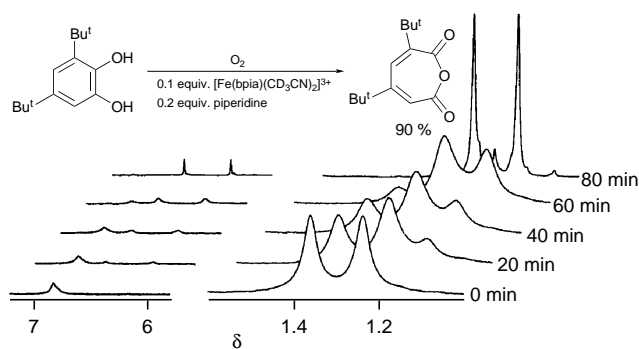


**Fig. 2** Progress of the reaction of  $[\text{Fe}(\text{bpia})(\text{dbc})]^+$  with air in methanol. Inset: plot of  $\ln(A)$  vs.  $t$  at  $25^\circ\text{C}$ .

$\text{ate})]^+$  complexes. Our observation supports the substrate activation mechanism proposed by Que.<sup>2</sup>

The system consisting of  $\text{Fe}(\text{ClO}_4)_3 \cdot 9\text{H}_2\text{O}$  and bpia in acetonitrile catalyses the oxidation of dbc to *cis,cis*-muconic anhydride rapidly and efficiently. In the presence of 10% of the catalyst 90% of the desired cleavage product is obtained. We have isolated 3,5-di-*tert*-butyl-*o*-benzoquinone (dbq) as a by-product in small amounts. By reducing the amount of the iron catalyst the yield of dbq increases, but even with 1%  $[\text{Fe}(\text{bpia})(\text{MeCN})_2]^{3+}$  nearly 80% of the catechol reacts with dioxygen in 12 h to 3,5-di-*tert*-butyl-1-oxacyclohepta-3,5-diene-2,7-dione. With turnover numbers up to 80 this iron(III) complex is the most effective catalyst for the oxidative cleavage of catechols reported yet.

Progress of the reaction can be followed by  $^1\text{H}$  NMR spectroscopy (Fig. 3). The signals of the free substrate ( $\delta$  6.82, 1.36, 1.24) disappear along with the appearance of signals of the muconic anhydride ( $\delta$  6.57, 6.16, 1.25, 1.14) and of the by-product, 3,5-di-*tert*-butyl-*o*-benzoquinone ( $\delta$  7.01, 6.14, 1.23, 1.19). The width of the signals is due to the formation of the paramagnetic  $[\text{Fe}(\text{bpia})(\text{dbc})]^+$  complex in solution during the reaction. At the end of the reaction the signals become sharp indicating a  $\mu$ -oxo-bridged dinuclear iron(III) complex with antiferromagnetic coupling in solution.



**Fig. 3** Catalytic oxidation of 3,5-di-*tert*-butylcatechol monitored by  $^1\text{H}$  NMR spectroscopy

We thank the Deutsche Forschungsgemeinschaft for financial support.

## Footnotes

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† Abbreviations used: bpia = bis[(2-pyridyl)methyl][(1-methylimidazol-2-yl)methyl]amine, dbc = 3,5-di-*tert*-butylcatechol, 4-bc = 4-*tert*-butylcatechol, 4-mc = 4-methylcatechol, cat = catechol, tcc = tetrachlorocatechol; dbq = 3,5-di-*tert*-butyl-*o*-benzoquinone.

‡ The oxidation product of tetrachlorocatechol has not been isolated, due to the high stability of the  $[\text{Fe}(\text{bpia})(\text{tcc})]^+$  complex.

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Received in Basel, Switzerland, 28th January 1997; Com. 7/00614D