J|A|C|S
COMMUNICATIONS

Aerobic Oxidation of Pinacol by Vanadium(V) Dipicolinate Complexes: Evidence for Reduction to Vanadium(III)

Susan K. Hanson,[†] R. Tom Baker,*[,†,¶] John C. Gordon,[†] Brian L. Scott,[‡] Andrew D. Sutton,[†] and David L. Thorn*[,§]

Chemistry and Materials Physics Applications Divisions and Chemistry, Life and Earth Sciences Directorate, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

Received September 22, 2008; E-mail: rbaker@uottawa.ca; dthorn@lanl.gov

Escalating global demand for energy, diminishing petroleum reserves, and concern over rising CO_2 emissions are driving interest in the use of nonfood-based biorenewable chemicals and fuels.[1] Lignocellulose is a particularly important resource, with US production potential estimated at 1 billion tons/year.[2] However, breakdown of the highly functionalized polymers lignin and cellulose for use in biofuels and chemical applications is a major challenge.[1,3] Some promising technologies that have emerged utilize C−O bond cleavage, such as in enzymatic and acid-catalyzed hydrolysis, as well as pyrolysis/gasification.[4,5]

Less attention has been directed at lignocellulose disassembly by selective C−C bond cleavage, which could provide alternative bioderived feedstocks. It has been recognized for some time that vanadium(V) complexes are capable of oxidative C−C bond cleavage reactions. Early work by Waters, West, Skoog, and others demonstrated that VO_2^+ in H_2SO_4 or $HClO_4$ could effect stoichiometric C−C bond cleavage in a range of substrates, including pinacol and glycerol (to give acetone and formic acid, respectively).[6] A catalytic aerobic reaction has been reported by Bregeault and co-workers, who found that $VO(O^iPr)_3/O_2$ catalyzed the conversion of 1,2-diphenyl-1,2-ethanediol to benzaldehyde with 11 turnovers.[7] Developing new vanadium-catalyzed aerobic oxidative C−C bond cleavage reactions of this type would complement related oxidation processes catalyzed by other metals[8] and could enable reactions that provide new chemical intermediates from cellulose and lignin.

The mechanisms of VO_2^+/H^+ alcohol oxidations have been studied in detail and generally appear to proceed via a one-electron redox pathway.[6,9] In contrast, a two electron pathway involving V^{III} intermediates has been proposed in the vanadium-catalyzed aerobic oxidation of activated alcohols reported by Toste, Chen, and Uemura; however, such intermediates have not yet been observed experimentally.[10,11] To investigate these oxidation reactions further, we prepared and characterized vanadium diolate complexes derived from dipicolinic acid (H_2dipic). We report herein our studies on the stoichiometric and catalytic oxidation of alcohols, including the isolation of a V^{III} species resulting from reaction under anaerobic conditions.

Reaction of (dipic)V^V(O)O^iPr (**1a**)[12] or (dipic)V^V(O)OEt (**1b**)[13] with pinacol (H_2pin) in CH_3CN gave the new yellow pinacolate complex (dipic)V^V(O)(Hpin) (**2**). Complex **2** was isolated in 88% yield and characterized by ^1H NMR and IR spectroscopy, elemental analysis, and X-ray crystallography.[14] The molecular structure of **2** (Figure 1) indicates that the monoanionic pinacolate ligand is bound unsymmetrically.

When complex **2** was dissolved in pyridine-d_5 and the reaction followed over the course of 4−6 days at room temperature, complete disappearance of **2** was observed, along with formation of acetone (1 equiv) and pinacol (0.5 equiv) (eq 1). The green V^{IV} product (dipic)V^{IV}(O)(pyr)$_2$ (**3**) could be isolated on a synthetic scale in 67% yield and was characterized by IR and UV−vis spectroscopy, elemental analysis, and X-ray crystallography (Figure 1).[14]

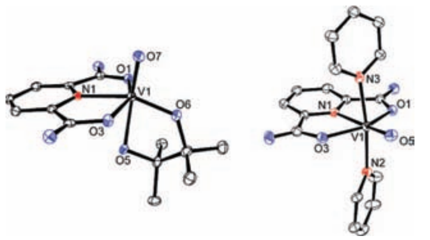
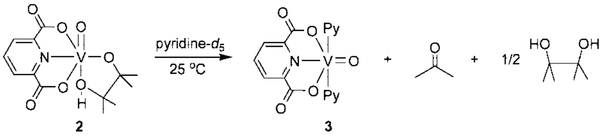
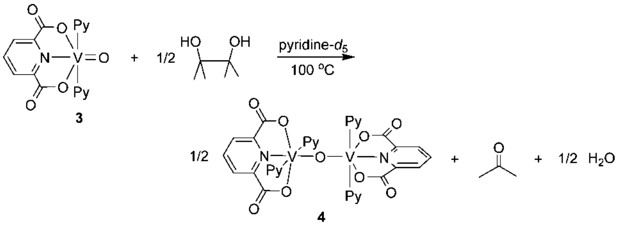


Figure 1. Molecular structures of pentavalent (dipic)V(O)(Hpin) (**2**, left) and tetravalent (dipic)V(O)(pyr)$_2$ (**3**, right) (thermal ellipsoids at 50% probability, H atoms omitted for clarity). Selected bond lengths (Å) for **2**: V1−O7 = 1.588(2), V1−O6 = 1.777(2), V1−O5 = 2.252(2), V1−N1 = 2.063(2), V1−O1 = 1.959(2), V1−O3 = 1.953(2). For **3**: V1−O5 = 1.611(2), V1−O1 = 2.013(2), V1−O3 = 2.009(2), V1−N3 = 2.170(2), V1−N2 = 2.141(2), V1−N1 = 2.148(2).



(1)

Under more forcing conditions, ^1H NMR spectroscopy revealed that complex **3** can facilitate a further C−C bond cleavage reaction. When the above reaction mixture containing **3** and 0.5 equiv of pinacol was heated in pyr-d_5 at 100 °C for 48 h, the pinacol was entirely consumed and acetone (1 equiv) was formed (eq 2).



(2)

A dark purple vanadium species (**4**) was also produced in this reaction. When the reaction was performed on a synthetic scale, dark purple crystals of **4** could be isolated in 60% yield and characterized by X-ray crystallography, UV−vis spectroscopy, and elemental analysis.[14] The X-ray structure (Figure 2) reveals that complex **4** is a V^{III} μ-oxo dimer. The V1−O5 bond length of 1.797(1) Å is typical of that observed for V^{III} μ-oxo dimers.[15] The dark purple color of this complex ($\lambda = 518$ nm, $\epsilon = 5000$ M^{-1} cm^{-1}; $\lambda = 598$ nm, $\epsilon = 4600$ M^{-1} cm^{-1}) is also consistent with reported complexes of this type and has been attributed to a V−O−V ligand to metal charge transfer.[15]

The reaction of complex **3** with pinacol to form V^{III} complex **4** is remarkable. Reactions of V^V complexes with alcohols generally afford V^{IV} products, and although V^{III} complexes have been

---

[†] Chemistry Division.
[‡] Materials Physics Applications Division.
[§] Chemistry, Life and Earth Sciences Directorate.
[¶] Current Address: Department of Chemistry, University of Ottawa, Ottawa, ON Canada K1N6N5.

10.1021/ja807522n CCC: $40.75

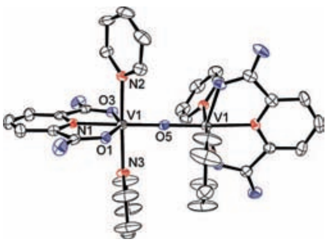
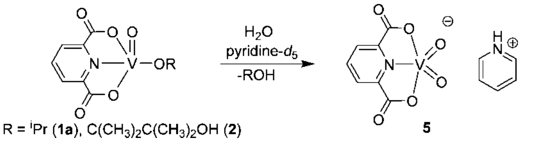


Figure 2. Molecular structure of trivalent $[(\text{dipic})V(\text{pyr})_2]_2(\mu\text{-O})$ (**4**) (thermal ellipsoids at 50% probability, H atoms, and cocrystallized pyr omitted for clarity). Selected bond lengths (Å): V1−O5 = 1.797(1), V1−O3 = 2.027(2), V1−O1 = 2.030(2), V1−N1 = 2.097(2), V1−N2 = 2.151(2), V1−N3 = 2.154(2).

proposed as intermediates in the vanadium-catalyzed aerobic oxidation of activated alcohols,[11] V^{III} products have never been isolated from such reactions. This reaction appears to be highly ligand-dependent; when the V^{IV} complex $V^{IV}(O)(acac)_2$ was treated with pinacol under the same reaction conditions employed to isolate **4** (pyr-d_5, 100 °C), formation of acetone was observed in less than 30% yield after 1 week (whereas reaction of **3** with pinacol to give **4** was complete in 48 h under these conditions).

Both complexes **3** and **4** could be oxidized by air, suggesting potential catalytic reactivity of (dipic)V toward polyalcohols. Reaction of a pyridine solution of **4** with air was followed by UV−vis spectroscopy, and yielded **3** after 1 h at room temperature.[14] Only trace oxidation of the V^{IV} complex **3** occurred under air in pyr-d_5 solution at room temperature over several weeks, but when the reaction was conducted at 100 °C, slow formation of *cis*-dioxo V^V complex **5** was observed (50% yield after 4 days). Complex **5** could also be prepared by reaction of **1a** or **2** with H_2O in pyridine (eq 3).[16]



(3)

Catalytic aerobic oxidative C−C bond cleavage of pinacol was achieved in both pyr-d_5 and NMP solvent (NMP = 1-methyl-2-pyrrolidinone), with the use of NMP resulting in better catalytic performance.[14] With **1a** (5 mol%) as the catalyst in NMP solvent, 19 turnovers (97% conversion, turnover = mol pinacol consumed per mol V) were observed after 3 days at 100 °C under air. Control experiments involving the thermolysis of pinacol in pyr-d_5 or NMP solvent under air with no vanadium showed no reaction under these conditions.[14]

The (dipic)V^V complexes were also found to oxidize unactivated aliphatic alcohols. Reaction of isopropoxide complex **1a** in pyr-d_5 at room temperature for 1−2 days yielded acetone (0.5 equiv) and V^{IV} complex **3**. In this case, further thermolysis at 100 °C in the presence of excess isopropyl alcohol did not result in formation of a V^{III} product. To gain insight into the mechanism of this alcohol oxidation, cyclobutanoxide complex $(\text{dipic})V^V(O)(OC_4H_7)$ (**6**) was prepared,[14] and its reactivity examined. Thermolysis of a pyridine-d_5 solution of **6** at 100 °C for 30 min produced cyclobutanone in 93% yield. The absence of ring-scission products in this reaction argues against radical intermediates and is more consistent with a two-electron pathway involving V^{III} intermediates.[17] In contrast, a one-electron pathway is implicated for VO_2^+ in $HClO_4$, where reaction with cyclobutanol was found to give primarily ring-opened products (94%), with less than 1.5% cyclobutanone formed.[9]

In conclusion, dipic V complexes are able to catalyze the aerobic oxidative C−C bond cleavage of pinacol. Reaction under anaerobic conditions allows for isolation of a V^{III} μ-oxo dimer, which provides strong support for the potential involvement of V^{III} in aerobic oxidation reactions. Experiments exploring the scope and mechanism of this reaction in more detail, including reactions with lignin and cellulose, are currently underway.

Acknowledgment. This work was supported by the NSF via the Center for Enabling New Technologies through Catalysis (CENTC). We thank Professors S. L. Scott and P. C. Ford (UCSB) for helpful discussions.

Supporting Information Available: Experimental procedures and details, characterization data for **2**−**6**, and X-ray crystallographic data and CIF files for **2**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Dodds, D. R.; Gross, R. A. *Science* **2007**, *318*, 1250–1251. (b) Huber, G. W.; Corma, A. *Angew. Chem., Int. Ed.* **2007**, *46*, 7184–7201. (c) Corma, A.; Iborra, S.; Velty, A. *Chem. Rev.* **2007**, *107*, 2411–2502.
(2) Perlack, R. D.; Wright, L. L.; Turhollow, A. F.; Graham, R. L.; Stokes, B. J.; Erbach, D. C. *Biomass as Feedstock for a Bioenergy and Bioproducts Industry: The Technical Feasibility of a Billion-Ton Annual Supply.* US Department of Energy Report, 2005, available online at http://www.eere.energy.gov/biomass/publications.html.
(3) (a) Emsley, A. M. *Cellulose* **2008**, *15*, 187–192. (b) Zhang, Y. H. P. *J. Ind. Microbiol. Biotechnol.* **2008**, *35*, 367–375.
(4) (a) Li, C.; Zhao, Z. K. *Adv. Synth. Catal.* **2007**, *349*, 1847–1850. (b) Dhepe, P. L.; Fukuoka, A. *Catal. Surv. Asia* **2007**, *11*, 186–191. (c) Fukuoka, A.; Dhepe, P. L. *Angew. Chem., Int. Ed.* **2006**, *45*, 5161–5163. (d) Zhang, Y. H. P.; Lynd, L. R. *Biotechnol. Bioeng.* **2004**, *88*, 797–824.
(5) Chheda, J. N.; Huber, G. W.; Dumesic, J. A. *Angew. Chem., Int. Ed.* **2007**, *46*, 7164–7183.
(6) (a) Kumar, A.; Mehrotra, R. N. *J. Org. Chem.* **1975**, *40*, 1248–1252. (b) Jones, J. R.; Waters, W. A.; Littler, J. S. *J. Chem. Soc.* **1961**, 630–633. (c) West, D. M.; Skoog, D. A. *J. Am. Chem. Soc.* **1960**, *82*, 280–283. (d) Littler, J. S.; Waters, W. A. *J. Chem. Soc.* **1959**, 1299–1305.
(7) Bregeault, J. M.; El Ali, B.; Mercier, J.; Martin, J.; Martin, C. C. R. *Acad. Sci. Paris* **1989**, *309*, 459–462.
(8) Catalytic aerobic C−C cleavage of diols has also been reported with Fe, Ru, Mn, and polyoxometalate complexes. See: (a) Murray, R. I.; Sligar, S. G. *J. Am. Chem. Soc.* **1985**, *107*, 2186–2187. (b) Riano, S.; Fernandez, D.; Fadini, L. *Catal. Commun.* **2008**, *9*, 1282–1285. (c) Barroso, S.; Blay, G.; Fernandez, I.; Pedro, J. R.; Ruiz-Garcia, R.; Pardo, E.; Lloret, F.; Munoz, M. C. *J. Mol. Catal., A.* **2006**, *243*, 214–220. (d) Takezawa, E.; Sakaguchi, S.; Ishii, Y. *Org. Lett.* **1999**, *1*, 713–715. (e) Khenkin, A. M.; Neumann, R. *J. Am. Chem. Soc.* **2008**, *130*, 14474–14476.
(9) Rocek, J.; Aylward, D. E. *J. Am. Chem. Soc.* **1975**, *97*, 5452–5456.
(10) See: (a) Jiang, N.; Ragauskas, A. J. *J. Org. Chem.* **2007**, *72*, 7030–7033. (b) Figiel, P. J.; Sobczak, J. M. *New. J. Chem.* **2007**, *31*, 1668–1673. (c) Velusamy, S.; Punniyamurthy, T. *Org. Lett.* **2004**, *6*, 217–219. (d) Maeda, Y.; Kakiuchi, N.; Matsumura, S.; Nishimura, T.; Kawamura, T.; Uemura, S. *J. Org. Chem.* **2002**, *67*, 6718–6724. (e) Kirihara, M.; Ochiai, Y.; Takizawa, S.; Takahata, H.; Nemoto, H. *Chem. Commun.* **1999**, *138*, 7–1388, and references therein.
(11) (a) Pawar, V. D.; Bettigeri, S.; Weng, S. S.; Kao, J. Q.; Chen, C. T. *J. Am. Chem. Soc.* **2006**, *128*, 6308–6309. (b) Weng, S. S.; Shen, M. W.; Kao, J. Q.; Munot, Y. S.; Chen, C. T. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 3522–3527. (c) Radosevich, A. T.; Musich, C.; Toste, F. D. *J. Am. Chem. Soc.* **2005**, *127*, 1090–1091.
(12) Thorn, D. L.; Harlow, R. L.; Herron, N. *Inorg. Chem.* **1996**, *35*, 547–548.
(13) Mimoun, H.; Chaumette, P.; Mignard, M.; Saussine, L.; Fischer, J.; Weiss, R. *Nouv. J. Chim.* **1983**, *7*, 467–475.
(14) See Supporting Information for details.
(15) See: (a) Cissell, J. A.; Kaur, N.; Nellutla, S.; Dalal, N. S.; Vaid, T. P. *Inorg. Chem.* **2007**, *46*, 9672–9677. (b) Kumagai, H.; Kitagawa, S.; Maekawa, M.; Kawata, S.; Kiso, H.; Munakata, M. *J. Chem. Soc., Dalton Trans.* **2002**, 2390–2396. (c) Zhang, Y.; Holm, R. H. *Inorg. Chem.* **1990**, *29*, 911–917, and references therein.
(16) NH_4^+ and K^+ salts of $(\text{dipic})V(O)_2^-$ have been previously reported: (a) Wieghardt, K. *Inorg. Chem.* **1978**, *17*, 57–64. (b) Crans, D. C.; Yang, L.; Jakusch, T.; Kiss, T. *Inorg. Chem.* **2000**, *39*, 4409–4416.
(17) (a) Chandler, W. D.; Wang, Z.; Lee, D. G. *Can. J. Chem.* **2005**, *83*, 1212–1221. (b) Oh, N. A.; Suh, Y.; Park, M. J.; Seo, M. S.; Kim, J.; Nam, W. *Angew. Chem., Int. Ed.* **2005**, *44*, 4235–4239.

JA807522N