trans-Dibromotetrakis(dimethyl sulfoxide)ruthenium(II): a Versatile Starting Material for the Synthesis of Ruthenium(II) Complexes for Use as Molecular Oxygen Oxidation Catalysts

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Received June 12, 1984

Abstract

The synthesis of neutral ruthenium(II) dihalo complexes of the type $RuX_2(Me_2SO)_3L$ and $RuX_2(L')_4$, using the easily prepared $RuBr_2(Me_2SO)_4$ complex is described. The synthesis of Ru(II) complexes of the type where L is a phoshine or arsine yields materials that are very active catalysts for the molecular oxygen oxidation of thioethers to sulfoxides. The new complexes are characterized via elemental analyses, ^1H NMR spectra, electronic spectra, their $E_{1/2}$ values (determined by cyclic voltammetry), and by their catalytic activity for the oxygen oxidation of thioethers to sulfoxides.

Introduction

The ruthenium complexes $RuX_2(Me_2SO)_4$, can function as catalysts in alcoholic solvents for the selective aerial oxidation of thioethers to their sulfoxides [1]. In our attempts to improve the activity of these ruthenium(II)-based catalysts we discovered that the anion plays a profound role in their activity [2]. Not only must two anions be coordinated to the ruthenium, but the identity of the anions play a major role in determining catalytic activity in these systems. For example, in methanol solvent the turn-over number (h^{-1}) for decyl methyl sulfide (0.15 M) oxidation (100 °C, 100 psi O_2, 3.0×10^{-3} M Ru) was 19 for X = Br, 6 for X = Cl, and 1 for X = I.

In our further attempts to optimize the activity of these ruthenium(II) complexes for this aerial oxidation of sulfides to sulfoxides, we synthesized several ruthenium(II) complexes having other neutral ligands. These complexes were also tested under similar conditions to determine their activities. Reported here are some representative examples of ruthenium(II) complexes which were screened for catalytic activity. For the synthesis of the ruthenium(II) complexes described here, we utilized the *trans*-$RuBr_2(Me_2SO)_4$ complex as the starting source of ruthenium, since the greatest activity is exhibited when the counterion is bromide. Using methodology that is similar to that reported for *cis*-$RuCl_2(Me_2SO)_4$ [3], we have found that phosphines can readily replace one Me_2SO ligand to afford complexes of the type $RuBr_2(Me_2SO)(L)$. This is different from that observed with the chloro complex [3], since the reaction product stoichiometry in those cases is $RuCl_2(Me_2SO)_2(PR_3)$. With other less bulky donors such as pyridine or acetonitrile, *trans*-$RuBr_2(L)_4$ complexes readily form.

The synthesis, characterization and electrochemistry of several new complexes are described in this report. Special emphasis is placed on the catalytic activity exhibited by these complexes for the aerial oxidation of sulfides to sulfoxides. Additionally, a kinetic study of this conversion catalyzed by one of these complexes, $RuBr_2(Me_2SO)_3(PPh_3)$, is discussed.

Experimental

General Information

All syntheses were carried out under a dry inert argon atmosphere using conventional Schlenk-ware techniques and dry degassed solvents to prevent oxygen oxidation of the Ru(II) complexes. Elemental analyses were done by Galbraith Laboratories, Knoxville, Tenn. Proton NMR spectra were recorded in $CDCl_3$ at 60 MHz on a Varian T-60 spectrometer using $(CH_3)_4Si$ as an internal standard. Infrared spectra were recorded as Nujol mulls between CsBr windows on Perkin-Elmer model 298 and 621 spectrophotometers. Electronic spectra were recorded in the UV/VIS regions on a Beckman DU-7

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0020-1693/85/$3.30

spectrophotometer using chloroform solutions in Teflon stoppered quartz cells.

All cyclic voltammograms were measured in 0.10 M tetra-n-butylammonium tetrafluoroborate in methylene chloride. The methylene chloride was dried by passing through two columns of dry alumina and then distilling over CaH_2 under dry N_2. The supporting electrolyte was twice recrystallized from ethyl acetate-hexane. A single compartment, three electrode cell was used. It had a platinum workking electrode, platinum wire auxiliary electrode, and a Ag/AgCl reference electrode in H_2O separated from the CH_2Cl_2 by a ceramic frit. The voltammograms were measured with a PAR 173 potentiostat and a PAR universal programmer and recorded on an oscilloscope. Oxidation reaction profiles under oxygen pressure were carried out by procedures described elsewhere [1]. The quantitative monitoring of reaction products from decyl methyl sulfide oxidations is also described elsewhere [1].

Syntheses

Trans-Dibromotetrakis(pyridine)ruthenium(II), trans-$RuBr_2(Pyr)_4$ [4, 5]

To a toluene solution (50 ml) containing 3.0 ml of pyridine was suspended 0.5 g of *trans*-$RuBr_2(Me_2SO)_4$. The suspension was refluxed under Ar for 30 min. During this period a deep red solution formed and crystals precipitated. After cooling, the orange crystalline product was collected by filtration, washed with diethyl ether, and dried *in vacuo* to yield 0.43 g (84%) of the desired product. The identity of this material was confirmed by comparison to authentic material and by elemental analysis. *Anal.* Calc. for $C_{20}H_{20}Br_2N_4Ru$: C, 41.61; H, 3.49; N, 27.68. Found: C, 41.38; H, 3.58; N, 27.88%.

Dibromotris(dimethylsulfoxide)(triphenylphosphine)ruthenium(II), $RuBr_2(Me_2SO)_3(PPh_3)$

To a toluene solution (50 ml) containing 0.23 g (0.87 mmol) of triphenylphosphine was suspended 0.50 g (0.87 mmol) of *trans*-$RuBr_2(Me_2SO)_4$. This suspension was refluxed under Ar for 30 min to give an orange solution which was then cooled. The toluene was removed via a vacuum and a pale-orange solid was dissolved in a minimum volume of warm acetone (~6 ml). To this solution diethyl ether was added dropwise till cloudiness developed. The solution was cooled at –40 °C for several hours and a pale orange microcrystalline product formed. This was collected by filtration, washed with diethyl ether and dried *in vacuo* for several hours. The yield was 55% of theoretical (0.36 g). *Anal.* Calc. for $C_{24}H_{33}Br_2O_3PRuS_3$: C, 38.05; H, 4.39; Br, 21.10; S, 12.70. Found: C, 38.29; H, 4.11; Br, 21.01; S, 12.57%.

Dibromotris(dimethyl sulfoxide)(triphenylarsine)ruthenium(II), $RuBr_2(Me_2SO)_3(AsPh_3)$

This complex was synthesized by the same procedure as outlined for the preceding triphenylphosphine complex. Using 0.5 g of $RuBr_2(Me_2SO)_4$, 0.41 g of the desired complex was obtained for a 61% yield. *Anal.* Calc. for $C_{24}H_{33}AsBr_2O_3RuS_3$: C, 35.96; H, 4.15; Br, 19.94; S, 12.00. Found: C, 36.26; H, 4.01; Br, 19.62; S, 11.77%.

Dibromotris(dimethyl sulfoxide)(tributylphosphite)ruthenium(II), $RuBr_2(Me_2SO)_3(P(OBu)_3)$

This complex was synthesized by the same procedure as described above for the preceding two complexes. This complex was much more soluble, as a consequence, hexanes were added to the diethyl ether solution to induce precipitation. The crude orange product was recrystallized from diethyl ether to give 0.24 g (37%) of pale-orange crystals. *Anal.* Calc. for $C_{18}H_{45}Br_2O_6PRuS_3$: C, 29.00; H, 6.08; Br, 21.43; S, 12.90. Found: C, 29.19; H, 6.17; Br, 21.63; S, 13.11%.

Dibromotris(dimethyl sulfoxide)(tri-n-butylphosphine)ruthenium(II), $RuBr_2(Me_2SO)_3(PBu_3)$

This complex was prepared in an analogous fashion to the preceding complexes, but 0.87 mmol of the $RuBr_2(Me_2SO)_4$ complex and 0.18 g tributylphosphine were used. After removal of the toluene, this product was dissolved in 15 ml of 1:1 MeOH/Et_2O. The diethyl ether was then removed on a rotovap and the concentrated methanol solution was cooled for two days at –40 °C. Bright yellow crystals formed and were collected via filtration and then dried *in vacuo* for 24 h. The yield was 0.31 g (51%). *Anal.* Calc. for $C_{18}H_{45}Br_2O_3PRuS_3$: C, 30.99; H, 6.50; Br, 22.91; S, 13.79. Found: C, 30.77; H, 6.62; Br, 22.71; S, 13.62%.

Dibromotris(dimethyl sulfoxide)(1,2-bis(diphenylphosphino)ethane)ruthenium(II), $RuBr_2(Me_2SO)_2(Diphos)$

To a toluene solution (75 ml) containing 0.62 g diphos (1.57 mmol) was suspended 0.90 g (1.57 mmol) of $RuBr_2(Me_2SO)_4$. The suspension was then refluxed for 30 minutes to give an orange-red solution. Upon cooling, yellow crystals precipitated. These were collected and recrystallized from hot toluene to give 0.73 g (57%) of the desired product. *Anal.* Calc. for $C_{30}H_{36}Br_2O_2P_2RuS_2$: C, 44.18; H, 4.45; Br, 19.60; S, 7.86. Found: C, 43.99; H, 4.52; Br, 19.74; S, 8.03%.

Trans-Dibromotetrakis(acetonitrile)ruthenium(II), trans-$RuBr_2(CH_3CN)_4$

One gram of $RuBr_2(Me_2SO)_4$ was stirred under Ar in refluxing acetonitrile for 16 h. A dull yellowish precipitate formed upon cooling and was collected

TABLE I. Selected Me_2SO Frequencies from the Solid State Infrared Spectra of the new Ru(II) Complexes.

Compound	Frequency (cm^{-1}) (Assignment) Intensity
$RuBr_2(Me_2SO)_3(PPh_3)$	1100^a and 1084 (ν_{SO}) broad
$RuBr_2(Me_2SO)_3(PBu_3)$	1075 (ν_{SO}) broad
	1025 (ρ_r, CH) broad
	977 and 942 (ρ_r, CH) sharp
	721 and 673 (ν_{CS}) sharp
$RuBr_2(Me_2SO)_3(P(OBu)_3$	1100 (ν_{SO}) broad
	1015 (ν_{SO}) $broad^b$
	980 and 940 (ρ_r, CH) broad, weak
	718 and 676 (ν_{CS}) sharp
$RuBr_2(Me_2SO)_2(diphos)$	1079 (ν_{SO}) sharp and intense
	1022 (ρ_r, CH) sharp
	972 and 935 (ρ_r, CH) weak
	740 and 694 (ν_{CS}) sharp

[a]Shoulder. [b]Shows a shoulder.

TABLE II. ^1H NMR of New Ru(II) Complexes.

Complex	Chemical Shift δ, ppm
trans-$RuBr_2(CH_3CN)_4$	2.1 (singlet)
$RuBr_2(Me_2SO)_3(PPh_3)$	2.6^a, 2.9^a, 3.2^a, 3.4^a, 3.6^a, 3.8^a, 7.4^a(broad)
$RuBr_2(Me_2SO)_2(diphos)$	PCH_2, 2.45^b (J_{PH} = 25 Hz), CH_3SO: 3.53: Ph–H, 7.2
$RuBr_2(Me_2SO)_3(PBu_3)$	1.25^c, CH_3SO: 2.62, 3.51
$RuBr_2(Me_2SO)_3(POBu_3)$	0.95^d, 1.41^d, 1.60^d, 2.15^d, 2.62^a, 3.41^a, 3.47^a, 3.52^a, 3.60^a

[a]See text. [b]Doublet. [c]Complex grouping due to PBu_3. [d]Due to $P(OBu)_3$.

by filtration, washed with Et_2O, and dried *in vacuo*. The yield of the desired complex was 0.61 g (82%). *Anal.* Calc. for $C_8H_{12}Br_2N_4Ru$: C, 22.60; H, 2.85; Br, 37.60; N, 13.18. Found: C, 22.79; H, 3.10; Br, 37.11; N, 13.30%.

Results

Synthesis and Characterizations

All of the synthesis described here utilized the *trans*-$RuBr_2(Me_2SO)_4$ complex as the starting material and were carried out under an inert atmosphere since the products are air-sensitive. All of the products were characterized via their elemental analyses, IR spectra, UV–Vis. spectra, and ^1H NMR spectra. The IR spectra of these complexes were particularly important for defining the solid state bonding mode of the residual Me_2SO ligands, while the ^1H NMR studies have advanced our understanding of the solution chemistry of these catalysts.

The infrared assignments of the new phosphine complexes are listed in Table I. The most significant feature these four complexes exhibit is the presence of intense absorptions near 1100 cm^{-1} attributable to the S–O stretch for S-bonded sulfoxide [2, 3, 6]. The relative weakness of the bands in the 900–1000 cm^{-1} region and the relative simplicity of their spectra in that region suggest that O-bonded Me_2SO ligands are not present in these complexes.

The solution ^1H NMR spectra of the $RuBr_2(Me_2SO)_3(L)$ complexes (Table II) suggest that the Me_2SO ligands are undergoing exchange, whereas the diphos complex shows no evidence of Me_2SO exchange. In the ^1H NMR spectrum of the $RuBr_2(Me_2SO)_3(PPh_3)$ complex, the integration of phenyl protons against Me_2SO protons confirms that three Me_2SO ligands are present. For this complex there are at least six chemically distinct singlets attributable to Me_2SO. The presence of a weak resonance at 2.9 δ (corresponding to O-bound Me_2SO [3]) suggests

TABLE III. Electronic Spectra of Ru(II) Complexes.

Complex	λmax (cm^{-1}), (ε)
cis-$RuCl_2(Me_2SO)_4$	27900(492), 32210(330), 39200(1670)
trans-$RuBr_2(Me_2SO)_4$	21380(207), 32050(Sh), 37600(2740)
trans-$RuBr_2(Pyr)_4$	25370(26430), 33333(2630), 40000(17,000)
$RuCl_2(Me_2SO)_2(PPh_3)$	21100(225,Sh), 27260(1455), 38840(15,030)
$RuBr_2(Me_2SO)_3(PPh_3)$	20420(293), 25450(1440), 39060(27,000)
$RuBr_2(Me_2SO)_3(PBu_3)$	21570(174), 27620(Sh), 39250(5400)
$RuBr_2(Me_2SO)_3(P(OBu)_3)$	20620(157), 27230(1020)
$RuBr_2(Me_2SO)_2$(diphos)	21370(76), 30300(Sh), 36760(4260)
$RuBr_2(Me_2SO)_3(AsPh_3)$	21740(270), 28370(Sh), 37600(4500)

TABLE IV. Comparison of the $E_{1/2}$ Values and Turnover Numbers for the Oxidation of Decyl Methyl Sulfide (at 100 °C, 100 psi O_2 in Methanol) Catalyzed by Ruthenium(II) Complexes.

Complex	$E_{1/2}$ (V)	T.N. (h^{-1})
cis-$RuCl_2(Me_2SO)_4$	+1.55[a]	6
trans-$RuBr_2(Me_2SO)_4$	+1.55[a]	19
trans-$RuBr_2(Pyr)_4$	+0.37	19[b]
trans-$RuBr_2(CH_3CN)_4$	+0.78	19[b]
$RuCl_2(PPh)_3$	+0.70	<1
$RuCl_2(Me_2SO)_2(PPh_3)$	+0.91	9
$RuBr_2(Me_2SO)_3(PPh_3)$	+0.94	22
$RuBr_2(Me_2SO)_3(PBu_3)$	+0.76	24
$RuBr_2(Me_2SO)_3(P(OBu)_3)$	+1.1	11
$RuBr_2(Me_2SO)_3(AsPh_3)$	+1.2[a]	22.5
$RuBr_2(Me_2SO)_2$(diphos)	+1.01	5

[a] Irreversible. [b] Initiation period.

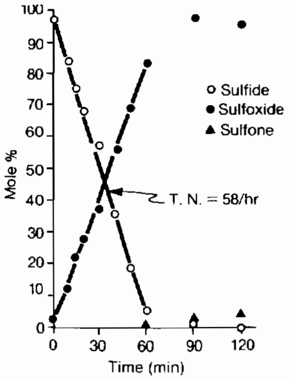

Fig. 1. Reaction profile for the oxidation of decyl methyl sulfide (0.15 M) with molecular oxygen (200 psi) in methanol (sub/cat = 60 and T = 105 °C).

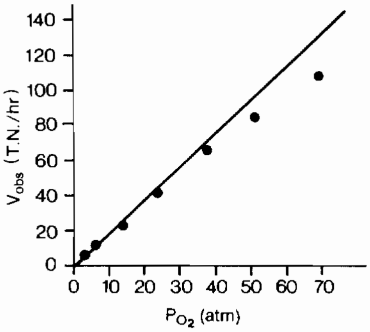

Fig. 2. Plot of the observed reaction rate V *vs.* oxygen pressure for the molecular oxygen oxidation of decyl methyl sulfide (0.13 M) at 95 °C in methanol catalyzed with $RuBr_2(Me_2SO)_3(PPh_3)$ (sub/cat = 70).

that some O-bound sulfoxide is present. The addition of d_6-Me_2SO causes an increase in the intensity of the 2.60 δ peak (free Me_2SO), and also results in the virtual disappearance of the 3.68 δ peak – the remainder of the spectrum is unchanged. This indicates that the O-bound Me_2SO (the 2.6 δ peak) and one S-bound sulfoxide are exchanging, whereas the remainder of the S-bound Me_2SO ligands are not. The tributylphosphine complex again shows the presence of free Me_2SO at 2.62 δ, but only one other Me_2SO resonance is observed (3.51 δ), corresponding to S-bound Me_2SO [3]. The integration reveals that the ratio of S-bound Me_2SO to free is 2 to 1. The tributylphosphite complex displays solution behavior similar to that observed for the PPh_3 complex; namely, the Me_2SO region is again complex for $RuBr_2(Me_2SO)_3(P(OBu)_3)$. Addition of d_6-Me_2SO causes the peak assigned to free Me_2SO at 2.62 δ to increase while causing the resonances at 3.41 δ and 3.47 δ to disappear. and leaves the remainder of the spectrum unchanged. The ^1H NMR of the diphos complex $RuBr_2(Me_2SO)_2$(diphos) shows but one type of S-bound Me_2SO ligand, consistent with a symmetrical *trans*-dibromo-*cis*-bis(dimethyl sulfoxide) structure.

Kinetic and Mechanistic Studies

The complexes reported here are all catalysts (Table IV) for the aerial oxidation of sulfides to sulfoxides in alcoholic solvents. In each case the catalytic oxidation is zero-order in the sulfide substrate and first-order in catalyst, while exhibiting variable and less than a first-order dependence in oxygen pressure. A reaction profile is shown in Fig. 1 for the $RuBr_2(Me_2SO)_3(PPh_3)$ catalyst (105 °C, 200 psi O_2, 0.15 M decyl methyl sulfide, 2.5×10^{-4} M = [Ru]). This plot shows the high selectivity for sulfoxide over sulfone product and the zero-order sulfide (and sulfoxide) dependence. Figure 2 shows that the dependence of the rate on oxygen pressure is not linear, but approaches first-order at low O_2 pressure and approaches zero-order at high O_2 pressure. That phosphine remains bound to the metal during the catalytic cycle was demonstrated by noting that phosphine oxide does not form when $RuX_2(Me_2SO)_{2,3}(PR_3)_{1,2}$ complexes are used and also that injection of additional sulfide into the reactor at the end of an experiment gives a second reaction profile identical to the first. The relative catalytic activities for the complexes reported here, are listed in Table IV. As can be seen, the replacement of one or two Me_2SO ligands with a single phosphine ligand gives an enhancement in the rate relative to that observed with the $RuX_2(Me_2SO)_4$ catalysts. For X = Cl, the rate enhancement is about 50% with L = PPh_3. When X = Br the activity increase is about 15% with L = PPh_3. When the phosphine is more electron rich, as with L = PBu_3, the rate enhancement is even greater (~26%) than the L = PPh_3 case, and when the weaker donor phosphite ligand L = $P(OBu)_3$ is used, the rate is actually diminished by 40%. The triphenylarsine complex has about the same rate as observed for the triphenylphosphine complex.

The reaction of *trans*-$RuBr_2(Me_2SO)_4$ with two equivalents of triphenylphosphine yields only the monophosphine substituted complex. But use of 1,2-bis(diphenylphosphino)ethane, diphos, did result in a bisphosphine substituted complex, $RuBr_2(Me_2SO)_2$ (diphos). Unfortunately the presence of the diphos ligand lowers the catalytic activity. And as can be seen with the $RuCl_2(PPh_3)_3$ complex, three phosphine ligands virtually eliminates any catalytic activity. The use of $RuX_2(L)_4$ complexes, where L = acetonitrile, pyridine, or other weak ligand monodentate donors, gives, after several minute initiation periods, the same reaction rates as observed with the parent Me_2SO complexes, $RuX_2(Me_2SO)_4$. All of the catalytic sulfide oxidations using the new ruthenium(II) complexes are first-order in total metal, as was observed previously for the parent $RuX_2(Me_2SO)_4$ catalysts.

Discussion

In earlier kinetic and mechanistic studies we demonstrated that the $RuX_2(Me_2SO)_4$ complexes act as catalyst precursors for the alcoholic molecular oxygen oxidation of thioethers to sulfoxides. From these studies we found that under the reaction conditions various mixed bis(halo)(thioether)(sulfoxide)ruthenium(II) complexes formed, any one (or several) of which could be the catalyst. Consequently, we wanted to ascertain if the presence of other less labile ligands in the ruthenium(II) coordination sphere would influence the observed reaction rates and in particular the reaction mechanism itself. Since the halo ligand that gives the fastest reaction rates is bromo, we largely concentrated our synthetic efforts on the synthesis of neutral dibromo sulfoxide ruthenium(II) complexes. The syntheses of the complexes described here are straightforward, but there were a few surprises as to the identity and solution behavior of some of these monophosphine substituted complexes.

When the starting complex $RuBr_2(Me_2SO)_4$ complex is reacted with an equivalent of phosphine ligand L (L = PBu_3, PPh_3, or $P(OBu)_3$), one Me_2SO ligand is replaced to give a complex with the stoichiometry $RuBr_2(Me_2SO)_3L$. This is in sharp contrast to the reactions with the *cis*-$RuCl_2(Me_2SO)_4$. In this case the isolated products contain only two Me_2SO ligands and are formally five-coordinate. The ^1H NMR spectra of the free monophosphine complexes $RuBr_2(Me_2SO)_3L$ reveal that each complex is undergoing exchange or loss of at least one Me_2SO ligand. In the L = PPh_3 case the ^1H NMR shows the presence of six different Me_2SO methyl resonances, including free Me_2SO. This spectrum can be rationalized on the basis of the presence of three different ruthenium(II) complexes in solution yielding five different methyl resonances and free Me_2SO accounting for the sixth resonance. The three species in solution could be: 1) a six-coordinate *trans*-dihalo complex with all S-bound Me_2SO – two different methyl resonances 2) a five-coordinate complex with two equivalent S-bound Me_2SO ligands – one methyl resonance, and 3) a six-coordinate *trans* dihalo complex with one O-bound sulfoxide *trans* to PPh_3 – three methyl resonances. When free d_6-Me_2SO is added (~5 eq.), the resonances that disappear include those assigned to the methyl of O-bound sulfoxide and two of the peaks assigned to S-bound methyl resonances. This result is consistent with the dissociation of the sulfoxide *trans* to the phosphine to give equilibrium mixtures of ruthenium species containing O-bound sulfoxide, S-bound sulfoxide, and the five-coordinate complex.

When L is tributylphosphine the facile dissociation of a sulfoxide ligand is again apparent, evidenced by the presence of free Me_2SO. But in this case there is only one other methyl resonance present, assigned to S-bound sulfoxide. The integrated ratio of these two peaks is two to one (free Me_2SO). Consequently, the $RuBr_2(Me_2SO)_3(PBu_3)$ complex must dissociate a Me_2SO ligand (most likely that Me_2SO *trans* to the phosphine) to generate a five-coordinate *trans*-dihalo-$RuBr_2(Me_2SO)_2(PBu_3)$ complex in chloroform solution. Finally, when L = $P(OBu)_3$ the ^1H NMR again is complex revealing at least five resonances due to Me_2SO. Free Me_2SO is again apparent at 2.62 δ but there is no evidence for the presence of O-bound sulfoxide. Addition of d_6-Me_2SO, as in the PPh_3 case, confirms that exchange of one phosphine is occurring, and that the minor species is a five-coordinate complex. Unlike the PPh_3 case there must be an equilibrium between five- and six-coordinate all S-bound complexes without formation of a six-coordinate O-bound Me_2SO complex.

The zero-order substrate (Fig. 1) kinetics observed with the complexes reported here is identical to that observed previously for the $RuX_2(Me_2SO)_4$ complexes. Our kinetic and mechanistic studies of these $RuX_2(Me_2SO)_4$ complexes support a catalytic scheme in which a ruthenium(II) complex generated *in situ* reacts with oxygen in an outer-sphere electron transfer step to yield a ruthenium(IV) complex and peroxide (eqn. 1):

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

The peroxide can then react with free thioether to give sulfoxide in a termolecular reaction with alcohol solvent (eqn. 2) [8]:

$$SR_2 + HO_2^- + ROH \xrightarrow{k_2} \overset{O}{SR_2} + OH^- + ROH \qquad (2)$$

The catalytic cycle is completed by the reduction of the ruthenium(IV) species by the solvent alcohol to give either an aldehyde or a ketone (eqn. 3):

$$\text{‘Ru(IV)’}, + ROH \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \text{‘Ru(II)’} + R_1R_2C{=}O + 2H^+ \qquad (3)$$

In order to confirm that these phosphine substituted complexes operated by the same mechanism as the $RuX_2(Me_2SO)_4$ complexes, the metal and oxygen dependences with the $RuBr_2(Me_2SO)_3(PPh_3)$ complex were studied. This complex exhibits the first-order catalyst dependence, zero-order sulfide dependence, and variable but less than first-order oxygen dependence as does the $RuX_2(Me_2SO)_4$ catalysts. Thus, we are confident that the same overall mechanism is operative for these phosphine substituted complexes as for the $RuX_2(Me_2SO)_4$ complexes.

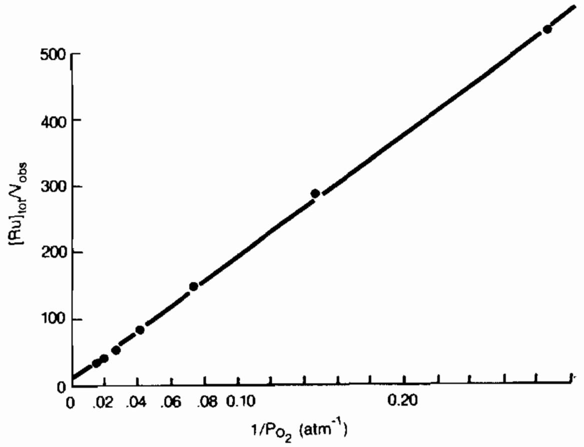

Fig. 3. Plot of $1/P_{O_2}$ *versus* $[Ru]_t/V_{obs}$ for the oxidation of decyl methyl sulfide (0.13 M) at 95 °C in methanol catalyzed by $RuBr_2(Me_2SO)_3(PPh_3)$ where sub/cat = 70.

For the $RuX_2(Me_2SO)_4$ catalysts an integrated rate expression was derived using eqns. 1–3 (assuming a double steady-state in peroxide and Ru^{IV}). This expression (eqn. 4) fits the observed kinetics and correctly predicts the form of the oxygen dependence; namely, a linear $1/V_{obs}$ *vs.* $1/P_{O_2}$ plot, whose slope equals $1/k_1$ and intercept equals $1/k_3[ROH]$.

$$V_{obs} = \frac{k_1k_3[Ru]_{tot}[O_2][ROH]}{k_1[O_2] + k_3[ROH]} \qquad (4)$$

A similar treatment of the oxygen dependence data for the $RuBr_2(Me_2SO)_3(PPh_3)$ catalyzed oxidation of decyl methyl sulfide at 95 °C in methanol (Fig. 3) gave a linear plot (>99% corr. coeff.). From these values k_1 and k_3 were determined: $k_1 = 5.6 \times 10^{-4}$ atm^{-1} s^{-1} ($\sim 6.3 \times 10^{-2}$ M^{-1} s^{-1}) and $k_3 = 3.75 \times 10^{-3}$ M^{-1} s^{-1}. It is interesting to compare these values to those obtained for the parent *trans*-$RuBr_2(Me_2SO)_4$ catalyst at 95 °C: $k_1 = 5.1 \times 10^{-4}$ atm^{-1} s^{-1} and $k_3 = 1.1 \times 10^{-3}$ M^{-1} s^{-1}. While the k_1 values for the two catalysts are similar, the k_3 value indicates that the reduction of Ru(IV) by alcohol is apparently three to four times faster with the $RuBr_2(Me_2SO)_3(PPh_3)$ catalyst. The relative magnitude of k_1 and k_3 for the $RuBr_2(Me_2SO)_3(PPh_3)$ catalyst means that eqn. 4 actually can be simplified at lower O_2 pressures to yield eqn. 5, since the $k_3[ROH]$ term completely dominates the denominator.

$$V_{obs} \approx k_1[Ru]_{tot}[O_2] \qquad (5)$$

While the details of the reduction of the oxidized metal with the solvent alcohol have as yet not been elucidated in this system, it is very likely that the reduction proceeds via coordination of the alcohol to the ruthenium(IV) ion [9]. The observed slow rates (k_3) of reduction of the oxidized metal would then reflect a kinetic problem and not an energetic one. The rate-controlling step for this reduction could very well be a dissociative step; namely, loss of a coordinated ligand from Ru(IV). This would be expected to be slow, while the resultant complexation of a molecule of the solvent alcohol would be essentially diffusion controlled. As a consequence of this, the origin of the enhanced rate (k_3) of reduction of oxidized metal with alcohol observed for the phosphine substituted complex may be attributed to the increased lability of a coordination site *trans* to the phosphine in the oxidized ruthenium complex. This is supported by the evidence from the ^{1}H NMR of the parent ruthenium(II) complexes. An increased *trans*-lability could conceivably permit the alcohol reductant greater access to the oxidized metal species and enhance the rate of reduction. It is also conceivable that the alcohol reduction occurs because a sulfoxide ligand dissociates in a stepwise fashion, proceeding through an O-bound intermediate [7] (as was observed here). If such is the case a sulfoxide *trans* to a phosphine ligand would be poised to dissociate most readily.

The electrochemical studies reported here are also significant since they allow us to compare the reaction rate with the ease of removal of an electron from the HOMO (d_π) of the complex [10]. In our kinetics studies we observed that k_3 is inherently on the order of 10 to 50 times smaller than k_1. Since the [ROH] concentration (the solvent) is so large, the actual observed rate-determining step is oxidation of the metal by oxygen (k_1, eqn. 5) especially at lower (<150 psi) oxygen pressures. Within the group of $RuBr_2(Me_2SO)_3L$ complexes (where L = PR_3 or $P(OR)_3$) there is a correspondence between redox potential and observed rate that is consistent with the complex that is easiest to oxidize (L = PBu_3) giving the fastest rate, while those that are the most difficult to oxidize yielding the slowest rate. Such trends are obviously limited since the $RuBr_2(Me_2SO)_3(AsPh_3)$ complex does not fit into this picture, nor does the $RuBr_2(Me_2SO)_2$(diphos) complex, which is much less active than $RuBr_2(Me_2SO)_3(P(OBu)_3)$, even though it is easier to oxidize.

Acknowledgement

The author would like to thank Mr. Robert Shumate for his excellent technical assistance in carrying out some of the work presented here.

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