Decatungstate Photocatalyzed Electron-Transfer Reactions of Alkenes. Interception of the Geminate Radical Ion Pair by Oxygen

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A combination of steady-state and time-resolved techniques has been used to investigate the mechanism of the decatungstate ($W_{10}O_{32}^{4-}$) photocatalyzed oxygenation of cyclohexene, and of a series of hexene isomers, as well as of their saturated counterparts, in acetonitrile. It is demonstrated that (i) alkenes react by both charge-transfer and hydrogen-atom-transfer mechanisms, the former being dominant in each case; (ii) alkanes exclusively react by hydrogen-atom abstraction; (iii) a previously unknown reaction pathway, resulting from interception of the geminate radical ion pair by molecular oxygen, and leading to quantitative formation of hydroperoxides without decatungstate reduction, can significantly contribute to the overall reaction; (iv) no back-electron transfer occurs prior to separation of the geminate pair or its interception by O_2; (v) the catalytic activity is strongly reduced in the presence of olefins, due to the formation of very long-lived complexes involving both one- and two-electron-reduced decatungstate; and (vi) the decatungstate anion undergoes strong precomplexation with the reactive solvent acetonitrile.

Introduction

Polyoxometalates, early-transition-metal-oxygen-anion-clusters, are a large and rapidly growing class of inorganic compounds with significant applications in a range of areas.[1] One of the most promising examples is the decatungstate anion $W_{10}O_{32}^{4-}$ which appears to be particularly interesting with regard to the light-induced transformation of organic materials.[2−16] It has been suggested 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 nonemissive transient,[3] which has been referred to as wO.[4] This latter species is a relaxed excited state, which bears a substantial charge, and exhibits oxyradical-like character due to the presence of an electron-deficient oxygen center. Also, it has been suggested that wO might have a distorted geometry with respect to $W_{10}O_{32}^{4-}$.[6] Its lifetime τ_{wO} was reported to vary from about 40 to 70 ns, depending on the nature of both the solvent and the counterion.[4−6] Transient absorbance measurements at 780 nm have shown that wO possesses an extraordinary reactivity toward virtually any organic substrate.[3−10] The decay profile at this wavelength follows second-order kinetics, and fails to reform the baseline after wO decay in many cases. This behavior demonstrates the existence of a third intermediate, which could be 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 of the transient absorbance spectrum with that of RF obtained by electrochemical reduction,[3a] or by pulse radiolysis.[4] This reduced species can be oxidized back to $W_{10}O_{32}^{4-}$ in the presence of oxygen with parallel formation of peroxy species.[4,5,7,9] Previous studies with alcohols and alkanes suggested that quenching of wO occurs by hydrogen-atom abstraction (HA) to give RF and an organic radical.[3a,4−12] For example, it has been shown that the reactivity of different alcohols, linear and branched, vary over 2 orders of magnitude for alcohols expected to have similar oxidation potential but containing hydrogen atoms of different bond-dissociation energy.[4] However, with easily oxidizable substrates (such as amines and aromatic hydrocarbons), direct electron transfer (ET) 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.[6,10] In any case, both mechanisms give rise to the same one-electron-reduced species, and to the corresponding substrate-derived radical. Thus, many aspects of the photocatalytic mechanism seem to be established from investigations carried out during the past few years.[3−10] However, several points remain unclear, with regard to both the primary photoevents and the cascade of subsequent chemical processes in the presence of oxygen.

The first determination of the quantum yield of formation of wO, Φ_{wO}, has been performed by continuous photolysis studies, using the extrapolation of substrate (XH) concentration dependent oxygen consumption yields $\Phi_{OX}{}^{XH}$ to their value at infinite XH concentration $\Phi_{OX}{}^{\infty}$.[4] Since the initial rates of O_2 consumption and hydroperoxide formation were found to be identical, it was concluded that $\Phi_{OX}{}^{\infty} = \Phi_{wO}$, and in the case of 2-propanol, a value of $\Phi_{wO} = 0.534$ was reported.[4] Later, Duncan et al.[6] determined extrapolated decatungstate reduction yields $\Phi_{RF}{}^{\infty}$, by laser flash photolysis experiments with cycloalkanes and 2-butanol in N_2-saturated CH_3CN, and arrived at values ranging from 0.44 to 0.50. In a simplified kinetic scheme, these values also represent the quantum yield of wO formation, if the separation of the geminate pair is quantitative. However, in a later study, $\Phi_{RF}{}^{\infty}$ values were found to be significantly lower in aerated acetonitrile for a range of substrates, including several alcohols.[10] With the exception of a few aliphatic halocarbons, all values were found to be within 0.075 and 0.35. Differences were also found between the rate

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constants k_{XH} for quenching of wO by the substrate. For example, $k_{XH} = 1.9 \times 10^8$ and 5.2×10^9 M^{-1} s^{-1} were reported for 2-butanol and ethanol in this study, which is significantly larger than other determinations (e.g., 9.9×10^7 M^{-1} s^{-1} for 2-butanol,[6] and 1.2×10^8 and 6.2×10^7 M^{-1} s^{-1} for 2-butanol and for ethanol (unpublished data)). Hence, there seems to be a certain inconsistency with respect to both quenching rate constants and quantum yields. Given the magnitude of these differences, which are far beyond experimental uncertainties, it seems probable that differences in experimental conditions and/or employed techniques have played a non negligible role. For example, it may be suggested that several of the observed discrepancies, especially those concerning $\Phi_{OX}{}^{\infty}$ and $\Phi_{RF}{}^{\infty}$, could be related to the relative efficiencies of thermal back reactions within solvent cages, and from freely diffusing intermediates.

To obtain further information on the primary photoevents, and to evaluate the uncertainties associated with the involved kinetic parameters, we have now undertaken a detailed study of the decatungstate photocatalyzed oxygenation of a series of hydrocarbons by steady-state (O_2 consumption) and time-resolved (laser flash photolysis) techniques. This approach provides quantitative data on substrate oxygenation and decatungstate reduction yields, as well as on the kinetics of wO decay, RF formation, O_2 uptake, and product formation. The investigation of the oxygenation of a series of alkenes and of their saturated counterparts allows us to compare the nature of products formed in both cases, to evaluate the contribution of ET and HA mechanisms to the overall process in each case, and to study the importance of back-electron-transfer or hydrogen-atom-transfer processes. Also, we report here the unexpected formation of very long-lived complexes of the decatungstate cluster with alkenes, which inhibit the photocatalytic activity of $W_{10}O_{32}{}^{4-}$ and have not been observed with any other type of substrate. Finally, we have also undertaken an electrospray mass spectrometry (ESMS) analysis of the decatungstate anion in acetonitrile, to determine the strength of its interactions with organic molecules, and to explore the role of preassociation in the previously reported unusual reactivity of wO with this solvent especially in the presence of oxygen.[4,7]

Experimental Section

Sodium and potassium decatungstate were synthesized and purified by literature procedures.[3a,17] All other chemicals were purchased at 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 5×10^{-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 $\Phi_{RF} = (OD_f/OD_i)(\Phi_{wO}\epsilon_{wO}/\epsilon_{RF})$, 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 $\epsilon_{RF} = 7000$ M^{-1} cm^{-1} of $W_{10}O_{32}{}^{5-}$ at 780 nm is known from the electrochemical reduction of $W_{10}O_{32}{}^{4-}$ [18] and the product $\Phi_{wO}\epsilon_{wO}$ of the quantum yield Φ_{wO} and extinction coefficient ϵ_{wO} of the wO transient was obtained from external actinometry experiments, using the triplet state of benzophenone in acetonitrile ($\epsilon_{BP} = 6500 \pm 400$ M^{-1} cm^{-1}).[19] Experiments in air-saturated and N_2-saturated solutions lead to significantly different values for this product. This is shown in Figure 1, which yields the values of $\Phi_{wO}\epsilon_{wO} = 4170 \pm 200$ M^{-1} cm^{-1} in air-saturated CH_3CN, and $\Phi_{wO}{}^{N2}\epsilon_{wO} = 4705 \pm 200$ M^{-1} cm^{-1} in N_2-saturated CH_3CN, which are somewhat larger than previous determinations.[6,10] Using $\Phi_{wO} = 0.567$ (mean value from 21 independent O_2 consumption determinations), these data yield $\epsilon_{wO} = 7012$ M^{-1} cm^{-1}, which is identical within experimental error to the extinction coefficient of $W_{10}O_{32}{}^{5-}$ at this wavelength, and is in good agreement with $\epsilon_{wO} = 6880$ M^{-1} cm^{-1} previously obtained by Duncan et al.[6] The value of $\epsilon_{wO} = 7012$ M^{-1} cm^{-1} leads to $\Phi_{wO}{}^{N2} = 0.67$ for the quantum yield of wO formation in N_2-saturated solution. However, the accuracy of the derived quantum yields is limited by the accuracy of primary actinometry reference data. Here, the most important source of uncertainty are ϵ_{BP} and ϵ_{RF}, for which values ranging from 7000 to 11000 M^{-1} cm^{-1} have been reported.[4,13,18,20,21]

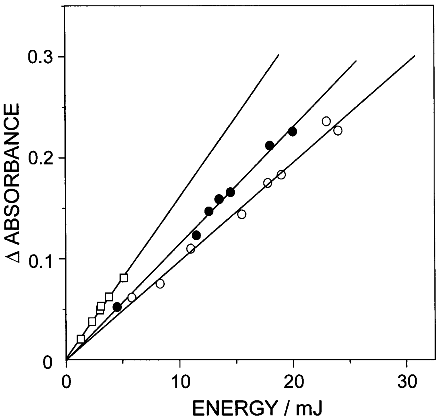


Figure 1. Pulse energy dependence of transient absorbance change extrapolated to laser pulse ignition time, for optically matched solutions of benzophenone (□) and sodium decatungstate (○ and ●), in air-saturated (○), and N_2-saturated (□ and ●) acetonitrile.

The photostationary state method consists of measuring the rate r_{OX} of substrate photooxygenation by following oxygen consumption as a function of irradiation time. The corresponding quantum yield Φ_{OX} is defined according to Φ_{OX} = (number of moles of O_2 consumed)/(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. O_2 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 O_2-saturated acetonitrile with phenalenone ($\Phi_{OX} = \Phi_{\Delta} = 0.98$) as sensitizer;[22]

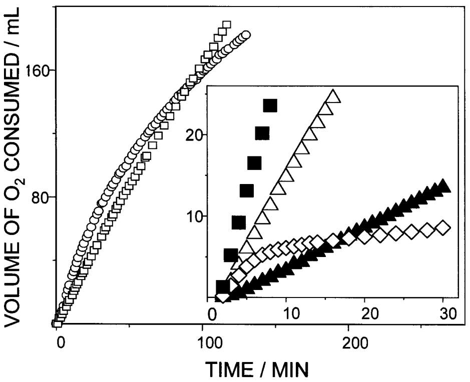


Figure 2. Time dependence of O_2 consumption measured for illumination of oxygen-saturated acetonitrile solutions of sodium decatungstate (5.5×10^{-4} M) in the presence of 0.8 M 2,3-dimethylbutene (○) and 0.8 M 2,3-dimethylbutane (□). Inset: Time dependence of O_2 consumption measured for illumination of oxygen-saturated acetonitrile solutions of sodium decatungstate (5.5×10^{-4} M) in the absence (▲) and presence of 0.1 M cyclohexene (◇), 0.1 M 2-methyl-2-pentene (Δ), and 0.1 M 2,3-dimethylbutene (■).

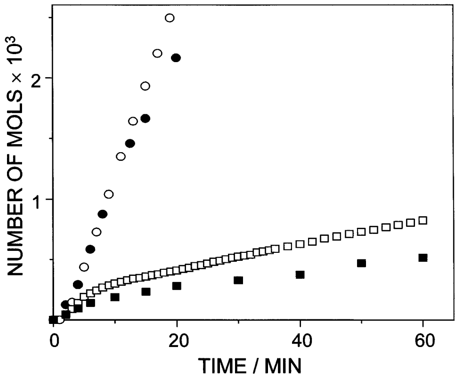


Figure 3. Correspondence between the number of moles of oxygen consumed (□ and ○) and of hydroperoxide formed (■ and ●) during continuous illumination of sodium decatungstate (5.5×10^{-4} M) in oxygen-saturated acetonitrile in the presence of 0.8 M cyclohexane (○ and ●) and 0.8 M cyclohexene (■ and □).

two filters were used successively (Pyrex filter, cutoff 296 nm, and 12% $NaNO_2$ in water, cutoff 370 nm) allowing the determination of the intensities of the bands of the lamp which are actually absorbed by decatungstate (296−365 nm). The concentration of decatungstate was sufficient to absorb all incident light. The intensity of absorbed light was 6.97×10^{-6} einstein s^{-1}. In contrast to transient absorbance-based determinations of quantum yields, the experimental uncertainties associated with O_2 consumption measurements are relatively small. All experiments described here follow the general procedure previously established using singlet oxygen-mediated oxygenations, for which the experimental error was found to be smaller than 3% for all r_{OX} measurements, and also for the $O_2(^1\Delta_g)$ yield of the universal reference sensitizer phenalenone in a wide range of solvents.[22−25]

Electrospray mass spectroscopy (ESMS) was performed at the Laboratoire de Spectrométrie de Masse Bio-Organique, Université Louis Pasteur, Strasbourg, France, on a Quattro triple-quadrupole mass spectrometer with a mass to charge (m/z) range of 4000 (Micromass, Manchester, UK) using a standard electrospray ion source. Resolution was usually set about 1000 at m/z 1000. Solutions (10^{-4}−10^{-5} M) were infused in the ion source in a continuous flow at about 5 L/min with a syringe pump. The source temperature was 70 °C. The accelerating cone voltage V_c was varied between 10 and 50 V.

Absorption spectra were recorded in quartz cells of 1 cm path length, using a Kontron Uvikon 930 spectrophotometer. Peroxide concentrations were determined by iodometric titration.[26]

Results

Steady-State Photolysis. Previous studies have shown that oxygen consumption measurements represent a very useful tool to investigate the reactivity of wO toward organic substrates.[4,7,9] This method allowed us to establish the rate constants for its reactions with several alcohols and alkanes, which were shown to yield quantitatively the respective hydroperoxides. It was demonstrated that even acetonitrile undergoes efficient photooxygenation in the presence of decatungstate. Additionally, the evolution of the hydroperoxides toward monooxygenated compounds could be simultaneously observed in the experimental conditions of their formation. We have now employed the same techniques for a comparative study of a set of olefins and their saturated counterparts. Figure 2 shows the profiles of O_2 consumption upon irradiation of oxygen-saturated acetonitrile solutions of sodium decatungstate, containing 0.8 M 2,3-dimethylbutene and 2,3-dimethylbutane, respectively. The oxygenation of the alkene is initially significantly faster than that of its saturated equivalent. This is in agreement with the involvement of a charge-transfer mechanism in this reaction. Surprisingly, after ca. 30 min of irradiation, the photooxygenation of the alkene rapidly slows down, and it becomes even slower than that of the alkane after 90 min. A similar curvature of the O_2 consumption profile is observed with any of the investigated alkenes, and is most striking in the case of cyclohexene, where the rate of O_2 consumption becomes even slower than that of neat acetonitrile, after 15 min of irradiation of a solution containing 0.1 M of this substrate (Figure 2). As previously discussed in the case of alkanes and alcohols, these oxygenation reactions lead to an initially quantitative formation of hydroperoxides, which are being decomposed under experimental conditions. Figure 3 demonstrates that the rate of hydroperoxide decomposition depends on the nature of the substrate, and is larger for the unsaturated compound than for the saturated one.

The astounding deceleration of the alkene photooxygenation process suggests that regeneration of the active form of the catalyst is being inhibited by a specific interaction with the olefins, such as the formation of a long-lived complex between at least one of the reduced forms of decatungstate, and the alkenes and/or their oxygenation products. The one-electron-reduced form, RF, and the two-electron-reduced form, RF^- (i.e., $H_xW_{10}O_{32}^{(6-x)-}$),[21] can be easily identified by their visible spectra, which exhibit specific peaks at 780 and 635 nm, respectively. Both one-electron-reduced species ($W_{10}O_{32}^{5-}$ and $HW_{10}O_{32}^{4-}$) exhibit identical absorption spectra at 780 nm, but differ by an UV absorption band which appears at 370 nm for $W_{10}O_{32}^{5-}$ and at 360 nm for $HW_{10}O_{32}^{4-}$.[8] Figure 4 shows the evolution with irradiation time of the absorption spectrum of an O_2-saturated acetonitrile solution of sodium decatungstate containing 0.1 M 2,3-dimethylbutene. Both RF and RF^- accumulate significantly in the medium, while the concentration of $W_{10}O_{32}^{4-}$ (absorption peak at 324 nm) diminishes. This is in accordance with the formation of long-lived complexes involving both reduced forms of decatungstate, where the spectra of the complexes and those of isolated RF and RF^- do not differ significantly. The absorption peak appearing at 360 nm is ascribed to the formation of the at least partially protonated reduced form $H_xW_{10}O_{32}^{(5-x)-}$. Figure 4 also shows that the decay of both reduced forms is indeed very slow under these

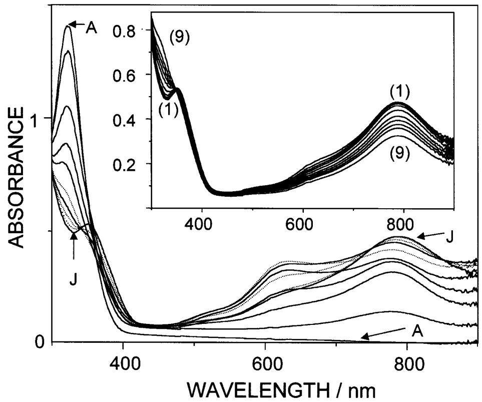


Figure 4. Absorption spectra of an oxygen-saturated acetonitrile solution of 0.1 M 2,3-dimethylbutene, recorded after 0 (A), 10, 20, 30, 40, 50, 60, 70, 90, and 110 (J) minutes of continuous illumination in the presence of 5.5×10^{-4} M sodium decatungstate. Inset: Evolution of the absorption spectrum of the same solution after irradiation end (Spectra recorded after 2 (1), 4, 8, 16, 30, 40, 50, 60, and 80 (9) minutes).

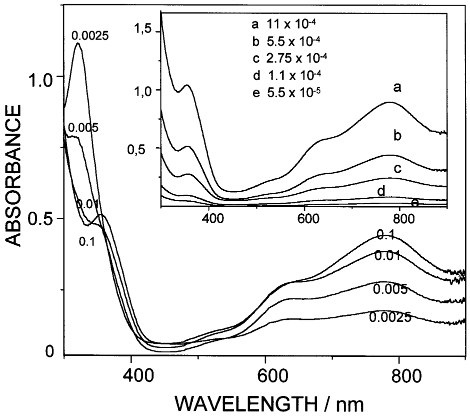


Figure 5. Dependence of the absorption spectrum of an oxygenated acetonitrile solution of sodium decatungstate and cyclohexene after 15 min of irradiation, on the concentration of the catalyst and the substrate (Spectra recorded with [decatungstate] = 5.5×10^{-4} M, for [cyclohexene] = 0.0025, 0.005, 0.01, and 0.1 M, respectively. Inset: Spectra recorded with [cyclohexene] = 0.1 M, for [decatungstate] = 0.55×10^{-4}, 1.1×10^{-4}, 2.75×10^{-4}, 5.5×10^{-4}, and 11×10^{-4} M, respectively).

conditions, and experiments in nitrogen-saturated solutions (not shown) reveal that reoxidation becomes even markedly slower in the absence of O_2. This is in support of the previously suggested role of molecular oxygen in the reoxidation of the catalyst. Analogous behavior is observed during the oxygenation of cyclohexene under the same conditions. In this case, even air-saturated solutions keep their blue coloration (which is due to the presence of reduced decatungstate) for several days after irradiation end. Furthermore, it is shown that the formation of both reduced forms depends strongly on the concentration of both $W_{10}O_{32}^{4-}$ and the substrate (Figure 5). This establishes clearly the involvement of both decatungstate and the alkenes in the formation of complexes. The fact that such long-lived species are not observed with any other type of substrate, including the saturated equivalents of the alkenes, shows that complexation is due to a very specific interaction of the metal cluster with the alkene double bond.

Using the extinction coefficients of 13500 M^{-1} cm^{-1} for $W_{10}O_{32}^{4-}$ at 324 nm, and 4850, 3300, and 7000 M^{-1} cm^{-1} for $W_{10}O_{32}^{5-}$ at 324, 630, and 780 nm, respectively, and 1780, 14000, and 5390 M^{-1} cm^{-1} for $W_{10}O_{32}^{6-}$ at 324, 630, and 780 nm, respectively,[18] we can calculate the molar concentrations $[W_{10}O_{32}^{4-}]$, $[W_{10}O_{32}^{5-}]$, and $[W_{10}O_{32}^{6-}]$ in a given system, and determine the evolution of the fractions $f = [W_{10}O_{32}^{4-}]/[W_{10}O_{32}^{4-}]_T$, $f' = [W_{10}O_{32}^{5-}]/[W_{10}O_{32}^{4-}]_T$, and $f'' = [W_{10}O_{32}^{6-}]/[W_{10}O_{32}^{4-}]_T$, of the individual forms of decatungstate to the total concentration of originally introduced decatungstate, as a function of irradiation time. Figure 6 shows the evolution of f, f', and f'' for illumination of 5.5×10^{-4} M decatungstate in the presence of 0.1 M cyclohexene, as well as of the corresponding O_2 consumption profile. This representation clearly shows that the deceleration of substrate oxygenation correlates with the formation of very long-lived complexes that mainly involve the one-electron-reduced form of decatungstate. Also, the figure provides a good illustration of the efficiency of complex formation in the case of cyclohexene, where more than 80% of the initial amount of catalyst (5.5×10^{-4} M) is shown to be inactivated after only 15 min of irradiation in the presence of 0.1 M of this substrate.

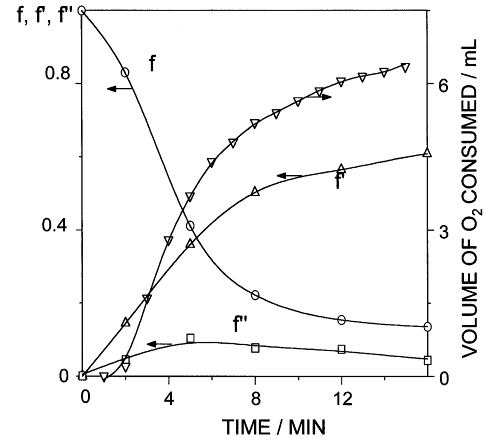


Figure 6. Time dependence of O_2 consumption and of the ratios f, f', and f'' of decatungstate and its one- and two-electron reduced forms to total $Na_4W_{10}O_{32}$, measured for illumination of oxygen-saturated acetonitrile solutions of sodium decatungstate ($[W_{10}O_{32}^{4-}]_T = 5.5 \times 10^{-4}$ M), in the presence of 0.1 M cyclohexene.

From the linear portion of the O_2 consumption profiles, one can obtain relative rates of O_2 consumption, which are converted into quantum yields Φ_{OX}^{XH} of O_2 consumption by comparison with the phenalenone-sensitized oxygenation of furfuryl alcohol (quantum yield 0.98).[22] In the case of the decatungstate-sensitized oxygenation of alkenes, this determination is only possible at low substrate concentrations, because the linear portion of the O_2 consumption persists for a few minutes of irradiation only, and is rapidly shortened with increasing substrate concentration. For example, in the case of cyclohexene, the highest utilizable concentration was 0.0025 M, where a linear evolution is observed during 8 min of irradiation (see Figure 7, compare with Figure 6, and also Figure 2).

As previously found with propan-2-ol,[4] Φ_{OX}^{XH} augments progressively with increasing substrate concentration (Figure 8). These data can be used to derive the rate constant k_{XH} for reaction between wO and the substrate, by considering the process in terms of a generalized Stern–Volmer treatment,[4,7,9]

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

where $K = k_{XH}\tau_{wO}$ is the Stern–Volmer constant. The quantum yields $\Phi_{OX} = 0.048 \pm 0.002$ of O_2 consumption by the solvent, and $\Phi_{wO} = 0.56 \pm 0.02$ of formation of wO, which are obtained from nonlinear least-squares analysis of the experimental data, are found to be equal in the presence of all investigated substrates, including alkenes, alkanes, and the previously

TABLE 1.

		transient absorbance at 780 nm					oxygen consumption		
		wO decay		$W_{10}O_{32}^{5-}$ formation					
substrate	IE/eV	$k_{XH}/10^7$ M^{-1} s^{-1}	K/M^{-1}	Φ_{RF}^0	Φ_{RF}^∞	K/M^{-1}	Φ_{OX}	Φ_{wO}	K/M^{-1}
alkenes									
1-hexene	9.44[a]	4.15	2.6	0.023	0.11	2.3			
trans-3-hexene	8.97[a]	5.9	3.7	0.023	0.25	3.6			
2-methyl-2-pentene	8.58[a]	10.1	6.9	0.022	0.23	6.1	0.048	0.55	6.8
2,3-dimethylbutene	8.16[a]	32.4	19.8	0.023	0.40	19.5	0.049	0.58	20.4
cyclohexene	8.95[a]	11.9	8.3	0.026	0.26	8.1	0.048	0.57	8.2
alkanes									
n-hexane	10.29[b]	0.79	0.55	0.025	0.38	0.74	0.044	0.57	0.54
2-methylpentane	10.04[b]	0.84	0.55	0.024	0.28	0.87			
2,3-dimethylbutane	10.04[b]	0.70	0.48				0.049	0.54	0.56
cyclohexane	9.88[a]	3.7	2.4	0.020	0.50	2.66	0.048	0.56	2.7

[a] Reference 34. [b] Reference 35.

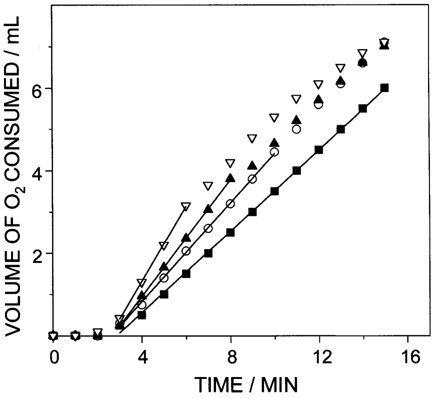


Figure 7. Time dependence of O_2 consumption measured for illumination of oxygen-saturated acetonitrile solutions of sodium decatungstate (5.5×10^{-4} M) in the absence (■) and presence of cyclohexene at 0.0025 M (○), 0.005 M (□), and 0.01 M (▽).

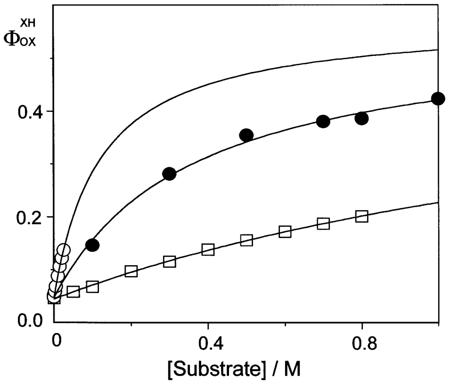


Figure 8. Dependence of the quantum yields Φ_{OX}^{XH}, of O_2 consumption on substrate concentration measured for illumination of oxygen-saturated acetonitrile solutions of sodium decatungstate (5.5×10^{-4} M), in the presence of cyclohexane (●), cyclohexene (○), and hexane (□). Solid lines are drawn in accordance with eq 1. For fit parameters, see Table 1.

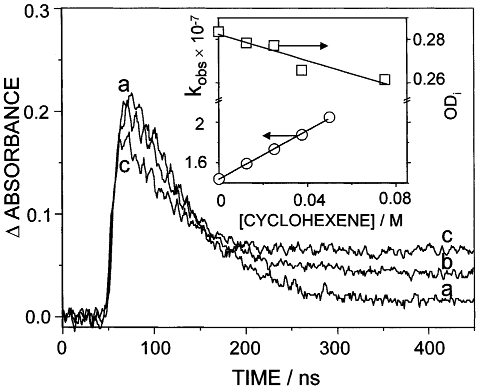


Figure 9. Time-profiles recorded at 780 nm following 355 nm excitation of air-saturated acetonitrile solutions of sodium decatungstate (5.5×10^{-4} M), in the presence of 0 M (a), 0.025 M (b), and 0.2 M (c) cyclohexene. Inset: Dependence of the corresponding first-order rate constants and end of pulse absorbances (OD_i) on the cyclohexene concentration.

investigated aromatic hydrocarbons and alcohols. The fact that these constants are very accurately reproduced even in the case of cyclohexene, suggests that despite the extrapolation over a wide concentration range, the cyclohexene oxygenation data of Figure 8 provide meaningful information on this process. This is further supported by the equivalence of the kinetic data from steady-state and time-resolved experiments (see below). Table 1 lists the fit parameters describing the O_2 consumption data for several alkenes and alkanes. It is interesting to note that K is significantly larger for the alkenes than for their saturated equivalents. This means that the reaction is enhanced by the interaction with the alkene double bond, which would be in agreement with an electron-transfer mechanism.

Laser Flash Photolysis. Additional unexpected features of the alkene photooxygenation mechanism are revealed by a time-resolved study of the same compounds. It is known from previous work that the initially formed charge-transfer excited state of decatungstate decays in a few tens of picoseconds to the longer-lived intermediate designated as wO. The reactivity of this species toward organic substrates can be observed at nanosecond time scale by transient absorbance measurements: Unlike $W_{10}O_{32}^{4-}$, wO absorbs strongly at 780 nm, and so do its longer-lived reduction products. This is the reason for the absorbance remaining after the end of wO disappearance (see Figure 9), which can be used to calculate the quantum yields Φ_{RF}^{XH} of formation of RF. 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,[4,7,9]

$$\Phi_{RF}^{XH} = (\Phi_{RF}^{0} + \Phi_{RF}^{\infty} K[XH])/(1 + K[XH]) \qquad (2)$$

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. The present experiments yield $\Phi_{RF}^0 = 0.023 \pm 0.002$ for the reaction of wO with acetonitrile. The Stern−Volmer constant $K = k_{XH}\tau_{wO}$ is additionally accessible from the first-order decay

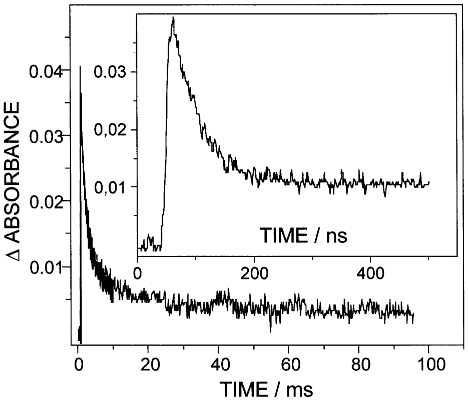


Figure 10. Nanosecond and millisecond decay profiles of the 780 nm absorbance, recorded following 355 nm excitation of air-saturated acetonitrile solutions of sodium decatungstate (5.5×10^{-4} M), in the presence of 0.05 M cyclohexene.

profiles at 780 nm, where k_{XH} and τ_{wO}^{-1} are the slope and the intercept of the respective Stern−Volmer plot. Our measurements yield a mean value of $\tau_{wO}^{-1} = (1.5 \pm 0.1) \times 10^7\ s^{-1}$ in air-saturated CH_3CN. All other results are listed in Table 1, together with the steady-state data. It is most remarkable that a good agreement is found between the values obtained from O_2 consumption, RF formation and wO decay. This indicates that all three approaches provide reliable data with no significant systematic errors, and also gives a good overview of the experimental uncertainties associated with the individual measurements.

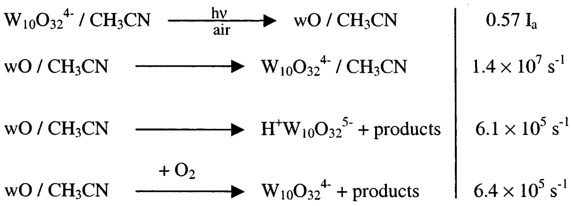
A thorough analysis of transient absorption spectra suggests that some additional information may be contained in the 780 nm profiles. Figure 9 shows typical spectra for the transient absorbance of wO in the presence of cyclohexene.

Rather surprisingly, we observe a regular decrease of the end of pulse absorbance with increasing substrate concentration. This decrease is reproduced with all the alkenes studied here, but is not observed with any other type of substrate (including the respective alkanes). If this observation is significant, it may be ascribed to the formation of any complex between the substrate and either a ground state or a CT excited state of $W_{10}O_{32}.^{4-}$ However, we failed to observe any changes in the absorption spectrum of $W_{10}O_{32}^{4-}$ upon addition of olefins. Since a constant value has been obtained for the quantum yield Φ_{wO} of formation of the reactive species from O_2 consumption measurements for all substrates, this suggests that wO is scavenged by the substrate during the laser pulse.

We have discussed above the formation of long-lived complexes involving both one and two electron reduced decatungstate, under steady-state conditions. The observation of the transient absorbance at longer time scales confirms that the interaction of wO with olefins leads to the formation of long-lived species that absorbs strongly at 780 nm (see Figure 10). Previous studies have shown that only RF is directly formed in this reaction, whereas RF^- is a disproportionation product of RF. Thus, the very slow absorbance decay shown here corresponds to both reoxidation of RF to $W_{10}O_{32}^{4-}$ and disproportionation reactions. This also demonstrates that the observed decatungstate reduction yields Φ_{RF}^{XH} will strongly depend on the time after which OD_f is recorded.

Electrospray Mass Spectroscopy. It was also hoped to gain further insight into the mechanism of the unusual reaction of wO with the solvent acetonitrile by an ESMS study of the decatungstate anion in this solvent. Lau et al.[27,28] have previously shown that this technique represents a powerful method for characterization of several ion metal species, including polyoxoanions. We present here ESMS results for dilute CH_3CN solutions of potassium decatungstate. Figure 11 shows the corresponding spectra for a variation of V_c from 10 to 50 V, and a detailed assignment for all species is given in Table 2.

SCHEME 1



Interestingly, at low cone voltage (i.e., $V_c = 10$ V), only solvated ions are detected, the most important being $W_{10}O_{32}^{4-}$ associated with 6 to 8 CH_3CN molecules, and $KW_{10}O_{32}^{3-}$ associated with 2−5 solvent molecules. Increase of voltage results in separation of ion and solvent molecules, and at $V_c = 20$ V, the dominant species is clearly the nonsolvated $KW_{10}O_{32}^{3-}$, although solvated ions (up to 4 CH_3CN molecules) are still significantly observed. At $V_c = 30$ V, the most abundant peaks correspond to $KW_{10}O_{32}^{3-}$ and $W_{10}O_{32},^{4-}$ and only two solvated species, namely $W_{10}O_{32}^{4-}\cdot CH_3CN$ and $W_{10}O_{32}^{4-}\cdot 2CH_3CN$, are present. Total separation of ions and solvent (i.e., no solvated ions detected) is only achieved at $V_c = 50$ V. However, at this voltage, even the decatungstate cluster undergoes significant fragmentation, as demonstrated by the presence of important peaks at $m/z = 703.51$, 819.43, and 935.35, which can be clearly attributed to $W_6O_{19}^{2-}$, $W_7O_{22}^{2-}$, and $W_8O_{25}^{2-}$, respectively. One more significant peak ($V_c = 50$ V, $m/z = 981.57$, and 12% BP) most probably also corresponds to a fragmented ion, but could not be unequivocally attributed due to the uncertainty of its charge. Thus, the present results provide clear evidence for very strong solvation (preassociation) interactions between the decatungstate cluster and the solvent acetonitrile. It is also remarkable that two protonated species, $KHW_{10}O_{32}^{2-}$ and $HW_{10}O_{32}^{3-}$, can be clearly identified at any cone voltage investigated here. This evidences the replacement of potassium counterions by solvent protons, thus suggesting that formation of the protonated one-electron-reduced photoproduct may originate from a protonated ground-state precursor complex.

Discussion

The reactivity of wO toward several types of organic substrates has been investigated by three methods, independently intervening at different stages of the reaction, namely the formation and disappearance of wO, the formation of RF, the interception of primary radicals by O_2, and the formation of reaction products. The data from all sources clearly confirm the-most remarkable-reaction of wO with the solvent acetonitrile, which is most probably favored by strong solvation interactions, as shown here by ESMS. We have shown above that the quantum yield of wO formation is significantly larger in N_2-saturated solutions than in air-saturated ones. Thus, it is suggested that O_2 intercepts solvated $W_{10}O_{32}^{4-*}$ and/or wO species during the laser pulse. Similarly, we have previously noted that the presence of small amounts of O_2 leads to a decrease in RF yield, and also shortens its lifetime.[4] Since additionally, the present results demonstrate clearly that $\Phi_{RF}^0 < \Phi_{OX}$, we conclude that interception by O_2 of solvated intermediate species results in a pathway leading to oxygenation of CH_3CN without formation of RF. The reaction of wO with acetonitrile can thus be described by Scheme 1, where the values

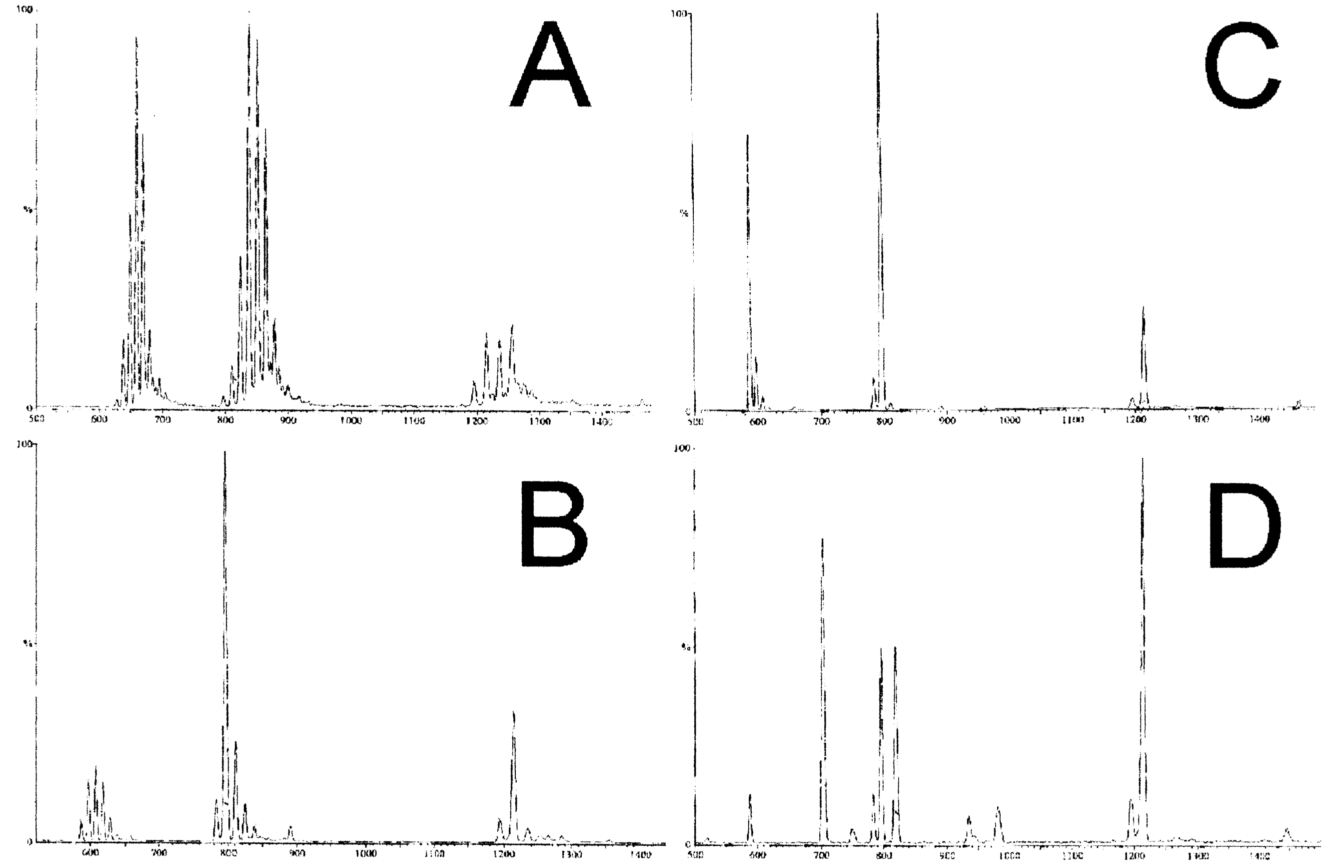


Figure 11. Electrospray mass spectra of potassium decatungstate in CH_3CN. Cone voltage set at 10 V (A), 20 V (B), 30 V (C), and 50 V (D).

TABLE 2

		m/*z* experimental (% base peak)			
	m/*z* theoretical	$V_c = 10$ V	$V_c = 20$ V	$V_c = 30$ V	$V_c = 50$ V
solvated ions					
$[K_2W_{10}O_{32}]^{2-}\cdot 2CH_3CN$	1255.38	1255.73(25)			
$[K_2W_{10}O_{32}]^{2-}\cdot CH_3CN$	1234.85	1234.92(22)	1235.10(4)		
$[KW_{10}O_{32}]^{3-}\cdot 6CH_3CN$	878.61	878.49(26)			
$[KW_{10}O_{32}]^{3-}\cdot 5CH_3CN$	864.93	864.66(74)			
$[KW_{10}O_{32}]^{3-}\cdot 4CH_3CN$	851.24	851.07(96)			
$[KW_{10}O_{32}]^{3-}\cdot 3CH_3CN$	837.55	837.67(100)	837.54(4)		
$[KW_{10}O_{32}]^{3-}\cdot 2CH_3CN$	823.87	823.95(42)	824.02(10)		
$[KW_{10}O_{32}]^{3-}\cdot CH_3CN$	810.20	810.61(14)	810.49(25)		
$[W_{10}O_{32}]^{4-}\cdot 9CH_3CN$	679.94	679.98(23)			
$[W_{10}O_{32}]^{4-}\cdot 8CH_3CN$	669.68	669.61(73)			
$[W_{10}O_{32}]^{4-}\cdot 7CH_3CN$	659.42	659.35(97)			
$[W_{10}O_{32}]^{4-}\cdot 6CH_3CN$	649.16	649.23(52)			
$[W_{10}O_{32}]^{4-}\cdot 5CH_3CN$	638.90	638.97(21)			
$[W_{10}O_{32}]^{4-}\cdot 4CH_3CN$	628.64		628.53(6)		
$[W_{10}O_{32}]^{4-}\cdot 3CH_3CN$	618.38		618.22(15)		
$[W_{10}O_{32}]^{4-}\cdot 2CH_3CN$	608.13		608.09(20)	608.09(4)	
$[W_{10}O_{32}]^{4-}\cdot CH_3CN$	597.87		597.84(15)	597.84(14)	
nonsolvated ions					
$[K_2W_{10}O_{32}]^{2-}$	1214.34	1214.10(24)	1214.35(34)	1214.16(26)	1213.91(100)
$[KW_{10}O_{32}]^{3-}$	796.53		796.53(100)	796.10(100)	
$[W_{10}O_{32}]^{4-}$	587.62		587.34(5)	587.52(70)	587.65(15)
protonated ions					
$[KHW_{10}O_{32}]^{2-}$	1195.29	1194.95(10)	1194.71(6)		1194.21(14)
$[HW_{10}O_{32}]^{3-}$	783.83		783.87(11)	783.44(8)	783.50(15)
fragmented ions					
$[W_8O_{25}]^{2-}$	935.35				934.45(10)
$[W_7O_{22}]^{2-}$	819.43				818.83(53)
$[W_6O_{19}]^{2-}$	703.51				702.96(80)

of the respective rate constants have been obtained from the wO lifetime and the solvent oxygenation and decatungstate reduction yields in oxygen-saturated solutions of the neat solvent (Table 1), as previously explained.[4,7] It is interesting to note that less than 10% of wO$-$CH$_3$CN interactions result in chemical transformations, half of which lead to formation of one-electron reduced decatungstate.

The investigation of a series of alkenes and alkanes shows that quenching of wO by organic substrates leads to formation of complexes of very variable lifetime, and in the presence of O_2, it results in a quantitative oxygenation of the substrate, as demonstrated by the general equivalence of the rate constants of wO decay, O_2 uptake, and hydroperoxide formation. The decrease of the end of pulse absorbance with increasing alkene concentration suggests that, similarly to the strong solvation observed with CH$_3$CN, strong interactions also exist between the decatungstate cluster and the olefins, leading to scavenging of $W_{10}O_{32}^{4-*}$ and/or wO species during the laser pulse. In this case, wO reactivity may be understood in terms of a combination of regular diffusion-controlled dynamic quenching and static quenching processes,[29a] the latter resulting from the formation of complexes between the alkenes and a precursor of wO, or from the statistical presence of the substrate next to wO or its precursors.[29b] Such a process would result in an increased reactivity, since diffusion is not required for the reaction to take place during the laser pulse. Similar suggestions have been previously made by Fox et al.,[30a] who found rate constants exceeding the diffusion controlled limit for reaction of polyoxometalates with organic substrates, by Hill et al.,[30b] who performed comparative experiments with alcohols and alkanes, and more recently also by Hiskia et al.,[31] who collected significant information suggesting that preassociation of catalyst and substrate is a general feature in photocatalyzed reactions of both polyoxometalates and aggregates of metal complexes.

Both ET and HA mechanisms may be suggested for the reactivity of wO toward organic substrates. In the case of alkenes, H-atom abstraction will occur at the allylic position to give the allyl radical, while electron transfer would lead to oxidation of the double bond, yielding the cation radical product. For the acyclic hexene isomers studied here, 1-hexene, 3-hexene, 2-methyl-2-pentene, and 2,3-dimethyl-2-butene, the allylic C$-$H bond strength is nearly constant, but the addition of electron-donating methyl groups to the vinyl position brings about a decrease in ionization energy by 1.28 eV across the series. Thus, if HA is the dominant pathway, we would expect similar k_{XH} values for all hexane isomers. If, in contrast, electron or charge-transfer processes take place, we expect the quenching rate constants to depend on the free energy for formation of an ion pair, which is a linear function of the substrate oxidation potential E_{ox} (or its gas-phase ionization energy IE, since E_{ox} and IE for structurally similar compounds are generally found to correlate linearly with each other). If we account for the diffusion-controlled (i.e., with rate constant $k_{diff} = 1.9 \times 10^{10}$ M^{-1} s^{-1}) formation of initial encounter complexes, the charge-transfer step can be described by $k_r/k_{-diff} = k_{XH}/(k_{diff} - k_{XH})$,[32] where k_r is the rate constant for electron transfer and k_{-diff} the rate constant for separation of encounter pairs. Figure 12 shows the dependence of $\ln[k_{XH}/(k_{diff} - k_{XH})]$ on substrate IE, for the olefins of Table 1. This dependence can be described by a linear fit with a slope of -1.5 eV^{-1}, which is much weaker than the slope of $-(RT)^{-1}$ expected for complete electron transfer. Thus, it is suggested that quenching of wO by alkenes leads to partial charge-transfer only. In a very simplified picture, the ratio of the experimental slope to the slope expected for complete electron transfer can be seen as the amount of charge transfer in intermediate complexes. This treatment leads to a value of 9% for the present series of alkenes. However, previous results for a series of aromatic hydrocarbons suggest that the dependence of wO quenching rate constants on E$_{ox}$ corresponds to a parabolic Marcus-type curve rather than to a linear plot.[10] It has been shown, for other photochemical systems involving partial electron transfer, that a Marcus-type interpretation can lead to significantly larger estimates for the charge-transfer character than a linear model.[33] Since the IE range of the present alkenes is relatively narrow, the data fit to both a parabolic and a linear model, and thus, the value of 9% charge transfer should be considered as a qualitative estimate. Also, the rate constants for decatungstate-alkene charge transfer are relatively small, compared with very easily oxidizable substrates, such as aromatic amines, for which wO quenching rate constants near diffusion control have been reported.[6] Assuming similar reorganization energies and regular Marcus behavior for forward and backward electron transfer, our data suggest that also back-electron transfer is comparatively unfavorable in the case of alkenes, and this could explain why interception of intermediate complexes by O_2 is faster than back-electron transfer for these substrates, as opposed to aromatic amines, where efficient back-electron transfer was demonstrated by a lack of $W_{10}O_{32}^{5-}$ formation during wO decay.[6]

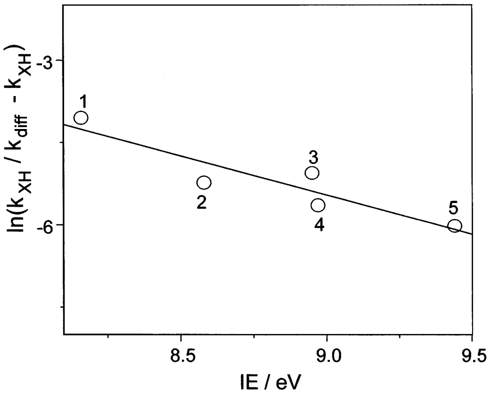


Figure 12. Dependence of $\ln[k_{XH}/(k_{diff} - k_{XH})]$ on substrate ionization energy. (1: 2,3-dimethylbutene. 2: 2-methyl-2-pentene. 3: cyclohexene. 4: *trans*-3-hexene. 5: 1-hexene.)

No IE dependence is observed when the alkenes are replaced by their saturated counterparts. The reactivity of these alkanes toward wO does not vary within experimental error, and is significantly weaker than for the respective alkenes. Since all C$-$H bond strengths are similar in these hexane isomers, this is in agreement with a HA mechanism. Given the low magnitude of reaction rate constants, the formation of a preassociated complex of $W_{10}O_{32}^{4-}$ with alkanes seems to be unlikely. It is believed that such a preassociated equilibrium should not be significantly more favorable than in the case of acetone, for which no solvated ions have been detected with several polyoxoanions including (Bu$_4$N)$_4$W$_{10}$O$_{32}$.[28] In this case, preassociation of $W_{10}O_{32}^{4-}$ with these substrates would be strongly disfavored compared with complexation with the solvent, and this could explain the nonselective reactivity of alkanes.

Moreover, the low and IE independent rate constants for the alkanes demonstrate that at least the major part of the charge-transfer interactions with the alkenes is due to the substrate C$-$C double bond, and it becomes clear that both ET and HA mechanisms may compete in the reactivity of wO toward organic substrates. In the case of the alkenes studied here, HA is negligible compared with ET, except for *n*-hexene and

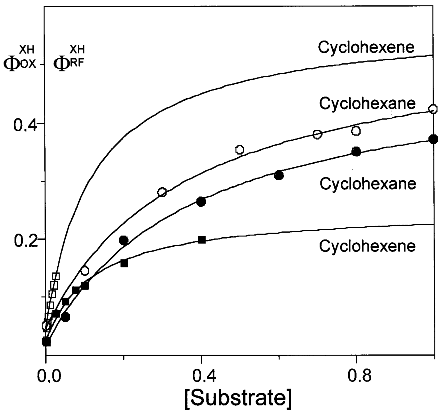


Figure 13. Dependence of the quantum yields Φ_{OX}^{XH}, of O_2 consumption (□ and ○), and Φ_{RF}^{XH}, and of decatungstate reduction (■ and ●) on substrate concentration. Data measured for illumination of acetonitrile solutions of sodium decatungstate (5.5×10^{-4} M) in the presence of cyclohexane (○ and ●) and cyclohexene (■ and □).

cyclohexene, where the rate constants for the corresponding alkanes are noticeable. We also note that the Stern–Volmer constants for wO decay, RF formation and O_2 consumption in the presence of cyclohexane are significantly larger than those observed for the other saturated compounds. Since the IE of cyclohexane is similar to that of the other alkanes, and additionally, the *K* values are much smaller than those found for cyclohexene, which also has a relatively high IE, these differences cannot be explained by an ET mechanism. Also, all *K* values for cyclohexene deviate from the value expected according to the correlation with IE, and thus, it is suggested that the reaction with wO is enhanced by a factor related to the structure of these cyclic compounds.

We have noted that the quantum yield Φ_{wO} of formation of wO, obtained from O_2 consumption measurements is constant, irrespective of the lifetime of the decatungstate-substrate complexes and of the mechanism dominating their reactivity. This means that backward reactions do not occur within these complexes. However, the reduction of $W_{10}O_{32}^{4-}$ is less than quantitative in any case, Φ_{RF}^{XH} is found to be significantly smaller than Φ_{OX}^{XH} at any substrate concentration. This is observed for all substrates investigated here, and is most prominent in the case of the alkenes (see Figure 13). It is also interesting to note that the experiments of Texier et al.,[10] which were also carried out in air-saturated CH_3CN, yielded even lower values for Φ_{RF}^{∞}, while measurements of Duncan et al. in N_2-saturated acetonitrile led to Φ_{RF}^{∞} values of ca. 0.5.[6]

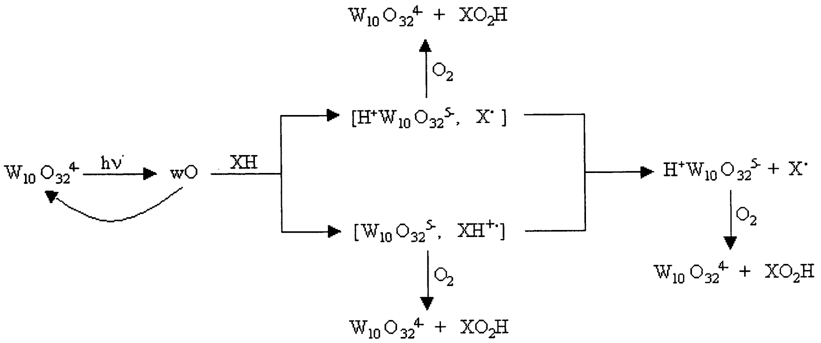
The only possible explanation for this behavior is the existence an alternative pathway resulting in substrate oxygenation, without production of $W_{10}O_{32}^{5-}$. Figure 13 shows that Φ_{RF}^{XH} and Φ_{OX}^{XH} increase regularly with [XH], until reaching their plateau values Φ_{RF}^{∞} and Φ_{OX}^{∞}, respectively. The above results on hydroperoxide formation from alkenes and alkanes are in agreement with the previous suggestion that O_2 consumption leads to an initially quantitative formation of hydroperoxides, which means that $\Phi_{OX}^{\infty} = \Phi_{wO}$. Thus, the ratio of the limiting decatungstate reduction and substrate oxygenation yields gives the probability $\alpha = \Phi_{RF}^{\infty}/\Phi_{wO}$ of formation of RF from wO. From the data of Table 1, we conclude that at least in the case of alkenes, α is significantly smaller than unity, and decreases, similarly to k_{XH}, with increasing IE. This indicates that the probability of decatungstate reduction is determined by the strength of charge-transfer interactions in the intermediate complexes. Also, it is known that the decatungstate reduction yields decrease with increasing O_2 concentration.[4] This is also confirmed in the case of alkenes. Hence, we conclude that reactions of intermediate complexes with O_2 are at least partially responsible for the nonreductive pathway leading to formation of $W_{10}O_{32}^{4-}$ and the hydroperoxide. The mechanism of the decatungstate-sensitized photooxygenation of organic substrates can thus be generally described by Scheme 2:

Illumination of $W_{10}O_{32}^{4-}$ leads, via the extremely short-lived excited state of decatungstate, to formation of the unexcited transient wO, which reacts with organic substrates XH by hydrogen-atom-abstraction and electron-transfer mechanisms. The efficiencies of formation of RF from the intermediate complexes can be less than unity. These intermediate species undergo oxidative interactions with molecular O_2, leading to substrate oxygenation without formation of one-electron reduced decatungstate.

Conclusions

The combination of time-resolved and steady-state studies on the reactivity of wO with several organic hydrocarbons reveals that any interaction of wO with the substrate leads to formation of the corresponding hydroperoxide. However, reductive and nonreductive pathways compete in the overall reaction. It is shown that the importance of molecular oxygen in the catalytic process goes beyond the simple reoxidation of $W_{10}O_{32}^{5-}$. Inhibition of $W_{10}O_{32}^{5-}$ formation represents an additional pathway by which O_2 enhances the catalytic process. Unexpected inhibition of photocatalysis is observed in the presence of olefins. It is shown that formation of very long-lived complexes involving the alkenes and both one- and two-electron-reduced decatungstate is responsible for this behavior. Thus, besides revealing new aspects of the photocatalytic mechanism, the present results also provide valuable information with regard to the practical operation of oxofunctionalization of hydrocarbons.

SCHEME 2



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