

Mechanism of decatungstate photocatalyzed oxygenation of aromatic alcohols

Part I. Continuous photolysis and laser flash photolysis studies

Charles Tanielian^{a,*}, Ioannis N. Lykakis^b, Rachid Seghrouchni^a,
Fabien Cougnon^a, Michael Orfanopoulos^{b,**}

^a Laboratoire de Photochimie/LIPHT, Ecole Européenne de Chimie Polymères et Matériaux de Strasbourg, 25 rue Becquerel, 67087 Strasbourg Cedex 2, France

^b Department of Chemistry, University of Crete, Iraklion, Voutes 71003, Crete, Greece

Available online 6 September 2006

Abstract

Previous studies on the mechanism of decatungstate photocatalyzed reactions of aliphatic alcohols and of aromatic hydrocarbons in the presence of oxygen suggest that in the corresponding reactions of aryl alcohols, direct electron transfer can compete with hydrogen-atom transfer. A combination of steady-state (O_2 consumption measurements under continuous photolysis) and of time-resolved (laser flash photolysis) techniques have been used to investigate the decatungstate photocatalyzed oxygenation of benzyl alcohol, 1-phenylethanol and 1-deuterium-1-phenylethanol. Based upon a series of observations (quantitative formation of peroxide, primary kinetic isotope effect) and the detailed examination of kinetic parameters derived from an extensive kinetic study, it is concluded that aromatic alcohols react by a hydrogen-atom transfer mechanism.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Photocatalytic oxygenation; Kinetics; Decatungstate; Aromatic alcohols; Hydrogen-atom transfer

1. Introduction

The polyoxotungstate $W_{10}O_{32}^{4-}$, which is among the most photochemically active polyoxometalates and appears to exhibit especially interesting properties as photocatalysts, has been intensively studied over the past 15 years or so [1–17]. Several aspects of the mechanism of photocatalysis by decatungstates may be considered as established in acetonitrile (Scheme 1).

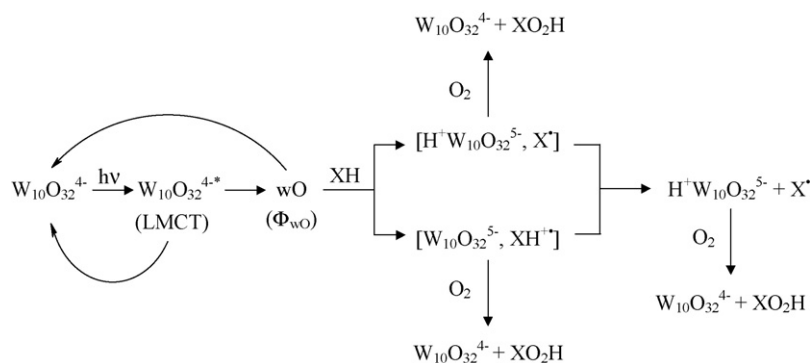
Illumination of $W_{10}O_{32}^{4-}$ leads to the formation of a locally excited ligand-to-metal charge transfer state $W_{10}O_{32}^{4-*}$ that decays in less than 30 ps to an extremely reactive nonemissive transient [2], which has been referred to as wO [3]. This latter species, which is a relaxed excited state, exhibits oxyradical-like character due to the presence of an electron-deficient oxygen center, and is the reactive species in photocatalytic systems, has a lifetime τ_{wO} of 65 ± 5 ns in the case of sodium decatungstate and its quantum yield of formation Φ_{wO} is 0.57 [3,10]. Transient

absorbance measurements at 780 nm have shown that wO possesses an extraordinary reactivity towards virtually any organic substrate XH [3–11]. The decay profile at this wavelength follows second-order kinetics, and fails to reform the baseline after wO decay in many cases. This behaviour demonstrates the existence of a third intermediate, which was identified as the one-electron-reduced form (RF or $H^+W_{10}O_{32}^{5-}$) of the catalyst (i.e., $W_{10}O_{32}^{5-}$ or its protonated form $HW_{10}O_{32}^{4-}$) by comparison with RF spectrum obtained by electrochemical reduction [2a] or pulse radiolysis [3]. Previous studies involving a wide variety of organic substrates suggested that quenching of wO may occur by hydrogen-atom abstraction (HA) and/or electron transfer (ET) mechanisms depending of the chemical nature of XH [3–15]. In any case, both mechanisms give rise to the same one-electron-reduced species, and to the corresponding substrate-derived radical. Both RF and X^\bullet were shown to react with molecular oxygen to regenerate the active form ($W_{10}O_{32}^{4-}$) of the catalyst, and to give the substrate derived hydroperoxide (XO_2H or H_2O_2), respectively [3,4,6,8–10]. Additionally, it was suggested that XO_2H can also be formed during interception by molecular oxygen of intermediate HA or ET complexes ($[H^+W_{10}O_{32}^{5-}, X^\bullet]$ and $[W_{10}O_{32}^{5-}, XH^{+\bullet}]$, respectively) [10], as shown in Scheme 1.

* Corresponding author. Tel.: +33 3 90 24 27 73; fax: +33 3 90 24 27 16.

** Corresponding author.

E-mail addresses: tanielian@chimie.u-strasbg.fr (C. Tanielian),
orfanop@chemistry.uoc.gr (M. Orfanopoulos).



Scheme 1.

In this work, we will focus on the mechanism of decatungstate oxygenation of aromatic alcohols. Previous studies with aliphatic alcohols suggested that quenching of wO occurs by hydrogen-atom abstraction. For example, it has been shown that the reactivity of different alcohols, linear and branched, vary over two orders of magnitude for alcohols expected to have similar oxidation potential but containing hydrogen atoms of different bond-dissociation energy [3]. However, with easily oxidizable substrates such as aromatic hydrocarbons [11] and alkenes [10], direct electron transfer can compete with hydrogen-atom transfer and even become the dominant pathway, as demonstrated by correlations of wO quenching rate constants with substrate redox properties. One can thus expect that, in the reaction of aromatic alcohols, HA and ET mechanisms may simultaneously contribute to the photochemical transformation. Such a competition has already been recently described in a recent investigation of decatungstate photocatalyzed oxygenation of a series of aliphatic hydrocarbons including cyclohexene, a series of hexene isomers, and their saturated counterparts [10]. Rate constants for alkenes were shown to correlate with substrate ionization energy (IE), while those for the corresponding alkanes were found to be significantly lower, and independent of IE. It was demonstrated that alkenes react by a combination of HA and ET mechanisms, whereas alkanes exclusively react by HA [10]. Here we will examine the mechanism of oxygenation of aromatic alcohols by using several complementary techniques and concepts. For clarity reasons, the results and the corresponding discussions will be presented in two parts. In Part I, continuous photolysis and laser flash photolysis studies on benzyl alcohol and deuterated or not 1-phenylethanol conclude that reactions of aromatic alcohols proceed essentially according to a HA mechanism, and in Part II, a kinetic isotope effects study confirms a HA process, and Hammett kinetics substantiates the existence of a radical intermediate and support an early transition state.

2. Experimental

Sodium decatungstate was synthesized and purified by literature procedures [2a]. All other chemicals were purchased at the highest purity available from Aldrich, and were used as received. All experiments described in this work have been performed in acetonitrile solution. Time-resolved spectroscopic studies were made at the Paterson Institute for Cancer Research

Free Radical Research Facility. Laser flash photolysis studies were made with the third harmonic of a Q-switched Nd:YAG laser, at 355 nm. Solutions of sodium decatungstate were made up to 1.1×10^{-4} M, corresponding to an absorbance value of ~ 0.4 at 355 nm. The sample solution, placed in a quartz cell having 1 cm path length, was excited with single pulses (100 mJ) delivered from the laser and analyzed with a pulsed Xe arc lamp. 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. Lifetimes of the reactive transient wO were obtained by computer extrapolation of the first order decay profiles recorded at 780 nm. 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:

$$\Phi_{RF} = \left(\frac{OD_f}{OD_i} \right) \left(\frac{\Phi_{wO} \epsilon_{wO}}{\epsilon_{RF}} \right),$$

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. The extinction coefficient $\epsilon_{RF} = 7000 \text{ M}^{-1} \text{ cm}^{-1}$ of $W_{10}O_{32}^{5-}$ at 780 nm is known from the electrochemical reduction of $W_{10}O_{32}^{4-}$, and the quantum yield $\Phi_{wO} = 0.567$ and extinction coefficient $\epsilon_{wO} = 7012 \text{ M}^{-1} \text{ cm}^{-1}$ of the wO transient have been previously obtained by O_2 consumption and laser spectroscopy experiments, respectively [10].

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:

$$\Phi_{OX} = \frac{(\text{number of moles of } O_2 \text{ consumed})}{(\text{number of einsteins absorbed by } W_{10}O_{32}^{4-})}.$$

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 an acetonitrile solution of decatungstate containing various amounts of substrate 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. O₂ consumption profiles generally display a short equilibration period, which is due to lamp stabilization and related thermal effects resulting from heating by the lamp. Light intensities were calibrated using the photooxygenation of furfuryl alcohol in O₂ saturated acetonitrile with phenalene ($\Phi_{\text{OX}} = 0.98$ [18]) as sensitizer. The concentration of decatungstate was sufficient to absorb all incident light. The intensity of absorbed light was 6.97×10^{-6} einstein s⁻¹. Peroxide concentrations were determined by iodometric titration [19].

3. Results and discussion

3.1. Steady-state photolysis

Previous studies have shown that oxygen consumption measurements represent a very useful tool to investigate the reactivity of wO towards organic substrates [3,6,8–10]. Fig. 1 shows the profiles of O₂ consumption upon irradiation of oxygen-

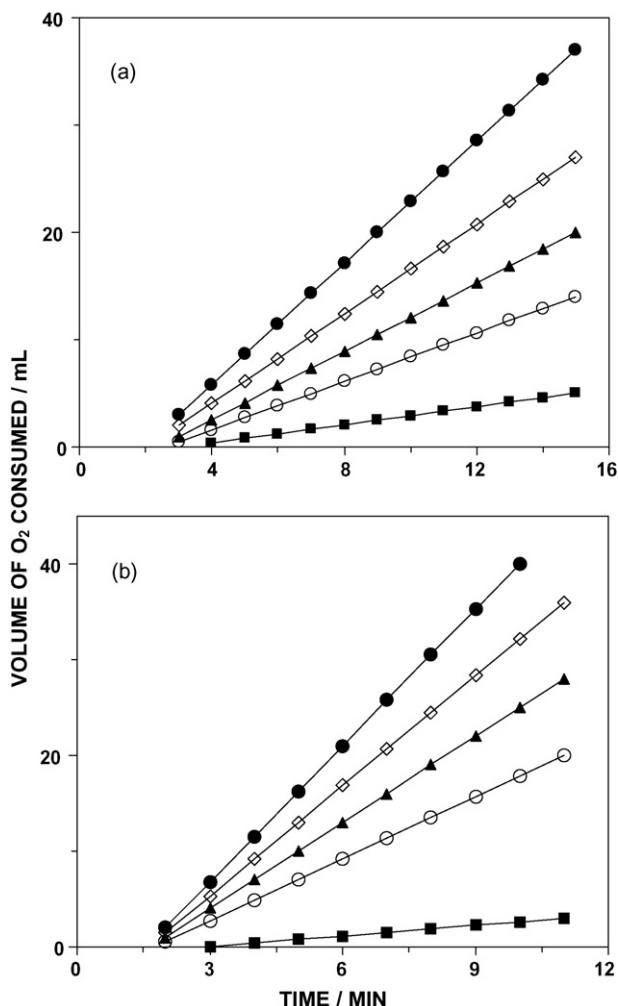


Fig. 1. Time dependence of O₂ consumption measured for illumination of oxygen-saturated solutions of sodium decatungstate (5.5×10^{-4} M) in oxygen-saturated acetonitrile: (a) in the absence (■) and presence of 1-phenylethanol at 0.02 M (○), 0.04 M (▲), 0.08 M (◇), and 0.2 M (●), and (b) in the absence (■) and presence of benzyl alcohol at 0.02 M (○), 0.05 M (▲), 0.1 M (◇), and 0.4 M (●).

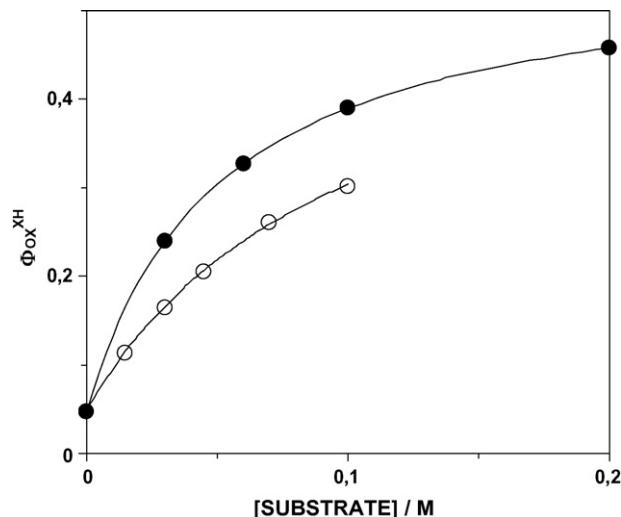


Fig. 2. Effect of benzyl alcohol (●) and 1-phenylethanol (○) concentration on the quantum yield of oxygen consumption measured for 5.5×10^{-4} M sodium decatungstate in oxygen-saturated acetonitrile. The solid lines are drawn in accordance with the equation $\Phi_{\text{OX}}^{\text{XH}} = (\Phi_{\text{OX}} + \Phi_{\text{wO}}K[\text{XH}])/(1 + K[\text{XH}])$, with $\Phi_{\text{OX}} = 0.047$, $\Phi_{\text{wO}} = 0.56$, $K = 9.9 \text{ M}^{-1}$ for 1-phenylethanol, and $\Phi_{\text{OX}} = 0.047$, $\Phi_{\text{wO}} = 0.56$, $K = 20.1 \text{ M}^{-1}$ for benzyl alcohol.

saturated acetonitrile solutions of sodium decatungstate, containing various concentrations of benzyl alcohol (Fig. 1a) and of 1-phenylethanol (Fig. 1b). After a short equilibration period due to lamp stabilization, consumption of O₂ increases linearly with irradiation time. The relative rates of O₂ 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 O₂ consumption for phenalene-sensitized oxygenation of furfuryl alcohol (quantum yield 0.98 [18]). Fig. 2 shows that the quantum yield for O₂ consumption, $\Phi_{\text{OX}}^{\text{XH}}$, increases progressively with increasing concentration of substrate, and that the value in the absence of substrate Φ_{OX} remains finite, confirming that acetonitrile itself acts as a substrate for wO.

These data can be used to derive the rate constant k_{XH} for reaction between wO and aromatic alcohols, because the experimental quantum yields can be described by the following expression [3,6]:

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

where Φ_{wO} is the quantum yield for formation of wO and $K = k_{\text{XH}}\tau_{\text{wO}}$ is the Stern–Volmer constant. From nonlinear least-squares analysis of the experimental data it may be deduced that the values of K are 20.1 M^{-1} and 9.9 M^{-1} for benzyl alcohol and 1-phenylethanol, respectively, and that the common values of $\Phi_{\text{OX}} = 0.047$ and of $\Phi_{\text{wO}} = 0.56$ obtained for the two substrates are identical to those previously found [10].

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 and hydrogen peroxide in essentially quantitative yield [3]. Fig. 3 shows the profile for oxygen consumption and peroxide formation as measured for decatungstate catalyzed

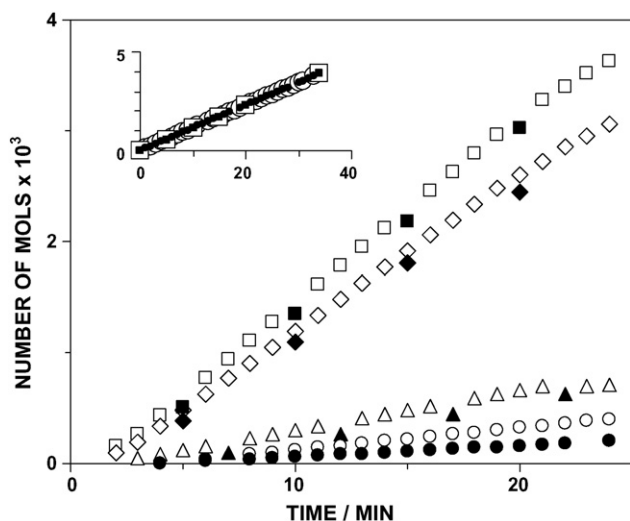
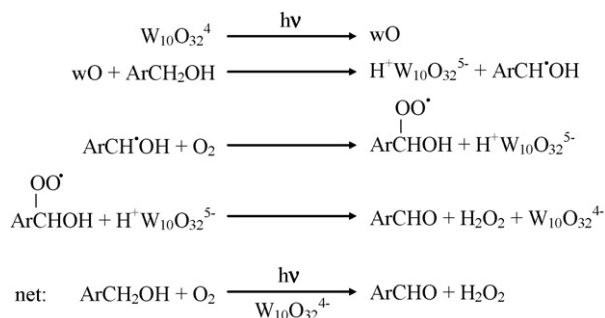


Fig. 3. Correspondence between the number of moles of oxygen consumed (open symbols) and of peroxide formed (solid symbols) during continuous illumination of sodium decatungstate (5.5×10^{-4} M) in air-saturated acetonitrile in the absence (\circ) and presence of benzyl alcohol at 0.01 M (Δ), 0.2 M (\diamond), and 0.8 M (\square). Inset: correspondence between the number of moles of oxygen consumed (circle) and of peroxide formed (square) during continuous illumination of sodium decatungstate (5.5×10^{-4} M) in oxygen (open symbols) and air (solid symbols) saturated acetonitrile in the presence of 1-phenylethanol at 0.8 M.

photooxygenation of benzyl alcohol at different concentrations and of 1-phenylethanol in acetonitrile. As in the case of propan-2-ol, the initial variations are linear, and except at low substrate concentrations, for which a noticeable contribution of direct photooxygenation 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 2 in the case of benzyl alcohol, which involves the intermediate formation of peroxy compound and is kinetically indistinguishable to that previously suggested for aliphatic alcohols [3].

Until now, we have (i) considered the kinetics of photooxygenation of substrates only in terms of initial rate of O_2 consumption and peroxide formation, an approach which is very useful in elucidating the mechanism of complex reactions such as processes in which oxygen is involved [8], and then (ii) implicitly assumed that the primary products were stable. In reality, the primary products of a photocatalyzed reaction can rapidly generate new products according to a cascade of secondary processes if they are unstable in the reaction medium [8]. These consecutive



Scheme 2.

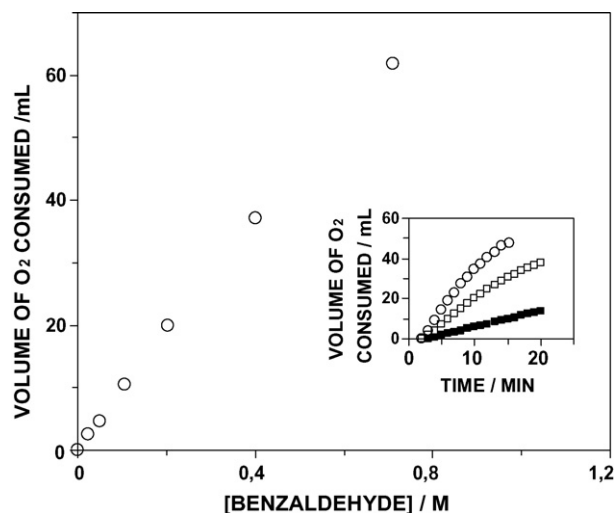
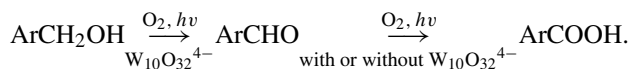


Fig. 4. Effect of benzaldehyde concentration on the rate of oxygen consumption measured for sodium decatungstate at 5.5×10^{-4} M in oxygen-saturated acetonitrile. Inset: time dependence of O_2 consumption measured for illumination of oxygen-saturated solutions of sodium decatungstate (5.5×10^{-4} M) in acetonitrile in the presence of benzaldehyde at 0.025 M (\square), 0.05 M (\circ), (\blacksquare) Like (\square) but without decatungstate.

reactions may be of thermal and/or of photochemical nature. In the decatungstate photocatalyzed oxygenation of benzyl alcohol, and for relatively high concentrations of substrate, the rate of O_2 consumption appears to be greater than expected (Fig. 4). This observation is related to the formation of benzaldehyde, directly derived from benzyl alcohol, which itself is converted to benzoic acid under the experimental conditions, simultaneously by decatungstate catalyzed oxygenation and by direct absorption of the incident irradiation (Fig. 4, inset)



This last process is well documented [20,21], and Bäckström found a quantum yield of about 10^4 for the self-photoinitiated oxidation of benzaldehyde [21].

3.2. Laser flash photolysis

Fig. 5 shows kinetic traces recorded at 780 nm following 355 nm excitation of air-saturated solutions of acetonitrile in the presence of variable concentrations of benzyl alcohol. These decays correspond to the wO transient, and yield the data displayed in the corresponding Stern–Volmer plot (Fig. 6), whose slope yields $k_{XH} = 28.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for benzyl alcohol, and, equivalently, $k_{XH} = 14.4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for 1-phenylethanol and $12.9 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for 1-deuterium-1-phenylethanol which corresponds to Stern–Volmer constants of 19.4 M^{-1} , 9.9 M^{-1} , and 7.9 M^{-1} , respectively. k_{XH} and K data obtained by this method are listed in Table 1. The lifetime of wO in air saturated CH_3CN is 65 ns.

We also note that the absorbance baseline is generally not reformed after wO decay. It has been previously shown that this absorbance is due to the one-electron-reduced form of decatungstate, $W_{10}O_{32}^{5-}$, or its protonated form $HW_{10}O_{32}^{4-}$. It

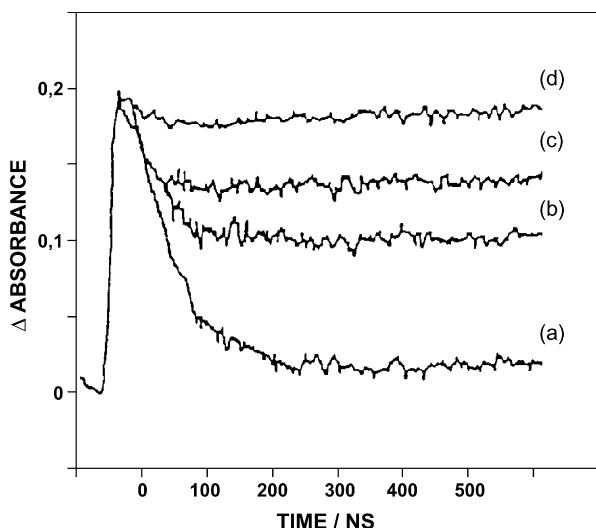


Fig. 5. Kinetics profiles observed at 780 nm showing decay of wO as generated following 355 nm excitation with a 15 ns laser pulse of 5×10^{-4} M sodium decatungstate air-saturated acetonitrile solution in the absence (a) and presence of benzyl alcohol at 0.025 M (b), 0.075 M (c) and 0.2 M (d).

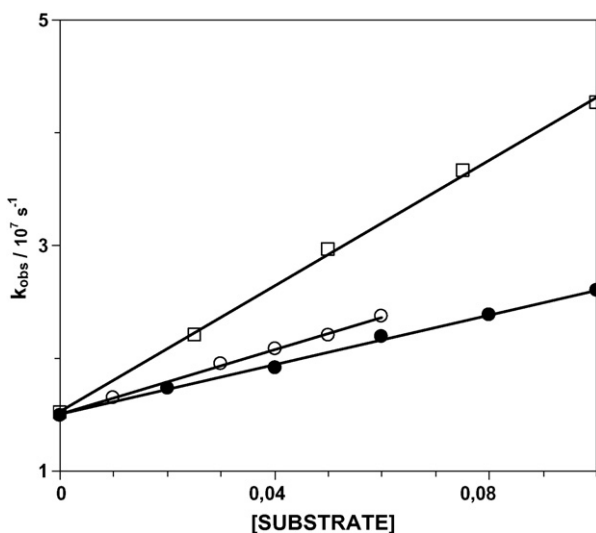


Fig. 6. Dependence of the pseudo-first-order rate constant of decay of wO measured at 780 nm on benzyl alcohol (\square), 1-phenylethanol (\circ), and 1-deuterium-1-phenylethanol (\bullet) concentration in air-saturated acetonitrile.

is known that these species are reoxidized to $W_{10}O_{32}^{4-}$, by interaction with molecular oxygen, or by disproportionation yielding $W_{10}O_{32}^{4-}$ and $W_{10}O_{32}^{6-}$. The transient absorbance change recorded at 780 nm, 450 ns following laser excitation, may be

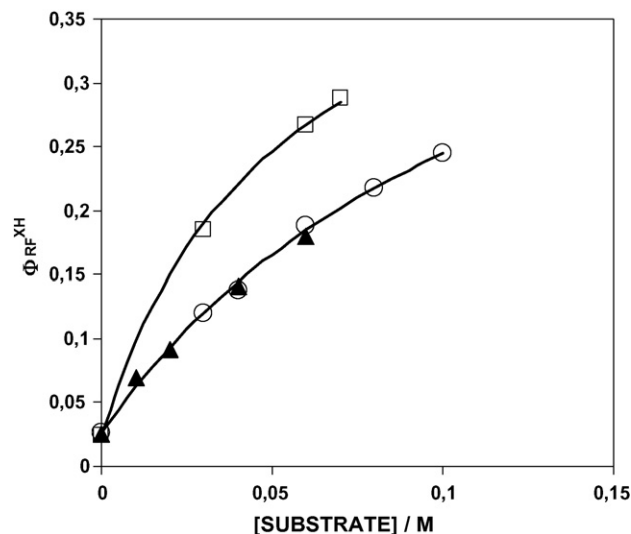


Fig. 7. Dependence of the quantum yield for formation of the reduced form of decatungstate, RF, on benzyl alcohol (\square), 1-phenylethanol (\circ), and 1-deuterium-1-phenylethanol (\blacktriangle) concentration, following 355 nm pulsed excitation (~ 20 mJ) of air-saturated acetonitrile solutions of sodium decatungstate (5×10^{-4} M). The solid lines are drawn in accordance with the equation $\Phi_{RF}^{XH} = (\Phi_{RF}^0 + \Phi_{RF}^\infty K[XH]) / (1 + K[XH])$, with $\Phi_{RF}^0 = 0.023$, $\Phi_{RF}^\infty = 0.45$, $K = 19.1 \text{ M}^{-1}$ for benzyl alcohol, and $\Phi_{RF}^0 = 0.024$, $\Phi_{RF}^\infty = 0.47$, $K = 8.1 \text{ M}^{-1}$ for 1-phenylethanol. For clarity reasons, the solid line is not drawn in the case of 1-deuterium-1-phenylethanol, for which we obtain $\Phi_{RF}^0 = 0.025$, $\Phi_{RF}^\infty = 0.50$, $K = 7.2 \text{ M}^{-1}$.

used to calculate the quantum yields Φ_{RF}^{XH} of formation of RF (see Section 2). Similarly to the analysis employed for the O_2 consumption quantum yields, the evolution of Φ_{RF}^{XH} with substrate concentration can be interpreted in terms 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. 7 shows the dependence of the quantum yield Φ_{RF}^{XH} of RF formation on aromatic alcohols concentration in acetonitrile. The kinetic analysis yields $\Phi_{RF}^0 = 0.023$, 0.024 and 0.025, $\Phi_{RF}^\infty = 0.45$, 0.47 and 0.50, and $K = 19.4 \text{ M}^{-1}$, 9.9 M^{-1} and 7.9 M^{-1} for benzyl alcohol, 1-phenylethanol and 1-deuterium-1-phenylethanol, respectively (Table 1). The value of $\Phi_{RF}^0 = 0.024 \pm 0.02$ is in excellent agreement with previous determinations [10] and, within the limit of experimental uncer-

Table 1
Kinetics parameters derived from laser flash photolysis and oxygen consumption studies

Substrate	Transient absorbance at 780 nm					Oxygen consumption		
	wO decay		$W_{10}O_{32}^{5-}$ formation			Φ_{OX}	Φ_{wO}	$K (\text{M}^{-1})$
	$k_{XH} (10^7 \text{ M}^{-1} \text{ s}^{-1})$	$K (\text{M}^{-1})$	Φ_{RF}^0	Φ_{RF}^∞	$K (\text{M}^{-1})$			
1-Phenylethanol	14.4	9.9	0.024	0.47	8.1	0.047	0.56	9.9
1-Deuterium-1-phenylethanol	12.9	7.9	0.025	0.50	7.2			
Benzyl alcohol	28	19.4	0.023	0.45	19.1	0.047	0.56	20.1

tainty, the value $\Phi_{\text{RF}}^{\infty} = 0.5 \pm 0.2$ may be considered as identical to that of the quantum yield for wO formation $\Phi_{\text{wO}} = 0.57$. This last result permits us to conclude that, contrary to the results obtained with olefins as substrates [10], the efficiency of formation of RF from the intermediate geminate pairs (Scheme 1) is close to unity for aromatic alcohols. In parallel, the reaction pathways resulting from interception of these geminate pairs by oxygen and leading to quantitative formation of peroxides without decatungstate reduction do not contribute to the overall reaction. This conclusion is consistent with a hydrogen-atom abstraction mechanism, which is confirmed by the observation of a primary kinetic isotope effect: the ratio of the values of k_{XH} obtained for 1-phenylethanol and 1-deuterium-1-phenylethanol is ~ 1.3 indicating carbon–tertiary hydrogen cleavage in the transition state consistent with the geminate pair $[\text{H}^+\text{W}_{10}\text{O}_{32}^{5-}, \text{X}^{\bullet}]$ (Scheme 1). This result can be connected to the primary kinetic isotope effect observed for the quenching of wO by cyclohexane- h_{12} /cyclohexane- d_{12} (ratio of the values of $k_{\text{XH}} = 3.0$) [5]. In addition, it is noteworthy that the rate constant k_{XH} for benzyl alcohol is the double of that for 1-phenylethanol, just as the number of hydrogen atoms on the carbon atom α to the hydroxyl group. In this connection, it must be noticed that, with aliphatic alcohols which are known to react by HA mechanism, wO also attacks predominantly C–H bonds α to an OH group (unpublished results).

It is remarkable that the three values of Stern–Volmer constants, obtained independently from both steady-state and time-resolved measurements are almost identical for the aromatic alcohols studied here (Table 1) and also for all previously investigated substrates [10]. This suggests that wO quenching generally leads to substrate oxygenation, i.e., the fraction of quenching events leading to substrate oxygenation equals unity in all cases, in contrast to the singlet oxygen mediated corresponding reactions [9].

4. Conclusions

The present study is the realization of a collaborative work devoted to the study of the mechanism of the decatungstate photocatalyzed oxygenation of aromatic alcohols in acetonitrile. In this Part I, a combination of steady-state (O_2 consumption measurements under continuous photolysis) and of time-resolved (laser flash photolysis) techniques have been used to investigate the photooxygenation of benzyl alcohol, 1-phenylethanol and 1-deuterium-1-phenylethanol. Based upon a series of observations (quantitative formation of peroxide, primary kinetic isotope effect) and the detailed examination of kinetic parameters derived from an extensive kinetic study, it is concluded that aromatic alcohols react with the transient wO by hydrogen-atom abstraction. In the accompanying paper, Part II, additional information will be gathered: supplementary kinetic isotope effects study confirms a HA process, and Hammett kinetics substantiates the existence of a radical intermediate and support an early transition state.

Acknowledgments

The laser flash photolysis studies were performed at the Pateron Institute for Cancer Research Free Radical Research Facility, Manchester, UK, with support of the European Commission through the Access to Large-Scale Facilities activity of the TMR Program. Financial support from ARC is gratefully acknowledged. We thank the French Direction de la coopération scientifique, universitaire et de la recherche (Ministère des Affaires Étrangères) and the Greek Secretariat of Research and Technology (Greek–French collaborative research program Platon 2001) for financial support and graduate fellowships to I.N.L.

References

- [1] (a) C.L. Hill, *Chem. Rev.* 98 (1998) 1–390; (b) E. Papaconstantinou, *Chem. Soc. Rev.* 18 (1989) 1–31; (c) A. Hiskia, A. Mylonas, E. Papaconstantinou, *Chem. Soc. Rev.* 30 (2001) 62–69; (d) C.L. Hill, C.M. Prosser-McCartha, in: K. Kalyanasundran, M. Grätzel (Eds.), *Photosensitization and Photocatalysis Using Inorganic and Organometallic Complexes*, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1993, pp. 307–330; (e) C.L. Hill (Ed.), *Activation and Functionalization of Alkanes*, Wiley, New York, 1989, and references cited in each.
- [2] (a) D.C. Duncan, T.L. Netzel, C.L. Hill, *Inorg. Chem.* 34 (1995) 4640; (b) I. Texier, J.F. Delouis, J.A. Delaire, C. Giannotti, P. Plaza, M.M. Martin, *Chem. Phys. Lett.* 311 (1999) 139.
- [3] C. Tanielian, K. Duffy, A. Jones, *J. Phys. Chem. B* 101 (1997) 4276–4282.
- [4] L.P. Ermolenko, C. Giannotti, J.A. Delaire, *J. Chem. Soc., Perkin Trans. 2* (1997) 25–30.
- [5] D.C. Duncan, M.A. Fox, *J. Phys. Chem. A* 102 (1998) 4559–4567.
- [6] C. Tanielian, *Coord. Chem. Rev.* 180 (1998) 1165–1181.
- [7] T. Kothe, R. Martschke, H. Fischer, *J. Chem. Soc., Perkin Trans. 2* (1998) 503–507.
- [8] C. Tanielian, R. Mechin, R. Seghrouchni, C. Schweitzer, *Photochem. Photobiol.* 71 (2000) 12–19.
- [9] C. Tanielian, C. Schweitzer, R. Seghrouchni, M. Esch, R. Mechin, *Photochem. Photobiol. Sci.* 2 (2003) 297–305.
- [10] C. Tanielian, R. Seghrouchni, C. Schweitzer, *J. Phys. Chem. A* 107 (2003) 1102–1111.
- [11] I. Texier, J.A. Delaire, C. Giannotti, *Phys. Chem. Chem. Phys.* 2 (2000) 1205–1212.
- [12] (a) A. Molinari, R. Amadelli, L. Andreotti, A. Maldotti, *J. Chem. Soc., Dalton Trans.* (1999) 1203–1204; (b) A. Maldotti, R. Amadelli, V. Carassiti, A. Molinari, *Inorg. Chim. Acta* 256 (1997) 309–312.
- [13] (a) C.L. Hill, *Synlett* (1995) 127–131; (b) R.F. Renneke, M. Pasquali, C.L. Hill, *J. Am. Chem. Soc.* 112 (1990) 6585–6594.
- [14] T. Yamase, N. Takabayashi, M. Kaji, *J. Chem. Soc., Dalton Trans.* (1984) 793–799.
- [15] T. Yamase, T. Usami, *J. Chem. Soc., Dalton Trans.* (1988) 183–190.
- [16] R. Akid, J.R. Darwent, *J. Chem. Soc., Dalton Trans.* (1985) 395–399.
- [17] A. Hiskia, E. Papaconstantinou, *Inorg. Chem.* 31 (1992) 163–167.
- [18] R. Schmidt, C. Tanielian, R. Dunsbach, C. Wolff, *J. Photochem. Photobiol. A: Chem.* 79 (1994) 11–17.
- [19] R.D. Mair, A.J. Graupner, *Anal. Chem.* 36 (1964) 194–204.
- [20] P.A.A. Van der Beek, *Rec. Trav. Chim. Pays-Bas* 47 (1928) 286–300.
- [21] H.L.J. Bäckström, *J. Am. Chem. Soc.* 49 (1927) 1460–1472.