A revised photocatalytic transformation mechanism for chlorinated VOCs: Experimental evidence from C_2Cl_4 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 Cl_2, $HClO$, ClO and ClO_2) was investigated both in the presence of oxygen and in anoxic conditions. At low O_2 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 O_2 the only possible form of active chlorine is Cl_2, this highlights that $Cl\cdot$ is not produced, and that chain reactions promoted by the chlorine radical do not occur on the TiO_2 surface.

The photocatalytic transformation of C_2Cl_4 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 TiO_2 surface slows down the PCE degradation rate and the production of gaseous CCl_4 but increments that of C_2Cl_6 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.

1. Introduction

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

The positive synergic effect, the formation of more halogenated intermediates, and the cited quantum yield greater than 1 for chlorinated compounds were ascribed to chain reactions promoted by the chlorine radical that is formed at the TiO_2 surface [3,10]. The chlorine radical can be formed a) from chloride oxidation by $\cdot OH$ or holes, or b) directly released from oxidized intermediates. The supposed $Cl\cdot$ formation by hydroxyl radicals produced at the surface of TiO_2 exposed to near-UV irradiation in the presence of adsorbed water vapor [11] was

able to justify the observed intermediates [8]. The role of chlorine radical was also supported by experiments in which chloride ions were added in the gas phase or at the surface. After addition of HCl in catalytic quantity in the air flow or by PCE overheating, a sensible increase of the reaction rate was obtained [12]. The addition of surface Cl^- through prechlorination with HCl increased the rate for toluene and hexane at the very beginning of the reaction when compared to the co-feeding with TCE, for which the enhancement was observed after some reaction time needed to accumulate a useful surface Cl^- level [13].

The chain reaction mechanism assumes that chlorine radical is an initiator which adds to TCE, forming a more halogenated radical, which in some further steps releases Cl· or HCl after reaction with oxygen [3]. The chain is terminated when Cl· reacts with water to form ·OH (a reaction possible only for pH > 2–2.5 as suggested by the standard redox potential for the couples $E^o(Cl·/Cl^-) = 2.60$ V and $E°(·OH,H^+/H_2O) = 2.73$ V [14]), or in dry conditions to form Cl_2 [15]. Chlorine radical could also be depleted by photoelectrons in the conduction bands (producing chloride ion that is adsorbed on the surface) or by reaction with O_2, forming ClO_2 [3].

The aforementioned framework based on the key role of Cl· seems to be consistent. However, parallel to earlier studies, alternative explanations could be suggested. For example, literature-reported values of photon efficiency are consistent with a photocatalytic mechanism without chain reactions mediated by Cl· radical. Using a fluorescence UV source and potassium ferrioxalate actinometry, the TCE photon efficiency was calculated as 13% over conditioned catalysts [16]. Jacoby et al. [1,2] measured quantum yields from 0.5 to 0.8 under high TCE concentration. In addition, the inhibition of the rate in the presence of halide ions in aqueous solution was suggested to be due to the competition with organic molecules for the oxidative species (i.e. photogenerated holes) [17]. The chlorine radical, if formed, is subjected to rapid recombination with conduction band electrons, creating a short-circuit cycle that depresses the conversion. An analogous inhibition was observed in the gas-phase photocatalytic degradation of $CHCl_3$ due to the increase of surface Cl^- with the space time [18]. The photoactivity was recovered washing the catalyst. Recently, EPR measurements were conducted to detect the presence of chlorine radicals by using the PBN spin-trap in chloroform solution [19]. The PBN–Cl· radical was not identified, suggesting that the existence of chlorine radical can be largely disregarded, although not completely excluded. Then the rate decrease was ascribed to the surface sites occupancy without a redox involvement of chloride ion. If so, also the formation of OH radicals, more endoergonic, could hardly be suggested.

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

To clarify the possible role of Cl· radical some new data on intermediate formation in the photocatalytic degradation of PCE are here reported, both in the presence and absence of O_2, together with the analysis of kinetic data. The formation of gaseous Cl_2 is assessed by a simple trapping experiment.

2. Materials and methods

Details on used materials, preparation of the catalyst, and experimental setup are reported in Supplementary Material (hereafter SM). The experiments of PCE transformation were carried out in a home-made flow-through photo-reactor working in a regime of perfect mixing (Continuous Stirred Tank Reactor, CSTR, see SM under 1.4) [25,26]. Under steady state the output concentration of gaseous C_2Cl_4 does not change with the time, if there is no change in the photoactivity of the catalyst, e.g. no poisoning or photo-activation as a consequence of the irradiation. Consequently, defining the conversion at the time t as $\eta(t) = (C_o-C_{out}(t))/C_o$, where C_o is the feed concentration and C_{out} the concentration inside the reactor and measured at its outlet, the rate under stationary conditions is directly obtained from the experiment (Eq. (1)) [25].

$$Rate(C_{out}) = \frac{C_0\eta_\infty F}{S} \tag{1}$$

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

The determination of the active chlorine formed during the photocatalytic test was carried out according to a standard spectrophotometric methods [27], based on the reaction of active chlorine ($Cl_2/HClO/ClO^-/ClO$) with N,N-diethyl-p-phenylenediamine (DPD). This reaction produces a pink coloured species that can be quantified spectrophotometrically at 510–515 nm. The gas flowing out of the reactor was bubbled through a fritted glass in a slightly basic solution (NaOH 2 mM). This solution favoured the trapping of volatile active chlorine species through: 1) deprotonation of the volatile hypochlorous acid into the non-volatile hypochlorite anion; 2) dismutation of Cl_2 into Cl^- and reactive ClO^- ($Cl_2 + 2\ OH^- \rightarrow H_2O + Cl^- + ClO^-$); 3) reaction of ClO with the excess of hydroxyl ions to form ClO^- ($ClO· + OH^- \rightarrow ClO^- + ·OH$); 4) dismutation of ClO_2 in chlorite and chlorate species ($2\ ClO_2 + H_2O \leftrightarrows HClO_2 + HClO_3$, K = 1.2×10^{-7}). At different irradiation times a fixed volume of the solution was withdrawn and mixed with DPD solution buffered at pH 6.2 (phosphate buffer, 0.17 mol L^{-1} HPO_4^{2-} e 0.33 mol L^{-1} H_2PO_4). The DPD produced pink colored species was quantified at 510 nm with a Cary 100 UV–vis spectrophotometer.

3. Results and discussion

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

The kinetic of the photocatalytic transformation of C_2Cl_4 was evaluated *i*) at different concentrations of the inlet flow (C_0) and *ii*) at different concentration of water vapor concentration. In both cases under stationary state the conversion was obtained and from this the transformation rate was computed (Eq. (1)). It is worth mentioning that the rate calculated from the experimental conversion refers to the concentration inside the reactor, and to $C_{out} = C_o(1–\eta)$.

Fig. 1A shows the photonic efficiency (PE) at different C_0, and plotted vs the actual concentration inside the reactor (C_{out}). The photocatalytic efficiency PE is given by the photocatalytic rate [mol m^{-2} s^{-1}] divided by the incoming light irradiance I_o [mol of photons m^{-2} s^{-1}]. The inset in Fig. 1A shows the stationary state (SS)