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Spectroscopic and electrochemical examination of the dark and photo-catalysed redox reactions that occur at the interface between solid α-$[Hex_4N]_4[S_2Mo_{18}O_{62}]$, solid triphenylphosphine and water

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Solid α-$[Hex_4N]_4[S_2Mo_{18}O_{62}]$ was found to be reduced by solid triphenylphosphine when the two species were ground together as powders and left for periods of several days in the presence of atmospheric water vapour. Electrospray mass spectrometry confirmed that the final product formed by oxidation of the phosphine was PPh_3O, while experiments in the presence of $H_2{}^{17}O$ demonstrated that the oxygen source was atmospheric water vapour rather than $[S_2Mo_{18}O_{62}]^{4-}$. Voltammetry and UV/visible spectroscopy of samples of reacted solids dissolved in MeCN imply that the two-electron, two-proton reduced species $[Hex_4N]_4[H_2S_2Mo_{18}O_{62}]$ was the major product formed upon reaction of an equimolar solid mixture of PPh_3 and $[Hex_4N]_4[S_2Mo_{18}O_{62}]$. The rate of this process is accelerated by irradiation with 300–400 nm light, corresponding to the wavelength of an absorption band of $[S_2Mo_{18}O_{62}]^{4-}$. When PPh_3 was in excess, three-electron and four-electron reduced forms of $[S_2Mo_{18}O_{62}]^{4-}$ were detected by EPR spectroscopy and voltammetry, respectively. Direct evidence for the photooxidation of PPh_3 was obtained through solid-state photovoltammetric experiments in which a phototransient response for the oxidation of reduced forms of $[S_2Mo_{18}O_{62}]^{4-}$ was recorded for solid state mixtures which were mechanically attached to a pyrolytic graphite electrode surface in contact with an aqueous medium.

Introduction

Polyoxometalate anions have a rich electrochemistry[1–3] and α-$[S_2Mo_{18}O_{62}]^{4-}$ (Fig. 1) is no exception, with multiply reduced forms being accessible in solution on the voltammetric and bulk electrolysis timescales.[4–11] In addition, many of these anions photooxidise a range of organic substances in the solution phase.[12] Yamase[13–15] has harnessed these properties to synthesize new anions and utilised the electrochromic properties of species such as $[EuW_{10}O_{35}]^{9-}$ to develop novel electroluminescent cells. We have demonstrated that $[S_2Mo_{18}O_{62}]^{4-}$ photooxidises a range of organic molecules such as toluene or tetrahydrofuran in acetonitrile forming the green one-electron ($1e^-$) and blue two-electron ($2e^-$) reduced forms.[16] We[17] and others[18] have also shown that redox chemistry occurs in the solution phase when $[S_2Mo_{18}O_{62}]^{4-}$ reacts with phosphines.

The above brief overview highlights the fact that a great deal is known about the solution phase redox reactions in both the presence and absence of light. However, there are virtually no data available on solid state reactivity, despite the fact that polyoxomolybdates are being used as heterogeneous catalysts.[1–3]

Recently, a new method of studying electron transfer at electrode–microcrystal–solvent interfaces has been developed, which is applicable to both, dark[19–22] and light[23] redox reaction pathways. Use of this new technique combined with spectroscopic studies enables us to show for the first time how microcrystals of $[Hex_4N]_4[S_2Mo_{18}O_{62}]$ (Hex = hexyl) and PPh_3 react in the solid state in the presence of water vapour and in the absence of light. Furthermore, the occurrence of photocatalysis is confirmed by solid-state photo-electrochemical voltammetry. The reactivity is quantitatively compared with that observed in the solution phase in order to establish whether the same products and analogous mechanistic behaviour is observed when a redox reaction occurs in a different phase.[17] Applications of this new electrochemical approach may assist the development of photovoltaic devices based upon solid state mixtures of polyoxometalates and a range of electron donors.

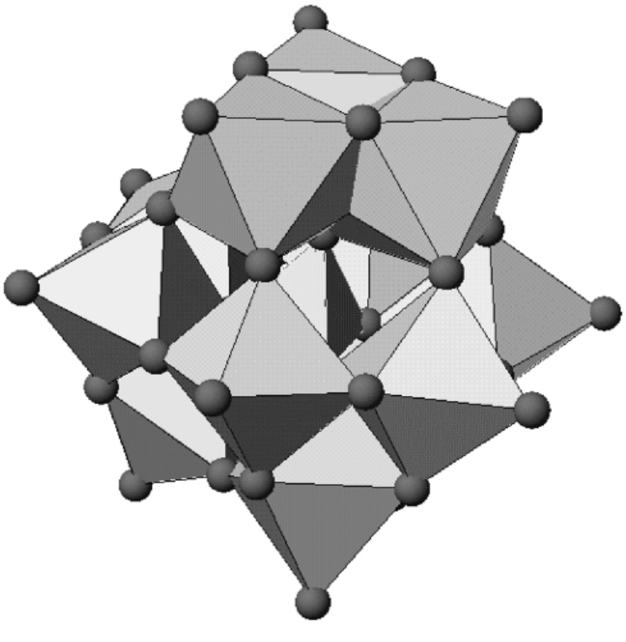

Fig. 1 Polyhedral representation of α-$[S_2Mo_{18}O_{62}]^{4-}$.

Results

Preliminary observations indicated that solid state mixtures of colourless PPh_3 and yellow $[Hex_4N]_4[S_2Mo_{18}O_{62}]$ turned green upon standing in air and that the colour change was promoted by filtered light of wavelength 300–400 nm. Electrospray ionisation mass spectrometry of products dissolved in MeCN detected PPh_3OH^+, confirming PPh_3O as the phosphorus product, and also protonated species derived from reduction of $[S_2Mo_{18}O_{62}]^{4-}$. A 1:1 mixture sealed under vacuum showed <2% reduction after 35 days, confirming the importance of atmospheric water in the solid state reaction. If the mixture was incubated in an atmosphere of H_2O (50 atom% ^{17}O), the PPh_3OH^+ ion is labelled, confirming H_2O as the source of oxygen. Control experiments confirmed that PPh_3O and H_2O do not exchange oxygen on the timescale of the incubation experiment.

(a) Voltammetric investigations on dissolved samples of reacted solids

Solid state mixtures of PPh_3 and $[Hex_4N]_4[S_2Mo_{18}O_{62}]$ were prepared in 1:1 and 5:1 molar ratios by grinding the components in a mortar and pestle. Some were kept in the dark while others were irradiated with 300–400 nm light (intensity = 10 mW cm^{-2}) corresponding to the wavelength region of an absorption band of $[S_2Mo_{18}O_{62}]^{4-}$.[16] Samples (about 30 mg) were dissolved in MeCN (10 ml; 0.1 M Bu_4NPF_6) for immediate analysis *via* steady-state voltammetry at a platinum microdisk electrode (diameter, d, 10.0 µm; scan rate, v 10 mV s^{-1}). Voltammograms were recorded immediately after solution preparation as a slow solution phase reaction ($t_{1/2} \approx 1$ h) occurs between $[S_2Mo_{18}O_{62}]^{4-}$ and PPh_3.[17]

Solutions of $[S_2Mo_{18}O_{62}]^{4-}$ in MeCN (0.1 M Bu_4NPF_6) under steady-state voltammetric conditions exhibit sequential 1e$^-$ reduction processes with $E_{1/2}$ values of +0.12 and −0.12 V *vs.* Fc$^+$/Fc for the first two processes.[11] In the presence of protons, positive shifts in $E_{1/2}$ occur and the reduction processes convert into 2e$^-$ events.[10,11] Proof that reduction of solid $[S_2Mo_{18}O_{62}]^{4-}$ occurred in the dark after 13 d was obtained by noting the presence of the oxidative current (Fig. 2) rather than a purely reductive current. In the 1:1 molar mixture two redox processes were observed at $E_{1/2}$ values of +0.17(2) and −0.10(1) V. The presence of protons is suggested by the positive shifts in potential from +0.12 and −0.12 V and the inequivalent current intensities.[11] The position of zero current after reaction shows that $[S_2Mo_{18}O_{62}]^{4-}$ has been partially reduced to the 1e$^-$ and (2e$^-$, 1H$^+$) $[HS_2Mo_{18}O_{62}]^{5-}$ or (2e$^-$, 2H$^+$) $[H_2S_2Mo_{18}O_{62}]^{4-}$ reduced products. In contrast, the 5:1 molar mixture under the same conditions exhibits $E_{1/2}$ values of +0.31(3) and +0.11(2) V (Fig. 2), consistent with the presence of a higher concentration of protons.[11,17] Importantly, the process at +0.31(3) V is now fully oxidative in nature and that at +0.11(2) V exhibits a partially oxidative component (Fig. 2), indicating that $[S_2Mo_{18}O_{62}]^{4-}$ has been reduced by more than 2e$^-$.

Cyclic voltammetric experiments at a macrodisk platinum electrode revealed that both 1:1 and 5:1 solid-phase mixtures still had significant amounts of unchanged PPh_3 after a 13 d reaction period (PPh_3 oxidation wave still present at E_p^{ox} +0.70 V). Longer reaction periods of 50 d showed that $[S_2Mo_{18}O_{62}]^{4-}$ in 1:1 mixtures was reduced by a maximum of 2e$^-$ and that the $E_{1/2}$ values indicated[11] that the (2e$^-$, 2H$^+$)-reduced form $[H_2S_2Mo_{18}O_{62}]^{4-}$ is the final product formed after dissolution in MeCN. In the 5:1 mixtures between 3 and 4 electrons were transferred, with the inferred level of reduction and concentration of protons increasing with increasing reaction time. Details of voltammetric results obtained after 35 d reaction time in the solid state, as well as under other conditions, are given in Table 1.

Data above refer to reaction of $[S_2Mo_{18}O_{62}]^{4-}$ and PPh_3 in the dark. Preliminary results for illuminated samples indicated a significant acceleration of the rate of reduction (*cf.* Table 1 and ref. 17). An order-of-magnitude comparison of rates can be made *via* a simple second order analysis of the voltammetric responses on dissolved reacted samples. For the 1:1 mixtures the measured oxidative component (*e.g.*, Fig. 2) is due to the two-electron oxidation (1) (x = 0, 1 or 2).

$$[H_xS_2Mo_{18}O_{62}]^{(6-x)-} \longrightarrow [S_2Mo_{18}O_{62}]^{4-} + xH^+ + 2e^- \quad (1)$$

The anions $[H_xS_2Mo_{18}O_{62}]^{(6-x)-}$ derive from disproportionation of the initial 1e$^-$-reduced product $[S_2Mo_{18}O_{62}]^{5-}$ in the presence of protons derived from water.[10,11,17] The magnitude of the oxidative limiting current (I_{lim}) measured by steady-state voltammetry at a microdisk electrode allows determination of the concentration of the product $[H_xS_2Mo_{18}O_{62}]^{(6-x)-}$ from the simple relationship (2)[24] where n is the number of electrons

$$I_{lim} = 4nFD[H_xS_2Mo_{18}O_{62}{}^{(6-x)-}]r \quad (2)$$

transferred in the charge transfer process and is assumed to be 2 in the presence of a proton source, F is 96485 C mol^{-1}, D is the

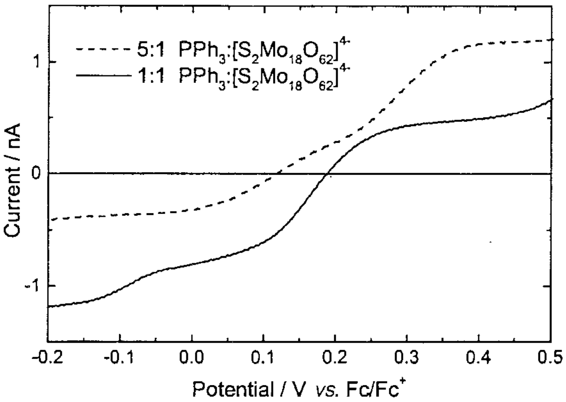

Fig. 2 Steady-state platinum microdisk electrode voltammograms (glassy carbon electrode; d, 10 µm; v, 10 mV s^{-1}) obtained for solid state reaction mixtures (13 d reaction time) of solid PPh_3 and $[Hex_4N]_4$-$[S_2Mo_{18}O_{62}]$ (30 mg) after dissolution in MeCN (0.1 M Bu_4PF_6).

Table 1 Steady-state voltammetric responses (10 µm diameter platinum disk electrode) obtained after dissolution in MeCN (0.1 M Bu_4NPF_6) of reacted solid phase mixtures of PPh_3 and $[Hex_4N]_4[S_2Mo_{18}O_{62}]$. Voltammetric data obtained for other solution phase combinations are included for purpose of comparison

$[PPh_3]:[Hex_4N]_4[S_2Mo_{18}O_{62}]$	Experimental conditions	Reaction time	Voltammetric[a] $E_{1/2}$ values/V[b]
1:1	Dark, exposed to atmospheric water	35 d	+0.34 (o/2e$^-$), +0.19 (r/2e$^-$)
5:1	Dark, exposed to atmospheric water	35 d	+0.33 (o/2e$^-$), +0.21 (o/r/2e$^-$)
1:1	Dark, sealed in vacuum	35 d	+0.21 (o/r/1–2 e$^-$), −0.09 (r/<1e$^-$)
1:1	Light, exposed to atmospheric water	150 min	+0.21 (o/r1–2 e$^-$), −0.07 (r/<1e$^-$)
1:1	Solution-phase reaction	48 h	+0.13 (o/2e$^-$), −0.02 (r/2e$^-$)
0:1	$[S_2Mo_{18}O_{62}]^{4-}$ in 95:5 MeCN–water (2 mM $HClO_4$)	—	+0.15 (r/2e$^-$), −0.01 (r/2e$^-$)
0:1	$[S_2Mo_{18}O_{62}]^{4-}$ in 95:5 MeCN–water (0.2 M $HClO_4$)	—	+0.31 (r/2e$^-$), +0.21 (r/2e$^-$)

[a] o = oxidative process, r = reductive process, o/r = partially oxidative and reductive. Assignment determined by the sign of the current for the appropriate process. In addition, the number of electrons transferred in the appropriate redox process is also included. [b] Quoted relative to Fc$^+$/Fc.

Table 2 Relative values of second-order rate constants k_{obs} for solid state reaction between PPh_3 and $[Hex_4N]_4[S_2Mo_{18}O_{62}]$ (1 : 1 molar ratio)

Experimental conditions	$10^6k_{obs}{}^a/\mu mol^{-1}\ min^{-1}$
Dark under vacuum	0.05
Dark in air	3
UV radiation[b] in air	50

[a] See text for definition of k_{obs}. [b] 300–400 nm; 10 mW cm^{-2}.

diffusion coefficient of the polyoxometalate species in MeCN (assumed to be 5×10^{-6} cm^2 s^{-1})[18] and r is the radius of the microelectrode. Eqn. (2) enables the mole fraction of reduced anion to be estimated and hence the second-order rate constant (k_{obs}) for the rate-limiting step of the overall reaction. The k_{obs} data in Table 2 show that UV/visible irradiation accelerates the overall rate of reaction by an order of magnitude, similar to the observation made in the solution phase reaction.[17] Further, the rate of reaction is reduced by three orders of magnitude in the absence of atmospheric water (Table 2).

(b) Spectroscopic investigations on dissolved samples of reacted solids

Fig. 3a shows the EPR spectrum recorded during the course of a coulometric titration (bulk electrolysis) at the $n = 1$ level (n = number of electrons added to each molecule of $[S_2Mo_{18}O_{62}]^{4-}$) on a frozen MeCN glass (4×10^{-3} M; 77 K). This intense, anisotropic signal ($g_{\parallel} = 1.964$, $g_{\perp} = 1.949$) was identical to that obtained from an authentic sample of 1e$^-$-reduced $[Bu_4N]_5[S_2Mo_{18}O_{62}]$.[11] This signal decayed progressively upon reduction to the $n = 2$ level, consistent with the likelihood that the 2e$^-$-reduced anion $[S_2Mo_{18}O_{62}]^{6-}$ is electronically coupled if not diamagnetic.[25] Upon further reduction to the $n = 3$ stage a new signal appeared and is assigned to the 3e$^-$-reduced species $[S_2Mo_{18}O_{62}]^{7-}$ (Fig. 3b; $g_{\parallel} = 1.930$). Reduction to the $n = 4$ level led to a progressive loss of this signal. The EPR spectra of 1 : 1 mixtures irradiated with UV/visible light for 15 d feature only the signal characteristic of the 1e$^-$-reduced species $[S_2Mo_{18}O_{62}]^{5-}$ (Fig. 3a). Those for 5 : 1 mixtures show features attributable to both the 1e$^-$- and 3e$^-$-reduced anions (Fig. 3c and 3d).

Electronic spectra of 15 d reacted solids dissolved in MeCN (0.1 M Bu_4NClO_4) exhibit an absorption maximum at about 16800 cm^{-1}, characteristic of protonated 2e$^-$-reduced anions (Table 3). In fact, the spectrum of the 35 d 1 : 1 reaction mixture dissolved in MeCN–water (95/5 vol%; 0.2 M $HClO_4$) provided an excellent match with that of the electrochemically (2e$^-$, 2H$^+$)-reduced complex (Table 3). Neither PPh_3 nor PPh_3O absorbs in the visible region.

Fig. 4 shows spectra of a 1 : 1 reaction mixture dissolved in MeCN (0.1 M Bu_4NClO_4) after reaction in air for 2.5 h. It is apparent that the reaction is accelerated significantly by light.

These spectroscopic results are consistent with the presence of 1e$^-$- and 2e$^-$-reduced anions in the 1 : 1 reaction mixtures with, additionally, 3e$^-$-reduced anions in the 5 : 1 mixture. The spectroscopic methods are insensitive to the presence of the 4e$^-$-reduced species detected voltammetrically.

(c) Solid-state electrochemical experiments

Solid state reaction mixtures of 1 : 1 and 10 : 1 molar ratios were attached mechanically to a pyrolytic graphite electrode which was then placed in aqueous solution (0.1 M NaCl). Voltammograms affected by reactions occurring at the solid–aqueous interface can be obtained conveniently by this technique.[19–23] Four chemically reversible reduction processes A–D are detected in the presence and absence of irradiation (Table 4, Fig. 5a) and correspond to a series of 2e$^-$-reduction processes in which the additional negative charge generated upon reduction is balanced by transport of protons from solution into the microcrystals of material attached to the electrode surface [eqn. (3)].[22]

$$[H_xS_2Mo_{18}O_{62}]^{4-}(s) + 2\,H^+(aq) + 2e^- \longrightarrow [H_{(x+2)}S_2Mo_{18}O_{62}]^{4-}(s) \quad (3)$$

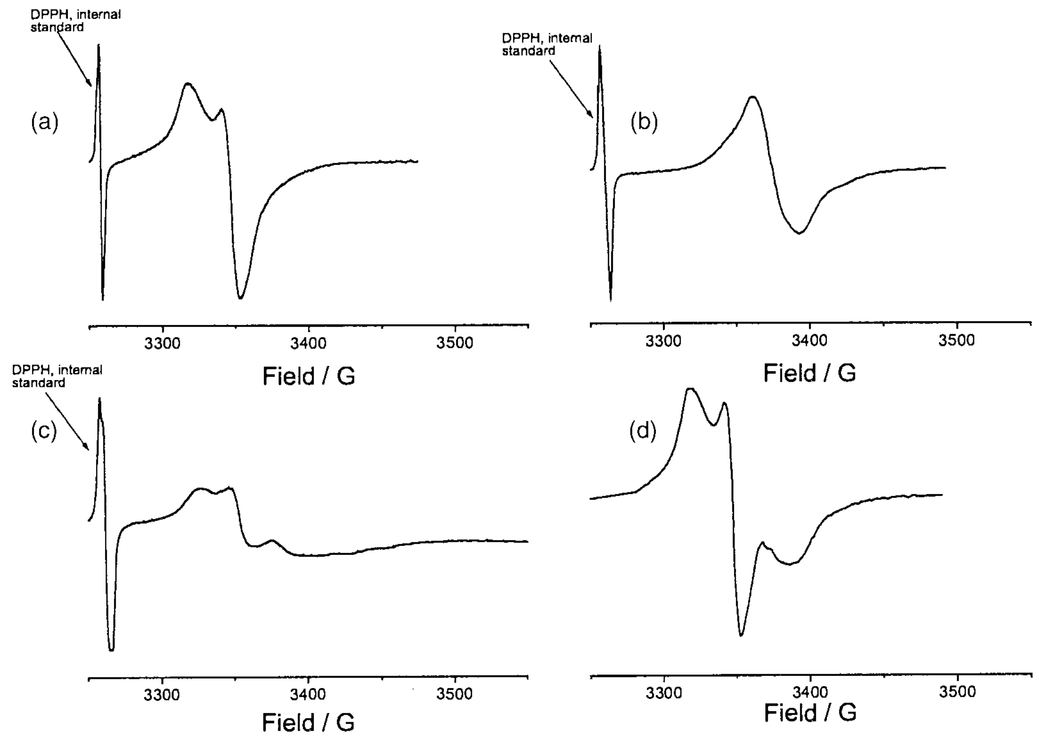

Fig. 3 Frozen solution (77 K) EPR spectra of (a) 1e$^-$-reduced $[S_2Mo_{18}O_{62}]^{5-}$ and (b) 3e$^-$-reduced $[S_2Mo_{18}O_{62}]^{7-}$ products formed by (coulometric) reduction of $[S_2Mo_{18}O_{62}]^{4-}$ (4×10^{-3} M) in MeCN (0.1 M Bu_4NClO_4). (c) Frozen solution (77K) EPR spectrum of a solid state mixture of PPh_3 and $[Hex_4N]_4[S_2Mo_{18}O_{62}]$ (5 : 1 molar ratio) after standing in air for 15 d and being dissolved in MeCN (0.1 M Bu_4NClO_4); (d) predicted EPR spectrum for a 1 : 1 mixture of 1e$^-$-reduced $[S_2Mo_{18}O_{62}]^{5-}$ and 3e$^-$-reduced $[S_2Mo_{18}O_{62}]^{7-}$ (addition of Fig. 3a and 3b). DPPH = Diphenylpicrylhydrazyl.

Table 3 Comparison of electronic spectra obtained in the range 5000–25000 cm^{-1} for electrochemically reduced forms of $[S_2Mo_{18}O_{62}]^{4-}$ (0.2–0.6 mM) and for reacted[a] solid state in MeCN media

Species	Medium	T/°C	Absorption maximum[b]/cm^{-1}	ε/M^{-1} cm^{-1}
$[S_2Mo_{18}O_{62}]^{5-}$ ($1e^-$)	[c]	−45[d]	9730	6000
$[S_2Mo_{18}O_{62}]^{6-}$ ($2e^-$)	[c]	−45[d]	12100	12500
	[c]		15370	7600
$[S_2Mo_{18}O_{62}]^{7-}$ ($3e^-$)	[c]	−45[d]	13260	17100
$[S_2Mo_{18}O_{62}]^{8-}$ ($4e^-$)	[c]	−45[d]	14130	25000
$[H_2S_2Mo_{18}O_{62}]^{4-}$ ($2e^-$, $2H^+$)	[e]	22[f]	8850	5100
			13130	12900
			16850	5900
$[H_4S_2Mo_{18}O_{62}]^{4-}$ ($4e^-$, $4H^+$)	[e]	22[f]	9730	13700
			14410	26700
$PPh_3:[S_2Mo_{18}O_{62}]^{4-} = 1:1$	[e]	22	9210	—
			13480	
			16730	
$PPh_3:[S_2Mo_{18}O_{62}]^{4-} = 1:1$	[c]	22[g]	8570	—
			13000	
			16860	
$PPh_3:[S_2Mo_{18}O_{62}]^{4-} = 5:1$	[c]	22	8840	—
			12950	
			16770	
$PPh_3:[S_2Mo_{18}O_{62}]^{4-} = 5:1$	[e]	22[g]	8630	—
			13110	
			16970	

[a] Reaction time of 13 d unless otherwise stated. [b] See references 3 and 26 for probable assignment of relevant intra-valence transitions that give rise to absorption bands. [c] In MeCN (0.1 M Bu_4NClO_4). [d] Data obtained by OTTLE experiments at a platinum gauze electrode at −45 °C. Well defined isosbestic points obtained during the course of electrolysis to each redox level confirm the absence of decomposition as do oxidation experiments after reduction which quantitatively regenerate the initial electronic spectrum of $[S_2Mo_{18}O_{62}]^{4-}$. [e] In MeCN–water (95:5; 0.2 M $HClO_4$). [f] Data obtained at 22 °C by sequential ($2e^-$, $2H^+$) reduction to form $[H_2S_2Mo_{18}O_{62}]^{4-}$ and $[H_4S_2Mo_{18}O_{62}]^{4-}$ in MeCN–water (95:5 vol%; 0.2 M $HClO_4$)[11] demonstrate that large shifts are observed in band maxima when protonation occurs. [g] Reaction time of 35 d.

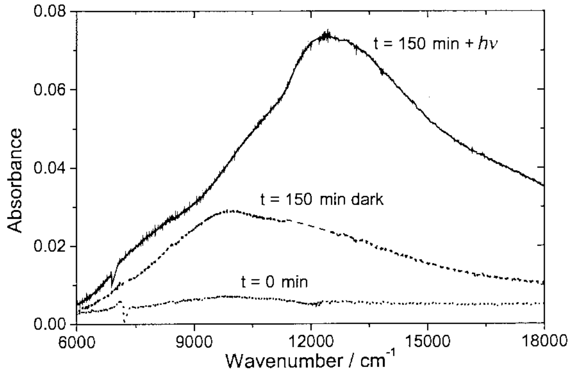

Fig. 4 The UV/visible spectrum of a solid state mixture of PPh_3 and $[Hex_4N]_4[S_2Mo_{18}O_{62}]$ (1 : 1 molar ratio; 5 mg) dissolved in MeCN (0.1 M Bu_4NClO_4, 10 ml).

Fig. 5b illustrates the effect of 300–400 nm irradiation on the electrode surface for the 1 : 1 molar mixture in the potential region 0.50 to 1.3 V (*vs.* Ag–AgCl). From potentials more positive than process A and up to potentials at which PPh_3 is oxidised, oxidative current is observed in the presence of radiation. This result is analogous with that obtained in the solution phase.[17] Thus, in the positive potential region, the reduced anion species formed by the photochemical reaction are oxidised at the electrode surface to give a Faradaic current above the background current until more positive potentials are reached when current from the phosphine oxidation response (E_p^{ox} = +0.90 V *vs.* Ag–AgCl) is significantly reduced in magnitude upon irradiation. This indicates that PPh_3 is photooxidised to a species (PPh_3O) which is electro-inactive in the potential range of Fig. 5b.

The photo-effect can be demonstrated further if the electrode potential is held at +0.60 V (*vs.* Ag–AgCl) with the electrode being periodically irradiated by 300–400 nm light. An oxidative 'photo-transient' response (current becomes more positive) is observed on irradiation of the pyrolytic graphite electrode surface (Fig. 6). The instantaneous rise in current following irradiation indicates that the current is photolytically, rather

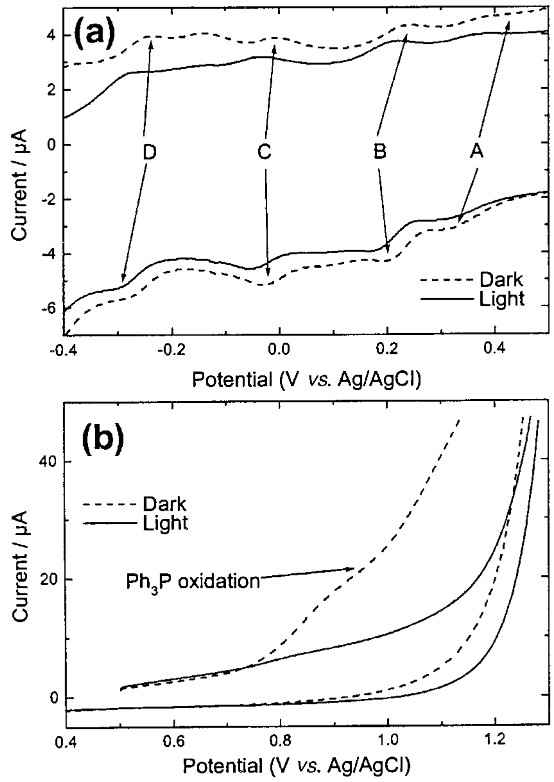

Fig. 5 Cyclic voltammograms (v 100 mV s^{-1}) of a solid state mixture of PPh_3 and $[Hex_4N]_4[S_2Mo_{18}O_{62}]$ (1 : 1 molar ratio) attached mechanically to a pyrolytic graphite electrode (d 5 mm) in contact with aqueous electrolyte (0.1 M NaCl) in the presence and absence of UV/visible light (300–400 nm). Potential ranges: (a) +0.50 to −0.40 V; (b) +0.50 to +1.20 V *vs.* Ag–AgCl.

Table 4 Peak potentials (mV *vs.* Ag–AgCl) for the four major reduction processes observed in the presence and absence of 300–400 nm UV/visible irradiation (intensity, 10 mW cm^{-2}) under conditions of cyclic voltammetry (scan rate 100 mV s^{-1}) when $[Hex_4N]_4[S_2Mo_{18}O_{62}]$ and PPh_3 (1 : 1 molar ratio) are mechanically attached to a pyrolytic graphite electrode immersed in aqueous 0.1 M NaCl

E_p^{red} (dark)	E_p^{red} (light)	E_p^{ox} (dark)	E_p^{ox} (light)	Reduction process[a]
304	306	396	390	A
196	172	252	224	B
−28	−58	20	30	C
−286	−306	−152	−264	D

[a] See Fig. 5.

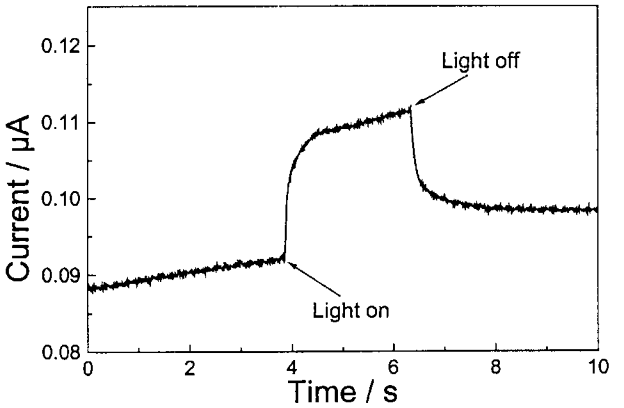

Fig. 6 Current–time curve under the conditions of Fig. 5. Potential is held at +0.60 V *vs.* Ag–AgCl. The wavelength of incident light is 300–400 nm.

than thermally, activated.† Further, using filters to vary wavelength showed that the maximum photocurrent response was attained at wavelengths between 300 and 400 nm, consistent with oxygen to metal charge transfer transitions which occur in $[S_2Mo_{18}O_{62}]^{4-,5-}$ in this wavelength region.[16]

Discussion

Solid state mixtures of PPh_3 and $[Hex_4N]_4[S_2Mo_{18}O_{62}]$ in contact with water (gaseous or solution phases) react to give PPh_3O and a range of reduced polyoxomolybdate species as the final products.

The EPR spectra on reacted solids confirm that $[S_2Mo_{18}O_{62}]^{5-}$ is the initial reduction product which implies that the first step in the overall reaction is transfer of a single electron between PPh_3 and $[S_2Mo_{18}O_{62}]^{4-}$ [eqn. (4)]. This step is

$$[S_2Mo_{18}O_{62}]^{4-} + PPh_3 \longrightarrow [S_2Mo_{18}O_{62}]^{5-} + PPh_3{}^{\bullet+} \quad (4)$$

accelerated photochemically by absorption of UV/visible light by the polyoxomolybdate since an order of magnitude increase in the rate of reaction occurs upon irradiation (see Table 2). However, $PPh_3{}^{\bullet+}$ must react rapidly with water and/or polyoxomolybdate by extracting an oxygen atom, *e.g.*, eqns. (5), (6), as this cation radical was not detected by EPR spectroscopy.

$$2PPh_3{}^{\bullet+} + H_2O \longrightarrow PPh_3O + PPh_3 + 2H^+ \quad (5)$$

$$[S_2Mo_{18}O_{62}]^{5-} + PPh_3{}^{\bullet+} + H_2O \longrightarrow [H_2S_2Mo_{18}O_{62}]^{4-} + PPh_3O \quad (6)$$

Interestingly, $[S_2Mo_{18}O_{62}]^{5-}$ formed in the solid state reaction apparently can exist in the presence of protons for considerable periods of time, in contrast to the analogous solution phase reaction.[17] This feature may have a kinetic explanation, since acid-catalysed disproportionation reactions are expected to be much faster in the solution phase. Alternatively, PPh_3 may be a relatively stronger base in the solid state regime and form PPh_3H^+, thereby protecting $[S_2Mo_{18}O_{62}]^{5-}$ formed in eqn. (4) from protonation and subsequent disproportionation.

Reaction of $[S_2Mo_{18}O_{62}]^{4-}$ with an excess of PPh_3 leads to polyoxomolybdate species reduced by more than two electrons as demonstrated by EPR spectroscopy (both one- and three-electron reduced forms were detected) and solution-phase voltammetry (an oxidative current of > 2e$^-$ was observed upon dissolution of solid reacted mixture). This suggests that in the presence of an excess of PPh_3 additional overall steps such as (7) and (8) occur with $PPh_3{}^+$ again being an intermediate.

$$[H_2S_2Mo_{18}O_{62}]^{4-} + PPh_3 + H_2O \longrightarrow [H_3S_2Mo_{18}O_{62}]^{5-} + PPh_3O + H^+ \quad (7)$$

$$[H_2S_2Mo_{18}O_{62}]^{4-} + PPh_3 + H_2O \longrightarrow [H_4S_2Mo_{18}O_{62}]^{4-} + PPh_3O \quad (8)$$

The fact that both one- and three-electron reduced species are detected by EPR spectroscopy upon reaction of a molar excess of PPh_3 and $[S_2Mo_{18}O_{62}]^{4-}$ is consistent with lack of complete homogeneity.

Voltammetric studies of MeCN solutions of products obtained in the solid state reactions allow the average level of reduction to be estimated. Complete reaction of an equimolar solid state mixture of $[Hex_4N]_4[S_2Mo_{18}O_{62}]$ with PPh_3 results in overall two-electron reduction of the polyoxomolybdate with further reduction being observed with an excess of PPh_3. However, solution phase studies cannot provide information on the exact nature of two electron reduced species present in this solid state as this could be the doubly protonated $[H_2S_2Mo_{18}O_{62}]^{4-}$ species, rather than $[HS_2Mo_{18}O_{62}]^{5-}$ formed in solution phase reactions; eqns. (9), (10), or even the non-protonated form [eqn. (11)].[17]

$$[S_2Mo_{18}O_{62}]^{4-} + PPh_3 + H_2O \longrightarrow [H_2S_2Mo_{18}O_{62}]^{4-} + PPh_3O \quad (9)$$

$$[S_2Mo_{18}O_{62}]^{4-} + PPh_3 + H_2O \longrightarrow [HS_2Mo_{18}O_{62}]^{5-} + PPh_3O + H^+ \quad (10)$$

$$[S_2Mo_{18}O_{62}]^{4-} + PPh_3 + H_2O \longrightarrow [S_2Mo_{18}O_{62}]^{6-} + PPh_3O + 2H^+ \quad (11)$$

Conclusion

The present work provides the first demonstration that microcrystals of PPh_3 in contact with microcrystals of polyoxometalates can lead to electron hopping between adjacent crystals with the reverse reaction being quenched by background water (vapour or liquid) reacting with the oxidised form of the phosphine molecule. Whilst the overall reaction is the same as in the solution phase reaction, the mechanisms of the reactions are distinctively different.

Experimental

(a) Reagents, compounds and solvents

The preparation of $[Hex_4N]_4[S_2Mo_{18}O_{62}]$ and $[Bu_4N]_5[S_2Mo_{18}O_{62}]$ as their *α* isomers has been described previously.[8] Tetra-*n*-butylammonium perchlorate (South Western Analytical, electrometric grade), 60% perchloric acid (BDH, Aristar grade), triphenylphosphine (Aldrich 99%), 2,2-diphenyl-1-

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† As the intensity of light was 10 mW cm^{-2} and the solution volume 20 cm^3, it was calculated that irradiation would alter the temperature of the aqueous solution by much less than 1 K during the course of a typical experiment.

picrylhydrazyl hydrate (DPPH) (Aldrich 95%) and $H_2{}^{17}O$ (50 atom% ^{17}O, Monsanto Research Corporation, Miamisburg, Ohio, US) were all used as received. Tetrabutylammonium hexafluorophosphate (Bu_4NPF_6), used as a supporting electrolyte in some experiments, was synthesized using literature methods.[27] Acetonitrile (Mallinckrodt, Biolab Scientific Pty Ltd; HPLC grade, 99.9%) was dried overnight over molecular sieves. Water was triply distilled.

(b) Instrumentation and procedures

Solution phase electrochemical experiments in acetonitrile (0.1 M Bu_4NClO_4 or 0.1 M Bu_4NPF_6) were performed at 22 ± 1 °C. Solutions were purged of dioxygen by degassing with dinitrogen. In voltammetric experiments, platinum disk (*d* 1 mm) or microdisk (*d* 10 μm) electrodes were used as working electrodes and calibrated with the ferrocenium–ferrocene Fc^+/Fc couple.[28] The counter electrode was a platinum wire. The Ag^+–Ag reference electrode consisted of a silver wire dipped in a 10 mM solution of $AgNO_3$ in acetonitrile (0.1 M Bu_4NClO_4) separated from the electroactive solution by a porous frit. Cypress Systems (model CYSY-1R), BAS100 (Bioanalytical System) and ADI instruments Maclab/4e computer controlled electroanalysis systems were used for potentiostatic control. The bulk electrolysis cell used for coulometric titrations contained two concentric platinum gauze baskets which served as the working and counter electrodes. They were separated by a glass cylinder with a porous glass frit in the base. The design is similar to that described previously.[29,30]

For photoelectrochemical voltammetric measurements on solid state mixtures of $[Hex_4N]_4[S_2Mo_{18}O_{62}]$ and PPh_3 the well ground mixtures were mechanically attached to a 5 mm diameter edge plane pyrolytic graphite disk electrode by gently rubbing the clean electrode surface against a filter paper onto which the powdered mixture had been placed. The electrode, containing mechanically attached microcrystals of the solid, was then placed into water with electrolyte. For these experiments an Ag–AgCl (3 M KCl in water) reference electrode was employed. An in-house built water-jacketed voltammetric cell was used, which allowed irradiation of the electrode surface through a quartz disk window. UV/visible irradiation was provided by a broad band 300 W xenon arc lamp (Cermax LX300; ILC technology, Sunnyvale, California). The light had its infrared component removed (using an infrared transparent mirror) and was then passed through a series of lenses and focused into an optic fibre (ILC technology) that was directed towards the surface of the relevant working electrode. The wavelength component of the incident light was controlled using 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 using this form of irradiation.

X-Band EPR measurements were made with a Varian E-12 spectrometer operating at 77 K. Gains in the range 8×10 to 2×10^4 and modulation amplitudes between 0.01 and 5.0 G were used. The *g* values were measured through calibration *versus* DPPH.[31] For EPR experiments on electrochemically generated species (coulometric titrations), the degassed, reduced solutions were transferred to a quartz EPR cell which was sealed. Samples were frozen in liquid nitrogen prior to measurements.

Positive and negative ion electrospray mass spectroscopic experiments were conducted on a Micromass Platform II quadrupole spectrometer. The reacted solid state mixtures were dissolved in acetonitrile at room temperature to provide concentrations in the 10^{-5}–10^{-6}M range and injected into the electrospray source. Voltages at the first skimmer electrode were the minimum necessary to maintain a stable spray (typically 10 to 25 V).

UV/visible/NIR Spectroelectrochemical experiments utilised an OTTLE cell located in the sample compartment of a Cary 5 spectrophotometer. The setup is described elsewhere.[32]

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References

Abbreviations: e^-, electronic charge; $E_p{}^{ox}$, oxidative peak potential; $E_p{}^{red}$, reductive peak potential; F, Faraday's constant.

1 M. T. Pope and A. Muller, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 34.
2 M. T. Pope and A. Muller, *Polyoxometalates: From Platonic Solids to Antiretroviral Activity*, Kluwer, Dordrecht, 1994.
3 M. T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer, Berlin, 1983.
4 S. Himeno, T. Osakai and A. Saito, *Bull. Chem. Soc., Jpn.*, 1989, **62**, 1335.
5 S. Himeno, T. Hori and A. Saito, *Bull. Chem. Soc. Jpn.*, 1989, **62**, 2184.
6 S. Himeno, T. Osakai, A. Saito, K. Maeda and T. Hori, *J. Electroanal. Chem. Interfacial Electrochem.*, 1992, **337**, 371.
7 S. Himeno, K. Maeda, T. Osakai, A. Saito and T. Hori, *Bull. Chem. Soc. Jpn.*, 1993, **66**, 109.
8 J. B. Cooper, D. M. Way, A. M. Bond and A. G. Wedd, *Inorg. Chem.*, 1993, **32**, 2416.
9 K. Maeda, S. Himeno, T. Osakaii, A. Saito and T. Hori, *J. Electroanal. Chem. Interfacial Electrochem.*, 1994, **364**, 149.
10 D. M. Way, A. M. Bond and A. G. Wedd, *Inorg. Chem.*, 1997, **36**, 2826.
11 D. M. Way, J. B. Cooper, M. Sadik, T. Vu, P. J. Mahon, A. M. Bond, R. T. C. Brownlee and A. G. Wedd, *Inorg. Chem.*, 1997, **36**, 4227; erratum: 1998, **37**, 604.
12 C. L. Hill and C. M. Prosser-McCartha, *Coord. Chem. Rev.*, 1995, **143**, 407.
13 T. Yamase, *J. Electrochem. Soc.*, 1993, **140**, 2378.
14 T. Yamase and K. Ohtaka, *J. Chem. Soc., Dalton Trans.*, 1994, 2599.
15 T. Yamase, *Chem. Rev.*, 1998, **98**, 307.
16 A. M. Bond, D. M. Way, A. G. Wedd, R. G. Compton, J. Booth and J. C. Eklund, *Inorg. Chem.*, 1995, **34**, 3378.
17 A. M. Bond, J. C. Eklund, V. Tedesco, T. Vu and A. G. Wedd, *Inorg. Chem.*, 1998, **37**, 2366.
18 R. Neier, C. Trojanowski and R. Mattes, *J. Chem. Soc., Dalton Trans.*, 1995, 2521.
19 A. M. Bond, R. Colton, F. Daniels, D. R. Fernando, F. Marken, Y. Nagaosa, R. F. M. Van Steveninck and J. N. Walter, *J. Am. Chem. Soc.*, 1993, **115**, 9556.
20 A. M. Bond and F. Marken, *J. Electroanal. Chem. Interfacial Electrochem.*, 1994, **372**, 125.
21 S. J. Shaw, F. Marken and A. M. Bond, *J. Electroanal. Chem. Interfacial Electrochem.*, 1996, **404**, 227.
22 A. M. Bond, J. B. Cooper, F. Marken and D. M. Way, *J. Electroanal. Chem. Interfacal Electrochem.*, 1995, **396**, 407.
23 A. M. Bond and J. C. Eklund, *J. Am. Chem. Soc.*, 1999, **121**, 8306.
24 M. I. Montenegro, *Res. Chem. Kin.*, 1994, **2**, 299.
25 N. Casan-Pastor and L. C. W. Baker, *J. Am. Chem. Soc.*, 1992, **114**, 10384 and refs. therein.
26 P. W. Atkins, D. F. Shriver and C. H. Langford, *Inorganic Chemistry*, OUP, Oxford, 1990.
27 A. J. Fry, *Laboratory Techniques in Electroanalytical Chemistry*, eds. P. T. Kissinger and W. R. Heineman, Marcel Dekker, New York, 1996, Ch. 15.
28 N. G. Connelly and W. E. Geiger, *Chem. Rev.*, 1996, **96**, 877.
29 C. Moinet and P. Peltier, *Bull. Soc. Chim. Fr.*, 1969, 690.
30 A. J. Fry, *Synthetic Organic Electrochemistry*, Wiley, New York, 1989, pp. 320–325.
31 J. E. Wertz and J. R. Bolton, *Electron Spin Resonance. Elementary Theory and Practical Applications*, McGraw-Hill, New York, 1972, p. 464.
32 C. M. Duff and G. A. Heath, *Inorg. Chem.*, 1991, **30**, 2528.

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