Homolytic Scission as the Main Pathway in the Liquid Chromatography/Electrospray Ionization Quadrupole Time-of-Flight Mass Spectrometry of Mesotrione and its Photoproducts

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Abstract
The indirect photochemical degradation of mesotrione induced by humic substances was studied by excitation with a solar light simulator. The disappearance rate constant increased by increasing the concentration of molecular oxygen. Three main byproducts were observed. They all arise from the dissociation of the non-aromatic cycle. Collision-induced dissociation tandem mass spectrometry (CID-MS/MS) of the deprotonated molecule was carried out and the effect of the collision energy as well as the elemental compositions of the products ions was used to propose the chemical structures. The presence in the chemical structure of the SO2-Me moiety permitted several types of homolytic scissions leading to the formation of radical anions.

Keywords: Mesotrione; Humic substances; Homolytic scission; ESI/MS/MS; Hydroxyl radical

Introduction
Nowadays, great concern deals with the effect of the contamination of groundwater and surface water owing to the extensive use of pesticides for agricultural purposes. Of course they play a beneficial role in agriculture, however, they have been largely described as causing important environmental problems. Thus, the extensive use of pesticides and therefore the contamination of air, soil, surface and ground waters has an unavoidable effect of human health.

Mesotrione [2-(4-methylsulfonyl-2-nitrobenzoyl)-1,3-cyclohexanedione] is a pesticide that belongs to a new class of triketone herbicides [1]. It is widely used for pre as well as post-emergence broadleaved weed control in corn. It is supposed to act by competitive inhibition of the enzyme 4-hydroxyphenylpyruvate dioxygenase (HPPD) [2,3]. The fate of mesotrione under various environmental conditions has been the subject of several research activities [4-8]. As examples:

• Two different and main metabolites were identified in soils and plant and mammal metabolisms, namely MNBA (4-(methylsulfonyl)-2-nitrobenzoic acid) and AMBA (4-(methylsulfonyl)-2-aminobenzoic acid) [9] (Scheme 1).

• The direct excitation upon 365 nm leads to the disappearance of mesotrione [10]. This study clearly demonstrates that mesotrione sensitizes its own oxidation by involving the triplet excited state. This proceeds through singlet oxygen formation and sensitizes the oxidation of H-donors through electron or H-atom transfer [10]. Besides MNBA, the photochemical degradation of mesotrione leads to the formation of two more byproducts arising from the scission of the non-aromatic cycle (Scheme 2).

Once mesotrione is in surface waters, it may undergo direct and/or indirect phototransformation. The direct phototransformation is observed when mesotrione absorbs itself the light while the indirect transformation is obtained when other substances absorb light and produce highly reactive species which can then react with mesotrione and induce its disappearance. Natural waters contain several species that may play the role of inducers such as nitrates, iron(III) species and of course dissolved organic matter DOM [11,12]. The latter substances are known to produce several kinds of reactive species such as: hydroxyl radicals, solvated electrons, reactive triplet excited states [13].

This paper deals with the photodegradation of mesotrione by commercial humic substances HS. It mainly concerns the analytical point of view of such photochemical point by the elucidation of the generated byproducts through their LC/MS/MS data. To our knowledge, no mechanisms of mesotrione and its byproducts electrospray fragmentation have been reported until no.

Experimental Section
Materials
Mesotrione, with a IUPAC name 2-[4-(Methylsulfonyl)-2-nitrobenzoyl]cyclohexane-1,3-dione (CAS number 104206-82-8), was obtained from Pestanal and was used as received. Humic substances (HS) were purchased Aldrich and used as received. Except when stated, all the other reagents were of the purest grade commercially available and were used without further purification. All the solutions were prepared with deionised ultrapure water that was purified with Milli-Q devise (Millipore) and its purity was controlled by its resistivity. pH measurements were carried out with a JENWAY 3310. For the irradiation with humic substances, the pH was adjusted to 6.5 with phosphates. The ionic strength was not controlled.

Irradiations setups
The Irradiation experiments using Humic substances (HS) were performed at 365 nm in an elliptical stainless steel cylinder. A high pressure mercury lamp (Philips HPW, 125 W) was located at a focal axis of the elliptical cylinder. An inner filter selected the emission at 365 nm. The irradiation experiments were performed at 365 nm permitting the selective excitation of Humic substances. The reactor (water-jacketed pyrex tube-diameter 2.8 cm) was centred at the other focal axis. The solution (roughly 30 ml) was continuously stirred with a magnetic bar during irradiation.

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The irradiations were also performed using a solar light simulator. The prepared samples were irradiated horizontally in a Suntest CPS photoreactor (Atlas, Moussy le neuf, France) equipped with a xenon lamp and a filter that prevents the transmission of wavelength below 290 nm. The lamp was operated at an intensity of 750 W/m². The temperature of the sample was roughly maintained at 20 °C by a continuous flow of cold water through the bottom of the photoreactor.

For direct excitation of mesotrione, the irradiations were performed in a cylinder reactor made in stainless steel equipped with two germicidal lamps (Mazda T815 15W) emitting selectively at 254 nm and symmetrically installed around the cylinder. The reactor, a quartz tube (d=2.5 cm) containing a maximum of 25 mL solution, was located in the centre of the container.

Analytical and spectroscopic equipments

The direct as well as the induced photodegradation by humic substances of mesotrione and the formation of the by-products were followed by Waters Alliance 2695 (Waters SA, St-Quentin en Yvelines, France) photodiode array detector (DAD) chromatograph. A reversed-phase column distributed by Phenomenex (Kinetex MS C18, 2.6 µm, 100 mm × 2.1 mm) was used at a flow rate of 0.2 mL min⁻¹ and the injected volume was 20 µL. The elution was accomplished, using an isocratic program, with water (0.1% formic acid) and acetonitrile at 60% and 40% respectively.

A Waters/Micromass LC/QTOF tandem mass spectrometer (Micromass, Manchester, UK), with an orthogonal geometry Z-spray ion source, was used for LC/ESI/MS and LC/ESI/MS² experiments. Eluate was subjected to electrospray ionization (ESI) in the positive as well as negative ion modes and resulted in the formation of protonated and deprotonated molecules of the sample components respectively. Scanning was performed in the range between m/z 60 and 600. The elemental composition of the recorded ions was further determined using MassLynx Elemental Composition software V4.1 (Micromass). The maximum deviation was set to 10 ppm, and C, H, N, O, Cl were selected as possible elements present. Five scans were combined before the integration of the individual peaks.

The desolation and ion source temperatures were set at 250°C and 100°C, respectively. Nitrogen was used as the nebulizer (35 L/h) as well as a desolation gas (350 L/h). The optimized voltages for the probe and ion source components (to produce maximum intensity) were 3 kV for the stainless-steel capillary, 35 V for the sample cone and 1 V for the extractor cone.

Tandem mass spectrometric (MS/MS) experiments in collisionally induced dissociation (CID) mode were performed using argon in the collision cell at a pressure of 4.0 × 10⁻³ mbar. A collision energy of 15–35 V was used for preliminary fingerprints and specific energies were then used to unambiguously assign the product ions. The [M+H]⁺ or [M-H]⁻ precursor ions were used as a lock masses for the MS/MS experiments and allowed for accurate mass measurements to be undertaken. The ion formulae were determined by restricting the possible elements present to those in the precursor ion formulae, and setting the maximum allowed deviation in the mass measurements to 20 ppm.
Results and Discussion

The UV-visible absorption spectrum of mesotrione highly depends on the pH of the solution. At pH<3, it exhibits two absorption bands at 274 and 220 nm with a shoulder at roughly 230 nm. However, at higher pH values, a unique band is observed at 255 nm with a shoulder at 291 nm. Such behaviour is owing to a protolytic equilibrium that involves the proton at the α-position of the three ketones functions. The pKa is estimated 3.1 [10]. The anionic form presents several mesomeric forms owing to the presence of the three ketones site (Scheme 3).

Aerated solutions of mesotrione (1.0 × 10⁻⁴ mol L⁻¹) and Humic substances HS (0.15 g L⁻¹) buffered at pH=5.6 were illuminated by a solar light simulator (sunteest photoreactor) under the conditions given in the experimental part. Under the irradiation wavelengths (λ>290 nm), the photons were mainly absorbed by HS. In the absence of HS, the conversion of mesotrione was estimated to less than 5% after about 5 hours of illumination. As observed in Figure 1, the conversion of mesotrione reached 60% within 7 hours irradiation time with a pseudo first order kinetics. The rate constant was estimated to 0.13 h⁻¹. When the irradiation was undertaken at 365 nm, the conversion was evaluated to about 19% after 7 hours owing to the low absorbance of HS at the excitation wavelength. The irradiation within the same conditions of the mixture mesotrione and HS (1.0 × 10⁻⁴ mol L⁻¹/ 0.15 g L⁻¹) at 254 nm leads to higher conversion percentage, roughly 90% after 4 hours irradiation time. It should be noted that at such wavelength, the photons were absorbed by both components, namely mesotrione and HS, and thus, the disappearance resulted from two pathways: direct phototransformation and transformation photoinduced by excitation of HS. In all cases, the degradation rate was much slower in oxygen free solutions, indicating that oxygen plays an important role in the photochemical behaviour of mesotrione.

Following irradiations and after a conversion of about 30% of mesotrione, three main byproducts were observed from the early stages of excitation (Figure 2). Their concentrations clearly increased as a function of irradiation time indicating their formation as primary products.

The three products P1, P2 and P3 were clearly detected by using HPLC equipped with a diode array detector at the retention times: 1.8; 3.3 and 8.2 minutes respectively when mesotrione was observed at 12.3 minutes. In order to identify the generated byproducts, HPLC/ESI/MS as well as HPLC/ESI/MS/MS experiments were undertaken in both positive and negative modes. The first set of experiments permitted us to obtain the accurate mass and the molecular formulae and mass error values were obtained using the elemental composition tool in the MassLync V4.1 software. In the second set of experiments, namely MS² data, the [M+H]⁺ or [M-H]⁻ accurate mass was used as a lock mass for the accurate mass determinations for the generated fragment ions.

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Table 1 gives the main results obtained by HPLC/ESI/MS. It shows that mesotrione was easily detected in both positive and negative modes while the byproducts were mainly observed at relatively high intensities in negative mode. The reason why the results will be give inhere in the negative mode. As shown in Figure 3, under our experimental conditions, the ESI-/MS spectrum of mesotrione is dominated by two peaks of the ions m/z 338 and 291 (ions 1a) corresponding to [mesotrione-H]+ and to the ion corresponding to the elimination of HNO. This shows that even in soft conditions, the parent ion easily decomposes with the formation of the ion 1a (referring to the text below). The accurate obtained mass of the deprotonated form of mesotrione (333.0332) is in perfect agreement with the elemental composition C18H17NO6S (mass error -0.7 ppm).

By close analyses of the elemental compositions we can conclude that the three formed byproducts present seven atoms of carbon which clearly indicates the loss of a part of mesotrione. Moreover, all the products contain the sulphur atom while one of them, namely P2, appears without the nitrogen atom.

In order to have useful information for the precise identification of the unknown generates, the fragmentation of the parent compound mesotrione was carefully studied.

### Mass spectra analyses of the parent compound mesotrione

Figure 4 represents the CID spectrum of [mesotrione-H]+ as obtained with a collision energy of 25 eV. It shows the presence of three major fragments ions: m/z 291 (1a), 249 (1b) and 212 (1c). Moreover, several minor ions are also obtained at m/z 276 (1d) 263 (1e), 227 (1f) and 184 (1g). All the data relative to these fragment ions are listed in Table 2.

The evolution of the intensities of the ions as a function of the collision energy clearly shows that the fragment ion 1a (m/z=291) is formed in a primary step. This was observed even in soft MS conditions as specified above. It should be noted that all the other fragments are more likely arising from 1a since their formations were only seen at collision energies higher than 15 eV.

The fragment ion 1a with the elemental composition C18H17O6S (error+2.3 ppm) corresponds to the elimination of nitrous acid (HNO2) as shown in Scheme 4. This proceeds through a cyclisation process and a transfer of hydrogen atom.

Once generated, the fragment ion 1a (m/z=291) may be involved in various secondary degradation pathways leading to the formation of the other fragment ions. These pathways are gathered in Scheme 4 and presented as follows:

- An intramolecular elimination of carbon monoxide leading to the formation of 1e (m/z 263; C16H15O5S; -1.2 ppm) that presents a furan structure. Such fragment further eliminates the radical SO2Me via a homolytic dissociation of the C-S bond that permits the generation the radical anion 1g (m/z=184; C16H13O4S; error=-6.7 ppm).

- A homolytic dissociation of the S-methyl bond leading to the loss of the methyl radical and the formation of the fragment radical 1d (m/z=276; C17H15O5S; error+6.4 ppm). The latter fragment...
may lose in its turn a neutral molecule of sulfur dioxide to form 1c (m/z=212; C_{13}H_{8}O_{3}^-).

- A homolytic scission of C-sulfur bond that correspond to an alternative second pathway for the formation of the fragment radical anion 1c (m/z=212; C_{13}H_{8}O_{3}^-).

- The formation of the fragment 1f (m/z=227; C_{14}H_{11}O_{3}^-) via an intramolecular sulphur dioxide elimination of SO_{2}.

- The formation of m/z=149 (1b; C_{12}H_{8}O_{2}^-) after the elimination of the neutral ketene structure CH_{2}CO.

As clearly shown above, homolytic scissions are largely presented as a guideline for the interpretation and elucidation of several fragment ions. These mainly involve the SO_{2}-CH_{3} moiety.

**Mass spectra analyses of the byproducts P1, P2 and P3**

The two byproducts P1 and P3 that elutes at the retention time of 1.8 and 8.2 minutes respectively have elemental compositions that are different from each other (C_{8}H_{8}NO_{4}S and C_{8}H_{6}NO_{6}S respectively) by the number of hydrogen and oxygen. P2 which has a retention time of 3.3 minutes and C_{8}H_{7}O_{5}S as elemental composition lost the nitrogen atom. These products were already presented in the literature [2-4] and they correspond to the following structures (Scheme 5).

As for the parent compound mesotrione, their fragmentations pathways were studied in order to establish a general scheme for the fragmentation of compounds that present SO_{2}-CH_{3} as a chemical moiety. The LC/ESI/MS/MS of P1 is given in Figure 5 and the main data extracted.

As clearly shown in Table 3, despite the difference in the elemental compositions, the patterns of the ESI fragmentation for P1 and P2 are more likely the same. As for the parent compound, the generated fragment ions are similar with one unit of mass difference indicating the same chemical squeleton except for the fragment ion m/z=79 that is common to both products. However, P3 presents only one main fragment ion corresponding the decarboxylation process. The fragmentation pathway of P1 is presented in Scheme 6 and the same scheme may be taken for P2 by replacing the NH_{2} group by a OH group. As for mesotrione, the fragmentation proceeds through several homolytic scission involving SO_{2}-CH_{3}.

From the photochemical point of view, the formation of P3 arises from the scission of non-aromatic moiety. This proceeds through the oxidation of mesotrione via direct oxidation or/and photosensitized by Humic substances (HS). The latter compounds are known to produce very reactive species such as hydroxyl radical or triplet excited states that are able to oxidize organic compounds. The formation of P2 is owing to the oxidation of P3 by the generated hydroxyl radical. P1
**Scheme 5:** Chemical structures for P1, P2 and P3.

**Scheme 6:** ESI/MS/MS fragmentation pathways of P1.

| m/z  | Accurate mass   | Calculated mass | Elemental composition | Error (ppm) |
|------|-----------------|-----------------|-----------------------|-------------|
| 170  | 170.0283        | 170.0276        | C₇H₈NO₄S⁻            | +4.3        |
| 155  | 155.0049        | 155.0041        | C₆H₅NO₂S⁻            | +5.2        |
| 106  | 106.0642        | 106.0657        | C₆H₅N                | -13.9       |
| 91   | 91.0410         | 91.0422         | C₆H₅N                | -13.2       |
| 79   | 78.9862         | 78.9854         | SO₂CH₃⁻               | +10.4       |

**P2 C₇H₆O₅S (m/z=215)**

| m/z  | Accurate mass   | Calculated mass | Elemental composition | Error (ppm) |
|------|-----------------|-----------------|-----------------------|-------------|
| 171  | 171.0108        | 171.0116        | C₇H₆O₅S⁻              | -4.6        |
| 156  | 155.9870        | 155.9881        | C₆H₅O₅S⁻              | -7.2        |
| 107  | 107.0480        | 107.0497        | C₆H₅O⁻                | -15.8       |
| 92   | 92.0273         | 92.0262         | C₆H₄O⁻                | +11.8       |
| 79   | 78.9850         | 78.9854         | SO₂CH₃⁻                | -4.8        |

**P3 C₇H₆NO₅S (m/z=244)**

| m/z  | Accurate mass   | Calculated mass | Elemental composition | Error (ppm) |
|------|-----------------|-----------------|-----------------------|-------------|
| 170  | 170.0283        | 170.0276        | C₇H₈NO₄S⁻            | +4.3        |
| 155  | 155.0049        | 155.0041        | C₆H₅NO₂S⁻            | +5.2        |
| 106  | 106.0642        | 106.0657        | C₆H₅N                | -13.9       |
| 91   | 91.0410         | 91.0422         | C₆H₅N                | -13.2       |
| 79   | 78.9862         | 78.9854         | SO₂CH₃⁻               | +10.4       |

**Table 3:** Accurate and exact masses and elemental composition of the fragment ions of the byproducts P1, P2 and P3 as obtained with a collision energy of 25 eV.

The spectrum is dominated by the fragment ion at m/z=200 corresponding to the loss of carbon dioxide.
is clearly formed via a reduction process. This is only observed in the presence of Humic substance (HS) and may be due to the formation of solvated electron from the excitation of HS.

**Conclusion**

The LC/MS fragmentation of mesotrione and its byproducts allows for unequivocal elucidation of the chemical structures during the photosensitized degradation of mesotrione with humic substances HS. Such degradation involves first the scission of the non-aromatic moiety leading to the formation of a carboxylic form (product P3) and second the oxidation of the generated compound by the hydroxyl radicals. It also involves, a reduction process via the formation of solvated electron from Humic substances.

The presence in the chemical structure of the SO₂-CH₃ group permitted the observation in LC/ESI/MS/MS fragmentation of mesotrione, P1 and P2 of various homolytic bond scissions via the dissociation of C-S and S-CH₃ bonds.

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