Probing the TiO_2 Photocatalytic Mechanisms in Water Purification by Use of Quinoline, Photo-Fenton Generated $OH^\bullet$ Radicals and Superoxide Dismutase†

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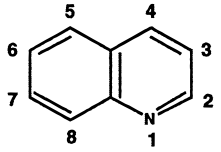
In an attempt to improve our understanding of the basic mechanisms of the degradation of aromatic pollutants in water by TiO_2 photocatalysis, quinoline (benzo[*b*]pyridine) was selected as a molecular probe, principally because of the difference in electron density over its two rings. This study was based on the identification and quantification of the primary products or principal secondary products of quinoline degradation either by TiO_2 photocatalysis at pH 3 and 6 or by $OH^\bullet$ radicals generated via the photo-Fenton reaction (Fe(II/III)−H_2O_2−UV) at pH 3. In this latter case, the three major products were those expected from the preferential electrophilic attack of $OH^\bullet$ radicals on the electron-richer benzene moiety, viz., 5-, and 8-hydroxyquinolines and quinoline-5,8-dione derived from them. TiO_2 photocatalysis did not yield this dione, and at the same percentages of degraded quinoline, the amounts of 5-hydroxyquinoline were lower by a factor of ca. 2 at pH 3 and ca. 10 at pH 6 (those of the 8-isomer were also decreased but no accurate measurements were obtained). In addition, at pH 6, we observed marked increases in the amounts of products corresponding to the oxidation of the pyridine moiety, viz., 4-quinolinone and especially 2-aminobenzaldehyde (the major product) and its *N*-formyl derivative. These results show that oxidative steps in TiO_2 photocatalysis do not involve only $OH^\bullet$ radicals. It was also observed that, at pH 6, superoxide dismutase (SOD), which catalyzes the elimination of $O_2^{\bullet-}$ species, decreased the TiO_2 photocatalytic rate of quinoline disappearance, almost suppressed the formation of 2-aminobenzaldehyde, and lowered the amount of 4-quinolinone. The SOD and pH effects suggest a mechanism involving quinoline activation by hole transfer, followed by superoxide addition to the resulting radical cation. The nucleophilic character of superoxide implies addition to the pyridine moiety, i.e., with a regioselectivity opposite that of the $OH^\bullet$ radical pathway.

Introduction

Heterogeneous photocatalysis over anatase TiO_2 samples is an appealing "advanced oxidation process" (AOP) to eliminate organic pollutants in water, and accordingly numerous studies have dealt with this field as it has been recently reviewed.[1] A better understanding of the basic mechanisms involved will certainly be useful to improve the efficiency of this AOP. That includes assessing the relative importances of the various reactions in which the photoproduced electrons and holes, as well as the radicals derived from them, are involved. Along this line, the present study addresses the debated question as to whether the hydroxyl radicals[1−18] formed at the surface of TiO_2 can totally account for the degradation of aromatic pollutants or whether other oxidative pathways also occur.[1,9−13,19−35] For that purpose, the following strategy was used: (i) choice of an appropriate probe pollutant, (ii) comparison between the primary intermediate products of this probe pollutant degraded either by TiO_2 heterogeneous photocatalysis or by a process generating hydroxyl radicals, and (iii) use of Cu−Zn superoxide dismutase (SOD),[36] an enzyme capable of decreasing the concentration in superoxide, to determine whether superoxide can be chemically involved in the degradation steps.

Previous comparisons of degradation intermediate products formed, either by heterogeneous photocatalysis or by methods yielding hydroxyl radicals in homogeneous phase, to assess the role of these radicals, in particular with respect to direct hole transfer to the pollutant, mainly concerned substituted benzene compounds, most often phenol derivatives.[19−23] Generally, these aromatic compounds lead to the same products whether they are degraded by $OH^\bullet$ radical attack or by electron transfer to the semiconductor followed by addition of a water molecule and loss of a proton, since a cyclohexadienyl radical can be formed by both pathways.[37,38] Effects of adding hydroxyl radical scavengers to the TiO_2−UV system have been investigated;[23] however, this method, although interesting, has the disadvantage of introducing a chemical compound which can also change the adsorption amount/mode of the probe molecule, and possibly compete with the probe molecule for reaction pathways other than those involving $OH^\bullet$ radicals.

The approach we chose was to select a probe molecule whose degradation intermediate products can be expected to allow one to discriminate between the $OH^\bullet$ radical pathway and other pathways. Quinoline was picked because it contains two



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different aromatic rings, the pyridine ring having a lower electron density than the benzene ring because of the larger electron affinity of the nitrogen atom.

As the hydroxyl radical is electrophilic, degradation of quinoline by this radical should generate primary products reflecting a preferential attack onto the benzene ring. By contrast, the formation of quinoline products in which the pyridine ring is affected will indicate the existence of other degradation pathways. Besides this difference in electron density over its two aromatic nuclei, quinoline offers other advantages to be used as a molecular probe. It is a sufficiently large and stable molecule to make it likely that primary products still possess at least one aromatic ring and therefore are easily detectable by HPLC−UV or by GC−MS without derivatization. The primary products can only result from transformations of the aromatic rings; therefore, interpretation of the results is expected to be less complex than if an alkyl side chain containing easily abstractable hydrogen atoms were present. Also, no steric hindrance can affect the product distribution. However, the lone electron pair of the nitrogen atom might orient the adsorption of quinoline on the TiO_2 surface and thus might lead to prevailing attacks at positions 1, 2, and 8; this concern is considered in the Discussion section. On the other hand, quinoline solubility in water is high enough to allow the use of an initial concentration sufficient for easily analyzing the degradation products. Quinoline is also moderately polar and basic, which prevents the degradation routes from being influenced by ionic associations. Finally, quinoline and its derivatives are common contaminants of groundwater near wood preservation and fossil fuel facilities[39] so that our study also represents a practical interest. Information about the products of the microbial degradation[39−42] and of the direct or indirect photolysis[43] of quinoline is available.

As a source of hydroxyl radicals in homogeneous medium we used the photo-Fenton reaction[44−49] which principally involves the absorption of UV light by the $Fe(OH)^{2+}$ complex, the most abundant complex of Fe(III) at pH 3 (eq 1), and the Fenton reaction (eq 2). This method of generating hydroxyl

$$Fe(OH)^{2+} \xrightarrow{h\nu} Fe^{2+} + OH^{\bullet} \quad (1)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^{\bullet} \quad (2)$$

radicals presents several advantages: (i) contrary to radiolysis it does not require heavy equipment, (ii) it is catalytic because of the interplay between eqs 1 and 2, (iii) the complex $Fe(OH)^{2+}$ is photoexcitable at 365 nm, as is TiO_2, which avoids any significant direct photolysis of quinoline within our degradation durations, and (iv) the rate of $OH^{\bullet}$ radical generation can easily be adjusted by varying the concentrations of the reagents and the radiant power.

The use of SOD[36] was an additional element of our research strategy. This enzyme, as well as catalase,[36] has previously been employed by two of us[29,30] to assess the chemical roles of superoxide and *in situ* formed hydrogen peroxide, respectively, in heterogeneous photocatalysis over TiO_2 or ZnO, 1,2-dimethoxybenzene being the probe pollutant. The use of SOD and catalase was based on the activity of these enzymes for catalyzing the dismutations of $O_2^{\bullet -}$ and H_2O_2, respectively.

$$2O_2^{\bullet -} + 2H^+ \rightarrow O_2 + H_2O_2 \quad (3)$$

$$2H_2O_2 \rightarrow 2\,H_2O + O_2 \quad (4)$$

From a series of experimental facts, it was inferred that the unfavorable effect of these enzymes on the disappearance rate of 1,2-dimethoxybenzene was not due to a competitive degradation of the enzyme and the pollutant, but really due to the enzymatic activity. These experimental facts included (i) the absence of significant change in the extent of adsorption of 1,2-dimethoxybenzene (and other aromatic pollutants) in the dark with or without enzyme at the concentrations that were employed, (ii) the absence of effect of catalase when ZnO, a semiconductor known for not photocatalytically decomposing H_2O_2, was used instead of TiO_2, and (iii) distinct distributions of intermediate degradation products of 1,2-dimethoxybenzene with or without SOD at equal percentages of pollutant elimination.[29] The most convincing argument was that the strong inhibition of SOD by CN^- ions (because of the complexation of the Cu−Zn SOD active centers by these anions), as checked by independent measurements of the enzyme activity, almost suppressed the SOD effect on the disappearance rate of the pollutant.[30]

To avoid either precipitating iron hydroxides or inhibiting SOD activity, the TiO_2 photocatalytic degradation of quinoline was carried out at pH 3 for comparison with the photo-Fenton reaction induced degradation, and at pH 6 for assessing the effect of superoxide which is inactive at pH 3. Herein we report the quinoline disappearance rates, as well as the identifications and kinetic variations of the primary products of quinoline degradation under these conditions. The mechanistic implications for heterogeneous photocatalysis with TiO_2 aqueous dispersions are discussed.

Experimental Section

Materials. All reagents and some of the intermediate products of quinoline degradation were purchased from Aldrich (maximum purity grade), except indole-2,3-dione (Fluka). Cu,Zn-superoxide dismutase E.C. 1.15.1.1. was obtained from Boehringer Mannheim. The following compounds were prepared and purified by published methods: 3-hydroxyquinoline;[50] 7-hydroxyquinoline;[51] 3-hydroxy-2-quinolinone;[52] 3-hydroxy-4-quinolinone;[53] 5,8-dihydroxyquinoline;[54] 6,7-dihydroxyquinoline;[55] quinoline-5,8-dione;[56] quinoline-2,3,4-trione;[57] 2-aminobenzaldehyde;[58] *N*-formyl-2-aminobenzaldehyde;[59] 2-oxoindole-1-carbaldehyde;[60] 2-oxoindole-3-carbaldehyde;[61] *N*-formyl-2,3-dihydroindole-2,3-dione (*N*-formylisatin);[62] 4-hydroxyindole-3-carbaldehyde.[63] Methanol (Aldrich, HPLC grade) was employed as an eluent. Tetraethylammonium bromide (eluent modificator) was also provided by Aldrich. Dichloromethane "Pestinorm" used for solvent extraction was obtained from Prolabo (GC grade, >99.9%). The water used for solution and eluent preparations was ultrapure water from Milli-Q plus (Millipore). The photocatalyst was TiO_2 Degussa P-25, mainly anatase, 50 $m^2\ g^{-1}$, non porous.

Photoreactor and Light Source. A cylindrical batch photoreactor (total volume ca. 80 mL) open to air with a bottom optical window of fused silica ca. 12 cm in surface area was used. The radiation from a Philips HPK 125-W high-pressure mercury lamp was filtered through a circulating water cuvette (thickness 2.2 cm) equipped with a 335 nm cut- off filter (Corning 0.52). The radiant flux of this system, measured with a UDT 21 A powermeter, was found to be 32.9 ± 1.6 mW cm^{-2}. The corresponding number of photons per second potentially absorbable by TiO_2 was estimated to be ca. (1.14 ± 0.05) × 10^{17}.[64]

Procedures. For studies of quinoline disappearance by GC−FID or HPLC, the starting solution contained 0.15 mmol L^{-1} quinoline (20 mg L^{-1}, pH ca. 6); 20 mL of this solution was introduced into the photoreactor and stirred with 70 mg of TiO_2 in the dark for 30 min, before irradiation, in order to reach

adsorption equilibrium. These initial conditions were also used to quantify intermediate products by HPLC.

Identifications of the intermediate products giving rise to HPLC peaks were first performed by comparing the retention times, t_R, and the UV spectra (photodiode array detector) with those of standards or home-prepared compounds. In addition, these intermediates were isolated and extracted with dichoromethane and analyzed by GC−MS. For these identifications the initial concentration of quinoline was 1.55 mmol L^{-1} (200 ppm) , and the irradiation time was 30 min.

The intermediate products not detected by HPLC under our conditions were identified by GC−MS; in that case the initial quinoline concentration was 7.55 mmol L^{-1} (1 g L^{-1}) and the irradiation time was 15 min.

For quinoline degradation in acidic medium, the pH of the solution was adjusted to pH 3 with HNO_3 because nitrate ions do not alter the TiO_2 photocatalytic activity, in contrast with chloride and sulfate ions.[65−67] Quinoline degradation in the presence of SOD at pH 6 was performed with 100 mg L^{-1} enzyme.

Photo-Fenton degradation of quinoline was carried out using $Fe_2(SO_4)_3 \cdot 5H_2O$ as Fe(III) source ([Fe(III)] = 0.304 mmol L^{-1}) and H_2O_2 (205 μL of 30% H_2O_2/20 mL) to reach a concentration of ca. 0.1 mol L^{-1} H_2O_2. The solution pH was naturally 3 when [quinoline] = 0.15 mmol L^{-1} and set to this value with H_2SO_4 when [quinoline] = 1.55 mmol/L^{-1}. The intermediate products were analyzed by HPLC and GC.

Analyses. *HPLC Analyses.* After each irradiation 20 mL of aqueous suspension was filtered through 0.45 μm Millipore HV filters to remove TiO_2 agglomerated particles before HPLC analysis. The HPLC system for quantitative analysis comprised an LDC Constameric 3200 isocratic pump and a Spectro Monitor D UV detector adjusted at 234 nm. A Varian Polychrom 9065 photodiode array detector (with a Varian LC start system and a Compaq 286-A microcomputer) and a Varian 9010 pump were used to obtain the UV spectra of intermediate products. In both HPLC systems a reverse-phase column Chromspher B (length 15 cm, inner diameter 4.6 mm) and a guard column Chromsep R.P. (10 × 2 mm) were employed. The mobile phase was composed of methanol (30% v/v) and ultrapure water into which tetraethylammonium bromide (5 mmol L^{-1}) was added, and a flow rate of 1 mL mn^{-1} was used. In all HPLC experiments the sample quantity injected was 20 μL.

GC−MS Analyses. Identification of the quinoline degradation intermediates was carried out using a gas chromatograph (HP 5890 series II) with a Chrompack CP-SIL 5-CB column (length 25 m, inner diameter 0.25 mm, film thickness 1.2 μm). The column was connected to a mass spectrometer (HP 5971 A) operated in electron impact (EI) or chemical ionization (CI) mode, with methane as a reagent gas, and an HP 386 microcomputer. The injections were made in the splitless mode. The column temperature program was 311−318 K (20 K min^{-1}, hold time = 1.5 min); 318−403 K (10 K min^{-1}, hold time = 10 min); 403−533 K (20 K min^{-1}, hold time = 10 min).

After each irradiation period (whose duration was such as to reach 5−7% quinoline transformation), the 20 mL of aqueous suspension was extracted, either at natural pH or at pH 2.5 after adding H_2SO_4, with twice ca. 10 mL of CH_2Cl_2, and the organic phase was evaporated down to a volume of ca. 0.2 mL before being analyzed.

GC−FID Analyses. After each irradiation period, to the 20 mL of aqueous solution (or TiO_2 suspension after adding H_2SO_4 to decrease the pH to 2.5) was added 2 mL of internal standard (4-cyanopyridine, 0.042 mmol L^{-1} in water). The aqueous mixture was then extracted three times with ca. 10 mL of CH_2Cl_2. The organic phase was reduced to ca. 0.3 mL before being analyzed.

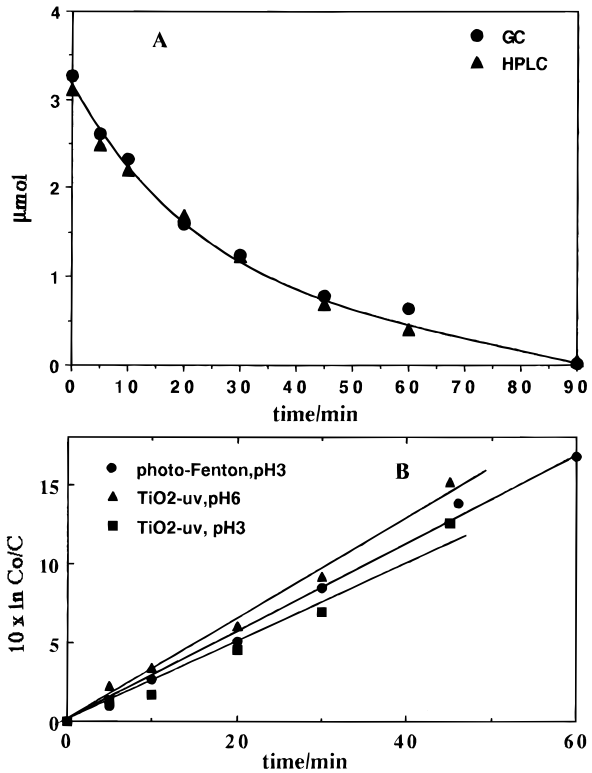


Figure 1. (A) Quinoline amount (GC and HPLC analyses) against irradiation time for degradation by TiO_2 heterogeneous photocatalysis at initial pH 6. (B) Linear transforms of the disappearance of quinoline during the degradation processes indicated. C_0 and C are initial and actual concentration of quinoline, respectively.

A Varian 3400 gas chromatograph with a flame ionization detector was used with a Chrompack CP-SIL 5CB column (length 25 m, inner diameter 0.32 mm, film thickness 1.2 μm). The injections were made in the on-column mode, with a septum-equipped programmable injector (T = 308−533 K, 150 K/min, hold time 10 min). The temperature program of the column was T = 318 K, hold time = 2 min; T = 318−403 K, 10 K/min, hold time = 10 min; T = 403−533 K, 20 K/min, hold time = 10 min. With this program, the retention times in GC−FID and GC−MS analyses were the same. The retention time of the internal standard was 13.8 min.

Results

Quinoline Disappearance. Figure 1A shows a typical disappearance profile of quinoline as a function of time. As the agreement between HPLC and GC analyses was very satisfactory (Figure 1A), HPLC was chosen for the experiments carried out under various conditions because of its convenience.

Upon UV irradiation with TiO_2 the kinetics of quinoline disappearance were apparently first order with respect to time for the first 50 min as illustrated in Figure 1B; the corresponding rate constant k_{app} was equal to (3.15 ± 0.05) × 10^{-2} min^{-1}. First order kinetics were also observed at pH 3 irrespective of the degradation process (Figure 1B).

Lowering the initial pH from 6 to 3, in which case quinoline (pK_a = 4.5) was present principally as quinolinium cation (as was clearly shown by the UV spectrum), decreased k_{app} by a factor of about 1.17 (Figure 1B). When SOD (100 mg L^{-1}) was added at pH 6, k_{app} was divided by ca. 4.5.

In the photo-Fenton experiments, the concentrations of H_2O_2 and Fe^{3+} ions were selected so as to obtain a k_{app} value ((3.00

TABLE 1: Gas Chromatographic Retention Times and Mass Peaks of Quinoline and Its Intermediate Products of Degradation

compounds	retention times (min)	mass peaks (CI methane) ($m/z = M + 1$; $M + 29$; $M + 41$)[a,b]	mass peaks (EI) (m/z)[a]
2-aminobenzaldehyde[c]	21.6		121; 93; 66; 65; 92; 39
quinoline[d]	22.3	130; 158; 170	129; 102; 76; 5039; 28
8-hydroxyquinoline[d]	25.2	146; 174; 186	145; 117; 89; 90; 63; 39
N-formyl-2-aminobenzaldehyde[c]	25.5	(121); 150; 178; 190	93; 121; 149; 66; 65; 92; 76; 39; 29
(2-formyl)phenyliminoethanal[c,e]	26.0		132; 104; 79; 51
A[f]	26.5	162; 190; 202	132; 104; 77; 51; 39; 29
quinoline-5,8-dione[c]	27.1	160; 188; 200	159; 103; 131; 77; 76; 108
B[f]	27.2	162; 190; 202	132; 104; 79; 51; 105; 133; 78; 77; 161
C[f]	27.3	(148); 176; 204; 216	147; 146; 119; 90; 175; 92; 63; 64; 39; 29; 76
5-hydroxyquinoline[d]	27.7	146; 174; 186	145; 117; 89; 90; 65; 50
2-quinolinone[d]	28.9	146; 174; 186	145; 117; 89; 90; 63

[a] In order of magnitude. [b] *M* is the molecular mass. [c] Synthesized compounds. [d] Mass spectrum and retention time equivalent to commercialized standards. [e] See Scheme 1C. [f] A, B, C: see text for a discussion on the nature of these compounds.

$\pm 0.05) \times 10^{-2}$ min^{-1}) close to that of the TiO_2 photocatalytic degradation (Figure 1B) to make comparisons easier between the distributions of intermediate products at equivalent percentages of degraded quinoline.

Main Degradation Products of Quinoline. *Identifications.* Table 1 shows the GC−MS characteristics of quinoline and the main products of degradation that were identified by this analytical technique through the use of authentic samples, among which some were synthesized for that purpose (see the Experimental Section).

Other products were formed for which identifications were not straightforward. Three intermediate products with molecular mass of 161 (quinoline + 2O) were detected in the case of the TiO_2−UV degradation of quinoline (Table 1). Comparison with several dihydroxyquinolines or their quinolinone tautomers (either by using authentic samples or by checking reported mass spectra) showed that the 1,2-, 1,8-, 2,3-, 2,4-, and 2,8-isomers were not present, whereas the 3,4- and 6,7-isomers were not determined under our analytical conditions. Another possibility considered was that these intermediate products were ring-cleaved dialdehydes. In support of this hypothesis, these products were not extracted when $NaHSO_3$ was added to the aqueous solution. Indeed, one of these products (Table 1) had a retention time and a mass spectrum identical to that of (2-formyl)phenyliminoethanal (Scheme 1B), a compound we prepared by condensation of 2-aminobenzaldehyde with ethanedial (glyoxal). On the other hand, some indole derivatives which were tested (4-hydroxyindole-3-carbaldehyde; 2-oxo-indole-1-carbaldehyde; 2-oxo-indole-1-carbaldehyde; 2-oxo-indole-3-carbaldehyde) were shown not to correspond to these quinoline products. Consequently, it was suggested that the two other isomers were also pyridinedialdehydes resulting from the cleavage of the quinoline carbocyclic ring, as for example 3-(2-formyl)pyridine-2-carbaldehyde. Finally, an intermediate product with molecular mass of 175 (quinoline + 3O − 2H) was also formed by TiO_2 photocatalytic degradation of quinoline (Table 1). *N*-Formyl-2,3-dihydroindole-2,3-dione (*N*-formylisatin) and quinoline-2,3,4-trione were synthesized for comparison. The former compound had GC−MS characteristics identical to those of the unknown product, but a slightly different HPLC retention time. The latter compound was not eluted by GC or HPLC under our conditions; during GC analysis it was partially transformed into 2,3-dihydroindole-2,3-dione (isatin) which was indeed found in the photocatalytically degraded quinoline solution. Therefore, the formation of these products, in particular quinoline-2,3,4-trione, was not excluded but the identifications were not definitive. In any event, assuming reasonable GC response coefficients, none of these products was formed in quantities susceptible of changing the conclusions drawn from the main products that have been surely identified and accordingly quantified (Figure 2, Table 2).

The identifications of 4-quinolinone and 6-hydroxyquinoline were performed only by comparing HPLC retention times and UV spectra (photodiode array) with those of standards. The reasons for that were 4-quinolinone was not extracted from the aqueous solutions by dichloromethane, the solvent utilized for GC analyses, and 6-hydroxyquinoline, formed in much lower amounts than 5-hydroxyquinoline, coeluted with this isomer under the GC conditions.

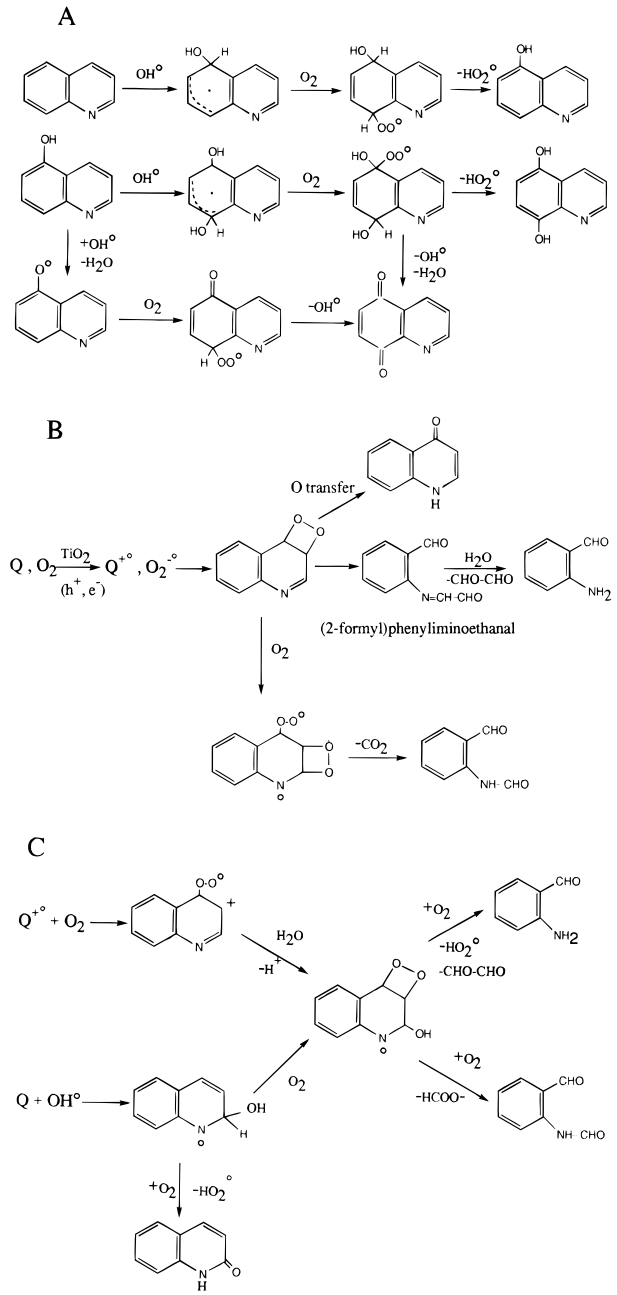
Quantifications. The amounts of hydroxyquinolines, quinolinones, quinoline-5,8-dione, 2-aminobenzaldehyde, and *N*-formyl-2-aminobenzaldehyde were measured by HPLC analysis. 8-Hydroxyquinoline was quantified by GC analysis because this product was not correctly eluted by HPLC, even when we used the conditions claimed in ref 43 to allow a correct HPLC analysis. Moreover, 8-hydroxyquinoline cannot be accurately quantified when TiO_2 is used for the quinoline degradation: as shown by control experiments, this compound was not completely extracted from TiO_2 by dichloromethane, unlike 2-and 4-quinolinones and 5-and 6-hydroxyquinolines. Note that quantification of quinoline-5,8-dione, 2-aminobenzaldehyde, and its *N*-formyl derivative required the preparation of pure standards.

Degradation by the Photo-Fenton Reaction. Several primary degradation products corresponded to the hydroxylation of quinoline, viz. 5-, 6-, and 8-hydroxyquinolines, as well as 2- and 4-quinolinones (the most stable tautomers of 2- and 4-hydroxyquinolines in water). As is shown in Figure 2A, 2-quinolinone and 6-hydroxyquinoline reached much lower concentrations than the other isomers. Moreover, the other hydroxyquinolines and quinoline 1-oxide were not detected. Another important degradation product was quinoline-5,8-dione, accompanied by traces of the corresponding dihydroxyquinoline. The maximum concentration of this dione was reached significantly later than those of the most abundant monohydroxyquinolines (Figure 2A); in addition, this product, unlike monohydroxyquinolines, was still present when quinoline was completely eliminated (Figure 2A); finally, it was formed as the main product of the separate degradations of 5- or 8-hydroxyquinoline under the same conditions as those employed to degrade quinoline. These results suggest that quinoline-5,8-dione was a secondary product.

2-Aminobenzaldehyde, a product from attack at the pyridine moiety of quinoline, was also formed but in much lower amounts than the products corresponding to the oxidation of the benzene nucleus (Figure 3A, Table 2).

Degradation by TiO_2 Heterogeneous Photocatalysis. The hydroxyquinoline and quinolinone isomers obtained in UV-

SCHEME 1: Suggested Mechanisms of Quinoline Degradation[a]



[a] Quinoline degradation: (A) *via* hydroxyl radicals (positions 5 and 8 are attacked preferentially; see text, Figure 2A, and Table 2); (B) via addition of superoxide to the quinoline radical cation (superoxide addition is supposed to preferentially occur on the pyridinic ring because of the nucleophilic character of $O_2^{\bullet -}$; for clarity, only the 3,4-dioxetane is shown, but other regioisomers as well as open-chain diradicals and zwitterions can be involved, see text); (C) to account for the formations of 2-aminobenzaldehyde and its *N*-formyl derivative by pathways that do not involve superoxide. Q is for quinoline.

irradiated TiO_2 suspensions were the same as those produced by the photo-Fenton reaction; however, the distribution of these isomers was different (Figure 2, Table 2). An influence of changing the pH from 3 to 6 was also noticeable (Figure 2B,C, Table 2). Above all, no quinoline-5,8-dione was detected in the course of the quinoline TiO_2 photocatalytic degradation in contrast to the degradation in homogeneous medium.

Regarding the main products corresponding to the opening of the pyridine moiety of quinoline, 2-aminobenzaldehyde and, to a lesser extent, its *N*-formyl derivative were formed and their

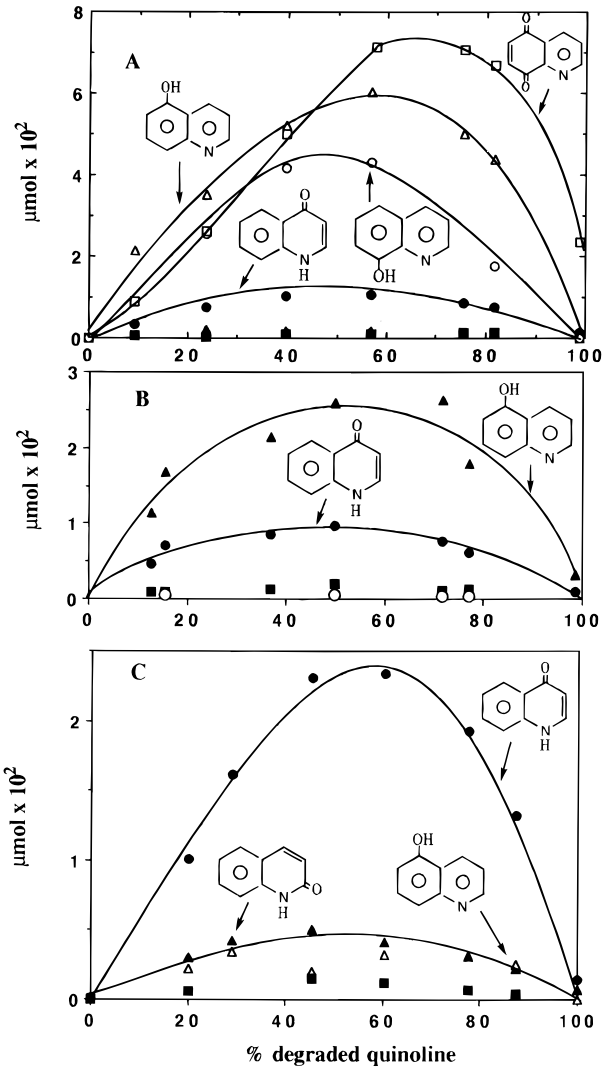


Figure 2. Variations in concentrations of the main hydroxyquinolines and quinolinones, and of quinoline-5,8-dione as a function of percentage of remaining quinoline during photo-Fenton degradation at initial pH 3 (A), TiO_2 heterogeneous photocatalytic degradation at initial pH 3 (B), or heterogenous photocatalytic degradation at initial pH 6 (C). 2-Quinolinone was formed in small amounts under the two former conditions (A and B), whereas 6-hydroquinoline was formed in small amounts under all three conditions (A, B, and C) (cf. experimental points close to the abscissa axis). All products were quantified by HPLC, except 8-hydroxyquinoline for which GC was used.

amounts increased from pH 3 to pH 6 (Table 2, Figure 3). By contrast, only traces of this latter product were detected when the photo-Fenton process was employed to degrade quinoline. Also, (2-formyl) phenyliminoethanal, which can be considered as a precursor of 2-aminobenzaldehyde (Scheme 1B), was detected only in the case of the degradation in heterogeneous phase.

At pH 6, for equal percentages of transformed quinoline, the presence of SOD changed the distribution of the three main degradation products. The amount of *N*-formyl-2-aminobenzaldehyde was not significantly affected (Figure 3B), whereas that of 4-quinolinone was substantially decreased and the formation of 2-aminobenzaldehyde was nearly nil (Table 2).

Discussion

Significance of the Distributions of the Quinoline Degradation Intermediates. The curves showing the variations in the concentrations of hydroxyquinolines or quinolinones as intermediate degradation products against the percentage of

TABLE 2: Amounts (in nmol) of the Intermediate Products of Quinoline Degradation under the Conditions Indicated[a]

	photo-Fenton pH 3		heterogeneous photocatalysis					
			pH 3		pH 6		pH 6 + SOD	
products	20%[b]	50%[b]	20%[b]	50%[b]	20%[b]	50%[b]	20%[b]	50%[b]
2-quinolinone	1.5	1.5	2	2	3	5	2.5	3
4-quinolinone	7	10	7	10	10	24	5	8
5-hydroxyquinoline	33	55	16	26	2	2.5	trace	trace
8- hydroxyquinoline	20	42	*c*	*c*	*c*	*c*	*c*	*c*
quinoline-5,8-dione	20	60	*d*	*d*	*d*	*d*	*d*	*d*
2-aminobenzaldehyde	6	8	8	10	50	80	trace	trace
N-formyl-2-aminobenzaldehyde	trace	trace	2.5	2.5	10	21	10	21

[a] Initial quinoline amount 3.2 μmol. Indicated pHs are initial pHs. The amounts of 6-hydroxyquinoline comprised between 0.5 and 1.5 nmol (traces in the presence of SOD). Traces of 5,8-dihydroxyquinoline were found in the case of the photo-Fenton degradation process. [b] Percentages of degraded quinoline. [c] 8-Hydroxyquinoline was incompletely extracted from TiO_2; however, the amount formed by heterogeneous photocatalysis was much smaller than that formed by the photo-Fenton reaction. [d] Not detected.

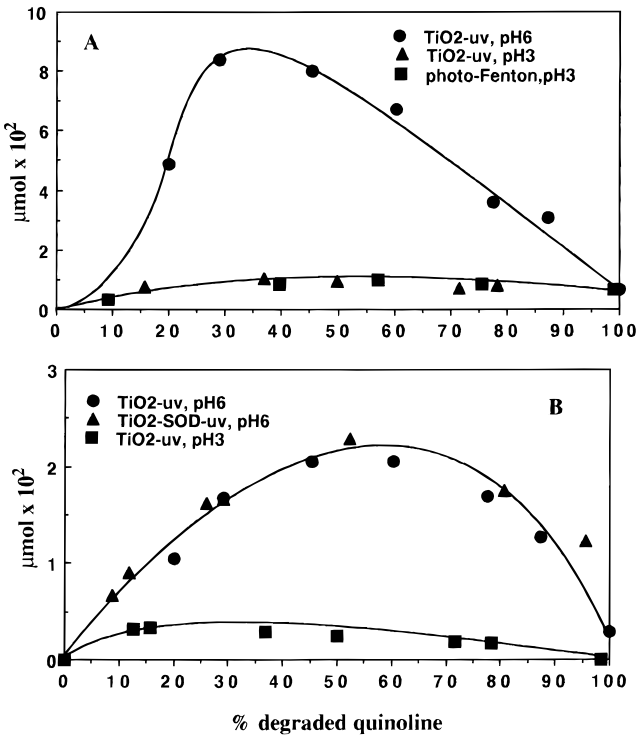


Figure 3. Variations in concentrations (HPLC analysis) of 2-aminobenzaldehyde (A) or *N*-formyl-2-aminobenzaldehyde (B) as a function of percentage of remaining quinoline under the degradation conditions indicated.

degraded quinoline (Figure 2) result from both the formation rate and the elimination rate of each of these products. However, these curves can be considered as essentially reflecting the formation rates, on which our conclusions are based, if the elimination rates do not differ much for each hydroxyquinoline or quinolinone. Indeed, control experiments showed that the elimination rates of 4-quinolinone and 5-hydroxyquinoline (initial concentration 0.186 mmol L^{-1} = 2.7 ppm) were sufficiently close to each other to allow this approximation: for the photo-Fenton process k_{app} = 0.116 and 0.128 min^{-1}, and for photocatalysis at pH 6 k_{app} = 0.182 and 0.156 min^{-1}, where the first figure in each couple relates to 4-quinolinone and the second one to 5-hydroxyquinoline.

It may also be questioned whether the presence of a large surface area onto which part of quinoline is adsorbed can *per se* affect the distribution of quinoline degradation products. To check that, the photo-Fenton degradation process was carried out in the presence of powder silica (Aerosil Degussa, 200 m^2 g^{-1}; 20 mg in 20 mL quinoline solution) which does not exhibit photocatalytic activity. Both the quinoline disappearance rate (0.027 min^{-1} instead of 0.03 min^{-1}) and the distribution of intermediate products resulting from the photo-Fenton reaction were little affected by the presence of silica. Thus the differences between the TiO_2−UV and the Fe(II/III)−H_2O_2−UV systems do not arise from the mere presence of a solid surface in the former case.

It may be further objected that the adsorption of quinoline by the nitrogen atom lone electron pair (note, however, that the difference in energy between the n and π orbitals is lower in quinoline than in pyridine) on TiO_2 Lewis acid sites can orient the attack of this pollutant by the active species photogenerated at the metal oxide surface. This hypothesis cannot be dismissed, since there are no spectroscopic data concerning the adsorption mode of quinoline. However, the following arguments suggest that it may not be valid under the conditions of this study. The density of Lewis acid sites on the TiO_2 surface was presumably weak, since this semiconductor was not pretreated under vacuum to create this type of sites. Furthermore, TiO_2 was dispersed in liquid water, which can behave as a Lewis base. In addition, the formations of 4-quinolinone and 5-hydroxyquinoline when quinoline was photocatalytically degraded suggest that the attack of quinoline was not restricted to positions 1, 2, and 8 as may be thought if quinoline were predominantly adsorbed *via* its nitrogen atom even in the presence of liquid water. Finally, a control experiment showed that quinoline impregnated on TiO_2 and UV irradiated in ambient air, *in the absence of liquid water*, indeed yielded quinoline 1-oxide, 2-quinolinone, and 8-hydroxyquinoline as primary products.

Comparison of the Product Distributions Obtained by $OH^\bullet$ Radicals and by TiO_2−UV. As has been amply demonstrated,[68] hydroxyl radicals add to aromatic derivatives, and the resulting cyclohexadienyl radicals evolve to phenols, mainly via addition of oxygen and elimination of $HO_2^\bullet$ radicals (Scheme 1A). In the case of quinoline, electrophilic species are expected to predominantly attack the benzene nucleus, preferentially at positions 5 and 8 with respect to positions 6 and 7. Attack at the less electron-rich pyridine ring to give 2- and 4-quinolinones is markedly less favored. By analogy with the case of pyridine itself, $OH^\bullet$ radical addition to position 1 is not expected.[69] Our results concerning quinoline degradation by the photo-Fenton reaction, which is assumed to produce hydroxyl radicals (eqs 1 and 2), are perfectly in accordance with these literature-based predictions (Figure 2A, Table 2). Also characteristic is the progressive oxidation of the primary products, viz. 5- and 8-hydroxyquinolines, *via* the further addition of a $OH^\bullet$ radical, yielding quinoline-5,8-dione principally and some 5,8-dihydroxyquinoline (Scheme 1A).

Table 2 shows that at pH 3 the amount of 5-hydroxyquinoline, for percentages of degraded quinoline equal to 20% or 50%, was decreased by a factor of about 2 when quinoline was

degraded by the TiO_2−UV system instead of the photo-Fenton reaction and no quinoline-5,8-dione was produced. In other words, position 5, viz. that with the highest electron density, was less attacked by heterogeneous photocatalysis than when the degradation was carried out by a reagent system assumed to produce only hydroxyl radicals. No definitive conclusion can be drawn from the amounts of 8-hydroxyquinoline, the other primary product expected from hydroxyl radical addition on the benzene nucleus, since this product was not entirely extracted from TiO_2 (see the Results Section); however, considering the high amount of 8-hydroxyquinoline formed by the photo-Fenton reaction, we can indicate that, in any event, a lower amount was formed by heterogeneous photocatalysis. Finally, large amounts of 2-aminobenzaldehyde and its *N*-formyl derivative were formed by the TiO_2−UV system at pH 6, but these amounts were much lower at pH 3 (Figure 3). Only the former product was present when the degrading agent was the photo-Fenton produced $OH^\bullet$ radical (Figure 3A, Table 2). All these observations illustrate that TiO_2 photocatalytic transformations concern predominantly the pyridine ring of quinoline, in contrast with the photo-Fenton induced transformations of quinoline.

Therefore it can be concluded that $OH^\bullet$ radical attack onto quinoline is not sufficient to explain the degradation of this pollutant by the TiO_2−UV system, since it is likely that a surface $OH^\bullet$ radical exhibits an electrophilic character as does a $OH^\bullet$ radical produced in the solution bulk by the photo-Fenton process.

Possible Additional Ways for Quinoline Degradation by Heterogeneous Catalysis. The decrease in the photocatalytic disappearance rate of quinoline when SOD was added indicated that superoxide anion radicals were chemically involved in quinoline degradation, if this decrease was really due to the enzymatic activity of SOD with respect to $O_2^{\bullet-}$ dismutation. As quinoline does not react significantly with KO_2, a source of superoxide, activation of quinoline appears as a prerequisite for reaction with superoxide. Quinoline activation can be the result of the tranfer of one electron from this compound to an electron vacancy (hole) in the valence band of photoexcited TiO_2. Comparison of the redox potential of quinoline in acetonitrile (1.73 V vs $Ag/AgNO_3$ electrode)[70] to that of the TiO_2 valence band (redox potential ca. 2.75 V vs NHE at pH 7)[71] shows this electron transfer is thermodynamically allowed. We suggest that the resulting quinoline radical cation, $Q^{\bullet+}$, combines with superoxide. Note that direct hole transfer from photoexcited TiO_2 to adsorbed phenol has been proposed from experiments comparing the hydroxylation products distribution of phenol obtained by γ-radiolysis, reaction with $SO_4^{\bullet-}$ ion radicals, and TiO_2 photocatalysis in aqueous solutions.[22]

The oppositely charged radical ions, $Q^{\bullet+}$ and $O_2^{\bullet-}$, are expected to react at a diffusion-controlled rate. The regioselectivity is expected to be determined by the spin density on the organic radical, which is reasonably larger at positions 2 and 4. This is in accordance with the fact that in photocatalysis functionalization occurs mainly at the heterocyclic ring, unlike the case of quinoline degradation produced by the photo-Fenton reaction. Relatively stabilized intermediates are formed in this way, and may include diradicals or zwitterions or, as invoked for oxidation of aromatics in acetonitrile, dioxetanes (as shown in Scheme 1B for one of the isomers).

Scheme 1B shows that these intermediates can lose oxygen to yield 2- and 4-quinolinones (for clarity, only the latter isomer is shown) considering the above-mentioned regioselective addition of superoxide. Moreover, the dioxetanes can be cleaved either directly or after addition of dioxygen as shown in Scheme 1B. These cleavages account for the observed formation of compounds derived from quinoline by oxidative opening of the pyridine ring without the loss of carbon atoms or with the loss of 1 or 2 carbon atoms from this ring.

Concerning the involvement of superoxide, apart from the previous results from two of us[29,30] also based on the use of SOD, another paper[32] has proposed that the protonated form of superoxide intervened in the degradation of *n*-octane, 3-octanol, 3-octanone, and *n*-octanoic acid by TiO_2 photocatalysis in water through the following sequence of reactions (Russell mechanism for aliphatic compounds).

$$RH \xrightarrow{h^+ \text{ and/or } OH^\bullet} R^\bullet \xrightarrow{O_2} RO_2^\bullet \xrightarrow{HO_2^\bullet} RO_4H \rightarrow \text{products} \quad (5)$$

Regarding photocatalysis in the gas phase, ESR experiments at 77 K have shown that the signal attributed to $HO_2^\bullet$ at the surface of outgassed TiO_2 disappeared in the presence of phenol.[72] From the use of Auger electron spectroscopy and low-energy electron diffraction techniques, it was concluded that the photoexcitation of dioxygen plays the more important role in the oxidation of methyl chloride on TiO_2 (110).[73] The same authors[74] have proposed that the role of superoxide should be reconsidered not only for gas-phase TiO_2 photocatalytic reactions but also for aqueous solutions.

In the following paragraphs, we further examine whether the effects of pH and of SOD on the product distribution of quinoline are all compatible with the addition to of $O_2^{\bullet-}$ to $Q^{\bullet+}$ (Scheme 1B) or whether other pathways should be envisaged.

An increase in pH from 3 to 6 causes the deprotonation of quinolinium cation to quinoline ($pK_a = 4.5$) and of the hydroperoxyl radical to superoxide ($pK_a = 4.8$). As a result, the concentration of both $Q^{\bullet+}$ and $O_2^{\bullet-}$ should increase. Therefore, if the hypothesis of a degradation pathway through a reaction between these ion radicals is correct, the differences in product distribution between degradations carried out by the photo-Fenton process and the TiO_2−UV process should be increased when this latter process is employed at pH 6 in place of pH 3. Indeed, concentrations of products stemming from the attack of the pyridine ring of quinoline (benzaldehyde derivatives and 4-quinolinone) increased when the pH was changed from 3 to 6, whereas the concentration of 5-hydroxyquinoline, arising from the $OH^\bullet$ radical pathway, decreased (Figure 2, Table 2).

The effects of adding SOD on the product distribution obtained by heterogeneous photocatalysis at pH 6 also provide information which appears to support the degradation pathways proposed in Scheme 1B. As 5- and 6-hydroxyquinolines and 2-quinolinone are minor compounds at pH 6, the effect of SOD on their formation cannot be meaningfully discussed. The presence of SOD at pH 6 causes the concentration of 4-quinolinone to be diminished to a value slightly lower than that obtained at pH 3 by heterogeneous photocatalysis without SOD or by the photo-Fenton reaction (Table 2). This observation suggests that the formation of 4-quinolinone *via* the superoxide pathway (Scheme 1B) is important at pH 6, but much less significant at pH 3.

The formation of 2-aminobenzaldehyde, the major product at pH 6, was almost suppressed in the presence of SOD (Table 2) in agreement with Scheme 1B. By contrast, the concentration of *N*-formyl-2-aminobenzaldehyde was not appreciably changed by addition of SOD at pH 6. This observation suggests that this product was not significantly formed by the pathway proposed in Scheme 1B. Therefore another pathway is envisaged in which $Q^{\bullet+}$ adds adsorbed neutral dioxygen, then water and deprotonates to yield the hydroxylated dioxetane neutral radical indicated in Scheme 1C. Oxidative cleavage of this radical can produce *N*-formyl-2-aminobenzaldehyde and/or

2-aminobenzaldehyde. Formation of the former product by this pathway does not involve superoxide; therefore it is not decreased by SOD. On the other hand, it involves $Q^{\bullet+}$ and accordingly it should be decreased at pH 3 because quinoline is then mostly present as quinolinium ion which is a poorer electron donor than quinoline; Table 2 shows that this expected decrease was indeed observed. Also, comparison of the amounts of 2-aminobenzaldehyde and its *N*-formyl derivative at pH 6 with and without SOD suggests that the addition of superoxide to $Q^{\bullet+}$ (Scheme 1B) prevails over the addition of neutral dioxygen to $Q^{\bullet+}$ (Scheme 1C) in the absence of SOD, as is expected from the nucleophilic character of superoxide.

Finally, the hydroxylated dioxetane neutral radical shown in Scheme 1C can also be formed in the hydroxyl radical-induced degradation of quinoline, which might explain the presence of 2-aminobenzaldehyde among the intermediates obtained through the photo-Fenton reaction (Figure 3). However, as already emphasized, the hydroxyl radical preferentially adds to the benzene ring of quinoline to yield 5- and 8-hydroxyquinoline, as well as quinoline-5,8-dione (Table 2, Scheme 1A).

Conclusions

First, the present results demonstrate that quinoline is an appropriate molecular probe to reveal the differences between oxidation processes based on $OH^{\bullet}$ radical production and the TiO_2 photocatalytic oxidative steps. Aromatic compounds with only one ring or two identical rings cannot easily be used for that purpose because the same products can be obtained through different pathways. In other words, quantitative analyses of the primary products formed by several degradation techniques are informative only if the studied compound has a suitable molecular structure.

Second, considering that the hypothesis according to which surface $OH^{\bullet}$ radicals have not the electrophilic character exhibited by free $OH^{\bullet}$ radicals can reasonably be ruled out, the quinoline products indicate that species other than the $OH^{\bullet}$ radicals are involved in TiO_2 photocatalytic oxidative degradations in water as was initially proposed for reactions carried out in acetonitrile.[75] Together with the increasing evidence regarding the role of reduction steps under TiO_2 photosensitization, that illustrates the variety of mechanisms involved and further enhances the interest for the use of this technique in pollutant control.

Third, considering that several experimental facts denote that superoxide dismutase is capable of exhibiting its expected enzymatic activity with respect to $O_2^{\bullet-}$ anion radicals in UV-irradiated TiO_2 aqueous suspensions, it is inferred that superoxide is chemically involved in photocatalytic oxidative steps.

Fourth, mechanisms consistent with the pH and SOD effects and based on the addition of either $O_2^{\bullet-}$ or, to a lesser extent, O_2 to the quinoline radical cation, have been suggested.

Fifth, inasmuch as the ionizing potential of quinoline is not dissimilar from that of many aromatic pollutants, the occurrence of several oxidative pathways in TiO_2 photocatalysis is of general significance. The relative importances of these pathways is influenced, *inter alia*, by the pH, in particular with respect to the pK_a of both the pollutant and superoxide, and by the surface coverage in pollutant because of competitive hole transfer to the pollutant or to H_2O/OH^- ions.

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(59) One gram of 2-aminobenzaldehyde and 1.5 g of anhydrous sodium formate in 5 mL of anhydrous ether + 3 mL of acetic formic anhydride (prepared from 3.4 mL of formic acid + 8.2 mL of acetic anhydride, 2 h at 50 °C) left overnight. Evaporation of the ether and stirring into 10 mL of iced water. The white precipitate filtered (1 g). Recrystallized from EtOH, mp 74−76, characterized by NMR 7.28, t, 7.52, t, 7.72, d, 8.55, s, 8.72, d, 9.95, s, 11.0, s, and IR 3380, 1695, 1675 cm^{-1}.

(60) Two grams of 2-indolenone and 3 g of sodium anhydrous formate in 6 mL of anhydrous ether and 6 mL of acetic formic anhydride overnight. Evaporation of the ether and stirring with water gave a mixture containing a GC−MS peak with the expected mass fragmentation; however, the largest part of the starting material was unchanged.

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