ChemComm

Cite this: *Chem. Commun.*, 2012, **48**, 7826–7828

www.rsc.org/chemcomm

COMMUNICATION

Published on 19 June 2012. Downloaded by University of California - Irvine on 31/10/2014 10:00:15.

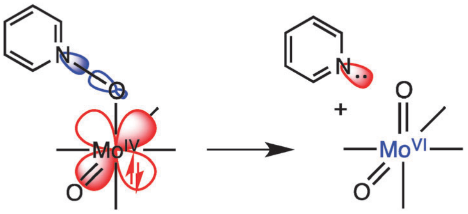
Nonclassical oxygen atom transfer reactions of oxomolybdenum(VI) bis(catecholate)†

Travis Marshall-Roth, Sean C. Liebscher, Karl Rickert, Nicholas J. Seewald, Allen G. Oliver and Seth N. Brown*

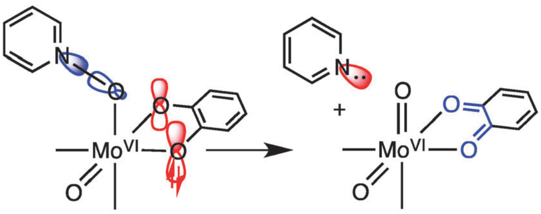
Received 16th May 2012, Accepted 15th June 2012
DOI: 10.1039/c2cc33523a

Mechanistic studies indicate that the oxomolybdenum(VI) bis(3,5-di-*tert*-butylcatecholate) fragment deoxygenates pyridine-*N*-oxides in a reaction where the oxygen is delivered to molybdenum but the electrons for substrate reduction are drawn from the bound catecholate ligands, forming 3,5-di-*tert*-butyl-1,2-benzoquinone.

Inner-sphere redox reactions involve both changes in oxidation state and changes in bonding. Classically, in reactions such as the oxygen atom transfer (OAT)[1] reaction depicted in eqn (1a), the changes in oxidation state and those in bonding are co-localized: molybdenum is both oxidized and forms a new bond to oxygen, while nitrogen is reduced and the N–O bond is broken. Co-localization is not, however, obligatory. For example, in complexes with redox-active ligands, bonding changes may take place at a redox-inert metal center while the corresponding changes in oxidation state take place at the coordinated ligand (eqn (1b)). The most thoroughly studied example of such a "non-classical" inner-sphere redox reaction is proton-coupled electron transfer (PCET), where the motion of the hydrogen nucleus may be quite separated from the motion of the electron.[2] In contrast to PCET, nonclassical OAT (eqn (1b)) would be a two-electron redox process.



(1a)



(1b)

Nonclassical OAT has been postulated for simple oxygen atom donors[3] but only observed using dioxygen as oxidant,[4] though nonclassical transfer reactions of the isoelectronic nitrene group from aryl azides to early metal complexes have been described.[5] Redox participation of catecholate in oxygen atom transfer to rhenium(V) has been proposed, but net oxidation takes place at the metal, not the ligands.[6] Reduced bipyridine complexes of uranium[7] and thorium[8] have been shown to abstract oxygen from pyridine-*N*-oxides, but it has not been established whether the electrons flow directly from the reduced bipyridine to the N–O bond while both ligands are coordinated, or whether neutral bipyridine dissociates from a reduced metal center prior to OAT. Here we describe the deoxygenation of pyridine-*N*-oxides by the bis(3,5-di-*tert*-butylcatecholato)oxomolybdenum(VI) fragment. Mechanistic data indicate that this reaction takes place by nonclassical oxygen atom transfer.

Air- and moisture-stable dark purple six-coordinate adducts $MoO(3,5\text{-}DBCat)_2(L)$ containing pyridine- or 4-picoline-*N*-oxide are readily prepared by mixing 2 equiv. of 3,5-di-*tert*-butylcatechol with $MoO_2(acac)_2$ in the presence of the appropriate *N*-oxide. The same adducts also form immediately on addition of pyridine-*N*-oxide to the catecholate-bridged dimer $Mo_2O_2(3,5\text{-}DBCat)_4$,[9] as judged by NMR spectroscopy. The molecular structure of $MoO(3,5\text{-}DBCat)_2(Opic)$ (Fig. 1) confirms that the molecule adopts a *cis* geometry, like its 3,6-di-*tert*-butylcatecholate analogue[3] and the bis(amidophenoxide) complex (^{t}BuClip)MoO(3,5-lutidine).[10] This geometry has been rationalized on the basis of maximizing π-donation by allowing the catecholate *trans* to the oxo to donate into the lone dπ orbital not involved in π bonding to the oxo group. The importance of π bonding is confirmed by structural features in the *trans* catecholate that show significant transfer of electron density to Mo (metrical oxidation state (MOS)[11] = −1.56(9)), which is not observed in the *cis* catecholate (MOS = −2.16(17)).

Department of Chemistry and Biochemistry, 251 Nieuwland Science Hall, University of Notre Dame, Notre Dame, IN 46556-5670, USA. E-mail: Seth.N.Brown.114@nd.edu; Fax: +1 574 631 6652; Tel: +1 574 631 4659

† Electronic supplementary information (ESI) available: Details of syntheses, variable-temperature NMR, and kinetics experiments. CCDC 882420. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2cc33523a

This journal is © The Royal Society of Chemistry 2012

Published on 19 June 2012. Downloaded by University of California - Irvine on 31/10/2014 10:00:15.

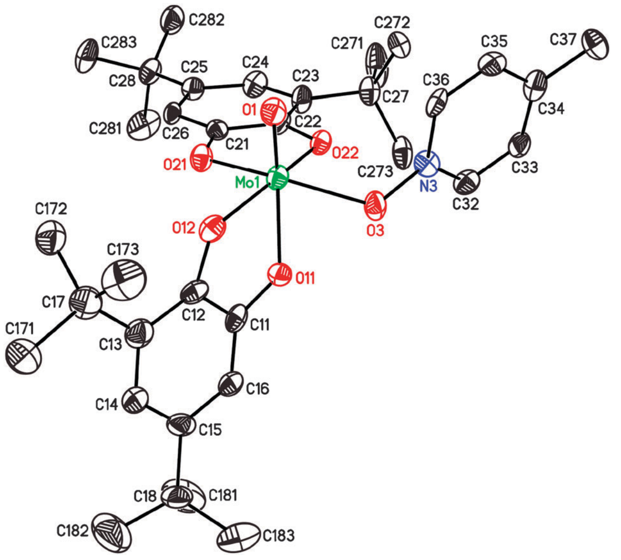
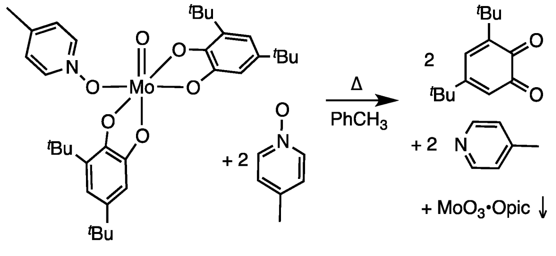


Fig. 1 Thermal ellipsoid plot of one of the two inequivalent complexes in $MoO(3,5\text{-}DBCat)_2(Opic)\cdot 1.5\ C_6H_{12}$. Selected distances (Å) and angles (°) [corresponding values for other molecule in brackets]: Mo1–O1 1.696(4) [1.689(4)], Mo1–O11 2.073(4) [2.074(5)], Mo1–O12 1.992(4) [1.994(4)], Mo1–O21 1.973(5) [1.970(5)], Mo1–O22 1.965(5) [1.950(4)], Mo1–O3 2.052(4) [2.059(4)], N3–O3 1.353(7) [1.371(7)], Mo1–O3–N3 120.7(4) [118.9(3)].

While only one of four possible stereoisomers (differing in the placement of the *tert*-butyl groups) is observed in the solid state, variable-temperature NMR studies of $MoO(3,5\text{-}DBCat)_2(Opic)$ confirm the presence of at least three stereoisomers. The isomers interconvert by Bailar ($\Delta G^\ddagger \approx 9$ kcal mol^{-1}) and Ray-Dutt ($\Delta G^\ddagger \approx 13$ kcal mol^{-1}) twists (Fig. S1, ESI†), with all isomers in rapid equilibrium at room temperature. Interchange of free and bound picoline-*N*-oxide can also be observed by dynamic NMR spectroscopy in $C_6D_5CD_3$ solution, with exchange taking place by an associative mechanism ($\Delta H^\ddagger = 7.8 \pm 0.2$ kcal mol^{-1}, $\Delta S^\ddagger = -19.1 \pm 0.5$ cal mol^{-1} K^{-1}, Fig. S2–S4, ESI†), contrasting with the dissociative mechanism observed for pyridine exchange in the bis(amidophenoxide) complex (^{t}BuClip)MoO(py).[10]

The picoline-*N*-oxide complex $MoO(3,5\text{-}DBCat)_2(Opic)$ is stable for extended periods at room temperature. However, upon heating to ~70 °C in toluene in the presence of excess picoline-*N*-oxide, the dark purple color due to the complex slowly fades and is replaced by the green color of 3,5-di-*tert*-butyl-1,2-benzoquinone according to eqn (2). *In situ* NMR spectroscopy using an internal standard confirms the production of quinone (2.07 ± 0.12 equiv.) and free 4-picoline (2.03 ± 0.09 equiv.). A total of 2.06 ± 0.06 equiv. of free 4-picoline-*N*-oxide is consumed, with 1 equiv. being deoxygenated and the second incorporated into a white solid, apparently $MoO_3\cdot$Opic,[12] which precipitates from the reaction in 81% yield.



(2)

The kinetics of reaction of $MoO(3,5\text{-}DBCat)_2(Opy)$ (in toluene in the presence of excess pyridine-*N*-oxide) have been measured by UV-visible spectroscopy, monitoring the disappearance of ligand-to-metal charge transfer bands at 500 and 800 nm. (At the low concentrations suitable for this measurement, [Mo] ≈ 1×10^{-4} mol L^{-1}, any adducts of MoO_3 remain dissolved in solution and do not scatter light appreciably.) Reactions are observed to be first-order in molybdenum, and identical results are obtained using isolated $MoO(3,5\text{-}DBCat)_2(Opy)$ or by generating the complex *in situ* from $Mo_2O_2(3,5\text{-}DBCat)_4$. Reaction rates identical within experimental uncertainty are also observed if the disappearance of $MoO(3,5\text{-}DBCat)_2(Opy)$ is monitored by ^{1}H NMR spectroscopy in toluene-d_8; the only 3,5-di-*tert*-butycatechol-containing species observed in significant concentration by ^{1}H NMR are $MoO(3,5\text{-}DBCat)_2(Opy)$ and free 3,5-di-*tert*-butyl-1,2-benzoquinone.

The observation of first-order decay indicates that the reaction is not significantly inhibited by 3,5-di-*tert*-butyl-1,2-benzoquinone or by pyridine. The lack of pyridine inhibition has been confirmed up to [py] = 0.083 mol L^{-1} (at [Opy] = 0.050 mol L^{-1}, Fig. S5, ESI†). The observed rate constant for disappearance of $MoO(3,5\text{-}DBCat)_2(Opy)$ is found to be independent of the concentration of excess Opy (0.01–0.05 mol L^{-1}), indicating that the rate-limiting step takes place from the intact pyridine-*N*-oxide adduct, which is the predominant form of the complex. Activation parameters of the reaction in toluene (62–92 °C) show a substantial activation enthalpy and a small entropy of activation ($\Delta H^\ddagger = 27.0 \pm 1.3$ kcal mol^{-1}, $\Delta S^\ddagger = +0.4 \pm 3.8$ cal mol^{-1} K^{-1}, Fig. S6, ESI†).

In order to gauge the electronic effects of the oxidant on the rate of reaction, the rates of reaction of a series of 4-substituted pyridine-*N*-oxides were compared (Fig. 2). There is a clear trend that electron-poor pyridine-*N*-oxides react faster than electron-rich ones, with a satisfactory correlation with Hammett substituent constants[13] ($\rho = +0.56$). This is qualitatively consistent with the trend seen in classical OAT from pyridine-*N*-oxides to $ReO(hoz)_2^+$ (hozH = 2-(2′-hydroxyphenyl)-2-oxazoline), though the cationic rhenium fragment is much more sensitive to *N*-oxide electronics ($\rho \approx +2.8$).[14] The enhanced rate of reaction of electron-poor pyridine-*N*-oxides is consistent with the pyridine acting as a leaving group in the rate-determining step of the reaction. A small rate acceleration is also observed on increasing the steric bulk of the pyridine, with 2,6-lutidine-*N*-oxide reacting 1.9 times faster than 4-picoline-*N*-oxide despite the greater basicity of 2,6-lutidine.[15]

Taken together, the kinetics, substituent effects, and activation parameters strongly suggest that the rate-limiting step in pyridine-*N*-oxide deoxygenation is expulsion of pyridine from the $MoO(3,5\text{-}DBCat)_2(Opy)$ complex (eqn (3)). Simultaneous expulsion of quinone and pyridine is unlikely given the modest $\Delta S^\ddagger$, pre-equilibrium loss of quinone is inconsistent with the lack of inhibition by quinone, and rate-limiting loss of quinone prior to N–O bond cleavage is difficult to reconcile with the observed substituent effects. This key step would produce, at least transiently, a dioxomolybdenum complex **1** containing two 3,5-DBCat ligands with a net 2− charge, either a pair of semiquinonates or a quinone and a catecholate ligand. (The species is depicted as the former, based on the electronic structure observed for the isoelectronic iminosemiquinonato

Published on 19 June 2012. Downloaded by University of California - Irvine on 31/10/2014 10:00:15.

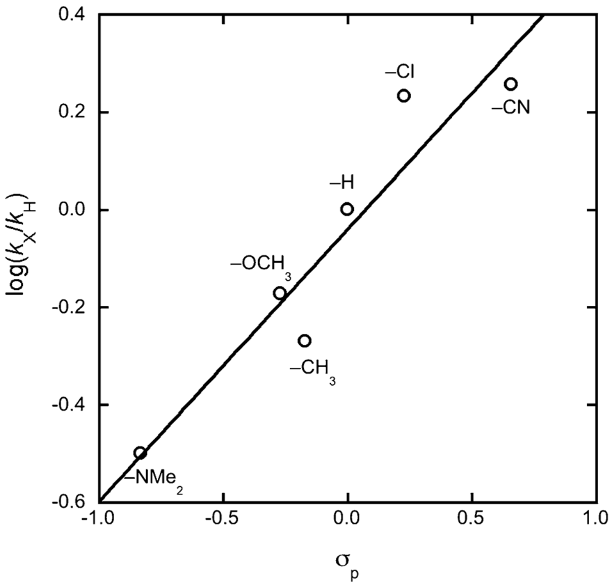
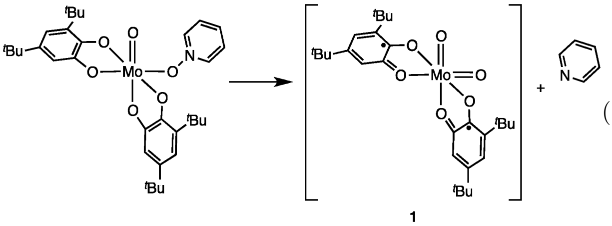


Fig. 2 Substituent effects on kinetics of reaction of $MoO(3,5\text{-}DBCat)_2(ONC_5H_4\text{-}4\text{-}X)$ in the presence of excess $4\text{-}X\text{-}C_5H_4NO$ (toluene, 79 °C).

complex $ZrCl_2(2\text{-}(^tBuN)\text{-}3,5\text{-}^tBu_2C_6H_2O)_2$,[16] but this is speculative.) Presumably **1**, once formed, rapidly dissociates quinone, and the monocatecholate species formed reacts either by disproportionation or by further oxidation by pyridine-*N*-oxide to produce MoO_3 in a kinetically invisible process.



(3)

These results indicate that a formally molybdenum(VI) species is capable of deoxygenating pyridine-*N*-oxide by a two-electron redox process where the electrons are drawn from catecholate co-ligands prior to their dissociation as quinone—in other words, a nonclassical oxygen atom transfer reaction. Given the covalency of the bonding between the *trans* catecholate and molybdenum, it can be argued that the electrons lost in the oxidation come to some extent from the molybdenum, and that the degree to which these electrons are localized on the molybdenum might well increase over the course of the reaction. Since all bonding is at least partially covalent, such arguments necessarily blur the distinction between formally "classical" and formally "nonclassical" reactions. Nevertheless, classifying this reaction as nonclassical is useful, as there can be little doubt that the electrons for the reaction are drawn substantially from the ligands, since the product **1** must have oxidized co-ligands lest the molybdenum be assigned an unreasonable oxidation state greater than +6. Finding which catecholate is more strongly engaged in the oxygen atom transfer—the *cis* catecholate, with its higher-energy filled orbital but less interaction with the molybdenum, or the less electron-rich but more delocalized *trans* catecholate—is a key question in learning what factors (redox potential or orbital overlap) are central in facilitating rapid nonclassical oxygen atom transfer. Experiments aimed at addressing this distinction, as well as those directed at producing stabilized analogues of the oxidized intermediate **1** to allow it to participate in catalytic OAT cycles, are currently in progress.

This work was supported by the US National Science Foundation (CHE-1112356). K.R. acknowledges summer fellowship support from the Notre Dame RESACC program.

Notes and references

1 (*a*) R. A. Holm and J. M. Berg, *Acc. Chem. Res.*, 1986, **19**, 363–370; (*b*) R. A. Holm, *Chem. Rev.*, 1987, **87**, 1401–1449; (*c*) M. A. Pietsch and M. B. Hall, *Inorg. Chem.*, 1996, **35**, 1273–1278; (*d*) L. M. Thomson and M. B. Hall, *J. Am. Chem. Soc.*, 2001, **123**, 3995–4002; (*e*) B. W. Kail, L. M. Pérez, S. D. Zarić, A. J. Millar, C. G. Young, M. B. Hall and P. Basu, *Chem.–Eur. J.*, 2006, **12**, 7501–7509; (*f*) J. M. Keith, Z. D. Tomić, S. D. Zarić and M. B. Hall, *J. Mol. Catal. A: Chem.*, 2010, **324**, 15–23.

2 (*a*) J. M. Mayer, *Annu. Rev. Phys. Chem.*, 2004, **55**, 363–390; (*b*) M. H. V. Huynh and T. J. Meyer, *Chem. Rev.*, 2007, **107**, 5004–5064.

3 C.-M. Liu, E. Nordlander, D. Schmeh, R. Shoemaker and C. G. Pierpont, *Inorg. Chem.*, 2004, **43**, 2114–2124.

4 (*a*) M. E. Cass and C. G. Pierpont, *Inorg. Chem.*, 1986, **25**, 122–123; (*b*) M. E. Cass, D. L. Greene, R. M. Buchanan and C. G. Pierpont, *J. Am. Chem. Soc.*, 1983, **105**, 2680–2686.

5 (*a*) A. I. Nguyen, K. J. Blackmore, S. M. Carter, R. A. Zarkesh and A. F. Heyduk, *J. Am. Chem. Soc.*, 2009, **131**, 3307–3316; (*b*) A. I. Nguyen, R. A. Zarkesh, D. C. Lacy, M. K. Thorson and A. F. Heyduk, *Chem. Sci.*, 2011, **2**, 166–169; (*c*) A. F. Heyduk, R. A. Zarkesh and A. I. Nguyen, *Inorg. Chem.*, 2011, **50**, 9849–9863.

6 C. A. Lippert and J. D. Soper, *Inorg. Chem.*, 2010, **49**, 3682–3684.

7 G. Zi, L. Jia, E. L. Werkema, M. D. Walter, J. P. Gottfriedsen and R. A. Andersen, *Organometallics*, 2005, **24**, 4251–4264.

8 W. Ren, G. Zi and M. D. Walter, *Organometallics*, 2012, **31**, 672–679.

9 R. M. Buchanan and C. G. Pierpont, *Inorg. Chem.*, 1979, **18**, 1616–1620.

10 J. A. Kopec, S. Shekar and S. N. Brown, *Inorg. Chem.*, 2012, **51**, 1239–1250.

11 S. N. Brown, *Inorg. Chem.*, 2012, **51**, 1251–1260.

12 Compare, *e.g.*, MoO_3·py: J. W. Johnson, A. J. Jacobson, S. M. Rich and J. F. Brody, *J. Am. Chem. Soc.*, 1981, **103**, 5246–5247.

13 C. Hansch, A. Leo and R. W. Taft, *Chem. Rev.*, 1991, **91**, 165–195.

14 L. D. McPherson, M. Drees, S. I. Khan, T. Strassner and M. M. Abu-Omar, *Inorg. Chem.*, 2004, **43**, 4036–4050.

15 K. Clarke and K. Rothwell, *J. Chem. Soc.*, 1960, 1885–1895.

16 K. J. Blackmore, M. B. Sly, M. R. Haneline, J. W. Ziller and A. F. Heyduk, *Inorg. Chem.*, 2008, **47**, 10522–10532.