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# Benzene and toluene gas-phase photocatalytic degradation over H<sub>2</sub>O and HCl pretreated TiO<sub>2</sub>: by-products and mechanisms

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## Abstract

Photocatalytic oxidations of toluene and benzene in air were carried out over water (TiO<sub>2</sub>/H<sub>2</sub>O) and HCl (TiO<sub>2</sub>/HCl) pretreated TiO<sub>2</sub> as this latter pretreatment enhances the toluene removal rate. The main purpose was to identify intermediate products. No gas-phase by-products were detected by direct GC/FID analysis under our conditions despite the high aromatic concentration (50 mg m<sup>-3</sup>) and the short contact time (ms); this result illustrates an attractive capability of this air purification method. Adsorbed intermediate products recovered by extraction from the used photocatalysts were the same over TiO<sub>2</sub>/H<sub>2</sub>O and TiO<sub>2</sub>/HCl; i.e. no chlorinated products were found in this latter case. Benzoic acid, benzaldehyde, and benzyl alcohol were three major toluene intermediate products identified; trace derivatives of these products and of toluene that were monohydroxylated on the ring were also detected in catalyst extract samples. The benzene major by-product was phenol which was accompanied by hydroquinone and 1,4-benzoquinone. Acetic and formic acids were also formed from both benzene and toluene. For both aromatics, a water extraction of the used photocatalysts permitted separation of a yellow viscous material that settled between water and TiO<sub>2</sub> after centrifugation. We have not identified the products contained in this material but believe them to be polymeric products which may be at the origin of the decreased photocatalytic activity of used TiO<sub>2</sub> with respect to fresh TiO<sub>2</sub>. Finally, we discuss the photocatalytic oxidation pathways. © 1998 Elsevier Science S.A. All rights reserved.

*Keywords:* Toluene; Benzene; TiO<sub>2</sub>; Photocatalytic oxidations

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## 1. Introduction

The TiO<sub>2</sub> photocatalytic oxidation of benzene and toluene in air or oxygen, generally in the 80–500 ppmv range, has been studied by several authors [1–13]. Formation of CO<sub>2</sub> was reported in all these studies. Also, the presence of CO in the exit gas flow was mentioned [11] in the case of benzene for a TiO<sub>2</sub>-coated annular flow reactor with a residence time of 4.9 s that presumably did not allow a long enough contact time between TiO<sub>2</sub> and the organic reactant products. For dynamic photoreactors, no gas-phase intermediate organic products were detected by on-line GC analysis, except by two groups of the investigators [5,7] who found the presence of benzaldehyde and even traces of benzene [7] when toluene was the reactant. The formation of gaseous acetone from benzene was reported by Sitkiewitz and Heller [13] but it occurred only in the absence of water vapor.

Analysis of the products recovered from used TiO<sub>2</sub> by various solvents showed the formation of benzyl alcohol and

benzaldehyde [6], and also benzoic acid [3,4] in the case of toluene oxidation, as well as the formation of phenol, hydroquinone, 1,4-benzoquinone and propanedioic acid in the case of benzene oxidation [11].

A yellowish discoloration of TiO<sub>2</sub> during photocatalytic treatment was mentioned by several investigators both for toluene [5,6] and for benzene [11–13]. Formation of polymeric species was proposed [13].

Concerning mechanisms, the benzyl radical has been suggested to be the key species at the origin of the formation of benzyl alcohol and benzaldehyde [7,13]. We have shown the photocatalytic degradation of toluene and benzene over TiO<sub>2</sub> in the presence and absence of trichloroethylene (TCE) [1]. The toluene degradation rate is enhanced by the simultaneous presence and degradation of TCE; the increase is assumed to be due to chlorine radicals. More recently [2], we have shown that a similar rate enhancement can be obtained through the prechlorination of the TiO<sub>2</sub> surface by use of aqueous HCl; we, therefore, proposed that Ti/Cl<sup>-</sup> surface species can trap photogenerated holes and degrade some organic pollutants owing to the resulting chlorine radical production.

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In this paper, we focus on the identification of intermediate products present on used TiO<sub>2</sub>, prechlorinated or not. We were interested in determining:

1. whether chlorinated products are formed when the photocatalyst is prechlorinated, and
2. whether the comparison between untreated and prechlorinated TiO<sub>2</sub> allows us to discriminate between basic mechanisms.

An additional objective was to better understand why TiO<sub>2</sub> can be partially deactivated in some cases, and we also demonstrated different catalyst deactivation and regeneration patterns depending on the aromatic contaminant and on TiO<sub>2</sub> prechlorination.

## 2. Experimental

### 2.1. Sample preparation

The samples were prepared from TiO<sub>2</sub> Degussa P-25, surface area 50 m<sup>2</sup> g<sup>-1</sup>, non porous about 80% anatase. TiO<sub>2</sub>/H<sub>2</sub>O was a water-impregnated and then dried TiO<sub>2</sub> sample; and TiO<sub>2</sub>/HCl, an aqueous HCl-impregnated and dried TiO<sub>2</sub> sample. Their detailed preparation is described elsewhere [2].

For each photocatalytic reaction a fresh catalyst charge was used (150 mg); this amount ensured an illuminated powder layer possessing an optical density  $\geq 2$  (i.e. complete light absorption).

### 2.2. Gas reservoir, photoreactor, and light source

The reservoir where the gas mixture (air + pollutant + water vapor) was prepared is a 12.5 l stainless steel cylinder. This reservoir can be pressurized up to 10 bar to provide the desired reactant gas flow rate over several days.

The photoreactor was a stainless steel cylinder 60 mm in diameter and 55 mm high, initially designed by Formenti et al. [14]. The upper part of the cylinder was sealed with an O-ring and a fused silica optical window. The powder catalyst was supported by a Whatman glass microfiber filter, and the reaction mixture was introduced above the catalyst bed.

Radiation from a Philips HPK 125-W mercury lamp was filtered through a circulating water cuvette (thickness 2.2 cm) equipped with a Corning 7–60 optical filter (300 nm  $\leq \lambda \leq$  400 nm). Consequently, the maximum peak intensity was at 365 nm. The lamp was placed at a fixed distance (approx. 8 cm) above the reactor.

### 2.3. Materials

Maximum purity grade compounds were purchased from Aldrich (toluene, benzyl alcohol, phenol, hydroquinone, formic acid, acetic acid, 3-hydroxybenzaldehyde, 1,4-benzoquinone, and muconic acid (2,4-hexadienedioic acid)),

Fluka (benzaldehyde, benzoic acid, 4-hydroxybenzaldehyde, and benzene), Merck (diethyl ether, and maleic acid (*cis*-butenedioic acid)), or Jansson Chimica (4-hydroxybenzyl alcohol). The water used for solution and eluent preparations was ultra-pure water from Milli-Q plus (Millipore). The pressurized gases (air, helium, hydrogen) were scientific grade furnished by Carboxyque.

### 2.4. Procedures

Inlet gas concentrations in air were 50 mg m<sup>-3</sup> toluene (13.1 ppmv) or benzene (15.5 ppmv) and 1000 mg m<sup>-3</sup> of water (1342 ppmv, ca. 5% relative humidity), achieved by mixing reactant gas flow from the reservoir with the tank air flow using regulation by mass flow controllers (Brooks Instrument 5850TR). The air flow rate was set at 1 or 2 cm<sup>3</sup> s<sup>-1</sup> and the reaction mixture was allowed to flow through the dark photoreactor until adsorption equilibrium was reached, then the UV light was turned on.

### 2.5. Analyses

#### 2.5.1. GC analysis

Toluene or benzene concentrations were measured on-line by an Intersmat IGC 120DFL Gas Chromatograph equipped with a HP1 semi-capillary column (length 30 m, i.d. 0.53 mm, film thickness 2.65  $\mu$ m) and a FID detector.

#### 2.5.2. GC/MS analysis

Adsorbed by-products were extracted from the used TiO<sub>2</sub> sample by diethyl ether and ultrasonication. Qualitative analysis of the filtrate was carried out by the use of a GC HP 5890 Series II, equipped with a splitless injector, a CP-SIL 5 CB capillary column (length 25 m, i.d. 0.25 mm, film thickness 1.2  $\mu$ m), and a HP 5971A mass analyzer detector.

#### 2.5.3. HPLC analysis

One milliliter of deionized water was added to the used catalyst. The solution was shaken and ultrasonicated before centrifugation. The separated clear aqueous solution was analyzed by HPLC using a Milton Roy ConstaMetric 3000 pump, a Waters 486 UV absorbance detector ( $\lambda = 220, 250, \text{ or } 270 \text{ nm}$ ), a Chrompack ODS-2 (length 250 mm, i.d. 4.6 mm) or CAR-H column (length 300 mm, i.d. 7.8 mm) and a guard column.

## 3. Results

### 3.1. Toluene and benzene removal rates

Toluene conversion rates vs. time over TiO<sub>2</sub> photocatalysts pretreated in either water (TiO<sub>2</sub>/H<sub>2</sub>O) or HCl solution (TiO<sub>2</sub>/HCl) are detailed in a recent paper [2]. Enhancement in the conversion of toluene over TiO<sub>2</sub>/HCl compared to TiO<sub>2</sub>/H<sub>2</sub>O was shown and a chlorine radical chain transfer

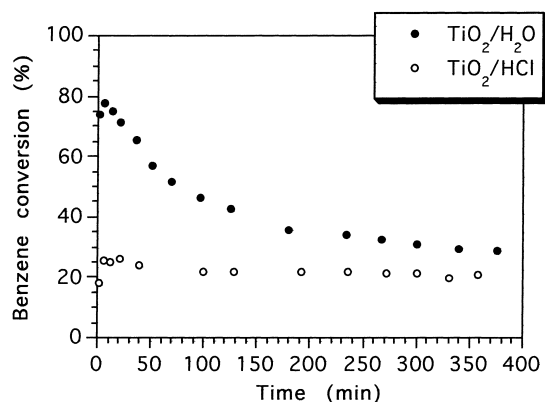


Fig. 1. Benzene conversion vs. time.  $[\text{Benzene}]_0 = 50 \pm 2 \text{ mg m}^{-3}$  (15.7 ppmv),  $[\text{H}_2\text{O}]_0 = 1000 \text{ mg m}^{-3}$  (1342 ppmv), flow rate =  $1 \text{ cm}^3 \text{ s}^{-1}$ .

mechanism was proposed to rationalize this effect, as before [1,3,4]. This enhancement was demonstrated for other branched aromatics but not for benzene [1].

The present work finds that benzene conversion over  $\text{TiO}_2/\text{H}_2\text{O}$  reached 80% and dropped slowly to 30% within about 3 h (Fig. 1). Over  $\text{TiO}_2/\text{HCl}$  the conversion remained nearly constant at about 25% for the entire 6 h run (Fig. 1). In both cases, the conversions reached similar steady-state values even though the photocatalysts have turned brown, a result in agreement with Ibusuki and Takeuchi [5] who noted a color change of  $\text{TiO}_2$  at 80 ppmv from white to light brown along with a maintenance of steady-state photocatalytic activity for toluene elimination.  $\text{TiO}_2$  prechlorination decreased rather than improved the activity for benzene removal, unlike what we earlier observed for toluene [2].

Benzene conversion was followed over  $\text{TiO}_2$  (not pretreated with either  $\text{H}_2\text{O}$  or aqueous  $\text{HCl}$ ) for three different inlet water concentrations (0, 1000, and  $8000 \text{ mg m}^{-3}$ , i.e. 0, 1342, and 10 800 ppmv). High initial conversion followed by a decrease over time was observed in all the three cases but the conversion after 3 h of reaction stabilized at 20%, 36%, and 40% conversion, respectively (Fig. 2). This con-

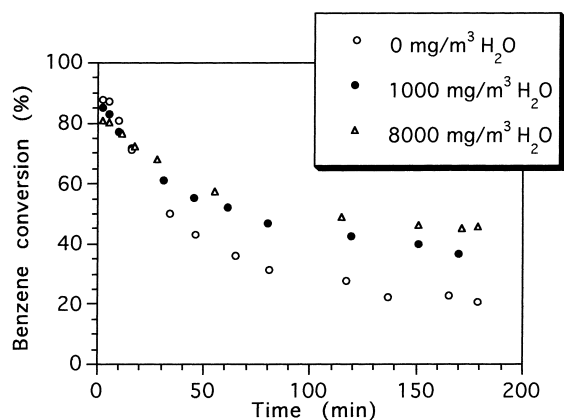


Fig. 2. Benzene conversion over untreated  $\text{TiO}_2$  vs. time.  $[\text{Benzene}]_0 = 50 \pm 2 \text{ mg m}^{-3}$  (15.7 ppmv), flow rate =  $1 \text{ cm}^3 \text{ s}^{-1}$ .

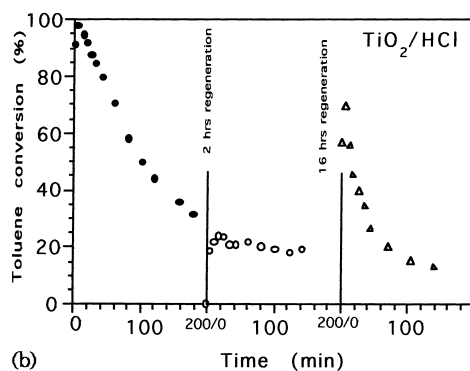
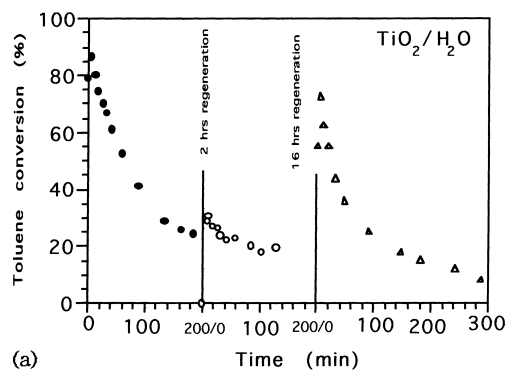


Fig. 3. Toluene conversion vs. time.  $[\text{Toluene}]_0 = 50 \pm 2 \text{ mg m}^{-3}$  (13.1 ppmv), flow rate =  $2 \text{ cm}^3 \text{ s}^{-1}$ ,  $[\text{H}_2\text{O}]_0 = 1000 \text{ mg m}^{-3}$  (1342 ppmv); (●) fresh  $\text{TiO}_2/\text{H}_2\text{O}$  or  $\text{TiO}_2/\text{HCl}$  regenerated in pure air flow during 2 h (○) or 16 h (△).

firms previous results [12,13] indicating that water vapour presence is necessary for continued high benzene conversion. Traces of water may also have been present in the formally noted 0% humidity run because of residual humidity in the reservoir, water initially present on the surface of  $\text{TiO}_2$ , and/or water produced via benzene oxidation.

### 3.2. Photocatalyst regeneration

Fig. 3(a) and (b) show toluene conversion over fresh and regenerated  $\text{TiO}_2/\text{H}_2\text{O}$  and  $\text{TiO}_2/\text{HCl}$ . The first interval (filled circles) presents the fresh catalyst activity, the second (empty circles) presents activity after the sample was regenerated in an air flow under UV irradiation for 2 h, and the third (triangles) presents the sample regenerated in an air flow under UV irradiation for 16 h. During the first interval,  $\text{TiO}_2/\text{H}_2\text{O}$  and  $\text{TiO}_2/\text{HCl}$  became brown. Neither photocatalyst recovered its white color after either regeneration, nor did the subsequent maximal initial conversion reach the fresh photocatalyst initial value. However, after the 16 h regeneration period, the initial conversion values (70–75%) were much higher than after the 2 h regeneration period (25–30%); regenerating the photocatalyst for only 2 h was ineffective.

Similarly, Fig. 4(a) and (b) present benzene conversion over fresh and regenerated  $\text{TiO}_2/\text{H}_2\text{O}$ , and  $\text{TiO}_2/\text{HCl}$ . For

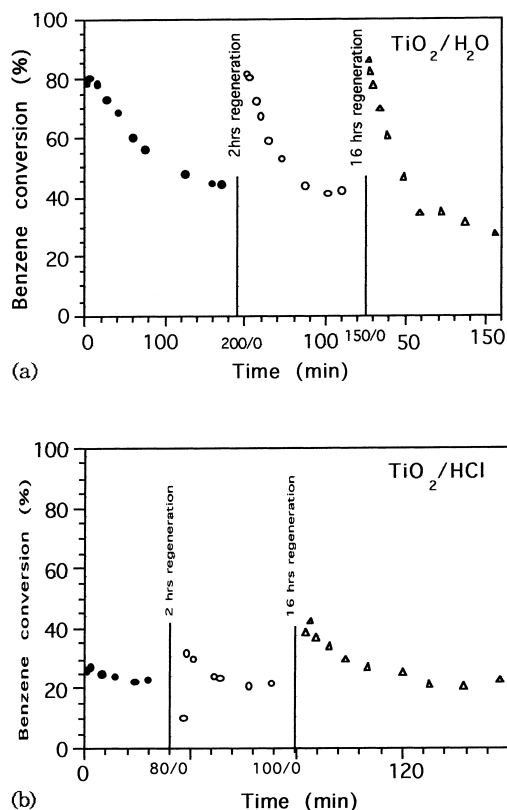


Fig. 4. Benzene conversion vs. time.  $[\text{Benzene}]_0 = 50 \pm 2 \text{ mg m}^{-3}$  (15.7 ppmv), flow rate =  $1 \text{ cm}^3 \text{ s}^{-1}$ ,  $[\text{H}_2\text{O}]_0 = 1000 \text{ mg m}^{-3}$  (1342 ppmv); (●) fresh  $\text{TiO}_2$ ;  $\text{TiO}_2$  regenerated in pure air flow during 2 h (○) or 16 h (△).

$\text{TiO}_2/\text{H}_2\text{O}$ , the 2 h regeneration did not completely recover the original white color, but the subsequent 16 h regeneration did. Also, the initial conversion exceeded 80% after both regenerations. With  $\text{TiO}_2/\text{HCl}$  initial activity was lower than with  $\text{TiO}_2/\text{H}_2\text{O}$ ; 2 h-regeneration did not recover a white catalyst color, but the initial conversion was about 10% higher than over the fresh sample. A 16 h-regeneration recovered the white color and gave a conversion about 15% higher than the original. These data show that the regeneration was easier after the photocatalysts were exposed to benzene than to toluene.

### 3.3. Toluene by-products

No gas-phase by-products were detected by on-line GC/FID under our conditions in agreement with other studies [3,4,6]. Some authors [5,7] have noted gas-phase benzaldehyde, but only when heating the catalyst or using larger benzene concentrations or different types of reactors. The products remaining on  $\text{TiO}_2/\text{H}_2\text{O}$  and  $\text{TiO}_2/\text{HCl}$  (both having a brownish color) were extracted by diethylether and ultrasonication. The brownish color of the solid was persistent, the filtrate containing the extracted products was clear to the eye. The GC/MS analyses of the extracts after 3 and 22 h of reaction over  $\text{TiO}_2/\text{H}_2\text{O}$  and  $\text{TiO}_2/\text{HCl}$  each showed

the presence of benzaldehyde and smaller amounts of benzyl alcohol. About the same amount of benzaldehyde was extracted from  $\text{TiO}_2/\text{H}_2\text{O}$  and  $\text{TiO}_2/\text{HCl}$  samples used either 3 or 22 h. Benzoic acid was present only in the filtrate obtained with  $\text{TiO}_2/\text{HCl}$  regardless of reaction duration or conversion; its quantity increased with increasing irradiation time. A second extraction with dichloromethane and a third extraction with methanol allowed recovery of only small additional amounts of the same products found via diethylether extraction.

Use of water as the solvent to extract the degradation products from the  $\text{TiO}_2$  samples, followed by HPLC analysis with a UV absorbance detector, was more sensitive and brought complementary information.  $\text{TiO}_2$  pelleted at the tube bottom with the clear aqueous phase at the top and a yellow viscous material at the interface. HPLC chromatograms of the clear liquid of  $\text{TiO}_2/\text{H}_2\text{O}$  and  $\text{TiO}_2/\text{HCl}$  extracts were similar and contained three major peaks having retention times equal to 13, 28, and 68 min (Chrompack ODS-2 column); these peaks corresponded to benzoic acid, benzyl alcohol, and benzaldehyde, respectively, in agreement with the GC/MS analysis. Note, however, that the quantity of benzoic acid adsorbed on the  $\text{TiO}_2/\text{H}_2\text{O}$  sample was too small to be extracted by the organic solvents we used and accordingly detected by GC/MS analysis. Less intense peaks with retention times of 4, 9, 25, and 31 min were identified, respectively, as 4-hydroxybenzoic acid, 4-hydroxybenzyl alcohol, 4-hydroxybenzaldehyde and 3-hydroxybenzaldehyde according to retention times of standards. The peaks with retention time shorter than 4 min presumably corresponded to aliphatic acids with a small number of carbon atoms; the same solution was, therefore, also analyzed using a CAR-H column more suited for separating this class of products.

Both  $\text{TiO}_2/\text{H}_2\text{O}$  and  $\text{TiO}_2/\text{HCl}$  extracts contained formic and acetic acids (retention time: 16 and 18 min, respectively). A peak at 35 min perhaps corresponded to muconic acid (2,4-hexadienedioic acid). If maleic acid (*cis*-butenedioic acid) was formed, its chromatograph peak would have been hidden under the injection peak at 7.3 min. Identification of these compounds was again based on the retention times of standard solutions.

### 3.4. Benzene by-products

No by-products were detected in the gas phase under our conditions.

Following photocatalyzed benzene destruction in air, the used  $\text{TiO}_2/\text{H}_2\text{O}$  and  $\text{TiO}_2/\text{HCl}$  were ultrasonicated in diethylether and the resulting solutions were analyzed by GC/MS for adsorbed by-products. Unlike the toluene case, no products were detected by this method even following partial evaporation of diethylether to concentrate any dissolved product.

Extraction of the used samples with water caused a yellow material to settle above the  $\text{TiO}_2$  pellet and below the clear

aqueous solution as in the case of toluene. HPLC analysis of the clear liquid permitted identification of hydroquinone (1,4-dihydroxybenzene), 1,4-benzoquinone, and phenol (Chrompack ODS-2 column) as well as formic and acetic acids (CAR-H column). These products were identified according to their retention times with respect to those of the standards. The phenol amount recovered was greater for  $\text{TiO}_2/\text{H}_2\text{O}$  than for  $\text{TiO}_2/\text{HCl}$ .

The products contained in the yellow material found at the  $\text{TiO}_2/\text{water}$  interface in both toluene and benzene samples were not identified by the methods we employed. Other analysis methods such as NMR and mass spectrometry with direct injection would perhaps allow one to identify these compounds.

## 4. Discussion

### 4.1. Benzene-suggested degradation pathways

We have reported [1] that benzene is less susceptible to photocatalytic oxidation than toluene. Wallington et al. [15] have studied chlorine radical and hydroxyl radical reactivities with toluene and benzene. Towards chlorine atoms, they noted that benzene is relatively unreactive and toluene is at least a factor 13 more reactive than benzene. This is in marked contrast with the corresponding reaction with hydroxyl radicals where benzene and toluene display much closer reactivities [15]. This difference could explain partially why the presence of chlorine does not enhance the degradation rate of benzene. The combination of low reactivity towards Cl and lower  $\text{TiO}_2$  coverage by benzene vs. toluene are presumed to be the primary factors responsible for the differences noted. We, therefore, propose two routes for benzene degradation (Fig. 5(a) and (b)).

1. Direct hole oxidation followed by reaction of the resulting radical cation with a surface basic OH group (or with an adsorbed water molecule and subsequent deprotonation) to yield phenol, the major intermediate detected. Over  $\text{TiO}_2/\text{HCl}$ , the radical cations may react with the OH groups not replaced by Cl. We found less

phenol on  $\text{TiO}_2/\text{HCl}$  than  $\text{TiO}_2/\text{H}_2\text{O}$ , consistent with fewer OH groups on the surface.

2.  $\text{OH}^\bullet$  radical addition to yield a cyclohexadienyl radical. Addition of oxygen to this radical and elimination of the radical  $\text{HO}_2^\bullet$  producing phenol by analogy with what has been determined in water [16].
3. An additional benzene conversion pathway is polymerization. The benzene radical cation might react with an incoming benzene molecule or a benzene molecule adsorbed on the surface to form polymers. Polymer formation during photocatalytic degradation of benzene was proposed by Sitkiewitz and Heller [13]. In the absence of  $\text{H}_2\text{O}$ , they suggested that the reaction proceeds via direct hole oxidation, which likely results in high levels of reaction intermediates that preferentially undergo free radical polymerizations to yield the observed stable brown material. During thermal catalytic partial oxidation of benzene to phenol over zeolites, Burch and Howitt [17] observed zeolite deactivation which they attributed to the deposition of carbonaceous material within the zeolite structure. They suggested that polyaromatic products such as biphenyl and 2-phenoxyphenol were responsible for this deactivation. We have not identified any bicyclic aromatics, but believe that the brown material we have separated from the aqueous phase was a polymer product containing chains of several aromatic rings.

In addition to phenol, other intermediate products of benzene photooxidation are 1,4-benzoquinone and hydroquinone. Since we have not identified catechol (1,2-dihydroxybenzene) as a by-product, we believe that phenol is predominantly degraded via a hole attack as proposed in Richard and Boule's study [18] for aqueous-phase photocatalytic oxidation of phenol. The phenolic radical cation loses a proton and the resulting phenoxy radical reacts with oxygen or more likely superoxide to yield 1,4-benzoquinone. Hydroquinone and 1,4-benzoquinone are known to be in equilibrium in UV-irradiated  $\text{TiO}_2$  aqueous suspensions [18–20].

The enhanced benzene conversion over  $\text{TiO}_2/\text{H}_2\text{O}$  vs.  $\text{TiO}_2/\text{HCl}$  could be due to a higher amount of OH groups

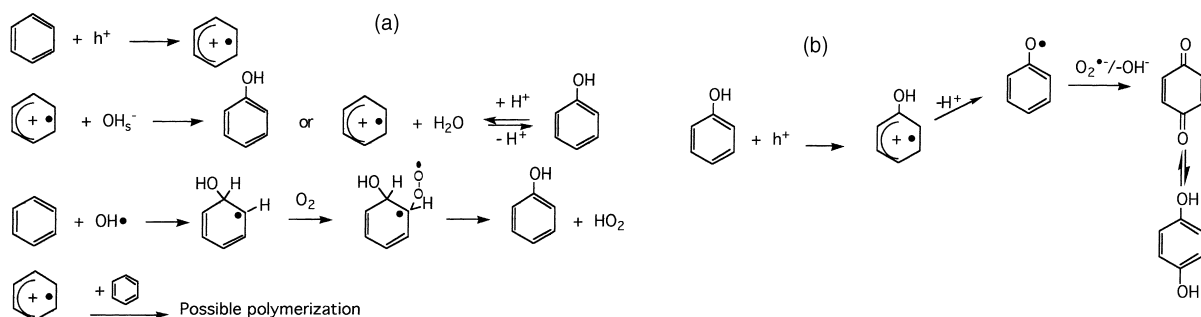


Fig. 5. (a) Primary benzene photocatalytic oxidation pathways. (b) Secondary benzene photocatalytic oxidation pathways.

on  $\text{TiO}_2/\text{H}_2\text{O}$  at the onset of the reaction. In particular, that favors the formation of phenol (Fig. 5(a)), thus, the degradation of benzene. On  $\text{TiO}_2/\text{HCl}$  the basic surface OH groups are replaced by chloride ions [21–24], thus, the density in OH groups is less at the onset of the reaction, and therefore, the conversion rate is lower. The favorable effect of a higher coverage of  $\text{TiO}_2$  by OH groups could also account for the increases in the steady-state values of benzene conversion that we observed for increasing water vapor concentrations and untreated  $\text{TiO}_2$ , in agreement with the previous results [12]. Also, the 10–15% increases in conversion over regenerated  $\text{TiO}_2/\text{HCl}$  compared with fresh  $\text{TiO}_2/\text{HCl}$  might reflect a surface rehydroxylation during the regeneration process.

#### 4.2. Toluene-suggested degradation pathways

The primary pathway in toluene photocatalytic oxidation is, we believe, the hydrogen abstraction from the methyl group leading to a benzyl radical; three initial routes are proposed for the formation of this radical (Fig. 6(a)).

1. Direct hole transfer to toluene. Andersson [25] proposed a mechanism in thermal heterogeneous catalysis of toluene oxidation where the first step is the reversible transfer of one electron from toluene to the metal oxide with the formation of an aromatic radical cation. This presumably slow, rate-determining step is followed by a faster proton release by the radical cation to form the benzyl radical. This mechanism is supported by the fact that the methyl hydrogen atom dissociation energy is lower by 28 kcal mol<sup>-1</sup> (117 kJ mol<sup>-1</sup>) for the radical cation than for toluene [26].
2. H abstraction by an OH radical. We believe that this is a minor pathway. We have proposed that OH<sup>•</sup> is not the dominant reactive species in gas-phase photocatalytic elimination of many common air contaminants [10]. In addition, OH radical abstraction of H atom from the toluene methyl group in gas-phase homogeneous photo-reactions is also not a dominant route [9,27].
3. H abstraction by chlorine radical. We have shown that over  $\text{TiO}_2/\text{HCl}$ , Cl<sup>•</sup> is most probably the reactive species for many contaminants [2]. In addition, homogeneous gas-phase literature [15] indicates that the Cl<sup>•</sup> reaction with toluene proceeds exclusively by hydrogen atom abstraction from the methyl group to form the benzyl radical.

The surface benzyl radical can then react with  $\text{O}_2$  to form a benzylperoxy radical (Fig. 6(a)), or with an incoming toluene molecule, thus, initiating a polymerization reaction as suggested by Sitkiewitz and Heller [13] for benzene photocatalyzed conversion. Also, in thermal heterogeneous catalysis, Andersson [25] reported that the second most important path (leading up to 30% by-products) for toluene vapor-phase oxidation is a methyl group attack with subsequent coupling to produce *o*- and *p*-methyl-diphenyl-

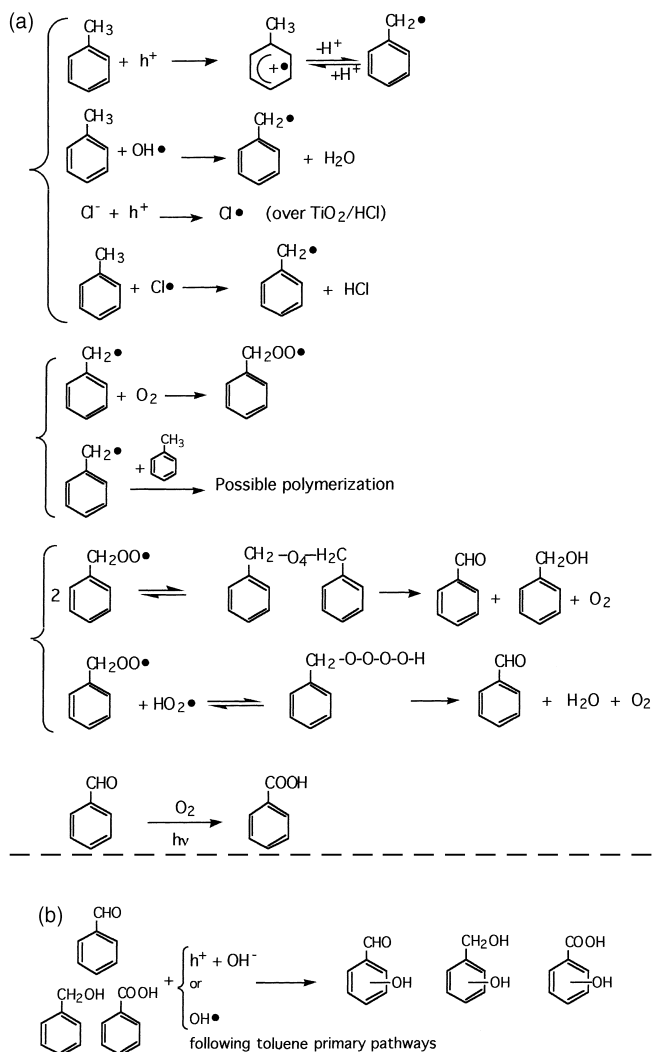


Fig. 6. (a) Primary toluene photocatalytic oxidation pathways. (b) Secondary toluene photocatalytic oxidation pathways.

methane isomers, and bibenzyl (1,2-biphenylethane). Coupling products have also been found in an aqueous phase photocatalysis over  $\text{TiO}_2$  [28–31] or  $\text{ZnO}$  [32]. We have not detected any bicyclic aromatics; however, we believe that the formation of higher condensed products (polymerization reaction) may occur in our continuous flow, ambient temperature, gas-phase photocatalytic system.

Only a prolonged regeneration in air and UV irradiation would permit the destruction of the polymer product. The yellow material that settles at the interface between the aqueous phase and used  $\text{TiO}_2/\text{H}_2\text{O}$  or  $\text{TiO}_2/\text{HCl}$  during centrifugation could be a polymer product.

The benzylperoxy radicals can couple to form a tetroxide (Fig. 6(a)) proposed by von Sonntag and Schuchmann for oxidation in aqueous phase [16] and applied in photocatalysis by Heller et al. [13,33]. The tetroxide decomposes to benzaldehyde, benzyl alcohol, and molecular oxygen (the Russell reaction [34]). The benzylperoxy radical can also react with a hydroperoxy radical to form a monoalkyl-

tetroxide that decomposes to benzaldehyde, molecular oxygen, and water (the 'Russell-like' reaction [35]). In the gas phase, Seuwen and Warneck [9] proposed that the benzylperoxy radicals undergo self-reaction to form either benzaldehyde via a benzyloxy radical or benzaldehyde and benzyl alcohol in equal amounts.

Benzaldehyde oxidizes easily into benzoic acid, especially in the presence of O<sub>2</sub> and UV irradiation similar to the transformation of 4-tertbutylbenzaldehyde into 4-tertbutylbenzoic acid [36].

The pathways proposed here are consistent with the three main by-products we identified: benzaldehyde, benzyl alcohol and benzoic acid. Over TiO<sub>2</sub>/HCl, the presence of chlorine provides an additional pathway to form the benzyl radical, which accounts for the faster initial rate of toluene degradation over TiO<sub>2</sub>/HCl, and the greater amounts of adsorbed benzoic acid which we find here.

A secondary, less important pathway in the degradation of the three main intermediate products, is an attack at the ring (Fig. 6(b)) leading to the corresponding mono-hydroxylated isomers (hydroxybenzaldehyde, hydroxybenzoic acid, and hydroxybenzyl alcohol). The small amounts of these hydroxylated products compared with the non-hydroxylated primary intermediate products confirm that initial OH radical addition to the aromatic ring is not a major pathway in the gas-phase photocatalytic system.

#### 4.3. TiO<sub>2</sub> discoloration and deactivation

The toluene and benzene intermediate products we identified were found in the clear portion of the extraction liquid and, therefore, are presumably not at the origin of the yellow coloration and the deactivation of the catalyst. Larson and Falconer [6] found that toluene oxidizes rapidly over UV-irradiated TiO<sub>2</sub> to form intermediate products that are strongly adsorbed and much less reactive than toluene. They also demonstrated that benzaldehyde and benzyl alcohol react 10–30 times faster than toluene. They, therefore, concluded that these compounds are not likely to be the stable intermediate products formed in a photocatalytic oxidation of toluene. The unidentified yellow material we recovered from used TiO<sub>2</sub> could correspond to these less reactive intermediates.

## 5. Conclusions

Different analytical methods (GC/FID, GC/MS, HPLC/UV), chromatographic columns (HP1, CP-SIL 5 CB, Chrompack ODS-2, and CAR-H), and solvents (water, diethylether, dichloromethane, methanol) permitted us to identify several adsorbed intermediate products, some of which have not been previously detected, during toluene or benzene photocatalytic conversion over TiO<sub>2</sub> prechlorinated or not. The relative amounts of toluene products suggest that direct hole transfer from the semiconductor to the aromatic

predominates over the attack by a OH radical, in agreement with our earlier indications for many organic contaminants [10]. The prechlorination of TiO<sub>2</sub> does not result in different intermediate products, but only in the respective quantities of these products and in the degradation rates. An important corollary is that prechlorination of the TiO<sub>2</sub> surface does not cause the formation of chlorinated products. The discoloration and concomitant deactivation of the photocatalyst during aromatic photocatalytic destruction appears largely due to the adsorbed polymeric products shown here to be separable by water extraction. Note that this phenomenon occurred for 50 mg m<sup>-3</sup> of aromatic pollutant, i.e. for concentrations that may correspond to some industrial effluents but are at least a thousand times higher than those found in indoor air. Regeneration in a pure air flow under UV-irradiation allowed gradual recovery of the photocatalytic activity.

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