

# Photocatalytic air oxidation of cyclohexane in $\text{CH}_2\text{Cl}_2\text{-C}_6\text{H}_{12}$ mixtures over $\text{TiO}_2$ particles

## An attempt to rationalize the positive effect of dichloromethane on the yields of valuable oxygenates

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### Abstract

Product selectivity and yields of cyclohexanol and cyclohexanone formation in the photocatalytic air oxidation of cyclohexane on  $\text{TiO}_2$  particles in the presence of dichloromethane were determined at  $303 \pm 5 \text{ nm}$  and  $4.35 \text{ nEinstein cm}^{-2} \text{ s}^{-1}$ , as a function of cyclohexane molar fraction,  $x$ . Apparent initial photonic efficiencies,  $\xi_{\text{ox}}$ , for total monooxygenated products (cyclohexanol + cyclohexanone) ranged from 19 to 51% depending on solvent composition, attaining a maximum for an equimolar mixture of  $\text{CH}_2\text{Cl}_2\text{-C}_6\text{H}_{12}$ . Singlet oxygen,  $^1\text{O}_2$ , formation was determined by the specific 2,2,6,6-tetramethyl-4-piperidone EPR assay. Yields of  $^1\text{O}_2$ , correlate with the amount of cyclohexanol detected in the mixtures, strongly suggesting that cyclohexanol is formed through the recombination of cyclohexylperoxy radicals which is favoured in the more polar media. Simultaneous determinations of chloride yields provide direct evidence of the active participation of dichloromethane in the photocatalytic system. A mechanism is proposed to account for the observed increment in the apparent efficiencies and the selectivity changes.

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### 1. Introduction

The controlled oxofunctionalization of hydrocarbons by molecular oxygen is a real challenging phenomena of practical interest in fine chemical synthesis [1,2].

It has earlier been reported that the  $\text{TiO}_2$ -photocatalytic oxidation of neat cyclohexane can proceed with high selectivity to cyclohexanone and cyclohexanol with minor amounts of carbon dioxide [3,4]. It was later observed, that the yields of monooxygenated products as well as product selectivity, *i.e.*, the ratio  $R$  between cyclohexanol and cyclohexanone, can be controlled by changing the nature of the solvent [5,6], the semiconductor structure [7,8] and/or by combining titanium dioxide with other catalysts such as titanium silicate [9]. In a recent study we have also shown that the value of  $R$  in neat cyclohexane critically depends on the frequency of photon absorption by  $\text{TiO}_2$  particles [10].

The effect of the solvent on the selectivity changes was first addressed by Amadelli and co-workers [5]. They showed that the rate of formation of monooxygenated products as well as the ratio between cyclohexanol and cyclohexanone could be improved by increasing the amount of dichloromethane in  $\text{C}_6\text{H}_{12}/\text{CH}_2\text{Cl}_2$  mixtures. However, no information was provided about the optimal composition of the solvent for a controlled oxidation. The higher yield of cyclohexanol as the mixtures become richer in  $\text{CH}_2\text{Cl}_2$  was explained by invoking the simultaneous desorption of the alcohol with increasing polarity, a fact that prevents its conversion to cyclohexanone and higher oxidation products. In fact, a following study of Almquist and Biswas [6] on cyclohexane photooxidation in different solvents showed that there is a strong correlation between cyclohexanol dark-adsorption isotherms and the predominance of the cyclohexanone among the monooxygenated products.

In the present study we have reinvestigated cyclohexane  $\text{TiO}_2$ -photocatalytic oxidation in  $\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{12}$  mixtures with cyclohexane molar fractions,  $x$ , ranging from 0.05 to 1. Besides determining the yields of carbon dioxide, cyclohexanone and

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cyclohexanol, we provide direct evidence of the active participation of dichloromethane in the photocatalytic system through the quantitative assessment of chloride ions as a function of  $x$ . In addition, we performed a detailed EPR spin trapping study of radical intermediates and  $^1\text{O}_2$ . The accumulated evidences are used to discuss the role of  $\text{CH}_2\text{Cl}_2$  in determining the yields of cyclohexanol.

## 2. Experimental

### 2.1. Materials

Degussa P25 was a commercial sample gently supplied by the manufacturers and used as provided. Cyclohexanone (Aldrich), cyclohexanol (Aldrich), dichloromethane (Merck) and all other chemicals were of analytical reagent grade and used as received. Cyclohexane (Cicarelli) was further purified to remove traces of benzene following standard procedures and dried over  $\text{CaCl}_2$  [11].

Stock solutions of the spin trapping reactivities phenyl-*tert*-butylnitron, (PBN, Aldrich), 5,5-dimethyl-1-pyrroline *N*-oxide, (DMPO, Aldrich) were prepared under nitrogen and stored at 268 K. 2,2,6,6-tetramethyl-4-piperidone (4-oxo-TMP) for the singlet oxygen assay as well as the stable 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) were purchased from Aldrich.

### 2.2. Irradiation procedures

Room-temperature, air saturated slurries ( $1\text{ cm}^3$ ,  $2\text{ g/L TiO}_2$ ) contained in square prismatic silica cells (volume =  $3\text{ cm}^3$ ) were fully illuminated with monochromatic radiation (from a Kratos-Schoeffel monochromator, 5 nm bandwidth) at 303 nm. A magnetic stirring bar was used to assure proper mixing and aeration during irradiation. The incident photon flux,  $I_0 = 4.35\text{ nEinstein cm}^{-2}\text{ s}^{-1}$ , was determined by chemical actinometry using phenylglyoxylic acid as actinometer [12].

### 2.3. Product analysis of stable species

Product analysis were carried out by gas chromatography using a GLC system consisting of a Tracor 540 gas chromatograph, equipped with flame ionization (FID) and thermal conductivity (TCD) detectors. Intermediate products giving rise to GLC peaks were identified by comparing the retention time,  $t_r$ , with those of commercial standards. The concentrations of cyclohexanol and cyclohexanone were determined using the flame ionization detector and a 6 in.  $\times$  1/8 ft stainless steel, packed, 80/100, 10% DEGS, Chromosorb W column, with nitrogen as the carrier gas. Alternatively the amount of cyclohexanone in some of the samples was also analyzed with an HPLC system equipped with a UV-vis photodiode array detector (UV2000-Thermo Separation Products), equipped with a ODS, 5  $\mu\text{m}$ , 250 mm  $\times$  4.6 mm, Phenomenex column. Methanol/water 50% by volume was used as eluent and the detection was performed at  $\lambda = 280\text{ nm}$ . This checking test was undertaken because cyclohexyl hydroperoxide, a plau-

sible intermediate in the early stages of cyclohexane oxidation [13] readily decomposes upon GC injection into cyclohexanone and cyclohexanol in a ratio that depends on the chromatographic conditions (injector temperature, column type, etc.) [14]. Additionally, total peroxides,  $P_T$ , were determined iodometrically following standard procedures [15].

$\text{CO}_2$  concentration in the gas phase was determined by gas chromatography with a 6 in.  $\times$  1/8 ft stainless steel, packed, 100/120, Porapak R column, helium as carrier gas, and a thermal conductivity detector.

The formation of chloride was monitored by HPLC suppressed ion chromatography using an Alltech 320 conductivity detector equipped with the Alltech 335 suppressor module and Allsep Anion IC Column (7  $\mu\text{m}$ , 4.60 mm  $\times$  150 mm). The eluent consisted in a  $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$  mixture at  $1.0\text{ mL min}^{-1}$ .

### 2.4. EPR experiments

EPR measurements were performed with a Bruker ER 200 X-band spectrometer (Bruker Analytische Messtechnik GMBH, Germany). Direct irradiation in the flat EPR cell was discarded as the suspensions require permanent agitation to ensure homogeneous mixing. Thus, for the EPR experiments the photolysis were performed following the same procedures described in Section 2.2. Well-determined volumes of the irradiated samples were withdrawn at the early times of the photolysis and their EPR spectra were immediately recorded at room temperature [16]. Blank experiments were periodically performed in order to check that the spin trap does not produce any paramagnetic signal under irradiation. Measurements of  $g$  values were made relative to TEMPO ( $g = 2.0051$ ) [17,18]. Typical instrumental conditions were: 3480 G, central field; 60 G, sweep width; 1–20 scans; 43 mW, microwave power; 100 kHz, modulation frequency; 1–50 ms, time constant; 1–5 s, sweep time; 0.5 Gpp, modulation amplitude; and  $4 \times 10^5$  receiver gain.

## 3. Results and discussion

### 3.1. Overall efficiency of cyclohexane oxidation

Excitation of  $\text{TiO}_2$  was carried out at  $\lambda = 303 \pm 5\text{ nm}$  in  $\text{CH}_2\text{Cl}_2$ - $\text{C}_6\text{H}_{12}$  mixtures of different compositions. Cyclohexanone, cyclohexanol, chloride and carbon dioxide were determined as a function of the irradiation time at different solvent composition covering the range  $0.05 \leq x \leq 1$ . No traces of cyclohexylperoxide could be detected in the course of these irradiation experiments. In fact, we established an upper limit for the steady state concentration of total peroxides:  $P_T < 50\text{ }\mu\text{M}$ , in the whole range of conditions investigated, by applying well established procedures [13,15]. Moreover, as already stated in the experimental section, the fact that the amount of cyclohexanone determined by GLC analysis was almost identical to that obtained by HPLC analysis, rules out the accumulation of cyclohexylperoxide at least at the millimolar level.

Initial photonic efficiencies for the sum of cyclohexanone and cyclohexanol,  $\xi_{\text{ox}}$ , were rather high and ranged from 19 to 51% depending on solvent composition as indicated in Table 1.  $\xi_{\text{ox}}$

Table 1

Apparent initial photonic efficiencies,  $\xi_{\text{ox}}$ , for total monoxygenated products (cyclohexanol + cyclohexanone) and ratio,  $R$ , between cyclohexanol and cyclohexanone yields in dichloromethane/cyclohexane mixtures as a function of cyclohexane molar fraction,  $x$

$x$	$\xi_{\text{ox}}$	$R^a$
0.03	19	0.30
0.1	27	0.45
0.2	38	0.58
0.3	46	0.71
0.4	47	0.75
0.5	51	0.82
0.6	49	0.78
0.70	45	0.71
0.8	39	0.59
0.9	28	0.43
1.0	25	0.34

<sup>a</sup> Determined after 45 min of irradiation at  $303 \pm 5$  nm.

was calculated as the ratio between the initial generation rates of total monoxygenated products and the incident photon flux,  $I_0$ . It is worthwhile to say that cyclohexanone and cyclohexanol build up in a linear fashion during the first 60 min of the irradiation experiments which typically represent between 1 and 5 mM of products.

Individual yields of cyclohexanone and cyclohexanol obtained after 45 min of irradiation at  $303 \pm 5$  nm are plotted in Fig. 1 and their relative values,  $R$ , are shown in Table 1. Both products displayed an optimal yield for  $x=0.5$ . Remarkably, apart from cyclohexanone and cyclohexanol, the *only* other product that could be detected after 45 min of irradiation, was carbon dioxide. Its concentration monotonously decreased from 14 to 5  $\mu\text{M}$  on going from pure cyclohexane to pure dichloromethane. Recall that, on the basis of carbon balance, the total moles of cyclohexane reacted,  $-n(\text{C}_6\text{H}_{12})$ , equals the sum  $n(\text{C}_6\text{H}_{10}\text{O}) + n(\text{C}_6\text{H}_{11}\text{OH}) + 1/6 n(\text{CO}_2)$ . Thus, the increment in the moles of cyclohexanol observed on going from  $x=1$  to  $x=0.5$  is far from been compensated by differences observed in the sum  $n(\text{C}_6\text{H}_{10}\text{O}) + 1/6 n(\text{CO}_2)$ . Accordingly, the results in Fig. 1 cannot be explained by invoking a different fate of cyclohexanol due to a change in solvent polarity, but clearly point to a better utilization of the photogenerated charges on going from pure cyclohexane to the equimolar mixture.

In the following sections we look for a rationalization of the above results through quantitative determinations of chloride yields -as a measure of dichloromethane involvement in the reaction scheme- and a detailed study of reaction intermediates by EPR spectroscopy.

### 3.2. Radical intermediates detected by EPR spectroscopy

The spin trapping technique using PBN has previously been employed to trap the intermediates formed during the photocatalytic oxidation of cyclohexane. A broad triplet and a triplet of doublets, ascribed to the alkoxy adducts, were respectively found for pure cyclohexane and 50% V dichloromethane:cyclohexane mixtures [5]. A similar pattern was found by us (see Fig. 2(a) and (c)). In fact, we performed

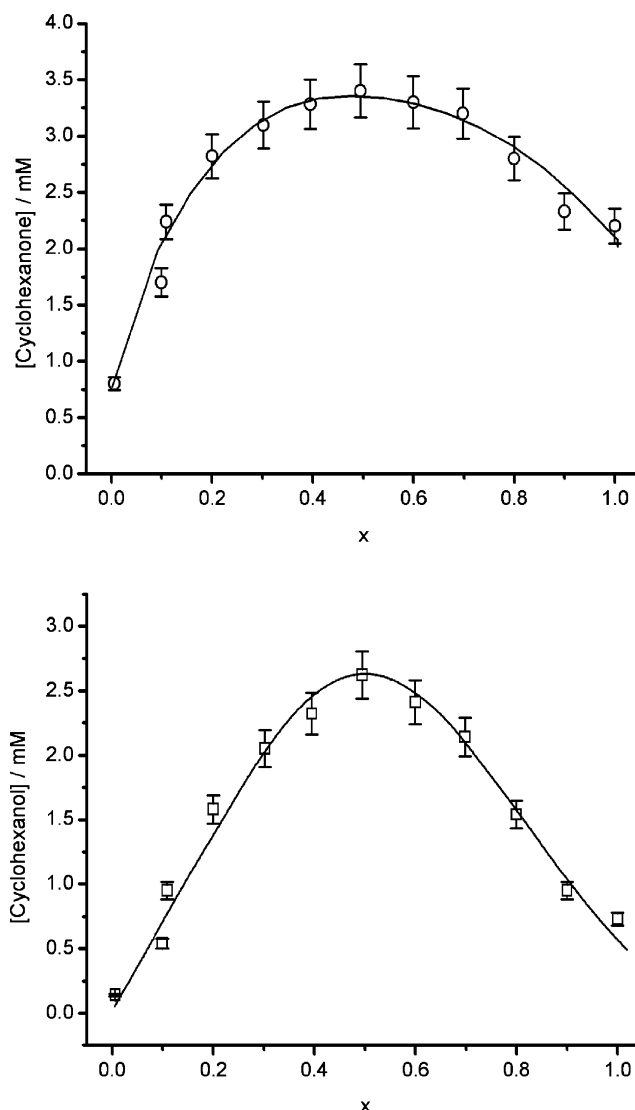


Fig. 1. Yields of cyclohexanone (○) and cyclohexanol (□) as a function of the cyclohexane molar fraction,  $x$ .  $[\text{TiO}_2]=2.0 \text{ g L}^{-1}$ ;  $I_0=4.34 \text{ nE cm}^{-2} \text{ s}^{-1}$ ;  $\lambda=303 \pm 5$  nm. Bars show the typical dispersion obtained for at least five independent determinations.

spin trapping experiments using PBN and DMPO in the whole range of the reaction mixtures carefully seeking for a change in the trapped intermediates with the solvent composition. DMPO was employed because the  $\beta$ -H hyperfine coupling constants,  $h_{\text{fcs}}$ , of their radical adducts are commonly larger and more sensitive to the structure of the trapped species than those for PBN, a fact that favours the analysis of a radical mixture [19].

Plots (b) and (d) in Fig. 2 illustrate the adducts formed in the presence of DMPO, upon irradiation of  $\text{TiO}_2$  suspensions in pure cyclohexane  $x=1$ , and for  $x=0.375$  as representative of  $\text{CH}_2\text{Cl}_2$ - $\text{C}_6\text{H}_{12}$  mixtures. The broad triplet shown in Fig. 2(a), ( $a^{\text{N}}=13.6 \pm 0.1 \text{ G}$ ), could be transformed in the spectra observed in cyclohexane-dichloromethane mixtures, Fig. 2(c), ( $a^{\text{N}}=13.85 \pm 0.15$  and  $a_{\beta}^{\text{H}}=2.08 \pm 0.05 \text{ G}$ ) by simply adding to the aliquots in pure cyclohexane the proper amount of  $\text{CH}_2\text{Cl}_2$  to get the same solvent composition of the mixture  $x=0.37$ . Similarly, the triplet of doublets obtained

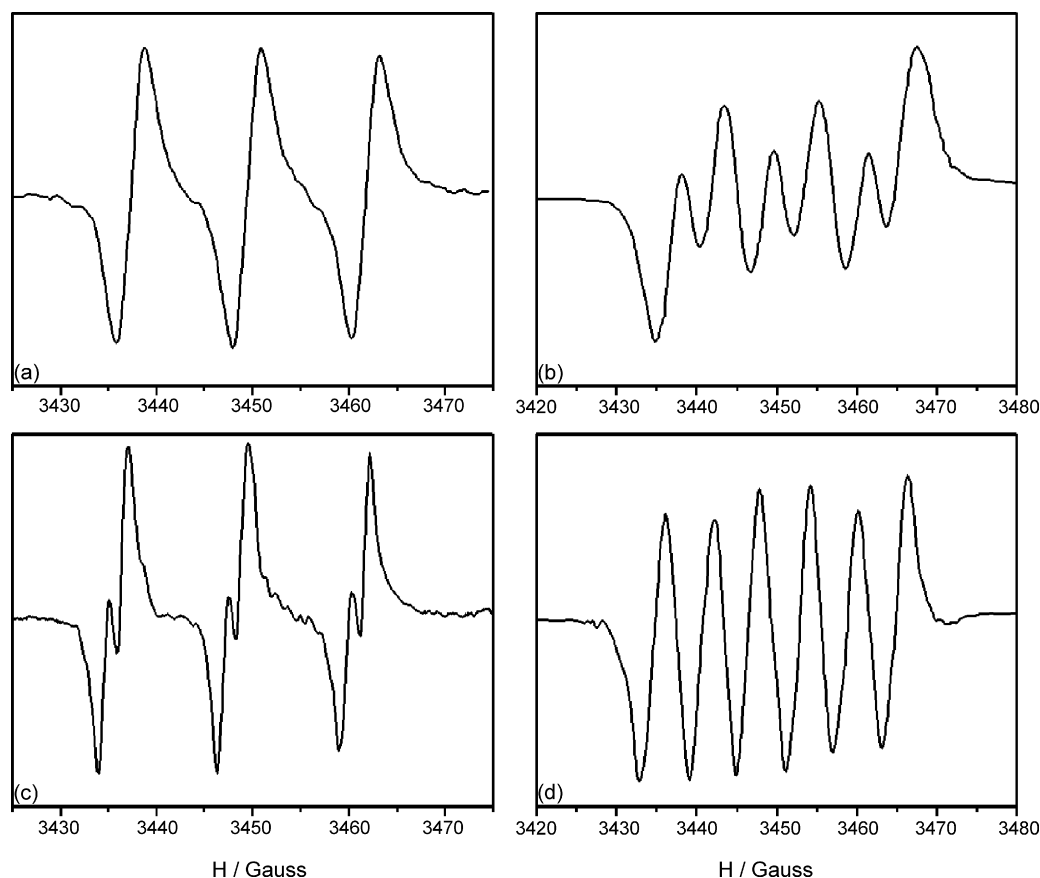


Fig. 2. EPR spectra of the radical adducts formed at the initial stages of irradiation of  $2.0 \text{ g L}^{-1}$   $\text{TiO}_2$  suspension in pure cyclohexane in the presence of (a) phenyl-*tert*-butyl nitron, (PBN) or (b) 5,5-dimethyl-1-pyrroline *N*-oxide, (DMPO). Plots (c) and (d) show the corresponding adducts for  $x=0.375$  as representative of dichloromethane-cyclohexane mixtures. Spin trap final concentration is 5 mM.

in pure cyclohexane depicted in Fig. 2(b) ( $a^{\text{N}} = 12.52 \pm 0.15$  and  $a_{\beta}^{\text{H}} = 5.97 \pm 0.05$  G), was transformed in that observed for  $x=0.37$ , Fig. 2(d), ( $a^{\text{N}} = 13.16 \pm 0.15$  and  $a_{\beta}^{\text{H}} = 6.95 \pm 0.05$  G). By these procedures we verified that the higher values of the nitrogen and  $\beta$ -H *hfc*s observed in the mixtures arise as a result of increased spin density on the *N* atom of the aminoxyl function in the more polar solvent, however, no matter the solvent composition, the same radical intermediates are trapped [19].

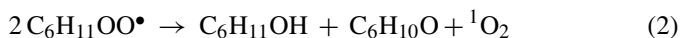
Comparison of the above *hfc*s with literature values for oxygen centred radicals indicates that the adduct detected in all cases is formed by the spin trap, ST=PBN or DMPO, and the  $\text{C}_6\text{H}_{11}\text{O}^{\bullet}$  radical. However, detailed investigations demonstrated that the trapping of organic peroxy radicals at room temperature produces alkoxy (RO-ST), rather than peroxy radical adducts (ROO-ST), according to the reaction sequence [20–23]:



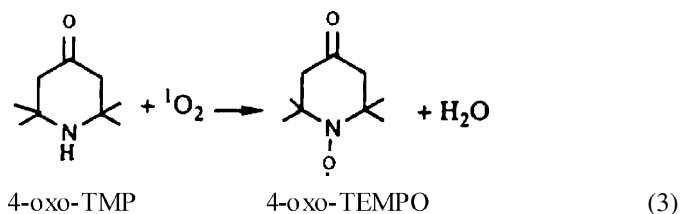
Considering the above arguments, the only definitive conclusion that can be obtained is that either  $\text{C}_6\text{H}_{11}\text{O}^{\bullet}$ ,  $\text{C}_6\text{H}_{11}\text{OO}^{\bullet}$ , or both species are the main intermediates in the reaction mechanism for all the studied solvent mixtures [24]. Remarkably, no evidence of radicals derived from dichloromethane could be achieved in the EPR experiments.

### 3.3. Relevance of the Russell mechanism in the yields of cyclohexanol

It is apparent from the results presented in Fig. 1 that the selectivity to cyclohexanol sharply increases with the addition of dichloromethane. Taking into account the relatively long time intervals between the absorption of successive photons by a single particle and the  $\text{O}_2$  concentration in air saturated organic solvents, we postulate that the formation of the alcohol via  $\text{C}_6\text{H}_{11}\text{O}^{\bullet} + \text{OH}^{\bullet}$  is highly unlikely, and turn to consider the possibility that most of the alcohol derives from the recombination of the cyclohexylperoxy radicals formed in reaction (2) [10,26]:



To test our hypothesis, the formation of singlet oxygen was investigated by EPR spectroscopy using the highly selective reaction of 2,2,6,6-tetramethyl-4-piperidone with  ${}^1\text{O}_2$ , [27–31] which gives the stable free radical 4-oxo-TEMPO according to (3):



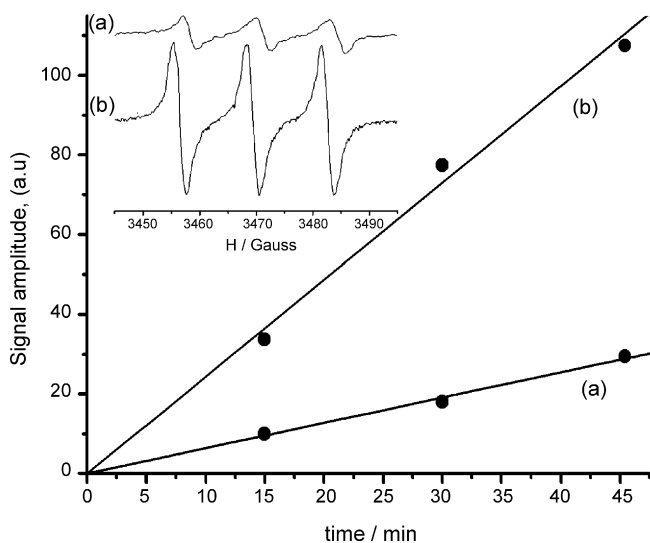


Fig. 3. Time evolution of the EPR signal amplitude of 4-oxo-TEMPO obtained under of continuous irradiation of  $2.0 \text{ g L}^{-1}$   $\text{TiO}_2$  suspension in the presence of 4-oxo-TMP (a) in pure cyclohexane,  $x=1$  and (b) in  $\text{C}_6\text{H}_{12}\text{-CH}_2\text{Cl}_2$  mixture,  $x=0.5$ . The inset shows the EPR spectra obtained in the same conditions after 45 min of irradiation.

Zang *et al.* [30] have demonstrated, using Rose Bengal as singlet oxygen generator, and Xanthine–Xanthine oxidase and  $\text{KO}_2$  as sources of superoxide radical, that this test is highly specific for  $^1\text{O}_2$  since the paramagnetic signal was formed in the presence of singlet oxygen but not with superoxide radicals.

Fig. 3 shows the time dependence and the spectra of the radicals obtained upon addition of 4-oxo-TMP for  $x=1$  and  $x=0.5$  as representative of the solvent mixtures. For this case we found that  $[\text{4-oxo-TEMPO}]_{x=0.5}/[\text{4-oxo-TEMPO}]_{x=1} = [\text{cyclohexanol}]_{x=0.5}/[\text{cyclohexanol}]_{x=1} = 4$ . Other tested compositions show the same pattern, that is: the yield of 4-oxo-TEMPO correlates with the amount of cyclohexanol detected in the mixtures, strongly suggesting that the alcohol is formed through the recombination of cyclohexylperoxy radicals according the Russell mechanism.

Recall that both, the desorption of cyclohexylperoxy radicals, and the specific rate of the Russell reaction are enhanced in a polar environment, thus one would expect an increase in  $R$  with the dielectric constant of the solvent. To test this hypothesis, we performed an experiment at  $x=0.03$  in acetonitrile, a composition that warrants perfect miscibility with cyclohexane, under the same irradiation conditions of the experiments shown in Table 1. The values obtained:  $\xi_{\text{ox}}=8\%$  and  $R=0.75$ , compared with those in dichloromethane ( $\xi_{\text{ox}}=19\%$ ,  $R=0.3$ ) are consistent with our assumptions and indicate that other factors besides solvent polarity determine the efficiency of cyclohexane oxidation in dichloromethane. It is worthwhile to say that cyclohexane photocatalytic oxidation in aqueous slurries – exceeding  $\text{C}_6\text{H}_{12}$  solubility – [32] results in a high cyclohexanol/ cyclohexanone ratio.

#### 3.4. Dichloromethane involvement in the reaction scheme

As already mentioned in Section 3.1, under our experimental conditions no chlorinated species could be detected among

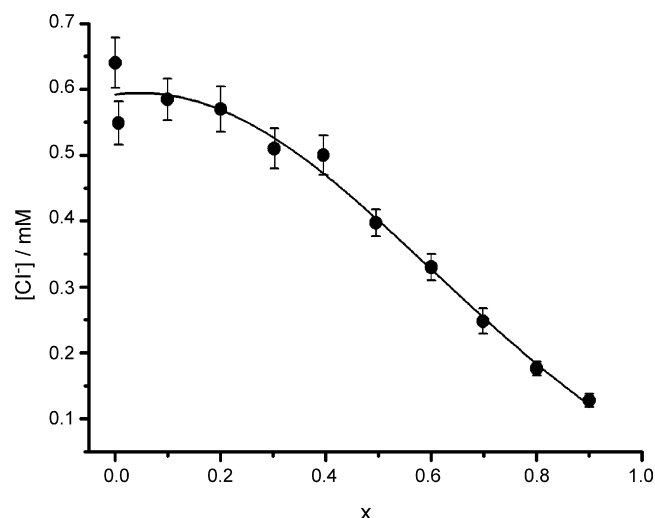
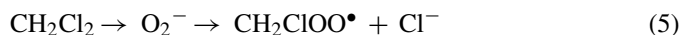
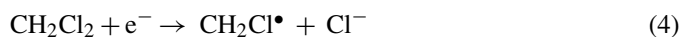


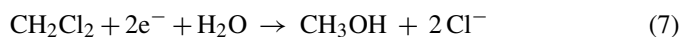
Fig. 4. Yield of chloride as a function of the cyclohexane molar fraction,  $x$ .  $[\text{TiO}_2]=2.0 \text{ g L}^{-1}$ ;  $I_0=3.64 \text{ nE cm}^{-2} \text{ s}^{-1}$ ;  $\lambda=303 \pm 5 \text{ nm}$ . Bars show the typical dispersion obtained for at least five independent determinations.

the reaction products. These findings are in good agreement with previous reports [5,6] in which negligible amounts of chlorinated cyclohexanol and cyclohexanone were found, despite both studies involve higher cyclohexane conversions. The low amount of chlorinated compounds has been previously considered as a good indication that cross-reactions involving hydrocarbon radicals and radicals deriving from a plausible oxidation of  $\text{CH}_2\text{Cl}_2$  are not significant [5]. Thus, although dichloromethane oxidation can not be completely ruled out, the above argument together with the fact that cyclohexane oxidation is not inhibited, but rather enhanced by the presence of  $\text{CH}_2\text{Cl}_2$ , seems to indicate that it does not compete with cyclohexane for the oxidative species (OH radicals or holes) to any considerable extent.

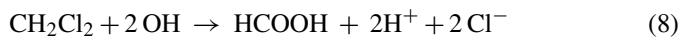
However, we were able to observe and quantified the formation of chloride ions in the extracted aliquots, as a function of cyclohexane molar fraction (see Fig. 4). For  $\text{Cl}^-$  we envisaged two possible mechanism of formation indicated as reactions (4) and (5):



It is well established that the photoreduction of carbon tetrachloride is feasible both in aqueous  $\text{TiO}_2$  dispersions under UV irradiation [33–35] and by visible light on  $\text{TiO}_2$  sensitized by tris-(4,4'-dicarboxy-2,2'-bipyridyl) ruthenium(II) complexes in anoxic conditions [36]. Although oxygen competes with  $\text{CCl}_4$  for conduction band electrons, carbon tetrachloride reduction is not fully inhibited in the presence of air [34,36]. Conversely, it is not clear if  $\text{CH}_2\text{Cl}_2$  photocatalytic reduction could be feasible by conduction band electrons. A careful study of Pelizzetti and coworkers [33] has shown that dichloromethane photocatalytic induced hydrolysis Eq. (6) is predominant over reductive and oxidative pathways, reactions (7) and (8),

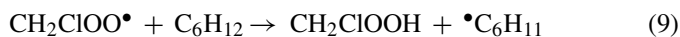






In fact, dichloromethane reduction potential is expected to be more negative than the corresponding value for carbon tetrachloride. Literature values for  $E^0(\text{CCl}_4/\bullet\text{CCl}_3 + \text{Cl}^-)$  range from  $-0.25$  to  $-0.54$  V vs NHE [33], while an estimation of the potential of the redox system  $\text{CH}_2\text{Cl}_2/\bullet\text{CH}_2\text{Cl} + \text{Cl}^-$  gives  $-0.7$  vs NHE [37]. Besides, the experimental half-wave potential determined in 1,4 dioxane  $E_0(\text{CH}_2\text{Cl}_2/\bullet\text{CH}_2\text{Cl} + \text{Cl}^-) = -1.6$  V vs SCE [38] renders reaction (4) thermodynamically inhibited unless the expected strong adsorption of  $\text{CH}_2\text{Cl}_2$  causes a positive shift of the reduction potential [39]. Nevertheless, it has been shown that superoxide exhibits an unexpected reactivity with  $\text{CCl}_4$ ,  $\text{CH}_3\text{Cl}$  and  $\text{CH}_2\text{Cl}_2$  [40,41]. Accordingly, we favour reaction (5) [42] over reaction (4) as the source of chloride ions.

It has been suggested that  $\text{O}_2^{\bullet-}$  recombination with trapped holes plays an important role in determining the quantum yields of photocatalytic reactions [43]. This may be particularly true in organic suspensions where  $\text{O}_2^{\bullet-}$  is expected to be relatively more long lived than in aqueous solutions. Accordingly  $\text{O}_2^{\bullet-}$  scavenging by  $\text{CH}_2\text{Cl}_2$  may contribute to improve the efficiency of charge utilization, leaving more holes available for cyclohexane oxidation. In addition, the  $\text{CH}_2\text{ClOO}\bullet$  radicals formed by the reaction of  $\text{O}_2$  reaction with  $\text{CH}_2\text{Cl}\bullet$  would probably generate cyclohexyl radicals:



thus enhancing cyclohexane oxidation. Notice that the contribution of reaction (9) depends on  $x$ , through the product of cyclohexane and  $\text{CH}_2\text{ClOO}\bullet$  concentrations. Given that the rate of formation of  $\text{CH}_2\text{ClOO}\bullet$  equals that of chloride, which monotonously increases on going from  $x = 1$  to  $x = 0.3$ , reaction (9) would attain its maximum relevance at  $x = 0.5$ , *i.e.* the solvent composition which incidentally produces the maximum rate of cyclohexane oxidation.

#### 4. Conclusions

A quantitative study of the apparent initial photonic efficiencies for valuable products (cyclohexanol + cyclohexanone) reveals that cyclohexanol/cyclohexanone ratio attains a maximum at  $x = 0.5$ . At this composition, cyclohexane photocatalytic oxidation proceeds with high efficiency: near 0.5 mol of products are formed by 1 mol of photons of 303 nm.

We provide direct evidence that cyclohexanol is formed by recombination of cyclohexylperoxy radicals and postulate that the chloride ions are formed by  $\text{O}_2^{\bullet-}$  reaction with  $\text{CH}_2\text{Cl}_2$ . This last process simultaneously produces  $\text{CH}_2\text{ClOO}\bullet$  radicals which in turn can abstract an H atom from cyclohexane improving the efficiency of charge utilization.

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