Inorg. Chem. **1987**, *26*, 779–781

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Oxygen Atom Transfer in the Oxidations of Dimethyl Sulfide and Dimethyl Sulfoxide by $[(bpy)_2(py)Ru(O)]^{2+}$

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Received July 7, 1986

The selective oxidation of sulfides to sulfoxides is an important reaction because of the synthetic versatility of sulfoxides.[1] A variety of transition-metal complexes have been used to carry out this oxidation including the catalytic system based on Fe(TPP)Cl (TPP is 5,10,15,20-tetraphenylporphyrinato) with iodosylbenzene as cooxidant.[2,3] With metal–oxo reagents such as chromic acid,[4] permanganate,[5] or OsO_4[5,6] however, selectivity is not observed because the sulfoxides are often more reactive than the corresponding sulfides. Riley and co-workers have investigated the oxidation of sulfides to sulfoxides by O_2 catalyzed with dihaloruthenium(II) complexes,[7,8] which give sulfoxide/sulfone ratios parallel to those observed in the H_2O_2 oxidation of sulfides,[9] and have proposed a Ru(IV) intermediate.

Here we report the results of a kinetic study on the oxidation of dimethyl sulfide to dimethyl sulfoxide and of dimethyl sulfoxide to dimethyl sulfone by the Ru(IV)–oxo complex $[(bpy)_2(py)Ru(O)]^{2+}$. Our goals were to establish the mechanisms of oxidation in order to make comparisons with mechanistic results obtained for other substrates,[10–15] to attempt to provide some insight into how sulfide oxidations based on $RuCl_3$[16] and $RuCl_2(PPh_3)_3$[17] occur, and to assess the possibility of developing an electrocatalytic procedure for the selective oxidation of sulfides to sulfoxides.[18]

Experimental Section

Materials. Acetonitrile (Baker) was distilled immediately before use from P_2O_5 under an argon atmosphere or used directly. Dimethyl sulfide (Aldrich) was distilled before use. Dimethyl sulfoxide (Burdick and Jackson) was distilled under vacuum before use.

Preparations. The salts $[(trpy)(bpy)Ru(OH_2)](ClO_4)_2$, $[(trpy)(bpy)Ru(O)](ClO_4)_2$, and $[(bpy)_2(py)Ru(O)](ClO_4)_2$ were prepared by previously reported procedures.[19,20]

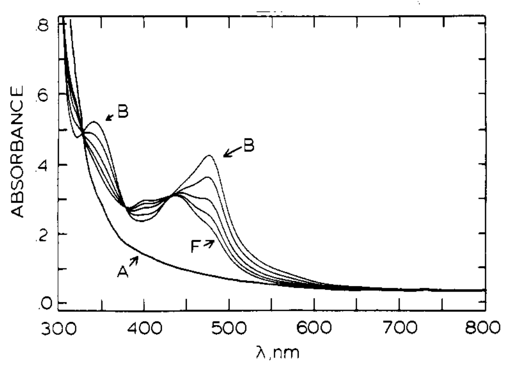
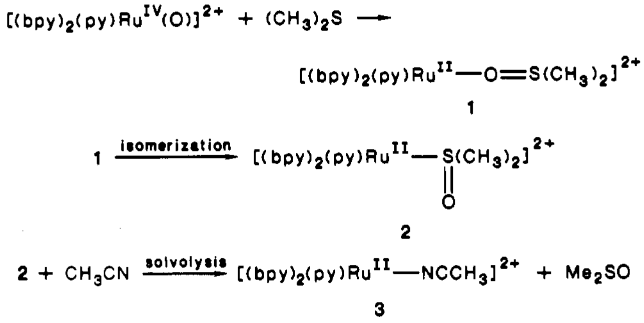


Figure 1. Spectral changes observed in the reaction of dimethyl sulfide, 0.82 M, with $[(bpy)_2(py)Ru(O)]^{2+}$ in CH_3CN after (A) 0, (B) 1, (C) 11, (D) 21, (E) 31, and (F) 41 min.

Scheme I



$$[(bpy)_2(py)Ru^{IV}(O)]^{2+} + (CH_3)_2S \longrightarrow \underset{\mathbf{1}}{[(bpy)_2(py)Ru^{II}{-}O{=}S(CH_3)_2]^{2+}}$$

$$1 \xrightarrow{\text{isomerization}} \underset{\mathbf{2}}{[(bpy)_2(py)Ru^{II}{-}\underset{\underset{O}{\|}}{S}(CH_3)_2]^{2+}}$$

$$2 + CH_3CN \xrightarrow{\text{solvolysis}} \underset{\mathbf{3}}{[(bpy)_2(py)Ru^{II}{-}NCCH_3]^{2+}} + Me_2SO$$

Instrumentation. UV-visible spectra were recorded on a Hewlett-Packard 8450A diode array spectrophotometer. Proton NMR spectra were recorded at room temperature on a Varian XL-400 400-MHz spectrophotometer and referenced to Me_4Si. Stopped-flow measurements were carried out on an Aminco-Morrow stopped-flow apparatus attached to a Beckman DU monochromator. Temperature was maintained to ±0.1 °C during kinetic runs with a Brinkman Lauda RM6 temperature bath. Kinetic calculations were performed on a Commodore PET Model 4032 computer using locally written software. Cyclic voltammetry (CV) and coulometric determinations were performed at room temperature by using a PAR Model 175 universal programmer and a PAR Model 173 potentiostat/galvanostat. In the coulometric determinations a Pt-gauze working electrode was used while in CV experiments a Teflon-shrouded glassy-carbon disk electrode (GC-30, Tokai Carbon, Inc.) was used as the working electrode.

Kinetic Measurements. Rate data for the disappearance of $[(bpy)_2(py)Ru(O)]^{2+}$ in CH_3CN were collected by following the absorbance increase at 440 nm for the dimethyl sulfoxide oxidation and at 480 nm for the dimethyl sulfide oxidation. Plots of $\ln|A_\infty - A_t|$ vs. time were usually linear, and first-order rate constants were calculated on the basis of a least-squares fit (uniform weighting) to the relation

$$\ln|A_\infty - A_t| = -kt + \ln|A_\infty - A_0|$$

where A_∞ is the absorbance at completion of the reaction, A_0 is the initial absorbance, A_t is the absorbance measured at time t, and k is the first-order rate constant. In some runs A_∞ drifted slightly upward; in these cases the value for A_∞ used to determine k was obtained by an iterative procedure to yield the best fit to the least-squares line. Values of A_∞ found in this manner were generally within 3% of the experimentally determined value. Substrate concentrations were calculated from the known densities of the liquid substrates. No attempt was made to exclude O_2 from the reactant solutions.

Results and Discussion

Dimethyl Sulfide Oxidation. Dimethyl sulfoxide was shown to be the oxidation product resulting from dimethyl sulfide reduction of $[(bpy)_2(py)Ru(O)]^{2+}$ by UV–vis spectroscopy, ^1H NMR spectroscopy, and electrochemical detection of the O-bound sulfoxide intermediate. In Figure 1 are shown the UV–vis spectral changes that accompany the oxidation in CH_3CN. Upon addition of substrate the initially featureless spectrum of $[(bpy)_2(py)Ru^{IV}(O)]^{2+}$ changes quickely to that of the O-bound sulfoxide complex (Figure 1B). The electronic spectral characteristics of the O-bound sulfoxide intermediate (λ_{max} = 476 nm (ϵ = 8200),

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Table I. Chemical Shifts of Intermediates in the Oxidation of $(CH_3)_2S$ by $[(bpy)_2(py)Ru^{IV}(O)]^{2+}$ [a]

	$\delta(CH_3)$	$\delta(6'\text{-}H)$ [b]
$[(bpy)_2(py)Ru^{II}—O{=}S(CH_3)_2]^{2+}$	2.32 (br)	9.28 (d)
$[(bpy)_2(py)Ru^{II}—S({=}O)(CH_3)_2]^{2+}$	2.61 (s) 2.35 (s)	10.23 (d)
$[(bpy)_2(py)Ru^{II}—NCCD_3]^{2+}$		9.42 (d)

[a] In CD_3CN, chemical shifts are referenced to Me_4Si. [b] See text for description of $\delta(6'\text{-}H)$.

343 nm (ϵ = 10300), 291 nm (ϵ = 50200)) are characteristic of bipyridine complexes of Ru(II) with oxygen-bound ligands. For the complexes $[(bpy)_2(py)Ru^{II}(L)]^{n+}$ in CH_3CN with L = H_2O, λ_{max} = 470 nm (ϵ = 8400), 335 nm (ϵ = 10500), and 290 nm (ϵ = 57200); with L = OH^-, λ_{max} = 505 nm (ϵ = 8000) and 363 nm, (ϵ = 10400); with L = $O{=}PPh_3$, λ_{max} = 479 nm (ϵ = 9000) and 338 nm (ϵ = 10300).[21]

After it is formed, the O-bound sulfoxide complex undergoes an isomerization to the S-bound sulfoxide complex. Ultimately, solvolysis of S-bound Me_2SO occurs to give $[(bpy)_2(py)Ru^{II}(NCCH_3)]^{2+}$ and free Me_2SO in solution but on a much longer time scale.

The sequence of reactions that appears to occur is shown in Scheme I (bpy is 2,2′-bipyridine). Corroboration of the scheme was obtained from an ^1H NMR experiment in which 5.2 μL (10-fold excess) of Me_2S were added to 5 mg of $[(bpy)_2(py)Ru^{IV}(O)]^{2+}$ dissolved in 1 mL of CD_3CN (Aldrich Chemical Co.). Rapid formation of the O-bound Me_2SO complex was observed in the ^1H NMR spectrum with the methyl groups of O-bound Me_2SO yielding a broad singlet at 2.32 ppm. In complexes of the type *cis*-$[(bpy)_2(py)Ru(L)]^{2+}$ the chemical shift of the 6′-proton of the bipyridine ring (the primed notation refers to those two of the four pyridyl groups of the cis bpy ligands that are trans to one another) that is nearest to L is shifted furthest downfield and is dramatically affected by the nature of L. For the O-bound sulfoxide complex **1**, the doublet of the 6′-proton occurs at 9.28 ppm. After 3 h, resonances associated with the O-bound isomer disappear and methyl resonances for the S-bound isomer appear at 2.61 and 2.35 ppm. The 6′-proton resonance for the S-bound Me_2SO complex **2** occurs at 10.23 ppm. The spectrum of the reaction mixture after 24 h shows the presence of both the S-bound Me_2SO complex **2** and the solvolysis product **3**, which has a characteristic 6′-proton resonance at 9.42 ppm. Table I summarizes the ^1H NMR results.

The UV-vis spectral changes in Figure 1 show that formation of the S-bound sulfoxide complex (λ_{max} = 400 nm) occurs with $t_{1/2}$ = 28 min. Deutsch and Root[22] have characterized the S-bound Me_2SO complex $[(trpy)(bpy)Ru(Me_2SO)]^{2+}$ (trpy is 2,2′:6′,2″-terpyridine) which has λ_{max} = 412 nm. The λ_{max} value for the S-bound complex $[(bpy)_2(py)Ru(Me_2SO)]^{2+}$ would be expected to have λ_{max} near 400 nm given the relative differences in electronic spectra for related $[(bpy)_2(py)Ru^{II}(L)]^{2+}$ and $[(trpy)(bpy)Ru^{II}(L)]^{2+}$ complexes. The spectral shift of λ_{max} to higher energy for the S-bound complex is consistent with the observation by Riley and Oliver that the S-bound sulfoxide ligand is either an excellent π acceptor and/or weak σ donor when coordinated to Ru(II).[8] Addition of dimethyl sulfide to a solution containing the terpyridine complex $[(trpy)(bpy)Ru^{IV}(O)]^{2+}$ in CH_3CN gives an initial intermediate having λ_{max} at 486 nm, which solvolyzes quantitatively to the CH_3CN complex with λ_{max} = 454 nm with no evidence for the S-bound sulfoxide complex with λ_{max} = 412 nm reported by Deutsch and Root.

From cyclic voltammetry, $E_{1/2}$ for the Ru(III/II) couple for the O-bound Me_2SO intermediate in the $[(bpy)_2(py)Ru^{IV}(O)]^{2+}$ + $(CH_3)_2S$ reaction occurs (Figure 2) at 1.0 V vs. SSCE ($E_{p,c}$ = 0.94, $E_{p,a}$ = 1.06) (Figure 2), which is considerably more positive than the potential for the $[(NH_3)_5Ru—O{=}SMe_2]^{3+/2+}$ couple at −0.05 V vs. SSCE.[23] The more positive potential is consistent with the stabilization of Ru(II) by the back-bonding pyridyl ligands.

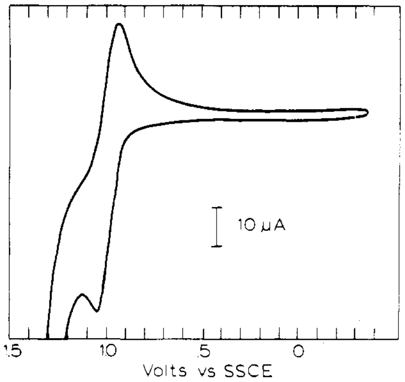

Figure 2. Cyclic voltammogram of the intermediate resulting from addition of $[(bpy)_2(py)Ru(O)]^{2+}$ to a solution of 0.1 M TEAP/CH_3CN containing dimethyl sulfide ca. 30 s after mixing (scan rate = 100 mv/s). A glassy carbon electrode was used and referenced vs. SSCE.

The lability of the S-bound sulfoxide complex toward Me_2SO loss is reminiscent of loss of H_2O or of $O{=}PPh_3$[21] in CH_3CN but is considerably slower. The isomerization of $[(NH_3)_5RuO{=}SMe_2]^{2+}$ to $[(NH_3)_5Ru—S(O)Me_2]^{2+}$ occurs much more rapidly, $k = 30 \pm 7\ s^{-1}$, consistent with the greater lability of the pentaammine complex.[23] In addition, Deutsch and Root report irreversible electrochemistry for the S-bound complex, $[(trpy)(bpy)Ru\text{-}S(O)Me_2]^{2+}$, which they attribute to S → O isomerization.[22] The normal preference of Ru(II) in an electron-rich environment is for S-bound Me_2SO because of the benefit of Ru → S back-bonding.[24-26]

The available evidence shows that the mechanisms of oxidation of dimethyl sulfide to Me_2SO occurs via $Ru^{IV}{=}O^{2+}$ attack on the S atom to give the O-bound Me_2SO complex followed by isomerization and subsequent ligand loss as depicted in Scheme I. There is no evidence for initial binding and coordination expansion at Ru, and the most reasonable mechanism for the redox step is via "O atom" transfer. The appearance of the Ru(II) O-bound sulfoxide product demonstrates that a net 2-electron transfer has occurred and that the oxo group is transferred quantitatively from Ru to S. In the O atom transfer 2 electrons are transferred from the largely S-based HOMO to the two vacancies in the d_{xz},d_{yz} orbitals at Ru(IV) accompanied by O^{2-} transfer to S. There is no basis for strong outer-sphere electronic coupling in the initial association complex between reactants

$$[b_2(py)Ru{=}O]^{2+} + S(CH_3)_2 \rightleftharpoons [b_2(py)Ru{=}O]^{2+},S(CH_3)_2$$

Consequently, in the redox step strong $\nu(Ru{=}O)$ vibrationally induced electronic coupling must occur

$$[b_2(py)Ru^{IV}{=}O]^{2+},S(CH_3)_2 \rightarrow [b_2(py)Ru^{II}—O{=}S(CH_3)_2]^{2+}$$

with the demand for six coordination at the metal met by retention of O-bound Me_2SO in the coordination sphere. The subsequent isomerization and ligand loss of bound Me_2SO follows on a far longer time scale.

The kinetics of the redox step were determined by monitoring the appearance of $[(bpy)_2(py)Ru—O{=}S(CH_3)_2]^{2+}$ at 480 nm. Over the limited concentration range studied, the reaction is first order in substrate and oxidant with $k_{IV} = 17.1 \pm 0.3\ M^{-1}\ s^{-1}$ (25 °C, CH_3CN). Activation parameters, determined from 287.7 to 308.8 K for a single substrate concentration are $\Delta H^{\ddagger} = 8.0 \pm 0.9$ kcal/mol and $\Delta S^{\ddagger} = -26 \pm 3$ eu. The kinetic parameters include contributions from the preassociation step including the orientational demands within the association complex arising from the

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Table II. Pseudo-First-Order Rate Constants and Second-Order Rate Constants for the Oxidation of $(CH_3)_2S$ by $[(bpy)_2(py)Ru(O)]^{2+}$ (5×10^{-5} M) in CH_3CN

[substrate], M	T, °C	k_{obsd}, s^{-1}	k_{IV},^{a} $M^{-1}\ s^{-1}$
0.817	14.7	8.56	10.5
		8.75	10.7
		8.97	11.0
	20.7	10.6	13.0
		11.0	13.5
	25.0	13.7	16.8
		13.8	16.9
	29.7	16.7	20.4
		17.4	21.3
	35.8	26.2	32.1
		24.2	29.6
0.408	25.0	7.12	17.5

$^a k_{IV} = k_{obsd}/[S(CH_3)_2]$.

Table III. Pseudo-First-Order Rate Constants and Calculated Second-Order Rate Constants for the Oxidation of $(CH_3)_2SO$ by $[(bpy)_2(py)Ru(O)]^{2+}$ (5×10^{-5} M) in CH_3CN

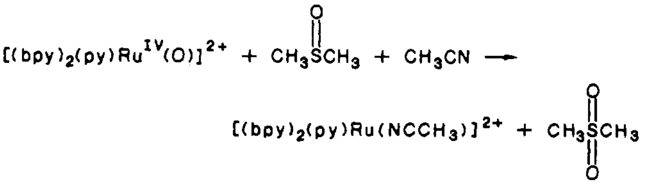
[substrate], M	T, °C	10^2k_{obsd}, s^{-1}	k_{IV},^{a} $M^{-1}\ s^{-1}$
0.846	13.2	6.94	0.0821
		6.81	0.0805
		6.82	0.0810
	19.9	9.54	0.113
		9.28	0.110
		9.51	0.112
	25.0	11.6	0.137
		11.8	0.140
		11.3	0.134
	35.4	17.6	0.208
		17.7	0.209
		17.7	0.209
0.169	25.0	2.07	0.123

^{a}Calculated from $k_{obsd}/[Me_2SO]$.

O atom transfer as well as from contributions of the redox step itself.

Oxidation of Dimethyl Sulfoxide to Dimethyl Sulfone. Dimethyl sulfone was shown to be the oxidation product by NMR in both the stoichiometric and electrocatalytic oxidation of DMSO by $[(bpy)_2(py)Ru^{IV}(O)]^{2+}$. In the electrocatalytic experiment, 10 mg of $[(trpy)(bpy)Ru(OH_2)](ClO_4)_2$ and 2 mL of Me_2SO were dissolved in 20 mL of water (pH 6.8, phosphate buffers) and electrolyzed at 0.8 V by using a Pt-gauze electrode in a three-compartment electrolysis cell.[18] In the experiment, $Ru^{IV}{=}O^{2+}$, generated electrochemically at the Pt-gauze working electrode with concomitant H_2 production at the auxiliary electrode, is reduced by Me_2SO to $Ru^{II}{-}OH_2^{2+}$ and then regenerated at the working electrode. After 537 C was passed, the solution was extracted with ether and 100 mg of dimethyl sulfone was isolated.

Shown in Figure 3 are the spectral changes that accompany the oxidation of Me_2SO by $[(bpy)_2(py)Ru(O)]^{2+}$ in CH_3CN. The spectral changes are distinct from those observed in the oxidation of dimethyl sulfide in that no intermediates are observed. The spectral changes are analogous to those previously observed in the epoxidation of olefins.[27] That an oxo atom transfer occurs, however, is clearly indicated by the appearance of $[(bpy)_2(py)Ru(CH_3CN)]^{2+}$ at 440 nm. Spectrophotometric titration experiments show the reaction stoichiometry to be



$$[(bpy)_2(py)Ru^{IV}(O)]^{2+} + CH_3\overset{O}{\overset{\|}{S}}CH_3 + CH_3CN \longrightarrow [(bpy)_2(py)Ru(NCCH_3)]^{2+} + CH_3\underset{O}{\underset{\|}{\overset{O}{\overset{\|}{S}}}}CH_3$$

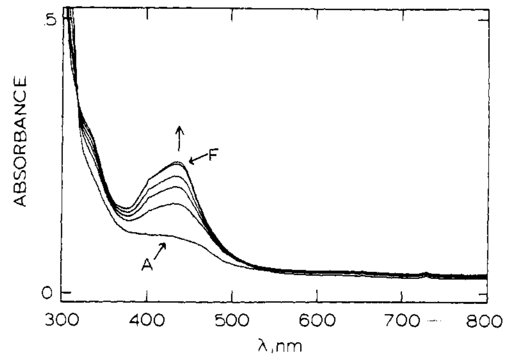
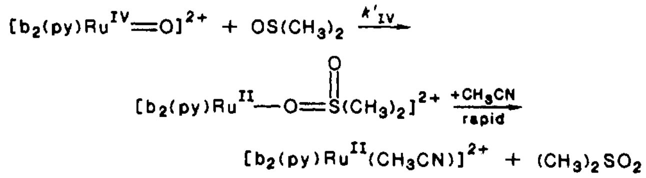


Figure 3. Spectral changes that accompany the oxidation of dimethyl sulfoxide, 0.85 M, by $[(bpy)_2(py)Ru(O)]^{2+}$ in CH_3CN after (A) 5, (B) 10, (C) 15, (D) 20, (E) 45, and (F) 180 s.

The kinetics for the appearance of $[(bpy)_2(py)Ru(CH_3CN)]^{2+}$ are first order in dimethyl sulfoxide and first order in $Ru^{IV}{=}O^{2+}$. From the rate studies the rate constant and activation parameters for the reaction are as follows: $k(25.0 \pm 0.1\ °C) = (1.34 \pm 0.06) \times 10^{-1}\ M^{-1}\ s^{-1}$; $\Delta H^{\ddagger} = 6.8 \pm 0.2$ kcal/mol; $\Delta S^{\ddagger} = -39 \pm 3$ eu.

Given the second-order kinetics and the observation of $[(bpy)_2(py)Ru(CH_3CN)]^{2+}$ and dimethyl sulfone as the reaction products, the oxidation mechanism must be



$$[b_2(py)Ru^{IV}{=}O]^{2+} + OS(CH_3)_2 \xrightarrow{k'_{IV}} [b_2(py)Ru^{II}{-}O{=}\overset{O}{\overset{\|}{S}}(CH_3)_2]^{2+} \xrightarrow[\text{rapid}]{+CH_3CN} [b_2(py)Ru^{II}(CH_3CN)]^{2+} + (CH_3)_2SO_2$$

In this case the slower redox step and more labile character of the sulfone product led to a circumstance where the solvolysis rate exceeds the rate of the redox step under our conditions and the sulfone complex is not observed as an intermediate.

Clearly, the same overall demands on the O atom transfer step exist in the oxidation of Me_2SO as for dimethyl sulfide including preassociation, utilization of preferred relative orientations, and $\nu(Ru{=}O)$ vibrationally induced electronic coupling in order to achieve the O atom transfer. An important factor in the decrease in k by a factor of ~120 for Me_2SO compared to dimethyl sulfide at 25 °C is, no doubt, a less favorable ΔG for the net reaction.

Implications for Catalysis. The oxidations of dimethyl sulfide to dimethyl sulfoxide and of dimethyl sulfoxide to dimethyl sulfone both occur by oxygen atom transfer in CH_3CN. The rate ratio for the two reactions at 25 °C, $k_{sulfide}/k_{sulfoxide} = 120$, is sufficient to provide a basis for the selective catalytic oxidation of the sulfide to the sulfoxide. Further, given the differences in activation parameters $\Delta H^{\ddagger}(Me_2S) - \Delta H^{\ddagger}(Me_2SO) = 1.2$ kcal/mol, selectivity for the sulfide over the sulfoxide would be even greater at higher temperatures.

We have not attempted here to develop a selective electrocatalytic procedure for the oxidation of sulfides to sulfoxides. However, we will return to this problem especially if we are successful in resolving optical isomers of the $[(bpy)_2(py)Ru^{IV}(O)]^{2+}/[(bpy)_2(py)Ru^{II}(OH_2)]^{2+}$ catalytic system with the goal of developing a procedure for the catalyzed electrochemical oxidation of sulfides to chiral sulfoxides.

Acknowledgments are made to the National Science Foundation under Grant No. CHE-8304230 for support of this research.

Registry No. Dimethyl sulfide, 75-18-3; dimethyl sulfoxide, 67-68-5; $[(bpy)_2(py)Ru^{IV}(O)]^{2+}$, 67202-43-1; $[(bpy)_2(py)Ru^{II}OS(CH_3)_2]^{2+}$, 106502-74-3; $[(bpy)_2(py)Ru^{II}S({=}O)(CH_3)_2]^{2+}$, 106502-75-4; $[(bpy)_2(py)Ru^{II}NCCD_3]^{2+}$, 106472-00-8.

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