Intramolecular Ligand-to-co-ordinated Dioxygen Proton Transfer in the Four-electron Reduction of Dioxygen by Tris(2,2′-bi-2-imidazoline)iron(II)

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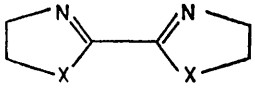
Summary The high-spin complex $[Fe^{II}$ (2,2′-bi-2-imidazoline)$_3]^{2+}$ reacts with dioxygen in aprotic media to form water and an iron(III) complex in which one ligand molecule is mono-deprotonated; a mechanism involving proton transfer from the ligand to the partially reduced co-ordinated dioxygen is suggested.

THERE has been considerable speculation concerning the role of the distal histidine in the reversible binding of dioxygen by myoglobin and haemoglobin, in particular whether the acidic hydrogen of the imidazole ring is hydrogen bonded to the co-ordinated dioxygen.[1] We here report on a study of the four-electron reduction of dioxygen by $[Fe^{II}(biH)_3][ClO_4]_2$[biH = 2,2′-bi-2-imidazoline (**1**)] in which an acidic hydrogen of the imidazoline ligand is clearly involved in the redox process.



(**1**) X = NH
(**2**) X = O
(**3**) X = S

$[Fe^{II}(biH)_3][ClO_4]_2$ (**4**) $[Fe^{III}(biH)_2(bi)][ClO_4]_2$ (**5**)

The red complex $[Fe^{II}(biH)_3][ClO_4]_2$ (**4**) reacts with O_2 in solution (EtOH, MeCN, acetone) to form the green complex $[Fe^{III}(biH)_2(bi)][ClO_4]_2$ (**5**), where bi is the uni-negative anion derived from biH by loss of a proton. High-spin† ($S = 2$, $S = \frac{5}{2}$, respectively) six-co-ordinate structures for (**4**) and (**5**), in which the bidentate ligands are co-ordinated *via* the α-di-imine group,[2] have been established by elemental analysis, by spectroscopic (i.r., visible, and Mössbauer) and magnetic susceptibility measurements, and by the reversible formation of $[Fe^{III}(biH)_2(bi)]^{2+}$ from $[Fe^{III}(biH)_3]^{3+}$ on treatment with one mole of strong base (NaOMe). The deprotonation is not effected by weaker bases such as pyridine (pK_a 5·23) nor is the iron(II) complex (**4**) deprotonated, even by NaOMe.

In contrast, the closely related complexes $[Fe(bt)_3]^{2+}$ and $[Fe(bo)_3]^{2+}$[bt = 2,2′-bi-2-thiazoline (**3**); bo = 2,2′-bi-2-oxazolidine (**2**)] are very much more stable to O_2, the former (low-spin)[3] apparently reacting not at all under comparable reaction conditions and the latter (high-spin) only very slowly. We therefore attribute the ready aerobic oxidation of (**4**) to the presence of acidic hydrogens in (**1**).

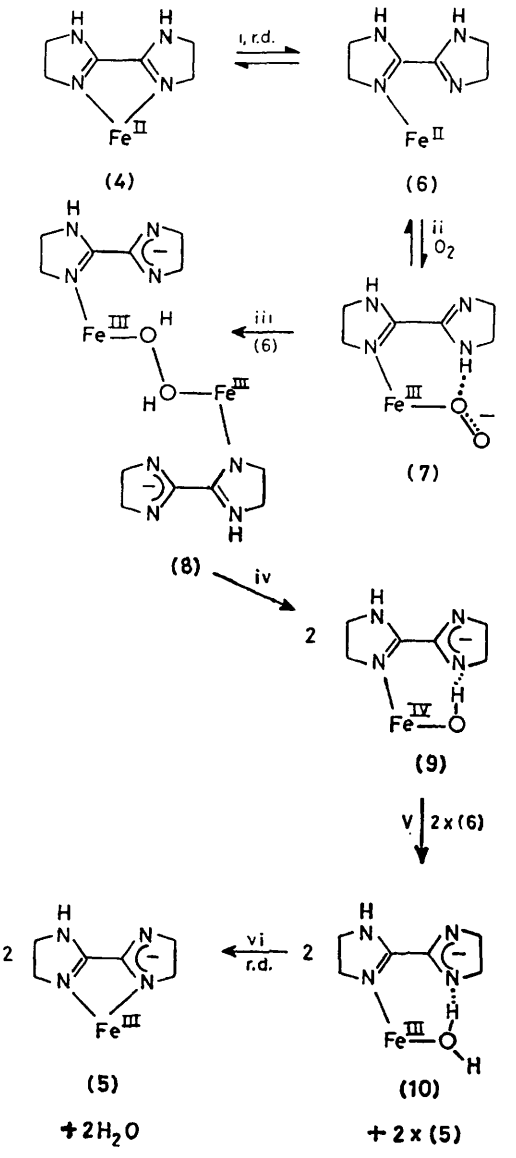
The stoicheiometry of the reaction (1) of (**4**) with O_2 in dry

$$4[Fe^{II}(biH)_3]^{2+} + O_2 = 4[Fe^{III}(biH)_2(bi)]^{2+} + 2H_2O \quad (1)$$

MeCN has been established by measurement of the O_2 consumed (pressure change at constant volume) and of the water produced (g.l.c.) The kinetics of the reaction were monitored spectrophotometrically in MeCN at 30 °C by following the growth of the 14,800 cm^{-1} band of the iron(III) product (**5**). The reaction occurs in two stages, each essentially first order in (**4**) and independent of $[O_2]$ except where $[O_2]$ is low (below *ca.* 0·05 atm.). However, at low concentrations of (**4**) (10^{-4} mol dm^{-3} and below) the final concentration of (**5**) is significantly lower than expected, an observation which suggests the occurrence of a bimolecular step in the reaction sequence. An unusual feature of the results is that while all the O_2 is consumed in the initial (fast) reaction ($t_{1/2}$ *ca.* 6 min) only about half the iron(III) product (**5**) is formed during this stage. It follows that the second reaction ($t_{1/2}$ *ca.* 60 min) involves the (slow) decay of some oxygen-containing intermediate to the remainder of the product (**5**).

The mechanism outlined in the Scheme fits the dissociative kinetics observed during the initial rapid O_2 uptake and the associated formation of half of the iron(III) product (**5**) [steps (i)—(v)], followed by the formation of the remainder of (**5**) *via* the slow step (vi). While we have no direct evidence for the intermediacy of the iron(IV)[4] species (**9**) in the present system, steps (i)—(iii) are supported by the results and are in full accord with accepted theories of iron(II)–O_2 interactions.[4,5]

The question then arises at what point in the sequential reduction of O_2 to H_2O does the proton transfer occur. The observation that $[Fe^{III}(biH)_3]^{3+}$ is deprotonated only by strong base argues strongly against the proton transfer occurring before the two-electron transfer *i.e.* before the irreversible[5] step (iii). This is because $[O_2]^-$ is a weak base (pK_a 4·8)[6] while $[O_2]^{2-}$ is a strong base ($pK_a > 14$).[6] It follows that while the acidic hydrogen of (**1**) appears to promote the oxidation of (**4**) (*cf.* the relative stability of $[Fe^{II}(bo)_3]^{2+}$) it is not the proton transfer itself which is crucial, but rather that the key role of the acidic hydrogen is exercised before the proton transfer, *i.e.* before step (iii).



SCHEME. r.d. = rate determining step. Only one of the three ligands is shown.

The implication is that there is a stabilizing hydrogen bonded interaction in the initially formed Fe^{II}–O_2 adduct (**7**) which increases the binding constant for its formation without which the reaction cannot proceed.

† Complex (**4**) undergoes a sharp $^5T_2 \rightleftharpoons {}^1A_1$ spin transition at *ca.* 125 K in the solid state.

Finally, the slowness of step (vi) requires comment in view of the known lability of high-spin iron(III) complexes.[7] Once again, we suggest a hydrogen bonded stabilization, this time of intermediate (**10**) for which dissociation of the co-ordinated water molecule may require the simultaneous rupture of both the Fe^{III}–O and hydrogen bonds.

(*Received, 25th February* 1980; *Com.* 210.)

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[2] A few complexes of (**1**) have been reported previously by J. C. Wang and J. E. Bauman, *Inorg. Chem.*, 1965, **4**, 1613. These authors appear to favour the view that chelation is *via* the secondary amine groups. Our results, to be published in detail, clearly indicate chelation *via* the α-di-imine group.

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[6] H. A. O. Hill, in 'New Trends in Bioinorganic Chemistry,' eds. R. J. P. Williams and J. R. R. F. Da Silva, Academic Press, London, 1978.

[7] See, for example, J. Burgess, 'Metal Ions in Solution,' Ellis Horwood, Chichester, 1978.