Oxidative Aromatic Ring Cleavage of 3,5-Di-t-Butylcatechol, with Total Insertion of Molecular Oxygen, Catalysed by 2,2′-Bipyridine–Iron(II) Complex

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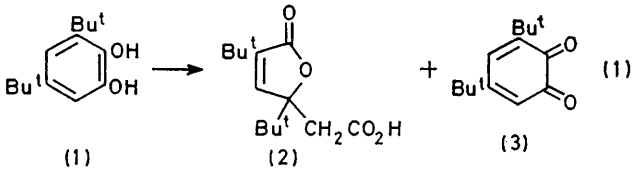
Summary The oxidative aromatic ring cleavage of 3,5-di-t-butylcatechol (**1**) by molecular oxygen to give the lactone (**2**) is catalysed by a non-enzymatic iron(II) complex co-ordinated by 2,2′-bipyridine and pyridine.

IRON(II) enzymes such as pyrocatechase catalyse the oxidative cleavage of aromatic rings; the total insertion of molecular oxygen is characteristic of these catalytic systems.[1] The reaction has attracted attention recently, and some analogous investigations with non-enzymatic systems have been reported,[2–11] but the total insertion of molecular oxygen has been achieved only in a non-catalytic reaction of oxygen with a copper(II)–3,5-di-t-butylcatecholate complex.[4] We report here the first example of the catalysis of reaction (1) by an Fe^{II} complex. Molecular oxygen was inserted, with O–O bond cleavage, to form the actone (**2**).



The oxidation of 3,5-di-t-butylcatechol (**1**) was performed at 25 °C in tetrahydrofuran (THF) under atmospheric oxygen in the presence of iron(II) chloride, 2,2′-bipyridine (bipy), and pyridine (py). After the cessation of oxygen absorption, the products were extracted with benzene by the method of Grinstead.[10] Two crystalline products were obtained, one of which was identified as the *ortho*-benzoquinone (**3**) by its m.p.,[10] i.r.,[12] and electronic spectra.[12] The other product was identified as the furanone (**2**) from the following data: m.p. 132—133 °C; i.r., ν_{max} 2962, 1748, 1721, 1702, and 1639 cm^{-1}; ^1H n.m.r., δ 0·98 (s), 1·23 (s), 2·81 (d, J 14·3 Hz), 2·95 (d, J 14·3 Hz), 6·94 (s), and 9·50 (s); ^{13}C n.m.r., δ 25·3 and 28·0 (CH_3), 37·5 (CH_2), 31·6, 37·8, and 88·1 (>C<), 143·9 (>C=), 145·5 (–CH=, J_{CH} 171 Hz), 171·2 (C:O), and 175·4 (CO_2H) p.p.m.

Results under various conditions are in the Table. The first three results show that the complex functions as a catalyst for the formation of (**2**). Increase in the catalyst concentration shortens the reaction time, but is not so effective in increasing the yield. This may be due to the low solubility of the complex and side reactions such as oxidation of the complex and polymerisation of (**1**). Compound (**2**) was produced without bipyridine in the presence of pyridine, but pyridine was essential for the formation of (**2**) and substituents on pyridine greatly affected the reactivity. This indicates that pyridine is an important ligand for this reaction. The use of 1,10-phenanthroline or ethylenediamine in place of bipyridine retarded the reaction, and (**2**) was not obtained in the latter system. This suggests that the presence of π-orbitals in pyridine, bipyridine, and phenanthroline is effective for the stabilisation of an intermediate for this reaction. Compound (**2**) was also formed in benzene or acetonitrile, but the reaction was slower and yields were lower than in tetrahydrofuran.

The structure of the active complex and the reaction mechanism are not clear at this stage. We examined whether the quinone (**3**) is a precursor for the formation of (**2**), since a similar lactone, 3,5-di-t-butyl-5-(carboxyhydroxymethyl)furan-2-one, was formed from (**3**) with hydrogen peroxide in basic aqueous methanol.[10] In the present case, addition of hydrogen peroxide did not lead to the production of (**2**) from (**3**), which indicates that (**2**) is formed directly from (**1**). The mechanism proposed for the Fe^{II}-enzyme system involves the direct reaction of catechol with oxygen activated by co-ordination to Fe^{II},[13] but by comparison with the reaction of the copper complex,[4] it also seems probable that catechol reacts after co-ordination to Fe^{II}. In order to attempt to detect an intermediate complex, we recorded electronic spectral changes during the reaction using a rapid scan spectrophotometer. When solutions of (**1**) and $[Fe(bipy)_3]^{2+}$ in acetonitrile containing pyridine were mixed, a new complex with a differential absorption maximum at 595 nm was observed, together with an isosbestic point at 555 nm. The peak was not observed in the absence of pyridine, (**1**), and oxygen. Since (**3**) was

TABLE. Oxidation of 3,5-di-t-butylcatechol (**1**) catalysed by 2,2′-bipyridine–iron(II) complex[a]

$FeCl_2·4H_2O$ (mmol)	bipy (mmol)	py (mmol)	Time (h)	Absd.O_2 (mmol)	Product (%)[b] (**2**)	[(**2**)/Fe]	(**3**)
0·1	0·1	23	8	1·97	8	[1·6]	35
0·1	0·2	23	10	1·96	9	[1·8]	35
0·1[c]	0·3[c]	23	12	1·97	11	[2·2]	36
1·0[d]	1·0	23	4	2·10	14	[0·3]	39
1·0[d]	0	23	2	1·90	9	[0·2]	18
1·0[d]	1·0	0	120	1·54	0	[0]	51
1·0[d]	(1·0)[e]	23	18	2·20	10	[0·2]	17
1·0[d]	1·0	(23)[f]	2	1·92	7	[0·2]	33
1·0[d]	1·0	(23)[g]	36	1·93	0	[0]	47

[a] (**1**) (0·2 mmol) in 20 cm^3 THF solution at 25 °C. [b] Yield of recrystallised products based on (**1**). [c] 0·1 mmol of $[Fe(bipy)_3]Cl_2·7H_2O$ was used. [d] The solution was inhomogeneous, containing undissolved complex. [e] 1,10-Phenanthroline was used in place of bipyridine. [f] γ-Picoline and [g] 4-cyanopyridine were used in place of pyridine.

formed without bipyridine and/or pyridine, the new peak is probably related to the formation of (**2**) and may correspond to an intermediate complex such as $[Fe(bipy)(\mathbf{1})(py)(O_2)]^{2+}$, in which py and O_2 are the axial ligands, although this is very speculative.

Work is continuing to increase the yield of (**2**) and the selectivity for its formation and to identify the intermediate, which should provide a better model complex for Fe^{II}-enzymes.

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