

Laser flash photolysis study of the mechanism of photooxidation of alkanes catalysed by decatungstate anion



Ludmila P. Ermolenko,^a Jacques A. Delaire^b and Charles Giannotti^{*,a}

^a Institut de Chimie des Substances Naturelles du CNRS, Avenue de la Terrasse, 91198 Gif-sur-Yvette Cedex, France

^b Laboratoire de Photophysique et de Photochimie Supramoléculaires et Macromoléculaires, URA 1906 du CNRS, Ecole Normale Supérieure de Cachan, 61 Avenue du Président Wilson, 94235 Cachan Cedex, France

Generated during light excitation, the O(2p) \rightarrow W(5d) ligand-to-metal charge transfer (LMCT) excited state of decatungstate anion ($W_{10}O_{32}^{4-}$) relaxes for $t < 30$ ps to a transient X which persists for 5 ns. In the nanosecond time domain, it reacts with all components of the photocatalytic system (substrate, organic counter-ion and solvent) to give a one-electron reduced decatungstate species $HW_{10}O_{32}^{4-}$ and an organic radical R \cdot . The latter is quenched by dioxygen at a near diffusion-controlled rate, forming a peroxy radical ROO \cdot . In the solvent cage, the peroxy radical ROO \cdot reoxidizes $HW_{10}O_{32}^{4-}$ to give the hydroperoxide ROOH and $W_{10}O_{32}^{4-}$, thus closing the catalytic cycle. The catalyst reoxidation is the rate-limiting step of the alkane oxidation.

Introduction

In the last decade, polyoxometalates (POM) have attracted increasing attention as catalysts for the photooxidation of organic substances because of their high selectivity, stability and efficiency.¹⁻³ These properties of POM have found diversified applications in heterogeneous and homogeneous catalysis,⁴ photomicroolithography³ and petrochemistry. More recently, POM have been proposed as photocatalysts for the photochemical degradation of pollutants of water and air.⁵ Several reviews have reported on various aspects of the decatungstate anion, including its structural and spectral properties⁶⁻⁸ and also its electrochemistry.⁹ However, our knowledge of the mechanism of the photocatalytic action of the decatungstate is still incomplete and there exist discrepancies in interpretation of the available experimental data, and most notably the primary photoevents.

Pioneering studies on laser flash photolysis of the decatungstate in the nanosecond time domain have suggested¹⁰ that upon laser pulse the O \rightarrow W charge-transfer excited state of $W_{10}O_{32}^{4-}$ undergoes a reversible electron transfer from organic substrate to form a cation-radical and a one-electron reduced $W_{10}O_{32}^{5-}$ with its characteristic λ_{max} 780 nm. The transfer of a proton to this latter species generates the corresponding radical and $HW_{10}O_{32}^{4-}$ which undergoes slow disproportionation to $W_{10}O_{32}^{4-}$ and a two-electron reduced diprotonated species $[H_2W_{10}O_{32}]^{4-}$.¹¹ However, time-resolved measurements of the decatungstate in the picosecond time domain made later have demonstrated that no chemical events take place during excitation time and the excited state of $W_{10}O_{32}^{4-}$ relaxes within $t < 30$ ps (a weak emission at λ_{max} 615 nm, with a lifetime of 21 ps, was found)³ to a 'long-lived' intermediate that persists for times longer than 15 ns. This long-lived intermediate has a substantial charge-transfer character itself (λ_{max} 780 nm) and is considered to be the real primary photoreactant in favour over the one-electron-reduced species $W_{10}O_{32}^{5-}$ or one of its protonated derivatives.¹²

Our recent studies on the decatungstate catalysed aerobic alkane oxidation under steady-state conditions led us to propose a catalytic cycle comprising the reoxidation of the reduced form of the decatungstate by peroxy radicals in the solvent cage as the main pathway of the catalyst regeneration.¹³ The suggested mechanism was deduced from the data of the alkane

transformation (selective hydroperoxide formation, stoichiometry of the oxidation). We report here an extensive laser flash photolysis study of the decatungstate cluster in the presence of all the components of the photocatalytic cycle—alkane substrate, counter-ions of the catalyst, nitrile solvents and dioxygen. Limited data on the decatungstate transformation under anaerobic conditions will also be given for the purposes of comparison.

Experimental

Materials

Acetonitrile (SDS, analytical grade) was used as purchased. Propionitrile (Fluka, reagent grade) was purified by filtration through a column with activity I basic aluminium oxide followed by fractionation. Doubly distilled water was used. Adamantane (Aldrich, reagent grade) was purified by recrystallization from heptane. The decatungstates $Q_4W_{10}O_{32}$ (Q = Na, Me₄N, Hex₄N) were prepared according to literature methods.^{13,14} All the decatungstates were crystallized from acetonitrile and checked for purity by UV-VIS spectroscopy and elemental analysis.

Transient absorption measurements

Transient absorption spectroscopy was carried out with a nanosecond and a picosecond Nd:YAG laser. Both set-ups have already been described.^{15,16} The mode-locked picosecond Nd:YAG laser was manufactured by BM Industries (model BMI 502 DPS). The pulse generator consisted of an oscillator in an actively-passively mode-locked cavity, an extra-cavity Pockels cell between crossed polarizers and two single-pass Nd:YAG amplifiers. At the output of the second amplifier, the energy was about 30 mJ in one single pulse (35 ps pulse width, 8 Hz) at 1064 nm. After passing through two harmonic generating KDP crystals, the beam was composed of three wavelengths (1064, 532 and 355 nm) which were split into three separated beams by appropriate dichroic mirrors. The third harmonic (355 nm) beam was used as the pump beam and the fundamental (1064 nm) was used to generate a probe beam in the following way. Using a procedure described by Yoshihara,¹⁵ the fundamental flash of the laser was focused on a tungsten electrode in a glass cell filled with

xenon at a pressure of 2 bars. The laser created a plasma, whose emission lifetime was *ca.* 50 ns with a rise time during the pulse width and an emission plateau after 10 ns delay. This light source did not need any electronic set-up and had an emission spectrum very similar to the emission of a xenon arc, continuous between 300 and 800 nm with a maximum near 400 nm. Both probe and pump beams were focused with separate lenses in the middle of a cell (1 mm optical path) in a nearly co-linear arrangement, with an angle of 20° between both beams. The probe beam volume is smaller than the excitation beam volume and contained inside it. At the output of the cell, the pump beam was blocked with an iris and the probe was focused on the entrance slit of a monochromator. The output signal at a selected wavelength was detected by a streak-camera (ARP Strasbourg, France) whose time resolution was 8 ps. The excitation signal was delayed relative to the probe signal by using different optical delays. The streak-camera was used in a single-shot mode and was triggered by the laser pulse itself: a part of the fundamental beam was extracted with a glass plate used as a reflector and focused on a germanium photodiode whose signal was used as a trigger after appropriated delay. The signal on the phosphor of the streak-camera was amplified by a microchannel plate and read by a photodiode array. Signal processing was made by a system developed by ARP company and the digitized voltages were then transmitted to a personal computer through an IEEE interface. Electronic shutters allowed data accumulation with and without sample excitation. Each absorbance change at a given wavelength was obtained by averaging the signal of both the probe light without excitation $I_0(t)$ and with excitation $I(t)$ over the same number of laser shots (10–200) and computing $\Delta[\text{OD}(t)] = \log [I_0(t)/I(t)]$. It had been verified prior to the experiment that the pulse-to-pulse reproducibility was such that this averaging procedure was valid. Kinetic analysis of the absorption signals according to simple orders (first or second order) was carried out employing a least-squares routine. The same experimental arrangement could be used to observe any fluorescent process: in order to do so, the probe beam shutter was turned off. Due to the wavelength sensitivity range of the photocathode (type S20) of the streak tube, the wavelength range was limited between 360 and 700 nm. The time range was also limited to $t \leq 5$ ns with this set-up.

The nanosecond laser was a Q-switched Nd:YAG laser manufactured by BM Industries (model BMI 502 DNS 77/10), delivering 7–8 ns pulses at 1064 nm. Q-switching was made with a Pockels cell inside the cavity. The giant pulse was amplified by passing through two Nd:YAG rods, and was then frequency doubled and tripled in KDP crystals. The output energy was 120 mJ at 353 nm. The energy deposited in the sample was lowered by interposing a diffusing plate in front of the irradiation cell. This energy was measured with a Gentec pyroelectric detector. The excitation beam and the probe beam generated by a pulsed xenon source were perpendicular to each other inside the 1 × 1 cm cell. The analysing beam was spectrally dispersed by a monochromator and converted to an electrical signal by a Hamamatsu R928 PM tube. The electric signal was recorded using a digital memory oscilloscope (Tektronix TDS 744 A) connected to a personal computer. The transient signals were analysed by a home-made routine using the Igor procedure. Every given rate constant reported is the mean value of at least five different measurements.

Initial absorption spectra of the solutions were recorded on a Perkin-Elmer Lambda 5 spectrometer.

Methods

The samples tested under aerobic conditions were saturated with oxygen for 5 min and then irradiated under slight pressure of oxygen. The same procedure was performed for the samples, tested under anaerobic conditions, using N_2 .

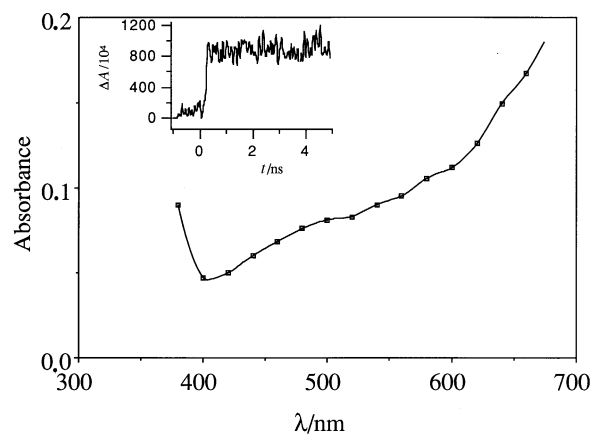


Fig. 1 Transient absorption spectrum obtained at the end of the picosecond laser pulse (355 nm) of 5.0×10^{-3} mol dm^{-3} sodium decatungstate solution in acetonitrile under anaerobic conditions. Insert: time dependence of absorbance measured during the first 5 ns at 380 nm.

Results

The picosecond flash photolysis studies were carried out on the following three systems: $\text{Na}_4\text{W}_{10}\text{O}_{32}-\text{H}_2\text{O}$ **1**, $\text{Na}_4\text{W}_{10}\text{O}_{32}-\text{CH}_3\text{CN}$ **2** and $\text{Na}_4\text{W}_{10}\text{O}_{32}-\text{CH}_3\text{CN}-\text{Ad}$ **3**, where Ad is adamantane. The picosecond laser flash excitation (λ 355 nm) of the 5.0×10^{-3} mol dm^{-3} decatungstate aqueous solution (system **1**) results in an emission at λ_{max} 615 nm with a lifetime <30 ps. Similar results are observed in acetonitrile (system **2**) and in the presence of adamantane (system **3**). Transient absorption spectrum of 5.0×10^{-3} mol dm^{-3} decatungstate solution (system **2**) obtained at the end of the laser pulse (100 ps after the beginning) showed significant increase in the 380–390 and 600–680 nm regions (Fig. 1). These changes are similar to those obtained for the systems **1** and **3**. The absorbance is equal for the three systems and it remained constant till 5 ns after excitation (Fig. 1, insert) from 380 to 680 nm.†

The nanosecond flash laser excitation (λ 355 nm, 10 ns) of 5.0×10^{-4} mol dm^{-3} decatungstate solutions (**1–3**) have a transient absorption spectrum similar to the one observed in the picosecond time domain. In the nanosecond time range this spectrum decreased with time during a period of a few hundred nanoseconds. In order to confirm the solvent and organic cation reactivity towards this transient, we also investigated the following three systems: $\text{Na}_4\text{W}_{10}\text{O}_{32}-\text{C}_2\text{H}_5\text{CN}$ **4**, $(\text{Me}_4\text{N})_4\text{W}_{10}\text{O}_{32}-\text{CH}_3\text{CN}$ **5** and $(\text{Hex}_4\text{N})_4\text{W}_{10}\text{O}_{32}-\text{CH}_3\text{CN}$ (Hex = hexyl) **6**. First, we noticed that the transient yields obtained at the end of the nanosecond pulse of these deaerated solutions were identical to those obtained without deaeration.

The end-of-pulse absorbance obtained in aqueous solution **1** was 10% lower than those observed in organic solutions **2–6**. This absorbance rapidly decreased with first-order kinetics, $k_1 = 2.7 \times 10^7 \text{ s}^{-1}$, and returned to base level in *ca.* 100 ns (Fig. 2). The transient spectra of solutions **2** and **5** are very similar in their shape and in their kinetics. The decay of the transient absorbance started after the end of the nanosecond pulse with first-order kinetics ($k_2 = k_5 = 1.3 \times 10^7 \text{ s}^{-1}$) and *ca.* 10% of initial absorbance values remained constant after 200 ns (Fig. 3). These decay constants k_1 , k_2 and k_5 were insensitive to the pres-

† The authors in ref. 12 reported a different transient behaviour at 390 nm during photoexcitation (355 nm, *ca.* 10 mJ cm^{-2}). After the initial rise, the transient decays rapidly (*ca.* 30 ps) to about half that of the peak maximum. This behaviour is consistent with assigning the prompt absorbance transient at 390 nm to ligand to metal charge-transfer excited state which subsequently generated the long-lived intermediate. They also reported the slowly rising absorbance in the presence of substrate at 390 nm (0–14 ns delay). We have not observed these phenomena under our conditions.

Table 1 Effect of substrate concentration of the values of decay absorption constant k_3 and of the persistent absorbance A_∞

[Adamantane]/ $10^{-2} \text{ mol dm}^{-3}$	A_0^a (± 0.002)	$k_3^b/10^7 \text{ s}^{-1}$ (± 0.001)	A_∞^c (± 0.002)
None	0.287	1.30	0.028
0.5	0.286	1.45	0.052
1.5	0.287	1.80	0.070
2.0	0.284	1.95	0.091

^a A_0 is the end-of-pulse absorbance (10 ns pulse). ^b k_3 is the transient absorbance decay constant. ^c A_∞ is the persistent absorbance 1 μs after the end of the nanosecond pulse.

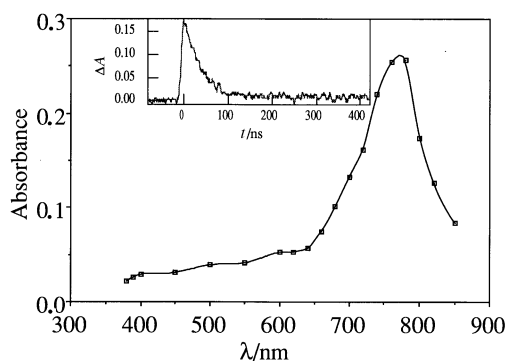


Fig. 2 Transient absorption spectra obtained at the end of the nanosecond laser pulse (355 nm) of $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ aqueous sodium decatungstate solution. Insert: decay curve at 780 nm.

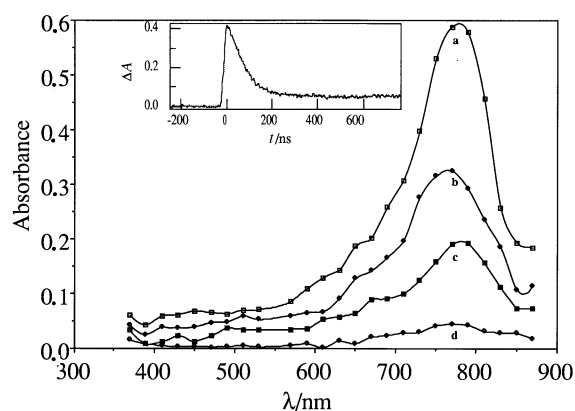


Fig. 3 Transient absorption spectra obtained by nanosecond laser photolysis (355 nm) of $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ $\text{Na}_4\text{W}_{10}\text{O}_{32}$ acetonitrile solution: (a) end of pulse, (b) 40, (c) 75 and (d) 200 ns after laser pulse. Insert: decay curve at 780 nm.

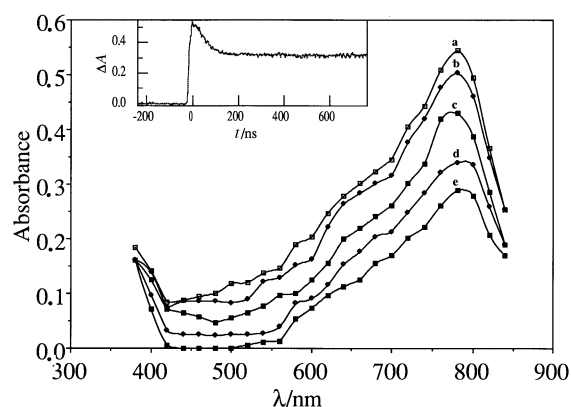


Fig. 4 Transient absorption spectra obtained by nanosecond laser flash photolysis (355 nm) of $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ $\text{Na}_4\text{W}_{10}\text{O}_{32}$ acetonitrile solution in the presence of adamantane ($2.0 \times 10^{-2} \text{ mol dm}^{-3}$): (a) end of pulse, (b) 15, (c) 35, (d) 70 and (e) 125 ns. Insert: decay curve at 780 nm.

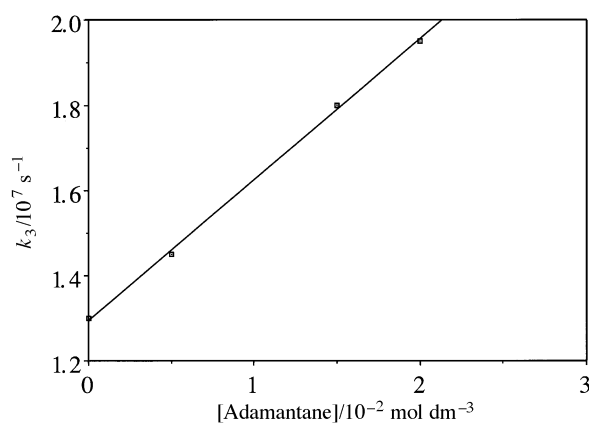


Fig. 5 Pseudo-first-order plot of the absorbance decay constant k_3 vs. [adamantane] (system **3**, 780 nm)

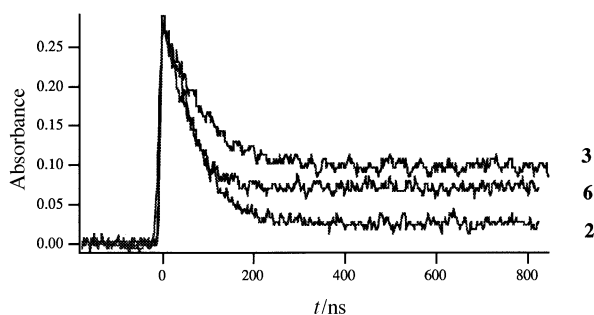


Fig. 6 Absorbance decay curves at 780 nm obtained by laser flash photolysis (355 nm) of systems **2**, **3**, **6** in the nanosecond time domain

ence of oxygen. The transient spectra of solutions **3**, **4** and **6** are also very similar (Fig. 4). The transient absorption decayed rapidly (125 ns) to a constant value (35, 81 and 57% of initial absorption value A_0 , respectively). The decay followed first-order kinetics with rate constants $k_3 = 1.9 \times 10^7$, $k_4 = 2.8 \times 10^7$ and $k_6 = 1.8 \times 10^7 \text{ s}^{-1}$.

Table 1 shows substrate concentration dependence of the transient absorbance decay constant k_3 and of the value of persistent absorbance A_∞ measured at 780 nm for solution **3**.

The values of the end-of-pulse absorbance are independent of adamantane concentration. Conversely, the constant k_3 and the value of the persistent absorbance increase with the increase of adamantane concentration. A plot of the dependence of the rate constant k_3 on adamantane concentration led to the second-order rate constant k_{3RH} of the reactivity of adamantane towards transient X. It was calculated to be $3.3 \times 10^8 \text{ dm}^3 \text{ mol}^{-1}$ (Fig. 5).

Fig. 6 shows the time dependence of the transient absorption measured at 780 nm in three different cases: activated primary C–H bond **2**, tertiary and secondary C–H bonds **3** and secondary C–H bond **6**. The value of the persistent absorbance (A_∞) is proportional to substrate reactivity, which increases in the order: primary < secondary < tertiary.

In the microsecond–millisecond time domain we have studied the decay of the transient absorption persistent at times longer than one microsecond for solutions **3**, **4** and **6** till its complete disappearance. For example, excitation by laser pulse (λ 355 nm) of $1.1 \times 10^{-3} \text{ mol dm}^{-3}$ decatungstate solution in propionitrile **4** produced the transient absorption spectra between 10 and 200 μs (Fig. 7), which were similar in shape to those obtained in the nanosecond time domain (Fig. 4). The absorption spectrum obtained 1 μs after the pulse in the presence of oxygen (Fig. 7) was similar to that of the deaerated sample (Fig. 8). However, the absorbance evolution was different in both cases. In aerated solution, the absorbance decayed to 30% of its initial value after the laser pulse till 0.5 ms without changing in shape (Fig.

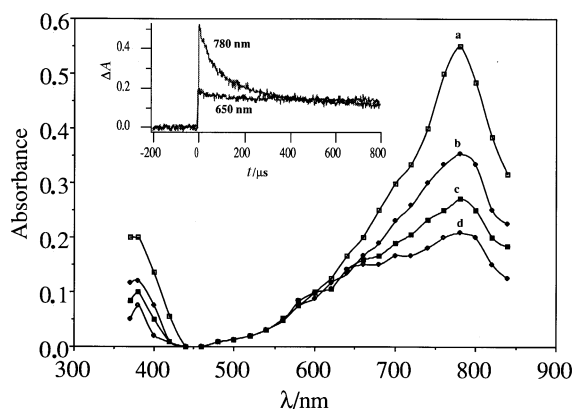


Fig. 7 Transient absorption spectra obtained by nanosecond laser flash photolysis (355 nm) of $1.1 \times 10^{-3} \text{ mol dm}^{-3}$ $\text{Na}_4\text{W}_{10}\text{O}_{32}$ propionitrile solution in the presence of dioxygen: (a) 1, (b) 50, (c) 100 and (d) 200 μs after laser pulse. Insert: decay curves at 650 and 780 nm.

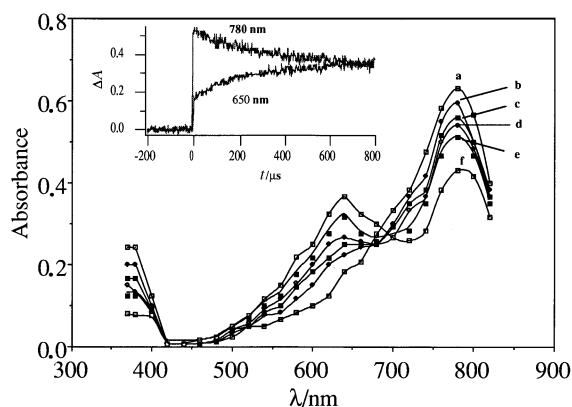
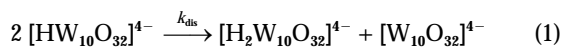


Fig. 8 Transient absorption spectra obtained by nanosecond laser flash photolysis (355 nm) of $1.1 \times 10^{-3} \text{ mol dm}^{-3}$ $\text{Na}_4\text{W}_{10}\text{O}_{32}$ deaerated propionitrile solution: (a) 1, (b) 50, (c) 100, (d) 150, (e) 200 and (f) 700 μs after laser pulse. Insert: decay curves at 650 and 780 nm.

7) and came to its base level after 17 s. After subtraction of the slowly decaying part of the signal, the decay kinetics of the transient obeyed first-order kinetics, with a rate constant $k_{\text{ox}} = 7.8 \times 10^3 \text{ s}^{-1}$. The fitting of this decay with a second-order kinetics gave a poorer standard deviation. The steady-state absorption spectra of solution **4** obtained before and after the photolysis were identical, showing the complete reversibility of the photochemical system.

For the same solution **4**, under N_2 , we observed the disproportionation of the reduced form of decatungstate as described by Yamase *et al.*,¹¹ eqn. (1). The partial decay of the absorbance



at 780 nm (Fig. 8) attributed to $[\text{HW}_{10}\text{O}_{32}]^{4-}$ was correlated with a slow increase in absorption at 650 nm (the two-electron reduced and diprotonated species denoted as $[\text{H}_2\text{W}_{10}\text{O}_{32}]^{4-}$). The absorption decay at 780 nm obeyed second-order kinetics. Using $\epsilon_{780} = 7.0 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ for the decatungstate reduced form⁸ in combination with the optical pathlength of the cell (1 cm), the rate constant for disproportionation was calculated to be $k_{\text{dis}} = 1.0 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

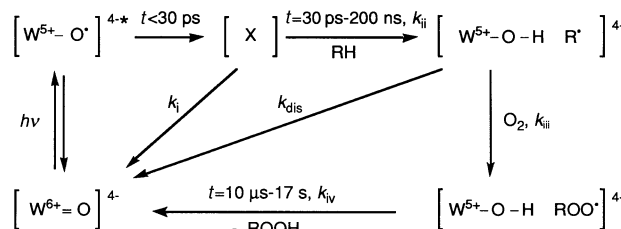
In the systems **3** and **6**, under dioxygen, 90% of the transient absorption value, which was attained by the end of the laser pulse, decayed with first-order kinetics to 3 ms for system **3** and 40 μs for system **6**. The residual absorbance decreased slowly to the base level in *ca.* 3 s in both cases. The rate constants of the transient absorption decay calculated assuming pseudo-

first-order kinetics were found to be $k_{3\text{ox}} = 1.3 \times 10^3$ and $k_{6\text{ox}} = 1.1 \times 10^5 \text{ s}^{-1}$ for systems **3** and **6**, respectively.

Under anaerobic conditions, the transient absorption behaviour observed in systems **3** and **6** was similar to that of system **4**. The rate constants for disproportionation of the reduced form of the decatungstate were calculated to be $k_{3\text{dis}} = 4.8 \times 10^7$ and $k_{6\text{dis}} = 1.8 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for systems **3** and **6**, respectively.

Discussion

The scheme for the photoinduced changes in the decatungstate anion, consistent with the transient absorption data for the catalytic cycle, is shown in Scheme 1.



Scheme 1

During the flash pulse $t < 30 \text{ ps}$ the intervalence $\text{O}(2p) \rightarrow \text{W}(5d)$ ligand-metal charge transfer (LMCT) excited state of decatungstate generates a transient X which persists for 5 ns. The picosecond transient absorption data obtained in aqueous and organic sodium decatungstate solutions (**1–3**) showed that the transient yields were identical and independent of organic scavengers. Furthermore, the transient absorbance (A_0) obtained after the nanosecond laser pulse was independent of the substrate concentration (Table 1). In contrast, the rate constants k_3 and the residual absorption values A_∞ were markedly increased with the increase of adamantane concentration. These observations rule out the suggestion that an electron transfer from a scavenger to the excited state of the decatungstate, leading to the formation of the reduced form of the decatungstate, occurs during the nanosecond laser pulse.^{10,11} The transient absorption spectrum obtained after the nanosecond laser pulse is not the spectrum of the reduced form of the decatungstate. Hill's group¹² has made the same suggestion, superimposing the transient absorption spectrum obtained in the picosecond domain and that of the reduced form of the decatungstate. This transient species exists during the first 100 ns, which allows us to determine the timescale for substrate reaction: it occurs after 10 ns.

In the nanosecond domain, the species X begins to react with the potential substrates. We consider the rate of transient X disappearance as the resulting rate of two parallel reactions: (i) back-to-ground state reaction of X (rate constant k_1 of Scheme 1 and (ii) the reaction with the C-H bond of organic compounds, resulting in the formation of the reduced form of the decatungstate (rate constant k_{ii} of Scheme 1).

Under laser-pulse conditions, the concentrations of all scavenger species are far above that of the transient X. A rate constant, k_{ii} , measured under pseudo-first-order kinetics leads to a rate constant for a second-order kinetics, $k_{\text{RH}} = k_{\text{ii}}/[\text{RH}]$. Using a pseudo-first-order analysis, the bimolecular rate constant of the reaction of adamantane with X could be determined (Fig. 5).

It has been noticed that the absorption spectra of the transient X and that of the reduced form of decatungstate are very similar in their shape because they are likely to have a similar W-orbital electron density.¹² Accordingly, both reactions (i) and (ii) should decrease the transient absorbance of the photocatalytic system but reaction (ii) also results in a simultaneous

absorption growth due to the formation of the reduced form of decatungstate, absorbing the same λ_{\max} 780 nm.

The study of water oxidation and reduction photocatalysed by POM^{9,17-19} has demonstrated that there is no observable photoreaction in the absence of organic scavengers such as a counter-ion or a substrate. So, we consider the rate constant of the absorption transient decay obtained in solution **1** as a back-to-ground state reaction constant k_{ii} ($k_{\text{ii}} = 2.7 \times 10^7 \text{ s}^{-1}$).

The availability of residual absorbance in the spectrum of solution **2** showed the reactivity of acetonitrile towards transient X. The identical behaviour of transient X in systems **2** and **5** demonstrated that tetramethylammonium cation is insensitive to photooxidation. These data are in agreement with those obtained in continuous photolysis studies.¹³ The rate constant of absorbance decay, $k_2 = 1.3 \times 10^7 \text{ s}^{-1}$, corresponds to a sum of a back-to-ground state reaction rate constant, $k_{2\text{i}}$, and a rate constant of reaction X with acetonitrile, $k_{2\text{ii}}$. It should be recalled that the back-to-ground state reaction rate constant measured in aqueous solution, $k_{\text{ii}} = 2.7 \times 10^7 \text{ s}^{-1}$, overrides that obtained in acetonitrile ($k_{\text{ii}} > k_{2\text{i}} + k_{2\text{ii}}$). This may be due to a specific effect of the solvent.

Fig. 6 and Table 1 show that the residual absorption value A_{c} increases with an increase in substrate concentration and with the rate constant of formation of the reduced form of decatungstate (k_{ii}).

The rate constants of absorbance decay k_3 and k_6 measured in solutions **3** and **6** may be denoted as eqns. (2) and (3).

$$k_3 = (k_{2\text{i}} + k_{2\text{ii}} + k_{3\text{ii}}) = (k_2 + k_{3\text{ii}}) = (k_2 + k_{3\text{RH}}[\text{Ad}]) \quad (2)$$

$$k_6 = (k_{2\text{i}} + k_{2\text{ii}} + k_{6\text{ii}}) = (k_2 + k_{6\text{ii}}) = (k_2 + k_{6\text{RH}}[\text{Hex}_4\text{N}^+]) \quad (3)$$

If we consider the rate constant of the absorbance decay, k_2 , to be the sum of rate constants of all interactions of X with acetonitrile, $k_2 = k_{2\text{i}} + k_{2\text{ii}}$, the second-order rate constants for the reactions of adamantane and counter-ion tetrahexylammonium with X were calculated to be $k_{3\text{RH}} = 3.3 \times 10^8$ and $k_{6\text{RH}} = 2.5 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, respectively. This high reactivity of tetrahexylammonium cation can be explained by an association phenomenon between decatungstate anion and the organic cation. The high reactivity of counter-ion has also been observed in steady-state photolysis of adamantane catalysed by the decatungstates.¹³

The different values of the rate constants of transient absorption decay ($k_2 = 1.3 \times 10^7$ and $k_4 = 2.8 \times 10^7 \text{ s}^{-1}$) measured in acetonitrile and propionitrile (solutions **2** and **4**) can only be explained by the different reactivity k_{ii} of X towards solvent. It is not possible to calculate correctly the rate constants $k_{2\text{ii}}$ and $k_{4\text{ii}}$ without knowing ϵ_{780} for the transient X which is probably different from that of the reduced form of decatungstate. But using the values of residual absorption ($A_{2\text{c}}$ and $A_{4\text{c}}$) and the rate constants of transient absorption decay in acetonitrile and propionitrile (k_2 and k_4), it is possible to estimate the pseudo-first-order rate constants ratio for the reactions of transient X with acetonitrile and propionitrile, eqn. (4). This ratio is

$$\frac{k_{2\text{ii}}}{k_{4\text{ii}}} = \frac{A_{4\text{c}} k_4}{A_{2\text{c}} k_2} \quad (4)$$

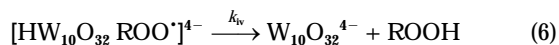
calculated to be 35. Assuming a bimolecular character for the reaction and taking into account the concentration values of acetonitrile and propionitrile, the ratio of second-order rate constants $k_{4\text{RH}}/k_{2\text{RH}}$ is found to be 50.

The reoxidation of the reduced form of decatungstate $\text{HW}_{10}\text{O}_{32}^{4-}$ becomes noticeable only in a microsecond-millisecond time domain. Three possible transformations for the reduced form of the decatungstate could be considered: (a) reoxidation of the reduced form by peroxy radicals (see Scheme 1) (b) its reoxidation by dioxygen¹³ and (c) disproportionation of $[\text{HW}_{10}\text{O}_{32}]^{4-}$ to $[\text{H}_2\text{W}_{10}\text{O}_{32}]^{4-}$ and $\text{W}_{10}\text{O}_{32}^{4-}$. The selective formation of the hydroperoxides and the overall

stoichiometry of alkane oxidation under continuous photolysis conditions allow us to consider the reoxidation of the reduced form of decatungstate by peroxy radicals [pathway (a)] as the principal pathway for regeneration of the catalyst in the presence of dioxygen.¹³ It follows two consecutive reactions (see Scheme 1): (iii) oxidation of the radical pair and formation of the peroxy radical reaction (5) and (iv) reoxidation of the pro-



tonated reduced form of decatungstate by the peroxy radical reaction (6). The alkyl radical R^\cdot reacts with dioxygen at a



near diffusion-controlled rate ($k > 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$),^{20,21} therefore, $k_{\text{iii}} \gg k_{\text{iv}}$. Accordingly, we can consider the absorption decay constants calculated by pseudo-first-order kinetics, $k_{3\text{ox}} = 1.3 \times 10^3$, $k_{4\text{ox}} = 7.8 \times 10^3$ and $k_{6\text{ox}} = 1.1 \times 10^5 \text{ s}^{-1}$, as the rate constants of the reoxidation of the reduced form by peroxy radicals in the solvent cage. This is in agreement with the unimolecular character of this reoxidation. We can explain the anomalously long lifetime of the solvent cage (near 1 ms) by supposing a strong stabilizing interaction between the peroxy radical ROO^\cdot and the protonated reduced form of decatungstate $\text{HW}_{10}\text{O}_{32}^{4-}$. This interaction could occur through an hydrogen bond. The existence of the solvent cage is also in agreement with the results of steady-state photolysis, principally the absence of recombination products of radicals.¹³

A rapid absorbance decay in the microsecond domain corresponds to pathway (a) and a further slow decay of the residual absorbance in the second domain could correspond to reoxidation of the reduced form of decatungstate by oxygen [pathway (b)]. In general, the peroxy radicals can escape from the solvent cage and/or react with it. If this is the case, the reduced form must be reoxidized by pathway (b). The evolution of absorption in systems **3** and **6** has demonstrated that only a small part of the molecules of the reduced form of decatungstate was reoxidized by pathway (b) when the solvent is acetonitrile. Propionitrile is more active as a potential substrate than acetonitrile towards peroxy radicals,²² so, there is competition between pathway (a) and the reaction of peroxy radicals with the solvent cage for system **4**: indeed, the decay kinetics of the reduced form of decatungstate is faster in acetonitrile than in propionitrile.

The rate constant reoxidation values are different for systems **3**, **4** and **6**. Such a difference is difficult to reconcile with the reoxidation of the reduced form of decatungstate by pathway (b) in the microsecond domain. It follows that pathway (c) does not take place, either, because $k_{\text{dis}} \ll k_{\text{ox}}$.

There are six stages in this catalytic cycle. Two of them are of special importance in understanding the mechanism of the alkane photooxidation. The reaction of a rupture of the C–H bond in the RH molecule is characterized by the rate constant for the formation of the reduced form (k_{ii}) and the reoxidation of the reduced form of the catalyst is characterized by the reoxidation rate constant (k_{ox}). A comparison of these values demonstrates that the reoxidation of the reduced form of the catalyst by peroxy radicals is the rate-limiting step of this catalytic cycle. This conclusion is corroborated by the small isotopic effect in the photooxidation of cyclohexane ($k_{\text{H}}/k_{\text{D}} = 1.2$).[‡]

‡ The isotopic effect ($k_{\text{H}}/k_{\text{D}}$) for the cyclohexane oxidation photocatalysed by $\text{Na}_4\text{W}_{10}\text{O}_{32}$ has been determined under competitive kinetic conditions ($0.9 \times 10^{-2} \text{ mol dm}^{-3}$ of both C_6H_{12} and C_6D_{12} in $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ sodium decatungstate acetonitrile solution). Additional reaction conditions are given in ref. 13.

It remains the puzzling question of the nature of transient X. As already noticed by Hill and co-workers,¹² this species is different from the one-electron reduced form of decatungstate but with a very similar absorption spectrum, and also different from the initial LMCT-excited state occurring in a very short picosecond timescale. These authors suggest that X could be a relaxed excited state with substantial charge transfer in it. As the electron density is similar on the W-orbital both in X and in the reduced form of decatungstate, the absorption spectra of both species are similar.

Conclusions

A laser flash photolysis study of the behaviour of decatungstate in the photocatalysed aerobic oxidation of alkanes leads us to conclude that: (a) all the components of the photocatalytic system—substrate, counter-ion and a solvent possessing an oxidizable C–H bond participate in the formation of the reduced form of decatungstate. (b) The reoxidation of the reduced form of decatungstate is mediated by peroxy radicals in the solvent cage. (c) The rate-limiting step of the catalytic cycle is the reoxidation of the reduced form of decatungstate. (d) Additional experiments are still needed to fully characterize the nature of the reactive intermediate X.

Acknowledgements

We gratefully acknowledge the efforts of Jean-François Delouis (LPPSM, Ecole Normale Supérieure de Cachan, France), who helped greatly with the laser experiments. We thank Club EDF Photochimie for financial support.

References

- 1 C. L. Hill and C. M. Prosser-McCartha, in *Photosensitization and Photocatalysis Using Inorganic and Organometallic Compounds*, eds. Kaliasundaram and M. Grätzel, Kluwer, Dordrecht, 1993, p. 307.

- 2 E. Papaconstantinou, *Chem. Soc. Rev.*, 1989, **18**, 1.
- 3 C. L. Hill, M. Kozik, J. Winkler, Y. Hou and C. M. Prosser-McCartha, in *ACS Advances in Chemistry Series No. 238. Photosensitive Metal-Organic Systems. Mechanistic Principles and Applications*, eds. C. Kotal and N. Serpone, ACS, Washington, DC, 1993, ch. 13.
- 4 C. L. Hill and C. M. Prosser-McCartha, *Coord. Chem. Rev.*, 1995, **143**, 407.
- 5 A. Mylonas and E. Papaconstantinou, *J. Photochem. Photobiol. A: Chem.*, 1996, **94**, 77.
- 6 M. T. Pope and A. Muller, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 34.
- 7 F. Chauveau, *Bull. Soc. Chim. Fr.*, 1986, **2**, 199.
- 8 A. Chemseddine, C. Sanchez, J. Livage, J. P. Launay and M. Fourmier, *Inorg. Chem.*, 1984, **23**, 2609.
- 9 G. Folcher, J. Paris and F. Chauveau, *Can. J. Chem.*, 1985, **63**, 2703.
- 10 T. Yamase and T. Usami, *J. Chem. Soc., Dalton Trans.*, 1988, 183.
- 11 T. Yamase, N. Takabayashi and M. Kaji, *J. Chem. Soc., Dalton Trans.*, 1984, 793.
- 12 D. C. Duncan, T. L. Netzel and C. L. Hill, *Inorg. Chem.*, 1995, **34**, 4640.
- 13 L. P. Ermolenko and C. Giannotti, *J. Chem. Soc., Perkin Trans. 2*, 1996, 1205.
- 14 R. F. Renneke, M. Pasquali and C. L. Hill, *J. Am. Chem. Soc.*, 1990, **112**, 6585.
- 15 M. Sumitani and K. Yoshihara, *Bull. Soc. Chim., Jpn.*, 1982, **55**, 85.
- 16 J. A. Delaire, M. Castella, J. Faure, P. Vanderauwera and F. C. De Schryver, *Nouv. J. Chim.*, 1984, **8**, 231.
- 17 T. Yamase, *Inorg. Chem. Acta*, 1983, **76**, 425.
- 18 R. Akid and J. R. Darvent, *J. Chem. Soc., Dalton Trans.*, 1985, 395.
- 19 T. Yamase and T. Kurozumi, *J. Chem. Soc., Dalton Trans.*, 1983, 2205.
- 20 B. Maillard, K. U. Ingold and J. C. Scaiano, *J. Am. Chem. Soc.*, 1983, **105**, 5095.
- 21 T. M. Lenhardt, C. E. McDade and K. D. Bayes, *J. Chem. Phys.*, 1980, **72**, 304.
- 22 D. F. McMillen and D. M. Golden, *Annu. Rev. Phys. Chem.*, 1982, **33**, 483.

Paper 6/04691F
Received 4th July 1996
Accepted 24th September 1996