

# The determination of ferrous and ferric iron in rocks and minerals—a comment

R. D. GILLARD

Department of Chemistry, University College, PO Box 78, Cardiff CF1 1XL, Wales, UK

**ABSTRACT.** Hey's observation of reduction of ferric ion bound to 1,10-phenanthroline in water is explained in terms of the analogy between quaternization of the ligand and its coordination by iron(III).

**KEYWORDS:** ferrous, ferric, iron.

IN his addendum (Hey, 1982*b*) to his useful paper (Hey, 1982*a*) on the determination of ferric and ferrous iron in rocks and minerals, Hey commented in detail on the rate of breakdown of 'ferric o-phenanthroline' solution as a source of some error in the measured  $\text{Fe}^{3+} : \text{Fe}^{2+}$  ratio.

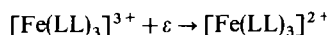
The initially yellow solution (obtained at pH around 5) from ferric iron and an excess of phenanthroline (here phen) soon became orange (that is, the optical density at 508 nm increased, indicating the formation of ferrous complex).

As Hey said, 'since the reaction involves reduction of ferric, something must be oxidised', although he then concluded that 'It seems probable that the ferric complex is capable of oxidising impurities in the solution.'

The purpose of my present note is to point out that this oxidizing property of 1,10-phenanthroline complexes of ferric iron in water is quite well known and that, even in the absence of oxidizable impurities, Hey's caveat applies: there is still an apparently spontaneous transformation of ferric to ferrous iron! The behaviour of such 1,10-phenanthroline

complexes of iron in aqueous media is surprisingly varied and fairly well studied.

For the tris-complexes such as  $[\text{Fe}(\text{phen})_3]^{3+}$ , ferriin (either pre-formed as its solid salts, or by oxidation of the tris-complex, ferriin, of iron(II)), it is a well-known anomaly (Dwyer and Gyrfas, 1952; Gillard and Williams, 1977) that the formal oxidation potentials for the half-cells



where LL = 2,2'-bipyridyl, 1,10-phenanthroline or their derivatives, vary strongly with the activity of the proton,  $\text{H}^+$ , although the half cell, *as written*, is independent of  $[\text{H}^+]$  and/or  $[\text{OH}^-]$ .

Essentially (and this has been known for many years) there is a special instability of the ferric-dimine system toward reduction in alkaline solutions. The ferric systems oxidize *water* and/or *hydroxide* ions, becoming ferrous. (Serpone *et al.*, 1983). It also seems (Nord *et al.*, 1983) that some of the phenanthroline or bipyridyl ligand becomes oxidized, to the N-oxide.

The view taken here (Gillard and Williams, 1978) of that special interaction of this type of ferric complex with hydroxide is that it is akin to the pseudo-base formation of quaternized N-heterocycles (see fig. 1). That is, the hydroxide ion adds to the coordinated phenanthroline, giving a dihydro-1,10-phenanthroline, which leads readily to intra-

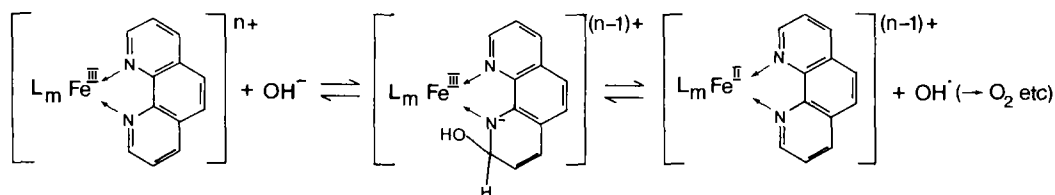
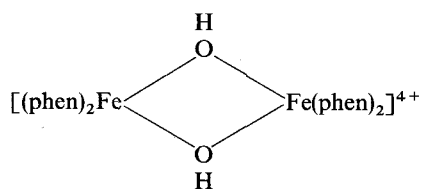


FIG. 1. The proposed mechanism of reduction of ferric ion complexed by phenanthroline to the corresponding ferrous ion. Here, L indicates other ligands attached to the iron ions, to make up their coordination numbers of six. Typically, for ferriin reducing to ferriin,  $L_m$  would mean 2 phenanthrolines. The overall charge of the ion is shown by  $n$  ( $n = 3$  for ferriin, 2 for ferriin).

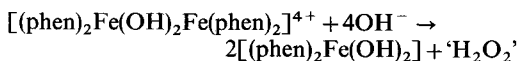
molecular reduction by hydroxide of iron(III). Exactly this intermediate is supported (Schmid and Han, 1983) in a study of the reduction of  $\text{Fe}(\text{phen})_3^{3+}$  by aqueous  $\text{Fe}^{2+}$ . The solvent influence on the redox properties of tris(5-nitro-1,10-phenanthroline)iron(II/III) was said (Mayer *et al.*, 1979) to arise from nucleophilic attack of solvent molecules *at the iron*. However, nucleophilic solvents were very recently shown (Bartolotta *et al.*, 1984) to add to the ligand in a fashion like that suggested here *for exactly such ions*,  $[\text{M}(\text{SNO}_2\text{phen})_3]^{n+}$ .

The case discussed by Hey (1982*b*) is a little more complicated, since, under his conditions, the tris-complex, ferriin, does not form. Instead, the yellow bridged dimeric species is dominant. It is the



reaction of this with hydroxide/water that Hey followed, in his fig. 5 (1982*a*) and discussed in the addendum (1982*b*).

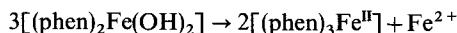
So we might expect to see



but even this is not the end of the road, because (Gillard, 1979), in water, the stepwise stability constants for the ferrous phenanthroline complexes manifest the unusual property

$$(K_3)^2 > K_1K_2.$$

That is to say, any high spin bis-complex of ferrous iron with phenanthroline will dismute to the low spin tris-complex. So, the equation



holds: the absorbing end-product of this is the orange tris-species ferriin (508 nm). In the presence of an excess of 1,10-phenanthroline, of course, all the ferrous iron formed by reduction of the ferric species will form this complex.

So, combining the three known properties of these systems:

(i)  $\text{Fe}^{3+}/\text{phen}$  is increasingly oxidizing as the pH increases, whether we speak of the yellow bis-phenanthroline dimer or the green-blue tris-phenanthroline monomer.

(ii) The yellow ferric dimer (in company with

many other phenanthroline complexes of trivalent metal ions) oxidizes hydroxide/water.

(iii) The bis-phenanthroline iron(II) species dismutates very rapidly in water to orange tris-phenanthroline iron(II) and aquo iron(II) which latter combines with the excess of o-phenanthroline to give more  $[\text{Fe}(\text{phen})_3]^{2+}$ . The net effect is that *all* the initial iron ions, whether ferrous or ferric, will eventually form ferriin.  $\text{Fe}^{2+}$  forms it rapidly,  $\text{Fe}^{3+}$  rather slowly, so an extrapolation of absorbance at 508 nm to zero time may be useful in the analytical determination.

The complicated nature of the equilibria and reactions in these bipyridyl and phenanthroline complexes of the two oxidation states of iron means that it is hard to fit rate curves quantitatively, but qualitatively we can account for the apparent increase (Hey, 1982*b*) in the ferrous concentration at the expense of ferric, in the medium range of pH, in the presence of these chelating di-imine ligands. The remarkable *decrease* [*sic*] with increasing temperature in reactivity of the ferriin recorded in the literature (Mason *et al.*, 1973) is not relevant: the observation is incorrect.

It is interesting that exactly the same problem addressed by Hey of possible change of oxidation state of an iron ion on removal from its original environment to the analytical solution vitiated some early results on metallo-enzymic and metallo-protein systems.

## REFERENCES

- Bartolotta, A., Cusumano, M., DiMarco, G., Giannetto, A., and Guglielmo, G. (1984) *Polyhedron*, **3**, 701.  
 Dwyer, F. P., and Gyrfas, E. C. (1952) *J. Am. Chem. Soc.* **74**, 4699.  
 Gillard, R. D. (1979) *Inorg. Chim. Acta* **37**, 103.  
 — and Williams, P. A. (1977) *Transition Metal Chem.* **2**, 109.  
 — (1978) *Clays Clay Minerals*, **26**, 178.  
 Hey, M. H. (1982*a*) *Mineral. Mag.* **46**, 111.  
 — (1982*b*) *Ibid.* **46**, 512.  
 Mason, S. F., Peart, B. J., and Waddell, R. E. (1973) *J. Chem. Soc. Dalton*, 943.  
 Mayer, U., Kotocova, A., and Gutmann, V. (1979) *J. Electroanal. Chem.* **103**, 409.  
 Nord, G., Pedersen, B., and Bjergbakke, E. (1983) *J. Am. Chem. Soc.* **105**, 1913.  
 Schmid, R., and Han, L. (1983) *Inorg. Chim. Acta*, **69**, 127.  
 Serpone, N., Ponterini, G., Jamieson, M. A., Bolletta, F., and Maestri, M. (1983) *Coordination Chem. Rev.* **50**, 209 (and especially pp. 275 ff.).

[Manuscript received 20 June 1984;  
 revised 28 September 1984]