# First Comparative Study of the Oxidation Properties of Dioxovanadium(V) Complex with Tris(2-pyridylmethyl)amine and Its Oxo-peroxo Analogue

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The oxidation reactions of $\alpha$-terpinene and 2,6-di-*tert*-butylphenol by vanadium(V) complexes were thoroughly examined using $^1$H NMR. The dioxovanadium(V) complex was more reactive than the corresponding oxo-peroxo vanadium(V) complex for the oxidation reaction of $\alpha$-terpinene and 2,6-di-*tert*-butylphenol.

High-valent oxovanadium compounds play important roles in various oxidation reactions such as epoxidation, haloperoxidase functions, and oxygen addition reactions.[1–4] The oxo-peroxo $V^V$ complexes have been the target of extensive studies of catalytic reactions using hydrogen peroxide as an oxidant.[1] In order to control the reactivities of oxo-peroxovanadium complexes, a variety of ligands ranging from monodentate to multidentate have been applied.[1,2]

The coreresponding dioxo $V^V$ complexes have often been assumed as an intermediate in the reaction processes, but the reactivities of the dioxo $V^V$ complexes themselves have not been examined so far.[4] This is because under catalytic reaction conditions with hydrogen peroxide, the dioxo complexes are converted to oxo-peroxo complexes, which prevents the examination of reactivity of the dioxo complexes. It is important to know the role of the dioxo complexes quantitatively for the understanding of the overall view of the $V^V$ oxidation reaction mechanisms. To the best of our knowledge, however, no clear result has been reported for the quantitative reactivities of dioxo $V^V$ complexes as an oxidation reagent.

Recently, we have isolated the dioxo and oxo-peroxo $V^V$ complexes with tris(3-pyridyl)methylamine (tpa), $[V(O)_2(tpa)]PF_6$, and $[VO(O_2)(tpa)]PF_6$.[5] These complexes provide an opportunity to make the comparison of the reactivities of dioxo and oxo-peroxo $V^V$ complexes. Here, we will demonstrate the first quantitative examination on the oxidation of organic substrates by the dioxo $V^V$ complex.

We chose $\alpha$-terpinene and 2,6-di-*tert*-butylphenol as organic substrates. The reaction of organic substrates with the tpa–$V^V$ complexes were carried out in deuterated acetonitrile, and was monitored by $^1$H NMR spectroscopy.[6] The reaction conditions are listed in Table 1.

During the reaction of the dioxo complex and $\alpha$-terpinene (Table 1a), intensities of the signals corresponding to the dioxo complex and $\alpha$-terpinene decreased with simultaneous appearance of the signals of the $\mu$-oxo divanadium(IV) complex $[\{V^{IV}O(tpa)\}_2(\mu\text{-}O)]^{2+}$ and *p*-cymene. The dioxo $V^V$ complex was almost quantitatively converted to the $\mu$-oxo divanadium(IV) complex in 10 d (Figure S1).[11] Although monomeic $V^{IV}$ complex is paramagnetic, the $\mu$-oxo divanadium(IV) complex shows the $^1$H NMR signals of their ligands in the diamagnetic region due to the spin coupling through the $\mu$-oxo bridge.[7] The signals of the divanadium(IV) complex were assigned by comparing with those of the independently prepared authentic dimer sample.[7] No product other than *p*-cymene and the divanadium(IV) complex was detected in the spectrum. Judging from the integrated signal intensities, the stoichiometry of the reaction is determined as shown in eq 1a.

**Table 1.** Reaction conditions

| Entry | Complex/Substrate | Complex /mM | Substrate /mM | $T$/°C |
|---|---|---|---|---|
| (a) | $[V(O)_2(tpa)]^+/\alpha$-terpinene | 10 | 70 | 70 |
| (b) | $[V(O)_2(tpa)]^+/Bu_2$-phenol | 10 | 56 | 65 |
| (c) | $[V(O)(O_2)(tpa)]^+/\alpha$-terpinene | 10 | 58 | 70 |
| (d) | $[V(O)(O_2)(tpa)]^+/$ $Bu_2$-phenol | 6.5 | 22 | 60 |

$$2[V^V(O)_2(tpa)]^+ + \alpha\text{-terpinene} \rightarrow [\{V^{IV}O(tpa)\}_2(\mu\text{-}O)]^{2+} + p\text{-cymene} + H_2O \qquad (1a)$$

As in the reaction with $\alpha$-terpinene, the intensities of the signals of dioxo complex and 2,6-di-*tert*-butylphenol ($Bu_2$-phenol) were decreased with increase of the signals of the divanadium(IV) complex and 3,3′,5,5′-tetra-*tert*-butyl-4,4′-diphenoquinone ($Bu_4$-dpq) during the reaction (Table 1b). After 65 h, the signals of the dioxo complex completely disappeared (Figure S2).[11] From the integrated intensities of the signals, the reaction ratio was determined as eq. 1b.

$$4[V^V(O)_2(tpa)]^+ + 2Bu_2\text{-phenol} \rightarrow 2[\{V^{IV}O(tpa)\}_2(\mu\text{-}O)]^{2+} + Bu_4\text{-dpq} + H_2O \qquad (1b)$$

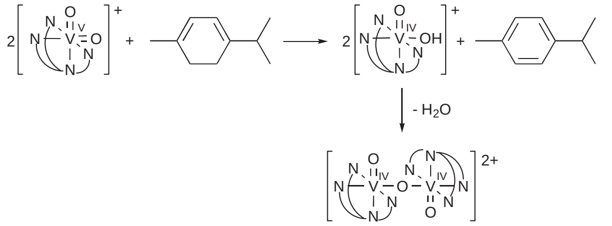
Thus, the dioxo complex was converted to the oxo-bridged $V^{IV}$ species upon the reaction with $\alpha$-terpinene as well as $Bu_2$-phenol. Oxidation reactions using the oxo-peroxo complex $[V^VO(O_2)(tpa)]^+$ were examined under similar conditions to those for the dioxo complex. To our surprise, the change in the NMR spectra revealed that the reaction is extremely slow.

Although the signals of the dioxo complex, $\mu$-oxo dimer and *p*-cymene appeared gradually at the expense of the signals of the oxo-peroxo complex and $\alpha$-terpinene, the reaction did not complete under the condition of (c) in 12 d (over 60% of the oxo-peroxo complex remained). More significantly, no appreciable change was observed for the reaction of oxo-peroxo complex with $Bu_2$-phenol under the condition (d) after a month.[8] It is concluded that the reactivity of the oxo-peroxo complex is significantly lower than that of the dioxo complex.

The proposed reaction scheme of the dioxo complex with $\alpha$-terpinene is depicted in Scheme 1.

It has been reported that the conversion of $\alpha$-terpinene into *p*-cymene proceeds via dehydrogenation process.

Therefore, the reaction should start with the hydrogen atom transfer from $\alpha$-terpinene to the dioxo vanadium complex to form $V^{IV}$-oxo-hydroxo complex (eq 2a).[9]



**Scheme 1.** Proposed reaction scheme of the oxidation of $\alpha$-terpinene by the dioxo complex.

$$\alpha\text{-terpinene} + [\mathrm{V^{V}(O)_2(tpa)}]^+ \rightarrow (\alpha\text{-terpinene} - \mathrm{H}) + [\mathrm{V^{IV}(O)(OH)(tpa)}]^+ \tag{2a}$$

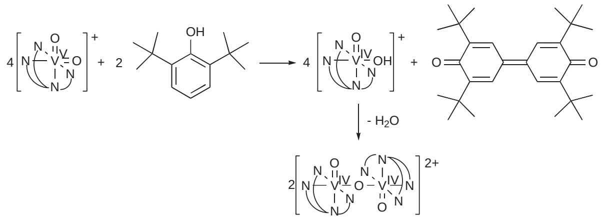
Monodehydrogenated $\alpha$-terpinene ($\alpha$-terpinene $-$ H) is quite unstable and should immediately react with another $\mathrm{V^V}$ dioxo complex to afford *p*-cymene and another $\mathrm{V^{IV}}$ oxo-hydroxo complex (eq 3a).

$$(\alpha\text{-terpinene} - \mathrm{H}) + [\mathrm{V^{V}(O)_2(tpa)}]^+ \xrightarrow{\text{very fast}} p\text{-cymene} + [\mathrm{V^{IV}(O)(OH)(tpa)}]^+ \tag{3a}$$

The $\mathrm{V^{IV}}$ oxo-hydroxo complex has high tendency to form oxo-bridged dimeric complex by dehydration reaction (eq 4a).

$$2[\mathrm{V^{IV}(O)(OH)(tpa)}]^+ \xrightarrow{\text{fast}} [\{\mathrm{V^{IV}O(tpa)}\}_2(\mu\text{-O})]^{2+} + \mathrm{H_2O} \tag{4a}$$

The reaction of dioxo complex with 2,6-di-*tert*-butylphenol also proceeded in the stoichiometric way as depicted in Scheme 2.



**Scheme 2.** Proposed reaction scheme for the oxidation of 2,6-di-*tert*-butylphenol by $[\mathrm{V(O)_2(tpa)}](\mathrm{PF_6})$.

As discussed for the reaction with $\alpha$-terpinene, the reaction should begin with the transfer of a hydrogen atom of a $\mathrm{Bu_2}$-phenol to the dioxo vanadium complex to form the $\mathrm{V^{IV}}$-oxo-hydroxo complex (eq 2b)

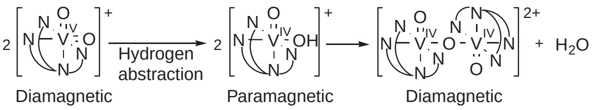
$$\mathrm{Bu_2\text{-}phenol} + [\mathrm{V^{V}(O)_2(tpa)}]^+ \rightarrow (\mathrm{Bu_2\text{-}phenol} - \mathrm{H}) + [\mathrm{V^{IV}(O)(OH)(tpa)}]^+ \tag{2b}$$

Again, monodehydrogenated $\mathrm{Bu_2}$-phenol ($\mathrm{Bu_2}$-phenol $-$ H) is quite unstable and should immediately react with another $\mathrm{V^V}$ dioxo complex to afford oxo-hydroxo $\mathrm{V^{IV}}$ complex and a radical coupled product, 3,3′,5,5′-tetra-*tert*-butyl-4,4′-diphenoquinone (eq 3b).

$$2(\mathrm{Bu_2\text{-}phenol} - \mathrm{H}) + 2[\mathrm{V^{V}(O)_2(tpa)}]^+ \xrightarrow{\text{very fast}} (\mathrm{Bu_4\text{-}dpq}) + 2[\mathrm{V^{IV}(O)(OH)(tpa)}]^+ \tag{3b}$$

The generated $\mathrm{V^{IV}}$ oxo-hydroxo complex is converted to oxo-bridged dimeric complex by dehydration reaction as 4a.
The overall reaction of the $\mathrm{Bu_2}$-phenol is given in 4b.[10]

$$2\mathrm{Bu_2\text{-}phenol} \rightarrow \mathrm{Bu_4\text{-}dpq} + 4\mathrm{H}\bullet \tag{4b}$$



**Scheme 3.** Conversion of the dioxo $\mathrm{V^V}$ complex into $\mu$-oxo divandium(IV) complex.

In summary, reactivity of dioxo and oxo-peroxo $\mathrm{V^V}$ complexes with organic substrates, $\alpha$-terpinene and 2,6-di-*tert*-butylphenol, were examined under noncatalytic reaction conditions. It turned out that the dioxo complex is significantly more reactive for the oxidation of the substrates. From the stoichiometries of the reactions, the reaction process of the dioxo complex with the substrates is initiated by the hydrogen atom abstraction (Scheme 3).

The result suggests the possible importance of the dioxo complex during catalytic oxidation reactions. As far as we know, the present results are the first unambiguous prove of the higher reactivity of a dioxo $\mathrm{V^V}$ complex as an oxidation reagent than the corresponding oxo-peroxo complex.

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6 The experimental detail and $^1$H NMR spectra during the reaction (Figures S1 and S2) are given in Supporting Information.

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8 By the limitation of sensitivity and solubility, the reaction with larger amount of $\mathrm{Bu_2}$-phenol was monitored by UV–vis absorption spectra at 50 °C ($[\mathrm{V(O)(O_2)(tpa)}]^+$:$\mathrm{Bu_2}$–phenol = 1:40). After several days, the formation of $\mathrm{Bu_4}$–dpq and $[\{\mathrm{V^{IV}O(tpa)}\}_2(\mu\text{-O})]^{2+}$ was observed. Therefore, the oxidation reaction by $[\mathrm{V(O)(O_2)(tpa)}]^+$ proceed very slowly. Because the small extinction coefficient of $[\mathrm{V(O)(O_2)(tpa)}]^+$ and possible products such as $[\mathrm{V(O)_2(tpa)}]^+$ and dibutylquinone, the discussion of reaction mechanism was not accomplished for the oxo-peroxo complex.

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11 Supporting Information is available electronically on the CSJ-Journal web site, http://www.csj.jp/journals/chem-lett/.

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