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Photochemistry of Polyoxometallates of Molybdenum and Tungsten and/or Vanadium

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1 Introduction

Over the past few years polyoxometallates (as they are now generally called), heteropoly (HPC) and isopoly compounds, have received increasing attention because of their participation in important industrial processes. Molybdenum and tungsten oxides and sulphides, and polyoxometallates in general, are extensively used as catalysts in a variety of commercially important chemical processes, such as hydrocracking, hydrogenation, isomerization, polymerization *etc.*[1] The blue reduction products of HPC, the so called heteropoly blues (HPB), are used in analytical chemistry in the colorimetric determination of several elements such as P, Si, As, Ge, and in biochemistry for determining uric acid, sugar *etc.*[2] Their ability to accept and release electrons has found use in efforts to elucidate the various steps in photosynthesis.[3] The motion of the electrons within the crystal lattice can be affected by applying an external potential. Several oxides in an externally applied electric field acquire a blue colour which disappears when the polarity is reversed. The electrochromism of these compounds is of interest because of its possible use in digital display devices.[4] The potentiality of these compounds in photochemical work was recognized in the past[5] and has been patented for possible use in photography.[6] Various Russian workers have investigated the photochemistry of molybdenum and tungsten for analytical purposes.[7]

Although various papers and review articles have concentrated on the general characteristics[8] of polyoxometallates and on thermal catalysis,[9] very little has been presented in the relatively new field of photocatalysis.

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[1] See for instance: (*a*) C. H. Kline and V. Kollonitsch, *Ind. Eng. Chem.*, 1965, **57**, 53; (*b*) G. A. Tsigdinos, 'Heteropoly Compounds of Molybdenum and Tungsten', Bulletin Cdb-12a Climax Molybdenum Co. of Michigan, U.S.A.

[2] (*a*) A. I. Vogel, 'A Text Book of Quantitative Inorganic Analysis', 3rd Edn., Wiley and Sons Inc., N.Y., 1966; (*b*) H. Wu, *J. Biol. Chem.*, 1920, **43**, 189.

[3] (*a*) See for instance: R. M. Bekina, A. F. Lebedeva, and V. A. Shuvalov, *Dokl. Akad. Nauk SSSR*, 1976, **231**, 739 (English translation); (*b*) S. P. Berg and S. Izava, *Biochim. Biophys. Acta*, 1977, **460**, 206.

[4] R. J. Cotton, A. M. Guzman, and J. W. Rabalais, *Acc. Chem. Res.*, 1978, **11**, 170.

[5] M. Rindl, *S. Afr. J. Sci.*, 1916, **11**, 362.

[6] L. Chalkley, *J. Phys. Chem.*, 1952, **56**, 1084.

[7] See for instance: (*a*) A. A. Nemodruk and E. V. Bezrogova, *Zh. Anal. Khim.*, 1969, **24**, 292 (English translation); (*b*) S. A. Morosanova, N. Ya. Kolli, and T. G. Kushinirenka, *ibid.*, 1977, **32**, 96; (*c*) M. N. Ptushkina and L. I. Lebedeva, *ibid.*, 1979, **49**, 1433.

This review gives a brief overall account of the thermal catalytic properties of polyoxometallates so that comparisons can be made between this field and polyoxometallate photocatalysis, which is the main subject of this review article. It is by no means an exhaustive literature survey of the subject. It presents ideas and thoughts developed by various workers over the past ten years or so, giving an edge, unavoidably, to our own work.

2 General Characteristics

A. Definition, Preparation, Structure.—HPC and isopoly electrolytes constitute large fundamental categories of polyoxometallates. Their general formula may be presented as: $[M_mO_y]^{p-}$ for isopoly anions, and $[X_xM_mO_y]^{q-}$ $(x < m)$ for heteropoly anions. M is usually Mo or W and to a lesser extent V, Nb, or Ta. The heteroatom X, can be one of 64 elements that belong to various groups of the periodic table except the noble gases. There exist also mixed polyoxometallates with general formulae $[M_mM'_nO_y]^{p-}$ and $[X_xM_mM'_nO_y]^{q-}$, where M can be one of the above metals or other metals. The metals are in high oxidation states (d^0, d^1).

Taking into consideration the various possible ratios m/x and the different atoms M, M′, and X that can participate in the formation of these compounds, the polyoxometallate field is indeed very large.

Typical examples that will be dealt with in this review are molybdates and tungstates with ratios x/m of 1/12 and 2/18—designated for simplicity as $X_xM_m{}^{q-}$ (*i.e.* $PW_{12}O_{40}^{3-} = PW_{12}^{3-}$)—and the corresponding mixed tungsto- and molybdovanadates; from the isopoly electrolytes section, the cases of $Mo_7O_{24}^{6-}$ and $W_{10}O_{32}^{4-}$ will be considered. Since this article deals mostly with heteropoly compounds (HPC), we will frequently refer to polyoxometallates as HPC and to their reduced products, heteropoly blues, as (HPB).

Polyoxometallates are generally prepared by the condensation reaction occurring upon acidification of solutions of MoO_4^{2-} or WO_4^{2-}. Whereas chromium, of the same group, undergoes upon acidification only dimerization ($Cr_2O_7^{2-}$ from CrO_4^{2-}), MoO_4^{2-} and WO_4^{2-} form a series of polyoxometallates (isopoly compounds) in equilibria with each other, typical representatives of which are $Mo_7O_{24}^{6-}$, $Mo_8O_{26}^{4-}$, $W_{10}O_{32}^{4-}$, and $H_2W_{12}O_{40}^{6-}$.[10] If the condensation takes place in the presence of a so called heteroatom X, *i.e.* P^{5+}, As^{5+}, Si^{4+}, Fe^{3+} *etc.* as mentioned earlier, the heteroatom becomes incorporated into the polyoxometal-

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[8] (*a*) M. T. Pope, 'Heteropoly and Isopoly Oxometallates' in 'Inorganic Chemistry Concepts 8', ed. C. K. Jorgensen *et al.*, Springer Verlag, West Berlin, 1983; (*b*) L. C. W. Baker in Advances in Chemistry of Coordination Compounds', ed. S. Kirschner, MacMillan, New York, 1961; (*c*) P. Souchay, 'Polyanions et Polycations', Gauthier-Villars, Paris, 1963; (*d*) T. J. R. Weakley, *Struct. Bonding* (*Berlin*), 1974, **18**, 131; (*e*) G. A. Tsigdinos, *Top. Curr. Chem.*, 1978, **76**, 1; (*f*) D. L. Kepert, 'Isopoly and Heteropolyanions' in 'Comprehensive Inorganic Chemistry', ed. J. C. Banlar, Jr., *et al.*, Pergamon Press, Oxford, 1973, Vol. 4, p. 607.

[9] (*a*) I. V. Kazhevnikov and K. I. Matveev, *Russ. Chem. Rev.*, 1982, **51**, 11; (*b*) N. Mizuko, K. Katamura, Y. Yoneda, and M. Misono, *J. Catal.*, 1983, **83**, 384; (*c*) Y. Izumi, K. Matsuo, and K. Urabe, *J. Mol. Catal.*, 1983, **18**, 299; (*d*) M. Misono, *Cat. Rev.*, 1987, **29**, 269.

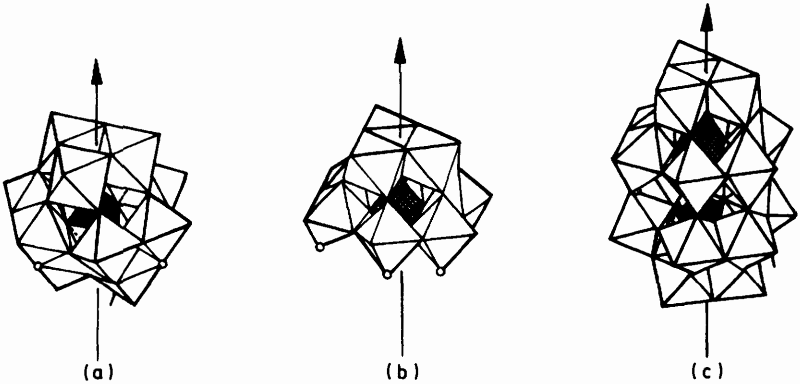

Figure 1 (*a*) *Keggin structure*[11] *for a* 1:12 *heteropoly anion. A* Mo *or* W *atom is within each octahedron, the heteroatom is within the central tetrahedron; a typical example is* $PW_{12}O_{40}^{3-}$. (*b*) *The half unit* PW_9O_{34} *from which the* 2:18 *heteropoly anions,* $P_2W_{18}O_{62}^{6-}$, *are made.* (*c*) *Dawson structure*[12] *of a* 2:18 *heteropoly anion, for instance* $P_2W_{18}O_{62}^{6-}$

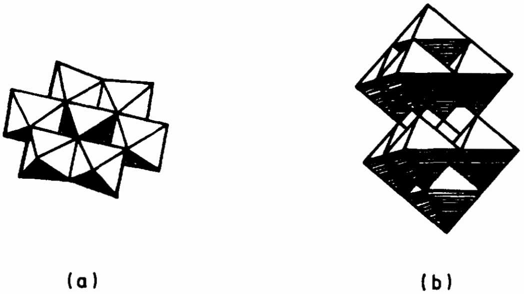

Figure 2 (*a*) *One of the structures in which* $Mo_7O_{24}^{6-}$ *exists.* (*b*) *Structure of* $W_{10}O_{32}^{4-}$

late and HPC are formed.[8] Typical structures of these polyoxometallates are shown in Figures 1 and 2. The 1:12 anions can be considered spherical with a diameter of about 1.2 nm, and the 2:18 anions can be considered as ellipsoids with axes of 1.2 and 1.7 nm. The much larger size of O^{2-} relative to Mo^{6+} and W^{6+} results in essentially a close-packed structure as far as oxygen atoms are concerned.

The structure of a 1:12 species was first elucidated by Keggin in 1933[11] for $PW_{12}O_{40}^{3-}$. Numerous other papers have verified and revealed details of the structure. The structure has an overall *Td* symmetry that is composed of a XO_4 tetrahedron surrounded by twelve MO_6 octahedra. These octahedra are organized in four groups of three MO_6, written as M_3O_{13}. The MO_6 units are

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[10] (*a*) K. H. Tytko and O. Glemser, *Adv. Inorg. Chem. Radiochem.*, 1976, **19**, 239; (*b*) M. T. Pope and B. W. Dale, *Q. Rev. Chem. Soc.*, 1968, **22**, 527; (*c*) E. Pungor and A. Halasz, *J. Inorg. Nucl. Chem.*, 1970, **32**, 1187.

[11] J. F. Keggin, *Nature*, 1933, **131**, 908.

joined to members of the same group through shared edges and to the MO_6 units of other groups and the XO_4 tetrahedron through shared corners.

As to the bonds in the 1:12 series, we distinguish twelve quasilinear M–O–M bonds, twelve M–O–M angular bonds, four X–O–M, and twelve M=O bonds with terminal O atoms.

The basic unit of the 2:18 HPC was elucidated first by Dawson in 1953 for $K_6[P_2W_{18}O_{62}]\cdot 14H_2O$ ($P_2W_{18}^{6-}$).[12] This structure can be thought of as arising from the Keggin structure in the following way: from the Keggin structure three MO_6 units are removed that belong to different M_3O_{13} groups that are in the same vicinity and share corners—the XM_9O_{39} unit results. Two of these units joined together through the free oxygens form the $X_2M_{18}O_{62}^{n-}$ anion. The two heteroatoms X are not joined together through O. The symmetry of the Dawson structure is D_{3h} and is of ellipsoid shape (Figure 1). Two groups of MO_6 octahedra may be considered, a group of six being located in the poles of the long axis and a group of twelve in the equator. By analogy with the 1:12 structure one distinguishes, roughly, the following types of bonds: eighteen M–O–M quasilinear bonds, eighteen M–O–M bent bonds, eight X–O–M bonds, and eighteen M=O bonds with terminal O atoms.

B. Properties.—(i) *Redox Reactions.* The redox chemistry of polyoxometallates is characterized by their ability to accept and subsequently release a certain number of electrons in distinct redox steps without decomposition. This has been shown by various methods, *viz.* potentiometric titrations using Cr^{2+}, Fe^{2+}, Eu^{2+} *etc.*, polarography, photoredox reactions, and high energy radiation through formation of reducing free radicals. The redox chemistry of polyoxometallates has been covered in various reviews.[8] The following is a brief account of these properties that refer mainly to HPC.

(a) Reduction of polyoxometallates proceeds without substantial change of their structure with addition of a certain characteristic number of electrons. On reduction they are coloured mainly blue, producing the so called heteropoly blues (HPB) which have a broad absorption at ~700 nm.

(b) Reduction is often followed by protonation that makes the corresponding potential pH-dependent. A pH increase shifts the redox potentials to more negative values and often splits the two-electron polarographic waves to two one-electron pH-independent waves.[13]

(c) The reduction potentials shift to more negative values with increasing negative charge on HPC.[13a]

(d) Molybdates are reduced more easily than the corresponding tungstates.[14]

(e) The 2:18 HPC are reduced at slightly more positive potentials and retain their structure upon addition of more electrons than the corresponding 1:12 compounds.

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[12] B. Dawson, *Acta Cryst.*, 1953, **6**, 113.

[13] (*a*) M. T. Pope and G. M. Varga, Jr., *Inorg. Chem.*, 1966, **5**, 1249; (*b*) M. T. Pope and E. Papaconstantinou, *Inorg. Chem.*, 1967, **6**, 1147.

[14] E. Papaconstantinou and M. T. Pope, *Inorg. Chem.*, 1967, **6**, 1152.

(f) The reduced HPC are more stable in basic solutions than the corresponding non-reduced compounds.[13] However, in some mixed HPC the reverse has been observed.[15,16]

(g) Addition of electrons beyond a certain number results in distortion of structure, formation of d^2 electronic configuration, and increased metal–metal bond character.[17,18]

(h) In mixed HPC the added electron is localized on the more electronegative metal.[19]

(ii) *Spectra.* Non-reduced polyoxometallates are characterized by O–M charge-transfer bands in the near visible and u.v. area. Generally molybdates absorb at higher wavelengths than tungstates. Upon reduction, polyoxometallates usually turn blue with a broad intense absorption at ~700 nm as mentioned earlier. Because the HPB contain metal ions in different oxidation states they are usually assigned to the category of mixed valence compounds.[20] The location of the electrons is of great interest. Extensive studies by e.s.r., n.m.r., and several other methods have shown that in one-electron reduction of HPC the electron is localized, at low temperatures, on one metal ion. E.s.r. spectra at low temperatures show hyperfine structure and asymmetry that is attributed to a localized electron. At higher temperatures the results indicate 'fast' intra electron-transfer between adjacent metal ions. Addition of a second electron results in the disappearance of the e.s.r. signal, indicating interaction with the metallic ions on which the electrons are located.

Pope has suggested that the two electrons are located on adjacent metal ions.[21] Heteropoly molybdates show no e.s.r. signal,[22] in accordance with the two-electron reduction shown by polarography.

Reduction of polyoxometallates to HPB results in a diminishing of the O–M CT band and in the formation of an intervalence CT band (IVCT) in the visible and near i.r.[13,14,22] (Figure 3). The intensities of absorption are approximately proportional to the number of added electrons. These observations are compatible with the model in which the added electrons enter the metal orbitals that are involved in the O–M CT bands.[22] The near i.r. and visible bands may be assigned in order of increasing energy to IVCT that involve metal ions in the

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[15] N. A. Polotebnova and L. A. Furtune *Russ. J. Inorg. Chem.*, 1969, **14**, 1615.

[16] V. F. Odyakov, L. I. Kuzuetsova, and K. I. Matveev, *Russ. J. Inorg. Chem.*, 1978, **23**, 254.

[17] J. P. Lanuay, *J. Inorg. Nucl. Chem.*, 1976, **38**, 807.

[18] L. P. Kazanskii and J. P. Launay, *Chem. Phys. Lett.*, 1977, **51**, 242.

[19] (*a*) M. T. Pope, S. E. O'Donnel, and R. A. Prados, *Adv. Chem. Ser.*, 1976, **150**, 82; (*b*) R. I. Maksimovskaya, M. A. Fedotov, L. I. Kuzuetsova, V. M. Mastinhin, and K. I. Matveev, *Dokl. Phys. Chem.*, 1975, **223**, 725; (*c*) M. M. Mossoba, C. J. O'Connor, M. T. Pope, E. Sinn, G. Herve, and A. Teze, *J. Am. Chem. Soc.*, 1980, **102**, 6864; (*d*) R. Acerete, S. P. Harmalker, C. F. Hammer, M. T. Pope, and L. C. W. Baker, *J. Chem. Soc., Chem. Commun.*, 1979, 777; (*e*) S. P. Harmalker and M. T. Pope, *J. Am. Chem. Soc.*, 1981, **103**, 7381; (*f*) J. J. Altenan, M. T. Pope, R. A. Prados, and H. So, *Inorg. Chem.*, 1975, **14**, 417.

[20] (*a*) M. B. Robin and P. Day, *Adv. Inorg. Chem. Radiochem.*, 1967, **10**, 247; (*b*) P. Day, *Int. Rev. Phys. Chem.*, 1981, **1**, 149.

[21] R. A. Prados and M. T. Pope, *Inorg. Chem.*, 1976, **15**, 2547.

[22] (*a*) G. M. Varga, Jr., E. Papaconstantinou, and M. T. Pope, *Inorg. Chem.*, 1970, **9**, 662; (*b*) E. Papaconstantinou and M. T. Pope, *ibid.*, 1970, **9**, 667.

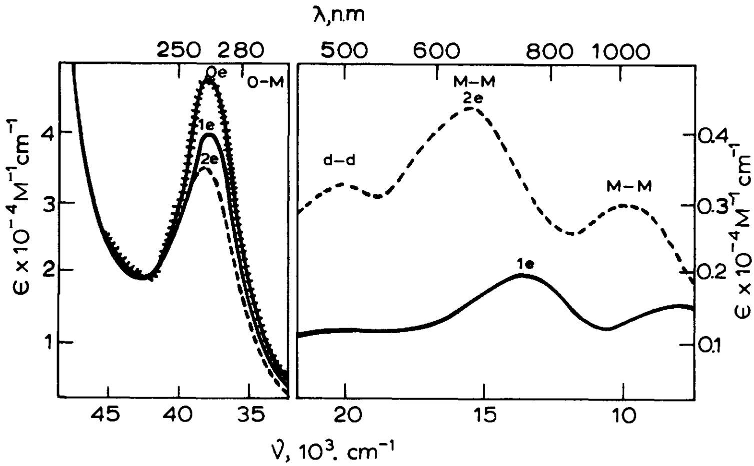

Figure 3 *Visible and near i.r. spectra of* $PW_{12}O_{40}^{3-}$ *in* 1M-H_2SO_4

same M_3O_{13} group of the Keggin structure, in different M_3O_{13} groups, and *d–d* transitions.[23] This assignment has been disputed in its details;[8a] nevertheless, it provides a good overall picture for the subject.

(iii) *Acid–base Properties.* Heteropoly acids (HPA) are strong Brönsted acids.[8] Generally tungstates are stronger acids than molybdates. Detailed pH titrations of the HPA as well as the variation of $E_{\frac{1}{2}}$ with pH have shown that tungstate acids, both the oxidized and the two-electron reduced species, are fully dissociated in aqueous solution whereas molybdates, being stronger bases than tungstates, are protonated upon reduction.[13,14] Figure 4 shows typical variation of $E_{\frac{1}{2}}$ with pH for $P_2W_{18}^{6-}$ and $P_2Mo_{18}^{6-}$, indicating the degree of protonation of reduced anions at various pHs, thus comparing the basicity of molybdate and the corresponding tungstate.

Two types of protons can be distinguished in HPA: hydrated protons that are loosely bound on the anion, and localized protons mainly located on the O-atoms of M–O–M bonds.

In a typical pH titration, Figure 5, addition of base to an HPA reveals the acid protons; further addition of base results in hydrolytic degradation of HPA. In non-aqueous media HPA are much more resistant to solvolysis. The acid strength of various HPA in various solvents is summarized by Matveev.[9a] Generally the acidity of HPA is stronger than the usual inorganic acids. For instance, $H_3PW_{12}O_{40}$ is stronger than both $HClO_4$ and H_2SO_4.

3 Catalytic Activity

A. Thermal Catalysis.—It has been stated earlier that oxides of Mo and W, and

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[23] J. M. Fruchart, G. Herve, J. P. Launay, and R. Mussart, *J. Inorg. Nucl. Chem.*, 1976, **38**, 1627.

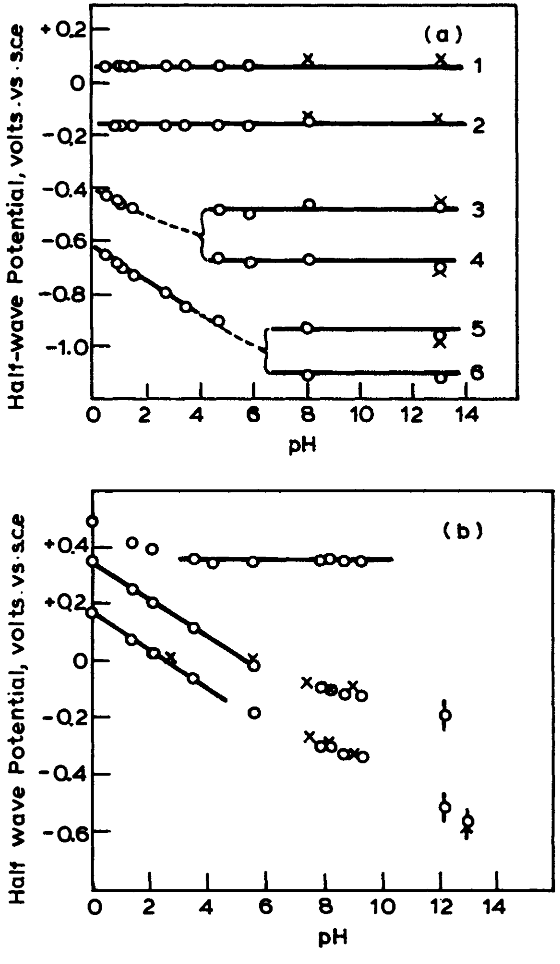

Figure 4 *Variation of half-wave potential with pH for:* (*a*) $P_2W_{18}O_{62}^{6-}$,[13b] (*b*) $P_2Mo_{18}O_{62}^{6-}$.[14]

polyoxometallates, in general, are important industrial catalysts.[1] Currently, there is extensive investigation on the subject by various groups, mainly Japanese and Russian.

It has been generally accepted that the catalytic activity of HPC is due to their acid–base properties, redox properties, and to the 'bulky size' of the anion.[9]

(i) *Ability to Function as Strong Acids.* The free acids of HPC, mainly the tungstates, are strong—stronger than the common inorganic acids.[9a] HPA are much more active acid catalysts in non-aqueous media due to their stronger

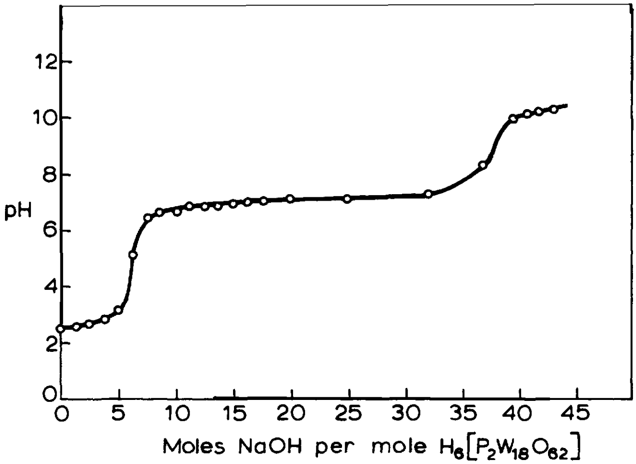

Figure 5 *Titration of* $H_6[P_2W_{18}O_{62}]$ *with* 0.1M-NaOH.[13b]

acidity than for instance *p*-toluenesulphonic acid, usually employed in organic media.[24]

(ii) *Redox Properties.* HPC undergo multi-electron redox reactions 'reversibly'—reversibly in the sense that they retain their structure, as mentioned earlier. This is a general statement that holds true for most cases. Re-oxidation is obtained with common oxidizing reagents: O_2 is very effective for reduced tungstates and mixed molybdovanadates.

More specifically, HPC redox ability, as far as catalysis is concerned, may be divided into two distinct categories: direct and indirect oxidation.

Direct oxidation, one component system. Several compounds are catalytically oxidized in the presence of HPC. The following scheme gives an overall account of this process:

$$S + M^{n-} \longrightarrow S^{2+} + M^{(n+2)-} \qquad (1)$$

$$M^{(n+2)-} + 1/2O_2 + 2H^+ \longrightarrow M^{n-} + H_2O \qquad (2)$$

$$\text{Overall} \quad S + 1/2O_2 + 2H^+ \longrightarrow S^{2+} + H_2O \qquad (3)$$

where S = substrate and M^{n-} a polyoxometallate ion.

Molybdates and mixed molybdo- and tungsto-vanadates are relatively powerful oxidizing reagents so that reaction 1 takes place with a variety of inorganic (mainly sulphur) compounds and organic reagents. Reaction 2 though, is not easily performed by O_2, especially with molybdates, and requires more effective oxidizing reagents such as H_2O_2 or O_2 in presence of active charcoal.

On the other hand, tungstates, with more negative redox potentials are less effective oxidizing reagents than molybdates and vanadates (reaction 1) whereas

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[24] Y. Izumi, 'U.S.–Japan Seminar on the Catalytic Activity of Polyoxoanions,' Shimoda, Japan, 1985, p. 40.

reaction 2 is fast with atmospheric O_2. The above gives an overall account of thermal catalysis by HPC, the mechanism of which varies considerably with the process.

HPC participate in redox reactions either through electron and H^+ transfer, or through oxygen transfer.[25]

Misono *et al.*[9b] were able to show that the reduction of PMo_{12}^{3-} by H_2 involved electrons and H^+ transfer, whereas O abstraction[25] took place in the case of oxidation of CO. The participation of lattice oxide ion was initially demonstrated by Keulks in the catalytic oxidation of propylene on bismuth molybdate,[26] and by Hockey *et al.*[27] In an effort to elucidate the catalytic sites of polyoxometallates, Misono *et al.* have shown that H_2 reduction of PMo_{12}^{3-} influences P–O and Mo–O–Mo, but not M–O i.r. frequencies.[9b]

Indirect oxidation, two-component system. Mixed molybdovanadates $PV_nMo_{12-n}O^{(3+n)-}$ have been used extensively by Matveev and co-workers in liquid-phase oxidation of several organic compounds. The method is based on the HPC-assisted regeneration of Pd catalysts, followed by re-oxidation of HPC by O_2, analogous to the Wacker process which uses Cu^{2+} for this purpose.[9a] The reactions are shown schematically below:

$$\begin{array}{rr}
S + Pd^{2+} \longrightarrow S^{2+} + Pd^0 & (4) \\
Pd^0 + M^{n-} \longrightarrow Pd^{2+} + M^{(n+2)-} & (5) \\
M^{(n+2)-} + 1/2O_2 + 2H^+ \longrightarrow M^{n-} + H_2O & (2) \\
\hline
\text{Overall} \quad S + 1/2O_2 + 2H^+ \longrightarrow S^{2+} + H_2O & (3)
\end{array}$$

where M^{n-} represents mainly mixed molybdovanadates and S = substrate.

B. Photocatalysis.—It has been stated before that it is generally accepted that the combination of acid–base properties, ability to function as 'reversible' redox reagents, and 'size' of the anions is responsible for the catalytic activity of HPC.

Although molybdates are generally more effective redox catalysts than tungstates, in the sense that they require lower temperatures for reduction, their re-oxidation by O_2 is not easily obtained. By contrast, tungstates are more difficult to reduce but are easily re-oxidized.

Now, as far as photochemistry and photocatalysis are concerned, it is known that the excited state of a redox reagent is both a better oxidant and a better reductant than the ground state (Scheme 1).[28] Thus tungstates that are otherwise thermally inactive become, under the influence of u.v. and near visible light, powerful oxidizing reagents capable of oxidizing a variety of organic compounds, *i.e.* reaction 1 followed by reaction 2.

(i) *Photochemistry, Basic Studies.* The potentiality of polyoxometallates in photochemical work has been recognized in the past and has been patented for

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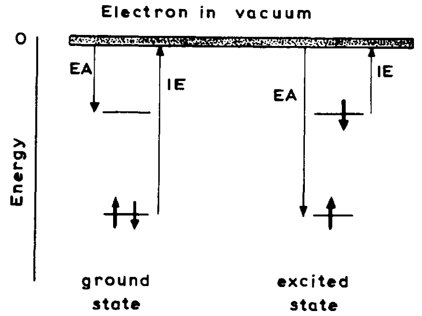
[25] N. Mizuno, T. Watanabe, and M. Misono, *J. Phys. Chem.*, 1985, **89**, 80.

[26] G. W. Keulks, *J. Catal.*, 1970, **19**, 232.

[27] R. D. Wragg, P. G. Ashmore, and J. A. Hockey, *J. Catal.*, 1971, **22**, 49.

[28] See for instance: V. Balzani, F. Bolletta, M. T Gandolfi, and M. Maestri, *Top. Curr. Chem.*, 1978, **75**, 1.



Scheme 1 *Schematic diagram showing that the excited state of a redox reagent is a better oxidant and a better reductant than the ground state*

Table 1 *Comparative quantum yield for the one-electron reduction products of various HPC in presence of* 5M propan-2-ol *at* 252 nm

HPC	Φ^a
PW_{12}^{3-}	0.12
SiW_{12}^{4-}	0.09
FeW_{12}^{5-}	0.02
$H_2W_{12}^{6-}$	<0.01
$P_2Mo_{18}^{6-}$	0.06^b
$P_2W_{18}^{6-}$	0.09

[a] Values within ~25%. [b] Photochemical, like chemical, reduction is a two-electron process for $P_2Mo_{18}^{6-}$. The quantum yield reported is per electron; it is also pH-dependent, see text.

possible use in photography.[5,6] It was also observed that solid HPC precipitated out with dioxane would turn blue on the surface upon exposure to sunlight.[29] In addition, various Russian workers have investigated the photochemistry of molybdenum and tungsten for analytical purposes.[7]

It is now well documented that polyoxometallates become photosensitized upon exposure to near visible and u.v. light in the presence of a great variety of organic compounds and give rise (generally) to blue species, with concomitant oxidation of the organic compounds. The organic compounds investigated (in approximate order of decreasing photosensitivity) include alcohols, glycols, hydroxy acids, amines, carboxylic, and dicarboxylic acids. Quantum yields vary with polyoxometallate, organic reagent, pH, and with reduction step. The quantum yield for PW_{12}^{3-}, for instance, drops from ~10% to ~1% in going from the first to the second reduction step in the presence of primary or secondary alcohols. Table 1 compares the quantum yield for the one-electron reduction product of various HPC in the presence of propan-2-ol. It can be seen that the quantum yield, *i.e.* the ease of photoreduction, is associated with the redox potential of the HPC, decreasing with increasing negative redox potential at least for the 1:12 tungstates (see also Table 2). Another parameter that affects photosensitivity, comes from the work of M. A. Fox. There is weak yet sufficient

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[29] M. T. Pope and E. Papaconstantinou, unpublished data.

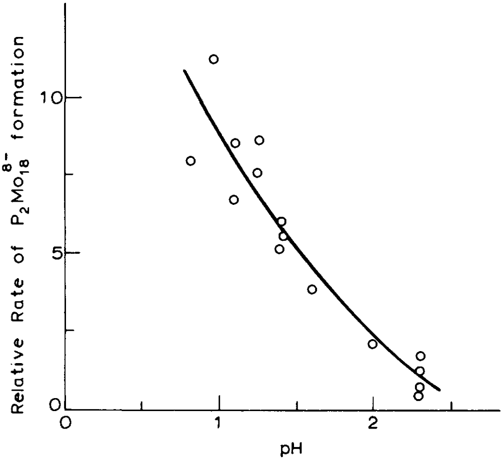

Figure 6 *Variation of relative rate of formation of* $P_2Mo_{18}^{8-}$ *with pH adjusted with* $HClO_4$ *at* 254 nm. $P_2Mo_{18}^{6-}$, 1 × 10^{-4}M; propan-2-ol, 2M. *Solutions deaerated with* Ar

evidence, from n.m.r., emission data and quenching rate constants, that a preassociation occurs between polyoxometallates and organic species.[30] This further supports previous work by Pope[29,31] and Hill.[31b] Thus Fox[30] associates the decrease in photosensitivity with replacement of tungsten for vanadium (see ref. 62), despite the more positive reduction potential, with the greater negative charge on polyoxometallate which disfavours preassociation with the organic species.

The dependence of photoreduction on [H^+] has a parallel in reduction by chemical means. For instance, the photoreduction of $P_2Mo_{18}^{6-}$ is pH-dependent. Figure 6 shows the variation of relative rate of formation of $P_2Mo_{18}^{8-}$ with pH adjusted with $HClO_4$.[32] This behaviour is reminiscent of the variation of $E_{\frac{1}{2}}$ of polarographic reduction with pH. It has been shown[14] that polarographic reduction involves addition of two H^+ per two electrons.

$$P_2Mo_{18}^{6-} + 2e^- + 2H^+ \longrightarrow H_2P_2Mo_{18}^{6-}$$

The variation of $\Phi(P_2Mo_{18}^{8-})$ with pH indicates also that protonation accompanies photoreduction. Unlike $P_2Mo_{18}^{6-}$,[32] the quantum yield of the one-electron reduction product of $P_2W_{18}^{6-}$ was independent of pH suggesting that H^+ does not participate in the photoreduction. This is in agreement with the fact that the thermal reduction $P_2W_{18}^{6-} + e^- \longrightarrow P_2W_{18}^{7-}$ is independent of H^+ which has been shown polarographically (Figure 4a).[13b]

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[30] M. A. Fox, R. Cardona, and E. Gailard, *J. Am. Chem. Soc.*, 1987, **109**, 6347.

[31] (*a*) L. Barcza and M. T. Pope, *J. Phys. Chem.*, 1975, **79**, 92; (*b*) C. L. Hill, R. F. Renneke, and M. M. Williamson, *J. Chem. Soc., Chem. Commun.*, 1986, 1747.

[32] E. Papaconstantinou, D. Dimotikali, and A. Politou, *Inorg. Chim. Acta*, 1980, **46**, 155.

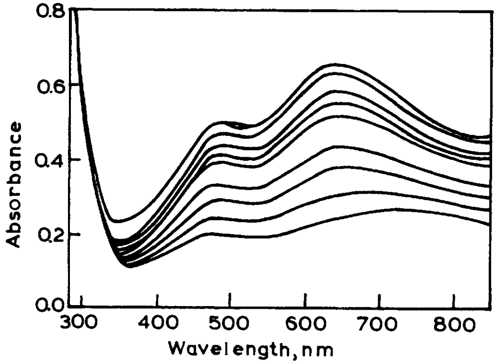

Figure 7 *Gradual photoreduction, showing the successive formation of one-electron* (750 nm) *and two-electron* (650 nm) *reduction products of* PW_{12}^{3-}. PW_{12}^{3-}, 1 × 10^{-4}M; *propan-2-ol*, 2M; *in* 0.1M-$HClO_4$; *deaeration with* Ar. *Photolysis at* 254 nm

The formation of the reduced HPC could be easily followed by their characteristic spectra (Figure 7). Photoreduction of HPC is accompanied by oxidation of organic compounds. Thus, primary alcohols give aldehydes and secondary alcohols give ketones (see below).

The extent of photoreduction depends, generally, on the organic reagent and the ease with which the HPC accept electrons. Thus, for instance, $P_2Mo_{18}^{6-}$ in the presence of propan-2-ol accepts six electrons photochemically, whereas PW_{12}^{3-} accepts two. This will be discussed below in connection with hydrogen production.

The relative rates of HPB formation are a function of HPC concentration and organic additive. The rates increase with concentration of organic compound up to 5—10 M for $P_2Mo_{18}^{6-}$,[32] whereas PW_{12}^{3-} needs considerably less alcohol (Figure 8).[33] This reflects, of course, on the lifetime of the excited states. Unfortunately HPC do not emit and no direct measurement of lifetimes could be made. However, Fox was able to observe very weak emission with some HPC.[30]

The isopoly compounds $Mo_7O_{24}^{6-}$ [34] and $W_{10}O_{32}^{4-}$ [35] have been studied by American, Japanese, and French groups. Apart from the details of the individual cases, the overall behaviour is that of HPC described above.

The spectra of the non-reduced HPC of both molybdates and tungstates are characterized by oxygen-to-metal charge-transfer bands in the near visible and u.v. regions and no absorption in the visible (all metals are Mo^{VI} or W^{VI} with d^0 configuration). The reduced forms present broad absorption bands around 700 nm. These bands are attributed to metal-to-metal charge transfer ($M^{5+} \longrightarrow M^{6+}$, M = Mo or W) which is responsible for the blue colour of

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[33] D. Dimotikali and E. Papaconstantinou, *Inorg. Chim. Acta*, 1984, **87**, 177.

[34] M. D. Ward, J. F. Bradzil, and R. K. Grasselli, *J. Phys. Chem.*, 1984, **88**, 4210.

[35] (*a*) A. Chemseddine, C. Sanchez, J. Livage, J. P. Launay, and M. Fournier, *Inorg. Chem.*, 1984, **23**, 2609; (*b*) T. Yamase, *Inorg. Chim. Acta Lett.*, 1983, **76**, L25; (*c*) K. Nomiya, Y. Sujie, T. Miyazaki, and M. Miwa, *Polyhedron*, 1986, **5**, 1267; (*d*) T. Yamase, N. Takabayashi, and M. Kaji, *J. Chem. Soc., Dalton Trans.*, 1984, 793.

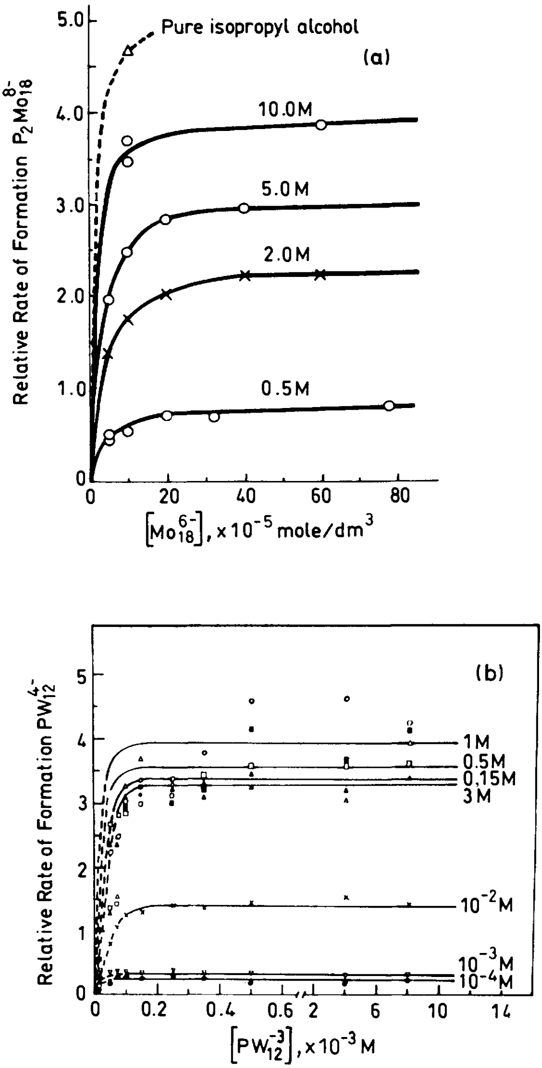

Figure 8 *Variation of the relative rates of formation of reduced HPC with concentration of HPC and various concentrations of propan-2-ol in* 0.1M-$HClO_4$

the compounds, and to *d–d* transitions of the d^1 metal ions, as has been stated earlier.[22,23,36]

The reduced HPC are not photosensitive at wavelengths over 500 nm in the

[36] H. Soo and M. T. Pope, *Inorg. Chem.*, 1972, **11**, 1441.

presence of organic additives, suggesting that the above mentioned bands of HPB are not responsible for the photochemistry.

Excitation seems to involve the oxygen-to-metal charge transfer of the HPC. Photoexcited polyoxometallates react with organic species mainly by H• and/or electron transfer, resulting in the reduction of the polyoxometallates and oxidation of the organic species through formation of radicals. One photon adds two electrons in the polyoxometallate and oxidizes one molecule of organic compound, as indicated in equations 6—9 below. The H-transfer mechanism is deduced from the fact that only species with easily removable hydrogen atoms, *e.g.* primary and secondary alcohols, act as effective photoreducing reagents whereas tertiary butyl alcohol is essentially inert.[51] This mechanism is generally accepted[37,38] and further supported by Ward's work[34] that showed a deuterium isotope effect $k_H/k_D \sim 3.7$ in the production of acetone when deuteriated Me_2CDOH was used with $Mo_7O_{24}^{6-}$, indicating that reaction 8 is the rate determining step in the scheme below. Further support arises from the fact that hydroxyalkyl radicals are effective reducing reagents; the rate of reduction of HPC by such radicals is diffusion controlled.[39]

Yamase, on the other hand, has studied extensively the photochemistry of alkyl ammonium heptamolybdates of the type $(RNH_3)_6Mo_7O_{24}$ both in aqueous solution and in the solid state. He postulates a mechanism (discussed below) that involves hydroxy radicals.[40]

Designating polyoxometallates as M^{n+} and using propan-2-ol, the photochemical reaction mechanism (mainly for tungstates) may be presented as follows:

$$M^{n-} \xrightarrow{h\nu} M^{*n-} \qquad (6)$$

$$^*M^{n-} \xrightarrow{k_{-1}} M^{n-} \qquad (7)$$

$$^*M^{n-} + Me_2CHOH \xrightarrow{k_Q} M^{(n+1)-} + Me_2\dot{C}OH + H^+ \qquad (8)$$

$$M^{n-} + Me_2\dot{C}OH \xrightarrow{k_R} M^{(n+1)-} + Me_2CO + H^+ \qquad (9a)$$

$$M^{(n+1)-} + Me_2\dot{C}OH \longrightarrow M^{(n+2)-} + Me_2CO + H^+ \qquad (9b)$$

$$M^{(n+2)-} + M^{n} \longrightarrow 2M^{(n+1)-} \qquad (9c)$$

(A slightly modified mechanism can be written for molybdates known to undergo a stepwise two-electron reduction process, at least in aqueous solutions.) Photoreduction proceeds to higher reduction steps depending on conditions.

From reactions 6, 7, and 8 (reactions 9 are too fast to interfere), applying the steady-state approximation for M^{n-}, we obtain from reaction 8:

$$R = \frac{d[M^{(n+1)-}]}{dt} = \frac{k_Q[Me_2CHCOH]I_0}{\mathrm{k}_{-1} + k_Q[Me_2CHOH]}$$

When $k_a Me_2CHOH \gg k_{-1}$, $R \approx I_0$, *i.e.* independent of Me_2CHOH as shown in Figure 8. This happens for $P_2Mo_{18}^{6-}$ at concentrations of isopropyl alcohol greater than 5—10M, but for PW_{12}^{3-} at concentrations greater than 0.1M.

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[37] R. Akid and J. Darwent, *J. Chem. Soc., Dalton Trans.*, 1985, 395.

[38] C. L. Hill and D. A. Bouhard, *J. Am. Chem. Soc.*, 1985, **107**, 5148.

[39] E. Papaconstantinou, *J. Chem. Soc., Faraday Trans. 1*, 1982, **78**, 2769.

[40] (*a*) T. Yamase, R. Sasaki, and T. Ikawa, *J. Chem. Soc., Dalton Trans.*, 1981, 628; (*b*) T. Yamase, *Polyhedron*, 1986, **5**, 79.

Taking the reciprocal of the above expression gives:

$$\frac{1}{R} = \frac{1}{I_0} + \frac{k_{-1}}{k_Q I_0[\mathrm{Me_2CHOH}]}$$

A similar expression was originally derived by Darwent for steady-state H_2 production[37] (see below). A plot of the reciprocal of the rate of formation of $P_2M_{18}^{8-}$ *vs.* 1/[Me_2CHOH] for various concentrations of $P_2Mo_{18}^{6-}$ gives a good straight line. However, this is not always the case, at least with other HPC, and possibly indicates that another type of mechanism might operate, *i.e.* the formation of a photosensitive aggregate precursor.

Ward[34] offers various mechanisms concerning the bond breaking and making during the process. Reactions 6, 8 are presented as follows:

$$-M^{6+}{=}\underset{\cdot\cdot}{\ddot{O}} \longrightarrow M^{5+}{-}\underset{\cdot\cdot}{\ddot{O}}$$

$$-M^{5+}{-}\underset{\cdot\cdot}{\ddot{O}}\cdot + H{-}(OH)CMe_2 \longrightarrow Me^{5+}{-}\underset{\cdot\cdot}{\ddot{O}}{:}H + HO\dot{C}Me_2$$

(where M^{6+} denotes the 6+ oxidation state of a Mo or W atom). The evidence provided by Ward for the above reactions was a deuterium isotope effect $k_H/k_D \sim 3.7$ when deuteriated Me_2CDOH was used as mentioned earlier. In a recent publication, however, Yamase working with $BW_{12}O_{40}^{5-}$ and CH_3OH reports an isotope effect of only 1.7 when CD_3OD was used. He concludes from this that C–H bond breaking, *i.e.* reaction 8, is not rate determining. Although agreeing with the above offered mechanism, reactions 6—9c, Yamase considers the rate determining step to be the breaking of the O–H bond and formation of the CH_3O radical, which subsequently converts into the $\dot{C}H_2OH$ radical. On the other hand, working with $W_{10}O_{32}^{4-}$ in presence of olefins, he has presented transient spectra to support a photochemical mechanism involving one-electron transfer to polytungstate, followed by protonation and disproportionation.[41] The possibility of photochemical reactions occurring through formation of OH radicals is also considered, in irradiated aqueous solutions of $(NH_3Pr)_6[Mo_7O_{24}]$, from e.s.r. spin trapping evidence[40a] (see below).

It appears that the most convincing picture, so far, as to the mechanism of photoredox reactions involving polyoxometallates, is that of a preassociated complex of polyoxometallate with the organic species undergoing, upon excitation with near visible and u.v. light, $H^{\cdot}$ and/or electron transfer that results in reduction of polyoxometallate and oxidation of the organic compound.

(ii) *Utilization of Polyoxometallates in Solar Energy Research.*—For a system to be suitable for solar energy conversion and storage, it is generally accepted that it ought to fulfil the following requirements: (a) to absorb considerably in the visible spectrum, (b) to have a long-lived excited state, (c) to participate in redox reactions that are able to store the absorbed energy, (d) to have a photoredox cycle of about one million times.

These are difficult requirements to match but efforts have led to systems that fulfil one or another of the requirements. In the field of polyoxometallates efforts

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[41] T. Yamase and T. Usami, *J. Chem. Soc., Dalton Trans.*, 1988, 183.

Table 2 *U.v. spectral data and half-wave potentials for the first two* 1-*electron reductions for oxidized* 1 : 12 *tungstates and* 2 : 18 *HPC*[13-22]

anion	λ^a, nm	$E^b_{\frac{1}{2}}$, V	*pH dependence*
PW_{12}^{3-}	265.0	−0.023	none
		−0.266	none
SiW_{12}^{4-}	262.0	−0.187	none
		−0.445	none
FeW_{12}^{5-}	264.0	−0.349	none
		−0.577	below pH 4.0
$H_2W_{12}^{6-}$	257.5	−0.581	below pH 4.9
		−0.730	
$P_2Mo_{18}^{6-}$	241[c] 312[c]	0.42[d]	below pH 4.0
		0.10[d]	
$P_2W_{18}^{6-}$	255 294[c]	0.10	none
		−0.10	

[a] In 1M-sulphuric acid. [b] *vs*. SCE. [c] Shoulder. [d] Refers to 2-electron wave

have been made in three directions: (a) hydrogen production, (b) photocatalytic oxidation of organic compounds, and (c) photogalvanic cells. Despite the obvious interrelation of these three cases, for reasons of clarity they will be presented separately.

Photocatalytic production of hydrogen. It has been stated before that polyoxometallates are photosensitive in near visible and u.v. light in the presence of organic compounds. Excitation leads to reduction of polyoxometallates and oxidation of organic compounds (reactions 6—9). The stepwise photoreduction of polyoxometallates, which is analogous to thermal reductions, drives the redox potential to more negative values which, as is known, are oxidized back, depending on the redox potential, to the original form by atmospheric oxygen (see below, in connection with photocatalytic oxidation of organic compounds). In the absence of oxygen the redox potentials, generally speaking, reach negative enough values to cause, from a thermodynamic point of view, reduction of H^+.[42] Table 2 shows u.v. spectral data and half-wave potentials for the first two one-electron reductions for 1 : 12-tungstates and two representative 2 : 18-tungstates and 2 : 18-molybdates. This is accomplished in the presence and in the absence of platinum catalyst (see below). Platinum catalyst is, of course, used to overcome the high potential necessary for the production of atomic hydrogen $H^+ + e^- \longrightarrow H$, $E^0 = -2.2$ V and produce instead molecular hydrogen $2H^+ + 2e^- \longrightarrow H_2$, $E_7 = -0.41$ V or $E_0 = 0.0$ V, where E_7 ane E_0 are potentials at pH 7 and 0 respectively.[43] The feasibility of H_2 evolution by reduced $S_1W_{12}^{4-}$ was established by Russian workers, who reduced $S_1W_{12}^{4-}$ with amalgamated zinc.[44]

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[42] E. Papaconstantinou, D. Dimotikali, A. Ioannidis, and P. Argitis, *J. Photochem.*, 1981, **178**, 171.

[43] See for instance: (*a*) 'Photogeneration of Hydrogen', ed. A. Harriman and M. A. West, Royal Institution Symposium, Academic Press N.Y., 1982; (*b*) 'Energy Resources through Photochemistry and Catalysis', ed. M. Gratzel, Academic Press, N.Y., 1983; (*c*) M. Kirch, J.-M. Lehn, and J.-P. Sauvage, *Helv. Chim. Acta*, 1979, **62**, 1345.

[44] E. N. Savinov, S. S. Saidkhanov, V. N. Parmon, and K. I. Zamaraev, *React. Kinet. Catal. Lett.*, 1981, **17**, 407.

Table 3 *Maximum number of electrons added photochemically on* 1 : 12-*tungstates in the presence of* 1.0M *isopropyl alcohol in* 0.1M $HClO_4$[a] (*ref.* 46)

	maximun no. of added electrons			*maximun no. of added electrons*	
Compound	*without platinum*[b]	*with platinum*[b]	*Compound*	*without platinum*[b]	*with platinum*[b]
PW_{12}^{3-}	2.2	1.3	FeW_{12}^{5-}	1.4	0.3
SiW_{12}^{4-}	1.7	0.9	$H_2W_{12}^{6-}$	1.2	0.2

[a] Conditions: [HPC] = 5×10^{-4}M; photolysis with Xe 150W lamp without filter (deaeration with Ar).
[b] Values within 20%; concentration of platinum catalyst ~ 5×10^{-6}M

Photocatalytic evolution of hydrogen has now been obtained by various laboratories.[37,45,46] H_2 evolution also takes place in the absence of platinum catalyst.[46]

Thus, polyoxometallates, generally, although they are not useful as sensitizers since they have a limited absorption in the visible spectrum, seem to be useful as electron carriers (relays). Photoreduction proceeds stepwise to the extent that the rate of photoreduction is matched by the rate of re-oxidation by H^+ (evolution of H_2). The reduction step at which this takes place depends on the polyoxometallate. To appreciate this we can observe the results with 1 : 12-tungstates. Thus with PW_{12}^{3-} the steady-state H_2 evolution takes place at a higher reduction step than with $H_2W_{12}^{6-}$ which is reduced at a more negative redox step. When platinum catalyst is used, the steady-state H_2 evolution is obtained at an even lower reduction step. Table 3 shows the degree of reduction, expressed as maximum number of electrons added at the steady state, which is associated with the redox potential of 1 : 2-tungstates since addition of electrons drives the redox potential to more negative values (see also Table 2). Apparently HPC also serve as heterogeneous catalysts in the absence of metallic platinum, but not as effectively. The photocatalytic cycle for H_2 production is depicted in Figure 9. The rate of H_2 production is limited by the low quantum yield of HPB formation. Re-oxidation of HPB by H^+, presented generally as shown in equation 10 seems to be 100% efficient. It can be seen from Table 3 that for

$$2M^{(n+1)-} + 2H^+ \longrightarrow 2M^{n-} + H_2 \qquad (10)$$

PW_{12}^{3-} reaction 10 involves roughly the $M^{(n+2)-}$ reduction product, whereas, for SiW_{12}^{4-}, FeW_{12}^{5-}, and $H_2W_{12}^{6-}$ it involves mainly the first reduction step, *i.e.* the $M^{(n+1)-}$ species. The overall process, reactions 6—10 is, in essence, dehydrogenation of alcohols, *i.e.* $Me_2CHOH \longrightarrow Me_2CO + H_2$ which, by the way, stores $\Delta H \sim 37$ kJ mol^{-1} of light energy. The rate of H_2 evolution, at the steady state, measured by g.c. matched the rate of reoxidation of HPB, at that stage, measured spectrophotometrically at ~750 nm (reaction 10). Figure 10 shows typical absorption spectra and kinetics of reoxidation by H^+. The pseudo first-order rate constants for reaction 10 at 0.1M $HClO_4$ for all photochemically reduced 1 : 12-

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[45] (*a*) S. S. Saidkhanov, A. I. Kokorin, E. N. Savinov, A. I. Vokov, and V. N. Parmon, *J. Mol. Catal.*, 1983, 31, 365.

[46] A. Ioannidis and E. Papaconstantinou, *Inorg. Chem.*, 1985, **24**, 439.

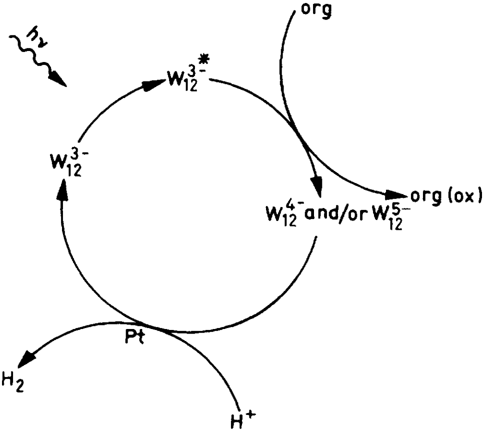

Figure 9 *Schematic diagram of* H_2 *evolution with* $PW_{12}O_{40}^{3-}$ (W_{12}^{3-}). *'Org' is a reductant that undergoes irreversible oxidation and* Pt *is a suitable platinum catalyst*

Table 4 *$E_{\frac{1}{2}}$ of various reduction steps at various pHs of* $P_2W_{18}^{6-}$ *obtained with a DME.*[13b]

pH	*$E_{\frac{1}{2}}$ (V versus NHE) for reduction step*				
	$1e^{-a}$	$1e^{-b}$		$2e^{-c}$	
			$1e^-$		$1e^-$
1	0.306	0.084		−0.213	
3	0.306	0.084		−0.304	
5	0.306	0.084	−0.233		−0.430

NHE, normal hydrogen electrode. DME, dropping mercury electrode. [a] Refers to $W_{18}^{6-} + e^- \longrightarrow W_{18}^{7-}$. [b] Refers to $W_{18}^{7-} + e^- \longrightarrow W_{18}^{8-}$. [c] Below pH 3, refers to $W_{18}^{6-} + 2e^- + 2H^+ \longrightarrow H_2W_{18}^{8-}$. Above pH 3, refers to $W_{18}^{8-} + e^- \longrightarrow W_{18}^{9-}$ and $W_{18}^{9-} + e^- \longrightarrow W_{18}^{10-}$

tungstates were $(5.6 \pm 3.1) \times 10^{-4}$ s^{-1} and $(2.6 \pm 1.8) \times 10^{-4}$ s^{-1} with and without platinum catalyst, respectively.

The pH of the solution is important in H_2 evolution (a) because of its effects on the redox potential of H^+ reduction, and (b) for driving, generally, the redox potential of HPC to more negative values.

Table 4 shows the values of $E_{\frac{1}{2}}$ for various reduction steps of $P_2W_{18}^{6-}$, at various pHs, obtained with a dropping mercury electrode.[13b] Table 5 shows the rate constants of reoxidation (H_2 evolution) of photoreduced one- and two-electron products of $P_2W_{18}^{6-}$, at various pHs, measured spectrophotometrically. It can be seen that as the reduction potential of H_2 evolution becomes more negative with increasing pH, only the higher reduction products produce H_2.

Yamase has recently studied the photochemistry of $BW_{12}O_{40}^{5-}$.[47] The overall behaviour is as described above for other similar compounds. However, this compound seems to present some special characteristics. At high pH (5.4) it presents two reversible waves −0.51 and −0.75 V *vs.* Ag/AgCl and at pH < 2 each wave is replaced by a 6-electron wave ($E_{\frac{1}{2}} = -0.52$—0.06 pH and −0.62—

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[47] T. Yamase and R. Watanabe, *J. Chem. Soc., Dalton Trans.*, 1986, 1669.

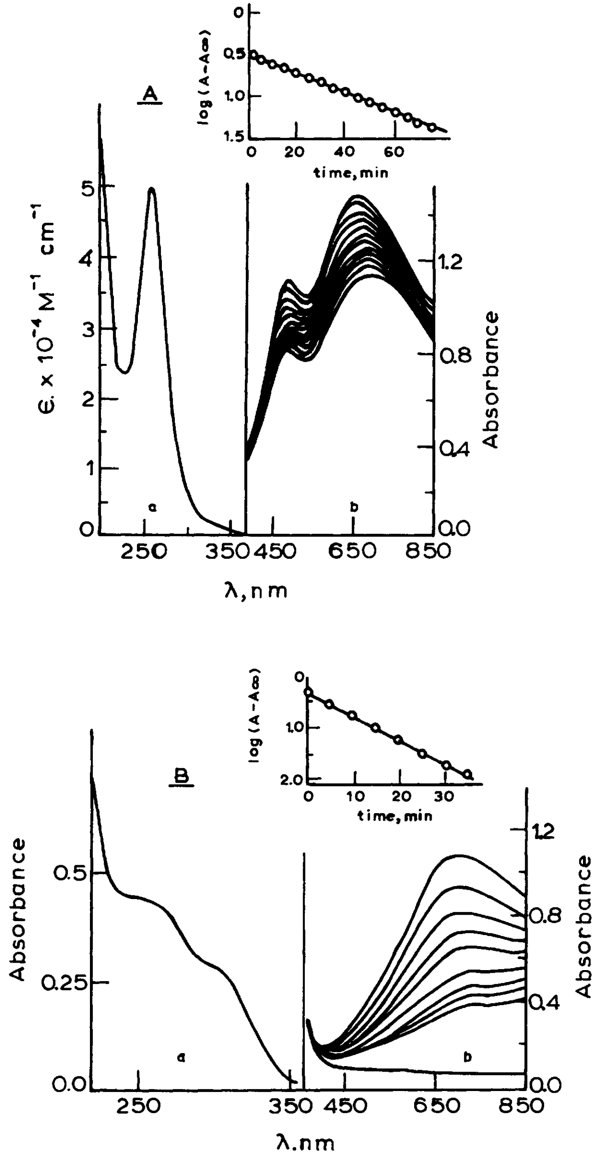

Figure 10 *Typical absorption spectra and kinetics of reoxidation of photoreduced HPC.* (*A*) PW_{12}^{3-}, 5 × 10^{-4}M; *propan-2-ol* 1.0M, *platinum catalyst* 5 × 10^{-6}M *in* 0.1M-$HClO_4$. (*B*) $P_2W_{18}^{6-}$ 1 × 10^{-4}M, *propan-2-ol* 1.1M, *in* 0.1M-$HClO_4$. *Photolysis with* Xe *lamp with pyrex filter. In both figures:* (*a*) *Spectra of non-reduced HPC showing the* O–M *CT bands responsible for the photosensitivity.* (*b*) *Photoreduced HPC showing gradual reoxidation by* H^+ *after illumination had been shut off. Insets: pseudo first-order plots of absorbance change, corresponding to reoxidation of HPC with concomitant* H_2 *evolution*

Table 5 *Rate constants*[a] *for hydrogen evolution measured spectrophotometrically at various pHs, adjusted with* $HClO_4$, *and various reduction stages*[48]

pH	E^0 *versus NHE*[b]	*k for reduction step* ($\times 10^{-4}$ s^{-1})			
		$1e^{-c}$	$1e^{-c}$	$2e^{-c}$	
				$1e^-$	$1e^-$
1	-0.059	0	4.0	0.73	
3	-0.177	0	0	0.77	
5	-0.295	0	0	0^d	0^d

[a] Values are within 50%. [b] Refers to the reduction potential of $2H^+ + 2e^- \longrightarrow H_2$ at the corresponding pH. [c] Numbers refer to electrons added photochemically. [d] Hydrogen is only evolved in the presence of the platinum catalyst and the k values are 1.6×10^{-4} s^{-1} and 2.9×10^{-4} s^{-1} for the third and fourth electron respectively

Table 6 *Rate constants*[a] *for hydrogen evolution for reactions measured spectrophtometrically with and without the platinum catalyst* $[P_2W_{18}^{6-}] = (0.5—1.0) \times 10^{-4}M$, [isopropyl alcohol] = 1—2M in 0.1M-$HClO_4$).[48]

	$k \times 10^4$ s^{-1}	
	$W_{18}^{8-} + H^+ \rightarrow$ $W_{18}^{7-} + 1/2H_2$	$W_{18}^{10-} + 2H^+ \rightarrow$ $W_{18}^{8-} + H_2$[b]
With platinum	6.1	17
Without platinum	4.0	0.73

[a] Calculated from pseudo first-order rate plots; values are within 50%. [b] It is known that W_{18}^{10-} is protonated at low pH so that the species exist as $H_2W_{18}^{8-}$

0.10 pH) so that in contrast to other HPC the quantum yield for H_2 production drops drastically at pH < 2.

The rate of H_2 evolution is a function of the reduction step. This is demonstrated in Table 6 with $P_2W_{18}^{6-}$.[48] Thermodynamics suggest that the rate of reoxidation of the 4-electron reduced product of $P_2W_{18}^{6-}$ by H^+ should be faster than that of the 2-electron reduced product $P_2W_{18}^{8-}$, on the basis of its more negative reduction potential (see Table 4). This is indeed the case when platinum is used as catalyst. In the absence of platinum reoxidation of $P_2W_{18}^{10-}$ is slower than $P_2W_{18}^{8-}$ contrary to their redox potentials. This suggests that addition of two more electrons and protons ($P_2W_{18}^{10-}$ is known to be protonated *i.e.* it exists as $H_2P_2W_{18}^{8-}$ at low pH [13b]) reduces the effectiveness of 2:18-tungstate as catalyst, apparently by distorting the structure of the anion. This observation is of interest in connection with the effectiveness of polyoxometallates as H_2 evolution catalysts. The total production of hydrogen, measured by gas chromatography, verified reaction 10. The efficiency of the process was of the order of one molecule of hydrogen per 100 photons absorbed. The low yield represents the low efficiency of photoproduction of higher reduction products which was mentioned earlier.[46]

With hydrogen production a second steady-state is established (reactions 8, 9, 10) that involves the reduction step from which H_2 is produced. Reaction 9 is fast and can be safely ignored. The H_2 produced matches, stoicheiometrically, the number of electrons added photochemically. Assuming for simplicity that

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[48] P. Argitis and E. Papaconstantinou, *J. Photochem.*, 1985, **30**, 445.

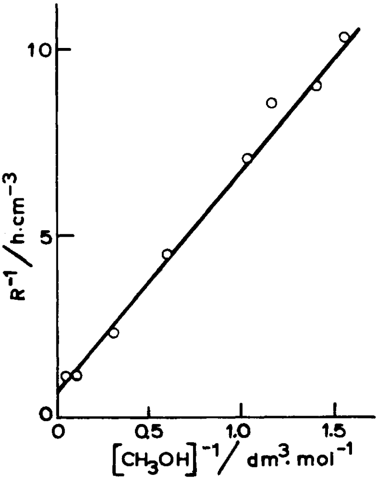

Figure 11 *Double reciprocal plot of initial rate of* H_2 *formation against concentration of* CH_3OH, *from a solution containing* SiW_{12}^{4-} $1 \times 10^{-3}M$, H_2SO_4 0.5M, *platinum catalyst* $2.4 \times 10^{-5}M$. *From ref.* 37

$M^{(n+1)-}$ is the reduction step from which H_2 is produced, and using steady states for $*M^{n-}$ and $M^{(n+1)-}$, we obtain from reaction 10:

$$R(H_2) = \frac{d[M^{(n+1)-}]}{dt} = \frac{k_Q[Me_2CHOH]I_0}{k_{-1} + K_Q[Me_2CHOH]}$$

This expression is identical with the previous expression. They both represent the rate of formation of some reduced tungstate, in this case $M^{(n+1)-}$. At sufficiently high concentrations of isopropyl alcohol, $k_Q[Me_2CHOH] \gg k_{-1}$ and the rate depends only on I_0.[37] The last equation can be rearranged to

$$\frac{1}{R(H_2)} = \frac{1}{I_0} + \frac{k_{-1}}{k_Q I_0[MeCHOH]}$$

A plot of the reciprocal of the initial rate of H_2 evolution *vs.* $1/Me_2CHOH$ gave a good straight line (Figure 11).[37]

The overall reaction is:

$$Me_2CHOH \longrightarrow Me_2CO + H_2$$

i.e. the production of H_2 is matched by concomitant production of acetone. The quantum yield for acetone production is 0.01, which represents the low quantum yield of that particular reduction step. In the case of PW_{12}^{3-}, for instance, it represents the second reduction step, *i.e.* $PW_{12}^{4-} + e^- \longrightarrow PW_{12}^{5-}$.

Selective photocatalytic oxidation of alcohols in the presence of oxygen. It has been stated earlier that a variety of organic compounds is oxidized photocatalytically in the presence of polyoxometallates. In this case reaction 10 is replaced by

$$M^{(n+1)-} + 1/4O_2 + H^+ \longrightarrow M^{n-} + 1/2H_2O \qquad (11)$$

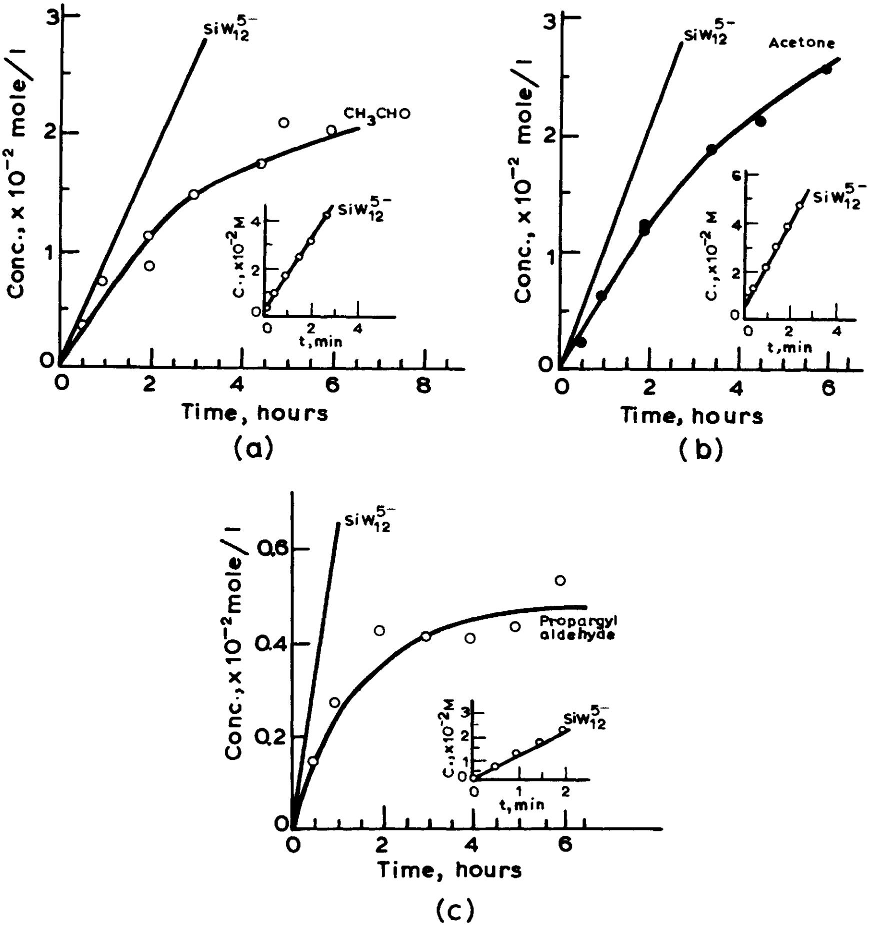

Figure 12 *Variation of concentrations of* MeCHO, Me_2CO, CH≡CCHO, *and* SiW_{12}^{5-} *with photolysis time in the presence of* O_2. SiW_{12}^{4-} 5 × 10^{-3}M, *alcohols* 2M, $HClO_4$ 10^{-4}M. *High pressure mercury lamp with pyrex filter. The variation of* SiW_{12}^{5-} *concentration with time was drawn by extrapolation of the corresponding curve, in de-aerated solutions, of the initial stages of photolysis (inset) followed spectrophotometrically* (λ ~ 700 nm)

reaction 11. The overall reaction for reactions 6—9c and 11 is, in essence, oxidation of alcohol, *i.e.* $Me_2CHOH + 1/2O_2 \longrightarrow Me_2CO + H_2O$.

Primary alcohols, *e.g.* methyl, ethyl, and propyl, give the corresponding aldehydes. Stoicheiometrically, one photon adds two electrons on the polyoxometallates and produces one molecule of oxidized organic compound. Figure 12 shows typical formation of reduced HPC (followed spectrophotometrically) and oxidized alcohols (followed by gas chromatography).

Secondary alcohols, *e.g.* propan-2-ol, under the same conditions give ketones. Figure 12b shows a corresponding diagram where the same 2:1 ratio (two electrons per molecule of oxidized alcohol) is observed, as is generally the case for redox reactions involving organic compounds.

By contrast tertiary alcohol Me_3COH presents a very low quantum yield indicating that H^+ transfer rather than electron transfer is mainly responsible for the photoredox reaction.

Photolysis of polyoxometallates in the presence of allyl, $CH_2{=}CHCH_2OH$, and prop-2-ynyl (propargyl), $CH{\equiv}CCH_2OH$, alcohols results in oxidation only of the alcoholic moieties, whereas the double and the triple carbon–carbon bonds remained intact. Allyl alcohol gave acrolein and propargyl alcohol the corresponding aldehyde. The method is useful for the selective oxidation of the above organic compounds (Figure 12c).[49]

Some mixed polytungstates are also claimed to functionalize alkanes photochemically, but we will not elaborate on this at present.[50]

The second-order rate constant for reoxidation of the blues by H^+ at the steady state, reaction 10, is $\sim 5 \times 10^{-3}\ M^{-1}\ s^{-1}$, whereas reoxidation of the first reduction product by oxygen, reaction 11, is considerably faster. This reaction is pH-dependent. Using laser flash photolysis to generate the reduced HPC, the second-order rate constant for reaction 11 was 88 $M^{-1}\ s^{-1}$[51] for $M^{(n+1)-} = PW_{12}^{4-}$. This work was expanded to other HPC and the values of k found were 75, 6.5×10^3, 2.8×10^5, and $1.75 \times 10^5\ M^{-1}\ s^{-1}$ for PW_{12}^{4-}, SiW_{12}^{5-}, FeW_{12}^{6-}, and $H_2W_{12}^{7-}$ respectively at 0.1M H^+.[37]

Detailed studies of the effect of pH were carried out using $P_2W_{18}^{6-}$, which is resistant to alkaline degradation up to pH 6, at a constant ionic strengh of 0.5M with $NaClO_4$. Despite the considerable scattering of the results, reaction 11 seems to be first-order in polyoxometallate and oxygen, whereas it follows a sigmoidal type of curve with pH, indicating that reaction 11 is zero-order in $[H^+]$ at low and high pH, and about first-order in between (inflection point).[52]

The upper limit to the quantum yield for the photocatalytic oxidation of organic compounds will be the quantum yield of formation of the first reduction step, Table 1. This is indeed the case where the steady state is established at the earliest possible stage of photoreduction, *i.e.* before the photoreduction of the second step becomes significant. Using, for simplicity, only the first reduction step, and applying the steady-state approximation for M^{n-} (reactions 6 and 11) we get

$$\frac{dM^{n-}}{dt} = k[H^+][O_2][M^{(n+1)-}] - \Phi_1 I_0 = 0$$

and

$$[M^{(n+1)-}] = \frac{\Phi_1 I_0}{k[H^+][O_2]} = \frac{\Phi_1 I_0}{k'}$$

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[49] A. Hiskia and E. Papaconstantinou, *Polyhedron*, 1988, **7**, 477.

[50] R. F. Renneke and C. L. Hill, *J. Am. Chem. Soc.*, 1986, **108**, 3528.

[51] E. Papaconstantinou, *J. Chem. Soc.. Chem. Commun.*, 1982, 12.

[52] A. Hiskia and E. Papaconstantinou, unpublished data.

where Φ_1 is the quantum yield of the first reduction step, I_0 is the intensity of radiation, assuming 100% absorption, and $k' = k[H^+][O_2]$. From reaction 11

$$\frac{d[M^{(n+1)-}]}{dt} = k[H^+][O_2][M^{(n+1)-}] = \Phi_1 I_0$$

Since, as we have discussed earlier, $M^{(n+1)-}$ oxidizes organic compounds stoicheiometrically, the quantum yield for the oxidation products will be the same. Table 1 shows that the best candidates for maximum yield of photo-oxidized organic compounds are PW_{12}^{3-} and SiW_{12}^{4-}. Using SiW_{12}^{4-} and Me_2CHOH in the presence of oxygen we were able to obtain, with a pyrex filter, a quantum yield for Me_2CO of ~ 0.1.

The isopoly compound $W_{10}O_{32}^{4-}$ has been studied by Japanese and French groups.[35] Although its overall photochemical behaviour is characteristic of polyoxometallates, it presents an interesting case in that its absorption peak is at higher wavelength (324 nm) than at least the 12-tungstates (265 nm), and photoreduction produces directly a $2e^-$ blue species in aprotic solvents that is reoxidized rapidly by O_2.[35c] It is claimed that the turnover number, *i.e.* the molar ratio of acetone produced to $W_{10}O_{32}^{4-}$ used, in organic solvents is better than, for instance, SiW_{12}^{4-} in aqueous solutions. It should be pointed out that $W_{10}O_{32}^{4-}$ absorption at 324 nm makes it more effective in organic solvents (*e.g.* DMF, DMSO, CH_3CN) which absorb strongly below 300 nm than the 1:12-tungstates at least. In the latter case we have found the quantum yield to diminish considerably owing to the elimination of active photons by the solvent.

Photogalvanic cells. The photogalvanic cells described in this review depend for their operation on the potential difference created between the photoreduced and oxidized forms of HPC. Although photogalvanic cells are easy to construct with many of the chemicals that undergo photoredox reactions, the requirement for regenerative photogalvanic cells limits the usefulness of these chemicals.[53] Yamase has reported a photogalvanic cell that is based on isopropyl ammonium heptamolybdate in aqueous solutions.[54] Using two platinum electrodes and illuminating with 313 nm light he was able to produce a photopotential that resulted in evolution of H_2 at the cathode. Yamase offers the following mechanism for the processes at the two electrodes.

Photoanode: $Mo^{VI}{=}O + H_2O \xrightarrow{h\nu} Mo^{V}{-}OH + \dot{O}H$
$Mo^{V}{-}OH \longrightarrow Mo^{VI}{=}O + H^+ + e^-$
Cathode: $H^+ + e^- \longrightarrow 1/2H_2$

However, the formation of hydroxy radicals has been generally disputed in processes of this kind, as mentioned earlier.[55]

Other photogalvanic cells using molybdenum compounds, but not polyoxometallates, have been reported. A. Heller *et al.* describe one constructed with Mo^{4+} and based on photoinduced disproportionation to Mo^{3+} and Mo^{5+}.[56]

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[53] See for instance: W. J. Albery and A. W. Foulds, *J. Photochem.*, 1981, **15**, 321.

[54] (*a*) T. Yamase and T. Ikawa, *Inorg. Chim. Acta*, 1979, **37**, L529; (*b*) T. Yamase and T. Ikawa, *ibid.*, 1980, **47**, L55.

[55] M. Gratzel, personal communication.

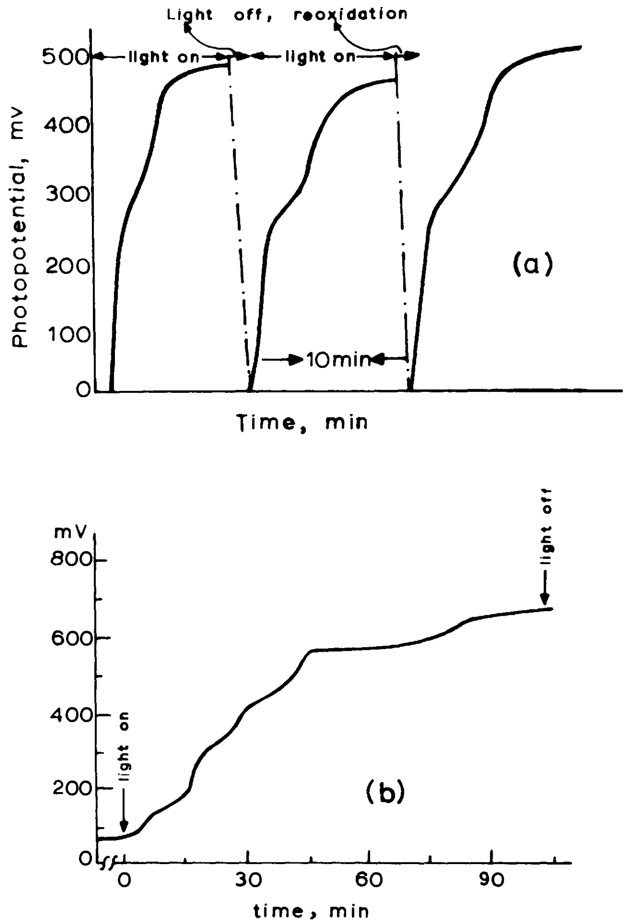

Figure 13 *Photopotentials developed between light and dark electrolytes composed of* (*a*) PW_{12}^{3-} 1 × 10^{-4}M, *propan-2-ol* 0.8M *in* 0.1M-$HClO_4$; *reoxidation by atmospheric oxygen.* (*b*) $P_2Mo_{18}^{6-}$ 5 × 10^{-5}M, *propan-2-ol* 1M, *in* 0.1M-$HClO_4$

The photogalvanic cells (in this case, strictly speaking, 'photofuel' cells) reported below, are based on the ease of reoxidation of some HPC by O_2 which regenerates the cells.

The electrolyte in both cells is composed of an HPC and an organic reagent which is consumed during the process. The pH was kept low with $HClO_4$ to avoid base hydrolysis of HPC. Photolysis of the electrolyte in the 'light' half-cell turned the solution blue, whereas the electrolyte in the 'dark' half-cell remained

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[56] M. H. Navidi, H. G. Brittain, and A. Heller, *Science*, 1970, **169**, 980.

colourless. Figure 13 shows the photopotential produced by a solution of PW_{12}^{3-} in the presence of isopropyl alcohol. The corresponding spectra of the photoreduced PW_{12}^{3-} can be easily followed in the visible (Figure 7).

The photopotential developed between the 'light' and 'dark' half-cells produced a current of 150 μA which dropped asymptotically to zero.[57] At the same time the dark electrolyte turned blue indicating a flow of electrons (reduction) through the electrolyte in the dark half-cell. Atmospheric oxygen reoxidizes the electrolyte in the dark cell to its original colourless form PW_{12}^{3-}. Further illumination restores the photopotential and the cycle is repeated. These 'cycles' were repeated at least thirty times with no loss in activity of PW_{12}^{3-}.

The stepwise development of photochemical potential (Figure 13a) parallels the stepwise reduction by two electrons in thermal reduction, for instance, by Cr^{2+} or polarography.[13a]

Photochemistry involves reactions 6—9b; the electrochemical reaction is 9c. The electrolyte in the 'dark' cell is reoxidized by oxygen (reaction 11) and the electrolyte in the 'light' cell is restored through the photochemical reactions 6—9b.

Similar results have been obtained with $P_2Mo_{18}^{6-}$. Figure 13b shows the stepwise photochemical potential developed with $P_2Mo_{18}^{6-}$ and propan-2-ol. Typical reactions (excited states and radical intermediates are not shown) are as follows:

$$P_2Mo_{18}^{6-} + Me_2CHOH \longrightarrow P_2Mo_{18}^{8-} + Me_2CO + 2H^+ \tag{12}$$

$$P_2Mo_{18}^{8-} + Me_2CHOH \longrightarrow P_2Mo_{18}^{10-} + Me_2CO + 2H^+ \tag{13}$$

$$P_2Mo_{18}^{10-} + Me_2CHOH \longrightarrow P_2Mo_{18}^{12-} + Me_2CO + 2H^+ \tag{14}$$

The overall electrochemical reaction is:

$$P_2Mo_{18}^{12-} + P_2Mo_{18}^{6-} \longrightarrow P_2Mo_{18}^{10-} + P_2Mo_{18}^{8-} \tag{15}$$

In the dark half-cell

$$P_2Mo_{18}^{10-} + 1/2O_2 + 2H^+ \longrightarrow P_2Mo_{18}^{8-} + 2H_2O \tag{16}$$

(Protonation of molybdates has been omitted for clarity). The situation is analogous to that for tungstates. Reaction 16 restores the electrolyte to the $P_2Mo_{18}^{8-}$ oxidation state. Further oxidation, *i.e.* to $P_2Mo_{18}^{6-}$, is not obtained in reasonable time with atmospheric oxygen. In the 'light' cell, photolysis regenerates the $P_2Mo_{18}^{12-}$ oxidation state (reaction 14) so that after the first cycle the electrochemical reaction involves mainly

$$P_2Mo_{18}^{12-} + P_2Mo_{18}^{8-} \longrightarrow 2P_2Mo_{18}^{10-}$$

contrary to the thermal data,[22b] this cell seems to be unstable when photoreduction reaches 6-electrons.

Coming back to 1 : 12-tungstates and using the half-wave potentials corresponding to reactions 6—9c for PW_{12}^{3-}

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[57] E. Papaconstantinou and A. Ioannidis, *Inorg. Chim. Acta*, 1983, **75**, 235.

$$\begin{array}{ll} PW_{12}^{3-} + e^{-} \longrightarrow PW_{12}^{4-} & E_{\frac{1}{2}} = -0.02\text{V } vs. \text{ SCE} \\ PW_{12}^{4-} + e^{-} \longrightarrow PW_{12}^{5-} & E_{\frac{1}{2}} = -0.26\text{V } vs. \text{ SCE} \\ \hline \end{array}$$

$$PW_{12}^{3-} + PW_{12}^{5-} \longrightarrow 2PW_{12}^{4-} \text{ (galvanic reaction) } E_{\frac{1}{2}} = 0.24\text{V},$$

we calculate the standard free-energy corresponding to the above galvanic reaction as ~24 kJ (it should be noted that reversible half-wave potentials correspond to standard redox potentials unless there is a marked difference between the diffusion coefficients of the oxidized and reduced forms). The corresponding value for $P_2Mo_8^{6-}$ is ~33 kJ (reaction 15). It is understood that other combinations of polyoxometallates/organic reagents can be used to optimize the energetics involved.

Sensitization. Polyoxometallates of molybdenum and tungsten in principle, present an advantage relative to other systems used in solar energy conversion and storage as H_2, in that one compound works as photosensitizer, relay, and catalyst. In reality, therefore, apart from the sacrificial reagent, it is a one component system. However, the wavelength of light suitable for excitation is limited to near visible and u.v. (essentially below 400 nm) at least for tungstates. Thus, these compounds have shown to be good relays but they are not effective photosensitizers.

Yamase[58] has tried as photosensitizers riboflavin derivatives that absorb strongly in the 400—500 nm wavelength region, with various ammonium salts of $Mo_7O_{24}^{6-}$. He found that under irradiation at 436 nm the molybdate was reduced but that the riboflavin decomposed. Similar work was performed with proflavin sulphate which absorbs strongly at 450 nm and emits at 500 nm. The presence of HPC quenched the emission thus indicating energy- or electron-transfer. However, this sensitization was again followed by degradation of the dye.[59] Balzani and co-workers have reported on dynamic and static quenching of the luminescence of Ru^{II} polypyridine complexes by some mixed 1:12-tungstates.[60] $Ru(bpy)_3^{2+}$ with various HPC has been tried but the efforts have been unsuccessful so far, owing to the insolubility of the salt formed between the positively charged $Ru(bpy)_3^{2+}$ and the highly negatively charged heteropoly anion (HPA). Using approximately ten times higher concentrations of HPC, precipitation is avoided (apparently by encapsulating $Ru(bpy)^{2+}$ with HPA). Under these conditions, quenching is 100% and no partial quenching data have so far been obtained.[61]

Another approach has been to incorporate chromophores into the system to move the absorption towards visible light. The most obvious and least troublesome method was to incorporate vanadium in HPC using mixed heteropoly vanadates known to absorb light well in the visible spectrum.

The compounds $PV_2Mo_{10}O_{40}^{5-}$ and $PV_2W_{10}O_{40}^{5-}$, designated for simplicity as V_2Mo_{10} and V_2W_{10}, were selected because of their stability against other mixed

[58] T. Yamase, *Inorg. Chim. Acta*, 1981, **54**, L207.

[59] A. Ioannidis, Doctoral Dissertation, The Technical University of Athens, 1987.

[60] R. Ballardini, M. T. Gandolfi, and V. Balzani, *Inorg. Chem.*, 1987, **26**, 862.

[61] E. Papaconstantinou, unpublished results.

Table 7 *Quantum yields for the one-electron photoreduced products of mixed HPC in the presence of organic compounds at various wavelengths*[62]

Organic Compound[c]	λ, nm	*assignment*	$\Phi(V^{IV}V^{V}W_{10})^{a}$	$\Phi(V^{IV}V^{V}Mo_{10})^{b}$
alcohols	509	O–V^{V} [19a]	0.02—0.03	0.001—0.003
alcohols	436	O–V^{V}	0.02—0.03	0.001—0.003
alcohols	365	O–V^{V}	0.02—0.03	0.001—0.003
alcohols	252	O–W^{VI}	0.08	0.02
ethanoic acid	*d*		0.0	0.0

[a] Conditions: $[V_2^{V}W_{10}] = 1 \times 10^{-3}$M and [organic compound] ~2 M, at pH 4.5—5.0 with phosphate buffer. [b] Conditions: $[V_2^{V}Mo_{10}] = 5 \times 10^{-4}$M, and [organic compound] ~8 M, pH 2.7 with $HClO_4$. Solutions were deaerated with Ar. [c] Alcohols studied were isopropyl alcohol, ethanol, and glycol. [d] At all above wavelengths

HPC. Figure 14 shows the spectra of the non-reduced mixed HPC together with those of the corresponding molybdates and tungstates for comparison.

The results obtained from selective irradiation of the O–V^{V}, O–Mo^{VI}, and O–W^{VI} CT bands are summarized in Table 7.[62]

Without going into details, the following conclusions can be drawn. Incorporation of vanadium into HPC of molybdenum and tungsten has shifted the absorption to higher wavelengths thus allowing photochemistry to be performed well into the area of high intensity solar light (Figure 14). This, however, is not without cost: (a) Generally, incorporation of vanadium into HPC (mainly tungstates) makes the reduced HPC less stable than the corresponding 'classical' heteropoly blues of the Keggin (1:12) and Dawson (2:18) structures.[8] Similar instability has been observed during photolysis. This may not necessarily be a serious problem, since catalysts of this kind operate effectively in thermal reactions.[9a] An equilibrium is established between the mixed HPC and the decomposition products thus allowing the system to operate despite partial decomposition. (b) Quantum yields of the one-electron photoreduced product obtained at the O–V^{V} CT bands are about four times less for tungstovanadates and about ten times less for molybdovanadates relative to quantum yields at the O–W^{VI} and O–Mo^{VI} CT bands respectively. (c) Irradiation with a 400 nm cut-off filter, *i.e.* in the area of O–V^{V} CT bands, would place a maximum of only two electrons on vanadium atoms. No further reduction that would place electrons on molybdenum or tungsten, as has been shown electrochemically, was observed on prolonged irradiation. Under these conditions no hydrogen was produced, in agreement with the thermodynamics. In connection with the location of the added electrons on mixed HPC, Figure 15 shows the e.s.r. spectrum of molybdovanadate photochemically reduced by one electron. The well defined eight-line hyperfine structure (^{51}V, $I = 7/2$) indicates that the electron is located on the vanadium ion, as is the case when reduction takes place by chemical means.[19b,63] Figure 16 shows the spectra of the photochemically reduced mixed HPC.

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[62] P. Argitis and E. Papaconstantinou, *Inorg. Chem.*, 1986, **25**, 4386.

[63] M. Otake, Y. Komigama, and T. Otaki, *J. Phys. Chem.*, 1973, **77**, 2896.

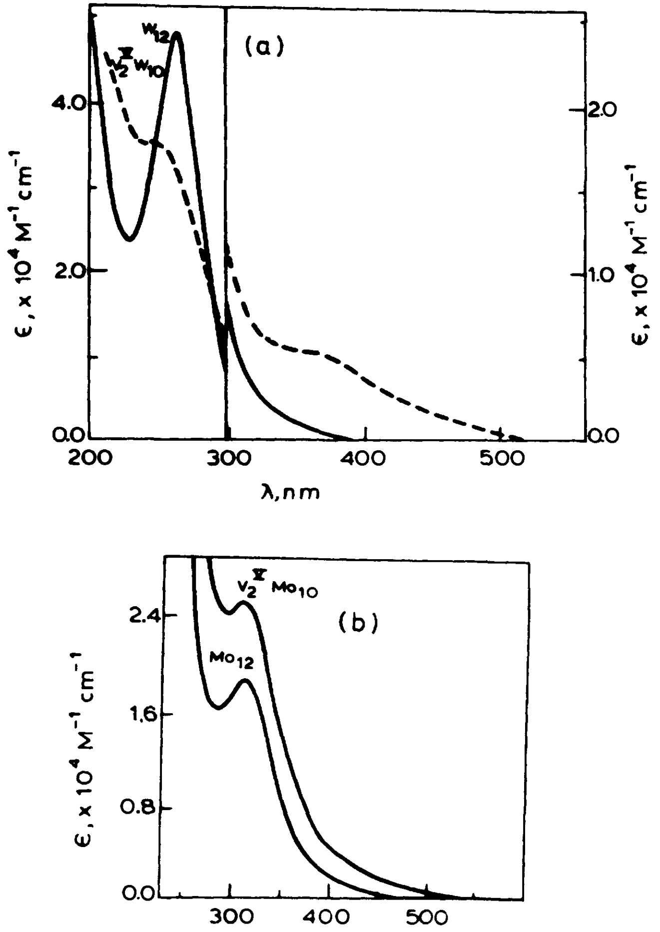

Figure 14 *Spectra of non-reduced HPC showing a red shift in absorbance with incorporation of* V^{5+} *ions.* $W_{12} = PW_{12}O_{40}^{3-}$, $V^VW_{10} = PV_2W_{10}O_{40}^{5-}$, $Mo_{12} = PMo_{12}O_{40}^{3-}$, $V^VMo_{10} = PV_2Mo_{10}O_{40}^{5-}$ (*ref.* 62)

For V_2W_{10}, reduction did not proceed beyond the addition of two electrons on vanadium atoms, even with u.v. irradiation, and no hydrogen was produced under any circumstances. On the other hand $V_2^VMo_{10}$ was reduced beyond two electrons when photolysed with $\lambda < 400$ nm (O–M^{VI} CT bands). Under these conditions the quantum yield for H_2 evolution was <0.01. An overall similar photochemical mechanism that involves mainly hydrogen transfer reactions 6—9c is suggested to operate with the mixed HPC.[62]

It has been reported that for tungstovanadate the absorption band around 500 nm corresponds to the $V^{IV} \longrightarrow W^{VI}$ CT band.[19a] It was thought that irradiation

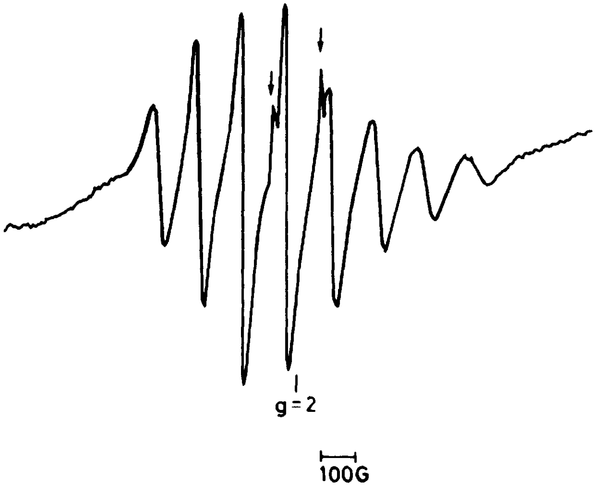

Figure 15 *E.s.r. spectra of photochemically produced* $V^{IV}V^{V}Mo_{10}$ (1×10^{-4}M) *in the presence of* 8M-*propan-2-ol*, pH 2.8 *with* $HClO_4$ *in aqueous solution at room temperature*[62]

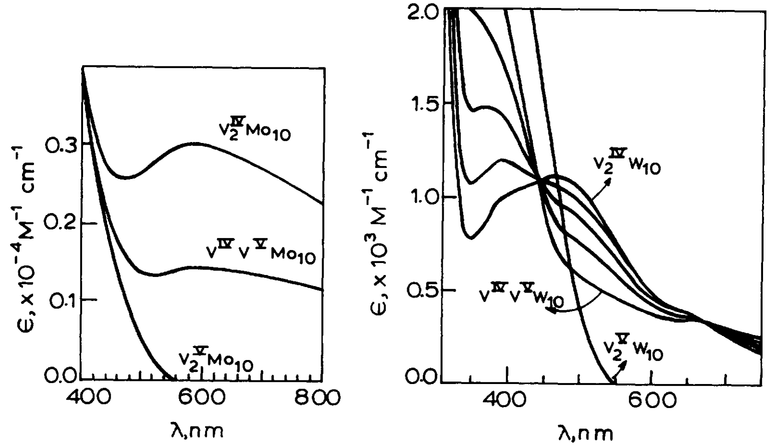

Figure 16 *Spectra of* $PV_2M_{10}O_{40}^{5-}$ ($V_2^{V}M_{10}$), *where* M = Mo *or* W, *photochemically reduced by one* ($V^{IV}V^{V}M_{10}$) *and two* ($V_2^{IV}M_{10}$) *electrons*

at this band would promote the electron on to tungsten atoms, thereby favouring reduction of H^+. So far the results have been negative.

4 Conclusions and Future Prospects

The photocatalytic behaviour of polyoxometallates consists of photoreduction of polyoxometallates with concomitant oxidation of organic compounds. Regeneration of the catalyst is obtained by reoxidation with oxygen, or in the absence of oxygen by H^+ (H_2 evolution). Generally, although molybdates are more effective redox catalysts than tungstates (they require lower temperatures for reduction), their reoxidation by oxygen is not easily obtained. By contrast tungstates are more difficult to reduce but they are easily oxidized back. Excitation with u.v. and near visible light renders tungstates effective oxidizing reagents and, owing to their fast reoxidation by oxygen, effective photocatalysts. The selective photocatalytic oxidation of alcohols, and for that matter the oxidation of other organic compounds, is promising if one considers the great number of polyoxometallates that exist and can be made, and their successful performance as thermal catalysts. In that respect, studies of the excitation and deactivation processes, and the ways that they are influenced by changes in the hetero atom, addenda atoms, extent of reduction, and incorporation of other metal ions into the structure, would be of interest. Although none of the HPC studied so far have shown any emission (weak emission has been recently observed[30]) indications are that the lifetime of the excited states varies considerably. Studies on how to prolong the excited state lifetimes would also be of interest. The chemistry of semiconductors is now moving fast and h^+ and e^- separation, mobility, and recombination are becoming better understood; studies on HPC have provided a step in this direction. The O–M charge-transfer band is now replaced by the band gap excitation from valence band to conduction band and to the generation of h^+ and e^-. The analogy is obvious and work in both subjects may be fulfilling. One is always hopeful that studies of this kind might lead to a process beyond academic interest.

Acknowledgements. I thank and appreciate the valuable contributions of my coworkers and students and NATO for financial support.