

# Comparison of monuron and isoproturon photodegradation processes in absence and in the presence of nitrate and nitrite in aqueous solution

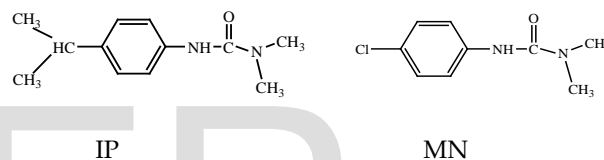
Hadjira Boucheloukh<sup>1,2</sup>, Wassila Remache<sup>1</sup>, Tahar Sehili<sup>1</sup>, Nadia Kouachi<sup>1</sup>

**Abstract**-The photodegradation of two phenylurea herbicides monuron 3-(4-chlorophenyl)-1,1 dimethylurea and isoproturon (3-(4-isopropylphenyl)-1,1 dimethylurea) in an aqueous solutions containing nitrates ( $10^{-3}$  M) and nitrites ( $10^{-3}$  M), using irradiation at 310 nm and at 365 nm respectively is investigated. In both cases MN ( $10^{-4}$  M) and IP ( $10^{-4}$  M) photodegradation followed pseudo-first order kinetics. The kinetics of monuron and isoproturon are accelerated in the presence of nitrates and nitrites. The major photodecomposition products from IP photolysis are detected through GC-MS, formed mainly through oxidation of the N-terminus group, deisopropylation are observed with isoproturon. Hydroxylation of the phenyl ring is observed with two herbicides.

**Keywords**- Isoproturon, Monuron, Nitrate, Nitrite, Photodegradation

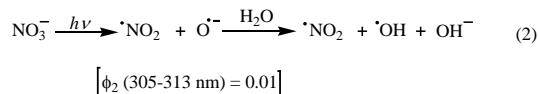
## 1 Introduction

The 3-(4-isopropylphenyl)-1, 1-dimethylurea called isoproturon (IP) and 3-(4-chlorophenyl)-1,1 dimethylurea called monuron (MN) were two herbicides non-biodegradable, used in agriculture (Fig.1). They cause harm and cancer [1, 2]. Due to Their solubility in water, it is often found in contaminated ground water, surface water and effluents of wastewater treatment plants [3]. Several authors have investigated the photodegradation of isoproturon and monuron in aqueous solution [4, 5], direct photolysis of monuron in water under solar and UV irradiations [6]. Photocatalytic degradation with TiO<sub>2</sub> [7], ozonation [8], and mineralization photoinduced by Fe(III) in aqueous solution [9, 10]. Different analytical methods were used to identify the different photoproducts and to propose a mechanism of phototransformation [8, 11]. Photocatalytic treatment and mineralization of isoproturon was very efficient in the destruction of isoproturon herbicide [12, 13].



Scheme 1. Structure of isoproturon and monuron

Nitrate ions are usually present in natural waters, their absorption spectra in aqueous solutions contain weak bands at  $\lambda_{\max}$  302 nm ( $\epsilon = 7.2 \text{ M}^{-1} \text{ cm}^{-1}$ ); and their photolysis results in two main processes [14]:



Due to the generation of hydroxyl radicals (powerful oxidant) and nitrogen dioxide;  $\text{NO}_3^-$  lead to the degradation of organic compounds, and could also induce the formation of nitro derivatives [15].

Nitrite ions that are obtained by photolysis of nitrate ions and by photodegradation of aquatic humic substances [16] are present in natural water but at lower rate than those of nitrate, their maximum absorption at 352 nm ( $\epsilon = 22 \text{ M}^{-1} \text{ cm}^{-1}$ ) is responsible for the photochemistry of nitrites in the environment. UV

irradiation of  $\text{NO}_2^-$  results in the formation of  $\cdot\text{NO}$  and  $\text{O}^-$  [17, 18].

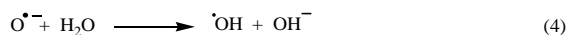
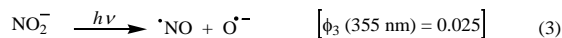
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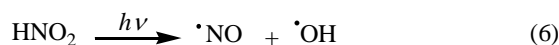


Differently from nitrate, nitrite is a sink for the hydroxyl radicals [19].



$$[k = 1.0 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}]$$

Formation of nitrogen dioxide obtained by oxidation of nitrite by  $\cdot\text{OH}$ , as a consequence the nitration of aromatic compounds is also obtained. Nitrous acid is a source of  $\cdot\text{OH}$  and  $\cdot\text{NO}$  upon photolysis, it is more reactive than nitrite because of a higher quantum yield for  $\cdot\text{OH}$  radicals [18].



$$\phi_6 (352 \text{ nm}) = 0.45$$

The goal of the present paper is to determine the difference between photolysis and photodegradation of monuron and isoproturon in the presence of nitrate and nitrite in aqueous solution.

## 2 Experiments

### 2.1 Chemicals

Deionized water from a Millipores device (Milli-Q) is used in all experiments. IP and MN analytical grade (>99.9% pure) is obtained from Riedel-de Hën.  $\text{KNO}_3$  and  $\text{HClO}_4$  (70%) are obtained from Merk (99%),  $\text{NaNO}_2$  from Prolabo (98%). Both acetonitril and methanol (99.9% Carlo Erba HPLC qualities) are used for chromatography analysis.

### 2.2 Photochemical Reactor

Devices used for irradiation at 310 nm are equipped with 6 lamps (Duke Sun Lamp GL 20 W). The reactor in cylindrical Pyrex glass (2 cm i.d), containing 100 mL of aqueous solution, and the temperature of samples did not exceed 20°C using tap-water cooling circuit for the UV-reactor. For irradiation of nitrite ions at 365 nm three HPW black light 125 W Philips lamps with a maximum emission at 365 nm are used. Cooling fan is fitted above the device to eliminate excess heat (3 cm i.d, 50 mL). For HPLC analysis, samples (1 mL) are taken before in regular intervals during the irradiation; followed by filtration through 0.45  $\mu\text{m}$  filters (Millipore).

## 2.3 Analyses

The analysis of the photodegradation kinetics is performed by using a Shimadzu HPLC-UV, a photodiode array UV detector programmable at a wavelength of 240 nm for isoproturon and at 244 nm for monuron, using C18 reverse phase column SupercosilTM LC-18 (250  $\times$  4.6 mm), and mobile phase Acetonitril/Water (1:1 v/v) at a flow rate of 1 mL.min<sup>-1</sup> for isoproturon and methanol /water (1:1 v/v) at a flow rate of 1 mL. min<sup>-1</sup> for monuron. For GC-MS analysis, after irradiation during several hours, the solutions are acidified with  $\text{HClO}_4$  (pH  $\leq$  2), extracted with diethyl ether and concentrated under a gentle stream of high purity nitrogen, then dried with anhydrous  $\text{Na}_2\text{SO}_4$ . A GC-MS, QP 2010 Shimadzu instrument equipped with a capillary column CP-SE30 (25 m  $\times$  0.25 mm  $\times$  0.25  $\mu\text{m}$ ), a trace GC 2010 gas chromatograph and GCQ plus ion trap mass spectrometer, is used for the identification under the following chromatographic conditions: an injector temperature 250 °C, oven temperature program 70°C (3 min), a gradient temperature of 5°C/min remaining at 280 °C for 5 min. Helium is used as the carrier gas at 0.76 mL/min and a manual splitless injection (1 $\mu\text{L}$ ).

## 3 Results and discussion

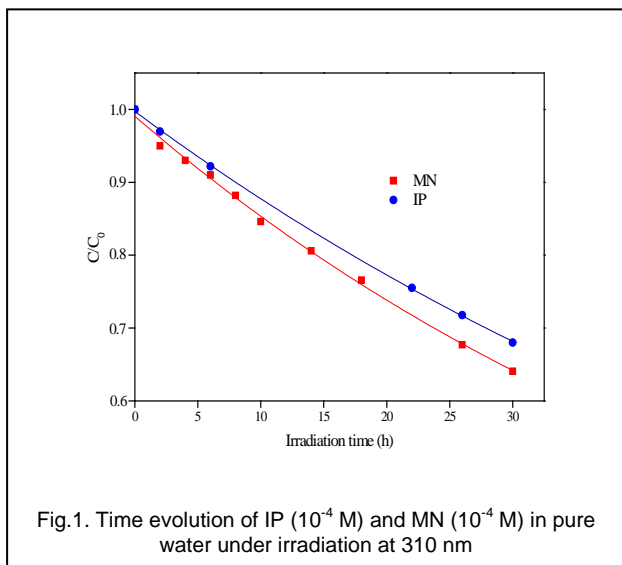
### 3.1 Direct Photolysis of phenylureas

#### 3.1.1 Kinetic study

The direct photolysis of IP and MN were previously studied by several authors [6, 20-22]. A test is realized qualitatively at the darkness to show that the irradiation is the principal factor of the evolution of the solution containing IP and MN. The direct photolysis is generally occurred when the substrate absorb solar light characterized by the wavelengths higher than 300 nm. Loss of IP (10<sup>-4</sup> M) and MN (10<sup>-4</sup> M) in aired pure aqueous solutions when irradiated at 310 nm is found to be very slowly photolysis. The variation of IP and MN concentration with reaction time is measured by HPLC, to determine rate

constants, we plotted  $\ln C_0/C$  vs irradiation time, where  $C_0$  is the initial concentration of IP and MN respectively and C the concentration at time t. IP and MN consumption followed pseudo first order

kinetics and rate constant are near ( $k_{IP'} = 0.0134 \text{ h}^{-1}$ ,  $t_{1/2} = 51.72 \text{ h}$  and  $k_{MN'} = k' = 0.0137 \text{ h}^{-1}$ ,  $t_{1/2} = 50.59 \text{ h}$ ) with  $R^2 = 0.99$ .



During the irradiation of isoproturon solutions several photoproducts could be detected by HPLC; six are identified using GC-MS arising from ring oxidation or elimination of N-methyl or isopropyl groups (Table 1).

The identified 4-isopropylphenylisocyanate (P1) has the same spectra compared with library mass spectra; appears at major byproduct. It is obtained by the cleavage of the terminal amine group  $-N(\text{CH}_3)_2$  followed by loss of an H atom to yield an isocyanate. The mono-hydroxylated byproduct P4 has molecular weight 222 amu obtained by addition of oxygen atom to IP. The intermediate P2 and P3 are forming due to successive oxidation of IP. The examination of mass spectra of P5 reveals the presence of peaks at  $m/z = 49 [M-1]$  and at  $m/z = 57$  showing that photodegradation transformation also yields IP demethylation and deisopropylation successively, but this pathway is very minor (Fig.2). The product of photorearrangement does not appear among the identified photoproducts because it involves excitation in a  $\pi-\pi^*$  band and usually requires approximately 250 nm photon energy, explained by the effect of wavelengths [24].

### 3.1.2 Analytical study

#### a) Photolysis of Isoproturon

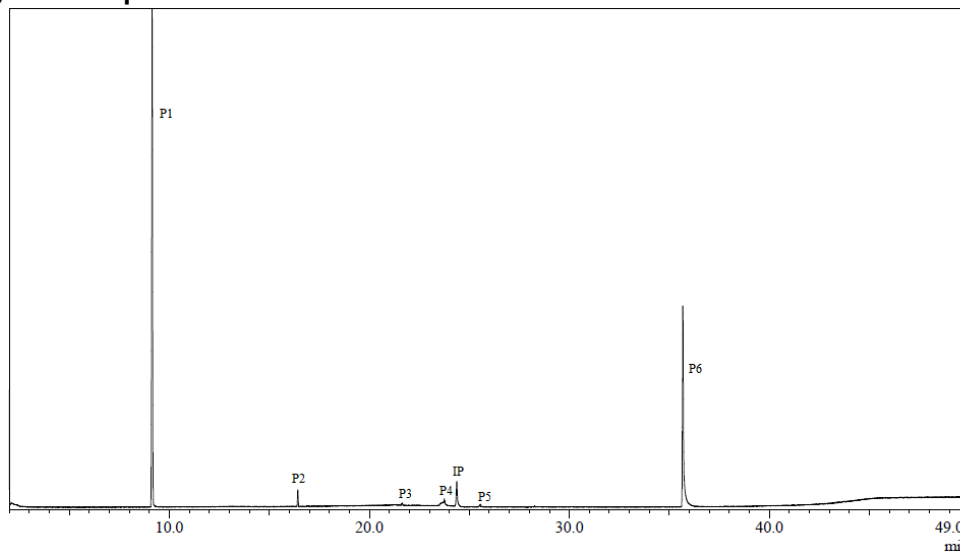
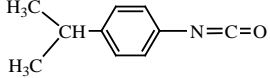
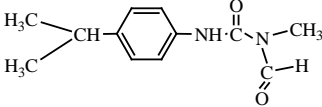
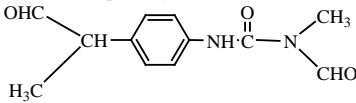
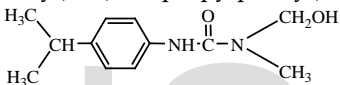
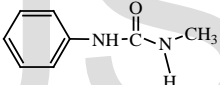
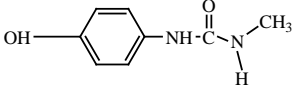
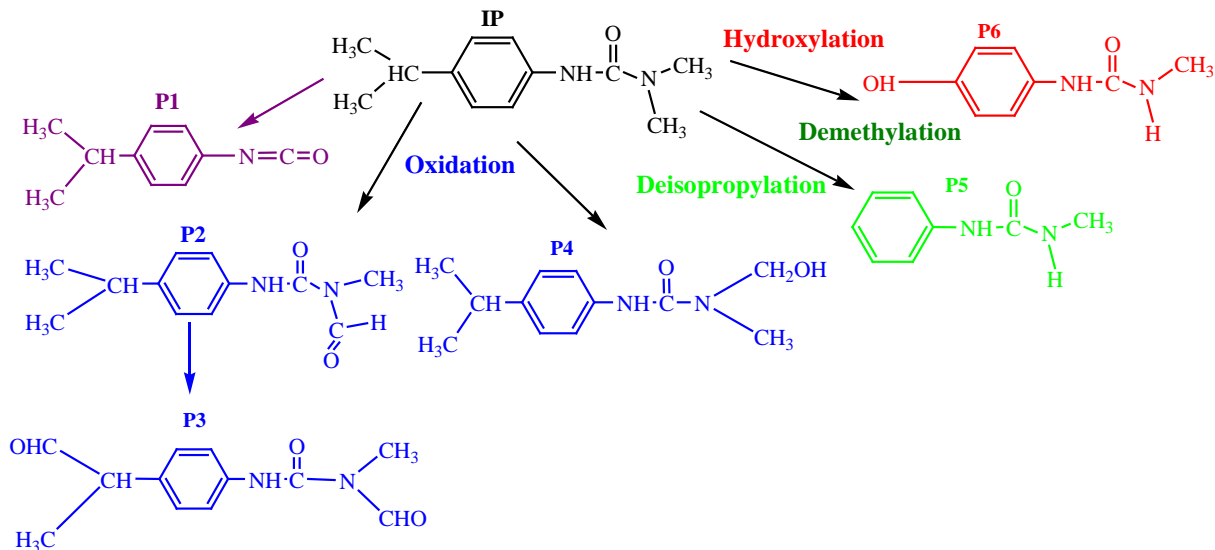


Fig.2 Chromatogram GC-MS obtained by direct photolysis of IP ( $10^{-4} \text{ M}$ ) irradiated during 58 h in aqueous solution

**Table 1**  
 Mass spectral data for the photolysis by-products of IP, analyzed by GC-MS

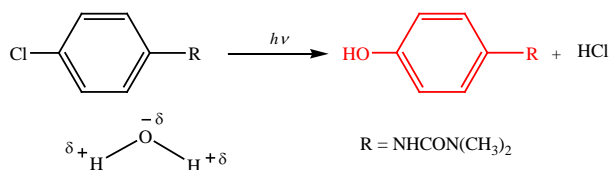
NO.	Name and structure	M. wt	Rt (min)	m/z ratios
P1	1-isocyanato-4-isopropylbenzene 	161	9.1	161, 146, 128, 91
P2	1-formyl-3-(4-isopropylphenyl)-1-methylurea 	220	16.4	220, 205, 145, 177
P3	1-formyl-1-methyl-3-(4-(1-oxopropan-2-yl)phenyl)- urea 	234	21.6	234, 219, 191, 161
P4	1-(hydroxymethyl)-3-(4-isopropylphenyl)-1- methylurea 	222	23.8	223, 149, 104, 57
P5	1-methyl-3-phenylurea 	150	25.6	149, 57, 41
P6	1-(4-hydroxyphenyl)-3-methylurea 	166	35.7	167, 149, 113, 71



Scheme 2: Main pathways in the photolysis of IP ( $10^{-4}$  M)

### b) Photolysis of monuron

Several studies had investigated the photolysis of MN in aqueous systems under solar and UV irradiations [6, 7]. In the present study, the photochemical degradation is investigated in order to compare the efficiency of photolysis of MN and IP. Analyses of the photolysis samples of MN ( $10^{-4}$  M) irradiate during 75 hours reveals the presence of only one photoproduct (Fig.3). The formation of hydrolyze products has also been reported, they generally result from the elimination of chlorine atom and the substitution by OH. However, when solution of MN irradiated at 254 nm, the main reaction is observed. The kinetics of photodegradation is influenced by the nature of the ring substituents. Degradation occurs faster with molecules substituted with electron-attractor, such as halogens because the presence of halogen on the aromatic ring introduces a relatively weaker bond that can be easily broken via a heterolytic mechanism.



Scheme 3: Photohydrolysis reaction of MN

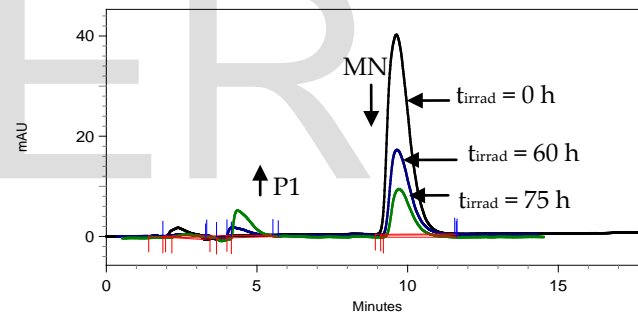


Fig. 3 Chromatogram HPLC-UV obtained by direct photolysis of MN ( $10^{-4}$  M) irradiated during 75 h in an aqueous solution

### 3.2. Photodegradation induced by nitrate ions

In order to understand the role of nitrate ions on photodegradation of IP and MN, a solution of IP ( $10^{-4}$  M) and another solution of MN ( $10^{-4}$  M) are irradiated at 310 nm during several hours in the presence of nitrate ions (1 mM). The data are plotted as the concentration versus irradiation time. Using a software program, the first-order rate constant is determined by least squares fitting of the data to a first-order kinetic equation. Results are presented in Table 2. The two phenylurea herbicides are

found to be photolyzed much more slowly in Milli-Q water than in the presence of nitrate ions. Thus; the

chromophoric constituents of water (nitrate) promotes IP and MN photodegradation.

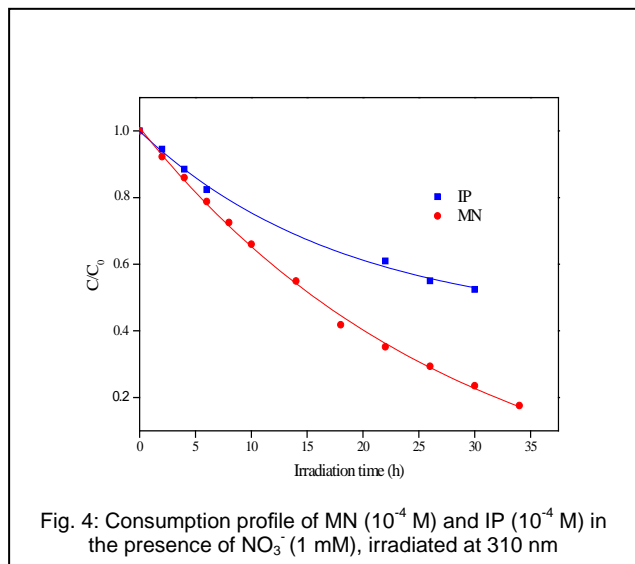


Fig. 4: Consumption profile of MN ( $10^{-4}$  M) and IP ( $10^{-4}$  M) in the presence of  $\text{NO}_3^-$  (1 mM), irradiated at 310 nm

### 3.3 Photodegradation induced by nitrite ions

Under irradiation and without nitrite inducer, phenylureas are not dissociated in aqueous solution this could be due to the phenylureas spectra that show no absorption at 365 nm. In order to examine the effect of nitrite, aqueous solutions of IP and MN ( $10^{-4}$  M) are exposed to irradiation at 365 nm in the presence of nitrites (1mM). Evaluation of rate pseudo-constants  $k'$  is achieved for each herbicide studied under the same conditions. The rate of IP and MN degradation (Fig.5) is observed as pseudo first order kinetics with both herbicides.

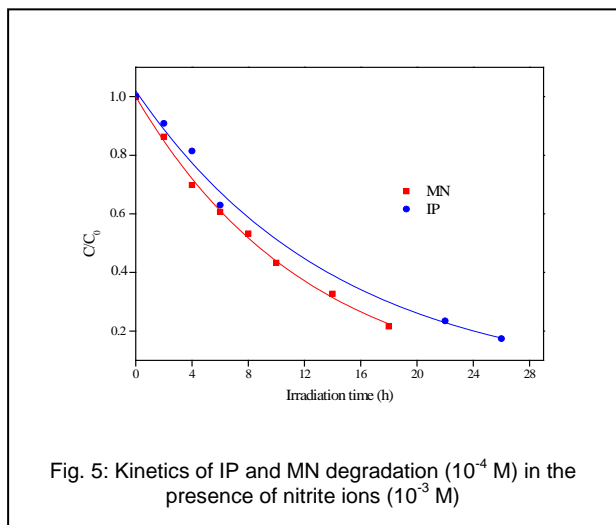


Fig. 5: Kinetics of IP and MN degradation ( $10^{-4}$  M) in the presence of nitrite ions ( $10^{-3}$  M)

Kinetic parameters for the photodegradation of MN and IP in absence and in the presence of nitrates and nitrites

Herbicides	$k'_{\text{Photolyse}} (\text{h}^{-1})$	$k'_{\text{nitrates}} (\text{h}^{-1})$	$k'_{\text{nitrites}} (\text{h}^{-1})$
MN	0.0137	0.04	0.08
IP	0.0134	0.03	0.06

### 3.4 Comparison of phenylureas

The direct photolysis is higher from MN compared to IP. The half time of IP and MN is found to be lower than that at 254 nm ( $k'_{\text{MN}} = 0.147 \text{ min}^{-1}$ ,  $t_{1/2} = 4.7 \text{ min}$  and  $k'_{\text{IP}} = 0.023 \text{ min}^{-1}$ ,  $t_{1/2} = 30 \text{ min}$ ). The low values observed for unhalogenated substrate (IP) indicate the lower photoreactivity of this compound, probably due to the strong bond which characterize the phephylurea herbicides. The analytical study of the photoproducts clearly indicates the influence of the structure on the reactivity of the herbicide; the MN gives rise to a single photoproduct whereas the photolysis of PI leads to several photoproducts. This difference is due to the difference in reactivity of the groups -Cl which are electroattractive and isopropyl at the time of photolysis; that due to the various substituents on the aromatic group, since the phenylurea group is the same. It is noted that the Cl atom would also be more reactive than the isopropyl group under UV and that below 270 nm, the absorption of the MN decreases to low values while that of the IP remains relatively high so that IP compensates low reactivity through better absorption. The half-life values of the MN and IP are 51 hours 52 hours respectively, these values show that the direct photolysis of the two herbicides is very difficult with the monochromatic lamp ( $\lambda = 310 \text{ nm}$ ). The degradation kinetics of MN and IP at 310 nm and at 365 nm increased in the presence of nitrate ions and nitrite ions, respectively. The results obtained show that the degradation kinetics is influenced by the presence of nitrate and nitrite ions in solution. Thus the isoproturon degrades more slowly than the monuron. The kinetic constants determined are very high compared to the direct photolysis and show the great reactivity of these herbicides with hydroxyl radicals. However the photoreactivity of  $\text{NO}_3^-$  is lower than that of  $\text{NO}_2^-$  for two herbicides.

Table 2

## 4 Conclusion

Photochemical behavior of IP and MN under irradiation is under the scope of the present work. Direct photolysis of aqueous IP and MN is slow but photosensitizing by nitrate and nitrite ions processes may promote their transformation in pure water. The observed kinetics never yields half-lives exceeding 100 hours. Numerous intermediary photoproducts obtained by irradiation of IP can be characterized using GC-MS. It is found that photolysis of IP and MN mainly formed hydroxylation reactions. It is noticeable, however, that by-product may differ substantially, and the importance of the structural factors has been evidenced at different levels. Experiments indicated that photodegradation rate of MN and IP increases in the following order: photolysis < herbicide with nitrate < herbicide with nitrite.

## Acknowledgment

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