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Journal of Photochemistry and Photobiology A: Chemistry 93 (1996) 7–19

Journal of
PHOTOCHEMISTRY
AND
PHOTOBIOLOGY
A: CHEMISTRY

Vacuum-UV photolysis of aqueous solutions of nitrate: effect of organic matter
I. Phenol

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Received 31 January 1995; accepted 24 May 1995

Abstract

Water homolyses on vacuum-UV excitation ($\lambda<200$ nm) to give $HO^{\bullet}$ radicals, $H^{\bullet}$ atoms and, with lower efficiency, hydrated electrons. These primary species induce a series of reactions partially depleting nitrate and quantitatively mineralizing organic compounds, e.g. phenol, in aqueous solutions.

The rates of oxidative degradation of phenol and its oxidation products strongly depend on the dissolved oxygen concentration. The formation of dihydroxybenzenes, trihydroxybenzene and oxalic acid as oxidation intermediates was observed in irradiation experiments with oxygen- and air-saturated solutions, but no significant concentrations of these compounds were observed in experiments with argon-saturated solutions.

The depletion rates of NO_3^- have been reported previously to be slow yielding mainly nitrite and N_2O as reaction products.

Vacuum-UV irradiation of aqueous solutions containing NO_3^- and phenol results in the simultaneous mineralization of phenol and depletion of NO_3^-, yielding mainly NH_4^+ and, in much lower yields, NO_2^-. The experimental observations indicate that the nitrogen-containing inorganic ions formed during NO_3^- depletion promote the oxidation of the dissolved organic matter independent of the presence of oxygen.

A possible reaction mechanism is discussed, in which the interaction of O_2NOOH, $ONOOH$, $NO_2^{\bullet}$ and $NO^{\bullet}$ with organic matter is proposed as being mainly responsible for the overall observed behaviour. The interaction between organic substrates and $NO^{\bullet}$ seems to favour further reduction to NH_4^+, whereas a one-electron reduction yielding N_2O is observed in the absence of organic substrates. The effect of CO_3^{2-} on these reactions is also discussed.

Under continuous irradiation, NH_4^+ is subsequently re-oxidized. Complete oxidation to NO_3^- is observed only in experiments with oxygen-saturated solutions. Experiments with air- or argon-saturated solutions show only 30% and 10% NO_3^- formation respectively due to the simultaneous formation of N_2.

The reduction of NO_3^- to NH_4^+ and the oxidation of NH_4^+ to NO_3^- seem to involve a series of common intermediates interrelated by many redox reactions and reaction equilibria where the pH, availability of electrons and the presence of protons or hydrogen donors and molecular oxygen determine their importance.

Keywords: Vacuum-UV excitation; Photolysis; Nitrate; Organic matter; Phenol

1. Introduction

Intensive human development and activities have resulted in the progressive deterioration of the water quality to the extent that water supplies formerly of good quality are now potentially hazardous to human health. Man has already recognized that the dilution of pollutants to concentrations below threshold levels and their transfer between environmental compartments are no longer viable solutions. Wastewater management procedures attempt to mineralize organic contaminants, i.e. convert them to carbon dioxide, water and mineral acids [1,2].

Recent developments in the field of chemical water treatment have led to an improvement in the oxidative degradation procedures for dissolved or dispersed organic compounds by applying catalytic and/or photochemical methods. They are generally referred to as advanced oxidation procedures [2,3]. Among the available methods, the vacuum-UV photolysis of water is of particular interest [3,4].

Water homolyses on vacuum-UV excitation to give hydrogen atoms, hydroxyl radicals and, with much less efficiency, hydrated electrons [5]. Previous reports on the mineralization of nitrogen-containing organic compounds by the vacuum-UV irradiation of water clearly indicate the important

SSDI 1010-6030(95)04127-3

participation of reductive reactions initiated by $H^•$ atoms and hydrated electrons in the overall mineralization process [6–8]. In a previous report [8], we studied the depletion of nitrate induced by the vacuum-UV irradiation of aqueous solutions under different experimental conditions. Hydrogen atoms and hydrated electrons produced by the homolysis of water induce a series of reactions partially depleting NO_3^-. The occurrence of these reactions strongly depends on the dissolved oxygen concentration, since molecular oxygen competes strongly with organic and inorganic substrates for $H^•$ atoms and hydrated electrons. NO_2^-, O_2NOO^- and N_2O were identified as reaction products after irradiation, and $NO_2^•$ and $NO^•$ were proposed as key intermediates in the overall process. The postulated reaction scheme is rather complex since, in the continuous vacuum-UV irradiation of aqueous solutions of nitrate, 28 species are interrelated by redox reactions and reaction equilibria, their importance depending on the pH and the availability of electrons.

$NO_2^•$, $NO^•$ and O_2NO^- are strong one-electron oxidants in aqueous systems [9–11], and we assume that these intermediates interact with organic matter during the vacuum-UV irradiation of aqueous systems containing both NO_3^- and organic matter. Phenol was chosen as a model compound because its pathways of oxidative degradation are well reported in the literature [12].

Taking into account that the Xe excimer lamps used for irradiation of the aqueous solutions present an emission band at 172 nm (MHW, 12 nm) and the linear absorption coefficient of water in this spectral range varies from 6000 to 200 cm^{-1} [3], the photolysis of water is the main photochemical reaction in aqueous systems containing concentrations of nitrate and phenol of the order of 1×10^{-2} M or lower.

2. Experimental details

2.1. Materials

KNO_3 and phenol (p.a. quality, Merck) were used without further purification. Pure water was provided by a UGH II system (Millipore; greater than 18 mΩ; less than 20 ppb of organic carbon).

2.2. Apparatus

A cylindrical Xe excimer lamp (length, 25 cm; external diameter, 3 cm) (ABB, Baden, Switzerland) emitting at 172 nm (MHW, 12 nm) was used as irradiation source [13]. The lamp was operated with an electrical power of 150 W and a frequency of 200–220 kHz, controlled by a high-frequency, high-voltage ENI model HPG-2 power supply.

The photochemical reactor was of annular geometry (volume, 220 ml; DEMA, Bornheim-Roisdorf) adapted for the Xe excimer lamp and fitted with a magnetic stirrer and external electrode [14].

Experiments were performed with the solutions maintained at 25 or 60 °C. However, it was not possible to control and measure the temperature in the irradiated annular reactor volume (optical path length, approximately 100 μm) where the photochemical homolysis of water and most of the subsequent primary reactions occurred.

2.3. Analytical methods

The analysis of phenol and its oxidation products was performed by high performance liquid chromatography (HPLC; Hewlett-Packard liquid chromatograph model 1090 with multiwavelength detection; column, ODS hypersil (particle size, 5 μm; 4.6 mm internal diameter (i.d.) × 100 mm); eluent, methanol–water (1:1); temperature, 30 °C).

Anion analysis was performed by ion chromatography (IC; Hewlett-Packard liquid chromatograph model 1050 (Ti series) with multiwavelength detection; column, Hewlett-Packard TSK Gel DEAE-5PW (4 mm i.d. × 50 mm); eluent, aqueous solution of 3×10^{-3} M KCl and 1×10^{-4} M KOH). Detection limits were normally 1×10^{-6} M. This method also allowed the determination of NH_4^+ with a detection limit of the order of 1×10^{-5} M, since NH_4^+ was observed to elute exhibiting a negative peak at 215 nm. The evolution of NH_4^+ was followed on a Dionex 5000 I ion analyser with suppressed conductivity detection (column, Dionex Ion Pac TS12 4 mm; eluent, HCl) or with NH_4^+ ion selective electrodes (Ecotest-110, ECONIX Ltd., Moscow, Russia) with a detection limit of 1×10^{-5} M.

The identification of compounds by HPLC and IC was performed by comparison of the UV–visible absorption spectra and co-injection of the corresponding standards.

Dissolved organic carbon (DOC) analysis was carried out with a Rosemount Analytical Instrument, Dohrmann DC-190. The lowest detection limit was 0.5 ppm. However, for samples containing between 10 and 50 ppm of CO_3^{2-} at pH 10 or higher, a positive and constant error of the order of 3–4 ppm was observed in the determination of DOC. This relatively high error limit has been reported to be a consequence of the inefficient removal of inorganic carbon by a simple sparging cycle under basic conditions [1a]. These observations are important for experiments with argon-saturated solutions containing high concentration ratios of NO_3^- to phenol, where final pH values of 10, inorganic carbon concentrations of 10–30 ppm and DOC values of the order of 3–4 ppm must be taken into account. The fact that no peaks are observed by HPLC and IC at long irradiation times, except for those corresponding to CO_3^{2-}, NO_2^- and NO_3^-, is a further and more conclusive indication of the complete mineralization under these conditions.

The analysis of gaseous products was performed by gas chromatography (GC; Hewlett-Packard gas chromatograph model 5890 series II with mass selective detector Hewlett-Packard series 5971; column, Hewlett-Packard Chrompack capillary column of PLOT fused silica with ParaPlotQ as the stationary phase). The analysis was performed at 30 °C with

He as the carrier gas. The lower detection limit was of the order of 10 ppm, which, under our experimental conditions, implies that approximately 2% of the potentially generated N_2O could be measured.

UV–visible spectra were obtained with a Hewlett-Packard diode array spectrophotometer model 8452A. The pH of the samples was periodically controlled with a Methrom-Herisau pH meter model E512.

2.4. *Experimental procedure*

The following procedure was standard for all the experiments performed. Approximately 250 ml of the aqueous solution was placed into the reactor and purged with oxygen, air or Ar for 20 min before being irradiated. Gas flow and magnetic stirring ensured good mixing of the solution during the entire period of irradiation. Samples (3 ml) were taken periodically and stored in capped vials for analysis.

Gaseous nitrogen oxides (N_2O and $NO^\bullet$) were analysed by collecting gases in a 500 ml Pyrex gas collector, from where gas samples were taken during the course of the reaction. For this purpose, purging with the saturating gas was stopped and the collecting system was opened 20 min before the collection of the gas sample.

3. Results

3.1. *Vacuum-UV irradiation of aqueous solutions of phenol*

Oxygen- or argon-saturated aqueous solutions containing approximately 7×10^{-4} M of phenol were irradiated. The depletion of phenol is slightly dependent on the dissolved oxygen concentration as shown in Fig. 1. However, as already reported for 4-chlorophenol [4], the depletion rate of DOC is strongly dependent on the dissolved oxygen concentration, and the highest rates are observed for oxygen-saturated solutions (see Fig. 2).

Experiments performed under air- or oxygen-saturated conditions show the formation of considerable amounts of 1,2-dihydroxybenzene, 1,3-dihydroxybenzene, 1,4-dihydroxybenzene, 1,2,3-trihydroxybenzene and oxalic acid. Their concentration profiles are shown in Fig. 3. Open-cycle oxidation products elute in liquid chromatography together with oxalic acid, but were not identified.

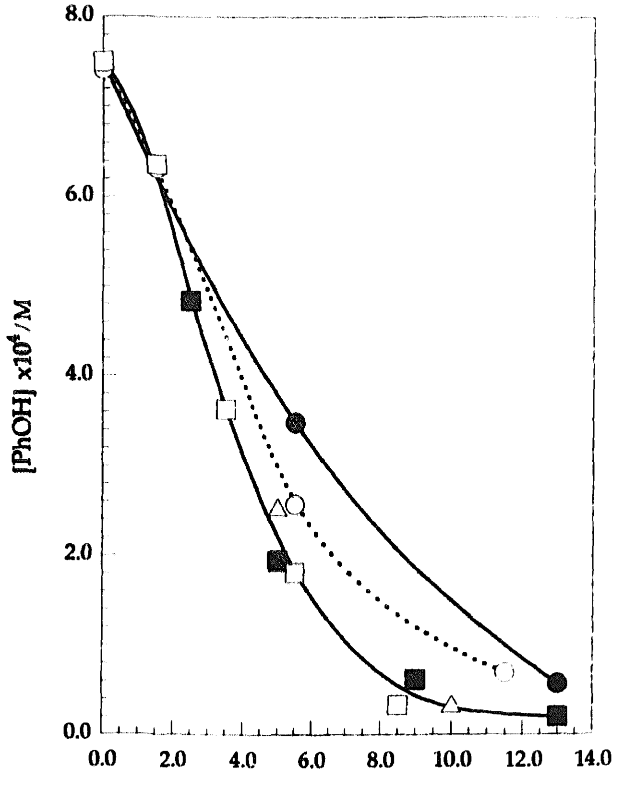

Fig. 1. Depletion of the phenol concentration [PhOH] vs. irradiation time for aqueous solutions containing 7.5×10^{-4} M of phenol at approximately 60 °C and different experimental conditions: Δ, O, ●, pure aqueous phenol solutions saturated with oxygen, air and argon respectively; □, oxygen-saturated aqueous phenol solutions containing 2.6×10^{-4} M of NO_3^-; ■, argon-saturated aqueous phenol solutions containing 2.3×10^{-3} M of NO_3^-.

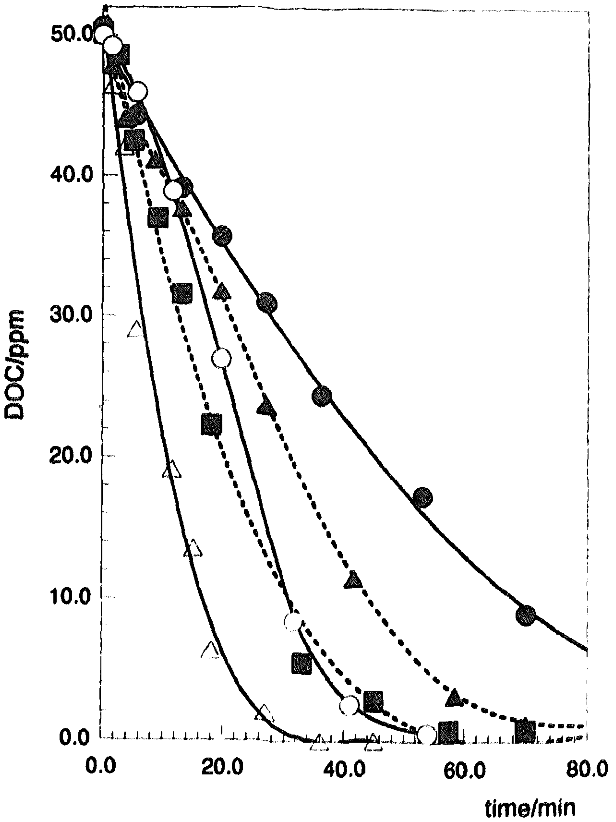

Fig. 2. Depletion of DOC vs. irradiation time for aqueous solutions containing 7.5×10^{-4} M of phenol at 60 °C and different experimental conditions: Δ, O, ●, aqueous solutions of phenol saturated with oxygen, air and argon respectively; ▲, ■, argon-saturated solutions of phenol containing approximately 2.7×10^{-4} M and 2.3×10^{-3} M of NO_3^- respectively. DOC values at irradiation times greater than 40 min for the last samples were corrected for an error of +3 ppm inherent in DOC determination for samples with pH ≥ 10 (see Section 2.3).

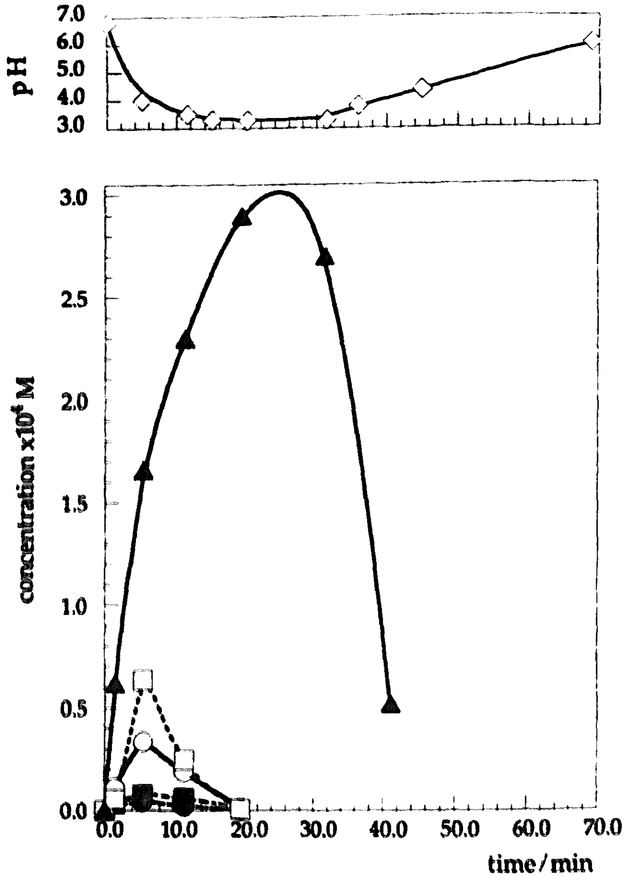

Fig. 3. Concentration profiles for different oxidation products of phenol observed during the vacuum-UV irradiation of aqueous solutions containing 7.5×10^{-4} M of phenol under an oxygen atmosphere at approximately 60 °C. ■, ○, ●, □ and ▼ correspond to 1,2,3-trihydroxybenzene, 1,4-dihydroxybenzene, 1,3-dihydroxybenzene, 1,2-dihydroxybenzene and oxalic acid respectively. Top: pH evolution vs. irradiation time.

The pH evolution (also shown in Fig. 3) decreases considerably during mineralization, reaching a minimum value after approximately 20 min of irradiation, then steadily increases at longer irradiation times to almost its original value. The minimum pH observed corresponds to irradiation times at which all hydroxybenzenes are depleted and mostly open-chain products remain in solution. The subsequent increase in pH may be explained by the complete removal of carboxylic acids.

Vacuum-UV irradiation experiments performed with argon-saturated solutions show the formation of important amounts of oxalic acid and open-cycle oxidation products, but hydroxybenzenes at concentrations higher than 1×10^{-6} M are not observed.

Vacuum-UV irradiation of oxygen-saturated aqueous solutions containing 3×10^{-3} M of phenol are completely mineralized to CO_2 and H_2O; however, higher concentrations lead to the formation of oligomers which remain adsorbed on the walls of the lamp, decreasing the efficiency of the mineralization process. Consequently, 3×10^{-3} M is the highest concentration of phenol that can be efficiently mineralized with our experimental apparatus.

3.2. Vacuum-UV irradiation of aqueous solutions containing nitrate and phenol

Oxygen-, air- and argon-saturated aqueous solutions containing 7×10^{-4} M of phenol and varying amounts of NO_3^- were vacuum-UV irradiated at 60 °C and, in some cases, 25 °C.

The depletion rates of phenol and DOC depend on the nitrate concentration; however, different behaviour is observed depending on the dissolved oxygen concentration as shown in Figs. 1 and 2. Irradiation experiments performed in the absence of dissolved oxygen show an increase in phenol and DOC depletion rates when nitrate is added. In contrast, no dependence on nitrate concentration is observed in experiments performed with air- or oxygen-saturated solutions.

Nitrate has a strong effect on the reactions involved in the oxidation of phenol in argon-saturated solutions. HPLC chromatograms taken at different irradiation times are completely different from those obtained under identical initial conditions but in the absence of NO_3^-. Indeed, in the presence of NO_3^-, 1,2,3-trihydroxybenzene, 1,2-dihydroxybenzene, 1,3-dihydroxybenzene, 1,4-dihydroxybenzene and oxalic acid are observed on irradiation of Ar-saturated solutions and quantified as intermediate products. Oxalic acid is identified although not quantified due to the superposition with NO_3^- in some of the samples. The potential formation of nitroaromatics was also checked, but could not be observed at concentrations above the detection limit of 5×10^{-6} M. Fig. 4 shows the concentration profiles of dihydroxybenzenes and trihydroxybenzene as a function of the irradiation time for solutions containing 2.3×10^{-3} M of NO_3^-. We may deduce from this figure that the oxidation sequence phenol → dihydroxybenzene → 1,2,3-trihydroxybenzene → open-chain products is an important reaction pathway of phenol mineralization. Although the same intermediates are found in oxygen- and air-saturated solutions on irradiation, a striking difference is their simultaneous formation under the latter conditions (Fig. 3).

Organic products formed at different irradiation times in corresponding experiments with air- or oxygen-saturated solutions do not show appreciable differences for solutions irradiated in the absence or presence of NO_3^-.

However, phenol greatly modifies the depletion rates and fate of NO_3^- during the vacuum-UV irradiation of aqueous solutions containing both reactants. The observed behaviour depends on the dissolved oxygen concentration and on the $[PhOH]/[NO_3^-]$ ratios. NO_2^- and NH_4^+ are the only nitrogen-containing inorganic ions observed in the aqueous phase after NO_3^- depletion.

Figs. 5(a)–5(c) show the concentration profiles vs. irradiation time for the depletion of NO_3^- and the formation of NO_2^- and NH_4^+ for irradiated aqueous solutions with $[PhOH]/[NO_3^-]$ ratios greater than 2.5 at 60 °C and saturated with oxygen, air or argon respectively. N_2O was not observed to be present in the gas phase at concentrations higher than 10 ppm, even after complete mineralization of

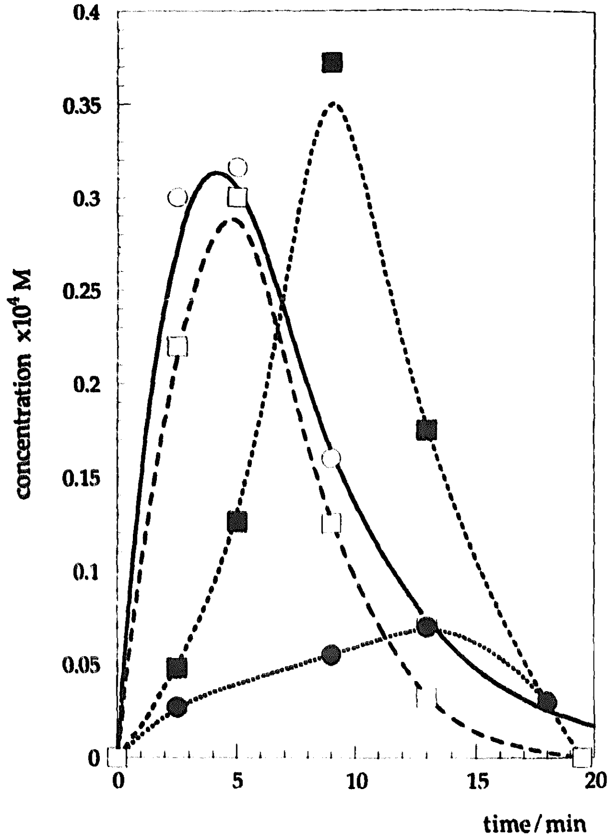

Fig. 4. Concentration profiles for different oxidation products of phenol observed during the vacuum-UV irradiation of aqueous solutions containing 7.5×10^{-4} M of phenol and approximately 2.7×10^{-4} M of NO_3^- under an argon atmosphere at about 60 °C. ■, ○, ● and □ correspond to 1,2,3-trihydroxybenzene, 1,4-dihydroxybenzene, 1,3-dihydroxybenzene and 1,2-dihydroxybenzene respectively.

the dissolved organic matter. Fig. 5(d) shows the concentration profiles for the same inorganic ions for irradiated argon-saturated solutions with $[PhOH]/[NO_3^-]$ ratios less than 0.3. The calculated total nitrogen concentrations $([N_T]_t=[NO_3^-]_t+[NO_2^-]_t+[NH_4^+]_t)$ and pH profiles vs. irradiation time are also shown.

The following general observations can be drawn from these figures.

(1) Irradiation experiments performed with argon- and air-saturated solutions yield the quantitative depletion of NO_3^-, whereas experiments performed with oxygen-saturated solutions result only in the partial depletion of NO_3^-. In all cases, nitrate depletion rates are slower than those of phenol.

(2) NH_4^+ is formed from NO_3^- depletion, but is partially re-oxidized to NO_3^- at longer irradiation times. NH_4^+ is almost quantitatively formed from NO_3^- in irradiated aqueous solutions with $[PhOH]/[NO_3^-]$ ratios greater than 2.5. Experiments with $[PhOH]/[NO_3^-]$ ratios less than 0.3 show only partial reduction of NO_3^- to NH_4^+.

(3) NO_2^- is formed immediately after irradiation is started, and its concentration profile follows qualitatively that of $[NO_3^-]_t$, its concentration always accounting for less than 10% of the actual concentration of NO_3^-. NO_2^- is therefore an intermediate product in the reduction of (oxidation to) NO_3^-.

(4) The total nitrogen concentration contained in the inorganic ions ($[N_T]_t$) and the pH show an evolution with irradiation time depending on the $[PhOH]/[NO_3^-]$ ratio and the dissolved oxygen concentration.

Irradiation experiments with argon- and air-saturated solutions with $[PhOH]/[NO_3^-]$ ratios greater than 2.5 show, within experimental error, a constant $[N_T]_t$ value until $[NH_4^+]$ reaches a maximum, thus indicating that NH_4^+ is readily formed from NO_3^- depletion. At longer irradiation times, $[N_T]_t$ steadily decreases until complete depletion of NH_4^+. Considering that NH_4^+ is only partially re-oxidized to NO_3^- and NO_2^-, the concomitant decrease in $[N_T]_t$ indicates a simultaneous elimination of nitrogen by the formation of gaseous products. The pH evolution during the irradiation of these solutions shows a steady increase from initial values of pH 6 to pH 8 at long irradiation times.

In corresponding experiments with oxygen-saturated solutions, $[N_T]_t$ decreases, reaching a minimum value after approximately 10 min of irradiation, and then increases at longer irradiation times to almost its initial value. A minimum in the $[N_T]_t$ profiles clearly indicates the involvement of nitrogen-containing species other than NH_4^+, NO_3^- and NO_2^- remaining in solution. The experimental observation that $[N_T]_t$ recovers to its original value at long irradiation times indicates a quantitative oxidation of NH_4^+ to NO_3^- and NO_2^-. The corresponding pH profiles are similar to those observed for $[N_T]_t$: the pH decreases considerably, reaching a minimum value at approximately 10 min of irradiation, and steadily increases at longer irradiation times to almost its original value. These observations seem to indicate that the formation of the unidentified nitrogen-containing species is intimately related to pH.

Experiments with argon-saturated solutions with $[PhOH]/[NO_3^-]$ ratios less than 0.3 show a steady decrease in $[N_T]_t$ with irradiation time until complete depletion of NH_4^+, NO_3^- and NO_2^-, thus indicating the formation of gaseous products starting at the initial stages of irradiation. The pH evolution during the irradiation of these solutions shows a continuous increase from initial values of pH 6 to pH 10 at long irradiation times.

The observed behaviour clearly indicates a strong relation between the different oxidation states of the dissolved nitrogen-containing species and the pH. An increase in pH seems to accompany the elimination of inorganic nitrogen as N_2 and/or N_2O.

The effect of temperature on the reaction kinetics was studied only under conditions of argon saturation. Similar experiments with oxygen-containing solutions will be reported when appropriate equipment is available to permit a precise determination of the simultaneous variation of the dissolved oxygen concentration with temperature. Fig. 6 shows the effect of temperature on the concentration profiles

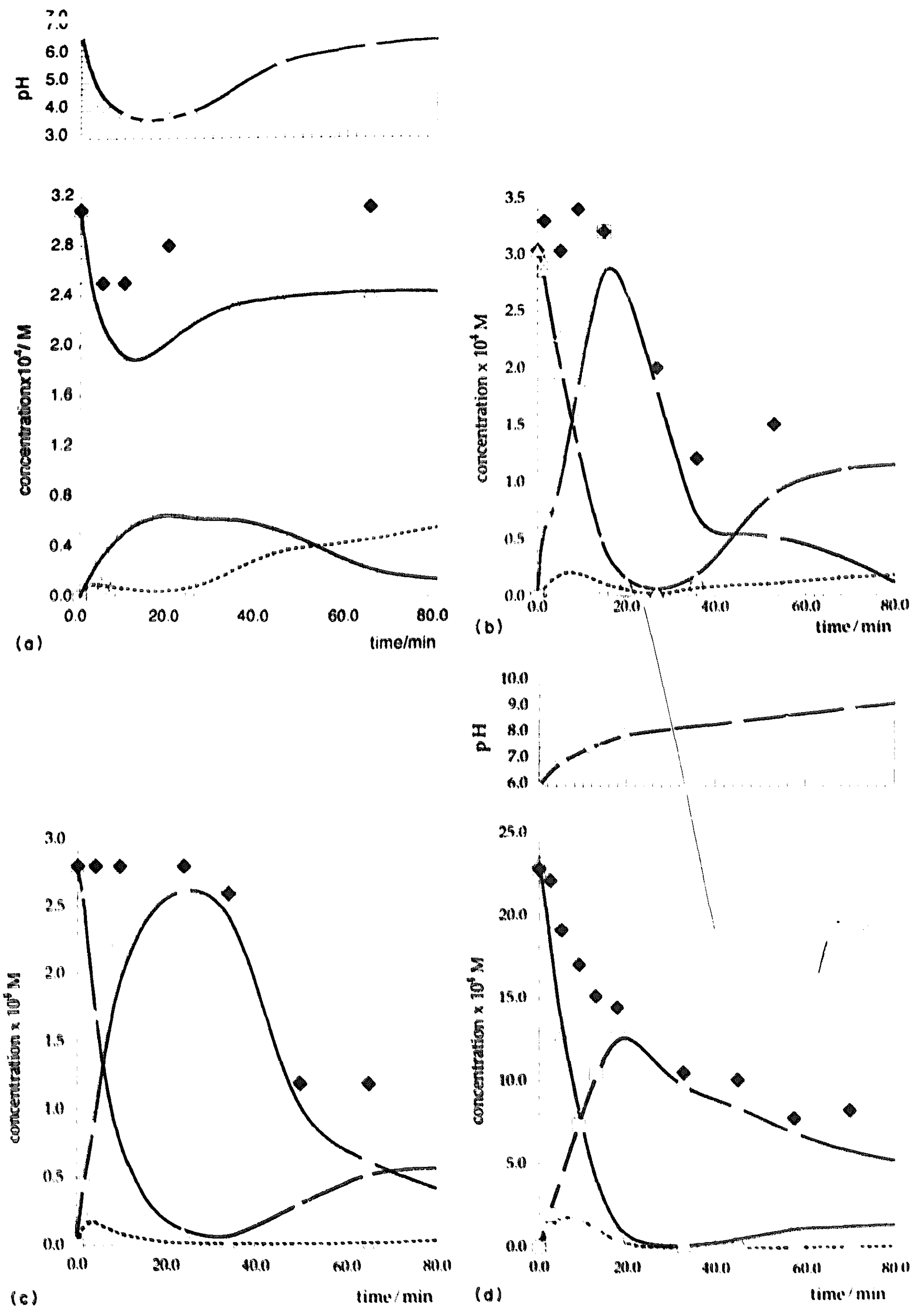

Fig. 5. Concentration profiles vs. irradiation time of NO_3^- (△), NO_2^- (○), NH_4^+ (□) and N_T (◆) during the vacuum-UV irradiation of aqueous solutions containing 7.5×10^{-4} M of phenol at 60 °C and different experimental conditions: (a), (b) and (c) correspond to vacuum-UV irradiation experiments of aqueous solutions of phenol containing 2.7×10^{-4} M of NO_3^- under oxygen, air and argon saturation respectively; (d) corresponds to the vacuum-UV irradiation of argon-saturated aqueous solutions of phenol containing 2.3×10^{-3} M of NO_3^-. The pH evolution vs. irradiation time is also shown in (a) and (d).

of NO_3^-, NO_2^-, NH_4^+ and DOC during the vacuum-UV irradiation of argon-saturated aqueous solutions at 25 °C. The results show that the temperature has a strong effect on the rate of NH_4^+ formation and depletion, as well as on the DOC depletion rate. NO_3^- and phenol depletion rates are not appreciably affected by temperature in the range 25–60 °C. $[N_T]_t$ decreases, reaching a minimum value after approximately 10 min of irradiation, and then increases to almost its initial value at irradiation times corresponding to a maximum of $[NH_4^+]$. A minimum in the $[N_T]_t$ profiles clearly suggests the involvement of nitrogen-containing species other than NO_3^- and NO_2^- present in solution before the formation of

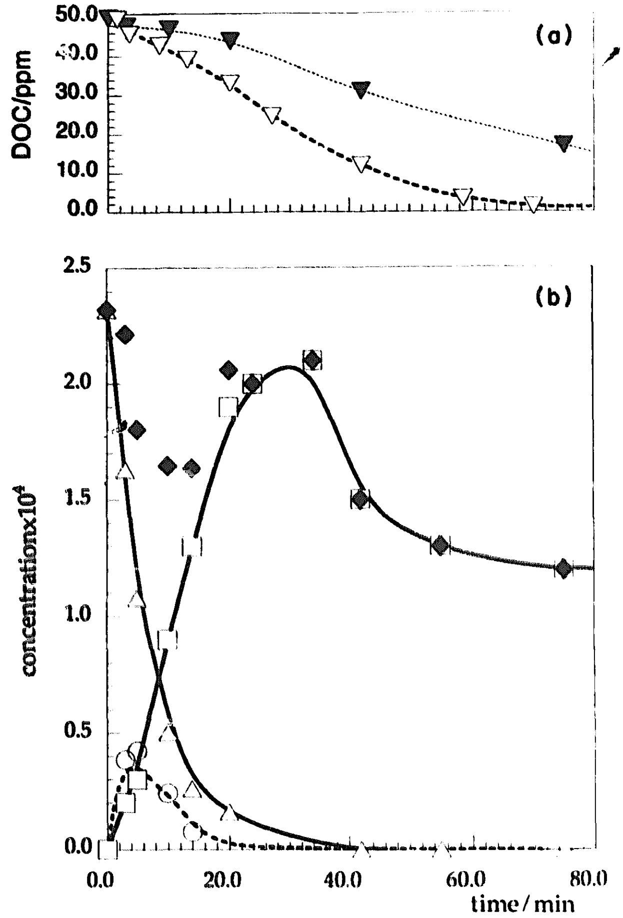

Fig. 6. (a) Depletion of DOC vs. irradiation time for argon-saturated aqueous solutions containing 7.5×10^{-4} M of phenol and 2.7×10^{-4} M of NO_3^- at 60 °C (▽) and 25 °C (▼). (b) Concentration profiles vs. irradiation time of NO_3^- (△), NO_2^- (○), NH_4^+ (□) and N_T (◆) during the vacuum-UV irradiation of argon-saturated aqueous solutions containing 7.5×10^{-4} M of phenol and 2.7×10^{-4} M of NO_3^- at 25 °C.

NH_4^+. Considering that no nitrogen-containing intermediates are observed during the reduction of NO_3^- to NH_4^+ in corresponding experiments at 60 °C, we may conclude that these intermediates are involved in thermally controlled reactions leading finally to NH_4^+. Indeed, NH_4^+ formation rates are temperature dependent.

3.3. Vacuum-UV irradiation of aqueous solutions containing nitrate and carbonate

Our studies clearly indicate that organic substrates have an important impact on the reduction of NO_3^- to NH_4^+. Considering that the vacuum-UV irradiation of water produces $H^\bullet$ atoms, hydrated electrons and $HO^\bullet$ radicals simultaneously, one possible effect of organic compounds is the efficient trapping of $HO^\bullet$ radicals. Low $HO^\bullet$ concentrations will favour the reduction pathway of NO_3^- to NH_4^+ and decrease the probability of oxidation reactions leading to the formation of inorganic nitrogen with high oxidation states [8]. In order to quantify the importance of $HO^\bullet$ trapping, aqueous solutions containing CO_3^{2-} and NO_3^- at pH 9 were irradiated. Carbonate ion was chosen as a specific $HO^\bullet$ scavenger reacting with hydroxyl radicals with a high rate constant and forming $CO_3^{\bullet-}$ radical anions which exhibit less oxidative reactivity than $HO^\bullet$ [5]. Moreover, depending on the pH of the aqueous system, CO_3^{2-} is the final reaction product formed after mineralization of the organic substrate, and is consequently present in all solutions of alkaline pH.

Air- and argon-saturated aqueous solutions containing 8.3×10^{-3} M of carbonate and 2.5×10^{-4} M of NO_3^- were vacuum-UV irradiated at 25 °C. NO_2^- is the only nitrogen-containing inorganic ion formed in the aqueous phase, and NH_4^+ was not detected even at concentrations less than 10^{-5} M. The fact that $[N_T]_t$ remains constant with irradiation time further indicates that NO_2^- is the only reaction product. Figs. 7(a) and 7(b) show the concentration profiles vs. irradiation time for NO_3^-, NO_2^- and $[N_T]_t$ during the irradiation of air- and argon-saturated aqueous solutions respectively. The observed results may be compared with corresponding irradiation experiments with pure nitrate solutions rather than with those containing organic compounds. Vacuum-UV irradiation experiments with argon-saturated aqueous solutions containing 3.0×10^{-4} M of NO_3^- at 25 °C show a 33%

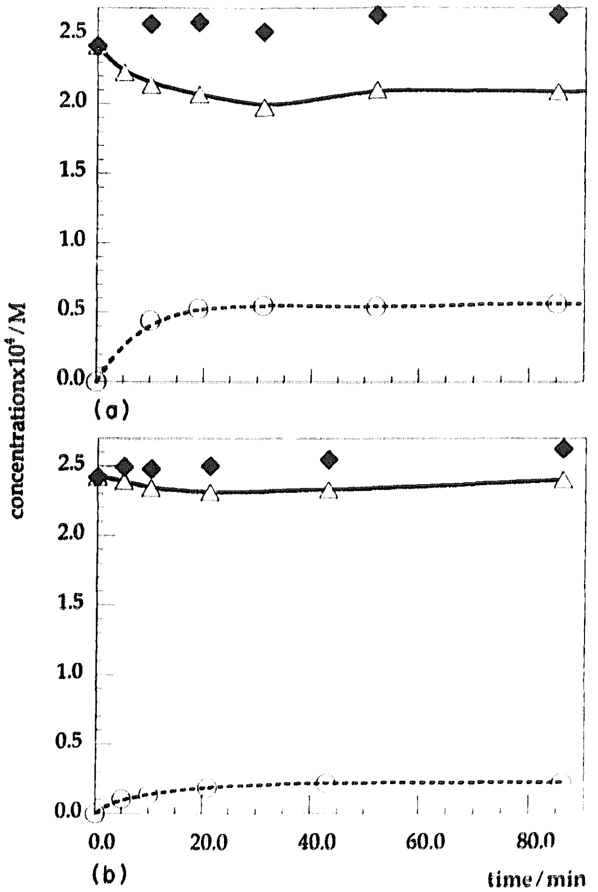

Fig. 7. Concentration profiles vs. irradiation time of NO_3^- (△), NO_2^- (○) and N_T (◆) during the vacuum-UV irradiation of aqueous solutions containing 4.5×10^{-3} M of Na_2CO_3 and 2.7×10^{-4} M of NO_3^- at 25 °C: (a) experiments performed with air-saturated solutions; (b) experiments performed with argon-saturated solutions.

depletion of NO_3^- after 100 min of irradiation yielding NO_2^- and N_2O as reaction products [8]. In contrast, corresponding experiments in the presence of carbonate show only an 8% depletion for the same irradiation time and no formation of N_2O within experimental error. It can therefore be concluded that the main effect of carbonate in the absence of dissolved oxygen is to reduce the efficiency of NO_3^- depletion and decrease the probability of the reaction pathway to N_2O formation.

However, carbonate shows no appreciable effect on nitrate depletion and reaction products in experiments with air-saturated solutions, as in both the presence and absence of carbonate, less than 20% depletion of NO_3^- after 100 min of irradiation is observed, yielding mainly NO_2^- as reaction product.

4. Discussion

The vacuum-UV photolysis of water produces $H^\cdot$, $HO^\cdot$ and hydrated electrons, according to reactions (1.1) and (1.2), with relatively high efficiency [5]. These photochemicaly generated reactive species initiate a series of diffusion-controlled secondary reactions yielding mild oxidative and reductive intermediates competing with organic and inorganic substrates for $H^\cdot$, $HO^\cdot$ and hydrated electrons. Twelve different species ($HO^\cdot$, $H^\cdot$, e_{aq}^-, $HO_2^\cdot$, $O_2^{\cdot -}$, H_2, O_2, H_2O_2, HO_2^-, H^+, HO^- and H_2O) and a minimum set of 28 reactions must be taken into account in a reaction scheme describing the vacuum-UV photolysis of pure water [8]. Table 1 contains the most important reactions efficiently reducing the availability of $H^\cdot$, $HO^\cdot$ and hydrated electrons for reactions with organic and inorganic substrates.

Table 1
Most important reactions during the vacuum-UV irradiation of pure water

Reaction	Rate constant	Number
$H_2O + h\nu \rightarrow HO^\cdot + H^\cdot$	$\Phi_{172\ nm} \approx 0.45$	(1.1)
$H_2O + h\nu \rightarrow HO^\cdot + H^+ + e_{aq}^-$	$\Phi_{172\ nm} \approx 0.05$	(1.2)
$O_2 + H^\cdot \rightarrow HO_2^\cdot$	$1 \times 10^{10}\ M^{-1}\ s^{-1}$	(1.3)
$O_2 + e_{aq}^- \rightarrow O_2^{\cdot -}$	$2 \times 10^{10}\ M^{-1}\ s^{-1}$	(1.4)

Table 2
Primary reactions depleting phenol during the vacuum-UV irradiation of phenol aqueous solutions

Reaction	Rate constant	Number
$C_6H_5OH + HO^\cdot \rightarrow C_6H_5(OH)_2^\cdot$	$\approx 1 \times 10^{10}\ M^{-1}\ s^{-1}$	(2.1a)
$C_6H_5OH + HO^\cdot \rightarrow C_6H_5O^\cdot + H_2O$		(2.1b)
$C_6H_5OH + HO^\cdot \rightarrow C_6H_5(OH)^{\cdot +} + OH^-$		(2.1c)
$C_6H_5OH + H^\cdot \rightarrow C_6H_6(OH)^\cdot$	$(2.0\text{–}7) \times 10^9\ M^{-1}\ s^{-1}$	(2.2)
$C_6H_5OH + e_{aq}^- \rightarrow C_6H_5(OH)^{\cdot -}$	$1.6 \times 10^7\ M^{-1}\ s^{-1}$	(2.3)

Table 3
Reactions retarding the depletion rate of phenol in the absence of dissolved oxygen

Reaction	Number
$C_6H_5(OH)_2^\cdot + H^\cdot \rightarrow H_2O + C_6H_5OH$	(3a)
$C_6H_5O^\cdot + H^\cdot \rightarrow C_6H_5OH$	(3b)

Therefore the ratio of $[HO^\cdot]$ to $[H^\cdot]$ reacting with the organic substrate or its degradation intermediates depends strongly on the experimental conditions, the concentration of dissolved oxygen being one of the important parameters. Less oxidative conditions may be obtained in experiments in which solutions are continuously purged with argon and an important contribution of the reactions involving $H^\cdot$ atoms may be expected. In contrast, molecular oxygen reacts efficiently with $H^\cdot$ and hydrated electrons (reactions (1.3) and (1.4)), decreasing the available concentrations of $H^\cdot$ and hydrated electrons. Consequently, a more oxidative medium is established in a reaction system saturated with oxygen.

The vacuum-UV irradiation of argon- or oxygen-saturated aqueous solutions of phenol at concentrations lower than 5×10^{-3} M yields CO_2 and water as the final products. As previously discussed [3,4,8,14], the photolysis of water is the main photochemical reaction in these systems, and reactions (2.1), (2.2) and (2.3) in Table 2 may be postulated as the primary reactions leading to the depletion of phenol [15].

Reactions following the formation of $C_6H_5(OH)_2^\cdot$, $C_6H_5O^\cdot$ and $C_6H_5(OH)^{\cdot +}$ are not well understood; they have been proposed to react further with O_2, $HO^\cdot$ and/or $HO_2^\cdot/O_2^{\cdot -}$ or undergo disproportionation yielding dihydroxybenzenes and phenol [16]. Otherwise they may undergo fragmentation leading to open-chain products [17].

Our experimental results in oxygen- and air-saturated solutions agree with those reported in the literature for the degradation of phenol using TiO_2 and H_2O_2 as the source of $HO^\cdot$ radicals [12,16]. 1,2-Dihydroxybenzene, 1,4-dihydroxybenzene and 1,2,3-trihydroxybenzene are the main products of oxidation. The observation that the concentration of 1,3-dihydroxybenzene is less than 10% of the concentrations of all other dihydroxybenzenes is consistent with the fact that hydroxyl radical addition in the meta position does not lead to a resonance-stabilized intermediate implying the corresponding phenoxy radical. Further oxidation of the dihydroxybenzenes and trihydroxybenzene results, finally, in the opening of the aromatic ring to yield aliphatic acids and aldehydes.

As indicated in Table 2, the reaction between phenol and $H^\cdot$ atoms (reaction (2.2)) is rather efficient and should make an important contribution to the overall depletion rate of phenol in the absence of dissolved oxygen. In experiments with high concentrations of dissolved oxygen, reactions (2.1a)–(2.1c) mainly lead to the depletion of phenol and, consequently, higher depletion rates should be expected in irradiated argon-saturated solutions. The experimental observation that the rate of disappearance of phenol increases with increasing concentration of dissolved oxygen does not support this simple hypothesis. Reactions other than those shown in Table 2, retarding the depletion rate of phenol in the absence of dissolved oxygen, should also be taken into account (see Table 3).

Our experimental observations show that the complete mineralization of phenol, although requiring longer irradiation times, is also achieved in irradiated argon-saturated solutions. Under these conditions, open-chain products rather than hydroxybenzenes are observed as reaction intermediates. We may conclude from these experiments that the presence of oxygen is decisive for the formation of dihydroxybenzenes. However, dihydroxybenzenes are reported to be formed from $C_6H_5(OH)_2^{\bullet}$ and $C_6H_5O^{\bullet}$ radicals generated by reactions (2.1a)–(2.1c) even in the absence of molecular oxygen [16]. Reactions (3a) and (3b) implicate the efficient depletion of $C_6H_5(OH)_2^{\bullet}$ and $C_6H_5O^{\bullet}$ in argon-saturated solutions, thus preventing the formation of dihydroxybenzenes. Subsequent reactions leading to phenol mineralization may then involve intermediates generated by reactions (2.2) and (2.3) from which dihydroxybenzenes are not produced by reactions with $H^{\bullet}$ atoms or $HO^{\bullet}$ radicals.

However, molecular oxygen is most efficient in decreasing $[H^{\bullet}]$. Under oxygen-saturated conditions, $H^{\bullet}$ atoms cannot compete with O_2, $HO^{\bullet}$ and/or $HO_2^{\bullet}/O_2^{\bullet -}$ radicals for $C_6H_5(OH)_2^{\bullet}$ and $C_6H_5O^{\bullet}$ and high yields of dihydroxybenzenes are obtained under these conditions. In addition, the possibility that $C_6H_5(OH)_2^{\bullet}$ and $C_6H_5O^{\bullet}$ radicals may react preferentially with open-chain products in the absence of molecular oxygen or $HO_2^{\bullet}/O_2^{\bullet -}$ radicals [18] should not be disregarded.

The vacuum-UV irradiation of aqueous solutions of phenol in the presence of NO_3^- results in the simultaneous removal of NO_3^- and the complete degradation of the organic matter to CO_2 and H_2O. In both the presence and absence of molecular oxygen, nitrate reduction intermediates clearly promote the oxidation of the organic substrate and its intermediates and/or act as a source of oxygen atoms for the complete oxidation to CO_2, being reduced themselves to NH_4^+.

In order to understand the cooperative effect of nitrate and organic matter during the vacuum-UV irradiation of aqueous solutions, an understanding of the reactions involved during the irradiation of aqueous solutions of phenol and nitrate is necessary. Having already discussed the reaction mechanisms involved during the vacuum-UV irradiation of aqueous phenol solutions, a brief introduction to the reactions involved during the irradiation of aqueous nitrate solutions is given.

In Table 4, some of the most important reactions leading from NO_3^- depletion to NO_2^- and N_2O formation during the vacuum-UV irradiation of aqueous solutions of nitrate are shown [8].

NO_3^- reacts with hydrated electrons at diffusion-controlled rates and with $H^{\bullet}$ atoms with much lower efficiency. However, NO_3^- is not an efficient $HO^{\bullet}$ scavenger (reaction (4.3)) and reactions (4.1) and (4.2) are the main primary reactions leading to nitrate depletion. Aqueous solutions of $NO_3H^{\bullet -}$ and $(NO_3^{\bullet})^{2-}$, formed by the one-electron reduction of NO_3^- (reactions (4.1) and (4.2)), decompose to $NO_2^{\bullet}$ radicals and hydroxide anion according to reaction (4.4). Consequently, an increase in pH with irradiation time is observed. In the absence of other substrates, $NO_2^{\bullet}$ dimerizes to N_2O_4 which subsequently disproportionates to NO_3^- and NO_2^- in the millisecond time range (reaction (4.5)).

Table 4
Most important reactions leading from NO_3^- depletion to NO_2^- and N_2O formation during continuous vacuum-UV irradiation of aqueous solutions of nitrate

Reaction	Reaction rate	Number
$NO_3^- + H^{\bullet} \rightarrow NO_3H^{\bullet -}$	$2.4 \times 10^7\ M^{-1}\ s^{-1}$	(4.1)
$NO_3^- + e_{aq}^- \rightarrow (NO_3^{\bullet})^{2-}$	$1 \times 10^{10}\ M^{-1}\ s^{-1}$	(4.2)
$NO_3^- + HO^{\bullet} \rightarrow NO_3^{\bullet} + HO^-$	$< 1 \times 10^5\ M^{-1}\ s^{-1}$	(4.3)
$NO_3H^{\bullet -}/(NO_3^{\bullet})^{2-} + H_2O \rightarrow NO_2^{\bullet} + 2HO^-$		(4.4)
$2NO_2^{\bullet} \rightleftarrows N_2O_4 \rightarrow NO_3^- + NO_2^-$		(4.5)
$NO_2^- + H^{\bullet} \rightarrow NO_2H^{\bullet -} \rightleftarrows (NO_2^{\bullet})^{2-} + H^+$		(4.6)
$NO_2^- + e_{aq}^- \rightarrow (NO_2^{\bullet})^{2-}$		(4.7)
$(NO_2^{\bullet})^{2-} \rightarrow NO^{\bullet} + 2HO^-$		(4.8)
$NO^{\bullet} + H^{\bullet} \rightarrow NOH \rightleftarrows NO^- + H^+$		(4.9)
$NO^{\bullet} + e_{aq}^- \rightarrow NO^-$		(4.10)
$2NOH \rightarrow N_2O + H_2O$		(4.11)
$NO_2^{\bullet} + HO^{\bullet} \rightarrow ONOOH \rightleftarrows ONOO^- + H^+$		(4.12)
$O_2 + (NO_3^{\bullet})^{2-} \rightarrow O_2^{\bullet -} + NO_3^-$		(4.13)
$NO^{\bullet} + O_2^{\bullet -} \rightarrow ONOO^-$		(4.14)
$NO_2^{\bullet} + HO_2^{\bullet} \rightleftarrows O_2NOOH$		(4.15)

Since the experiments were performed under conditions of continuous irradiation, the NO_2^- formed during NO_3^- depletion further reacts with $HO^{\bullet}$ radicals, $H^{\bullet}$ atoms and hydrated electrons. Reaction of NO_2^- with $H^{\bullet}$ atoms and hydrated electrons yields $NO_2H^{\bullet -}$ and $(NO_2^{\bullet})^{2-}$ respectively (reactions (4.6) and (4.7)), which decompose into hydroxide anion and $NO^{\bullet}$ (reaction (4.8)).

Although we were unable to confirm experimentally the formation of $NO^{\bullet}$, the radical was postulated as a key intermediate in the sequence of reactions producing N_2O. $NO^{\bullet}$ may efficiently react with $H^{\bullet}$ and e_{aq}^-, yielding NOH and NO^- respectively (reactions (4.9) and (4.10)). NOH decomposes to yield N_2O by a complex bimolecular reaction (reaction (4.11)).

The average lifetime of $NO_2^{\bullet}$ in aqueous solutions before disproportionation to NO_3^- and NO_2^- is of the order of milliseconds (reaction (4.5)). In the presence of high local concentrations of $HO^{\bullet}$, reaction (4.12) produces peroxynitrous acid.

Oxygen scavenges $H^{\bullet}$ atoms and hydrated electrons efficiently to yield $HO_2^{\bullet}$ and $O_2^{\bullet -}$ respectively (reactions (1.3) and (1.4)). $O_2^{\bullet -}$ and $HO_2^{\bullet}$ are mild oxidants that can oxidize $NO^{\bullet}$ and $NO_2^{\bullet}$ to peroxynitrous and peroxynitric acid respectively (reactions (4.14) and (4.15)).

We assume that reactions (4.1) and (4.2) also initiate the depletion of NO_3^- during the irradiation of aqueous solutions containing both nitrate and organic matter. Moreover, the reactions shown in Table 4 can be taken as a base set of reactions and specific reactions involving the participation of organic matter and leading to NH_4^+ formation should be added. Irradiation experiments with $[PhOH]/[NO_3^-]$ ratios

Table 5
Primary reactions involving CO_3^{2-} during the vacuum-UV irradiation of aqueous solutions containing CO_3^{2-} and NO_3^- at pH ≈ 9

Reaction	Rate constant	Number
$CO_3^{2-} + HO^{\bullet} \rightarrow CO_3^{\bullet -}$	4×10^8 M^{-1} s^{-1}	(5.1)
$NO_2^{\bullet} + CO_3^{\bullet -} \rightarrow NO_3^- + CO_2$	1.0×10^9 M^{-1} s^{-1}	(5.2)
$O_2 + CO_3^{\bullet -} \rightarrow O_2 + CO_3^{2-}$	6.5×10^8 M^{-1} s^{-1}	(5.3)

Table 6
Possible reactions between $NO_2^{\bullet}$, ONOOH and phenolic substrates (PheOH)

Reaction	Number
$NO_2^{\bullet}$ + PheOH → HNO_2 + PheO$^{\bullet}$	(6.1)
$NO_2^{\bullet}$ + PheO$^{\bullet}$ → Phe(OH)NO_2	(6.2)
$NO_2^{\bullet}$ + PheO$^{\bullet}$ → Phe(OH)ONO	(6.3)
Phe(OH)ONO + H_2O → Phe$(OH)_2$ + HNO_2	(6.4)
trans-ONOOH + PheOH → PheO$^{\bullet}$ + $NO_2^{\bullet}$	(6.5)

of less than 0.3, showing the partial reduction of NO_3^- to NH_4^+ and the formation of nitrogen-containing gaseous products, clearly indicate the importance of the reactions in Table 4 when organic matter is a limiting factor.

NO_3^- may be reduced electrochemically to NH_4^+, NH_2OH and N_2O, the relative yield of the reduction products depending on the availability of proton donors in the solution [19]. On the basis of these results, we may only achieve the reduction of NO_3^- to N_2O by irradiation experiments in the presence of organic substrates. The DOC may effectively deplete the available concentration of $HO^{\bullet}$ radicals, such that mostly $H^{\bullet}$ atoms and hydrated electrons are available for the reduction of the intermediates formed after NO_3^- depletion. Experiments with CO_3^{2-} as the $HO^{\bullet}$ scavenger do not even yield traces of NH_4^+. This means that it is the interaction between organic matter and nitrogen-containing inorganic intermediates which is essential for the final evolution of NH_4^+, rather than efficient $HO^{\bullet}$ scavenging.

The effect of CO_3^{2-} in the vacuum-UV irradiation of aqueous solutions containing NO_3^- is explained in Table 5. CO_3^{2-} reacts with $HO^{\bullet}$ radicals (reaction (5.1)) to yield $CO_3^{\bullet -}$, which efficiently reacts with $NO_2^{\bullet}$ (reaction (5.2)) yielding NO_3^- [20]. The participation of reaction (5.2) is important for the inhibiting effect of CO_3^{2-} on the depletion rate of NO_3^-, as observed in experiments with argon-saturated solutions. However, high concentrations of dissolved molecular oxygen may effectively compete with $NO_2^{\bullet}$ for $CO_3^{\bullet -}$ yielding CO_3^{2-} (reaction (5.3)) and, consequently, under conditions of oxygen saturation, CO_3^{2-} shows no appreciable effect on nitrate depletion.

According to Table 4, $NO_2^{\bullet}$, $NO^{\bullet}$ and ONOOH or $ONOO^-$ are formed after NO_3^- depletion. These nitrogen-containing species are strong one-electron oxidants in aqueous systems [9–11] and may be responsible for the higher rates of mineralization of the organic matter in the presence of NO_3^-. However, as previously discussed, the interaction between these intermediates and organic matter should yield NH_4^+ or an inorganic nitrogen species capable of being effectively reduced to NH_4^+.

$NO_2^{\bullet}$ acts as a one-electron oxidant in aqueous systems, and the oxidation of phenolic compounds (reaction (6.1), see Table 6) has been reported to compete favourably with disproportionation to NO_2^- and NO_3^- (reaction (4.5)) even at low concentrations of organic substrates [9a]. Hydrogen abstraction has been proposed as the primary reaction, yielding phenoxyl radicals and nitrite. However, these reactions are slower than the diffusion-controlled limit and strongly pH dependent [19]. Reactions (6.2) and (6.3) between phenoxyl radicals and $NO_2^{\bullet}$ have also been postulated in the chemistry of nitration reactions. The experimental observation that no hydroxynitrobenzenes are formed in detectable yields, as would be expected from reaction (6.2), indicates that nitration reactions are not important in the overall reaction mechanism. It appears that phenoxyl radicals react with $NO_2^{\bullet}$ radicals producing phenolic nitrites (reaction (6.3)), which may undergo rapid hydrolysis yielding the corresponding dihydroxybenzenes and nitrite (reaction (6.4)) [9,11b,21].

Peroxynitrite is a strong oxidant capable of reacting by a variety of oxidative mechanisms. Protonation of peroxynitrite yields HO_2NO ($pK_a = 6.8$). The trans configuration of peroxynitrous acid is thought to react with organic matter via an energetic intermediate complex with hydroxyl-like oxidant properties (reaction (6.5)) [11a]. Peroxynitrite nitration of phenolic compounds seems to take place mainly during the mediation of metal catalysts [22].

The relatively long lifetimes of $NO_2^{\bullet}$ and ONOOH (approximately 3×10^{-3} s and 1 s respectively under our experimental conditions) allow diffusion into the dark volume of the reactor. Consequently, even when reactions (6.1) and (6.5) are not diffusion controlled, their contribution to the total rate of depletion of phenol may still be important, as shown by our experiments where higher depletion rates of phenol are observed during the irradiation of aqueous solutions containing nitrate.

However, the one-electron oxidation of phenolic substrates by $NO_2^{\bullet}$ and ONOOH has been reported to yield the corresponding dihydroxylated products. We find complete agreement as our experimental results show important yields of dihydroxybenzenes and trihydroxybenzene in irradiated argon- saturated solutions containing nitrate, while none of these products is observed in the absence of nitrate [9a,9b].

Reactions of $NO^{\bullet}$ with organic radicals have been extensively investigated in the gas phase and liquid media involving organic solvents [10a]. Under these conditions, $NO^{\bullet}$ efficiently reacts with organic radicals to yield unstable nitrous compounds which can then rearrange to oximes [23] (reaction (7.1), see Table 7). However, reactions with alkoxy radicals have been reported to yield organic nitrites or to induce oxidation of the organic substrates (reactions (7.3) and (7.4) respectively) [24]. We may expect that such reactions also take place in the aqueous phase, but the nature

Table 7
Possible reactions between $NO^{\bullet}$ and organic radicals ($R^{\bullet}$ indicates a hypothetical organic radical and $RO^{\bullet}$ alkoxy radicals)

Reaction	Number
$NO^{\bullet}+R^{\bullet}\rightarrow RNO$	(7.1)
$RNO\rightleftharpoons R'CH{=}NOH$	(7.2)
$NO^{\bullet}+RO^{\bullet}\rightarrow RONO$	(7.3)
$NO^{\bullet}+RO^{\bullet}\rightarrow R'O+HNO$	(7.4)

and distribution of the final products may be different because of the solvating properties, thermalization of radicals and the dielectric constant of water.

The experimental observation that the rates of nitrate depletion are two or three orders of magnitude faster in the presence of organic substrates stresses the importance of the reactions of $NO_2^{\bullet}$ and $NO^{\bullet}$ with organic radicals, which compete with reaction pathways retarding NO_3^- depletion, such as reaction (4.5) [8]. The depletion of nitrate should be mainly controlled by its rate of reaction with $H^{\bullet}$ atoms and hydrated electrons (reactions (4.1) and (4.2)) which, in turn, depends on their yield of production and is, consequently, independent of temperature. The experimental observation that the depletion rates of NO_3^- are temperature independent in the range 25–70 °C and of the same order of magnitude as the phenol depletion rates further supports our mechanistic interpretations.

However, the participation of thermally controlled reactions, such as reaction (7.2), in the reduction pathways to NH_4^+ implicate a temperature dependence of the rate of NH_4^+ production, as shown by our experimental results.

Molecular oxygen has a strong effect on the efficiency and depletion rates of NO_3^-. Several reasons may lead simultaneously to lower NO_3^- depletion in the presence of dissolved oxygen: (a) molecular oxygen competes efficiently for $H^{\bullet}$ radicals and hydrated electrons (reactions (1.3) and (1.4)) with reactions (4.1) and (4.2); (b) the one-electron reduction product of nitrate $(NO_3^{\bullet})^{2-}$ is efficiently scavenged by O_2 yielding NO_3^- (reaction (4.13); (c) $O_2^{\bullet-}$ and $HO_2^{\bullet}$, produced in high concentrations in oxygen-saturated solutions (reactions (1.3) and (1.4)), compete with organic substrates for $NO^{\bullet}$ and $NO_2^{\bullet}$, yielding peroxynitrite and peroxynitrate (reactions (4.14) and (4.15)) which decompose to NO_3^- and NO_2^- respectively.

Mineralization of DOC requires at least stoichiometric amounts of molecular oxygen. Since primary reactions initiating oxidative degradation take place at very short distances (less than 100 μm) from the surface of the lamp, the concentration of molecular oxygen may be considerably depleted in the effective optical path length, if diffusion of oxygen is slower than its consumption even under continuous oxygenation of the solutions. Local depletion of dissolved molecular oxygen has been quantified [25], and may explain the polymerization of the organic intermediates at the lamp surface as well as the similar depletion rates of NO_3^- in argon- and air-saturated solutions of phenol and nitrate.

Although the reactions postulated in Table 6 explain the increased depletion rates of DOC and phenol in nitrate-containing solutions, the fast release of ammonium is still not explained. However, we conclude that reactions (7.1)–(7.4) between organic substrates and $NO^{\bullet}$ may induce further reduction of $NO^{\bullet}$ to NH_4^+.

The reduction of NO_3^- to NH_4^+ is an eight-electron process involving a step by step reduction: two electrons for the reduction to NO_2^-, one electron for the reduction of NO_2^- to $NO^{\bullet}$, three electrons for the reduction NO• to NH_2OH and two electrons for the reduction of NH_2OH to NH_4OH [19]. The reduction of NO_3^- during the vacuum-UV irradiation of aqueous nitrate solutions at low concentrations (less than 10^{-3} M) takes place mainly by reaction with $H^{\bullet}$ atoms and hydrated electrons; consequently, a stepwise reduction can only be achieved under experimental conditions of oxygen exclusion. The one-electron reduction of $NO^{\bullet}$ yields NO^- or NOH, and the further reduction of NO^- or NOH by reaction with $H^{\bullet}$ atoms or hydrated electrons does not seem to be favoured when compared with dimerization (reaction (4.11)) yielding N_2O. Unfortunately, no data on the kinetic parameters of the reactions between $H^{\bullet}$ atoms or hydrated electrons and NO^- or NOH exist in the literature. We assume that chemical interaction between $NO^{\bullet}$ and the organic substrate sustains a multiple electron reduction of $NO^{\bullet}$ to hydroxylamine or ammonium without the evolution of N_2O. Our observations are in agreement with electrochemical studies [19] indicating the involvement of high concentrations of proton donors in the three-electron reduction of $NO^{\bullet}$ to NH_2OH, which can then be reduced to NH_4^+. In the absence of proton donors, a one-electron reduction of $NO^{\bullet}$ to NO^-, leading to N_2O as the final product of reduction, is observed.

The concentration profiles of NH_4^+ vs. irradiation time show the same characteristics for the vacuum-UV irradiation experiments with argon- and air-saturated solutions containing NO_3^- and organic substrates. NH_4^+ formation reaches a maximum concentration, and under continued irradiation is re-oxidized to NO_3^-. Complete oxidation of NH_4^+ to NO_3^- and NO_2^- is observed only for irradiation experiments with oxygen-saturated solutions. Corresponding experiments with air- or argon-saturated solutions show 30% and 10%–15% re-oxidation respectively, as competing reactions yielding gaseous nitrogen-containing products occur. N_2 is most probably formed, since no nitrogen oxides were detected in the gas phase.

NH_4^+ does not react with $HO^{\bullet}$; however, NH_3 related to NH_4^+ by equilibrium (8.1) may be efficiently oxidized by $HO^{\bullet}$ radicals to $NH_2^{\bullet}$ (reaction (8.2), see Table 8). In addition, NH_3 may be formed with much lower efficiency by the reaction of NH_4^+ with hydrated electrons (reaction (8.3)) [15]. The need for an alkaline medium to provide a minimum concentration of NH_3 for this oxidation is indicated by our experimental results which show that NH_4^+ is oxidized only at long irradiation times where $pH > 8$. $NH_2^{\bullet}$ radicals may be further oxidized to hydroxylamine by $HO^{\bullet}$ radicals (reaction

Table 8
Reactions oxidizing NH_4^+ during the vacuum-UV irradiation of aqueous solutions

Reaction	Reaction rate	Number
$H_2O + NH_3(aq) \rightleftarrows NH_4^+ + HO^-$	$pK_b = 4.75$	(8.1)
$HO^{\bullet} + NH_3 \rightarrow H_2O + NH_2^{\bullet}$	$1 \times 10^8\ M^{-1}\ s^{-1}$	(8.2)
$NH_4^+ + e_{aq}^- \rightarrow H^{\bullet} + NH_3$	$2 \times 10^6\ M^{-1}\ s^{-1}$	(8.3)
$HO^{\bullet} + NH_2^{\bullet} \rightarrow NH_2OH$	$9.5 \times 10^9\ M^{-1}\ s^{-1}$	(8.4)
$NH_2^{\bullet} + CO_3^{\bullet -} \rightarrow CO_2 + NH_2O^-$	$1.5 \times 10^9\ M^{-1}\ s^{-1}$	(8.5)
$NH_2O^- + H^+ \rightleftarrows NH_2OH$	$pK_a = 6.0$	(8.6a)
$NH_2OH + e_{aq}^- \rightarrow NH_2^{\bullet} + HO^-$	$9.2 \times 10^8\ M^{-1}\ s^{-1}$	(8.6b)
$NH_2OH + HO^{\bullet} \rightarrow NHOH^{\bullet} + H_2O$	$9.5 \times 10^9\ M^{-1}\ s^{-1}$	(8.7)
$NHOH^{\bullet} + NHOH^{\bullet} \rightarrow N_2 + 2H_2O$		(8.8)
$NH_2^{\bullet} + O_2 \rightarrow NH_2O_2^{\bullet}$	$3 \times 10^8\ M^{-1}\ s^{-1}$	(8.9)

(8.4)) or by carbonate radicals (reaction (8.5)) [20]. Reaction (8.5) may open an efficient reaction pathway in our experimental system, since CO_3^{2-}, formed during the mineralization of organic substrates, is present in high concentrations at irradiation times at which NH_4^+ is efficiently depleted from the reaction system.

Hydroxylamine further reacts with hydrated electrons and $HO^{\bullet}$ radicals yielding $NHOH^{\bullet}$ radicals (reactions (8.6) and (8.7)). Pulse radiolysis experiments and photolysis of hydroxylamine in aqueous solutions have shown efficient recombination of $NHOH^{\bullet}$ radicals yielding N_2 [26] (reaction (8.8)). Moreover, anodic oxidation studies on hydroxylamine suggest that the oxidation of $NHOH^{\bullet}$ radicals produces NO_2^- [27]. In the presence of high concentrations of dissolved oxygen, the reaction of $NH_2^{\bullet}$ radicals with molecular oxygen (reaction (8.9)) may be an efficient reaction path leading to nitrogen compounds of higher oxidation states.

Although we were unable to detect hydroxylamine in the irradiated samples, our previous discussion strongly indicates that hydroxylamine is a possible intermediate in the oxidation of (or reduction to) NH_4^+. Since reactions (8.6) and (8.7) involving hydroxylamine are very efficient, its steady state concentration may be no higher than 10^{-5} M and, consequently, not appropriate for detection by standard colorimetric methods.

The reduction of NO_3^- to NH_4^+ and the oxidation of NH_4^+ to NO_3^- seem to involve a series of common intermediates interrelated by many redox reactions and reaction equilibria in which the pH, availability of electrons and the presence of proton or hydrogen donors and molecular oxygen determine their rate and probability. Further studies are currently underway to understand in more detail the role of $NO^{\bullet}$ and hydroxylamine in the reaction schemes involved.

Acknowledgements

The authors acknowledge financial support from Hewlett-Packard GmbH, Germany. M.C.G. wishes to thank the Fundación Antorchas, Argentina, for taking care of travelling expenses.

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