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NMR, Voltammetric, and Photoelectrochemical Studies on the Dark and Light-Catalyzed Reactions of α-$[S_2Mo_{18}O_{62}]^{4-}$ with Aryl- and Alkylphosphines

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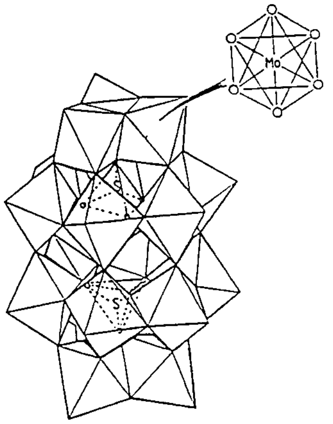
The polyoxometalate, α-$[S_2Mo_{18}O_{62}]^{4-}$ is reduced by phosphines in the mixed-solvent medium CH_3CN/H_2O (95/5 v/v). Monitoring of reaction pathways by voltammetric and NMR (^{17}O, ^{31}P) techniques shows that the identity of the final products is determined by the basicity of the phosphine. Thus reaction with aryl- (Ph_3P, $Ph_2PCH_2PPh_2$, and $Ph_2PCH_2CH_2PPh_2$) and alkyl- (Et_3P and $^nBu_3P$) phosphines leads to two- and one-electron reduced polyoxometalate products, respectively, for example: $[S_2Mo_{18}O_{62}]^{4-} + Ph_3P + H_2O \rightarrow [HS_2Mo_{18}O_{62}]^{5-} + Ph_3PO + H^+$; $2[S_2Mo_{18}O_{62}]^{4-} + 3^nBu_3P + H_2O \rightarrow 2[S_2Mo_{18}O_{62}]^{5-} + {}^nBu_3PO + 2^nBu_3PH^+$. For each reaction, the primary electron-transfer step is believed to be $[S_2Mo_{18}O_{62}]^{4-} + R_3P \rightarrow [S_2Mo_{18}O_{62}]^{5-} + R_3P^{\bullet+}$with $R_3P^{\bullet+}$ then reacting with water to generate R_3PO and protons. If R_3P is relatively basic (R = ^{n}Bu, Et), a 1:2 mixture of R_3PO and R_3PH^+ is formed due to the protonation of R_3P. However, if R_3P (R = Ph) is a weak base, H^+ preferentially initiates the following disproportionation reaction: $2[S_2Mo_{18}O_{62}]^{5-} + H^+ \rightleftarrows [HS_2Mo_{18}O_{62}]^{5-} + [S_2Mo_{18}O_{62}]^{4-}$. Reactions in the presence of light lead to significant photocatalysis. A quantitative photoelectrochemical channel electrode study demonstrates that oxidation of Ph_3P by $[S_2Mo_{18}O_{62}]^{4-}$ is accelerated substantially by irradiation in the 300−400 nm wavelength range, where absorption bands of both $[S_2Mo_{18}O_{62}]^{4-}$ and $[S_2Mo_{18}O_{62}]^{5-}$ are present.

Introduction[1]

Polyoxometalate anions[2−8] exhibit varied structures, rich redox chemistry, photochemistry, and an ability to catalyze a wide range of industrially and biologically significant reactions.[7,8]

The compound of interest in this investigation is α-$[S_2Mo_{18}O_{62}]^{4-}$ (structure **1**, D_{3h} point group symmetry). Its redox chemistry has been well established. Up to eight reversible one-electron reduction processes can be observed in aprotic media.[9−13] In the presence of proton sources, the reduction steps are facilitated by protonation of the highly reduced compounds so that in excess of 18 electrons (one electron per Mo center) can be added.[13] One- to four-electron reduced species have been isolated as solids.[14,15] In the presence of light, α-$[S_2Mo_{18}O_{62}]^{4-}$ becomes an extremely powerful oxidant, reacting for example with toluene when irradiated with 325 nm light.[16]



polyhedral representation of α-$[S_2Mo_{18}O_{62}]^{4-}$ (**1**)

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(1) Abbreviations: $[A]_0$, bulk concentration of species A; Bu, n-C_4H_9; δ, chemical shift; *d*, diameter; *D*, diffusion coefficient; $E_{1/2}$, reversible half-wave potential; E_p^{ox}, peak oxidation potential; *F*, 96485 C mol^{-1}; h, hours; Hex, n-C_6H_{13}; I_{lim}, limiting current; *J*, coupling constant; K_a, acid dissociation constant; *n*, number of electrons transferred; ν, scan rate; $pK_a = -\log K_a$; *r*, radius; THF, tetrahydrofuran; v/v, volume by volume.

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Recent data from Mattes et al.[15] imply that α-$[S_2Mo_{18}O_{62}]^{4-}$ is reduced by four electrons in the presence of Ph_3P since refluxing for 72 h in acetonitrile led to crystals of α-$[H_3S_2Mo_{18}O_{62}]^{5-}$. The process appears to correspond to the following overall reaction:

$$\alpha\text{-}[S_2Mo_{18}O_{62}]^{4-} + 2Ph_3P + 2H_2O \rightarrow \alpha\text{-}[H_3S_2Mo_{18}O_{62}]^{5-} + 2Ph_3PO + H^+ \quad (1)$$

In recent studies in these laboratories, quantitative details of the redox chemistry (electron transfer and accompanying proton transfer) have been extracted for the initial two-electron transfer processes in the mixed-solvent medium CH_3CN/H_2O (95/5 v/v). That is, a complete thermodynamic description of the reversible potentials, acid−base equilibria, and disproportionation reactions of the one-electron reduced state is available which has established the relationships between the species α-$[S_2Mo_{18}O_{62}]^{4-,5-,6-}$, α-$[HS_2Mo_{18}O_{62}]^{4-,5-}$, and α-$[H_2S_2Mo_{18}O_{62}]^{4-}$.[14] Since the reaction of α-$[S_2Mo_{18}O_{62}]^{4-}$ with Ph_3P (eq 1, for example) is likely to involve both electron- and proton-transfer reactions, we have now undertaken a detailed study of the redox chemistry associated with the reaction of α-$[S_2Mo_{18}O_{62}]^{4-}$ with aryl- and alkylphosphines of varying base strengths (Ph_3P, $Ph_2PCH_2PPh_2$ (dpm), $Ph_2PCH_2CH_2PPh_2$ (dpe), $^nBu_3P$, and Et_3P). ^{31}P and ^{17}O NMR techniques have been used to identify the phosphorus-containing products, whereas voltammetric monitoring of reactions under steady-state conditions was used to determine the oxidation state of the polyoxoanion during the course of the reactions. Finally, photoelectrochemical channel electrode techniques were used to quantitatively study the effect of light on the redox chemistry.

Experimental Section

Reagents, Compounds, and Solvents. Triphenylphosphine (Aldrich 99%), 1,2-bis(diphenylphosphino)ethane (Strem chemicals, 97%), bis(diphenylphosphino)methane (Strem chemicals 97%), triphenylphosphine oxide (Strem chemicals), tri-*n*-butylphosphine oxide (Strem chemicals), tetrabutylammonium perchlorate (Bu_4NClO_4; SACHEM, Austin, TX (Electrometric grade)), $H_2{}^{17}O$ (50 atom % ^{17}O, Monsanto Research Corp., Miamisburg, OH), perchloric acid (BDH, Analar 60% aqueous solution), and ^2H_2O (Cambridge Isotope Laboratory, Andover, MA) were all used as received. Tri-*n*-butylphosphine (Strem chemicals) was purified by vacuum distillation. Acetonitrile (MeCN; Mallinckrodt, Biolab Scientific Pty Ltd. (HPLC grade, 99.9%)) was dried over molecular sieves overnight while water was triply distilled. The synthesis of α-$[S_2Mo_{18}O_{62}]^{4-}$ as its Hex_4N^+ salt is described in ref 12. All solutions were purged of oxygen by outgassing with nitrogen that had been presaturated with acetonitrile. All experiments were conducted at ambient temperature conditions (22 ± 1 °C).

Instrumentation and Procedures. Voltammetric experiments in stationary solutions were performed in $MeCN/H_2O$ (95/5 v/v) mixtures containing 0.1 M Bu_4NClO_4 as supporting electrolyte. A glassy carbon disk (diameter = 3 mm) or microdisk (diameter = 10 μm) electrode was used as the working electrode. The counter electrode was a platinum wire, and the reference electrode was a silver wire dipped in a saturated solution of $AgNO_3$/0.1 M Bu_4NClO_4 in acetonitrile separated from the electroactive solution by a porous frit. A Cypress Systems (model CYSY-1R) computer-controlled electroanalysis system was used for potentiostatic control. Rotating disk electrode experiments used a glassy carbon disk electrode (diameter = 3 mm) which was rotated by a variable-speed rotator (Metrohm 628-10). All electrode potentials are quoted relative to the ferricinium/ferrocene redox couple (Fc^+/Fc).

For the photochemical experiments, UV/visible irradiation was provided by a broad band 300 W xenon arc lamp (Cermax LX300; ILC technology, Sunnyvale, CA) enclosed in a R400 lamp holder (ILC technology). The infrared component of the light was removed by an infrared transparent mirror. It was then passed through a series of lenses and focused into an optic fiber (ILC technology) directed at the surface of the working electrode. The wavelength was controlled via a range of colored-glass filters (Jena Glaswerk, Schott & Gen., Mainz, Germany). Typical intensities of 10−12 mW cm^{-2} were obtainable in the UV/visible region.

Details of the channel electrode flow system used in this work are given elsewhere.[16,17] The channel electrode unit was constructed in PTFE, and the associated cover plate was made of optical quality synthetic silica. The working electrodes consisted of 4 × 4 mm platinum blocks sealed flush into the PTFE channel unit. Precise dimensions were determined by a traveling microscope. The electrodes were polished using a succession of finer grade alumina slurries down to 0.1 μm. A silver wire pseudoreference electrode was located in the quartz cover plate of the channel unit, the electrode being sealed flush to the coverplate surface using Araldite adhesive. The potential of this reference electrode was calibrated with the ferricinium/ferrocene couple. A platinum gauze counter electrode was located upstream of the working electrode so as to avoid counter electrode products contaminating the channel cell. Flow rates in the range 10^{-3}−10^{-1} $cm^3\ s^{-1}$ were employed in the quantitative experiments described below. An ADI instruments Maclab 4e/potentiostat system controlled by a Macintosh Powerbook microcomputer was used in order to undertake electrochemical measurements at the channel electrode.

Channel electrode mechanistic BIFD simulations were conducted using programs written in FORTRAN 77 and run using a commercial FORTRAN compiler (Watcom) on a 120 MHz Pentium PC or on a Silicon graphics Iris workstation. Cyclic voltammograms were simulated using the package DIGISIM V 2.0 (Bioanalytical Systems, West Lafayette, IN) run on a 150 MHz Pentium PC.[18]

Phosphorus-31 NMR spectra were recorded on a Bruker AM300 spectrometer operating at 121.4 MHz, and chemical shifts were referenced against an external aqueous solution of 85% H_3PO_4. Some experiments used an internal Ph_3P standard (contained in a 5 mm diameter tube within the 10 mm diameter sample tube) whose single ^{31}P line could be used as a calibrant against which the generation/removal of other phosphorus-containing species could be compared. Oxygen-17 NMR spectra were recorded on a Bruker AM300 spectrometer operating at 40.7 MHz, and chemical shifts were referenced against external neat ^2H_2O. Samples for ^{17}O NMR were prepared by dissolving α-$[S_2Mo_{18}O_{62}]^{4-}$ (5 mM) and Ph_3P (5 mM) in $MeCN/H_2{}^{17}O$ (95/5 v/v); the solution was then left for 24 h. Next, the solvent was evaporated to leave a solid residue of the polyoxomolybdate and phosphine, which was subsequently dissolved in acetonitrile. This solution was finally dried over magnesium sulfate for 12 h before running spectra. All NMR spectra were recorded at 293 K.

Electron impact mass spectra were recorded on a VG-Trio-1 quadrupole mass spectrometer. The temperature and voltage of the ion source were 200 °C and 70 eV, respectively, and the solid probe was heated to 300 °C. Solvent in the solution phase mixtures of the polyoxo species and phosphine was removed by evaporation, and the solid residue was introduced into the mass spectrometer.

Results and Discussion

A. Reaction of α-$[S_2Mo_{18}O_{62}]^{4-}$ with Ph_3P in the Absence of Light. The visual observation of a gradual color change from yellow to green confirmed that a reaction occurs between Ph_3P and α-$[S_2Mo_{18}O_{62}]^{4-}$ when these reactants are dissolved in a 1:1 molar ratio in $MeCN/H_2O$ (95/5 v/v).

Figure 1a shows cyclic voltammograms obtained over the potential range −0.30 to + 1.10 V (vs Fc^+/Fc) of a solution of $[(Hex)_4N]_4[S_2Mo_{18}O_{62}]$ (1mM) in $MeCN/H_2O$ (95% v/v; 0.1 M Bu_4NClO_4) recorded in the absence and presence of Ph_3P (1 mM) at a glassy carbon macrodisk electrode. Note that for convenience, the α designation of the isomeric form of α-[S2-

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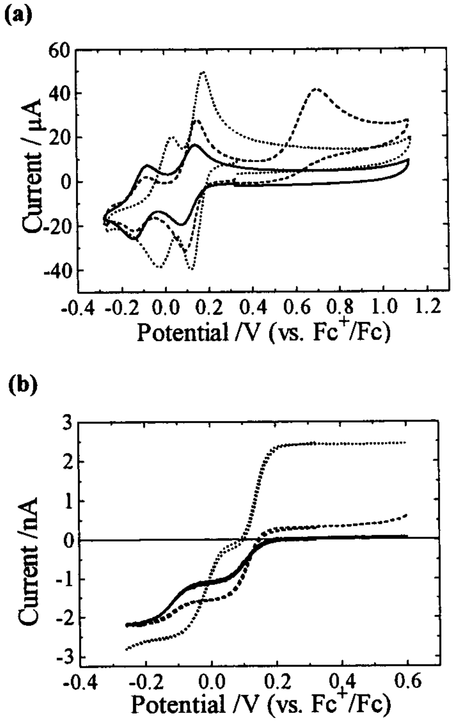

Figure 1. Voltammograms of $[S_2Mo_{18}O_{62}]^{4-}$ (1 mM) in MeCN/H_2O (95/5 v/v; 0.1 M Bu_4NClO_4) before and after addition of Ph_3P (1 mM): (a) cyclic voltammograms at a glassy carbon disk electrode (d, 3.0 mm; ν, 100 mV s^{-1}); (b) steady-state voltammograms at a glassy carbon microdisk electrode (d, 10 μm; ν, 10 mV s^{-1}). Key: —, no Ph_3P; - - -, Ph_3P (1 mM), 1 h; ···, Ph_3P (1 mM), 48 h.

Table 1. $E_{1/2}$ Values for the Reduction of $(Hex_4N)_4[S_2Mo_{18}O_{62}]$(1.0 mM) in MeCN/$H_2O$ (95/5 v/v; 0.1 M Bu_4NClO_4) in the Potential Range +1.1 to −0.3 V

	$E_{1/2}$/V^b		
n^a		1.0 mM Ph_3P (48 h)^b	2.0 mM $HClO_4$^{b}
1	0.12 (r)		
2	−0.11 (r)	0.13 (o)	0.15 (r)
3	−0.73 (r)		
4	−0.90 (r)	−0.02 (r)	−0.01 (r)

[a] Total number of electrons added at this potential. [b] Potentials versus Fc^+/Fc; estimated from a combination of cyclic voltammetry (ν = 100 mV s^{-1}) and microdisk voltammetry (ν = 10 mV s^{-1}) at glassy carbon electrodes (o, oxidation; r, reduction).

$Mo_{18}O_{62}]^{4-}$ and all related species will be omitted in the remainder of the text. Figure 1b shows equivalent steady-state voltammograms measured at a glassy carbon microdisk electrode over the range −0.30 to + 0.60 V. In the absence of Ph_3P, two reversible one-electron waves are observed over the potential range studied (Figure 1a,b) with reversible half-wave potentials ($E_{1/2}$) of 0.12 and −0.11 V (Table 1). Ph_3P itself is irreversibly oxidized at +0.70 V under the conditions of Figure 1a, in agreement with other studies in different media.[19−23] In the presence of Ph_3P, the nature of the voltammograms change slowly with time.

In particular, while redistribution of current between the two processes associated with the polyoxomolybdate system occurs, the total current increases and shifts in half-wave potential to more positive values occurs. In contrast, the peak current for the Ph_3P oxidation wave simply decreases with reaction time, as can be seen by comparing the voltammetric feature in Figure 1a at E^{ox}_p = +0.70 V 1 and 48 h after addition of Ph_3P to the polyoxometalate solution. Monitoring of the reaction by steady-state voltammetry at a microdisk electrode (Figure 1b; note position of zero current) reveals that the $[S_2Mo_{18}O_{62}]^{4-}$ system is partially reduced after 1 h of reaction time. After 48 h, two polyoxomolybdate processes of almost equal height can be detected (Figure 1b), one oxidation wave ($E_{1/2}$, 0.13 V) and one reduction wave ($E_{1/2}$, −0.02 V). The current values and wave shapes now correspond to the presence of two reversible two-electron charge-transfer processes (if the sloping nature of the plateau and baseline are taken account of) rather than two reversible one-electron processes as observed before addition of Ph_3P. Furthermore, the voltammetric feature associated with oxidation of Ph_3P is almost undetectable (Figure 1a) indicating almost complete reaction with $[S_2Mo_{18}O_{62}]^{4-}$ has now occurred

The change in voltammetric peak heights and potentials of the polyoxomolybdate processes as a function of time suggested that an increase in proton concentration may be occurring during the course of the reaction. With respect to the potential range of interest in this study, the redox system in the presence of acid is quantified by the following reactions:[14]

$$[S_2Mo_{18}O_{62}]^{4-} + e^- \rightleftarrows [S_2Mo_{18}O_{62}]^{5-} \qquad (E_{1/2} = 0.12\ \text{V}) \quad (2)$$

$$[S_2Mo_{18}O_{62}]^{5-} + e^- \rightleftarrows [S_2Mo_{18}O_{62}]^{6-} \qquad (E_{1/2} = -0.11\ \text{V}) \quad (3)$$

$$[HS_2Mo_{18}O_{62}]^{4-} + e^- \rightleftarrows [HS_2Mo_{18}O_{62}]^{5-} \qquad (E_{1/2} = 0.35\ \text{V}) \quad (4)$$

$$[S_2Mo_{18}O_{62}]^{5-} + H^+ \rightleftarrows [HS_2Mo_{18}O_{62}]^{4-} \qquad (K = 1.4\ \text{M}^{-1}) \quad (5)$$

$$[S_2Mo_{18}O_{62}]^{6-} + H^+ \rightleftarrows [HS_2Mo_{18}O_{62}]^{5-} \qquad (K = 1.6 \times 10^8\ \text{M}^{-1}) \quad (6)$$

$$[HS_2Mo_{18}O_{62}]^{5-} + H^+ \rightleftarrows [H_2S_2Mo_{18}O_{62}]^{4-} \qquad (K = 10^2\ \text{M}^{-1}) \quad (7)$$

$$[S_2Mo_{18}O_{62}]^{5-} + [HS_2Mo_{18}O_{62}]^{4-} \rightleftarrows [S_2Mo_{18}O_{62}]^{4-} + [HS_2Mo_{18}O_{62}]^{5-} \qquad (K = 1.6 \times 10^4) \quad (8)$$

$$[S_2Mo_{18}O_{62}]^{5-} + [HS_2Mo_{18}O_{62}]^{4-} + H^+ \rightleftarrows [S_2Mo_{18}O_{62}]^{4-} + [H_2S_2Mo_{18}O_{62}]^{4-} \qquad (K = 1.6 \times 10^4\ \text{M}^{-1}) \quad (9)$$

where the K values represent the equilibrium constants for the relevant reactions as a function of proton concentration. An important conclusion from the magnitudes of these equilibrium constants, with respect to the results presented later, is that, in the presence of acid, $[S_2Mo_{18}O_{62}]^{5-}$ disproportionates to $[S_2Mo_{18}O_{62}]^{4-}$ and $[HS_2Mo_{18}O_{62}]^{5-}$ (low acid concentrations)

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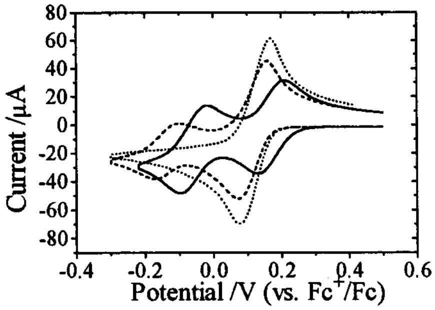

Figure 2. Simulation of cyclic voltammograms of $[S_2Mo_{18}O_{62}]^{4-}$ (1 mM) in MeCN/H_2O (95/5 v/v; 0.1 M Bu_4NClO_4) in the presence of differing concentrations of acid using the parameters and mechanistic scheme described in the text. (—, $[H^+] = 0$ mM; - - -, $[H^+] = 0.3$ mM; ···, $[H^+] = 0.7$ mM).

or $[H_2S_2Mo_{18}O_{62}]^{4-}$ (high acid concentrations). The simulated cyclic voltammograms shown in Figure 2 were calculated assuming that steps 2−9 were reversible and the forward constants, k_f, for the protonation equilibria were large (10^{10} M^{-1} s^{-1}). The heterogeneous rate constants for steps 2−4 were also assumed to be high (>1 cm s^{-1}), and charge-transfer coefficients (α) were set to 0.5. Figure 2 shows simulated cyclic voltammograms using the thermodynamic parameters given above, the diffusion coefficients contained in ref 14, and the experimental conditions of Figure 1. Note that as the acid concentration increases, the two one-electron processes present initially convert to a reversible two-electron process as observed experimentally. The theoretical voltammograms obtained from simulating the mechanism described by eqs 2−9 in the presence of varying amounts of acid (Figure 2) clearly resemble those obtained experimentally (Figure 1a) if loss of 1 mol of Ph_3P is accompanied by generation of 2 mol of H^+.

To test this hypothesis, the voltammetry of 1 mM $[S_2Mo_{18}O_{62}]^{4-}$ was examined in the presence of 2 mM $HClO_4$ (Figure 3). The voltammetric response is virtually identical with that of the reaction solution after 48 h (Table 1; compare Figures 1−3). The only difference is that the first two-electron wave of the reaction solution (Figure 1) is an *oxidation* rather than a reduction process. On the basis of the simulated and experimental data, it is apparent that the final product in this reaction is the two-electron reduced species, $[HS_2Mo_{18}O_{62}]^{5-}$, generated by the initial one-electron reduction of $[S_2Mo_{18}O_{62}]^{4-}$ to $[S_2Mo_{18}O_{62}]^{5-}$ by Ph_3P followed by its disproportionation in the presence of the protons released during the Ph_3P oxidation process (eq 8).[13,14] It has been noted that, at higher proton concentrations (>120 mM), an additional proton is added to the two-electron reduced form of the polyoxomolybdate anion, making $[H_2S_2Mo_{18}O_{62}]^{4-}$ the major product (eq 9).[14]

Monitoring the reaction of a 1:1 molar ratio solution of $[S_2Mo_{18}O_{62}]^{4-}$ and Ph_3P in the acetonitrile/water (95/5 v/v) medium by ^{31}P NMR spectroscopy in both the presence and absence of electrolyte showed that Ph_3P ($\delta = -4.4$ ppm) is oxidized to Ph_3PO ($\delta = 30.1$ ppm). However, the rate of reaction was found to be much faster in the absence of electrolyte, presumably because of ion pairing of the very negatively charged polyoxomolybdate species with Bu_4N^+ that occurs when 0.1 M Bu_4NClO_4 is present. ^{17}O NMR experiments on solutions enriched in $H_2{}^{17}O$ (50% ^{17}O) confirmed that the source of the oxygen atom in the product Ph_3PO was solvent water and not $[S_2Mo_{18}O_{62}]^{4-}$. Electron impact mass spectra on solids obtained from this ^{17}O-enriched reaction solution exhibited peaks at $m/z = 278$ and 279 in the intensity ratios expected for $Ph_3P^{16}O$ and $Ph_3P^{17}O$ produced from the presence of $H_2{}^{17}O$ (50% ^{17}O).

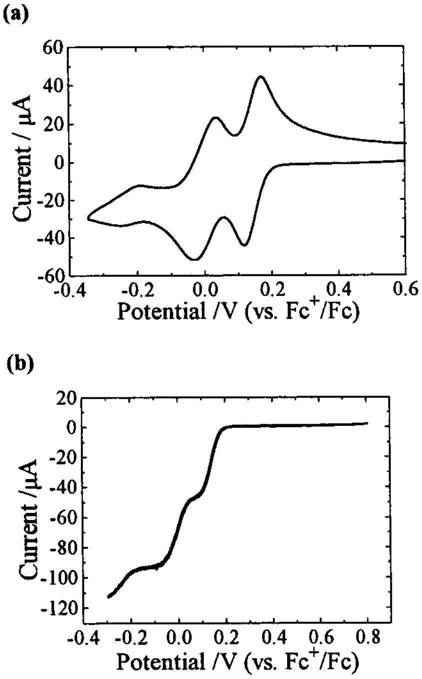

Figure 3. (a) Cyclic voltammogram of a solution of $[S_2Mo_{18}O_{62}]^{4-}$ (1 mM) and $HClO_4$ (2 mM) in MeCN/H_2O (95/5 v/v; 0.1 M Bu_4NClO_4) at a glassy carbon disk (d, 3.0 mm; ν, 100 mV s^{-1}). (b) Steady-state voltammogram of the solution in (a) using a glassy carbon rotating disk electrode (d, 3.0 mm; rotation speed, 500 rpm; ν, 10 mV s^{-1}).

A combination of cyclic voltammetric, steady-state voltammetric, and ^{31}P NMR experiments for solutions of $Ph_2P(CH_2)_nPPh_2$ ($n = 1$ or 2) showed qualitatively that their mode of reaction with an equimolar amount of $[S_2Mo_{18}O_{62}]^{4-}$ was the same as that for Ph_3P described above. This is expected as the measured oxidation potentials (ca. $E_p^{ox} = +0.6$ to $+0.7$ V) for both these species are similar to that for Ph_3P.[19−23] The final phosphine product was $Ph_2P(CH_2)P(O)Ph_2$ for the methane analogue ($n = 1$) as the singlet in the ^{31}P NMR spectrum ($\delta = -21.0$ ppm) was converted to two doublets ($\delta_P = -27.4$; $\delta_{PO} = 31.2$; $J(^{31}P-^{31}P) = 49$ Hz), corresponding to inequivalent P atoms in the final product.[24] The polyoxomolybdate steady-state voltammetric response of a reaction mixture of $[S_2Mo_{18}O_{62}]^{4-}$ and $Ph_2P(CH_2)_nPPh_2$ ($n = 1$ or 2) after 24 h was identical to that shown in Figure 1b after 48 h. Consequently, the final polyoxomolybdate species formed is identical to that produced on reaction with Ph_3P.

Both the NMR and voltammetric data indicate that $[S_2Mo_{18}O_{62}]^{4-}$ undergoes an overall two-electron reduction process to form $[HS_2Mo_{18}O_{62}]^{5-}$ while oxidizing Ph_3P to Ph_3PO. On the basis of the above results an overall reaction scheme can be proposed:

$$[S_2Mo_{18}O_{62}]^{4-} + Ph_3P + H_2O \rightarrow [HS_2Mo_{18}O_{62}]^{5-} + Ph_3PO + H^+ \quad (10)$$

Ph_3P undergoes an irreversible one-electron oxidation at platinum electrodes in acetonitrile solution, and the initial product of this reaction is believed to be the phosphinium radical cation ($Ph_3P^{\bullet+}$).[19−23,25] Hence it is postulated that, in the rate-determining step, Ph_3P initially transfers one electron to

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[24] Grim, S. O.; Briggs, W. L.; Barth, R. L.; Tolman, C. A.; Jesson, J. P. *Inorg. Chem.* **1974**, *13*, 1095.

[25] Rhodes, C. J.; Symons, C. R. *J. Chem. Soc., Dalton Trans.* **1989**, 1393.

$[S_2Mo_{18}O_{62}]^{4-}$:

$$[S_2Mo_{18}O_{62}]^{4-} + Ph_3P \xrightarrow{k_1/\text{slow}} [S_2Mo_{18}O_{62}]^{5-} + Ph_3P^{\bullet +} \quad (11)$$

Although the Ph_3P peak oxidative potential is substantially more positive than the reversible potential for reduction of $[S_2Mo_{18}O_{62}]^{4-}$, the equivalent reversible potential for Ph_3P may be much less positive. Further, this step is kinetically favored due to the rapid reaction of the $Ph_3P^{\bullet +}$ cation with water possibly forming a phosphine oxide precursor (such as the radical $Ph_3P^{\bullet}$-OH)[19] thus preventing the back-reaction in eq 11:

$$Ph_3P^{\bullet +} + H_2O \xrightarrow{\text{fast}} Ph_3P^{\bullet}OH + H^+ \quad (12)$$

The phosphine oxide precursor could react rapidly with $[S_2Mo_{18}O_{62}]^{4-}$ to form the oxide and $[S_2Mo_{18}O_{62}]^{5-}$:

$$[S_2Mo_{18}O_{62}]^{4-} + Ph_3P^{\bullet}OH \xrightarrow{\text{fast}} [S_2Mo_{18}O_{62}]^{5-} + Ph_3PO + H^+ \quad (13)$$

In the presence of protons, $[S_2Mo_{18}O_{62}]^{5-}$ disproportionates, as illustrated by eqs 5, 8, and 9, resulting in $[HS_2Mo_{18}O_{62}]^{5-}$ being the final polyoxomolybdate product.[12,14]

After addition of Ph_3P to the solution of $[S_2Mo_{18}O_{62}]^{4-}$, the oxidative component detected in voltammograms obtained under steady-state conditions is predominantly due to the two-electron oxidation of the stable final product $[HS_2Mo_{18}O_{62}]^{5-}$ back to $[S_2Mo_{18}O_{62}]^{4-}$. It is assumed that the concentration of $[S_2Mo_{18}O_{62}]^{5-}$ available for electrode reduction is negligible due to its rapid disproportionation to the final product and starting material in the presence of protons.[12,14] Under such conditions, an estimate of the concentration of $[HS_2Mo_{18}O_{62}]^{5-}$ formed may be obtained from the equation for the limiting current at a microdisk electrode:

$$I_{\text{lim}} = 4nFD[A]_0 r \quad (14)$$

where n is the number of electrons transferred (in this case $n = 2$), F is Faraday's constant (96485 C mol^{-1}), D is the diffusion coefficient of the electroactive species (a value of 6.4×10^{-6} $\text{cm}^2\ \text{s}^{-1}$ was utilized as measured for $[S_2Mo_{18}O_{62}]^{4-}$ by rotating-disk voltammetry;[13] the same value was assumed for each polyoxomolybdate anion), $[A]_0$ is the concentration of $[HS_2Mo_{18}O_{62}]^{5-}$ (mol cm^{-3}), r is the radius of the microelectrode (cm), and I_{lim} is the measured oxidative current (A). Knowledge of the initial concentrations of Ph_3P and $[S_2Mo_{18}O_{62}]^{4-}$ in solution and the concentration of the reaction product, $[HS_2Mo_{18}O_{62}]^{5-}$, as a function of time (as determined from microdisk voltammetry) enables a second-order kinetic analysis[26] to be developed which may then be utilized to estimate the rate constant, k_1, for the overall rate of reaction between Ph_3P and $[S_2Mo_{18}O_{62}]^{4-}$ (eq 11). A representative second-order plot is shown in Figure 4. A value of 0.06 (±0.04) $\text{M}^{-1}\ \text{s}^{-1}$ was obtained for k_1 under nonirradiative conditions using a range of initial equimolar concentrations of Ph_3P and $[S_2Mo_{18}O_{62}]^{4-}$ (0.2−2.0 mM).

B. Reaction of α-$[S_2Mo_{18}O_{62}]^{4-}$ with Ph_3P under Irradiative Conditions. The photoreaction between $[S_2Mo_{18}O_{62}]^{4-}$ and Ph_3P was examined in the presence of filtered light (10 mW cm^{-2}, 300−400 nm). Irradiation of an equimolar solution of $[S_2Mo_{18}O_{62}]^{4-}$ and Ph_3P in $MeCN/H_2O$ (95/5 v/v; 0.1 M Bu_4NClO_4) resulted in a color change from yellow to blue-green and a voltammetric response identical to that shown in Figure 1 for equivalent nonirradiated solutions. ^{31}P NMR confirmed Ph_3PO as the sole phosphorus-containing product of the photoreaction. It is therefore concluded that the overall reaction in the presence of light is identical to that observed in its absence, the light merely accelerating the rate-determining electron-transfer reaction between Ph_3P and $[S_2Mo_{18}O_{62}]^{4-}$.

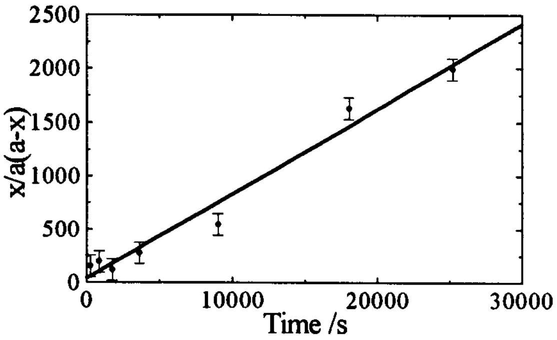

Figure 4. Second-order kinetic plot of $x/a(a - x)$ vs time, where x is the concentration of $[HS_2Mo_{18}O_{62}]^{5-}$ at time t and a is the initial concentration of $[S_2Mo_{18}O_{62}]$.$^{4-}$ The initial concentrations of $[S_2Mo_{18}O_{62}]^{4-}$ and Ph_3P in $MeCN/H_2O$ (95/5 v/v; 0.1 M Bu_4NClO_4) were 1 mM. The slope of the plot yields k_1 directly.

The effect of UV/visible irradiation on the kinetics of the reaction was quantified by channel electrode experiments conducted as rapidly as possible (<1 h) in order to minimize the effects of the equivalent "dark" reaction. An equimolar solution of Ph_3P and $[S_2Mo_{18}O_{62}]^{4-}$ in $MeCN/H_2O$ (95:5 v/v; 0.1 M Bu_4NClO_4) was irradiated by light filtered down to 300−400 nm corresponding to the lowest energy electronic absorption band ($\epsilon = 3.4 \times 10^4\ \text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$) of $[S_2Mo_{18}O_{62}]^{4-}$ in acetonitrile.[16] The platinum channel electrode was held at a potential of +0.30 V which will oxidize photoreduced forms of $[S_2Mo_{18}O_{62}]^{4-}$, so permitting rapid detection of such species. Neither Ph_3P nor Ph_3PO undergo redox processes at +0.30 V in acetonitrile, with the former species being oxidized only at potentials above +0.60 V.[19−23]

Light (300−400 nm; intensity ~10 mW cm^{-2}) periodically irradiated the platinum working electrode surface, providing a phototransient response, similar to that observed on irradiation of solutions of $[S_2Mo_{18}O_{62}]^{4-}$ and toluene/THF.[16] The resultant photocurrent generated at the working electrode was measured as a function of the flow rate ($V_f = 10^{-3}$−$10^{-1}\ \text{cm}^3\ \text{s}^{-1}$) of the reaction solution over the electrode surface (Figure 5).

It was postulated above that the rate-limiting step in the dark reaction between Ph_3P and $[S_2Mo_{18}O_{62}]^{4-}$ is the one-electron-transfer process, eq 11. This step may be photo-accelerated by a positive shift in redox potential in the photoexcited state:

$$[S_2Mo_{18}O_{62}]^{4-} \xrightarrow{h\nu} [S_2Mo_{18}O_{62}]^{*4-} \quad (15)$$

$$[S_2Mo_{18}O_{62}]^{*4-} + Ph_3P \xrightarrow{\text{accelerated rate}} \text{products} \quad (16)$$

One of the products, $[HS_2Mo_{18}O_{62}]^{5-}$ (eq 10), is detected at the electrode surface by its two-electron oxidation to the original $[S_2Mo_{18}O_{62}]^{4-}$ anion. Therefore, the reaction mechanism measured photoelectrochemically is postulated to be a photo C_2E reaction, where C_2 represents the second-order reaction

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(26) Atkins, P. W. *Physical Chemistry;* OUP: Oxford, U.K., 1986; Chapter 28.

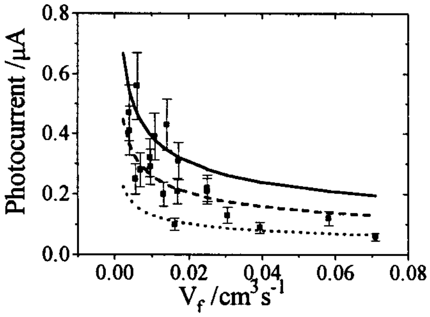

Figure 5. Plot of experimentally measured and theoretical photocurrents as a function of the electrolyte flow rate for the reaction between Ph_3P (0.48 mM) and $[S_2Mo_{18}O_{62}]^{4-}$ (0.44 mM) in $MeCN/H_2O$ (95/5 v/v; 0.1 M Bu_4NClO_4) (■, experiment (with error bars); —, BI theory ($k_1^* = 3.0$ M^{-1} s^{-1}); - - -, BI theory ($k_1^* = 2.0$ M^{-1} s^{-1}); ···, BI theory ($k_1^* = 1.0$ M^{-1} s^{-1})).

Table 2. Calculated Values of k_1^* as a Function of Electrolyte Flow Rate for the Photolysis (300−400 nm; intensity ~ 10 mW cm^{-2}) of a Solution of $[S_2Mo_{18}O_{62}]^{4-}$ (0.44 mM) and Ph_3P (0.48 mM) in $MeCN/H_2O$ (95/5 v/v; 0.1 M Bu_4NClO_4)

10^3V_f/cm^3 s^{-1}	I^{photo}/μA	k_1^*/M^{-1} s^{-1}
3.86	0.47	2.6
4.01	0.41	2.3
6.85	0.28	1.9
9.52	0.32	2.6
9.58	0.29	2.2
10.72	0.39	3.0
14.10	0.43	3.7
16.13	0.10	1.0
16.90	0.21	2.0
17.22	0.31	2.9
25.02	0.21	2.3
25.08	0.22	2.4
30.56	0.13	1.6
39.38	0.09	1.2
58.16	0.12	1.8
		2.2 (±0.7) (av)

between Ph_3P and $[S_2Mo_{18}O_{62}]^{*4-}$ (eq 17) in the presence of

$$C_2:\ [S_2Mo_{18}O_{62}]^{4-} + Ph_3P \xrightarrow{k_1/h\nu} \text{products} \xrightarrow{H_2O/\text{fast}} [HS_2Mo_{18}O_{62}]^{5-} + Ph_3PO + H^+ \quad (17)$$

$$E:\ [HS_2Mo_{18}O_{62}]^{5-} \rightleftarrows [S_2Mo_{18}O_{62}]^{4-} + H^+ + 2e^- \quad (18)$$

water and E represents the electro-oxidation of the reduced species $[HS_2Mo_{18}O_{62}]^{5-}$ to $[S_2Mo_{18}O_{62}]^{4-}$ (eq 18). That is k_1^* represents the second-order rate constant for eq 16 in the presence of light and is analogous to the rate constant k_1 (for eq 11) obtained in the absence of light. A theoretical model for a C_2E process has been derived by solution of the relevant convective−diffusion equations of each species to the channel electrode surface using backward implicit (BI) theory.[16,17]

The theoretically expected results for the variation of photocurrent with flow rate for three different values of k_1^* are shown in Figure 5, while Table 2 documents how k_1^* varies for a typical data set. The larger than expected scatter of data from the theory is attributed to the dark reaction resulting in a lower concentration of the available reactants for the photoreaction and lower than expected experimental photocurrents. In summary, average k_1^* values obtained are in the range 0.6−3.0 M^{-1} s^{-1} for a variety of equimolar concentrations of Ph_3P and $[S_2Mo_{18}O_{62}]^{4-}$ (0.4−1.0 mM) and water contents (0−5% v/v added H_2O). From comparison of these values with that for the equivalent dark reaction (0.06 M^{-1} s^{-1}), it can be seen that the redox reaction associated with eq 11 is accelerated by up to 2 orders of magnitude in the presence of light. This substantial acceleration in rate indicates a significant positive shift in the excited-state redox potential of the $[S_2Mo_{18}O_{62}]^{4-/5-}$ couple over that of the ground state.

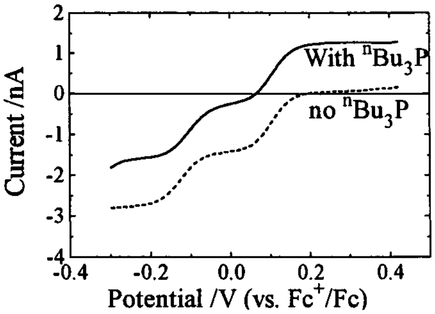

Figure 6. Steady-state voltammograms of $[S_2Mo_{18}O_{62}]^{4-}$ (1 mM) in $MeCN/H_2O$ (95/5 v/v; 0.1 M Bu_4NClO_4) before and after addition of $^nBu_3P$ (1.5 mM) at a glassy carbon electrode (d, 10.0 μm; ν, 10 mV s^{-1}).

The results obtained with Ph_3P can be compared with a study in which photoexcited $[S_2Mo_{18}O_{62}]^{4-}$ acts as a powerful oxidizing agent forming $[S_2Mo_{18}O_{62}]^{5-}$ and $[S_2Mo_{18}O_{62}]^{6-}$ with species of high formal oxidation potentials such as toluene and tetrahydrofuran.[16] The oxidizing power of polyoxometalate species has been reviewed recently.[7] Whereas toluene and THF have formal oxidation potentials greater than +1.1 V (vs Fc$^+$/Fc) and require photoexcitation of the polyoxo-cluster to undergo oxidation, the peak potential (and hence the formal oxidation potential) of Ph_3P is lower (+0.6 to +1.0 V[19−23]) and it is oxidized slowly in the absence of light. Ferrocene has a much lower formal oxidation potential (0.0 V) and is oxidized rapidly in the absence of light.[16] The dependence on redox potential is consistent with Marcus theory for outer-sphere electron transfers outside the inverted region.[16]

C. Reaction of $[S_2Mo_{18}O_{62}]^{4-}$ with $^nBu_3P$. Again a color change from yellow to green occurs upon mixing of equimolar solutions of $[S_2Mo_{18}O_{62}]^{4-}$ and $^nBu_3P$ in CH_3CN/H_2O (95/5 v/v). However, for this reaction, the current magnitudes of steady-state voltammograms obtained at a microdisk electrode are virtually independent of time in the sense that two reversible processes are observed irrespective of the color of the solution (Figure 6). This behavior is very different from that obtained in the presence of Ph_3P since no change in wave heights or potentials occurs. Rather, the first two one-electron charge-transfer processes associated with $[S_2Mo_{18}O_{62}]^{4-}$ remain, but the position of zero current observed in steady-state voltammograms at a microdisk electrode (Figure 6) has shifted toward the plateau region separating the two waves; i.e., the initial one-electron reduction process has now become a one-electron oxidation process. The end point when this is achieved is at a molar ratio of $[S_2Mo_{18}O_{62}]^{4-}$:$^nBu_3P$ = 1:1.5. The voltammetric oxidation of $^nBu_3P$ occurs at about +0.5 V,[23] however no oxidation peak associated with $^nBu_3P$ was observed as complete reaction between the phosphine and polyoxomolybdate occurred on initial mixing, with 1.5 mM being required to convert 1 mM $[S_2Mo_{18}O_{62}]^{4-}$ to 1 mM $[S_2Mo_{18}O_{62}]^{5-}$. This result is consistent with chemical production of one-electron reduced $[S_2Mo_{18}O_{62}]^{5-}$ rather than a protonated form of the two-electron reduced species, $[HS_2Mo_{18}O_{62}]^{5-}$.[12−14]

^{31}P NMR spectra for a 5 mM equimolar reaction mixture revealed the generation of a combination of $^nBu_3PO$ (δ = 57.6 ppm) and $^nBu_3PH^+$ (δ = 13.7 ppm; $J(^{31}P - {}^1H)$ = 480 Hz).

Equivalent experiments in MeCN/^2H_2O showed that the source of hydrogen in $^nBu_3P^2H^+$ was water, via observation of a triplet ($J(^{31}P-^2H) = 74$ Hz) in place of the doublet observed in ^1H_2O solutions. In summary, the natures of both the polyoxometalate anion and phosphorus containing products are different from those formed when $[S_2Mo_{18}O_{62}]^{4-}$ is reacted with Ph_3P. This difference may be rationalized by proposing that, again (cf. eq 11), $^nBu_3P$ reacts with $[S_2Mo_{18}O_{62}]^{4-}$ in an initial one-electron-transfer step:

$$^nBu_3P + [S_2Mo_{18}O_{62}]^{4-} \rightarrow {}^nBu_3P^{\bullet+} + [S_2Mo_{18}O_{62}]^{5-} \quad (19)$$

The $^nBu_3P^{\bullet+}$ cation radical, also reacts with water in analogous manner:

$$^nBu_3P^{\bullet+} + H_2O \rightarrow {}^nBu_3P^{\bullet}OH + H^+ \quad (20)$$

However, $^nBu_3P$ is a much stronger base than Ph_3P ($^nBu_3PH^+$, $pK_a = 8.43$; Ph_3PH^+, $pK_a = 2.73$ [27]) so it reacts with the protons generated in eq 20 to form $^nBu_3PH^+$:

$$^nBu_3P + H^+ \rightarrow {}^nBu_3PH^+ \quad (21)$$

and also with the protons generated in the reaction:

$$[S_2Mo_{18}O_{62}]^{4-} + {}^nBu_3P^{\bullet}OH \xrightarrow{\text{fast}} [S_2Mo_{18}O_{62}]^{5-} + {}^nBu_3PO + H^+ \quad (22)$$

This leaves $[S_2Mo_{18}O_{62}]^{5-}$ as the finally observed polyoxomolybdate species. The removal of protons by $^nBu_3P$ prevents the disproportionation of $[S_2Mo_{18}O_{62}]^{5-}$ (eqs 8 and 9) from occurring, and as a result, $[S_2Mo_{18}O_{62}]^{5-}$ is the final polyoxomolybdate product of the redox reaction between $^nBu_3P$ and $[S_2Mo_{18}O_{62}]^{4-}$. The overall reaction in this case is as follows:

$$2[S_2Mo_{18}O_{62}]^{4-} + 3{}^nBu_3P + H_2O \rightarrow 2[S_2Mo_{18}O_{62}]^{5-} + {}^nBu_3PO + 2{}^nBu_3PH^+ \quad (23)$$

Analogous results also were obtained for Et_3P, which has a similar oxidation potential and pK_a value to those of $^nBu_3P$ (∼+0.5 V[23] and 8.69,[27] respectively).

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