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VANADIUM-CATECHOLATO COMPLEXES AS REACTION INTERMEDIATES IN THE VANADIUM CATALYZED OXYGENATION OF CATECHOLS

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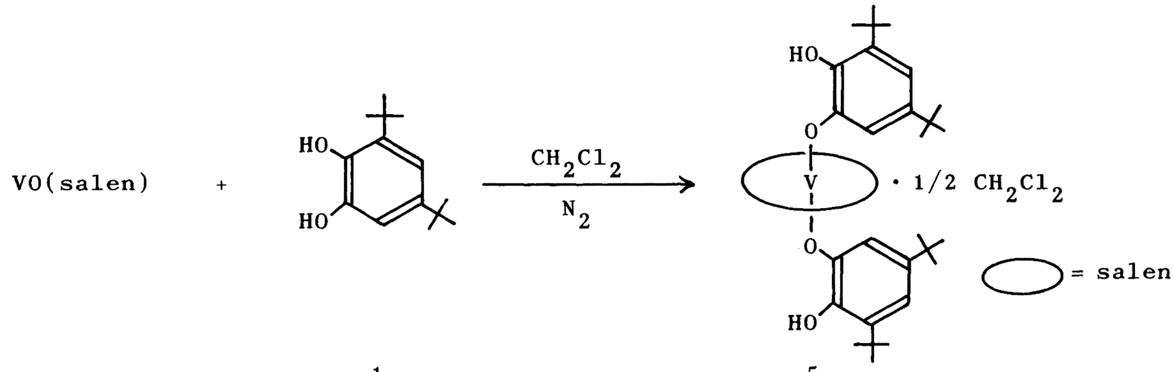
New vanadium-catecholato complexes containing a Schiff base ligand, $[V(salen)(DBcatH)_2]\cdot 1/2\ CH_2Cl_2$, $[V(salen)(DBpyrH_2)_2]\cdot 1/2\ H_2O$, $[V(salen)(cat)]\cdot 1/10\ CH_2Cl_2$, $[V(salen)(Bcat)]\cdot H_2O$, $[V(saldpt)(DBcatH)]\cdot CH_2Cl_2$ were prepared and characterized by elemental analyses and spectroscopic methods. Their relationship to the vanadium(III or IV)-catalyzed oxygenation of catechol was discussed.

Pyrocatechase is an enzyme capable of catalyzing the oxidative ring cleavage of pyrocatechol with dioxygen.1) Metal-catalyzed oxygenations of catechols have received considerable attention in recent years in the light of the elucidation of the enzymatic reaction mechanism.2-5) However, none of them could not offer enough information for a complete understanding of the reaction mechanism. Even the roles of metal ions in the model reactions still remain uncertain. Vanadium-catecholato complexes such as $[VO(DBcat)_2]^{2-}$ and $[V(DBcat)_3]^{3-}$,6) have also been reported in recent publications.7-11) Their relationship to the oxygenation catalysis, however, has not been examined. Recently, we have first reported12) that several vanadium(III or IV) complexes catalyze the oxygenation of 3,5-di-t-butylcatechol(**1**) with dioxygen to give 2,4-di-t-butylmuconic acid anhydride(**2**) and 4,6-di-t-butyl-2-pyrone(**3**) in addition to 3,5-di-t-butyl-o-benzoquinone(**4**). Here we wish to report the isolation of several new vanadium-catecholato complexes considered to be reaction intermediates in the catalysis and their characterization by elemental analyses and spectroscopic methods. From their reactivities toward dioxygen the role of vanadium complexes in the catalysis is also suggested.

An excess of the catechol **1** was added to a green solution of [VO(salen)] in

CH_2Cl_2 under nitrogen atmosphere at ambient temperature to give a dark brown solution from which, after being stirred overnight, a biscatecholato complex containing a half mole of solvated dichloromethane $[V(salen)(DBcatH)_2]\cdot 1/2\ CH_2Cl_2$ (5) was isolated as dark brown powder upon addition of a large excess of hexane (Eq.1).



(1)

1 5

The elemental analyses (Table 1) were conformed to the empirical formula of 5. Its IR spectrum (nujol mull) showed one sharp ν_{OH} at 3510 cm^{-1} besides absorption bands due to the coordinated salen moiety but no $\nu_{V=O}$ around 990 cm^{-1}. The EPR spectrum (CH_2Cl_2, 25 °C) showed a typical vanadium(IV) spectrum of eight lines at $g=1.98(A_{av}=98\ G)$. These data suggested trans-ligation of two catechol monoanions to vanadium(IV) for the structure of 5 as shown in Eq.1. Such coordination of the catechol monoanion to a metal ion has not been observed in the vanadium-catecholato complexes so far isolated,[7-11] while a similar coordination has been proposed in [Fe(salen)(DBcatH)].[13] From a reaction mixture of [VO(salen)]-catalyzed oxygenation of 1 in CH_2Cl_2 obtained after a half mole of dioxygen per mole of 1 had been consumed, the complex 5 was also isolated by addition of hexane. In contrast to [Fe(salen)(DBcatH)] which is inactive for the oxygenation of 1, the complex 5 itself showed a similar catalytic activity for the oxidation of 1 with dioxygen to that of the catalyst precursor, [VO(salen)] (1 atm, at ambient temperature, 20 h, in CH_2Cl_2) (Eq.2).

$$\underset{}{1} + O_2 \xrightarrow{5\ (1\ mol\%)} \underset{42}{2} + \underset{11}{3} + \underset{24\%\ (based\ on\ 1)}{4} \qquad (2)$$

The complex 5, reacted with dioxygen in the absence of the substrate 1 (1 atm, at ambient temperature, in CH_2Cl_2, 12 h), decomposed to give the oxygenated products 2 and 3, the quinone 4, and the original complex [VO(salen)](Eq.3). In contrast to the great stability of typical vanadium(IV) complexes such as $[VO(acac)_2]$

$$\underset{1}{5} + O_2 \longrightarrow \underset{0.7}{2} + \underset{0.1}{3} + \underset{1.14}{4} + \underset{0.7\ (mole\ ratio)}{[VO(salen)]} \qquad (3)$$

Table 1. Analytical and Physical Data

Complex	Color	Mp $\theta m/^{\circ}C$	Yield %	Found(Calcd) (%) C	H	N	Cl	IR spectra[a)]
$[V(salen)(DBcatH)_2]\cdot$ $1/2\ CH_2Cl_2$ 5	black brown	216-22	97	66.64 (66.62)	7.19 (7.16)	3.54 (3.49)	4.74 (4.42)	3510 $cm^{-1}(\nu_{OH})$
$[V(salen)(DBpyrH_2)_2]\cdot$ $1/2\ H_2O$ 6	black brown	130-40 (decomp)	98	66.19 (65.99)	7.48 (7.17)	3.30 (3.49)		3510 $cm^{-1}(\nu_{OH})$ 3340 $cm^{-1}(H_2O)$
$[V(salen)(cat)]\cdot$ $1/10\ CH_2Cl_2$ 7	black brown	235 (decomp)	93	60.95 (61.19)	4.15 (4.23)	6.53 (6.46)	1.80 (1.63)	
$[V(salen)(Bcat)]\cdot$ H_2O 8	black brown	180-2	89	62.77 (62.55)	5.37 (5.65)	5.86 (5.61)		3400 $cm^{-1}(H_2O)$
$[V(saldpt)(DBcatH)]\cdot$ CH_2Cl_2 9	orange red	162-5 (decomp)	64	60.88 (60.52)	6.75 (6.68)	6.14 (6.05)	9.48 (10.21)	3300 $cm^{-1}(\nu_{OH})$ 3230 $cm^{-1}(\nu_{NH})$

a) Nujol mull.

or [VO(salen)] toward dioxygen, this instability of 5 seems to be intriguing. Presumably the instability is due to activation of the catecholato ligand through coordination. This activation of the catecholato ligands can be considered to be an important step in the catalytic oxygenation of catechols.

4,6-Di-t-butylpyrogallol is also oxygenated with dioxygen in the presence of catalytic amounts of [VO(salen)] as reported previously.[14)] Reaction of [VO(salen)] and the pyrogallol under nitrogen atmosphere gave a complex $[V(salen)(DBpyrH_2)_2]\cdot 1/2\ H_2O$ (6) analogous to 5, where two pyrogallol monoanions are ligating to vanadium(IV) in trans position (see Table 1). Presence of a half mole of solvated water molecule was shown from its IR spectrum and the elemental analyses. The complex 6 showed also a catalytic activity for oxygenation of the pyrogallol.

Pyrocatechol, which did not undergo oxidative ring cleavage in this catalysis, also reacted with [VO(salen)] to give an unstable complex $[V(salen)(cat)]\cdot 1/10\ CH_2Cl_2$(7) after recrystallization from CH_2Cl_2-hexane. Different from 5 or 6, one pyrocatechol dianion in 7 coordinates to vanadium(IV) as a bidentate ligand.

Although a CH_2Cl_2 solution of 4-t-butylcatechol absorbed about one mole of dioxygen per mole of the substrate at ambient temperature in the presence of a catalytic amount of [VO(salen)] (1 mol%), no distinct oxygenated products of 3-t-butylmuconic acid anhydride have been isolated so far. The catechol reacted with [VO(salen)] under nitrogen atmosphere to give a complex $[V(salen)(Bcat)]\cdot H_2O$ (8) similar to 7. In complexes 7 and 8, a salen moiety could not be planar but should have a bent structure as in [Fe(salen)(DBSQ)].[15] In contrast to monodentate catecholato complexes **5** and **6**, these bidentate catecholato complexes **7** and **8** showed only poor catalytic activity for oxygenation of catechols. The reason of these poor catalytic activity shown by the bidentate catecholato complexes is not clear at the moment.

Reaction of [VCl(saldpt)] with one mole of **1** in CH_2Cl_2 in the presence of one mole of triethylamine afforded an orange red crystal [V(saldpt)(DBcatH)]·CH_2Cl_2(**9**) which was also active for the catalytic oxygenation of **1**. Coordination of the catechol monoanion to vanadium has been proposed for the structure of **9** just as that of the complex **5** on the basis of the physical properties.

Crystal structure of these complexes are now in progress.

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6) Abbrevations used are as follows: DBcat, 3,5-di-t-butylcatechol dianion; salen, ethylenebis(salicylideneaminato); DBcatH, 3,5-di-t-butylcatechol monoanion; $DBpyrH_2$, 4,6-di-t-butylpyrogallol monoanion; cat, pyrocatechol dianion; Bcat, 4-t-butylcatechol dianion; DBSQ, 3,5-di-t-butyl-o-semiquinone anion; saldpt, N,N'-(3,3'-dipropylamine)bis(salicylideneaminato).
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