

Photocatalytic transformation of organic compounds in the presence of inorganic ions*

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Abstract: The influence of halide ions on the photocatalytic process on titanium dioxide has been investigated carefully. Chloride and bromide ions, acting as hole scavengers, generate active radical species (e.g., $\cdot\text{Cl}$ and $\cdot\text{Br}$) that participate in reactions with the organic compounds and the transient intermediates. Chloride and bromide ions have shown to deeply inhibit the degradation rate of chloroform and tetrachloromethane and to modify both the qualitative and quantitative distribution of their intermediates formed during the degradation process. In the presence of bromide, CBrCl_3 is detected as intermediate during CCl_4 degradation, while in the presence of chloride, formation of CCl_4 is observed in the CHCl_3 degradation. Fluoride ions, differently from the other halides, cannot be oxidized by the valence hole and may be used as a diagnostic tool in mechanistic studies. The influence of fluoride on phenol has been investigated, and, by choosing appropriate experimental conditions, it was possible to evaluate the role of the different active species in the photocatalytic process.

INTRODUCTION

Photocatalytic oxidation of organic molecules in aqueous aerated suspensions leads in almost all cases and through a sequence of reactions to the stoichiometric formation of carbon dioxide and, eventually, to inorganic ions. Besides, reductive photocatalytically induced processes are responsible for the degradation of halogenated compounds as tetrachloromethane.

However, the presence of inorganic ions has been shown to influence the kinetics and mechanism of the transformation processes of organic compounds. It is well known that the photocatalytic reactions occur at the surface of the semiconductor particle [1], so that specific adsorption of ions may affect the system performance. Specific adsorption of ions can give surficial coordination reactions at the oxide–water interface [2]. The adsorption degree is dependent on the value of pH and on the exchange reactions with the surface hydroxyl groups. The surface occupation by anions may be competitive with the adsorption of organic molecules, this effect being directly related to their coverage fraction.

Inhibition by strongly adsorbed anions has been reported, while for weakly adsorbed anions such as nitrate and perchlorate, a negligible effect has been observed [3–5]. In this paper, the effect of halides (chloride, bromide) on chloromethanes and of fluoride on phenol will be considered. The purpose of this investigation was to get information on the effect of these anions on the photocatalytic pathways of organic transformations and the extent of inhibition as a function of the nature of the anions. In particular, the TiO_2/F system may be used as a diagnostic tool in describing the role of active species involved in oxidation processes.

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EXPERIMENTAL CONDITIONS

Materials and reagents

Dichloromethane (Aldrich), chloroform (Aldrich), tetrachloromethane (Aldrich), and phenol (Aldrich) were used as received for all the tests. Experiments were carried out using TiO₂ Degussa P25 (surface area 50 m²g⁻¹). In order to avoid possible interference from ions adsorbed on the photocatalyst, the TiO₂ Degussa P25 powder was irradiated and washed with double distilled water until no signal due to chloride, sulphate, or sodium ions could be detected by ion chromatography. HClO₄, HNO₃, and NaOH (reagent grade) were used to adjust the pH.

Irradiation procedures

The irradiation was carried out on suspensions containing TiO₂ and the organic compound. The irradiation experiments have been carried out in Pyrex glass cells (cut-off at 295 nm, 4.0 cm diameter, 2.3 cm height), containing 5 ml of the aqueous suspension of the photocatalyst powder and substrate, using a 1500 W xenon lamp (CO.FO.MEGRA, Milan, Italy) equipped with a cut-off filter of 340 nm. Total photon flux entering in the irradiation cell was 8.1×10^{19} quanta sec⁻¹ m⁻², as determined by ferrioxalate actinometry.

The cell temperature during irradiation was 50 °C. The suspension homogeneity, as well as good oxygen exchange with the gaseous phase (air) contained in the cell, is assured by magnetic stirring.

Analytical procedures

The cooled sample (around 5 °C) was preliminarily filtered through 0.45 µm cellulose acetate membranes (Millipore HA). The entire content of the cell was analyzed for dichloromethane, chloroform, and tetrachloromethane after the established irradiation time by Purge and Trap/GC. A purge-and-trap system (Tekmar LSC 2000) with criofocusing connected to a gas-chromatograph (Varian STAR 3400) equipped with 1 FID detector and 60 m DB5 column (Supelco, 0.25 µm coating) was used. The samples were analyzed after proper dilution directly into P&G vessel (10–100 µL to 5 ml). The Purge and Trap's operative parameters were: standby 35 °C, purge 15 min, dry purge 3 min., desorb preheat 255 °C, desorb at 260 for 3 min, cryo cool down at -100 °C, inject at 220 °C, and bake at 250 °C for 7 min. The analyses were performed using a double gradient; temperature was linearly increased at 12 °C/min from 37 to 157 °C and then was brought to 300 °C at a rate of 30 °C/min. Phenol and dihydroxybenzenes were detected by HPLC using a Rheodyne 7125 injector, an RP C18 column (Lichrochart, Merck 12.5 × 0.4 cm), and a UV-vis detector (Merck Hitachi L-4200).

Total organic carbon (TOC) was measured on filtered suspensions using a Shimadzu TOC-5000 analyzer (catalytic oxidation on Pt at 680 °C). Calibration was achieved by injecting standards of potassium phthalate.

The formation of chloride and bromide ions was monitored by suppressed ion chromatography, using a Biotronik IC 5000 apparatus with a BTIAN separation column (20 cm length, 4 mm i.d., Biotronik) and an alkaline buffer eluant containing NaHCO₃ (3 mM) at the flow rate of 1.5 mL min⁻¹. Under these conditions, the retention time of chloride and bromide ions were 4.3 min and 5.5 min, respectively.

DISCUSSION

Interaction of inorganic ions at the oxide surface

If it is assumed that the chemical events occur predominantly at the surface, only those ions that are bound to TiO₂ or are very close to its surface can have significant effects. Consequently, the point of zero charge (PZC) should be a determining property; for TiO₂ Degussa P25, the pH_{PZC} is 6.3 [6].

The two surfacial acid-basic equilibria are:



At $\text{pH} > \text{pH}_{\text{PZC}}$, several anions, such as chloride, sulphate, and nitrate have been found to have no effect on the initial rate of disappearance of 3-chlorophenol [5] and phenol [7]. Since at $\text{pH} > \text{pH}_{\text{PZC}}$, the surface is negatively charge (see equilibrium 2), the concentration in anions is lower near the TiO_2 surface than in the bulk of the solution [8].

In the literature studies at $\text{pH} < \text{pH}_{\text{PZC}}$, including the effect of Cl^- , SO_4^{2-} , and NO_3^- [5], H_2PO_4^- and ClO_4^- [9] on several organic compounds, such as 3-chlorophenol [5], salicylic acid, aniline, and ethanol [9] are also available. No effect of nitrate and perchlorate was observed, while chloride, sulfate, and phosphate have detrimental effect.

At $\text{pH} < \text{PZC}$, the surface is positively charged as is expressed by eq. 1. The concentration of monovalent anions at the surface, $[\text{A}^-]_{\text{S}}$, is linked to the concentration in the bulk $[\text{A}^-]_{\text{b}}$ and to the surface charge σ [8], according to eq. 3:

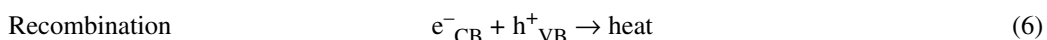
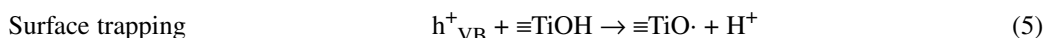
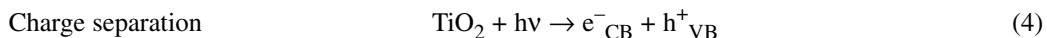
$$[\text{A}^-]_{\text{S}} = \sigma/2\epsilon\epsilon_0KT + 2[\text{A}^-]_{\text{b}} \quad (3)$$

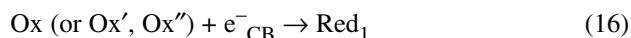
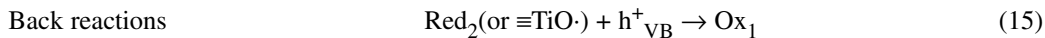
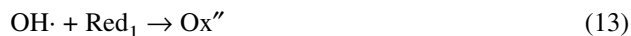
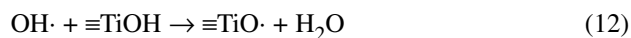
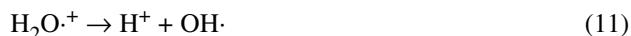
Although this coulombic treatment shows a marked excess of anions close to the surface, it does not predict differences between the various monovalent anions considered [10]. The contrasting effects of the anions at the acidic pH indicate either a competition between the inorganic salt and the organic compound for the surface oxidizing species (holes, OH radicals) and/or a competitive adsorption. In the latter case, as in the case of chloride, the Langmuir–Hinshelwood kinetic model would indicate that the reciprocal of the initial rate, r_0 , of disappearance of the organic substrate increases linearly with the concentration of anion. However, the Langmuir–Hinshelwood model is not compatible with the fact that the surface concentration of chloride ions does not depend much on the bulk concentration if only electrostatic forced is taken into account. Then, the participation of halides in the photocatalytic process will be discussed below.

PHOTOCATALYTIC PROCESS

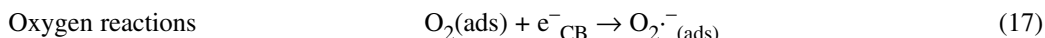
TiO_2 photoactivity is due to the adsorption of UV light (of energies with $\lambda < 380$ nm) that generates active species (electron/holes pairs) in the bulk of the semiconductor (reaction 4). Heterogeneous photocatalysis occurs over semiconductor oxides in which the charge carriers are ultimately positioned at the particle surface to undergo a variety of events (recombination, trapping) in competition with the redox chemistry involving solubilize and solvent molecules.

The photogenerated pairs can recombine according to reactions 6 and 7 or be trapped at the surface (reaction 5). If electron acceptors (Ox_1) or electron donors (Red_1 , H_2O) are present at the surface, interfacial electron transfers may occur according to reactions 8–14. The overall reactions involved are reported below.

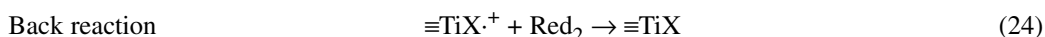
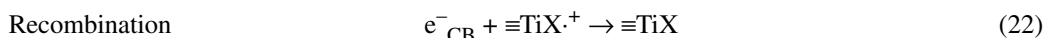
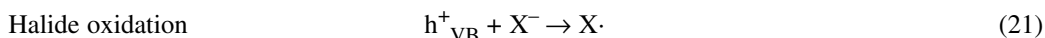
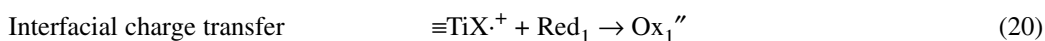
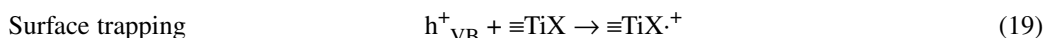
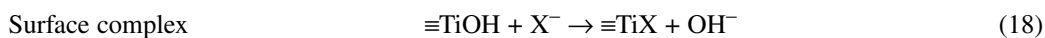




In aerated systems, oxygen acts as an efficient electron scavenger in reaction 14:



If halides (X^-) are present, some more reactions can occur. The primary events occurring at the catalyst surface in the presence of an anion X^- may be summarized as follows:



Effect of halides on the photocatalytic transformation of organic compounds

Some of the halides (chloride, bromide, and iodide) can be thermodynamically oxidized by valence band holes, thus acting as hole scavenging. At pH 5, the titania valence band hole is able to oxidize chloride ions to chlorine radical according to reaction 21 [11–13], for which the standard reduction potential is $E_0 = +2.5$ V [14], and bromide to bromine radical ($E_0 = 2.0$ V). However, the formed radical could back-react with conduction band electrons, according to reaction 20. This gives a null process, which lowers the concentration of available holes and electrons. The radical species $X\cdot$ can attack the organic compound through an addition/elimination reaction with a specific rate constant lower of radicals.

Fluoride anion shows strong adsorption on TiO_2 [15]. The estimated redox potential of the couple $\cdot F/F^-$ is 3.6 V [16], which makes fluoride stable against oxidation by TiO_2 valence holes, even in acidic media. Thus, for this anion, the redox competition with the organics is not possible.

The different effects of such halides have been investigated on several organic compounds, in order to stress their different way of action, as will be discussed below.

CHLORIDE AND BROMIDE

The influence of chloride and bromide has been studied on $CHCl_3$ and CCl_4 degradation rate. The phototransformation of these chloromethanes on TiO_2 proceeds through an oxidation/reduction sequence that brings to their dechlorination and mineralization [17,18]. The presence of NaCl (5×10^{-2} M) modifies the degradation rate of CCl_4 (see Fig. 1). The degradation rate is significantly decreased, and also

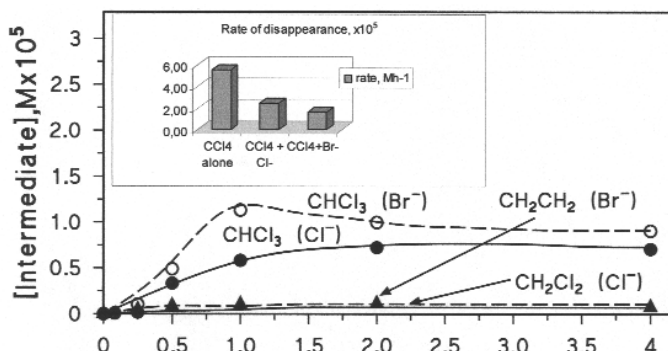


Fig. 1 Photocatalytic transformation of CCl_4 (10 mgL^{-1}) on TiO_2 200 mgL^{-1} after addition of NaCl (or KBr) 0.05 M at $\text{pH } 5$. Intermediates evolution both with Cl^- (continued line) and Br^- (dotted lines). Inset: rate of disappearance of CCl_4 with or without halide.

the intermediates evolution is influenced (i.e., CHCl_3 is formed in larger amount [18]). The main reactions involved in the one-electron oxidation of halides lead to a very fast formation of an adsorbed Cl^- followed by formation of $\text{Cl}_2^{\cdot-}$ (through reaction with Cl^-).

The electron recapture by adsorbed Cl^- and $\text{Cl}_2^{\cdot-}$ may follow the same mechanism in competition with other electron-capturing species [19], while the disproportionation reaction ($2\text{Cl}_2^{\cdot-} \rightarrow \text{Cl}_2 + 2\text{Cl}^-$) seems to play only a minor role.

The photogenerated holes are scavenged by chloride ions, so that they should increase the electron availability and the degradation rate of CCl_4 . The experimentally observed decrease suggests that the reaction:



and the electron recapture by adsorbed Cl^- and $\text{Cl}_2^{\cdot-}$ overcome the scavenging effects of reaction 21.

The addition of KBr ($5 \times 10^{-2} \text{ M}$) induces a similar decrease in the degradation rate of CCl_4 (see Fig. 1). A process similar to the one described with chloride occurs. Since bromide is an even better hole scavenging than Cl^- , the hole-scavenging effects are balanced by the electron-scavenging effect of $\cdot\text{Br}$ (or $\text{Br}_2^{\cdot-}$):



By analogy with Cl^- , if Br radical is formed, mixed halomethanes should be originated according to reactions 27 and 28:



Small quantities of CBrCl_3 and traces of CHCl_2Br have been experimentally detected, so confirming the occurrence of reactions 27 and 28.

The influence of chloride and bromide on chloroform degradation rate is represented in Fig. 2. In the presence of chloride, CHCl_3 can be concurrently reduced by e^-_{CB} (formation of $\cdot\text{CHCl}_2$) or oxidized [21] according to reactions 29 and 30:



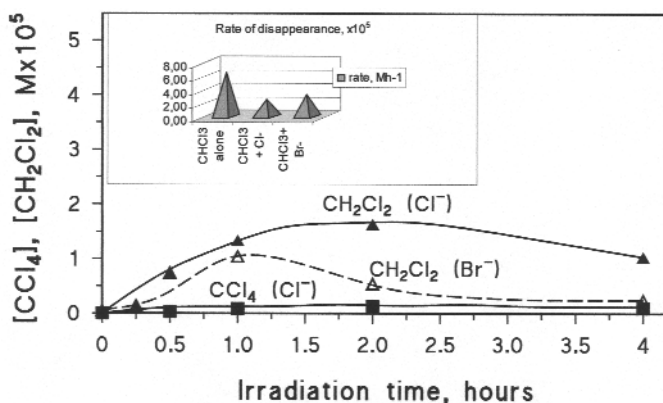


Fig. 2 Photocatalytic transformation of CHCl_3 (10 mgL^{-1}) on TiO_2 200 mgL^{-1} after addition of NaCl (or KBr) 0.05 M at $\text{pH } 5$. Intermediates evolution both with Cl^- (continued line) and Br^- (dotted lines). Inset: rate of disappearance of CHCl_3 with or without halide.

The contribution of reductive pathway should be decreased either by reaction 31 (giving a null effect when combined with reactions 29 and 30):



or by electron scavenging through the reduction of chlorine radical according to eq. 23. The formation of chlorine radical is evidenced by the appreciable production of CCl_4 [22], as shown in Fig. 2, according to reaction 25.

The degradation rate of chloroform in presence of Br^- decreases slightly less than in the presence of chloride (Fig. 2). Traces of CBrCl_3 are observed [18] and are generated through a pathway similar to the one followed in the presence of chloride. From such experiments, it may be concluded that a photocatalytic process in presence of chloride or bromide may originate heavily halogenated chloromethanes.

It is noteworthy that no significant effect of Cl^- and Br^- is observed at $\text{pH } 11$. Above pH_{PZC} [20], no adsorption of anions on TiO_2 occurs, and, as a consequence, the formation of $\text{X}\cdot$ is strongly inhibited, in agreement with the considerations previously reported.

Effect of fluoride

Mechanistic details of photocatalytic process (bound vs. free hydroxyl, direct electron transfer to the hole, back reaction, adsorption at the catalyst surface, kinetic model, etc.) are still unravelled and could shed light on the parameters affecting the quantum efficiency of the process.

Recent studies on the effect of fluoride added to TiO_2 suspensions have contributed to insight on the photocatalytic events [23,24].

Surficial charge and distribution on TiO_2 and TiO_2/F

Adsorption experiments and XPS measurement [25] indicate that fluoride ions strongly interact with TiO_2 . A variety of anionic species in aqueous solution undergo inner-sphere ligand substitution reaction with the surface hydroxyl.

In presence of fluoride, it is supposed a simple exchange equilibrium as indicated below, where A and B indicate the acidic and basic sites, respectively.



Fluoride ion replaces the basic hydroxyls, indicated as B, (as confirmed by IR and XPS spectroscopy [25,26]) according to the above reaction for which an equilibrium constant $k_1 = 8 \times 10^{-7}$ has been reported [27], and coordinates the surface-bound titanium atoms directly.

Considering the above equilibrium and the number balance for surface sites $C_S = [\text{TiOH}_2^+] + [\text{TiOH}] + [\text{TiO}^-] + [\text{TiF}]$ (calculated according to eqs. 1 and 2), the surface coverage in the dark can be calculated [23]. It is worth mentioning that for 0.01 M F^- and pH 3.6 the surface coverage by fluoride ions was maximum [23]. For this reason, the experiments described below have been performed at pH 3.6. The fluoride still remains the prevalent species at this pH.

The fluoride displacement of the surficial hydroxyl group of titanium dioxide in aqueous solution has been shown to introduce relevant modifications in the properties of titanium dioxide, either in the physical aspects or in the photocatalytic properties. A milky suspension of naked Degussa P25 is stable for days, whereas after addition of 0.01 M NaF (pH 3.6 with HF) the suspension stability changes and settles down in 30 min. There is also an enlarged region of small surface charge, extended from pH 3 to 6 (see Fig. 3). This may be important particularly for charged substrates or intermediates and for the possibility of interfacial electron transfer.

The low value of the surface charge in the pH range 3–6 causes coagulation of the particles. This could modify the reactive surface area [28] and the scattering of incident photons. The measurements of electrophoretic mobilities [29] confirm the modest charge of the colloidal particles of TiO_2/F in the range 4–6, thus explaining the flocculation observed in the presence of 0.01 M fluoride in this pH domain.

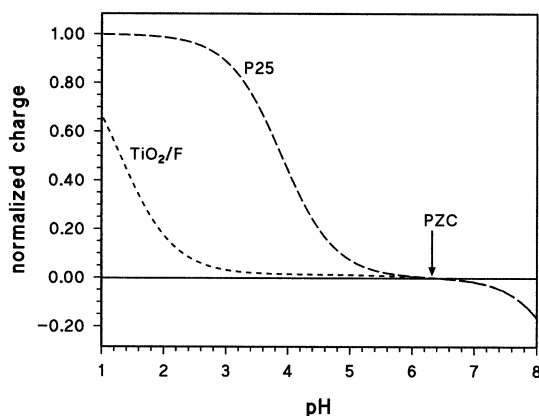


Fig. 3 Surficial distribution and surface charge for TiO_2 Degussa P25 and TiO_2/F as a function of pH.

Influence on phenol degradation

Phenol photocatalytic degradation has been extensively investigated [8,30]. However, the fluoride displacement of the surficial hydroxyl groups of TiO_2 in aqueous solution has been shown to introduce relevant modifications in the kinetics and mechanism of the photocatalytic degradation of phenol. We will focus on the modifications induced in the degradation rates, while the mechanistic details have been fully discussed in a previous paper [23].

Phenol 2×10^{-4} M has been irradiated both adopting TiO_2 naked and fluorinated. The rate of disappearance of phenol alone and in presence of different concentrations of fluoride anions is represented in Table 1, from which emerges that on TiO_2 fluorinated an increase in the rate of disappearance occurs. The reaction rate was strongly dependent on the surface coverage by $\equiv\text{TiF}$ species (concentration of fluoride ions and pH). In fact, the degradation rate increases while increasing the fluoride concentration (rate passes from 0.098 min^{-1} with $\text{F}^- 1 \times 10^{-3} \text{ M}$ to 0.15 min^{-1} with $\text{F}^- 0.01 \text{ M}$) and is maximum for pH ranging from 3.6 to 5, thus reflecting the TiF distribution.

Table 1 Observed rate constant of disappearance of phenol (2×10^{-4} M) on TiO_2 0.1 g L^{-1} as a function of pH and fluoride concentration.

Rate, min^{-1}	0 F^-	$1 \times 10^{-3} \text{ M F}^-$	$3 \times 10^{-3} \text{ M F}^-$	$1 \times 10^{-2} \text{ M F}^-$
pH 2.5	–	–	–	0.09
pH 3.6	0.056	0.098	0.12	0.15
pH 4	–	–	–	0.17
pH 5	–	–	–	0.17
pH 6	–	–	–	0.11

The variation of the degradation rate due to the presence of fluoride anions could be attributed to several causes. The diminution of $\equiv\text{TiOH}$ as increasing $[\text{F}^-]$ will decrease the ability to trap the holes as $\equiv\text{TiO} \cdot (\cdot\text{OH ads})$ as expected according to reaction 5. Because reaction 19 is not allowed for $\text{X} = \text{F}$, this will increase h^+_{VB} availability and consequently affect either the direct electron transfer to the organic electron donors or recombination of the charge carriers. In addition, the depletion of $\equiv\text{TiOH}$ will inhibit the formation of surficial peroxide. Moreover, fluoride anion is well known as the inhibitor of the complex formation between Ti(IV) and peroxide[31].

The displacement of OH^- by F^- changes the adsorption and the surface interactions. In particular, for organic compounds that interact with $-\text{OH}$ groups, the extent of this interaction is largely modified, as is reported elsewhere for catechol [32,33]. Also, the rate of electron scavenging by O_2 and of superoxide formation will be influenced.

The shift of the potential of the valence and conduction band may be induced by fluoride substitution of OH [34]. However, controversial was the role of direct electron transfer to the hole vs. OH radical oxidation of organic compounds. Hole oxidation has been suggested for compounds lacking abstractable hydrogen and for some aromatic compounds, as evidenced by diffused reflectance flash photolysis [35].

Different oxidant species might be present in the photocatalytic system; the hole, the surface-trapped hole ($\text{TiO} \cdot$), and the free $\cdot\text{OH}$ radical. The bulk holes, formed upon photon adsorption, migrate to the surface where they can interact with surficial water or hydroxyl groups to form $\cdot\text{OH}$ or $\equiv\text{TiO} \cdot$, respectively, or be trapped as subsurface holes. As trapped, the hole may interact with organic compounds through direct electron transfer both through $-\text{O}-$ or $-\text{Ti}-$ species.

Their presence and their role in the oxidation depend both on photocatalyst surface characteristics and solution composition. Some clarification has come from experiments performed in the presence of alcohols, which can be used as diagnostic tools since suppressing the OH radical-mediated process.

Considering the effect of several alcohols on the kinetics of degradation of phenol both on naked TiO_2 and TiO_2/F , the surface coverage by fluoride ions impedes the surface trapping of photogenerated holes (as $\equiv\text{TiO} \cdot$) with the possibility to discriminate, by comparison with naked TiO_2 , the surface-mediated pathway from that taking place via free $\cdot\text{OH}$ radicals. A quantitative study of this process is reported elsewhere [24].

On naked TiO_2 , increasing evidences are given for a surface mechanism. The comparison of the kinetics of the photocatalytic transformation of phenol on naked TiO_2 in the presence of different alco-

holes suggests that its oxidation proceeds either through the reaction with surficial bound hydroxyl and via a direct interaction with the holes. At large alcohol concentration, the rate mediated by surface-trapped hydroxyl radicals is very low; the only possible pathway is through direct electron transfer.

On TiO_2/F the effect of alcohol inhibition is pronounced (see Table 2). In the absence of any scavenger with phenol 2×10^{-4} M, the rate constant is 0.15 min^{-1} , which decreases to 0.057 (with 0.01 M tert-butanol) and to $6.7 \times 10^{-3} \text{ min}^{-1}$ (with 0.1 M tert-butanol). On fluorinated TiO_2 , the reaction proceeds almost entirely via homogeneous hydroxyl radicals owing to the unavailability of surface-bound hydroxyl in the presence of fluoride.

Table 2 Observed rate constant of disappearance of phenol (2×10^{-4} M) on TiO_2 0.1 gL^{-1} naked or TiO_2/F 0.01 M as a function alcohols concentration.

Rate, min^{-1}	[alcohol], M	t-butanol	2-propanol
TiO_2 naked	0	5.6×10^{-2}	5.6×10^{-2}
	0.01	2.6×10^{-2}	1.9×10^{-2}
	0.02	1.4×10^{-2}	1.1×10^{-2}
	0.1	7.8×10^{-3}	4.5×10^{-3}
TiO_2/F	0	0.15	0.15
	0.01	5.7×10^{-2}	3.2×10^{-2}
	0.02	2.8×10^{-2}	1.8×10^{-2}
	0.1	6.7×10^{-3}	3.8×10^{-3}

CONCLUSIONS

The presence of chloride and bromide on the photocatalytic degradation of CHCl_3 leads to the formation of more halogenated methanes. The scavenging mechanism of such halides is the competition with organic compounds for the photogenerated oxidative species rather than a mere site occupation.

The most important conclusions in the presence of fluoride are related to the substitution of the hydroxyl groups by fluoride on the TiO_2 surface in the range pH 2–6. The primary aim of this work was to achieve evaluation of the extent of the different pathways operating in the photocatalytic transformation of phenol chosen as a model organic molecule. The degradation rate of phenol increases as a function of the fluoride concentration, and its dependence on pH reflects that of the surficial $\equiv\text{TiF}$ distribution. This rate increase can be explained by the major extent of homogeneous OH reaction and direct electron transfer from the aromatic ring to the hole and by a decrease in the back reaction extent.

Alcohols have been used as diagnostic tools for suppressing the OH radical-mediated process. On naked TiO_2 , the mechanism may involve direct electron transfer and/or reaction with the bound surficial hydroxyl. For phenol, which is poorly interacting with the surface, the last mechanism is prevailing. Only this path is efficiently inhibited by alcohols such as tert-butyl alcohol and 2-propanol. It may be concluded that on TiO_2/F , the phenol degradation proceeds almost entirely through homogeneous OH radical reaction.

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