Effective Oxygenation of 3,5-Di-t-butylpyrocatechol catalysed by Vanadium(III or IV) Complexes

Yoshitaka Tatsuno,* Masanobu Tatsuda, and Sei Otsuka

Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka, Japan 560

Oxygenation of 3,5-di-t-butylpyrocatechol (**1**) to the corresponding muconic acid anhydride (**2**) and 2-pyrone (**3**) is efficiently catalysed by vanadium(III or IV) complexes.

In the past decade, several oxidative ring cleavage reactions of pyrocatechols with activated oxygen,[1,2] or with molecular oxygen in the presence of metal complexes[3–8] or bases,[9,10] have been studied in connection with an enzyme pyrocatechase[11] which catalyses the intra-diol cleavage of pyrocatechol to *cis*, *cis*-muconic acid. However, most of these reactions are stoicheiometric, or even if the reactions are catalytic, the catalytic activities are very low. During an investigation of the metal-catalysed oxidation of pyrocatechols, we found that several vanadium(III or IV) complexes efficiently catalysed the oxygenation of 3,5-di-t-butylpyrocatechol (**1**) to 3,5-di-t-butylmuconic acid anhydride (**2**) and 4,6-di-t-butyl-2-pyrone (**3**).

In the presence of catalytic amounts (1 mol%) of bis(acetylacetonato)oxovanadium, $VO(acac)_2$, the pyrocatechol (**1**) was easily oxidised in CH_2Cl_2 with molecular oxygen (1 atm) at room temperature to afford the muconic acid anhydride (**2**) (41%) and the 2-pyrone (**3**) (15%) together with 3,5-di-t-butyl-*o*-benzoquinone (**4**) (27%) [see equation (1)]. The reaction products (**2**), (**3**), and (**4**) were separated by column chromatography on silica gel ($CHCl_3$ eluant), recrystallized from n-hexane, and characterized by elemental analyses, i.r., ^1H n.m.r., and mass spectra.

A recent paper[8] reported that the ruthenium-catalysed oxygenation of (**1**) afforded products (**2**) and (**3**) which arose from

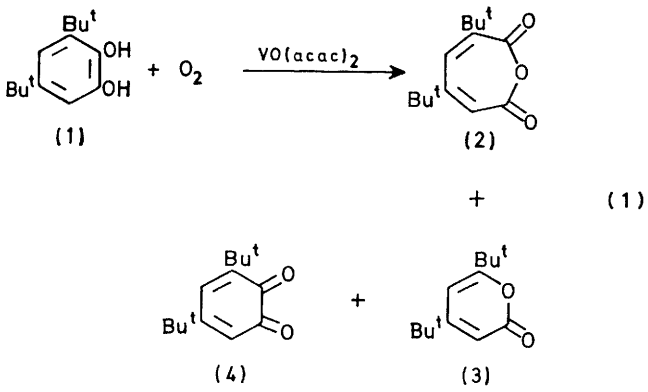


Table 1. Catalytic oxidation of 3,5-di-t-butylpyrocatechol (**1**) by vanadium complexes.[a]

Catalyst	Amount of catalyst (mol%)[b]	Conversion (%)	Products (%)[c] (2)	(3)	(4)
$VO(acac)_2$	1	100	41	15	27
	0.1	100	43	7	25
VO(salen)	1	100	39	7	22
VCl(salen)	1	100	43	7	28
VCl(saldpt)	1	100	41	6	23

[a] Reaction conditions: concentration of pyrocatechol (**1**), 0.1 M in CH_2Cl_2; room temp., 20 h; 1 atm of O_2. [b] Based on pyrocatechol (**1**). [c] The yield of the isolated products is based on pyrocatechol (**1**).

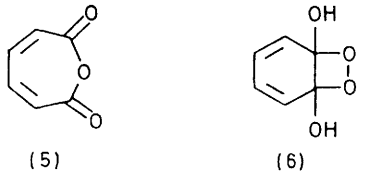
an intra-diol and an extra-diol cleavage of the pyrocatechol (**1**), respectively, with incorporation of one oxygen atom from molecular oxygen. The muconic acid anhydride (**2**) was the main product in this reaction, indicating that the vanadium complex catalyses intra-diol cleavage of the pyrocatechol-like pyrocatechase.

Among other vanadium(III or IV) complexes, VO(salen)[12] [salen = ethylenebis(salicylideneaminato)], VCl(salen), and VCl(saldpt) [saldpt = *N*,*N*′-(3,3′-dipropylamine)bis(salicylideneaminato)]† were also effective for the catalytic oxidation of (**1**) as shown in Table 1. However, VO(ttp)[13] (ttp = tetra-*p*-tolylporphyrinato) and VO(saldpt),† despite being V^{IV} complexes, did not catalyse the oxidation of (**1**) under the same conditions as those mentioned above, and the starting pyrocatechol was recovered. When Schiff-base complexes of iron, manganese, or cobalt, such as Fe(salen),[14] Fe(salen)-dbcatH[15] (dbcatH = 3,5-di-t-butylpyrocatecholato), Fe(salen)-dbsq[14] (dbsq = 3,5-di-t-butylsemiquinolato), Mn(salen),[14] or Co(salen)[14] were examined as catalysts for the oxidation of (**1**), only the quinone (**4**) was obtained in almost quantitative yield and no oxygenated products were detected.

As solvent, MeCN or benzene can be used, whereas MeOH, dimethylformamide, or tetrahydrofuran lead to poor yields of the oxygenated products (**2**) and (**3**), and pyridine completely inhibits the oxidation.

The remarkable feature of this reaction is the high catalytic activity for the oxygenation. As Table 1 shows, the pyrocatechol (**1**) can be easily oxidised even with 0.1 mol % of the catalyst $VO(acac)_2$ to give (**2**), (**3**), and (**4**) in good yields. Thus,

† V^{III} complexes were prepared from VCl_3 and the Schiff-bases in EtOH in the presence of Et_3N: VCl(salen)·2EtOH, golden brown powder, m.p. 298 °C; VCl(saldpt), orange crystals, m.p. 256—270 °C. VO(saldpt) was prepared from $VO(acac)_2$ and saldpt in EtOH: VO(saldpt), orange yellow crystals, m.p. 257—259 °C. Elemental analyses of these complexes were in good agreement with the calculated values.



the maximum turnover of the catalyst for the oxygenation amounted to about 500. This is the first report of such a high value. Furthermore, on raising the reaction temperature to 70 °C, the reaction (MeCN, solvent) was completed within 4 h without a decrease in the yield of the oxygenated products (**2**) and (**3**).

As the main product (**2**) is analogous to the Hamilton intermediate[16] (**5**) in the enzymatic reaction, the vanadium-catalysed oxygenation favours the Hamilton intermediate rather than the dioxetan intermediate[9,17] (**6**) in oxidative ring cleavage reactions of the pyrocatechols.

Although the quinone (**4**) was an intermediate product and was oxidised further to give the oxygenated product in several ring cleavage reactions[6,8,10] studied thus far, (**4**) could not be oxidised in this reaction just as in the enzyme reaction.

The characteristic features of this reaction can be summarised as follows: 1) the intra-diol cleavage product is mainly formed, 2) the vanadium complexes show a high catalytic activity (turnover 500), 3) the quinone can not be oxidised. From these results, we concluded that the vanadium-catalysed oxygenation was very similar to pyrocatechase-catalysed oxygenation.

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan.

Received, 15th June 1982; Com 685

References

1 T. Matsuura, H. Matsushita, S. Kato, and I. Saito, *Tetrahedron*, 1972, **28**, 5119.
2 Y. Moro-oka and C. S. Foote, *J. Am. Chem. Soc.*, 1976, **98**, 1510.
3 J. Tsuji and H. Takayanagi, *J. Am. Chem. Soc.*, 1974, **96**, 7349; *Tetrahedron Lett.*, 1975, 1245.
4 M. M. Rogić, T. R. Demmin, and W. B. Hammond, *J. Am. Chem. Soc.*, 1976, **98**, 7441; M. M. Rogić and T. R. Demmin, *J. Am. Chem. Soc.*, 1978, **100**, 5472.
5 D. G. Brown, L. Beckmann, C. G. Ashby, G. C. Vogel, and J. T. Reimprecht, *Tetrahedron Lett.*, 1977, 1363.
6 G. Speier and Z. Tyeklár, *J. Mol. Catal.*, 1980, **9**, 233.
7 T. Funabiki, H. Sakamoto, S. Yoshida, and K. Tarama, *J. Chem. Soc., Chem. Commun.*, 1979, 754.
8 M. Matsumoto and K. Kuroda, *J. Am. Chem. Soc.*, 1982, **104**, 1433.
9 R. R. Grinstead, *Biochemistry*, 1964, **3**, 1308.
10 A. Nishinaga, T. Itahara, and T. Matsuura, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 3353.
11 M. Nozaki, in 'Molecular Mechanism of Oxygen Activation,' ed. O. Hayaishi, Academic Press, New York, 1974, pp. 135—167.
12 K. Dey, R. M. Maiti, and S. K. Sen, *Inorg. Chim. Acta*, 1976, **20**, 197.
13 F. A. Walker, E. Hui, and J. M. Walker, *J. Am. Chem. Soc.*, 1975, **97**, 2390.
14 S. L. Kessel, R. M. Emberson, P. G. Debrunner, and D. N. Hendrickson, *Inorg. Chem.*, 1980, **19**, 1170.
15 L. Que, Jr., and R. H. Heistand, II, *J. Am. Chem. Soc.*, 1979, **101**, 2219.
16 G. A. Hamilton, in 'Molecular Mechanism of Oxygen Activation,' ed. O. Hayaishi, Academic Press, New York, 1974, pp. 405—451.
17 O. Hayaishi, M. Katagiri, and S. Rothberg, *J. Am. Chem. Soc.*, 1955, **77**, 5450; *J. Biol. Chem.*, 1957, **229**, 905.