Photochemistry of Tetrasulfido Complexes of Molybdenum(VI), Tungsten(VI), Vanadium(V), and Rhenium(VII)

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The tetrasulfido complexes [MoS₄]²⁻, [WS₄]²⁻, [VS₄]³⁻, and [ReS₄]²⁻ photoitize in solution in the presence of air according to the stoichiometry [MS₄]²⁻ + O₂ → [MoS₂O₄]²⁻ + S₈. The diatomic sulfur can be scavenged by norbornadiene or tetramerizes to yield stable S₈. Quantum yields are strongly wavelength-dependent. For all complexes the reactive excited states are of the ligand to metal charge transfer type.

Introduction

Sulfido complexes of transition metals, particularly those of molybdenum, have been investigated extensively during recent years.¹,² This interest is related to the importance of these compounds in biological redox processes³ and industrial applications such as the hydrodesulfurization reaction.⁴⁻⁵ Transition-metal sulfide compounds are also involved in some remarkable photochemical reactions. As semiconductors, metal sulfides participate in light-induced reactions of organic and inorganic substrates.⁶⁻¹² Metallasulfur compounds are active in the photosynthesis¹³ and sulfur metabolism of phototropic bacteria.¹⁴ Despite these observations, not much is known about the light sensitivity of simple transition-metal complexes containing sulfur coordinating ligands. While some studies on complexes with more complicated sulfur ligands were reported,¹⁵⁻²³ the photochemical behavior of simple thiometales is virtually unknown. This lack is quite surprising since the electronic spectra of complexes such as [MoS₄]²⁻ are fairly well understood.¹² In addition, even some information on the structures of electronically excited states of [MoS₄]²⁻ and [WS₄]²⁻ is available.²⁵,²⁶ Finally, the photochemistry of the isoelectronic oxyanion MnO₄⁻ has been investigated in detail recently.²⁷

Internal redox processes between an oxidizing metal such as Mo(VI) and reducing sulfide ligands seem to be a characteristic feature of the chemistry of thiometales.¹,²⁻³⁴ Due to the charge-transfer (CT) nature of electronically excited states of [MoS₄]²⁻ and related complexes,²⁴ such an intramolecular ligand to metal (LM) electron transfer may easily occur as a photochemical reaction. On the basis of these considerations, we started an investigation of the photochemistry of tetrasulfido complexes of oxidizing metals with a d⁰ electron configuration. We report here on light-induced redox reactions of [MoS₄]²⁻, [WS₄]²⁻, [VS₄]³⁻, and [ReS₄]²⁻.

Experimental Section

Materials. The compounds (NH₄)₂[MoS₄]³⁻, [Ni(C₅H₅)₂]₂[MoS₄]²⁻, (NH₄)₂[WS₄]³⁻, (NH₄)₂[VS₄]³⁻, and [Ni(CH₃)₄][ReS₄]²⁻ were prepared according to published procedures. Their electronic absorption spectra agreed well with those reported previously.¹³⁻⁴¹ The water used in the photochemical experiments was triply distilled. Acetonitrile was Spectro Grade. Norbornadiene was purified by distillation.

Photolysis. The light sources were an Osram HBO 100 W/2 and a Hanovia Xe/Hg 977 B-1 (1 kW) lamp. The mercury lines at 254, 313, and 546 nm were selected by Schott FIL/IL interference filters. Irradiations at 241, 277, and 508 nm were achieved with a Schoeffel GM 250-1 monochromator. Solutions of the complexes were photolized in 1-cm spectrophotometer cells at room temperature. For quantum yield determinations the complex concentrations were such as to have essentially complete light absorption. The total amount of photolysis was limited to less than 5% to avoid light absorption by the photoproducts. Absorbed light intensities were determined by a Polytec pyroelectric radiometer that was calibrated and equipped with an R&P-345 detector.

Progress of the photolysis was monitored by UV-visible spectral measurements with a Uvikon 810 recording spectrophotometer and a...
Zeiss PMQ II spectrometer for measurements at selected wavelengths. The photoproducts \([\text{MoO}_2\text{S}_2]^{2-}\), \([\text{WO}_4\text{S}_2]^{2-}\), \([\text{V}O_2\text{S}_2]^{2-}\) were identified by their absorption spectra. As indicated by the spectral changes (Figures 1–3), the photolyses took place without side reactions. The photoproducts \([\text{MoO}_2\text{S}_2]^{2-}\) have the same extinction coefficients: \(\varepsilon_{300} = 0.6 \text{ M}^{-1} \text{cm}^{-1}\) and a 1-cm cell.

The isolate of \([\text{ReO}_2\text{S}_2]^{-}\) was not described in the literature. The decrease of concentration of \([\text{ReO}_2\text{S}_2]^{-}\) during the photolysis was expected according to the proposed stoichiometry (see below). The decrease of concentration of \([\text{ReO}_2\text{S}_2]^{-}\) during the photolysis was determined by measuring the extinction at its absorption maximum \(\lambda_{\text{max}} = 508 \text{ nm} (\varepsilon = 9700)\). At this wavelength the small absorption of the photoproduct (Figure 4) was neglected.

Elemental sulfur as other photoproduct was separated by centrifuging and dissolved in \(\text{CHCl}_3\). It was determined by its extinction at \(\lambda = 300 \text{ nm} (\varepsilon = 2940)\). As an example, an aqueous solution (100 mL) of 3.3 \(\times 10^{-3} \text{ M} \) \(\text{NH}_3\)[\(\text{MoS}_4\)] was photolyzed with light of \(\lambda = 254 \text{ nm}\) in the presence of oxygen. After 20-min irradiation time 1.17 \(\times 10^{-4} \text{ M} \) \(\text{MoS}_4\) was converted to \(\text{MoO}_2\text{S}_2\), as determined by spectrophotometric analysis. The sulfur was dissolved in \(\text{CHCl}_3\) (100 mL). The concentration of sulfur was 0.24 \(\times 10^{-4} \text{ M}\). This is 18% less than expected according to the proposed stoichiometry (see below).

**Results**

In the presence of air the irradiation of diluted (~10⁻²) aqueous solutions of \([\text{MoS}_4]^{2-}\) with white light was accompanied by spectral changes (Figure 1) that clearly indicated the formation of \([\text{MoO}_2\text{S}_2]^{2-}\). The final spectrum (Figure 1) corresponds to 80% conversion of \([\text{MoS}_4]^{2-}\) to \([\text{MoO}_2\text{S}_2]^{2-}\). In solutions that were deaerated by saturation with argon, \([\text{MoS}_4]^{2-}\) was essentially not light-sensitive. However, a very slow and incomplete photolysis took place with the same spectral variations as those that were observed in the presence of air. It was assumed that the photolysis in deaerated solutions was caused by trace amounts of oxygen,

\[\lambda_{\text{max}} = 490 \text{ nm and a 1-cm cell.}\]

The photolysis of all four complexes are rather similar. Some deviations are explained below. The decrease of concentration of \([\text{ReO}_2\text{S}_2]^{-}\) during the photolysis was determined by measuring the extinction at its absorption maximum \(\lambda_{\text{max}} = 508 \text{ nm} (\varepsilon = 9700)\). At this wavelength the small absorption of the photoproduct (Figure 4) was neglected.

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The isolation of \([\text{ReO}_2\text{S}_2]^{-}\) was not described in the literature. The reported absorption maxima at \(\lambda = 400 \text{ and } 312 \text{ nm were}


\[(44)\] The spectrophotometric analysis of elemental sulfur was described previously. However, the extinction coefficient at 300 nm was different from that of the present work.

which are difficult to remove. In the presence of oxygen the formation of [MoO(S2)]2− was accompanied by the release of elemental sulfur:

\[ \text{[MoS}_2\text{]}^2− + O_2 → [\text{MoO(S}_2\text{]}]^2− + 1/2 \text{S}_2 \]

At low complex concentrations (≈10−5 M) the formation of elemental sulfur could not be detected. But at higher concentrations (>10−3 M) sulfur formed a colloid, which led to light scattering over the entire absorption spectrum. At complex concentrations of ~10−3 M the elemental sulfur precipitated. It was separated by centrifuging and determined spectrophotometrically. This analysis agreed fairly well with the stoichiometry of the equation as proposed above. At λmax = 254 nm the quantum yield of this photoreaction was Φ = 0.15. It dropped to Φ < 10−3 for λirr > 300 nm. In alkaline solution the efficiency of the photolysis did not depend on the pH.

It was assumed that sulfur was initially released as S2, which finally yields stable S4. Diatomic sulfur is known to undergo efficient Diels–Alder trapping by certain olefins such as norbornadiene.4 The photolysis (λirr = 313 nm) of 10−2 M [N-(C6H5)2]2[M0(S2)] in acetonitrile was carried out in the presence of 2 × 10−3 M norbornadiene. The olefin does not absorb at this wavelength. After an irradiation time of 5 h, the starting complex and the photoproduct [N-(C6H5)2][M02S2−] were separated by the addition of ether. The filtered solution was evaporated at room temperature. The residue was analyzed by mass spectroscopy. The presence of the mass 188 clearly indicated the formation of the trisulfide C7H8S3 by the reaction of norbornadiene with diatomic sulfur.47

The irradiation of aqueous solutions of [WS4]2− led to results that were very similar to those obtained for [MoS4]2−. In the presence of air the photolysis of [WS4]2− was accompanied by spectral changes (Figure 2) that indicated clearly the formation of [VO2S4]2−.48 At higher complex concentrations (>10−3 M) the photochemical formation of elemental sulfur was detected. The photolysis proceeds apparently by the same stoichiometry as that of [MoS4]2−. At λirr = 214 nm the quantum yield was Φ = 0.038. It dropped to Φ = 4 × 10−3 at λirr = 277 nm. The photolysis of [VS2]2− was carried out in alkaline (1 M NaOH) solution since this complex is not stable in neutral solution. The spectral changes (Figure 3) are in agreement with the formation of [VO2S2]2−.49 The photolysis that proceeds only in the presence of oxygen was accompanied by the formation of sulfur. In contrast to the corresponding molybdenum and tungsten complexes, [VS2]2− was quite light-sensitive upon irradiation of its long-wavelength band. [VO2S2]2− was formed with a quantum yield Φ = 0.14 at λirr = 546 nm.

Since [ReS2]2− can be isolated only as the tetraalkylammonium or phosphonium salt, both of which are insoluble in water, the photolysis was carried out in acetonitrile. The spectral changes that accompanied the photoreaction in the presence of air (Figure 4) are qualitatively similar to those of the other tetrathiosulfide complexes. It was assumed that [ReO2S2]2− was formed. However, in acetonitrile the formation of colloidal sulfur occurred already at very low concentrations. The spectral variations (Figure 4) include an apparent extinction due to light scattering by the colloidal sulfur. This extinction increases with decreasing wavelength. In analogy to [VS2]2− the light sensitivity of [ReS2]2− extends to the long-wavelength band. [ReS2]2− disappeared with a quantum yield of Φ = 0.14 at λirr = 313 nm and Φ = 0.08 at λirr > 508 nm.

Discussion

Electronic Spectra. All four complexes [MS]n+ with M = Mo(VI), W(VI), V(V), and Re(VII) are tetrahedral and contain the metal with a d8 electron configuration. At low energies all electronic transitions are then LMCT transitions from the sulfide ligands to the metal.5 However, at these high formal oxidation states of the metal, the bonding in these complexes must have large covalent contributions. It follows that some of the MO’s are strongly delocalized between metal and ligands. LMCT transitions may then not be associated with the transfer of much charge from the ligand to the metal.

The absorption spectra of the four [MS]n+ complexes are rather similar (Figures 1–4). Since the electronic structure of [MoS4]2− has been investigated in detail,1,24,40,48 only the spectrum of this complex will be discussed here. Appropriate assignments of absorption bands of the other complexes are then quite obvious. The red shift of the LMCT absorption bands from W(VI) to Mo(VI), Re(VII), and V(V) (Figure 1–4) reflects certainly the increasing oxidation strength in this series. In comparison to those of the corresponding oxyniums MO+4, the absorption bands of MS+4 are shifted to longer wavelength since sulfide is a stronger reductant than oxide.

The MO’s of [MoS4]2− that are involved in electronic transitions above 200 nm are the filled 3t2 and 1t1 (HOMO) and the empty 2e* (LUMO) and 4t2* orbitals.1,24 The 1t1 level is a pure sulfur orbital that is slightly antibonding with respect to the sulfur–sulfur interaction.24 The 3t2 level is largely composed of sulfur orbitals (~90%) with a minor contribution by the metal (~10%). This 3t2 orbital is weakly S–S bonding. The empty MO’s 2e* and 4t2*, which are antibonding with respect to metal–ligand interaction, are composed of comparable portions of metal and ligand orbitals. It follows that all electronic transitions are of the LMCT type and are associated with the transfer of a considerable fraction of charge from the ligand to the metal. While there is a general agreement that the longest wavelength band of [MoS4]2− at λmax = 468 nm (ε = 13800) is assigned to the 1t1 → 2e* transition, the origin of the higher energy transitions (3t2 → 2e*, 1t1 → 4t2*, 3t2 → 4t2*) is not quite clear. By resonance Raman spectroscopy of [MoS4]2− and [WS4]2−, it was shown that LMCT excitation (1t1 → 2e*) leads indeed to a M–S bond extension of 0.058 and 0.07 Å, respectively. This is not as large as that of MnO−4 (0.09 Å).

Photochemistry. The photochemistry of all four [MS]n+ complexes can be described by the following scheme (* = LMCT state):
LMCT state of [MoS₄]²⁻ and [WS₄]²⁻ is not much distorted with regard to the ground state while [MnO₄]²⁻, which photoyses efficiently upon long-wavelength irradiation, is distorted much more strongly. Unfortunately, the excited-state distortions of [VS₄]³⁻ and [ReS₄]²⁻ are not known to establish a correlation between the extent of excited state distortion and the efficiency of the photoreaction.

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Registry No. [MoS₄]²⁻, 16330-92-0; [WS₄]²⁻, 14916-78-0; [V₅S₄]²⁻, 14791-51-6; [ReS₄]²⁻, 16829-47-3; [MoS₅]²⁻, 16680-22-3; [WO₃S₂]²⁻, 16450-49-0; [VO₅S₃]²⁻, 26815-91-8; [ReO₃S₃]²⁻, 112113-55-0; O₂, 7782-44-7; S₂, 23550-45-0; S₈, 10544-50-0.

Metal/Sulfide/Thiolate Chemistry for an Early 3d Transition Metal: Variation of Product Identity as a Function of V:S Reaction Ratio and Structure and Redox Properties of Discrete V:S/edt Complexes

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A systematic investigation of the VCl₄/elemental S/Na₂-edt reaction system in MeCN is described. Particular emphasis has been placed on determining the influence of the S/V ratio (n) on the identity of the reaction product(s). Values of n in the 0–2.5 range have been employed. In some cases, the influence of the edt⁻:V ratio on reaction product(s) has also been investigated. These combined variations have led to the synthesis of five discrete complexes, the structures of two of which are described. The n = 0 reaction ratio leads to high-yield preparation of (PPH₄)₃[V₇(edt)₃] (1). The n = 0.5 reaction ratio yields a mixture of products, being composed of an approximately 3:1 ratio of (NEt₄)₂[V₄(edt)₂] and (NEt₄)₂[V₃S₄(edt)] (2). Complex 2 crystallizes in the monoclinic space group P2₁/n with the following unit cell dimensions at -154 °C: a = 14.168 (5) Å, b = 18.446 (7) Å, c = 19.803 (8) Å, β = 104.91 (2)°, and Z = 4. A total of 3806 unique reflections with F > 2.33σ(F) were collected, and the structure solution was refined to values of conventional indices R and R_w of 8.39 and 8.59%, respectively. The structure of the anion of 2 consists of a V₇ triangle with one central capping μ-S atom and a μ-S atom bridging each edge. A terminal edt completes five-coordination at each metal. The V₅S₄ core can be described as a “partial cube” and is isostructural with the more common Mo₅S₄ cores in Mo/S chemistry. Charge considerations necessitate a mixed-valence trivanadium(III,2IV) description, but on the basis of inspection of structural parameters, there is no justification for a trapped-valence assignment, and the anion is best described as electronically delocalized with an average metal oxidation state of +3.2. The n = 1 reaction ratio yields (NEt₄)₂Na₂[V₃S₄(edt)] (3), the structure of which had been determined in previous work and contains the multiply bonded VS₂⁻ unit. The n = 1.5 reaction ratio gave differing products depending on the edt⁻:V ratio employed. When edt⁻:V = 3:1, high yields of 3 were obtained, whereas an edt⁻:V = 2:1 ratio yielded a preparative route to pure 2. This difference in behavior is attributed to the strongly chelating nature of the edt⁻ ligand favoring complex 3 when sufficient edt⁻ is available and preventing aggregation by further incorporation of available S⁻². The n = 2 ratio also yielded differing products, depending on the edt⁻:V ratio. When this ratio was 3:1, the product again was 3. When this ratio was 2:1, a mixture of highly crystalline (NEt₄)₂[V₂S₃(edt)] (4) and microcrystalline (NEt₄)₂Na₂[V₃S₄(edt)] (5) was obtained; the two materials have been satisfactorily separated manually. Complex 4 crystallizes in the monoclinic space group P2₁/c with the following unit cell dimensions at -155 °C: a = 12.955 (6) Å, b = 15.963 (8) Å, c = 15.338 (8) Å, β = 109.83 (2)°, and Z = 4. A total of 3112 unique reflections with F > 3.00σ(F) were employed, and the structure solution was refined to values of conventional indices R and R_w of 4.34 and 4.37%, respectively. The anion of 4 consists of a five-coordinate vanadium(VI) atom bridged by two μ-S²⁻ species to a four-coordinate vanadium(V) atom. The former additionally contains terminal edt⁻ and O⁻ groups, while the latter contains two terminal S⁻² groups. Complex 5 is assigned the same structure but with O⁻ replaced by S⁻². The n = 2.5 reaction ratio was found to yield only complex 5. The cyclic voltammetric properties of these complexes are also described, and the isolated oxidation levels are shown to be members of multicomponent electron-transfer series, with the exception of 3, which shows no reversible behavior.

Introduction

It is becoming increasingly apparent that the chemistry of vanadium bound to sulfur is of great relevance and/or importance to a wide variety of chemical, industrial, and biological systems. For example, the polymeric group 5 sulfides have exhibited interesting magnetic and electrical properties, and substances such as Li₅VS₄ and (the group 4 sulfide Li₂TiS₄) have been attracting the attention of industrial researchers seeking novel conducting materials for use as electrodes in solid-state batteries. In addition, the large amounts of vanadium impurities in the heavier crude oils result in conversion of the former to vanadium sulfide deposits, which help to poison the Mo/Co catalyst during hydrodesulfurization (HDS). This has stimulated interest in both the identity of the crude oil impurities and the mechanism of their subsequent conversion to vanadium sulfide. Finally, the recent identification of a vanadium nitrogenase, its subsequent study by the EXAFS technique, and comparison with the better understood Mo nitrogenase suggest that the vanadium is located in a complete or partial environment of sulfur.

The combined developments described above have suggested to us that the time had come for a better understanding of the fundamental chemistry and properties of discrete complexes containing vanadium bound to sulfide and/or sulfur-based ligands such as thiolate (RS⁻). This belief represents the primary stimulus for the work described herein. In addition, such studies with a 3d metal would provide illuminating comparisons and contrasts with 4d Mo/S and 5d W/S chemistry, both of which have already been extensively developed.
