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Phototransformation of monuron induced by nitrate and nitrite ions in water: Contribution of photonitration

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Abstract

The nitrate and nitrite-induced phototransformation of monuron in aqueous solution has been investigated using 300–450 nm light irradiation. The degradation kinetics was estimated under various conditions of concentrations of substrate and inducer, oxygen content and pH. From the numerous photoproducts identified using LC–ESI-MS–MS and their evolution curves a degradation scheme was proposed. Besides oxidation of the N-terminus group (major pathway in the presence of NO_3^-) and a minor contribution of direct photolysis, the other photoproducts originated from Cl/OH substitution, regiospecific hydroxylation and/or nitration of the phenyl ring. The two last processes occurred competitively under the NO_3^- conditions even at “environmental” concentrations of the inducer yielding significant levels of nitro-derivatives. Their production was found to be oxygen-dependent in contrast to the NO_2^- conditions.

Keywords: Monuron; Nitrate; Nitrite; Induced phototransformation; Photonitration

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1. Introduction

Substituted phenylureas constitute a group of herbicides widely used for general weed control of non-crop area and as pre-emergence treatment on cereals and vegetable crops. Due to their persistence (*ca.* weeks or months) they represent a risk of contamination for natural waters. It is further admitted that transformation products have now to be considered for risk assessment which give rise to an increasing amount of studies. This work is focused on the induced photodegradation of monuron used herein as a representative model due to its known characteristics in water and soil [1,2] and relatively simple structure. Such process is supposed to be competitive with biodegradation [3], whereas hydrolysis, another abiotic event, is unlikely to take place under environmental conditions [4].

Direct photolysis of monuron has been studied in water under UV, solar and simulated solar irradiations. The absorption spectrum of monuron shows a maximum at 245 nm (ε 17,800 L mol^{-1} cm^{-1}) and a weak band at 280 nm. The small overlap with sunlight spectrum ($\lambda > 300$ nm) may lead to a weak degradation [5]. Under UV and low substrate concentration, the main photoproduct results from the substitution of chlorine by a hydroxyl group [6], whereas biphenyl derivatives can be formed at high concentration [7]. The N-terminal substituent may be oxidised to some extent to give demethylation and intermediates. In some conditions the C–Cl bond can be reduced particularly in the presence of methanol or surfactants [8,9].

The photodegradation of monuron can also be induced by photocatalysis, iron salts or humic substances. The heterogeneous TiO_2 photocatalysis is known to proceed through the generation of $^{\bullet}OH$ radicals and positive holes (h^+) on the semiconductor surface. In the case of monuron, this process leads to the formation of *N*-demethylated products, chlorophenyl-isocyanate, chlorophenols, chloroaniline and finally mineralization [10,11]. In the presence of aqueous iron(III) species (particularly $Fe(OH)^{2+}$) which also produce $^{\bullet}OH$ radicals, monuron was shown to undergo mineralization as well [12]. Humic and fulvic acids can induce the degradation of the pesticide through energy transfer (sensitization) or hydrogen atom transfer from their excited triplet states [13]. Both these reactions yield Cl/OH substitution. Nitrates have also been shown to induce photodegradation of phenylureas [14,15]. But no study on the fate of monuron has been reported in this context.

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Sunlight irradiation of nitrate ions, which are often present in natural waters, gives rise to the reactive $^{\bullet}OH$ radicals, and to $NO_2^{\bullet}$ and N_2O_4 species through reactions (1)–(4) [16,17]. The nitrite ions resulting from reaction (3) or from the photodegradation of humic substances [18] are usually present too, but at lower concentrations. However, NO_2^- can absorb solar radiation more efficiently (NO_2^-: λ_{max} 352 nm, ε 22 L mol^{-1} s^{-1} *versus* NO_3^-: λ_{max} 302 nm, ε 7 L mol^{-1} s^{-1}) and produce subsequently reactive species (Eqs. (5)–(8)) with higher quantum yields [19]. Conversely, NO_2^- can also be regarded as a scavenger towards hydroxyl radicals (Eq. (9)).

$$NO_3^- + h\nu \rightarrow {}^{\bullet}NO_2 + O^{\bullet -}$$
$$[\Phi_1\,(305\text{–}313\,\text{nm}) = (0.009\text{–}0.017)] \qquad (1)$$

$$O^{\bullet -} + H^+ \leftrightarrows {}^{\bullet}OH \qquad [pK_a = 11.9] \qquad (2)$$

$$NO_3^- + h\nu \rightarrow NO_2^- + O(^3P) \qquad [\Phi_2\,(305\,\text{nm}) = 0.001] \qquad (3)$$

$${}^{\bullet}NO_2 + {}^{\bullet}NO_2 \rightarrow N_2O_4 \qquad [k = 4.5 \times 10^8\,\text{L mol}^{-1}\,\text{s}^{-1}] \qquad (4)$$

$$NO_2^- + h\nu \rightarrow {}^{\bullet}NO + O^{\bullet -} \qquad [\Phi_3\,(355\,\text{nm})\,0.02\text{–}0.07] \qquad (5)$$

$$NO_2^- + h\nu \rightarrow {}^{\bullet}NO_2 + e^-_{aq} \qquad [\Phi_4\,(355\,\text{nm})\,0.076] \qquad (6)$$

$$e^-_{aq} + O_2 \rightarrow O_2^{\bullet -} \qquad [k = 1.9 \times 10^{10}\,\text{L mol}^{-1}\,\text{s}^{-1}] \qquad (7)$$

$$O_2^{\bullet -} + NO_2^- + 2H^+ \rightarrow H_2O_2 + {}^{\bullet}NO_2$$
$$[k = 5 \times 10^6\,\text{L mol}^{-1}\,\text{s}^{-1}] \qquad (8)$$

$${}^{\bullet}OH + NO_2^- \rightarrow {}^{\bullet}NO_2 + OH^-$$
$$[k = 1.0 \times 10^{10}\,\text{L mol}^{-1}\,\text{s}^{-1}] \qquad (9)$$

The $^{\bullet}NO_2$ radicals may thus result from various routes (Eqs. (1), (6) and (9)) and at a lesser extent from Eqs. (10) and (11). Their production may be limited by radical duplication (Eqs. (4) and (13)) or inhibited by oxygen (reaction (12) with $O_2^{\bullet -}$ issuing from (7)):

$$2{}^{\bullet}NO + O_2 \rightarrow 2{}^{\bullet}NO_2 \qquad [2k = 4.2 \times 10^6\,\text{L}^2\,\text{mol}^{-2}\,\text{s}^{-1}] \qquad (10)$$

$$NO_3^- + {}^{\bullet}NO \rightarrow {}^{\bullet}NO_2 + NO_2^-$$
$$[k \leq 4 \times 10^4\,\text{L mol}^{-1}\,\text{s}^{-1}] \qquad (11)$$

$${}^{\bullet}NO_2 + O_2^{\bullet -} \rightarrow NO_2^- + O_2$$
$$[k = 4.5 \times 10^9\,\text{L mol}^{-1}\,\text{s}^{-1}] \qquad (12)$$

$${}^{\bullet}NO_2 + {}^{\bullet}NO\,(+H_2O) \rightarrow 2NO_2^- + 2H^+$$
$$[k = 1.6 \times 10^8\,\text{L mol}^{-1}\,\text{s}^{-1}] \qquad (13)$$

Hence, the aim of the present study was to determine the kinetics and pathways of monuron photodegradation induced by nitrate and nitrite ions in water. A special attention was given to the relative reactivity of $^{\bullet}OH$ *versus* $^{\bullet}NO_2$ or $^{\bullet}NO$ through examination of the proportions between their respective products in function of environmental factors.

2. Experimental

2.1. Chemicals

Monuron (3-(4-chlorophenyl)-1-1-dimethylurea, 99.5%) was purchased from Cluzeau-Info-Labo (Ste Foy-la-Grande, France). Sodium nitrate and sodium nitrite (ACS reagent grade) were obtained from Sigma–Aldrich (St Quentin Fallavier, France). HPLC plus grade acetonitrile and RPE methanol were purchased from Carlo Erba (Val-de-Reuil, France). LC-grade water was prepared by purification of reverse osmosis water in an Elgastat UHP system (Elga, High Wycombe, UK). Monuron aqueous solutions were prepared by ultra-sound activated dissolution, followed by filtration through 0.45 μm membrane (Millipore, St Quentin-en-Yvelines, France). When necessary, pH was adjusted by addition of dilute solutions of sulphuric acid or sodium hydroxide (VWR, Fontenay-sous-Bois, France).

2.2. Irradiations

Polychromatic irradiations were performed using a cylindrical device equipped with six lamps (TLD 15 W, Philips) emitting within 300–450 nm with a maximum emission at 365 nm. Light intensity measured by a radiometer (Vilber Lourmat, Marne la Vallée, France) at 312 and 365 nm was 0.18 and 2.4 mW cm^{-2}, respectively. A cooling fan was fitted at the bottom of lamp house to eliminate excess heat. The test solution (300 mL) containing the pesticide and spiked with freshly prepared nitrite/nitrate was placed in a 3 cm i.d. tubular Pyrex reactor at the centre of the lamp housing, with open-top access for sampling. The solution was thoroughly mixed with gas sparging (150 mL min^{-1}). Pure oxygen or nitrogen gas was used as an alternative to air (purging from 20 min before starting irradiation to the end). Samples (1 mL) were taken at selected intervals during the irradiation and analysed by HPLC.

Direct photolysis was performed using 60 mL aqueous solution of the pesticide in a 2 cm i.d. quartz tube, under magnetic stirring and with gas purging as previously. The reactor was positioned parallel to a monochromatic 254 nm low-pressure mercury lamp (germicide TUV 15 W, Philips) with an incident photon flow evaluated as 2.6×10^{15} photons cm^{-2} s^{-1} by ferrioxalate actinometry [20]. Monuron quantum yield and evolution of UV spectrum were determined by irradiation in a 1 cm path length quartz cell with a 6 W low-pressure mercury lamp (Philips) equipped with a metallic cover to allow parallel beam along the 5 cm distance between lamp and cell (incident photon flow 3.7×10^{14} photons cm^{-2} s^{-1}).

2.3. Analytical determinations

Analysis of monuron and its photoproducts was performed by HPLC using a Waters system (600 MS pump equipped with automatic injector 717 and photodiode array UV-detector