

# Evaluation of the Efficiency of Photodegradation of Nitroaromatics Applying the UV/H<sub>2</sub>O<sub>2</sub> Technique

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Photolysis of nitroaromatic compounds in aqueous solution is a very slow and inefficient process. As already observed for a variety of organic pollutants, considerably faster degradation rates of nitrobenzene (NBE), 1-chloro-2,4-dinitrobenzene (CDNB), 2,4-dinitrophenol (DNP), and 4-nitrophenol (PNP) could be achieved, when the oxidative degradation of these compounds was initiated by hydroxyl radicals produced by UV-C photolysis of H<sub>2</sub>O<sub>2</sub>. Analysis of intermediate products formed during irradiation by HPLC and IC showed that cleavage of the aromatic ring should occur at an early stage of the oxidation process and that organic nitrogen was almost completely converted to nitrate. The optimal initial concentration of hydrogen peroxide ([H<sub>2</sub>O<sub>2</sub>]<sub>OPT</sub>) leading to the fastest oxidation rate, which depends on the initial substrate concentration ([S]<sub>0</sub>), could be evaluated using a simplified expression based on the main reactions involved in the first stages of the degradation process. Using only a minimum of kinetic and analytical information, this expression shows that the ratio  $R_{OPT} (= [H_2O_2]_{OPT}/[S]_0)$  is related to the bimolecular rate constants for the reactions of hydroxyl radicals with substrate ( $k_S$ ) and H<sub>2</sub>O<sub>2</sub> ( $k_{HP}$ ) and to the corresponding molar absorption coefficients ( $\epsilon_S$ ,  $\epsilon_{HP}$ ). Competition experiments between selected pairs of the substrates showed that their relative reactivity toward hydroxyl radicals could be correctly predicted using the same simplified approach. The results of our investigations as well as literature data support the general validity of the proposed procedure for optimizing oxidation rates of the UV/H<sub>2</sub>O<sub>2</sub> process.

## Introduction

Chemical remediation of wastewaters is one of the main aspects in modern environmental chemistry. Biological treatment uses microorganisms to metabolize the pollutants, a technique broadly applied to the treatment of wastewater from urban areas. However a large number of compounds are not biodegradable or cannot be destroyed by biological

treatment due to their toxicity. Research on alternative or additional methods of wastewater treatment is of current interest and has led already to the development of photochemical processes for the oxidative degradation of pollutants in aqueous solution. In general, the use of UV/visible radiation can lead to the degradation of organic pollutants by two main processes (I): (I) excitation of the substrate and its subsequent decomposition (photolysis) and (II) generation of highly oxidizing species able to attack the substrate. The latter is primarily based on the generation of hydroxyl radicals (Advanced Oxidation Procedures (AOP) (1–3) and include UV/H<sub>2</sub>O<sub>2</sub> (1, 2, 4), UV/TiO<sub>2</sub> (3), UV/H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> (5), UV/H<sub>2</sub>O<sub>2</sub>/Fe(II) or Fe(III) (photoassisted Fenton reaction) (6), and VUV photolysis of water (7), among others.

In the UV/H<sub>2</sub>O<sub>2</sub> process, photolysis of H<sub>2</sub>O<sub>2</sub> results in the homolysis of the oxygen–oxygen bond and the production of hydroxyl radicals (HO•). This technique presents a series of advantages (2, 8): (a) HO• radicals are highly reactive species, (b) H<sub>2</sub>O<sub>2</sub> can be readily mixed with water in all proportions, (c) costs associated to production and handling of H<sub>2</sub>O<sub>2</sub> are smaller than the corresponding ones for e.g. ozone. The process leads in most cases to the mineralization of the organic substrate, i.e. to the production of CO<sub>2</sub>, water, and mineral acids (when the substrates contain heteroatoms). It should be noted, however that complete mineralization by the UV/H<sub>2</sub>O<sub>2</sub> process may be an uneconomical goal for treatment and would not be required when intermediate products are nontoxic and biodegradable.

The UV/H<sub>2</sub>O<sub>2</sub> method has been applied to the degradation of a variety of pollutants (1, 2, 4, 8–12). Experimental results show that the efficiency of the process strongly depends on the initial concentrations of substrate and additive as well as on the chemical structure of the substrate. Hydroxyl radicals react by addition to aromatic substrates and by hydrogen abstraction from aliphatic compounds, yielding carbon centered radicals. The latter add molecular oxygen and the resulting peroxy radicals undergo further thermal reactions, leading eventually to substrate mineralization (13, 14).

In a previous study on the photodegradation of 4-chloro-3,5-dinitrobenzoic acid (CDNBA) (2) using the UV/H<sub>2</sub>O<sub>2</sub> technique, we have proposed a simple method for predicting the amount of H<sub>2</sub>O<sub>2</sub> leading to the highest degradation efficiency. However, the analysis was restricted to one compound, and a more general application of this method remained to be tested. In this work we analyze the effect of H<sub>2</sub>O<sub>2</sub> and substrate concentrations on the efficiency of the UV/H<sub>2</sub>O<sub>2</sub> technique and correlate the optimal conditions for the process with the absorption characteristics of the substrates and with their reactivity toward HO•. Four nitroaromatic compounds were chosen as model substrates: 1-chloro-2,4-dinitrobenzene (CDNB), 2,4-dinitrophenol (DNP); 4-nitrophenol (PNP), and nitrobenzene (NBE). Previous results on CDNBA (2) were used for comparison.

## Experimental Section

**Chemicals.** 1-Chloro-2,4-dinitrobenzene (99%, Aldrich), 2,4-dinitrophenol (99%, Riedel de Haën), 4-nitrophenol (99%, Fluka and Riedel de Haën), and nitrobenzene (95%, May&Baker) were used without further purification for preparing aqueous solutions containing 15–200 mg L<sup>-1</sup> of substrate. Unless otherwise indicated, the initial pH was adjusted to 2.5 using H<sub>2</sub>SO<sub>4</sub> (Merk). Dissolution of the organic compounds was facilitated by sonication (when required, solutions were cooled in order to avoid heating induced by ultrasonic waves). Concentrations of H<sub>2</sub>O<sub>2</sub> (30% Perhydrol,

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Merck) ranged from  $5.5 \times 10^{-3}$  to 0.6 M. Water was of Milli-Q quality. 4-Chloro-2,5-dinitrobenzoic acid (Aldrich) was also employed in competition experiments. This substance was previously purified as already described (2).

All other chemicals used were ACS grade.  $\text{H}_2\text{O}_2$  (30% w/w in  $\text{H}_2\text{O}$ ),  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{KMnO}_4$ , triethanolamine (TEA), oxalic acid, formic acid, acetonitrile, and acetic acid were purchased from Merck.  $\text{H}_2\text{O}_2$  was analyzed by the classic  $\text{KMnO}_4$ -titration.

**Absorbance Measurements.** Absorption spectra were registered on a double beam Cary 3 spectrophotometer. Measurements were made using quartz cells of 0.2 cm optical path length.

**HPLC Measurements.** HPLC analyses were carried out using an HP1100 Ti-series equipment with a LiChrospher 100 RP-18 column (length: 125 mm, diameter: 4 mm, film thickness: 5 mm); the eluent was a mixture of acetonitrile and water (40/60). The aqueous phase contained 3.75 mL of TEA and 2 mL of  $\text{H}_3\text{PO}_4$  dissolved in 1 L of water. A flow rate of 1 mL/min was used. Calibration curves for CDNB, DNP, PNP, and NBE were established under identical conditions.

**Ionic Chromatography.** IC measurements of inorganic and organic anions were performed on a DIONEX DX500 series equipment using an IONPAC AS14 DIONEX column (length: 240 mm, diameter: 4 mm); an aqueous solution (pH 10) of  $\text{Na}_2\text{CO}_3$  ( $2.7 \times 10^{-3}$  M) and  $\text{NaHCO}_3$  ( $3 \times 10^{-4}$  M) was employed as eluent at a flow rate of 1.2 mL/min. The presence of cations, such as  $\text{NH}_4^+$ , was investigated using a DIONEX CD12 column (length: 240 mm, diameter: 4 mm); the mobile phase was an aqueous solution of methanesulfonic acid at a flow rate of 1.0 mL/min. Calibration curves were established for all ionic species investigated.

**Other Measurements.** Dissolved organic carbon (DOC) was analyzed with a Beckman Tocamaster 915-B equipment (oven temperature 950 °C). The experimental error on DOC values was  $\pm 8\%$ . The pH of the irradiated solutions was determined using a PHM220 Radiometer pH meter. Selective electrodes (Radiometer F1012Cl and ISE25NO3) were used to determine  $\text{Cl}^-$  and  $\text{NO}_3^-$  concentrations. Calomel and Ag/AgCl electrodes were used as reference electrodes. Organic compounds were previously extracted from aqueous samples with isooctane in order to avoid adsorption of nitrocompounds on the PVC selective membrane.

**Photochemical Reactors.** The experiments were performed in two annular photochemical reactors (Nr 1326, DEMA, Mangels, Bornheim-Roisdorf, Germany). The reactors are similar but they have different capacities. One of them had a volume of 750 mL (internal radius = 2.0 cm, external radius = 4.0 cm and height = 20.0 cm) and was equipped with a medium-pressure Hg arc (Philips HPK 125 W), positioned in the axis of the reactor in a quartz well. The second reactor had a capacity of 800 mL (internal radius = 2.5 cm, external radius = 4.0 cm and height = 26.0 cm) and was operated with a medium-pressure Hg lamp TQ 150 (150 W) from Heraeus Nobellight (Hanau, Germany). The spectral distribution of the emission of this lamp has been published elsewhere (15). The photon fluxes entering the reactors were  $9.8 \times 10^{-6}$  einstein  $\text{s}^{-1}$  (HPK 125) and  $1.2 \times 10^{-5}$  einstein  $\text{s}^{-1}$  (TQ 150) in the wavelength range 200–450 nm, as estimated from potassium ferrioxalate actinometry and the spectral emission profiles of the lamps (6). The reactors were equipped with ports for sample withdrawing. The purging gas was introduced from below through a glass frit. Solutions were continuously purged with synthetic air (21%  $\text{O}_2$  in  $\text{N}_2$ ), and the temperature was maintained at 25 °C ( $\pm 1$  °C) and 21 °C ( $\pm 1$  °C) for the experiments performed in the first and the second reactor, respectively.  $\text{H}_2\text{O}_2$  was added to the reaction system just before starting the irradiation.

## Results

**UV Photolysis.** Aqueous solutions of CDNB, DNP, NBE, and PNP were photolyzed at pH 2.5 in the DEMA reactor using the HPK 125 lamp (Experimental Section). In all cases, no significant changes in the absorption spectra could be detected during irradiation (not shown). Less than 4% of the substrates were degraded under continuous irradiation for 2–3 h in the absence of  $\text{H}_2\text{O}_2$ .

**Oxidative Photodegradation in the Presence of  $\text{H}_2\text{O}_2$ : Intermediate and Final Products.** Dramatic changes were observed in the absorption spectra of aqueous solutions of CDNB, DNP, NBE, and PNP during irradiation in the presence of  $\text{H}_2\text{O}_2$ , as shown in Figure 1 for selected runs. The absorbance decrease indicates that the four nitroaromatic substrates are rapidly consumed under these conditions.

Substrates, intermediate, and final products were analyzed using HPLC and IC techniques. As an example, IC results for CDNB at different irradiation times are shown in Figure 2. In all cases, formate, oxalate,  $\text{NO}_2^-$  (traces),  $\text{Cl}^-$ , and  $\text{NO}_3^-$  anions were detected as intermediate and final products.  $\text{PO}_4^{3-}$  and  $\text{SO}_4^{2-}$  were observed at constant concentrations in all the samples. The presence of  $\text{SO}_4^{2-}$  results from initial pH adjustment using  $\text{H}_2\text{SO}_4$ , whereas small concentrations of  $\text{PO}_4^{3-}$  might be due to a possible contamination during dilution. DOC and electrochemical determinations (for  $\text{Cl}^-$  and  $\text{NO}_3^-$ ) were also carried out.

Concentration profiles of substrates, intermediate, and final products analyzed in irradiated solutions in the presence of  $\text{H}_2\text{O}_2$  are shown in Figure 3 for selected runs. Note that experimental conditions differ from one compound to another, and, therefore, concentration profiles cannot be directly compared (relative oxidation efficiencies are discussed below in the section on “Competitive photodegradation”).

The following general remarks hold for the four compounds investigated (Figure 3): (a) complete depletion of substrates could be achieved; (b) formation of organic oxidation products (such as formic acid and oxalic acid) and inorganic ions ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ) was observed; (c) concentrations of formic and oxalic acids reached maximum values and then decreased due to further oxidation to  $\text{CO}_2$ ; formic acid reached its highest concentration before or when the substrate was completely oxidized, whereas the maximum concentration of oxalic acid was observed at longer irradiation times; (d) the pH value of the solution decreased during photolysis; (e) the amount of  $\text{NO}_3^-$  formed was almost stoichiometric in relation with the total initial nitrogen content; (f) DOC measurements showed that complete mineralization can be achieved only after relatively long irradiation times; (g) carbon and nitrogen balances suggest that, during the degradation process, some organic intermediates in addition to those mentioned above were formed but not always detected by the applied analytical methods. This might be of importance in applications: toxicity controls would be required when treatment is not carried out until complete mineralization is achieved (most cases), as some of the organic intermediates could be biocidal.

In the case of CDNB (Figure 3a), the organic chlorine was quantitatively released from the substrate as chloride anion. The rate of  $\text{Cl}^-$  production was coincident with the rate of substrate depletion. This result strongly suggests that the carbon–chlorine bond was cleaved during the initial stages of the process. A similar behavior was reported for CDNB (2).  $\text{NO}_2^-$  was generated during the first minutes of irradiation (not shown), but its concentration was very low (less than  $1.5 \times 10^{-5}$  M) and dropped below the detection limit as soon as the substrate was completely depleted. Most probably, organic nitrogen was released as  $\text{NO}_2^-$  in the early stages of the photolysis, but was rapidly oxidized to  $\text{NO}_3^-$  in the strongly

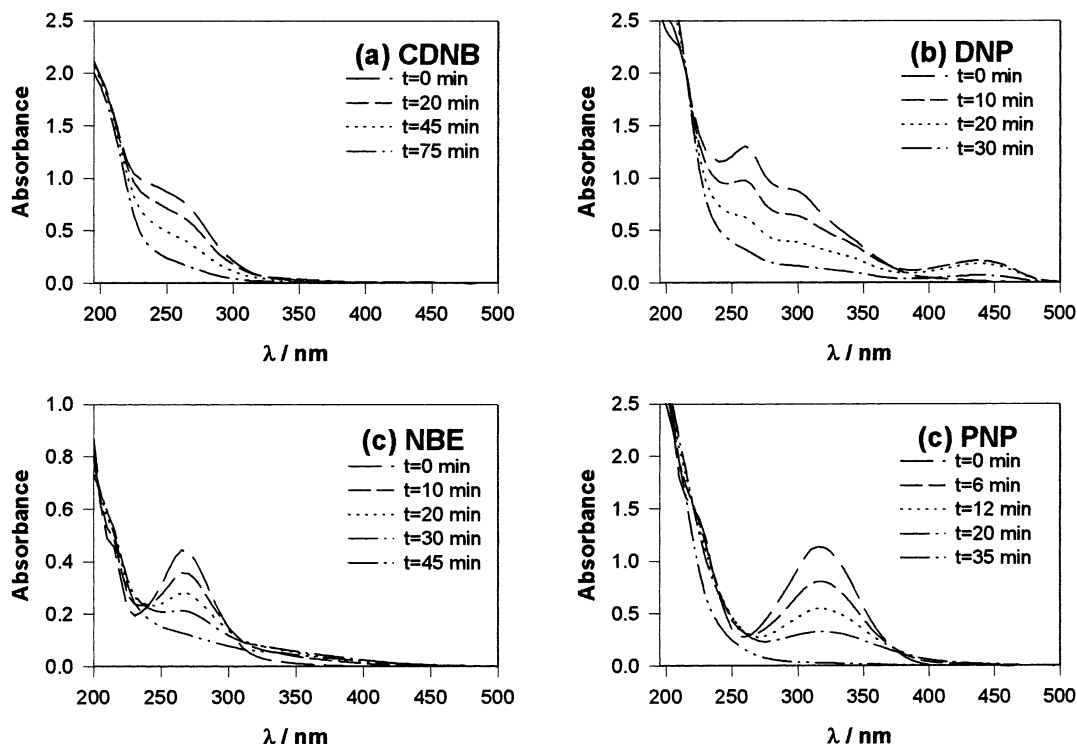


FIGURE 1. Absorption spectra of aqueous solutions of the nitroaromatic derivatives investigated in the presence of  $\text{H}_2\text{O}_2$  at different irradiation times (initial concentrations: (a) CDNB:  $2.9 \times 10^{-4}$  M,  $\text{H}_2\text{O}_2$ : 0.034 M; (b) DNP:  $5.0 \times 10^{-4}$  M,  $\text{H}_2\text{O}_2$ : 0.045 M; (c) NBE:  $2.9 \times 10^{-4}$  M,  $\text{H}_2\text{O}_2$ :  $5.5 \times 10^{-3}$  M; and (d) PNP:  $5.8 \times 10^{-4}$  M,  $\text{H}_2\text{O}_2$ :  $4.5 \times 10^{-3}$  M; optical path length of spectroscopic cell: 0.2 cm; initial absorbance in photoreactor (optical thickness: 2.25 cm) > 2 below 320 nm).

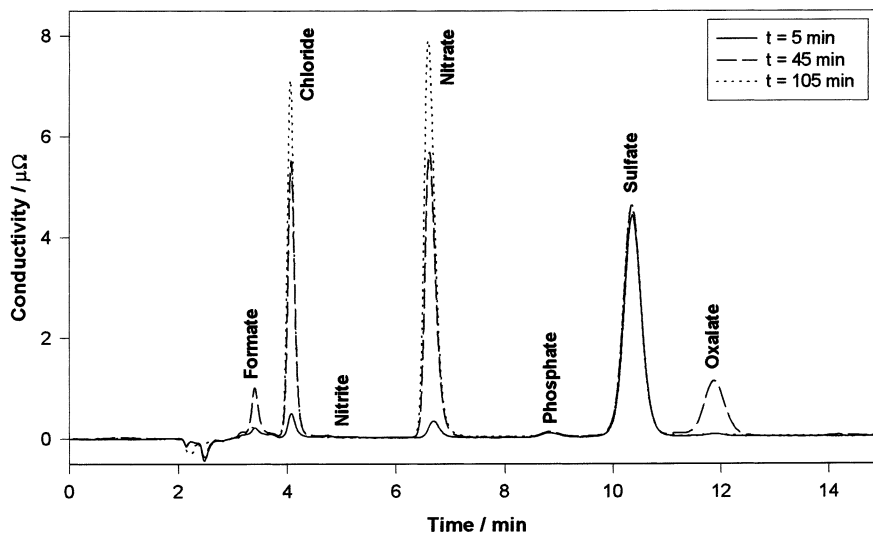


FIGURE 2. Ion chromatography profiles for the photodegradation of CDNB in aqueous solution in the presence of  $\text{H}_2\text{O}_2$  (initial concentrations: CDNB:  $5.2 \times 10^{-4}$  M,  $\text{H}_2\text{O}_2$ : 0.044 M).

oxidizing medium. The initial rate of formic acid generation was approximately 2.2 times higher than the rate of substrate oxidation. Therefore at least two molecules of formic acid were produced per molecule of substrate. In the case of DNP (Figure 3b), the initial rate of formation of formic acid relative to substrate depletion was slower than for CDNB, and the maximum concentration of formic acid was observed when the substrate was completely depleted. For the dinitro aromatics, CDNB and DNP (Figure 3a,b), the amount of  $\text{NO}_3^-$  produced corresponds to the stoichiometric molar ratio of 2/1 that would be expected if all the organic nitrogen content was mineralized to  $\text{NO}_3^-$  ( $2\text{NO}_3^-$  anions formed per molecule of substrate mineralized).

In the case of NBE, besides production of  $\text{NO}_3^-$ , formate, and oxalate (Figure 3c), 2-nitrophenol, 3-nitrophenol, and 4-nitrophenol were formed (detected by HPLC, not shown). These intermediates were subsequently oxidized, and, under the experimental conditions shown in Figure 3c, the rate of production of  $\text{NO}_3^-$  was 30% smaller than that observed for substrate depletion. The relative amounts of the intermediate nitrophenols are in agreement with the expected reactivity of hydroxyl radicals in their electrophilic attack at the aromatic ring of NBE. Under similar experimental conditions, oxidative degradation of PNP was faster than that of the other compounds investigated. Formation of formic and oxalic acids was however delayed in comparison with the other

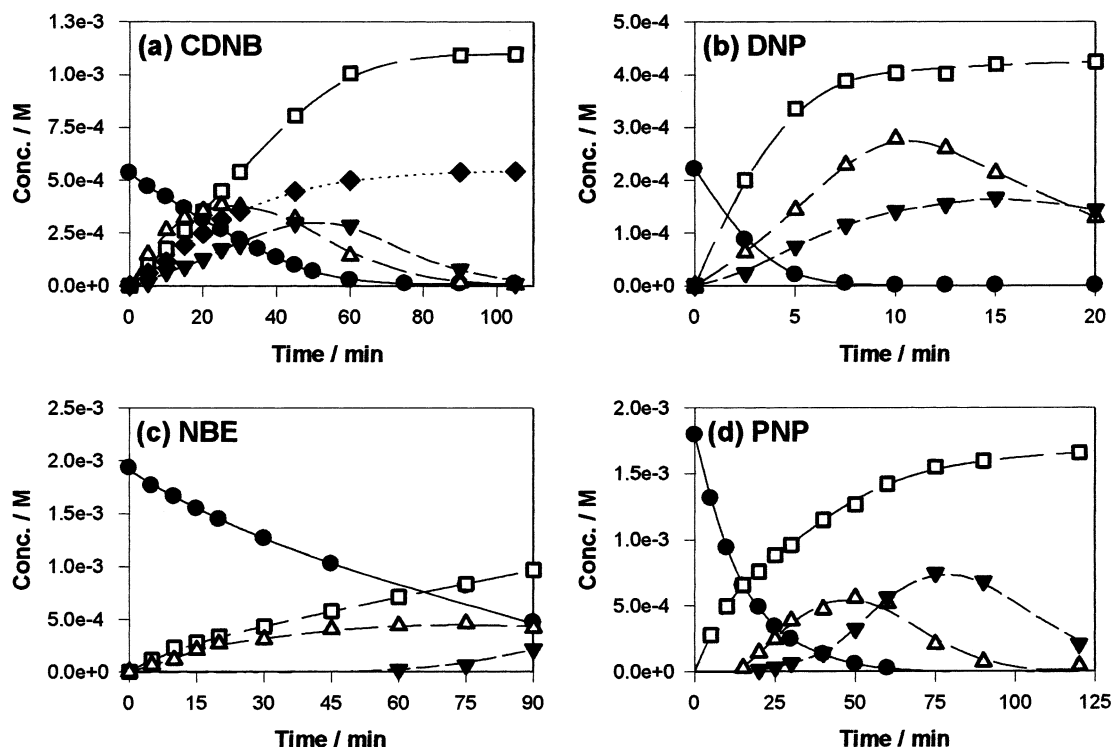


FIGURE 3. Concentration profiles for irradiated solutions of the nitroaromatic derivatives investigated in the presence of  $\text{H}_2\text{O}_2$ : filled circles: substrates, squares: nitrate, open triangles: formate, filled triangles: oxalate, diamonds: chloride (initial concentrations: (a) CDNB:  $5.2 \times 10^{-4}$  M,  $\text{H}_2\text{O}_2$ : 0.044 M; (b) DNP:  $2.2 \times 10^{-4}$  M,  $\text{H}_2\text{O}_2$ : 0.044 M; (c) NBE:  $1.9 \times 10^{-3}$  M,  $\text{H}_2\text{O}_2$ : 0.011 M; and (d) PNP:  $1.8 \times 10^{-3}$  M,  $\text{H}_2\text{O}_2$ : 0.022 M; initial pH = 2.50).

compounds (Figure 3d). For the two mononitro derivatives (NBE and PNP),  $\text{NO}_3^-$  production was significantly slower than substrate depletion (Figure 3c,d), but at longer irradiation times when mineralization was achieved, stoichiometric formation of  $\text{NO}_3^-$  was observed, as in the case of CDNB and DNP.

More investigations aiming at the identification of all organic intermediates would be necessary before a detailed mechanistic scheme can be proposed for the oxidation of nitroaromatic compounds by the UV/ $\text{H}_2\text{O}_2$  process. It should be noted however that the results presented in this work and those obtained previously for CDNB (2) show that  $\text{Cl}^-$  and  $\text{NO}_3^-$  are produced almost stoichiometrically with respect to the initial chlorine and nitrogen contents of the substrates. This result may be explained by a mechanism involving electrophilic attack of  $\text{HO}^\bullet$  on a carbon atom substituted by Cl (or  $\text{NO}_2$ ) followed by HCl (or  $\text{HNO}_2$ ) elimination. It has been already shown that the addition of  $\text{HO}^\bullet$  may take place at various sites of an aromatic nucleus (4). In most cases, cleavage of the aromatic ring should occur at an early stage of the oxidation process, as indicated by the early release of formic acid (Figure 3). It is worthwhile to note that (i) hydroxylated aromatic intermediates were only detected in substantial amounts in the case of NBE, a monosubstituted aromatic compound; (ii) formation of  $\text{NO}_3^-$  was delayed with respect to substrate depletion for the less substituted derivatives, NBE and PNP, where more positions on the aromatic ring are available for addition of  $\text{HO}^\bullet$ ; and (iii) depending on their structure, some of the aromatic intermediates might be rapidly depleted and be present only at very low concentrations.

**Oxidative Photodegradation in the Presence of  $\text{H}_2\text{O}_2$ : Oxidation Rates.** The effect of the initial  $\text{H}_2\text{O}_2$  concentration on the efficiency of the UV/ $\text{H}_2\text{O}_2$  process was analyzed in a series of experiments using different initial concentrations of substrates ( $[\text{S}]_0$ ) ranging from 15 to 100 mg  $\text{L}^{-1}$ . The concentration of  $\text{H}_2\text{O}_2$  was varied in a wide range depending

on the nature of the substrate (e.g., in the case of CDNB, from  $3.3 \times 10^{-3}$  up to  $3.5 \times 10^{-1}$  M). Initial rates of substrate disappearance ( $r = -d[\text{S}]/dt$ ) under different conditions were determined. In all cases, when increasing the concentration of  $\text{H}_2\text{O}_2$ , a maximum rate ( $r_{\text{max}}$ ) could be observed (Figure 4). A similar trend was also reported for CDNB (2) and for a variety of aromatic and aliphatic compounds [see e.g. refs 8 and 16–18]. When increasing the initial substrate load  $[\text{S}]_0$ , the optimal  $\text{H}_2\text{O}_2$  concentration ( $[\text{H}_2\text{O}_2]_{\text{OPT}}$ , defined as the initial  $\text{H}_2\text{O}_2$  concentration for which  $r_{\text{max}}$  was reached) increased proportionally. Figure 4 shows the behavior of the normalized initial rates of oxidation ( $r/r_{\text{max}}$ ) under different experimental conditions. In these plots,  $r/r_{\text{max}}$  is represented as a function of the parameter  $R$  (defined as  $[\text{H}_2\text{O}_2]_0/[\text{S}]_0$ ), for each nitroaromatic derivative investigated. It is worthwhile to mention that optimal concentration ratios  $R_{\text{OPT}}$  ( $=[\text{H}_2\text{O}_2]_{\text{OPT}}/[\text{S}]_0$ ) were independent of  $[\text{S}]_0$  and of the reaction volumes used in these experiments.

The analysis of the shape of the curves reveals a marked asymmetry. As the initial concentration of  $\text{H}_2\text{O}_2$  increases for a given  $[\text{S}]_0$ , a dramatic change in the initial oxidation rate can be observed, but when  $R > R_{\text{OPT}}$ , this rate shows a smooth decrease (Figure 4). This behavior is of great importance from both a practical and an economical point of view, since there is a wide range of  $R$  values corresponding to oxidation rates of at least 90% of the optimal rate. DOC depletion and  $\text{NO}_3^-$  production rates show similar  $R_{\text{OPT}}$  values, within experimental error.

## Discussion

**Simplified Mechanism of Oxidative Photodegradation.** The degradation of pollutants by the UV/ $\text{H}_2\text{O}_2$  technique is initiated by the attack of  $\text{HO}^\bullet$  radicals generated by photolysis of  $\text{H}_2\text{O}_2$ . Hydroxyl radicals may react with the substrate,  $\text{H}_2\text{O}_2$ , and with the intermediate products of the degradation process. From the initial oxidation of the substrate until

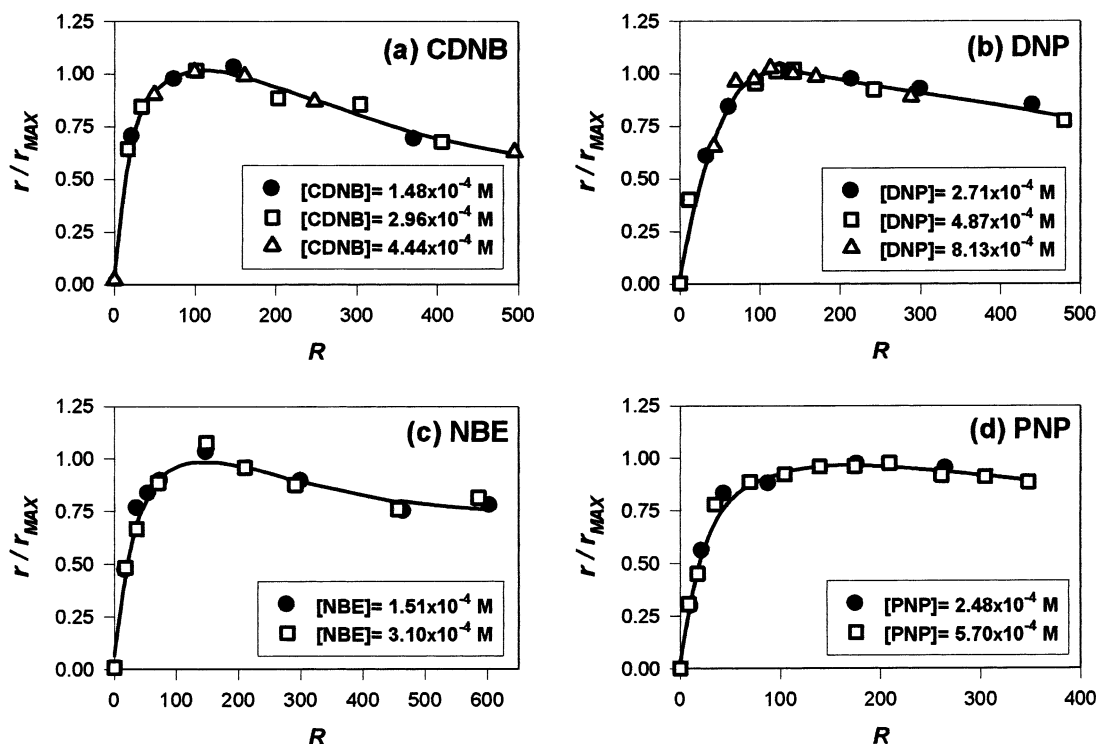
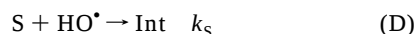
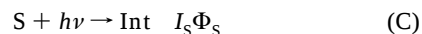
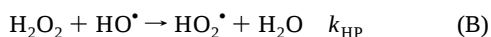
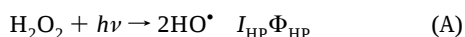


FIGURE 4. Normalized initial rates of substrate disappearance  $r/r_{\max}$  vs  $R$  ( $=[\text{H}_2\text{O}_2]_0/[\text{S}]_0$ ) for the photodegradation of CDNB, DNP, NBE, and PNP in aqueous solution in the presence of  $\text{H}_2\text{O}_2$ .

complete depletion, a complex set of reactions takes place, where other oxidizing species (e.g. hydroperoxyl radical ( $\text{HO}_2^\bullet$ ), nitrogen containing radicals) might participate in the reaction mechanism (10, 19), and a detailed analysis of all the reactions involved in the manifold of oxidative degradation is very complex (8, 10, 11, 20, 21). However, the general trends observed for the different substrates are very similar under all experimental conditions applied. Hence a simple kinetic model for describing the observed behavior for the initial oxidation rates of all substrates tested might be found.

During the initial stages of the oxidation process, only substrate and  $\text{H}_2\text{O}_2$  are present in substantial amounts, and the following main reactions may be considered (8, 9, 12)



where  $I_{\text{HP}}$  and  $I_{\text{S}}$  are the rates of photons absorbed by  $\text{H}_2\text{O}_2$  and by the substrate, respectively,  $\Phi_{\text{HP}}$  and  $\Phi_{\text{S}}$  are the quantum yields of respective photolyses, and  $k_{\text{HP}}$  and  $k_{\text{S}}$  are the bimolecular rate constants for the corresponding reactions with hydroxyl radicals.

In this reaction scheme, reactions implying  $\text{HO}_2^\bullet$  or  $\text{O}_2^{\bullet-}$  radicals have not been considered, as their reactivity is much lower than that of  $\text{HO}^\bullet$  (22–25). A similar remark applies to the reactions associated with the intermediate products (Int), whose concentrations during the first minutes of irradiation may be neglected. At this point a comment related to the use of  $\text{H}_2\text{SO}_4$  for adjusting the initial pH of the solutions seems necessary. The reaction of  $\text{HO}^\bullet$  with  $\text{HSO}_4^-$  generates  $\text{SO}_4^{\bullet-}$  radicals, which are able to react with organic substrates and may introduce alternative reaction pathways. Control experiments in the absence and presence of  $\text{H}_2\text{SO}_4$  did not

yield significant differences. This result may be explained by the relatively low reactivity of  $\text{HO}^\bullet$  toward  $\text{HSO}_4^-$  ( $k = 3.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  (26)). Consequently, the results discussed below refer indistinctly to experiments in the presence or in the absence of  $\text{H}_2\text{SO}_4$ .

Considering the simplified mechanism proposed, the rate of substrate consumption ( $r$ ) is given by the sum of the rates of reactions (C) and (D):

$$r = \frac{-d[\text{S}]}{dt} = I_{\text{S}}\Phi_{\text{S}} + k_{\text{S}}[\text{S}][\text{HO}^\bullet] \quad (1)$$

In a solution where several species absorb radiation at the same wavelengths, the total number of photons absorbed is the sum of the photons absorbed by each species (27, 28). If Lambert–Beer's law holds under the present experimental conditions, the rate of photons absorbed by the substrate ( $I_{\text{S}}$ ) at a given wavelength of irradiation is given by

$$I_{\text{S}} = I_0(1 - 10^{-A}) \frac{\epsilon_{\text{S}}c_{\text{S}}}{\epsilon_{\text{HP}}c_{\text{HP}} + \epsilon_{\text{S}}c_{\text{S}}} \quad (2)$$

where  $I_0$  is the incident photon rate ( $\text{einstein L}^{-1} \text{ s}^{-1}$ ),  $\epsilon_{\text{S}}c_{\text{S}}/(\epsilon_{\text{HP}}c_{\text{HP}} + \epsilon_{\text{S}}c_{\text{S}})$  is the fraction of photons absorbed by the substrate,  $\epsilon_{\text{S}}$  and  $\epsilon_{\text{HP}}$  are the molar absorption coefficients of substrate and  $\text{H}_2\text{O}_2$ , respectively ( $\text{M}^{-1} \text{ cm}^{-1}$ ),  $c_{\text{S}}$  and  $c_{\text{HP}}$  are the corresponding concentrations (M), and  $A$  ( $= \sum \epsilon_i c_i d$ ) represents the total absorbance of the solution ( $d$ : optical path length).

The steady-state concentration of  $\text{HO}^\bullet$  radicals is given by eq 3

$$[\text{HO}^\bullet] = \frac{r_{\text{HO}}}{k_{\text{HP}}c_{\text{HP}} + k_{\text{S}}c_{\text{S}}} \quad (3)$$

where  $r_{\text{HO}}$  is the rate of  $\text{HO}^\bullet$  production.

In the UV/ $\text{H}_2\text{O}_2$  process, the main path for the generation of  $\text{HO}^\bullet$  radicals is the photodissociation of  $\text{H}_2\text{O}_2$ . The quantum

yield of photolysis of  $\text{H}_2\text{O}_2$  ( $\Phi_{\text{HP}}$ ) is approximately 0.5 in the wavelength range from 200 to 300 nm (29). The rate of  $\text{HO}^\bullet$  production ( $r_{\text{HO}}$ ) may be expressed as

$$r_{\text{HO}} = \frac{2I_0\Phi_{\text{HP}}(1 - 10^{-A})\epsilon_{\text{HP}}c_{\text{HP}}}{\epsilon_{\text{HP}}c_{\text{HP}} + \epsilon_{\text{S}}c_{\text{S}}} \quad (4)$$

where  $\epsilon_{\text{HP}}c_{\text{HP}}/(\epsilon_{\text{HP}}c_{\text{HP}} + \epsilon_{\text{S}}c_{\text{S}})$  is the fraction of photons absorbed by  $\text{H}_2\text{O}_2$ .

Combining eqs 1–4 and under conditions where the absorbance of the solution is greater than 2, the oxidation rate of the substrate ( $r$ ) may be expressed as

$$r = \frac{I_0}{\epsilon_{\text{HP}}R + \epsilon_{\text{S}}} \left\{ \Phi_{\text{S}}\epsilon_{\text{S}} + \frac{2\Phi_{\text{HP}}k_{\text{S}}\epsilon_{\text{HP}}R}{k_{\text{HP}}R + k_{\text{S}}} \right\} \quad (5)$$

where  $R = [\text{H}_2\text{O}_2]_0/[\text{S}]_0$  (see results).

The optimal ratio  $R_{\text{OPT}}$  leading to the highest initial oxidation rate can be obtained by differentiation of eq 5 (i.e.  $R = R_{\text{OPT}}$  for  $dr/dR = 0$ )

$$R_{\text{OPT}} = \frac{\sqrt{4\Phi_{\text{HP}}^2\epsilon k + 2\Phi_{\text{HP}}\Phi_{\text{S}}(k^2 - \epsilon k) - 2\Phi_{\text{S}}k}}{k(2\Phi_{\text{HP}}\epsilon + \Phi_{\text{S}}k)} \quad (6)$$

where  $\epsilon = \epsilon_{\text{HP}}/\epsilon_{\text{S}}$  and  $k = k_{\text{HP}}/k_{\text{S}}$ .

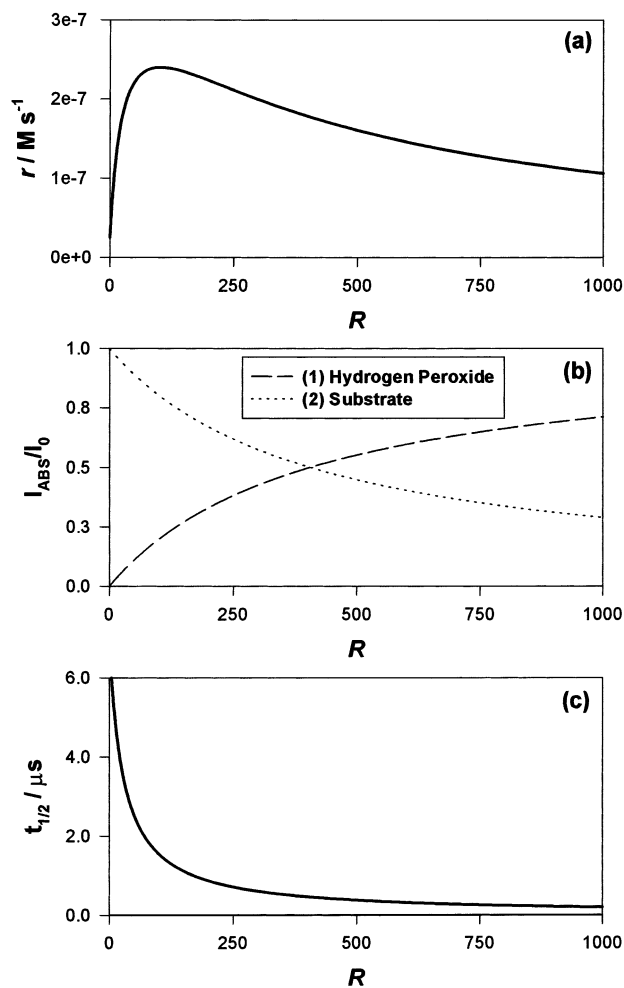
Equation 6 was obtained taking into account the initial rate of disappearance of the substrate by photolysis (reaction C) and by oxidative degradation initiated by  $\text{HO}^\bullet$  radicals (reaction D). However, in most cases, reaction C can be neglected in the presence of  $\text{H}_2\text{O}_2$ . Moreover, the fraction of the incident photons absorbed by the substrate diminishes as  $R$  increases. Under these conditions, eq 5 simplifies to eq 7, and eq 6 gives eq 8.

$$r = \frac{2I_0\Phi_{\text{HP}}\epsilon R}{(\epsilon R + 1)(kR + 1)} \quad (7)$$

$$R_{\text{OPT}} = \sqrt{\frac{1}{k\epsilon}} = \sqrt{\frac{k_{\text{S}}\epsilon_{\text{S}}}{k_{\text{HP}}\epsilon_{\text{HP}}}} \quad (8)$$

This simple expression of  $R_{\text{OPT}}$  ( $= [\text{H}_2\text{O}_2]_{\text{OPT}}/[\text{S}]_0$ ) might be used, either to evaluate  $[\text{H}_2\text{O}_2]_{\text{OPT}}$  if  $k_{\text{S}}$  and  $\epsilon_{\text{S}}$  at a given  $\lambda$  are known or to estimate  $k_{\text{S}}$  if  $[\text{H}_2\text{O}_2]_{\text{OPT}}$  is determined experimentally. The validity of eqs 5–8 was tested by comparing experimental and simulated variations of the oxidation rates.

**Simulation of the Rate of Substrate Consumption.** The variation of the initial rate of substrate disappearance ( $r$ ) as a function of  $R$  predicted by eq 5 is shown in Figure 5a for a hypothetical pollutant (irradiation at 254 nm). The following data were taken into account for the calculations: (i) quantum yields of photolysis of various aromatic compounds ( $\Phi_{\text{S}}$ ) have been determined to be between  $10^{-3}$  and  $10^{-4}$  (2, 30); (ii) molar absorption coefficients ( $\epsilon_{\text{S}}$ ) at 254 nm for the studied compounds are in the range between  $5.4 \times 10^3$  and  $1.4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  and rate constants for the reaction of  $\text{HO}^\bullet$  with different aromatic compounds ( $k_{\text{S}}$ ) are in the range  $10^8$ – $10^{10} \text{ M}^{-1} \text{ s}^{-1}$  (31); and (iii) the molar absorption coefficient of  $\text{H}_2\text{O}_2$  ( $\epsilon_{\text{HP}}$ ) at 254 nm is  $18.7 \text{ M}^{-1} \text{ cm}^{-1}$  (29) and the rate constant for the bimolecular reaction between  $\text{H}_2\text{O}_2$  and  $\text{HO}^\bullet$  radicals ( $k_{\text{HP}}$ ) has a value of  $2.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  (31). The general trend predicted for  $r$  as represented in Figure 5a is in very good agreement with the variations of  $r$  observed experimentally for the four nitroaromatic derivatives investigated (Figures 4a–d) as well as with results previously reported for the degradation of CDNBA (2) and a variety of aromatic and aliphatic compounds (8, 16–18).



**FIGURE 5.** Simulation of (a) initial rate of substrate disappearance ( $r$ ) using eq 6, (b) initial fraction of photons absorbed by the substrate and by  $\text{H}_2\text{O}_2$  ( $I_{\text{ABS}}/I_0$ ), and (c) half-life of  $\text{HO}^\bullet$  radicals ( $t_{1/2}$ , eq 9) as a function of  $R$  for a hypothetical pollutant ( $\Phi_{\text{S}} = 10^{-3}$ ,  $\epsilon_{\text{S}} = 7500 \text{ M}^{-1} \text{ cm}^{-1}$ ,  $k_{\text{S}} = 1.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , wavelength of irradiation: 254 nm).

In fact, in the presence of  $\text{H}_2\text{O}_2$ , consumption of the substrate by photolysis (reaction C) is negligible, and eq 7 may be used instead of eq 5 for the simulations. On the basis of eq 7, the trend observed for the variation of the initial rate of substrate disappearance ( $r$ ) as a function of  $R$  may be qualitatively explained. This equation indicates that, for a given substrate and a given experimental design (reactor volume, geometry, incident photon rate, etc.),  $r$  depends only on the ratio  $R$  ( $= [\text{H}_2\text{O}_2]_0/[\text{S}]_0$ ). Therefore solutions with different initial pollutant concentrations but with the same value of  $R$  should have the same initial rate of disappearance. Moreover, eq 7 shows that the variation of  $r$  as a function of  $R$  should exhibit a maximum, since  $r$  is the ratio of a first degree polynomial to a second degree polynomial (both in terms of parameter  $R$ ). For small values of  $R$ , the linear term of the numerator will dominate, while for larger values, the quadratic term in the denominator will be more important (2). The observed behavior is due to two contradictory effects. On one hand, as the value of  $R$  increases, the fraction of photons absorbed by  $\text{H}_2\text{O}_2$  increases (Figure 5b), leading to an increase in the production of  $\text{HO}^\bullet$  radicals (reaction A). On the other hand, at high values of  $R$ , reaction B (trapping of  $\text{HO}^\bullet$  by  $\text{H}_2\text{O}_2$ ) competes more effectively with reaction D (attack of the substrate by  $\text{HO}^\bullet$ ). This latter effect can be also represented by the decrease of  $\text{HO}^\bullet$  half-life ( $t_{1/2}$ , as defined

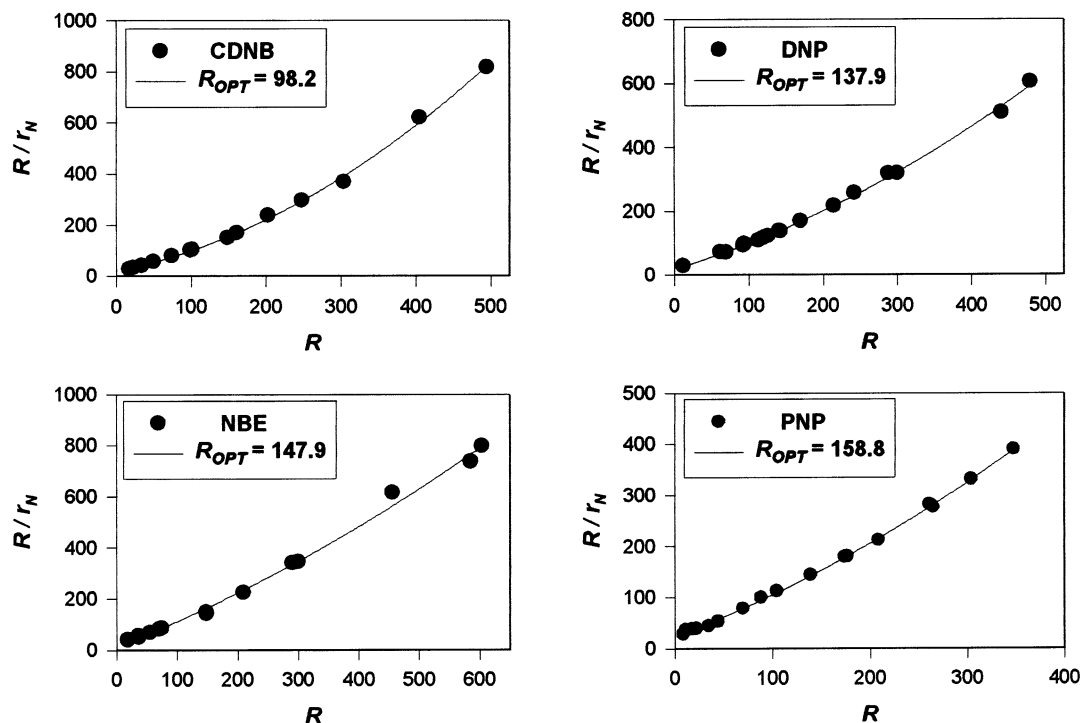


FIGURE 6. Plots of  $R/r_N$  vs  $R$  for the nitroaromatic derivatives investigated ( $r_N = r/r_{max}$  is the normalized initial rate of substrate disappearance).

in eq 9, Figure 5c).

$$t_{1/2} = \frac{\ln(2)}{k_{HP}C_{HP} + k_S C_S} \quad (9)$$

**Estimation of Experimental Values of  $R_{OPT}$ .** When the rate constant of the reaction between a substrate and  $HO^\bullet$  ( $k_S$ ) is not known, an estimate of  $k_S$  may be obtained using eq 8 if the value of  $R_{OPT}$  is experimentally determined from the experimental curves shown in Figure 4. Two different methods have been developed to estimate with good precision the values of  $R_{OPT}$ . The first method does not require any kinetic model and uses an algorithm that combines a Taylor series around each experimental point with polynomial regression analysis. The function obtained represents the behavior of the data in the whole experimental domain (Figure 4, solid lines), and the determination of the value of  $R_{OPT}$  is made by taking its numerical derivative (32). The second method uses the expression for the initial rate of substrate disappearance. After reordering eq 7, the following expression is obtained

$$\frac{R}{r} = aR^2 + bR + c \quad (10)$$

where  $a = \epsilon k / (2I_0 \Phi_{HP} \epsilon)$ ,  $b = (\epsilon + k) / (2I_0 \Phi_{HP} \epsilon)$ , and  $c = 1 / (2I_0 \Phi_{HP} \epsilon)$  are the coefficients of the polynomial function.

From the coefficients  $a$  and  $c$ ,  $R_{OPT}$  is directly calculated as  $(c/a)^{1/2}$ . Figure 6 shows the variation of  $R/r_N$  ( $r_N = r/r_{max}$ : normalized initial rate) vs  $R$  for each substrate investigated. In all cases, the experimental behavior may be fitted by a quadratic polynomial as predicted by eq 10.

Table 1 shows the results obtained for  $R_{OPT}$  using both methods for the four studied compounds as well as for CDNBA (2). No significant differences were observed between both procedures.

**Competitive Photodegradation.** A quantitative description of the kinetics of photooxidation requires the knowledge of the rate constants of the reactions of  $HO^\bullet$  radicals with the substrate as well as with the intermediates of the degradation manifold. Absolute rate constants for the reactions of  $HO^\bullet$

TABLE 1. Values of  $R_{OPT}$  ( $= [H_2O_2]_{OPT} / [S]_0$ ) Obtained from the Curves in Figures 4a–d by Two Different Methods: (A) Taylor Analysis around the Maximum and (B) Quadratic Approach (Eq 10)

| substrate | method A | method B |
|-----------|----------|----------|
| DNP       | 134 ± 9  | 138 ± 9  |
| CDNBA     | 57 ± 9   | 61 ± 7   |
| CDNB      | 105 ± 18 | 98 ± 15  |
| NBE       | 152 ± 13 | 148 ± 12 |
| PNP       | 165 ± 7  | 159 ± 10 |

with organic compounds are most often evaluated using pulse radiolysis or are obtained in some cases from EPR measurements. However, an evaluation of these rate constants is also possible by performing experiments where a given substrate competes for  $HO^\bullet$  radicals with a reference compound whose reactivity toward  $HO^\bullet$  is already known (33–35). To determine values of relative rate constants, competition experiments among pairs of the investigated substrates were carried out. Results obtained for the pair PNP-NBE are shown in Figure 7. The substrate disappearance follows first-order kinetics for both PNP and NBE (Figure 7, inset), as predicted by eq 1 if UV photolysis of the substrate is neglected.

Under these conditions, eq 1 can be rewritten as

$$\frac{-d[S]}{dt} = k_S [S] [HO^\bullet] \quad (1a)$$

$$\frac{-d[R]}{dt} = k_R [R] [HO^\bullet] \quad (1b)$$

where the subscripts R and S refer to the reference compound and the substrate investigated, respectively (in case of Figure 7, S = PNP and R = NBE).

The ratio  $\beta$  ( $= k_S / k_R$ ) is equal to the ratio of the pseudo-first-order rate constants  $k'_S$  ( $= k_S [HO^\bullet]$ , eq 1a) and  $k'_R$  ( $= k_R [HO^\bullet]$ , eq 1b).  $\beta$  was calculated from the slopes of the plots of  $\ln([S])$  and  $\ln([R])$  as a function of irradiation time (see inset of Figure 7). In all cases investigated in this work,

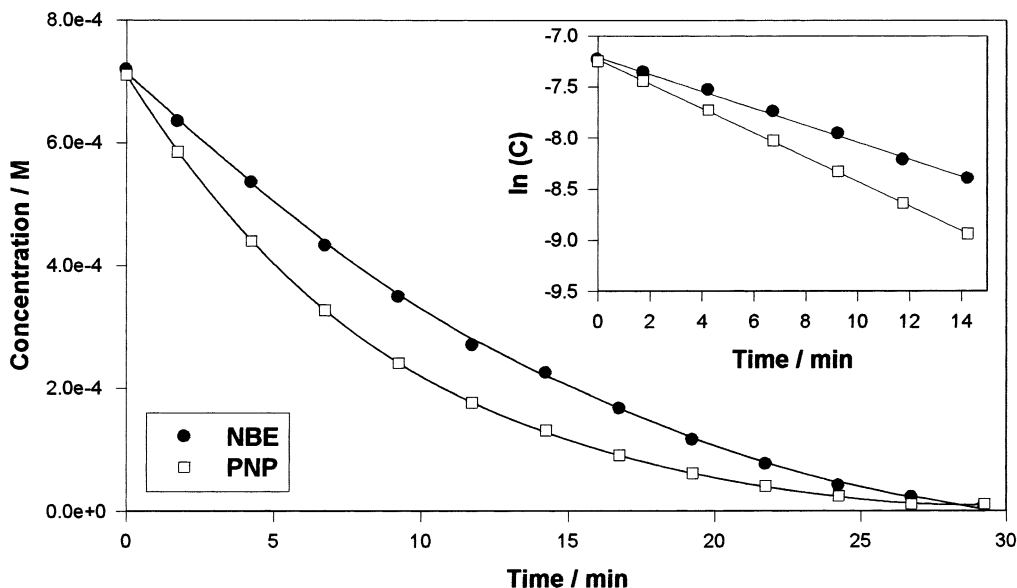


FIGURE 7. Concentration profiles obtained in a competition experiment using an aqueous solution containing  $7.2 \times 10^{-4}$  M of NBE and PNP ( $[H_2O_2]_0 = 5.0 \times 10^{-2}$  M; concentrations of substrates determined by HPLC as described in the Experimental Section).

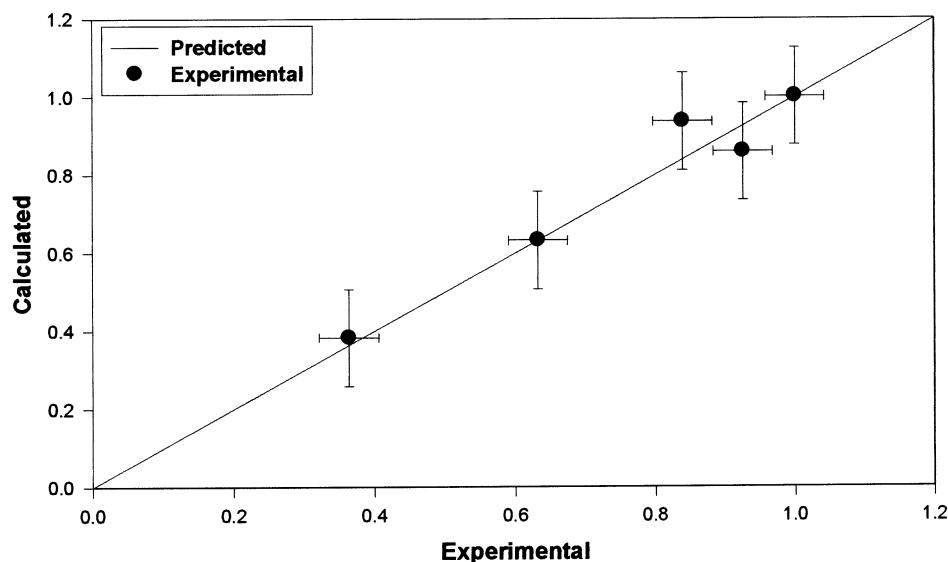


FIGURE 8. Comparison between experimental results of  $R_{OPT}^S/R_{OPT}^{PNP}$  (Table 1) and values calculated using eq 11 (see text).

pseudo-first-order oxidation rates were observed. The rate constants of the reaction of  $HO^\bullet$  radicals with PNP and NBE have been reported in the literature:  $k_{PNP} = 3.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  and  $k_{NBE} = 3.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  (36, 37) (values measured the same year with the same technique), resulting in a value of  $\beta (= k_{PNP}/k_{NBE})$  of 1.2. The experiments shown in Figure 7 give a value of  $1.4 \pm 0.2$ , in agreement with the literature value.  $\beta$  values for different pairs of substrates (including CDNBA) are shown in Table 2. Despite some data dispersion, the values listed show that the reactivity order toward  $HO^\bullet$  radicals for the substrates investigated is  $PNP > NBE > DNP > CDNBA$ . This reactivity order is in agreement with that expected from the electrophilic nature of the hydroxyl radical and the electron-withdrawing or -donating substituents on the aromatic ring (38). It should be noted that, under the same experimental conditions and when  $R = R_{OPT}$ , the initial oxidation rates of the substrates investigated in this work follow the same order as the values of  $k_S$ . This is a consequence of the relative values of  $k_S$  and  $\epsilon_S$  of the specific compounds investigated in this work. In general, for  $R = R_{OPT}$ , the initial rate of substrate oxidation ( $r_{max}$ ) is obtained by combining eqs 7 and 8. When the behavior of

TABLE 2. Relative Rate Constants ( $\beta$ ) of the Reaction with  $HO^\bullet$  for Different Couples of Nitroaromatic Derivatives Investigated

| couple of substrates | $\beta$        |
|----------------------|----------------|
| PNP/NBE              | $1.4 \pm 0.2$  |
| DNP/CDNB             | $2.7 \pm 0.1$  |
| PNP/CDNB             | $9.5 \pm 1.0$  |
| NBE/CDNB             | $6.1 \pm 0.6$  |
| DNP/CDNBA            | $7.5 \pm 0.5$  |
| CDNB/CDNBA           | $2.8 \pm 0.2$  |
| PNP/CDNBA            | $26.9 \pm 2.8$ |
| NBE/CDNBA            | $16.4 \pm 1.4$ |

$r_{max}$  is dominated by the numerator of eq 7,  $r_{max}$  should be proportional to  $(\epsilon/k)^{0.5}$  i.e. to  $(k_S/\epsilon_S)^{0.5}$  and, if the values of  $\epsilon_S$  are of the same order of magnitude, the ranking of  $r_{max}$  among the various substrates will be the same as the ranking of  $k_S$ .

**Rate Constants for Reaction with Hydroxyl Radicals and  $R_{OPT}$ .** It is interesting to observe that the variation of  $R_{OPT}$  values among the different compounds is similar to that observed for the rate constants obtained in the competition

experiments. Equation 8 deduced from a simplified reaction scheme establishes that  $R_{OPT} = (k\epsilon)^{-0.5}$ . This relation is only valid for a given wavelength of excitation. In fact, in the present study, polychromatic radiation sources were employed as is most often the case in technical applications. In this case, the spectral distribution of the radiation source as well as the molar absorption coefficients of substrate and  $H_2O_2$  in the whole spectral range of absorption are required for a detailed study. In a simplified approach, we calculated an average molar absorption coefficient  $\langle\epsilon_i\rangle$  for each compound in the wavelength range of 230–255 nm and assumed that under polychromatic irradiation  $R_{OPT} \approx [k_S \langle\epsilon_S\rangle / k_{HP} \langle\epsilon_{HP}\rangle]^{0.5}$ . To test this assumption, values of  $\langle\epsilon_i\rangle$  and of  $\beta$  (Table 2) were introduced in eq 11 for estimating  $R_{S_{OPT}}/R_{PNP_{OPT}}$ . Experimental results (Table 1) and values calculated using eq 11 are compared in Figure 8. They are in good agreement within experimental error.

$$\sqrt{\beta_{S/PNP} \frac{\langle\epsilon_S\rangle}{\langle\epsilon_{PNP}\rangle}} \approx \frac{R_{S_{OPT}}}{R_{PNP_{OPT}}} \quad (11)$$

where  $\beta_{S/PNP} = k_S/k_{PNP}$ .

Therefore a simple predictive model, useful in technical applications of the UV/ $H_2O_2$  process, could be established.

**Practical Implications.** The results obtained for the nitroaromatic compounds investigated in this work as well as literature data (2, 8, 16–18) support the potential of the proposed approach to improve the efficiency of the UV/ $H_2O_2$  process. The simplified mechanism for the oxidative photodegradation leads to very simple expressions (eqs 7 and 8) that describe well the experimental behavior observed (Figure 4). Equation 7 gives the oxidation rate as a function of the operating conditions (i.e.  $H_2O_2$  and substrate concentrations), whereas eq 8 defines the optimal conditions that lead to the fastest rate. Since the variation of the oxidation rate is relatively flat around  $R_{OPT}$ , there is a wide range of  $R$  values corresponding to oxidation rates of at least 90% of the optimal one. This range can be easily estimated using eqs 7 and 8 as design tools for technical development. When necessary,  $R_{OPT}$  ( $=[H_2O_2]_{OPT}/[S_0]$ ) may be experimentally determined at the laboratory scale before implementing the process at the pilot or production level, since  $R_{OPT}$  does not depend on the reaction volume. Furthermore, the results shown in Figure 8 indicate that the model proposed may also be used when polychromatic radiation sources are employed, although a detailed analysis would require a rather complex mathematical treatment (39).

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