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Reversible Binding of Dioxygen by an Iron Complex of 3,5-Di-t-butylcatechol

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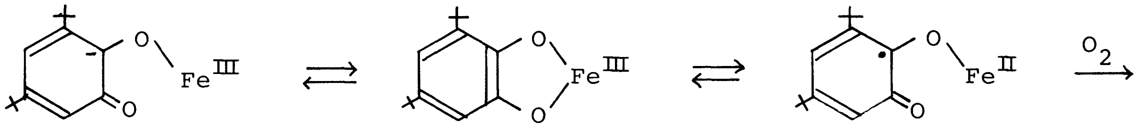
Reversible electronic and ESR spectral changes have been observed by oxygenation and deaeration of $[Fe(DTBC)_3]^{3-}$ ($DTBCH_2$: 3,5-di-t-butylcatechol) in organic solvents, suggesting formation of a ternary catechol-iron-oxygen complex. The reaction of $[Fe(DTBC)_3]^{3-}$ with oxygen yielded intra- and extradiol oxygenation products, whose ratio was dependent on solvent.

Previously we have reported that the oxygenation of 3,5-di-t-butylcatechol, **1**, by iron(III) complex proceeds in a similar fashion to pyrocatechase with insertion of molecular oxygen.[1-3] One of the most important problems to be clarified in the mechanism of oxygenation by enzyme or model iron complexes is whether the oxygen activation by coordination to iron, i.e., formation of a catechol-iron-oxygen ternary complex, is involved or not. Although it is proposed that oxygenation proceeds via an catecholatoiron(III) species based on the spectroscopic information that the Fe(III) state is maintained throughout the oxygenation by enzyme,[4] we have proposed the oxygenation process via a semequinonatoiron(II) species (Eq. 1), based on the electronic and Mössbauer spectroscopic evidences.[5,6]



(1)

Formation of a ternary complex was found with a manganese complex, i.e., the reversible binding of oxygen by $[Mn(DTBC)_3]^{2-}$ in slightly alkaline acetonitrile (Eq. 2, DTBSQ and DTBQ denote semiquinonate and quinone forms of $DTBCH_2$, respectively).[7,8] The reversibility was claimed to be erroneous,[9] but this claim has been rebutted on the basis of the absorption spectral evidences.[8]

$$[Mn(DTBC)_3]^{2-} + O_2 + OH^- \rightleftarrows [Mn(DTBSQ)_2(DTBC)(O_2^-)(OH)]^{2-} \rightarrow [Mn(DTBC)_2(O_2^-)(OH)]^{3-} + DTBQ \quad (2)$$

We report here that the very similar spectral changes is observed with an iron complex, $[Fe(DTBC)_3]^{3-}$, in organic solvents, which suggests strongly the reversible binding of O_2 to catecholatoiron complex. The use of alkali complicated the situation in the case of the manganese complex, but the reversibility was observed without the use of alkali in the case of the iron complex. The reaction of the complex with oxygen yielded intra- and extradiol oxygenation products, indicating that the ternary complex may be an intermediate for the oxygenation of **1**.

$K_3[Fe(DTBC)_3]$ (8.4 mg, 0.01 mmol)[10] was dissolved in 5 cm^3 dimethyl formamide (DMF), tetrahydrofuran (THF), or acetonitrile in an argon atmosphere at room temperature. The solution was bubbled with O_2 for 1 min, and then with argon for 5 min. The argon bubbling was continued intermittently for 2 h. Colour of the solution changed from red-violet to brown-violet after the O_2 bubbling and then to red-violet again after the argon bubbling. In these procedures a small amount of the solution was taken out and absorption spectra were recorded at room temperature using a cell of 1 mm light path. The spectral changes of the solution under O_2 were also followed for 24 h.

Figure 1 shows the spectral changes in DMF. Under an argon atmosphere, the complex exhibited a peak at λ_{max}=505 nm (a). The introduction of oxygen shifted the maximum peak to 425 nm and the intensity at 505 nm decreased (b). The argon bubbling to remove oxygen shifted back the maximum peak to 510 nm with isosbestic points at 362 and 462 nm (c-e). The peak height recovered by the argon bubbling was lower than that of (a), and the spectrum (a) did not pass through the isosbestic points. The spectral changes by oxygen bubbling (f) and argon bubbling (g) indicated that the reversibility is repetitive. We observed the reversible change of intensity of the peak at 300 nm which was assigned to the π-π^* band of the catecholate ligand.

Figure 2 shows the spectral changes under an O_2 atmosphere. The peak intensity of $K_3[Fe(DTBC)_3]$ at 505 nm decreased fairly slowly and a gradual red shift of λ_{max} was observed (550 nm after 24 h). The peak at 425 nm once appeared after introduction of O_2 disappeared and a peak at 394 nm appeared which was assigned to DTBQ **2**. The peak of catecholate ligand at 300 nm also disappeared gradually. The solution became yellow-brown after 24 h.

The spectral changes as shown in Figs. 1 and 2 were observed also in THF and CH_3CN. The maximum peak of $K_3[Fe(DTBC)_3]$ under argon was observed at 510 nm in THF and at 525 nm in CH_3CN and hardly shifted after oxygenation and deaeration. The change of colour was more clear in CH_3CN, i.e., red-violet (under Ar) → yellow-brown (under O_2) → red-violet (under Ar). The isosbestic points were also observed, e.g., at 385 and 455 nm in CH_3CN.

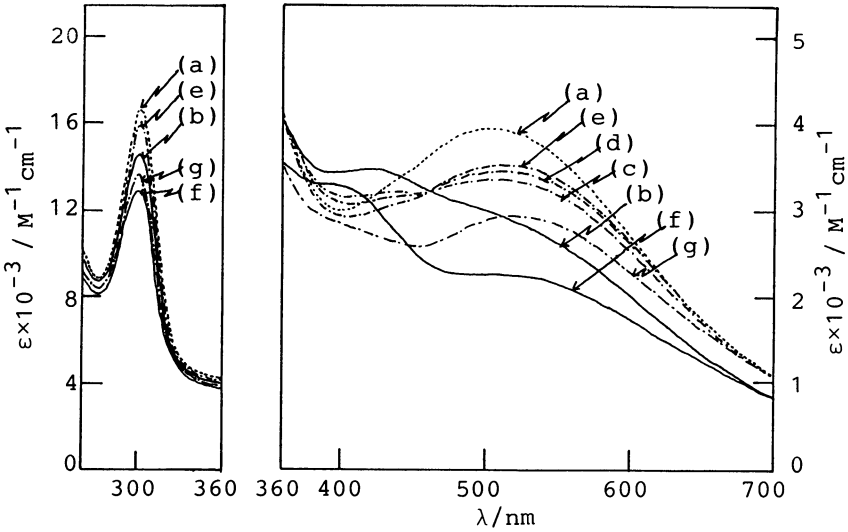


Fig. 1. Reversible changes of electronic spectra of $K_3[Fe(DTBC)_3]$ in DMF at 25 °C.

(a)Under Ar ([Fe]= 2 mM); (b)After O_2bubbling to (a) for 1 min; (c)-(e)After Ar bubbling to (b) for 5 min (c), 0.5 h (d), and 2 h (e); (f)After O_2 bubbling to (e) for 1 min; (g)After Ar bubbling to (f) for 0.5 h.

ESR spectra were measured at 77 K. In DMF, a signal was observed at g=4.35 together with a very weak signal at g= 2.00. As shown in Fig. 3, the former, which is assigned to the high-spin Fe(III) complex decreased after the O_2 bubbling (a → b) and increased after the argon bubbling (b→c). The intensity of (c) was lower than that of (a). Although we should be careful in the quantitative discussion on the peak intensity of ESR, but the reversibility as shown in Fig. 3 was repetitive and observed also in other solvents. In THF, a sharp resonance at g=2.0038 was observed in addition to that of Fe(III) even under an argon atmosphere. The same sharp resonance was also observed with $[Mn(DTBC)_3]^{2-}$,[7] and assigned to a free DTBSQ radical. The peak intensity increased after introduction of oxygen and decreased after the argon bubbling. This may be due to the formation of DTBSQ and its conversion into DTBQ.

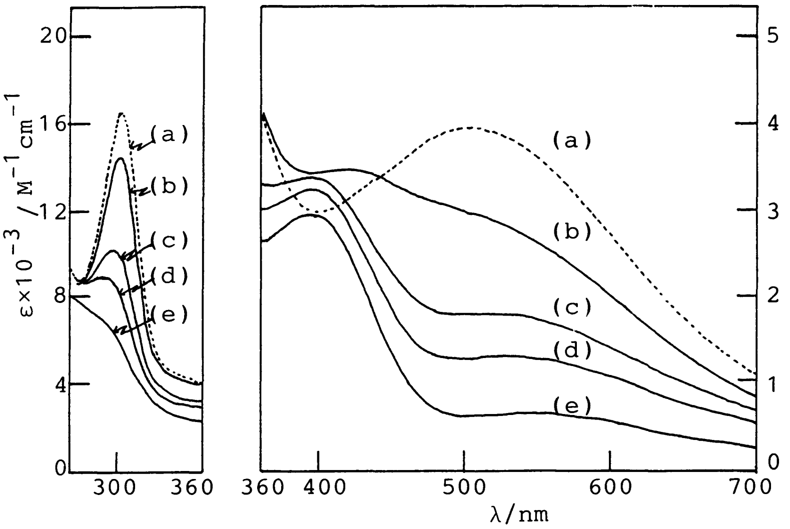


Fig. 2. Spectral changes of $K_3[Fe(DTBC)_3]$ under an O_2 atmosphere in DMF at 25 °C.
(a)Under Ar ([Fe]=2 mM); (b)After O_2 bubbling to (a) for 1 min; (c)-(e)Under O_2 for 1 h (c), 2 h (d), and 24 h (e)

The change of intensity of the Fe(III) species in Fig. 3 parallels to that shown in Fig. 1. The electronic and ESR spectral changes observed here are very similar to those observed with the manganese complex,[8] and suggest strongly the reversible oxygen binding to the iron complex. The spectral change may be represented by Eq. 3 in reference to the reaction of the manganese complex (Eq. 2).

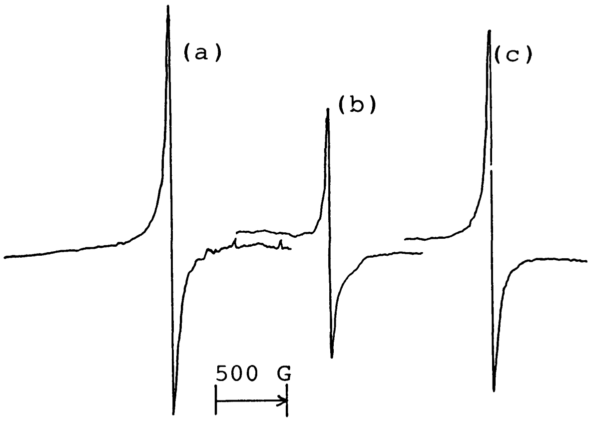


Fig. 3. ESR spectral changes in DMF observed at 77 K.
(a)-(c): same as those in Fig. 1.

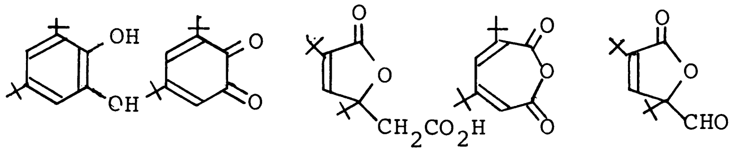
$$\underset{(A)}{[Fe(DTBC)_3]^{3-}} + O_2 \rightleftarrows \underset{(B)}{[Fe(DTBC)_2(DTBSQ)(O_2^{-\bullet})]^{3-}} \rightarrow \text{oxygenation products} \qquad (3)$$

The decrease in the ESR intensity observed after introduction of oxygen, i.e., (a) (b), is consistent with the formation of (B), because (B) may not exhibit an ESR resonance due to the spin-spin interaction between Fe(III) and DTBSQ and $O_2^{-\bullet}$ ligands. The decrease in the ESR intensity by the the formation of high-spin Fe(II) species seems less probable because it may not explain the reversible change of the spectra after deaeration. The results that the spectrum (a) in Fig. 1 does not pass through the isosbestic points and that the diminish of the intensity after oxygenation and deaeration cycle as shown in Figs. 1 and 3 are ascribable to the formation of DTBQ. The shift of 505 nm to 550 nm observed in DMF may be due to the formation of solvent coordinated complexes after replacement of some DTBC ligands with solvent, because it was not so significant in other solvents.

Table 1. Oxygenated products from $K_3[Fe(DTBC)_3]$[a)]

Solvent[b)]	Yield of products/mol%[c)]				
	1	**2**	**3**	**4**	**5**
DMF	9	43	2	1	17
CH_3CN	3	37	20	0	4
THF	6	34	40	0	4

a)$K_3[Fe(DTBC)_3]$:0.05 mmol, 25 °C. b)2 cm^3. c)Based on 1 DTBC ligand of **1**, after 24 h.



1 **2** **3** **4** **5**

As shown in Table 1, the reaction of $[Fe(DTBC)_3]^{3-}$ with oxygen forms intradiol oxygenation products, **3** and **4**, and extradiol oxygenation product **5** as well as quinone **2**. This suggests that the ternary complex is an intermediate for the oxygenation of $[Fe(DTBC)_3]^{3-}$. Interestingly, the composition of oxygenated products was found to be greatly dependent on solvent, i.e., the intradiol oxygenation was predominant in THF and CH_3CN and extradiol in DMF. The role of solvent on the selectivity of reaction is not clear at present and should be clarified in further studies. Since oxygenation was not observed with the manganese complex,[7,8)] the result indicates a characteristic ability of iron complex for oxygenation of catechol.

The reversible spectral changes observed here suggest strongly the reversible oxygen binding to iron and that the formation of a catechol-iron-oxygen ternary complex, i.e., activation of both catechol and oxygen coordination to iron and is involved in the oxygenation of catechol by enzymes and model iron complexes. However, further detailed studies are necessary since we have not obtained any direct evidence for the coordination of oxygen to iron.

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