FEATURE ARTICLE

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Swift oxo transfer reactions of perchlorate and other substrates catalyzed by rhenium oxazoline and thiazoline complexes†

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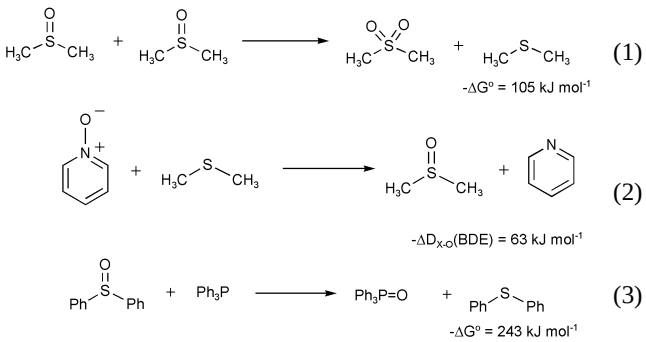
The reaction kinetics and mechanisms of catalytic oxygen atom transfer (OAT) with rhenium oxazoline and thiazoline complexes are described in this feature article. The striking features of this new family of molecular oxotransferases are their rapid kinetics and their surpassed ability in catalyzing the very difficult reduction of perchlorate by atom transfer. The diverse and competing pathways that make these catalysts efficient and practical have been delineated. Factors that govern the rates of OAT reactions have been elucidated on the basis of substrate variation, substituent and steric effects, subtle changes in the coordination environment, and geometrical transformations. This account also presents comparisons of our abiological OAT catalysis to mechanistically related enzymes and model complexes of molybdenum and tungsten.

Introduction

Atom transfer reactions between closed shell molecules rarely occur under normal conditions irrespective of the thermodynamic driving force. A good case in point is the transfer of an oxygen atom (formally a two electron redox process) from a donor to an acceptor, a reaction of extraordinary importance in both chemistry and biology.[1,2] Examples of energetically favorable oxygen atom transfer (OAT) reactions between organic molecules are plentiful; a sample of reactions that illustrate this point is given in eqns. 1–3.[3] However, none of these reactions proceeds at reasonable rates, if at all, under ambient and non-forcing conditions. The extremely slow kinetics prevents sulfoxide disproportionation to sulfide and sulfone, a thermodynamically favorable OAT process (eqn. 1), and renders sulfoxides stable indefinitely. In contrast, intermetal multi-electron atom transfer reactions are facile and have precedence in the literature.[4–7] Also, transition metal complexes have a long history of catalyzing oxidations of organic compounds.[8,9]



In biology, enzymes have evolved to address the kinetic inertness of OAT reactions involving closed shell organic molecules. There is ample evidence to support the involvement of OAT in the reactions of dimethyl sulfoxide (DMSO) reductase, sulfite oxidase, and nitrate reductase.[10–12] These enzymes contain Mo (or W, in the case of thermophilic bacteria)[13,14] that cycles between the +4 (d^2) and +6 (d^0) oxidation states during catalysis. While Mo(IV) desoxo and Mo(VI) monooxo are the players in DMSO reductase,[15,16] the sulfite oxidase family features monooxomolybdenum(IV) in the reduced state and dioxomolybdenum(VI) in the oxidized state.[2,17,18] Modeling the active sites of these molybdenum enzymes has received much attention with a focus on effecting oxo transfer from sulfoxides to tertiary phosphines.[19–24] Most of the known molybdenum model complexes are ineffective catalysts for OAT reactions because they display sluggish kinetics and deactivate *via* the irreversible formation of dimeric μ-oxo-Mo(V) species as a result of the facile reaction between $Mo^{IV}(O)$ and $Mo^{VI}(O)_2$. Concurrently, in the past decade a number of rhenium catalysts have been shown to effect OAT reactions between suitable donors and acceptors such as the examples given in eqns. 1–3 above.[25–33] Two different mechanisms have been recognized for rhenium. In one mechanism, catalysis is realized by rhenium(V) complexes acting as Lewis acids, Scheme 1, in which the oxo donor is coordinated to rhenium and hence electrophilically activated.[29,34] The other mechanism features a metal-centered oxygen transfer, Scheme 2.[28,30,32,33] It is in the latter mechanism the rhenium chemistry parallels that of molybdenum oxotransferases from a mechanistic standpoint while bypassing the kinetic inertness inherent in molybdenum coordination complexes.

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† Electronic supplementary information (ESI) available: colour versions of Figs. 3 and 4. See http://www.rsc.org/suppdata/cc/b3/b300189j/

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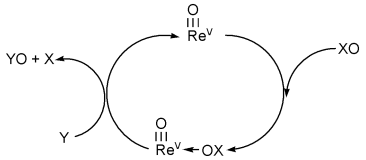
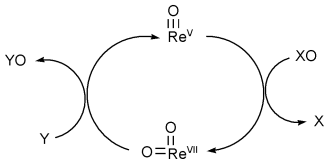
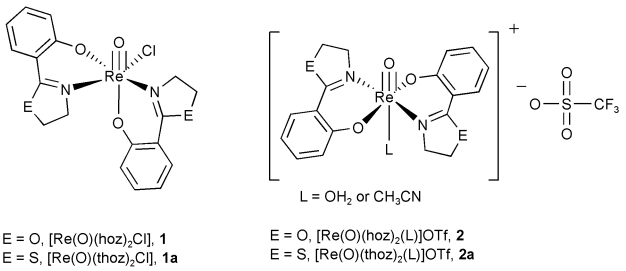


Scheme 1 Lewis acid catalyzed OAT.



Scheme 2 Metal centered OAT.

We have developed a new class of oxotransferase rhenium catalysts that contain oxazoline and thiazoline moieties as ancillary ligands, Fig. 1. The oxazoline ligand is found in the



E = O, [Re(O)(hoz)$_2$Cl], **1**
E = S, [Re(O)(thoz)$_2$Cl], **1a**

E = O, [Re(O)(hoz)$_2$(L)]OTf, **2**
E = S, [Re(O)(thoz)$_2$(L)]OTf, **2a**

Fig. 1 Rhenium oxazoline and thiozaline catalysts. Abbreviations: hoz = 2-(2′-hydroxyphenyl)-2-oxazoline, thoz = 2-(2′-hydroxyphenyl)-2-thiazoline, and OTf = trifluoromethanesulfonate.

siderophores mycobactin and agrobactin.[35,36] In some respect, the oxazoline ligand could be considered biology's answer to Schiff bases, since transition metal complexes of oxazoline are less susceptible to hydrolytic and oxidative degradation than their Schiff base analogues. Our systems have been shown to be highly effective in catalyzing OAT from several oxo donors to organic thioethers *via* a mechanism that involves $Re^{V}(O)$ in the reduced state and $Re^{VII}(O)_2$ in the oxidized state.[33,37] Thus, these rhenium catalysts are comparable in terms of their intimate mechanism and chemistry to the Mo^{IV}/Mo^{VI} couple (isoelectronic to Re^{V}/R^{VII}) in biological oxotransferases. One of the remarkable reactions of the oxazoline rhenium complexes is their surpassed ability to catalyze perchlorate reduction by pure atom transfer to chloride, which is extremely difficult kinetically, at record rates under mild conditions.[37]

Even though many thermodynamically sound reactions can be written for perchlorate (ClO_4^-), eqns. 4–6, they do not occur in solution under ambient conditions due to kinetic factors that dictate perchlorate's chemical reactivity. For example, the reduction of perchlorate to chlorate is favorable (eqn. 7), but

$$ClO_4^- \rightarrow Cl^- + 2O_2\ (g) \quad (4)$$

$$4ClO_4^- + 2H_2O \rightarrow 2Cl_2 + 7O_2 + 4OH^- \quad (5)$$

$$ClO_4^- + 8M^{2+} + 8H^+ \rightarrow Cl^- + 8M^{3+} + 4H_2O \quad (6)$$

M = 3d metals Fe, Cr, Mn, *etc*.

$$ClO_4^- + 2H^+ + 2e^- \rightarrow ClO_3^- + H_2O \quad E° = 1.23\ V \quad (7)$$

often takes place at rates that are miserably slow because ClO_4^- is nonlabile and the redox center, Cl^{VII}, is shielded by the oxygens.[38–43] Consequently, perchlorate salts are widely used to adjust ionic strength in kinetics and electrochemical studies. In the last few years, perchlorate has been recognized as an environmental contaminant in water supplies in several states in the U.S.[44] Perchlorate toxicity stems from its irreversible binding to the thyroid gland inhibiting the production of vital hormones.[45] Although the sources of perchlorate in the environment are not always identifiable, $[NH_4][ClO_4]$ is a major ingredient in rocket fuel, and military and aerospace activities have undergone scrutiny in the past few years.[46] Perchlorate poses serious challenges for remediation due to the high solubility of its salts in both aqueous and organic solvents, and due to its kinetic inertness towards reductants in solution. Therefore, typical water treatments such as precipitation, carbon adsorption, and air stripping are not effective.[44] Anion exchange and microbiological reduction of perchlorate have been the dominant areas in remediation research.[47–51] Microbes most likely utilize nitrate reductases in the reduction of perchlorate under anaerobic conditions, since perchlorate is not reduced in the presence of nitrate. Another approach to developing a practical treatment of perchlorate is the employment of chemical catalysts, since the barrier to perchlorate reduction is kinetic.

As will be shown in this article, rhenium complexes featuring the anionic phenoxy-oxazoline or -thiazoline ligand are effective oxo transfer catalysts. These systems present clean reaction chemistry that makes them ideal for quantitative studies. Fully detailed mechanisms for different oxo transfer reactions will be presented based on extensive chemical kinetics, spectroscopic identification of relevant intermediates, substrate variation, and electronic effects. The reaction kinetics and mechanisms reveal the factors that control the rate of OAT reactions. The kinetics of oxo transfer from donor substrates to our $Re^{V}(O)$ and from $Re^{VII}(O)_2$ to organic acceptors will be related and compared to other oxotransferase systems in the literature.

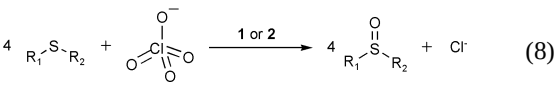
Synthesis of catalysts

The ease of catalyst preparation and its amenability to fine tuning the catalyst's physical properties are prerequisites to having a functional and useful catalyst. The oxazoline (Hhoz) and thiazoline (Hthoz) ligands employed in our catalysts are easy to make from inexpensive and commercially available starting materials at multi gram scale reproducibly in excess of 85% yield.[52,53] Furthermore, the ligands can be easily functionalized and modified (electronically and sterically), since they are synthesized from ethyl salicylate derivatives and amino alcohols; the latter is obtained by LDA reduction of amino acids. Complex **1** can be prepared from the reaction of either $Re(O)Cl_3(OPPh_3)(SMe_2)$[54] (80% yield) or $Re(O)Cl_3(PPh_3)_2$[55] (45% yield) with the free ligand in the presence of a mild base.[33] Synthesis of the rhenium thiazoline complex **1a** requires the use of $[NBu_4][Re(O)Cl_4]$[56] as a precursor.[57,58] Both complexes **2** and **2a** are made in essentially quantitative yields (~ 95%) from the metathesis of **1** and **1a**, respectively, with AgOTf.

The rhenium complexes **1–2** are air and water stable, and have a bench life of more than one year. These properties are extremely attractive because they reduce the amount of time spent on catalyst preparation and provide the researcher with greater flexibility in tailoring and exploring their catalytic chemistry. Both ^1H NMR spectra and single crystal X-ray structures of complexes **1–2** show the chloride ligand *cis* to oxo in complexes **1** and **1a**, and the solvent ligand (whether H_2O or CH_3CN) *trans* to the Re≡O bond.

Catalytic reduction of ClO_4^- and other catalytic oxo transfers

Both oxazoline rhenium catalysts **1** and **2** exhibit comparable activity in reducing perchlorate with sulfides under ambient conditions, eqn. 8, indicating that the two precursor complexes yield the same active catalytic species.[37] The stoichiometry of the reaction was established based on the yields of isolated

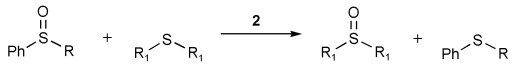


(8)

sulfoxide under conditions of limiting ClO_4^-, and addition of $AgBF_4$ at the end of reaction yields a quantitative amount of AgCl. Under steady-state conditions the rate of perchlorate reduction is independent of the nature of sulfide. Aryl and alkyl sulfides give comparable conversion rates. The catalytic kinetics is first-order in rhenium and perchlorate, shows zeroth-order dependence on [sulfide], and approaches a turnover number of 360 h^{-1} (0.10 s^{-1}). Thus, the rate-determining step (RDS) involves the reaction of perchlorate and oxorhenium(V). After a couple of hundred turnovers, the catalyst activity is significantly compromised, not due to deactivation, but rather due to product inhibition. Chloride inhibits the reaction since it competes with perchlorate for coordination on rhenium. The thiazoline rhenium complexes are comparable in their catalytic activity to the oxazoline analogues. Nevertheless, the details of their reaction kinetics do differ as will be shown in a later section.

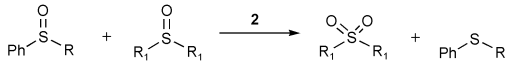
For comparison purposes, we prepared oxorhenium(V) saldmpen [*N*,*N*′-bis(salicylidene)-1,3-diamino-2,2′-dimethylpropane] and investigated its activity for perchlorate reduction.[37] Although the saldmpen complex displayed some activity, it was clearly inferior to the oxazoline complexes. For example, under conditions in which reaction 8 is complete in less than half an hour with **1** or **2** as catalyst, the oxorhenium(V) Schiff base complex required two days for 69% conversion.

Other OAT reactions that complexes **1–2** catalyze effectively are shown in eqns. 9–11.[33,58] The current list is by no means exhaustive as other reactions might be feasible, but have not yet been explored. Certainly, **1** and **2** would be efficient catalysts for OAT to organic phosphines and arsines, but these are less desirable and easier reactions to accomplish.



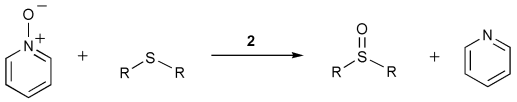
(9)

where R = Ph or Me and R_1 = akyl group



(10)

where R = Ph or Me and R_1 = akyl group



(11)

where R = akyl or aryl.

Oxo transfer from substrate

The catalytic reduction of perchlorate proceeds *via* an OAT mechanism in which the RDS is the oxidation of the rhenium(V) complex to a cationic dioxorhenium(VII) complex and the reduction of ClO_4^- to ClO_3^-. In the absence of sulfide (or a reductant), complex **2**, which is green in color, reacts with ClO_4^- to give a red compound, λ_{max} = 500 nm (ε = 1300 L mol^{-1} cm^{-1}). The kinetics of this reaction was investigated on the stopped-flow, and featured first-order dependence on [**2**] and saturation in rate with respect to [ClO_4^-], Fig. 2a. The

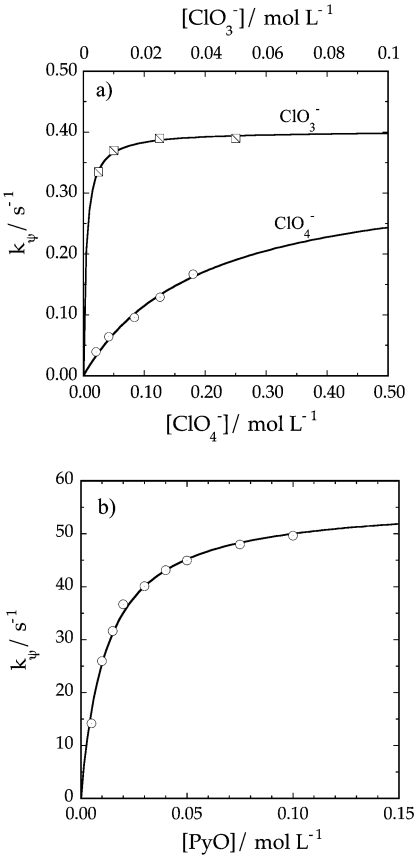
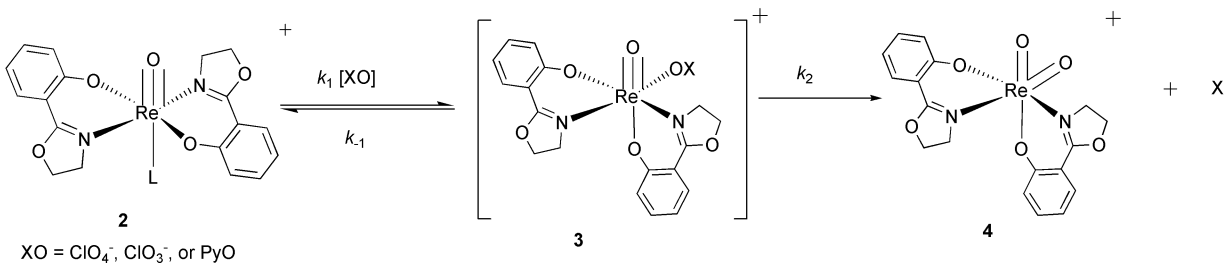


Fig. 2 Dependence of the observed rate constant on substrate concentration for the oxidation of complex **2** by (a) ClO_4^- and ClO_3^-, and (b) PyO.

reaction kinetics for other oxygen donor substrates such as ClO_3^- and pyridine *N*-oxide (PyO) also display saturation in rate, Fig. 2. It is worth noting that while rate saturation sets in at high concentrations (0.10 M) for ClO_4^-, it is clearly evident at low concentrations (0.0050 M) for ClO_3^-. Since the oxidation of **2** by ClO_3^- is faster than by ClO_4^-, the RDS in the catalytic reduction of perchlorate is the initial OAT from ClO_4^- to afford chlorate; the subsequent steps all the way to Cl^- are fast. The fact that different oxo donor substrates give different plateau values (saturation rates), Fig. 2, is in agreement with a prior equilibrium mechanism in which the oxo donor coordinates to the rhenium catalyst followed by O-atom transfer, Scheme 3 and eqn. 12.

$$\frac{d[L_2Re(O)_2]}{dt} = \frac{k_\psi}{[Re]} = \frac{nk_2[XO]}{k_{-1}/k_1 + [XO]} \qquad (12)$$

where n = stoichiometric coefficient: n = 4 for ClO_4^-, n = 3 for ClO_3^-, and n = 1 for PyO.



Scheme 3 Mechanism of oxo transfer from substrate.

The rate of OAT (k_2) for PyO is two orders of magnitude ($\sim 500\times$) faster than the values observed for the oxyanions ClO_4^- and ClO_3^-, despite the higher driving force for the oxyanions, Table 1. This is a recurring theme in metal mediated OAT reactions, and the systems presented here are no exception. Factors other than thermodynamics dictate the rate of atom transfer, namely, the accessibility of the transition state. Chlorate reacts faster with complex **2** not because it is a better oxo donor than perchlorate, but rather because it is a better ligand (Table 1). Note that the values of k_2 for both oxyanions are comparable but the values of K_1 differ significantly.

One of the most attractive features of the reaction kinetics of our rhenium oxazoline system is the separation of the oxo donor coordination step from the atom transfer event, Fig. 2 and Scheme 3. For most systems the kinetics are first-order in the transition metal complex and in the oxo donor substrate, and as a result the kinetic information is a composite of ligand substitution (oxo donor coordination to the metal center) and oxo transfer.[20,21,28] Furthermore, examples have been noted in the literature in which ligand substitution is rate determining.[19] Therefore, the rhenium oxazoline complex presents an excellent opportunity to investigate factors that affect the rate of OAT reactions. In order to understand these factors, we investigated the kinetics of OAT to complex **2** employing pyridine *N*-oxide substrates with different substituents in the *para* position, Table 1. As evident by the values of K_1 and k_2 for the different PyO substrates, an electron-donating substituent makes the PyO substrate a better ligand but an inferior oxygen donor. On the other hand, an electron-withdrawing substituent enhances the kinetics of atom transfer (k_2) but yields a weaker ligand. Therefore, from a structure–reactivity standpoint, the transition-state for OAT (k_2) features a negative charge buildup on the PyO nitrogen as the N–O bond weakens and the Re=O bond is formed. It is worth noting that the electronic effects on OAT would not have been as easily deciphered if the coordination step is not separated from the kinetics of atom transfer, see the composite second-order rate constants (K_1k_2) in Table 1.

The activation parameters in the limit of substrate saturation (k_2) were determined for ClO_3^- and *p*-CH_3-PyO (Table 1). The enthalpy of activation for both ClO_3^- and *p*-CH_3-PyO are comparable, and they are consistent with what has been measured for other OAT systems.[19,21,28,59,60] The entropy of activation values are, on the other hand, different for the two oxo donors. Oxygen atom transfer from *p*-CH_3-PyO has a $\Delta S^{\ddagger}$ of zero indicating an early transition-state that is very similar geometrically to the adduct precursor complex [Re^V–OX]. The $\Delta S^{\ddagger}$ for ClO_3^- is negative, but much smaller than previously observed for OAT reactions of rhenium and molybdenum complexes.[19,21,28,59,60] Typical values of $\Delta S^{\ddagger}$ for oxo transfer from substrates to metal complexes have been noted in the range of -80 to -140 J mol^{-1} K^{-1}. The source of the difference in $\Delta S^{\ddagger}$ for ClO_3^- and *p*-CH_3-PyO is not fully understood, except that the transition state for the ClO_3^- must involve more geometrical changes from the structure of the precursor ClO_3^- adduct than in the case of *p*-CH_3-PyO. Furthermore, our findings seem to contradict the Hammond postulate. On the basis of energetics, the reaction with ClO_3^- would be expected to have an early (or an earlier) transition state in comparison to *p*-CH_3-PyO. Therefore, the transition-state for OAT from ClO_3^- should more closely resemble the structure of the precursor complex [Re^V–$OClO_2$]. However, our results indicate the opposite.

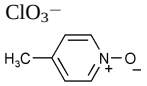
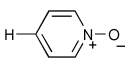
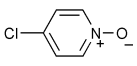
In conclusion, OAT from substrate proceeds *via* the formation of a precursor adduct [Re^V–OX], which is supported by saturation kinetics. The atom transfer step is very sensitive to electronic changes on the substrate. Electron-withdrawing substituents enhance the rate of oxo transfer (k_2) demonstrating a negative charge build up on the substrate in the transition state. The bulk of the activation barrier to oxo transfer is enthalpic, and in the case of *p*-CH_3-PyO the $\Delta S^{\ddagger}$ is zero. The factors that control the rate of OAT thus are (1) facile precursor adduct formation, (2) the resemblance of the complex [Re^V–OX] to the transition state structure, (3) and minimization of the reorganization energy required to make products from the precursor complex. The last point is especially important for reactions at low thermodynamic driving force. The reaction of PyO and complex **2** proceeds with a k_2 that is two orders of magnitude faster than k_2 for ClO_4^- and ClO_3^-, despite the lower driving force for the PyO reaction.

Relevant issues of substitution mechanism

The most significant structural reorganization along the reaction pathway takes place during the formation of the adduct complex [Re^V–OX], Scheme 3. The solvent ligand (H_2O or CH_3CN) is coordinated *trans* to the oxo ligand, and the OAT product, $(hoz)_2Re(O)_2^+$, has the two oxo ligands *cis* since its electronic configuration is d^0. Therefore, the substitution reaction with oxo donors such as ClO_4^- and PyO could give initially the *trans* adduct, which has to rearrange to *cis* prior to atom transfer. Thus, the mechanism of ligand substitution in this case would be relevant to understanding how the oxo donor adduct is formed.

Since substitution reactions of **2** follow a dissociative mechanism, we investigated the fluxional behavior of complexes **2** and **2a** by variable temperature ^{1}H NMR. The solvated complexes were found to be in dynamic equilibrium with a five-coordinate species. The coalescence temperature for the oxazoline complex **2** in CD_3CN is 263 K and the first-order rate constant (k_D) in either direction at the coalescence temperature, according to the approximate equation $k \approx \pi(\delta\nu)/\sqrt{2}$, is 200 s^{-1}. The thiazoline complex exhibits similar behavior and has a coalescence temperature of 275 K and $k_D = 160$ s^{-1}, Scheme 4. Therefore, the formation of the precursor adduct with oxygen

Table 1 Kinetics data for oxo transfer from substrate (XO) to complex **2**[a]

Oxo donor (XO)	K_1/M^{-1}	k_2/s^{-1}	K_1k_2/M^{-1} s^{-1}	$-\Delta G°_{rxn}$[b]/kJ mol^{-1}	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J mol^{-1} K^{-1}
ClO_4^-	5 ± 1	0.09 ± 1	0.45	75		
ClO_3^-	208 ± 26	0.134 ± 0.002	15	63	54 ± 1	−28 ± 3
	714 ± 60	11 ± 1	7,854	—	66 ± 2	1 ± 5
	83 ± 5	56 ± 1	4,648	(17)[c]		
	44 ± 5	154 ± 6	6,776	—		

[a] The reactions with ClO_4^- and ClO_3^- were carried out in 9 : 1 v/v CH_3CN : H_2O at 293 K, and reactions with PyO substrates were done in CH_3CN at 293 K. Activation parameters for k_2 in the limit of substrate saturation were determined over a temperature range of 278–308 K. [b] From ref. 3. [c] Estimated from BDE.

donor substrates proceeds through a five-coordinate intermediate, and the rapid kinetics of formation of this adduct facilitate OAT. In summary, it is desirable to have a stable but yet fluxional ligand system that can accommodate with ease the necessary geometrical changes for binding oxo donor substrates. It is clear from the kinetic constants that the rhenium oxazoline complex **2** is more labile than its thiazoline analogue, **2a**. However, in both cases the formation of the five-coordinate intermediate is rapid relative to the rate of oxo transfer.

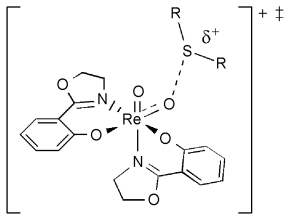
Oxo transfer to substrate

The red dioxorhenium(VII) complex **4** can be prepared *in situ* by the stoichiometric reaction of **2** with PyO. Even though **4** decomposes with water (*vide infra*), it persists for weeks in dry acetonitrile. Therefore, its reactions with organic thioethers and other substrates were investigated under pseudo-first order conditions by stopped-flow techniques. The progress of reaction was monitored at 500 nm, where complex **4** absorbs but not **2**. The second-order rate constants (k_3) for the reactions of **4** with thioether substrates and other oxygen atom acceptors are summarized in Table 2. The rate constants of oxo transfer to substrate amazingly span seven orders of magnitude over a range of > 200 kJ mol^{-1} in ΔG of reaction.

Table 2 Second-order rate constants for the oxo transfer reaction: $(hoz)_2Re(O)_2^+ + Y \rightarrow (hoz)_2Re(O)^+ + YO$

Substrate (Y)	k_3 (293 K)/L mol^{-1} s^{-1}	$-\Delta G°_{rxn}$/kJ mol^{-1}	σ_p
H_3CSCH_3	7500 ± 300	25	
$H_3CS(O)CH_3$	0.85 ± 0.05	134	
$CH_3CH_2SCH_2CH_3$	6900 ± 200		
$(CH_3)_3CSC(CH_3)_3$	1400 ± 50		
$(p\text{-}OCH_3\text{-}C_6H_4)SCH_3$	1271 ± 100		−0.27
$(p\text{-}CH_3\text{-}C_6H_4)SCH_3$	367 ± 25		−0.17
$(C_6H_5)SCH_3$	110 ± 8	16	0.00
$(p\text{-}Cl\text{-}C_6H_4)SCH_3$	2.6 ± 0.2		+0.23
$(p\text{-}CN\text{-}C_6H_4)SCH_3$	0.091 ± 0.005		+0.66
$(C_6H_5)S(C_6H_5)$	1.1 ± 0.1	8	
$(C_6H_5)_3P$	$> 10^6$	242	

The general trend of the rate constants (k_3) is indicative of electrophilic oxo transfer from **4** to the substrate. Aryl sulfides are less reactive than alkyl sulfides, and sulfides are much more reactive than the corresponding sulfoxides, which explains the high product selectivity for sulfoxide. Furthermore, only a lower limit can be put on the reaction of **4** with PPh_3, since the reaction is faster than the stopped-flow dead time. In order to probe the electronic sensitivity of OAT from complex **4**, we determined the rate constants for a few phenylmethyl sulfide derivatives containing susbtituents in the *para* position (Table 2). The structure–reactivity correlation of Hammett was employed to gain insights into the nature of the transition state.[61] The Hammett plot of $\log(k_3^H/k_3^X)$ *versus* σ_p yielded a reaction constant $\rho = -4.6 \pm 0.4$ ($R = 0.991$). The negative sign of the reaction constant indicates a positive charge buildup on the sulfur in the transition state, and is in agreement with nucleophilic attack of substrate on an electrophilic oxo ligand. The large value of ρ demonstrates that the reaction is much more sensitive to electronic variation than benzoic acid, the reference substrate for the Hammett linear free energy relationship. The origins of this conspicuous sensitivity can be attributed to the charge on complex **4** as well as the high activity of dioxorhenium(VII) species *versus* trioxorhenium complexes in which the π-bonding of three oxo ligands in the latter stabilizes the +7 oxidation state. A suggested structure of the transition state that is consistent with all experimental observations is given below.



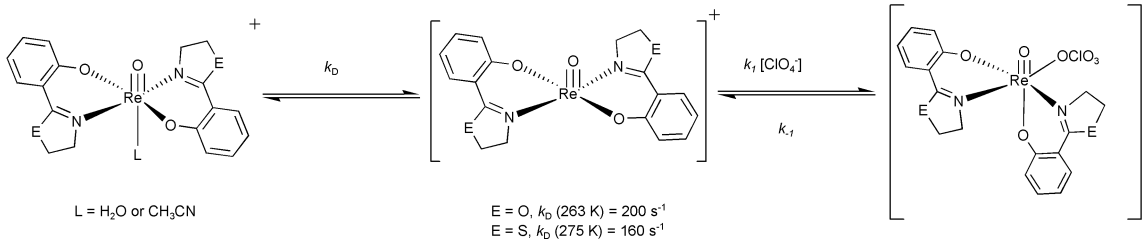
The thermodynamics of the $Re^V(O)$, **2**, and $Re^{VII}(O)_2$, **4**, couple were determined from its catalytic reactions with sulfides and sulfoxides (eqn. 9).[33] For the reaction

$$(hoz)_2Re^{VII}(O)_2 \rightarrow (hoz)_2Re^{V}(O) + 1/2O_2$$

$\Delta G°$ is ≤ 84 kJ mol^{-1}. Even though the reactions of **4** with sulfides are not exergonic, the rates of oxo transfer are swift. The transition state resemblance to the initial sulfoxido product, $(hoz)_2Re(O)(O{=}SR_2)$, is responsible for the low reorganization energy of atom transfer, and hence the fast kinetics. It is worth noting that the second-order rate constants (k_3) for sulfides are larger than K_1k_2 (apparent second-order rate constant, Scheme 3) for perchlorate reduction. Therefore, under steady-state (catalytic) conditions the formation of dioxorhenium(VII) **4** is rate-determining and the dominant form of the catalyst is rhenium(V), **2**.

The fate of the active catalyst

In the absence of an oxo acceptor (sulfide), the red dioxorhenium(VII) complex **4** hydrolyzes to $(hoz)Re(O)_3$, **5**, with first-order dependence on [Re] and [H_2O] (k_4 (293 K) = $(2.8 \pm 0.2) \times 10^{-4}$ L mol^{-1} s^{-1}).[37] Interestingly, the resulting neutral trioxorhenium(VII) is not active in OAT reactions. It neither reacts with sulfides nor with organic phosphines. The three π-donating oxo ligands stabilize the +7 oxidation state. In comparison, PPh_3 reduces the cationic dioxo complex **4** with a second-order rate constant that is $> 10^6$ L mol^{-1} s^{-1}. However, under dry conditions, complex **4** persists for days in solution, and it has been fully characterized by mass spectrometry and ^{1}H NMR. Crystallization of **4** in the glove box yielded single-crystals of a neutral amidato complex, **6**, Fig. 3, which contains a ring-opened oxazoline ligand in accordance with eqn. 13. The Re–N(2) (anionic amidato ligand) distance is 2.018(3) Å *versus* a Re–N(1) (neutral oxazoline ligand) distance of 2.272(3) Å. The C(16)–O(6) distance of the amidato ring-opened ligand is



Scheme 4 Mechanism of ligand substitution for rhenium oxazoline and thiazoline complexes.

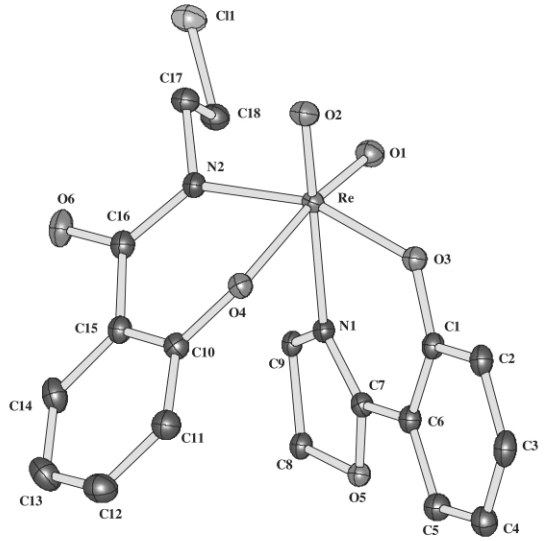
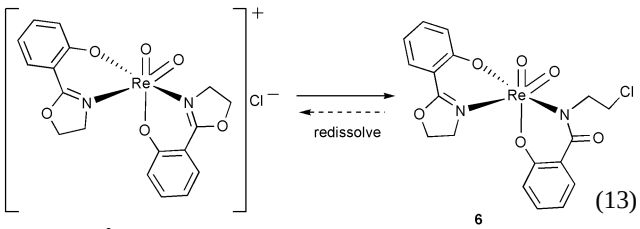


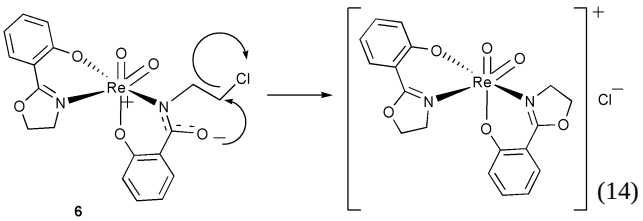
Fig. 3 Structure of dioxorhenium(VII) complex **6** showing 50% probability ellipsoids and atom labeling scheme. Hydrogen atoms are not included for clarity. Selected bond lengths (Å) and angles (°): Re–O(1) 1.717(3), Re–O(2) 1.712(3), Re–O(3) 1.917(2), Re–O(4) 1.970(2), Re–N(1) 2.272(3), Re–N(2) 2.018(3), C(16)–O(6) 1.235(4), C(16)–N(2) 1.380(5), C(17)–N(2) 1.490(4), C(18)–Cl(1) 1.794(4), C(7)–N(1) 1.286(4), C(9)–N(1) 1.485(4), C(7)–O(5) 1.332(4), C(8)–O(5) 1.470(4); O(1)–Re–O(2) 102.36(13), O(4)–Re–N(2) 83.17(11), C(17)–N(2)–C(16) 113.8(3), O(6)–C(16)–N(2) 120.5(3), Cl(1)–C(18)–C(17) 109.5(3), C(9)–N(1)–C(7) 107.3(3), N(1)–C(7)–O(5) 117.3(3), C(7)–O(5)–C(8) 106.3(3).



(13)

1.235(4) Å, which is consistent with a C=O double bond. However, some electron delocalization with the amidato nitrogen is evident in the structural data as the C(16)–N(2) distance is 1.380(5) Å *versus* a C(17)–N(2) distance of 1.490(4) Å. The latter distance is typical for a C–N single bond and the earlier distance (C(16)–N(2)) is between a single and a double bond, and similar to the C–N distance observed in aromatic rings. We also observe similar delocalization in the oxazoline ring ligands; for example, the C(7)–O(5) distance is 1.332(4) Å *versus* a C(8)–O(5) distance of 1.470(4) Å. The C(18)–Cl distance is 1.794(4) Å, which is in the expected range for a C–Cl single bond.

In order to better understand the role of **6** in catalytic oxo transfer from perchlorate, we measured the kinetics of oxo transfer from **6** to thioethers. Upon dissolution of crystalline **6** into acetonitrile, it reverted to the cationic complex **4**, eqn. 13. Even though puzzling at the offset, this observation can be understood once the synthesis of the oxazoline ligand is carefully considered. Following the reaction of ethyl salicylate with amino alcohol, the amide product is treated with thionyl chloride to replace the OH group with a better leaving group, namely, Cl. The oxazoline ring is then closed upon treatment with mild base. Therefore, the amidato ligand in complex **6** is activated for ring closure by the Lewis acidic rhenium center (eqn. 14). The X-ray structure of **6** also provides support for this ring closing mechanism as the amidato ligand shows some electron delocalization in the solid-state structure based on bond distances. The C(16)–N(2) distance is significantly shorter than C(17)–N(2) and the expected value for a C–N single bond (*vide supra*).



(14)

When sulfoxides are used as the oxygen donor, the equilibrium lies in favor of rhenium(V). Thus, even in the absence of a reductant, only diphenyl sulfoxide gives detectable amounts of dioxorhenium(VII) **4** (Ph_2S + **4** = = $Ph_2S(O)$ + **2**, K (293 K) = 27). However, it is a reasonable extrapolation given the thermodynamic values to expect that OAT from aryl sulfoxides to alkyl sulfides or sulfoxides (eqns. 9 and 10) proceed *via* the intermediacy of complex **4**.

In summary, the ring opened amidato product is not pertinent to catalyst deactivation, since its formation is slow and the resulting complex (**6**) repairs itself by reverting back to the active form of the catalyst, complex **4**. The hydrolytic decomposition pathway to give complex **5** is insignificant under steady-state conditions because the catalyst is present predominantly (≥99%) in the rhenium(V) form, which is stable indefinitely, and the rate of oxo transfer to sulfides is much faster than deactivation by water ($k_3 \gg k_4$). In fact, the only noticeable deceleration of the catalyst's activity is due to product (Cl^-) inhibition. Once chloride is removed by precipitation with $AgBF_4$, the catalyst regains full activity in successive cycles without any sign of catalyst loss even after thousands of turnovers.

Effects of ligand electronics on reactivity: thiazoline *vs*. oxazoline

Metalloenzymes utilize the second coordination sphere in their active sites to control substrate binding as well as to tune substrate activation and accessibility of the transition state.[62,63] A thiazoline analogue of oxazoline (Fig. 1) was investigated in the context of oxo transfer chemistry because it allows direct comparisons between oxygen and sulfur in the second coordination shell of rhenium. The phenoxy-thiazoline ligand chelates rhenium through the anionic phenoxide oxygen and the neutral thiazoline nitrogen (Fig. 4). The sulfur of thiazoline does not

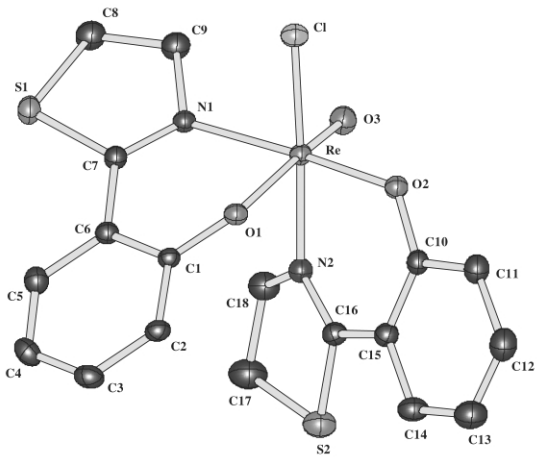


Fig. 4 Structure of rhenium(V) thiazoline complex **1a** showing 50% probability ellipsoids and atom labeling scheme. Selected bond lengths (Å) and angles (°): Re–O(3) 1.688(3), Re–Cl 2.3669(11), Re–O(1) 1.997(3), Re–O(2) 1.983(3), Re–N(1) 2.111(3), Re–N(2) 2.103(4), C(7)–N(1) 1.298(5), C(9)–N(1) 1.474(5), C(7)–S(1) 1.743(4), C(8)–S(1) 1.795(6), C(6)–C(7) 1.457(6), C(16)–S(2) 1.754(4), C(17)–S(2) 1.798(7); O(1)–Re–O(3) 165.13(15), Cl–Re–O(3) 102.62(13), N(1)–Re–O(2) 166.10(13), C(1)–O(1)–Re 127.4(2), C(7)–N(1)–Re 127.6(3).

bind to rhenium. Complex **2a**, which is green in color, reacts with perchlorate to give a red dioxorhenium(VII) complex, **4a**, similar to that observed for the oxazoline complex. The rate constant for the reaction of **2a** with ClO_4^- is less than that measured for **2** by a factor of two. Furthermore, the kinetics of the reaction of **2a** with PyO is comparable to that observed with the parent oxazoline complex **2**, Table 3. Hence, the rate of oxo

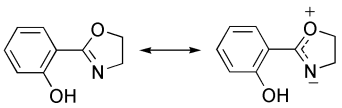
Table 3 Comparison of the kinetic constants for rhenium thiozaline *versus* oxazoline complexes[a]

Reaction	K_1/M^{-1}	k_2/s^{-1}	K_1k_2/M^{-1} s^{-1}	k_3/M^{-1} s^{-1}
Oxo transfer from substrate				
$(thoz)_2Re(O)(L)^+ + PyO \rightarrow$				
$(thoz)_2Re(O)_2^+ + Py$	32 ± 2	46 ± 1	1472	
$(hoz)_2Re(O)(L)^+ + PyO \rightarrow$				
$(hoz)_2Re(O)_2^+ + Py$	83 ± 5	56 ± 1	4648	
Oxo transfer to substrate[b]				
$(thoz)_2Re(O)_2^+ + {}^tBu_2S \rightarrow$				
$(thoz)_2Re(O)^+ + {}^tBu_2S(O)$				27000
$(hoz)_2Re(O)_2^+ + {}^tBu_2S \rightarrow$				
$(hoz)_2Re(O)^+ + {}^tBu_2S(O)$				1400
$(thoz)_2Re(O)_2^+ + PhSMe \rightarrow$				
$(thoz)_2Re(O)^+ + PhS(O)Me$				2300
$(hoz)_2Re(O)_2^+ + PhSMe \rightarrow$				
$(hoz)_2Re(O)^+ + PhS(O)Me$				110

[a] Rate constants were measured in acetonitrile at 293 K. [b] Kinetics determinations for the thiazoline complex were performed by sequential stopped-flow techniques.

transfer from substrate to rhenium is not influenced significantly by varying O to S in the oxazoline moiety; the reaction proceeds slightly slower with thiazoline than with oxazoline. However, when the kinetics of OAT from the dioxorhenium(VII) complexes, **4** *versus* **4a**, were compared, the rate of oxo transfer from the thiazoline complex **4a** was found to be 20 times faster than that measured for its oxazoline counterpart, complex **4**, Table 3. This difference is much larger than the factor of two or three observed for oxo transfer from substrate. Furthermore, $(thoz)_2Re^{VII}(O)_2^+$ (**4a**) is less stable than complex **4**, and is more susceptible to hydrolysis (k_4^{thoz} (293 K) = $(5.0 \pm 0.3) \times 10^{-3}$ compared to $k_4^{hoz} = (2.8 \pm 0.2) \times 10^{-4}$ L mol^{-1} s^{-1}).

The differences in reactivity and stability between the dioxorhenium(VII) oxazoline and thiazoline complexes can be reconciled by considering the size differences between sulfur and oxygen as well as the extent of π-electrons delocalization in the respective ring structures. Since sulfur has larger and more diffused 3p orbitals than oxygen, its ability to π-conjugate with the C=N double bond is less than that of oxygen in oxazoline, eqn. 15. This rationalization is supported by structural data on



(15)

oxazoline and thiazoline complexes. For instance, the X-ray structure of complex **1a** shows no delocalization of the C=N π-electrons with sulfur, C(7)–S(1) = 1.743(4) Å and C(8)–S(1) = 1.795(6) Å (Fig. 4). In contrast the structures of rhenium(V) oxazoline complexes as well as dioxorhenium(VII) complex **6** display significant delocalization of the π-electrons with oxygen.[33] The distance between oxygen and the sp^2 carbon (the 2 position) in the oxazoline ring is in the range 1.32–1.36 Å, which is significantly shorter than a C–O single bond and shorter than the C(sp^3)–O distance (1.45–1.48 Å) in the oxazoline ring. Therefore, the oxazoline ligand stabilizes the higher oxidation state of rhenium (+7) more effectively than thiazoline.

The possibility that the lack of stability of $(thoz)_2Re^{VII}(O)_2^+$ (**4a**) originates from ligand oxidation at sulfur was explored. No evidence of ligand oxidation was found, and addition of exogenous free ligand (Hthoz) did not affect the kinetics of decomposition and no oxidized ligand (Hthoz-SO) was recovered. Furthermore, the kinetics of decomposition of complex **4a** is first- and not second-order in rhenium.

Since the RDS in perchlorate reduction is oxo transfer from ClO_4^- to rhenium(V), the thiazoline complex (**2a**) is not a better catalyst than its oxazoline analogue (**2**), despite its enhanced rate of reaction with sulfides (oxo acceptors). On the contrary, the lower stability of the dioxorhenium(VII) thiazoline complex **4a** makes it the lesser catalyst of the two.

Rhenium *versus* molybdenum and tungsten

The parallel between the OAT mechanism of the rhenium catalysts presented here and molybdenum model oxotransferases cannot be underestimated. We shall now contrast the two related chemistries. Two drawbacks in obtaining functional OAT catalysts with molybdenum are the facile and irreversible coproportion of $Mo^{IV}(O)$ and $Mo^{VI}(O)_2$ complexes to μ-oxo-Mo^V dimers, and the sluggish kinetics of oxo transfer. Careful interrogation of the literature showed that the rates of OAT with our rhenium catalysts are 10^6–10^8 faster than those reported for the most active molybdenum and tungsten model complexes. Representative comparisons are illustrated in Table 4. The observed kinetic trends cannot be rationalized on the basis of thermodynamics. The Re^{VII}=O bond strength in complex **4**, $(hoz)_2Re(O)_2^+$, (~84 kJ mol^{-1}) is weaker than the range observed for the isoelectronic Mo^{VI}=O (134–176 kJ mol^{-1}) in enzymes and model coordination complexes.[64] Hence, based on thermodynamics oxo transfer to substrate is more favorable for rhenium, but oxo transfer from substrate should be more facile for molybdenum. Furthermore, W^{VI} is least oxidizing of the three metals and the high stability of the W^{VI}=O bond should favor its formation. However, the kinetics of oxo transfer is drastically faster for rhenium in both directions (Table 4). For example, the second-order rate constant of OAT from PyO to complex **2** (entry 6) is ~10^7 higher than that to (L-pz_3)Mo(O)(S_2PPr_2) (entry 1), and the rate of OAT to PPh_3 from **4** (entry 12) is at least 10^9 (billion times!) faster than oxo transfer from (L-pz_3)$Mo(O)_2$(S_2PPr_2) to the same substrate (entry 8).[21] While oxo transfer from $W^{VI}(O)_2$ is much slower than from $Mo^{VI}(O)_2$ analogues (entries 10 and 11), an observation that correlates well with the driving force of reaction, the kinetics of oxo transfer from substrate to W^{IV} are not always very different from the rates measured for Mo^{IV} complexes (entries 4 *vs.* 5, and 2 *vs.* 3).[24,65]

The difference in the rates of OAT reactions between rhenium and analogous systems of molybdenum and tungsten, albeit the ligands are dissimilar, is enormous spanning nine orders of magnitude. A variation of 10^9 in rate constant is comparable to the difference between a reaction that is completed in 1 h, and one that takes 100,000 years (10^9 h) under the same conditions. In other words, the difference in reactivity between rhenium and molybdenum noted herein is like comparing human and geological time scales! Over this broad range of activity, it is clearly evident from Table 4 that factors other than thermodynamics, namely, kinetics, dictate the reactivity of oxo transfer catalysts (reagents). In the case of enzymes, it is the cumulative effects of several primary and secondary shell interactions in the active site that facilitate access to transition-state conformations and hence induce a huge acceleration in the rate of reaction. In recent years, computational methods have made it possible to predict near attack conformers, which precede and resemble the enzyme's

Table 4 Rates of OAT reactions for molybdenum, tungsten, and rhenium[a]

Entry	Reaction[b]	$k/M^{-1}\ s^{-1}$	Ref.
Oxo transfer from substrate			
1	$(L\text{-}pz_3)Mo(O)(S_2PPr_2) + PyO \rightarrow (L\text{-}pz_3)Mo(O)_2(S_2PPr_2) + Py$	4.8×10^{-4}	21
2	$[(S_2C_2Me_2)_2Mo(OPh)]^- + Me_2SO \rightarrow [(S_2C_2Me_2)_2Mo(O)(OPh)]^- + Me_2S$	1.3×10^{-6}	24
3	$[(S_2C_2Me_2)_2W(OPh)]^- + Me_2SO \rightarrow [(S_2C_2Me_2)_2W(O)(OPh)]^- + Me_2S$	3.9×10^{-5}	65
4	$[(bdt)_2Mo(O)]^{2-} + Me_3NO \rightarrow [(bdt)_2Mo(O)_2]^{2-} + Me_3N$	2.0×10^{-3}	66
5	$[(bdt)_2W(O)]^{2-} + Me_3NO \rightarrow [(bdt)_2W(O)_2]^{2-} + Me_3N$	5.0×10^{-3}	66
6	$[(hoz)_2Re(O)]^+ + PyO \rightarrow [(hoz)_2Re(O)_2]^+ + Py$	4.7×10^3 (293 K)	58, 67
7	$[(thoz)_2Re(O)]^+ + PyO \rightarrow [(thoz)_2Re(O)_2]^+ + Py$	1.5×10^3 (293 K)	67
Oxo transfer to substrate			
8	$(L\text{-}pz_3)Mo(O)_2(S_2PPr_2) + Ph_3P \rightarrow (L\text{-}pz_3)Mo(O)(S_2PPr_2) + Ph_3P(O)$	2.5×10^{-4} (303 K)	21
9	$(L\text{-}NS_2)Mo(O)_2 + (p\text{-}F\text{-}C_6H_4)_3P \rightarrow (L\text{-}NS_2)Mo(O) + R_3P(O)$	9.7×10^{-3}	19
10	$[(mnt)_2Mo(O)_2]^{2-} + (MeO)_2PhP \rightarrow [(mnt)_2Mo(O)]^{2-} + (MeO)_2PhP(O)$	0.45	68
11	$[(mnt)_2W(O)_2]^{2-} + (MeO)_2PhP \rightarrow [(mnt)_2W(O)]^{2-} + (MeO)_2PhP(O)$	4.5×10^{-4}	68
12	$[(hoz)_2Re(O)_2]^+ + Ph_3P \rightarrow [(hoz)_2Re(O)]^+ + Ph_3P(O)$	$> 10^6$ (293 K)	58
13	$[(hoz)_2Re(O)_2]^+ + PhSMe \rightarrow [(hoz)_2Re(O)]^+ + PhS(O)Me$	110 (293 K)	37
14	$[(thoz)_2Re(O)_2]^+ + PhSMe \rightarrow [(thoz)_2Re(O)]^+ + PhS(O)Me$	2300 (293 K)	67

[a] Reported rate constants were measured at 298 K unless specified otherwise. [b] Abbreviations: L-pz_3 = hydrotris(3,5-dimethylpyrazol-1-yl)borate, bdt = benzene-1,2-dithiolate(2−), hoz = 2-(2′-hydroxyphenyl)-2-oxazoline, thoz = 2-(2′-hydroxyphenyl)-2-thiozaline, L-NS_2 = 2,6-bis(2,2-diphenyl-2-mercaptoethyl)pyridine(2−), mnt = maleonitriledithiolate(2−).

transition state.[69] By analogy, in molecular oxotransferase systems (both rhenium and molybdenum) structural and electronic similarities between the precursor adduct, $[M^n \leftarrow OX]$, and the transition state that leads to oxo transfer products, $M^{n+2}{=}O$, determine the nuclear and geometrical reorganization energies, which most likely define the kinetics of atom transfer.

In contrasting our molecular catalysts, it is remarkable that the reactivity of rhenium(V) oxazoline and thiazoline complexes with oxo donors (k_2^{hoz} (PyO) = 56 s^{-1}) is comparable to, and for some substrates supersedes, enzymatic activity observed for trimethylamine *N*-oxide reductase and dimethylsulfoxide reductase.[70,71] Of course, the second-order rate constants (k_{cat}/K_M) for these enzymes with various XO substrates are one to two orders of magnitude greater than that measured for our molecular catalysts (K_1k_2) due to the higher substrate affinity (low K_M) of enzymes. The involvement of non-covalent interactions and residues in the second coordination shell are responsible for the improved selectivity and substrate binding affinity in the enzymes. Thus, for a small molecular weight catalyst, our complexes exhibit truly impressive activity.

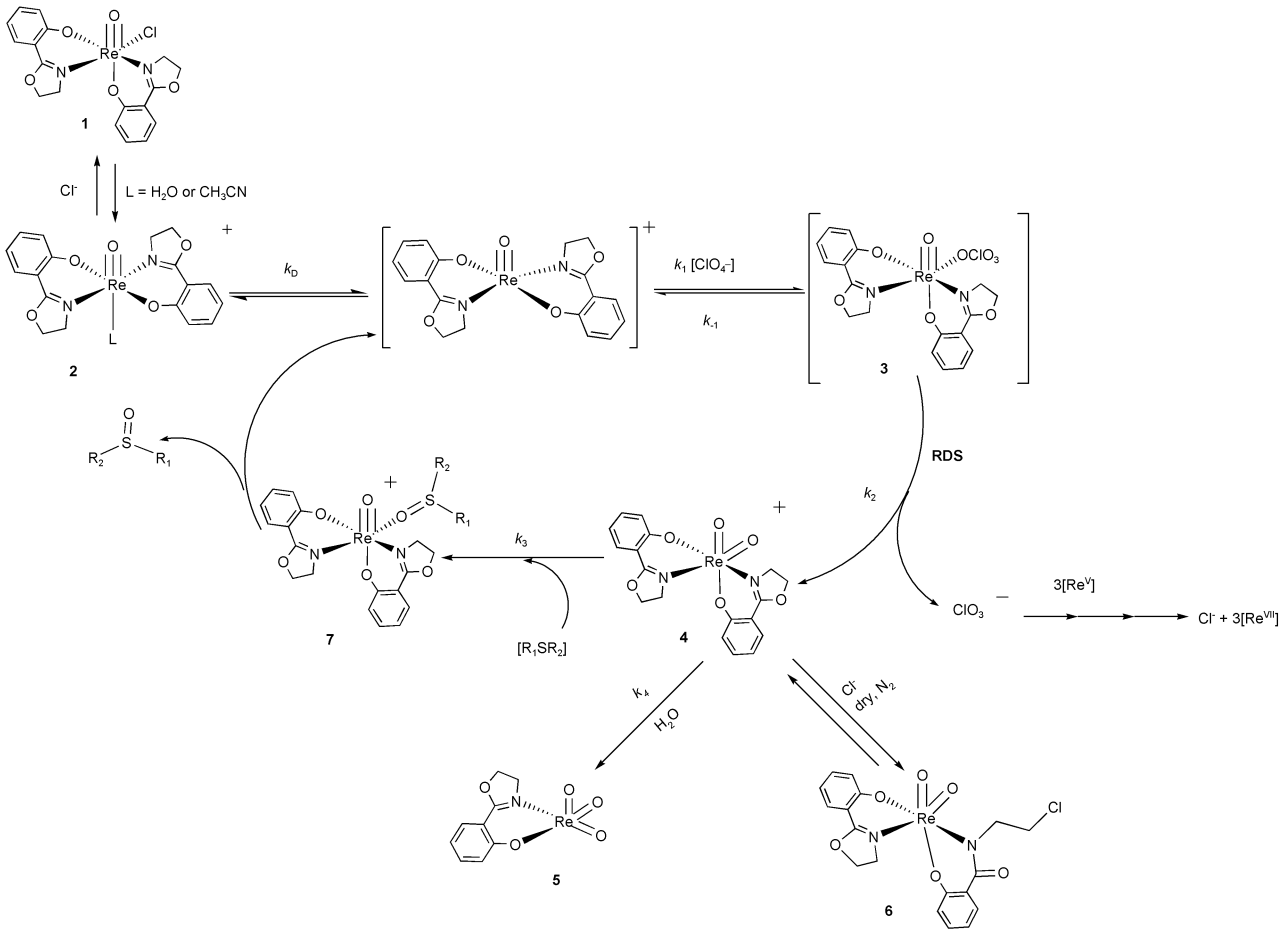
The complete picture with some future prospects

Simple rhenium oxazoline and thiazoline complexes are versatile catalysts for a variety of OAT reactions. A testament to their remarkable activity is their ability to catalyze perchlorate reduction efficiently by pure oxo transfer, an extremely challenging reaction. The kinetics of oxo transfer from substrates to give a cationic dioxorhenium(VII) as well as the kinetics from the latter (the active form of the catalyst) to acceptor substrates is impressively fast, approaching enzymatic activity. For example, the turnover rates for perchlorate and pyridine *N*-oxide reduction by rhenium(V) oxazoline catalyst **2** are 360 and 2×10^5 h^{-1}, respectively. All of the chemical transformations that have been fully characterized (chemically and kinetically) are presented in the catalytic cycle in Scheme 5 for the perchlorate reaction; similar mechanisms can be drawn for other oxo donors and acceptors. In the case of perchlorate reduction, the RDS is oxo transfer from perchlorate to form the dioxorhenium(VII) complex **4**, and the substitution kinetics of rhenium(V) complex **2** in coordinating solvents such as acetonitrile or mixtures of water and acetonitrile are rapid. In non-coordinating media such as chloroform or dichloromethane with organic oxygen donor substrates such as PyO, product dissociation (exchange of sulfoxido for PyO on rhenium) becomes rate limiting under steady-state conditions.

Chemical reduction of perchlorate under ambient conditions is very difficult and rare even with transition metal complexes. The potent reductant $Cr_{(aq)}^{2+}$ does not react with perchlorate and is totally stable in 1.0 M $HClO_4$ solution![72] As a consequence catalytic reduction of perchlorate is essentially unprecedented. Methylrhenium dioxide reduces perchlorate with a second-order rate constant that is an order of magnitude faster than that for our rhenium oxazoline complex **2**.[73] However, methylrhenium dioxide cannot be an effective catalyst for perchlorate reduction for two reasons. Methylrhenium trioxide, the product from the reaction with perchlorate, requires strong reducing agents such as organic phosphines or hypophosphorus acid to regenerate the dioxide. Secondly, under steady-state (catalytic) conditions the reduction of methylrhenium trioxide is rate controlling, and the rate constant for that reaction is slow, 3×10^{-2} L mol^{-1} s^{-1}.[28] Therefore, the reduction of ClO_4^- catalyzed by methylrhenium trioxide is more than an order of magnitude slower than by our rhenium oxazoline complex. Furthermore, the facile polymerization of methylrhenium dioxide, which renders the catalyst inactive, is another setback.

The separation of XO (oxo donor substrates) coordination to rhenium from the kinetics of atom transfer allowed us to establish structure–reactivity correlations and define the factors that control the rates of oxo transfer. Substituent variation on substrates demonstrated high electronic sensitivity of OAT in both reduction and oxidation of substrates. Minimization of nuclear reorganization is crucial in promoting OAT reactions at low driving force, and minimization of precursor adduct to product structural changes are likely responsible for the efficient kinetics. Further insights into transition-state structures along the reaction pathways can be sought by computational methods employing density functional theory (DFT). A theoretical study has appeared on the mechanism of OAT from a simplified dioxomolybdenum(VI) complex to PMe_3.[74] We have already calculated all the ground state structures presented in Scheme 5, and a promising future direction is calculating transition-state structures to better understand and accurately predict kinetic constants.[75]

The oxazoline and thiazoline ligands could be easily functionalized by straightforward organic synthesis, and thus the catalysts presented here could be easily tethered to solid



Scheme 5 The catalytic cycle and all the characterized reactions for OAT with complex **2** illustrated for the reduction of perchlorate with organic thioethers.

support or mesoporous materials, extending the catalysis to heterogeneous systems. From a practical standpoint effective heterogeneous catalysts are needed for any practical method for perchlorate destruction or for carrying out other useful oxo transfer reactions. Rhenium oxazoline and thiazoline complexes are very promising molecular oxotransferases that could be utilized in other challenging reductions and oxidations; examples would include NO_3^- and NO reduction, deoxygenation of epoxides, the use of environmentally relevant reagents such as N_2O in novel O-atom transfer reactions under mild conditions, and the oxidation of olefinic and nitrogen containing organic molecules. The use of enantiomerically pure amino alcohols in the synthesis of oxazoline ligands would allow the extension of this chemistry to asymmetric OAT reactions. Finally, incorporation of rhenium active sites into oxotransferase enzymes and contrasting their physical properties and catalytic activity with native molybdenum or tungsten proteins would be an interesting and challenging venue that will bridge our understanding of chemical and biological oxo transfer. Efforts along these general directions are currently underway in this laboratory.

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