Spectroscopic Evidence for the Formation of Catecholato-Fe^{III} and Semiquinonato-Fe^{II} Pyridine Complexes in the Oxygenation of Catechol by a Pyridineiron(III) Complex

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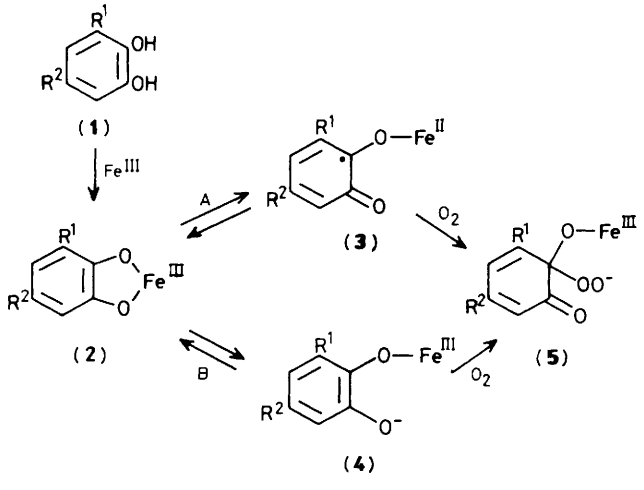
300 MHz ^{1}H N.m.r. and Mössbauer spectra of the solutions prepared by mixing catechol and iron(III) chloride in pyridine indicated clearly the formation of catecholato-Fe^{III} and semiquinonato-Fe^{II} pyridine complexes in equilibrium, suggesting the probability of oxygenation of catechol *via* the latter.

In the oxygenation of catechols by nonhaemiron-enzymes and model iron complexes, the importance of activation of catechol by co-ordination to iron is well recognized, but that of oxygen remains to be demonstrated. In early work on the mechanism it was suggested that an Fe^{II} intermediate which reacts with oxygen is formed in the course of oxygenation by Fe^{III}-containing enzymes,[1] but recent spectroscopic studies have indicated that the Fe^{III} state is retained throughout the oxygenation reaction.[2] However, that no Fe^{II} species were detected is not enough to exclude the possibility of the former mechanism, which is a spin-allowed process. We have reported previously that 3,5-di-t-butylcatechol (**1a**) is oxygenated by (bipyridine)(pyridine)iron(III) or a pyridineiron(III) complex in tetrahydrofuran to give intra- and extra-diol oxygenation products in addition to quinone.[3] An oxygenation mechanism, which involves stepwise oxygen incorporation, has been proposed mainly on the basis of product analysis, kinetics, and $^{18}O_2$ tracer studies, but little information has been obtained on the intermediate complex. We have obtained spectroscopic evidence for the formation of the Fe^{II} and Fe^{III} species suggesting the equilibria A and B in Scheme 1.



a; R^1 = R^2 = Bu^t
b; R^1 = Me, R^2 = H
c; R^1 = R^2 = H

Scheme 1

A pyridine solution of the iron complex of (**1a**) in an argon atmosphere exhibits characteristic bands in visible spectra at 550 nm (ε 1.3 × 10^3) and 975 nm (ε 2.1 × 10^3), which correspond to a 1:1 complex between (**1a**) and iron and disappear in an oxygen atmosphere.[4] A Mössbauer spectrum of this solution in argon exhibited four peaks as shown in Figure 1. Deconvolution of the bands indicated clearly the formation of nearly equimolar amounts of a high-spin Fe^{II} complex (IS = 1.23 mm s^{-1}, ΔE = 3.41 mm s^{-1}) and a high-spin Fe^{III} complex (IS = 0.51 mm s^{-1}, ΔE = 0.89 mm s^{-1}). The former peak disappeared after the addition of oxygen. An e.s.r. spectrum measured at 77 K indicated the formation of a high-spin Fe^{III} complex (g = 3.8, 4.2, 4.6, 8.7). The strong bands in the visible region which may be assigned to the intervalence charge-transfer bands from Fe^{II} to Fe^{III},[5] and the promoted formation of quinone in the solution of higher pyridine concentration[4] support the equilibrium between a catecholato-Fe^{III} and a semiquinonato-Fe^{II} complex, *e.g.* the equilibrium A in Scheme 1.

^{1}H N.m.r. spectra of the complex were measured by using 3-methylcatechol (**1b**) and pyrocatechol (**1c**) in place of (**1a**). The formation of complexes analogous to that of (**1a**) was shown by characteristic visible spectra at 500 nm (ε 1.5 × 10^3) and 880 nm (ε 2.1 × 10^3) with (**1b**), and 480 nm (ε 1.4 × 10^3) and 870 nm (ε 1.9 × 10^3) with (**1c**). As shown in Figure 2, the complex of (**1b**) prepared in [$^2H_5$]pyridine in argon exhibited one broad peak at δ 63 at room temperature. The peak became sharper and shifted to δ 56 at 40 °C, and two peaks were observed at ≤0 °C, *i.e.*, δ 37 and 85 at 0 °C and δ 45 and 93 at −30 °C. Between 0 and 23 °C, peaks were too broad to be discriminated. Chemical shift values of the single peaks at 23 and 40 °C are intermediate between those expected from

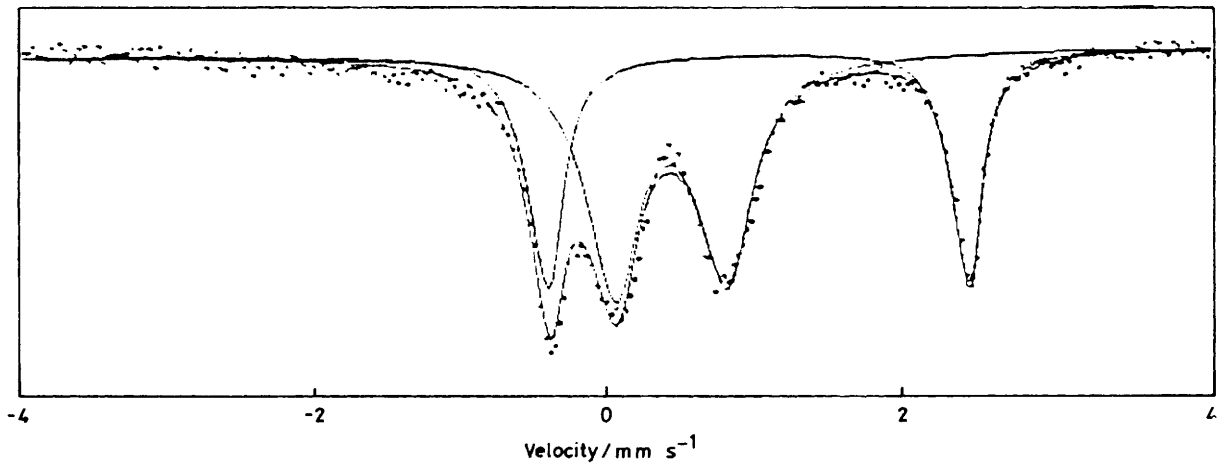


Figure 1. Mössbauer spectrum of the 3,5-di-t-butylcatechol–iron complex in pyridine, observed at 100 K. [$FeCl_3$] = 0.0125, [3,5-di-t-butylcatechol] = 0.1 M, in argon.

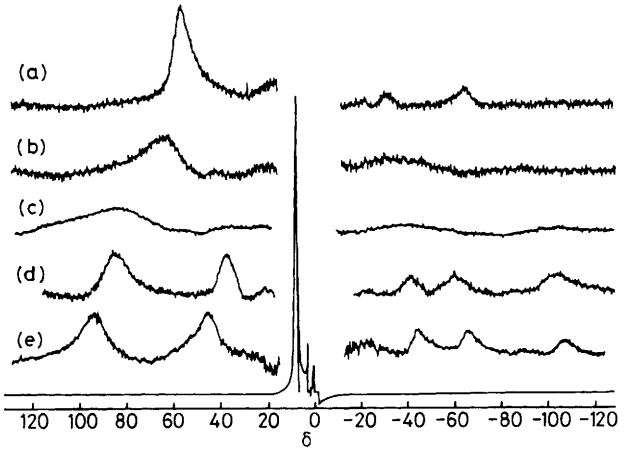


Figure 2. 300 MHz ^1H N.m.r. spectra of 3-methylcatechol–iron complexes in [$^2H_5$]pyridine. [$FeCl_3$] = 0.0125, [3-methylcatechol] = 0.1 M, in argon, observed at (°C) (a) 40, (b) 23, (c) 10, (d) 0, (e) −30.

straight lines of chemical shifts of two peaks observed at lower temperature *vs.* $1/T$. These peaks are assigned to methyl groups of catechol (**1b**), since no peak was observed in the low field region when (**1c**) was used in place of (**1b**). This temperature dependence of the n.m.r. spectra indicates the chemical equilibrium between two complexes, which exhibit a small and a large downfield shift of their methyl resonances.

The two complexes in equilibrium observed by n.m.r. may be the high-spin Fe^{II} and Fe^{III} complexes which were detected by Mössbauer spectroscopy. In this case, the peaks at small and large downfield shifts observed below 0 °C may correspond to (**2b**) and (**3b**), respectively, as shown by equilibrium A. However, the ^1H n.m.r. spectrum of a semiquinonato-Fe^{II} complex has not been reported, and the free radical centre of (**3b**) may broaden the semiquinone signals beyond detection. The other probable equilibrium is that between two high-spin catecholato-Fe^{III} complexes. Since it is reported that the methyl signal of the (3-Me-catecholato)-Fe(salen) [*N*,*N*′-ethylenebis(salicylideneaminato)] complex appears at δ 32 (chelated complex), and δ 89 and −28 (monodentate complex co-ordinated by 2- and 1-OH groups, respectively),[6] the equilibrium B between (**2b**) and (**4b**) may be more probable than that between two monodentate catecholate complexes.† The broadness of the n.m.r. peaks seems to reflect the effect of the presence of the Fe^{II} species. At present, the latter explanation for the n.m.r. spectra seems more probable although the former cannot be excluded.

The above results indicate the formation of three types of catecholate–iron complex and the presence of both A and B equilibria. This may be applicable to the enzymatic system even though a semiquinonato-Fe^{II} species was not detected. As active species for the reaction with oxygen, the monodentate species (**3**) and (**4**) are more probable than the chelated catecholate species (**2**) which may be the most stable.[7] Although species of type (**4**) have been proposed as active species, the detection of the semiquinonato-Fe^{II} complex suggests the probability of the pathway of the oxygen insertion *via* the Fe^{II} species, (**3**).

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† Equilibrium between two monodentate catecholate Fe^{III} complexes has been suggested by a referee as more favourable based on the single Fe^{III} Mössbauer signal, but it is possible to deconvolute the rather broad signal into two types of Fe^{III} species and this is consistent with the n.m.r. result.