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Deoxygenation of Nitroxyl Radicals by Oxorhenium(V) Complexes with Redox-Active Ligands

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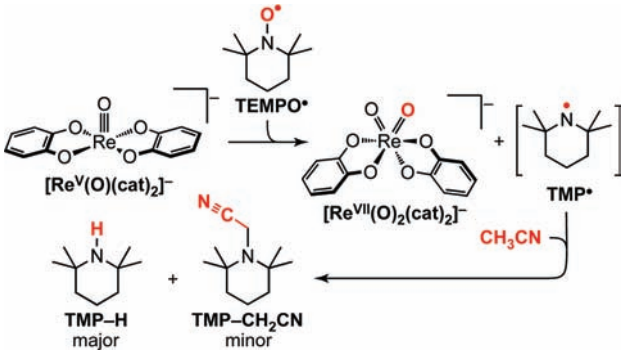
Five-coordinate oxorhenium(V) anions with redox-active catecholate ligands deoxygenate stable nitroxyl radicals, including TEMPO•, to afford dioxorhenium(VII) complexes and aminyl radical-derived products. A structural homologue with redox-inert oxalate ligands does not react with TEMPO•. Redox-active ligands are proposed to lower the kinetic barrier to TEMPO• deoxygenation by giving access to $1e^-$ redox steps that are crucial for the formation and stabilization of intermediate species.

An ability to engender $1e^-$ versus $2e^-$ redox selectivity is paramount for realizing a variety of synthetically important bond-making and -breaking redox reactions.[1] Low-coordinate oxorhenium(V) complexes are prototypical $2e^-$ redox reagents, with particular utility for mediating oxygen-atom transfer.[2,3] We speculated that coordination to a redox-active ligand may afford access to $1e^-$ redox reactions that are atypical of oxorhenium(V) complexes, while preserving the ability of the metal to mediate $2e^-$ oxo-transfer reactivity.[4] This strategy was successfully applied to bimetallic O_2 homolysis at five-coordinate oxorhenium(V) species.[5] Reported herein are remarkable $2e^-$ deoxygenation reactions of stable nitroxyl radicals by five-coordinate oxorhenium(V) anions. Kinetics studies suggest a multistep reaction mechanism, where, by analogy to the first step of O_2 activation, redox-active ligands are proposed to facilitate $1e^-$ trapping of oxygen radicals.

Scheme 1



The addition of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO•) to tan solutions containing the five-coordinate monooxo anion $[Re^V(O)(cat)_2]^-$ ([cat]$^{2-}$ = 1,2-catecholate) in CH_3CN immediately produces a dark-purple solution containing the *cis*-dioxo $[Re^{VII}(O)_2(cat)_2]^-$ complex. When the reaction is performed at 25 °C in NMR tubes containing CD_3CN, the oxidation is complete prior to acquisition of an initial spectrum (< 10 min).[6] Integration of the ^{1}H NMR resonances for $[Re^{VII}(O)_2(cat)_2]^-$ confirms the stoichiometry shown in Scheme 1. Two new methyl resonances are also observed in a 3:1 ratio. Analysis of a similarly prepared purple CH_3CN solution by gas chromatography−mass spectrometry (GC−MS) confirms that these correspond to 2,2,6,6-tetramethylpiperidine (TMP-H) and the *N*-cyanomethyl congener (TMP-CH_2CN) (Scheme 1). When the reaction is performed in CD_3CN, the molecular ion peaks increase by 1 and 2 atomic mass units, respectively, implicating the solvent in the reaction (Figures S1 and S2 in the Supporting Information, SI).

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(1) For example, see: (a) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic Press: New York, 1981. (b) *Comprehensive Organic Synthesis: Selectivity, Strategy and Efficiency in Modern Organic Chemistry, Vol. 7: Oxidation*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, U.K., 1991. (c) *Report of the Basic Energy Sciences Workshop on Solar Energy Utilization*; U.S. Department of Energy: Washington, DC, **2005**.

(2) Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401–1449.

(3) (a) Espenson, J. H. *Adv. Inorg. Chem.* **2003**, *54*, 157–202. (b) Owens, G. S.; Arias, J.; Abu-Omar, M. M. *Catal. Today* **2000**, *55*, 317–363. (c) Herrmann, W. A.; Kuhn, F. E. *Acc. Chem. Res.* **1997**, *30*, 169–180.

(4) For recent examples of redox-active ligands in bond-making and -breaking reactions at coordinatively unsaturated metals, see: (a) Blackmore, K. J.; Ziller, J. W.; Heyduk, A. F. *Inorg. Chem.* **2005**, *44*, 5559–5561. (b) Haneline, M. R.; Heyduk, A. F. *J. Am. Chem. Soc.* **2006**, *128*, 8410–8411. (c) Zarkesh, R. A.; Ziller, J. W.; Heyduk, A. F. *Angew. Chem., Int. Ed.* **2008**, *47*, 4715–4718. (d) Bart, S. C.; Lobkovsky, E.; Bill, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 5302–5303. (e) Bouwkamp, M. W.; Bowman, A. C.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 13340–13341. (f) Stanciu, C.; Jones, M. E.; Fanwick, P. E.; Abu-Omar, M. M. *J. Am. Chem. Soc.* **2007**, *129*, 12400–12401. (g) Lu, C. C.; Weyhermuller, T.; Bill, E.; Wieghardt, K. *Inorg. Chem.* **2009**, *48*, 6055–6064. (h) Smith, A. L.; Soper, J. D. *Polyhedron* **2010**, *29*, 164–169.

(5) Lippert, C. A.; Arnstein, S. A.; Sherrill, C. D.; Soper, J. D. *J. Am. Chem. Soc.* **2010**, *132*, 3879–3892.

(6) Under identical conditions, the oxidation of $[Re^V(O)(cat)_2]^-$ with 1 atm of air requires > 3 h, indicating that the observed process does not result from O_2 contamination.

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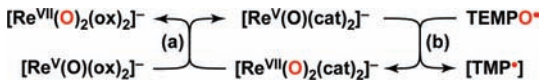
Both amine products derive from the same piperidyl radical (TMP$^{\bullet}$) intermediate. TMP-CH_2CN was previously reported from the electrochemical oxidation of TMP-H in CH_3CN and was proposed to arise from the trapping of TMP$^{\bullet}$ by $^{\bullet}CH_2CN$ (generated in situ by the net abstraction of H$^{\bullet}$ from CH_3CN).[7−9] Accordingly, performing a reaction of $[Re^{V}(O)(cat)_2]^-$ with 1 equiv of TEMPO$^{\bullet}$ in the presence of excess (13 equiv) 9,10-dihydroanthracene (DHA) as a sacrificial H$^{\bullet}$ source affords TMP-H as the only observable product by GC−MS (Figure S3 in the SI).[10]

Reactions of $[Re^{V}(O)(cat)_2]^-$ with TEMPO$^{\bullet}$ in ethanol, tetrahydrofuran, or CH_2Cl_2 all gave clean and quantitative conversion to $[Re^{VII}(O)_2(cat)_2]^-$, as evidenced by ^{1}H NMR and UV−vis spectroscopy. All of the reactions contained TMP-H as the major TEMPO$^{\bullet}$-derived organic product (65−100%), with minor species apparently arising from radical decomposition of the solvent. Clean conversion of $[Re^{V}(O)(cat)_2]^-$ to $[Re^{VII}(O)_2(cat)_2]^-$ was similarly achieved in stoichiometric reactions with the stable di-*tert*-butylnitroxyl and *tert*-amyl-*tert*-butylnitroxyl radicals. For both, a complex mixture of amine-containing organic products was observed in neat CH_3CN solutions, but reactions performed in the presence of excess DHA (10−15 equiv) gave only the expected R_2N-H products by GC−MS.

In total, the data suggest that $[Re^{V}(O)(cat)_2]^-$ efficiently abstracts an oxygen atom from nitroxyl radicals to afford $[Re^{VII}(O)_2(cat)_2]^-$ and aminyl radical transients (Scheme 1). The reaction is a 2e$^-$ oxygen-atom transfer that is reminiscent of oxo transfer from amine *N*-oxides.[5] However, this is apparently a very unusual reaction for nitroxyl radicals, such as TEMPO$^{\bullet}$,[11] which are more typically 1e$^-$ redox reagents. Because related radical Re−O bond-forming reactions proceed with the initial 1e$^-$ oxidation of a redox-active ligand,[5] we hypothesized that this reaction may be similarly sensitive to substitution of the redox-active ligand.

Structural homologues of $[Re^{V}(O)(cat)_2]^-$ were prepared by both new and previously reported methods. As detailed elsewhere,[5] $[Re^{V}(O)(OPPh_3)(Br_4cat)_2]^-$ and $[Re^{V}(O)(PPh_3)(ox)_2]^-$ ($[Br_4cat]^{2-}$ = tetrabromo-1,2-catecholate; $[ox]^{2-}$ = ethanedioate, $C_2O_4^{2-}$) have labile $OPPh_3$ and PPh_3 ligands, which make them precursors to the corresponding five-coordinate oxorhenium(V) fragments. Square-pyramidal $(Et_4N)[Re(O)(3,5\text{-}^tBu_2cat)_2]$ ($[3,5\text{-}^tBu_2cat]^{2-}$ = 3,5-di-*tert*-butylcatecholate; Figure S4 in the SI) was obtained in high yield by adaptation of a procedure for the preparation of closely related species.[5,12]

Scheme 2



The addition of 1 equiv of TEMPO$^{\bullet}$ to CH_3CN solutions containing the redox-active ligand complex $[Re^{V}(O)(3,5\text{-}^tBu_2cat)_2]^-$ or $[Re^{V}(O)(OPPh_3)(Br_4cat)_2]^-$ affords clean and quantitative conversion to the corresponding dioxorhenium(VII) products. In contrast, GC−MS analysis of CH_3CN solutions containing $[Re^{V}(O)(PPh_3)(ox)_2]^-$ and 1−3 equiv of TEMPO$^{\bullet}$ shows no TMP-H or TMP-CH_2CN over 3 days at 25 °C and < 5% TMP-H after 42 h at 70 °C. Oxidation of $[Re^{V}(O)(PPh_3)(ox)_2]^-$ by strong oxygen-atom donors, including pyridine *N*-oxide, leads to rapid decomposition to ReO_4^-,[5] so the stability of TEMPO$^{\bullet}$ in $[Re^{V}(O)(PPh_3)(ox)_2]^-$ solutions implies that the $[Re^{V}(O)(ox)_2]^-$ core does not abstract an oxygen atom from TEMPO$^{\bullet}$. We previously noted that $[Re^{VII}(O)_2(cat)_2]^-$ decomposes $[Re^{V}(O)(PPh_3)(ox)_2]^-$ by apparent oxo transfer to the $[Re^{V}(O)(ox)_2]^-$ fragment (Scheme 2a).[5] Because $[Re^{VII}(O)_2(cat)_2]^-$ is itself generated in reactions with TEMPO$^{\bullet}$ (Scheme 2b), $[Re^{V}(O)(cat)_2]^-$ mediates net oxo-group transfer from TEMPO$^{\bullet}$ to $[Re^{V}(O)(ox)_2]^-$, implying that the reaction thermodynamics are not prohibitive. The inability of $[Re^{V}(O)(PPh_3)(ox)_2]^-$ to directly deoxygenate TEMPO$^{\bullet}$ must then arise from a kinetic impediment.

The reaction of $[Re^{V}(O)(cat)_2]^-$ with TEMPO$^{\bullet}$ in a dilute CH_3CN solution is sufficiently slow to permit monitoring by UV−vis absorption spectroscopy. Under pseudo-first-order conditions ($[Re^{V}]$ = 0.15 mM; $[TEMPO^{\bullet}]$ = 1.5−6.0 mM), the concentration−time data are clearly biphasic, indicating that an intermediate species accumulates during the reaction (Figures 1 and S5 and S6 in the SI). Global iterative analysis of the full spectral window using an A → B → C integrated rate law model yields good first-order fits to both the growth and decay phases of the reaction, with two exponential equations corresponding to consecutive first-order processes. The reactions performed with varied concentrations of $[Re^{V}(O)(cat)_2]^-$ and TEMPO$^{\bullet}$ indicate that the first phase of the reaction is first-order with respect to both reactants; the rate constant for the second reaction phase shows a zero-order dependence on the TEMPO$^{\bullet}$ concentration (Figure S7 and Table S1 in the SI). The reactions of TEMPO$^{\bullet}$ with $[Re^{V}(O)(3,5\text{-}^tBu_2cat)_2]^-$ are also biphasic (Figure S8 in the SI), but analogous reactions with $[Re^{V}(O)(OPPh_3)(Br_4cat)_2]^-$ are instead fit best by an A → B → C → D rate law model (Figure S9 in the SI). The generation of $[Re^{VII}(O)_2(Br_4cat)_2]^-$ in the C → D phase occurs very slowly, but formation of the immediate precursor occurs in two phases with distinct rates (Table 1).

We tentatively rationalize these experimental observations by the two-step mechanism shown in Scheme 3. In the first reaction step, the observed first-order dependence on both reactants is consistent with the initial attack of 1 equiv of TEMPO$^{\bullet}$ on 1 equiv of $[Re^{V}(O)(cat)_2]^-$. The most common mode of TEMPO$^{\bullet}$ complexation to redox-active metal ions involves reduction to the closed-shell $[TEMPO]^-$ anion with

(7) (a) Masui, M.; Yamagata, K.; Ueda, C.; Ohmori, H. *J. Chem. Soc., Chem. Commun.* **1985**, 272–273. (b) Ohmori, H.; Ueda, C.; Yamagata, K.; Masui, M.; Sayo, H. *J. Chem. Soc., Perkin. Trans. 2* **1987**, 1065–1069.

(8) Assuming that radical combination is rapid compared to H$^{\bullet}$ abstraction from CH_3CN,[9] the consumption of 2 equiv of TEMPO to generate 1 equiv of TMP-CH_2CN and 1 equiv of TMP-H is a balanced reaction. The excess of the TMP-H product in our reactions may implicate some reaction with adventitious sources of H$^{\bullet}$.

(9) CH_3CN can be a kinetically poor H$^{\bullet}$ donor. See: (a) Roberts, B. P. *Chem. Soc. Rev.* **1999**, *28*, 25–35. (b) Tsentalovish, Y. P.; Kulik, L. V.; Gritsan, N. P.; Yurkovskaya, A. V. *J. Phys. Chem. A* **1998**, *102*, 7975–7980.

(10) The reaction of $[Re^{V}(O)(cat)_2]^-$ with 1 equiv of TEMPO$^{\bullet}$ in a 80:20 CD_3CN:CH_3CN mixture gives only the protio amine species (TMP-H and TMP-CH_2CN), as determined by analysis of their respective isotopic compositions by GC−MS. Assuming a detection limit of 10%, the selectivity of > 90% for protio products gives an estimate of the lower limit for k_H/k_D > 36, which is in excellent agreement with a reported value.[7b]

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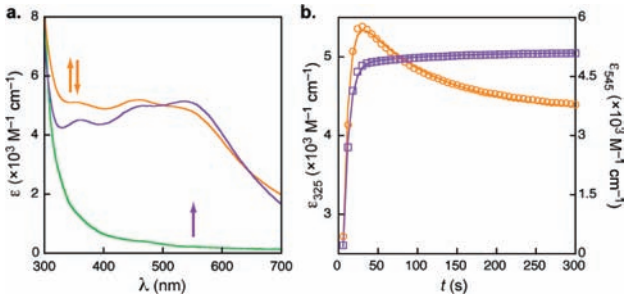


Figure 1. UV−vis absorption data for a reaction of 0.14 mM $[Re^{V}(O)(cat)_2]^-$ with 1.5 mM TEMPO• at 25 °C in CH_3CN to generate $[Re^{VII}(O)_2(cat)_2]^-$. (a) Spectra at $t = 0$ (green line), $t = 30$ s (orange line), and $t = 720$ s (purple line). (b) Time-resolved data at 325 nm (orange ○) and 545 nm (purple □). The fits (orange and purple lines) were obtained simultaneously from iterative analysis of the full spectral window (300−700 nm) using a biexponential A → B → C integrated rate law model, giving the rate constants shown in Table 1.

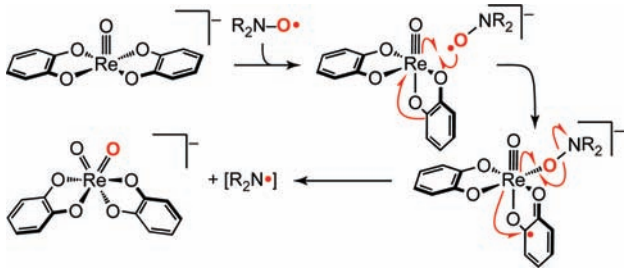
Table 1. Rate Constants for TEMPO• Oxidations of Oxorhenium(V)[a]

	k_1 (s^{-1})	k_2 (s^{-1})
$[Re^{V}(O)(cat)_2]^-$ [b]	0.14 ± 0.04	(1.3 ± 0.2) × 10^{-2}
$[Re^{V}(O)(3,5\text{-}^{t}Bu_2cat)_2]^-$ [b]	0.033 ± 0.001	(9 ± 2) × 10^{-4}
$[Re^{V}(O)(OPPh_3)(Br_4cat)_2]^-$ [c]	0.16 ± 0.03, (1.2 ± 0.6) × 10^{-3}	(1.7 ± 0.5) × 10^{-4}

[a] All reactions performed in CH_3CN at 25 °C with $[Re^{V}] = 0.14$ mM and [TEMPO•] = 1.5 mM. [b] Fit to a biexponential A → B → C integrated rate law model. [c] Fit to an A → B → C → D rate law model. The two values of k_1 are the successive rate constants for formation of the immediate precursor to $[Re^{VII}(O)_2(Br_4cat)_2]^-$, so k_2 corresponds to product formation.

concomitant $1e^-$ oxidation of the metal.[13,14] In $[Re^{V}(O)(cat)_2]^-$, this $1e^-$ could derive from either the metal center or a redox-active $[cat]^{2-}$ ligand. Attempts to isolate and further characterize the intermediate are ongoing, so the locus of oxidation is not known. However, d^1 oxorhenium(VI) complexes are comparatively rare compared to d^0 and d^2 analogues.[3a] Also, computational studies of O_2 activation at $[Re^{V}(O)(cat)_2]^-$ clearly implicate ligand-centered redox in radical Re−O bond formation.[5] By analogy, we propose this nitroxyl-binding step: (1) is accompanied by the isomerization of *trans*-$[Re^{V}(O)(cat)_2]^-$ to the cis conformer; (2) occurs with oxidation of a redox-active $[cat]^{2-}$ ligand to give a semiquinonate $[sq^•]^-$ free-radical intermediate. The reaction is completed by a second oxidation of the oxorhenium fragment, which homolyzes the nitroxyl-derived N−O bond. The dioxo product is d^0, implying that this second $1e^-$ step

Scheme 3



occurs with intramolecular reduction of the coordinated semiquinonate radical $[sq^•]^-$ ligands.[15]

The trends in the reaction rates (Table 1) do not cleanly parallel the oxidation potentials of the redox-active ligands ($[3,5\text{-}^{t}Bu_2cat]^{2-} > [cat]^{2-} > [Br_4cat]^{2-}$).[16] The comparatively slow TEMPO• deoxygenation by $[Re^{V}(O)(3,5\text{-}^{t}Bu_2cat)_2]^-$ versus $[Re^{V}(O)(cat)_2]^-$ is surprising and suggests that steric hindrance by the *tert*-butyl groups may inhibit equilibrium formation of the $[TEMPO]^-$-complex intermediate. The very slow rate of $[Re^{VII}(O)_2(Br_4cat)_2]^-$ formation is consistent with the proposed mechanism, but generation of the precursor complex is more complex. The very fast A → B phase may reflect the enhanced Lewis acidity of the $[Re^{V}(O)(Br_4cat)_2]^-$ core.[5,17] In the context of this proposed mechanism, we attribute the kinetic inertness of $[Re^{V}(O)(ox)_2]^-$ toward TEMPO• to its reluctance to undergo $1e^-$ transfer. Binding $R_2N-O^•$ to $[Re^{V}(O)(ox)_2]^-$ would require metal-centered $1e^-$ oxidation because the $[ox]^{2-}$ ligands are not redox-active.

In summary, $[Re^{V}(O)(cat)_2]^-$ and its analogues exhibit a remarkable ability to deoxygenate nitroxyl radicals, which may be a function of their capacity to undergo both ligand-centered $1e^-$ and metal-centered $2e^-$ redox reactions. Metal ions that bind TEMPO• as $[TEMPO]^-$ often cannot undergo further $1e^-$ oxidation (e.g., Ti^{III}),[13] or they have high d-electron counts that disfavor terminal oxo formation.[14] In contrast, most oxorhenium(V) complexes that mediate $2e^-$ oxo transfer do not undergo $1e^-$ transfer.[2,3a] Ongoing efforts in our laboratory are utilizing the ability of redox-active ligands to orthogonalize $1e^-$ and $2e^-$ redox reactions for redox selectivity in other reactions with small molecules.

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Supporting Information Available: Details of general experimental and synthetic procedures, GC−MS data for reactions with nitroxyl radicals, selected UV−vis spectra and kinetics data, X-ray crystal structure of $(Et_4N)[Re(O)(3,5\text{-}^{t}Bu_2cat)_2]$, and X-ray crystallographic information in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) An alternative mechanism of initial outer-sphere electron transfer can be ruled out. $[Re^{V}(O)(cat)_2]^-$ is not a strong outer-sphere reductant; quasi-reversible oxidation of $[Re^{V}(O)(cat)_2]^-$ occurs at ca. +0.04 V versus Fc^+/Fc in CH_3CN. TEMPO• is reduced at −1.48 V versus SHE in H_2O. See: (a) Hodgson, J. L.; Namazian, M.; Bottle, S. E.; Coote, M. L. *J. Phys. Chem. A* **2007**, *111*, 13595–13605.

(16) Pascaly, M.; Duda, M.; Schweppe, F.; Zurlinden, K.; Müller, F. K.; Krebs, B. *J. Chem. Soc., Dalton Trans.* **2001**, 828–837.

(17) TEMPO• can bind Lewis acids by a nonredox mechanism. See: (a) Hoffman, B. M.; Eames, T. B. *J. Am. Chem. Soc.* **1969**, *91*, 5168–5170. (b) Cohen, A. H.; Hoffman, B. A. *Inorg. Chem.* **1974**, *13*, 1484–1491.