

Kinetic and Mechanistic Aspects of Photocatalysis by Polyoxotungstates: A Laser Flash Photolysis, Pulse Radiolysis, and Continuous Photolysis Study

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Illumination of polyoxotungstates generates a short-lived excited state which decays to form the reactive intermediate wO that is responsible for subsequent transformation of organic substrates. It is shown by laser flash photolysis that wO is formed with a quantum yield of 0.6 and that it survives for ca. 55 ns in deoxygenated acetonitrile. In the presence of a substrate such as propan-2-ol wO reacts to produce the one-electron-reduced species, as characterized by transient spectroscopy and as confirmed by pulse radiolysis. Oxygen intercepts the initially-formed radicals so that this methodology may be used to follow the course of the reaction. Under continuous photolysis, propan-2-ol is converted into acetone and hydrogen peroxide but with adamantane as substrate the corresponding hydroperoxides are formed. Quantum yields of oxygen consumption have been measured for a variety of other substrates and range from ca. 0.05 for pure acetonitrile to ca. 0.5 for propan-2-ol. In the absence of other substrates, reaction of organic counterions may be observed. All these observations are consistent with hydrogen-atom abstraction from an organic substrate by wO, followed by rapid deprotonation of $\cdot\text{wOH}$ and/or trapping by O_2 . A concise reaction scheme involving coupling between oxyradicals is proposed that adequately describes the overall chemistry.

Introduction

Oxide-based, inorganic networks, such as TiO_2 , RuO_2 , IrO_2 , and WO_3 , can display important catalytic properties with regard to the light-induced transformation of organic materials.¹ Of the many oxidic clusters studied to date, the polyoxometallates, such as decatungstate $\text{W}_{10}\text{O}_{32}^{4-}$, appear to exhibit especially interesting properties as photocatalysts.² Such materials have been studied in detail over the past 10 years or so, particularly under anaerobic conditions, and these oxides may possess genuine applications in catalysis. In marked contrast to the corresponding organic-based photocatalysts, such as the fullerenes, it is difficult to specify the exact nature of the reactive species present in the polyoxometallates. Indeed, the cascade of events that follows light absorption by such materials is somewhat confusing, even in the absence of an added substrate. It is clear, however, that proper utilization of these photocatalysts demands an improved understanding of the nature and lifetime of the primary species that result from light absorption. We address these issues here by a combination of laser flash photolysis, pulse radiolysis, and steady-state irradiation experiments with specific reference to tetra-*n*-butylammonium decatungstate.

Earlier studies by Hill and colleagues 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.³ The quoted lifetime is close to the temporal resolution of the picosecond laser setup used for these studies but it is clear that the initial excited state decays rapidly. Formation of this primary species is thought to take place *via* charge transfer from oxygen to metal.^{4–6} Decay of the excited state generates an intermediate that persists for many nanoseconds (i.e., >20 ns) but its lifetime and deactivation route remain obscure. On the basis of laser flash photolysis studies³ it seems likely that the longer-lived intermediate (wO) is the normal reactant in dehydrogenation processes. Not unsurprisingly,

neither the excited state nor wO reacts with molecular oxygen to produce singlet molecular oxygen but extremely weak emission has been reported for the excited state.⁷ Reaction with certain substrates, such as hydrocarbons, alcohols, alkyl halides, and ketones, is known to result in formation of the one-electron-reduced form of decatungstate.^{2,6,8} This latter species, which is readily detected from its characteristic absorption spectrum,^{9–11} is quite stable in the absence of an oxidizing agent. Its involvement in the overall photoprocess suggests that electron transfer plays an important role in the transformation of organic substrates. In most cases, however, it is likely that wO reacts with organic substrates by way of hydrogen-atom abstraction to give radicaloid species.^{12–14}

Further progress in this area is hampered by lack of clear information regarding the nature, reactivity, and energetics of the primary intermediates. Realistically, the excited state is too short-lived to be useful as a reactant in bimolecular reactions and, consequently, it is the second intermediate wO that requires detailed characterization. Without proper knowledge of its lifetime it is difficult to provide rate constants for its subsequent reaction with different organic substrates. Equally important, it is difficult to assess the ability of wO to abstract particular hydrogen atoms in the absence of more information about its energetics. Here, we address the first issue and provide compelling results that indicate the lifetime of wO is on the order of a few tens of nanoseconds. Additional studies suggest that the one-electron-reduced species plays an active role in the overall chemistry and it is further shown that normally inert substrates, such as acetonitrile, display significant activity toward wO.

Experimental Section

Sodium decatungstate,¹² together with its potassium¹⁵ and tetrabutylammonium⁹ counterparts, was synthesized and purified by literature procedures. The tetrabutylammonium salt was analyzed by electrospray mass spectrometry, elemental composition, and infrared spectroscopy. This material was used for

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most of the studies reported here. The potassium salt is easily prepared but is poorly soluble in acetonitrile, while the sodium salt is more difficult to prepare in a pure form. All time-resolved spectroscopic studies were made with the tetrabutylammonium salt but steady-state irradiations were made with the different salts in order to assess the importance of the cation. Solvents were obtained from commercial sources and were used as received.

All time-resolved studies were made at the Paterson Institute for Cancer Research using the Free Radical Research Facility. Laser flash photolysis studies were made with the third harmonic from a Q-switched Nd-YAG laser ($\lambda = 355$ nm, fwhm = 15 ns). The sample solution, placed in a quartz cell having 1 mm path length, was irradiated with single pulses (100 mJ) delivered from the laser and analyzed with a pulsed Xe arc lamp. Solutions of tetrabutylammonium decatungstate were made up to be either 1×10^{-4} or 5×10^{-4} M, corresponding to absorbance values of ca. 0.1 and 0.4, respectively, at 355 nm. The sample solution was replenished after each excitation flash by way of a flow system. Spectra were compiled point-by-point and kinetic studies were made at fixed wavelength. Pulse radiolysis studies were made with the 10 MeV electron-beam accelerator after purging the solution with oxygen-free nitrogen. Solutions of tetrabutylammonium decatungstate in acetonitrile were prepared in the concentration range 0–250 μ M. A fresh aliquot of solution was used for each pulse and transient spectra were compiled point by point. All studies were made in acetonitrile and actinometric measurements were made by reference to the reduced solvent.¹⁶ A pulsed Xe arc lamp was used for the monitoring beam. Spectra were corrected for variations in the dose. Kinetic measurements were made at fixed wavelength.

The photostationary state method used in this work consists of measuring the rate r_{OX} of substrate photooxygenation by following oxygen consumption as a function of irradiation time. The corresponding quantum yield Φ_{OX} is defined according to $\Phi_{\text{OX}} = (\text{number of moles of O}_2 \text{ consumed})/(\text{number of einsteins absorbed by W}_{10}\text{O}_{32}^{4-})$. These experiments followed the general procedures described previously for the measurement of the quantum yield Φ_{Δ} of singlet oxygen production under carefully controlled conditions.¹⁷ All photoreactions were carried out in an internal cylindrical photoreactor (volume 100 mL) or, for a limited number of experiments, in an external cylindrical photoreactor (volume 40 mL) illuminated with a Philips HPK 125 mercury lamp. The apparatus consists of a closed system comprising an acetonitrile solution of decatungstate (5.5×10^{-4} M) containing various amounts of substrate and about 250 mL (150 mL) of O₂ gas for external (internal) photoreactors. A vigorous O₂ gas stream produced by a gas pump provides for rapid circulation of the solution and supplies simultaneously that amount of dissolved O₂ which is consumed in the reaction. The consumption of oxygen was measured under steady-state irradiation using a gas buret. Light intensities were calibrated using the photooxygenation of furfurylic alcohol in O₂-saturated acetonitrile with phenalenone ($\Phi_{\text{OX}} = \Phi_{\Delta} = 0.98$)¹⁸ as sensitizer. The concentration of decatungstate was sufficient to absorb practically all the incident light. The intensity of absorbed light was 6.2 and 82 einsteins s⁻¹ for external and internal cylindrical photoreactor, respectively.

For the systems containing adamantane as substrate, excess trimethylphosphite was added to the reaction mixture to reduce adamantane hydroperoxides. The disappearance of adamantane and formation of the corresponding alcohols were measured on a Carlo Erba HRGC 5300 gas chromatograph with cyclodode-

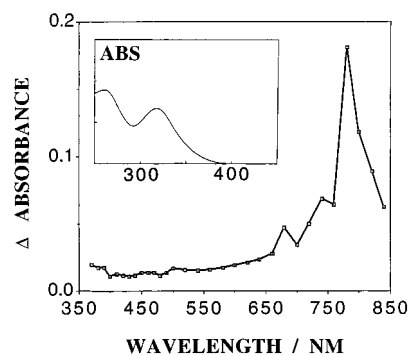


Figure 1. Transient absorption spectrum obtained 60 ns after 355 nm excitation with a 15 ns laser pulse of a 5×10^{-4} M tetrabutylammonium decatungstate air-saturated acetonitrile solution. Inset: Absorption spectrum of sodium decatungstate in air-saturated acetonitrile.

cane being used as internal standard. Peroxide concentrations were measured by iodometric titration.¹⁹

Results

Laser Flash Photolysis. Previous work³ has established that the initially-formed, charge-transfer (CT) excited state of decatungstate has a lifetime in the region of ca. 30 ps and that this species decays to form a longer-lived intermediate, designated herein as wO. In the present work, we specifically address the issue of the lifetime and nature of the longer-lived intermediate wO since this is the more likely reactant in subsequent photocatalytic reactions. The earlier studies of Hill and co-workers,³ together with those by other researchers working with closely-related polyoxometallates,^{9,11,20,21} can be interpreted in terms of the CT excited state possessing both an oxyradical and a reduced metallic center. The fraction of this CT species that decays to wO is unknown but, from quantitative product determinations, this interconversion of the species might be less than quantitative.

Decatungstate absorbs only in the UV region of the spectrum (Figure 1) where the maximum of absorption is around 325 nm. This corresponds to an excitation energy of ca. 3.8 eV, this being the maximum energy content of the CT excited state. Following excitation of decatungstate in aerated acetonitrile solution with a 15 ns laser pulse, a long-lived transient species could be observed by time-resolved optical spectroscopy. This intermediate absorbs strongly around 780 nm (Figure 1) and, on the basis of its characteristic absorption spectrum, can be identified as being wO. Under these conditions, wO decays *via* first-order kinetics with a lifetime of $\tau = 55 \pm 20$ ns. This derived lifetime agrees well with the results of Hill *et al.* who, from picosecond laser flash spectroscopy, concluded that wO persists for more than 15 ns. Our value of 55 ns is the first definite assignment of a lifetime for this species. Repeating the experiment under different pressures of oxygen showed that the lifetime is not quenched by O₂ within the limit of experimental uncertainty, while separate studies confirmed that neither the CT state nor wO produced singlet molecular oxygen under illumination in O₂-saturated acetonitrile solution.

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 (Figure 2). 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 re-form the prepulse baseline. The yield of this long-lived species was decreased in the presence of small concentrations of O₂ and its lifetime was shortened. It appears,

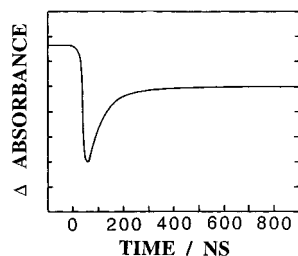


Figure 2. Profile recorded at 760 nm showing decay of wO as generated following 355 nm excitation of a 5×10^{-4} M tetrabutylammonium decatungstate nitrogen-saturated acetonitrile solution. The species remaining after decay of wO is assigned to the one-electron-reduced species. One division represents $\Delta A = 0.018$.

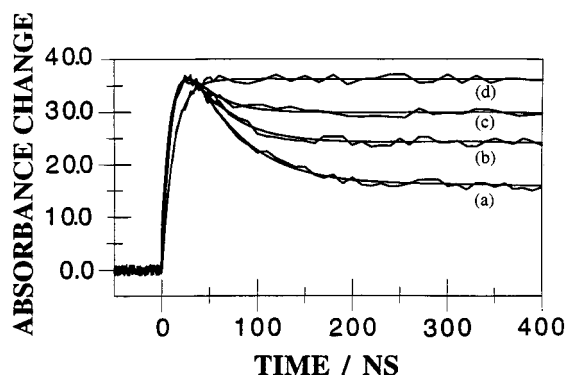
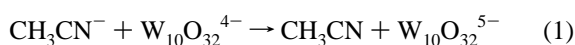


Figure 3. Effect of propan-2-ol [XH] on the decay of wO in an air-saturated acetonitrile solution of 5×10^{-4} M tetrabutylammonium decatungstate observed at 760 nm following 355 nm excitation with a 15 ns laser pulse: (a) [XH] = 0.01 M, (b) [XH] = 0.10 M, (c) [XH] = 0.30 M, and (d) XH/CH₃CN (1/1). The profiles have been normalized to the initial absorbance and show the progressive increase in yield of the one-electron-reduced species.

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. Thus, addition of 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 (Figure 3). This investigation has also shown that the bimolecular rate constant for reaction between wO and propan-2-ol in aerated acetonitrile solution is ca. $1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. The spectrum of the long-lived species obtained in the presence of propan-2-ol is given in Figure 4a.

Pulse Radiolysis. 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.¹⁶ 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 $3.5 \times 10^5 \text{ s}^{-1}$. 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 (Figure 5).



The bimolecular rate constant for this electron-transfer process corresponds to $5.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The absorption spectrum

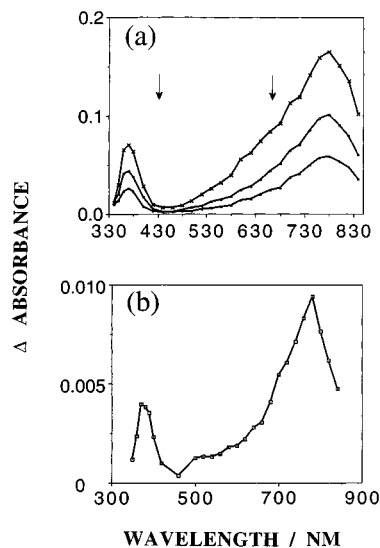


Figure 4. Transient absorption spectra recorded for the one-electron-reduced form generated by (a) 355 nm excitation with a 15 ns laser pulse of a 5×10^{-4} M tetrabutylammonium decatungstate air-saturated acetonitrile/propan-2-ol (1/1 vol) solution after 230 μs , 1.3 ms, and 8 ms; (b) injection of a 20 ns pulse of high-energy electrons into a 2.5×10^{-4} M tetrabutylammonium decatungstate N₂-saturated solution after 220 μs .

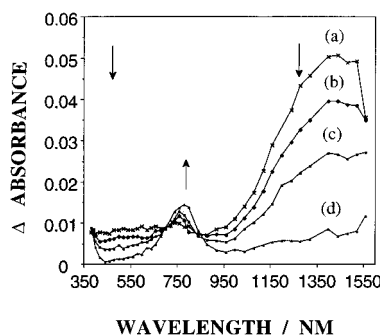


Figure 5. Decay of CH_3CN^- and growth of $\text{W}_{10}\text{O}_{32}^{5-}$. Transient absorption spectra obtained after injection of a 20 ns pulse of high-energy electrons into a 2.5×10^{-4} M tetrabutylammonium decatungstate N₂-saturated acetonitrile solution after (a) 120 ns, (b) 270 ns, (c) 520 ns, and (d) 3.12 μs .

of the reduced product is given in Figure 4b and, by reference to CH_3CN^- , the molar extinction coefficient at the absorption maximum of 780 nm can be assigned a value of $\sim 10\,000 \text{ M}^{-1} \text{ cm}^{-1}$ in agreement with literature data which range^{6,9,10} from ~ 7500 to $11\,000 \text{ M}^{-1} \text{ cm}^{-1}$. The transient possesses a second absorption band centered around 370 nm whose molar extinction coefficient is $\sim 4500 \text{ M}^{-1} \text{ cm}^{-1}$. 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 (Figure 4).

Steady-State Photolysis. In order to learn more about the nature and reactivity of the primary species, especially wO, a series of steady-state irradiations was made both in the absence and presence of an added substrate. These reactions were made under aerated conditions so that the course of reaction could be followed by monitoring the uptake of dissolved O₂. In O₂-saturated acetonitrile, it is assumed that O₂ intercepts all species derived from interaction between wO and an organic substrate (including acetonitrile itself). In fact, wO does not react with O₂ but the rate of O₂ uptake remains constant in aerated and O₂-saturated solution. On the basis of this assumption, we can

equate the quantum yield for consumption of O₂ with the quantum yield for formation of radicals derived from wO. These quantum yields are measured by following the rate of O₂ consumption under illumination, over short irradiation periods where O₂ consumption depends linearly on illumination time.

Illumination in the absence of an added substrate results in slow but definite consumption of O₂, 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 O₂ consumption, and at [propan-2-ol] = 1.0 M the quantum yield for O₂ consumption was found to be 0.5. In fact, the quantum yield measured in the presence of a substrate ($\Phi_{\text{OH}}^{\text{XH}}$) was found to depend upon both the concentration and nature of that substrate (Table 1) 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 (Table 1). 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 O₂ consumption increased progressively with increasing concentration of substrate until reaching a plateau value of ca. 0.5 (Figure 6). It was also noted that the value, although approaching zero at low concentrations of substrate, remained finite in the absence of substrate. We regard this latter observation as confirming the notion that acetonitrile itself acts as a substrate for wO. The data expressed in Figure 6 can be used to derive a bimolecular rate 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

$$(\Phi_{\text{wO}} - \Phi_{\text{OX}})/(\Phi_{\text{wO}} - \Phi_{\text{OX}}^{\text{XH}}) = 1 + K[\text{XH}] \quad (2)$$

where Φ_{wO} is the quantum yield for formation of wO and K is the corresponding Stern–Volmer constant. From nonlinear least-squares analysis of the experimental data (Figure 6) we derive that $K = 6.2 \pm 2 \text{ M}^{-1}$ while the quantum yield for formation of wO becomes 0.53 ± 0.17 . An independent estimate of K was made by laser flash photolysis studies where $K = 4.4 \text{ M}^{-1}$ since under these conditions $\tau = 55 \text{ ns}$ and $k_{\text{XH}} = (8 \pm 4) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$.

Illumination in the presence of O₂ seems likely to result in formation of peroxides and/or hydroperoxides derived from the organic substrates and from consumption of O₂, and it has been shown that decatungstate catalyzes conversion of propan-2-ol into acetone in essentially quantitative yield.^{22–24} Figure 7a shows the profile for oxygen consumption and hydrogen peroxide formation as measured for sensitized photooxygenation 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 photooxygenation of solvent is expected, the rate of peroxide formation is equal to

TABLE 1: Quantum Yield for O₂ Consumption Measured for Illumination of Sodium Decatungstate (WO-Na), Potassium Decatungstate (WO-K), or tetra-*N*-Butylammonium Decatungstate (WO-Bu) in the Absence and Presence of Various Substrates XH in O₂-Saturated Acetonitrile at 25 °C^a

decatungstate	WO	[WO]/mM	substrate XH	[XH]/M	$\Phi_{\text{OX}}^{\text{XH}}$
WO-Na		0.2–1.2			0.09
WO-Na		0.2–1.2	AdH	0.018	0.15
WO-Na		0.54	CdH	0.018	0.15
WO-Bu		0.54			0.19
WO-Bu		0.27	AdH	0.018	0.18
WO-Bu		0.54	AdH	0.018	0.23
WO-Bu		1.08	AdH	0.018	0.25
WO-K		0.55			0.04
WO-K		0.55	AdH	0.018	0.14
WO-K		0.55	Me ₂ CHOH	0.0055	0.065
WO-K		0.55	Me ₂ CHOH	0.1	0.24
WO-K		0.55	Me ₂ CHOH	0.2	0.34
WO-K		0.55	Me ₂ CHOH	0.5	0.46
WO-K		0.55	Me ₂ CHOH	1.0	0.50
WO-K		0.55	Me ₂ CHOH	1.0	0.49
WO-K		0.55	BuOH	0.1	0.23
WO-K		0.55	Me ₃ COH	0.1	0.05
WO-K		0.55	Me ₃ COH	1.0	0.08

^a AdH = adamantane, CdH = cyclododecane, Me₂CHOH = propan-2-ol, BuOH = butan-1-ol, Me₃COH = 2-methylpropan-2-ol.

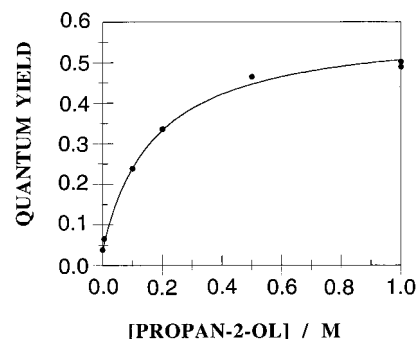


Figure 6. Effect of concentration of propan-2-ol on the quantum yield of oxygen consumption measured for potassium decatungstate in O₂-saturated acetonitrile. The solid line is drawn in accordance with equation $\Phi_{\text{OX}}^{\text{XH}} = (\Phi_{\text{OX}} + \Phi_{\text{wO}}K[\text{XH}])/(1 + K[\text{XH}])$ with $\Phi_{\text{OX}} = 0.042$, $\Phi_{\text{wO}} = 0.534$, and $K = 6.2$.

the rate of O₂ consumption. This result confirms the mechanism proposed in Scheme 1. Under these conditions, reaction does not involve any 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, Figure 7b shows the variation of the number of moles of O₂ consumed and 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 O₂ 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 disappearance of adamantane and for formation of the hydroperoxide were identical within experimental limits but significantly less than the quantum yield for consumption of O₂ (ratio ~ 0.75:1). This latter finding is consistent with part of the consumed O₂ being associated with oxygenation of the solvent. In fact, the contribution of solvent oxygenation becomes noticeable when

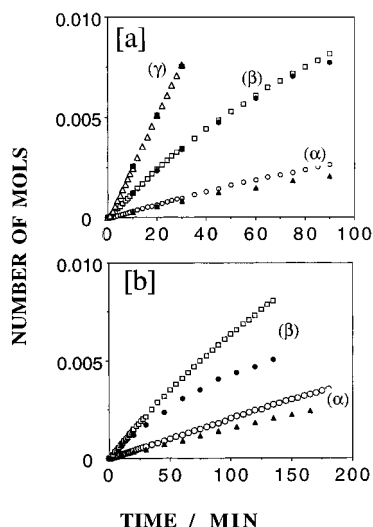
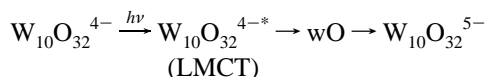


Figure 7. Correspondence between the number of mols of oxygen consumed (open symbols) and of peroxide formed (solid symbols) during continuous illumination of potassium decatungstate (5.5×10^{-4} M) in oxygen-saturated acetonitrile. Panel (a) shows the effect of propan-2-ol at 5.5×10^{-3} M (α), 0.1 M (β), and 1.0 M (γ). Panel (b) shows results collected in the absence (α) and presence (β) of 0.018 M adamantane.

$k_{\text{XH}}[\text{XH}]$ for the substrate is close to the corresponding value for acetonitrile ($k \sim 2 \times 10^6 \text{ s}^{-1}$). The quantitative formation of hydroperoxides from adamantane is consistent with a precedent observation made with isobutane.²⁵

Discussion

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 as follows:



Here, the initially produced excited state is of CT character and decays in about 30 ps³ 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. 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 under deoxygenated conditions^{2c,6,12,13,26,27} 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.

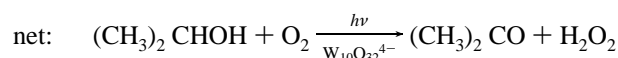
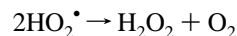
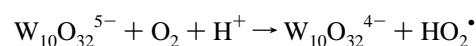
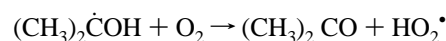
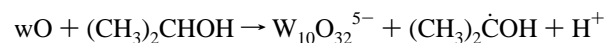
In the absence of O₂, wO decays to form the one-electron-reduced species as demonstrated by laser flash photolysis techniques. It has been shown that O₂ inhibits formation of the one-electron-reduced species and that $\text{W}_{10}\text{O}_{32}^{5-}$ reacts with O₂ to provide a source of peroxy species.^{6,8,28,29} 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 our

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 $\cdot\text{CH}_2\text{-CN}$ radical which dimerizes to form succinonitrile.³⁰ The same radical can be formed by reaction between the *tert*-butoxyl radical and acetonitrile under milder conditions.³¹ The cyanomethyl radical, being a carbon-centered radical, reacts with oxygen to form the corresponding peroxy species.³² 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 $(\text{NBu}_4)_4[\text{W}_{10}\text{O}_{32}]$ in deoxygenated acetonitrile.⁶ We might expect, therefore, that illumination of decatungstate in aerated acetonitrile will result in formation of the cyanomethylperoxy radical, at least in low yield. In this regard the observed quantum yield seems to be in the expected order of magnitude.

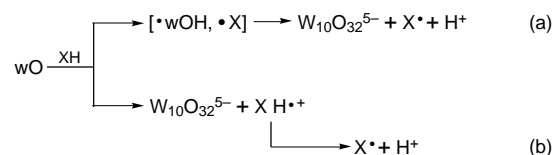
Although direct interaction between wO and solvent is interesting in itself, a more important aspect of this work concerns the reactions that occur with added substrate. In particular, it is important to assess the reaction mechanism by which decatungstate is able to oxygenate organic compounds and to 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 (Figure 3). Irradiation in the presence of both propan-2-ol and O₂ results in formation of acetone and hydrogen peroxide and can be expressed by the following sequence of reactions:³³

SCHEME 1



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



XH = solvent, added substrate
(a) hydrogen-atom transfer mechanism
(b) electron-transfer mechanism

We have found that irradiation of decatungstate in the presence of many different alcohols, linear and branched, results in consumption of oxygen. From the measured rates of oxygen consumption, the Stern–Volmer constants K could be determined from eq 2. The observed reactivities vary over 2 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 is ca. 70-fold, although the value for 2-methylpropan-2-ol relates to a single concentration. 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. Our observation that propan-2-ol reacts very much faster than acetonitrile is also consistent with a hydrogen atom abstraction mechanism. The similarity of the spectra obtained by pulse radiolysis and laser flash photolysis in the presence of propan-2-ol (Figure 4) suggests that the initially formed radical $^{\bullet}wOH$ undergoes rapid deprotonation in non-aqueous solvent (Scheme 2).

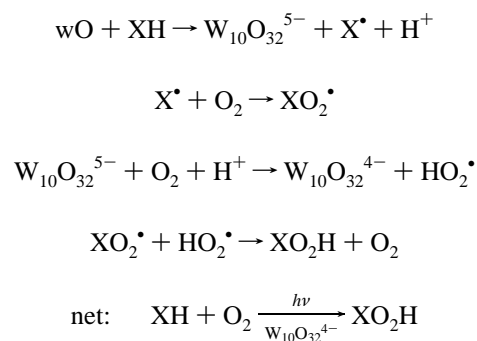
Light-induced hydrogen-atom abstraction is also entirely consistent with our observations made in the absence of added substrate. Thus, illumination of $Na_4[W_{10}O_{32}]$ (0.2–1.2 mM) in aerated or O_2 -saturated acetonitrile results in a quantum yield for oxygen consumption of 0.09 (Table 1). This 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.

Continuing this argument, we can use these observations to derive approximate rate constants for hydrogen-atom abstraction from the counterion and from acetonitrile. For $(NBu_4)_4[W_{10}O_{32}]$ in the absence of added substrate, the quantum yield for O_2 consumption can be expressed as $\Phi_{OX} = \Phi_{wO/H}$, where f_H is the probability that hydrogen abstraction competes with inherent deactivation of wO . In turn, we can define this latter probability as $f_H = (k_{AN}[AN] + k_{CI}[CI])\tau$, where k_{AN} and k_{CI} refer, respectively, to rate constants for hydrogen abstraction from solvent and counterion. Combining steady-state and flash photolysis results gives $[k_{AN}[AN] + k_{CI}[CI]] \sim 6.4 \times 10^6 s^{-1}$. Comparing quantum yields measured for $(NBu_4)_4[W_{10}O_{32}]$ and for $Na_4[W_{10}O_{32}]$, we find $k_{AN}[AN] \sim 2.4 \times 10^6 s^{-1}$ and $k_{CI}[CI] \sim 4.0 \times 10^6 s^{-1}$. Furthermore, the rate constant for overall deactivation of wO can be expressed as $k = k_1 + k_{AN}[AN] + k_{CI}[CI]$, where k_1 is the rate constant for inherent [i.e., non-hydrogen atom abstraction] decay of wO . For deoxygenated acetonitrile at room temperature, we find $k_1 \sim 1.2 \times 10^7 s^{-1}$ which corresponds to an inherent lifetime of ca. 85 ns.

Irradiations made in the presence of alkanols as reactive substrate result in formation of hydrogen peroxide according to the sequence of reactions in Scheme 1. 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 formation of more useful products. For example, alkanes are converted into the corresponding carbon-centered hydroperoxides as shown in

Scheme 3 and as demonstrated in the specific case of adamantane.³⁵

SCHEME 3



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 we consider to be the reactive entity toward added organic substrates, is formed from the initial CT state in ca. 60% yield. The exact nature of this species remains obscure but its reaction with most organic materials is likely to involve hydrogen-atom abstraction. This could imply that wO 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. These latter species react quantitatively with oxygen to form hydrogen peroxide and/or organic hydroperoxides as final products. Current studies, using a variety of organic substrates, are intended to better define the ability of wO to function in hydrogen-atom abstraction processes and, in particular, to estimate the dissociation energy of the resultant $wO-H$ bond.

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