

The first evidence for activation of exogenous O₂ on a vanadium(IV) center: synthesis and characterization of a peroxo vanadium(V) complex with hydrotris(3,5-diisopropylpyrazol-1-yl)borate

Masahiro Kosugi, Shiro Hikichi,* Munetaka Akita and Yoshihiko Moro-oka *

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan. E-mail: shikichi@res.titech.ac.jp

Received 8th February 1999, Accepted 19th March 1999

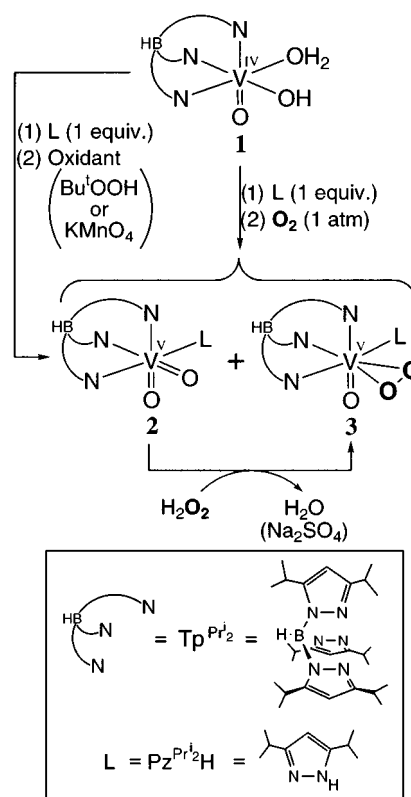
Reaction of a vanadium(IV) hydroxo complex bearing hydrotris(3,5-diisopropylpyrazol-1-yl)borate (Tp^{Pr²}) with O₂ results in reductive O₂ activation to give Tp^{Pr²}V^V(O)(η²-O₂)(L); the first example of the formation of a peroxo vanadium complex from molecular oxygen.

Reductive O₂ activation (O₂ → O₂⁻ → O₂²⁻ → 2 × O²⁻) via oxidative addition of molecular oxygen to a transition metal center is a fundamental process in various synthetic O₂ oxidation reactions and physiological O₂ metabolism. Therefore, research into the reactivity of transition metal complexes toward O₂ activation and the characterization of the resulting peroxo complexes is essential to the understanding of the synthetic and metabolic O₂ activation mechanisms.¹ It is known that vanadium–peroxo species take part in various catalytic oxidations ranging from industrial processes to enzymatic reactions.² However, the oxidant used in most of these processes (including halide oxidation by haloperoxidases) is not O₂ but ROOH (R = H, alkyl); only a limited number of aerobic oxidation reactions by vanadium catalysts have been reported. Moreover, the role of the vanadium center in aerobic oxidation processes is proposed to assist the autoxidation reaction (*i.e.* degradation of the alkylhydroperoxides to induce radical chain reaction).³ In addition, previously reported vanadium(V)–peroxo complexes were prepared by the reaction of appropriate V(V)–oxo or –hydroxo precursors with ROOH,² and no examples of the formation of a peroxo complex *via* incorporation of an external O₂ molecule was known to date.⁴ In this communication, we report the first evidence for the activation of exogenous O₂ on V(IV) centers resulting in formation of V(V)–peroxo species.[†]

We have been investigating the peroxo and related complexes of various first- and second-row, late transition metals (Mn, Fe, Co, Ni, Cu, Ru, Rh, Pd) with the hindered hydrotris(pyrazolyl)borate ligands (Tp^R) in order to obtain comprehensive insights into the role of metal ions in various oxidation processes.⁵ Recently, our research target has been extended to the early transition metals, and a V(IV)–hydroxo complex with hydrotris(3,5-diisopropylpyrazol-1-yl)borate (Tp^{Pr²}), Tp^{Pr²}-V^{IV}(O)(OH)(OH₂) **1**, has been synthesized and characterized successfully.⁶ When a toluene solution of **1** was exposed to O₂ (1 atm) in the presence of 1 equiv. of 3,5-diisopropylpyrazole (Pz^{Pr²}H) ‡ at room temperature, the purple solution changed to a dark red one within 2 h. NMR (⁵¹V, ¹³C and ¹H) and IR spectra of the resulting products clearly indicated the existence of two sets of Tp^{Pr²}-V^V(Pz^{Pr²}H) moieties in a 1:1 molar ratio and, in addition, two sets of ν(V=O) and ν(O–O) vibration bands appeared in the 960–890 cm⁻¹ region (in the IR region). Finally, these two products were identified as mononuclear V(V)–*cis*-dioxo and –oxo–peroxo complexes, Tp^{Pr²}-V^V(O)₂(Pz^{Pr²}H) **2** and Tp^{Pr²}-V^V(O)(η²-O₂)(Pz^{Pr²}H) **3**, respectively, by comparison of the spectral data with those of the independ-

ently prepared authentic samples whose molecular structures were successfully determined by X-ray crystallography (see below).§

An authentic sample of **2** was synthesized by chemical oxidation of **1** with Bu^tOOH or KMnO₄ in the presence of 1 equiv. of the pyrazole ligand (Pz^{Pr²}H), and subsequent dehydrative condensation of the isolated **2** with H₂O₂ (in the presence of Na₂SO₄ as dehydrating reagent) yielded the corresponding V(V)–oxo–peroxo complex **3** (Scheme 1).¶ The pale yellow dioxo complex **2** involves a slightly distorted octahedral vanadium center coordinated by two terminal oxo ligands in *cis* configuration [Fig. 1(a)]. The structural and spectral features of **2** [(i) somewhat long V=O lengths: V–O(1) 1.621(3), V–O(2) 1.636(3) Å, (ii) elongation of two of the three V–N_{TP} bond lengths *trans* to the oxo ligands are due to the strong *trans* effect from the terminal oxo ligands, and (iii) relatively low ν(V=O) vibration frequencies (921 and 893 cm⁻¹)] are similar to those found for the previously reported V(V)–*cis*-dioxo complexes.⁷



Scheme 1

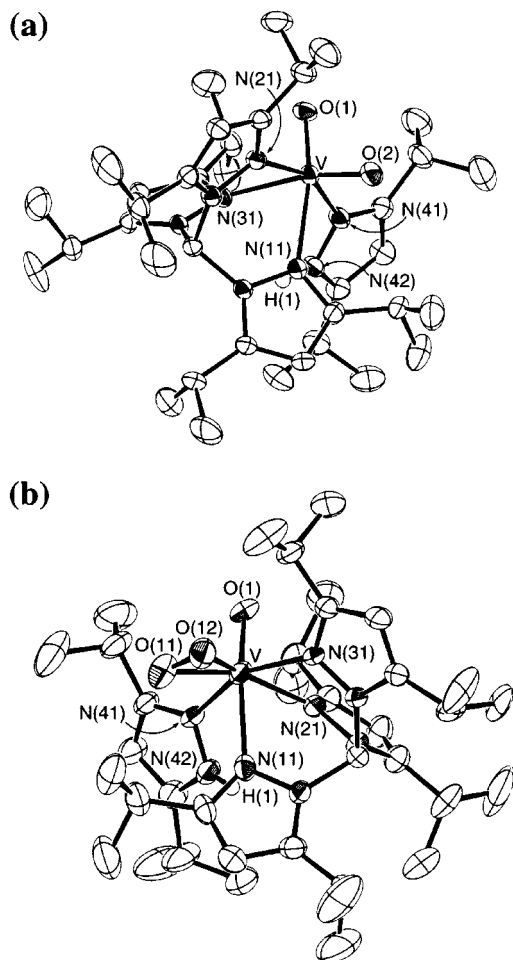
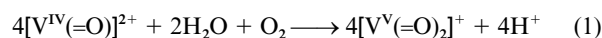


Fig. 1 Molecular structures of $\text{Tp}^{\text{Pr}_2}\text{V}(\text{O})_2(\text{Pz}^{\text{Pr}_2}\text{H})$ **2** (a) and $\text{Tp}^{\text{Pr}_2}\text{V}(\text{O})(\eta^2\text{-O}_2)(\text{Pz}^{\text{Pr}_2}\text{H})\cdot\text{THF}$ **3**·THF at the 50% probability level. All hydrogen atoms except those attached to the nitrogen atoms [N(42)] of the coordinating pyrazole ligands (**2** and **3**), the disordered carbon atoms of one of the three 5- Pr^i groups in the Tp^{Pr_2} ligand and the THF solvate (**3**) are omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): (a) *cis*-dioxo complex **2** V–O(1) 1.621(3), V–O(2) 1.636(3), V–N(11) 2.324(5), V–N(21) 2.203(5), V–N(31) 2.122(5), V–N(41) 2.161(5), O(1)–V–O(2), 103.8(1); (b) oxo- η^2 -peroxo complex **3** O(11)–O(12) 1.379(6), V–O(1), 1.603(4), V–O(11), 1.862(5), V–O(12), 1.887(5), V–N(11) 2.324(5), V–N(21) 2.203(5), V–N(31) 2.122(5), V–N(41) 2.161(5); O(11)–V–O(12), 43.2(2).

The red peroxo complex **3** has a seven-coordinated pentagonal-bipyramidal metal center containing an η^2 -peroxo ligand [V–O(11) 1.862(5), V–O(12) 1.887(5) Å; O(11)–V–O(12) 43.2(2) $^\circ$], and the overall structures of **2** and **3** are very similar when it is assumed that the peroxo ligand occupies a single coordination site [Fig. 1(b)]. The distance from the vanadium center to the terminal oxo ligand [V–O(1) 1.603(4) Å, $\nu(\text{V}=\text{O})$ 947 cm^{-1}] is shorter than those found for the dioxo complex **2**. The relatively short O–O length [O(11)–O(12) 1.379(6) Å] is almost at the shortest end of the typical range for the O–O distances of peroxide ligands,⁸ and is indicated by the relatively high $\nu(\text{O}=\text{O})$ value of 960 cm^{-1} . Retention of the side-on bound peroxo ligand in solution is supported by a UV-vis spectrum of a toluene solution involving the peroxo-to-vanadium charge-transfer band around 495 nm ($\epsilon = 280 \text{ M}^{-1} \text{ cm}^{-1}$).²

The O_2 activation on the V(IV) center of the hydroxo complex **1** was evidenced by a labeling experiment with $^{18}\text{O}_2$ and an external substrate oxidation ability. Of the four characteristic vibrations [$\nu(\text{O}=\text{O})$ and $\nu(\text{V}=\text{O})$, see above] of a reaction mixture of **1** and O_2 , only the $\nu(\text{O}=\text{O})$ band at 960 cm^{-1} disappeared upon treatment with $^{18}\text{O}_2$ [overlapped with the tail of the $\nu(\text{V}=\text{O})$ peak at 893 cm^{-1} (**2**); observed $\nu(^{18}\text{O}=\text{O})$ value = 900 cm^{-1} in the sample prepared by the reaction of **2** with $\text{H}_2^{18}\text{O}_2$], and the remaining three $\nu(\text{V}=\text{O})$ bands were not shifted. We thus conclude that the peroxo ligand in **3** arises from the

external dioxygen molecule and the origin of the terminal oxo ligands in both **2** and **3** is the oxygen atoms of the oxo and the hydroxo ligands in **1** (not O_2). Trapping of the external O_2 molecule as the peroxide ($=\text{O}_2^{2-}$) ligand on the vanadium center (*i.e.* formation of **3**) indicates that the present aerobic oxidation of **1** is clearly different from the usual $4e^-$ oxidation process of $[\text{V}^{\text{IV}}(\text{O})]^{2+}$ compounds yielding the vanadium(V)-dioxo compounds [eqn. (1)].²



Remarkably, the V(IV)-hydroxo complex **1** showed aerobic PPh_3 oxygenation activity [under 1 atm O_2 , r.t., reaction time: 30 min, yield of $\text{O}=\text{PPh}_3$: 150% (based on **1** in the presence of 30 equiv. of PPh_3)], whereas the isolated mononuclear V(V)- η^2 -peroxo complex **3** exhibited relatively low oxo-transfer activity under the same condition (yield 31% based on **3**) and the V(V)-dioxo complex **2** could not oxidize PPh_3 under any conditions. These observations supported the fact that the reductive O_2 activation was mediated by another vanadium- O_2 species formed at an initial stage of the oxygenation of **1**. In the present vanadium system, the electron donating ability of Tp^{Pr_2} might make the reductive O_2 activation on the vanadium(IV) center possible.⁹

In conclusion, the reductive O_2 activation took place on the V(IV) center of the hydroxo complex containing Tp^{Pr_2} . The resulting monomeric V(V)- η^2 -peroxo complex is the first example of the V(V)-peroxo complex derived from the direct oxygenation of the V(IV) precursor. Detailed investigation of the reactivities of the vanadium-peroxo species is now underway.

Acknowledgements

We are grateful to the Ministry of Education, Science, Sports and Culture of the Japanese government for financial support of the research (Grant-in-Aid for Specially Promoted Scientific Research: No. 08102006).

Notes and references

† Abbreviations used in this paper: Tp^{R} , hydrotris(3,5-substituted-pyrazol-1-yl)borate; Tp^{Pr_2} , hydrotris(3,5-diisopropylpyrazol-1-yl)borate; $\text{Pz}^{\text{Pr}_2}\text{H}$, 3,5-diisopropylpyrazole.

‡ Reaction of **1** with O_2 in the absence of the additional $\text{Pz}^{\text{Pr}_2}\text{H}$ also resulted in the formation of the $\text{Pz}^{\text{Pr}_2}\text{H}$ containing complexes **2** and **3**, although the yields of them were quite low (>30% based on **1**) due to partial decomposition of the Tp^{Pr_2} ligand providing the $\text{Pz}^{\text{Pr}_2}\text{H}$ ligands.
§ Crystal data. For **2**: $\text{C}_{36}\text{H}_{62}\text{N}_8\text{O}_5\text{BV}$, $M = 700.69$, monoclinic, space group $P2_1/n$ (no. 14), $a = 9.698(10)$, $b = 20.54(2)$, $c = 22.84(1)$ Å, $\beta = 92.51(4)^\circ$, $V = 4018(2)$ Å³, $Z = 4$, $D_c = 1.16 \text{ g cm}^{-3}$, $\mu(\text{Mo-K}\alpha) = 2.87 \text{ cm}^{-1}$, $T = -60^\circ\text{C}$, $R(R_w) = 0.043$ (0.046) (based on F) for 3613 [$I > 3\sigma(I)$] reflections with 442 parameters. For **3**·THF: $\text{C}_{40}\text{H}_{70}\text{N}_8\text{O}_5\text{BV}$, $M = 788.80$, monoclinic, space group $P2_1/n$ (no. 14), $a = 9.171(2)$, $b = 17.458(4)$, $c = 25.12(1)$ Å, $\beta = 98.97(8)^\circ$, $V = 4493(6)$ Å³, $Z = 4$, $D_c = 1.17 \text{ g cm}^{-3}$, $\mu(\text{Mo-K}\alpha) = 2.67 \text{ cm}^{-1}$, $T = -60^\circ\text{C}$, $R(R_w) = 0.077$, (0.068) (based on F) for 4472 [$I > 3\sigma(I)$] reflections with 509 parameters. CCDC reference number 186/1394.

¶ Selected spectroscopic data. For **2**: IR (KBr pellet, ν/cm^{-1}): 3433(N–H), 2541(B–H), 921, 893(V=O). FD-MS: m/z 702 ($M + \text{H}^+$). UV-vis (toluene, λ/nm , $\epsilon/\text{M}^{-1} \text{ cm}^{-1}$): 749 (7.3). ^{51}V NMR (C_6D_6 , reference; VOCl_3): δ 541. ^1H NMR (C_6D_6): δ 9.03 (1H, pyrazole N–H). For **3**: IR (KBr pellet, ν/cm^{-1}): 3436(N–H), 2543(B–H), 960 ($^{16}\text{O}=\text{O}$), 900 ($^{18}\text{O}=\text{O}$); prepared by reaction of **2** with $\text{H}_2^{18}\text{O}_2$, 947(V=O). FD-MS: m/z 718 ($M + \text{H}^+$). UV-vis (toluene, λ/nm , $\epsilon/\text{M}^{-1} \text{ cm}^{-1}$): 495 (280). ^{51}V NMR (C_6D_6 , reference; VOCl_3): δ 552. ^1H NMR (C_6D_6): δ 8.43 (1H, pyrazole N–H).

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