Production of Hydrogen by Ultraviolet Irradiation of $Mo_2(SO_4)_4{}^{4-}$ in Aqueous Sulfuric Acid. Electronic Absorption Spectrum of $K_3Mo_2(SO_4)_4 \cdot 3.5H_2O$ at 15 K

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Abstract: Ultraviolet irradiation (λ 254 nm) of $Mo_2(SO_4)_4{}^{4-}$ in 5 M H_2SO_4 produces H_2 and the one-electron oxidation product $Mo_2(SO_4)_4{}^{3-}$. The disappearance quantum yield of $Mo_2(SO_4)_4{}^{4-}$ is 0.17 at 254 nm. The spectrum of $K_3Mo_2(SO_4)_4 \cdot 3.5H_2O$ exhibits an absorption band at 1405 nm (ϵ 143); this band shows a vibrational progression in a 350-cm^{-1} fundamental even in 5 M D_2SO_4 solution at room temperature. At 15 K additional vibronic structure is resolved. This band is assigned to the N → E type transition $\delta \rightarrow \delta^*$ ($^2B_{2g} \rightarrow {}^2B_{1u}$).

It has been shown previously that ultraviolet irradiation of aqueous acidic solutions containing one-electron reductants such as Fe^{2+} yield hydrogen.[2] We are presently exploring the photoredox behavior of low-valent molybdenum complexes containing strong metal-metal bonds, and in particular are directing our attention to systems that are capable of reducing hydronium ions. Herein we report the results of an investigation of the photoreactivity of $Mo_2(SO_4)_4{}^{4-}$ in aqueous sulfuric acid. The near infrared spectrum of $K_3Mo_2(SO_4)_4 \cdot 3.5H_2O$ at 15 K has also been studied.

Experimental Section

The compounds $K_4Mo_2(SO_4)_4$[3,4] and $K_3Mo_2(SO_4)_4 \cdot 3.5H_2O$[5] were prepared according to standard procedures. All manipulations with the molybdenum complexes were conducted under nitrogen or in degassed solution. For the irradiations, the appropriate solution was placed in a special vacuum-tight, 1-cm quartz spectrophotometer cell and degassed through three freeze-pump-thaw cycles. Low-pressure Hg lamps were used for the 254-nm irradiations. The electronic absorption spectra of the reaction solutions were monitored using a Cary 17 spectrophotometer. Quantum yields at 254 nm were determined using ferrioxalate actinometry such that the sample absorbed 5.77 × 10^{-7} einsteins/min. Mass spectral analyses of the gas above the irradiated solutions were obtained with an AEI-MS-902 high-resolution mass spectrometer. The low-temperature near IR spectrum of $K_3Mo_2(SO_4)_4 \cdot 3.5H_2O$ was obtained by positioning a sample in a Cary liquid helium Dewar. X-ray photoelectron spectra were obtained with a HP5950A spectrometer from powdered samples on double-stick tape.

Evolution of H_2 was measured for exhaustively photolyzed samples of $Mo_2(SO_4)_4{}^{4-}$ in vacuum-tight 1-cm spectrophotometer cells equipped with a glass side chamber and needle valve. The amount of evolved H_2 was determined by Toepler pumping the stirred photolyzed solution through three liquid nitrogen traps into a calibrated volume and manometrically measuring the pressure. To ensure that only H_2 was collected, the gas was then passed over hot copper oxide, yielding water that was condensed in a liquid nitrogen trap, leaving no detectable gas.

Photochemistry of $Mo_2(SO_4)_4{}^{4-}$

Irradiation (254 nm) of $Mo_2(SO_4)_4{}^{4-}$ in 5 M D_2SO_4 results in the spectral changes shown in Figure 1. As irradiation proceeds, small gas bubbles are formed. The band at 515 nm (ϵ ~170) characteristic[3,4] of $Mo_2(SO_4)_4{}^{4-}$ decreases in intensity, whereas a structured absorption system diagnostic (vide infra) of $Mo_2(SO_4)_4{}^{3-}$ grows in at 1200-1600 nm (ϵ_{max} of 143). Isosbestic points are initially maintained at 578 and 420 nm and shoulders develop at 570 and 405 nm. A quantum yield of 0.17 was obtained for disappearance of $Mo_2(SO_4)_4{}^{4-}$.

Mass spectral analysis of the gas formed by irradiating $Mo_2(SO_4)_4{}^{4-}$ in 5 M H_2SO_4 solution confirmed that H_2 was produced. Thus the principal photoreaction must correspond to

$$H^+(aq) + Mo_2(SO_4)_4{}^{4-} \xrightarrow{254\ nm} \tfrac{1}{2}H_2 + Mo_2(SO_4)_4{}^{3-} \quad (1)$$

An exhaustively photolyzed solution yielded 0.31 mol of H_2/mol of $K_4Mo_2(SO_4)_4$. The fact that this is less than the theoretical amount of H_2 (0.5 mol) is not unexpected, as isosbestic points are not maintained (Figure 1); that is, the reaction observed upon 254-nm irradiation is not stoichiometric at high conversion.[6]

Near Infrared Spectrum of $Mo_2(SO_4)_4{}^{3-}$

We have found that $Mo_2(SO_4)_4{}^{3-}$ exhibits a previously unreported[5] absorption band in the near IR at 1405 nm (ϵ_{max} 143 for a 5 M D_2SO_4 solution). Remarkably, a vibrational progression with a spacing of 350 cm^{-1} attributable to a_{1g} (MoMo) was observed even in solution at room temperature. In contrast, the lowest energy electronic absorption band of $K_4Mo_2(SO_4)_4$, which occurs at 519 nm (ϵ 170), has been shown[7] to be due to the transition $\delta \rightarrow \delta^*$ ($^1A_{1g} \rightarrow {}^1A_{2u}$). There are two plausible explanations for the near IR band of $K_3Mo_2(SO_4)_4 \cdot 3.5H_2O$. As the compound is formally of mixed valence, the transition could be assigned intervalence charge transfer in the weak interaction description.[8,9] Alternatively, the transition could be viewed as the N → E type[10] transition $\delta \rightarrow \delta^*$ ($^2B_{2g} \rightarrow {}^2B_{1u}$). The former description seems inappropriate for several reasons. Firstly, the MoMo bond lengths[11] and stretching frequencies[12] are approximately equal in $K_4Mo_2(SO_4)_4$ and $K_3Mo_2(SO_4)_4 \cdot 3.5H_2O$. Therefore, the δ-bonding model applicable to $K_4Mo_2(SO_4)_4$ would be expected to obtain for $K_3Mo_2(SO_4)_4 \cdot 3H_2O$ as well. EPR measurements for $K_3Mo_2(SO_4)_4 \cdot 3.5H_2O$ suggest that the odd electron occupies a δ orbital delocalized over both metal centers.[13] We also have examined the x-ray photoelectron spectrum of $K_3Mo_2(SO_4)_4 \cdot 3.5H_2O$ and have found no splitting of the Mo $3p_{1/2}$ signal. One final point, and most convincing, is the fact that the 1405-nm band in the spectrum of $K_3Mo_2(SO_4)_4 \cdot 3.5H_2O$ shows sharp vibronic structure at 15

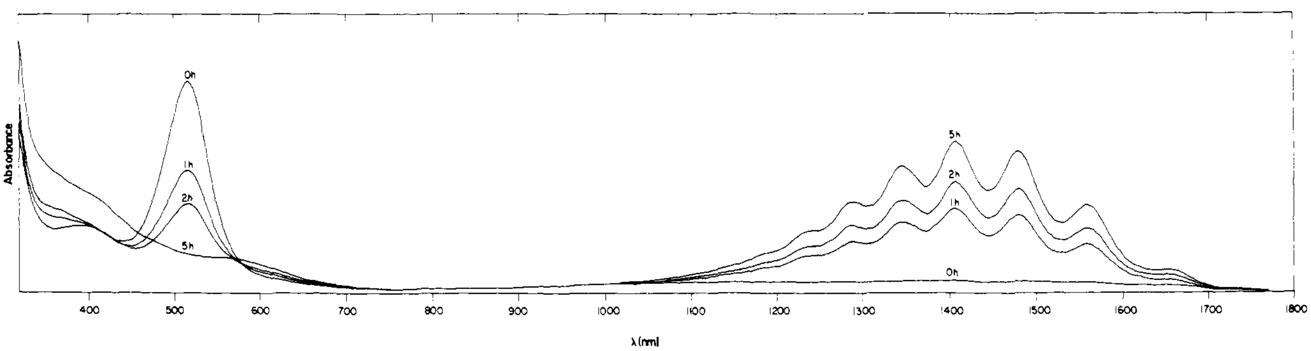

Figure 1. Electronic absorption spectral changes during 254-nm irradiation of $K_4Mo_2(SO_4)_4$ in 5 M D_2SO_4 solution.

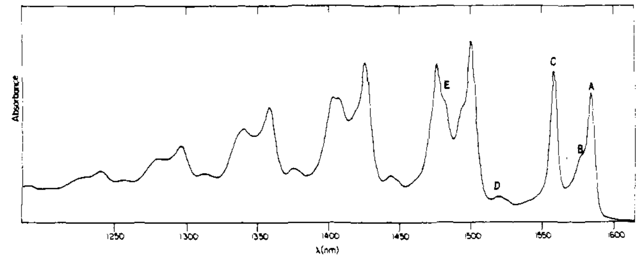

Figure 2. Electronic absorption spectrum of $K_3Mo_2(SO_4)_4 \cdot 3.5H_2O$ in a KBr pellet at 15 K.

Table I. Vibronic Structure of the Near IR Band in the Spectrum of $K_3Mo_2(SO_4)_4 \cdot 3.5H_2O$ *in a* KBr Pellet at 15 K

nm	cm^{-1}	A	B	C	D	E
1583.7	6314	┌				
1575.6	6347		┌			
1558.2	6418			┌		
1520.0	6579	351			┌	
1500.3	6665	–	354			
1492.3	6701		–			
1482.4	6746			358		┌
1475.9	6776			–	351	
1442.9	6930	353			–	
1425.0	7018	–	354			
1417.3	7055		└			363
1406.7	7109			355		–
1402.3	7131			└		
1374.0	7278	350			└348	
1357.2	7368	–				
1339.0	7468					└359
1312.9	7616					
1296.2	7715	└347				

K (Figure 2, Table I). An intervalence charge transfer band, because the transition is a multiphonon excitation,[9,14] would not be expected to exhibit well resolved molecular vibronic structure. Both the vibrational progression in quanta of 350 cm^{-1} and the Franck-Condon factor of about 1.5 are more consistent with the $\delta \rightarrow \delta^*$ assignment.

The vibrational structure of the 1405-nm band in the spectrum of $K_3Mo_2(SO_4)_4 \cdot 3.5H_2O$ is assigned as follows: There are five (A–E, Figure 2, Table I) origins for progressions in a_{1g}(MoMo). Conspicuous is the presence of the two major components A and C with slightly different Franck-Condon factors. The progression that begins at C has a slightly higher progressional frequency than that beginning at A. These split components are interpreted to result from the $\delta \rightarrow \delta^*$ transition of two crystallographically nonequivalent[11] $Mo_2(SO_4)_4^{3-}$ ions in the unit cell. Previously, it has been noted[12] that this nonequivalence results in slightly different ground-state values of a_{1g}(MoMo) (373 and 386 cm^{-1}). The two weak peaks, B and E, might possibly represent transitions involving quanta of a_{1g} modes built on A and C, respectively. Alternatively, these weak peaks could result from Davydov splitting of the pure origins (A and C). The other weak peak, D, may be attributed to a transition involving a quantum of an a_{1g} mode built on either A or C. It is apparent, however, that definitive assignments of the three weak peaks cannot be made with the limited data available.

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References and Notes

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(6) Irradiation of $Mo_2(SO_4)_4^{4-}$ in 5 M H_2SO_4 with visible light also produces $Mo_2(SO_4)_4^{3-}$ and hydrogen (W. C. Trogler and H. B. Gray, unpublished results). Preliminary experiments have shown that the photoreaction under these conditions is stoichiometric at high conversion (0.49 mol of H_2 were liberated per mole of $Mo_2(SO_4)_4^{4-}$ irradiated). Experiments directed toward the elucidation of the mechanistic features of the photoreaction are in progress.
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