Autoxidation of Iron(II) Di-imine Complexes

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Summary Tris(biacetylbismethylimine)iron(II), in acid aqueous media, undergoes a free-radical chain autoxidation process, promoted by iron(III) and inhibited by iron(II), in which ligands are oxidized without breaking the metal–ligand bond or oxidation of the iron(II).

THERE are several recent reports on the activation of saturated amines towards oxidation by molecular oxygen, on co-ordination to Ru[1] and Fe.[2] In all those cases, the oxidized forms are stronger ligands (CN^- or di-imines) than the original amine ligand, which might provide the driving force for those unusual reactions. We now report a novel kind of ligand activation, in which aliphatic di-imines co-ordinated to Fe^{II} are oxidized by molecular oxygen in strongly acid media, without an apparent change of the basic ligand function.

It has been observed[3] that tris(biacetylbismethylimine)-iron(II), in acid aqueous media, undergoes a slow and irreversible change of the absorption spectrum. This change is now shown to be caused by an attack on the co-ordinated ligands by molecular oxygen.

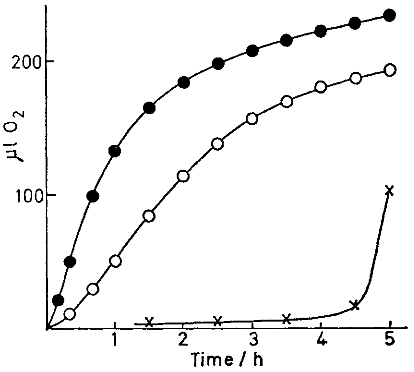

FIGURE. *Absorption of* O_2 *from air by* 3 ml *of a* 10^{-3}M *solution of tris(biacetylbismethylimine)iron*(II) *in* 0·5M-H_2SO_4 *at* 45°. ○, *without addition;* ×, 10^{-4}M-Fe^{II}; ●, 10^{-4}MFe^{III}.

Solutions of the complex in 0·5 M-aqueous H_2SO_4 absorb, from air, in 10 h at 45° *ca.* four moles of oxygen. The reaction profile (see Figure) displays an induction period characteristic of free-radical chain processes. Formation of free radicals was confirmed by the polymerisation of acrylonitrile added to the reaction mixture. The rate of oxygen absorption is roughly proportional to the concentration of the complex and decreases with decreasing acidity. The reaction is initially strongly inhibited by Fe^{II} ions and promoted by Fe^{III} ions, at a concentration of 10^{-4}M (see Figure).

Analysis of the spectral changes during the course of the oxidation process reveals successive formation (and slow decomposition) of several complex species. In their shape and intensity, the spectra of the oxidized species are characteristic of complexes containing the iron(II)–di-imine chromophore.[4]

The oxidized complexes have been isolated as tarry polyiodides in 75% yield. Analysis reveals that the original Fe:N ratio of 1:6 is maintained in the oxidized forms.

Under the above conditions, tris(glyoxalbismethylimine) iron(II) is not attacked by molecular oxygen. The corresponding cyclohexane-1,2-dionebismethylimine complex, on the other hand, absorbs oxygen at a faster rate than the biacetylbismethylimine complex. It is concluded that oxidation occurs at the methyl (or methylene) groups attached to the carbon atoms of the di-imine skeleton.

This work was supported by the Fundação de Amparo a Pesquisa do Estado de São Paulo.

(*Received*, 1*st May* 1972; *Com.* 741.)

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