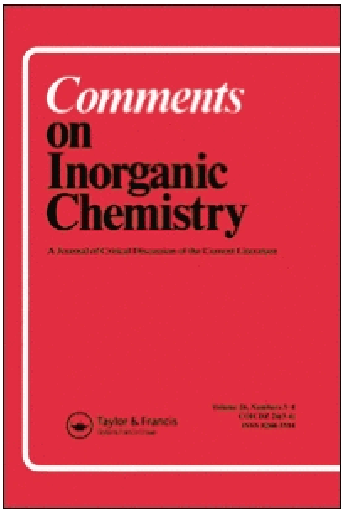
This article was downloaded by:
On: *15 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Comments on Inorganic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

Effective and Catalytic Reduction of Perchlorate by Atom Transfer-Reaction Kinetics and Mechanisms

Mahdi M. Abu-Omar

Online publication date: 24 June 2010

To cite this Article Abu-Omar, Mahdi M.(2003) 'Effective and Catalytic Reduction of Perchlorate by Atom Transfer-Reaction Kinetics and Mechanisms', Comments on Inorganic Chemistry, 24: 1, 15 — 37

To link to this Article: DOI: 10.1080/02603590390228326

URL: http://dx.doi.org/10.1080/02603590390228326

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Comments on Inorganic Chemistry, 24: 15–37, 2003
Copyright © Taylor & Francis Inc.
ISSN: 0260-3594 print
DOI: 10.1080/02603590390228326

Taylor & Francis
Taylor & Francis Group

Effective and Catalytic Reduction of Perchlorate by Atom Transfer–Reaction Kinetics and Mechanisms

Mahdi M. Abu-Omar
Department of Chemistry and Biochemistry,
University of California, Los Angeles,
Los Angeles, CA 90095-1569, USA

The reaction kinetics and mechanisms of catalytic reduction of perchlorate and chlorate ions by organic thioethers are described. Oxazoline and thiazoline oxorhenium complexes serve as efficient catalysts for the reduction of perchlorate under mild conditions by a pure oxygen atom transfer mechanism. The observed rate law features saturation kinetics with respect to oxo donor (perchlorate or chlorate) concentration. The factors that make this new family of catalytsts effective and viable have been delineated including different pathways of catalyst deactivation and inhibition. Comparisons to other transition metal complexes that do react controllably with perchlorate are presented.

INTRODUCTION

Perchlorate (ClO_4^-) holds a special place among the inorganic oxyanions in that it is weakly coordinating and when used as the counter anion with transition metal complexes it furnishes high-quality single crystals that are often difficult to obtain with other inorganic anions. However, perchlorate's most fascinating chemical property is its dual character. In aqueous media under ambient conditions, ClO_4^- is very inert, but in the solid state its salts are potentially explosive, especially in the presence of organic ligands. Ammonium perchlorate continues to be an important ingredient in propulsion systems, both as a solid oxidant when reacted with powdered aluminum as a reducing agent and as an energy booster.[1] Even though perchlorate is a reasonably strong oxidant thermodynamically (Eq. 1), its reactions in solution are very sluggish due to kinetic barriers.[2,3] Of particular interest is perchlorate's reduction by divalent transition metals (Eq. 2), which either does not occur in solution under ambient conditions or takes place at rates that are miserably slow.[4–8] As a matter of fact, Taube used $Cr_{(aq)}{}^{2+}$ solutions prepared in 1.0 M $HClO_4$ in his infamous inner-sphere electron transfer experiment with $(NH_3)_5Co^{III}Cl^{2+}$.[9,10] Despite the driving force, Cr^{2+} is stable indefinitely towards perchlorate as long as the perchlorate is free of chlorate impurities; the latter does oxidize $Cr_{(aq)}{}^{2+}$.[11,12] Even labile reductants such as Ti^{3+} react with perchlorate very slowly.[8,13] As a consequence of this kinetic inertness in aqueous solution, perchlorate salts are widely used to adjust ionic strength in kinetics and electrochemical studies.

$$ClO_4^- + 2H^+ + 2e^- \rightarrow ClO_3^- + H_2O \qquad E^\circ = 1.23\ \text{V} \tag{1}$$

$$\begin{gathered} ClO_4^- + 8M^{2+} + 8H^+ \rightarrow Cl^- + 8M^{3+} + 4H_2O \\ M = 3\text{d metals} : \text{Fe, Cr, Mn, etc.} \end{gathered} \tag{2}$$

In 1997, perchlorate was discovered in aquifers and natural waterways around the western United States.[14] Affected regions include southern California, greater Las Vegas, and northwestern Arizona (Figure 1). Since its original detection as an environmental contaminant and by 1999, environmental releases of perchlorate have been reported in many states in the Midwest and Northeast (Figure 2).[14] Although the complete sources of perchlorate in the environment are not always traceable, the majority of perchlorate contamination probably resulted from previously legal dumping of wastewater from military installations. Aerospace and military programs consume ~90% of the NH_4ClO_4 produced each year.[15] Perchlorate toxicity stems from its irreversible binding to the thyroid gland, inhibiting the production of vital hormones.[16] The proposed oral human health risk benchmark is 0.9 μg/kg-day, and it is an estimate of the amount of perchlorate, which, when ingested daily over a lifetime, is anticipated to be without adverse health effects.[14] Based on available information about the risk to human health, a provisional action level of 18 μg/L has been adopted by the state of California, which resulted in closing more than 30 wells in California.[17] In 1999, the United States Environmental Protection Agency's Office of Water concluded that there was sufficient chance for perchlorate contamination throughout the country to merit adding perchlorate to the Unregulated Contaminants Monitoring Rule (UCMR).[18]

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 toward reductants in solution.[19–21] Therefore, typical water treatments such as precipitation, carbon adsorption, and air stripping are not effective. Anion exchange and microbiological reduction of perchlorate have attracted most attention in remediation research.[22–26] Microbes most likely utilize nitrate reductases in the reduction of perchlorate under

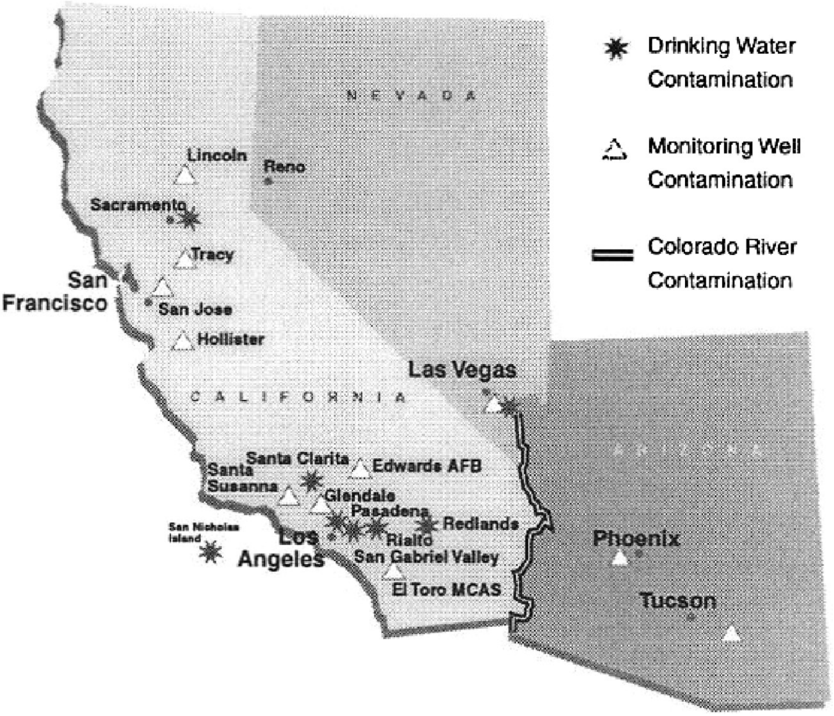


FIGURE 1 Observed perchlorate contamination in water supplies in the southwestern region of the United States (source: http://www.epa.gov/ncea/perch.htm).

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, we have developed a new class of molecular rhenium oxotransferases that contain the anionic phenoxy-oxazoline or -thiazoline as ancillary ligands (Figure 3). The oxazoline ligand is found in the siderophores mycobactin and agrobactin.[27,28] These systems are highly effective in catalyzing oxygen atom transfer (OAT) from perchlorate to organic thioethers at record rates under mild conditions and present clean reaction chemistry that makes them ideal for quantitative studies. Fully detailed mechanisms for their 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 these important OAT reactions.

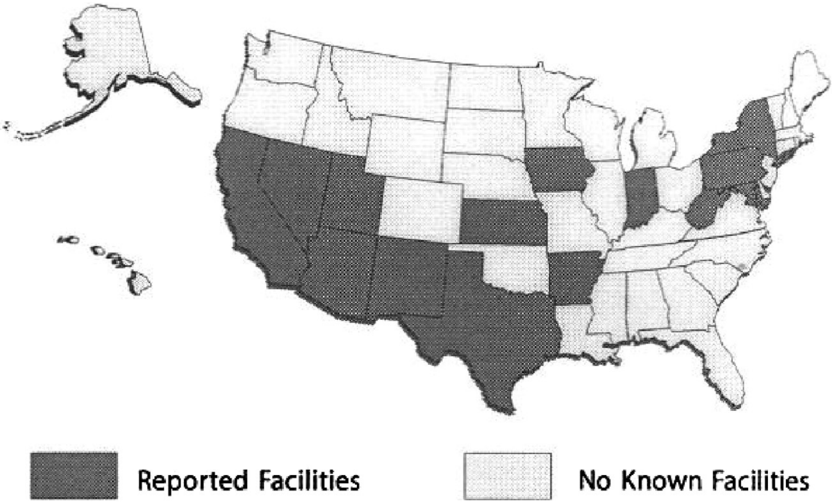
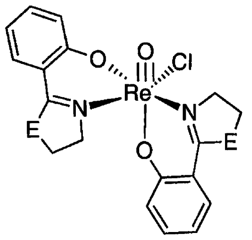


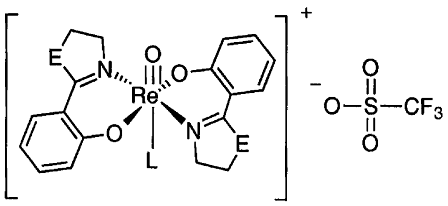
FIGURE 2 States with identified environmental releases of perchlorate (source: http://www.epa.gov/ncea/perch.htm).

SYNTHESIS OF CATALYSTS

A functional catalyst must be easy to prepare and modify. Additionally, a catalyst must be stable toward water and air, and its resting state should have a prolonged bench life. The oxazoline (Hhoz) and thiazoline (Hthoz)



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



L = OH_2 or CH_3CN

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

FIGURE 3 Rhenium oxazoline and thiozaline catalysts. Abbreviations: hoz = 2-(2'-hydroxyphenyl)-2-oxazoline, thoz = 2-(2'-hydroxyphenyl)-2-thiazoline, and OTf = trifluoromethanesulfonate.

ligands employed in our catalysts are easy to make from inexpensive and commercially available starting materials in two steps.[29,30] Furthermore, the ligands are 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. The ligands are isolated on multi-gram scale reproducibly in access of 85% yield. Two methods can be employed in the preparation of complex **1**, Eqs. 3 and 4. The use of $Re(O)Cl_3(OPPh_3)(SMe_2)$[31] affords higher yields (80%), but produces toxic dimethylsulfide as a byproduct.[32] Also, $Re(O)Cl_3(OPPh_3)(SMe_2)$ is prepared from $Re(O)Cl_3(PPh_3)_2$[33] on ~5 g scale over a period of days while $Re(O)Cl_3(PPh_3)_2$ is synthesized in quantitative yields (>95%) directly from $KReO_4$ in a one-pot synthesis at ~25 g scale in a few hours. Even though the precursor $Re(O)Cl_3(PPh_3)_2$ affords lower yields of **1**, it reduces the time and number of steps required in the synthesis. Synthesis of the rhenium thiazoline complex **1a** requires the use of $[NBu_4][Re(O)Cl_4]$ as a precursor, Eq. 5.[34] $[NBu_4][Re(O)Cl_4]$ is highly reactive with moisture, and thus the synthesis of **1a** has to be done with dry solvent under inert atmosphere. Both complexes **2** and **2a** are made in quantitative yields (~95%) from the metathesis of **1** and **1a**, respectively, with AgOTf.

$$\mathrm{Re(O)Cl_3(OPPh_3)(SMe_2) + 2Hhoz} \xrightarrow[\substack{\mathrm{EtOH,reflux,3\,h} \\ \mathrm{yield} = 80\%}]{\text{2,6-lutidene}} \mathrm{Re(O)(hoz)_2Cl + OPPh_3 + Me_2S} + 2[\mathrm{H-lutidene}]\mathrm{Cl} \tag{3}$$

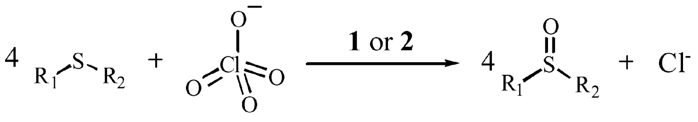
$$\mathrm{Re(O)Cl_3(PPh_3)_2 + 2Hhoz} \xrightarrow[\substack{\mathrm{EtOH,reflux,3\,h} \\ \mathrm{yield} = 45\%}]{\text{2,6-lutidene}} \mathrm{Re(O)(hoz)_2Cl + 2PPh_3 + 2[H\text{-}lutidene]Cl} \tag{4}$$

$$\mathrm{[NBu_4][Re(O)Cl_4] + 2Hthoz} \xrightarrow[\substack{\mathrm{EtOH,25^\circ C,30\ mins} \\ \mathrm{yield} = 68\%}]{\text{2,6-lutidene}} \mathrm{Re(O)(thoz)_2Cl + NBu_4Cl + 2[H\text{-}lutidene]Cl} \tag{5}$$

The rhenium complexes **1–2** are air and water stable and have a bench life of years. 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 $Re\equiv O$ bond.

CATALYTIC REDUCTION OF ClO_4^- BY PURE ATOM TRANSFER

Both oxazoline rhenium catalysts **1** and **2** exhibit comparable activity in reducing perchlorate with sulfides under ambient conditions, Eq. 6, indicating that the two precursor complexes yield the same active catalytic species.[35] The stoichiometry of the reaction was established based on the yields of isolated 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 (Table 1). Aryl and alkyl sulfides give comparable conversion rates. 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 (Table 1).[35] Although the saldmpen complex displayed some activity, it was clearly inferior to the oxazoline complexes. For example, under conditions in which reaction 6 is complete in less than half an hour with **1** or **2** as catalyst, the oxorhenium(V) saldmpen complex required two days for only 69% conversion.



(6)

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}). A typical time profile for the oxidation of thioanisole demonstrating zeroth-order dependence on [PhSMe] is shown in Figure 4.

TABLE 1. Catalytic reduction of perchlorate by organic thioethers.

		Catalyst: $Re(O)(hoz)_2Cl$ or $Re(O)(hoz)_2(OTf)$		Catalyst: Re(O) (saldmpen)Cl	
Entry	Substrate	*t*/hr.	$R_1S(O)R_2$ % yield	*t*/hr.	$R_1S(O)R_2$ % yield
1	Me_2S	2	100	48	69
2	Et_2S	2	100	48	62
3	PhSMe	2	98	48	69
4	PhSMe	6[a]	83	–	–
5	Ph_2S	4	90	38	57

Conditions: [Re] = 0.0020 M, [$LiClO_4$] = 0.10 M, [Sulfide] = 0.50 M at 20°C.
[a][LiCl] = 0.10 M

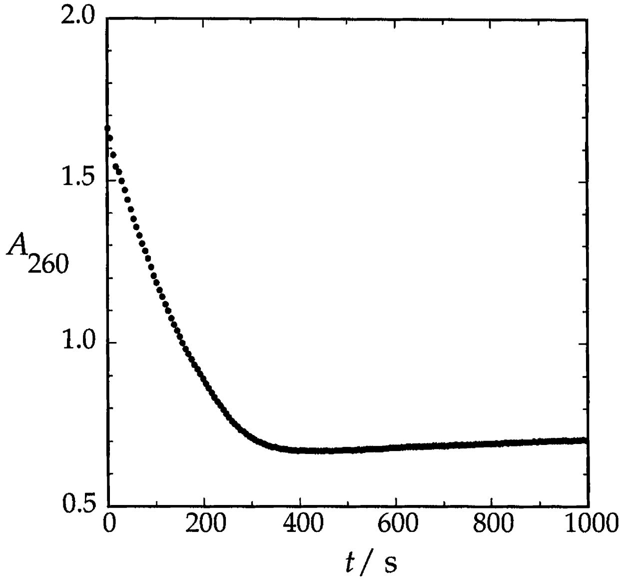


FIGURE 4 Time profile for the oxidation of thioanisole (PhSMe), monitored at 260 nm (path length 1.00 mm), with ClO_4^- as catalyzed by rhenium(V) oxazoline complex **2**. Conditions: [PhSMe] = 2.0 mM, [$LiClO_4$] = 0.020 M, [**2**] = 2.0×10^{-4} M at 293 K.

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.

KINETICS AND MECHANISM OF OXO TRANSFER FROM PERCHLORATE

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, $\lambda_{max} = 500$ nm. The kinetics of this reaction was investigated on the stopped-flow and featured first-order dependence

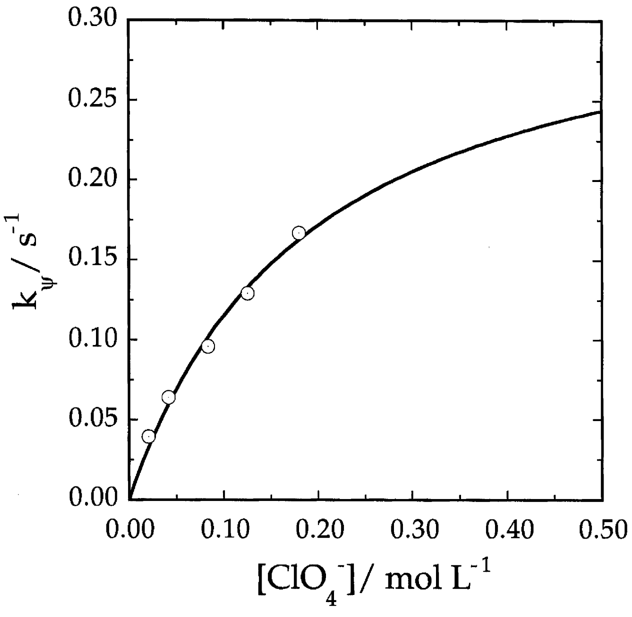


FIGURE 5 Dependence of the observed rate constant on perchlorate concentration for the oxidation of complex **2**.

on (**2**) and saturation in rate with respect to $[ClO_4^-]$, Figure 5. The reaction kinetics for OAT from ClO_3^- also display saturation in rate, Figure 6. 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 plateau values (saturation rates) are observed is in agreement with a prior equilibrium mechanism in which the oxo donor anion coordinates to the rhenium catalyst followed by O-atom transfer, Scheme 1 and Eq. 7.

$$\frac{d[L_2Re(O)_2]}{dt} = \frac{k_\psi}{[Re]} = \frac{nk_2[ClO_n^-]}{\frac{k_{-1}}{k_1} + [ClO_n^-]} \tag{7}$$

Other organic oxygen donor substrates such as PyO react with complex **2** to give dioxorhenium(VII), and feature saturation kinetics with k_2 values that are approximately two orders of magnitude faster than that observed for ClO_4^-. The rate constants alongside the driving force for the oxygen atom

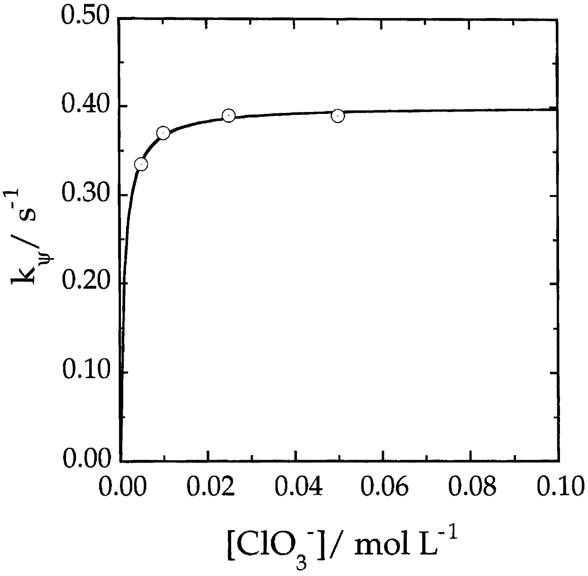
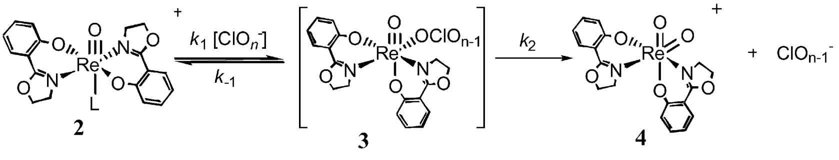


FIGURE 6 Dependence of the observed rate constant on chlorate concentration for the oxidation of complex **2**.

transfer reactions for ClO_4^- and ClO_3^- are summarized in Table 2. 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 2). Note that the values of k_2 for both oxyanions are comparable but the values of K_1 differ significantly. The temperature dependence of OAT (k_2) was determined for ClO_3^- in the limit of substrate saturation (Table 2). The enthalpy of activation for ClO_3^- is consistent with what has been measured for other OAT systems.[36–40] The entropy of activation, however, is much smaller than previously observed for OAT reactions of rhenium and molybdenum complexes.[36–40] Typical values of $\Delta S^\ddagger$ for oxo transfer from substrates to metal complexes have been noted in the range of -80 to $-140\,\mathrm{J\,mol^{-1}\,K^{-1}}$. $\Delta S^\ddagger$ for ClO_3^- is only



SCHEME 1 Mechanism of oxo transfer from oxyanions of chlorine.

TABLE 2 Kinetics data for oxo transfer from substrate ClO_4^- and ClO_3^- 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}	$\Delta H^‡$/kJ mol^{-1}	$\Delta S^‡$/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

[a] The reactions with ClO_4^- and ClO_3^- were carried out in 9:1 v/v CH_3CN:H_2O 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 reference [48].

−28 J mol^{-1} K^{-1}, which indicates minor geometrical changes in the transition-state from the adduct precursor complex [Re^V-$OClO_2$].

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. 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.[39–41] Furthermore, in some instances ligand substitution is rate determining.[38]

The most significant structural reorganization along the reaction pathway takes place during the formation of the adduct complex [$L_2(O)Re^V$-$OClO_{n-1}$], Scheme 1. The solvent ligand (H_2O or CH_3CN) is coordinated trans to the oxo ligand, and because of its electronic configuration (d^0), the OAT product is *cis*-$(hoz)_2Re(O)_2^+$. Therefore, the substitution reaction with oxo donors such as ClO_4^- and ClO_3^- could give initially the trans adduct, which has to rearrange to *cis* prior to atom transfer. That possibility is less favored on the basis that most ligands (for example, Cl^- and $O = PR_3$) other than solvent molecules coordinate *cis* to the $Re \equiv O$ bond. 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 ^1H NMR. The solvated complexes were found to be in dynamic equilibrium with five coordinate species, Figure 7. 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 $k \approx \pi(\delta v)/\sqrt{2}$, 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 2. Therefore, the formation of the precursor adduct

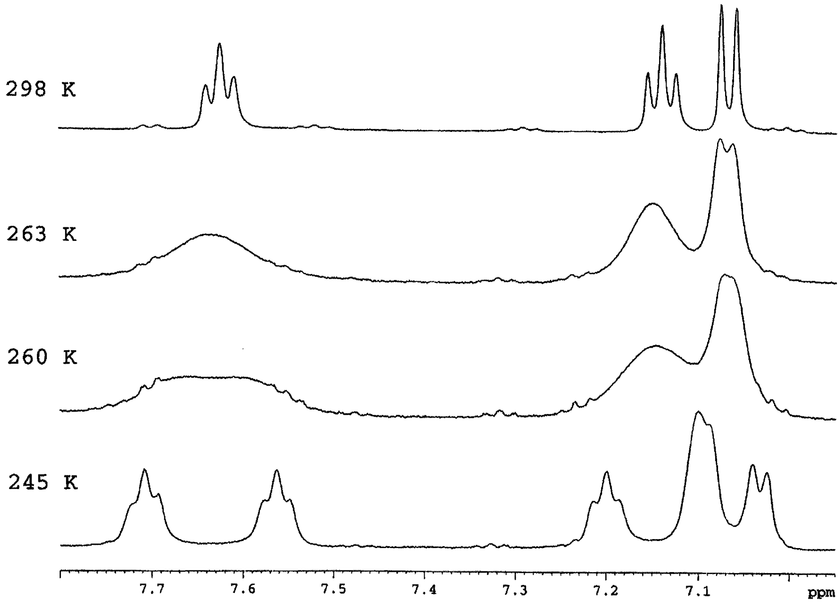
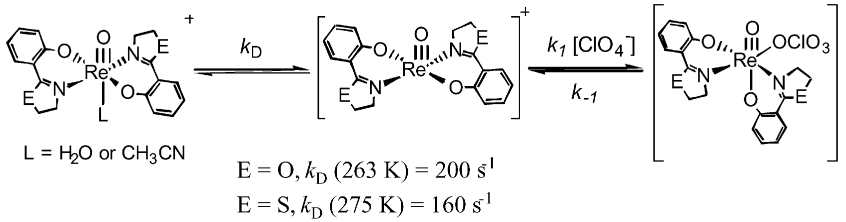


FIGURE 7 Variable temperature ^1H spectra of complex **2** in CD_3CN showing the aromatic region.

with oxygen 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 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 fast relative to the rate of oxo transfer.



L = H_2O or CH_3CN

E = O, k_D (263 K) = 200 s^{-1}

E = S, k_D (275 K) = 160 s^{-1}

SCHEME 2 Mechanism of ligand substitution for rhenium oxazoline and thiazoline complexes.

In conclusion, OAT from ClO_4^- proceeds via the formation of a precursor adduct $[L_2(O)Re^{V}\text{-}OClO_3]$, which is supported by saturation kinetics. The bulk of the activation barrier to oxo transfer is enthalpic. The factors that control the rate of OAT are facile precursor adduct formation, the resemblance of the adduct precursor complex to the transition state structure, and minimization of the reorganization energy required to make products from the precursor complex.

KINETICS AND MECHANISM OF OXO TRANSFER FROM DIOXORHENIUM(VII), THE ACTIVE CATALYST

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 on the stopped-flow. The progress of reaction was monitored at 500 nm, where complex **4** absorbs but not **2**. Another method of following oxo transfer to substrate from **4** that verifies the integrity of complex **4** is employing sequential mixing on the stopped-flow. A stoichiometric amount of PyO and **2** were mixed to allow for complete formation of dioxorhenium(VII) followed by the addition of excess sulfide (or other O-acceptor) after a programmed time delay. In this second method, the formation of **4** is followed to completion, and it is reacted immediately with substrate. The values from both methods were in total agreement. The second-order rate constants (k_3) for the reactions of **4** with thioether substrates are summarized in Table 3. The rate constants of oxo transfer to substrate amazingly span seven orders of magnitude over a range of $>200\,\text{kJ mol}^{-1}$ in driving force.

TABLE 3 Second-order rate constants for the oxo transfer reaction: $(hoz)_2\text{-}Re(O)_2{}^+ + Y \rightarrow (hoz)_2Re(O)^+ + YO$.

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	

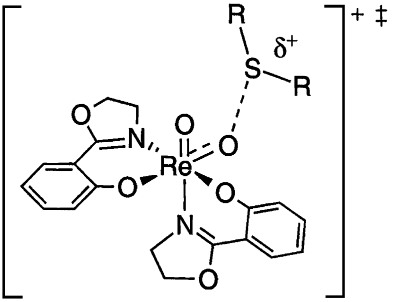


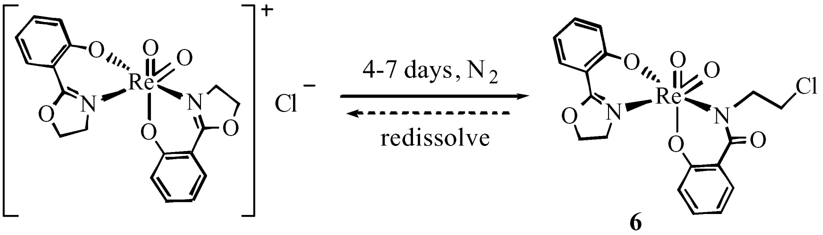
FIGURE 8 Transition-state structure of oxygen atom transfer to substrate.

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. 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 3). The structure-reactivity correlation of Hammett was employed to gain insights into the nature of the transition state.[42] The 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. A proposed structure of the transition state is given in Figure 8.

THERMODYNAMIC CONSIDERATIONS AND DEACTIVATION OF THE CATALYST

The thermodynamics of the $Re^{V}(O)$, **2**, and $Re^{VII}(O)_2$, **4**, couple have been determined by means of thermodynamic cycles.[32] For the reaction $(hoz)_2Re^{VII}(O)_2 \rightarrow (hoz)_2Re^{V}(O) + 1/2O_2$, ΔG° is $\leq 84\,kJ\ mol^{-1}$. Even though the reactions of **4** with sulfides are not exergonic, the rates of oxo transfer are fast. 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 1 and Table 2) for perchlorate reduction. Therefore, under steady-state (catalytic) conditions the formation of dioxorhenium(VII) **4** is rate-determining (Figure 4 shows zero-order dependence in [sulfide]) and the dominant form of the catalyst is rhenium(V), **2**.

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 ± 0.2] × 10^{-4} L mol^{-1} s^{-1}).[35] 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. However, under dry conditions, complex **4** persists for days, and it has been fully characterized by mass spectrometry and ^{1}H NMR. Crystallization of **4** in the glove box yielded single crystals after a few days of a neutral amidato complex, **6**, Figure 9, which contains a ring-opened oxazoline ligand in accordance to Eq. 8. The Re-N(2) (anionic amidato ligand) distance is 2.018(3) Å versus an 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 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 C(17)-N(2) distance of 1.490(4). The latter distance is typical for C-N single bond and the earlier distance (C[16]-N[2]) is between a single and a double bond, and similar to 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 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.



(8)

In order to better understand the role of **6** in catalytic oxo transfer from perchlorate, we decided to measure the kinetics of oxo transfer from **6** to thioethers. Upon dissolution of crystalline **6** into acetonitrile, it reverted to the cationic complex **4**, Eq. 8. Even though puzzling at the offset, this observation can be understood in light of the synthesis of the oxazoline ligand. 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. The X-ray structure of **6** also provides support for this ring closing mechanism as the amidato ligand shows

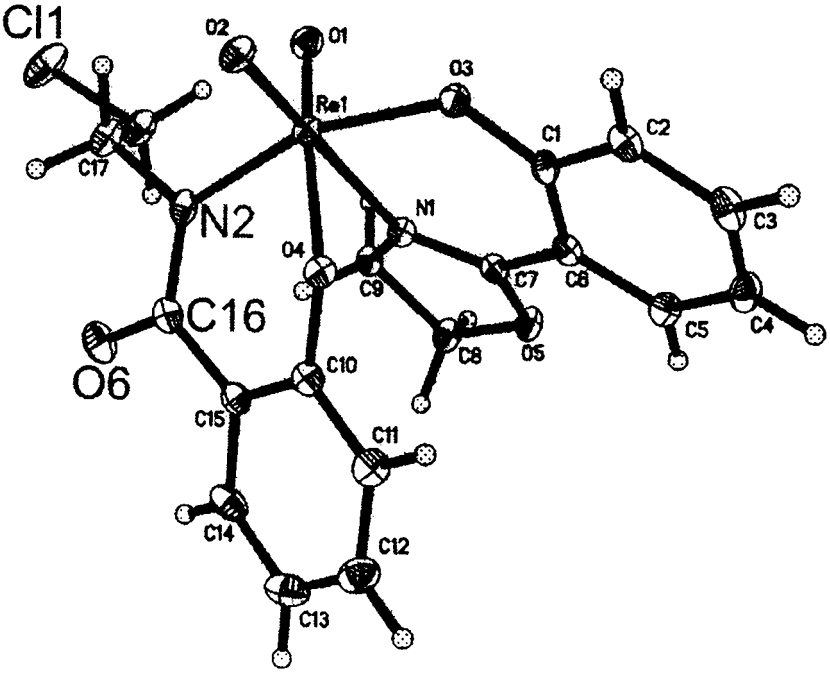
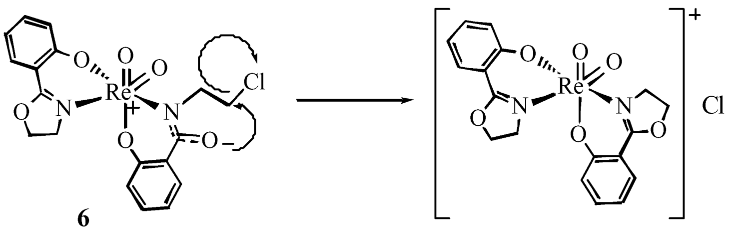


FIGURE 9. Structure of dioxorhenium(VII) complex **6** showing 50% probability ellipsoids and atom labeling scheme. Selected bond lengths (Å) and angles (°): Re-O1 = 1.717(3), Re-O2 = 1.712(3), Re-O3 = 1.917(2), Re-O4 = 1.970(2), Re-N1 = 2.272(3), Re-N2 = 2.018(3), C16-O6 = 1.235(4), C16-N2 = 1.380(5), C17-N2 = 1.490(4), C18-Cl1 = 1.794(4), C7-N1 = 1.286(4), C9-N1 = 1.485(4), C7-O5 = 1.332(4), C8-O5 = 1.470 (4), O1-Re-O2 = 102.36(13), O4-Re-N2 = 83.17(11), C17-N2-C16 = 113.8(3), O6-C16-N2 = 120.5(3), Cl-C18-C17 = 109.5(3), C9-N1-C7 = 107.3(3), N1-C7-O5 = 117.3(3), and C7-O5-C8 = 106.3(3).

some electron delocalization in the solid-state structure. 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*), Figure 9 and Eq. 9.



6

(9)

The ring opened amidato product is not pertinent to catalyst deactivation, since it takes place over a period of days 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 ($\geq 99\%$) in the rhenium(V) form, which is stable indefinitely, and the rate of oxo transfer to sulfides is much faster than deactivation by water ($k_3 >> k_4$). In fact, the only noticeable deceleration 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.

COMPARATIVE KINETICS OF S VERSUS O IN THE SECOND COORDINATION SHELL: THIAZOLINE VS. OXAZOLINE

Metalloenzymes utilize non-covalent interactions in their active sites to control substrate binding as well as to tune substrate activation and accessibility of the transition state.[43,44] Thiazoline analogue of oxazoline (Figure 3) was investigated in the context of oxo transfer chemistry because it allows direct comparisons between oxygen and sulfur in the second coordination sphere of rhenium. Both thiazoline complexes **1a** and **2a** were successfully synthesized and fully characterized (^{1}H NMR, MS, x-ray, and elemental analysis). The phenoxy-thiazoline ligand chelates rhenium through the anionic phenoxide oxygen and the neutral thiazoline nitrogen (Figure 10). The sulfur of thiazoline does not 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. However, when the rate 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 4. 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 understood 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, Eq. 10. This rationalization is supported by structural data on oxazoline and thiazoline

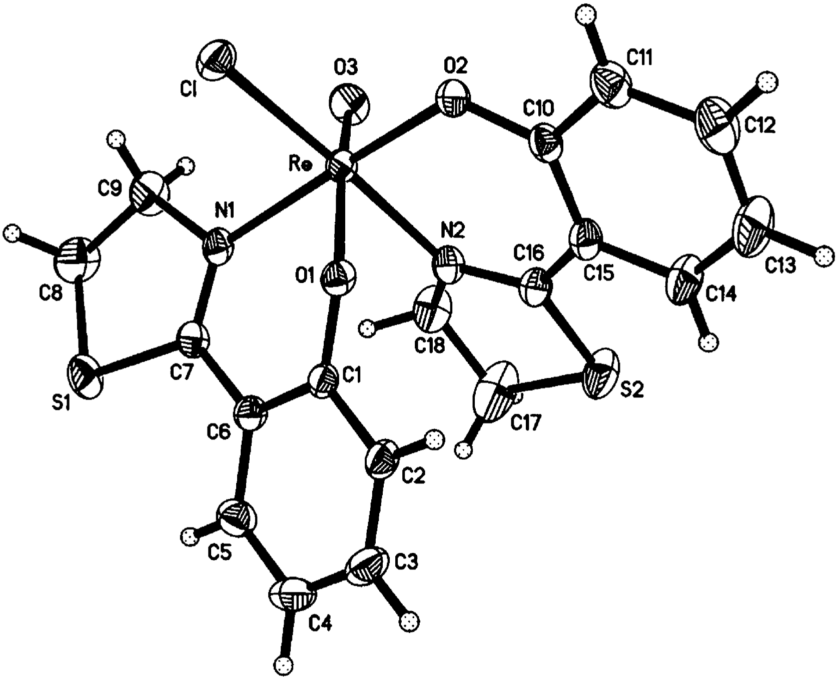


FIGURE 10 Structure of rhenium(V) thiazoline complex **1a** showing 50% probability ellipsoids and atom labeling scheme. Selected bond lengths (Å) and angles (°): Re-O3 = 1.688(3), Re-Cl = 2.3669(11), Re-O1 = 1.997(3), Re-O2 = 1.983(3), Re-N1 = 2.111(3), Re-N2 = 2.103(4), C7-N1 = 1.298(5), C9-N1 = 1.474(5), C7-S1 = 1.743(4), C8-S1 = 1.795(6), C6-C7 = 1.457(6), C16-S2 = 1.754(4), C17-S2 = 1.798(7), O1-Re-O3 = 165.13(15), Cl-Re-O3 = 102.62(13), N1-Re-O2 = 166.10(13), C1-O1-Re = 127.4(2), and C7-N1-Re = 127.6(3).

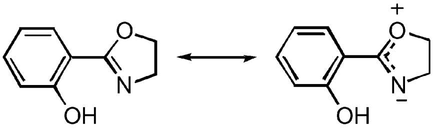
TABLE 4 Comparison of the kinetic constants for rhenium thiazoline versus oxazoline complexes.[a]

Reaction[b]	k_3/M^{-1} s^{-1}
$(\mathrm{thoz})_2\mathrm{Re(O)}_2{}^+ + {}^t\mathrm{Bu}_2\mathrm{S} \rightarrow (\mathrm{thoz})_2\mathrm{Re(O)}^+ + {}^t\mathrm{Bu}_2\mathrm{S(O)}$	27,000
$(\mathrm{hoz})_2\mathrm{Re(O)}_2{}^+ + {}^t\mathrm{Bu}_2\mathrm{S} \rightarrow (\mathrm{hoz})_2\mathrm{Re(O)}^+ + {}^t\mathrm{Bu}_2\mathrm{S(O)}$	1400
$(\mathrm{thoz})_2\mathrm{Re(O)}_2{}^+ + \mathrm{PhSMe} \rightarrow (\mathrm{thoz})_2\mathrm{Re(O)}^+ + \mathrm{PhS(O)Me}$	2300
$(\mathrm{hoz})_2\mathrm{Re(O)}_2{}^+ + \mathrm{PhSMe} \rightarrow (\mathrm{hoz})_2\mathrm{Re(O)}^+ + \mathrm{PhS(O)Me}$	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.

complexes. For instance, the x-ray of complex **1a** (Figure 10) shows no delocalization of the C = N π-electrons with sulfur, C(7)-S1 = 1.743(4) Å and C(8)-S1 = 1.795(6) Å. In contrast the structures of rhenium(V) oxazoline complexes as well as dioxorhenium(VII) complex **6** (see Figure 5 above) display significant delocalization of the π-electrons with oxygen. 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.



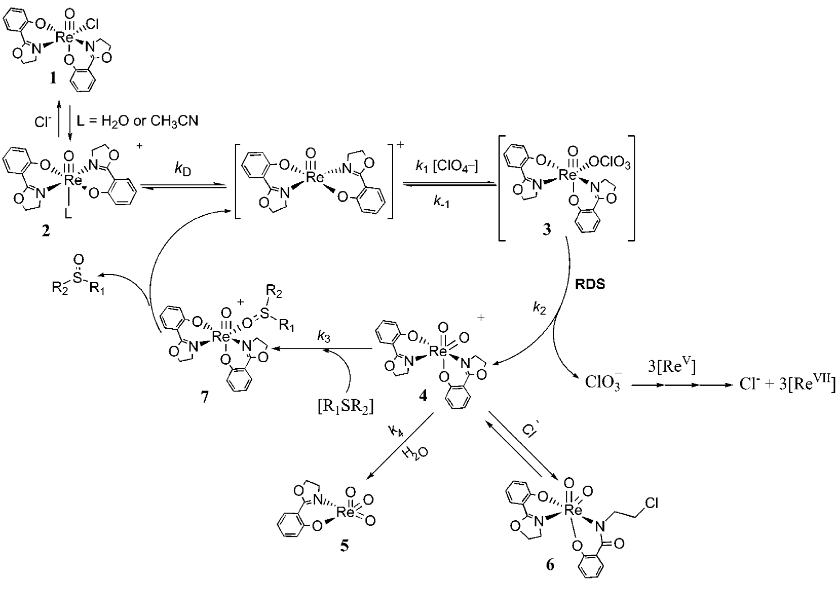
(10)

The possibility that the lack of stability of (thoz)$_2$Re^{VII}(O)$_2$$^+$ (**4a**) is originating 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-order 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 thioether substrates (oxo acceptors). On the contrary, the lower stability of the dioxorhenium(VII) thiazoline complex **4a** makes it the inferior catalyst of the two.

THE FULL CATALYTIC MECHANISM, SOME COMPARISONS TO OTHER TRANSITION METAL COMPLEXES, AND FUTURE DIRECTIONS

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. For example, the turnover rate for perchlorate reduction by rhenium(V) oxazoline catalyst **2** is 360 h^{-1}. All of the chemical transformations that have been fully characterized (chemically and kinetically) are presented in the catalytic cycle in Scheme 3. The RDS is oxo transfer from perchlorate to form the dioxorhenium(VII) complex **4**, and



SCHEME 3 The catalytic cycle and all the characterized reactions for OAT with complex **2** illustrated for the reduction of perchlorate with organic thioethers.

the substitution kinetics of rhenium(V) complex **2** in coordinating solvents such as acetonitrile or mixtures of water and acetonitrile are rapid.

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![11] As a consequence, catalytic reduction of perchlorate is rare. However, there are few examples of certain transition metal complexes that do react with perchlorate in a controlled fashion even in dilute solutions. Table 5 presents a list of these metal complexes and their rate of reaction with perchlorate and chlorate ions. It is evident from Table 5 that the rate of reaction is not dictated by the thermodynamic driving force of reaction as evidenced by the entries for Cr^{2+} and Eu^{2+}. As advocated by Taube and has been shown for our rhenium oxotransferase system, the reduction of perchlorate must proceed via OAT and formation of a favorable M = O bond.[2]

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**.[45] 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

TABLE 5. Rate constants for the reduction of perchlorate and chlorate ions in a controlled fashion by certain transition metal complexes.

Transition metal complexes	$\Delta G°$/kJ mol^{-1}	T/°C	k/L mol^{-1} s^{-1}		Ref.
			ClO_4^-	ClO_3^-	
$[(hoz)_2Re(O)(OH_2)]^+$	75	20	0.45	15	[35]
$CH_3ReO_2(OH_2)_n$	218	25	7.1	4×10^4	[45]
$[V(OH_2)_6]^{2+}$	213	50	2×10^{-5}		[4]
$[V(OH_2)_6]^{2+}$	213	20		18	[49]
$[V(OH_2)_6]^{3+}$	201	50	3×10^{-6}		[4]
$[Ru(NH_3)_6]^{2+}$	~117	25	3×10^{-4}	3.2×10^{-2}	[50]
$[Ru(H_2O)_6]^{2+}$	~117	25	3.2×10^{-3}	3×10^{-2}	[5]
Ti(Hedta)		25	2×10^{-3}		[51]
$[L_2Mo_2(H_2O)_2(\mu\text{-}OH)_2]^{4+}$ L = 1,4,7 = triazacyclononane	138	21	2×10^{-3}		[7]
$[Fe(H_2O)_6]^{2+}$			nr	2×10^{-2}	[11]
Eu_{aq}^{2+}		28	$\sim 10^{-8}$		[6]
$[Cr(OH_2)_6]^{2+}$	88	25	nr	39	[11]

methylrhenium trioxide is rate controlling, and the rate constant for that reaction is slow, 3×10^{-2} L mol^{-1} s^{-1}.[40] 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.

Worthy of special mention in the context of catalytic reduction of perchlorate is an older study in which molybdate and tungstate are the active catalysts for perchlorate reduction by stannous chloride in concentrated acidic media.[46,47] The molybdate catalysis is observed in 2.5 M sulfuric acid, and the tungstate catalysis in 10 M hydrochloric acid. The kinetics for the earlier system are complex with fractional dependences, but Mo^{IV} was suggested as the active catalyst. In contrast, the reduction of perchlorate catalyzed by tungstate was proposed to proceed via a W^{VI} perchlorate adduct. These studies are in need of re-examination.

Our rhenium systems demonstrate that minimization of nuclear reorganization is crucial in promoting OAT reactions, 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).

The oxazoline and thiazoline ligands are easily functionalized by straightforward organic synthesis, and thus the catalysts presented herein can be tethered to solid support or incorporated into mesoporous materials, extending the catalysis to heterogeneous systems. From a practical standpoint, effective heterogeneous catalysts are needed for any practical method for perchlorate destruction. In summary, rhenium oxazoline and thiazoline complexes are very promising molecular oxotransferases that could be utilized in other challenging reductions; examples would include NO_3^- and NO reduction, deoxygenation of epoxides, and the use of environmentally relevant reagents such as N_2O in novel O-atom transfer reactions under mild conditions. Efforts along these general directions are currently underway in this laboratory.

ACKNOWLEDGMENTS

My most sincere thanks are to my coworkers, the graduate students, who conducted most of the described experiments. Financial support from the National Science Foundation and the Arnold and Mabel Beckman Foundation is gratefully acknowledged. I wish to also thank Dr. Saeed I. Khan for his assistance in the x-ray structural determinations.

REFERENCES

1. Schilt, A. A. 1979. *Perchloric Acid and Perchlorates*. Columbus: GFS Chemicals, Inc.
2. Taube, H. 1982. Observations on atom-transfer reactions. *Adv. in Chem.* 198, 151–171.
3. Espenson, J. H. 2000. *The Problem and Perversity of Perchlorate, in Perchlorate in the Environment*. E.T. Urbansky, ed. Washington, DC: American Chemical Society.
4. King, W. R. and Garner, C. S. 1954. Kinetics of the oxidation of vanadium(II) and vanadium(III) ions by perchlorate ion. *J. Phys. Chem.* 58, 29–33.
5. Kallen, T. W. and Earley, J. E. 1971. Reduction of the perchlorate ion by aquoruthenium(II). *Inorg. Chem.* 10, 1152–1155.
6. Adin, A. and Sykes, A. G. 1966. The kinetics of oxidation of europium(II) with vanadium (III) and chromiun(III) in aqueous perchloric acid solutions. *J. Chem. Soc. A.* 1230–1236.
7. Hahn, M. and Wieghardt, K. 1984. Kinetics and mechanism of the oxidation of $[L_2Mo_2(H_2O)_2(\mu\text{-}OH)_2]^{4+}$ (L = TACN) with perchlorate. *Inorg. Chem.* 23, 3977–3982.
8. Amadei, G. A. and Earley, J. E. 2001. Effect of some macrocyclic ligands on the rate of reduction of perchlorate ion by titanium(III). *Croat. Chem. Acta.* 74, 601–606.
9. Taube, H. Myers, H. and Rich, R. L. 1953. Observations on the mechanism of electron transfer in solution. *J. Am. Chem. Soc.* 75: 4118–4119.
10. Taube, H. and Myers, H. 1954. Evidence for a bridged activated complex for electron transfer reactions. *J. Am. Chem. Soc.* 76, 2103–2111.
11. Thompson, R. C. and Gordon, G. 1966. Kinetics of the reaction between chromium(II) and the chlorine oxidants in aqueous perchloric acid. *Inorg. Chem.* 5, 562–569.
12. Thompson, R. C. and Gordon, G. 1966. Stoichiometry of the reaction between chromium(II) and the chlorine oxidants in aqueous perchloric acid. *Inorg. Chem.* 5, 557–562.

13. Early, J. E. Tofan, D. C. and Amadei, G. A. 2000. *Reduction of Perchlorate Ion by Titanous Ions in Ethanolic Solution, in Perchlorate in the Environment.* E. T. Urbansky, Ed. Washington, DC: American Chemical Society.
14. EPA's National Center for Environmental Assessment report titled "Perchlorate Environmental Contamination: Toxicological Review and Risk Characterization Based on Emerging Information" on the Web, http://www.epa.gov/ncea/perch.htm
15. Linke, S. R. 1990. *Managing Crises in Defense Industry: The PEPCON and Avex Cases.* Washington, DC: Institute for National Strategic Studies.
16. Greer, M. A. Goodman, G. Pleus, R. C. and Greer, S. E. 2002. Health effects assessment for environmental perchlorate contamination: The dose response for inhibition of thyroidal radioiodine uptake in humans. *Environ. Health Perspect.* 110, 927–937.
17. California Department of Health Services, Perchlorate in California Drinking Water, http://www.dhs.cahwnet.gov/ps/ddwem/chemicals/perchl/perchlindex.htm
18. Browner, C. M. 1999. Part II. Environmental Protection Agency. 40 CFR Parts 9, 141 and 142. Revisions to the unregulated contaminant monitoring regulation for public water systems; final rule. *Federal Register.* 64, 50555–50620.
19. Urbansky, E. T. 1998. Perchlorate chemistry: Implications for analysis and remediation. *Bioremediation J.* 2, 81–95.
20. Urbansky, E. T. and Schock, M. R. 1999. Issues in managing the risks associated with perchlorate in drinking water. *J. Environ. Manage.* 56: 79–95.
21. Urbansky, E. T. 2000. Quantitation of perchlorate ion: Practices and advances applied to the analysis of common matrices. *Critical Reviews in Analytical Chemistry.* 30, 311–343.
22. Logan, B. E. 1998. A review of chlorate- and perchlorate-respiring microorganisms. *Bioremediation J.* 2, 69–79.
23. Herman, D. C. and Frankenberger, W. T. 1999. Bacterial reduction of perchlorate and nitrate in water. *J. Environ. Qual.* 28, 1018–1024.
24. Wallace, W. Beshear, S. Williams, D. and Hospadar, S. 1998. Perchlorate reduction by a mixed culture in an up-flow anaerobic fixed bed reactor. *J. Indust. Microbiol. Biotechnol.* 20, 126–131.
25. Chambliss, C. K. Odom, M. A. Martin, C. R. Moyer, B. A. and Strauss, S. H. 1998. Rapid and selective redox-recyclable anion-exchange materials containing polyalkylated ferricenium anion-exchange sites. *Inorg. Chem. Commun.* 1, 435–438.
26. Gu, B. Brown, G. M. Maya, L. Lance, M. J. and Moyer, B. A. 2001. Regeneration of perchlorate (ClO_4^-)-loaded anion exchange resins by a novel tetrachloroferrate ($FeCl_4^-$) displacement technique. *Environ. Sci. & Technol.* 35, 3363–3368.
27. D.L. Eng-Wilmot, D. L. and Van der Helm, D. 1980. Molecular and crystal structure of the linear tricatechol siderophore, agrobactin. *J. Am. Chem. Soc.* 102, 7719–7725.
28. Maurer, P. J. and Miller, M. J. 1983. Total synthesis of a mycobactin: Mycobactin S2. *J. Am. Chem. Soc.* 105, 240–245.
29. Nishiyama, H. Yamaguchi, S. Kondo, M. and Itoh, K. 1992. Electronic substituent effect of nitrogen ligands in catalytic asymmetric hydrosilylation of ketones: Chiral 4-substituted bis(oxazolinyl)pyridines. *J. Org. Chem.* 57, 4306–4309.
30. Hoveyda, H. R. Rettig, S. J. and Orvig, C. 1992. Coordination chemistry of 2-(2'-hydroxyphenyl)-2-oxazolines with aluminum, gallium, and indium: First tris(ligand)metal(III) complexes of this naturally occurring binding group. *Inorg. Chem.* 31, 5408–5416.
31. Grove, D. E. and Wilkinson, G. J. 1966. Oxo-complexes of rhenium(V). *J. Chem. Soc. A.* 1224–1230.

32. Arias, J. Newlands, C. R. Abu-Omar, M. M. 2001. Kinetics and mechanisms of catalytic oxygen atom transfer with oxorhenium(V) oxazoline complexes. *Inorg. Chem.* 40, 2185–2192.
33. G.W. Parshall. 1977. Phosphine complexes of rhenium. *Inorg. Synth.* 17, 110–112.
34. Alberto, R. Schibli, R. Egli, A. Schubiger, P. A. Herrmann, W. A. Artus, G. Abram, U. and Kaden, T. A. 1995. Metal carbonyl syntheses XXII. Low-pressure carbonylation of $[MOCl_4]^-$ and $[MO_4]^-$. The technetium(I) and rhenium(I) complexes $[NEt_4]_2$ $[MCl_3(CO)_3]$. *J. Organomet. Chem.* 492, 217–224.
35. Abu-Omar, M. M. McPherson, L. D. Arias, J. Béreau, V. M. 2000. Clean and efficient catalytic reduction of perchlorate. *Angew. Chem. Int. Ed.* 39, 4310–4313.
36. Topich, J. and Lyon, J. T., III. 1984. Ligand control of *cis*-dioxomolybdenum(VI) redox chemistry: Kinetic and activation parameter data for oxygen atom transfer. *Inorg. Chem.* 23, 3202–3206.
37. Roberts, S. A. Young, C. G. Cleland, W. E. Ortega, R. B. and Enemark, J. H. 1988. Synthesis, characterization, and oxygen atom transfer reactions of $\{HB(Me_2C_3N_2H)_3\}$-$MoO\{S_2P(OR)_2\}$ and $\{HB(Me_2C_3N_2H)_3\}MoO_2\{.eta.1\text{-}S_2P(OEt)_2\}$. *Inorg. Chem.* 27, 3044–3051.
38. Caradonna, J. P. Reddy, P. R. Holm, R. H. 1988. Kinetics, mechanisms, and catalysis of oxygen atom transfer reactions of *S*-oxide and pyridine *N*-oxide substrates with molybdenum(IV,VI) complexes: Relevance to molybdoenzymes. *J. Am. Chem. Soc.* 110, 2139–2144.
39. Laughlin, L. J. and Young, C. G. 1996. Oxygen atom transfer, coupled electron-proton transfer, and correlated electron-nucleophile transfer reactions of oxomolybdenum(IV) and dioxomolybdenum(VI) complexes. *Inorg. Chem.* 35, 1050–1058.
40. Abu-Omar, M. M. Appelman, E. H. and Espenson, J. H. 1996. Oxygen-transfer reactions of methylrhenium oxides. *Inorg. Chem.* 35, 7751–7757.
41. Schultz, B. E. and Holm, R. H. 1993. Kinetics of oxygen atom transfer in an analogue reaction system of the molybdenum oxotransferases. *Inorg. Chem.* 32, 4244–4248.
42. Hammett, L. P. 1940. *Physical Organic Chemistry*. New York: McGraw-Hill Book Co.
43. Lipscomb, W. N. and Strater, N. 1996. Recent advances in zinc enzymology. *Chem. Rev.* 96, 2375–2434.
44. Lu, Y. and Valentine, J. S. 1997. Engineering metal-binding sites in proteins. *Curr. Opin. Struct. Biol.* 7, 495–500.
45. Abu-Omar, M. M. and Espenson, J. H. 1995. Facile abstraction of successive oxygen atoms from perchlorate ions by methylrhenium dioxide. *Inorg. Chem.* 34, 6239–6240.
46. Haight, G. P. and Sager, W. F. 1952. Evidence for preferential one-step divalent changes in the molybdate catalyzed reduction of perchlorate by stannous ion in sulfuric acid solution. *J. Am. Chem. Soc.* 74, 6056–6059.
47. Haight, G. P. 1954. Mechanism of the tungstate catalyzed reduction of perchlorate by stannous chloride. *J. Am. Chem. Soc.* 76, 4718–4721.
48. Holm, R. H. and Donahue, J. P. 1993. A thermodynamic scale for oxygen atom transfer reactions. *Polyhedron.* 12, 571–589.
49. Gordon, G. and Tewari, P. 1966. The kinetics of the reaction between vanadium(II) and chlorate in aqueous perchloric acid. *J. Phys. Chem.* 70, 200–204.
50. Endicott, J. F. and Taube, H. 1965. Studies on oxidation-reduction reactions of ruthenium ammines. *Inorg. Chem.* 4, 437–445.
51. Liu, B. Wagner, P. A. and Earley, J. E. 1984. Reduction of perchlorate ion by (N-(hydroxyethyl)ethylenediaminetriacetato) aquatitanium(III). *Inorg. Chem.* 23, 3418–3420.