Kinetic and analytical study of the photo-induced degradation of monuron by nitrates and nitrites under irradiation or in the dark

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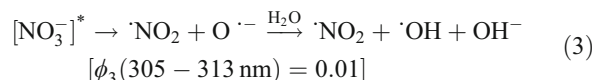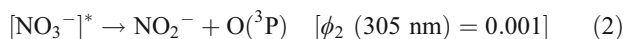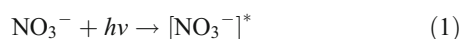
The photo-induced transformation of monuron (3-(4-chlorophenyl)-1,1 dimethylurea) was investigated in an aqueous solution containing nitrates and nitrites at 310 nm and 365 nm, respectively. In both NO_3^- and NO_2^- conditions, the degradation of monuron followed pseudo-first order kinetics. The intermediate products were identified by GC-MS, and the nitration, hydroxylation and coupling reactions were determined. In addition, the oxidation of the N-terminus group, the substitution of chlorine by ·OH and the nitration by ·NO_2 radical onto the phenyl ring were observed. The photo-induced transformation of monuron was studied under variable conditions of pH, inducer concentration, substrate concentration, humic acids, oxygen content and salts used as hydroxyl radical scavengers. The photodegradation rates were strongly influenced by all the above parameters. The degradation of monuron was also studied in the dark and in the presence of NO_2^- as well as in an aqueous solution with the addition of hydrogen peroxide.
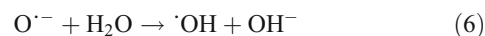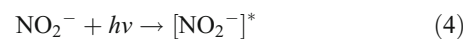
1. Introduction

Monuron (MN) is a phenylurea herbicide that is commonly used for weed control[1] because of its toxicity, and it has received more attention in recent years.[2] Many reports have focused on the photodegradation of monuron, which can occur either by photolysis in water or under solar or UV irradiation.[3] The primary by-product results from the substitution of chlorine by a hydroxyl group.[4] Some of these studies have reported the following: indirect photodegradation by heterogeneous TiO_2 photocatalysis;[5,6] mineralization, which is photo-induced by Fe(III) in aqueous solutions;[7] sensitization by humic acids;[8] ozonation;[9] or by advanced oxidation processes that generate *in situ* hydroxyl radicals (·OH).[10] Nitrates (NO_3^-) and nitrites (NO_2^-) are inorganic ions present in natural waters and can also induce the photodegradation of phenylureas.[11,12]

The absorption spectra of NO_3^- and NO_2^- ions in aqueous solutions contain weak bands at λ_{max} 302 nm ($\varepsilon = 7.2$ M^{-1} cm^{-1}) and 352 nm ($\varepsilon = 22$ M^{-1} cm^{-1}), respectively; in addition, they can absorb solar radiation ($\lambda > 295$ nm).[13] The photochemistry of NO_3^- ions in aerated aqueous solutions results in two main processes. The first yields ·NO_2 and ·OH, and the second yields NO_2^- and O(^{3}P):[13,14]

$$NO_3^- + h\nu \rightarrow [NO_3^-]^* \qquad (1)$$

$$[NO_3^-]^* \rightarrow NO_2^- + O(^3P) \quad [\phi_2 \ (305 \ nm) = 0.001] \qquad (2)$$

$$[NO_3^-]^* \rightarrow \,^·NO_2 + O^{·-} \xrightarrow{H_2O} \,^·NO_2 + \,^·OH + OH^- \atop [\phi_3(305 - 313 \ nm) = 0.01] \qquad (3)$$

Nitrate ions are a source of hydroxyl radicals, and their quantum yield for the formation rate of hydroxyl radicals at 313 nm in the pH range of 6.2–8.2 has been evaluated by Zepp *et al.*[15] ($\Phi_{·OH} = (13 \pm 2) \times 10^{-3}$ and $\Phi_{·OH} = (17 \pm 3) \times 10^{-3}$ at 20 °C and 30 °C, respectively). The quantum yield of the formation of hydroxyl radicals increases with decreasing wavelength from 0.015 ± 0.005 at 370 nm[16] to 0.11 ± 0.01 at 254 nm.[17] Hydroxyl radicals quickly oxidize the majority of organic compounds.[18,19]

Nitrite ions are usually present in water but at a lower concentration than those of nitrate, but its higher molar absorptivity and photolysis quantum yield can make it a competitive photoreactant under environmental conditions.[14] The main pathway of UV irradiation of nitrite yields ·OH + ·NO:

$$NO_2^- + h\nu \rightarrow [NO_2^-]^* \qquad (4)$$

$$[NO_2^-]^* \rightarrow \,^·NO + O^{·-} \quad [\phi_5 \ (355 \ nm) = 0.025] \qquad (5)$$

$$O^{·-} + H_2O \rightarrow \,^·OH + OH^- \qquad (6)$$

The quantum yield for the formation of hydroxyl radicals decreases with increasing wavelength from approximately 0.07 near 300 nm to 0.025 at 355 nm and to 0.015 at 371 nm.[16,20] Nitrite ions are very good scavengers of hydroxyl radicals, which is a disadvantage.

$$NO_2^- + \,^·OH \rightarrow \,^·NO_2 + OH^- \atop [k = 1.0 \times 10^{10} \ L \ mol^{-1} \ s^{-1}] \qquad (7)$$
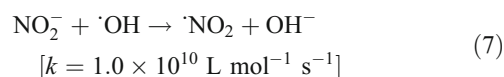
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In an acidic medium, NO_2^- is in its acidic form (HNO_2, $pK_a =$ 3.37) and becomes more reactive because of both a higher absorption and a higher quantum yield for the $\cdot OH$ radical ($\lambda_{max} = 352$ nm, $\varepsilon = 51.9$ M^{-1} cm^{-1}, $\Phi = 0.45$).[20]

$$HNO_2 + h\nu \rightarrow \cdot NO + \cdot OH \qquad (8)$$
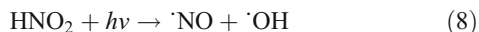
HNO_2 can also nitrate phenol in the dark[21] and react with H_2O_2 to yield peroxynitrous acid (HOONO), an isomer of nitric acid, where oxidation and nitration of aromatic compounds can take place.[22]

The purpose of the present study was to identify the photo-products resulting from the excitation of nitrate and nitrite ions in the presence of MN and to observe the formation of oxidation by-products, which are beneficial to the environment. The kinetic studies were performed in detail to explore the MN re-activity and the effects of environmental parameters. Vione et al.[19,22] have concluded that HOONO transformed the benzene and phenols. Thus, we observed the behavior of MN in the presence of peroxynitrous acid in the dark and in an acidic medium.

2. Experiment

2.1. Chemicals

All the chemicals were of analytical grade and used as such without further purification. The MN standard was purchased from Riedel-de Haën (Seelze, Germany) with a purity of 99.9%. The following are chemicals utilized for this study along with the distributors from which they were purchased: KNO_3 (99%) and $HClO_4$ (70%) from Merck (Oulchy-Le-Chateau, France), $NaNO_2$ (98%) from Prolabo (Poole, England), humic acids from Aldrich (Steinhein, Germany), H_2O_2 (33%), KI and KBr from Fisher Scientific Labosi (Elancourt, France), and KSCN from Panreac (Barcelona, Spain). The pH of the solutions was measured using an Orion pH-meter (Maryland, USA) with a combined electrode. The buffered solutions were made from solutions of $Na_2HPO_4 \cdot 12H_2O$ and KH_2PO_4 obtained from Merck (Darmstadt, Germany). The HPLC grade methanol (99.9%) was purchased from Carlo Erba Reagents (Val de Reuil, France). All the solutions were prepared with deionized water from a Millipore device (Milli-Q) or the bidistilled water followed by filtration through a 0.45 μm sieve (Millipore).

2.2. Photochemical reactor

Several devices were used to study the photochemical transform-ations of the substrate (MN). Solutions containing nitrate ions were irradiated at 310 nm in a 60 × 2 cm i.d. cylindrical Pyrex reactor with six lamps (Duke Sun Lamp GL 20 W). The nitrite ions were irradiated at 365 nm using three HPW black light 125 W Philips lamps with a maximum emission at 365 nm. The Pyrex cylindrical reactor (20 × 3 cm i.d.) was equipped with a water-cooling jacket to eliminate excess heat. The solutions were magnetically stirred, and the dark experiments were performed in magnetically stirred vials wrapped in aluminum foil. Light inten-sity measured by a radiometer (Vilber Lourmat, Marne la Vallée, France) at 310 nm and 365 nm was 0.18 and 2.5 mW cm^{-2}.

2.3. Analyses

The UV spectra were recorded on a Helios Alpha Spectronic Unicam (Cambridge, England). The MN degradation was moni-tored using a Shimadzu HPLC-UV (Kyoto, Japan), a photodiode array UV detector at a wavelength of 244 nm, a C_{18} reverse phase column Supercosil™ LC-18 (250 × 4.6 mm), and a mobile phase consisting of methanol–water (50 : 50 v/v%) at a flow rate of 1 mL min^{-1}.

After two days of irradiation, the aqueous samples were acidified with HCl (pH ≤ 2), extracted with diethyl ether and concentrated under a gentle stream of high-purity nitrogen; then, the samples were dried with anhydrous Na_2SO_4. The concentrated extract was injected into a Shimadzu GC-MS QP 2010 (Kyoto, Japan) equipped with a Trace GC 2010 gas chromatograph, a GCQ plus ion trap mass spectrometer, and a Varian WCOT fused silica column (CP-SE30, 25 m length, 0.25 mm i.d.). The conditions employed were as follows: a 0.76 mL min^{-1} carrier flow (He), an oven temperature of 70 °C (3 min), an increasing gradient temperature of 10 °C min^{-1} that was steady at 280 °C for 5 min, an injector tem-perature of 250 °C, and a manual splitless injection (1 μL). The MS was operated in an electron ionization mode with a potential of 70 eV, and the spectra were obtained in the full scan mode.[23]

## 3. Results and discussion

3.1. Photolysis (310 nm irradiation)

We first investigated the photodegradation of MN (10^{-4} M) in pure water at 310 nm. When the reaction was monitored by UV-Vis the intense band of MN (244 nm; $\varepsilon = 17\,800$ M^{-1} cm^{-1}) decreased, and new absorption bands appeared at 280 nm. MN was photolyzed much more slowly in Milli-Q water than in the presence of nitrate and nitrite, and its transformation followed pseudo-first order kinetics with an apparent first-order rate con-stant of $k' = 0.0137$ h^{-1}, which was determined according to the following equation:

$$\ln(C_0/C) = k't \qquad (9)$$

where C represents the MN concentration at time t, C_0 represents the MN concentration at time 0, and k' represents the apparent first order rate constant of MN consumption. The HPLC chroma-togram of a solution of MN irradiated during several hours showed the formation of only one by-product. Its UV spectrum showed a high absorption at 238 nm and a weak band at 280 nm. This by-product (3-(4-hydroxyphenyl)-1,1-dimethyl-urea) results from the photohydrolysis reaction of MN, which is commonly encountered in the phototransformation of haloge-nated aromatic compounds,[4,24,25] due to the substitution of chlor-ine by OH (Cl/OH). A molecule of water $H^{\delta+}$–$OH^{\delta-}$ reacts with a $C^{\delta+}$–$Cl^{\delta-}$ polarized carbon–halogen bond, which can be acti-vated and further polarized through the absorption of a photon by the MN molecule; thus, a heterolytic rupture of the connec-tion and the substitution can occur at the same stage of the halogen atom by OH.[8,25] Previously, it has been suggested[4,8] that this compound probably originates from a carbene formed during the irradiation of MN after the elimination of HCl,
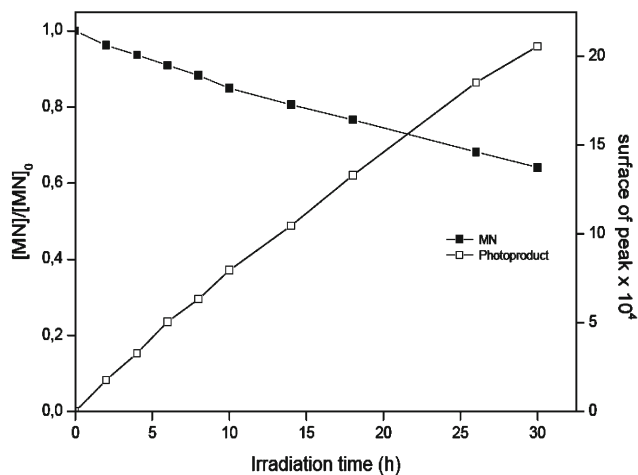
Fig. 1 Time evolution of MN (10^{-4} M) and the by-product upon irradiation at 310 nm in an aerated aqueous solution.
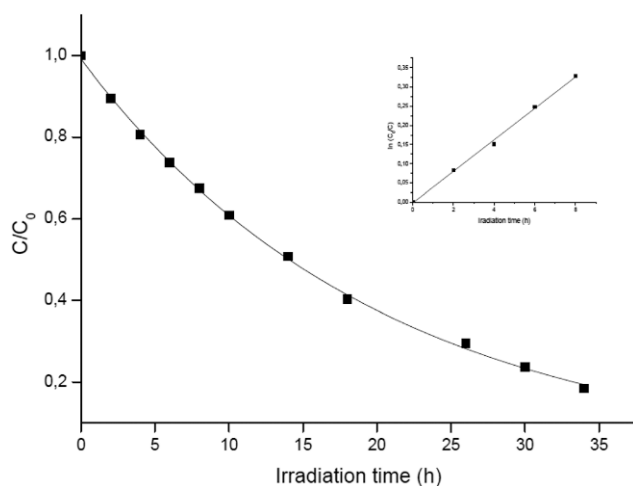
Fig. 2 Consumption profile of MN (10^{-4} M) in the presence of NO_3^- (1 mM), which was irradiated at 310 nm in an aqueous solution. Insert: plot of $\ln(C_0/C)$ versus t, where C represents the MN concentration at time t and C_0 the MN concentration at time 0.

assuming that the photohydrolysis simply results from addition of this carbene to water.

The evolution curve of 3-(4-hydroxyphenyl)-1,1-dimethylurea (Fig. 1) indicated that it is a primary by-product; a similar by-product was observed for the MN photolysis at 254 nm compared to its UV-Visible spectrum and its retention time.

3.2. Photodegradation induced by nitrate ions

3.2.1. Kinetic study. After a solution of MN (10^{-4} M) was irradiated at 310 nm in the presence of nitrates (1 mM) for 34 h, 40% of MN was practically degraded in approximately 10 h (Fig. 2). The transformation followed pseudo-first order kinetics with an apparent first order rate constant of $k' = 0.04$ h^{-1} ($R^2 = 0.99$) and a half-life time of $t_{1/2} = 17.35$ h.

$t_{1/2}$ was calculated using eqn (10) which was derived from eqn (9) by replacing C with $C_0/2$:

$$t_{1/2} = \ln 2/k' \qquad (10)$$

Table 1 Kinetic parameters for the photodegradation of MN in the presence of NO_3^- under different conditions after 10 h of irradiation at 310 nm

[MN]$_0 \times (10^4$ M)	[NO$_3^-$]$_0$ (mM)	k' (h^{-1})	$t_{1/2}$ (h)
1	50	0.15	4.62
1	20	0.09	7.70
1	1	0.04	17.32
1	0.1	0.03	23.10
1	0.01	0.02	34.65
0.5	1	0.05	13.86
5	1	0.03	23.10

Thus, MN was found to be photolyzed much more slowly in Milli-Q water than in the presence of NO_3^-. The kinetics of MN's disappearance was accelerated twice as much in the presence of nitrate irradiated with 6 lamps (intensity = 120 W, $k' = 0.04$ h^{-1}) than that irradiated with 3 lamps (intensity = 60 W, $k' = 0.02$ h^{-1}). Thus, intensive irradiation can significantly enhance the rate of MN degradation. It is very obvious that the photodegradation of MN strongly depends on light intensity in this system.

3.2.2. Inducer concentration. We investigated the photo-transformation of MN (10^{-4} M) in the presence of NO_3^- varying from 0.01 mM to 50 mM. The MN photodegradation rates increase when the initial concentration of the nitrate ions increases (Table 1). These results were directly linked to the production rates of the ·OH radical reactive species and constituted the main active species generated after irradiation.

3.2.3. Effect of substrate concentration. The influence of substrate concentration on the photodegradation rate was studied at different concentrations varying from 0.5×10^{-4} to 5.0×10^{-4} M with NO_3^- as the photoinducer (1 mM). The photodegradation reactions followed pseudo-first order kinetics and the k' values that were obtained clearly depended on the substrate concentration. The photodegradation rate decreased with an increase in substrate concentration (Table 1), which could be explained by competitive absorption between nitrate and MN; therefore, an indirect reduction in ·OH radicals (screen effect)[26] or the production of ·OH was not in excess compared to the MN molecules.
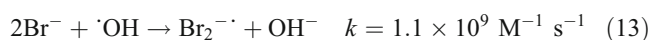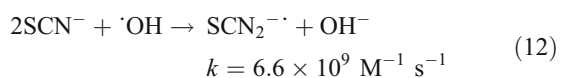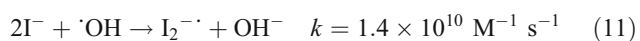
3.2.4. Effect of oxygen concentration. The solutions containing nitrates (1 mM) and MN (10^{-4} M) were irradiated and the oxygen content was varied using nitrogen, air or oxygen as purging gases. The k' values obtained were 0.0198, 0.04 and 0.0799 h^{-1}, respectively. The kinetic values increased in oxygenated medium and indicated that oxygen is involved in the phototransformation process to some extent.

3.2.5. Effect of ·OH scavengers. Organic matter and other components present in natural waters might be involved in the nitrate induced photodegradation process. The influence of I$^-$, SCN$^-$ and Br$^-$ on the photodegradation of phenylureas in the presence of NO_3^- is poorly documented; and it would be very interesting to study the effect of Br$^-$, I$^-$ and SCN$^-$ ions in the phototransformation of MN because the role of these ions is not negligible and their effect should not be excluded in certain

Table 2 Effects of HA and HA + NO_3^- on the photodegradation of MN. Initial conditions $[MN]_0 = 10^{-4}$ M, $[NO_3^-]_0 = 1$ mM, $[HA]_0 = 0.1$ g L^{-1}

	k' (h^{-1})	$t_{1/2}$ (h)
MN + HA	0.026	26.65
MN + NO_3^- + HA	0.021	33.00

Table 3 Effects of nitrate, nitrite, and nitrate + nitrite on the phototransformation of MN (10^{-4} M) in aqueous solutions, irradiation at 310 nm

$[NO_3^-]_0$ (mM)	$[NO_2^-]_0$ (mM)	k' (h^{-1})	$t_{1/2}$ (h)
0	1	0.07	9.90
1	0	0.04	17.32
0.5	0.5	0.06	11.55

circumstances. KI, KSCN and KBr react with $^{\cdot}OH$ to form dihalogeno radical anions, which are reactive, but less than hydroxyls, toward organic and inorganic compounds as well as OH^- according to eqn (11)–(13).[27,28]

$$2I^- + {}^{\cdot}OH \rightarrow I_2^{-\cdot} + OH^- \quad k = 1.4 \times 10^{10}\ M^{-1}\ s^{-1} \quad (11)$$

$$2SCN^- + {}^{\cdot}OH \rightarrow SCN_2^{-\cdot} + OH^-$$
$$k = 6.6 \times 10^9\ M^{-1}\ s^{-1} \quad (12)$$

$$2Br^- + {}^{\cdot}OH \rightarrow Br_2^{-\cdot} + OH^- \quad k = 1.1 \times 10^9\ M^{-1}\ s^{-1} \quad (13)$$

Bromide, iodide and sulfocyanide ions are primary scavengers of $^{\cdot}OH$ in natural waters. They are able to scavenge approximately 97% of the photo-generated $^{\cdot}OH$ radicals. Addition of the scavengers (10^{-2} M) to the solution containing 10^{-4} M of MN and nitrate (1 mM) irradiated during several hours inhibited the MN photodegradation processes initiated by $^{\cdot}OH$. The rate constants were determined as 0.0226, 0.0259 and 0.036 h^{-1} for KI, KSCN and KBr, respectively; the photodegradation rate of MN was a bit higher compared to trials in the absence of these scavengers. These findings provided much needed information on Br^-, I^- and SCN^- in saltwater photochemistry.

3.2.6. Effect of humic acids. Humic acids (HA) are natural organic materials that play an important role in the photochemical processes that occur in surface waters.[29] When MN was irradiated at 310 nm in the presence of HA (0.1 g L^{-1}), the rate of MN photodegradation significantly increased to approximately 50%. In the presence of both HA (0.1 g L^{-1}) and nitrate ions (1 mM), MN disappeared more slowly than in the presence of nitrates alone. The k' and $t_{1/2}$ values are reported in Table 2.

The inhibiting effect of HA on nitrate photolysis is due to a screen effect. The remaining 50% inhibition might have been partly due to the scavenging of hydroxyl radicals by HA.[30]

3.3. Photodegradation induced by nitrite ions

3.3.1. Kinetic study. No photodegradation of MN was observed when it was irradiated alone at 365 nm using black light lamps (no absorbance of MN at wavelengths greater than 300 nm). However, the MN was more efficiently degraded when it was irradiated in the presence of NO_2^- at 365 nm ($\lambda_{max} = 352$ nm, $\varepsilon = 22\ M^{-1}\ cm^{-1}$, $\Phi_{(^{\cdot}OH)\ 355\ nm} = 0.025$, $k' = 0.08\ h^{-1}$)[16] than with NO_3^- at 310 nm ($\lambda_{max} = 302$ nm, $\varepsilon = 7.2\ M^{-1}\ cm^{-1}$, $\Phi_{(^{\cdot}OH)\ 313\ nm} = 0.013$, $k' = 0.04\ h^{-1}$).[15] These results were directly linked to the production rates of the reactive species ($^{\cdot}OH$ radicals) and the absorption characteristics of the inducer.

3.3.2. Effect of nitrite concentration. The effect of NO_2^- concentration on the photodegradation kinetics was studied. The half-lives shifted from 17.32 to 8.66 h when the NO_2^- concentration decreased from 10 to 1 mM; this behavior indicated that with the highest concentration of inducer, the reagent supplement was used as a scavenger toward the produced $^{\cdot}OH$ radicals (eqn (7)), which limited the expected increase in kinetics. The effect of nitrite as an inducer was also observed at a 10^{-5} M concentration, where 50% of the MN degradation was produced within 34.6 h ($k' = 0.02\ h^{-1}$).

3.3.3. Effect of pH. The effect of pH on nitrite induced photodegradation was studied at a pH range of 2–5. The decrease in pH accelerated the kinetics induced by nitrites: half-lives of 3.44, 4.95 and 6.93 h were obtained at pH 2, 4 and 5, respectively. This phenomenon was due to an increase in the $^{\cdot}OH$ formation and in the more efficient HNO_2 form of the inducer, whose pK_a is 3.37; in addition, the λ_{max} of HNO_2 matched the maximum lamp emission of approximately 365 nm and showed superior quantum yield compared to the NO_2^- species in forming $^{\cdot}OH$ radicals ($\lambda_{max} = 352$ nm, $\varepsilon = 51.9\ M^{-1}\ cm^{-1}$, $\Phi = 0.45$).[20] The NO_2^-–HNO_2 relative quantum yields at 365 nm, lowering the pH, accelerated the photodegradation induced by nitrites.

3.4. Combined NO_3^-–NO_2^- induced degradation

The NO_3^-–NO_2^- induced photodegradation experiments were performed with 1 mM NO_3^-, 1 mM NO_2^-, a mixture of 0.5 mM NO_2^-–0.5 mM NO_3^- and 10^{-4} M MN, which was the same concentration used in other experiments. The k' obtained for the NO_2^- induced photo process was twice more compared to the NO_3^- induced process, and the k' of the mixture was similar to the NO_2^- k' value. Under these conditions, the reactivity of NO_3^- was lower than NO_2^-, and the reactivity of the NO_3^-–NO_2^- system resembled NO_2^- alone, which possibly indicated a slight additive effect (Table 3). The role of NO_2^- should not be neglected because this species is characterized by a higher UV absorbance value and a greater quantum yield for $^{\cdot}OH$ production compared to NO_3^- at 310 nm.[15,16]

## 3.5. Degradation of MN by HNO_2 and H_2O_2 in the dark

Peroxynitrous acid (HOONO) is formed through the reaction of superoxide and nitric oxide, from HNO_2 with H_2O_2, and as an intermediate in the oxidation of nitrites to nitrates with hydrogen peroxide in acidic media. Peroxynitrous acid is an isomer of nitric acid ($pK_a = 6.8$), and it is a strong oxidant, which easily

oxidizes and nitrates organic compounds in aqueous solutions.[22,31]

$$HNO_2 + H_2O_2 \rightarrow HOONO + H_2O \qquad (14)$$

$$HOONO \rightleftharpoons [\cdot OH + \cdot NO_2]_{cage} \rightleftharpoons \cdot OH + \cdot NO_2 \qquad (15)$$

The MN transformation reaction occurred at ambient temperature under acidic conditions in the presence of peroxynitrous acid. MN reacts with $\cdot OH$ to form hydroxylated products or with $\cdot NO_2$ to form nitrated products. Some main intermediate products were detected and identified as well as their formation rates, which increased with decreasing pH in the presence of $HNO_2 + H_2O_2$ in the dark and reflected the formation rate of HOONO. The MN did not react with H_2O_2 alone in the dark without HNO_2.

At pH = 4.0, the reaction rate of MN transformation was much slower (Fig. 3), which was most likely due to the slower
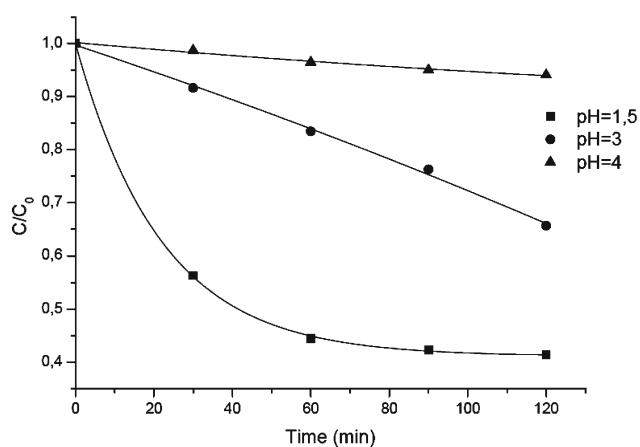
Fig. 3 Time evolution of MN (10^{-4} M) in the presence of NaNO₂ (1 mM) and H₂O₂ (1 mM) at various acidic pH values (adjusted by HClO₄).

formation rate of HOONO.[32] Compared to catechol and 1-naphthol, MN was not nitrated or hydroxylated by HNO₂ in the dark.[33] This suggests that the OH group was necessary for the oxidation and nitration by HNO₂. HOONO is an important oxidizing and nitrating agent.

3.6. Analytical study

The present work focused on the identification of the by-products obtained by the reaction of phenylurea herbicides induced by nitrate, which has been discussed in several publications.[11,26,34] The principal objective of this study was to provide a detailed description of a mechanism to clearly understand the degradation pathways of an aromatic compound (MN) with hydroxyls, which usually has anti-pollution effects. To our knowledge, the transformation of MN in the presence of HOONO has not been subjected to photochemical studies. The transformation intermediates for the degradation of MN were identified.

The by-products were characterized by mass spectrometry and compared to others obtained in previous studies of the phenylurea group transformation through the advanced oxidation processes (AOPs)[7,9,10] or NO₃⁻ and NO₂⁻ induced photodegradation.[26,34,35] Mass spectral data for the photodegradation of MN in the presence of NO₃⁻ or with HNO₂ and H₂O₂ in the dark analyzed by GC-MS are presented in Scheme 1 and Table 4.

3.7. Reactional pathways

When MN was degraded by NO₃⁻ and HOONO, numerous products appeared. The elucidated structures were acquired from the molecular mass of the major fragment peaks in the spectra. The data analysis revealed four reactions that primarily involved the following: (1) hydroxylation on the methyl group or the aromatic ring, (2) oxidation of the N-terminus group, (3) Cl/OH substitution, and (4) nitration resulting from the reaction of the nitrogen species to the phenyl ring (Scheme 2).
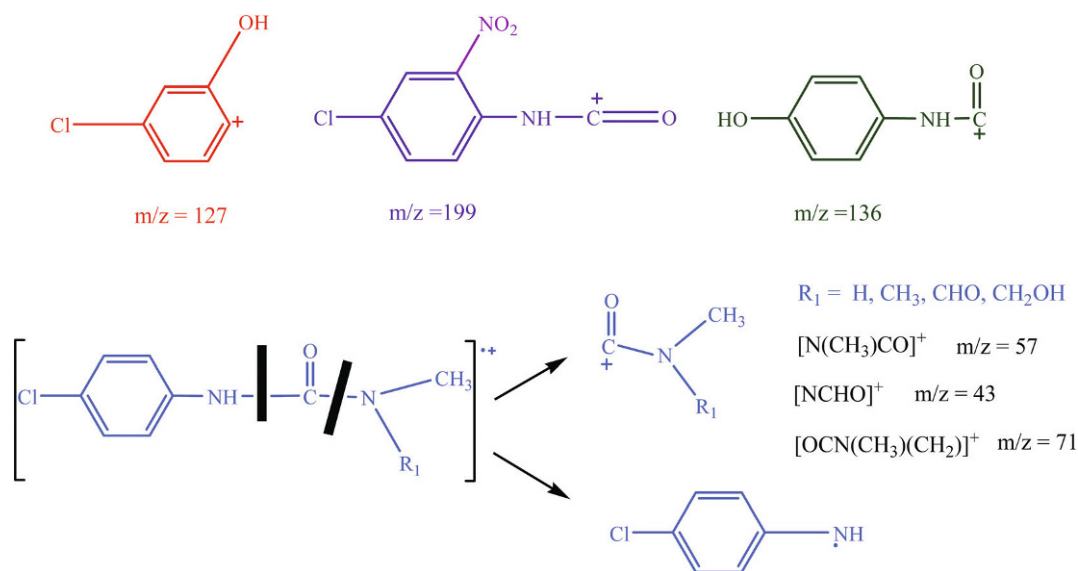
Scheme 1 Main fragments of by-products.

In this study, the P3 and P14 by-products were assumed to originate from the OH radical attack. Furthermore, the aromatic ring of MN was hydroxylated in the experiment to give P6 and P7. The NO_2 su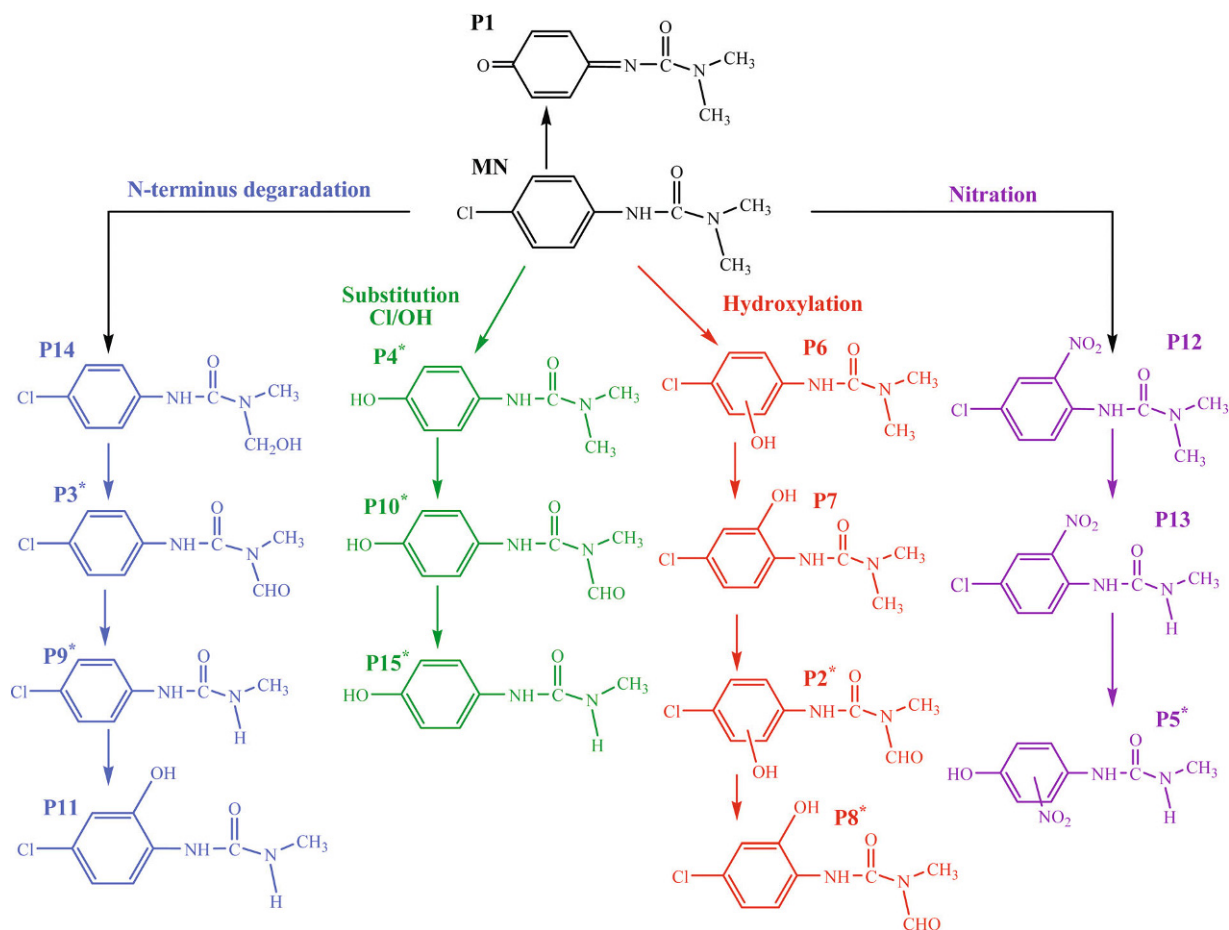bstitution was due to the $^{\cdot}NO_2$, which produced the nitrated derivatives. All these by-products (P3, P14, P6 and P7) had been previously observed under other $^{\cdot}OH$ generating processes (AOP), such as in the O_3/H_2O_2 or Fenton reactions.[9] The Cl/OH substitution might occur either by a $^{\cdot}OH$-mediated reaction or by photolysis. The P1 compound must have originated from a carbene, as has been suggested in previous studies.[4]

4. Conclusion

MN was efficiently photodegraded in the presence of NO_3^- and NO_2^-. The reactions followed pseudo-first order kinetics and depended on several parameters, such as the concentration of MN, the inductor, oxygen, salts, HA, and pH, which indicated the importance of these parameters in risk assessment. Numerous intermediary by-products were characterized using GC-MS. The MN primarily underwent oxidation reactions *via* hydroxyl radicals produced during the nitrate photolysis. The nitration was a minor pathway, and the substitution of chlorine by $^{\cdot}OH$ was also observed. HOONO could induce oxidation, hydroxylation and nitration processes with MN in the dark, and the formation of the by-products was favored by decreasing pH. These reactions can take place in natural waters containing nitrate, nitrite, and a combination of nitrite with oxidants in acidic water. It is necessary to study the toxicity of MN's by-products in water because the nitration reactions can lead to mutagenic compounds.

Table 4 Mass spectral data for the photodegradation of MN in the presence of NO_3^- or with HNO_2 and H_2O_2 in the dark analyzed by GC-MS

Compound	Mol. wt.	R_t (min)	m/z Ratios of main mass (MS) fragments
P1	178	11.0	177, 161, 146, 105, 91, 77
P2	228	12.9	226, 155, 141, 127/129, 113, 85, 57
P3	212	13.5	212, 197, 183, 169, 153/155, 127, 57
P4	180	14.1	180, 165, 151, 137, 57
P5	225	14.6	223, 206, 177, 149, 135, 121, 91
P6	214	16.0	214, 180, 149, 137, 111/113, 43
P7	214	16.1	214, 181, 111/113, 97, 57
P8	228	16.2	227, 199, 171, 143, 127/129, 74
P9	184	16.5	183, 152, 168, 111/113, 71, 57
P10	194	17.2	192, 177, 161, 135, 120, 91
P11	200	18.1	199, 185, 141/143, 129, 74, 57, 43
P12	243	18.4	241, 196, 168, 111/113, 71, 57
P13	229	19.3	229, 199, 153/155, 127, 74, 46
P14	214	19.5	214, 200, 185, 111/113, 71, 43
MN	198	19.8	196, 125/127, 161, 155, 57
P15	166	21.4	167, 149, 132, 57, 43

Scheme 2 Degradation pathways of monuron photo-induced by NO_3^-* by-products obtained in the dark (MN with HNO_2 and H_2O_2).

References

1 J. W. Eichelberger and J. J. Lichtenberg, Persistence of pesticide in river water, *Environ. Sci. Technol.*, 1971, **5**, 541–544.

2 K. H. Chan and W. Chu, Riboflavin-sensitized photooxidation of phenylurea herbicide monuron in aqueous peroxide solution, *Chem. Eng. J.*, 2009, **152**, 103–109.

3 D. G. Crosby and C. S. Tang, Photodecomposition of 3-(*p*-chlorophenyl) 1,1dimethylurea (monuron), *J. Agric. Food Chem.*, 1969, **17**, 1041–1044.

4 A. Boulkamh and C. Richard, Photochemical transformation of aqueous *para* palogenophenylureas: evidence for the intermediary formation of carbenes, *New J. Chem.*, 2000, **24**, 849–851.

5 H. Mešt'ánková, J. Krýsa, J. Jirkovský, G. Mailhot and M. Bolte, The influence of Fe(III) speciation on supported TiO$_2$ efficiency: example of monuron photocatalytic degradation, *Appl. Catal., B: Environ.*, 2005, **58** (3–4), 185–191.

6 M. A. Oturan, M. C. Edelahi, N. Oturan, K. El Kacemi and J. J. Aaron, Kinetics of oxidative degradation/mineralization pathways of the phenylurea herbicides diuron, monuron and fenuron in water during application of the electro-Fenton process, *Appl. Catal., B: Environ.*, 2010, **97**, 82–89.

7 H. Mešt'ánková, G. Mailhot, J. F. Pilichowski, J. Krýsa, J. Jirkovský and M. Bolte, Mineralisation of monuron photoinduced by Fe(III) in aqueous solution, *Chemosphere*, 2004, **57**, 1307–1315.

8 C. Richard, D. Vialaton, J. P. Aguer and F. Andreux, Transformation of monuron photosensitised by soil extracted humic substances: energy or hydrogen transfer mechanism, *J. Photochem. Photobiol., A: Chem.*, 1997, **111**, 265–271.

9 L. Amir Tahmasseb, S. Nélieu, L. Kerhoas and J. Einhorn, Ozonation of chlorophenylurea pesticides in water: reaction monitoring and degradation pathways, *Sci. Total Environ.*, 2002, **291**, 33–44.

10 M. Bobu, S. Wilson, T. Greibrokk, E. Lundanes and I. Siminiceanu, Comparison of advanced oxidation processes and identification of monuron photodegradation products in aqueous solution, *Chemosphere*, 2006, **63**, 1718–1727.

11 M. V. Shankar, S. Nélieu, L. Kerhoas and J. Einhorn, Natural sunlight NO$_3^-$/NO$_2^-$ induced photo-degradation of phenylurea herbicides in water, *Chemosphere*, 2008, **71**, 1461–1468.

12 S. Nélieu, L. Kerhoas, M. Sarakha and J. Einhorn, Nitrite and nitrate induced photodegradation of monolinuron in aqueous solution, *Environ. Chem. Lett.*, 2004, **2**, 83–87.

13 J. Mack and J. R. Bolton, A review, photochemistry of nitrite and nitrate in aqueous solution, *J. Photochem. Photobiol., A: Chem.*, 1999, **128**, 1–13.

14 P. Warneck and C. Wurzinger, Product quantum yields for the 305 nm photodecomposition of NO$_3^-$ in aqueous solution, *J. Phys. Chem.*, 1988, **92**, 6278–6283.

15 R. G. Zepp, J. Hoigné and H. Bader, Nitrate-induced photooxidation of trace organic chemicals in water, *Environ. Sci. Technol.*, 1987, **21**, 443–450.

16 O. C. Zafiriou and R. Bonneau, Wavelength-dependent quantum yield of OH radical formation from photolysis of nitrite ion in water, *J. Photochem. Photobiol., A: Chem.*, 1987, **45**, 723–727.

17 A. Alif and P. Boule, Photochemistry and environment part XIV. Phototransformation of nitrophenols induced by excitation of nitrite and nitrate ions, *J. Photochem. Photobiol., A: Chem.*, 1991, **59**, 357–367.

18 J. Fulkerson Brekken and P. L. Brezonik, Indirect photolysis of acetochlor: rate constant of a nitrate-mediated hydroxyl radical reaction, *Chemosphere*, 1998, **36**, 2699–2704.

19 D. Vione, V. Maurino, C. Minero and E. Pelizzetti, Reactions induced in natural waters by irradiation of nitrate and nitrite ions, in *The Handbook of Environmental Chemistry Vol. 2-M (Environmental Photochemistry Part II)*, ed. P. Boule, D. W. Bahnemann and P. K. J. Robertson, Springer, Berlin, 2005, pp. 221–253.

20 M. Fischer and P. Warneck, Photodecomposition of nitrite and undissociated nitrous acid in aqueous solution, *J. Phys. Chem.*, 1996, **100**, 18749–18756.

21 D. Vione, V. Maurino, C. Minero and E. Pelizzetti, Phenol nitration upon oxidation of nitrite by Mn(III,IV) (hydr)oxides, *Chemosphere*, 2004, **55**, 941–949.

22 D. Vione, V. Maurino, C. Minero, M. Lucchiari and E. Pelizzetti, Nitration and hydroxylation of benzene in the presence of nitrite/nitrous acid in aqueous solution, *Chemosphere*, 2004, **56**, 1049–1059.

23 M. M. Haque and M. Muneer, Heterogeneous photocatalysed degradation of a herbicide derivative, isoproturon in aqueous suspension of titanium dioxide, *J. Environ. Manage.*, 2003, **69**, 169–176.

24 P. Boule, L. Meunier, F. Bonnemoy, A. Boulkamh, A. Zertal and B. Lavedrine, Direct phototransformation of aromatic pesticides in aqueous solution, *Int. J. Photoenergy*, 2002, **4**, 69–78.

25 A. Amine-Khodja, A. Boulkamh and P. Boule, Photochemical behaviour of phenylurea herbicides, *Photochem. Photobiol. Sci.*, 2004, **3**, 145–156.

26 S. Nélieu, L. Kerhoas, M. Sarakha, J. Einhorn and J. Einhorn, Phototransformation of monuron induced by nitrate and nitrite ions in water: contribution of photonitration, *J. Photochem. Photobiol., A. Chem.*, 2008, **193**, 1–9.

27 P. Neta, R. E. Huie and A. B. Ross, Rate constants for reactions of inorganic radicals in aqueous solution, *J. Phys. Chem. Ref. Data*, 1988, **17** (3), 1027–1284.

28 R. Das, B. K. Dutta, V. Maurino, D. Vione and C. Minero, Suppression of inhibition of substrate photodegradation by scavengers of hydroxyl radicals: the solvent-cage effect of bromide on nitrate photolysis, *Environ. Chem. Lett.*, 2009, **7**, 337–342.

29 W. J. Cooper, R. G. Zika, R. G. Petasne and A. M. Fischer, Sunlight-induced photochemistry of humic substances in natural waters: major reactive specie, *Adv. Chem. Ser.*, 1989, **219**, 333–362.

30 P. L. Brezonik and J. Fulkerson-Brekken, Nitrate-induced photolysis in natural waters: controls on concentrations of hydroxyl radical photo-intermediates by natural scavenging agents, *Environ. Sci. Technol.*, 1998, **32**, 3004–3010.

31 V. Anan'ev and M. Miklin, The peroxynitrite formation under photolysis of alkali nitrates, *J. Photochem. Photobiol., A Chem.*, 2005, **72**, 289–292.

32 D. Vione, V. Maurino, C. Minero, D. Borghesi, M. Lucchiari and E. Pelizzetti, New processes in the environmental chemistry of nitrite 2. The role of hydrogen peroxide, *Environ. Sci. Technol.*, 2003, **37**, 4635–4641.

33 C. Minero, F. Bono, F. Rubertelli, D. Pavino, V. Maurino, E. Pelizzetti and D. Vione, On the effect of pH in aromatic photonitration upon nitrate photolysis, *Chemosphere*, 2007, **66**, 650–656.

34 M. V. Shankar, S. Nélieu, L. Kerhoas and J. Einhorn, Photo-induced degradation of diuron in aqueous solution by nitrites and nitrates: kinetics and pathways, *Chemosphere*, 2007, **66**, 767–774.

35 P. Patnaik and J. N. Khoury, Reaction of phenol with nitrite ion: pathways of formation of nitrophenols in environmental waters, *Water Res.*, 2004, **38**, 206–210.