Photocatalytic and catalytic activity of heterogenized $W_{10}O_{32}{}^{4-}$ in the bromide-assisted bromination of arenes and alkenes in the presence of oxygen

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Abstract

Photochemical excitation ($\lambda > 300$ nm) of the decatungstate $(n\text{Bu}_4\text{N})_4\text{W}_{10}\text{O}_{32}$, heterogenized with Amberlite IRA-900 and dispersed in a $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ mixture, causes the reductive activation of O_2 to alkyl hydroperoxides. The light-assisted formation of these intermediates represents a new approach for inducing the bromination of activated arenes and cycloalkenes at atmospheric pressure and room temperature. The active species "Br^+" is formed as a consequence of a two-electron oxidation of Br^- by the photogenerated hydroperoxides. This process is catalyzed by the decatungstate, which, therefore, plays also a catalytic role in addition to the photocatalytic one. Phenol and anisole can be converted to the corresponding mono-brominated derivatives, and a wide range of cycloalkenes to the corresponding bromohydrins and dibromides, with bromohydrins as intermediates for the formation of epoxides. The anionic exchange resin plays a crucial role in fostering the enrichment of bromide anions close to the surface and, consequently, their reaction with the photogenerated hydroperoxides. As a matter of fact, the efficiency of the bromination photocatalytic processes may benefit by the heterogenization of the decatungstate.

As to the chemoselectivity of the photocatalytic process, we have found that the solid matrix plays the important function of increasing the yields of epoxides and bromohydrins from cyclohexene, 1-methyl-1-cyclohexene, and styrene, upon heterogenization of the decatungstate. The solid matrix can also control the chemoselectivity in anisole bromination, by favoring the functionalization of the *para* position.
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Keywords: Photocatalysis; Heterogenized polyoxotungstates; Bromination; Epoxidation; Hydroperoxides
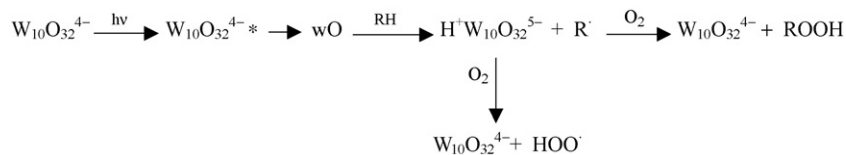
1. Introduction

Bromination represents a key-reaction for the production of many fine chemicals, such as pharmaceuticals, agrochemicals and flame retardants. However, there is a strong demand for the development of new strategies to induce this process, since the conventional methods use hazardous and expensive reactants, like elemental bromine or stoichiometric brominating reagents, that can also produce organic waste. An alternative and more benign approach is based on the production of brominating intermediates through oxidation of bromide salts with hydrogen peroxide. Bromoperoxidase enzymes have attracted particular interest in this regard [1,2], and several inorganic catalysts mimicking their activity are now available [3–7]. In all cases, H_2O_2-assisted bromination occurs as a consequence of a

two-electron oxidation of Br^- to the active species Br^+ or BrO^-. Herein, we investigate the possibility that brominating species may be obtained from bromide salts, through photochemical excitation of the $\text{W}_{10}\text{O}_{32}{}^{4-}$ polyoxoanion in the presence of molecular oxygen. We were prompted to follow this strategy because $\text{W}_{10}\text{O}_{32}{}^{4-}$ is able to induce the photocatalytic oxidation of organic compounds to peroxidic species according to the literature data briefly summarized in the following.

The decatungstate $\text{W}_{10}\text{O}_{32}{}^{4-}$ has been intensively studied as very attractive photocatalyst for the transformation of organic compounds [8–12]. It is generally accepted that illumination of this polyoxoanion leads to the formation of a charge transfer excited state, which, in few ps, decays to an extremely reactive transient referred as wO (Scheme 1) [13–15]. Previous studies [13–23] indicate that the intermediate wO is able to initiate the oxidation of the substrate (RH) through either hydrogen abstraction or direct electron transfer to give, in any case, the same one-electron reduced species of the decatungstate. The substrate-derived radical, thus obtained, in the presence of

$$W_{10}O_{32}{}^{4-} \xrightarrow{h\nu} W_{10}O_{32}{}^{4-}* \longrightarrow wO \xrightarrow{RH} H^+W_{10}O_{32}{}^{5-} + R^{\cdot} \xrightarrow{O_2} W_{10}O_{32}{}^{4-} + ROOH$$

$$\downarrow {O_2}$$

$$W_{10}O_{32}{}^{4-} + HOO^{\cdot}$$

Scheme 1. Mechanism of decatungstate-assisted photooxygenation of hydrocarbons.

O_2 and $H^+W_{10}O_{32}{}^{5-}$ is converted to the corresponding alkyl hydroperoxide. Reoxidation of $H^+W_{10}O_{32}{}^{5-}$ by O_2 may also lead to the formation of peroxy radicals.

Heterogenization of polyoxoanions for photocatalytic purposes has attracted particular attention, since the solid support: (i) makes the handling and recycling of the system easier; (ii) allows a more free choice of the reaction medium; (iii) can sometimes control the efficiency and selectivity of the photocatalytic processes. Some of our contributions in this research area have dealt with the use of $(nBu_4N)_4W_{10}O_{32}$ on amorphous or mesoporous silica [19,24,25].

We discuss here our results on the reactivity of bromide ions in the presence of $(nBu_4N)_4W_{10}O_{32}$ heterogenized with Amberlite IRA-900. This support is a macroreticular styrene-divinylbenzene copolymer, bearing $-N(CH_3)_3{}^+$ functional groups. It consists of spherically shaped particles with diameters of about 0.5 mm and it is commercially available in its chloride form. The photocatalytic ability of this system (Amb/$W_{10}O_{32}{}^{4-}$) to induce bromide-assisted functionalization processes is assessed in the bromination of some aromatics and alkenes, paying particular attention to the role played by the solid matrix on its efficiency and selectivity. The possibility that the overall process may benefit by non-photoassisted catalytic reactions involving decatungstate is also taken into account.

2. Experimental

2.1. Materials

The decatungstate $(nBu_4N)_4W_{10}O_{32}$ was synthesized according to literature procedures [21]; CH_3CN was a spectroscopic grade Aldrich solvent; arenes (phenol and anisole) and alkenes (cyclohexene, 1-methyl-1-cyclohexene, 1-phenyl-1-cyclohexene, indene, and styrene) were purchased from Aldrich and distilled before use; NaBr (Carlo Erba) and HBr (Aldrich) were used without further purification.

2.2. Preparation of the heterogeneous catalyst

Amberlite IRA-900 (1 g, commercial from Fluka, Cl^- form) was added to $(nBu_4N)_4W_{10}O_{32}$ (0.25 g) dissolved in CH_3CN. The suspension was stirred at room temperature for several hours, until the lack of the typical UV–vis spectrum of the dissolved decatungstate ($\lambda_{max} = 323$ nm) showed that the adsorption was complete. The exchanged resin (Amb/$W_{10}O_{32}{}^{4-}$) was filtered off, washed successively with water, water–acetone (1/1) and acetone.

2.3. Apparatus

Photochemical excitations were performed at room temperature (298 ± 1 K) with a Helios Italquartz Q400 medium-pressure mercury lamp (for alkenes), and with a xenon mercury lamp by Oriel (for arenes), using a cut-off filter to select excitation wavelengths higher than 300 nm. Gas chromatographic (GC) analyses were carried out using a HP6890 Series Instrument equipped with a flame ionization detector and a HP-5 (Crosslinked 5% PH ME Siloxane, 30 m; $0.32\,\mu m \times 0.25\,\mu m$ film thickness) capillary column. Quantitative analysis was performed with calibration curves obtained from commercial or synthesized standards. GC–MS analyses were performed using a GC-8000 Fisons Instrument equipped with a Mega OV1 (25 m; i.d. = 0.32 mm) capillary column and a mass spectrometer MD-800 as a detector. UV–vis spectra were recorded using a Kontron Uvikon 943 spectrophotometer. IR spectra were obtained with a Nicolet 510P FTIR spectrometer, fitted with a Spectra-Tech collector diffuse reflectance accessory (range $4000–200\,cm^{-1}$).

2.4. Photocatalytic reactions

The Amb/$W_{10}O_{32}{}^{4-}$ system ($33\,g\,dm^{-3}$) was suspended under vigorous stirring in CH_3CN/H_2O mixtures (3 mL) at different ratios. These mixtures contained either the dissolved olefin ($3 \times 10^{-2}\,mol\,dm^{-3}$) or the arene ($1 \times 10^{-2}\,mol\,dm^{-3}$), and, when necessary, Br^- ($0.2\,mol\,dm^{-3}$). Four hours irradiations were performed inside a Pyrex reactor at 298 ± 1 K in the presence of 760 Torr of O_2. After irradiation, the dispersing medium was analyzed by GC. Peroxide concentrations were measured by iodometric titration [26]. A possible release of decatungstate from the resin was evaluated following the UV–vis spectrum of the dispersing medium. If necessary, the products adsorbed on the solid matrix were extracted with CH_3CN and analyzed.

Control experiments were carried out irradiating the resin without decatungstate, or keeping the sample in the dark after addition of H_2O_2 ($4 \times 10^{-3}\,mol\,dm^{-3}$). Irradiations in homogeneous solutions were performed dissolving $(nBu_4N)_4W_{10}O_{32}$ ($2 \times 10^{-4}\,mol\,dm^{-3}$) and the olefin ($3 \times 10^{-2}\,mol\,dm^{-3}$), or the arene ($1 \times 10^{-2}\,mol\,dm^{-3}$), in CH_3CN/H_2O mixtures (3 mL), with or without Br^- ($0.2\,mol\,dm^{-3}$). Each photocatalytic experiment was repeated at least three times in order to evaluate errors, that never exceeded ±5%.

In order to evaluate the ability of photogenerated peroxides to oxidize bromide ions, Amb/$W_{10}O_{32}{}^{4-}$ system ($33\,g\,dm^{-3}$) was suspended under vigorous stirring in water or in CH_3CN/H_2O mixtures (3 mL) containing Br^- ($2 \times 10^{-2}\,mol\,dm^{-3}$), and

irradiated for 22 h. Such a long irradiation time was necessary in order to measure a significant decrease in bromide concentration. The final concentration of residual Br^- was estimated by potentiometric titration with $AgNO_3$. Adsorbed bromide ions were previously brought into the solution by exchanging them with ClO_4^-.

2.5. Product analyses

The reaction mixtures were analyzed by GC. The identification of the major products was systematically confirmed by GC–MS. Bromination and epoxidation products were identified by comparing their retention times with those of commercial products (Aldrich) or specifically prepared compounds. All 2-bromo and 4-bromo derivatives of phenol and anisole were commercial. Indene epoxide was prepared adding an excess of NaOH to a CH_3CN solution of 2-bromo-1-indanol. The other non-commercial epoxides were synthesized according to standard literature procedures [27]. Bromohydrins were prepared adding HBr to solutions of the starting epoxides in CH_3CN. *Trans*-1,2-dibromocyclohexane, cyclohex-2-en-1-ol, cyclohex-2-en-1-one, and benzaldehyde were purchased from Aldrich. Non-commercial dibromides were prepared from CH_3CN acidified solutions containing the corresponding epoxide and an excess of NH_4Br. Commercial 2-indanol, 2-indanone, 3-methyl-2-cyclohexen-1-ol, 3-methyl-2-cyclohexen-1-one, 2-phenyl-1-cyclohexanol, and 2-phenyl-2 cyclohexanone were used as standards for all monooxygenation products (OMP) obtained from 1-methyl-1-cyclohexene, 1-phenyl-1-cyclohexene, and from indene, respectively, assuming that there is no significant difference in the instrumental answer between monooxygenated compounds with the same number of carbon atoms.

3. Results and discussion

3.1. Preparation and photoreactivity of the Amb/$W_{10}O_{32}^{4-}$ system

The Amb/$W_{10}O_{32}^{4-}$ system was prepared by addition of Amberlite IRA 900 to CH_3CN solutions of $(nBu_4N)_4W_{10}O_{32}$ according to the procedure reported in the experimental section. The UV–vis spectrum of the dissolved decatungstate disappeared after few hours of contact with the polymer, thus indicating that the exchange of Cl^- for $W_{10}O_{32}^{4-}$ anions on the polymer surface is favored by the soft character of the organic cation. A comparison of the infrared spectrum of the resin treated with $(nBu_4N)_4W_{10}O_{32}$ with that of pure Amberlite (Fig. 1) shows absorptions at frequencies typical of the decatungstate (962.68, 805.32, and 442.64 cm^{-1}) [21]. This result indicates that $W_{10}O_{32}^{4-}$ anions are supported on the resin without undergoing appreciable changes in their structure.

Several photocatalytic experiments were carried out suspending the Amb/$W_{10}O_{32}^{4-}$ system (33 g dm^{-3}) in a CH_3CN/H_2O mixture (3 mL, 1/1, v/v). The well-stirred samples were irradiated ($\lambda > 300$ nm) at atmospheric pressure and room temperature for 4 h in the presence of 760 Torr of oxygen. Iodometric analyses gave evidence that irradiation led to the formation of
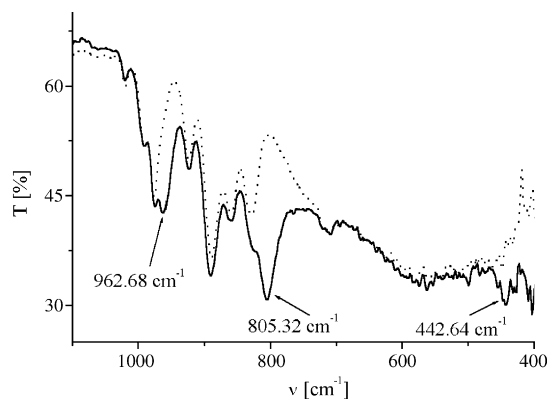

Fig. 1. IR spectra of Amb/$W_{10}O_{32}^{4-}$ (—) and of unmodified Amberlite (····).

1.7×10^{-3} mol dm^{-3} of peroxides at the end of the experiment. In order to evaluate the amount of H_2O_2 among them, a portion of the irradiated mixture was treated with Catalase (Sigma, 10 U/mL), which is known to decompose H_2O_2, but does not react with alkyl peroxides. On the basis of this analysis, we concluded that about 90% of the overall peroxides were of organic nature, likely deriving from CH_3CN, in agreement with previously reported literature data [14]. Control experiments were carried out varying the amount of suspended photocatalyst. The yield in peroxides indicated that the quantity (33 g dm^{-3}) of photocatalyst used was the optimum in order to ensure the maximum of light absorption and efficiency.

On the basis of the described results, we can state that heterogenization with Amberlite does not affect the typical photocatalytic activity of $W_{10}O_{32}^{4-}$, that induces the formation of alkyl hydroperoxides according to Scheme 1. A possible reactivity of these species towards Br^- ion has been assessed irradiating the Amb/$W_{10}O_{32}^{4-}$ system dispersed in CH_3CN/H_2O in the presence of NaBr (2×10^{-2} mol dm^{-3}). The results reported in the first row of Table 1 show that 22 h irradiation led to the disappearance of 10% of the initial Br^-. This fact is a clear indication that the photogenerated peroxides are able to oxidize Br^- ions.

When the photocatalytic experiment was carried out in the presence of cyclohexene, as additional organic substrate, a higher amount of alkyl hydroperoxide was obtained: 2.3×10^{-3} mol dm^{-3}. In line with this finding, the results reported in the second row of Table 1 show that a higher amount of Br^- disappeared with respect to the experiments carried out in the absence of cyclohexene. The peroxides detected in this

Table 1
Photocatalytic oxidation[a] of Br^- by the Amb/$W_{10}O_{32}^{4-}$ system

Dispersing medium	Consumed Br^- ($\times 10^{+3}$ mol dm^{-3})
CH_3CN/H_2O	2
CH_3CN/H_2O, cyclohexene (3×10^{-2} mol dm^{-3})	3.4
H_2O	<0.5

[a] The Amb/$W_{10}O_{32}^{4-}$ system (0.1 g) was suspended in a CH_3CN/H_2O mixture (3 mL, 1/1, v/v) or H_2O in the presence of NaBr (2×10^{-2} mol dm^{-3}). The well-stirred samples were irradiated ($\lambda > 300$ nm) at atmospheric pressure and room temperature for 22 h in the presence of 760 Torr of oxygen. Reported values are the average of three repeated experiments.

system should originate from the oxidation of both CH_3CN and the olefinic substrate because H-abstraction from its allylic position is easy. Since addition of the reducing agent KI to the irradiated solution produced 5.8×10^{-4} mol dm^{-3} of allylic alcohol, we could conclude that about 25% of the detected alkyl peroxides originated from cyclohexene.

It is rather unlikely that a direct oxidation of Br$^-$ by the photoexcited decatungstate can occur without the involvement of an alkyl hydroperoxide, since the interaction between these two anions is not favorable because of their negative charges. Accordingly, the third row of Table 1 shows that irradiation of the Amb/$W_{10}O_{32}{}^{4-}$ system in the absence of any organic substrate yields only negligible variations of the Br$^-$ initial concentration.

According to the followed procedure of Amberlite loading, we can estimate that 0.8 mequiv. g^{-1} are occupied by the decatungstate. Since the anion exchange capacity of Amberlite is about 4.2 mequiv. g^{-1}, the obtained heterogeneous photocatalyst should be able to support Br$^-$ ions too. Bromide adsorption is also favored by an easy interaction of these anions with the soft positive functional groups of the surface. Therefore, it is likely that the formation of the brominating species occurs in proximity of the solid surface, where the photoinduced formation of peroxides also takes place. Later, we have examined the possibility that the reaction between peroxides and Br$^-$ can be catalyzed by $W_{10}O_{32}{}^{4-}$ itself to give a two-electron oxidation of Br$^-$ to the active species Br$^+$ or BrO$^-$. The further brominating activity of these intermediates was investigated for some activated arenes and alkenes.

3.2. Photocatalytic bromination of activated arenes

Phenol has been chosen as the simplest activated arene for testing the brominating properties of the described photocatalytic system. The Amb/$W_{10}O_{32}{}^{4-}$ photocatalyst (33 g dm^{-3}) was suspended in a CH_3CN/H_2O mixture (3 ml, 1/1, v/v) containing NaBr (1×10^{-1} mol dm^{-3}) and phenol (1×10^{-2} mol dm^{-3}). HBr (1×10^{-1} mol dm^{-3}) was also added, since aromatic bromination through peroxide-mediated oxidation of bromide is known to be fostered by acidic conditions [28]. GC analysis of this suspension after 4 h in the dark showed a 20% decrease in the initial phenol concentration, thus indicating a significant interaction of the aromatic substrate with the surface of the polymeric support.

The well-stirred Amb/$W_{10}O_{32}{}^{4-}$ system was then irradiated at atmospheric pressure and room temperature for 6 h in the presence of 760 Torr of oxygen. Fig. 2 shows that the formation of alkyl peroxides was accompanied by the bromination of phenol to give only the mono-brominated derivatives, 4- and 2-bromophenol. The amounts of brominated products at the end of the experiment corresponded to more than 90% of the overall consumed phenol.

Control experiments indicated that the bromination reaction did not occur in the dark or in the absence of either Amb/$W_{10}O_{32}{}^{4-}$ or O_2. We have also found that the use of HCl instead of HBr caused only a 15% decrease in the substrate conversion without any significant effect on the nature of the brominated products and on their molar ratio. Finally, we ver-
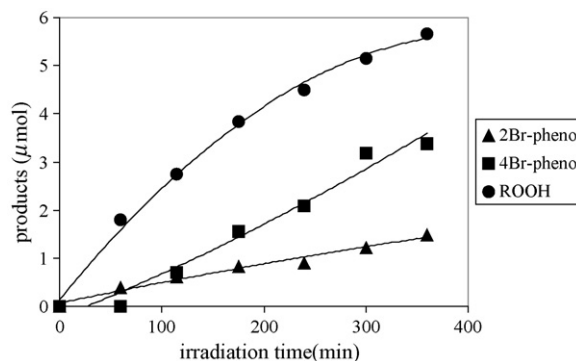

Fig. 2. Evolution of photoproducts as a function of irradiation time.

ified that the photocatalytic efficiency decreased significantly (about 80%) when irradiation was carried out in not acidic conditions.

Table 2 enables us to evaluate the effect of the polymeric support on the $W_{10}O_{32}{}^{4-}$-assisted bromination of phenol. This reaction is strongly influenced by heterogenization, being 10 times more efficient in phenol bromination than the corresponding process in homogeneous phase. The observed matrix effect is most likely due to surface effects, which can control in different ways the local concentration of reagents and reaction intermediates. On the other hand, the amounts of 4-bromophenol and 2-bromophenol in the homogeneous system are only 10% of the consumed phenol. This result implies that homogenous reaction conditions favor the reaction between phenol and the radical intermediates formed according to Scheme 1 to give phenoxy radicals, which can then couple to yield oligomeric products, not detected by gas chromatographic analysis.

Photochemical excitation of the Amb/$W_{10}O_{32}{}^{4-}$ photocatalyst in the presence of NaBr and HBr induced also the functionalization of anisole with formation of 4-bromoanisole as the only brominated product (see Table 2). In this case, the solid matrix did not significantly affect the total yield with respect to the homogeneous solution, but surface effects controlled the chemoselectivity of the process, driving the attack in para, the less hindered position of anisole.
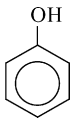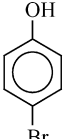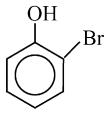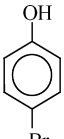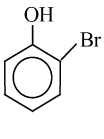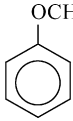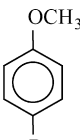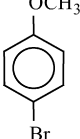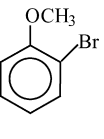
The stability of the photocatalyst was tested by separation of the used Amb/$W_{10}O_{32}{}^{4-}$ from the irradiated reaction mixture, washing, and reuse in repeated reaction cycles. GC-analyses revealed that the decrease in activity of the supported photocatalyst, in terms of detected end products, was about 20% after three cycles. Furthermore, UV–vis spectra indicated that decatungstate anion was not released in detectable amounts into the solution, thus confirming that we were in the presence of a real heterogeneous photocatalytic process.

3.3. Photocatalytic functionalization of alkenes

Epoxide formation is a major reaction in the functionalization of many molecules. In this framework, much effort is addressed to find suitable solid supports for tungsten-based compounds, in order to make the handling and recycling easier in view of large-scale applications. For instance, the Venturello peroxotungsten catalyst $[PW_4O_{24}]^{3-}$ anchored on Amberlite IRA 900

Table 2
Photocatalytic properties[a] of $Amb/W_{10}O_{32}{}^{4-}$ and $W_{10}O_{32}{}^{4-}$ in the bromide-assisted functionalization of phenol and anisole

Arene	System	Brominated products distribution (%)		Total yields in brominated products[b] (μmol)
OH	$Amb/W_{10}O_{32}{}^{4-}$	OH, Br (para) 70	OH, Br (ortho) 30	3.0
	$W_{10}O_{32}{}^{4-}$	OH, Br (para) 62	OH, Br (ortho) 38	0.3
OCH₃	$Amb/W_{10}O_{32}{}^{4-}$	OCH₃, Br (para) 100		1.6
	$W_{10}O_{32}{}^{4-}$	OCH₃, Br (para) 59	OCH₃, Br (ortho) 41	1.2

[a] In a typical experiment $Amb/W_{10}O_{32}{}^{4-}$ (1×10^{-1} g) or $W_{10}O_{32}{}^{4-}$ (2×10^{-4} mol dm^{-3}) were suspended/dissolved in a CH$_3$CN/H$_2$O mixture (3 mL, 1/1, v/v) containing the arene (1×10^{-2} M), NaBr (1×10^{-1} mol dm^{-3}), HBr (1×10^{-1} mol dm^{-3}), and irradiated (4 h, $\lambda > 300$ nm) at 298 ± 1 K and 760 Torr of oxygen. Reported values are the mean of three repeated experiments.
[b] Amount of brominated products in μmol accumulated in 3 mL of CH$_3$CN/H$_2$O mixture.

has been successfully used for terpenes epoxidation [29,30]. Venturello's anion and Neumann's sandwich-type compound $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$ have been also supported on silica bearing phenyl and quaternary ammonium groups, and used for the epoxidation of olefins such as cyclooctene and norbornene [31,32].

Cyclohexene has been chosen here as a reference unsaturated hydrocarbon. Typical photocatalytic experiments were carried out with $Amb/W_{10}O_{32}{}^{4-}$ (33 g dm^{-3}) suspended in a CH$_3$CN/H$_2$O mixture (3 mL) containing the olefinic substrate (3×10^{-2} mol dm^{-3}) and NaBr (2×10^{-1} mol dm^{-3}). Evolution of products during the photocatalytic experiment is shown in Fig. 3, while overall yield and products distribution after 4 h irradiation are reported in the first row of Table 3.

Iodometric analysis gave evidence that irradiation led to the formation of alkyl hydroperoxides. Since addition of the reducing agent KI to aliquots of irradiated solutions did not produce additional amount of allylic alcohol, we concluded that the alkyl hydroperoxides accumulated during the photochemical experiment came mainly from CH$_3$CN. Formation of hydroperoxides was accompanied by functionalization of the alkene to yield the corresponding epoxide (EP), bromohydrin (BrOH), dibromide (BrBr), and monooxygenated species (OMP). The detected

products accounted for about the 80% of the overall converted cyclohexene. Since the complete conversion of the bromohydrin to the corresponding cyclohexene epoxide was achieved by simply adjusting the pH, we could estimate that the overall yield in epoxide was about 36%.

Photocatalytic experiments with other alkenes led to analogous results. In particular we have investigated the following olefinic substrates: 1-methyl-1-cyclohexene, 1-phenyl-1-cyclohexene, indene, and styrene. Different compositions of the
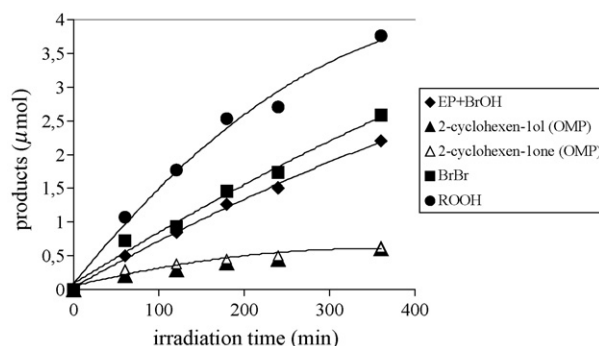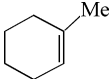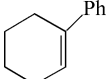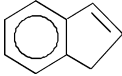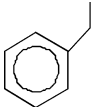

Fig. 3. Evolution of photoproducts as a function of irradiation time.

Table 3
Photocatalytic properties[a] of Amb/$W_{10}O_{32}^{4-}$ and $W_{10}O_{32}^{4-}$ in the bromide-assisted functionalization of alkenes

Alkene	System	Alkene products distribution[b] (%)				Alkene total yield[c] (μmol)
		EP	BrOH	BrBr	OMP	
(cyclohexene)	Amb/$W_{10}O_{32}^{4-}$	13	23	42	22	4.2
	$W_{10}O_{32}^{4-}$	12	12	7	69	4.5
(1-methyl-1-cyclohexene)	Amb/$W_{10}O_{32}^{4-}$	56	13	5	26	4.8
	$W_{10}O_{32}^{4-}$	37	1	4	58	14
(1-phenyl-1-cyclohexene)	Amb/$W_{10}O_{32}^{4-}$	38	8	0	54	11
	$W_{10}O_{32}^{4-}$	47	5	0	48	17
(indene)	Amb/$W_{10}O_{32}^{4-}$	51	12	0	35[d]	22
	$W_{10}O_{32}^{4-}$	55	10	0	34[d]	20
(styrene)	Amb/$W_{10}O_{32}^{4-}$	13	31	2	50[e]	29
	$W_{10}O_{32}^{4-}$	14	8	0	70[e]	20

[a] In a typical experiment Amb/$W_{10}O_{32}^{4-}$ (0.1 g) or $W_{10}O_{32}^{4-}$ (2×10^{-4} mol dm^{-3}) were suspended/dissolved in a CH_3CN/H_2O 1/1 mixture (3 mL) containing the alkene (3×10^{-2} mol dm^{-3}) and NaBr (2×10^{-1} mol dm^{-3}), and irradiated (4 h, $\lambda > 300$ nm) under aerobic conditions at 298 ± 1 K. Reported values are the average of three repeated experiments.

[b] By GC analysis—EP: epoxide; BrOH: bromohydrin; BrBr: dibromo derivative; OMP: other monooxygenated products, such as alcohols, ketones, aldehydes (benzaldehyde from styrene, 2-methyl benzaldehyde from indene), and lactones (benzofuranone from indene).

[c] Amount of products in μmol accumulated in 3 mL of CH_3CN/H_2O mixture.

[d] For indene, 2-bromo-3-phenyl propenale is also produced (the missing amount to give 100%).

[e] The missing amount to give 100% consists of dimeric products.

dispersing CH_3CN/H_2O mixture were required to dissolve the alkenes under investigation. In all cases the formation of hydroperoxides was accompanied by the functionalization of the alkenes to yield epoxides (EP), bromohydrins (BrOH), dibromides (BrBr), and monooxygenated species such as alcohols, ketones, and aldehydes (OMP) with a mass balance of about 80%.

Overall yields and product distribution of these compounds are reported in Table 3 (first row for each alkene). It can be seen that epoxides and bromohydrins represent an important fraction in the final product distribution, with the best yield in these products (69%) when irradiation of the Amb/$W_{10}O_{32}^{4-}$ system was carried out in the presence of 1-methyl-1-cyclohexene. Photoexcitation of the Amb/$W_{10}O_{32}^{4-}$ system without bromide (data not reported in Table 3) always yielded a large fraction of monooxygenated products (OMP), such as alcohols, ketones, and aldehydes with a minor amount of epoxides. These oxygenated products derive from the photogenerated hydroperoxides, which undergo degenerate branching reactions [13].
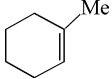
The second row for each alkene in Table 3 reports the results obtained with homogeneous $W_{10}O_{32}^{4-}$ (2×10^{-4} mol dm^{-3}) and enable us to evaluate how much the polymeric support affects the photocatalytic properties of decatungstate. The effect of heterogenization on efficiency seems to be strongly influenced by the degree of sterical hindrance of the double bond. As a matter of fact, in the case of styrene, whose double bond is the less hindered in the series of the studied olefins,

the heterogeneous system results more efficient than the homogeneous one. Moreover, when the catalyst is immobilized, the extent of competing polymerization processes is reduced. As to cyclohexene and indene, heterogenization did not reduce significantly the total amount of end products, but had a negative effect on the reactivity of 1-methyl-1-cyclohexene and 1-phenyl-1-cyclohexene. It is likely that the methyl or phenyl groups hinder the interaction of these two alkenes with the active solid surface.

As far as the chemoselectivity of the photocatalytic process is concerned, an important result is the increase in the yields of epoxides and bromohydrins from cyclohexene, 1-methyl-1-cyclohexene, and styrene upon heterogenization of the decatungstate. Moreover, the solid matrix plays the important function of inhibiting the formation of monooxygenated products (OMP). A possible explanation is that the enrichment of bromide anions on the surface of amberlite may favor their reaction with the photogenerated hydroperoxides, which, otherwise, are able to diffuse into the solution bulk to give oxygen-containing products.

Another remarkable result caused by heterogenization is the increased stability of the decatungstate. GC-analyses revealed that the decrease in activity of the supported photocatalyst in terms of detected end products was less than 5% after three repeated cycles. On the contrary, we observed about 50% degradation of the polyoxoanion at the end of analogous experiments carried out in homogeneous solution.

Table 4
Effect of the dispersing medium on the photocatalytic properties[a] of Amb/$W_{10}O_{32}^{4-}$ in the bromide-assisted functionalization of alkenes

Alkene	Dispersing medium	Alkene products distribution[b] (%)				Alkene total yield[c] (μmol)
		EP	BrOH	BrBr	OMP	
(cyclohexene)	CH_3CN/H_2O 1/5; Br^- 2×10^{-1} mol dm^{-3}	27	46	27	0	3.6
	CH_3CN/H_2O 1/5; Br^- 3×10^{-2} mol dm^{-3}	25	60	10	5	3.6
(1-methyl-cyclohexene, Me)	CH_3CN/H_2O 19/1; Br^- 2×10^{-1} mol dm^{-3}	21	4	41	34	4.8

[a] In a typical experiment Amb/$W_{10}O_{32}^{4-}$ (0.1 g) was suspended in the chosen dispersing medium (3 mL) containing the alkene (3×10^{-2}), and irradiated (4 h, $\lambda > 300$ nm) under aerobic conditions at 298 ± 1 K. Reported values are the average values of three repeated experiments.
[b] By GC analysis—EP: epoxide; BrOH: bromohydrin; BrBr: dibromo derivative; OMP: other monooxygenated products (alcohols and ketones).
[c] Amount of products in μmol accumulated in 3 mL of CH_3CN/H_2O mixture.

3.4. Reactivity of peroxides in the presence of Br^- and $W_{10}O_{32}^{4-}$

The following experiments were carried out in order to gain more insight into the role of the photogenerated hydroperoxides in the described bromination processes. The Amb/$W_{10}O_{32}^{4-}$ system was irradiated in CH_3CN/H_2O/phenol or CH_3CN/H_2O/cyclohexene mixtures in the absence of bromide to accumulate organic hydroperoxides up to a final concentration of about 3×10^{-3} mol dm^{-3}. A subsequent addition of Br^- in the dark led to the disappearance of the photogenerated peroxides and to the formation, after 4 h, of comparable amounts of the same products obtained during the photocatalytic experiments. Control experiments demonstrated that no appreciable reactivity of the substrate occurred in the absence of Br^- within 4 h in the dark. These results indicate that the bromination of the organic substrates takes place as a consequence of non-photoassisted reactions, that follow the photocatalytic production of hydroperoxides. This reaction should be able to induce a two-electron oxidation of Br^- to an active species, whose electrophilic attack on carbon–carbon double bond gives the observed brominated products (Scheme 2).

Other experiments were performed using a CH_3CN/H_2O/substrate mixture containing the photogenerated hydroperoxides after removal of the solid Amb/$W_{10}O_{32}^{4-}$ system. The addition of Br^- ions did not induce any detectable decrease in the hydroperoxides concentration and any functionalization of the substrate after 4 h in the dark. These results clearly indicate that the decatungstate is necessary not only for inducing the light-assisted formation of hydroperoxides, but also for catalyzing their reaction with Br^- to form the brominating species. On

the basis of literature data [33,34], it is reasonable to assume that the decatungstate-assisted activation of hydroperoxides occurs through the formation of peroxo-tungsten species.

The H_2O and Br^- ions are in competition as nucleophilic reagents (see Scheme 2). In order to favor the formation of bromohydrins and, consequently, of epoxides, we increased the amount of water in the dispersing medium as much as possible (first row in Table 4). The concentration ratio [epoxide + bromohydrin/dibromide] increased from 0.86 to 2.7 in the case of cyclohexene (to be compared with the product distribution in Table 3). This ratio reached a value of 8.5, if the increase in water was accompanied by a decrease in the initial concentration of bromide ions (second row in Table 4). In the case of 1-methyl-1-cyclohexene the ratio [epoxide + bromohydrin/dibromo derivative] increased from 0.6 to 13.8 increasing the amount of water from 5 to 50% (to be compared with the product distribution in Tables 3 and 4).

The matrix effect is in line with previous works of Jacobs and coworkers [7,33,35,36]. They found that the layered double hydroxides (LDH) exchanged with WO_4^{2-} were active in the epoxidation of allylic and homoallylic alcohols in the presence of an excess of H_2O_2 and Br^- anions. The positive effect of the LDH matrix on the catalytic activity of WO_4^{2-} was ascribed to the positive electric potential of its solid surface, which favors the approach of Br^- to the adsorbed peroxotungstate active species.

4. Conclusions

Photochemical excitation of $(nBu_4N)_4W_{10}O_{32}$ heterogenized with Amberlite IRA-900 and dispersed in a CH_3CN/H_2O mixture causes the reductive activation of O_2 to alkyl hydroperoxides. Suitable experimental conditions have been found for the conversion of activated arenes to monobrominated derivatives, and of cycloalkenes to the corresponding bromohydrins and dibromides, with bromohydrins as intermediates for the formation of epoxides. These results are particularly interesting since with classical organic methods it is quite difficult to stop the functionalization of activated arenes at the monobromination stage, and epoxides are important building blocks in applied syntheses.
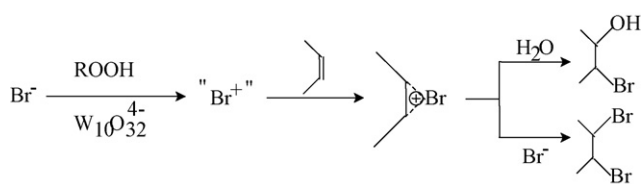
Scheme 2. Mechanism for the Br^--assisted bromination of olefinic substrates by photogenerated hydroperoxides and $W_{10}O_{32}^{4-}$.

In all investigated systems, the detected products accounted for about the 80% of the overall consumed substrate. The Amb/$W_{10}O_{32}{}^{4-}$ system is leak-free under irradiation and reusable up to three runs in the Br^--assisted functionalization of alkenes, and without significant loss of activity. The decrease in activity of the supported photocatalyst observed in the case of arenes was about 20% after three repeated cycles.

The brominating species is generated in situ, as a consequence of the oxidation of Br^- by the photogenerated peroxides. This process is catalyzed by the decatungstate, which, therefore, plays also a catalytic role in addition to the photocatalytic one.

The anionic exchange resin plays a crucial role in fostering the enrichment of bromide anions close to the surface and, consequently, their reaction with the photogenerated hydroperoxides. As a matter of fact, the efficiency of the bromination photocatalytic processes benefit sometimes by the heterogenization of the decatungstate. Phenol bromination, for example, occurs with 10 times higher efficiency compared with the same process carried in homogeneous phase. In most cases, however, heterogenization did not reduce significantly the total amount of end products. This is an interesting result in view of the use of the described photoactive system in heterogeneous catalysis, since a significant loss of activity usually occurs when a homogeneous catalyst is immobilized on a solid support.

As to the chemoselectivity of the photocatalytic process, we have found that the solid matrix plays the important function of increasing the yields of epoxides and bromohydrins from cyclohexene, 1-methyl-1-cyclohexene, and styrene, upon heterogenization of the decatungstate. The solid matrix can also control the chemoselectivity in anisole bromination, by favoring the functionalization of the *para* position. The chemoselectivity of the alkene bromination is also affected by the nature of the dispersing medium. In fact, the yields in bromohydrins can be enhanced increasing the amount of water.

Acknowledgements

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