caused by something other than (+)-(S)-2-butanol. Snyder and Johnson's attribution of this rotational strength to the hydrocarbon σ–σ^* transitions[5] must be ruled out since all such possible transitions were considered in our calculation.

Although we cannot predict the exact quantitative features of the CD spectrum of 2-butanol, we can make some general qualitative comments on its form. When the data of Table II are used, the first CD band should be very small and positive (16→17). The second CD band would be larger and also positive (16→18). The next three transitions 16→19, 16→20, and 15→17 fall in the same energy range; the CD spectrum should exhibit a small, negative band. The region above about 69 000 cm^{-1} would be dominated by a very large positive band; it would include contributions from the transitions 16→21 and 14→17.

V. Conclusions

We have calculated the singlet Rydberg excited states of 2-butanol in the energy range of 7–9 eV in two basis sets. The CI calculations, which include the generation of more than a million distinct spatial configurations, are probably among the largest ever performed. The energies and oscillator strengths of the lowest states agree well with the experimental UV spectrum. The calculated rotational strengths represent the two lowest bands of the CD spectrum reasonably. The calculations do not entirely reproduce the third, large, negative CD band observed experimentally. They do, in accord with the transferability hypothesis, correctly predict the observed CD spectrum of 1-borneol for all three bands, and it is our belief that these calculations correctly represent the CD spectrum of the first three UV bands of 2-butanol in particular and, in a more qualitative sense, alcohols in general.

Acknowledgment. This work was supported by NIH Grant GM 30114.

Registry No. (+)-(S)-2-Butanol, 4221-99-2; l-borneol, 464-45-9.

Mechanistic Studies of the Selective Oxygen Oxidation of Sulfides to Sulfoxides Catalyzed by Dihaloruthenium(II) Complexes

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Abstract: The selective and facile molecular oxygen oxidation of dialkyl sulfides to their sulfoxides can be effectively catalyzed by neutral ruthenium(II) complexes of the type *cis*- or *trans*-$RuX_2(Me_2SO)_4$. The results of kinetic studies for two of these catalysts, *cis*-$RuCl_2(Me_2SO)_4$ and *trans*-$RuBr_2(Me_2SO)_4$, show that these catalytic oxidations are first order with respect to total catalyst concentration, less than first order in oxygen concentration, zero order in the sulfide substrate, and approximately first order in alcohol. These and other observations plus ^{18}O-labeling studies support a mechanism involving oxidation of a "Ru(II)" species to give an oxidized metal species, probably "Ru(IV)" and peroxide. The active sulfide oxidant is peroxide, whose concentration is approximated by the steady-state assumption. The reductant of the oxidized metal is the solvent alcohol, thus completing the catalytic cycle.

For several years we have been investigating the possibility of using metal-based catalysts to promote the selective air oxidation of dialkyl sulfides to their sulfoxides. There are only a very few examples of metal-based sulfide oxidation catalysts that utilize O_2 as the oxidant, and these catalysts suffer from poor selectivities and very slow rates.[1] In contrast to the sulfide dioxygen oxidation, a large number of transition-metal complexes are known to function as homogeneous catalysts for the molecular oxygen oxidation of phosphines to phosphine oxides. Using such catalyzed phosphine oxidation reactions as models for the sulfide oxidation, we screened all of the metal complexes known to us to catalyze the oxidation of phosphines to phosphine oxides[2–4] or to form metal–O_2 adducts.[2,5] There was no activity associated with any of these complexes for the oxidation of sulfides. For many of these complexes, such results are perhaps not unexpected since from the work of Halpern et al.[3a] it is known that the dioxygen oxidation of phosphines to phosphine oxides catalyzed with $Pt^0(PPh_3)_4$ generates peroxide as the active oxidant. These catalysts form inner-sphere peroxide complexes (O_2 adducts); thus for an oxidation to occur the substrate must be able to displace peroxide from the coordination sphere. Phosphines are excellent ligands and are able to displace O_2^{2-}, but sulfides are generally considered to be poorer ligands and are apparently not able to displace peroxide.

For this reason we believed that to achieve effective dioxygen catalysis with substrates that are poor ligands, such as sulfides, it would be essential to use metal complexes that can undergo outer-sphere electron transfer to give free peroxide in solution. We chose to investigate ruthenium(II) complexes as potential catalysts, since there are a number of Ru(II) compounds known to undergo outer-sphere oxidation with molecular oxygen to yield peroxide and Ru(III)[6,7] or Ru(IV).[8] Our choice of ruthenium(II)

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was also supported by some of our observations in the ruthenium-catalyzed oxygen oxidation of tertiary amines in which a Ru(II)/Ru(IV) redox couple is apparently operative.[9] Based on this reasoning it was believed that with a suitable ligand environment about ruthenium(II) we could generate an active catalyst for sulfide oxidations. After screening a large number of ruthenium(II) complexes, we have found that the selective and facile molecular oxygen oxidation of dialkyl sulfides to their sulfoxides can be accomplished with dihalotetrakis(dimethyl sulfoxide)ruthenium(II) complexes.[10] In particular, the *cis*-dichlorotetrakis(dimethyl sulfoxide)ruthenium(II) and the *trans*-dibromotetrakis(dimethyl sulfoxide)ruthenium(II) complexes are excellent catalysts for the oxygen-driven conversion of sulfides to sulfoxides, giving high selectivities for sulfoxide over sulfone (sulfoxide/sulfone ratio ≥25).

In an earlier communication we reported that the *cis*-$RuCl_2(Me_2SO)_4$ complex was an excellent catalyst for this oxidation.[10] Subsequently we found that the *trans*-$RuBr_2(Me_2SO)_4$ complex is an even better catalyst giving rates that are over three times as fast as the *cis*-$RuCl_2(Me_2SO)_4$ catalyst under comparable conditions. This work describes these catalysts, their reactivities, their utility, and our attempts to elucidate the mechanism of the catalytic dioxygen oxidation reaction via kinetic and mechanistic studies.

Experimental Section

Materials. The starting sources for the ruthenium complexes were either anhydrous $RuBr_3$ (Alfa) or $RuCl_3 \cdot xH_2O$ (Strem Chemical). To monitor the Ru(IV) impurity levels in the $RuCl_3 \cdot xH_2O$ samples, the UV–vis spectra were routinely run. All traces of Ru(IV) were removed by dissolving the Ru salts in 0.1 N HCl and bubbling H_2 through the solutions at 60 °C until no evidence of Ru(IV) was observed in the spectrum.[11,12] The solution was then dried on a rotary evaporator and the solid $RuCl_3 \cdot xH_2O$ collected. Solvents used for kinetic studies and catalyst screening (methanol, ethanol, 2-propanol, and acetone) were always dried by distillation from CaH_2 prior to use. The organic sulfides (dimethyl sulfide, diethyl sulfide, tetrahydrothiophene, and thioanisole) were used as supplied by Aldrich. Other sulfides (di-*n*-propyl sulfide, di-*n*-butyl sulfide, diiso-propyl sulfide, diiso-butyl sulfide, di-*tert*-butyl sulfide, and di-*sec*-butyl sulfide) were used as supplied by Fairfield Chemical Co. The sulfoxides (dimethyl sulfoxide, dibutyl sulfoxide, and tetramethylene sulfoxide) were used as supplied by Aldrich Chemical Co., while decyl methyl sulfoxide and diethyl sulfoxide were synthesized by standard techniques.[13] The sulfones used as standards (di-*n*-butyl sulfone, diethyl sulfone, dimethyl sulfone, and tetramethylene sulfone) were used as supplied by Aldrich Chemical Co., while decyl methyl sulfone was synthesized by standard methods.[13] Labeled water $H_2{}^{18}O$ was purchased from Norell. Anhydrous lithium iodide was used as supplied by Alfa. Ultrahigh purity oxygen (99.99%) was supplied by Matheson.

The following Ru(II) complexes were used as received from Strem Chemical Co.: tris(2,2′-bipyridyl)ruthenium(II) chloride, chloropentaammineruthenium(III) chloride, *cis*-dichlorobis(2,2′-bipyridine)ruthenium(II) dihydrate, dichlorotricarbonylruthenium(II) dimer, dichlorodicarbonylbis(triphenylphosphine)ruthenium(II), dichlorotris(triphenylphosphine)ruthenium(II), hexammineruthenium(III) chloride, and hydrido(acetato)tris(triphenylphosphine)ruthenium(II).

Procedures. Reaction mixtures in the concentration range of 0.1–0.2 M in substrate and 2 mM in catalyst were placed in a Griffen-Worden pressure vessel and shaken in a thermostatically controlled oil bath under an atmosphere of oxygen. These reaction mixtures were sampled periodically in order to determine the reaction kinetics.[14] These kinetic samples were analyzed directly by using a Hewlett-Packard 5880A gas chromatograph with a level IV terminal and flame ionization detector.

Oxidation products of *n*-decyl methyl sulfide were analyzed by using a 30M × 0.25 mM DB-1 (J&W Scientific) capillary column with a 0.25-μm film thickness. Helium was used as the carrier and makeup gas. Other chromatographic conditions were as follows: sample volume, 2 μL; column flow, 1.9 mL/min; split ratio, 81:1; injector temperature, 280 °C; detector temperature, 325 °C; oven temperature program, 120 °C for 5 min then increased at a rate of 10 °C per min and holding at 315 °C for 10 min.

Table I. Results of Catalytic Dioxygen Oxidations (0.2 M Solutions in 2-Propanol) of Decyl Methyl Sulfide for 16 h under 100 psi of O_2 Pressure and at 100 °C

complex[a]	% conversion	products (% yield)
$[Ru(bpy)_3]Cl_2$	no rxn.	
$[Ru(bpy)_2Cl_2]$	no rnx.	
$[Ru(CO)_3Cl_2]_2$	no rxn.	
$[Ru(CO)_2Cl_2(PPh_3)_2]$	no rxn.	
$[RuCl_2(\eta_6\text{-}C_6H_6)]_2$	no rxn.	
$[RuH(OAc)(PPh_3)_3]$	no rxn.	
[Ru(TPP)CO]	25	sulfoxide (20), sulfone (trace)
$[Ru(NH_3)_5(N_2)]Cl_2$	no rxn.	
$[Ru(NH_3)_6]Cl_2$	no rxn.	
$[Ru(NH_3)_6](BF_4)_2$	no rxn.	
$[RuCl_2(PPh_3)_3]$	46	sulfoxide (36), sulfone (12)
cis-$RuCl_2(Me_2SO)_4$	100	sulfoxide (88), sulfone (10)
trans-$RuCl_2(CH_3CN)_4$	17	sulfoxide (17)
$RuCl_3 \cdot xH_2O$	no rxn.	
$[Ru(NH_3)_6]Cl_3$	no rxn.	
$[Ru(MeSPh)_3Cl_3]$	no rxn.	
$[Ru(Me_2S)_3Cl_3]$	no rxn.	

[a] $[Ru]_t = 4.00 \times 10^{-3}$ M.

Reaction samples contained dodecane as an internal standard (ISTD) and were compared against standard solutions. The analysis of *n*-butyl sulfide oxidation components was possible with use of the same chromatographic conditions. The analysis of dimethyl sulfide oxidation components requires the use of a different oven temperature program: 40 °C was the initial temperature then increased at 30 °C/min until reaching 250 °C and holding for 3 min.

When 2-propanol was used as a solvent, the detection of acetone from its oxidation was possible with use of the same chromatography equipment but different chromatography conditions. a 6-ft × 2-mm glass column was used containing 80/100 Carbopack C with 0.1% SP1000. A column temperature of 65 °C isothermal was used. The injector and detector temperatures were both 100 °C. The column flow was 20 mL/min of helium. A flame ionization detector was used. Retention times were as follows: acetone, 1.7 min; 2-propanol, 1.9 min.

Syntheses. Dibromotetrakis(dimethyl sulfoxide)ruthenium(II) $[RuBr_2(Me_2SO)_4]$. The synthesis of this material has been reported previously[15] and has been shown to have the *trans*-dibromo structure with all S-bonded Me_2SO ligands.[16]

***cis*-Dichlorotetrakis(dimethyl sulfoxide)ruthenium $[RuCl_2(Me_2SO)_4]$.** This complex has been synthesized previously[15] and shown to have the *cis*-dichloro structure with one O-bonded Me_2SO ligand trans to an S-bonded Me_2SO ligand.[17]

***trans*-Diiodotetrakis(dimethyl sulfoxide)ruthenium $[RuI_2(Me_2SO)_4]$.** One gram of the *trans*-$RuBr_2(Me_2SO)_4$ (1.75 mmol) complex was added to a dry degassed ethanolic solution containing 2.0 g (15 mmol) of anhydrous LiI. This solution was then refluxed under Ar for 1 h. A beige precipitate formed which was collected by filtration, washed with degassed ethanol and then ether, and then dried in a vacuum for 2 h. The yield was 0.73 g (62.5% theoretical yield based on $RuBr_2(Me_2SO)_4$). Anal. Calcd for $C_8H_{24}I_2O_4RuS_4$: C, 14.40; H, 3.62; I, 38.03. Found: C, 14.71; H, 3.48; I, 38.83. Selected IR absorptions (in cm^{-1}): 1082 (γ_{SO}, s), 1028 (CH rock, (s), 979 (s), 940 (s); 720 (γ_{CS}, s), 674 (γ_{CS}, s).

The following complexes were prepared by published procedures: *trans*-dichlorotetrakis(acetonitrile)ruthenium(II),[18] trichlorotris(dimethyl sulfide)ruthenium(III),[19] trichlorotris(methyl phenyl sulfide)ruthenium(III),[19] dichloro(2,2′-bipyridyl)bis(dimethyl sulfoxide)ruthenium(II),[20] di(μ-chloro)bis[(η_6-benzene)chlororuthenium(II)],[21] pentaammine(nitrogen)ruthenium(II) chloride,[22] hexammineruthenium(II) chloride,[23]

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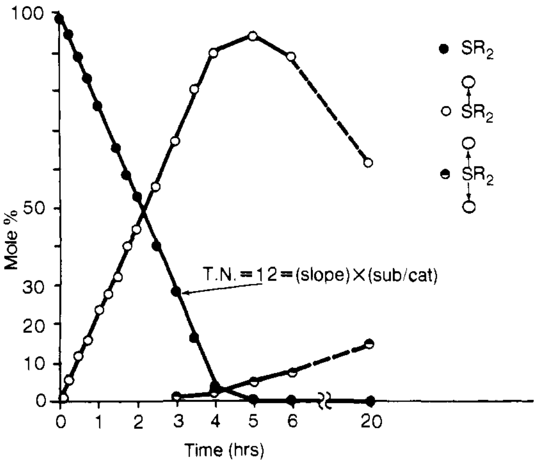

Figure 1. The reaction of decyl methyl sulfide (0.15 M) with molecular oxygen (100 psi) at 108 °C in dry MeOH catalyzed with *cis*-$RuCl_2(Me_2SO)_4$ (3.0 mmol).

Table II. Turnover Numbers for the Catalytic O_2 Oxidation (100 psi) of Decyl Methyl Sulfide (0.15 M) at 100 °C with Various Catalysts, $RuX_2(Me_2SO)_4$ (3.0×10^{-3} M) in Methanol

complex	turnover no. (mol of sub/mol of cat. per h)
cis-$RuCl_2(Me_2SO)_4$	6
$Ru(SnCl_3)_2(Me_2SO)_4$	11
trans-$RuBr_2(Me_2SO)_4$	19
trans-$RuI_2(Me_2SO)_4$	1

pentaammine(nitrogen)ruthenium(II) tetrafluoroborate,[22] carbonyl(tetraphenylporphyrinato)ruthenium(II), [Ru(TPP)CO],[24] and bis(trichlorostannate)tetrakis(dimethyl sulfoxide)ruthenium(II).[20]

Results

General Observations. Table I is a partial list of the complexes that were tested as catalysts, and it gives a representative sampling of the structural types of complexes that were tested. In all of the initial catalyst screening runs, the reactions were allowed to proceed for 16 h at 100 °C under 100 psi of O_2 pressure with use of the nonvolatile and low-stench substrate decyl methyl sulfide (0.2 M) in 2-propanol solvent. The results show that very little catalytic activity is exhibited by any of these ruthenium(II) complexes except for the *cis*-$RuCl_2(Me_2SO)_4$ complex. Even the seemingly similar $RuCl_2(CH_3CN)_4$ complex is barely catalytic compared to the dichlorotetrakis(dimethyl sulfoxide)ruthenium(II) complex. Additionally, a number of ruthenium(III) complexes were tested for activity in the catalytic O_2 oxidation of sulfides. These were in all cases completely inactive.

As a consequence of the activity and selectivity that the *cis*-$RuCl_2(Me_2SO)_4$ complex exhibits, this catalyst was studied in greater detail. In Figure 1 is shown a typical reaction profile for the oxidation of decyl methyl sulfide (0.15 M) with molecular oxygen (100 psi) using *cis*-$RuCl_2(Me_2SO)_4$ as catalyst in dry methanol at 108 °C. Two features are immediately obvious. First, the high selectivity for sulfoxide is apparent and is observed for all the oxidations we have studied with this catalyst. Second, the reaction is zero order in the decyl methyl sulfide substrate.

Since the dichloro complex exhibited catalytic activity, we synthesized analogous complexes differing only in the coordinated anion. We found that the anion plays a major role in the catalyst activity. In Table II are listed the four complexes $RuX_2(Me_2SO)_4$ where X = Cl^-, $SnCl_3^-$, Br^-, and I^-. Clearly the bromide ligand gives the best catalyst and the iodide ligand gives the poorest catalyst. The solid-state IR spectrum of the iodide complex is identical with that of the bromide complex, thus indicating that their structures are identical in the solid state: *trans*-halides with all S-bound sulfoxides.[16] The reaction rate profile for the molecular oxygen oxidation of decyl methyl sulfide catalyzed with each of these $RuX_2(Me_2SO)_4$ complexes is similar to that shown in Figure 1; namely, they give high conversions to sulfoxide and exhibit zero-order kinetics.

Table III. Turnover Numbers for the Catalytic O_2 Oxidations of Various Sulfide Substrates (0.15 M) at 105 °C and 100 psi of O_2 in MeOH

substrate	turnover number (mol of sub/mol of cat. per h)	
	cis-$RuCl_2(Me_2SO)_4$[a]	*trans*-$RuBr_2(Me_2SO)_4$[b]
dimethyl sulfide	7.2	24
tetrahydrothiophene	4.0	9.5
decyl methyl sulfide	8.5	27
diethyl sulfide	52	121
di-*n*-butyl sulfide	78	172
diisobutyl sulfide		131
di-*tert*-butyl sulfide	0	0
thioanisole ($PhSCH_3$)	4	8
diisopropyl sulfide		*sec*-CH autoxidation
di-*sec*-butyl sulfide		*sec*-CH autoxidation

[a] $[Ru]_t = 3.00 \times 10^{-3}$ M. [b] $[Ru]_t = 1.5 \times 10^{-3}$ M.

We have studied these catalysts using a variety of sulfide substrates and in all cases the gross kinetic behavior is the same as with the decyl methyl sulfide substrate; viz., the reactions are always zero order in the sulfide substrate. Surprisingly, even though the reaction rates are zero order in substrate, the reaction rates observed for the different substrates vary markedly. In Table III are listed the turnover numbers for the O_2 oxidations of several different substrates (0.15 M) under 100 psi of O_2 at 105 °C in MeOH with use of the *cis*-$RuCl_2(Me_2SO)_4$ and *trans*-$RuBr_2(Me_2SO)_4$ catalysts. In all cases the reactions are zero order in substrate and the reactions exhibit very high selectivities at 100% sulfide conversion (≥25:1). The substrate has a profound effect on the reaction rates, which vary over an order of magnitude. Tetrahydrothiophene is the slowest substrate with each catalyst (except for di-*tert*-butyl sulfide, which is not oxidized), and di-*n*-butyl sulfide is the best substrate; e.g., with the *trans*-$RuBr_2(Me_2SO)_4$ catalyst at 105 °C under 100 psi of O_2, a turnover number of about 3 min^{-1} is observed! When sulfide substrates containing "*sec*-CH groups" α to the sulfur atom are used, substantial autoxidation of the substrate resulted giving α-oxidation products. Control reactions in the absence of catalyst showed that these *sec*-CH sulfides do indeed react with O_2 by a noncatalytic pathway as well. In contrast, no autoxidation of *n*-alkylthioether substrates occurs in either the catalyzed or uncatalyzed reactions.

The effect of solvent was investigated early in our studies and found to be very significant. For both of these catalysts the reaction rates at 100 °C and 100 psi of O_2 for the oxidation of decyl methyl sulfide are identical in the alcoholic solvents, MeOH, EtOH, and *i*-PrOH. However, in acetone the reaction does not occur. Also, these catalyst systems are relatively immune to the presence of water or added acid. The reaction rates for both catalysts are unchanged when low levels of water are present, e.g., 1% v/v of H_2O has no effect on the reaction rates. When water is present at higher levels, e.g., greater than 10%, the reaction rates do suffer and a black precipitate forms. Apparently, hydrolysis of higher valent ruthenium complexes occurs, since chemical analysis of the precipitate reveals only Ru, O, and H (in variable amounts). Also since control reactions with ruthenium(III) complexes give no precipitate under the reaction conditions (0.2 M decyl methyl sulfide, 10% H_2O in methanol, 100 °C, 100 psi of O_2), the precipitates in the actual reactions are very likely hydrated ruthenium(IV) oxides.

Kinetic Studies. To determine the overall kinetics for these sulfide oxidations the rates of both loss of sulfide (k_{obsd}) and appearance of sulfoxide were monitored with time. With the two catalysts, *cis*-$RuCl_2(Me_2SO)_4$ and *trans*-$RuBr_2(Me_2SO)_4$, for over

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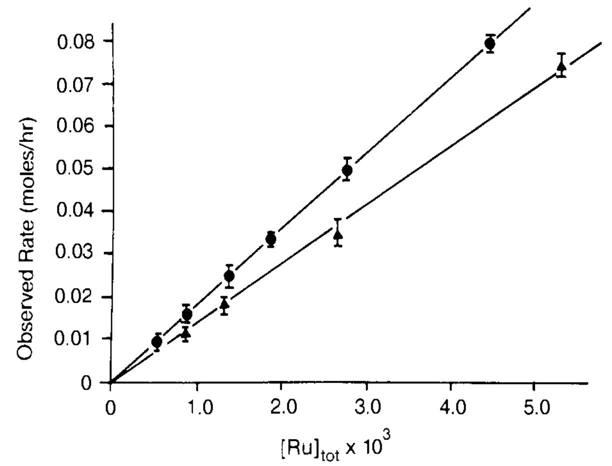

Figure 2. Plot of k_{obsd} vs. $[Ru]_{tot}$ for the O_2 (100 psi) oxidation of decyl methyl sulfide (0.133 M) in methanol: (▲) *cis*-$RuCl_2(Me_2SO)_4$, T = 110 °C, and (●) *trans*-$RuBr_2(Me_2SO)_4$, T = 100 °C.

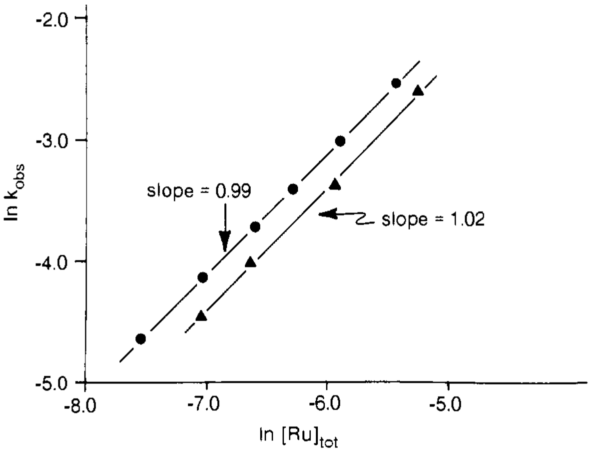

Figure 3. Plots of ln k_{obsd} vs. ln $[Ru]_{tot}$ for decyl methyl sulfide (0.133 M) oxidations with O_2 (100 psi) in methanol: (▲) *cis*-$RuCl_2(Me_2SO)_4$, T = 110 °C, and (●) *trans*-$RuBr_2(Me_2SO)_4$, T = 100 °C.

the course of 90% of the reaction, the rate of appearance of product sulfoxide was equal to that for loss of sulfide. In all the oxidations the O_2 pressure was maintained constant throughout the course of the reaction. The linear plots of k_{obsd} vs. $[Ru]_{tot}$ (Figure 2) and the plots for ln k_{obsd} vs. ln $[Ru]_{tot}$ (Figure 3) clearly demonstrate the first-order dependency in $[Ru]_{tot}$. The ln–ln plot gives a linear relation with a slope of 0.99 for the *trans*-$RuBr_2(Me_2SO)_4$ catalyst, and similarly for the *cis*-$RuCl_2(Me_2SO)_4$ catalyst, a linear relation with a slope of 1.02 was observed. Consequently, these oxidations are first order in the total ruthenium concentration.

The dependence of the reaction rates on oxygen for these two catalysts was also studied (see Figure 4). For both the *cis*-$RuCl_2(Me_2SO)_4$ and *trans*-$RuBr_2(Me_2SO)_4$ catalysts plots of the observed reaction rate vs. pressure of oxygen exhibit nonlinear behavior. In fact, at sufficiently large oxygen pressures the reactions approach zero order in oxygen for both catalysts. At lower oxygen pressures the oxygen dependence approaches a linear first-order dependence. Thus, assuming Henry's law is valid under these conditions, these reactions clearly exhibit a variable and less than unity oxygen dependence with both catalysts.

The effect of varying the alcohol solvent concentration was studied. These studies were done in both dry 2-propanol and methanol solvent systems with varying amounts of dry acetone added as an inert diluent. The rate of conversion of decyl methyl sulfide (0.15 M) to its sulfoxide at 100 °C and 100 psi of O_2 with the *trans*-$RuBr_2(Me_2SO)_4$ catalyst decreased as the percent acetone in the solvent increased for both systems. The complex shape of the plot of observed rate vs. methanol concentration indicates that there is an alcohol dependence on the reaction rate but that this dependence cannot be precisely defined by studying solvent changes directly. This is not a surprising conclusion since we know that in changing the solvent system a change in the oxygen concentration[25] will result. Further, a change in the solvent composition will certainly change the solvent dielectric, as well as affecting more subtle factors such as ionic strength, pH, etc. All such factors will effect the rate of electron-transfer reactions.

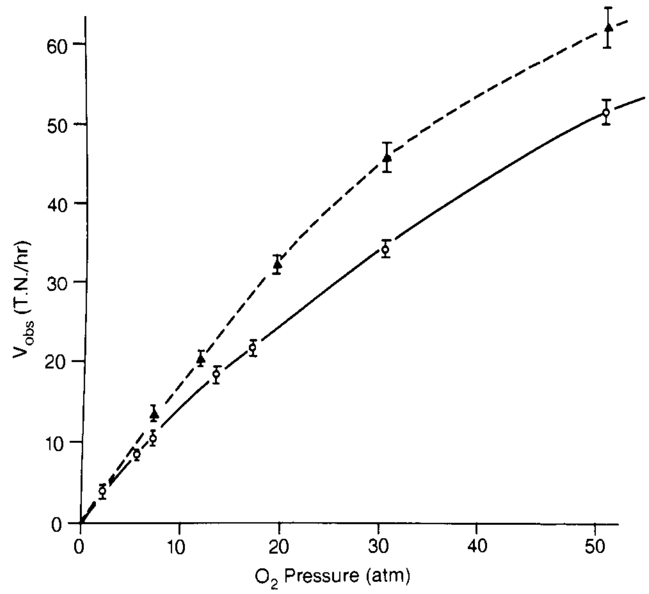

Figure 4. Plot of $(k_{obsd}/[Ru]_{tot})$ vs. P_{O_2} for the O_2 oxidation of decyl methyl sulfide (0.15 M) in methanol (sub/cat. = 50): (▲) *cis*-$RuCl_2(Me_2SO)_4$, T = 108 °C, and (○) *trans*-$RuBr_2(Me_2SO)_4$, T = 95 °C.

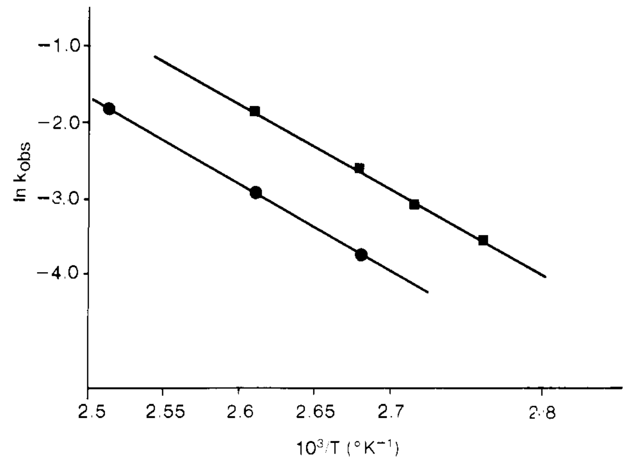

Figure 5. Arrhenius plots (ln k_{obsd} vs. $1/T$) for the $RuX_2(Me_2SO)_4$ catalyzed O_2 (100 psi) oxidation of decyl methyl sulfide (0.15 M) with sub/cat. = 50: (●)-*cis*-$RuCl_2(Me_2SO)_4$ and (■) *trans*-$RuBr_2(Me_2SO)_4$.

Temperature Studies. In Figure 5 are shown linear Arrhenius plots for the *trans*-$RuBr_2(Me_2SO)_4$ and *cis*-$RuCl_2(Me_2SO)_4$ catalysts under 100 psi of O_2.[25] The plots of ln k_{obsd} vs. $1/T_{abs}$ for these two catalysts give straight lines over the temperature ranges investigated. For the *cis*-$RuCl_2(Me_2SO)_4$ catalyst E_a and $\Delta S^{\ddagger}$ are calculated to be 22.3 kcal/mol and −8.6 eu, respectively. For the *trans*-$RuBr_2(Me_2SO)_4$ catalyst E_a and S are calculated to be 23.7 kcal and −2.6 eu, respectively.

Mechanistic Studies. The sulfide oxidation is visualized to occur by either of two mechanisms: a direct reaction with either free or coordinated peroxide[27,28] (eq 2) produced by the O_2 oxidation

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(25) Oxygen concentration in MeOH and acetone can be approximated from published data. Since changes in the oxygen concentration over the temperature range −25 to +50 °C in these solvents are virtually linear and quite small, an extrapolation to 100 °C gives an approximate O_2 solubility in MeOH of 6.7 × 10^{-2} M and in acetone of 13.0 × 10^{-2} M.[26]

(26) Kretschmar, C. B.; Nowakowski, J.; Wiebe, R. *Ind. Eng. Chem.* **1946**, *38*, 506.

of a ruthenium(II) complex (eq 1) or by a direct nucleophilic attack of H_2O on a sulfide coordinated to the oxidized metal complex, presumably a Ru(IV) complex, followed by an internal two-electron transfer (eq 3). The last step (eq 3) has precedent

$$\text{``Ru(II)''} + O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{``Ru(IV)''} + O_2^{2-} \qquad (1)$$

$$SR_2 + H_2O_2\ (HO_2^-) + ROH \xrightarrow{k_2} S(\rightarrow O)R_2 + H_2O\ (OH^-) + ROH \qquad (2)$$

$$\text{``Ru(IV)-SR}_2\text{''} + H_2O \xrightarrow{k_3} \text{``Ru(II)''} + S(\rightarrow O)R_2 + 2H^+ \qquad (3)$$

in Au(III) chemistry where $AuCl_3 + (PhCH_2)_2S + H_2O \rightarrow AuCl + (PhCH_2)_2SO + 2HCl$.[29] Alternatively, the reduction of a "Ru(IV)" complex back to the Ru(II) state could be achieved by electron transfer from the solvent alcohol (eq 4).[8] To better define

$$\text{``Ru(IV)''} + R_1R_2CHOH \xrightarrow{k_3} Ru(II) + R_1R_2C{=}O + 2H^+ \qquad (4)$$

the chemical possibilities, a number of separate studies were carried out to determine if sulfide or alcohol or both were functioning as the reductant of the oxidized metal. During the course of the entire reaction with both the *cis*-$RuCl_2(Me_2SO)_4$ and *trans*-$RuBr_2(Me_2SO)_4$ catalysts (0.15 M decyl methyl sulfide, sub/cat. = 100, 100 °C, 2-propanol solvent, 100 psi of O_2), the molar ratio of solvent oxidation product, acetone, relative to sulfoxide was constant and equaled 1.05 ± 0.05. Additional experiments with both catalysts under the same conditions using a 98% 2-propanol–2% $H_2{}^{18}O$ solvent system were performed. Thus, in these studies if any sulfide is oxidized by the metal and water (eq 3), the product sulfoxide should contain some ^{18}O-sulfoxide. Quantitative studies by GC–mass spectral analyses reveal that no oxygen-18 incorporation occurs during the entire catalytic reaction.

Finally, the role of added protons was investigated with both catalysts for the oxidation of decyl methyl sulfide (0.2 M, sub/cat. = 50) in methanol using added HSO_3CF_3 (0.2 mmol). For both catalysts added acid had no effect upon the observed kinetics or on the measured rates of sulfide conversion to sulfoxide.

Discussion

Mechanism. A mechanism consistent with the data can be deduced. The active oxidant in these reactions is peroxide (eq 2) generated in an oxidation of a Ru(II) complex (vide infra) with molecular oxygen (eq 1). The high selectivities for sulfoxide over sulfone are consistent with selectivities observed for sulfide oxidations with hydrogen peroxide (at low H_2O_2/SR_2 levels) at lower temperatures where sulfoxide is favored by factors of at least 100.[27] The molecular oxygen oxidation of a ruthenium(II) complex can either involve direct two-electron transfer from the metal to form a Ru(IV) complex and peroxide[6,8] (indistinguishable from two successive one-electron transfer steps) or a one-electron transfer to give a Ru(III) complex and superoxide,[6,7] which itself could disproportionate to yield peroxide.[30] The catalytic redox cycle on the ruthenium could either involve a Ru(II,IV) or Ru(II,III) couple. It is known, for example, that both the Ru^{III}(terpyridine)(bipyridine)OH^{2+} and Ru^{IV}(terpyridine)(bipyridine)O^{2+} complexes will oxidize 2-propanol to acetone competitively in water, although the Ru(IV) pathway is faster than the Ru(III) path.[31]

While our kinetic results do not unequivocally discern between the two choices, a number of different results suggest that Ru(III) is not involved in this redox chemistry. For example, various studies with discrete Ru(III) complexes (including some with various combinations of thioether and sulfoxide ligands present) indicate that Ru(III) is very likely not involved in this redox chemistry. Additionally, if ruthenium(III) were the active oxidant of solvent in these catalytic oxidations, the oxidation of the alcohol would proceed via a radical pathway consisting of two successive one-electron steps, as has been demonstrated as in eq 5 and 6.[31]

$$\text{``Ru(III)''} + R_1R_2CHOH \xrightarrow{k_3} \text{``Ru(II)''} + R_1R_2\dot{C}OH + H^+ \qquad (5)$$

$$\text{``Ru(III)''} + R_1R_2\dot{C}OH \xrightarrow{\text{fast}} \text{``Ru(II)''} + R_1R_2C{=}O + H^+ \qquad (6)$$

The catalytic oxidations reported here were monitored for the presence of coupled alcohol products (e.g., glycols) and, most especially, for α-oxidation products of the sulfide substrates.[32] In no instance was the formation of the α-H atom abstraction pathway products (decanal or decanoic acid) observed in these catalytic oxidations with primary thioether substrates. Since thioethers are susceptible to initiated autoxidation, the absence of any radical pathway induced products suggests that the catalytic oxidation of the primary thioether substrates described here does not produce such free-radical species as the alcohol radical and that Ru(III) is not the oxidant of the solvent.

"Ruthenium(III) chloride" in alcohol solvents has been reported to catalyze the molecular oxygen oxidation of sulfides affording mixtures of sulfoxides and sulfones.[1] When we repeated this work with ruthenium(III) chloride hydrate which had been treated with hydrogen (see Experimental Section) to remove Ru(IV) impurities, there was no catalytic activity observed. But when crude "ruthenium(III) chloride" containing Ru(IV) was used, oxidation of the decyl methyl sulfide substrate in 2-propanol does afford about 20% conversion to sulfoxide with a few percent sulfone (same experimental as Table I). While this is not a very active catalytic system, it does provide additional evidence that Ru(IV) and not Ru(III) is involved in this catalytic redox chemistry producing peroxide (eq 1).

When several catalytic reactions were carried out in the presence of added acid ($[HSO_3CF_3] \leq [Ru]_{tot}$), no effect was observed on the rate or on the types of products formed. These results are consistent with the mechanism as written in eq 1, where there is no proton dependence on the electron-transfer step, but is inconsistent with the intermediate production of Ru(III) and superoxide.[7] If superoxide is involved and if ruthenium(III) is the fate of the metal when oxidized, then acid should increase the rate of the reaction by promoting the formation of a more active oxidant, $HO_2\cdot$ (eq 7 and 8).[7] Since added protons have no effect, this suggests that superoxide and also ruthenium(III) are not involved in this redox chemistry.

$$Ru(II) + H^+ + HO_2\cdot \rightarrow Ru(III) + H_2O_2 \qquad (7)$$

$$Ru(II) + HO_2\cdot \rightarrow Ru(III) + HO_2^- \qquad (8)$$

The second step in this catalytic cycle involves the oxidation of sulfide with the peroxide in the alcoholic solvent (a termolecular reaction[28]) to yield sulfoxide (eq 2). That peroxide and not the oxidized metal complex is the sole oxidant of the sulfide is supported by ^{18}O-water labeling experiments and by the fact that the rate of solvent oxidation is virtually identical with the rate of sulfoxide production. This latter fact is also consistent with solvent acting as the sole reductant of the oxidized metal. This and the observed alcohol solvent concentration dependence is consistent with reduction of the oxidized species—a ruthenium(IV) complex—by the solvent alcohol (eq 4). The actual thioether oxidant is very likely HO_2^- or H_2O_2 and not free O_2^{2-}. Since the chemistry is carried out in hydroxylic solvents and since reduction of the oxidized ruthenium by alcohol solvent must produce protons,

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[27] Edwards, J. O. "Peroxide Reaction Mechanism"; J. Wiley & Sons: New York, 1962; Chapter 5, p 96.

[28] Overberger, C. C.; Cummins, R. W. *J. Am. Chem. Soc.* **1953**, *75*, 4783.

[29] Herman, F. *Ber.* **1905**, *38*, 2813.

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[31] Thompson, M. S.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 4106.

[32] (a) Howard, J. A.; Korcek, S. *Can. J. Chem.* **1971**, *49*, 2178. (b) Bateman, L.; Cunneen, J. I.; Ford, J. *J. Chem. Soc.*, **1956**, 3056 and references therein.

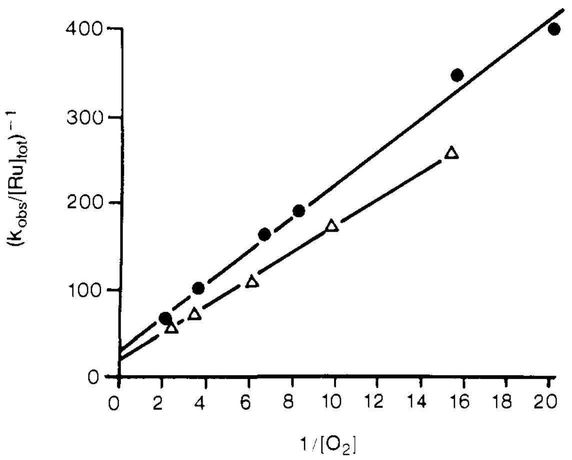

Figure 6. Plot of $[O_2]^{-1}$ vs. $(k_{obsd}/[Ru]_{tot})^{-1}$ for the oxidation of decyl methyl sulfide with conditions the same as for Figure 4: (△) *cis*-$RuCl_2(Me_2SO)_4$ and (●) *trans*-$RuBr_2(Me_2SO)_4$.

there is an abundant source of protons.

In order to test this mechanistic scheme, an integrated rate expression was derived by using eq 1, 2, and 4. The observed reaction velocity V is simply the rate of loss of sulfide (eq 9). Since

$$V = -d[SR_2]/dt = k_2[SR_2][O_2^{2-}][ROH] \qquad (9)$$

there is no evidence for a k_{-2} term, there is only one reaction rate constant in this expression. Using a steady-state approximation for the concentration of peroxide and the assumption that k_{-3} is also vanishingly small gives

$$V = k_2[SR_2][ROH]\left[\frac{k_1[Ru^{II}][O_2]}{k_{-1}[Ru^{IV}] + k_2[SR_2][ROH]}\right] \qquad (10)$$

In addition, assuming that the steady-state treatment for oxidized Ru, $[Ru^{IV}]$, is valid[33] and that the $[Ru]_{tot} = [Ru^{IV}] + [Ru^{II}]$, where the term $k_{-1}[Ru^{IV}]/k_2[SR_2][ROH]$ is small,[27,34] then with suitable manipulations the rate law (eq 11) can be derived.

$$V = \frac{k_1k_3[Ru]_{tot}[O_2][ROH]}{k_1[O_2] + k_3[ROH]} \qquad (11)$$

This rate law expression is in excellent agreement with our observed kinetics. It correctly predicts the first order dependence on total metal catalyst added, as well as the zero order dependence on the sulfide substrate concentration. Even more significant is that it also predicts a less than unity reaction order for the oxygen concentration. This expression implies that plots of $[Ru]_{tot}/V$ vs. $[O_2]^{-1}$ should be linear with a slope equal to $1/k_1$ and an intercept of $1/(k_3[ROH])$. Such plots (Figure 6) for both the *cis*-$RuCl_2(Me_2SO)_4$ and *trans*-$RuBr_2(Me_2SO)_4$ catalysts are indeed linear (correction coefficient ≥0.98). The values of k_1 and k_3 for the *cis*-$RuCl_2(Me_2SO)_4$ catalyst at 108 °C are 5.1×10^{-4} atm^{-1} s^{-1} ($k_1 \sim 6 \times 10^{-2}$ M^{-1} s^{-1}) and 2.1×10^{-3}, M^{-1} s^{-1}, respectively. Values of k_1 and k_3 for the $RuBr_2(Me_2SO)_4$ catalyst at 95 °C are 4.7×10^{-4} atm^{-1} s^{-1} ($k_1 \sim 5.3 \times 10^{-2}$ M^{-1} s^{-1}) and 1.1×10^{-3} M^{-1} s^{-1}) and 1.1×10^{-3} M^{-1} s^{-1}, respectively. Thus, the kinetic rate expression (eq 11) derived from eq 1, 2, and 4 is in excellent agreement with experimental results and provides kinetic support for the proposed mechanism of these selective and facile sulfide oxidations utilizing molecular oxygen.

The values obtained for k_1 and k_3 for these catalysts suggest that the oxidation of a ruthenium(II) complex with oxygen is inherently on the order of 50 times as fast as the reduction of the oxidized metal with alcohol. However, since the concentration of solvent methanol is about 24.0 M and the concentration of O_2 at 100 psi is about 0.06 M,[25] the denominator of eq 11 is dominated by the $k_3[ROH]$ term. As a consequence, at lower O_2 pressures and high methanol concentration the observed rate of sulfide consumption is given by the approximation

$$-d[SR_2]/dt = k_1[Ru]_{tot}[O_2] \qquad (12)$$

Thus, the rate-determining step at lower oxygen pressures is oxidation of the metal with oxygen. Since Arrhenius plots were made at 100 psi, the low activation entropy values measured for these two catalytic systems are consistent with an outer-sphere electron transfer for the oxygen oxidation of Ru(II). These values are similar in magnitude to the value reported for the oxidation of $Ru(NH_3)_6^{2+}$ with O_2 at 11 °C, $\Delta S^{\ddagger} = -10.4 \pm 1.0$ eu.[6] Indeed, we believe that these results provide support for our original contention that to achieve dioxygen catalysis with poor ligands, such as sulfides, it would be necessary to use metal complexes that can undergo outer-sphere electron transfer to give free peroxide in solution.

The reduction of the oxidized ruthenium (presumably Ru(IV)) with alcohol very likely would occur by a mechanism similar to that reported previously for the reduction of Ru(IV) with alcohols.[8] Either a six- or seven-coordinate intermediate alcohol adduct could lose a proton to form an alkoxide complex which could undergo internal two-electron transfer to give Ru(II) and aldehyde or ketone. Alternatively, this could be viewed as the transfer of a β-hydride (α-CH) from a coordinated alkoxide,[35] followed by reductive elimination of a proton from the high-valent metal to give Ru(II).

An observation that requires discussion is the origin of the profound effect of the sulfide substrate on the rate. In this regard we have shown in a control reaction in which sulfide is not present that no catalytic oxidation of the alcohol will occur in the presence of the $RuX_2(DMSO)_4$ complexes. However, the mechanism of eq 1, 2, and 4 predicts that a catalytic oxygen oxidation of the alcohol solvent should occur and that sulfide or perhaps other substrates[36] simply trap the peroxide as it forms. This observation, as well as the profound effect of substrate (Table III) on the reaction rates, implies that these $RuX_2(Me_2SO)_4$ complexes must react with sulfide to form the actual catalyst in situ:

$$RuX_2(Me_2SO)_4 + \text{excess } SR_2 \rightarrow RuX_2(Me_2SO)_{4-x}(SR_2)_x + xMe_2SO \qquad (13)$$

We have observed that facile substitution of Me_2SO ligands does occur with sulfide ligands present in excess.[36] Thus, to complete our understanding of this active and selective oxygen oxidation system, we are studying the nature of the species formed in situ. By isolating such complexes and studying their chemistry, we hope to be able to identify the structure of the catalyst and to solve the question of whether or not the oxidized metal is indeed Ru(IV). Such a characterization will make it possible to obtain a complete kinetic picture, with the true values of k_1 and k_3. Since we are dealing with the possibility that a small percentage of added metal actually forms the catalyst, the true rate constants may be very fast indeed. In fact, from the substrate dependence data one can see that large rate enhancements are possible. Furthermore, it appears that electronic factors are not the sole source of the rate differences observed with the different sulfides but that subtle steric effects must play a dramatic role in determining the structure (cis or trans), as well as the degree of substitution, of any $RuX_2(Me_2SO)_{4-x}(SR_2)_x$ complex.

Registry No. Ru(TPP)CO, 32073-84-0; $RuCl_2(PPh_3)_3$, 15529-49-4; *cis*-$RuCl_2(Me_2SO)_4$, 59091-96-2; *trans*-$RuCl_2(CH_3CN)_4$, 30066-40-1; $Ru(SnCl_3)_2(Me_2SO)_4$, 41290-69-1; *trans*-$RuBr_2(Me_2SO)_4$, 72904-46-2; *trans*-$RuI_2(Me_2SO)_4$, 72907-35-8; $PhSCH_3$, 100-68-5; dimethyl sulfide, 75-18-3; tetrahydrothiophene, 110-01-0; decyl methyl sulfide, 22438-39-7; diethyl sulfide, 352-93-2; di-*n*-butyl sulfide, 544-40-1; diisobutyl sulfide, 592-65-4; di-*tert*-butyl sulfide, 107-47-1.

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[33] The solution of $[Ru^{IV}] = k_1[Ru^{II}][O_2]/(k_{-1}[O_2^{2-}] + k_3[ROH])$ can be simplified by assuming that $k_{-1}[O_2^{2-}] \ll k_3[ROH]$ which yields $[Ru^{IV}] = k_1[Ru^{II}][O_2]/k_3[ROH]$.

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[36] Subject of further reports.