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Quantitative and Qualitative Photoelectrochemical Studies on the 18-Molybdodisulfate Anion $[S_2Mo_{18}O_{62}]^{4-}$

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The heteropoly anion clusters $[S_2Mo_{18}O_{62}]^{4-}$ and $[S_2Mo_{18}O_{62}]^{5-}$ may be photochemically activated to generate extremely powerful oxidants. Quantitative photoelectrochemical measurements using laser excitation at 325 nm of acetonitrile solutions of $[S_2Mo_{18}O_{62}]^{4-}$ containing the electron donors (ED), toluene and tetrahydrofuran, with hydrodynamic voltammetric monitoring at a platinum channel electrode are consistent with the following CECE mechanism: $[S_2Mo_{18}O_{62}]^{4-} + ED\ (k_1(h\nu)) \rightarrow [S_2Mo_{18}O_{62}]^{5-} + ED^+$ (C); $[S_2Mo_{18}O_{62}]^{5-} \rightleftharpoons [S_2Mo_{18}O_{62}]^{4-} + e^-$ (E); $[S_2Mo_{18}O_{62}]^{5-} + ED\ (k_2(h\nu)) \rightarrow [S_2Mo_{18}O_{62}]^{6-} + ED^+$ (C); $[S_2Mo_{18}O_{62}]^{6-} \rightleftharpoons [S_2Mo_{18}O_{62}]^{4-} + 2e^-$ (E); ED^+ (fast) $\rightarrow$ products. Photochemical oxidation of other electron donors such as methanol, $[BPh_4]^-$, ferrocene, and $Cr(CO)_3$ (arene) also occurs to generate $[S_2Mo_{18}O_{62}]^{5-}$ and $[S_2Mo_{18}O_{62}]^{6-}$ but not the more highly reduced $[S_2Mo_{18}O_{62}]^{7-}$ and $[S_2Mo_{18}O_{62}]^{8-}$ anions. It is concluded on the basis of these studies that $[S_2Mo_{18}O_{62}]^{4-}$ is a potentially valuable photooxidant in the synthetic sense, since it may be readily synthesised in large quantities from inexpensive materials.

Introduction

Polyoxometalates are an important group of metal-oxygen clusters formed by early transition metals such as Mo(VI), W(VI), and V(V).[2] The polyoxometalate ions usually consist of highly symmetrical core assemblies into which many elements may be incorporated. Some examples are $[SiW_{12}O_{40}]^{4-}$, $[P_2W_{18}O_{62}]^{6-}$, and the compound of interest in this work, $[S_2Mo_{18}O_{62}]^{4-}$, which has the α-Dawson structure shown in Figure 1.[3] In these examples, Si, P, and S are referred to as heteroatoms. Since the initial discovery of polyoxometalates more than 100 years ago,[2] their interesting properties have been exploited in diverse areas such as analytical and medical chemistry and catalysis, especially photocatalysis (see for example refs 4–19). Important applications are generally attributed to their very high stability at very low concentrations over wide pH ranges, their electron transfer and electron sink properties, the intense color of reduced forms, and their large size.

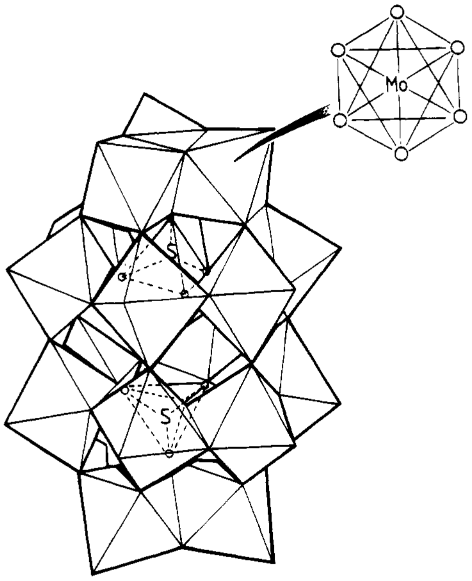

Figure 1. Dawson polyhedral representation of $[S_2Mo_{18}O_{62}]^{4-}$.

In medical chemistry, useful properties demonstrated so far include highly selective enzyme inhibition,[8–10] antitumoral

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activity,[11] and anti−viral activity against HIV.[2] In analytical chemistry, polyoxometalates have been used for many years for the detection and/or separation[4,5] of many elements, often exploiting their ease of reduction and the formation of the highly colored species formed upon reduction. The redox properties are often remarkable and for example, $[H_2W_{12}O_{40}]^{6-}$ has been reported to undergo a 32 electron reduction process in aqueous media.[20] Heteropolyoxoanions are widely used as oxidative catalysts and, for example, have been used to convert aldehydes to their corresponding carboxylic acids, and for the formation of C=C and C=O bonds through dehydrogenation of aldehydes, alcohols, and carboxylic acids.[2] Recently, $[(Ph_3P)_2Rh(CO)_4][SiW_{12}O_{40}]$ has been developed as a bifunctional catalyst for sequentially hydroformulating and oxidising olefins.[6,7]

During the numerous studies of polyoxometalates, photochemical and associated redox activity has been commonly observed although $[S_2Mo_{18}O_{62}]^{4-}$, which is of interest in this work, has not specifically been reported to be photoactive. However, the redox properties of $[S_2Mo_{18}O_{62}]^{4-}$ has been subjected to intensive study.[21−23] In (95:5) acetonitrile:water mixtures containing 0.1 M perchloric acid, at least four reversible two electron processes were detected by cyclic voltammetry.[21] These processes involve both proton and electron transfer steps. In nonaqueous aprotic media, at least four reversible one-electron processes have been reported[22,23] and $[S_2Mo_{18}O_{62}]^{5-}$ and $[S_2Mo_{18}O_{62}]^{6-}$ have been isolated after bulk reductive electrolysis.[22] An extensive series of reduction processes is typical of this class of compound.[20−25]

In view of the established redox activity and if $[S_2Mo_{18}O_{62}]^{4-}$ is photoactive as may be expected on the basis of studies on related compounds, then the products formed during photochemical reactions are likely to be the well-characterized reduced forms which should be amenable to electrochemical detection. Consequently, we have now undertaken a study of the photoelectrochemistry of $[S_2Mo_{18}O_{62}]^{4-}$ in the presence of a variety of electron donors both to confirm the expected photochemistry of this compound and to provide quantitative data which may lead to a better understanding of the systematics of heteropolyoxometalate photochemistry. Recently, quantitative photoelectrochemical techniques have been developed by irradiation of flowing solutions containing compounds of interest, followed by electrochemical detection in a flow-through channel electrode.[26−28] The use of flowing solutions greatly minimizes problems with thermal effects and the well-defined hydrodynamics associated with the channel electrode provides a mathematically tractable solution to the normally difficult problem of relating the photochemistry to the detection of the redox active product.[29,30] The present study now demonstrates that this particular form of methodology is highly suitable for quantitative photoelectrochemical studies of this important class of compound.

Experimental Section

Reagents, Compounds, and Solvents. Acetonitrile (Fisons or Mallinkrodt, HPLC grade) was purified by the method of Kiesele.[30] Other organic solvent also were of HPLC grade, but used as provided by the manufacture (Mallinkrodt) except for drying over molecular sieves. Water was obtained from a Barnstead (NANO-pure) purification system.

The synthesis of $[S_2Mo_{18}O_{62}]^{4-}$ and $[S_2Mo_{18}O_{62}]^{5-}$ as their Bu_4N^+ or Hex_4N^+ salts is described in ref 22.

The electrolyte, Bu_4NClO_4 (South Western Analytical or Fluka), and the electron donor compounds, ferrocene (Aldrich), $Cr(CO)_3(TMPD)$, $Cr(CO)_3(C_6H_6)$ (Aldrich), $Cr(CO)_3(C_6Me_6)$, $Cr(CO)_3(C_6Et_6)$, and $[Bu_4N]^+[BPh_4]^-$ (Fluka), were used as supplied by the manufacturer or as synthesised in ref 28.

Instrumentation and Procedures. All qualitative photoelectrochemical voltammetry experiments were conducted using a channel electrode made of optical quality synthetic silica to standard construction and dimensions.[31−34] Electrolyte flow rates in the range $10^{-4}-10^{-1}$ $cm^3\ s^{-1}$ were employed. Working electrodes were fabricated from platinum foils (purity of 99.95%, thickness 0.025 mm) of approximate size 4 mm × 4 mm, supplied by Goodfellow Advanced Materials. Precise electrode dimensions were determined using a travelling microscope. A silver wire pseudoreference electrode was located upstream and a platinum foil counterelectrode downstream of the channel electrode. The silver wire reference electrode was found to be steady throughout the period of our experiments: consistent values for the oxidation potential of *N,N,N′,N′*-tetramethyl-1,4-phenylenediamine (TMPD) were observed. However, potentials are reported relative to the saturated calomel electrode (SCE) with 0.20 V being subtracted from the measured values to obtain the potentials quoted.

Electrochemical measurements associated with the photoelectrochemistry were made using an Oxford Electrodes potentiostat modified to boost the counter electrode voltage (up to 200V). Other methodological details were as described previously.[32−34] Irradiation was provided by an Omnichrome continuous wave 3112XM He-Cd UV source (maximum incident power 40 ± 5 mW cm^{-2}). Variable light intensity measurements were made by attenuation of the beam as described previously.[32] UV/visible measurements were made with a Perkin-Elmer Lambda-5 spectrometer. Complementary rotating platinum disk or platinum microdisk electrode (10 μm diameter) measurements were conducted in conventional electrochemical cells using Oxford Electrodes equipment (rotating disk voltammetry) or a Cypress Systems Model CS-1190 computer-controlled electroanalysis system (microelectrode voltammetry).

Voltammetric experiments were performed at 25 °C using solutions of $[S_2Mo_{18}O_{62}]^{4-}$ (ca 0.05−0.2 mM) in acetonitrile solution containing 0.1 M (recrystallized) tetrabutylammonium perchlorate as the supporting electrolyte. Solutions were purged of oxygen by outgassing with prepurified argon prior to electrolysis. Experimental details for the qualitative photochemical studies are contained in the text (see later).

Results and Discussion

Photoelectrochemical Experiments in the Presence of Toluene and Tetrahydrofuran. Cyclic voltammograms (Figure 2, first two processes of interest in this work only included) and hydrodynamic chemical electrode voltammograms at plati-

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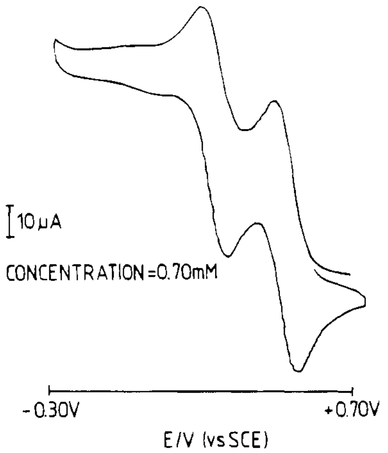

Figure 2. Cyclic voltammograms obtained at a platinum electrode using a scan rate of 100 mV s^{-1} for the $[S_2Mo_{18}O_{62}]^{4-/5-}$ and $[S_2Mo_{18}O_{62}]^{5-/6-}$ processes in acetonitrile (0.1 M Bu_4NClO_4).

num electrodes for reduction of $[S_2Mo_{18}O_{62}]^{4-}$ exhibit at least four chemically reversible reduction processes over the potential range +0.7 to −1.3 V vs SCE in acetonitrile. The reversible half-wave potentials ($E_{1/2}$ values) were found to be +0.49, +0.19, −0.46, and −1.20 V vs SCE. These processes correspond to the previously reported[22,23] extended electron transfer species

$$[S_2Mo_{18}O_{62}]^{4-} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [S_2Mo_{18}O_{62}]^{5-} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [S_2Mo_{18}O_{62}]^{6-} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [S_2Mo_{18}O_{62}]^{7-} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [S_2Mo_{18}O_{62}]^{8-} \quad (1)$$

As will emerge, only the yellow $[S_2Mo_{18}O_{62}]^{4-}$, green $[S_2Mo_{18}O_{62}]^{5-}$, and blue $[S_2Mo_{18}O_{62}]^{6-}$ are relevant to the photochemistry so that the processes relating to the formation of the 7− and 8− anions are not considered further.

At the rotating disk platinum electrode, a plot of E versus ln $(i_L - i)/i$ (E = potential, i = current, i_L = limiting current) for the first reduction step of $[S_2Mo_{18}O_{62}]^{4-}$ gave a slope of 63 mV and the second gave a slope of 89 mV (theoretical = 59 mV for a reversible one electron charge transfer process at 25 °C). The limiting current for both processes were equal in magnitude and analysis of the limiting current as a function of the square root of the rotation rate gave a diffusion coefficient for $[S_2Mo_{18}O_{62}]^{4-}$ of $(5.0 \pm 0.5) \times 10^{-6}$ cm^2 s^{-1} at 25 °C. This relatively small value is consistent with the large molecular volume of the polyanion.

From the above data, it can be deduced that if the potential of a channel electrode is held at a value which is more positive than the first reduction step, that zero current (relative to the background) should be observed. However, if $[S_2Mo_{18}O_{62}]^{5-}$ or $[S_2Mo_{18}O_{62}]^{6-}$ are generated photochemically, then an oxidation current will be detected at these positive potentials.

UV/visible spectra of $[S_2Mo_{18}O_{62}]^{4-}$ and $[S_2Mo_{18}O_{62}]^{5-}$ were recorded in acetonitrile (Figure 3). Weak shoulders were observed at 310 mm and 290 mm respectively. The extinction coefficient at these wavelengths and at 325 nm which is the wavelength used in the quantitative photoelectrochemical measurements are given in Table 1.

Use of the platinum channel electrode, acetonitrile (0.1 M Bu_4NClO_4) solution containing 10^{-3} M $[S_2Mo_{18}O_{62}]^{4-}$, and irradiation with laser light of wavelength of 325 nm, introduced no new features into the hydrodynamic voltammetry over the potential range +0.9 to +0.2 V vs SCE. However, on irradiation of $[S_2Mo_{18}O_{62}]^{4-}$, in the presence of 0.6 M toluene or tetrahydrofuran, steady state oxidative currents were observed in the range +0.9 to +0.2 V. These mass transport limited currents are consistent with photochemical generation of reduced forms of $[S_2Mo_{18}O_{62}]^{4-}$ which are then detected by their transport limited oxidation. Equations 2 and 3 summarize likely photochemically induced processes, where ED = the electron donor (toluene or tetrahydrofuran).

$$[S_2Mo_{18}O_{62}]^{4-} \xrightarrow{h\nu} ([S_2Mo_{18}O_{62}]^{4-})^* + \mathrm{ED} \xrightarrow{k_1} [S_2Mo_{18}O_{62}]^{5-} + \mathrm{ED}^+ \quad (2)$$

$$[S_2Mo_{18}O_{62}]^{5-} \xrightarrow{h\nu} ([S_2Mo_{18}O_{62}]^{5-})^* + \mathrm{ED} \xrightarrow{k_2} [S_2Mo_{18}O_{62}]^{6-} + \mathrm{ED}^+ \quad (3)$$

The "photo current" is much larger in the presence of tetrahydrofuran than toluene, suggesting that the kinetics of the reaction of the photoexcited state molecule(s) with tetrahydrofuran must be faster than with toluene.

In initial experiments, electrode passivation was substantial in the presence of light and toluene or tetrahydrofuran and the photocurrent decayed steadily with time. However, this problem was minimized by the use of a "sacrificial electrode" which was irradiated upstream of the channel detector electrode. The sacrificial electrode consisted of a platinum foil (4 × 5 mm) located in the irradiation zone, immediately upstream of the working electrode but insulated from it. Its purpose was to act as an adsorptive surface for any surface active minority species photogenerated in solution, so preventing them from reaching and contaminating the working electrode surface. The latter electrode was screened from the light source using masking tape. In this way $[S_2Mo_{18}O_{62}]^{5-}$ or $[S_2Mo_{18}O_{62}]^{6-}$ formed upstream were swept to the working electrode for voltammetric interrogation while passivating species were removed.

Using the above protocol, solutions containing $[S_2Mo_{18}O_{62}]^{4-}$ and toluene or tetrahydrofuran were flowed through the channel electrode and the working electrode held at +0.8 V (v SCE) (corresponding to transport limited oxidation of $[S_2Mo_{18}O_{62}]^{5-}$ and $[S_2Mo_{18}O_{62}]^{6-}$ to $[S_2Mo_{18}O_{62}]^{4-}$. Laser light of wavelength 325 nm and intensity of 40 ± 5 mW cm^{-2} was periodically used to irradiate the area immediately upstream of the working electrode. The resulting total steady state transport limited current (Figure 4) was measured under irradiative conditions (λ = 325 nm) as a function of flow rate of solution over the electrode. After each measurement, the potential was switched to reducing potentials of −2.00 V vs SCE for a period of time (ca. 1 min) in order to clean the electrode. The photocurrents at 0.8 V vs SCE were measured over a wide range of flow rates (6×10^{-4} cm^3 s^{-1} to 5×10^{-2} cm^3 s^{-1}) and concentration (0.05–0.2 mM) and at two light intensities (I_0) of 40 and 18 mW cm^{-2}. In the absence of light there was negligible oxidative current. Also negligible photocurrent was observed in the case of irradiation of $[S_2Mo_{18}O_{62}]^{4-}$ in acetonitrile (0.1 M Bu_4NClO_4) without 0.6 M toluene or 0.6 M tetrahydrofuran.

It is clear from the above results that $[S_2Mo_{18}O_{62}]^{4-}$ is excited by the 325 nm irradiation and not the electron donors and that excited $[S_2Mo_{18}O_{62}]^{4-}$ reacts with toluene or tetrahydrofuran oxidatively, thereby gaining an electron. It was also considered likely that a second electron transfer could occur between photoexcited $[S_2Mo_{18}O_{62}]^{5-}$ and the electron donor, since $[S_2Mo_{18}O_{62}]^{5-}$ also has a strong absorption at 325 nm ($\epsilon = 3.3 \times 10^4$ M^{-1} cm^{-1}) as shown in Figure 3. A theoretical CECEC

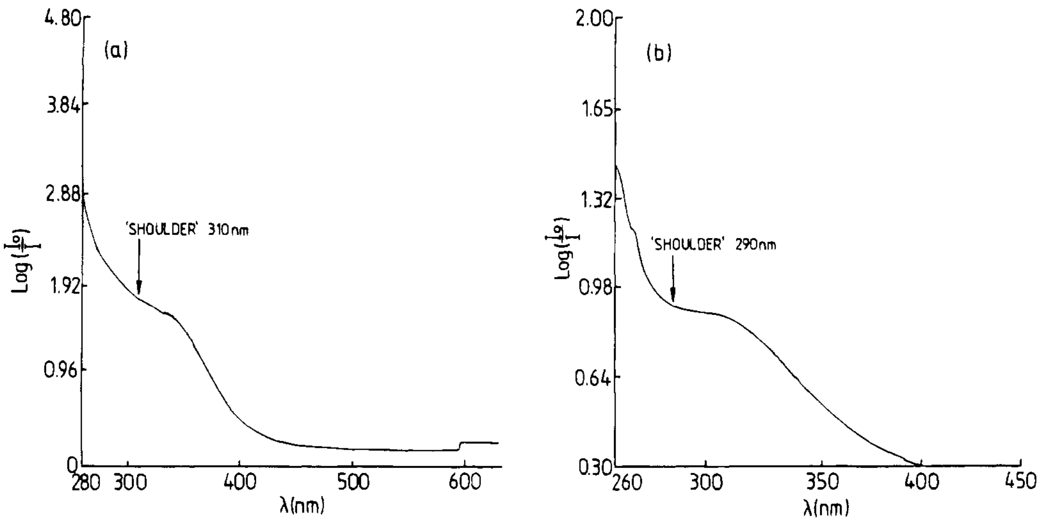

Figure 3. UV–visible spectra of (a) $[S_2Mo_{18}O_{62}]^{4-}$ and (b) $[S_2Mo_{18}O_{62}]^{5-}$ in acetonitrile.

model assuming that formation of $[S_2Mo_{18}O_{62}]^{5-}$ and $[S_2Mo_{18}O_{62}]^{6-}$ leads to the observed photocurrents at potentials corresponding to their transport limited oxidation was therefore developed as in eqs 4–8 when ED = toluene or tetrahydrofuran.

$$\text{(C)}\quad [S_2Mo_{18}O_{62}]^{4-} + ED \xrightarrow{k_1\,(h\nu)} [S_2Mo_{18}O_{62}]^{5-} + ED^{+} \quad (4)$$

$$\text{(E)}\quad [S_2Mo_{18}O_{62}]^{5-} \rightleftharpoons [S_2Mo_{18}O_{62}]^{4-} + e^{-} \quad (5)$$

$$\text{(C)}\quad [S_2Mo_{18}O_{62}]^{5-} + ED \xrightarrow{k_2\,(h\nu)} [S_2Mo_{18}O_{62}]^{6-} + ED^{+} \quad (6)$$

$$\text{(E)}\quad [S_2Mo_{18}O_{62}]^{6-} \rightleftharpoons [S_2Mo_{18}O_{62}]^{4-} + 2e^{-} \quad (7)$$

$$\text{(C)}\quad ED^{+} \xrightarrow{\text{fast}} \text{products} \quad (8)$$

Since the donor was in considerable excess, it was postulated that the photoreduction reactions occur to form $[S_2Mo_{18}O_{62}]^{5-}$ and $[S_2Mo_{18}O_{62}]^{6-}$ (eqs 4 and 6) via a pseudo-first-order process which is followed by detection by electrochemical oxidation (eqs 5 and 7). The final step postulated involves decomposition of the donor cations, [toluene^{+}] and [THF^{+}]. It was assumed that these cations decompose instantaneously on the timescale of the experiments[34] and that this rapid decomposition therefore precludes the occurrence of any back-electron-transfer reaction. Possible protonation of the polyoxometalate $[S_2Mo_{18}O_{62}]^{6-}$ by H^{+} formed by decomposition of ED^{+} also was neglected because these voltammetrically distinguishable forms of the metalate were not detected. The generation of $[S_2Mo_{18}O_{62}]^{7-}$ and $[S_2Mo_{18}O_{62}]^{8-}$ or even more highly reduced species was not included in the model as the much higher energies required for their formation made this a less likely event than the generation or $[S_2Mo_{18}O_{62}]^{5-}$ and $[S_2Mo_{18}O_{62}]^{6-}$. No account was taken in the modelling of the disproportionation step shown in eq 9, since there is known to be less than 1% disproportionation at equilibrium in CH_3CN.[22]

$$2[S_2Mo_{18}O_{62}]^{5-} \rightarrow [S_2Mo_{18}O_{62}]^{6-} + [S_2Mo_{18}O_{62}]^{4-} \quad (9)$$

The experimental results were compared with the theoretical model for CECE process derived from the solution of the relevant convective-diffusion equations using backwards implicit (BI) theory. The matrix elements for the BI analysis of this mechanism are given in the Appendix. $[S_2Mo_{18}O_{62}]^{4-}$, $[S_2Mo_{18}O_{62}]^{5-}$, and $[S_2Mo_{18}O_{62}]^{6-}$ were assumed to have equal diffusion coefficients of magnitude equal to that deduced above for $[S_2Mo_{18}O_{62}]^{4-}$.

Table 1. Extinction Coefficient Data Obtained in Acetonitrile for the $[S_2Mo_{18}O_{62}]^{4-}$ and $[S_2Mo_{18}O_{62}]^{5-}$ Complexes

extinction coeff ($M^{-1}\,cm^{-1}$)	$[S_2Mo_{18}O_{62}]^{4-}$	$[S_2Mo_{18}O_{62}]^{5-}$
ε(wavelength of shoulder)	3.4×10^4 (310 nm)	3.8×10^4 (290 nm)
ε(325 nm)	3.2×10^4	3.3×10^4

Additional modelling work was carried out to check if alternative mechanisms could give agreement with the experimental data for the photocurrent variation with flow rate observed. The alternative mechanisms postulated all had reversible chemical steps in which ED^{+} reacted with $[S_2Mo_{18}O_{62}]^{5-}$ or $[S_2Mo_{18}O_{62}]^{6-}$ to re-form $[S_2Mo_{18}O_{62}]^{4-}$ or $[S_2Mo_{18}O_{62}]^{5-}$ respectively so that the step for the decomposition of the donor cation became kinetically significant. For these alternative mechanisms, the diffusion coefficients for THF and toluene were estimated empirically from the Wilke–Chang correlation.[35]

The experimental fits for the CECE mechanism for both the toluene and THF cases are shown in Figures 5 and 6. The high correlation between theory and experiment is indicative that the CECE mechanism provides an accurate representation of the reaction with the rate constants given in Table 2. Furthermore, it is claimed that the mechanism suggested gives a uniquely good fit to the experimental data. In particular, if the rate of electron donor cation decomposition was assumed to be kinetically significant, the quality of fit markedly deteriorated irrespective of the assumed values of k_1 and k_2.

The best fit values of k_1 and k_2 were found to be independent of $[S_2Mo_{18}O_{62}]^{4-}$ concentration in the range 0.05 mM to 0.2 mM as required for pseudo-first order processes (studies using higher concentrations were precluded due to electrode passivation, notwithstanding the sacrificial electrode approach) and as expected theoretically, the rate constants were found to have a linear dependence on light intensity for the two light intensities investigated in this study.

Photochemical Experiment in the Presence of Other Electron Donors. An additional series of qualitative photo-

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(35) Wilke, C. R.; Chang, P. *AIChE J.* **1955**, *1*, 261.

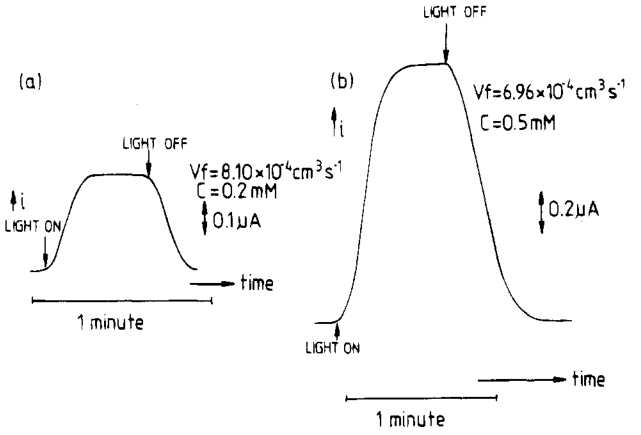

Figure 4. Photocurrent obtained in a channel electrode in acetonitrile (0.1 M Bu_4NClO_4) for $[S_2Mo_{18}O_{62}]^{4+}$ in the presence of (a) toluene and (b) tetrahydrofuran.

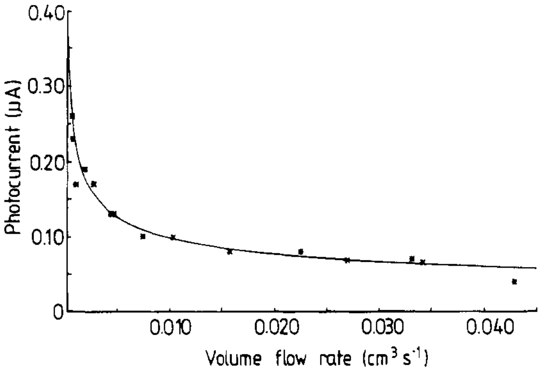

Figure 5. CECE mechanism experiment and theory comparison for photocurrents obtained in a channel electrode for 0.2 mM$[S_2Mo_{18}O_{62}]^{4-}$ when toluene is the electron donor and when a light intensity of (40 ± 5) mW cm^{-2} is used.

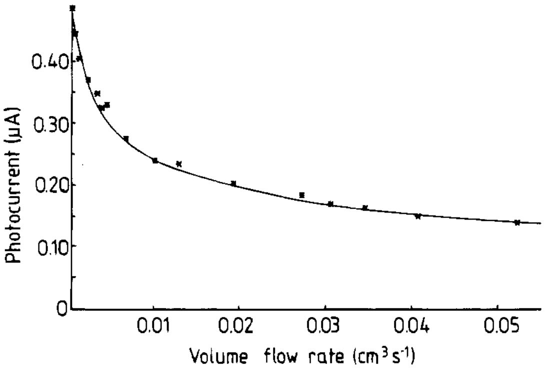

Figure 6. CECE mechanism experiment and theory comparison for photocurrents obtained in a chemical electrode for 0.1 mM $[S_2Mo_{18}O_{62}]^{4-}$ when tetrahydrofuran is the electron donor and when a light intensity of (40 ± 5) mW cm^{-2} is used.

chemical experiments were performed on $[S_2Mo_{18}O_{62}]^{4-}$ with a variety of other potential electron donors in order to establish the generality of the proposed mechanism. In the first set of experiments, a solution containing (0.1−1.0 mM) $[S_2Mo_{18}O_{62}]^{4-}$ was combined with potential electron donors (0.1 mM to 0.6 M) in acetonitrile as the solvent, in a standard UV/visible curvette (Perkin-Elmer) and irradiated by a continuous UV/visible light source (1000 W xenon arc lamp) for a period of 30 min. Any color change from the yellow $[S_2Mo_{18}O_{62}]^{4-}$ in solution detected visually was noted and taken to be indicative of reaction, recognizing that $[S_2Mo_{18}O_{62}]^{5-}$ is green and $[S_2Mo_{18}O_{62}]^{6-}$ blue.[22]

The following results were obtained.

Table 2. Kinetic Data Obtained from Photoelectrochemical Measurements on $[S_2Mo_{18}O_{62}]^{4-}$ in the Presence of Toluene and Tetrahydrofuran in Acetonitrile (0.1 M Bu_4NClO_4), Using a Platinum Channel Electrode with Experimental Details Contained in the Text

rate const (s^{-1})	value (I_o = 55 mW cm^2)	value (I_o = 25 mW cm^{-2})
k_1(toluene)	0.0085 (±0.0005)	0.0041 (±0.0005)
k_2(toluene)	0.0047 (±0.0002)	0.0020 (±0.0003)
k_1(THF)	0.0410 (±0.0050)	0.0190 (±0.0060)
k_2(THF)	0.0370 (±0.0030)	0.0150 (±0.0050)

(i) ED = CH_3CN. The color of the mixed $[S_2Mo_{18}O_{62}]^{4-}$ and ED solution remained yellow during a 30 min irradiation period. Hence no photoredox reaction was inferred to have taken place on this time scale.

(ii) ED = MeOH, Toluene. The color of the $[S_2Mo_{18}O_{62}]^{4-}$/ED solution was yellow before irradiation. After 30 min of irradiation the solution was green. This implied that the photoexcited ($[S_2Mo_{18}O_{62}]^{4-}$)* had been reduced by ED to form $[S_2Mo_{18}O_{62}]^{5-}$.

(iii) ED = Tetrahydrofuran, Dimethylformamide, $[Bu_4N]^+[BPh_4]^-$. The initially yellow solution immediately went green upon irradiation and the final color after 30 min of irradiation was blue. Thus, it is concluded that $[S_2Mo_{18}O_{62}]^{4-}$ is reduced to $[S_2Mo_{18}O_{62}]^{5-}$ and then to $[S_2Mo_{18}O_{62}]^{6-}$. $[BPh_4]^-$ is known to transfer an electron to photoexcited anthroquinone.[26] Apparently, it also transfers electrons to photoexcited ($[S_2Mo_{18}O_{62}]^{4-}$)*.

(iv) ED = Ferrocene, $Cr(CO)_3$(Arene) (Arene = TMPD, C_6H_6, C_6Me_6, C_6Et_6). On addition of the yellow $[S_2Mo_{18}O_{62}]^{4-}$ solution to ED, the solution immediately went blue for ED = ferrocene, $Cr(CO)_3(C_6H_6)$, and $Cr(CO)_3$(TMPD), whereas for ED = $Cr(CO)_3(C_6Me_6)$ and $Cr(CO)_3(C_6Et_6)$ the mixture initially turned green and then after a short period of irradiation (ca. 5 min) the solution turned blue. Thus, for these donors, $[S_2Mo_{18}O_{62}]^{4-}$ is reduced to $[S_2Mo_{18}O_{62}]^{5-}$ and then $[S_2Mo_{18}O_{62}]^{6-}$.

In another series of experiments, the reactivity of the photoexcited ($[S_2Mo_{18}O_{62}]^{4-}$)* with the electron donors $TBA^+BPh_4^-$, toluene and THF were monitored spectrophotometrically. These electron donors were found to absorb negligibly in the range 270−400 nm (ϵ < 10 M^{-1} cm^{-1}). Solutions containing $[S_2Mo_{18}O_{62}]^{4-}$ (0.01−0.2 mM) and the relevant electron donor (0.005−0.6 M) in acetonitrile solvent were irradiated as before, but for a shorter period of 10 min, and the UV/visible spectra in the range 270−450 nm recorded. Control solutions of $[S_2Mo_{18}O_{62}]^{4-}$ and electron donors were kept in the dark for the same period and their spectra also recorded for comparison. In all three cases, when an electron donor was present, the shoulder at 310 nm in the UV/visible spectrum for pure $[S_2Mo_{18}O_{62}]^{4-}$ moved to a lower wavelength consistent with partial conversion to $[S_2Mo_{18}O_{62}]^{5-}$. The shifts in the position of the shoulder were as follows: (a) $[Bu_4N]^+[BPh_4]^-$; 310 to 295 nm; (b) toluene, 310 to 300 nm; (c) THF, 310 to 295 nm; (d) CH_3CN, no change. These experiments reveal that $[S_2Mo_{18}O_{62}]^{5-}$ is an intermediate in the overall photochemical conversion of $[S_2Mo_{18}O_{62}]^{4-}$ to $[S_2Mo_{18}O_{62}]^{6-}$.

It can be seen from the above that the kinetic ease of electron transfer correlates well with the oxidation potential of the electron donor. Thus, acetonitrile has a voltammetric oxidation potential greater than +2.0 V vs SCE,[36] and no color or spectral change was seen under any conditions. Tetrahydrofuran, dimethylformamide, and toluene[37] all have oxidation potentials greater than +1.5 V vs SCE and were observed to relatively slowly convert $[S_2Mo_{18}O_{62}]^{4-}$ to $[S_2Mo_{18}O_{62}]^{5-}$ and $[S_2Mo_{18}O_{62}]^{6-}$. In contrast, ferrocene and the chromium arene tricarbonyl compounds all have formal oxidation potentials less than +0.8 V vs SCE and reduce $[S_2Mo_{18}O_{62}]^{4-}$ to $[S_2Mo_{18}O_{62}]^{5-}$ and/or $[S_2Mo_{18}O_{62}]^{6-}$ effectively instantaneously. This correlation of rate of reduction with oxidation potential is consistent with Marcus theory for outer sphere electron transfers provided the energetics are such that the electron transfer is outside of the inverted Marcus region.

All of the above observations provide supporting evidence for the postulated photochemical electron transfer mechanism.

The Electron Transfer Process. Little work has been reported concerning the electronic structure of $[S_2Mo_{18}O_{62}]^{4-}$. However, it is likely on reduction that an electron enters a "MoO_6" LUMO. ESR evidence[22] suggests that the additional electron in $[S_2Mo_{18}O_{62}]^{5-}$ is dynamically distributed over the entire molecule and that electron transfer reactions between $[S_2Mo_{18}O_{62}]^{4-}$, $[S_2Mo_{18}O_{62}]^{5-}$, and $[S_2Mo_{18}O_{62}]^{6-}$ are extremely rapid since no great structural distortion is involved in the course of the electron transfer step. When $[S_2Mo_{18}O_{62}]^{4-}$ or $[S_2Mo_{18}O_{62}]^{5-}$ are photoexcited it is likely that an electron also is transferred to an "MoO_6" LUMO, thereby labelizing an adjacent "MoO_6" site toward reduction by an electron donor. Again, presumably, only negligibly small changes in geometry are required in the excited state electron transfer reactions. In the ground state, the reversible redox potentials are +0.49 and +0.19 V vs SCE for the $[S_2Mo_{18}O_{62}]^{4-/5-}$ and $[S_2Mo_{18}O_{62}]^{5-/6-}$ redox couples respectively. In the excited state, the redox potentials must have been shifted to considerably more positive potentials since $([S_2Mo_{18}O_{62}]^{4-})^*$ can oxidize toluene.

Conclusions

It has been shown that the photoexcited polyanion cluster $([S_2Mo_{18}O_{62}]^{4-})^*$ will accept electrons from a wide range of electron donors including toluene and THF with the formation of the pentaanion $[S_2Mo_{18}O_{62}]^{5-}$ and the hexaanion $[S_2Mo_{18}O_{62}]^{6-}$ but not the heptaanion $[S_2Mo_{18}O_{62}]^{7-}$ or octaanion $[S_2Mo_{18}O_{62}]^{8-}$. In the absence of photo-excited $[S_2Mo_{18}O_{62}]^{4-}$ these electron donor species are typically extremely hard to oxidize. The photoelectrochemical mechanism for the reaction of toluene and tetrahydrofuran with $[S_2Mo_{18}O_{62}]^{4-}$ has been shown to occur via a CECE mechanism in which the two C steps are pseudo-first-order photochemical reduction processes and the E steps are the corresponding electrochemical reoxidations of $[S_2Mo_{18}O_{62}]^{6-}$ and $[S_2Mo_{18}O_{62}]^{5-}$ back to $[S_2Mo_{18}O_{62}]^{4-}$.

The merits of hydrodynamic voltammetric methods for mechanistic studies are therefore again apparent by providing a simple, unambiguous, and quantitative determination of the mechanistic photochemical pathways. Importantly, in the case of the compound studied in this work $[S_2Mo_{18}O_{62}]^{4-}$ is a potentially valuable photooxidant since it is readily synthesized in high yield from inexpensive reagents.

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Appendix

We consider a modified "CECE" scheme where irradiation of the species takes place upstream of the electrode

"C" $A \xrightarrow{k_1} B$ upstream of electrode

"C" $B \xrightarrow{k_2} C$

"E" $B \rightleftharpoons A + e^-$ at the electrode

"E" $C \rightleftharpoons A + 2e^-$

where A is $[S_2Mo_{18}O_{62}]^{4-}$, B is $[S_2Mo_{18}O_{62}]^{5-}$, and C is $[S_2Mo_{18}O_{62}]^{6-}$.

This mechanism is used to describe the pseudo-first-order electron transfer mechanism between $[S_2Mo_{18}O_{62}]^{4-}$ and toluene and THF described in this paper.

The steady state transport equations for A, B and C are as follows using the coordinates specified in ref 29.

$$D_A\frac{\partial^2 a}{\partial y^2} - v_x\frac{\partial a}{\partial x} - k_1 a = 0$$

$$D_B\frac{\partial^2 b}{\partial y^2} - v_x\frac{\partial b}{\partial x} + k_1 a - k_2 b = 0$$

$$D_C\frac{\partial^2 c}{\partial y^2} - v_x\frac{\partial c}{\partial x} + k_2 b = 0$$

where $a = [A]$, $b = [B]$, and $c = [C]$.

The channel is divided into two areas whose total length is l. If x_e is the length of the electrode then the length of the irradiation zone before the electrode is $l - x_e$.

The boundary conditions for the irradiation zone and working electrode zone differ.

(a) Upstream of the electrode ($x < l - x_e$, where $x = 0$ is the upstream edge of the irradiation zone and $x = l$ is the downstream edge of the electrode):

$$x = 0:\ a = a_0, b = 0, c = 0$$

$$y = 0:\ \frac{\partial a}{\partial y} = \frac{\partial b}{\partial y} = \frac{\partial c}{\partial y} = 0$$

$$y = 2h:\ \frac{\partial a}{\partial y} = \frac{\partial b}{\partial y} = \frac{\partial c}{\partial y} = 0$$

(b) Over the electrode ($x > l - x_e$):

$$y = 0:\ -\frac{\partial a}{\partial y} = \frac{\partial b}{\partial y} + \frac{\partial c}{\partial y}, b = 0, c = 0$$

$$y = 2h:\ \frac{\partial a}{\partial y} = \frac{\partial b}{\partial y} = \frac{\partial c}{\partial y} = 0$$

Matrix Elements. The elements given below are the only ones that are dependent upon the electroactivity of the species, A, B, and C, and the identity and kinetics of the mechanism.

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(36) Yoshida, K. *Electroxidation in Organic Chemistry*; Wiley: New York, 1989.

(37) Eberson, L. *Electron Transfer Reactions in Organic Chemistry*; Springer Verlag: Berlin, 1987.

(38) Greenwood, N. N.; Earnshaw, A. E. *Chemistry of the Elements*; Pergamon Press: Oxford, England, 1984.

The notation follows that used in ref 29. All other matrix elements are independent of mechanism and have been calculated and detailed earlier.[29] These are as follows:

(a) $x < l - x_e$

for A

$$b_1 = 1 + \lambda^{A}{}_{1} \qquad d_j = g^{A}{}_{j,k} - g^{A}{}_{j,k} k_1 (\Delta y)^2 \lambda^{A}{}_{j} D^{-1}$$

$$j = 1, 2, ..., J - 1$$

for B

$$b_1 = 1 + \lambda^{B}{}_{1}$$

$$d_j = g^{B}{}_{j,k} + g^{A}{}_{j,k} k_1 (\Delta y)^2 \lambda^{B}{}_{j} D^{-1} + g^{B}{}_{j,k} k_2 (\Delta y)^2 \lambda^{b}{}_{j} D^{-1}$$

$$j = 1$$

for C

$$b_1 = 1 + \lambda^{C}{}_{1} \qquad d_j = g^{C}{}_{j,k} - g^{B}{}_{j,k} k_2 (\Delta y)^2 \lambda^{C}{}_{j} D^{-1}$$

$$j = 1, 2, ..., J - 1$$

(b) $x > l - x_e$

for A

$$b_1 = 1 + \lambda^{A}{}_{1} \qquad d_j = g^{A}{}_{j,k} \qquad j = 1, 2, ..., J - 1$$

for B

$$b_1 = 1 + 2\lambda^{B}{}_{1} \qquad d_j = g^{B}{}_{j,k} \qquad j = 1, 2, ..., J - 1$$

for C

$$b_1 = 1 + 2\lambda^{C}{}_{1} \qquad d_j = g^{C}{}_{j,k} \qquad j = 1, 2, ..., J - 1$$

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