



CH₂Cl₂-assisted functionalization of cycloalkenes by photoexcited (nBu₄N)₄W₁₀O₃₂ heterogenized on SiO₂

A. Maldotti*, R. Amadelli, I. Vitali, L. Borgatti, A. Molinari

Dipartimento di Chimica, I.S.O.F. C.N.R., Sezione di Ferrara, Università di Ferrara, Via L. Borsari 46, 44100 Ferrara, Italy

Received 29 August 2002; received in revised form 23 January 2003; accepted 12 February 2003

Dedicated to Professor Renato Ugo on the occasion of his 65th birthday

Abstract

The photocatalytic oxidation of cyclohexene and cyclooctene by (nBu₄N)₄W₁₀O₃₂ supported on silica is strongly affected by the presence of CH₂Cl₂ as co-substrate. CH₂Cl₂ undergoes oxidative pathway yielding radical intermediates. This species are involved in the subsequent epoxidation of cyclohexene and cyclooctene, which occurs with a selectivity higher than 50%. A major competing reaction is the well known oxidation of the alkenes to the corresponding allylic hydroperoxides. Cyclooctene epoxide is stable enough to be accumulated in the irradiated solution. On the contrary, cyclohexene epoxide undergoes ring opening to form 2-chlorocyclohexanol. The good stability of the heterogenized decatungstate is demonstrated by the fact that it could be employed at least three times without suffering any appreciable loss of photocatalytic activity. Decatungstate loading and initial cyclohexene concentration influence the chemoselectivity of the photocatalytic process. In particular a high number of active centers and a low cyclohexene concentration favor a chlorination pathway of cyclohexene, which leads to the formation of 20% of 3-chlorocyclohexene.

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Keywords: Heterogeneous photocatalysis; Photoexcited polyoxotungstate; CH₂Cl₂ photooxidation; Epoxidation with O₂; Oxychlorination

1. Introduction

Catalytic oxidation represents an ever expanding area of interest for industrial preparation of functionalized hydrocarbons and fine chemicals [1–3]. In this framework, it has been well established that photocatalysis can provide an alternative approach to more conventional synthetic pathways, giving innovative and economically advantageous oxofunctionalization of hydrocarbons by O₂ in mild conditions [4]. A number of examples of oxidative photocatalysts are

based on the use of polyoxometallates, thanks to their ability to undergo photoinduced electron transfers without irreversible modifications [5–14].

Heterogenization of polyoxometallates has attracted particular attention since it presents some important advantages [15]: (i) the solid surface may control efficiency and selectivity of the photocatalytic processes; (ii) the support makes the systems more easily handled and recycled than in homogeneous solution; (iii) it allows a more free choice of the reaction medium. Some of our contributions in this research area have dealt with the use of (nBu₄N)₄W₁₀O₃₂ on solid matrices, such as amorphous silica and MCM-41 materials [16–19]. We demonstrated that suitable experimental conditions can be found in organic dispersing media

* Corresponding author. Tel.: +39-0532-291-147;

fax: +39-0532-240-709.

E-mail address: mld@unife.it (A. Maldotti).

in order to avoid photoinduced mineralization of the substrate by these photocatalytic systems [16]. This is a major advantage when accumulation of valuable oxidation intermediates is sought and total photodegradation is an unwanted competing reaction.

In this work, we investigate the possibility that photocatalytic oxidation of alkenes by $(n\text{Bu}_4\text{N})_4\text{W}_{10}\text{O}_{32}$ anchored on SiO_2 may be affected by the presence of CH_2Cl_2 as co-substrate. It is known from literature data that the excited state potential of $(n\text{Bu}_4\text{N})_4\text{W}_{10}\text{O}_{32}$ is positive enough to oxidize CH_2Cl_2 [20]. We explore the possibility that the oxidizing properties of the photoexcited decatungstate may lead to the formation of highly reactive chloro-intermediates able to induce mono-oxygenation and/or chlorination of alkenes in mild temperature and pressure conditions [21–24]. These objectives are of great interest in applied synthesis, since epoxides are very versatile building blocks in fine chemistry and organic synthesis [25] and chlorination of alkenes is still carried out by petrochemical industry using hazardous reagents and drastic conditions [26].

The decatungstate $(n\text{Bu}_4\text{N})_4\text{W}_{10}\text{O}_{32}$ is immobilized on silica following a previously reported procedure [27,16–19]. The loading is 10 and 60% (w/w) to give the heterogeneous systems $\text{SiO}_2/\text{W}10\%$ and $\text{SiO}_2/\text{W}60\%$, respectively. Their photocatalytic properties are assessed in the oxidation of cyclohexene and cyclooctene in the presence of CH_2Cl_2 . We have chosen these two substrates as representative unsaturated alkenes [28]. Different factors such as decatungstate loading, nature and concentration of the substrate are investigated. The primary radical species are detected by the electron paramagnetic resonance (epr) spin trapping technique.

2. Experimental section

2.1. Materials

The synthesis of $(n\text{Bu}_4\text{N})_4\text{W}_{10}\text{O}_{32}$ was performed following literature procedure [29]. Its subsequent heterogenization on silica, to give $\text{SiO}_2/\text{W}10\%$ and $\text{SiO}_2/\text{W}60\%$ was carried out according to literature methods [16–19]. The decatungstate (0.1 or 0.6 g) was dissolved in a $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ mixture (4/1) con-

taining 1 g of colloidal silica (0.012 micron, Strem Chemicals). The suspensions were shaken at room temperature (1 h) and then the excess of solvent was evaporated. The sample was dried at 100°C for 24 h.

The commercial products CH_3CN , CH_2Cl_2 from Fluka were spectrophotometric grade. Cyclohexene and cyclooctene from Aldrich were distilled before use. The spin trap α -phenyl *N*-tert-butyl-nitron (pbn), 2-cyclohexen-1-one, 2-cyclohexen-1-ol and cyclohexene and cyclooctene epoxides were obtained from Aldrich. 2-Chlorocyclohexanol was prepared by addition of HCl to a solution of cyclohexene epoxide of known concentration. The concentration of 3-chlorocyclohexene, which is not a commercial product, was estimated using the calibration curve of 2-cyclohexen-1-one, assuming that the answer of the FID detector is similar for the two compounds.

2.2. Apparatus

Photochemical excitations were performed with a Helios Italquartz Q400 medium-pressure mercury lamp, selecting wavelengths higher than 300 nm with a cut-off filter, at room temperature ($298 \pm 1\text{ K}$) and 760 Torr of O_2 . Gas chromatographic 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; $0.32\ \mu\text{m} \times 0.25\ \mu\text{m}$ film thickness) capillary column. Quantitative analysis has been carried out with calibration curves obtained from authentic samples. Each photocatalytic experiment was repeated four times in order to evaluate the errors, which never exceeded $\pm 10\%$. GC-MS analyses were performed using a GC-8000 (Fisons Instrument) equipped with a Mega OV1 (25 m; i.d. = $0.32\ \text{mm}$) capillary column and with a mass spectrometer MD-800 as a detector. The epr spectra were recorded with a X-band Bruker 220 SE spectrometer.

2.3. Procedures

$\text{SiO}_2/\text{W}10\%$ or $\text{SiO}_2/\text{W}60\%$ ($15\ \text{g dm}^{-3}$, 1.35 and $8.2\ \mu\text{mol}$ of $\text{W}_{10}\text{O}_{32}^{4-}$, respectively) were kept in suspension under magnetic stirring at 1000 rotation/min in 3 ml of CH_2Cl_2 or CH_3CN containing cyclohexene or cyclooctene (1×10^{-1} or $1 \times 10^{-2}\ \text{mol dm}^{-3}$) and irradiated ($\lambda > 300\ \text{nm}$) for 60 min inside a Pyrex

reactor and under an atmosphere of 101.3 kPa of O₂. When necessary, deaeration of the samples was done by means of a vacuum line equipped with diffusive pump. The chosen amount of photocatalyst was such that the maximum absorption of incident light was ensured. After irradiation the sample was centrifuged, the products that remained adsorbed were extracted with CH₂Cl₂ (2 × 3 ml) and the collected organic phases were analysed by GC or GC–MS. The determination of hydroperoxides was carried out by a spectrophotometric standard method reported in the literature [30] while the evaluation of Cl[−] was performed through potentiometric titration with AgNO₃. When necessary, GC analyses were done after addition of an excess of NaOH. Control measurements showed that no detectable oxidation products were observed when blank experiments were carried out in the absence of light or O₂. Likewise, no oxidation product was also observed irradiating the pristine SiO₂. Photocatalytic experiments were also done using cyclohexene epoxide (1 × 10^{−2} mol dm^{−3}) as substrate.

The epr spin trapping experiments were carried out by irradiating the heterogeneous photocatalyst dispersed in CH₂Cl₂/cyclohexene 6/1 or in CH₂Cl₂ in the presence of pbn (5 × 10^{−2} mol dm^{−3}). Photochemical excitation was performed directly inside the epr cavity, using a flat quartz cell as reaction vessel. Signals were not observed in the dark or in the absence of photocatalyst.

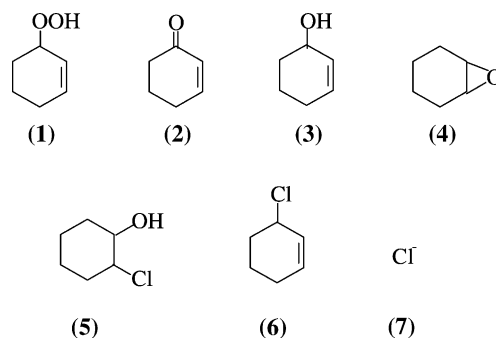
3. Results and discussion

We have previously carried out a structural characterization of the SiO₂/W10% and SiO₂/W60% systems by spectroscopic and N₂-adsorption–desorption techniques [18,19]. One of the main conclusion was that both the anion W₁₀O₃₂^{4−} and its counterions are anchored on the surface of silica without undergoing any appreciable modification. Although the precise stoichiometry of association complexes counter-ion⁺/W₁₀O₃₂^{4−} on silica is not an easy task [31–33], we could state that *n*Bu₄N⁺ cations act as a bridge between the negative surface of silica and the W₁₀O₃₂^{4−} anions, according to an ion-mediated adsorption pathway of the type SiO[−]/counter-ion⁺/W₁₀O₃₂^{4−}.

N₂-adsorption–desorption experiments [18] have shown that all the systems SiO₂, SiO₂/W10% and SiO₂/W60% present a disordered pore distribution and that the majority of the pores is larger than 10 nm in size. The surface area of SiO₂ is reduced from 95 to 54 or 40 m²/g when the support is impregnated with 10 or 60% decatungstate, respectively. A parallel decrease of the total pore volume with increasing amounts of (*n*Bu₄N)₄W₁₀O₃₂ has been also found. In particular, SiO₂/W60% loses more than 50% of the initial porosity.

3.1. Photocatalytic oxidation of cyclohexene with SiO₂/W10% dispersed in CH₃CN

SiO₂/W10% (15 g dm^{−3}) was dispersed in CH₃CN and irradiated (λ > 300 nm) in the presence of cyclohexene (1 × 10^{−1} mol dm^{−3}) and O₂ (101.3 kPa). GC–MS and iodometric analyses gave evidence that the allylic hydroperoxide (1), 2-cyclohexen-1-one (2), 2-cyclohexen-1-ol (3) and cyclohexene epoxide (4) were formed (Scheme 1), and that they represented more than 90% of the oxidized alkene. Overall yield and product distribution after 60 min irradiation are reported in Table 1 (Entry 2). Previous experiments carried out with cyclohexene that was one order of magnitude more concentrated led to very similar results (Entry 1) [17]. According to literature data the photocatalytic oxidation of cyclohexene by W₁₀O₃₂^{4−} leads to the formation of 1 as major product [7,14,17]. Generally speaking, hydroperoxides are widely used as intermediates for oxidative syntheses, such as the hydrocarbon monooxygenation catalyzed by iron porphyrins [8,17,34].



Scheme 1. Obtained products from the CH₂Cl₂-assisted photocatalytic oxidation of cyclohexene.

Table 1
Photocatalytic properties^a of heterogenized $W_{10}O_{32}^{4-}$ in the oxygenation of cyclohexene

Entry	Photocatalytic system	Product distribution (%)									Total concentration ^b ($\times 10^3$ mol dm ⁻³)
		1	2	3	4	5	6	7	Other ^c		
1 ^d	SiO ₂ /W10% CH ₃ CN/C ₆ H ₁₀ (1 mol dm ⁻³)	89	6.4	1.9	1.2	–	–	–	–	1.5	8.0
2	SiO ₂ /W10% CH ₃ CN/C ₆ H ₁₀ (1×10^{-1} mol dm ⁻³)	82.5	10	6	1.5	–	–	–	–	–	2.9
3	SiO ₂ /W10% CH ₂ Cl ₂ /C ₆ H ₁₀ (1×10^{-1} mol dm ⁻³)	24.5	16	8.5	1.5	42.5	1.5	5.5	–	–	8.7
4	SiO ₂ /W60% CH ₂ Cl ₂ /C ₆ H ₁₀ (1×10^{-1} mol dm ⁻³)	34.6	14	7.3	0.8	35.3	3.7	4.3	–	–	15.0
5	SiO ₂ /W10% CH ₂ Cl ₂ /C ₆ H ₁₀ (1×10^{-2} mol dm ⁻³)	30	6.5	0.5	1.5	54	7.5	^e	–	–	4.2
6	SiO ₂ /W60% CH ₂ Cl ₂ /C ₆ H ₁₀ (1×10^{-2} mol dm ⁻³)	29	3.5	4.5	2.0	42	19	^e	–	–	4.5

^a SiO₂/W10% or SiO₂/W60% (15 g dm⁻³) were dispersed in 3 ml of CH₃CN or of CH₂Cl₂ containing C₆H₁₀ (1×10^{-1} or 1×10^{-2} mol dm⁻³) and irradiated ($\lambda > 300$ nm) at 25 ± 1 °C under 101.3 kPa of O₂. Reported values are the mean of four repeated experiments.

^b After 60 min irradiation.

^c *trans*-Cyclohexane-1,2-diol monocyclohexenyl ether.

^d See [17].

^e Not determined.

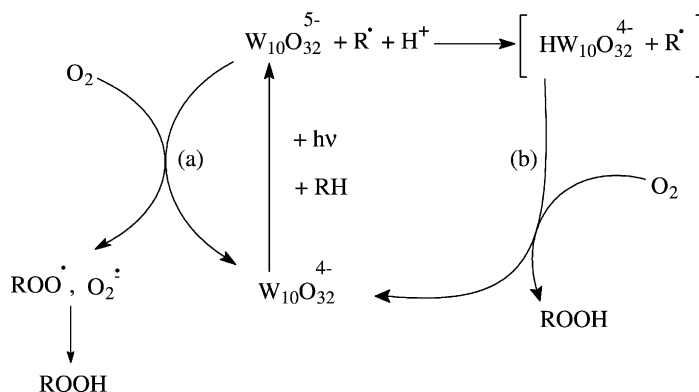
As summarized by Scheme 2 for a generic substrate RH [7,14,17], the photoexcited decatungstate is able to initiate the oxidation of the substrate through hydrogen abstraction. A key step in the photocatalytic cycle under aerobic conditions is the subsequent reoxidation of the decatungstate by O₂. This process may lead to the reductive activation of O₂ to O₂^{•-} and to peroxy radicals, according to pathway (a). Alternatively, the photocatalytic cycle involves the formation of a protonated one-electron-reduced decatungstate, which should react with peroxy radicals inside the solvent cage to give the hydroperoxide as schematized by pathway (b). The formation of other minor photo-products, such as **2**, **3** and **4**, occurs through subsequent reactions, which involve hydroperoxides, radical

species, O₂ and the decatungstate both in its oxidized and photoreduced forms [14,17,35].

The possibility that **1** can react with cyclohexene in the dark without the involvement of the photoexcited decatungstate can be ruled out since the concentration of oxidation products remains constant when irradiation is interrupted. Direct photochemistry of **1** to give **2** and **3** can be also excluded because the chosen amount of decatungstate avoids any possible light absorption by the hydroperoxide.

3.2. Hydroxychlorination of cyclohexene

The above photocatalytic experiments were repeated using CH₂Cl₂ as dispersing medium instead



Scheme 2. Photocatalytic cycle of $W_{10}O_{32}^{4-}$ in the presence of an organic substrate RH and of O₂.

of CH_3CN . The reaction products reported in Table 1 (Entry 3) account for more than 90% of the oxidized cyclohexene. A comparison with the results of Entry 2 indicates that the presence of CH_2Cl_2 significantly affects the photocatalytic activity of $\text{SiO}_2/\text{W}10\%$, both in terms of product distribution and overall conversion yield.

The first important effect consists in the formation of a considerable amount of 2-chlorocyclohexanol (**5**) as additional product (Scheme 1). Halohydrines are well known to undergo facile conversion to the corresponding epoxides under alkaline conditions. Accordingly, we could easily transform **5** into **4** by addition of an excess of NaOH to the irradiated sample. The observed formation of 3-chlorocyclohexene (**6**) and Cl^- ions (**7**) will be discussed in the following paragraphs.

Table 1 shows that a second important effect of CH_2Cl_2 is that of increasing of about three times the overall yield of the photocatalytic conversion of cyclohexene. As far as the stability of the heterogeneous photocatalyst is concerned, it is worth noting that it could be employed at least three times without suffering any appreciable loss of photocatalytic activity.

3.3. Oxidation to radical species

The epr spin trapping technique is a powerful means of collecting information about the reaction mechanism. In fact, this technique can help identification of short-lived radical species, which eventually derive from primary photochemical processes [8,20,36]. Few seconds irradiation of $\text{SiO}_2/\text{W}10\%$ in $\text{CH}_2\text{Cl}_2/\text{cyclohexene}$ in the presence of the spin trap pbn gives the epr spectrum reported in Fig. 1A. It consists of a triplet of doublets with hyperfine coupling constants $a_N = 13.8\text{ G}$ and $a_H = 2.1\text{ G}$. These values indicate that, in agreement with the results previously obtained in CH_3CN homogeneous solutions [17], $\text{C}_6\text{H}_9\cdot$ are formed and trapped according to Scheme 2 and Eq. (1).

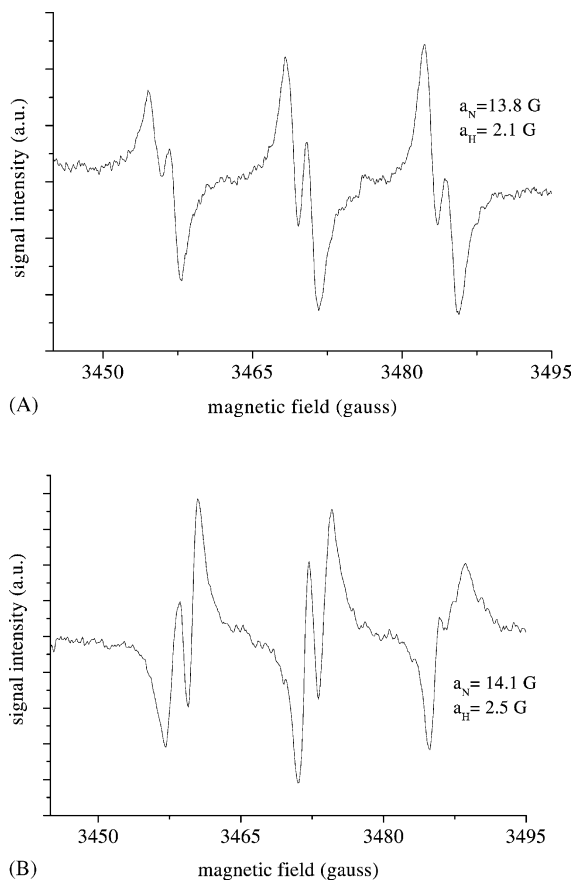
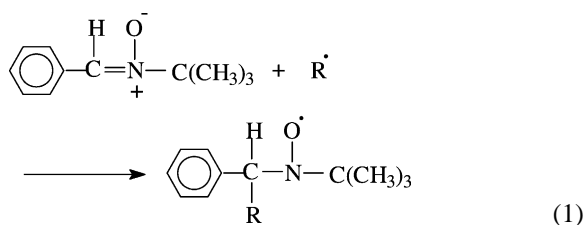


Fig. 1. The epr spectra obtained upon irradiation ($\lambda > 300\text{ nm}$) of $\text{SiO}_2/\text{W}10\%$ dispersed in $\text{CH}_2\text{Cl}_2/\text{cyclohexene}$ 6/1 (A) and in CH_2Cl_2 (B) in the presence of pbn ($5 \times 10^{-2}\text{ mol dm}^{-3}$).

Literature data regarding the photocatalytic oxidation of CH_2Cl_2 by the semiconducting oxide TiO_2 have been previously reported by other authors [37,38]. The possibility that CH_2Cl_2 may undergo direct oxidation by photoexcited $(n\text{Bu}_4\text{N})_4\text{W}_{10}\text{O}_{32}$ is here demonstrated by the observation that irradiation of $\text{SiO}_2/\text{W}10\%$ in neat CH_2Cl_2 yields the epr spectrum shown in Fig. 1B. This spectrum, which presents hyperfine coupling constants ($a_N = 14.1\text{ G}$ and $a_H = 2.5\text{ G}$) that are sensibly different from those of the $\text{C}_6\text{H}_9\text{-pbn}^\cdot$ adduct, can be ascribed to the formation of the $\text{CHCl}_2\text{-pbn}^\cdot$ paramagnetic species [39].

The lack of epr signals due to the adduct $\text{CHCl}_2\text{-pbn}^\cdot$ when also cyclohexene is present in the reaction medium is not surprising. In fact, the relative intensities of different superimposed spectra of radical

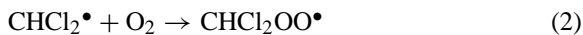
adducts with pbn depends on various factors, such as the lifetimes of the radicals, their reaction rates with the trap, the stabilities of the paramagnetic adducts [40]. For the same reasons, it is not possible to obtain quantitative information about the relative rates of formation of CHCl_2^\bullet and $\text{C}_6\text{H}_9^\bullet$ by comparing the intensities of the spectra of Fig. 1.

However, on the basis of the above results we can state that both CH_2Cl_2 and cyclohexene can be oxidized to the corresponding radical species by photoexcited decatungstate; in fact CHCl_2^\bullet may be formed thanks to the high concentration of the former, while $\text{C}_6\text{H}_9^\bullet$ are easily produced from the latter due to its activated allylic position.

3.4. The role of O_2

No oxidation product of cyclohexene was observed when the photocatalytic experiments were performed in deaerated CH_2Cl_2 . The only effect in this case was an irreversible reduction of $\text{W}_{10}\text{O}_{32}^{4-}$ to $\text{W}_{10}\text{O}_{32}^{5-}$, as demonstrated by the blue color of the irradiated solution. These results indicate that (i) the electron scavenging properties of CH_2Cl_2 are not sufficient to avoid the accumulation of $\text{W}_{10}\text{O}_{32}^{5-}$, (ii) O_2 plays a main role in the photocatalytic process and (iii) the observed effects of CH_2Cl_2 on the overall yield of the photocatalytic process may be ascribed to its oxidative pathway.

The molecule of oxygen may react with the photo-generated CHCl_2^\bullet to give the corresponding peroxy radicals according to Eq. (2). There is ample evidence that this reaction occurs and is very fast [37,41]. According to literature data on the nucleophilic reactivity of $\text{O}_2^{\bullet-}$ [42] halogenated peroxy radicals may be also formed as a consequence of Eq. (3), which involves the photogenerated $\text{O}_2^{\bullet-}$ (see Scheme 2a).



One possible reaction pathway for peroxy radicals is hydrogen abstraction to yield the corresponding hydroperoxides. Accordingly, we accumulated $0.8 \times 10^{-3} \text{ mol dm}^{-3}$ of halogenated hydroperoxides when the photocatalytic experiment was carried out in neat CH_2Cl_2 . Subsequent addition of cyclohexene to the irradiated mixture was accompanied by an instantane-

ous disappearance of these hydroperoxides. Due to their low stability in the presence of cyclohexene, we can safely assume that total amount of peroxides reported in Table 1 only refers to $\text{C}_6\text{H}_9\text{OOH}$.

The formation of cyclohexene oxide **4** may be ascribed to Eq. (4), possibly in competition with hydrogen abstraction. In fact, literature data report that the reaction of peroxy radicals with alkenes to give epoxides is possible [43,44] and that halogenated peroxy radicals are particularly reactive towards alkenes [45]. Furthermore, we cannot rule out the possibility that RO^\bullet formed following equation 4 could react with the alkene giving an additional amount of $\text{C}_6\text{H}_9^\bullet$.

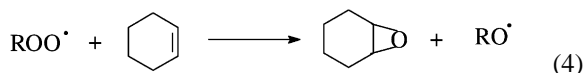
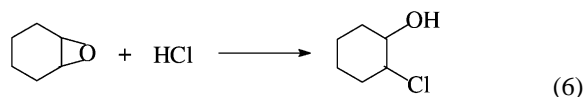


Fig. 2 reports the formation trends of **4** and **5**: both are formed in comparable amounts in the first 30 min, then the epoxide concentration decreases and simultaneously that of 2-chlorocyclohexanol increases so much that it becomes the main oxidation product. This strongly suggests that **5** may originate from **4**, likely from the opening of the epoxide ring by acid catalysis. In fact enough amount of HCl can be probably formed during photomineralization of CH_2Cl_2 following equation 5 [37,38]. Then the epoxide ring opens as a consequence of a nucleophilic attack by Cl^- catalyzed by the H^+ (see Scheme 2), giving 2-chlorocyclohexanol, as shown in Eq. (6). The following results are in agreement with the above statement: (i) addition of HCl to CH_2Cl_2 solution of **4** results in the formation of **5** also in the dark; (ii) irradiation of $\text{SiO}_2/\text{W}10\%$ dispersed in CH_2Cl_2 containing **4** as substrate yields **5** as single product.



3.5. Epoxidation of cyclooctene

Treatments with HCl indicate that cyclooctene epoxide is more stable than cyclohexene epoxide towards ring opening and should, therefore, be accumulated under photocatalytic conditions. Consequently, irradiation of $\text{SiO}_2/\text{W}10\%$ dispersed in CH_2Cl_2 containing cyclooctene ($1 \times 10^{-1} \text{ mol dm}^{-3}$) and O_2

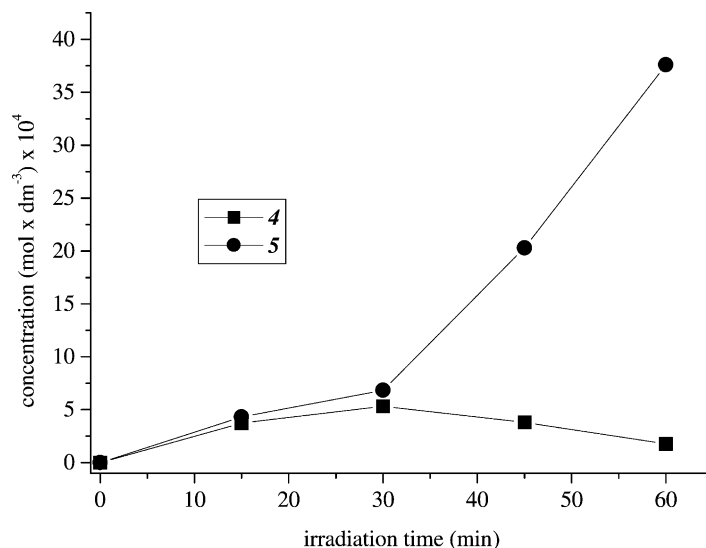


Fig. 2. Molar concentrations of cyclohexene epoxide (4) and of 2-chlorocyclohexanol (5) vs. time obtained upon irradiation ($\lambda > 300$ nm) of $\text{SiO}_2/\text{W}10\%$ (15 g dm^{-3}) in CH_2Cl_2 containing cyclohexene ($1 \times 10^{-1} \text{ mol dm}^{-3}$) under 101.3 kPa of O_2 .

(101.3 kPa) gave cyclooctene epoxide (63%) and the allyl hydroperoxide (37%) as main products. The important role of CH_2Cl_2 in the photocatalytic epoxidation of the double bond is confirmed by the observation that a reverse trend in the formation of products was obtained when the experiment was carried out in CH_3CN as dispersing medium. In fact, in this case the main product was the hydroperoxide (90%) and cyclooctene epoxide was obtained in minor amount (10%).

3.6. Chlorination of cyclohexene

The effect of increasing the decatungstate loading on silica up to 60% was examined in some experiments. Entry 4 of Table 1 shows that the use of this system has two main effects: a significant increase of the overall oxidation yield and a higher selectivity in the formation of 6. Entries 5 and 6 demonstrate that the formation of 6 is also favored by low initial concentration of cyclohexene.

A great number of factors, including adsorption–desorption equilibria of reagents and reaction intermediates, may affect the chemoselectivity of the photocatalytic process. Generally speaking, a higher loading of decatungstate on the support is expected to enhance the oxidizing properties of the photocatalyst

as a consequence of higher number of photoactive sites dispersed on the surface. This statement is confirmed by previous measurements of BET areas [18].

An increase in the number of the active sites, together with a reduced initial concentration of cyclohexene can create a very strong oxidizing environment for CH_2Cl_2 , which is, in some way, analogous to that typical in the industrial oxychlorination of alkenes. The exact mechanism of this process is unknown, but it requires very high temperature, the presence of peroxides and chloride ions.

4. Conclusions

The presence of CH_2Cl_2 as co-substrate strongly affects the photocatalytic activity of heterogenized $(n\text{Bu}_4\text{N})_4\text{W}_{10}\text{O}_{32}$ in the oxidation of cyclohexene and cyclooctene. The effect of CH_2Cl_2 is ascribed to its oxidation pathway, which leads to the formation of highly reactive radical intermediates. These species are likely involved in the monooxygenation of cyclohexene and cyclooctene to give the corresponding epoxides. Cyclooctene epoxide is stable enough to be accumulated in the irradiated solution. On the contrary, cyclohexene epoxide undergoes ring opening to form 2-chlorocyclohexanol. However, it is worth noting that

a facile conversion of this halohydrine to cyclohexene epoxide is possible in alkaline solution. On this basis, we can claim that a CH_2Cl_2 -assisted photocatalytic epoxidation of alkenes with O_2 is here realized for the first time. This process occurs with a selectivity higher than 50%. A major competing reaction is the well known oxidation of the alkenes to the corresponding allylic hydroperoxides, which, however, are intermediates of interest in oxidative syntheses.

Other results of particular relevance from a synthetic point of view are the following: (i) the process occurs with light of the near ultraviolet and in mild temperature and pressure conditions; (ii) the positive effect of CH_2Cl_2 on the overall oxidation process of cyclohexene is very significant, increasing it to about three times; (iii) the stability of the heterogenized decatungstate is demonstrated by the fact that it could be employed at least three times without suffering any appreciable loss of photocatalytic activity; (iv) the good mass balance obtained indicates that the photocatalyst does not cause mineralization of the alkene to CO_2 .

Both decatungstate loading and initial concentration of the alkene influence the chemoselectivity of the photocatalytic process. In particular, a high number of active centers and a low cyclohexene concentration favor a chlorination pathway of cyclohexene, which leads to the formation of appreciable amounts (20%) of 3-chlorocyclohexene.

Further experiments are in progress to investigate the possibility to improve efficiency and selectivity of either epoxidation or halogenation of alkenes by photoexcited heterogenized polyoxometallates using more easily oxidizable inorganic halides. These compounds also present the important advantage of being less expensive and health hazardous than CH_2Cl_2 in view of further developments of this method in applied synthesis.

Acknowledgements

The authors are very grateful for the financial support of MIUR, CNR, INCA Consortium.

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