biphasic kinetics, while for the BPA and BPED complexes the two phases are indistinguishable; the BPDO complexes are compact but the BPA and BPED complexes are extended; the BPDO complexes have greater $\Delta E_{1/2,\mathrm{cor}}$ than the BPA and BPED complexes; and the BPDO complexes show greater deviations from the LFER than do the BPA and BPED complexes. The ligand systems are all saturated, which means that these effects must be electrostatic in origin, and this explains the dependence of $\Delta E_{1/2,\mathrm{cor}}$ on ligand conformation. The greater electrostatic effect for the BPDO complexes means that w_{22} should be more sensitive to charge type; thus $k_2 > k_1$ and biphasic kinetics are observed. The more compact complexes should have a *greater* effective radius which decreases ΔG_0^*, and so the BPDO binuclear species deviate more strongly from the LFER.

The above considerations provide qualitative support for the proposed mechanism involving one-electron generation of superoxide for both the fully reduced and mixed-valence binuclear complexes. The results demonstrate that simple proximity of two Ru(II) centers is not sufficient to induce the multielectron reduction of dioxygen. The analysis presented provides a general basis for interpreting the redox reactions of binuclear complexes in the search for effects ascribable to cooperativity.

Acknowledgment. Support of this work by National Science Foundation Grant No. CHE77-22722 is gratefully acknowledged. We wish also to thank Professor A. Haim for his help in the discussion of the effects of the work terms in the Marcus calculations.

Appendix

Rate law 10 was derived as follows: Ru(III,III) does not absorb appreciably in the region being monitored, so

$$\mathrm{Abs} = \epsilon_{\mathrm{II,II}}[(\mathrm{II,II})] + \epsilon_{\mathrm{III,II}}[(\mathrm{III,II})] \qquad (\mathrm{A1})$$

Thus

$$[(\mathrm{II,II})] = \frac{\mathrm{Abs} - \epsilon_{\mathrm{III,II}}[(\mathrm{III,II})]}{\epsilon_{\mathrm{II,II}}} \qquad (\mathrm{A2})$$

By the definition of K_{com}

$$[(\mathrm{III,III})] = \frac{[(\mathrm{III,II})]^2}{K_{\mathrm{com}}[(\mathrm{II,II})]} \qquad (\mathrm{A3})$$

so

$$\frac{[\mathrm{Ru}]_0}{2} = \frac{\mathrm{Abs} - \epsilon_{\mathrm{III,II}}[(\mathrm{III,II})]}{\epsilon_{\mathrm{II,II}}} + [(\mathrm{III,II})] + \frac{[(\mathrm{III,II})]^2\epsilon_{\mathrm{II,II}}}{K_{\mathrm{com}}(\mathrm{Abs} - \epsilon_{\mathrm{III,II}}[(\mathrm{III,II})])} \qquad (\mathrm{A4})$$

or

$$0 = \mathrm{Abs}\left(\frac{[\mathrm{Ru}]_0}{2} - \frac{\mathrm{Abs}}{\epsilon_{\mathrm{II,II}}}\right) + [(\mathrm{III,II})]B - [(\mathrm{III,II})]^2 A \qquad (\mathrm{A5})$$

Using the correct root of the quadratic equation leads to

$$[(\mathrm{III,II})] = \frac{(B - C)}{A} \qquad (\mathrm{A6})$$

where A, B, and C have been defined in the text.

From the proposed mechanism

$$\frac{-\mathrm{d}[\mathrm{Ru(II)}]}{\mathrm{d}t} = 2[\mathrm{O_2}](k_1[(\mathrm{II,II})] + k_2[(\mathrm{III,II})]) \qquad (\mathrm{A7})$$

and since

$$[\mathrm{Ru(II)}] = 2[(\mathrm{II,II})] + [(\mathrm{III,II})] \qquad (\mathrm{A8})$$

then

$$\frac{-\mathrm{d}[\mathrm{Ru(II)}]}{\mathrm{d}t} = \frac{-2\mathrm{d}[(\mathrm{II,II})]}{\mathrm{d}t} - \frac{\mathrm{d}[(\mathrm{III,II})]}{\mathrm{d}t} \qquad (\mathrm{A9})$$

Equations A2 and A6 give [(II,II)] and [(III,II)] in terms of the absorbance, and so the two derivatives on the right-hand side of eq A9 can be solved. This leads to

$$2[\mathrm{O_2}](k_1[(\mathrm{II,II})] + k_2[(\mathrm{III,II})]) = \frac{-\mathrm{d(Abs)}}{\mathrm{d}t}\alpha \qquad (\mathrm{A10})$$

where α is defined after eq 10. Rearrangement of eq A10 gives eq 10.

Registry No. $[(\mathrm{Ru(NH_3)_5})_2\mathrm{BPDO}](\mathrm{TFMS})_4$, 85894-02-6; $[\mathrm{Ru(NH_3)_5BPDO}]^{2+}$, 85894-06-0; $[\mathrm{Ru(NH_3)_5BPDOH}](\mathrm{PF_6})_3$, 85894-08-2; *cis*-$[(\mathrm{Ru(NH_3)_4(H_2O)})_2\mathrm{BPDO}]^{4+}$, 85894-10-6; $[(\mathrm{Ru(NH_3)_5})_2\mathrm{BPA}](\mathrm{PF_6})_4$, 85894-04-8; $[(\mathrm{Ru(NH_3)_5})_2\mathrm{BPA}](\mathrm{CF_3SO_3})_6$, 85894-05-9; $[\mathrm{Ru(NH_3)_5BPAH}](\mathrm{PF_6})_3$, 85894-09-3; $[(\mathrm{Ru(NH_3)_5})_2\mathrm{BPED}]^{4+}$, 85894-11-7; $[\mathrm{Ru(NH_3)_5(H_2O)}](\mathrm{TFMS})_3$, 53195-18-9; BPDO, 85894-00-4; O_2, 7782-44-7; H_2O_2, 7722-84-1; *meso*-1,2-bis(4-pyridyl)ethane-1,2-diol, 4972-49-0; 2,2-dimethoxypropane, 77-76-9.

Contribution from the Department of Chemistry,
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Photochemical Studies of Bis(dibenzoylmethanato)dioxomolybdenum

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We have observed the photochemistry of bis(dibenzoylmethanato)dioxomolybdenum(VI), $\mathrm{MoO_2(DBM)_2}$, at 380 nm in 1,2-dichloroethane at 23 °C. The primary photoprocess is loss of ligand to form $\mathrm{MoO_2(DBM)}$ and DBM. The quantum yield for loss of $\mathrm{MoO_2(DBM)_2}$ exhibits apparent Stern–Volmer behavior without addition of any quencher: this is attributed to a back-reaction that regenerates $\mathrm{MoO_2(DBM)_2}$. Quantum yield extrapolated to zero time is 0.097. Ideas concerning the identity of the ESR-active molybdenum-containing photoproduct are discussed.

Introduction

Molybdenum(VI) complexes have been shown to be strong oxidants in both biological and chemical systems.[1,2] In particular, complexes of the general form $\mathrm{MoO_2L_2}$ (L = bidentate ligand) have been shown to oxidize $\mathrm{PPh_3}$ to $\mathrm{OPPh_3}$ with production of $\mathrm{MoOL_2}$. Excited states are known to be even stronger oxidants and reductants than ground states.[3] We have recently examined the photochemistry and subsequent thermal chemistry of $\mathrm{MoO_2(Et_2NCS_2)_2}$, which results in

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[1] Stiefel, E. I. *Prog. Inorg. Chem.* **1977**, *22*, 1.

[2] Peterson, M. W.; Richman, R. M. *Inorg. Chem.* **1982**, *21*, 2609.

[3] Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1976**, *98*, 6384.

0020-1669/83/1322-1982$01.50/0 © 1983 American Chemical Society

dissociation and dimerization of the ligand.[2]

We now report a second photochemical study of this type of complex where L = dibenzoylmethanato (DBM). The photochemistry is characterized by generation of free ligand and production of an isolable Mo(V) complex from irradiation into the lowest energy band of $MoO_2(DBM)_2$.

Experimental Section

Materials and Chemicals. $MoO_2(C_6H_5COCHCOC_6H_5)_2$ (**1**) was synthesized according to a previously described procedure.[4] Recrystallization was performed from warm benzene. Anal. Calcd for $MoO_2(C_6H_5COCHCOC_6H_5)_2$: C, 62.73; H, 3.86; O, 16.71; Mo, 16.70. Found: C, 62.96; H, 3.90; O, 16.55; Mo, 16.63.

Phenyl-*N*-*tert*-butylnitrone (PBN) was obtained from Aldrich Chemical Co. and used without further purification. Reagent grade 1,2-dichloroethane was distilled and stored over molecular sieves. Spectral grade pyridine, benzene, toluene, and methylene chloride were used without further purification.

Quantum Yield Measurements. All quantum yields were determined as described earlier.[2] Since both free ligand and Mo(V) complex absorb at 380 nm, the quantum yield was calculated from the following equations:[5]

for absorbance at 380 nm > 2.0

$$\phi_{\text{obsd}} = \frac{1}{I_0 t}\left[(1-y)([\mathbf{1}]_0 - [\mathbf{1}]) + y[\mathbf{1}]_0 \ln\left(\frac{[\mathbf{1}]_0}{[\mathbf{1}]}\right)\right]$$

for absorbance at 380 nm < 2.0

$$\phi_{\text{obsd}} = \frac{1}{I_0 t}\Bigg[(1-y)([\mathbf{1}]_0 - [\mathbf{1}]) + y[\mathbf{1}]_0 \ln\left(\frac{[\mathbf{1}]_0}{[\mathbf{1}]}\right) + \frac{1}{2.303\epsilon_1 b}\ln\left(\frac{1-10^{-\epsilon_1[\mathbf{1}]_0 b}}{1-10^{-[(\epsilon_1-\epsilon_p)[\mathbf{1}]+\epsilon_p[\mathbf{1}]_0]b}}\right) + y[\mathbf{1}]_0\sum_{j=1}^{\infty}10^{-\epsilon_p[\mathbf{1}]_0 bj} \times [\mathrm{Ei}(-(\epsilon_1-\epsilon_p)[\mathbf{1}]_0 b(2.303j)) - \mathrm{Ei}(-(\epsilon_1-\epsilon_p)[\mathbf{1}]b(2.303j))]\Bigg]$$

where I_0 is the lamp intensity as determined by standard ferrioxalate actimetry, t is the irradiation time, $[\mathbf{1}]_0$ is the initial concentration of **1**, $[\mathbf{1}]$ is the concentration of **1** after irradiation, ϵ_1 is the extinction coefficient of **1** at 380 nm, ϵ_p is the extinction coefficient of the photoproducts being produced at 380 nm, y is the ratio ϵ_1/ϵ_p, b is the cell path length, and $\mathrm{Ei}(x)$ is the exponential integral.

Instrumentation. All UV-visible spectra were recorded on a Perkin-Elmer Model 330 spectrophotometer that has been interfaced to a Digital Equipment Corp. MINC-11 computer. ESR spectra were recorded on a Varian E-4 spectrophotometer. Illumination into an ESR cavity was done by using a 300-W tungsten projector lamp with a Corning 3-75 cutoff filter. IR spectra were recorded on a Perkin-Elmer Model 580 spectrophotometer that has been interfaced to a Perkin-Elmer CDS-2 data station.

Results and Discussion

The lowest energy electronic transition of **1** is at 380 nm and can be assumed to be the reactive excited state since the photochemistry displays no wavelength dependence below 380 nm ($\phi_0(380) = 0.097$, $\phi_0(300) = 0.096$, $\phi_0(280) = 0.097$). Moore and Rice[4] have assigned this transition to the internal ligand $\pi \rightarrow \pi^*$ transition with some ligand-to-metal charge transfer $p\pi \rightarrow d\pi$ character. Either class of excited state could be responsible for the photochemistry observed here.[2,7]

When a solution of **1** is irradiated in the region of 300–400 nm, the initially yellow solution slowly turns green. When this experiment is performed in benzene at high concentrations of **1** (10^{-3}–10^{-2} M), a molybdenum-containing photoproduct precipitates that may be isolated as a dark green powder. This precipitate is unstable in most organic solvents, decomposing to HDBM, **1**, and a diamagnetic blue precipitate (perhaps $Mo_2O_5 \cdot nH_2O$).

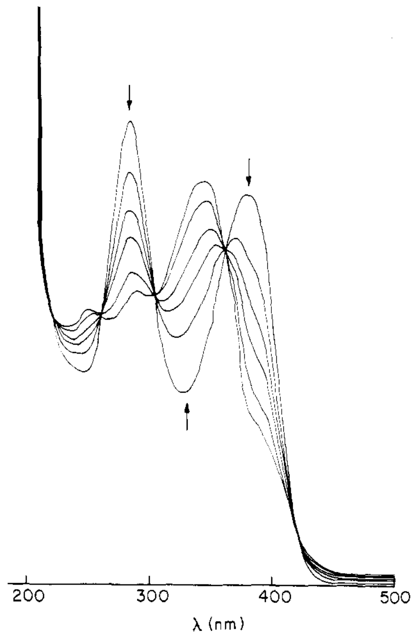

Figure 1. Spectral changes during photolysis of **1** in 1,2-dichloroethane at 23 °C. Peaks growing in at 250 and 340 nm are characteristic of the free ligand.

The crude photoproduct decomposes when recrystallization is attempted. Attempts to use column and thin-layer chromatography have also failed to produce a clean molybdenum photoproduct. Hence, we have not obtained reproducible elemental analyses. TLC of a benzene solution of the photoproduct does confirm the presence of both biphenyl and free HDBM.

A pyridine solution of **7** rapidly bleaches. However, if an excess of HDBM (~1 M) is added, the characteristic yellow color of **1** persists. Irradiation of such a solution causes it to turn orange. The molybdenum photoproduct can be isolated and recrystallized from a benzene/petroleum ether solution. Elemental analysis is consistent with the formulation $MoO_2(DBM)(py)$ (or $Mo_2O_4(DBM)_2(py)_2$). Anal. Calcd: C, 55.81; H, 3.72; N, 3.26. Found: C, 55.67; H, 3.98; N, 2.47.

The spectral changes during photolysis of **1** in 1,2-dichloroethane at 380 nm are shown in Figure 1. It can be seen that the peaks due to **1** (282 and 380 nm) diminish with irradiation time while peaks grow in at 340 and ~250 nm. Isosbestic points are maintained at 428, 367, 307, and 258 nm. The peaks growing in at 340 and 250 nm may be attributed in part to free ligand (HDBM), as determined by both ultraviolet and infrared spectra. However, there is also an increase in absorbance at longer wavelengths ($\lambda_{max} \cong 650$ nm) that leads into the 380-nm band, indicating that a third absorbing species is being formed in constant proportion.

When a sample of **1** is irradiated in an ESR cavity, a signal slowly grows in. This signal is typical of monomeric Mo(V) complexes.[6] If irradiation is stopped, the signal remains with no further change. Table I shows that the same isotropic ESR parameters are obtained in several solvents, implying that the Mo(V) complex being produced does not incorporate noncoordinating solvents. Furthermore, if the crude photoproduct isolated from a saturated benzene solution is redissolved in a solution of **1**, the same ESR parameters are obtained. This indicates that the isolated photoproduct is the same as that observed during photolysis.

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(4) Moore, F.; Rice, R. *Inorg. Chem.* **1968**, *7*, 2510.
(5) Kling, Von O.; Nikolaishi, E.; Schläfer, H. *Ber. Bunsenges. Phys. Chem.* **1963**, *67*, 833.
(6) See ref 1, pp 70–71.
(7) Filipeseu, N.; Way, H. *Inorg. Chem.* **1969**, *8*, 1863.

Table I

solvent	Stern–Volmer slope × 10^6	Mo(V) ESR parameters g_{iso}	Mo(V) ESR parameters $a_{iso}{}^a$	PBN adduct ESR parameters $a_N{}^d$	PBN adduct ESR parameters a_H
benzene	3.15	1.936 ± 0.002	53 ± 2	14.3 ± 0.3 14.2^b	2.2 ± 0.05 2.4^b
dichloromethane	2.00	1.936	52	14.6	2.2
1,2-dichloroethane	1.80	1.938	53	14.4	2.6
toluene	0.61	1.937	53	14.0	2.4
pyridine	*c*	1.927	~50	14.6	2.4

[a] Hyperfine due to ^{97,95}Mo. [b] Approximate parameters for a second trapped radical at high intensity. [c] The high concentration of HDBM necessary to stabilize **1** precludes accurate determination of the quantum yield vs. time. [d] The PBN adduct signal lies on one of the Mo(V) hyperfine signals. Hence, a_N is measured with relatively low precision.

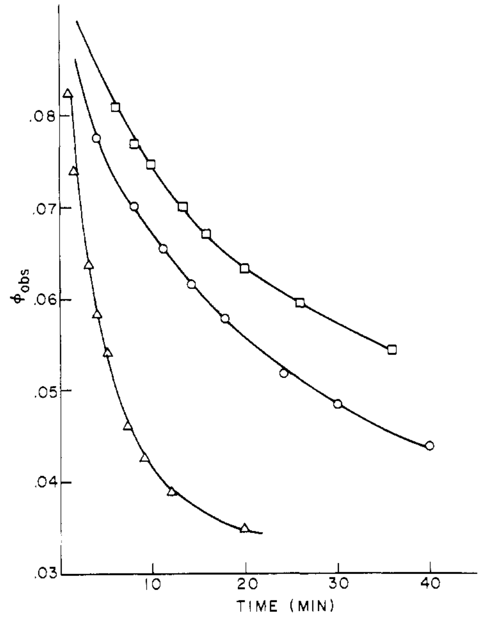

Figure 2. Variation of quantum yield for loss of **1** as a function of irradiation time for three different lamp intensities: □, 1.16 × 10^{-10}; ○, 1.43 × 10^{-10}; △, 3.32 × 10^{-10} einstein.

Continuous irradiation of a pyridine solution of **1** in an ESR cavity again leads to a signal characteristic of Mo(V). This signal is weak and disappears when irradiation is stopped. Both *g* and *a* values differ from those obtained in other solvents (Table I). The same *g* and *a* values are obtained by addition of pyridine to a photolyzed 1,2-dichloroethane solution of **1**. These results suggest that a good coordinating solvent can be incorporated into the photoproduct.

If these experiments are performed in the presence of O_2, no ESR signal is produced, during photolysis there is no observed growth at $\lambda > 380$ nm, and no isosbestic points are observed. At high concentrations of **1** in any solvent a white precipitate is formed. It has been isolated and shown to contain $MoO_4{}^{2-}$ (λ(UV) = 210 and 233 nm).[1] If a sample of **1** is degassed and photolyzed, the UV and ESR spectral changes persist even after the sample is exposed to O_2 for days. This implies that an intermediate (not the ultimate photoproducts) is O_2 sensitive.

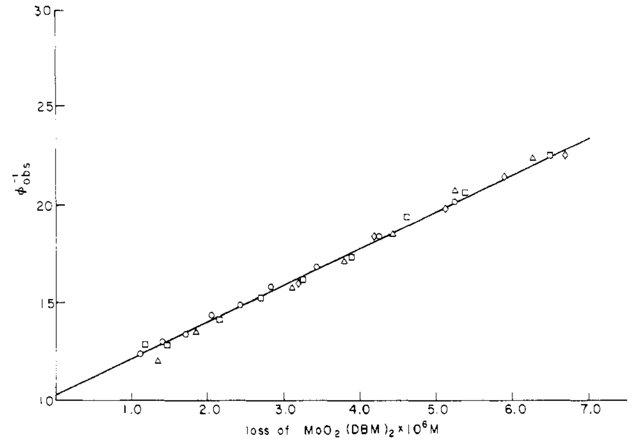

Figure 3. Plot of the reciprocal observed quantum yield vs. loss of $MoO_2(DBM)_2$ for four different lamp intensities: ○, 1.16 × 10^{-10}; ◇, 1.43 × 10^{-10}; △, 3.32 × 10^{-10}; □, 9.01 × 10^{-10} einstein. Photolysis is at 380 nm in 1,2-dichloroethane at 23 °C.

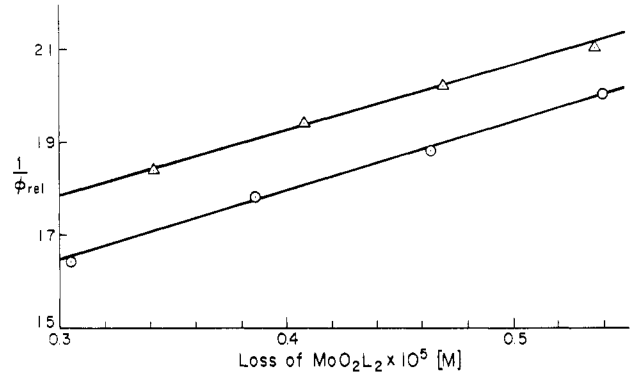

Figure 4. Plots of the reciprocal relative quantum yield vs. loss of $MoO_2(DBM)_2$ with (△) and without (○) added molybdenum photoproduct. Photolysis at 380 nm in 1,2-dichloroethane at 28 °C.

Addition of a spin trap, PBN, to a degassed solution of **1**, followed by irradiation in an ESR cavity, leads to a signal typical of solvent radicals (Table I). In benzene irradiation outside the cavity at a 100-fold greater intensity, two radicals are trapped, phenyl[8,9] and, presumably, DBM. This supports a primary photostep of production of Mo(V) and DBM, where one potential fate of DBM is hydrogen atom abstraction from solvent.

The quantum yield for disappearance of **1** is found not to be constant with irradiation time. Figure 2 shows this variation for three different lamp intensities. If these data are plotted with respect to photoproduct being produced, a linear Stern–Volmer relationship is obtained, as shown in Figure 3 for 1,2-dichloroethane with $\phi_0 = 0.097 \pm 0.005$ and slope of 1.8 × 10^6. Excited-state quenching of **1** by photoproduct has been eliminated as a possible explanation for this behavior since **1** shows no emission below 800 nm at room temperature or 77 K. We therefore propose some type of postphotolytic thermal reaction that leads to regeneration of **1** from photoproducts. The slope of the Stern–Volmer plot shows a large solvent dependence, again indicating involvement of the solvent in the postphotolytic chemistry.

In separate experiments both free ligand and crude photoproduct were added to solutions of **1** and photolyzed. While addition of free ligand has no effect on the slope or intercept of the Stern–Volmer type relationship, addition of the crude photoproduct (Figure 4) causes a shift in the curve from the experiment without added photoproduct. This implies that the isolable Mo(V)-containing photoproduct participates in the thermal reaction to regenerate **1**.

These results are quite interesting with respect to the nature of the Mo(V)-containing photoproduct. The ESR spectrum is the same with irradiation on and off, and it does not change

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(8) Janzen, E. G. *Acc. Chem. Res.* **1971**, *4*, 31.

(9) Janzen, E. G.; Blackburn, H. J. *J. Am. Chem. Soc.* **1969**, *91*, 4481.

Scheme I

$$\left.\begin{array}{l} MoO_2(DBM)_2 \overset{h\nu}{\rightleftharpoons} MoO_2(DBM)_2^* \\ MoO_2(DBM)_2^* \longrightarrow MoO_2(DBM) + DBM \end{array}\right\} I_m, \phi_0$$

$$(DBM)\cdot + MoO_2(DBM) \longrightarrow MoO_2(DBM)_2 \quad k_3$$

$$(DBM)\cdot \xrightarrow{\text{solvent}} HDBM \quad k_4$$

with different noncoordinating solvents. Furthermore, the Stern–Volmer type of plot shows no dependence on the initial concentration of **1**. Hence, it is likely that, in solution at least, we have a four-coordinate Mo(V) complex, $MoO_2(DBM)$. This notion is also supported by the results obtained with pyridine, since addition of pyridine to the stable ESR-active photoproduct leads to an immediate shift in the ESR parameters. This implies rapid coordination of pyridine to the photoproduct.

The possibility of a coordinatively unsaturated Mo(V) complex $MoO_2(DBM)$ leads to the most straightforward analysis of the quantum yield variation (Scheme I). If steady-state concentrations of $MoO_2(DBM)_2^*$ and (DBM)· in Scheme I are assumed, then

$$\frac{1}{\phi_{\text{obsd}}} = \frac{1}{\phi_0} + \frac{k_3[MoO_2(DBM)]}{2\phi_0 k_4}$$

As we have pointed out, it has not been possible to isolate the green photoproduct in a pure form; however, it has been possible to identify several infrared absorptions in the crude photoproduct. Peaks have been identified at 956 (m), 714 (s), and 453 cm^{-1} (m). Similar results are obtained from the pyridine photoproduct (935, 714, and 450 cm^{-1}). These values are quite similar to those reported for the $Mo_2O_4^{2+}$ μ-dioxo bridging system.[1]

A reasonable extension of Scheme I to account for the presence of $Mo_2O_4^{2+}$ in the solid state would be to add

$$2MoO_2(DBM) \rightleftharpoons Mo_2O_4(DBM)_2 \quad k_5$$

This equilibrium must lie largely to the left in dilute solution for two reasons. First, the $Mo_2O_4^{2+}$ unit is diamagnetic, and second, isosbestic points are maintained to over 90% conversion.

We have also been able to generate a UV–visible spectrum of the photoproduct. A sample of **1** was irradiated until no further spectral changes were observed. From that spectrum, the spectrum of the free ligand was quantitatively subtracted ($[HDBM] = [\mathbf{1}]_0$). The result is shown in Figure 5. The common peaks with **1** have been red shifted, the extinction coefficients are substantially smaller, and two new peaks appear at 250 and ~650 nm.

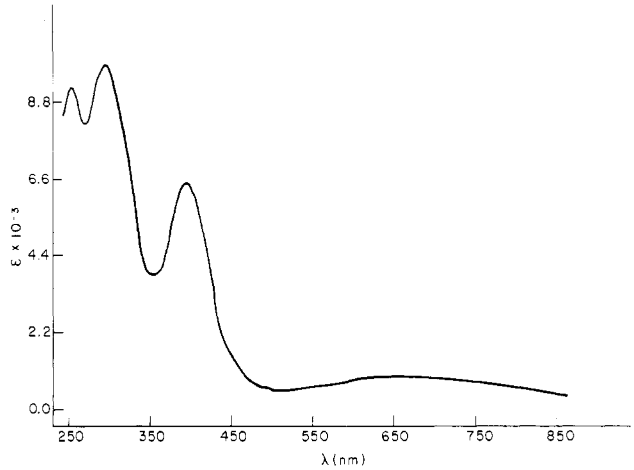

Figure 5. UV–visible spectrum of the Mo(V) photoproduct generated by computer subtraction of the free-ligand spectrum from the total photoproduct spectrum.

Finally, we explain the O_2 sensitivity in analogy with the work of Filipeseu and Way.[7] They demonstrated that in the presence of O_2, photoproduction of $Co(DBM)_2$ from $Co(DBM)_3$ is partially irreversible due to the action of $(DBM)O_2H$ on Co(II). It is likely that $(DBM)O_2H$ would similarly quench the Mo(V) ESR signal here.

Conclusion

We have demonstrated the second example of redox photochemistry for an MoO_2L_2 complex. Like $MoO_2(Et_2NCS_2)_2$,[2] $MoO_2(DBM)_2$ dissociates a ligand radical in the primary photoprocess. In the former case, the stability of $(Et_2NCS_2)_2$ is the driving force for a radical chain mechanism that ultimately leads to MoO_2. In the present case, however, DBM· rapidly abstracts a hydrogen atom from solvent, and there is only a slow tendency for the molybdenum-containing photoproduct to lose further ligands. An ESR-active molybdenum compound persists. We assign this as the first reported four-coordinate complex of Mo(V) containing the MoO_2^+ unit.[10]

Acknowledgment. This work was supported by the Office of Basic Energy Sciences, Department of Energy.

Registry No. **1**, 21884-97-9; $MoO_2(DBM)$, 85735-71-3; DBM, 19274-26-1.

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(10) Recently Zubieta and co-workers have reported a Mo(V) complex with the MoO_2^+ unit, a complex of the form $[MoO_2L]^-$ ($L = C_8H_{18}N_2S_2$).[11] However, that complex is not stable at ambient temperatures and L is tetradentate.

(11) Pickett, C.; Kumar, S.; Vella, P. H.; Zubieta, J. *Inorg. Chem.* **1982**, *21*, 908.