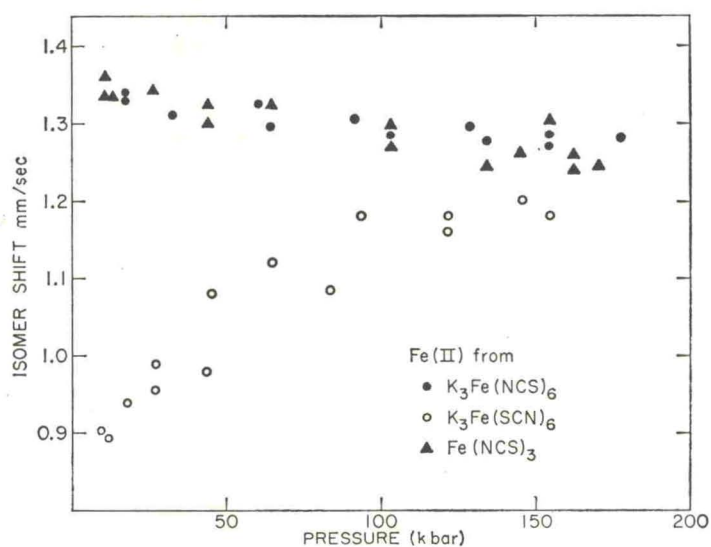


Fig. 9 (above right). Isomer shift vs. pressure—Thiocyanate and isothiocyanate.

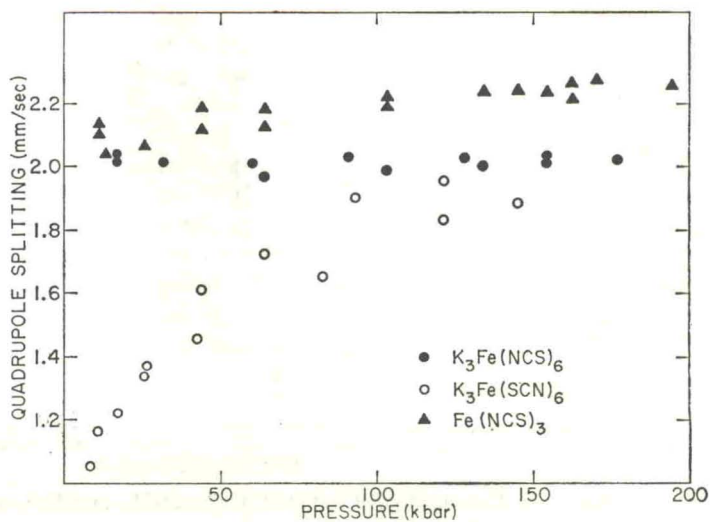


Fig. 10 (bottom right). Quadrupole splitting vs. pressure—Thiocyanate and isothiocyanate.

analysis for $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$. The hydrated ferric fluoride soaked in water just before loading gave the same value of B but higher conversions, very close to those for $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. The substitution of D_2O for H_2O made no difference within our accuracy.

The results for $\text{FeCl}_3 \cdot 6\text{NH}_3$ exhibit a new feature. The data can be fitted with two straight lines with a distinct break near 25 kilobars. Orgel (15) has pointed out that in $\text{Co}(\text{NH}_3)_6\text{I}_2$ the optical charge transfer observed is probably from I^- to $\text{Co}(\text{NH}_3)_6^{2+}$. It is possible that for the thermal transfer observed here, in one region the NH_3 to $\text{Fe}(\text{III})$ electron transfer dominates, and in another the Cl^- transfer to the iron-ammonia complex controls.

Hemin and hematin are both prototype molecules for hemoglobin. In both molecules ferric iron is at the center of four pyrrole rings held together by CH_2 groups. Various organic groups attach to the outside of the rings. In the first approximation, iron is in a site of square planar symmetry. In hemin a Cl^- is attached to the ring with the bond perpendicular to the ring. This pulls the iron 0.47 angstrom out of the plane of the organic skeleton. In hematin an OH^- replaces the Cl^- . As can be seen from Fig. 6, hemin reduces with increasing pressure (5) with a rather large value of B . The most surprising feature is the fact that the reaction is exothermic, with a ΔH which decreases rapidly with increasing pressure. Evidently thermal deformation of the potential wells is large and overcomes the effect of thermal promotion of the electron transfer. This deformation is rapidly reduced by increasing pressure. Hematin (Fig. 7) also reduces with increasing pressure in a manner qualitatively similar to hemin. However, the amount of reduction at a given pressure is distinctly less for hematin than for hemin, which indicates that the external ion (Cl^- or OH^-) plays a significant role in the electron transfer process.

Transition metal complexes with the $(\text{SCN})^-$ ion are of considerable interest especially because of the fact that they can attach to the metal either through the sulfur (thiocyanate) or through the nitrogen (isothiocyanate). Generally the first row transition metals

form isothiocyanates, while the heavier metals tend to form thiocyanates. The type of bonding is established from small differences in the infrared spectrum. Burmeister and Basolo (16) have shown that one can obtain thiocyanate-isothiocyanate isomerization in the solid state.

$\text{Fe}(\text{NCS})_3 \cdot 6\text{H}_2\text{O}$ has the isothiocyanate structure. It reduces with increasing pressure (6) in a manner much like a number of rather ionic complexes (see Fig. 8 and Table 1). The ferrous ion formed has as isomer shift (about 1.35 mm/sec) and quadrupole splitting (about 2.1 mm/sec) within the usual range for high spin "ionic" ferrous compounds (see Figs. 9 and 10). The reduction process is reversible, as it is for all the materials discussed above.

On the other hand, the $\text{K}_3\text{Fe}(\text{SCN})_6$ appears to have the thiocyanate arrangement. The isomer shift is within the usual ferric range, but the Mössbauer spectrum is highly asymmetric. The reduction at low pressure is considerably larger than for the $\text{Fe}(\text{NCS})_3 \cdot 6\text{H}_2\text{O}$. The $\text{Fe}(\text{II})$ formed has more nearly the isomer shift and quadrupole splitting characteristic of FeS and FeSe than of typical ionic materials. The amount of $\text{Fe}(\text{II})$ increases slowly with pressure up to about 100 kilobars, then drops off (open circles in Fig. 8). With increasing pressure the isomer shift and quadrupole splitting of the $\text{Fe}(\text{II})$ increase rapidly and approach usual high spin ferrous values (Figs. 9 and 10). Upon release of pressure the $\text{Fe}(\text{II})$ spectrum disappears and one obtains a symmetric $\text{Fe}(\text{III})$ spectrum. If a sample which has been taken to high pressure is reloaded in the cell and subjected to pressure, it shows a symmetric ferric spectrum; and as pressure is increased, a characteristic high spin ferrous spectrum appears. The conversion increases with pressure in a manner very much like other ionic materials (solid circles in Fig. 8). As seen in Figs. 9 and 10, the isomer shift and quadrupole splitting are very similar to the values obtained for $\text{Fe}(\text{NCS})_3 \cdot 6\text{H}_2\text{O}$. The converted material appears to have an isothiocyanate infrared spectrum.

It seems clear that isomerization as well as reduction takes place with in-

creasing pressure, and that the reduction is reversible, but the isomerization is not. There is no tendency for the $\text{Fe}(\text{II})$ peaks to broaden or split as the pressure increases and the isomerization takes place. Apparently, at any one pressure there is essentially only one entity present; i.e. each ion has the same distribution of $(-\text{NCS})^-$ and $(-\text{SCN})^-$ neighbors. The difference in Mössbauer spectrum between ferric thiocyanate and isothiocyanate is sufficiently small that it is difficult to determine to what extent isomerization precedes or follows reduction.

VI. Summary

Ferric ion reduces to the ferrous state with increasing pressure in a reversible manner, with a wide variety of ligands. The phenomenon can be described in terms of changes in the electronic energy levels of the ferric ion vis à vis the ligands, and of strain-induced deformation of the potential wells of the ground and excited electronic states. For one system, pressure-induced isomerization is observed. An understanding of the high pressure chemistry of iron could be significant in biology and geophysics as well as in chemistry and physics.

References and Notes

1. A. R. Champion, R. W. Vaughan, H. G. Drickamer, *J. Chem. Phys.* **47**, 2583 (1967).
2. A. R. Champion and H. G. Drickamer, *ibid.*, p. 2591.
3. G. K. Lewis, Jr., and H. G. Drickamer, *Proc. Nat. Acad. Sci. U.S.* **61**, 414 (1968).
4. S. C. Fung, G. K. Lewis, Jr., H. G. Drickamer, *ibid.*, p. 812.
5. D. C. Grenoble and H. G. Drickamer, *ibid.*, in press.
6. S. C. Fung and H. G. Drickamer, *ibid.*, in press.
7. W. Holzapfel and H. G. Drickamer, *J. Chem. Phys.*, in press.
8. H. Frauenfelder, *The Mössbauer Effect* (Benjamin, New York, 1963).
9. G. K. Wertheim, *Mössbauer Effect; Principles and Applications* (Academic Press, New York, 1964).
10. R. W. Vaughan, private communication (1968).
11. W. M. Riggs and C. E. Bricker, *Anal. Chem.* **38**, 897 (1966).
12. N. Saito, H. Sano, T. Tominaga, F. Ambe, *Bull. Phys. Soc. Japan* **38**, 681 (1965).
13. P. K. Gallagher and C. R. Kurkjian, *Inorg. Chem.* **5**, 214 (1966).
14. M. Lind, *J. Chem. Phys.* **47**, 990 (1967).
15. L. E. Orgel, *Quarterly Reviews* **9**, 422 (1954).
16. J. L. Burmeister and F. Basolo, *Inorg. Chem.* **3**, 1587 (1964).
17. The authors wish to acknowledge very helpful conversations and collaboration with R. W. Vaughan, C. P. Slichter, and R. A. Marcus. The research has been supported by the United States Atomic Energy Commission.