halamide A was revised unambiguously to the one represented by structure **24** (*ent*-**1**).

In summary, we have accomplished the first synthesis of (+)-salicylihalamide A and revised the absolute configuration of the natural product to 12*S*,13*R*,15*S*. Our approach features a highly efficient, *trans*-selective ring-closing olefin metathesis for the assembly of the 12-membered salicylate skeleton and can be readily adapted to obtain the natural enantiomer.

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[1] K. L. Erickson, J. A. Beutler, J. A. Cardellina II, M. R. Boyd, *J. Org. Chem.* **1997**, *62*, 8188 – 8192.

[2] a) T. C. McKee, D. L. Galinis, L. K. Pannell, J. H. Cardellina II, J. Laakso, C. M. Ireland, L. Murray, R. J. Capon, M. R. Boyd, *J. Org. Chem.* **1998**, *63*, 7805 – 7810; b) lobatamide A is identical to the structure of YM-75518; see: K.-I. Suzumura, I. Takahashi, H. Matsumoto, K. Nagai, B. Setiawan, R. M. Rantiatmodjo, K.-I. Suzuki, N. Nagano, *Tetrahedron Lett.* **1997**, *38*, 7573 – 7576.

[3] a) B. Kunze, R. Jansen, F. Sasse, G. Höfle, H. Reichenbach, *J. Antibiot.* **1998**, *51*, 1075 – 1080; b) R. Jansen, B. Kunze, H. Reichenbach, G. Höfle, *Eur. J. Org. Chem.* **2000**, 913 – 919.

[4] J. W. Kim, K. Shin-ya, K. Furihata, Y. Hayakawa, H. Seto, *J. Org. Chem.* **1999**, *64*, 153 – 155.

[5] K. A. Dekker, R. J. Aiello, H. Hirai, T. Inagaki, T. Sakakibara, Y. Suzuki, J. F. Thompson, Y. Yamauchi, N. Kojima, *J. Antibiot.* **1998**, *51*, 14 – 20.

[6] We recently reported an enantioselective synthesis of side chain truncated apicularen A; see A. Bhattacharjee, J. K. De Brabander, *Tetrahedron Lett.* **2000**, accepted.

[7] a) A similar strategy has been proposed recently; see B. B. Snider, F. Song, *Org. Lett.* **2000**, *2*, 407 – 408; b) for a related example, see K. Kuramochi, H. Watanabe, T. Kitahara, *Synlett* **2000**, 397 – 399; c) for an alternative approach using a copper(I)-catalyzed substitution of vinyl iodides with amides, see R. Shen, J. A. Porco, Jr., *Org. Lett.* **2000**, *2*, 1333 – 1336.

[8] H. C. Brown, R. S. Randad, K. S. Bhat, M. Zaidlewicz, U. S. Racherla, *J. Am. Chem. Soc.* **1990**, *112*, 2389 – 2392.

[9] D. A. Evans, D. L. Rieger, M. T. Bilodeau, F. Urpí, *J. Am. Chem. Soc.* **1991**, *113*, 1047 – 1049.

[10] W. Oppolzer, T. Osamu, J. Deerberg, *Helv. Chim. Acta* **1992**, *75*, 1965 – 1978.

[11] Since no diastereomeric aldol products were detected by ^{1}H NMR spectroscopic analysis of the crude reaction mixture, including C15 epimers which would have arisen from an enantiomeric C15 aldehyde, we conclude that aldehyde **10** was essentially enantiomerically pure.

[12] For recent reviews on ring-closing metathesis, see a) R. H. Grubbs, S. Chang, *Tetrahedron* **1998**, *54*, 4413 – 4450; b) A. Fürstner, *Top. Organomet. Chem.* **1998**, *1*, 37 – 72; c) S. K. Armstrong, *J. Chem. Soc. Perkin Trans. 1* **1998**, 371 – 388; d) M. Schuster, S. Blechert, *Angew. Chem.* **1997**, *109*, 2124 – 2144; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2037 – 2056; e) A. Fürstner, *Top. Catal.* **1997**, *4*, 285 – 299.

[13] Prepared from 2,2-dimethyl-5-(trifluoromethanesulfonyl)benzo[1,3]-dioxin-4-one (A. Fürstner, I. Konetzki, *Tetrahedron* **1996**, *52*, 15071 – 15078) as follows: a) allylSnBu$_3$ (1.2 equiv), Pd$_2$(dba)$_3$ (2 mol%), tri(2-furyl)phosphine (8 mol%), LiCl (3 equiv), 4-methyl-2-pyrrolidinone, RT, 48 h; b) CH$_2$=CHCH$_2$OMgBr (4 equiv, prepared from allyl alcohol and EtMgBr), THF, reflux, 3 h, 90% (steps a, b); c) MeI (3 equiv), K$_2$CO$_3$ (1.1 equiv), acetone, RT, 40 h, 98%; d) Pd(Ph$_3$)$_4$ (5 mol%), morpholine (10 equiv), THF, RT, 1 h, 96%. dba = *trans,trans*-dibenzylideneacetone.

[14] O. Mitsunobu, *Synthesis* **1981**, 1 – 28.

[15] R. H. Grubbs, S. J. Miller, G. C. Fu, *Acc. Chem. Res.* **1995**, *28*, 446 – 452.

[16] Fürstner and co-workers observed a modest selectivity for the *E* isomer (*E*:*Z* = 2.3:1) of a related 12-membered resorcylic benzolactone; see A. Fürstner, G. Seidel, N. Kindler, *Tetrahedron* **1999**, *55*, 8215 – 8230.

[17] D. B. Dess, J. C. Martin, *J. Am. Chem. Soc.* **1991**, *113*, 7277 – 7287.

[18] Note that **19** is a useful intermediate for the synthesis of *ent*-salicylihalamide B (**2**).

[19] Bromide **22** was obtained from 1-trimethylsilyl-3-hexen-1-yne (G. Arsequell, F. Camps, G. Fabriàs, A. Guerrero, *Tetrahedron Lett.* **1990**, *31*, 2739 – 2742) by treatment with *N*-bromosuccinimide and AgNO$_3$ according to: T. Nishikawa, S. Shibuya, S. Hosakawa, M. Isobe, *Synlett* **1994**, 485 – 486, followed by reduction of the corresponding 1-bromo-3-hexen-1-yne according to the method in: H. C. Brown, C. D. Blue, D. J. Nelson, N. G. Bhat, *J. Org. Chem.* **1989**, *54*, 6064 – 6067. The (1*Z*,3*Z*)-1-bromo-1,3-hexadiene (**22**) thus obtained was contaminated with ≈20% of (1*Z*,3*E*)-1-bromo-1,3-hexadiene but was used as such.

[20] The 22*E* isomer (≈20%) was removed by preparative HPLC (normal phase, acetone/hexanes (3/7)).[19]

[21] A sample and the NMR spectra of natural (−)-salicylihalamide A were kindly provided by Dr. M. R. Boyd, National Cancer Institute (Frederick, MD, USA).

[22] This derivative was prepared from **16**: 1) DDQ, CH$_2$Cl$_2$/H$_2$O, RT; 2) *para*-bromobenzoic acid, PPh$_3$, DEAD, Et$_2$O, RT; 3) BBr$_3$ (3 equiv), CH$_2$Cl$_2$, −78 °C.

[23] Crystallographic data (excluding structure factors) for the structure reported in this paper (**23**) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-147019. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Clean and Efficient Catalytic Reduction of Perchlorate**

Mahdi M. Abu-Omar,* Lee D. McPherson,
Joachin Arias, and Virginie M. Béreau

Even though perchlorate is a strong oxidizing agent thermodynamically [Eq. (1)], its reactions are very slow

$$\mathrm{ClO_4^- + 2\,H^+ + 2\,e^- \longrightarrow ClO_3^- + H_2O} \quad (1)$$
$$E^\circ = 1.23\ \mathrm{V}$$

because it is nonlabile.[1–3] Consequently, perchlorate salts are often used to adjust ionic strength in kinetics and electrochemical investigations. Perchlorate is also a poor complexing ("innocent") anion.[4] In 1997, $\mathrm{ClO_4^-}$ was found in ground and surface waters in several U.S. western states at concentrations up to 3700 mg L^{-1}.[5–7] For example, 30% of the wells sampled

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[*] Prof. M. M. Abu-Omar, L. D. McPherson, J. Arias, Dr. V. M. Béreau
Department of Chemistry and Biochemistry
University of California at Los Angeles
405 Hilgard Avenue
Los Angeles, CA 90095 – 1569 (USA)
Fax: (+1)310-206-9130
E-mail: mao@chem.ucla.edu

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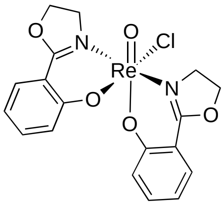
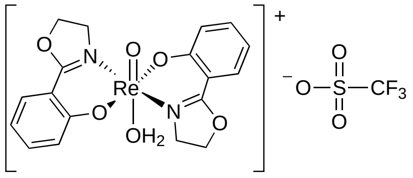
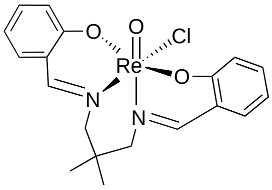
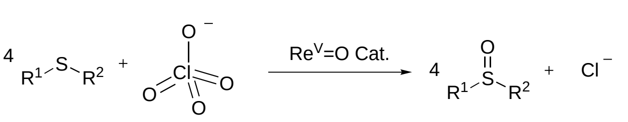
Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/angewandte/ or from the author.

in California were contaminated with perchlorate, and 9% exceeded the state's provisional action level of 18 µgL^{-1}.[8] The oxoanion ClO_4^- targets the thyroid gland and muscle tissue.[9] Most perchlorate in the environment comes from defense and aerospace activities since ammonium perchlorate is an ingredient in rocket fuels.[6] Perchlorate poses serious challenges for remediation due to the high solubility of its salts (in both water and organic solvents) and its extreme chemical inertness. Therefore, typical water treatment technologies such as ion exchange, carbon adsorption, and air stripping are not effective.[7] Recent research efforts have focused on bioremediation as a possible treatment for perchlorate-contaminated water.[10–12] We discovered in our laboratory that the simple oxorhenium(v) coordination complexes **1**–**3** (hoz = [2-(2′-hydroxyphenyl)-2-oxazoline], OTf = trifluoromethanesulfonate, saldmpen = [*N*,*N*′-bis(salicylidene)-1,3-diamino-2,2′-dimethylpropane]) are effective catalysts for the reduction of perchlorate with sulfides under mild conditions [Eq. (2)].


[Re(O)(hoz)$_2$Cl] **1**


[Re(O)(hoz)$_2$(OH$_2$)]OTf **2**


[Re(O)(saldmpen)Cl] **3**


$$4\,R^1{-}S{-}R^2 + ClO_4^- \xrightarrow{Re^V{=}O\ Cat.} 4\,R^1{-}S(O){-}R^2 + Cl^- \qquad (2)$$

The reduction of perchlorate and other oxoanions by methylrhenium dioxide ($CH_3ReO_2 \cdot nH_2O$, or MDO) has been reported.[13, 14] Nevertheless, the need for highly acidic media and the facile polymerization of MDO rendered this system impractical.[14] Another setback was the fact that the product, methylrhenium trioxide (MTO), required strong reducing agents such as hypophosphorus acid to regenerate MDO.[14]

The occurrence of the reaction in Equation (2) was established by the following: 1) sulfoxide is the only organic product in the ^{1}H NMR spectra; 2) the stoichiometry ClO_4^-:R^1SR^2 = 1:4 is based on the yield of sulfoxide as determined by ^{1}H NMR spectroscopy under conditions in which ClO_4^- is limiting; 3) the product from perchlorate, Cl^-, is precipitated and isolated as AgCl upon the addition of $AgBF_4$ at the end of the reaction. The reactivity of the rhenium catalysts **1**–**3** was probed under steady-state conditions with a variety of sulfides and 0.8% catalyst (Table 1).

Table 1. Catalytic reduction of ClO_4^- with sulfides.[a]

Entry	Substrate	Catalyst **1** or **2**		Catalyst **3**	
		t [h]	yield [%][b]	*t* [h]	yield [%][b]
1	CH_3SCH_3	4	100	48	69
2	$CH_3CH_2SCH_2CH_3$	4	100	48	62
3	$(C_6H_5)SCH_3$	5	96	48	69
4	$(C_6H_5)SCH_3$[c]	7	83	–	–
5	$(C_6H_5)S(C_6H_5)$	7	87	38	57

[a] Conditions: 0.0030 M catalyst, 0.092 M $LiClO_4$, 0.50 M sulfide in CD_3CN/D_2O (v/v 95/5) at 20 °C. [b] Yield of sulfoxide. [c] In the presence of 0.10 M LiCl.

Catalysts **1** and **2** gave rise to identical results, indicating that the two precursors yield the same active catalyst. On the other hand, the rhenium–saldmpen compound **3**,[15] even though reactive, was clearly inferior to **1** and **2**. The catalytic kinetics are independent of the nature of the sulfide; aryl and alkyl sulfides give comparable conversion rates. Thus the rate-determining step (RDS) involves the reaction of perchlorate and oxorhenium(v). Addition of LiCl showed product inhibition (Table 1, entry 4).[16]

The catalytic reaction proceeds initially through oxidation of the rhenium(v) complex (green) to a cationic dioxorhenium(vii) complex (red),[17] followed by the rapid reduction of dioxorhenium(vii) back to oxorhenium(v) with organic sulfides. This color change of the rhenium complex is significant because spectrophotometric methods for the detection of perchlorates are nonexistent.[18]

The reaction of perchlorate with oxorhenium(v) complexes **1** and **2** was studied by stopped-flow spectrophotometry, following the newly formed peak at 500 nm due to the dioxorhenium(vii).[19] The two rhenium complexes display identical kinetics; compound **1** undergoes chloride dissociation initially to give $[Re(O)(hoz)_2(OH_2)]^+$ with Cl^- as the counteranion. The kinetics were first-order in $[Re]_T$ and saturation in rate was observed with respect to $[ClO_4^-]$ (Figure 1). The kinetics were conducted in CH_3CN and the rate was independent of the H_2O concentration over a wide range (0.70–5.3 M). At saturation in $[ClO_4^-]$, k_{max} from the nonlinear least-squares fitting is $0.34 \pm 0.05\ s^{-1}$. When chlorate (ClO_3^-) was used as the oxidant (in place of perchlorate) the kinetics were first-order in $[Re]_T$ but zero-order in $[ClO_3^-]$, even at concentrations as low as 0.0050 M ClO_3^- (Figure 1). It is worth noting that k_{max} at the plateau for both perchlorate and chlorate is the same ($\approx 0.35\ s^{-1}$), indicating a RDS that is dependent on the catalyst but not the oxoanion [Scheme 1, Eq. (3)].[20] Indeed, substitution reactions of these oxorhenium(v) complexes are dissociative, and intermediate [I] in Scheme 1 is most likely a five-coordinate complex.

Since the red dioxorhenium(vii) complex persists over a reasonable amount of time (see below), its reaction with sulfides was investigated independently by stopped-flow spectrophotometry. Solutions of dioxorhenium(vii) were pre-

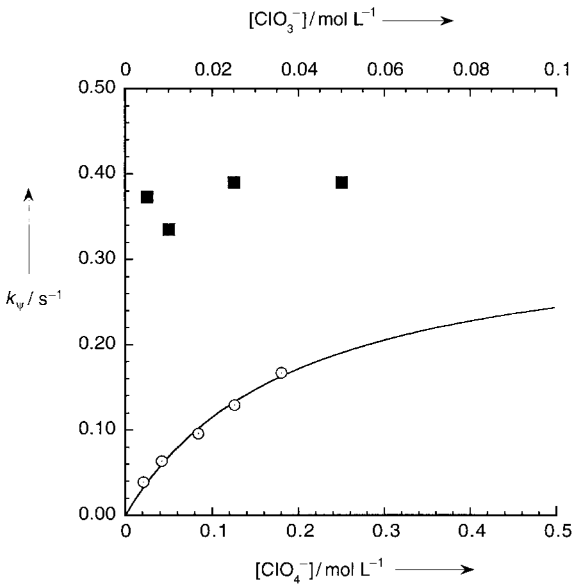


Figure 1. Concentration dependencies for the oxidation of $[Re(O)(hoz)_2(OH_2)]^+$ to $[Re(O)_2(hoz)_2]^+$ by ClO_4^- (○) and ClO_3^- (■) as measured by stopped-flow kinetics.

$$[\mathrm{Re(O)(hoz)_2(OH_2)}]^+ \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} [\mathrm{I}]$$

$$[\mathrm{I}] + \mathrm{ClO_4^-} \xrightarrow{k_2} [\mathrm{Re(O)_2(hoz)_2}]^+ + \mathrm{ClO_3^-}$$

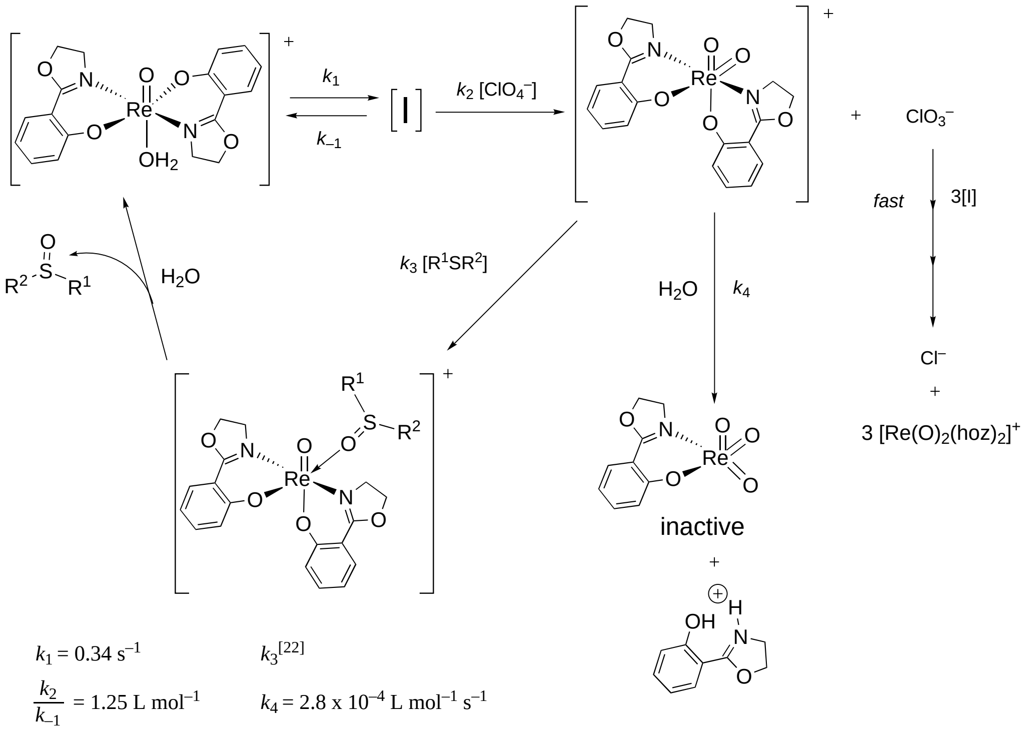
Scheme 1. Mechanism of ClO_4^- reduction by $[Re(O)(hoz)_2(OH_2)]^+$ ($k_1 = 0.34 \pm 0.05\ s^{-1}$, $k_{-1}/k_2 = 0.80 \pm 0.16\ mol L^{-1}$). [I] = intermediate.

$$v = \frac{-\mathrm{d}[\mathrm{ClO_4^-}]}{\mathrm{d}t} = \frac{k_1 k_2 [\mathrm{Re}][\mathrm{ClO_4^-}]}{k_{-1} + k_2[\mathrm{ClO_4^-}]} \qquad (3)$$

pared from the reaction of $LiClO_4$ or pyridine-*N*-oxide and complex **2** in situ, then mixed with sulfide, and the decay of the peak at 500 nm was monitored.[21] The second-order rate constants for a few sulfides were determined (Scheme 2).[22] The trend in the kinetics is in agreement with the cationic dioxorhenium(VII) complex acting as an electrophilic oxygen donor. Sulfoxides are much less reactive than their corresponding sulfides;[22] this fact is consistent with the observation that under steady-state catalysis sulfoxide is the only product and no sulfone is detected. The second-order rate constants for most sulfides, Ph_2S being the exception, are much larger than k^{app} ($k^{app} = k_1k_2/k_{-1} = 0.43\ L mol^{-1} s^{-1}$, Scheme 1) for the perchlorate reaction with rhenium(V). Thus, under catalytic conditions rhenium is dominantly present as oxorhenium(V).

In the absence of a reductant, sulfide, the red dioxorhenium(VII) complex decomposes with first-order dependence on [Re] and [H_2O] ($k_4 = 2.8 \pm 0.2 \times 10^{-4}\ L mol^{-1} s^{-1}$; Scheme 2).[23] The rate of decomposition is independent of [ClO_4^-]. The formed yellow compound $[(hoz)Re^{VII}O_3]$ is inactive; it is reduced by neither sulfides nor phosphanes. This decomposition pathway, however, is insignificant under steady-state conditions since the catalyst is present dominantly (≥99%) in the oxorhenium(V) form (see above), which is indefinitely stable, and the reduction of $[Re^{VII}(O)_2(hoz)_2]^+$ by most sulfides is faster than decomposition ($k_3 \gg k_4$).

Since aryl sulfides absorb in the UV range much more intensely than sulfoxides, we studied the kinetics of catalytic reduction of perchlorate with thioanisole, PhSMe, at 260 nm. A typical kinetic trace is shown in Figure 2a. The rate is zero-order with respect to [PhSMe], first-order in [ClO_4^-], and first-order in catalyst ($[\mathbf{1}]_T$). Thus, the RDS is the reaction of perchlorate with **1**. The rise in absorption following the zero-order consumption of PhSMe is due to the formation of the dioxorhenium(VII) species once PhSMe is depleted. Under these conditions, PhSMe is limiting (1.0–2.0 mM) and ClO_4^- is in excess (0.0050–0.025 M). The program KINSIM[24] was used to simulate the kinetics under these conditions (Figure 2b). The simulated data clearly show that the major form of the catalyst under steady-state conditions is rhenium(V), and dioxorhenium(VII) only evolves after PhSMe is depleted. From a plot of the initial rate (V_i) versus $[\mathbf{1}]_T[ClO_4^-]$, an experimental second-order rate constant was computed and found to be $0.33 \pm 0.04\ L mol^{-1} s^{-1}$, which is in excellent agreement with that determined independently by stopped-



Scheme 2. Mechanism and rate constants for the catalytic reduction of perchlorate.

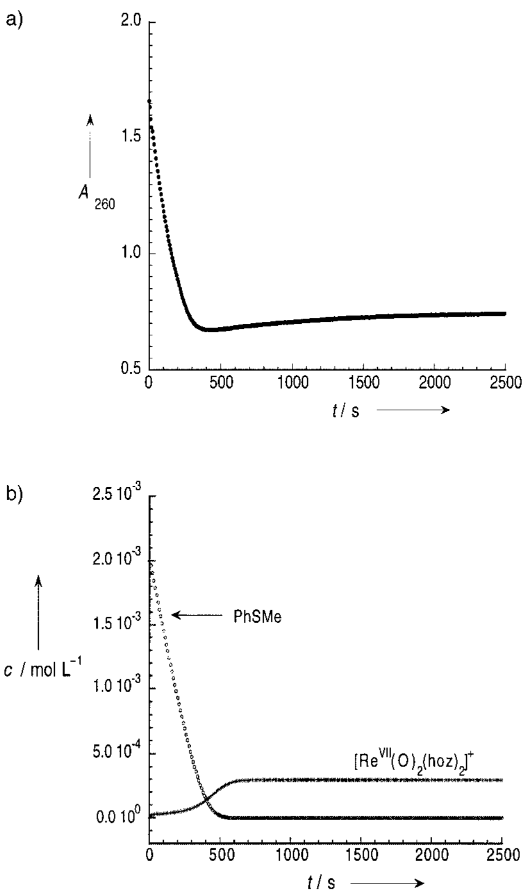


Figure 2. a) Time profile for the oxidation of thioanisole (PhSMe), monitored at 260 nm (pathlength 1.00 mm), with ClO_4^- as catalyzed by complex **1**. Conditions: [PhSMe] = 2.0 mM, [$LiClO_4$] = 0.022 M, [**1**] = 3.0×10^{-4} M, [H_2O] = 1.0 M in CH_3CN at 20.0 °C. b) Simulated kinetics using the program KINSIM, showing the evolution of the dioxorhenium(VII) complex after the zero-order consumption of PhSMe.

flow methods for the reaction of **1** with ClO_4^- (k_1k_2/k_{-1}, Scheme 2).

Complexes **1** and **2** are promising catalysts for the chemical treatment of perchlorate because of the following advantages: 1) They are stable towards air and moisture; 2) they show very little decomposition even after hundreds of turnovers;[25] 3) they are easily prepared from the readily available compound [$Re(O)Cl_3(OPPh_3)(Me_2S)$];[26] 4) the reduction of perchlorate proceeds cleanly to sulfoxide and chloride;[27] and 5) the oxazoline ligands employed in these catalysts are easy to make from inexpensive and commercially available starting materials.[28] Furthermore, the ligands could be easily functionalized by straightforward organic synthesis,[29] and thus, these catalysts could be tethered to a resin or support, allowing the treatment of perchlorate heterogeneously. In addition to the possible application to remediation, the color change associated with the reaction of **1** with ClO_4^- could be utilized in analysis of perchlorate at submillimolar levels based on the molar absorptivity of the dioxorhenium(VII) product.

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[1] H. Taube, *ACS Symp. Ser.* **1982**, *198*, 151–171.
[2] B. Y. Liu, P. A. Wagner, J. E. Earley, *Inorg. Chem.* **1984**, *23*, 3418–3420.
[3] W. R. King, C. S. Garner, *J. Phys. Chem.* **1954**, *58*, 29–33.
[4] F. A. Cotton, G. Wilkinson, C. A. Murillo, M. Bochmann, *Advanced Inorganic Chemistry*, 6th ed., Wiley, New York, **1999**, pp. 568–569.
[5] See the Environmental Protection Agency's National Center for Environmental Assessment report entitled: "Perchlorate Environmental Contamination: Toxicological Review and Risk Characterization Based on Emerging Information" on the web: http://www.epa.gov/ncea/perch.htm.
[6] E. T. Urbansky, *Biorem. J.* **1998**, *2*, 81–95.
[7] E. T. Urbansky, M. R. Schock, *J. Environ. Manage.* **1999**, *56*, 79–95.
[8] California Department of Health Services, Perchlorate in California Drinking Water, http://www.dhs.cahwnet.gov/ps/ddwem/chemicals/perchl/perchlindex.htm.
[9] R. V. Burg, *J. Appl. Toxicol.* **1995**, *15*, 237–241.
[10] D. C. Herman, W. T. Frankenberger, *J. Environ. Qual.* **1999**, *28*, 1018–1024.
[11] W. Wallace, S. Beshear, D. Williams, S. Hospadar, *J. Indust. Microbiol. Biotechnol.* **1998**, *20*, 126–131.
[12] B. E. Logan, *Biorem. J.* **1998**, *2*, 69–79.
[13] M. M. Abu-Omar, J. H. Espenson, *Inorg. Chem.* **1995**, *34*, 6239–6240.
[14] M. M. Abu-Omar, E. H. Appelman, J. H. Espenson, *Inorg. Chem.* **1996**, *35*, 7751–7757.
[15] W. A. Herrmann, M. U. Rauch, G. R. J. Artus, *Inorg. Chem.* **1996**, *35*, 1988–1991.
[16] Even "noncoordinating" anions such as triflate and hexafluorophosphate inhibit the reduction of ClO_4^-. Reduction of ClO_4^- by aquaruthenium(II) is inhibited by Cl^- as well: T. W. Kallen, J. E. Earley, *Inorg. Chem.* **1971**, *10*, 1152–1155.
[17] The dioxorhenium(VII) complex is detected by fast atom bombardment mass spectrometry (FAB/MS; nitrobenzyl alcohol (NBA)): m/z: 543 ($MO_2L_2^+$), 527 (MOL_2^+), 381 (MO_2L^+) with correct rhenium 187/185 isotope ratios.
[18] For alternate methods for the detection of perchlorate, see E. T. Urbansky, M. L. Magnuson, D. Freeman, C. Jelks, *J. Anal. At. Spectrom.* **1999**, *14*, 1861–1866; M. L. Magnuson, E. T. Urbansky, C. A. Kelty, *Anal. Chem.* **2000**, *72*, 25–29.
[19] An orange dioxorhenium(VII) complex is formed from the reaction of [($HBpz_3$)Re(O)(Ph)(OTf)] ($HBpz_3$ = hydrotris(1-pyrazolyl)borate) and pyridine-*N*-oxide: S. N. Brown, J. M. Mayer, *J. Am. Chem. Soc.* **1996**, *118*, 12119–12133.
[20] The oxidation of complex **1** by ClO_4^- is inhibited by other anions such as Cl^-, OTf^-, and PF_6^-. For example, the second-order rate constant $k^{app} = 0.08\ L\,mol^{-1}\,s^{-1}$ in 0.075 M LiOTf and 0.025 M $LiClO_4$ ($\mu = 0.10$), but $k^{app} = 0.24\ L\,mol^{-1}\,s^{-1}$ with 0.10 M $LiClO_4$ ($\mu = 0.10$). However, the reaction of **1** with ClO_3^- is unaffected by LiOTf.
[21] In a typical experiment, compound **2** (1.0 mM) is treated with $LiClO_4$ or pyridine-*N*-oxide (1.0–5.0 mM), and the resulting red solution is allowed to react on the stopped-flow instrument with the reagent (0.01–0.10 M; for $CH_3S(O)CH_3$ 0.50–2.0 M) at 20.0 ± 0.2 °C. An Applied Photophysics SX18.MV stopped-flow spectrophotometer was employed.
[22] Several values for k_3 [$L\ mol^{-1}\,s^{-1}$] (Scheme 2): Me_2S: 7500 ± 300, Et_2S: 6900 ± 200, PhSMe: 110 ± 8, Ph_2S: 1.1 ± 0.1, $Me_2S(O)$: 0.85 ± 0.04.
[23] [**1**] = 5.0×10^{-4} M, [$LiClO_4$] = 0.010–0.025 M, [H_2O] = 1.0–5.0 M, μ = 0.10, $T = 20.0 + 0.2$ °C.
[24] B. A. Barshop, R. F. Wrenn, C. Frieden, *Anal. Biochem.* **1983**, *130*, 134–145.
[25] When dialkyl sulfides or thioanisole are employed, the catalytic reaction mixture retains its green color (that of the oxorhenium(V) complex), even after 120 turnovers.
[26] See the Supporting Information for detailed synthetic procedures and characterizations of the oxorhenium(V) complexes **1** and **2**.
[27] Dimethyl sulfoxide (DMSO) is essentially nontoxic, especially at the low concentrations that would be employed in water treatment (LD_{50} orally in rats is greater than 20 $g\,Kg^{-1}$), and is used as a topical antiinflammatory agent (*The Merck Index*, 11th ed., Merck & Co., Rahway, NJ, USA, **1989**).
[28] H. R. Hoveyada, V. Karunaratne, S. J. Rettig, C. Orvig, *Inorg. Chem.* **1992**, *31*, 5408–5416.
[29] H. Nishiyama, S. Yamaguchi, M. Kondo, K. Itoh, *J. Org. Chem.* **1992**, *57*, 4306–4309.