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A revised photocatalytic transformation mechanism for chlorinated VOCs: experimental evidence from C₂Cl₄ in the gas phase

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Abstract

The photodegradation of gaseous perchloroethylene (PCE) was investigated on titanium dioxide under UV light at 365 nm at the gas/solid interface in a CSTR photo-reactor (Continuous Stirred Tank Reactor). The rate and products are strongly affected by oxygen presence. Gaseous products of PCE degradation agree with literature. The production of active chlorine (sum of Cl₂, HClO, ClO and ClO₂) was investigated both in the presence of oxygen and in anoxic conditions. At low O₂ concentration no gaseous active chlorine was determined, while a significant amount was measured in the presence of oxygen. By considering that in the absence of O₂ the only possible form of active chlorine is Cl₂, this highlights that Cl[•] is not produced, and that chain reactions promoted by the chlorine radical do not occur on the TiO₂ surface.

The photocatalytic transformation of C₂Cl₄ was investigated at different concentrations. The rate follows a first order kinetic that is rationalized with a photocatalytic kinetic model in which the substrate is able to react simultaneously with both photogenerated holes and electrons. In anoxic conditions adsorbed halogenated organic compounds with molecular weights higher than that of PCE were produced and chloride ions accumulated at the surface. Reductive pathways have a key role in PCE degradation. The water vapor has a detrimental role on the PCE transformation rate due to the competition with PCE adsorption on reactive sites with 2:1 stoichiometry.

The addition of chloride ions on TiO₂ surface slows down the PCE degradation rate and the production of gaseous CCl₄ but increments that of C₂Cl₆ in anoxic conditions. This is rationalized by a mechanism in which direct hole transfer to substrate occurs followed by chloride anion addition to the carbocation.

Keywords

Photocatalysis, Titanium Dioxide, Perchloroethylene, Chlorine radical, Gas/solid interface, Active chlorine

40 1 Introduction

41 The photocatalytic process is a well-known method for abatement of air pollutants. Early
42 studies showed that alkanes, aromatic hydrocarbons, alcohols, aldehydes, ketones, and
43 halogenated solvents can be degraded although in a different extent. The studies on
44 halogenated solvents, namely trichloroethylene (TCE), tetrachloroethylene (PCE) and
45 chloroform date at late 80's.[1] The main products observed were DCAC (dichloroacetyl
46 chloride), COCl_2 (phosgene), CO_2 , CO and HCl . Nimlos et al. [2] were also able to identify
47 Cl_2 using a molecular beam mass spectrometer. In the degradation of TCE and PCE, CHCl_3
48 and CCl_4 [3,4] were formed as the O_2 mole fraction in the feed gas decreases. The formation
49 of more halogenated products was ascribed to the initial formation of Cl^\bullet radicals, and the
50 subsequent preferential attack at the $-\text{CHCl}$ side.[3] Comparison of literature data [5] under
51 similar conditions and reactor configuration using the Langmuir Hinshelwood model showed
52 that toluene, m-xylene, acetone and TCE have similar order of magnitude rate constant and
53 apparent binding constant.[6] A photocatalytic rate enhancement for the conversion of many
54 pollutants was reported when co-fed with chloro-olefins.[7] Quantum yield greater than 1 has
55 been cited several times [1,8], although the original papers are almost not available. A
56 detailed mechanism was also proposed through ab initio molecular orbital calculations,
57 showing that addition of $^\bullet\text{OH}$ and Cl^\bullet radicals to TCE is possible, being the first more
58 exothermic than the second one.[3,8] Nowadays, PCE and TCE are still used as model
59 pollutants for reactor configuration studies.[9]

60 The positive synergic effect, the formation of more halogenated intermediates, and the
61 cited quantum yield greater than 1 for chlorinated compounds were ascribed to chain reactions
62 promoted by the chlorine radical that is formed at the TiO_2 surface.[3,10] The chlorine radical
63 can be formed a) from chloride oxidation by $^\bullet\text{OH}$ or holes, or b) directly released from
64 oxidized intermediates. The supposed Cl^\bullet formation by hydroxyl radicals produced at the
65 surface of TiO_2 exposed to near-UV irradiation in the presence of adsorbed water vapor [11]
66 was able to justify the observed intermediates.[8] The role of chlorine radical was also
67 supported by experiments in which chloride ions were added in the gas phase or at the
68 surface. After addition of HCl in catalytic quantity in the air flow or by PCE overheating, a
69 sensible increase of the reaction rate was obtained.[12] The addition of surface Cl^- through
70 prechlorination with HCl increased the rate for toluene and hexane at the very beginning of
71 the reaction when compared to the co-feeding with TCE, for which the enhancement was
72 observed after some reaction time needed to accumulate a useful surface Cl^- level.[13]

73 The chain reaction mechanism assumes that chlorine radical is an initiator which adds to
74 TCE, forming a more halogenated radical, which in some further steps releases Cl^\bullet or HCl
75 after reaction with oxygen.[3] The chain is terminated when Cl^\bullet reacts with water to form $^\bullet\text{OH}$
76 (a reaction possible only for $\text{pH} > 2-2.5$ as suggested by the standard redox potential for the
77 couples $E^\circ(\text{Cl}^\bullet/\text{Cl}^-) = 2.60 \text{ V}$ and $E^\circ(^\bullet\text{OH}, \text{H}^+/\text{H}_2\text{O}) = 2.73 \text{ V}$ [14]), or in dry conditions to form
78 Cl_2 . [15] Chlorine radical could also be depleted by photoelectrons in the conduction bands
79 (reducing to chloride ion that is adsorbed on the surface) or by reaction with O_2 , forming
80 ClO_2 . [3]

81 The aforementioned framework based on the key role of Cl^\bullet seems to be consistent.
82 However, parallel to earlier studies, alternative explanations could be suggested. For example,
83 literature-reported values of photon efficiency are consistent with a photocatalytic mechanism

84 without chain reactions mediated by Cl^\bullet radical. Using a fluorescence UV source and
85 potassium ferrioxalate actinometry, the TCE photon efficiency was calculated as 13% over
86 conditioned catalysts.[16] Jacoby et al.[1,2] measured quantum yields from 0.5 to 0.8 under
87 high TCE concentration. In addition, the inhibition of the rate in the presence of halide ions in
88 aqueous solution was suggested to be due to the competition with organic molecules for the
89 oxidative species (i.e. photogenerated holes).[17] The chlorine radical, if formed, is subjected
90 to rapid recombination with conduction band electrons, creating a short-circuit cycle that
91 depresses the conversion. An analogous inhibition was observed in the gas-phase
92 photocatalytic degradation of CHCl_3 due to the increase of surface Cl^- with the space
93 time.[18] The photoactivity was recovered washing the catalyst. Recently, EPR measurements
94 were conducted to detect the presence of chlorine radicals by using the PBN spin-trap in
95 chloroform solution.[19] The PBN- Cl^\bullet radical was not identified, suggesting that the
96 existence of chlorine radical can be largely disregarded, although not completely excluded.
97 Then the rate decrease was ascribed to the surface sites occupancy without a redox
98 involvement of chloride ion. If so, also the formation of $\bullet\text{OH}$ radicals, more endoergonic,
99 could hardly be suggested.

100 The existence of $\bullet\text{OH}$ radicals in photocatalysis was debated for years.[20] Although free
101 $\bullet\text{OH}$ is still often invoked in the recent literature, the surface trapped hole is most probably the
102 reactive species, often indistinguishable as reactivity from $\bullet\text{OH}$ radical. In the photocatalyzed
103 oxidation of TCE in the presence of $^{18}\text{O}_2$, oxygen-18 is incorporated into DCAC, phosgene,
104 and CO, indicating that only the oxygen from the gas phase is involved in the oxidation of
105 TCE, whilst oxygen-16 from H_2^{16}O is not incorporated in the photooxidation products.[21]
106 This proved that $\bullet\text{OH}$ driven oxidation mechanism is not operative in the photooxidation of
107 TCE. The direct electron transfer from organic substrate to the photogenerated holes was
108 recently demonstrated as a unique electron transfer mechanism in the case of photocatalytic
109 transformation of melamine, which is unreactive toward $\bullet\text{OH}$ radical.[22] This indicates that
110 direct electron transfer from the surface trapped hole could be in general the sole process
111 responsible for oxidation.[23] Consistently, the product analysis obtained with O_2 -sensitised
112 photo-oxidation of indane and some of its hetero-analogs in deaerated CH_3CN and in the
113 presence of Ag_2SO_4 was explained with the intervention of a carbocation in the first reaction
114 event resulting from an electron-transfer mechanism (from the substrate to the photogenerated
115 hole).[24]

116 To clarify the possible role of $\bullet\text{Cl}$ radical some new data on intermediate formation in the
117 photocatalytic degradation of PCE are here reported, both in the presence and absence of O_2 ,
118 together with the analysis of kinetic data. The formation of gaseous Cl_2 is assessed by a
119 simple trapping experiment.

120 **2 Materials and Methods**

121 Details on used materials, preparation of the catalyst, and experimental setup are reported
122 in Supplementary Material (hereafter SM). The experiments of PCE transformation were
123 carried out in a homemade flow-through photo-reactor working in a regime of perfect mixing
124 (Continuous Stirred Tank Reactor, CSTR, see SM under 1.4).[25,26] Under steady state the
125 output concentration of gaseous C_2Cl_4 does not change with the time, if there is no change in
126 the photoactivity of the catalyst, e.g. no poisoning or photo-activation as a consequence of the
127 irradiation. Consequently, defining the conversion at the time t as $\eta(t) = (C_o - C_{out}(t))/C_o$, where

128 C_o is the feed concentration and C_{out} the concentration inside the reactor and measured at its
129 outlet, the rate under stationary conditions is directly obtained from the experiment (eq.
130 1).[25]

$$131 \quad Rate(C_{out}) = \frac{C_o \eta_{\infty} F}{S} \quad (\text{eq. 1})$$

132 The monitoring of C_2Cl_4 flowing out of the reactor was carried out with a Photo Ionization
133 Detector. The volatile VOCs were analysed through both GC-MS after cryofocusing and
134 directly through an FTIR spectrophotometer equipped with a cell for gases with 8 m long
135 optical path length. The catalyst surface modification was assessed through UV-Vis
136 reflectance spectra and FT-IR. The surface-deposited compounds have been extracted and
137 analysed with GC/MS and IC. All details are reported in SM.

138 The determination of the active chlorine formed during the photocatalytic test was carried
139 out according to a standard spectrophotometric methods,[27] based on the reaction of active
140 chlorine ($Cl_2/HClO/ClO^-/ClO$) with N,N-diethyl-p-phenylenediamine (DPD). This reaction
141 produces a pink coloured species that can be quantified spectrophotometrically at 510-515
142 nm. The gas flowing out of the reactor was bubbled through a fritted glass in a slightly basic
143 solution (NaOH 2 mM). This solution favoured the trapping of volatile active chlorine species
144 through: 1) deprotonation of the volatile hypochlorous acid into the non-volatile hypochlorite
145 anion; 2) dismutation of Cl_2 into Cl^- and reactive ClO^- ($Cl_2 + 2 OH^- \rightarrow H_2O + Cl^- + ClO^-$); 3)
146 reaction of ClO with the excess of hydroxyl ions to form ClO^- ($ClO^{\bullet} + OH^- \rightarrow ClO^- + \bullet OH$);
147 4) dismutation of ClO_2 in chlorite and chlorate species ($2 ClO_2 + H_2O \rightleftharpoons HClO_2 + HClO_3$,
148 $K=1.2 \times 10^{-7}$). At different irradiation times a fixed volume of the solution was withdrawn and
149 mixed with DPD solution buffered at pH 6.2 (phosphate buffer, $0.17 \text{ mol} \cdot \text{L}^{-1} \text{ HPO}_4^{2-}$ e 0.33
150 $\text{mol} \cdot \text{L}^{-1} \text{ H}_2\text{PO}_4$). The DPD produced pink colored species was quantified at 510 nm with a
151 Cary 100 UV-Vis spectrophotometer.

152 3 Results and Discussion

153 3.1 Rate as a function of the inlet C_2Cl_4 and water vapor concentration

154 The kinetic of the photocatalytic transformation of C_2Cl_4 was evaluated *i*) at different
155 concentrations of the inlet flow (C_o) and *ii*) at different concentration of water vapor
156 concentration. In both cases under stationary state the conversion was obtained and from this
157 the transformation rate was computed (eq. 1). It is worth mentioning that the rate calculated
158 from the experimental conversion refers to the concentration inside the reactor, and to
159 $C_{out}=C_o(1-\eta)$.

160 Fig. 1A shows the photonic efficiency (PE) at different C_o , and plotted vs the actual
161 concentration inside the reactor (C_{out}). The photocatalytic efficiency PE is given by the
162 photocatalytic rate [$\text{mol m}^{-2} \text{ s}^{-1}$] divided by the incoming light irradiance I_o [mol of photons
163 $\text{m}^{-2} \text{ s}^{-1}$]. The inset in Fig. 1A shows the stationary state (SS) conversion as a function of the
164 inlet concentration of perchloroethylene. As the conversion is almost independent of the inlet
165 concentration, a quasi-first order kinetic was observed ($rate=m \times C_{out}^n$ where $n=1$ for first
166 order, observed $n=0.90$).

167 A basic kinetic approach to the photocatalytic process previously reported [28] and widely
168 discussed,[23] based on 5 primary steps (light absorption with production of an exciton in the
169 bulk, charge carriers migration to the surface, recombination of the charge carriers at the

170 surface, interface charge transfer of holes to a reduced substrate and conduction band
 171 electrons transfer to an oxidant species), gives the $rate = \phi \times QY$, where the quantum yield (QY)
 172 of the photocatalytic process is:

$$173 \quad QY = \left(-y + \sqrt{y(y+2)} \right) \quad (\text{eq. 2})$$

174 The master variable y in eq. 2 is formally the ratio of two rates, the chemical rate at the
 175 catalyst surface and ϕ , which is the rate of absorption of photons in units consistent with those
 176 of the chemical rate (e.g. $\text{mol m}^{-2} \text{s}^{-1}$):

$$177 \quad y = k_0 \frac{\{C_{red}\}\{C_{ox}\}}{\phi} \quad (\text{eq. 3})$$

178 where k_0 is a combination of microscopic kinetic constants, and $\{C_{red}\}$ and $\{C_{ox}\}$ are the
 179 concentrations of the reduced and oxidized species adsorbed at the surface according to a
 180 proper adsorption isotherm (e.g. in the most simplified case a Langmuir isotherm). The above
 181 model, where the oxidant and reductant are different species, foresees a reaction order $0 \leq n \leq$
 182 0.5 , often experimentally verified [22,28] and recently deeply tested for the oxidation reaction
 183 of formic acid in the presence of oxygen.[29]

184 The first order observed in the case of PCE (see Fig. 1A) can be rationalized in the
 185 framework of the basic kinetic model briefly summarized above considering the possibility
 186 that C_2Cl_4 reacts *both* with h_s^+ and e_s^- . This double reactivity of the substrate has been hardly
 187 ever considered in the gas-phase halocarbon degradation because *i*) the most of the
 188 experiments are carried out in the presence of O_2 , *ii*) oxygen is believed to be an efficient
 189 electron scavenger and *iii*) the main goal of the photocatalytic processes is the full oxidation
 190 (abatement) of the substrate. An effective competition between O_2 and PCE for the
 191 photoproduced electrons can be operating also in the presence of excess oxygen as few PCE
 192 ppm were able to increase toluene degradation in the presence of air (200000 ppm).[7]

193 The importance of reductive pathways was proved in aqueous slurry in the study of photo-
 194 induced hydrolysis of chlorinated methanes under anaerobic conditions [30], in which the
 195 interconversion of CCl_4 , CHCl_3 and CH_2Cl_2 was supposed to proceed by reductive release of
 196 chloride ions. An initial reductive dominance of the reductive pathway was observed for CCl_4
 197 even in the presence of oxygen. Reductants such as alcohols (methanol, propan-2-ol, tert-
 198 butanol) remarkably enhance CCl_4 degradation as they scavenge holes.[31] Accordingly, it is
 199 worth noting that the early literature reported that compounds exhibiting TCE rate promotion
 200 were toluene, ethylbenzene, m-xylene,[7] methyl ethyl ketone (MEK), acetaldehyde,
 201 butyraldehyde, methyl tert-butyl ether (MTBE), methyl acrylate, 1,4-dioxane,[32] and
 202 methanol.[33] All these compounds are degraded mainly by an oxidative pathway. Then e_{CB}^-
 203 scavenging by TCE would increase the rate. Rate inhibition by TCE was exhibited for
 204 acetone, methylene chloride, chloroform, and 1,1,1-trichloroethane.[32] These compounds are
 205 more likely degraded by a first reduction step like TCE, which then acts as a competitor
 206 reducing their transformation rate.

207 On the hypothesis that C_2Cl_4 reacts *both* with h_s^+ and e_s^- , it is possible to predict that the
 208 presence of oxygen is not mandatory for an effective transformation of PCE (*vide infra*),
 209 because both surface holes and electrons are able to be scavenged by the substrate itself (i.e.
 210 $\{C_{red}\} = \{C_{ox}\}$). In this case

$$211 \quad QY = 2 \left(-y + \sqrt{y(y+2)} \right) \quad (\text{eq. 4})$$

212 where the master variable $y = k_o\{PCE\}^2/\varphi$. Eq. 4 shows that when the substrate can be
 213 simultaneously oxidized and reduced the reaction order is $0 \leq n \leq 1$. The first order at low
 214 $\{PCE\}$ (low value of y and then low value of QY or PE, see Fig. 1) is evident when y value is
 215 significantly lower than 2. For this case

$$216 \quad QY \approx 2\{PCE\}\sqrt{\frac{2k_o}{\varphi}} \quad (\text{eq. 5})$$

217 As the absorbed light is proportional to the incident one ($\varphi = \alpha I_o$), and the photocatalytic
 218 rate is given by $rate = \varphi QY$, the photonic efficiency $PE = rate/I_o$ is

$$219 \quad PE = 2\{PCE\}\sqrt{2\alpha k_o I_o} = k'\{PCE\} \quad (\text{eq. 6})$$

220 where $k' = \sqrt{8\alpha k_o I_o}$. This equation justifies the first order rate observed for the PCE
 221 photocatalytic transformation (Fig. 1A), and supports the role of the reductive pathway, that
 222 will be deeply investigated under anoxic conditions (see below).

223 The transformation rate of PCE was also investigated at increasing relative humidity. Fig.
 224 1B shows that the rate normalized for the incoming light intensity I_o decreases with increasing
 225 water vapor content, as previously reported when the mole fraction of H_2O is 50–60 times
 226 higher than that of PCE.[34] The inhibition of the PCE photocatalytic rate with the increment
 227 of the water vapor concentration can be rationalized by considering the competitive
 228 adsorption of PCE with water (W) for the same adsorption sites s , and can be modeled using a
 229 competitive Langmuir isotherm

$$230 \quad \{PCE\} = \frac{K_{ads}^{PCE}\{s\}[PCE]}{1 + K_{ads}^{PCE}[PCE] + K_{ads}^W[W]^n} \quad (\text{eq. 7})$$

231 where $\{ \}$ and $[]$ are concentrations at the surface and in the gas phase, respectively, and $\{s\}$ is
 232 the concentration of adsorption sites. The above isotherm can be easily derived using the
 233 balance of surface sites and the equilibrium constants of reactions $s + PCE \rightleftharpoons s\text{-}PCE$ and $s +$
 234 $nW \rightleftharpoons s\text{-}W_n$, which are K_{ads}^{PCE} and K_{ads}^W , respectively.

235 Combining equations (6) and (7) the experimentally determined PE is related to the
 236 concentration of gaseous water in the reactor by

$$237 \quad \frac{1}{PE} = a + b[W]^n \quad (\text{eq. 8})$$

238 where $a = \frac{1 + K_{ads}^{PCE}[PCE]}{k' K_{ads}^{PCE}\{s\}[PCE]}$ and $b = \frac{K_{ads}^W}{k' K_{ads}^{PCE}\{s\}[PCE]}$. In the used experimental conditions

239 a and b are constants ($[PCE] = 3$ ppm, constant surface area, constant light intensity).

240 By numerical fit of experimental data $n = 2.2 \pm 0.1$ was obtained, suggesting a displacement
 241 of 2 molecules of water for molecule of adsorbed PCE. The dashed curve in Fig. 1B is
 242 obtained with $n=2.2$, $a=18.3$, $b=920$ and shows the goodness of the model. Also linearization
 243 with eq. 8 has $R^2=0.992$. The model also predicts that PE is not dependent of the humidity at
 244 low water content, supplementing literature data [34] and confirming that traces of water are
 245 uninfluential for experiments carried out under dry condition. From the ratio a/b and under the
 246 reasonable hypothesis that $K_{ads}^{PCE}[PCE] \gg 1$ one obtains $K_{ads}^{PCE} = (1.6 \pm 0.2) \times 10^2 K_{ads}^W$. Because
 247 the dependence of the photocatalytic rate from the water content is highly dependent on the
 248 catalyst preparation [35], the reported value refers to the catalyst specimen used in this work.

249 As H₂O is needed to compensate surface unoccupied atomic orbitals,[36] the calculated value
250 indicates that PCE is strongly adsorbed.

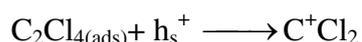
251 The competitive adsorption of H₂O and C₂Cl₄ on the same reactive sites is a strong proof
252 that the photocatalytic transformation of PCE takes place at the TiO₂ surface, where the direct
253 electron transfer occurs.

254 As a consequence of the detrimental role of water in the PCE photocatalytic
255 transformation, the below reported experiments were carried out in dry gas. Although under
256 this condition, traces of water are unavoidable, but such traces are uninfluential (see above).

257 **3.2 Basic mechanism**

258 The reactivity (transformation kinetics and by-products) was compared in the presence of
259 synthetic air (N₂ 80% + O₂ 20%) and in anoxic conditions (N₂ 100%) with the aim to give
260 insights on the role of oxidative and reductive pathways. A complete anoxia cannot be
261 reached as a consequence of the ubiquitous atmospheric oxygen which unavoidably diffuses
262 into the reactor and tubes, even though a continuous flow through the reactor with N₂ is fed.
263 This hinders to reach a complete anoxia even at very long irradiation time. On the contrary in
264 an ideal batch reactor in which diffusion of O₂ from the atmosphere is absent, initial traces of
265 oxygen would be easily removed during the photocatalytic process and authentic anoxic
266 condition would be reached. In actual anoxic experimental conditions a residual O₂
267 concentration ≤ 10 ppm was attained.

268 Fig. 2A shows the residual concentration of PCE going out of the reactor under irradiation.
269 A significant photocatalytic transformation of PCE was observed both in the presence and in
270 the absence of oxygen with a slightly higher conversion in oxygenated atmosphere. Despite of
271 the most common photocatalytic transformations of organic substrates are completely blocked
272 in the absence of electron scavengers (when {C_{ox}}=0, in eq. 3 y = 0, and consequently QY and
273 the rate are null), the rate of PCE degradation is only partially depressed with oxygen
274 shortage. This supports the previous hypothesis that C₂Cl₄ is able to be concurrently oxidized
275 by holes and reduced by the photoelectrons, as depicted in the following reactions:



292 reaction (r2) and that, in oxic conditions, it reacts in later steps of degradation. Then reductive
293 electron transfer, which occurs only at the catalyst surface, is always operating.

294 From the comparison between the amount of cumulated chloride and the total amount of
295 PCE photocatalytically transformed in the same time, the molar fraction χ of C_2Cl_4 converted
296 in chloride was computed (ratio between the μmol of C_2Cl_4 degraded and the μmol of
297 deposited chloride, both normalized per unit area). The values of χ are reported as inset in
298 Fig. 2B. In the presence of O_2 larger values of χ were observed, which indicate that PCE is
299 oxidized according to reaction (r1) without losing chloride anion, and later reactions with O_2
300 increment its degradation rate. Then organic chlorine must be released in some other forms as
301 well as chloride.

302 The transformation of PCE was investigated on TiO_2 films on which different amount of
303 chloride ion was deposited through evaporation of an aerosol of sodium chloride solution. To
304 prevent that the amount of surface chloride changed significantly during the photocatalyzed
305 reaction, the experiments were carried out at low conversion and shortly terminated (after 10
306 minutes of irradiation). Fig. 3A shows the PE with and without oxygen as a function of the
307 chloride amount added at the surface. In both oxic and anoxic condition the addition of
308 chloride ion had a detrimental effect on the PCE degradation rate for the reasons already
309 discussed (a redox null cycle or physical occupation of sites, preventing PCE adsorption).

310 The former hypothesis was that organic chlorine could be released as Cl^\bullet , which also
311 favors chain reactions useful for further degradation, and that also chloride ion can be
312 oxidized to Cl^\bullet radical as mentioned in the Introduction. Then, the production of active
313 chlorine gives insights not only on the role of the surface chloride in the photocatalytic
314 process, but also on some other peculiar aspects of the photocatalytic transformation of PCE.

315 The production of active chlorine (AC, i.e. $HClO/ClO^-$, Cl_2 , ClO and ClO_2) in the gaseous
316 phase is reported in Fig. 3B as a function of the irradiation time under the four investigated
317 conditions. Only in the presence of oxygen the production of a significant amount of AC was
318 observed (after a delay time of roughly 30 minutes due to the exponential dilution in the CST
319 reactor) while in anoxic conditions the concentration of AC is lower than the limit of
320 detection. Because in the absence of O_2 the only active chlorine species that can be produced
321 is Cl_2 , the transformation of PCE does not involve pathways in which the production of Cl_2 is
322 operational. The absence of Cl_2 excludes that Cl^\bullet radicals are produced through oxidation by
323 holes of chloride ion self-released or added as $NaCl$, or through release from intermediates,
324 and agrees with the absence of Cl^\bullet evidenced by EPR spectroscopy.[19] The holes at the
325 surface (h_s^+) have a sufficient redox potential for the oxidation of Cl^- to Cl^\bullet .[17] A possible
326 competition of chloride ion for h_{VB}^+ is possible as a decrease of the rate was observed (Fig.
327 3A). However, this radical is evidently not formed because surface mediated recombination
328 processes with e_{CB}^- could be operational. Then, the suggested production of a significant
329 amount of chlorine radical at the irradiated surface [2,4,39] is not in agreement with the
330 absence of AC observed here without oxygen.

331 Conversely, in the presence of oxygen there is production of AC. Even if the eventually
332 formed chlorine radical reacts with oxygen to give ClO_2 , under irradiation it can be
333 immediately transformed into ClO through its photolysis via the reaction $ClO_2 (^2B_2) \rightarrow$
334 $ClO(2\Pi) + O(^3P)$ [38], and then the detected AC is composed of $HClO$ and/or ClO . However,
335 because Cl_2 is not formed under anoxic conditions as above reported, there is good reason to
336 assume that only oxygenated species such as $HClO/ClO^-$, and ClO are produced in the

337 presence of oxygen. Furthermore, as no significant difference between the production of AC
338 in the presence of oxygen was observed for the pristine and surface chlorinated catalysts (see
339 Fig. 3B), these species must derive from intermediates, and are produced through their
340 dehalogenation, that is organic chlorine is directly released as HClO or ClO. Then, in the
341 presence of oxygen the operational mechanism for PCE transformation would imply the
342 production of oxygenated chlorinated species.

343 **3.3 Main intermediates**

344 The main by-products of the PCE photocatalytic transformation are those previously
345 reported [2,4,39], namely phosgene, trichloroacetyl chloride (TCAC), tetrachloromethane and
346 esachloroethane. The gaseous species were identified through FT-IR spectrophotometry
347 equipped with a cell with long optical path (8 m) and GC-MS. From FT-IR spectra (see Fig.
348 3-SM) in the 2500-500 cm^{-1} CO_2 , COCl_2 , traces of TCAC and other unknown chlorinated
349 compounds were detected (see SM under 3.). The identification of the main products was
350 carried out by comparing the recorded spectra with the spectra of pure gaseous standard.[40]
351 From GC-MS with cryofocusing the residual C_2Cl_4 , the produced CCl_4 and C_2Cl_6 were
352 detected (see Fig. 4-SM).

353 Fig. 4A shows the concentration of photocatalytic produced carbon tetrachloride in the
354 presence and absence of oxygen. The presence of chlorides has a detrimental effect on the
355 production of CCl_4 both with and without O_2 . The effect is larger under anoxic conditions.
356 The production of CCl_4 is strongly inhibited in the presence of oxygen. The concentration of
357 this molecule increased monotonically during the experiments in both cases, but the
358 concentrations reached in anoxic conditions are roughly 1-2 order of magnitude higher than in
359 the presence of oxygen (see Fig. 5-SM). Then the increase of CCl_4 with irradiation time is
360 *NOT* correlated with the concomitant increase of released chloride observed during the
361 photocatalytic degradation of PCE (see Fig. 2B). CCl_4 must be released from intermediates
362 formed upon further chlorination, favored under anoxic conditions, and the chlorination is not
363 due to chlorine radical, as discussed before.

364 During the same experiments the evolution of hexachloroethane was also monitored. As
365 for CCl_4 , the production of C_2Cl_6 is totally impeded by an excess of oxygen and favored by
366 anoxic conditions. Conversely, chloride ions at the surface favor its production (Fig. 4B).
367 Given that $\bullet\text{Cl}$ radical is not present and that the primary reducing step decrements by one the
number of organic chlorine, there is the sole possibility that the carbocation C^+Cl_2

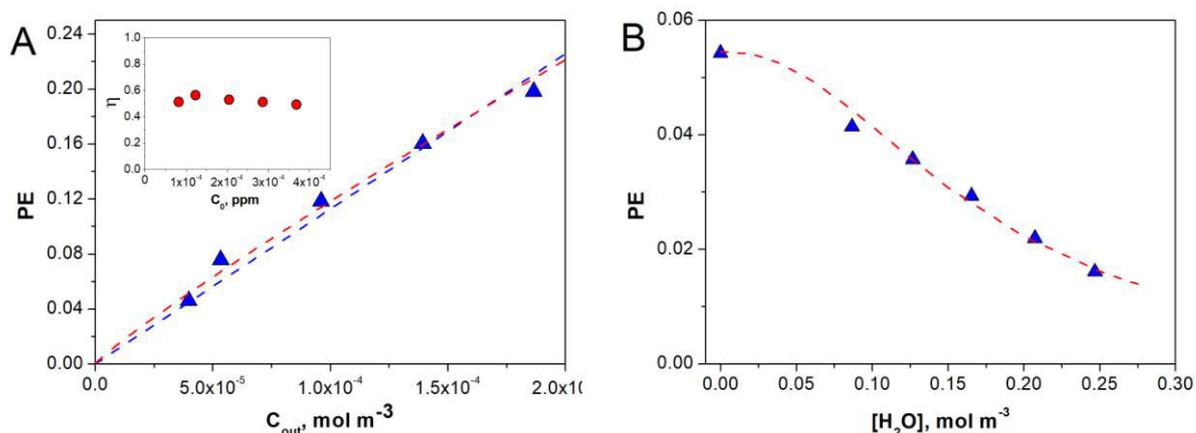
381 carbocation was demonstrated as necessary to justify observed reaction products.[24] The
382 reaction of an anion with a carbocation, actually formed for direct hole transfer to PCE
(reaction r1) and with CCl_3

425 The mechanism of formation of the detected compounds and of higher MW compounds
426 with conjugated double bonds could be sketched as: 1) the addition of C₂Cl₄ to neutral radical
427 formed upon reduction (r2); 2) the arrangement of the radical by chlorine transposition; 3)
428 loss of CCl₄ (as suggested before). Amongst these steps the oxidation of intermediates by
429 holes forms a carbocation that adds one chloride anion, giving molecules with less double
430 bonds and more chlorine (toward chloroalkanes, as depicted in r4 and r5). Alternatively,
431 amongst these steps, the reduction of intermediates by e_s⁻ and loss of chloride ion forms a
432 neutral molecule or radical that can undergo the previous reactions. The formation of the
433 detected 1,1,2,3,4,4-hexachlorobuta-1,3-diene is here proposed as an example (see also Fig.
434 6).



462 **FIGURE CAPTIONS**

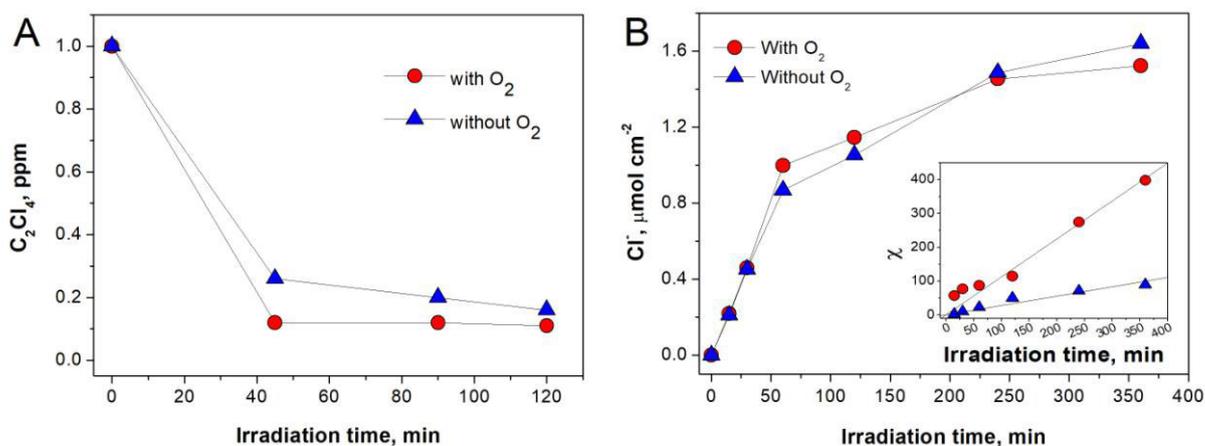
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465 **Fig. 1.** (A) Photon efficiency $PE = \text{rate}/I_0$ of PCE transformation as a function of actual
 466 concentration in the reactor. Inset: conversion as a function of inlet concentration C_0 .
 467 Conditions: $C_0 = 2\text{-}9$ ppm, total flow = 3.0 L min^{-1} (N_2 80%, O_2 20%), $S = 15 \text{ cm}^2$, $I_0 = 10 \text{ W m}^{-2}$. (B) Photon efficiency PE of PCE transformation as a function of actual water vapor
 468 concentration. The dashed line shows the data interpolation with eq. 8 (see text). Conditions:
 469 $C_0 = 3$ ppm, total flow = 1.6 L min^{-1} (N_2 80%, O_2 20%), $S = 15 \text{ cm}^2$, $I_0 = 10 \text{ W m}^{-2}$.
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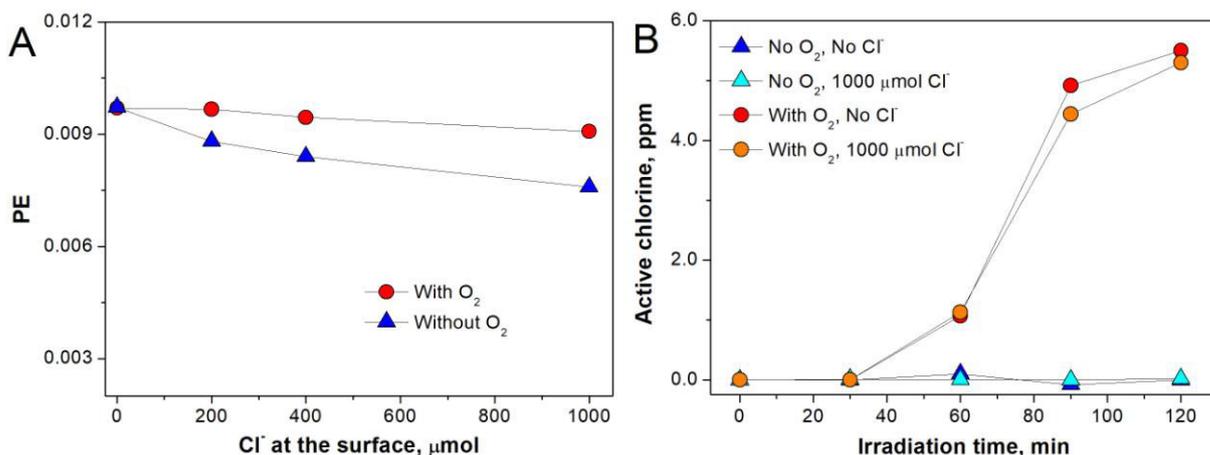


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475 **Fig. 2.** (A) residual concentration of PCE going out of the reactor in the presence of
 476 oxygen (N_2 80% + O_2 20%) and in quasi-anoxic conditions (N_2 100 %) as a function of the
 477 irradiation time. Experimental conditions: $C_0 = 1$ ppm, total flow = 1.6 L min^{-1} (N_2 80% + O_2
 478 20% or N_2 100%), $S = 100 \text{ cm}^2$, $I_0 = 10 \text{ W m}^{-2}$, volume sampled in the cryogenic trap = 50 mL.
 479 (B) Evolution of the surface concentration of Cl^- as a function of the irradiation time. Inset:
 480 molar fraction χ of C_2Cl_4 converted in chloride ion. Experimental conditions: $C_0 = 3$ ppm,
 481 total flow = 1.6 L min^{-1} (N_2 80% + O_2 20% or N_2 100%), $S = 15 \text{ cm}^2$, $I_0 = 10 \text{ W m}^{-2}$.

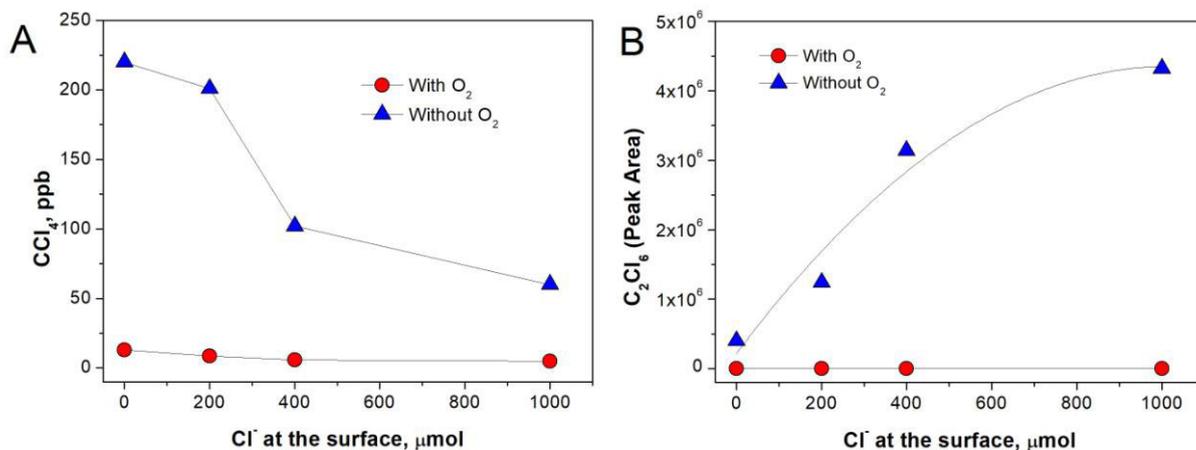


482

483 **Fig. 3.** (A) Photon efficiency $PE = \text{Rate}/I_0$ for C_2Cl_4 degradation (after 10 minutes of
 484 irradiation) in the presence or absence of oxygen as a function of the amount of chloride ions
 485 added (as NaCl) at the TiO_2 film surface. Experimental conditions: $C_0 = 3 \text{ ppm}$, total flow =
 486 1.6 L min^{-1} (N_2 80% + O_2 20% or N_2 100%), $S = 100 \text{ cm}^2$, 10 W m^{-2} . (B) Concentration of
 487 active chlorine flowing out of the reactor as a function of the irradiation time in the presence
 488 or absence of added chloride (1000 μmol NaCl) at the TiO_2 film surface. Experimental
 489 conditions: $C_0 = 10 \text{ ppm}$, total flow = 2.4 L min^{-1} (N_2 80% + O_2 20% or N_2 100%), $S = 100$
 490 cm^2 , 10 W m^{-2} .

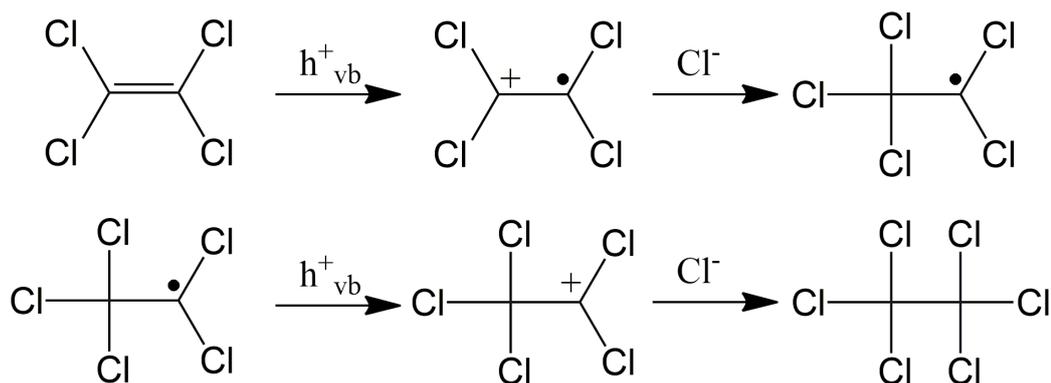
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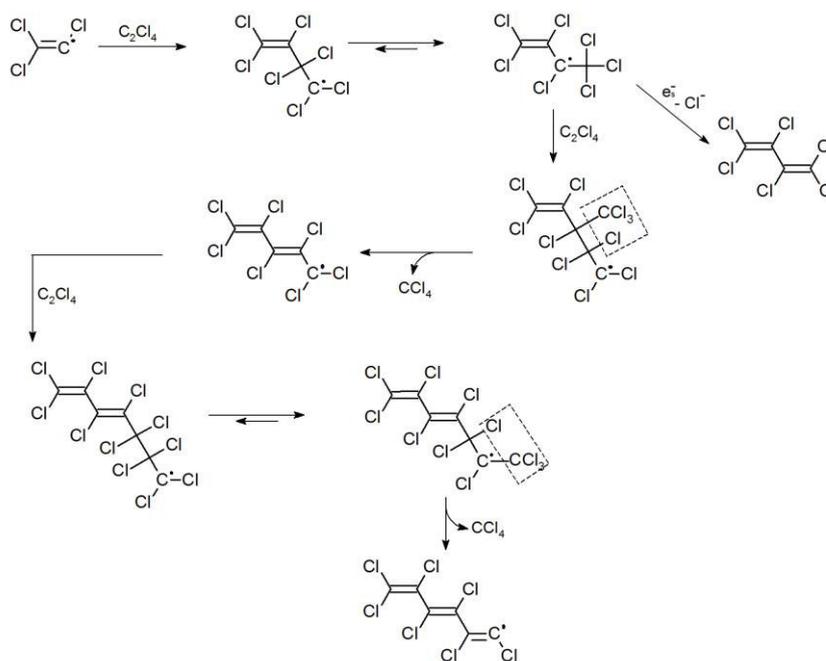
493

494 **Fig. 4.** Concentration of formed CCl_4 (A) and Chromatographic peak area for C_2Cl_6 (B)
 495 after 10 minutes of irradiation during the photocatalytic transformation of C_2Cl_4 in the
 496 presence or absence of oxygen as a function of the amount of chloride ions added (as NaCl) at
 497 the TiO_2 film surface. Experimental conditions: $C_0 = 3 \text{ ppm}$, total flow = 1.6 L min^{-1} (N_2 80%
 498 + O_2 20% or N_2 100%), $S = 100 \text{ cm}^2$, $I_0 = 10 \text{ W m}^{-2}$.



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Fig. 5. Mechanism of reaction for the production of C_2Cl_6 during the photocatalytic transformation of gaseous PCE under irradiated TiO_2 in anoxic condition.



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Fig. 6. Suggested mechanism proposed for the production of polyene compounds at the surface of the photocatalyst in anoxic conditions. The structural analogy between the first and the last radicals of the reaction chain allows the perpetuation of the reaction with the production of compounds with higher molecular weight.

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1 **A revised photocatalytic transformation mechanism for**
2 **chlorinated VOCs: experimental evidence from C₂Cl₄ in**
3 **the gas phase**

4
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6

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21 **SUPPLEMENTARY MATERIAL**

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25 **1 MATERIALS AND METHODS 2**
26 1.1 MATERIALS 2
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41 1 Materials and Methods

42 1.1 Materials

43 Titanium dioxide (Hombikat N100: 100% anatase, BET specific surface area $100 \text{ m}^2 \text{ g}^{-1}$,
44 average crystal size 20 nm) was purchased from Sachtleben Chemie GmbH (Duisburg,
45 Germany). Perchloroethylene (PCE, 99.9%), Titanium(IV) isopropoxide (97%), N,N-Diethyl-
46 p-phenylenediamine (97%), NaOH ($\geq 98\%$), Na_2HPO_4 ($\geq 98\%$) and NaH_2PO_4 (99%) were
47 purchased from Sigma Aldrich and absolute ethanol from Fluka ($\geq 98\%$). Nitrogen was
48 obtained from the evaporation of pure liquid nitrogen (99.999%, SIAD, Italy) while gaseous
49 oxygen (research grade 99.9%) and chromatographic grade Helium (5.5 grade) were supplied
50 by SIAD (Italy). Gaseous standards of PCE were prepared in 15 L SilcoCan™ (Restek)
51 canisters diluting PCE in nitrogen at the desired concentration. All the compounds were used
52 as received without any further purification step. Water was purified with a MilliQ plus
53 apparatus (TOC = 2 ppb, conductivity $18.2 \text{ M}\Omega \text{ cm}$).

54 1.2 Preparation of the TiO_2 films

55 TiO_2 films were prepared as follow. 12.5 g of TiO_2 Hombikat N100 were suspended in 50 mL
56 of a Titanium(IV) isopropoxide (TIP, 0.33 mol L^{-1}) in absolute ethanol. 2 mL of the
57 suspension were deposited on the surface of $10 \times 10 \text{ cm}^2$ Pyrex glass substrates, in this way
58 0.55 g of TiO_2 were deposited on each Pyrex glass substrate as sum of the nanocrystalline
59 catalyst (0.50 g) and the amorphous TiO_2 phase obtained from the hydrolysis of TIP (0.05 g).
60 The samples were dyed at $100 \text{ }^\circ\text{C}$ for 150 min and UV irradiated (18 W m^{-2} in the 300-400
61 nm range) for 18 hours with the aim to photocatalytically remove the organic residues from
62 the catalyst surface. The hydrolysis of TIP is essential to obtain a compact and well anchored
63 films. The TiO_2 film samples were storage in the dark and in a closed box to avoid possible
64 poisoning of the surface before use.

65 1.3 Methods and experimental set-up

66 The monitoring of C_2Cl_4 flowing out the reactor was carried out with a Photo Ionization
67 Detector PID-AH (from α -Sense with Kr as filling gas for the glow discharge lamp) which
68 signal was amplified (model AD327 amplifier, Analog device), digitalized and recorded by
69 using an analog-to-digital converter (model NI USB-6221, National Instruments).

70 The volatile VOCs flowing out the reactor were analysed by both GC-MS after cryofocusing
71 and directly by FTIR spectrophotometry.

72 The cryofocusing system was a Model 7000 Entech system able to focus at the temperature of
73 liquid nitrogen the VOCs, eliminate both CO_2 and water vapour, and inject into the
74 chromatographic system the preconcentrated samples. The GC-MS system used for the VOCs
75 determination was a 6890 GC hyphenated with a 5973 Mass Selective Detector (Agilent
76 Technologies). The column was an Agilent CP-Sil 5 CB column (length 60 m, i.d. 0.32 mm,
77 film thickness $0.1 \mu\text{m}$). The analyses were carried out starting from 35°C , increasing the
78 temperature at $5 \text{ }^\circ\text{C}/\text{min}$ up to 140°C and from 140°C to 240°C at $15 \text{ }^\circ\text{C}/\text{min}$.

79
80 Volatile by-products of the PCE photocatalytic transformation were also detected through FT-
81 IR (Cary 670 spectrophotometer, Agilent Technologies) equipped with a cell for gases with 8
82 m long optical path length. Both the cell and the transfer line were thermostated at $150 \text{ }^\circ\text{C}$.
83 The FT-IR spectrophotometer was equipped with a KBr bean splitter and a MCT detector.

84
85 The organic compounds cumulated at the catalyst surface in the anoxic conditions were
86 determined through extraction with dichloromethane after irradiation of the film of TiO_2 and

87 analysed through an Agilent 6890 GC equipped with a GERSTEL CIS4 PTV injector
88 (injection volume 2 μL in splitless mode). The column used was an Agilent HP-5MS (length
89 30 m, i.d. 0.25 mm, film thickness 0.25 μm). The starting oven temperature was 40 $^{\circ}\text{C}$ for 3
90 min with a ramp of 5 $^{\circ}\text{C}/\text{min}$ up to 320 $^{\circ}\text{C}$ (maintained for 9 minutes). The mass spectra
91 obtained were interpreted for comparison with the standard spectra reported in the Wiley 7n
92 library (Agilent part No. G1035B). For both the GC analysis the carrier gas was He of
93 chromatographic grade (Sapio, Italy).

94
95 The deposition of water soluble anions at the TiO_2 film surface during the photocatalytic
96 transformation of PCE with and without oxygen was evaluated. After different irradiation
97 times in condition of constant flow of PCE, the films were removed from their Pyrex glass
98 supports, extracted with ultrapure water and the aqueous samples analyzed. The determination
99 of water extractable anions cumulated at the catalyst surface was done through ion
100 chromatography (Dionex 500, with GP40 pump, Rheodyne 9126, 50 μL loop, LC30 oven,
101 ASRS-II Ultra conductivity suppressor and ED40 detector) with the analytical column AS9-
102 HC and column guard AG9-HC. The eluent was K_2CO_3 9 mM, and the flow rate adopted was
103 1 mL/min keeping the column temperature oven at 30 $^{\circ}\text{C}$.

104
105 Some TiO_2 samples obtained at different irradiation times and conditions were analysed by
106 FT-IR Spectrophotometry to investigate the changes in the surface properties. The samples
107 were pressed in self-supporting pellets (“optical thickness” of $\approx 10 \text{ mg cm}^{-2}$) and placed in an
108 IR cell with KBr windows (Aabspec), permanently attached to a vacuum line (residual
109 pressure = 1.0×10^{-6} Torr), allowing desorption and thermal treatments to be carried out *in*
110 *situ*. We used a Perkin-Elmer System 2000 FT-IR spectrophotometer equipped with a MCT
111 cryodetector able to record spectra in the 7200-580 cm^{-1} range.

112
113 Finally, the UV-Vis reflectance spectra of the film obtained at different irradiation time in the
114 presence of C_2Cl_4 both in oxygen rich and in anoxic conditions were recorded by a Cary 5000
115 (Varian) spectrophotometer with an integration sphere in polytetrafluoroethylene (PTFE)
116 with a 150 mm diameter. The elaboration of the %R spectra was carried out by the Kubelka-
117 Munk equation using a PTFE standard sample as reference blank.

118 119 **1.4 Photochemical reactor and related kinetic treatment**

120 The experiments of PCE transformation were carried out through the experimental set up
121 schematized in Fig. 1-SM. The homemade flow-through photo-reactor worked in a regime of
122 perfect mixing (Continuous Stirred Tank Reactor, CSTR). An internal fan allows the absence
123 of any concentration gradient inside the reactor. The reaction chamber (340 \times 180 \times 90 mm) was
124 in poly-methyl-methacrylate (PMMA) sealed with epoxy glue to avoid air leakage. The cover
125 of the reactor was a Pyrex glass 5 mm thick with a full optical transparency in the emission
126 wavelength range of the adopted light source. A set of two Philips PL-S 9W/2P BLB lamps
127 was used as irradiation source with an emission spectra in the 350-400 nm range with a
128 maximum of emission at 365 nm. To modify the UV irradiance reaching the sample the
129 relative distance between the light source and the sample was properly modified. The light
130 irradiance was measured through a photometer purchased by the Italian vendor
131 CO.FO.MEGRA. The radiative power [W m^{-2}] was converted in the related photon flux [mol
132 of photons $\text{m}^{-2} \text{s}^{-1}$] on the basis of the lamp spectrum. A homogeneous irradiation of the whole
133 catalyst surface was always assured. The reactor was built according to the CEN/TS 16980-
134 1:2016 Technical Specification proposed for the Determination of the degradation of nitric
135 oxide (NO) in the air by photocatalytic material.[1] A set of valves allowed the regulation of

136 the inlet/outlet gas flow and the by-pass of the reactor chamber. The gas flow flowing out the
 137 reactors is properly analysed as reported above. For a detailed description of the testing
 138 procedure see ref.[2].

139 The mass balance for C_2Cl_4 in the reactor as a function of the reaction time (for
 140 photochemical transformation the irradiation time (t) is

$$V_R \frac{d}{dt} C_{out}(t) = F[C_0 - C_{out}(t)] - S Rate(t) \quad (\text{eq. 1-SM})$$

141 where V_R is the reactor volume, $C_{out}(t)$ is the concentration of C_2Cl_4 going out the reactor at
 142 the irradiation time t , F is the total flow, S is the geometric area of the TiO_2 film, C_0 is the
 143 concentration of the reactant entering the reactor and $Rate(t)$ is the transformation rate
 144 normalized for unit area of C_2Cl_4 in the reactor at the irradiation time t .

146 In condition of steady state (SS , $t \rightarrow \infty$ and no change in the photoactivity of the catalyst, e.g. no
 147 poisoning or photo-activation as a consequence of the irradiation) the concentration of C_2Cl_4

148 does not change with the time ($V_R \frac{d}{dt} C_{out}(t) = 0$) and consequently

$$F[C_0 - C_{out}(t)] - S Rate^{SS}(t) = 0 \quad (\text{eq. 2-SM})$$

149 Defining the conversion at the time t as

$$\eta(t) = \frac{C_0 - C_{out}(t)}{C_0} \quad (\text{eq. 3-SM})$$

152 The transformation rate can be expressed as a function of the conversion and so directly
 153 measured from the experimental profiles in steady state conditions (eq. 4-SM) [2].

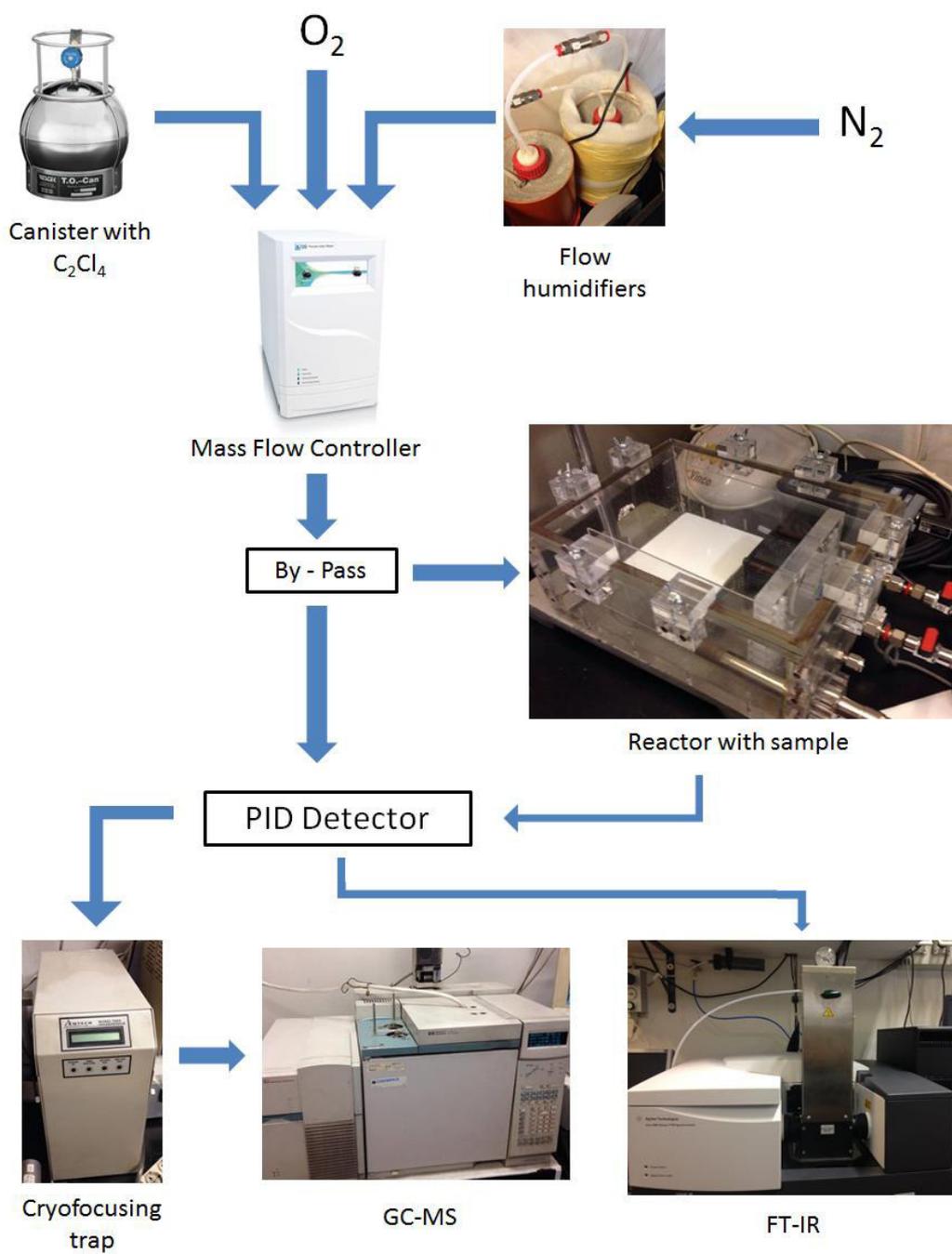
$$Rate^{SS} = \frac{C_0 \eta_{\infty} F}{S} \quad (\text{eq. 4-SM})$$

155 The inlet gas flows and their concentrations were set with an Entech-4600A Mass Flow
 156 Controller (MFC) mixing pure N_2 , O_2 , and concentrated C_2Cl_4 in N_2 . Relative humidity was
 157 set by bubbling dry N_2 in thermostated pure water under a fixed pressure.

158
 159 A thermohygrometric sensor placed in the reaction chamber allowed the determination of
 160 both the relative humidity and the temperature. The absolute humidity was computed on the
 161 basis of eq. 5-SM [3]

$$p_{H_2O} = 6.11 \frac{RH\%}{100} 10^{\frac{7.5T}{237.7+T}} \quad (\text{eq.5-SM})$$

162 in which p_{H_2O} is the absolute humidity (atm), $RH\%$ is the relative humidity % and T is the
 163 temperature ($^{\circ}C$). In order to express the absolute humidity in ppm the value of p_{H_2O} [atm]
 164 was multiplied for 10^6 (the atmospheric pressure was considered stable and equal to 1 atm).
 165
 166



167

168 **Fig. 1-SM** Scheme of the experimental apparatus adopted for the investigation of the
 169 photocatalytic transformation of C_2Cl_4 .

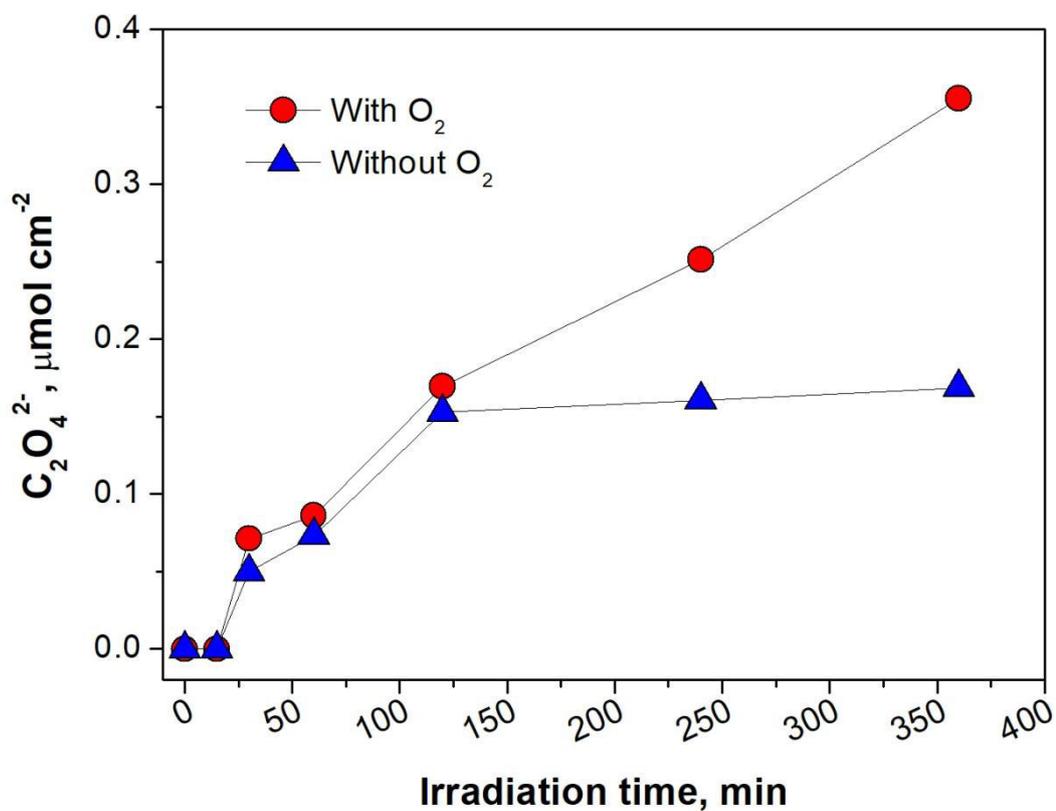
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173 **2 Main Intermediates**

174 Evolution of the amount of oxalate (normalized for the film surface area) deposited on the
175 TiO₂ surface in the presence or absence of oxygen



176

177

178 **Fig. 2-SM** Evolution of the amount of oxalate (normalized for the film surface area) deposited
179 on the TiO₂ surface in the presence or absence of oxygen as a function of the irradiation time
180 during the photocatalytic transformation of gaseous C₂Cl₄. Experimental conditions: C₀ = 3
181 ppm, total flow = 1.6 L min⁻¹ (N₂ 80% + O₂ 20% or N₂ 100%), S = 15 cm², 10 W m⁻².

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183

184 3 Detection of gas species

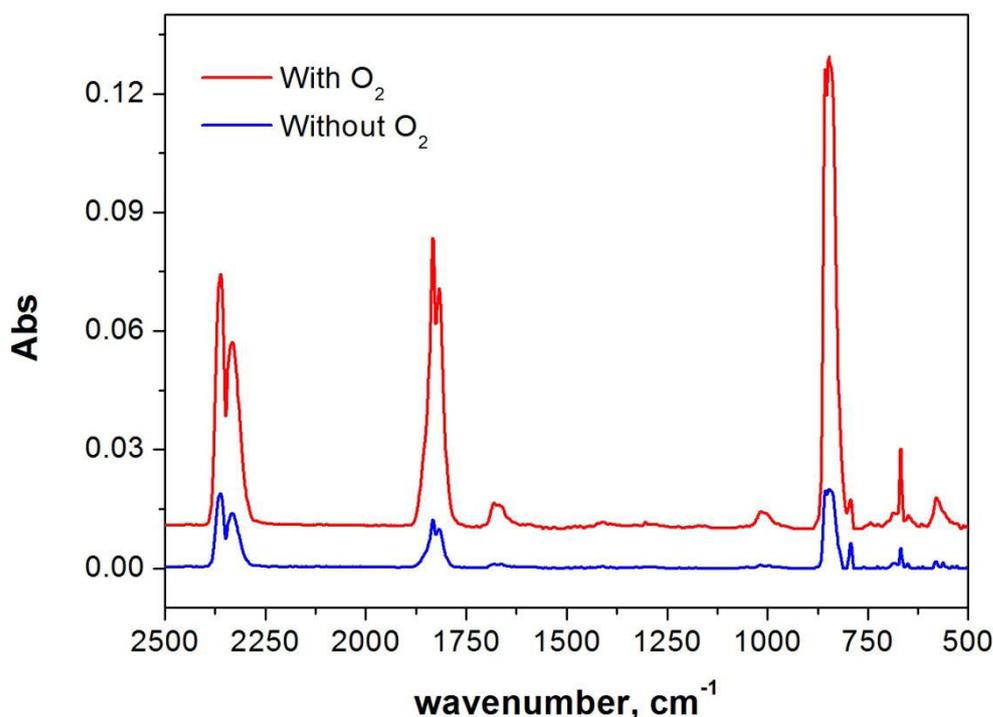
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186 The gaseous species were identified through FT-IR spectrophotometry with long optical path
187 cell (8 m) and GC-MS.

188 In FT-IR spectra (see Fig. 3-SM) there is the absence of the two main IR signals of the PCE at
189 914 and 780 cm^{-1} due to the abatement of C_2Cl_4 at concentration lower than the limit of
190 detection of the technique. The main products observed both in the presence and absence of
191 oxygen are carbon dioxide (see the doublet with maxima at 2330 and 2360 cm^{-1} related to its
192 asymmetric stretching) and phosgene (main peaks at 794, 846, 856, 1016, 1680, 1818 and
193 1834 cm^{-1}). Furthermore, traces of both TCAC and other chlorinated compounds can be
194 hypothesized due to the presence of other minor peaks (e.g. 794, 668 and 569 cm^{-1}) not
195 ascribable to the main transformation products.

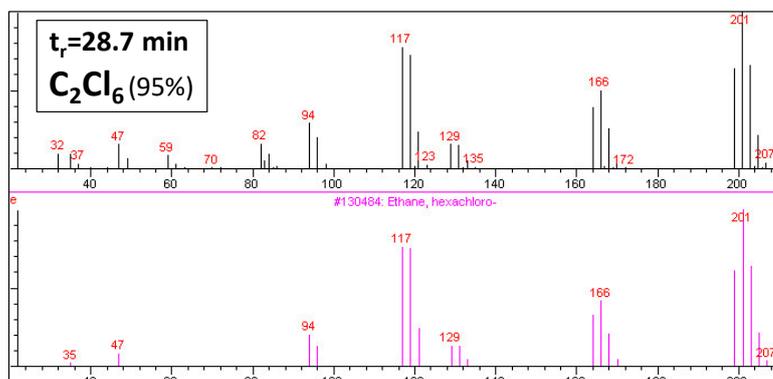
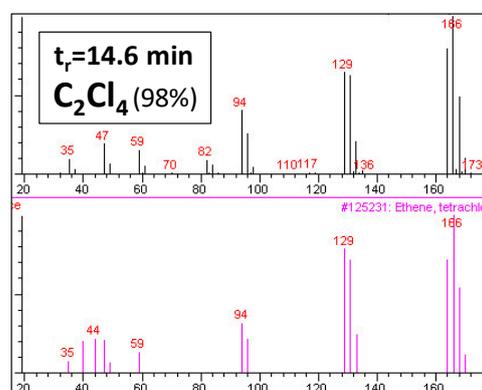
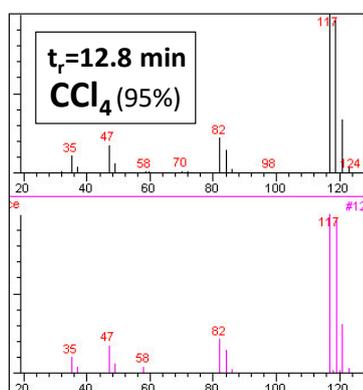
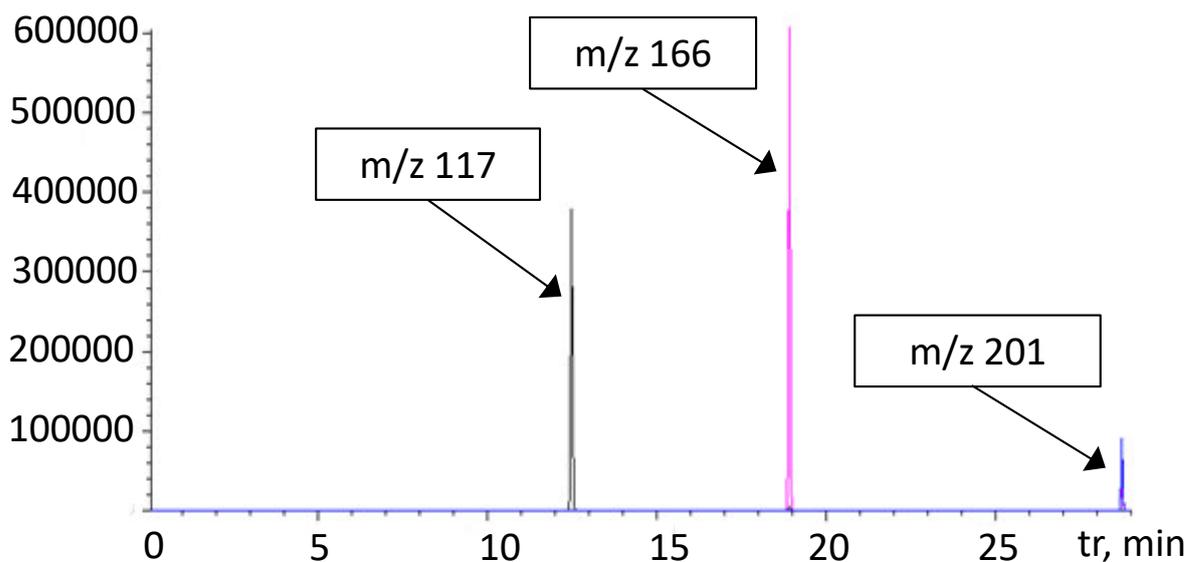
196 The analysis of the by-products formed during the photocatalytic transformation of PCE were
197 carried out also by GC-MS through cryofocusing at the temperature of the liquid nitrogen.
198 The chromatograms obtained (an example is reported in Fig. 4-SM) are dominated by 3 main
199 peaks related to the presence of the residual C_2Cl_4 ($t_r = 14.6$ min), the photocatalytically
200 produced CCl_4 ($t_r = 12.8$ min) and C_2Cl_6 ($t_r = 28.7$ min). The identification of the nature of
201 these compounds were carried out on the basis of the mass spectra (matching between the
202 recorded spectra and the spectra reported in the NIST library $\geq 95\%$). Note that the absence of
203 phosgene in the chromatogram can be easily explained considering that this compound reacts
204 in the focusing system with the traces of water producing CO_2 and HCl and consequently
205 cannot be determine by the adopted GC-MS system.

206



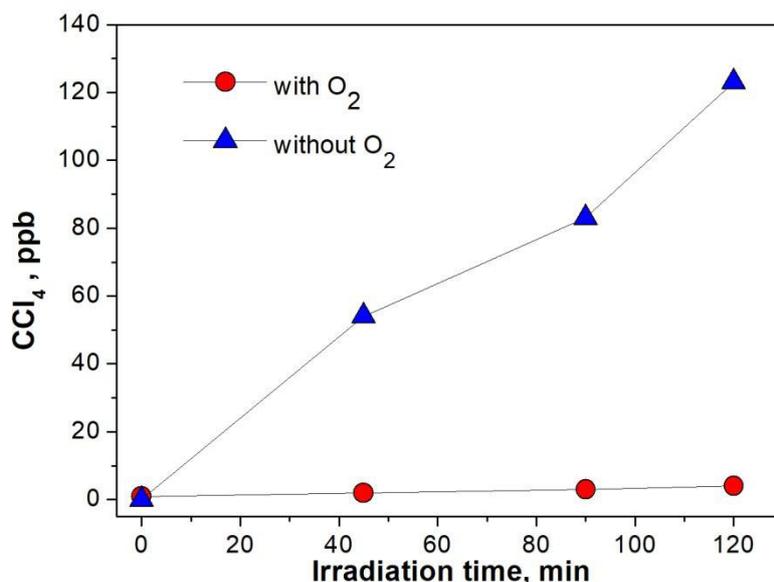
207

208 **Fig. 3-SM** FT-IR spectra in the 2500-500 cm^{-1} range of the gaseous species flowing out of
209 the reactor chamber during the photocatalytic transformation of C_2Cl_4 in the presence of
210 oxygen (red line) and in quasi-anoxic conditions (blue line). Experimental conditions: $C_0 = 20$
211 ppm, total flow = 2.0 L min^{-1} (N_2 80% + O_2 20% or N_2 100%), $S = 100 \text{ cm}^2$, 10 W m^{-2} ,
212 resolution 4 cm^{-1} .



213
214

215 **Fig. 4-SM** GC analysis of the gaseous species flowing out of the reactor during the C_2Cl_4
 216 photocatalytic transformation under UV-irradiated TiO_2 film. Example of chromatogram
 217 (Selective Ion Monitoring (SIM) mode, m/z 117, 166 and 201) and Mass Spectra of the main
 218 compounds. For the three compounds identified the related spectra present in the MS library
 219 Wiley 7n library were reported together with the goodness of fit ($\geq 95\%$). Experimental
 220 conditions: $C_0 = 1$ ppm, total flow = 1.6 L min^{-1} (N_2 80% + O_2 20%), $S = 100$ cm^2 , 10 W m^{-2} ,
 221 volume sampled in the cryogenic trap = 50 mL.

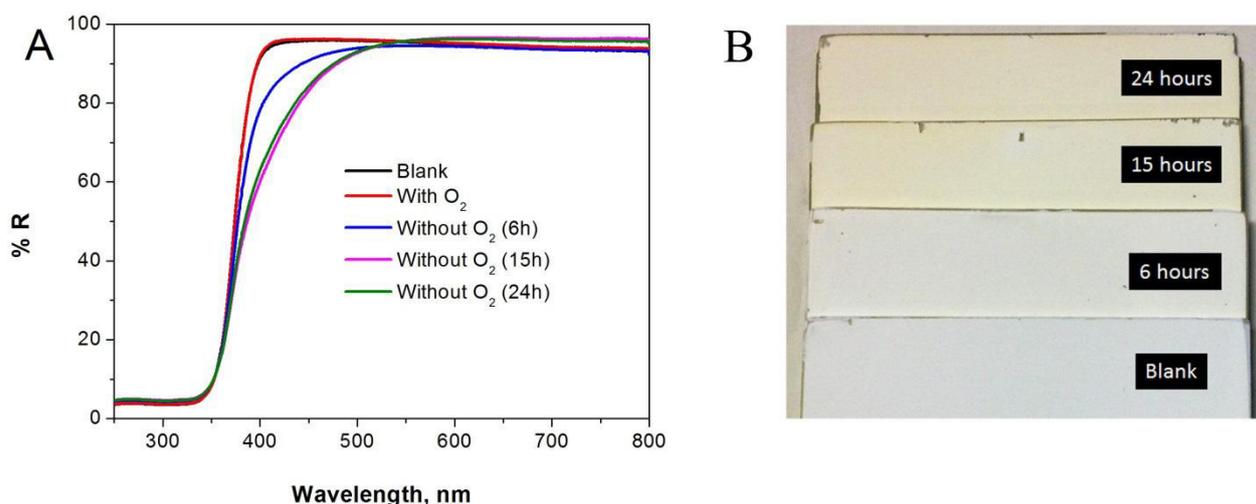


222
 223 **Fig. 5-SM** Concentration of the photocatalytically generated CCl₄ (B) in the presence of
 224 oxygen (N₂ 80% + O₂ 20%) and in anoxic conditions (N₂ 100 %) as a function of the
 225 irradiation time. Experimental conditions: C₀ = 1 ppm, total flow = 1.6 L min⁻¹ (N₂ 80% + O₂
 226 20% or N₂ 100%), S = 100 cm², 10 W m⁻², volume sampled in the cryogenic trap = 50 mL.
 227

228 4 Surface species

229 4.1 UV-Vis reflectance measurements and poisoning

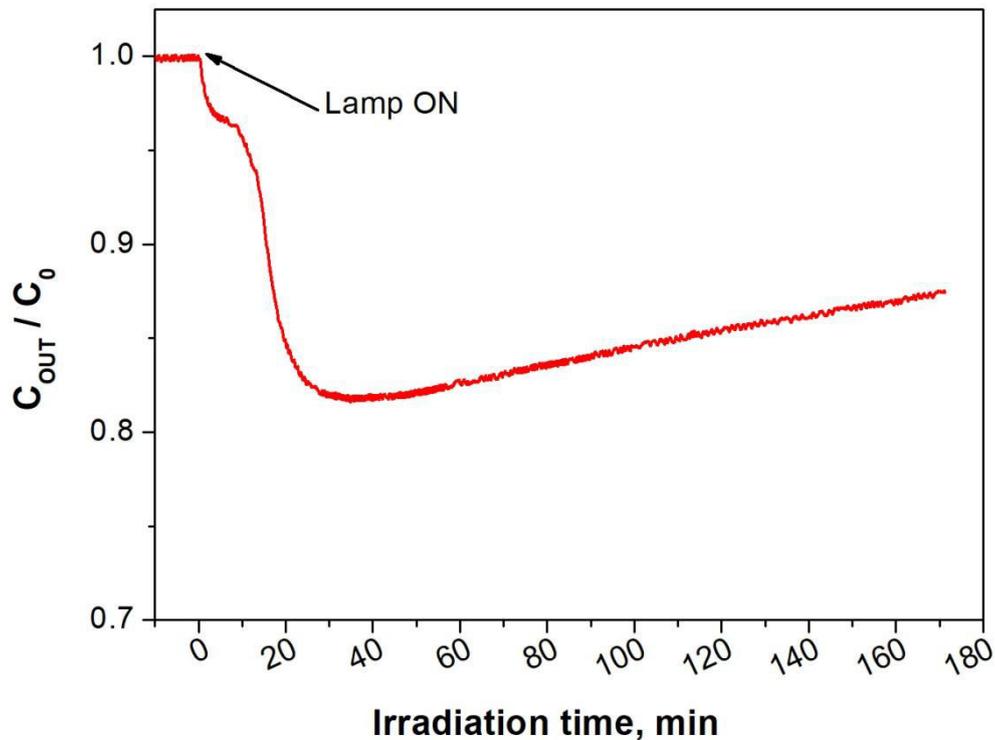
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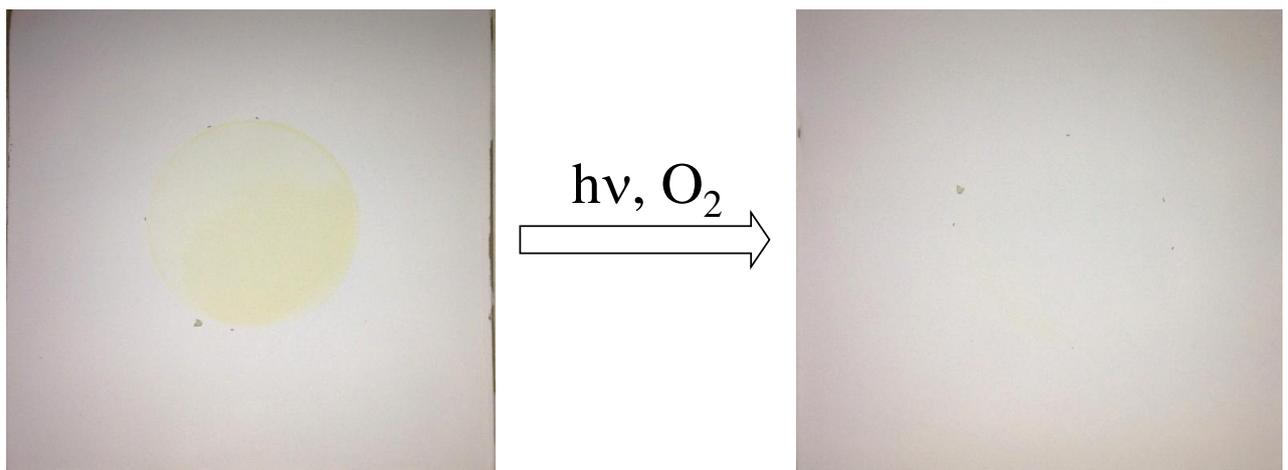
231
 232 **Fig. 6-SM** Evolution of the TiO₂ film surface during the photocatalytic transformation of
 233 C₂Cl₄ in quasi anoxic-condition under prolonged UV-irradiation (from 0 to 24 hours of
 234 continuous irradiation). A) UV-Vis reflectance spectra of the TiO₂ films; B) Pictures of the
 235 films obtained after different irradiation times (note the progressive evolution of the surface
 236 color toward pale yellow). Experimental conditions: C₀ = 10 ppm, total flow = 2.1 L min⁻¹
 237 (N₂ 100%), S = 100 cm², 10 W m⁻².
 238

239 **4.2 Conversion in CSTR in anoxic conditions**

240 During irradiation the experimental conversion in CSTR (after the first transient) decreases,
241 due to poisoning. This effect can't be diagnosed in batch experiments.



242 **Fig. 7-SM** Residual concentration of C_2Cl_4 under anoxic-condition as a function of the
243 irradiation time. Experimental conditions: $C_0 = 10$ ppm, total flow = 2.1 L min^{-1} (N_2 100%), S
244 = 100 cm^2 , 10 W m^{-2} .
245
246
247



248 **Fig. 8-SM** Effect of the irradiation in the presence of oxygen on the TiO_2 film obtained at the
249 end of a long time irradiation in the presence of C_2Cl_4 in quasi anoxic-condition. Note that the
250 yellow-pale compounds deposited during in the anoxic phase disappeared during the
251 irradiation in the presence of oxygen. Experimental conditions: $C_0 = 10$ ppm, total flow = 2.1
252 L min^{-1} (N_2 100%), $S = 15 \text{ cm}^2$, 10 W m^{-2} .
253
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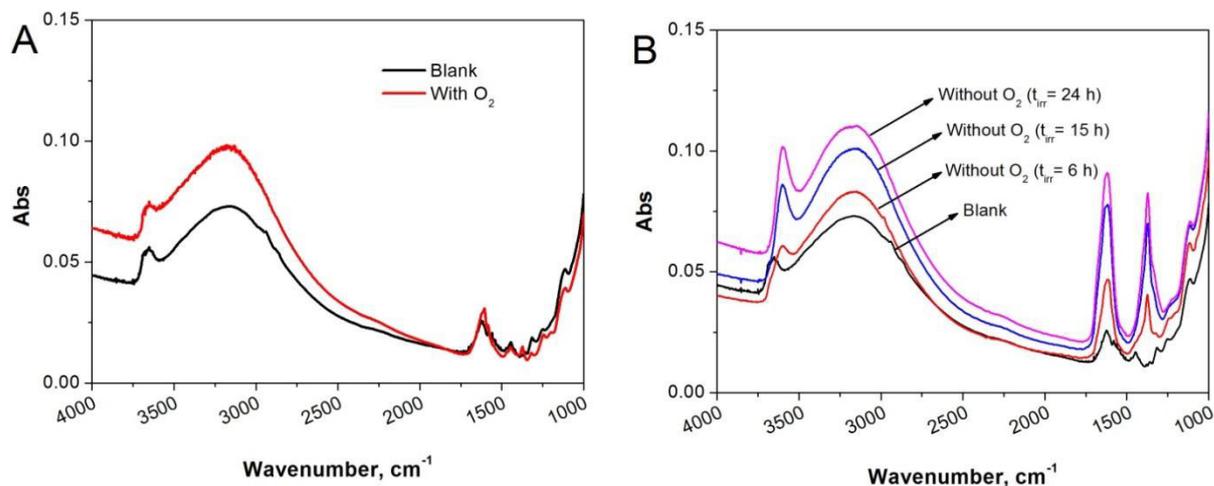
256 4.3 FT-IR spectroscopy of surface species

257 Film samples at different irradiation times were removed from their Pyrex glass substrate and
258 pressed as self-supported pellets. The spectra of the samples in the $1000\text{-}4000\text{ cm}^{-1}$ range
259 were recorded after out-gassing at room temperature and at $50\text{ }^\circ\text{C}$ for 30 minutes. The spectra
260 of samples before and after 6 hour of irradiation in the presence of oxygen almost overlap
261 (Fig. 9A-SM), indicating a negligible accumulation. The comparison among the spectra
262 obtained after 0, 6, 15 and 24 hours of irradiation in anoxic conditions (Fig. 9B-SM) show a
263 progressive increment of the intensity of: 1) the peak at 1620 cm^{-1} is related to the bending of
264 the water molecules adsorbed at the TiO_2 surface; 2) a new peak formed at 1370 cm^{-1} ; 3) the
265 broad absorption band spread over the $3550\text{-}2500\text{ cm}^{-1}$ interval and the partly resolved
266 components between 3750 and 3550 cm^{-1} .

267 As already stated, water traces are always present in the experimental system. The peaks in
268 $3550\text{-}2500\text{ cm}^{-1}$ interval are attributed to O–H stretching bond of hydroxyl surface groups
269 (linear or bridged) and adsorbed water. The pattern at $3750\text{-}3550\text{ cm}^{-1}$ is commonly attributed
270 to free νOH oscillators while the broad band at $3550\text{-}2500\text{ cm}^{-1}$ to H-bonded νOH
271 oscillators.[4,5] The increment of the intensity of these signals, together with the concomitant
272 increment of the 1620 cm^{-1} peak can be related to the increase of the hydration state of the
273 TiO_2 surface. The higher amount of surface water can be related to the presence at the surface
274 of species able to increase the Lewis acidity, and consequently to increase the ability to
275 adsorb water molecules [5], and to the production of water soluble species (e.g. Cl^-), which
276 are able to decrease the vapor tension of the water multilayers located at the TiO_2 surface, and
277 consequently hinder their desorption.

278 The 1370 cm^{-1} peak can be attributed to the vibration modes of C–Cl bond closed to
279 carbon/carbon double bonds. As an example, 3-chloropropene shows an intense absorption
280 band in the same region with a maximum located at 1417 cm^{-1} .[6] Then compounds of similar
281 structure are cumulated, most probably with increased conjugated double bonds as Vis
282 absorption is developed with irradiation time.

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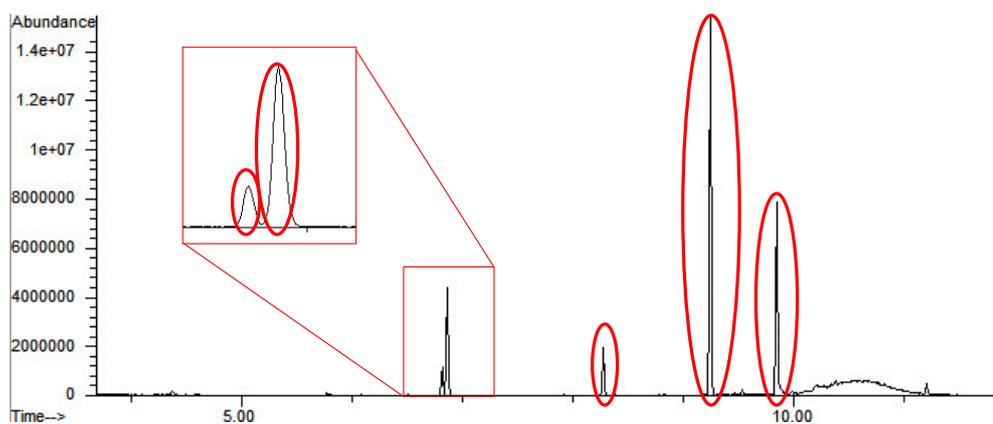


286
287 **Fig. 9-SM** Evolution of the FT-IR spectra of the TiO_2 films removed from the support and
288 analyzed as self-supported pellets during the photocatalytic transformation of C_2Cl_4 . (A)
289 Comparison between the samples before and after 6 hour of irradiation in the presence of
290 oxygen; (B) Comparison among the spectra before and after 6, 15 and 24 hours of irradiation
291 in quasi-anoxic conditions. Experimental conditions: $C_0 = 10\text{ ppm}$, total flow = 2.1 L min^{-1}
292 ($\text{N}_2\text{ }80\% + \text{O}_2\text{ }20\%$ or $\text{N}_2\text{ }100\%$), $S = 100\text{ cm}^2$, 10 W m^{-2} .
293

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295 4.4 GC-MS analysis of surface species

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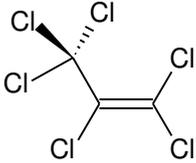
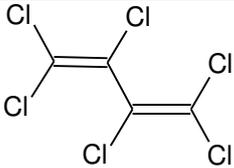
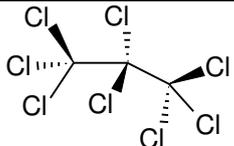
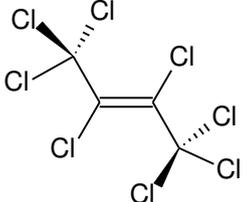
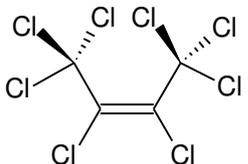
298

299 **Fig. 10-SM** Gas chromatogram (TIC mode) of the sample obtained extracting with CH_2Cl_2
300 the TiO_2 film after the photocatalytic transformation of C_2Cl_4 in quasi-anoxic condition ($C_0 =$
301 10 ppm, flow = 2100 cm^2 (N_2 100%), $S = 100 \text{ cm}^2$). The peaks of the five main
302 compounds formed are highlighted in red.

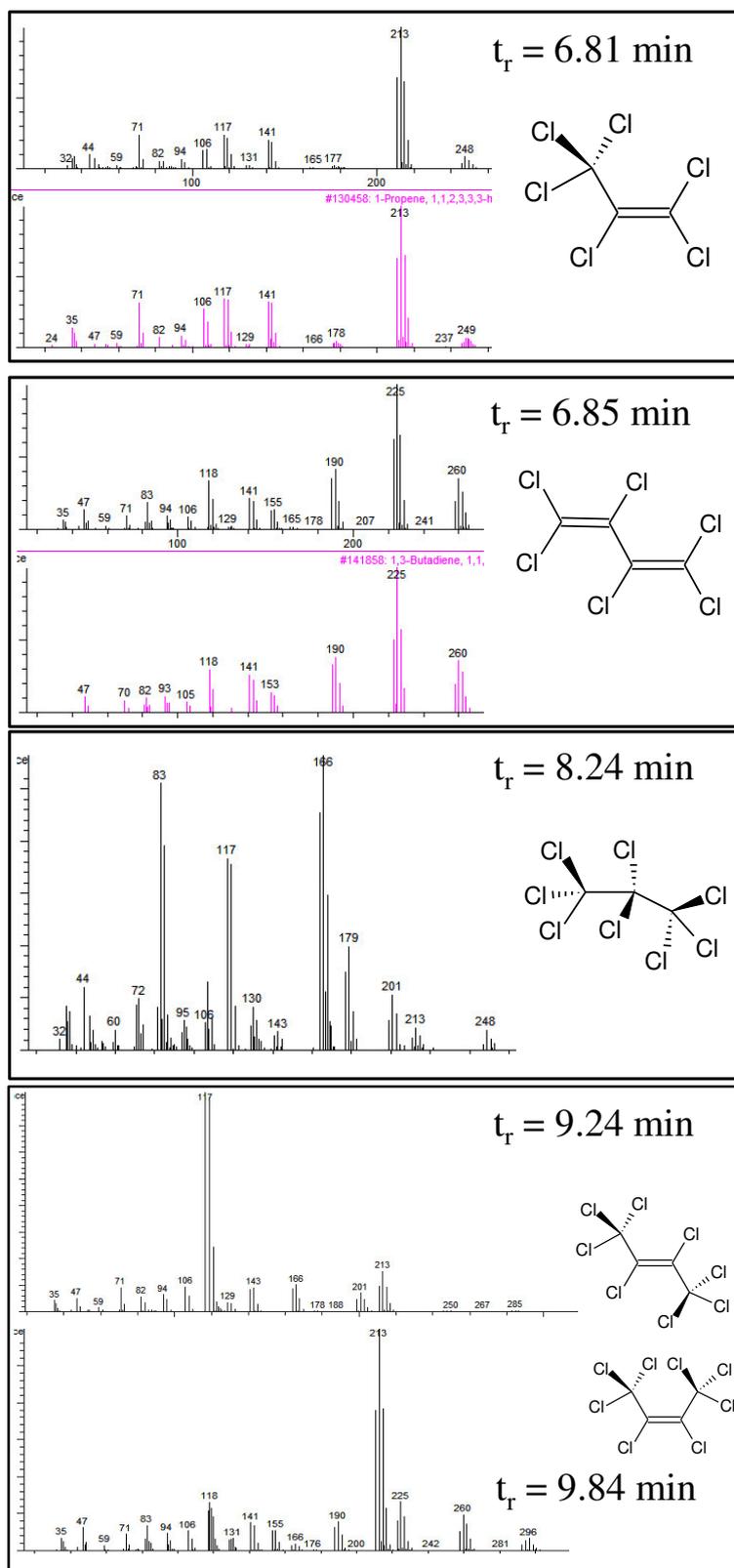
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305 **Table 1-SM** Retention time, molecular weight and molecular structure of the 5 compounds
 306 formed and deposited on the TiO₂ film during the photocatalytic transformation of C₂Cl₄
 307 under irradiated TiO₂ film in quasi-anoxic conditions (C₀ = 1 ppm ppm, flow = 1600 cm² (N₂
 308 100%), S = 100 cm²).
 309

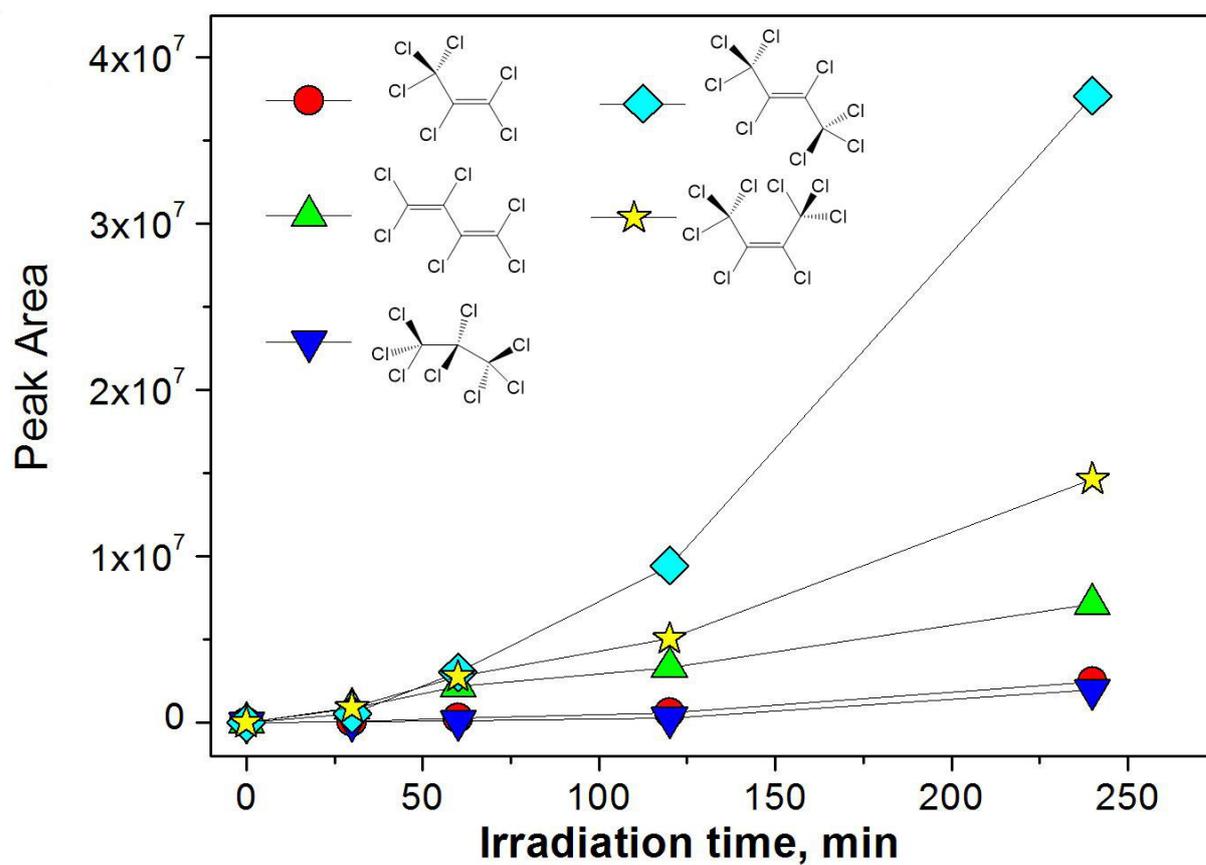
t _r (min)	Compounds	Molecular weight
6,81	 <i>1,1,2,3,3,3-hexachloropropene</i>	249
6,85	 <i>1,1,2,3,4,4-hexachlorobuta-1,3-diene</i>	261
8,24	 <i>perchloropropane</i>	320
9,24 - 9,84	 <i>Trans-1,1,1,2,3,4,4,4-octachlorobut-2-ene</i>	332
	 <i>Cis-1,1,1,2,3,4,4,4-octachlorobut-2-ene</i>	

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Fig. 11-SM Mass spectra of the molecules formed during the photocatalytic transformation of C_2Cl_4 under irradiated TiO_2 film in quasi-anoxic conditions ($C_0 = 1$ ppm ppm, flow = 1600 cm^2 (N_2 100%), $S = 100$ cm^2). For the compounds with $t_r = 6.81$ and 6.85 min the spectra present in the MS library Wiley 7n library for the related compounds were reported for comparison with the experimental data.



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Fig. 12-SM. Area of the peaks of species formed during the photocatalytic transformation of C_2Cl_4 and deposited on the TiO_2 films under anoxic condition as a function of the irradiation time. Experimental conditions: $C_0 = 10$ ppm, total flow = 2.1 L min^{-1} (N_2 100%), $S = 100 \text{ cm}^2$, $I_0 = 10 \text{ W m}^{-2}$.

326 **5 References**

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