

Acetone, a substrate and a new solvent in decatungstate photocatalysis

Charles Tanielian*, Fabien Cougnon, Rachid Seghrouchni

Universite Louis Pasteur, Laboratoire de Photochimie/LIPHT, Ecole Européenne de Chimie Polymères et Matériaux de Strasbourg, 25, rue Becquerel, F-67087 Strasbourg Cedex 2, France

Available online 1 September 2006

Abstract

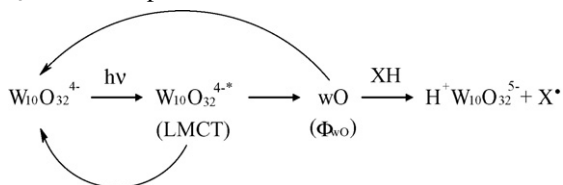
It is shown that acetone may accompany acetonitrile and water in the very restricted category of conventional solvents for polyoxometalates and more specially decatungstate photocatalyzed reactions. The values of the lifetime, rate constant for inherent decay, and quantum yield for formation of the reactive wO transient in both solvents are practically identical. The only differences relate: (i) to the reactivity of acetone toward wO which is three to four times higher than that of acetonitrile, but remains relatively weak compared to the less reactive substrates, such as alkanes and (ii) to the fact that, in contrast to acetonitrile, no solvated ions have been detected in solutions of decatungstate in acetone by ESMS, thus excluding strong precomplexation. The relative values of the rate constants of reaction of wO with propan-2-ol in acetone, acetonitrile, and water are 1/1.8/23, respectively. This first solvent effect study is consistent with the oxyradical-like character of the reactive transient wO due to the presence of an electron-deficient oxygen center.

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Keywords: Photocatalytic oxygenation; Decatungstate; Acetone as substrate/solvent; Solvent effect; Propan-2-ol

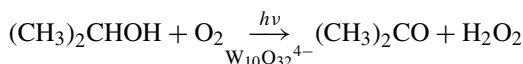
1. Introduction

Polyoxometalates, such as decatungstate $W_{10}O_{32}^{4-}$, appears to exhibit especially interesting properties as photocatalysts [1–17]. It is now admitted that illumination of $W_{10}O_{32}^{4-}$ leads to the formation of a locally excited ligand-to-metal charge transfer state $W_{10}O_{32}^{4-*}$, that decays in less than 30 ps to an extremely reactive non-emissive transient [2] designated as wO [3]. This latter intermediate, which in the case of sodium decatungstate has a lifetime τ_{wO} of 65 ± 5 ns in acetonitrile (AN), is the reactive species in photocatalytic systems. In the presence of a substrate XH, wO reacts to produce a substrate derived radical, X^\bullet , and the one-electron-reduced form (RF or $H^+W_{10}O_{32}^{5-}$) $W_{10}O_{32}^{5-}$ and/or protonated form.



Both RF and X^\bullet react with molecular oxygen, to regenerate the active form ($W_{10}O_{32}^{4-}$) of the catalyst, and to form per-

oxy compounds [3,8–10]. Interestingly, no chain reactions are observed [6]. In this way, propan-2-ol in acetonitrile was shown to be converted quantitatively into acetone (AC) and hydrogen peroxide under continuous photolysis [3]:



The relative contribution of solvent, added substrate, and corresponding peroxide formed to the overall photooxygenation has been previously discussed [6].

The conventional solvents used for a great majority, if not all, of the polyoxometalates (and in particular of the decatungstates) photocatalyzed reactions are limited to water and acetonitrile. However, it would be interesting to have the use of several solvents for both practical and fundamental reasons. For example, to overcome limitations due to a low solubility, and to permit solvent effect studies in polyoxometalates photocatalysis. The principal difficulty to find new solvents is due to the very high reactivity of wO towards virtually any organic substrate [3–11]. Thus, all the traditional organic solvents are likely to react with it. Previous studies have already provided detailed information on reaction products, yields, and kinetics of the decatungstate photocatalyzed oxygenation of acetonitrile, which was shown to be favoured by extraordinarily strong precomplexation of $W_{10}O_{32}^{4-}$ with this solvent [10]. A significant number of O_2

* Corresponding author. Tel.: +33 3 90 24 27 73; fax: +33 3 90 24 27 16.
E-mail address: tanielian@chimie.u-strasbg.fr (C. Tanielian).

consumption and transient absorbance spectroscopy measurements established the values of $\Phi_{\text{OX}} = 0.047$ and $\Phi_{\text{RF}}^0 = 0.023$ for the quantum yields of AN oxygenation and RF formation during reaction with wO [10].

We now show, after having eliminated alcohols for this purpose, that acetone can be included in the very restricted category of conventional solvents for polyoxometalate photocatalyzed chemical reactions such as decatungstate photosensitized oxygenation of propan-2-ol. Additionally, its photoproperties, in the absence of added substrate, will be examined and compared with those of acetonitrile.

2. Experimental

Sodium decatungstate was synthesized and purified by literature procedures [2(a)]. All other chemicals were purchased at highest purity available from Aldrich, and were used as received. Laser flash photolysis studies were made with the third harmonic of a Q-switched Nd:YAG laser, at 355 nm. Transient absorbance measurements were made at the Free Radical Research Facility in the Synchrotron Radiation Department of the CLRC Daresbury Laboratory, Warrington, UK. All spectra were recorded at 780 nm using a pulsed Xe arc lamp. Solutions of sodium decatungstate were made up to 5×10^{-4} M, corresponding to an absorbance value of ~ 0.4 at 355 nm. All signals were digitized using a digital storage oscilloscope. Lifetimes of the reactive transient were obtained by computer extrapolation of the first-order decay profiles recorded at 780 nm. Bimolecular rate constants k_{XH} for reactions with organic substrates were obtained from the slopes of the respective Stern–Volmer plots. Quantum yields Φ_{RF} of formation of RF were obtained from the 450 ns absorption at 780 nm, using the wO transient as an internal actinometric standard at this wavelength, according to

$$\Phi_{\text{RF}} = \left(\frac{\text{OD}_i}{\text{OD}_f} \right) \left(\frac{\Phi_{\text{wO}} \varepsilon_{\text{wO}}}{\varepsilon_{\text{RF}}} \right),$$

where OD_f and OD_i correspond to the transient absorbance change of the sample solution at 450 ns and 0 ns after laser pulse ignition, respectively, and $\Phi_{\text{wO}} \varepsilon_{\text{wO}}$ is the product of the quantum yield (Φ_{wO}) and the extinction coefficient ($\varepsilon_{\text{wO}} \sim \varepsilon_{\text{RF}} = 7000 \text{ M}^{-1} \text{ cm}^{-1}$ at 780 nm [10]) of wO. The photostationary state method consists in 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

$$\Phi_{\text{OX}} = \frac{\text{number of moles of O}_2 \text{ consumed}}{\text{number of einsteins absorbed by } \text{W}_{10}\text{O}_{32}^{4-}}.$$

All photoreactions were carried out in an internal cylindrical photoreactor (volume 100 mL) illuminated with a Philips HPK 125 mercury lamp. The apparatus consists of a closed system comprising a solution of decatungstate (5.5×10^{-4} M) in acetonitrile, in acetone, or in a mixture of AN and AC, and about 250 mL of O_2 . A vigorous O_2 gas stream produced by a gas pump provides for rapid circulation of the solution and supplies simultaneously that amount of dissolved O_2 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 furfuryl alcohol in O_2 -saturated acetonitrile with phenalenone ($\Phi_{\text{OX}} = \Phi_{\Delta} = 0.98$ [18]) as sensitizer. In acetone solutions of decatungstate, the rate r_{OX} was corrected for direct absorption of incident light by the solvent. Peroxide concentrations were determined by iodometric titration [19].

3. Results and discussion

3.1. Comparison of acetonitrile, acetone, and methanol as solvents by nanosecond laser transient investigation

Alcohols have been mentioned as being traditional solvents for polyoxometalates and, in addition, from some exploratory experiments using O_2 consumption technique, we felt that acetone may also be an acceptable candidate for decatungstates. As a first evaluation, we compared the decay of wO in different alcohols, acetone, and acetonitrile following excitation with a 15 ns laser pulse. Fig. 1 shows the profiles recorded for wO at 780 nm following 355 nm excitation of 1.1×10^{-4} M sodium decatungstate in air saturated acetonitrile, acetone, and methanol (which is the less reactive of common aliphatic alcohols) solutions. The decay profiles recorded for wO at 780 nm are similar for AC and AN, the species remaining after decay of wO being assigned to the one-electron-reduced species RF. It is apparent that the yield of RF is higher in acetone which suggests that the reactivity of wO is higher with AC than with AN (Table 1). From the rate of decay, it may also be deduced that in acetone wO has a lifetime τ_{wO} of 62 ± 5 ns, practically identical to the value in acetonitrile (65 ± 5 ns).

By comparison, it is apparent that the reactivity of wO with methanol is so important that the reactive intermediate is scavenged by the solvent during the laser pulse since only the reduced form RF is detected (Fig. 1), and that the nanosecond time scale

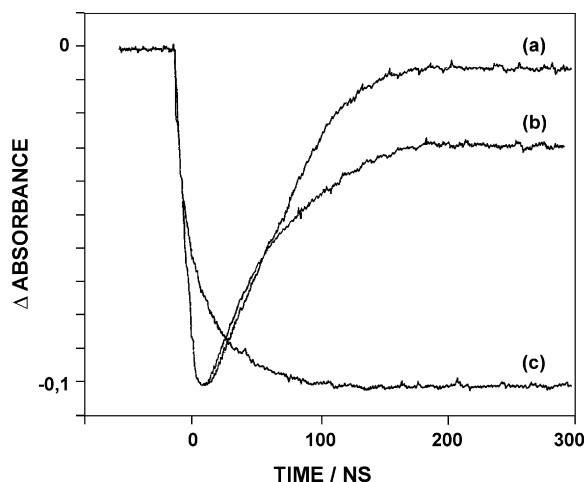


Fig. 1. Kinetics profiles, normalized to the initial absorbance, observed at 780 nm showing decay of wO as generated following 355 nm excitation with a 15 ns laser pulse of 1.1×10^{-4} M sodium decatungstate air-saturated acetonitrile (a), acetone (b), and methanol (c) solutions.

Table 1

Properties of acetone as substrate and solvent in decatungstate photocatalysis, and comparison with acetonitrile

	Acetone	Acetonitrile
τ_{wO}^a (ns)	62 ± 5	65 ± 5
Φ_{OX}^b	0.175	0.047
K_{AC}^c (M^{-1})	–	0.024
k_l^d ($10^7 s^{-1}$)	1.1	1.4
$k_{AC, AN}^e$ ($10^6 s^{-1}$)	$k_{AC} = 5$	$k_{AN} = 1.25$
Φ_{RF}^f	0.11	0.023
$\Phi_{wO} \epsilon_{wO}^g$ ($M^{-1} cm^{-1}$)	4 090	4 170
Φ_{wO}	0.57	–
Φ_{RF}^h	0.63 ± 0.2	–
k_{IPA}^i ($10^7 M^{-1} s^{-1}$)	4.9	8.9
K_{IPA}^j (M^{-1}) (α)	3.1	5.8
K_{IPA} (M^{-1}) (β)	3.2	–
K_{IPA} (M^{-1}) (γ)	–	5.6
Precomplexation with $W_{10}O_{32}^{4-}$	No	Yes

^a Lifetime of wO.

^b Quantum yield of solvent oxygenation.

^c Stern–Volmer constant for acetone as substrate.

^d Rate constant for inherent decay of wO.

^e Pseudo-first-order rate constant for hydrogen atom abstraction from solvent.

^f Quantum yield of $W_{10}O_{32}^{5-}$ formation in pure solvent.

^g Product of the quantum yield of wO formation and the extinction coefficient of wO at 780 nm.

^h Quantum yield of $W_{10}O_{32}^{5-}$ formation at infinite substrate concentration.

ⁱ Rate constant for reaction of wO with propan-2-ol.

^j Stern–Volmer constant for reaction of wO with propan-2-ol, obtained from (α) wO decay, (β) RF formation, and (γ) O_2 consumption.

laser flash photolysis technique is not adapted for investigations in alcohols. The continuous photolysis methodology (O_2 consumption) could be used, but it would be delicate to obtain very precise kinetic data for added substrates because of the important contribution of the solvent.

3.2. Chemical reactivity of acetone and of its mixtures with acetonitrile

3.2.1. Quantum yields of photooxygenation in the absence of added substrate

Fig. 2 shows the profiles for O_2 consumption measured for various concentrations of acetone in oxygen-saturated acetonitrile. After a short equilibration period due to lamp stabilization and related thermal effects, consumption of O_2 increases linearly with irradiation time. The relative rates of O_2 consumption are calculated from the slope of the linear portion of these plots. They can be converted into quantum yield values by comparison with the rate of O_2 consumption for phenalenone-sensitized oxygenation of furfurylic alcohol (quantum yield 0.98 [18]). The quantum yield for O_2 consumption Φ_{OX}^{XH} (Fig. 3) increases progressively with increasing concentration of AC up to a value of $(\Phi_{OX})_{AC} = 0.175$ in pure acetone. The value in the absence of acetone remains finite, $(\Phi_{OX})_{AN} = 0.047$, confirming that acetonitrile itself, as acetone, acts as a substrate for wO. These data can be used to derive the Stern–Volmer constant $K_{AC} = k_{AC}\tau_{wO}$ and the corresponding rate constant k_{AC} for the reaction of wO with acetone in acetonitrile, because the experimental quantum

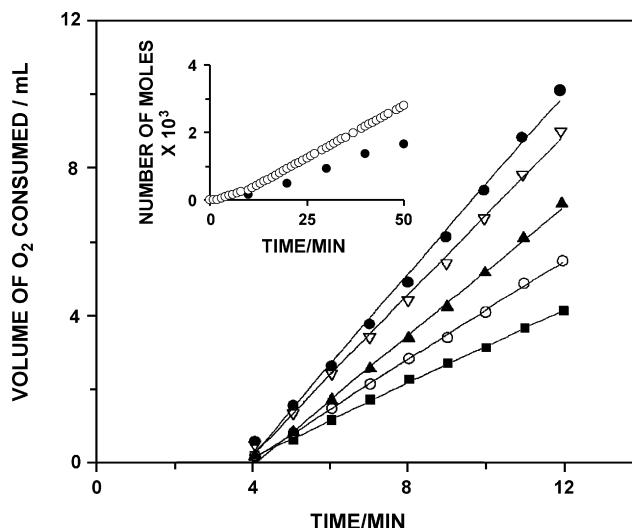


Fig. 2. Time dependence of O_2 consumption measured for illumination of oxygen-saturated solutions of sodium decatungstate ($5.5 \times 10^{-4} M$) in acetonitrile in the absence (\blacksquare) and presence of acetone at 2.7 M (\circ), 6.8 M (\blacktriangle), 10.9 M (∇), and 13.6 M (\bullet). Inset: correspondence between the number of moles of oxygen consumed (\circ) and hydroperoxide formed (\bullet) during continuous illumination of sodium decatungstate ($5.5 \times 10^{-4} M$) in oxygen saturated acetonitrile in the presence of acetone (10.9 M).

yields can be described by the following expression [3]:

$$\frac{\Phi_{wO} - \Phi_{OX}}{\Phi_{wO} - \Phi_{OX}^{XH}} = 1 + K[XH],$$

where Φ_{wO} and Φ_{OX} are the quantum yields for formation of wO and for O_2 consumption in the absence of added substrate, respectively. From non-linear least-squares analysis of the experimental data one obtain $K_{AC} = 0.024 M^{-1}$, $\Phi_{wO} = 0.57$, and $\Phi_{OX} = 0.047$. The kinetic parameters are listed in Table 1. It may be noticed that: (i) the values obtained for Φ_{wO} and Φ_{OX} in acetonitrile are identical to those found previously [3,9,10], (ii) the reactivity of wO with acetone is three to four times

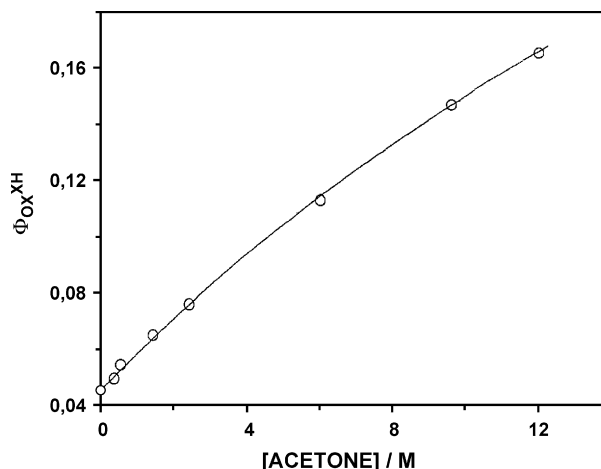
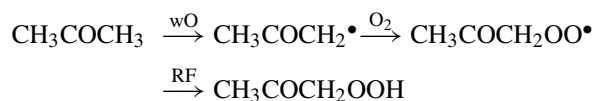


Fig. 3. Effect of acetone concentration on the quantum yield of oxygen consumption measured for $5.5 \times 10^{-4} M$ sodium decatungstate in oxygen-saturated acetonitrile. The solid line is drawn in accordance with equation $\Phi_{OX}^{XH} = (\Phi_{OX} + \Phi_{wO}K[XH]) / (1 + [XH])$, with $\Phi_{OX} = 0.047$, $\Phi_{wO} = 0.57$, and $K = 0.024 M^{-1}$.

higher than with acetonitrile, but (iii) this reactivity remains relatively weak ($K_{AC} = 0.024 \text{ M}^{-1}$) compared to the less reactive substrates, such as *n*-hexane ($K = 0.54 \text{ M}^{-1}$) [10].

3.2.2. O_2 consumption and hydroperoxide formation

It has been previously shown that illumination of a solution of decatungstate in pure acetonitrile results in a parallel O_2 consumption and hydroperoxide formation [3]. Similarly, Fig. 2 shows the variation of the number of moles of O_2 consumed and of total hydroperoxide formed as a function of illumination time for a solution of sodium decatungstate ($5.5 \times 10^{-4} \text{ M}$) in oxygen saturated acetone/acetonitrile 80/20 mixture (corresponding to a concentration of 10.9 M of acetone in acetonitrile). The quantum yield of O_2 consumption is 0.155 against 0.047 in pure acetonitrile. After ca. 10 min a separation of O_2 consumption and hydroperoxide formation curves is clearly observed. This observation reveals a progressive decomposition of hydroperoxides under experimental conditions and the possible existence of a reactive pathway which does not yield the hydroperoxide. The formation of $\text{CH}_3\text{COCH}_2\text{OOH}$, the main initial product of acetone decatungstate photocatalyzed oxygenation, can be described by the following simplified scheme:



where the propanone radical, resulting from an hydrogen-atom abstraction from acetone by wO, reacts with oxygen to give the peroxy radical which generate the hydroperoxide. The unstable alkylperoxy radical $\text{CH}_3\text{COCH}_2\text{OO}\cdot$ has recently been identified as intermediate in the photocatalytic oxidation of acetone over TiO_2 in the presence of oxygen [20].

3.3. Quantum yield Φ_{wO} for wO production in acetone

The product $\Phi_{\text{wO}}\epsilon_{\text{wO}}$ of the quantum yield (Φ_{wO}) and the extinction coefficient (ϵ_{wO}) of the wO transient in air saturated acetone was obtained from external actinometry experiments by comparison with the corresponding value in acetonitrile already determined ($\Phi_{\text{wO}}\epsilon_{\text{wO}} = 4170 \pm 200 \text{ M}^{-1} \text{ cm}^{-1}$ in air-saturated solution [10]). Fig. 4 shows the pulse energy dependence of transient absorbance change for sodium decatungstate in air-saturated acetone and air-saturated acetonitrile. From the comparison of the initial slopes of the two plots, a value of $\Phi_{\text{wO}}\epsilon_{\text{wO}} = 4090 \text{ M}^{-1} \text{ cm}^{-1}$ is found in AC which is practically identical to that in AN. As the photophysical properties of wO in AN and AC are also practically identical, it may be assumed that the value of the extinction coefficient ϵ_{wO} is the same in the two solvents ($\epsilon_{\text{wO}} \sim \epsilon_{\text{RF}} = 7000 \text{ M}^{-1} \text{ cm}^{-1}$ at 780 nm [10]), and then that the value of the quantum yield $\Phi_{\text{wO}} \sim 0.57$ is also the same in AC and AN.

3.4. Rate constants for inherent decay of wO, k_I , and for hydrogen atom abstraction from acetone, k_{AC}

Combining steady-state and flash photolysis results, the approximate rate constants for inherent [i.e. non-hydrogen

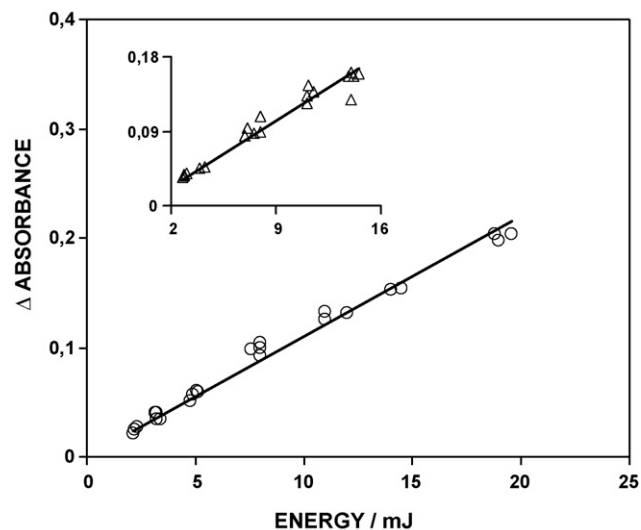
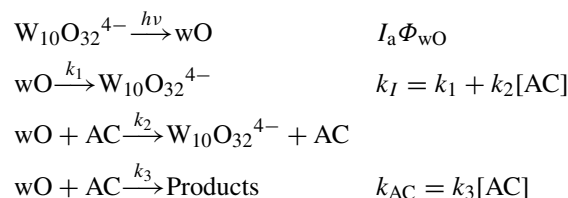


Fig. 4. Pulse energy dependence of transient absorbance change extrapolated to laser pulse ignition time for solutions of sodium decatungstate in air-saturated acetone (○) and acetonitrile (△).

abstraction] decay of wO, k_I , and for hydrogen atom abstraction from acetone, k_{AC} , may be derived.



As the quantum yield of photooxygenation of the solvent, Φ_{OX} , is given by

$$\Phi_{\text{OX}} = \frac{\Phi_{\text{wO}} k_{AC}}{k_I + k_{AC}},$$

and using previously determined parameters, it may be deduced that $k_I = 1.1 \times 10^7 \text{ s}^{-1}$ and $k_{AC} = 5 \times 10^6 \text{ s}^{-1}$. The value of k_I , which corresponds to an inherent lifetime of wO of 90 ns, is close to that obtained in acetonitrile [6,10], thus confirming the similarities of the photophysical properties of the two solvents; but the rate constant k_{AC} is four times higher than k_{AN} which reflects the difference of chemical reactivity of AC and AN with respect to hydrogen atom abstraction by wO (Table 1).

3.5. Decatungstate photocatalyzed oxygenation of propan-2-ol in acetone. A laser flash photolysis study

Unlike $\text{W}_{10}\text{O}_{32}^{4-}$, wO absorbs strongly at 780 nm, and so does its longer-lived reduction product. This is the reason for the absorbance remaining after the end of wO disappearance (see Fig. 1), which can be used to calculate the quantum yields $\Phi_{\text{RF}}^{\text{XH}}$ of formation of RF (see Section 2). Similarly to the analysis employed for the O_2 consumption quantum yields, the evolution of $\Phi_{\text{RF}}^{\text{XH}}$ with substrate concentration can be interpreted in terms

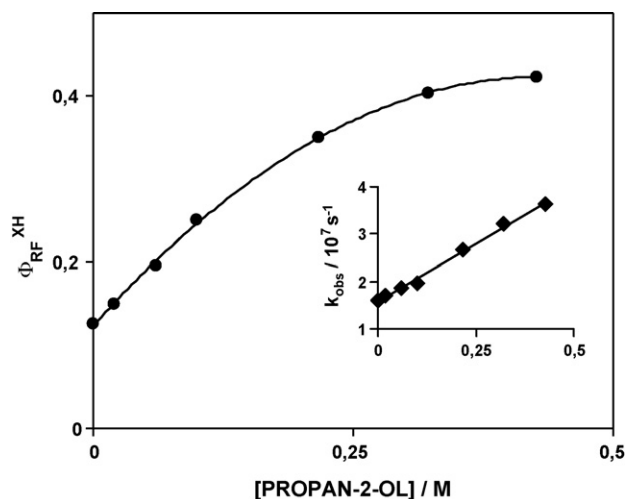


Fig. 5. Dependence of the quantum yield Φ_{RF}^{XH} of decatungstate reduction on propan-2-ol concentration (●). Inset: dependence of the corresponding pseudo-first-order rate constant on propan-2-ol concentration (◆). For fit parameters, see Table 1.

of a generalized Stern–Volmer treatment [10]:

$$\Phi_{RF}^{XH} = \frac{\Phi_{RF}^0 + \Phi_{RF}^\infty K[XH]}{1 + K[XH]}$$

where Φ_{RF}^0 is the quantum yield of formation of $W_{10}O_{32}^{5-}$ in the absence of added substrates and Φ_{RF}^∞ is the quantum yield of $W_{10}O_{32}^{5-}$ formation at infinite substrate concentration. Fig. 5 shows the dependence of the quantum yield Φ_{RF}^{XH} of RF formation on propan-2-ol concentration in acetone. The kinetic analysis yields $K_{IPA} = 3.2 \pm 0.7 M^{-1}$, $\Phi_{RF}^\infty = 0.63 \pm 0.2$, and $\Phi_{RF}^0 = 0.11 \pm 0.01$ for the reaction of wO with propan-2-ol. The Stern–Volmer constant $K_{IPA} = k_{IPA}\tau_{wO}$ is additionally accessible from the pseudo-first-order decay profiles at 780 nm, where k_{IPA} and τ_{wO}^{-1} are the slope and the intercept of the respective Stern–Volmer plot (Fig. 5, inset). From least-squares analysis of the experimental data we obtained $k_{IPA} = 4.9 \times 10^7 M^{-1} s^{-1}$, $K_{IPA} = 3.1 M^{-1}$, and $\tau_{wO}^{-1} = (1.6 \pm 0.1) \times 10^7 s^{-1}$ in air-saturated acetone. A very good agreement is found between the values of K_{IPA} obtained from RF formation, wO decay and O_2 consumption (for values in acetonitrile) which indicates that all three approaches provide reliable data. Both values of Φ_{RF}^0 and of Φ_{OX} for acetone are four to five times higher than for acetonitrile, which reflects the relative reactivities of the two solvents towards wO. Additionally, the value of Φ_{OX} is greater than that of Φ_{RF}^0 for AC, as for AN [10], which means that also for acetone, interception by oxygen of intermediate species directly formed from interaction of wO with $(CH_3)_2CO$, results in a pathway leading to oxygenation of acetone without formation of RF. The values of Φ_{RF}^∞ and of Φ_{wO} may be considered as identical within experimental uncertainties, and it may be concluded that, contrary to the results obtained with olefins in acetonitrile [10], the efficiency of formation of RF from the intermediate complex $[H^+W_{10}O_{32}^{5-}, X^\bullet]$ is close to unity for propan-2-ol in acetone.

All results are listed in Table 1 from which it appears, combined with previous investigations, that acetone, acetonitrile,

and propan-2-ol react exclusively with wO by hydrogen-atom abstraction.

4. Conclusions

There are great analogies between the photoproperties of acetone and acetonitrile as solvents as well as substrates in decatungstate photocatalysis. The values of the lifetime of wO, τ_{wO} , of the rate constant for inherent decay of wO, k_I , of the product $\Phi_{wO}\epsilon_{wO}$ of the quantum yield (Φ_{wO}) and the extinction coefficient (ϵ_{wO}) of the wO transient, and then of Φ_{wO} , are close to one another in both solvents. The only major differences are: (i) that the reactivity of acetone toward wO is three to four times higher than that of acetonitrile, but remains relatively weak compared to the less reactive substrates such as alkanes and (ii) that, in contrast to acetonitrile, no solvated ions have been detected in solutions of decatungstate in acetone by ESMS [21], thus excluding strong precomplexation. It may be concluded that acetone may accompany acetonitrile and water in the very restricted category of conventional solvents, a result which permits to have a better approach of solvent effect in decatungstate photocatalysis. As a first example, if we compare the rate constant k_{IPA} of reaction of propan-2-ol in the two solvents and in H_2O (data not shown), the relative reactivities of wO in acetone, acetonitrile, and water are 1/1.8/23. It appears that the reactivity of wO is slightly lower in AC than in AN (factor 1.8), but much more important in water. This solvent effect sheds a new light on the nature of the reactive transient wO which strongly supports an oxyradical-like character due to the presence of an electron-deficient oxygen center.

Acknowledgments

The time-resolved experiments were performed at the Free Radical Research Facility in the Synchrotron Radiation Department of the CLRC Daresbury Laboratory, Warrington, UK, with the support of the European Commission through a TMR Programme. We thank Dr. S. Navaratnam and Dr. R. Edge for their excellent technical assistance.

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