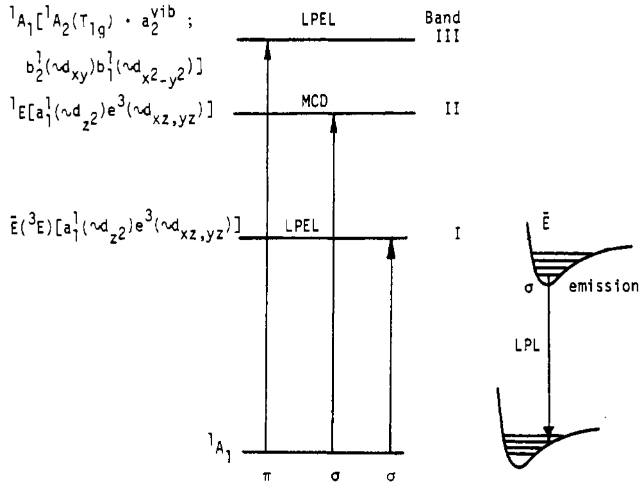

Figure 2. Direct excited state (and MO) assignments based on the quadruple-probe data of MCD, LPL, LPEL, and optical absorption techniques.

since in principle it might equally well have been $\pi(z)$ polarized. With this knowledge the emission monochromator was held at 535 nm and the excitation monochromator was scanned several times in the averaging mode for each of several solutions over the absorption region of bands I (~430 nm), II (~400 nm), and III (~340 nm). Figure 1 shows the positive degree of polarization,[6] P ($P = (I_\parallel - I_\perp)/(I_\parallel + I_\perp)$), for bands I and II, but P is negative for band III. These results now enable us to make two new direct polarization excitation assignments for which *direct* assignments were not previously possible. Thus *it is found now that the degree of polarization, P, of band I is experimentally the same as of* $^1E \leftarrow {}^1A_1$ *(band II)*, for which reason band I, previously suggested[1-3,5] to be $^3E \leftarrow {}^1A_1$ (vide supra), *is dominated by molecular in-plane* $\sigma(x,y)$ *polarization*, or $\bar{E}(^3E) \xleftarrow{\sigma} A_1$. On the basis of group theory band I might equally well have been dominated by out-of-plane $\pi(z)$ polarization, e.g., $\bar{A}_1(^3E) \leftarrow {}^1A_1$, to one of the energy-distinct spin–orbit components of ^3E. Previously observed[1,3] *A*-term-like MCD intensity for band I could not unambiguously be ascribed to a genuine *A* term of $\bar{E} \leftarrow A_1$ or to opposite signed *B* terms of adjacent spin–orbit components of a $^3\Gamma$ state such as ^3E.

The second new direct polarization assignment for optical excitation is that of band III (~335 nm). The polarization of $^1E \leftarrow {}^1A_1$ (band II) and $\bar{E} \rightarrow A_1$ from MCD and *P* of the LPEL–LPL experiments having been established, *the negative degree of polarization establishes that band III (~335 nm) is* $\pi(z)$ *polarized corresponding to excitation* $A_1 \xleftarrow{\pi} A_1$. If III is the transition $^1A_2(T_{1g})[b_2{}^1(\sim d_{xy})b_1{}^1(\sim d_{x^2-y^2})] \leftarrow {}^1A_1$ as proposed,[1,2] then the present experimental polarization finding leads to the *new conclusion that the electric dipole enabling vibronically coupled vibration is of symmetry* $a_2{}^{vib}$, e.g., $^1A_2(a_2{}^{vib}) \xleftarrow{\sigma} {}^1A_1$ or $^1A_2 \xleftarrow{\pi} {}^1A_1(a_2{}^{vib})$, ruling out the alternative group theoretically possible coupling vibration(s) of symmetry e^{vib}, e.g., $^1A_2(e^{vib}) \xleftarrow{\sigma} {}^1A_1$. The a_2 vibration of $W(CO)_5N$ is one of the type δ(W–C–O). The measured polarization does not support an assignment[3] $^1E[b_1{}^1(\sim d_{x^2-y^2})e^3] \leftarrow {}^1A_1$, since it requires *P* to be positive. The above amplitudes of *P* are below the extrema of depolarization-free ones,[6] $+^1/_7$ ($E_1 \leftarrow A_1$) and $-^1/_3$ ($A_1 \leftarrow A_1$), and will be discussed in our next paper.

The assignment composite is summarized in Figure 2. The generalization inherent in these results resides in the fact that the analysis should be applicable to similar excitation and emission bands of all nominally "$nt_{2g}{}^6$" low-spin tetragonal complexes, ML_5X and *trans*-ML_4XY, including other carbonyl complexes.

In summary, it is shown that multiply probing electronic excited states by LPL, LPEL, MCD, and optical absorption techniques can lead to complementing and definitive new information of great importance to photochemists as well as spectroscopists. For the present case of $W(CO)_5$pip it became possible to make direct polarization assignments of a sequence of three absorption and one emission state and to associate the MO's with them. The direct polarized measurements for excitation bands I and III are new, as is that of the dominant σ polarization of the emission band. The photochemical implication of excitations I and II is dominantly σ labilization (with some *xz*, *yz* π labilization) of the axial N–W–CO, with magnitudes of effects W–N > W–CO as photochemically found. The implications of excitation III are equatorial W–CO σ labilization and π labilization of in-plane (*xy*) type. However, these one-electron effects are distributed over four W–CO bonds. Also, since there is only one photoemission band, it is considered that at 80 K there is no emission corresponding to excitation III. Thus, the lower quantum yields[7,8] (e.g., $W(CO)_5L + L' \rightarrow W(CO)_5L' + L$) with excitation III compared to excitation II may be due to $^{1,3}A_2$ nonradiative losses, $^{1,3}A_2 \rightsquigarrow$ "^3E"$[(\sim d_{z^2})^1(\sim d_{xz},d_{yz})^3]$, detracting from internal conversion to the most likely photoreactive state, "^3E".

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Selective Molecular Oxygen Oxidation of Alkyl Sulfides to Sulfoxides Catalyzed by Dichlorotetrakis(dimethyl sulfoxide)ruthenium(II)

Sir:

In the past, attempts to use metal-based catalysts to promote the selective oxidation of dialkyl sulfides to their sulfoxides have met with only limited success. Known catalysts for this oxidation suffer not only from slow rates but also from poor selectivities with high levels of sulfone as byproducts. We have found that the Ru(II) complex *cis*-dichlorotetrakis(dimethyl sulfoxide)ruthenium in alcohol solvents is an excellent catalyst for the selective molecular oxygen oxidation of dialkyl sulfides to their sulfoxides. The observed reaction rates at 100 °C and 100 psig O_2 pressure are much faster than reported rates for other metal catalysts such as $RuCl_3$[1,2] or $RuCl_2(Ph_3)_3$.[1] In addition, unlike metal-based literature catalysts,[1] the *cis*-$RuCl_2(Me_2SO)_4$ complex[4,5] affords high selectivities for the

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(1) Ledlie, M. A.; Allum, K. G.; Howell, I. V.; Pitkethly, R. C. *J. Chem. Soc., Perkin Trans. 1* **1976**, 1734–8.
(2) Contrary to ref 3, $RuCl_3 \cdot xH_2O$ (when reduced with H_2 to ensure that all Ru present is in the +3 oxidation state[3]) will not function as a catalyst. This offers further support for the presence of Ru(IV) since the authors of ref 3 were very likely dealing with a Ru(IV) contaminant as active catalyst material in their work.[3]
(3) Harrod, J. F.; Ciccone, S.; Halpern, J. *Can. J. Chem.* **1961**, *39*, 1372.
(4) James, B. R.; Ochiai, E.; Rempel, G. I. *Inorg. Nucl. Chem. Lett.* **1971**, *7*, 781–4.
(5) The complex used in the catalytic studies was recrystallized from MeOH and has been shown to possess a cis–chloro arrangement with two S-bonded Me_2SO groups trans to the chloride ligands, one axial Me_2SO O-bonded, and the other axial Me_2SO S-bonded: Mercer, A.; Trotter, J. *J. Chem. Soc., Dalton Trans.* **1975**, 2480–3.

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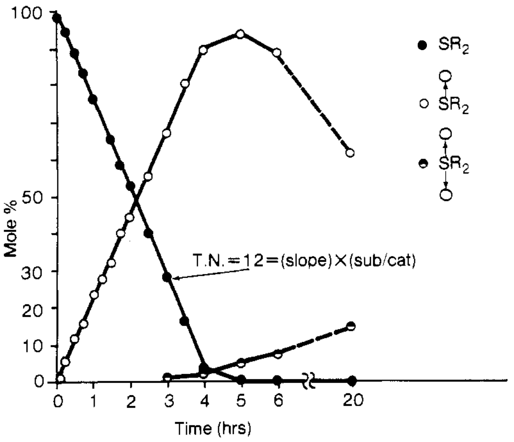
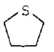


Figure 1. Molecular oxygen oxidation of decyl methyl sulfide (0.15 M) in MeOH catalyzed with *cis*-$Ru(Me_2SO)_4Cl_2$ at 110 °C and 110 psig O_2 pressure with substrate/catalyst = 50: (●) sulfide; (○) sulfoxide; (◒) sulfone.

Table I. Turnover Numbers for O_2 Oxidations of Sulfide Substrates under Various Conditions Using the Catalyst *cis*-$Ru(Me_2SO)_4Cl_2$

substrate[a]	solvent	temp, °C	O_2 pressure, psig	TN,[b] mol of substrate/ (mol of catalyst h)
decyl methyl sulfide	MeOH	110	110	12.0
decyl methyl sulfide	*i*-PrOH	110	110	11.0
decyl methyl sulfide	95% MeOH-5% H_2O	110	110	11.5
decyl methyl sulfide	MeOH	105	110	8.5
Me_2S	MeOH	105	110	7.2
Bu_2S	MeOH	105	110	77.8
	MeOH	105	110	3.4
C_6H_5SMe	MeOH	105	110	4.0

[a] Initial concentration 0.1 M. [b] TN's calculated from the zero-order plots of $[SR_2]$ vs. time.

sulfide oxidation; i.e., the sulfoxide to sulfone ratio at 100% sulfide conversion is ≥20 for all the sulfides we have investigated.

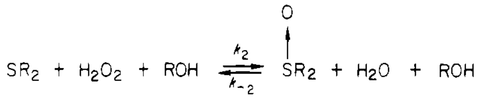
A typical reaction profile is shown in Figure 1 for the oxidation of decyl methyl sulfide with O_2 at 110 °C in dry MeOH ($[SR_2]/[RuCl_2(Me_2SO)_4] = 50$). Two features are immediately obvious. First, the high selectivity for sulfoxide is apparent and is observed for all the oxidations we have studied with this catalyst over the temperature range from 90 to 135 °C. Second, the reaction is zero order in decyl methyl sulfide, as it is for all the sulfide oxidations we have studied with this catalyst. The rates are dependent on the substrate (Table I), but are, nevertheless, always zero order in sulfide. This suggests that for each type of sulfide substrate different catalysts are generated in solution:

$$Ru(Me_2SO)_4Cl_2 + SR_2 \rightleftarrows Ru(SR_2)_x(Me_2SO)_{4-x}Cl_2 \qquad (1)$$

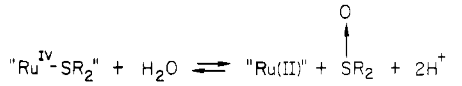
This is also supported by separate experiments which indicate the facile replacement of Me_2SO ligands by other ligands in solution.[6,7]

The sulfide oxidation can be visualized to occur either by a direct reaction with either free or coordinated peroxide[8-10] (eq 3) or by nucleophilic attack of H_2O on a sulfide coordinated to Ru(IV)[11] followed by an internal two-electron transfer (eq 4).[12] Alternatively, the reduction of a "Ru(IV)" complex back to the "Ru(II)" state could be achieved by electron transfer from the alcohol solvent (eq 5).[13] The results of mechanistic studies which are presented here for this sulfide system and results from the study of an analogous catalytic tertiary amine oxidation[14] indicate that the mechanism expressed by eq 2, 3, and 5 is operative. To determine whether sulfide (eq 4) or alcohol (eq 5) or both are the reducing agents in this system, the reaction was run in a 98% MeOH-2% $H_2{}^{18}O$ solvent system. Prior experiments demonstrated that water at this concentration has no effect on the kinetics. Thus, if the sulfide is oxidized by Ru(IV) and H_2O (eq 5), the product sulfoxide should contain some (^{18}O)sulfoxide that could be detected quantitatively via GC-mass spectral analyses. Our labeling studies show that no oxygen-18 incorporation occurs during the catalytic cycle. In additional experiments using isopropyl alcohol solvent it was found that, for each mole of sulfoxide formed, approximately 1.0 mol of acetone is formed during the course of a reaction. Also the reaction rate is markedly reduced when acetone replaces a substantial portion of isopropyl alcohol as the solvent. These results clearly establish that eq 4 is not operative, that the alcohol solvent is oxidized by "Ru(IV)" (eq 5), and that the sulfide is oxidized to sulfoxide by peroxide or its equivalent (eq 3).

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



$$SR_2 + H_2O_2 + ROH \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \overset{\displaystyle O}{\overset{\uparrow}{S}}R_2 + H_2O + ROH \qquad (3)$$



$$\text{"Ru}^{IV}\text{-SR}_2\text{"} + H_2O \rightleftarrows \text{"Ru(II)"} + \overset{\displaystyle O}{\overset{\uparrow}{S}}R_2 + 2H^+ \qquad (4)$$

$$\text{"Ru(IV)"} + R_2CHOH \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} \text{"Ru(II)"} + R_2C{=}O + 2H^+ \qquad (5)$$

To better develop our understanding of this chemistry, the kinetics of the catalyzed reaction of decyl methyl sulfide with O_2 was studied in detail. The reaction is less than first order in oxygen pressure ($n \approx 0.8$) over the pressure range investigated (100–700 psig O_2), and is first order in catalyst over the substrate/catalyst concentration ratio range investigated, 25–250 ($[SR_2] = 0.15$ M). The effects of sulfide concentrations on observed rates were also investigated, and the rates were found to be independent of sulfide at lower concentrations ($[SR_2] \leq 0.5$ M), but at high $[SR_2]$ the reaction rate was somewhat slower (~40% slower at 5 M in MeOH).

The reaction was also studied over the temperature range from 90 to 135 °C at 110 psig O_2 pressure. The plot of ln k_{obsd} vs. $1/T$ was linear and gave a value for $\Delta E_a = 22.3$ kcal/mol with an activation entropy value of −9 eu at 100 °C.

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[6] Evans, I. P.; Spencer, A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1973**, 204–9.

[7] The complexes $[Ru(Me_2SO)_{4-x}(Me_2S)_xCl_2]$ (where x = 2–4) have been characterized after isolation via silica gel chromatography from the reaction of excess Me_2S with *cis*-$Ru(Me_2SO)_4Cl_2$ for 1 h in hot EtOH under Ar.

[8] Such high selectivities for sulfoxide over sulfone are consistent with selectivities observed for H_2O_2 oxidations of sulfides at lower temperatures where sulfoxide is favored by about a factor of 100.[9]

[9] Edwards, J. O. "Peroxide Reaction Mechanisms"; Wiley: New York, 1962; Chapter 5, p 96.

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

[11] In studies using discrete Ru(III) complexes as catalysts no oxidation of sulfides was observed.

[12] This has an analogy in Au(III) chemistry where $AuCl_3 + (PhCH_2)_2S + H_2O \rightarrow AuCl + (PhCH_2)_2SO + 2HCl$: Herman, F. *Ber. Dtsch. Chem. Ges.* **1905**, *38*, 2813.

[13] Tovrog, B. S.; Diamond, S. E.; Mares, F. *J. Am. Chem. Soc.* **1979**, *101*, 5067.

[14] Riley, D. P. "Abstracts of Papers", 185th National Meeting of the American Chemical Society, Seattle, WA, March 1983; American Chemical Society: Washington, DC, 1983; INOR 272.

Such a ΔE_a value is consistent with a bimolecular process, and the activation entropy value is remarkably similar to the value reported for the oxidation of $Ru(NH_3)_6^{2+}$ to $Ru(NH_3)_6^{4+}$ with oxygen at 25 °C ($\Delta S^{\ddagger} = -10$ eu).[15]

A rate law (eq 6) for sulfide loss that is consistent with our

$$-d[SR_2]/dt = \frac{k_1k_3[Ru]_{tot}[O_2][ROH]}{k_1[O_2] + k_3[ROH]} \qquad (6)$$

observations was derived by using a steady-state approximation for [peroxide] and the assumption that k_{-2} and k_{-3} are vanishingly small, where $[Ru]_{tot} = [Ru(IV)] + [Ru(II)]$ and where the term $k_{-1}[Ru^{IV}]/k_2[SR_2][ROH]$ is small.[10,16] The linear plot of $[Ru]_{tot}$/Rate vs. $[O_2]^{-1}$ is consistent with the rate expression of eq 6. The values of k_1 and k_3 for the oxidation of decyl methyl sulfide at 108 °C in methanol, derived from the slope and intercept of such a plot, are 5.1×10^{-4} atm^{-1} s^{-1} and 2.1×10^{-3} M^{-1} s^{-1}, respectively. This rate law correctly predicts the less than unity order for the oxygen dependence, as well as the profound effect of solvent. Thus, the kinetic expression derived from eq 2, 3, and 5 is in excellent agreement with experimental results and provides kinetic support for the proposed catalytic mechanism of this facile and selective sulfide oxidation utilizing molecular oxygen.

Registry No. Decyl methyl sulfide, 22438-39-7; dimethyl sulfide, 75-18-3; dibutyl sulfide, 544-40-1; tetrahydrothiophene, 110-01-0; phenyl methyl sulfide, 100-68-5; *cis*-$Ru(Me_2SO)_4Cl_2$, 64376-67-6.

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(15) Pladziewicz, J. R.; Meyer, T. J.; Broomhead, J. A.; Taube, H. *Inorg. Chem.* **1973**, *12*, 639.

(16) Ross, S. D. *J. Am. Chem. Soc.* **1946**, *68*, 1484–5.

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Does CeSbO$_3$ Exist?

Sir:

The synthesis of a new defect cubic pyrochlore, $CeSbO_3$, was recently reported.[1] Several aspects of this report seemed rather unusual, and since then the preparation has been carefully repeated and the conclusion drawn that the product is not a new compound but rather a mixture of the starting materials, one crystalline and the other amorphous.

Our attention was drawn to this report for the following reasons:

First, according to the formula, one must assume trivalent oxidation states for both cerium and antimony. This seemed somewhat unusual, since the authors reported a closed-system preparation expressed by the equation

$$2CeO_2 + Sb_2O_3 \rightarrow 2CeSbO_3 + {}^1/_2O_2$$

which would have produced an endogenous oxygen pressure. In such an oxidizing atmosphere, one would not expect to obtain relatively reduced forms of cerium and antimony.

Second, the existence of the pyrochlore structure with either the Ce(III)/Sb(III) or the Sb(III)/Ce(IV) combination would be unusual from a crystal chemical point of view. The pyrochlore structure, ${}^{VIII}A_2{}^{VI}B_2O_7$, consists of a rather open BO_3 framework of octahedra sharing all vertices. The seventh oxygen, nonessential to the structure, resides in a large cavity formed by the octahedral framework. The eight-coordinate A cation resides in a hexagon of anions from surrounding framework octahedra. Each hexagon joins two of the large cavities, the anions therein bringing the coordination to eight in a bicapping fashion. Thus, even in the defect pyrochlore, $A_2B_2O_6$ (ABO_3), where the large cavities are not occupied by oxygens and the coordination number of both cations is formally 6, the geometry of the cation sites is quite different and requires a "larger" A cation for structural stability. Substantial empirical data have accrued in the literature outlining stability fields for this structure according to the relative cation sizes,[2,3] considerable extension having been obtained with high-pressure techniques.[4] Cerium/antimony combinations fall either outside of known stability regions or near boundaries.

Third, the interpretation of the crystallographic data, in which oxygen was randomly distributed among both the (f) positions (essential framework octahedra) and the (a) positions (within the large cavities), is disturbing since in the defect pyrochlore ABO_3 the cavity sites are not occupied by anions.

Fourth, it was eventually realized that the X-ray powder diffraction pattern given by the authors for $CeSbO_3$ was essentially identical with that of CeO_2,[5] one of the reactants, except for the (111) reflection at $d = 6.18$, which, at a relative intensity of 1%, could well be spurious. CeO_2 has the fluorite structure with a unit cell parameter of 5.4110 Å. The authors reported that the X-ray data for $CeSbO_3$ could be indexed on the basis of a cubic cell of the fluorite type with a cell edge of 5.4123 Å.

It was decided to carefully repeat the preparation as reported.[1] Reagent grade starting materials were used, and a green-white mass with a glassy texture was obtained. Optical inspection revealed orange streaks in regions of the mass. The product was very hard and difficult to grind to a powder, and the Debye–Scherrer X-ray powder photograph gave a diffraction pattern identical with that of CeO_2. Although qualitative analysis with sulfide ion was positive for antimony, no trace of the oxide was evident in the X-ray diffraction pattern. The melting point of Sb_2O_3 is 656 °C, and thus at the reaction temperature of 690 °C, this compound is molten. To determine if quenching in liquid nitrogen would produce an amorphous solid, Sb_2O_3 alone was treated according to the $CeSbO_3$ preparation procedure. At 690 °C, Sb_2O_3 is a clear orange liquid. After quenching in liquid nitrogen, a yellow-orange glass is obtained, which is very hard and difficult to grind. Before the heat treatment, the X-ray diffraction pattern corresponded to that of the Sb_2O_3 polymorph, senarmontite. After quenching from the molten state, the powdered glassy product gave no diffraction pattern.

In an effort to separate the two presumed phases, CeO_2 and Sb_2O_3, the product from the $CeSbO_3$ preparation procedure was heated at 700 °C under flowing argon. A white cloudy ring was deposited on a cooler section of the quartz tube. The white substance gave an X-ray diffraction pattern corresponding to that of Sb_2O_3, senarmontite. Examination of the "$CeSbO_3$" product using electron microscopy also indicated the presence of two types of particles, one amorphous and the other crystalline. The diffraction patterns of crystalline particles could be indexed on the basis of the unit cell of fluorite-type CeO_2.

These results seem to indicate rather conclusively that CeO_2 and Sb_2O_3 do not react under the given conditions to form a new defect pyrochlore: "$CeSbO_3$" consists of a mixture of crystalline CeO_2 embedded in a glassy Sb_2O_3 matrix.

Registry No. $CeSbO_3$, 81642-86-6; CeO_2, 1306-38-3; Sb_2O_3, 1309-64-4.

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(5) "Powder Diffraction File"; JCPDS: Swarthmore, Pennsylvania; Card No. 4-0593.

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