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Oxidation of Thioanisoles and Methyl Phenyl Sulfoxides by Oxo(phosphine)ruthenium(IV) Complexes

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The oxo(phosphine)ruthenium(IV) complexes $[Ru(bpy)_2(O)PR_3](ClO_4)_2$ (bpy = 2,2′-bipyridine; $PR_3 = P(C_6H_5)_3$, $P(p\text{-}C_6H_4OCH_3)_3$, $P(p\text{-}C_6H_4CH_3)_3$, $P(p\text{-}C_6H_4F)_3$, $P(C_6H_5)(p\text{-}C_6H_4CF_3)_2$, $P(p\text{-}C_6H_4CF_3)_3$) cleanly oxidize sulfides to sulfoxides and in separate experiments oxidize sulfoxides to sulfones. The substrate oxidations are second order overall, first order in substrate concentration and first order in ruthenium concentration. Through the use of para-substituted thioanisoles and para-substituted methyl phenyl sulfoxides, linear free energy relationship analyses of the kinetics of substrate oxidations by $[Ru(bpy)_2(O)P(C_6H_5)_3](ClO_4)_2$ were conducted. For the oxidation of sulfides to sulfoxides, an excellent correlation ($R^2 = 0.99$) was obtained between log (k_X/k_H) and the σ^- values for the substituents of para-substituted thioanisoles ($\rho = -1.56$). For the oxidation of sulfoxides to sulfones, a good correlation ($R^2 = 0.98$) was obtained between log (k_X/k_H) and the σ^+ values for the substituents of para-substituted methyl phenyl sulfoxides ($\rho = -0.42$). In addition, the kinetic isotope effect for the oxidation of thioanisole and methyl-d_3 phenyl sulfide produced $k_H/k_D = 1.14$, and the oxidation of methyl phenyl sulfoxide and methyl-d_3 phenyl sulfoxide resulted in an inverse isotope effect of $k_H/k_D = 0.64$. Finally, through the use of $[Ru(bpy)_2(O)PR_3](ClO_4)_2$ complexes, Hammett-type analyses of the kinetics of thioanisole oxidation and methyl phenyl sulfoxide oxidation by the $[Ru(bpy)_2(O)PR_3](ClO_4)_2$ complexes afford a different approach in analysis of the mechanism of sulfide and sulfoxide oxidation. Hammett correlations of log (k_X/k_H) versus $\sum\sigma$ (where σ is the Hammett substituent constant for each of the para substituents on the triphenylphosphine ligands) also show linear relationships. The slopes of these plots gave $\rho = 0.49$ ($R^2 = 0.99$) for the oxidation of thioanisole and $\rho = 0.37$ ($R^2 = 0.99$) for the oxidation of methyl phenyl sulfoxide by the $[Ru(bpy)_2(O)PR_3](ClO_4)_2$ complexes. The results of all our experiments suggest that the rate-determining step in the oxidation of thioanisole by $[Ru(bpy)_2(O)P(C_6H_5)_3](ClO_4)_2$ involves primarily single-electron transfer, whereas the rate-determining step of the oxidation of methyl phenyl sulfoxide involves primarily an S_N2 mechanism.

Introduction

There have been a number of reports concerning the oxidation of organic sulfides, with particular focus on the synthetic applications on the oxidized products in asymmetric synthesis[1–5] and also on the mechanisms of sulfide oxidation.[6–17] A large variety of reagents such as peroxides,[18] sodium periodate,[19] enzymatic systems,[12,20,21] and transition metal-based oxidants[8,9,11,13–14,22–34] have been utilized for the oxidation of sulfides. Notably, transition metal–oxo systems such as $KMnO_4$[33] frequently react to give unselective products and thus are not suitable for mechanistic studies.

There are two different proposed mechanisms for the oxygenation of organosulfur compounds. A single-electron-transfer mechanism has been proposed for the oxidation of sulfides by peroxybenzoate,[6] hydroperoxidase,[7] Cr(VI),[8] Ce(IV),[14] and metalloporphyrin systems.[28] The second mechanism, S_N2, involving a nucleophilic attack by sulfur on an electrophilic oxygen center, leading to the formation of a trivalent sulfur, has been proposed for reactions involving oxidants such as molybdenum peroxopolyoxoanions,[13] sulfamyloxaziridines,[35] and pyridinium chlorochromate.[36] For the majority of studies of the oxidation of

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organosulfur compounds, the effects of the electronic nature of the substrate have been studied in detail, but the effects of the electronic nature of the oxidant have not been studied as carefully.

Oxo(phosphine)ruthenium(IV) complexes cleanly oxidize a variety of organic substrates,[37-40] including organosulfur compounds.[30] In addition, by varying the substituents at the para position of the phenyl rings of the triphenylphosphine ligand, it is possible to vary the electronic properties of the metal complex while maintaining the steric properties constant.[41] Thus oxo(phosphine)ruthenium(IV) complexes are particularly suitable for the mechanistic investigation of the oxidation of organosulfur compounds.

We wish to report here the kinetic and mechanistic studies of the oxidation of thioanisoles and sulfoxides by oxo(phosphine)ruthenium(IV) complexes. The oxidants were found to selectively oxidize sulfides to sulfoxides and in separate experiments oxidize sulfoxides to sulfones. Hammett analyses of the kinetic data indicate excellent correlation ($R^2 = 0.99$) between log (k_X/k_H) and the substituent constant σ^- for the oxidation of para-substituted thioanisoles whereas a good correlation ($R^2 = 0.98$) was found between log (k_X/k_H) and σ^+ for the oxidation of para-substituted phenyl methyl sulfoxides. Also, a plot of the natural logarithm of the second-order rate constant (k) for the oxidation of thioanisole versus the $E_{1/2}$ values of the ruthenium(IV/III) couples gives a linear relationship with $R^2 = 0.98$. Similarly, a plot of log (k_X/k_H) versus the $E_{p,a}$ values of the para-substituted thioanisoles shows a linear relationship with $R^2 = 0.96$. The kinetic isotope effect of the oxidation of thioanisole and methyl-d_3 phenyl sulfide (k_H/k_D) is 1.14, where the kinetic isotope effect of the oxidation of methyl phenyl sulfoxide and methyl-d_3 phenyl sulfoxide (k_H/k_D) is 0.64. Finally, Hammett correlations of log (k_X/k_H) versus $\sum\sigma$ (where σ is the Hammett substituent constant for para substituents on the triphenylphosphine ligands) yield $\rho = 0.49$ ($R^2 = 0.99$) for the oxidation of thioanisole and $\rho = 0.37$ ($R^2 = 0.99$) for the oxidation of methyl phenyl sulfoxide by the $[Ru(bpy)_2(O)PR_3](ClO_4)_2$ complexes. From these observations, we propose that a rate-determining single-electron-transfer mechanism is indicated in the thioanisole oxidation whereas an S_N2 mechanism is proposed for the oxidation of the sulfoxide.

Experimental Section

Materials. Acetonitrile (Fisher Scientific) was stirred overnight over activated 3-Å molecular sieves and distilled before use. Methylene chloride (Baker, reagent grade) was used as received. Thioanisole, methyl *p*-tolyl sulfide, *p*-chlorothioanisole, *p*-bromothioanisole, *p*-chlorophenyl methyl sulfone, and methyl phenyl sulfoxide were purchased from Lancaster Synthesis. 1-Methoxy-4-(methylthio)benzene and 2-bromothioanisole were purchased from Aldrich Chemical Co. All other sulfoxides and sulfones were prepared according to the literature procedure.[19]

Syntheses. *p*-(Trifluoromethyl)thioanisole. This compound was prepared by a modification of the literature procedure.[42,43] 4-Chlorobenzotrifluoride (4 mL) was added to DMF (50 mL) in a 100-mL round-bottom flask, and the resulting solution was degassed with $N_2(g)$ for 5 min. Sodium metal (2 g) and dimethyl disulfide (6 mL) were added to the mixture. The flask was equipped with a long reflux condenser and was heated until the sodium metal melted. Upon melting, the sodium reacted vigorously with the dimethyl disulfide, liberating a large amount of heat. The mixture was heated for 1 h and then allowed to cool to room temperature, after which 2 mL of methyl iodide was added and the mixture was then stirred for 1 h. The mixture was poured into a saturated aqueous sodium chloride solution, stirred for 5 min, and extracted with four 50-mL portions of methylene chloride. The combined organic layer was dried with anhydrous sodium sulfate and filtered. The solvent was removed by distillation, and the crude product was passed through a silica gel column using hexane as eluant. The product was then purified by distillation under reduced pressure. Yield: 4.32 g (76% based on 4-chlorobenzotrifluoride). Mp: 31–32 °C. Anal. Calcd for $C_8H_7F_3S$: C, 49.99; H, 3.67. Found: C, 49.99; H, 3.67. ^{1}H NMR ($CDCl_3$): δ = 2.45 (s, 3H, CH_3), 7.35 (dd, 4H, phenyl protons).

Methyl *p*-(Trifluoromethyl)phenyl Sulfoxide. The sulfoxide was synthesized according to the literature procedure[19] for the synthesis of methyl phenyl sulfoxide. *p*-(Trifluoromethyl)thioanisole (0.46 g) was reacted with $NaIO_4$ (0.54 g) to yield 0.37 g (74%) of methyl *p*-(trifluoromethyl)phenyl sulfoxide. Mp: 39–41 °C. Anal. Calcd for $C_8H_7F_3OS$: C, 46.15; H, 3.39. Found: C, 46.23; H, 3.39.

Methyl *p*-(Trifluoromethyl)phenyl Sulfone. This sulfone was synthesized from the corresponding sulfoxide according to the literature procedure.[19] *p*-(Trifluoromethyl)phenyl methyl sulfoxide (0.25 g) was reacted with $NaIO_4$ (0.32 g) to give 0.15 g (54%) of product. Mp: 101–102 °C. Anal. Calcd for $C_8H_7F_3O_2S$: C, 42.86; H, 3.15. Found: C, 42.76; H, 3.14.

Methyl-d_3 Phenyl Sulfide. Diphenyl disulfide (3.5 g) was reacted with sodium metal[42] (1.5 g) in DMF (70 mL) by heating the reaction mixture gently for about 30 min until the sodium melted. After the mixture was cooled to room temperature, methyl-d_3 iodide (4.65 g; Aldrich, 99+ atom % D) was added and the solution was stirred overnight. The workup and purification procedures are the same as those described in the synthesis of *p*-(trifluoromethyl)thioanisole (see above). Yield: 2.5 g (61%). The ^{1}H NMR spectrum showed no detectable amount of CH_3 present, and a gas chromatographic analysis indicated a pure product.

Methyl-d_3 Phenyl Sulfoxide. The literature procedure[19] for the oxidation of the sulfide was used. Methyl-d_3 phenyl sulfide (0.31 g) yielded 0.24 g (70%) of the sulfoxide. Both the ^{1}H NMR spectrum and the gas chromatographic analysis indicated a pure product.

$[Ru(bpy)_2(O)PR_3](ClO_4)_2$ (bpy = 2,2′-Bipyridine; $PR_3 = P(C_6H_5)_3$, $P(p\text{-}C_6H_4OCH_3)_3$, $P(p\text{-}C_6H_4CH_3)_3$, $P(p\text{-}C_6H_4F)_3$, $P(C_6H_5)(p\text{-}C_6H_4CF_3)_2$, $P(p\text{-}C_6H_4CF_3)_3$). These complexes were prepared according to published procedures.[38,40]

$[Ru(bpy)_2(OS(CH_3)(C_6H_5))P(C_6H_5)_3](ClO_4)_2\cdot H_2O$. Thioanisole (0.7 mL) was transferred into a 25-mL round-bottom flask equipped with a magnetic stirrer. Methylene chloride (4 mL) was added, and the solution was degassed with $N_2(g)$ for 3 min. $[Ru(bpy)_2(O)P(C_6H_5)_3](ClO_4)_2\cdot H_2O$ (15.85 mg) was added, and the solution was stirred under a blanket of $N_2(g)$ for 30 min. At the end of 30 min, the product was precipitated by the addition of pentane (10 mL). The mixture was subjected to centrifugation for 5 min, and the solvent was decanted. The product was washed several times with pentane and dried in a vacuum oven at room temperature. A quantitative yield of 100% based on the amount of oxidant was obtained. Anal. Calcd for $C_{45}H_{39}Cl_2O_9PSRu\cdot H_2O$: C, 52.33; H, 4.00. Found: C, 52.53; H, 4.23.

Instrumentation. Electronic spectra were recorded either on a Bausch and Lomb Spectronic 2000 spectrophotometer equipped with a Houston Instruments Model 200 X-Y recorder or on a Milton Roy Spectronic 3000 array spectrophotometer equipped with a Hewlett-Packard 7470A plotter. Cyclic voltammetric and differential pulse experiments were performed using an IBM EC/225 polarographic analyzer equipped with a Houston Instruments Model 100 recorder. Acetonitrile was used as the solvent with tetra-*n*-butylammonium tetrafluoroborate (0.1 M) as the supporting electrolyte. A platinum disk working electrode, a platinum auxiliary electrode, and a saturated sodium chloride calomel reference electrode (SSCE) were used. ^{1}H NMR spectra were recorded using either a Varian EM-390 or a Varian Gemini 300 NMR spectrometer. Elemental analyses were conducted by Atlantic Microlabs, Norcross, GA.

The product analyses were done using a Shimadzu GC 8A gas chromatograph equipped with a flame ionization detector and a split/splitless injector. A Restek Corp. wide-bore capillary column of 0.32-mm i.d. and 35-m length, with a 5% diphenylpolysiloxane stationary phase, was used. The kinetics measurements were performed spectrophotometrically using Beckman DU spectrophotometers retrofitted with Gilford accessories. Thermostated temperature baths were used to maintain the temperature of the cell blocks at 15 °C.

Product Distributions. In a typical experiment a 50–100-fold excess of the sulfide was weighed into a 25-mL round-bottom flask equipped with a magnetic stir bar. Acetonitrile (2 mL) was added, and the solution was degassed with $N_2(g)$ for 3 min. A weighed amount (6–8 mg) of the oxidant was then added, and the solution was stirred under a blanket of $N_2(g)$ for 3 h. Methylene chloride (2 mL) was added, followed by the

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addition 8 mL of pentane or hexane to precipitate the metal complex. The mixture was stirred for 30 min, and then transferred into centrifuge tubes and subjected to centrifugation for 5 min. The clear solution was decanted from the precipitated metal complex, and the solvent was removed with a rotary evaporator. The residue was then dissolved in methylene chloride, and a weighed amount of *o*-dibromobenzene was added as internal standard. Samples were then injected into the gas chromatograph for analysis. Blank reactions using the corresponding aqua complex were conducted as described above to calculate the amount of product lost in the manipulations.

Kinetic Measurements. The rates of the oxidation of sulfides and sulfoxides were measured at 15 °C in acetonitrile by monitoring the wavelength maximum of the metal to ligand charge-transfer band of the ruthenium(II) species which is formed during the substrate oxidation. By using a minimum of a 100-fold excess of the substrate, pseudo-first-order conditions were achieved. In a typical kinetics experiment, the reaction was initiated by quickly mixing together a 2-mL solution of the oxidant (which had been thermostated at 15 °C) with a 1-mL solution of the substrate in a glass cuvette. The progress of the reaction was monitored by the use of a chart drive as the time base. The absorbance versus time curves were recorded for seven solutions of different substrate concentrations. Plots of ln $[(A_\infty - A_0)/(A_\infty - A_t)]$ versus time were linear, and the pseudo-first-order rate constants were calculated by least-squares treatment of data using the relationship

$$-\ln(A_\infty - A_t) = k_{\mathrm{obs}}t - \ln(A_\infty - A_0) \qquad (1)$$

where A_∞ is the final absorbance at the completion of the reaction, A_0 is the initial absorbance, A_t is the absorbance at time t, and k_{obs} is the observed rate constant. A plot of k_{obs} versus substrate concentration yielded a slope which is equal to the second-order rate constant for the substrate oxidation.

Results

Product Distributions. The $[\mathrm{Ru(bpy)_2(O)PR_3}](\mathrm{ClO_4})_2$ complexes (bpy = 2,2′-bipyridine; $\mathrm{PR_3} = \mathrm{P(C_6H_5)_3}$, $\mathrm{P}(p\text{-}\mathrm{C_6H_4OCH_3})_3$, $\mathrm{P}(p\text{-}\mathrm{C_6H_4CH_3})_3$, $\mathrm{P}(p\text{-}\mathrm{C_6H_4F})_3$, $\mathrm{P(C_6H_5)}(p\text{-}\mathrm{C_6H_4CF_3})_2$, $\mathrm{P}(p\text{-}\mathrm{C_6H_4CF_3})_3$ were found to selectively oxidize thioanisoles to the corresponding sulfoxides and in separate experiments oxidize the sulfoxides to sulfones, in high yields. The sulfoxide yields ranged from 81% to 98%, with an average yield of 89%. The sulfone yields ranged from 80% to 92%, with an average yield of 87%.

Study of the Intermediate $[\mathrm{Ru(bpy)_2(OS(CH_3)(C_6H_5))P(C_6H_5)_3}]^{2+}$. We observed evidence of an intermediate in the oxidation of thioanisole by $[\mathrm{Ru(bpy)_2(O)P(C_6H_5)_3}](\mathrm{ClO_4})_2$ reminiscent of our observations regarding the oxidation of dibutyl sulfide by $[\mathrm{Ru(bpy)_2(O)PEt_3}](\mathrm{ClO_4})_2$.[30] When the reaction between $[\mathrm{Ru(bpy)_2(O)P(C_6H_5)_3}](\mathrm{ClO_4})_2$ and thioanisole was performed in a noncoordinating solvent such as *o*-dichlorobenzene or methylene chloride, the GC analysis of the reaction mixture showed no evidence of the formation of methyl phenyl sulfoxide, and the complex $[\mathrm{Ru(bpy)_2(OS(CH_3)(C_6H_5))P(C_6H_5)_3}]^{2+}$ was isolated from the reaction mixture. Also, spectrophotometric studies of the reaction between $[\mathrm{Ru(bpy)_2(O)P(C_6H_5)_3}](\mathrm{ClO_4})_2$ and thioanisole carried out in *o*-dichlorobenzene or methylene chloride indicate the formation of the $[\mathrm{Ru(bpy)_2(OS(CH_3)(C_6H_5))P(C_6H_5)_3}]^{2+}$ complex in solution. However, if acetonitrile was added to the *o*-dichlorobenzene or methylene chloride solution, the formation of the analogous $[\mathrm{Ru(bpy)_2(CH_3CN)P(C_6H_5)_3}]^{2+}$ complex was observed, and the presence of the sulfoxide was observed by GC analysis. These observations combine to suggest that, in the reaction between $[\mathrm{Ru(bpy)_2(O)P(C_6H_5)_3}](\mathrm{ClO_4})_2$ and thioanisole, the intermediate complex $[\mathrm{Ru(bpy)_2(OS(CH_3)(C_6H_5))P(C_6H_5)_3}]^{2+}$ is first formed, followed by the acetonitrile displacement of the bound $\mathrm{OS(CH_3)(C_6H_5)}$. Notably, the intermediate is not observed spectrally if acetonitrile is used as the solvent; therefore the kinetics studies of sulfide and sulfoxide oxidation were conducted using acetonitrile as the solvent.

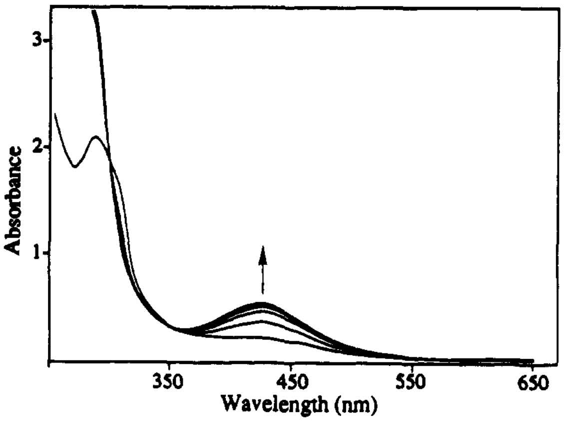

Figure 1. Repetitive scan of the reaction of $[\mathrm{Ru(bpy)_2(O)P(C_6H_5)_3}](\mathrm{ClO_4})_2$ (7.0×10^{-5} M) with thioanisole (1.1×10^{-3} M) in acetonitrile at 15 °C.

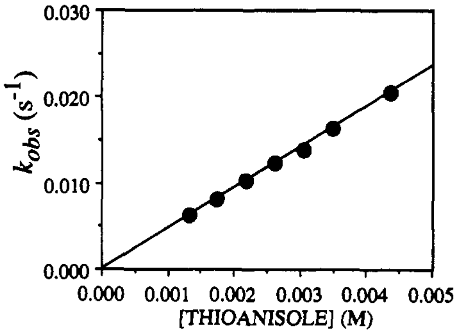

Figure 2. Plot of the observed pseudo-first-order rate constant, k_{obs}, as a function of thioanisole concentration for the oxidation of thioanisole by $[\mathrm{Ru(bpy)_2(O)P}(p\text{-}\mathrm{C_6H_4F})_3](\mathrm{ClO_4})_2$ in acetonitrile at 15 °C.

Kinetic Studies. The kinetics of the oxidation of the sulfides and sulfoxides by $[\mathrm{Ru(bpy)_2(O)PR_3}](\mathrm{ClO_4})_2$ showed first-order behavior with respect to the substrate and first-order behavior with respect to the oxidant. Figure 1 shows an example of the isosbestic spectral changes that occur in the oxidation of thioanisoles by an (oxo)ruthenium(IV) complex, $[\mathrm{Ru(bpy)_2(O)P(C_6H_5)_3}](\mathrm{ClO_4})_2$ in acetonitrile, where a clean (oxo)ruthenium(IV) to (acetonitrile)ruthenium(II) conversion is observed. Similar (oxo)ruthenium(IV) to (acetonitrile)ruthenium(II) spectral changes were also observed for the oxidations of the sulfoxides to the corresponding sulfones using the $[\mathrm{Ru(bpy)_2(O)PR_3}](\mathrm{ClO_4})_2$ complexes.

Linear plots of k_{obs} versus substrate concentrations were made using the relationship in eq 2. Figure 2 shows the plot of k_{obs}

$$-d[\mathrm{Ru(IV)}]/dt = d[\mathrm{Ru(II)}]/dt = k[\mathrm{substrate}][\mathrm{Ru(IV)}] = k_{\mathrm{obs}}[\mathrm{Ru(IV)}] \qquad (2)$$

versus substrate concentration for the oxidation of thioanisole by $[\mathrm{Ru(bpy)_2(O)P}(p\text{-}\mathrm{C_6H_4F})_3](\mathrm{ClO_4})_2$, where the slope of the plot is equal to the second-order rate constant. Results of the second-order rate constants for the oxidations of the thioanisoles and the methyl phenyl sulfoxides by $[\mathrm{Ru(bpy)_2(O)PR_3}](\mathrm{ClO_4})_2$ are shown in Tables I and II.

The effects of substituents at the para position of the phenyl ring of thioanisole and the methyl phenyl sulfoxide were studied by the reaction of para-substituted thioanisoles and sulfoxides with $[\mathrm{Ru(bpy)_2(O)P(C_6H_5)_3}](\mathrm{ClO_4})_2$. Tables I and II show the second-order rate constants for the oxidation of para-substituted thioanisoles and sulfoxides. A plot of log (k_X/k_H) versus the $E_{p,a}$ values for the one-electron oxidation of the substituted thioanisoles is shown in Figure 3. The linearity of the correlation suggests a one-electron transfer occurs in the rate-determining step of thioanisole oxidation.[44]

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Table I. Second-Order Rate Constants for Oxidation of Thioanisoles by $[Ru(bpy)_2(O)PR_3](ClO_4)_2$ Complexes[a]

PR_3	substrate	k (M^{-1} s^{-1})
$P(p\text{-}C_6H_4CF_3)_3$	thioanisole	17.90 ± 1.67
$P(p\text{-}C_6H_4CF_3)_2(C_6H_5)$	thioanisole	10.11 ± 0.65
$P(p\text{-}C_6H_4F)_3$	thioanisole	4.70 ± 0.17
$P(C_6H_5)_3$	thioanisole	2.30 ± 0.19
$P(p\text{-}C_6H_4CH_3)_3$	thioanisole	1.47 ± 0.16
$P(p\text{-}C_6H_4OCH_3)_3$	thioanisole	1.31 ± 0.09
$P(C_6H_5)_3$	*p*-methoxythioanisole	8.59 ± 0.55
$P(C_6H_5)_3$	*p*-methylthioanisole	5.49 ± 0.41
$P(C_6H_5)_3$	*p*-chlorothioanisole	1.55 ± 0.11
$P(C_6H_5)_3$	*p*-bromothioanisole	1.26 ± 0.10
$P(C_6H_5)_3$	*p*-(trifluoromethyl)thioanisole	0.24 ± 0.04

[a] Conditions described in text.

Table II. Second-Order Rate Constants for Oxidation of Methyl Phenyl Sulfoxides by $[Ru(bpy)_2(O)PR_3](ClO_4)_2$ Complexes[a]

PR_3	substrate	k (M^{-1} s^{-1})
$P(p\text{-}C_6H_4CF_3)_3$	methyl phenyl sulfoxide	0.29 ± 0.04
$P(p\text{-}C_6H_4CF_3)_2(C_6H_5)$	methyl phenyl sulfoxide	0.16 ± 0.01
$P(p\text{-}C_6H_4F)_3$	methyl phenyl sulfoxide	0.10 ± 0.01
$P(C_6H_5)_3$	methyl phenyl sulfoxide	0.06 ± 0.01
$P(p\text{-}C_6H_4CH_3)_3$	methyl phenyl sulfoxide	0.043 ± 0.004
$P(p\text{-}C_6H_4OCH_3)_3$	methyl phenyl sulfoxide	0.038 ± 0.003
$P(C_6H_5)_3$	methyl *p*-methoxyphenyl sulfoxide	0.114 ± 0.002
$P(C_6H_5)_3$	methyl *p*-methylphenyl sulfoxide	0.073 ± 0.008
$P(C_6H_5)_3$	methyl *p*-chlorophenyl sulfoxide	0.053 ± 0.002
$P(C_6H_5)_3$	methyl *p*-bromophenyl sulfoxide	0.043 ± 0.007
$P(C_6H_5)_3$	methyl *p*-(trifluoromethyl)phenyl sulfoxide	0.030 ± 0.006

[a] Conditions described in text.

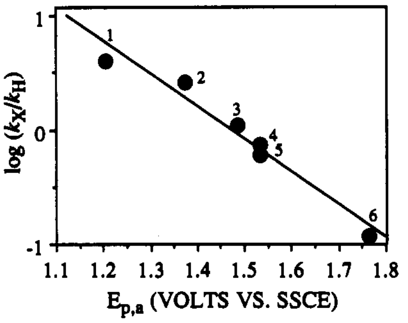

Figure 3. Plot of log (k_X/k_H) versus the $E_{p,a}$ values of the para-substituted thioanisoles from the reaction with $[Ru(bpy)_2(O)P(C_6H_5)_3](ClO_4)_2$. The para substituents are (1) OCH_3, (2) CH_3, (3) H, (4) Cl, (5) Br, and (6) CF_3.

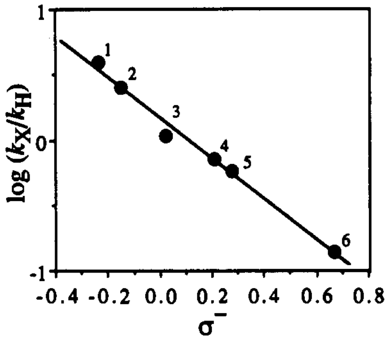

Figure 4. Hammett correlation of log (k_X/k_H) versus σ^- for the reaction of para-substituted thioanisoles with $[Ru(bpy)_2(O)P(C_6H_5)_3](ClO_4)_2$. The para substituents are (1) OCH_3, (2) CH_3, (3) H, (4) Cl, (5) Br, and (6) CF_3.

The relative rates for the oxidation of the para-substituted thioanisoles showed an excellent correlation with σ^-, $\rho = -1.56$ ($R^2 = 0.99$) (see Figure 4), compared with σ, $\rho = -1.80$ ($R^2 = 0.97$), and σ^+, $\rho = -1.12$ ($R^2 = 0.93$). For the oxidation of the para-substituted sulfoxides, log (k_X/k_H) gave the best correlation with σ^+, $\rho = -0.42$ ($R^2 = 0.98$) (see Figure 5), compared with σ, $\rho = -0.64$ ($R^2 = 0.92$), and σ^-, $\rho = -0.57$ ($R^2 = 0.92$). In both cases, the negative values of ρ indicate an accumulation of positive charge at the sulfur center, while the relative magnitudes of the ρ values indicate the extent of charge development on the sulfur atom, in the transition state of the rate-determining step.[45]

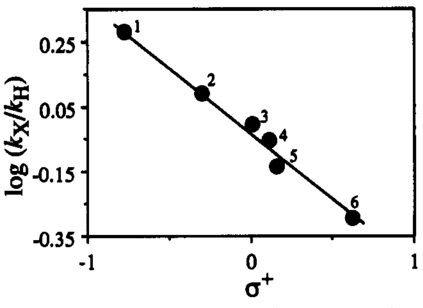

Figure 5. Hammett correlation of log (k_X/k_H) versus σ^+ for the reaction of methyl para-substituted phenyl sulfoxides with $[Ru(bpy)_2(O)P(C_6H_5)_3](ClO_4)_2$. The para substituents are (1) OCH_3, (2) CH_3, (3) H, (4) Cl, (5) Br, and (6) CF_3.

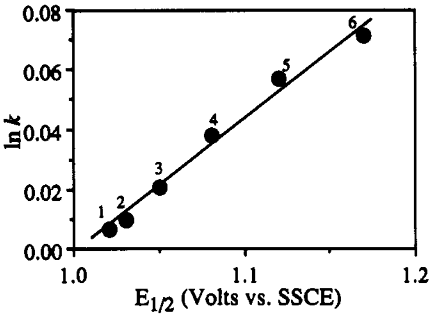

Figure 6. Plot of the natural logarithm of the second-order rate constants (k) versus $E_{1/2}$ values of the ruthenium(IV/III) couples for the oxidation of thioanisole by $[Ru(bpy)_2(O)PR_3](ClO_4)_2$ where PR_3 corresponds to (1) $P(p\text{-}C_6H_4OCH_3)_3$, (2) $P(p\text{-}C_6H_4CH_3)_3$, (3) $P(C_6H_5)_3$, (4) $P(p\text{-}C_6H_4F)_3$, (5) $P(C_6H_5)(p\text{-}C_6H_4CF_3)_2$, and (6) $P(p\text{-}C_6H_4CF_3)_3$.

The effect of changes in the electronic nature of the oxidants is shown in Figure 6, where a plot of the natural logarithm of k versus the $E_{1/2}$ values for the ruthenium(IV/III) couples[40] is linear for the oxidation of thioanisole by the $[Ru(bpy)_2(O)PR_3](ClO_4)_2$ complexes. A similar plot can be made for the oxidation of methyl phenyl sulfoxide by the $[Ru(bpy)_2(O)PR_3](ClO_4)_2$ complexes. Thus, for the oxidation of organosulfur compounds by the $[Ru(bpy)_2(O)PR_3](ClO_4)_2$ complexes, log k values are a direct function of the electron density at the ruthenium(IV) center. Since the cone angles of the para-substituted triphenylphosphine ligands are constant, as suggested by Tolman,[41] the above observation is solely due to the electronic effects of the phosphine ligands.

Hammett correlations of log (k_X/k_H) versus $\Sigma\sigma$ (where σ is the Hammett substituent constant for para-substituted triphenylphosphine ligands) also show a linear relationship. The slopes of these plots gave $\rho = 0.49$ ($R^2 = 0.99$) for the oxidation of thioanisole (see Figure 7) and $\rho = 0.37$ ($R^2 = 0.99$) for the oxidation of methyl phenyl sulfoxide (see Figure 8) by the $[Ru(bpy)_2(O)PR_3](ClO_4)_2$ complexes. The positive values of ρ indicate a buildup of negative charge on the metal center in the transition state of the rate-determining step, as would be expected in the reduction of ruthenium(IV) to ruthenium(II).[45]

Isotope Effects. The k_H/k_D ratio for the oxidation of thioanisole and methyl-d_3 phenyl sulfide by $[Ru(bpy)_2(O)P(C_6H_5)_3](ClO_4)_2$ is 1.14. Notably, an inverse isotope effect of $k_H/k_D = 0.64$ was observed for the oxidation of methyl phenyl sulfoxide and methyl-d_3 phenyl sulfoxide by $[Ru(bpy)_2(O)P(C_6H_5)_3](ClO_4)_2$.

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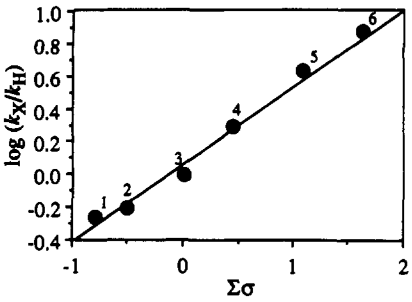

Figure 7. Hammett correlation of log (k_X/k_H) versus $\Sigma\sigma$ for the reaction of thioanisole with $[Ru(bpy)_2(O)PR_3](ClO_4)_2$ where PR_3 corresponds to (1) $P(p\text{-}C_6H_4OCH_3)_3$, (2) $P(p\text{-}C_6H_4CH_3)_3$, (3) $P(C_6H_5)_3$, (4) $P(p\text{-}C_6H_4F)_3$, (5) $P(C_6H_5)(p\text{-}C_6H_4CF_3)_2$, and (6) $P(p\text{-}C_6H_4CF_3)_3$.

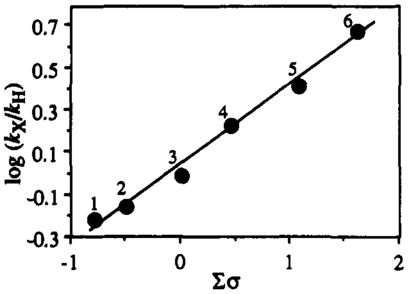

Figure 8. Hammett correlation of log (k_X/k_H) versus $\Sigma\sigma$ for the reaction of methyl phenyl sulfoxide with $[Ru(bpy)_2(O)PR_3](ClO_4)_2$ where PR_3 corresponds to (1) $P(p\text{-}C_6H_4OCH_3)_3$, (2) $P(p\text{-}C_6H_4CH_3)_3$, (3) $P(C_6H_5)_3$, (4) $P(p\text{-}C_6H_4F)_3$, (5) $P(C_6H_5)(p\text{-}C_6H_4CF_3)_2$, and (6) $P(p\text{-}C_6H_4CF_3)_3$.

Discussion

Electronic Substrate Effects. The oxidation of para-substituted thioanisoles with $[Ru(bpy)_2(O)P(C_6H_5)_3](ClO_4)_2$ was studied to evaluate the substrate electronic effects on thioanisole oxidation. A ρ value of −1.56 was obtained, and this is reminiscent of the ρ values found for the oxidation of substituted thioanisoles by isoalloxazine hydroperoxide and *tert*-butyl *p*-chloroperoxybenzoate ($\rho = -1.68$)[7,8] and by singlet oxygen ($\rho = -1.63$).[46] For all three cases, single-electron-transfer (SET) mechanisms were proposed. In contrast, a ρ value of −0.42 was obtained in the oxidation of para-substituted methyl phenyl sulfoxides by $[Ru(bpy)_2(O)P(C_6H_5)_3](ClO_4)_2$. The ρ value of −0.42 is similar to the values of $\rho = -0.76$ for the oxidation of substituted methyl phenyl sulfoxides by dioxiranes[47] and to the value of $\rho = -0.83$ for the oxidation of sulfoxides by *gem*-dialkylperoxonium ions.[48] These reactions were characterized as undergoing an S_N2 rate-determining step.

An excellent correlation was obtained from the plot of log (k_X/k_H) versus σ^-, $\rho = -1.56$, ($R^2 = 0.99$), for the oxidation of the substituted thioanisoles by $[Ru(bpy)_2(O)P(C_6H_5)_3](ClO_4)_2$, whereas the plots with σ and σ^+ showed $\rho = -1.8$ ($R^2 = 0.97$) and $\rho = -1.1$ ($R^2 = 0.93$), respectively. The excellent correlation produced by σ^- is in contrast to a number of studies where σ or σ^+ has usually been used.[7] In several cases, a combination of σ^+ and σ^- has been used in the Hammett correlation of thioanisole oxidation. For example, σ^+/σ^- was employed in the oxidations of thioanisoles by peroxydisulfate[49] and ($\sigma^+ - \sigma^-$) was used in the oxidations by pyridinium chlorochromate.[36] To the best of our knowledge, this is the first reported correlation of log (k_X/k_H) versus σ^- for thioanisole oxidation. However, a survey of the literature showed analogous results were obtained for the oxidation of aniline by pyridinium chlorochromate,[50] for the benzolation of anilines[45] and the reaction of *N*,*N*-dimethylanilines with methyl iodide.[45] These are reactions which involve the development of positive charge at the reaction site in the transition state but give the best correlations of log (k_X/k_H) versus σ^- instead of σ^+ or σ. It is noteworthy that σ^- values were derived for systems such as phenols and anilines, where the lone pairs of electrons are in conjugation with electron-withdrawing groups at the para position of the benzene ring.[45] In accordance with this, since the sulfur atom in thioanisole has unshared electron pairs, it is conceivable that conjugation of the lone pair of electrons does occur with sulfides, as has been observed with phenols and anilines.

Although the sign and magnitude of the ρ values for the oxidations of thioanisole suggest an SET mechanism while the values for the oxidation of methyl phenyl sulfoxide indicate an S_N2 mechanism, Miller has pointed out that misleading conclusions can result if the interpretation of reaction mechanism is based solely on Hammett correlations.[7] Therefore to verify our conclusion, we also conducted kinetic isotope effect studies.

Kinetic Isotope Effects. Deuterium isotope effects have been utilized to distinguish between SET and S_N2 mechanisms,[6,7] where k_H/k_D values greater than 1 suggest an SET mechanism and k_H/k_D values less than 1 suggest an S_N2 mechanism. The oxidation of thioanisole and methyl-d_3 phenyl sulfide by $[Ru(bpy)_2(O)P(C_6H_5)_3](ClO_4)_2$ yields a k_H/k_D value of 1.14, which is in good agreement with that found by Miller[7] for the oxidation of thioanisole by 4α-(hydroperoxy)isoalloxazine ($k_H/k_D = 1.04$) and the k_H/k_D value of 1.2 obtained for the oxidation of phenacyl phenyl sulfide by microsomal cytochrome P-450,[51] where SET mechanisms were assigned for both oxidations. Hyperconjugative stabilization of CH_3 over CD_3 in the transition state has been used to explain this type of secondary isotope effect.[52] The electron-deficient sulfide center, which results from an electron transfer, will cause a shift in electron density from the methyl C–H bond to the electron-deficient center. This results in a greater weakening of the C–H bond relative to the C–D bond. The hyperconjugative stabilization will therefore be greater for CH_3 than for CD_3, resulting in the observed rate constant differences.

The inverse isotope effect observed for the oxidation of methyl phenyl sulfoxide and methyl-d_3 phenyl sulfoxide by $[Ru(bpy)_2(O)P(C_6H_5)_3](ClO_4)_2$ suggests an S_N2 mechanism. Kaplan and Thornton[53] studied the S_N2 reaction of methyl *p*-toluenesulfonate with *N*,*N*-dimethylaniline and *N*,*N*-di(methyl-d_6)aniline to form trimethylammonium and methyldi(methyl-d_6)phenylammonium *p*-toluenesulfonates, respectively, and observed an inverse isotope effect of $k_H/k_D = 0.88$. The observation was suggested to be due to the steric effects arising from the overcrowding of the methyl groups in the ions compared to the free amines. The consequence of the steric crowding is to favor the deuterated amine in an S_N2 rate-determining step. In a similar fashion, we suggest that the inverse isotope effect observed for the oxidation of the sulfoxides by $[Ru(bpy)_2(O)P(C_6H_5)_3](ClO_4)_2$ is due to an S_N2 rate-determining step, which leads to the formation of a sulfoxide-bound ruthenium intermediate.

Electronic Oxidant Effects. Electron-donating and -withdrawing para substituents on the phenyl ring of the triphenylphosphine ligands were used to vary the electronic properties of the oxidants. The Hammett correlation for the oxidation of thioanisole by $[Ru(bpy)_2(O)PR_3](ClO_4)_2$ shows an excellent correlation with $\rho = 0.49$ ($R^2 = 0.99$) between log (k_X/k_H) and $\Sigma\sigma$. Also, the plot of the natural logarithm of k versus $E_{1/2}$ of the Ru(IV/III) couple of the $[Ru(bpy)_2(O)PR_3](ClO_4)_2$ complexes is in accord with Marcus' prediction of an α value (transfer

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coefficient) of 0.5 for an outer-sphere electron-transfer mechanism.[54] Our results give an α value of 0.45, which is in good agreement with other observed values such as $\alpha = 0.46$ for the V^{2+}/V^{3+} couple at a dropping mercury electrode[55] and 0.50 for the square-wave electrolysis of the $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ couple.[56] An α value of 0.51 was also obtained for the reduction of (polypyridine)ruthenium(III) complexes by Fe(II).[57] The close agreement of these values with our results suggests that the rate-determining step involves a single-electron-transfer mechanism in the oxidation of thioanisole.

The rate constants for the oxidation of methyl phenyl sulfoxide by $[Ru(bpy)_2(O)PR_3](ClO_4)_2$ were 30–60 times smaller than the rate constants for thioanisoles oxidation. The Hammett correlation of log (k_X/k_H) versus $\Sigma\sigma$ for the phosphine ligands was linear with $\rho = 0.37$ ($R^2 = 0.99$). Again, the plot of the natural logarithm of k versus $E_{1/2}$ values of the Ru(IV/III) couple is linear ($R^2 = 0.99$) with $\alpha = 0.34$. The smaller values of ρ and α obtained for the sulfoxide oxidation, relative to sulfide oxidation, suggest that a mechanism different from SET may be in operation for the oxidation of sulfoxides. We propose that the smaller ρ and α values suggest that an S_N2 mechanism is occurring for sulfoxide oxidation, because the charge development for an S_N2 mechanism would be centered more on oxygen than on the ruthenium center, relative to an SET mechanism. Thus, the reaction center for an S_N2 mechanism is one bond further from the triphenylphosphine substituent than the reaction center for the SET reaction, resulting in the observed smaller ρ and α values.

Conclusion. We have shown that (1) oxo(phosphine)ruthenium(IV) complexes oxidize thioanisoles cleanly to sulfoxides and in separate experiments oxidize sulfoxides to sulfones, (2) the mechanisms of thioanisole oxidation and methyl phenyl sulfoxide oxidation can be elucidated by varying the electronic nature of the substrates and by a deuterium isotope study, and (3) thioanisole oxidation and methyl phenyl sulfoxide oxidation can be further studied by varying the electronic nature of the ruthenium-based oxidants. All of our observations combine to suggest that an SET mechanism occurs for the thioanisole oxidation, while an S_N2 mechanism occurs for methyl phenyl sulfoxide oxidation. In addition, we propose that our interpretation of ρ values obtained from the electronic variation of the ruthenium-based oxidants demonstrates the utility of the electronic variability of the oxidant in the mechanistic study of the oxidation of organosulfur compounds.

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