Heteropolytungstates as Catalysts for the Photochemical Reduction of Oxygen and Water

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A series of polytungstate anions $[XW_{12}O_{40}]^{n-}$ (X = P, Si, Fe, Co, or H_2; n = 3, 4, 5, 6, and 6 respectively), spanning a range of reduction potentials, have been studied as sensitizers for the photoreduction of water and O_2. $[SiW_{12}O_{40}]^{4-}$ was the most efficient sensitizer for H_2 evolution in the presence of colloidal platinum. Saturation kinetics were found with respect to the concentrations of Pt, $[SiW_{12}O_{40}]^{4-}$, and CH_3OH as predicted by a simple kinetic scheme. The maximum rate depended on competition between the natural decay of the excited polyanion and quenching by alcohol. Electron transfer from photoreduced polyanions to O_2 was also investigated by flash photolysis. Rate constants depended on the reduction potential of the polyanion and increased by a factor of 3 700 on going from $[PW_{12}O_{40}]^{3-}$ to $[FeW_{12}O_{40}]^{5-}$, in line with the Marcus equation for adiabatic electron-transfer reactions.

Heteropolyanions such as $[SiW_{12}O_{40}]^{4-}$ can be reduced in a series of reversible steps to give the familiar heteropoly blue compounds.[1] As a result they are widely used as redox catalysts for multi-electron transfer reactions,[2] such as the iodometric determination of H_2O_2.[3] The polyanions can also be photoreduced in the presence of organic electron donors such as alcohols.[4,5] In the case of polytungstates, the blue compounds which are formed are moderate reducing agents, so that these polyanions can sensitize the photochemical reduction of oxygen and water.[6,7] Both of these reactions have been suggested as potential routes for conversion and storage of solar energy.[5-9] Cuendet and Grätzel[10] recently established that sodium metatungstate, $Na_6[H_2W_{12}O_{40}]$, can act as a redox relay in the photoreduction of water by chloroplasts.[10] In a preliminary communication one of us demonstrated that platinum sols catalyse the photosensitized reduction of water by $[SiW_{12}O_{40}]^{4-}$.[6] Here we wish to report this work in detail together with a comparison of other polytungstates and a discussion of the effect of redox potential on the rate of electron transfer from reduced polyanions to O_2.

Experimental

Steady-state experiments were performed with an Applied Photophysics UV90 photoirradiation system using a 900-W xenon lamp and monochromator. Light intensities were measured with a calibrated thermopile and absorption spectra were recorded with a Perkin-Elmer 554 spectrophotometer. Conventional flash photolysis measurements were made with an Applied Photophysics K200 system using quartz cells with a 10-cm path length. For H_2 evolution solutions were purged with N_2 before illumination. In a typical experiment 50 cm³ of solution was illuminated in a 75-cm³ Pyrex flask together with a Pyrex cut off ($\lambda > 300$ nm) filter and a 5-cm cold water infrared filter. H_2 was detected by injecting 50 µl from the gas phase above the solution into a Perkin-Elmer Sigma 4B gas chromatograph.

Colloidal platinum was formed by boiling aqueous sodium citrate (160 cm³, 1.7×10^{-3} mol dm^{-3}) and $H_2[PtCl_6]$ (2.4×10^{-4} mol dm^{-3})[11] for 4 h. Sodium metatungstate, $Na_6[H_2W_{12}O_{40}]$,[10,12] 12-tungstoferric acid, $H_5[FeW_{12}O_{40}]$,[13] and potassium monohydrogen 12-tungstocobaltate, $K_5H[CoW_{12}O_{40}]$,[14] were prepared by established methods. $Na_3[PW_{12}O_{40}]$, $K_4[SiW_{12}O_{40}]$, and H_2SO_4 were supplied by B.D.H. Solutions of the polytungstates were made with doubly-distilled water and Pr^{i}OH was distilled at 81.5 °C.

Results and Discussion

Hydrogen Generation.—Anaerobic solutions of $[SiW_{12}O_{40}]^{4-}$ are rapidly photoreduced in the presence of alcohols to give a deep blue species $[SiW_{12}O_{40}]^{5-}$ ($\lambda_{max.}$ 730 nm). Colloidal platinum is known to catalyse the reduction of water by reduced methyl viologen (1,1′-dimethyl-4,4′-bipyridinium),[15,16] metal ions (Cr^{2+} and Eu^{2+}),[16] and organic radicals such as $Ph_2\dot{C}OH$.[17] When colloidal platinum was added to solutions of $[SiW_{12}O_{40}]^{4-}$ and the samples illuminated with near-u.v. light ($\lambda > 300$ nm), production of the blue polyanion was inhibited and H_2 was evolved. The rate of H_2 generation is illustrated in Figure 1. Over a period of 11 h, 0.5 mmol of H_2 was produced from a sample containing 50 µmol of $[SiW_{12}O_{40}]^{4-}$ and 0.4 µmol of Pt, indicating that the process is truly catalytic with respect to $[SiW_{12}O_{40}]^{4-}$ and Pt. During this time H_2 evolution dropped to 20% of the initial rate, although less than 1% of the methanol had been consumed. When an additional aliquot of Pt (2.4×10^{-6} mol dm^{-3}) was added, the rate returned to nearly the initial high rate [curve (*b*) in Figure 1]. This suggests that the decrease in rate is due to loss of the colloidal catalyst, which tends to precipitate at the high ionic strengths (0.5 mol dm^{-3} H_2SO_4) used in this study.

No H_2 was detected in the absence of light, $[SiW_{12}O_{40}]^{4-}$, or methanol, although trace amounts (5 µl h^{-1}) were observed when

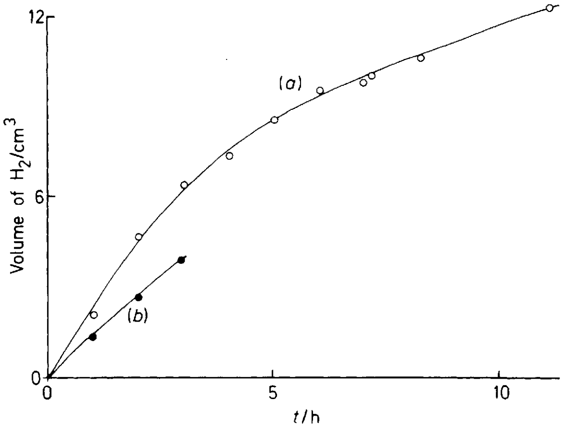

Figure 1. (*a*) Evolution of H_2 from a solution containing 10^{-3} mol dm^{-3} $[SiW_{12}O_{40}]^{4-}$, H_2SO_4 0.5 mol dm^{-3}, 2.4×10^{-5} mol dm^{-3} Pt, and 10% CH_3OH; (*b*) is a continuation of (*a*) after addition of a fresh aliquot of Pt ($\lambda > 300$ nm)

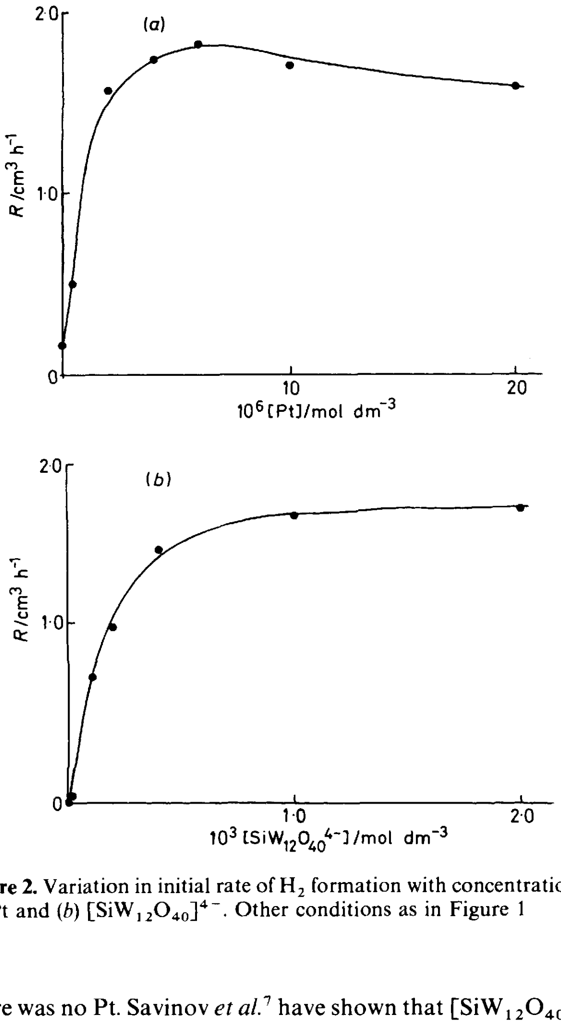

Figure 2. Variation in initial rate of H_2 formation with concentration of (*a*) Pt and (*b*) $[SiW_{12}O_{40}]^{4-}$. Other conditions as in Figure 1

there was no Pt. Savinov *et al.*[7] have shown that $[SiW_{12}O_{40}]^{4-}$ will reduce water directly *via* the doubly-reduced anion $[SiW_{12}O_{40}]^{6-}$.[7] In the absence of Pt, $[SiW_{12}O_{40}]^{4-}$ can be photoreduced through $[SiW_{12}O_{40}]^{5-}$ to give $[SiW_{12}O_{40}]^{6-}$, which can then slowly reduce water to give H_2.

The effect of Pt and $[SiW_{12}O_{40}]^{4-}$ concentrations on the initial rate of H_2 formation is described in Figure 2. Low concentrations of $[SiW_{12}O_{40}]^{4-}$ and Pt lead to a dramatic increase in the rate of H_2 formation, which reaches a maximum value at *ca.* 10^{-3} mol dm^{-3} $[SiW_{12}O_{40}]^{4-}$ and *ca.* 10^{-5} mol dm^{-3} Pt. The rate decreases slightly for higher Pt concentrations. Simple saturation kinetics might have been expected, since at higher concentrations ($>10^{-5}$ mol dm^{-3}) sufficient Pt will be available to scavenge all of the $[SiW_{12}O_{40}]^{5-}$.

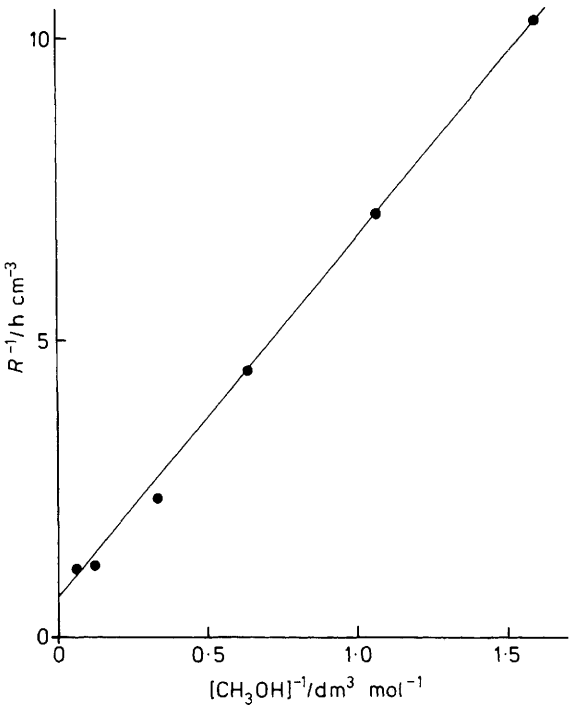

Figure 3. Double reciprocal plot of initial rate of H_2 formation against concentration of CH_3OH. Other conditions as in Figure 1

The simplest mechanism consistent with these observations would involve reactions (1)—(5) shown below, where I_A (mol dm^{-3} s^{-1}) is the rate of photon absorption by $[SiW_{12}O_{40}]^{4-}$ and α is the quantum yield for production of the reactive excited state, $[{}^*SiW_{12}O_{40}]^{4-}$. k_D (s^{-1}) is the rate constant for the decay of $[{}^*SiW_{12}O_{40}]^{4-}$. $\dot{C}H_2OH$ is a strong reducing agent [$E_{\frac{1}{2}} = -1.1$ V *vs.* saturated calomel electrode (s.c.e.)][18] and is known to react with $[SiW_{12}O_{40}]^{4-}$ at a rate close to the diffusion limit ($k_R = 9.1 \times 10^8$ dm^3 mol^{-1} s^{-1})[19] so that two $[SiW_{12}O_{40}]^{5-}$ ions are produced per photon, *via* reactions (3) and (4). Above 10^{-5} mol dm^{-3} Pt, $[{}^*SiW_{12}O_{40}]^{4-}$ and $[SiW_{12}O_{40}]^{5-}$ rapidly establish a photostationary state, in which the rate of H_2 (R/mol dm^{-3} s^{-1}) generation is controlled by reactions (1), (2), and (3). Consequently the steady-state approximation can be applied to $[{}^*SiW_{12}O_{40}]^{4-}$ and $[SiW_{12}O_{40}]^{5-}$ in which case equation (6) and hence equation (7) apply. Figure 3 shows a plot of $1/R$

$$R = \frac{d[H_2]}{dt} = \frac{k_Q \alpha I_A [CH_3OH]}{k_D + k_Q[CH_3OH]} \qquad (6)$$

$$1/R = 1/\alpha I_A + k_D/\alpha I_A k_Q [CH_3OH] \qquad (7)$$

against $1/[CH_3OH]$, which agrees well with equation (7). From this Figure, αI_A is 1.7×10^{-6} mol dm^{-3} s^{-1} and k_D/k_Q is 10 mol dm^{-3}.

Equation (6) also predicts that the rate of H_2 formation will depend on I_A and hence on the concentration of $[SiW_{12}O_{40}]^{4-}$. From the Beer–Lambert law [equation (8)], where ε is the absorption coefficient for $[SiW_{12}O_{40}]^{4-}$, L is the pathlength (5

Rate (mol dm^{-3} s^{-1})

$$[SiW_{12}O_{40}]^{4-} + h\nu \longrightarrow [{}^*SiW_{12}O_{40}]^{4-} \qquad \alpha I_A \quad (1)$$

$$[{}^*SiW_{12}O_{40}]^{4-} \longrightarrow [SiW_{12}O_{40}]^{4-} \qquad k_D[{}^*SiW_{12}O_{40}{}^{4-}] \quad (2)$$

$$[{}^*SiW_{12}O_{40}]^{4-} + CH_3OH \longrightarrow [SiW_{12}O_{40}]^{5-} + \dot{C}H_2OH + H^+ \qquad k_Q[{}^*SiW_{12}O_{40}{}^{4-}][CH_3OH] \quad (3)$$

$$\dot{C}H_2OH + [SiW_{12}O_{40}]^{4-} \longrightarrow [SiW_{12}O_{40}]^{5-} + CH_2O + H^+ \qquad k_R[\dot{C}H_2OH][SiW_{12}O_{40}{}^{4-}] \quad (4)$$

$$2[SiW_{12}O_{40}]^{5-} + 2H^+ + Pt \longrightarrow 2[SiW_{12}O_{40}]^{4-} + Pt + H_2 \qquad (5)$$

$$\log\left(\frac{I_0}{I_0 - I_A}\right) = \varepsilon L[\mathrm{SiW_{12}O_{40}}^{4-}] \qquad (8)$$

cm), and I_0 is the incident light intensity, the maximum rate ($R_{\mathrm{max.}}$) for a given CH_3OH concentration will occur when all available protons are absorbed by $[SiW_{12}O_{40}]^{4-}$, *i.e.* when I_A

$$\log\left(\frac{R_{\mathrm{max.}}}{R_{\mathrm{max.}} - R}\right) = \varepsilon L[\mathrm{SiW_{12}O_{40}}^{4-}] \qquad (9)$$

equals I_0; hence equation (9). Equation (9) is plotted in Figure 4 and gives $\varepsilon = 400$ dm^3 mol^{-1} cm^{-1} which is close to the absorption coefficient for $[SiW_{12}O_{40}]^{4-}$ at 340 nm ($\varepsilon = 500$ dm^3 mol^{-1} cm^{-1}). Equation (9) clearly explains the variation in rate of H_2 formation with $[SiW_{12}O_{40}]^{4-}$ concentration which was shown in Figure 2(*b*). The good agreement between the absorption coefficients also shows that the photoactive species is derived from $[SiW_{12}O_{40}]^{4-}$ and the rate of H_2 evolution is proportional to I_A.

Dihydrogen formation also showed a marked pH dependence. This is illustrated by Figure 5. Since the blue reduced polyanion $[SiW_{12}O_{40}]^{5-}$ is formed at a constant rate in this pH range, the drop in rate probably reflects the close balance between the redox potential of $[SiW_{12}O_{40}]^{4-}$ ($E_{\frac{1}{2}} = -0.187$ V *vs.* s.c.e.)[1] and water [$E_0' = -(0.24 + 0.059\ \mathrm{pH})$ V *vs.* s.c.e.]. The redox potential for the polyanion is independent of pH,[1] whereas the potential for water becomes more negative as the pH increases in line with the Nernst equation. As a result reduction of water by $[SiW_{12}O_{40}]^{5-}$ is only thermodynamically favourable at high proton concentrations.

Figure 5 also shows the relative rates of H_2 evolution for a range of aliphatic alcohols (Pr^{n}OH, EtOH, MeOH, and Pr^{i}OH). Equation (6) will apply to all four alcohols so that the variation in H_2 generation will reflect changes in k_Q. This will have the largest value for those alcohols which possess readily abstractable H atoms.

Four other polyanions, $[XW_{12}O_{40}]^{n-}$ (X = P, Fe, Co, or H_2; n = 3, 5, 6, and 6 respectively), which are structurally related to $[SiW_{12}O_{40}]^{4-}$, were also tested for their ability to sensitize the reduction of water. Results for all five of the polytungstates are summarized in the Table which also includes the first reduction potentials[1] for these anions in 0.05 mol dm^{-3} H_2SO_4 and the relative quantum yields for formation of the reduced blue compounds $[XW_{12}O_{40}]^{(n+1)-}$ (X = P, Si, or H_2; n = 3, 4, and 6 respectively) and $[XW_{12}O_{40}]^{(n+2)-}$ (X = Fe or Co; n = 5 and 6 respectively). In the case of $[CoW_{12}O_{40}]^{6-}$ and $[FeW_{12}O_{40}]^{5-}$ the absorption spectra showed that only the doubly-reduced anions were formed ($\lambda_{\mathrm{max.}}$ = 630 nm for $[CoW_{12}O_{40}]^{8-}$ and $[FeW_{12}O_{40}]^{7-}$).[20] Although the rate of H_2 production increased on going from $[PW_{12}O_{40}]^{3-}$ to $[SiW_{12}O_{40}]^{4-}$, the most notable feature in the Table is the large decrease in the yield of polyanion as the reduction potential of $[XW_{12}O_{40}]^{n-}$ becomes more negative. Thus the low reduction

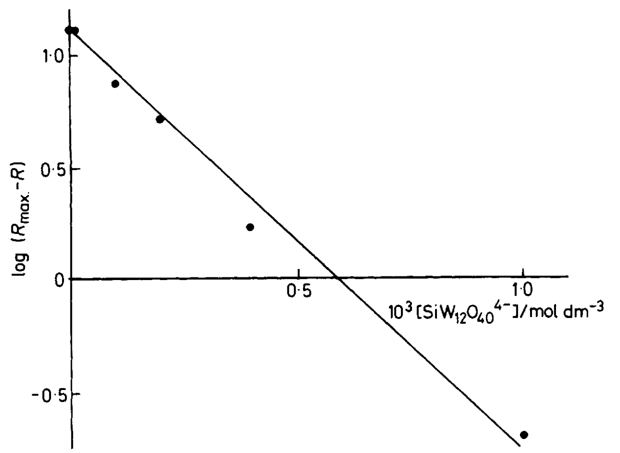

Figure 4. Plot of equation (9) showing that $[SiW_{12}O_{40}]^{4-}$ concentration affects the initial rate of H_2 formation in line with the Beer–Lambert law

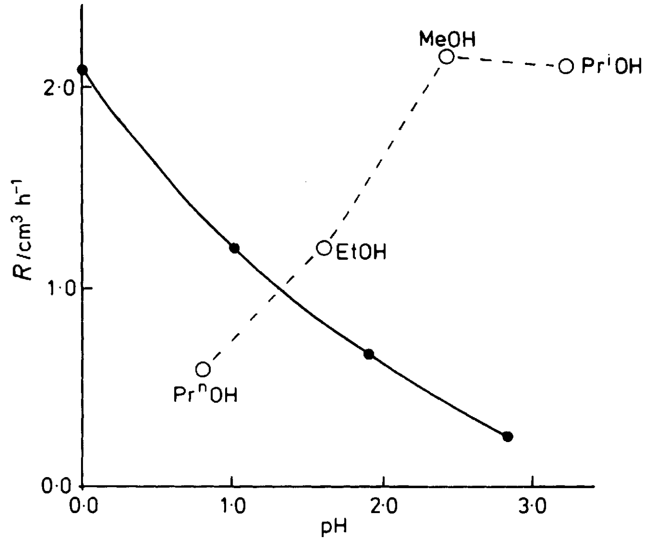

Figure 5. Effect of pH (●) and type of alcohol (○) on the initial rate of H_2 generation. The pH scale does not refer to the different alcohols where the experiments were all performed in 0.5 mol dm^{-3} H_2SO_4. Other conditions as in Figure 1

Table. Relative quantum yields and rate constants for the formation of reduced polyanions, photoreductions of water, and electron transfer to O_2

Anion	E/V[a]	$\Phi_{\mathrm{rel.}}[XW_{12}O_{40}]^{(n+1)-}$[b]	$\Phi_{\mathrm{rel.}}H_2$[c]	$k_{\mathrm{obs.}}/\mathrm{s}^{-1}$[d]
$[PW_{12}O_{40}]^{3-}$	−0.023	1.00	0.04	15 × 10^{-3}
$[SiW_{12}O_{40}]^{4-}$	−0.187	0.70	1.00	1.3
$[FeW_{12}O_{40}]^{5-}$	−0.410[e]	0.09[e]	0.01[e]	56[e]
$[H_2W_{12}O_{40}]^{6-}$	−0.403	0.13	0.20	35
$[CoW_{12}O_{40}]^{6-}$	−0.390	0.004	0.00	

[a] Reduction potential for first reduction step at pH 1.0 from ref. 1 *vs.* s.c.e. [b] Relative quantum yields for formation of reduced polyanions; conditions as in Figure 1 except [Pt] = 0. [c] Relative quantum yields for H_2 generation. Conditions as Figure 1. Absolute quantum yield for λ = 340 nm was 0.1 for 10^{-3} mol dm^{-3} $[SiW_{12}O_{40}]^{4-}$, 0.5 mol dm^{-3} H_2SO_4, 15 mol dm^{-3} CH_3OH, and 10^{-5} mol dm^{-3} Pt. [d] Observed pseudo-first-order rate constants for electron transfer to O_2 ([O_2] *ca.* 2 × 10^{-4} mol dm^{-3}), [H^+] 10^{-1} mol dm^{-3}. [e] Doubly-reduced anion was formed for $[FeW_{12}O_{40}]^{5-}$ at this pH.

potential of $[H_2W_{12}O_{40}]^{6-}$ will favour H_2 formation in reaction (5), but this benefit is offset by the low yield of $[H_2W_{12}O_{40}]^{7-}$, which results from the competition between reactions (2) and (3). This yield will depend on the ratio k_Q/k_D and k_Q is expected to decrease, in line with the Marcus equation,[21] as reaction (3) becomes less thermodynamically favourable. In addition, low-energy metal centred *d–d* transitions are likely to reduce the excited state lifetimes of $[CoW_{12}O_{40}]^{6-}$ and $[FeW_{12}O_{40}]^{5-}$.

Kinetics of O_2 *Reduction.*—Polyanions can sensitize the photo-oxidation of alcohols by transferring an electron from $[XW_{12}O_{40}]^{(n+1)-}$ [generated as in reactions (1)—(3)] to O_2 to form superoxide. In the pH range in this study, superoxide will be protonated ($pK_a = 4.69$),[22] equation (10). This process is

$$[XW_{12}O_{40}]^{(n+1)-} + O_2 + H^+ \longrightarrow [XW_{12}O_{40}]^{n-} + HO_2^{\bullet} \qquad (10)$$

also important in many of the systems where polyanions are used as redox catalysts.[2] Reaction (10) would severely limit the applicability of polyanions as redox relays for water photolysis. $[XW_{12}O_{40}]^{(n+1)-}$ can be produced photochemically in the presence of alcohols, so that electron transfer to O_2 can be monitored directly by microsecond flash photolysis.

When a solution containing $[XW_{12}O_{40}]^{n-}$ ions (2×10^{-6} mol dm^{-3}) and Pr^{i}OH (1.7 mol dm^{-3}) was subjected to a 10-μs photoflash, $[XW_{12}O_{40}]^{(n+1)-}$* was produced during the flash and readily detected by its broad absorption above 400 nm. In anaerobic solutions $[XW_{12}O_{40}]^{(n+1)-}$*was produced as a permanent product but when O_2 was present the signal due to $[XW_{12}O_{40}]^{(n+1)-}$ decays away rapidly. The decay rate was first order with respect to $[XW_{12}O_{40}{}^{(n+1)-}]$ and $[O_2]$ (2×10^{-4}—10^{-3} mol dm^{-3}). It was also proportional to the proton concentration, which suggests that $HO_2^{\bullet}$ is formed in the rate-determining step rather than O_2 [equation (11)]. The con-

$$-\frac{d[XW_{12}O_{40}{}^{(n+1)-}]}{dt} = k[XW_{12}O_{40}{}^{(n+1)-}][H^+][O_2] = k_{obs.}[XW_{12}O_{40}{}^{(n+1)-}] \qquad (11)$$

centration of $[XW_{12}O_{40}]^{(n+1)-}$ formed during the flash was (5—8) $\times 10^{-7}$ mol dm^{-3}, so that at pH 1.0 and $[O_2] = 2 \times 10^{-4}$ mol dm^{-3} the reaction was always pseudo-first-order and the values for $k_{obs.}$ (s^{-1}) are collected in the Table.

The value of $k_{obs.}$ increases by a factor of 3 700 on going from $[PW_{12}O_{40}]^{3-}$ to $[FeW_{12}O_{40}]^{5-}$. This large change as $E_{\frac{1}{2}}$ decreases agrees well with predictions based on the Marcus equation[21] and related theories for adiabatic electron-transfer reactions.[23] Marcus has suggested that the free energy of activation ($\Delta G^{\neq}$) will be related to the overall free energy change ($\Delta G^{\ominus}$) for the electron-transfer reaction and the reorganization energy, λ, according to equation (12).

$$\Delta G^{\neq} = \frac{\lambda}{4}(1 + \Delta G^{\ominus}/\lambda)^2 \qquad (12)$$

$$k = Z \exp(-\Delta G^{\neq}/RT) \qquad (13)$$

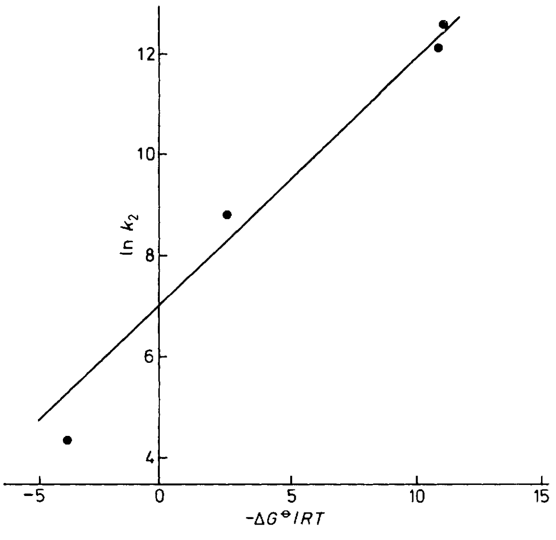

Figure 6. Effect of overall free energy change on the second-order rate constant for electron transfer to O_2; k_2 was calculated assuming an O_2 concentration of 2×10^{-4} mol dm^{-3} in air-equilibrated samples. Other conditions: $[XW_{12}O_{40}{}^{n-}] = 10^{-6}$ mol dm^{-3} (X = P, Si, Fe, Co, or H_2; *n* = 3, 4, 5, 6, and 6 respectively), 0.05 mol dm^{-3} H_2SO_4, 10% Pr^{i}OH)

For reactions in solution equation (13) applies, where *Z* is the collision frequency (*ca.* 10^{11} dm^3 mol^{-1} s^{-1}).[24] Combining (12) and (13) gives (14). When $(\Delta H^{\ominus})^2$ is small compared to $4RT\lambda$ this simplifies to the linear equation (15). This relationship is

$$\ln k = \ln Z - \frac{\lambda}{4RT} - \frac{\Delta G^{\ominus}}{2RT} - \frac{(\Delta G^{\ominus})^2}{4RT\lambda} \qquad (14)$$

$$\ln k = \ln Z - \frac{\lambda}{4RT} - \frac{\Delta G^{\ominus}}{2RT} \qquad (15)$$

plotted in Figure 6, where $\Delta G^{\ominus}$ was calculated for reaction (10) with $E_0{}'$ ($O_2/HO_2^{\bullet}$) equal to −0.12 V (*vs.* s.c.e.) at pH 0.0.[22] The line plot has a slope of 0.5 in agreement with equation (15). Also from this figure ln $Z - (\lambda/4RT) = 7.0$. If the collision frequency is 10^{11} dm^3 mol^{-1} s^{-1}, then the reorganization energy (λ) is 180 kJ mol^{-1}. This large value shows that $(\Delta G^{\ominus})^2$ is much less than $4RT\lambda$, so that equation (15) is justified. $[XW_{12}O_{40}]^{n-}$ anions are large symmetrical molecules with a hydrodynamic radius of 5.6 Å and are thought to show very little distortion following reduction.[1] Consequently the large value of λ presumably reflects desolvation of H^+ and changes in the geometry of O_2 on forming HO_2.†

Conclusions

The photoreduction of water by alcohols has been optimized with $[SiW_{12}O_{40}]^{4-}$ as sensitizer. Alternative polyanions, with a more negative reduction potential, are less efficient due to lower yields of $[XW_{12}O_{40}]^{(n+1)-}$. In contrast $[PW_{12}O_{40}]^{3-}$ is photoreduced more rapidly than $[SiW_{12}O_{40}]^{4-}$ but also produces H_2 more slowly, since its less negative reduction potential results in a low rate of electron transfer to the Pt catalyst. The energy stored in this reaction is small (0.57 eV) in comparison with the minimum energy required to excite the polyanions (3.2 eV). If polyanions are to be used for solar energy conversion, it will be necessary to find suitable additional sensitizers which extend the photoresponse of the system across the visible spectrum. This is not a trivial problem, since the large polyanions form insoluble salts with most

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* $[XW_{12}O_{40}]^{(n+2)-}$ for X = Fe and Co.

† We are grateful to one referee, who drew attention to the applicability of equation (12). In this case, where the reorganization energies for the separate redox couples may be very different (λ_1, λ_2), then it is unlikely that the normal cross-reaction formula (ref. 21), $\lambda = \frac{1}{2}(\lambda_1 + \lambda_2)$, will apply and the absolute numerical relationship between λ and λ_1 is not known.

cationic dyes, and alternative anionic sensitizers generally protonate and dimerize at high acid strengths, which were employed in this study.

Electron transfer from the reduced polyanions to O_2 showed excellent agreement with the Marcus theory. The rate constants for this reaction ranged from 75 $dm^3 mol^{-1} s^{-1}$ for $[PW_{12}O_{40}]^{3-}$ to 2.8×10^5 $dm^3 mol^{-1} s^{-1}$ for $[FeW_{12}O_{40}]^{5-}$ and were well below the diffusion limit.

Acknowledgements

This work was supported by the S.E.R.C. and London University Central Research Fund.

References

1 M. T. Pope and G. M. Varga, *Inorg. Chem.*, 1966, **5**, 1249.
2 I. V. Kozhevnikov and K. I. Matveev, *Russ. Chem. Rev.*, 1982, **51**, 1075.
3 J. A. Basset, R. C. Denney, G. H. Jeffrey, and J. Mendham, in 'Vogel's Textbook of Quantitative Inorganic Analysis,' Longman, London, 1978.
4 L. Chalkley, *J. Phys. Chem.*, 1952, **56**, 1084.
5 E. Papaconstantinou, *J. Chem. Soc., Chem. Commun.*, 1982, 12.
6 J. R. Darwent, *J. Chem. Soc., Chem. Commun.*, 1982, 798.
7 E. N. Savinov, S. S. Saidkhanov, V. N. Parmon, and K. I. Zamaraev, *React. Kinet. Catal. Lett.*, 1981, **17**, 407.
8 E. Papaconstantinou, D. Dimoticali, A. Ionnidis, and P. Argitis, *J. Photochem.*, 1981, **17**, 171.
9 T. Yamase, *Inorg. Chim. Acta*, 1982, **64**, L155 and refs. therein.
10 P. Cuendet and M. Grätzel, *Photochem. Photobiol.*, 1982, **36**, 203.
11 R. M. Wilenzick, D. C. Russell, and R. H. Morriss, *J. Chem. Phys.*, 1967, **47**, 533.
12 J. A. Mair, *J. Chem. Soc.*, 1950, 2364; D. H. Brown and J. A. Mair, *ibid.*, 1962, 1512.
13 M. L. Freedman, *J. Am. Chem. Soc.*, 1959, **81**, 3834.
14 V. E. Simmons, Doctoral Dissertation, Boston University, 1963.
15 J. Kiwi and M. Grätzel, *Nature (London)*, 1979, **281**, 657.
16 B. V. Koryakin, T. S. Dzhabiev, and A. E. Shilov, *Dokl. Akad. Nauk. SSSR*, 1977, **233**, 620.
17 C. K. Grätzel and M. Grätzel, *J. Am. Chem. Soc.*, 1979, **101**, 7741.
18 J. Lilie, G. Beck, and A. Henglein, *Ber. Bunsenges Phys. Chem.*, 1971, **75**, 458.
19 E. Papaconstantinou, *J. Chem. Soc., Faraday Trans. 1*, 1982, 2769.
20 G. M. Varga, E. Papaconstantinou, and M. T. Pope, *Inorg. Chem.*, 1970, **9**, 662.
21 R. A. Marcus, *J. Phys. Chem.*, 1963, **67**, 853; *Ann. Rev. Phys. Chem.*, 1964, **15**, 155; *J. Chem. Phys.*, 1965, **43**, 679.
22 D. T. Sawyer and J. S. Valentine, *Acc. Chem. Res.*, 1981, **14**, 393.
23 D. Rehm and A. Weller, *Ber. Bunsenges Phys. Chem.*, 1968, **72**, 839.
24 W. J. Albery, *Ann. Rev. Phys. Chem.*, 1980, **31**, 227.

Received 14*th May* 1984; *Paper* 4/785