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Decatungstate photocatalysis

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Contents

Abstract

Polyoxometalates, such as decatungstates $W_{10}O_{32}^{4-}$, appear to exhibit especially interesting properties as photocatalysts. The current review is specifically concerned with (i) the primary photoevents and in particular the nature, lifetime and quantum yield of formation of the primary species that result from light absorption, and (ii) the sequence of reactions resulting in product formation under aerobic conditions.

Keywords: Polyoxotungstates; Photocatalysis; Photochemistry; Photooxygenation; Peroxides; Radicals

1. Introduction

Polyoxometalates, early-transition-metal-oxygen-anion clusters, are a large and rapidly growing class of inorganic compounds with significant applications in a range of areas. In an excellent general review devoted to homogeneous catalysis by polyoxoanions [1], Hill and Prosser-McCartha indicate that more than 30 reviews on some aspects of polyoxometalates have been published since 1983. [Since submission of the present paper, a Special Issue of Chemical Reviews on Polyoxometalates,

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C.L. Hill (Ed.) [Chem. Rev., 98 (1998) 1–387] has just appeared. Photochemistry and photocatalysis of polyoxometalates is one of the few topics that is not reviewed in this comprehensive and up-to-date reference volume on the subject.] These oxides, such as decatungstates $W_{10}O_{32}^{4-}$, appear to exhibit especially interesting properties as photocatalysts. They have been intensively studied over the past 10 years or so, particularly under anaerobic conditions [2–7]. [For interesting papers on mechanisms involving decatungstates photochemistry, including introduction of functionality into unactivated carbon–hydrogen bonds, see refs. [8–16].] This review focuses on the kinetic and mechanistic aspects of photocatalysis by polyoxotungstates. Although previous reviews on photocatalytic properties of polyoxometalate systems are relatively recent [1–7], they have not covered these aspects very adequately and are in part out of date as research in this area has developed considerably in the last two or three years. In fact, hard mechanistic information on photocatalysis by polyoxotungstates is limited to a few papers. It is clear, however, that proper utilization of these photocatalysts demands an improved understanding of the cascade of events that follow light absorption by polyoxotungstates, finally yielding reaction products. The current review is specifically concerned with (i) the primary photoevents, and in particular the nature, lifetime and quantum yield of formation of the primary species that result from light absorption, and (ii) the sequence of reactions resulting in product formation under aerobic conditions, and especially on the role played by oxygen in such processes.

2. Laser flash photolysis and pulse radiolysis studies

Previous studies on nano- and microsecond laser flash photolysis of tetrabutylammonium decatungstate in deaerated acetonitrile led to the proposal that the oxygen-to-metal charge-transfer (LMCT) excited state of $W_{10}O_{32}^{4-}$, which is thought to be the primary species formed [17–19], undergoes an electron transfer from a substrate to yield the one-electron reduced form of decatungstate [20]. The protonation of $W_{10}O_{32}^{5-}$ produces $HW_{10}O_{32}^{4-}$ which undergoes a slow disproportionation to $H_2W_{10}O_{32}^{4-}$ as expected from the results for tetrabutylammonium decatungstate photolysis [19].

Recently, Hill and colleagues [21,22] have demonstrated that the primary excited state produced following absorption of a UV photon by sodium or tetrabutylammonium decatungstate survives for ca. 30 ps in both aerated and deaerated acetonitrile solutions (Fig. 1). The quoted lifetime is close to the temporal resolution of the picosecond laser set-up used for these studies, but it is clear that the initial excited state decays rapidly to generate an intermediate that absorbs strongly around 780 nm and persists for many nanoseconds (i.e. >20 ns) (Fig. 2). But the lifetime and deactivation route of this intermediate, which will be designed as wO [23], remain obscure. Fig. 2 shows distinct differences between the transient absorbance spectrum of the intermediate and that calculated for $W_{10}O_{32}^{5-}$ or $H_xW_{10}O_{32}^{5-x}$. This suggests that the intermediate wO is not the one-electron reduced form of decatungstate as proposed previously [20].

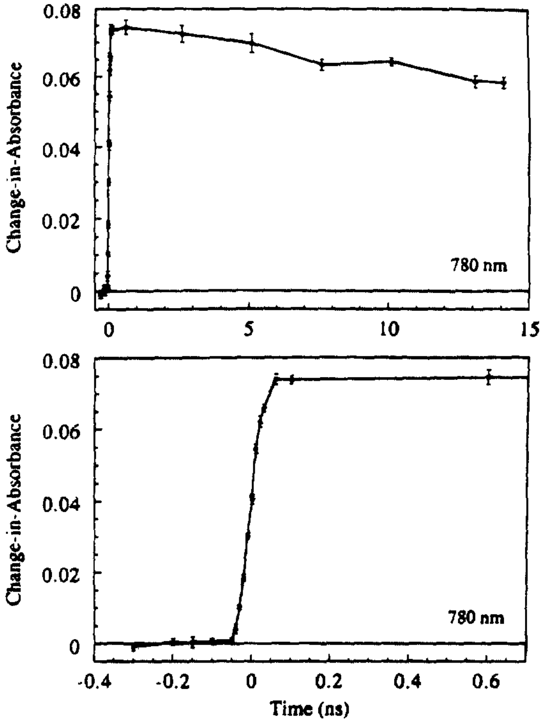


Fig. 1. Representative kinetics observed at 780 nm for the absorbance transient produced following 355 nm excitation of a 5×10^{-4} M tetrabutylammonium decatungstate acetonitrile solution: (top) 0–15 ns delay; (bottom) −0.2 to +0.4 ns delay. Reprinted with permission from ref. [21]. Copyright 1995 American Chemical Society.

Following excitation ($\lambda = 355$ nm) of tetrabutylammonium decatungstate in acetonitrile with a 15 ns laser pulse, a long-lived transient species could be observed by time-resolved optical spectroscopy [23]. This intermediate absorbs strongly around 780 nm and, on the basis of its characteristic absorption spectrum, can be identified as being wO. It decays via first-order kinetics with a lifetime of $\tau = 55 \pm 20$ ns (Fig. 3). Repeating the experiment under various pressures of oxygen showed that the lifetime is not quenched by O_2 within the limit of experimental uncertainty. Separate studies confirmed that neither the CT state nor wO produced singlet molecular oxygen under illumination in O_2-saturated acetonitrile solution, suggesting that wO is a relaxed excited state.

The decay profile recorded for wO at 760 nm is complex and indicates the existence of a further intermediate that survives on much longer time scales (Fig. 3). This latter species absorbs both at 780 nm and in the near UV region, and its rate of formation exactly equals the rate of decay of wO. Clearly, this long-lived intermediate is formed from wO under these conditions. It decays via second-order kinetics with a first half-life of ca. 700 ns to reform the prepulse baseline. The yield of this long-lived species is reduced by the presence of small concentrations of O_2, and its lifetime

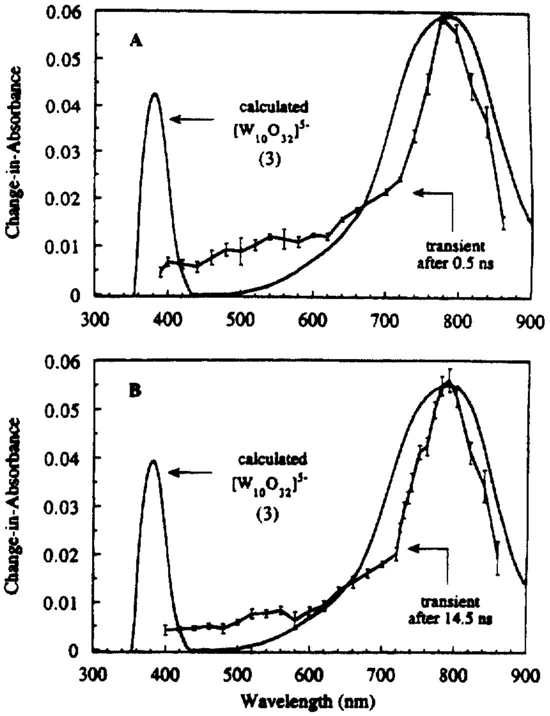


Fig. 2. Transient absorbance (ΔA) spectra obtained following 355 nm excitation of a 5×10^{-4} M tetrabutylammonium decatungstate acetonitrile solution: (A) 0.5 ns delay; (B) 14.5 ns delay. Also shown is a calculated difference spectrum of the one-electron-reduced species in acetonitrile. Reprinted with permission from ref. [21]. Copyright 1995 American Chemical Society.

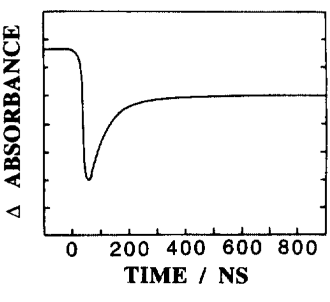


Fig. 3. Profile recorded at 760 nm showing decay of wO as generated following 355 nm excitation of a 5×10^{-4} M tetrabutylammonium decatungstate nitrogen-saturated acetonitrile solution. The species remaining after decay of wO is assigned to the one-electron-reduced species. One division represents ΔA = 0.018. Reprinted with permission from ref. [23]. Copyright 1997 American Chemical Society.

is shortened. It appears, therefore, that oxygen both competes with formation of the long-lived species and reacts with it. The absorption spectrum of this long-lived species has some of the characteristics of the one-electron-reduced form of decatungstate, such that it might arise by way of electron transfer. If this is so, it is likely that acetonitrile plays some part in the overall process and this possibility was addressed by performing pulse radiolysis studies and by adding a more-reactive substrate (i.e. propan-2-ol) to the solution [23]. Thus, addition of increasing amounts of propan-2-ol to an acetonitrile solution of decatungstate results in an enhanced yield of the one-electron-reduced species (Fig. 4). This investigation has also shown that the bimolecular rate constant for reaction between wO and propan-2-ol in aerated acetonitrile solution is ca. 1×10^{8} M^{-1} s^{-1}. The spectrum of the long-lived species obtained in the presence of propan-2-ol is given in Fig. 5(a).

Injection of a pulse of high-energy electrons into deoxygenated acetonitrile gives rise to a highly reducing species exhibiting an intense absorption band centered around 1500 nm that is similar to the transient described by Bell et al. [24]. This species may be generalized as being a reduced solvent molecule CH_3CN^-. In the absence of an added substrate, CH_3CN^- decays rapidly with a first-order rate constant of 3.5×10^{5} s^{-1}. Addition of increasing amounts of decatungstate enhances the rate of decay of CH_3CN^- and causes the appearance of the one-electron-reduced form of decatungstate [23].

$$CH_3CN^- + W_{10}O_{32}^{4-} \rightarrow CH_3CN + W_{10}O_{32}^{5-}$$

The bimolecular rate constant for this electron-transfer process corresponds to 5.5×10^{9} M^{-1} s^{-1}. The absorption spectrum of the reduced product is given in Fig. 5(b) and, by reference to CH_3CN^-, the molar extinction coefficient at the absorption maximum of 780 nm can be assigned a value of ~10 000 M^{-1} cm^{-1}, in agreement with literature data which range [20,25,26] from ~7500 M^{-1} cm^{-1} to 11 000 M^{-1} cm^{-1}. The transient possesses a second absorption band centered around 370 nm whose molar extinction coefficient is ~4500 M^{-1} cm^{-1}. [For synthesis and characterization of $W_{10}O_{32}^{6-}$ and electronic absorbance data for $H_x[W_{10}O_{32}]^{(6-x)-}$ ($x=0$–4) in CH_3CN, see ref. [27]. Molecular orbital calculations

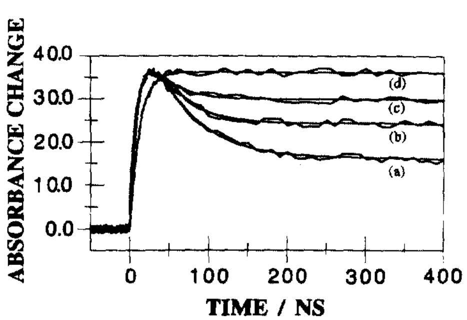


Fig. 4. Effect of propan-2-ol [XH] on the decay of wO in an air-saturated acetonitrile solution of 5×10^{-4} M tetrabutylammonium decatungstate observed at 760 nm following 355 nm excitation with a 15 ns laser pulse: (a) [XH]=0.01 M, (b) [XH]=0.10 M, (c) [XH]=0.30 M, and (d) XH/CH_3CN (1/1). The profiles have been normalized to the initial absorbance and show the progressive increase in yield of the one-electron-reduced species. Reprinted with permission from ref. [23]. Copyright 1997 American Chemical Society.

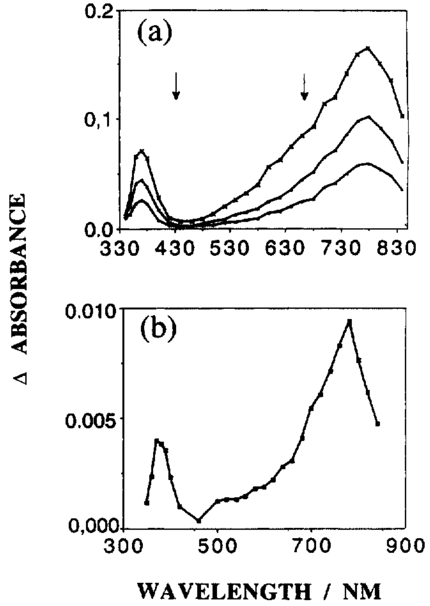
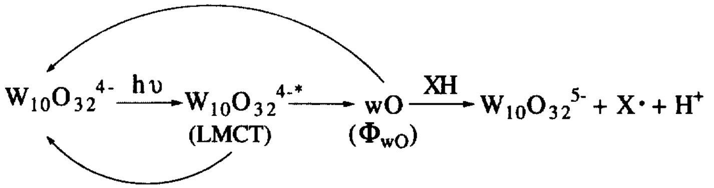


Fig. 5. Transient absorption spectra recorded for the one-electron-reduced form generated by (a) 355 nm excitation with a 15 ns laser pulse of a 5×10^{-4} M tetrabutylammonium decatungstate air-saturated acetonitrile/propan-2-ol (1/1 vol) solution after 230 μs, 1.3 ms and 8 ms; (b) injection of a 20 ns pulse of high energy electrons into a 2.5×10^{-4} M tetrabutylammonium decatungstate N_2-saturated solution after 220 μs. Reprinted with permission from ref. [23]. Copyright 1997 American Chemical Society.

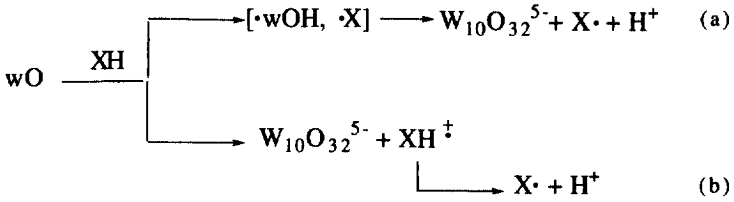
support the effect of acid and $W_{10}O_{32}^{4-}$ protonation on photoactivated hydrogen atom abstraction from alkanes [28].] Under pulse radiolytic conditions, the one-electron-reduced form of decatungstate does not decay over a few milliseconds. Careful comparison of the transient spectroscopic records shows that the long-lived species generated by laser photolysis of decatungstate in acetonitrile can be identified as being the one-electron reduced species (Fig. 5).

By combination of laser flash photolysis and pulse radiolysis studies, together with literature data, the course of events following light absorption by decatungstate in acetonitrile can be expressed by Schemes 1 and 2, where XH denotes a substrate.

A pico- and nanosecond laser flash photolysis study confirms the formation of



Scheme 1.



(a) Hydrogen-atom transfer mechanism
(b) Electron-transfer mechanism

Scheme 2.

the short-lived LMCT excited state and of the transient wO, and determines the rate of decay of this last intermediate for decatungstate with different counterions in nitrile solvents [29]. It also suggests that wO reacts with any substrate XH to give the one-electron-reduced decatungstate species $HW_{10}O_{32}^{4-}$ and the radical X·. This proposal is not consistent with the similarity of the spectra obtained by pulse radiolysis and laser flash photolysis in the presence of propan-2-ol (Fig. 5) which suggests that the initially formed radical ·wOH undergoes rapid deprotonation in non-aqueous solvent (Scheme 2).

3. Continuous photolysis studies

Until the last few years, most studies were made under anaerobic conditions and the proposed mechanisms were founded on indirect evidence. They were essentially derived from product yields and kinetic measurements obtained under steady-state illumination. It was generally believed that, in the presence of oxygen, autoxidation initiated by radicals generated in the photoinduced redox chemistry was responsible for product formation. The recent progress made in the understanding of the mechanism of catalysis by polyoxotungstates is mainly the consequence of a new approach based on the simultaneous determination of substrate disappearance, product formation and dissolved O_2 uptake as a function of irradiation time [23]. These last experiments followed the general procedures described previously for the measurement of the quantum yield of singlet oxygen production under carefully controlled conditions [30–32].

Since the initially formed charge-transfer excited state of decatungstate has a very short lifetime, the longer lived intermediate wO is the more likely reactant in subsequent photocatalytic reactions. In order to learn more about its nature and reactivity, a series of steady-state irradiations was made both in the absence and the presence of an added substrate [23]. These reactions were made under aerated conditions so that the course of the reaction could be followed by monitoring the uptake of dissolved O_2. In O_2-saturated acetonitrile, it is assumed that O_2 intercepts all species derived from interaction between wO and an organic substrate (including acetonitrile itself). In fact, wO does not react with O_2 but the rate of O_2 uptake remains constant in aerated and O_2-saturated solution. Based on this assumption, the quantum yield for consumption of O_2 may be equated with the quantum yield for formation of radicals derived from wO. These quantum yields are measured by following the rate of O_2 consumption under illumination, over short irradiation periods where O_2 consumption depends linearly on illumination time.

Illumination in the absence of an added substrate results in slow but definite consumption of O_2, a finding consistent with the involvement of acetonitrile in the overall reaction scheme. Addition of a suitable organic substrate, such as propan-2-ol, caused a significant increase in the rate of O_2 consumption, and at [propan-2-ol] = 1.0 M the quantum yield for O_2 consumption was found to be 0.5 (Table 1). In fact, the quantum yield measured in the presence of a substrate (Φ_{OX}^{XH}) was found to depend upon both the concentration and nature of that substrate, but always exceeded that found in neat acetonitrile (Φ_{OX}). The highest quantum yields observed during these experiments are restricted to values <0.6, suggesting that effective radical chain propagation is unlikely. Different values for the quantum yield are found for different counterions, with the tetrabutylammonium salt being the more reactive species. With this latter sensitizer it was noted that the quantum yield increased with increasing concentration of counterion, as varied by changing the concentration of sensitizer or by adding tetra-*n*-butylammonium bromide. For the corresponding sodium salt, the quantum yield remains strictly independent of sensitizer concentration. This suggests that the organic counterion competes with solvent and/or substrate.

Concerning the use of propan-2-ol as substrate, it was found that the quantum yield for O_2 consumption increased progressively with increasing concentration of substrate to a limiting value of ca. 0.5 (Table 1). It was also noted that the value, although approaching zero at low concentrations of substrate, remained finite in the absence of substrate, confirming the notion that acetonitrile itself acts as a substrate for wO. The data expressed in Table 1 can be used to derive a bimolecular rate

Table 1
Quantum yield of oxygen consumption measured for illumination of potassium decatungstate (0.55 mM) in the absence and presence of alcohols ROH in oxygen-saturated acetonitrile[a]

Alcohol ROH	ROH (M)	Φ_{ox}^{ROH}
—	—	0.04
Me_2CHOH	0.0055	0.065
Me_2CHOH	0.1	0.24
Me_2CHOH	0.2	0.34
Me_2CHOH	0.5	0.46
Me_2CHOH	1.0	0.50
Me_2CHOH	1.0	0.49
BuOH	0.1	0.23
Me_3COH	0.1	0.05
Me_3COH	1.0	0.08

[a] Me_2CHOH = propan-2-ol, BuOH = butan-1-ol, Me_3COH = 2-methylpropan-2-ol.

constant (k_{XH}) for reaction between wO and propan-2-ol by considering the reaction in terms of a generalized Stern–Volmer treatment. Thus, the experimental quantum yields can be described by the following expression:

$$(\Phi_{wO} - \Phi_{OX})/(\Phi_{wO} - \Phi_{OX}^{XH}) = 1 + K[XH] \tag{1}$$

where Φ_{wO} is the quantum yield for formation of wO and $K = k_{XH}\tau$ is the corresponding Stern–Volmer constant. From non-linear least-squares analysis of the experimental data, it was derived that $K = 6.2 \pm 2\ M^{-1}$ while the quantum yield for formation of wO becomes 0.53 ± 0.17 [23]. An independent estimate of K was made by laser flash photolysis studies where $K = 4.4\ M^{-1}$ since under these conditions $\tau = 55$ ns and $k_{XH} = (8 \pm 4) \times 10^7\ M^{-1}\ s^{-1}$. More generally, knowing the values of τ and Φ_{wO} permits the determination of k_{XH} for any substrate if the quantum yield of XH disappearance or of product formation has been measured. Thus, for a value of 0.35 found for a solution of 2.8 M cyclohexane in CH_2Cl_2–CH_3CN solution [33], it may be deduced that $k_{XH} \approx 1 \times 10^7\ M^{-1}\ s^{-1}$.

Illumination in the presence of O_2 seems likely to result in formation of peroxides and/or hydroperoxides derived from the organic substrates and from consumption of O_2, and it has been shown that decatungstate catalyses conversion of propan-2-ol into acetone in essentially quantitative yield [34–36]. Fig. 6 shows the profile for oxygen consumption and hydrogen peroxide formation as measured for sensitized

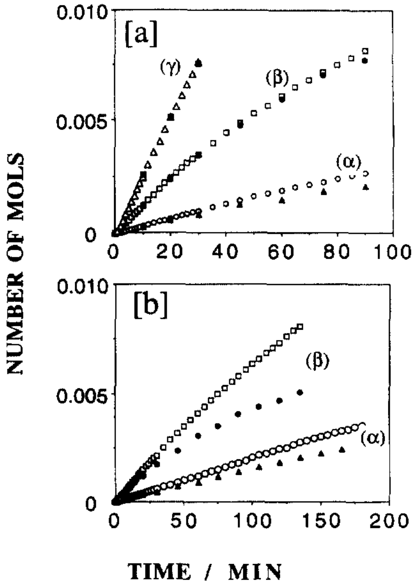
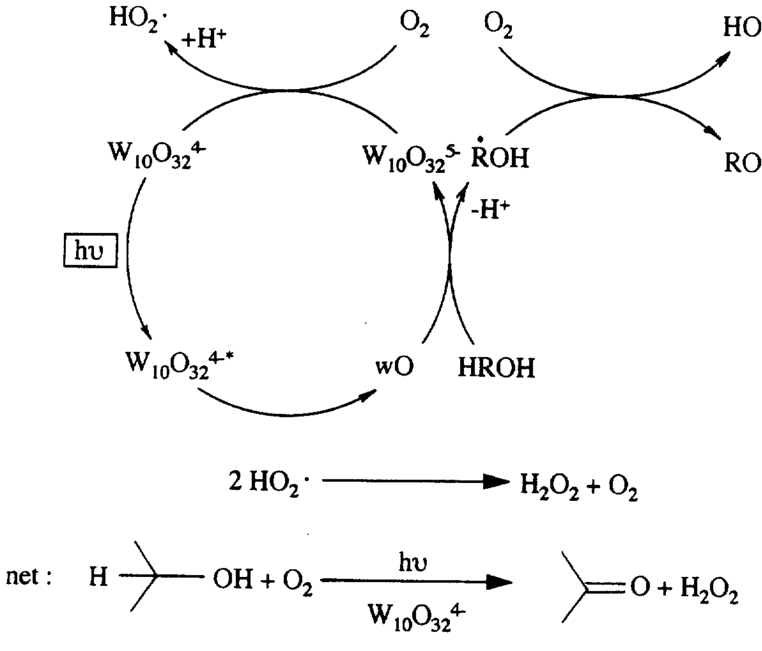


Fig. 6. Correspondence between the number of moles of oxygen consumed [open symbols] and of peroxide formed [solid symbols] during continuous illumination of potassium decatungstate (5.5×10^{-4} M) in oxygen-saturated acetonitrile. Panel (a) shows the effect of propan-2-ol at 5.5×10^{-3} M (α), 0.1 M (β) and 1.0 M (γ). Panel (b) shows results collected in the absence (α) and presence (β) of 0.018 M adamantane. Reprinted with permission from ref. [23]. Copyright 1997 American Chemical Society.

photo-oxygenation of propan-2-ol at different concentrations of substrate. The initial variations are linear over a relatively long period, deviations from linearity beginning as the concentration of remaining substrate is no longer sufficient to quantitatively intercept wO. Except at low propan-2-ol concentrations, for which a noticeable contribution of direct photo-oxygenation of solvent is expected, the rate of peroxide formation is equal to the rate of O_2 consumption. This result confirms the mechanism proposed in Scheme 3, under reaction conditions not involving a radical chain component and, consequently, the limiting value of Φ_{OX} is Φ_{wO}. This situation corresponds to the case where the intermediate wO is intercepted quantitatively by substrate.

Similarly, Fig. 6 shows the variation of the number of moles of O_2 consumed and the total peroxide formed as a function of illumination time in the absence and presence of adamantane. Initially, the concentration of peroxide formed corresponds to the number of molecules of O_2 consumed, within the limit of experimental uncertainty. But after ca. 10 min the molar ratio of peroxide formed to oxygen consumed remains constant and then, after 1 h decreases again when adamantane is present. Gas chromatography was used to follow both the disappearance of adamantane and the formation of oxygenated products of the substrate, the corresponding hydroperoxides, after their reduction with trimethylphosphite. Quantum yields measured for the disappearance of the adamantane and for the formation of the hydroperoxide were identical within experimental limits but significantly less than the quantum yield for the consumption of O_2 (ratio ~0.75:1). This latter



Scheme 3.

finding is consistent with part of the consumed O_2 being associated with oxygenation of the solvent. In fact, the contribution of solvent oxygenation becomes noticeable when $k_{XH}[XH]$ for the substrate is close to the corresponding value for acetonitrile ($k \sim 2 \times 10^6\ s^{-1}$). The quantitative formation of hydroperoxides from adamantane is consistent with a precedent observation made with isobutane [37].

4. Mechanism of catalysis under aerobic conditions

The course of events following light absorption by decatungstate in acetonitrile is expressed in Scheme 1.

Here, the initially produced excited state is of CT character and decays in about 30 ps to form the longer lived species designated as wO. This latter intermediate, which has a lifetime of ca. 55 ns in deoxygenated acetonitrile, is most likely the reactive species in photocatalytic systems. From steady-state irradiation experiments made in the presence of propan-2-ol as substrate, the quantum yield for formation of wO appears to be ca. 0.6 [23]. In fact, this value for the quantum yield for formation of wO (Φ_{wO}) appears to be entirely consistent with the large body of product determination studies made mainly under deoxygenated conditions [4,20,33,38–41], where quantum yields approach but never exceed 0.6. On this basis, ca. 40% of the initially formed CT excited state must undergo rapid internal conversion to restore the ground state since emission is very weak [42].

In the absence of O_2, wO decays to form the one-electron-reduced species as demonstrated by laser flash photolysis techniques. It has been shown that O_2 inhibits formation of the one-electron-reduced species and that $W_{10}O_{32}^{5-}$ reacts with O_2 to provide a source of peroxy species [19,20,43,44]. The yield of the one-electron-reduced species increases in the presence of a reactive substrate, such as propan-2-ol, but the origin of this species in neat acetonitrile is unclear. In fact, two limiting cases can be considered to account for formation of the one-electron-reduced species in the absence of a substrate; namely, intramolecular rearrangement of wO or bimolecular interaction between wO and acetonitrile. Either process could account for the observations, and it is of particular interest to learn if the solvent is acting as a quencher for wO since this would affect its inherent lifetime.

Acetonitrile is not normally regarded as a reactive substrate, being favored by electrochemists as an inert solvent. Under more drastic conditions such as those attained in γ-radiolysis experiments, acetonitrile appears quite reactive. In the absence of oxygen, one of the primary radiolysis products is the $\cdot CH_2CN$ radical which dimerizes to form succinonitrile [45]. The same radical can be formed by reaction between the *tert*-butoxyl radical and acetonitrile under milder conditions [46]. The cyanomethyl radical, being a carbon centered radical, reacts with oxygen to form the corresponding peroxyl species [47]. On this basis, and bearing in mind that high energies are available, it is not unrealistic to expect [ineffective] direct reaction between wO and acetonitrile. In fact, succinonitrile has been detected (quantum yield $<10^{-5}$) from the photolysis of $(NBu_4)_4[W_{10}O_{32}]$ in deoxygenated acetonitrile [19]. It might be expected, therefore, that illumination of decatungstate in aerated acetonitrile will result in formation of the cyanomethyl peroxy radical, at least in low yield. In this regard the observed quantum yield seems to be of the expected order of magnitude. These considerations are substantiated by the recent isolation of hydroperoxyacetonitrile [48].

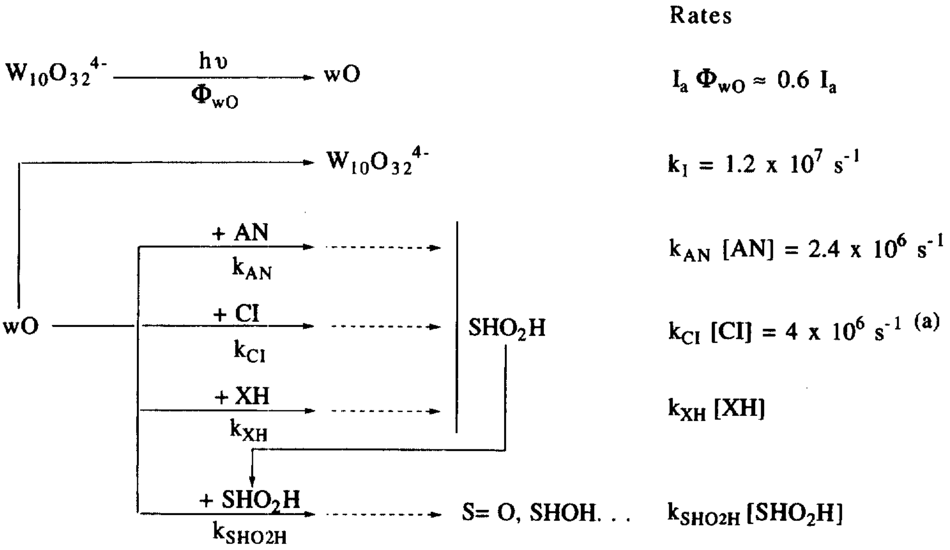
Although direct interaction between wO and solvent is interesting in itself, a more important aspect concerns the reactions that occur with added substrate. In particular, it is important to assess the reaction mechanism by which decatungstate is able to oxygenate organic compounds and to ascertain if such reactions are catalytic and/or selective. Reactions with substrate can be considered as an extreme form of the reaction which occurs with acetonitrile. This point is made clear by the realization that adding increasing amounts of propan-2-ol to an acetonitrile solution of decatungstate results in an enhancement in the yield of the one-electron-reduced species (Fig. 4). Irradiation in the presence of both propan-2-ol and O_2 results in formation of acetone and hydrogen peroxide and can be expressed by Scheme 3. An alternative mechanism involving intermediate formation of 2-propylperoxyl may be suggested for the propagation step [49].

Formation of the one-electron-reduced species under illumination of decatungstate in the presence of a substrate might involve hydrogen-atom abstraction from the substrate by wO, followed by rapid deprotonation of the resultant radical, and/or electron transfer (Scheme 2).

It has been found that irradiation of decatungstate in the presence of many different alcohols, linear and branched, results in consumption of oxygen (Table 1). From the measured rates of oxygen consumption, the Stern–Volmer constants K could be determined from Eq. (1). The observed reactivities vary over two orders of magnitude for alcohols expected to have similar oxidation potentials but containing hydrogen atoms of different bond-dissociation energy. Throughout this set of experiments, wO reacts as expected for a reactive oxyradical. Thus, the relative reactivities of propan-2-ol and 2-methylpropan-2-ol are ca. 70-fold. On this basis, it seems most likely that the primary reaction between wO and alcoholic substrates involves hydrogen-atom abstraction for which the selectivity is marginal. The observation that propan-2-ol reacts very much faster than acetonitrile is also consistent with a hydrogen-atom abstraction mechanism.

Light-induced hydrogen-atom abstraction is also entirely consistent with the observations made in the absence of added substrate [23]. Thus, illumination of $Na_4[W_{10}O_{32}]$ (0.2–1.2 mM) in aerated or O_2-saturated acetonitrile results in a quantum yield for oxygen consumption of 0.09. This value is very much lower than the limiting value of ca. 0.6, despite the high concentration of substrate. The reaction efficiency increases when an organic counterion is present, and with $(NBu_4)_4[W_{10}O_{32}]$ (0.54 mM) the quantum yield becomes 0.19. Clearly, in the latter case the counterion provides an additional source of abstractable hydrogen and, indeed, addition of tetra-*n*-butylammonium bromide further augments the quantum yield. It is unlikely that these observations can be explained by a mechanism other than hydrogen-atom abstraction.

Combining steady-state and flash photolysis results [23] the approximate rate constants for inherent [i.e. non-hydrogen abstraction] decay of wO, k_I, and for



(a) for [tetrabutylammonium decatungstate] = 0.54 mM

Scheme 4.

hydrogen atom abstraction from the counterion k_{CI} and from acetonitrile k_{AN} have been derived (Scheme 4).

Irradiations made in the presence of alkanols as reactive substrate result in the formation of hydrogen peroxide according to the sequence of reactions shown in Scheme 3. In principle, such photoprocesses could be utilized for reactions requiring the controlled release of peroxide. With other types of substrate irradiation might be expected to result in the formation of more useful products. For example, alkanes

$$\begin{array}{lcll}
 & W_{10}O_{32}^{4-} \xrightarrow[\Phi_{wO}]{h\upsilon} wO & & (a) \\
 & wO + XH \longrightarrow W_{10}O_{32}^{5-} + X\cdot + H^+ & & (b) \\
 & X\cdot + O_2 \longrightarrow XO_2\cdot & & (c) \\
 & W_{10}O_{32}^{5-} + O_2 + H^+ \longrightarrow W_{10}O_{32}^{4-} + HO_2\cdot & & (d) \\
 & XO_2\cdot + HO_2\cdot \longrightarrow XO_2H + O_2 & & (e) \\
\text{net} & XH + O_2 \xrightarrow[W_{10}O_{32}^{4-}]{h\upsilon} XO_2H & &
\end{array}$$

Scheme 5.

are converted into the corresponding carbon centered hydroperoxides as shown in Scheme 5 and as demonstrated in the specific case of adamantane [23].

A different mechanism has been proposed [29,48] in which (i) the intermediate wO reacts with an alkane XH to give $HW_{10}O_{32}$, the protonated form of the one-electron-reduced species $W_{10}O_{32}{}^{5-}$, and the corresponding radical X·, (ii) this latter is quenched by O_2 forming a peroxy radical $XO_2\cdot$, (iii) in the solvent cage, which is supposed to have an anomalously long lifetime (near 1 ms), the peroxy radical reoxidizes $HW_{10}O_{32}{}^{4-}$ to give the hydroperoxide ROOH and $W_{10}O_{32}{}^{4-}$, and (iv) the catalyst reoxidation is the rate-limiting step of the alkane oxidation. This alternative mechanism involving hydrogen-atom transfer from ·wOH to $XO_2\cdot$ seems much less likely because the concentration of ·wOH will be kept low by deprotonation and interception with O_2 as suggested by the similarity of the spectra obtained by pulse radiolysis and laser photolysis (Fig. 5). In addition, the results of continuous photolysis studies in oxygen-saturated acetonitrile in a well-agitated system under low near UV irradiance [23] (conditions in which the concentration of O_2 is much higher than the steady-state concentration of any radical) are consistent with a quantitative direct reoxidation of $W_{10}O_{32}{}^{5-}$ by O_2 (Schemes 3 and 5) and with a hydrogen-atom abstraction by wO being the rate-limiting step of the catalytic cycle (Table 1). It may be noticed that the reoxidation of the one-electron-reduced form of polyoxometalates is often represented by:

$$2W_{10}O_{32}{}^{5-}+\tfrac{1}{2}O_2+2H^+\rightarrow 2W_{10}O_{32}{}^{4-}+H_2O$$

which is inconsistent with the initial equality of the rate of peroxide formation and the rate of O_2 consumption discussed precedently (Fig. 6).

A radical chain autoxidation mechanism has frequently been evoked to explain at least partially the oxygenation of various substrates. Autoxidation is characterized by initiation reactions generating free radicals ($XH\rightarrow X\cdot$), the propagation reactions yielding oxidation products ($X\cdot+O_2\rightarrow XO_2\cdot$; $XO_2\cdot+XH\rightarrow XO_2H+X\cdot$) and termination reactions eliminating free radicals from the system [50]. The fixation of an oxygen molecule into a carbon atom centered free radical X· is generally a very fast reaction close to diffusion-controlled rates [49,51]. It transforms alkyl radicals X· into peroxy radicals $XO_2\cdot$. As the enthalpy of reaction for hydrogen atom abstraction is directly related to the difference in the dissociation energy of the bond being broken and the dissociation energy of the bond being formed [52], the organoperoxy radical $XO_2\cdot$ is much less reactive than the radical X· and does not rapidly abstract hydrogen atoms from most of the substrates studied to date in photocatalysis by polyoxotungstates at room temperature. Then the formation of hydroperoxides does not result from propagation reactions but essentially from the interaction between $XO_2\cdot$ and $HO_2\cdot\rightleftarrows O_2^-\cdot+H^+$. As shown in Scheme 5, the primary radicals $W_{10}O_{32}{}^{5-}$ and X· are formed through the processes (a) and (b), peroxy and perhydroxyl radicals result from propagation steps (c) and (d) not involving hydrogen atom abstraction, and hydroperoxide is the product of the termination reaction (e). As previously described, initially the variations of the number of moles of O_2 consumed and total peroxide formed as a function of irradiation time are identical

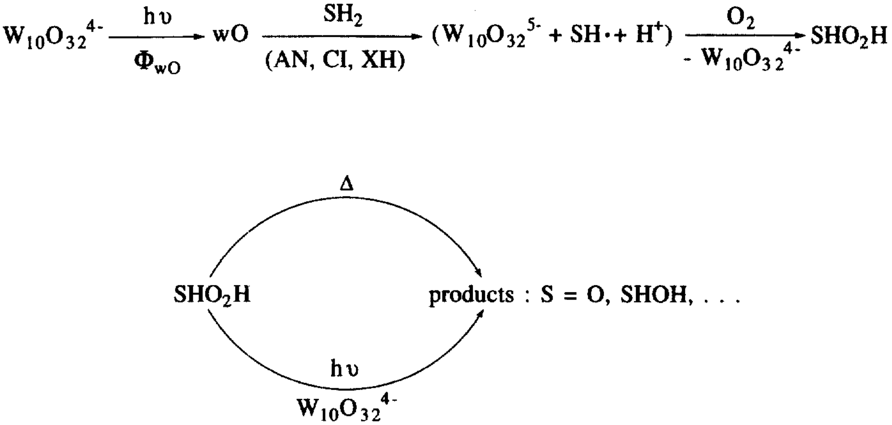
(Fig. 6). But progressively the molar ratio of peroxide formed to oxygen consumed decreases demonstrating (i) a progressive decomposition of peroxides under experimental conditions, and (ii) parallel formation of oxygen-containing products such as alcohols, ketones and aldehydes. Most of the results of photocatalysis by polyoxotungstates under aerobic conditions may be represented by Scheme 6, which suggests that the oxygenated products other than peroxides derive from these last species and not from coupling of intermediate radicals such as organoperoxy radicals. In other terms, hydroperoxides undergo degenerate branching reactions which result in oxygen-containing product formation.

The relative contribution of solvent, counterion, added substrate and corresponding primary peroxide formed to the overall photo-oxygenation may be rationalized in terms of Scheme 4 from which it may be deduced that the probability f_{XH} that hydrogen abstraction competes with inherent deactivation of wO is given by:

$$f_{XH} = \Phi^{XH}_{OX}/\Phi_{wO} = (k_{AN}[AN] + k_{CI}[CI] + k_{XH}[XH] + k_{SHO_2H}[SHO_2H])\tau$$

where $\tau^{-1} = k_I + k_{AN}[AN] + k_{CI}[CI] + k_{XH}[XH] + k_{SHO_2H}[SHO_2H]$, as long as reactions of decomposition products of SHO_2H may be neglected. The relative contribution of each component SH_2 of the system (Schemes 4 and 6) is given by $k_{SH_2}[SH_2]\tau$. Initially, the selective formation of peroxide is observed if $k_{XH}[XH]\tau \approx 1$, when a significant contribution of photo-oxygenation of solvent is expected at low substrate concentration where this last condition is not (or no longer) fulfilled. The decomposition of hydroperoxide XO_2H will become noticeable when the conversion of XH will be significant and $k_{XO_2H}[XO_2H]$ close to $k_{XH}[XH]$.

In conclusion, the lifetime of wO in deoxygenated acetonitrile solution has been found to be 55 ns but, since acetonitrile functions as a substrate, the inherent lifetime is estimated to be around 85 ns. This species, which is considered to be the reactive entity towards added organic substrates, is formed from the initial CT state in ca.



Scheme 6.

60% yield. The exact nature of this species remains obscure, but (i) it does not produce singlet molecular oxygen, (ii) it absorbs strongly at 780 nm as $W_{10}O_{32}{}^{5-}$, and (iii) its reaction with most organic materials is likely to involve hydrogen atom abstraction. This could imply that wO is a relaxed excited state with substantial charge in it and which exhibits oxyradical-like character due to the presence of an electron-deficient oxygen center. With easily oxidized substrates, it is likely that direct electron transfer could compete with hydrogen atom transfer and, in any case, both mechanisms give rise to the same one-electron reduced species and the corresponding substrate-derived radical. In acetonitrile these latter species react quantitatively with oxygen to form hydrogen peroxide or organic hydroperoxides which may themselves be decomposed to give oxygenated products. In aqueous solution, substrates such as phenol and p-cresol undergo complete mineralization upon photolysis in the presence of polyoxometallates [53–55]. The main oxidant is said to be hydroxyl radicals, but the mechanism remains to be established.

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