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Photolytic degradation of the insecticide thiamethoxam in aqueous medium monitored by direct infusion electrospray ionization mass spectrometry

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Photodegradation of the insecticide thiamethoxam (1), 3-[(2-chloro-5-thiazolyl)methyl]tetrahydro-5-methyl-*N*-nitro-4H-1,3,5-oxadiazin-4-imine, in an aqueous medium was monitored by electrospray ionization mass spectrometry in the positive ion mode, ESI(+)-MS. An aqueous solution of (1) was incessantly exposed to a UV radiation source and aliquots were taken after reaction times of 1, 2, 3, and 4 h. Analysis by GC/NCI-MS revealed that (1) was continuously degraded under these experimental conditions. However, the total organic carbon (TOC) content remained practically constant during the exposition period, thereby indicating that 1 was not mineralized but continuously converted into other compounds. ESI(+)-MS monitoring revealed that whereas the intensity of the ions of *m/z* 292/294 ($[1 + H]^+$) constantly decreased, there was the emergence of other ions of *m/z* 247/249, 197, 168, and 116 whose intensities simultaneously increased. Their structures were proposed on the basis of: (1) the data of their ESI(+)-MS/MS; (2) their high resolution *m/z* values; and (3) a plausible reactivity of the thiamethoxam molecule exposed to UV radiation in aqueous solution. Finally, these data allowed us to suggest a reaction route for the photodegradation of 1 in an aqueous medium. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: thiamethoxam; photodegradation; electrospray ionization; mass spectrometry; reaction monitoring

INTRODUCTION

Pesticides play a beneficial role in agriculture because they help combat a variety of pests that destroy crops. However, several studies have been described on the environmental contamination by pesticides as a result of agricultural practices, accidental spillage, or uncontrolled release of industrial effluents. The contamination of air, soil, surface, groundwater, and the trophic chain by pesticides has evident negative impacts on public health and on biological diversity.[1]

Thiamethoxam (**1**) (3-[(2-chloro-5-thiazolyl)methyl] tetrahydro-5-methyl-*N*-nitro-4H-1,3,5-oxadiazin-4-imine), a neonicotinoid insecticide, has been widely applied to crop protection against a broad spectrum of chewing and sucking pests and used for a variety of other purposes such as in seed and pet treatment.[2] However, its characteristic properties, such as low soil sorption and high leaching capability, make it a potential contamination source of underground and surface waters[3] (Scheme 1).

Advanced oxidation processes (AOPs) have provided a promising alternative for the remediation of contaminated water when compared to other treatment methods.[4–6] The most efficient and convenient of them involves the use of UV irradiation, which promotes the absorbing target molecules to their excited triplet states. Such excited states can then undergo, among other chemical processes, homolysis, heterolysis, or photoionization. Alternatively, UV-sensitive materials may be added to the aqueous solutions, thereby allowing the use of wavelengths that are not absorbed by the target molecules.[7] Other reactive species, especially hydroxyl radicals ($HO^{\bullet}$), can also be generated *in situ* by exposing aqueous solutions to UV radiation. These radicals characteristically promote a nonselective attack on the organic molecules, thereby being useful oxidant species widely employed in wastewater treatment.[5]

Mass spectrometry (MS) has been extensively used to monitor the degradation of organic compounds in the environment but, owing to the limitations of the classical ionization techniques, it has been commonly restricted to the more volatile and lighter components.[8,9] Molecular analysis by MS has, however, benefited significantly from the advance of electrospray ionization (ESI),[10] which has permitted the ionization of heavier, more polar, and less volatile molecules.[11,12] ESI has also shown a remarkable capability to gently transfer transient and unstable species to the gas phase without inducing undesirable fragmentations. It has

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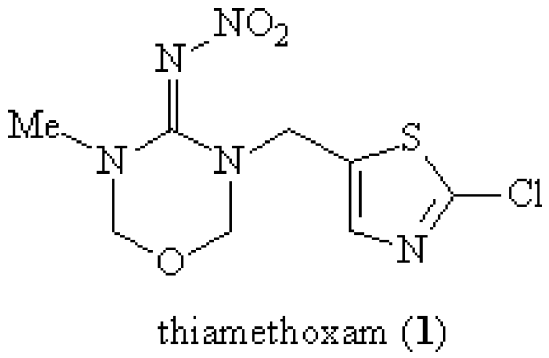

thiamethoxam (**1**)

Scheme 1. Chemical structure of the insecticide thiamethoxam (**1**).

also been postulated that the composition of ESI-generated ions closely reflect that of the condensed phase.[13–18] ESI-MS (as well as ESI-MS/MS) with its unique features is, therefore, becoming the foremost technique in elucidating reaction pathways, especially in aqueous solutions, via the detection and identification of reactants, products, and intermediates, even the transient ones occurring at very low concentrations.[19,20]

In this study the electrospray ionization mass spectrometry in the positive ion mode (ESI(+)-MS) monitoring of the photolytic degradation of the insecticide thiamethoxam in an aqueous medium was performed aiming to obtain novel and relevant information on the products and unstable intermediates formed under these experimental conditions.

EXPERIMENTAL

Chemicals

Thiamethoxam and HPLC grade dichloromethane were purchased from Sigma-Aldrich (Milwaukee, WI, USA) and Merck (Whitehouse Station, NJ, USA), respectively. Ultrapure water, from a Millipore Milli-Q system (Milford, MA, USA), was used to prepare the solutions in all experiments.

Kinetic studies

To determine the degradation kinetic, experiments were performed in a 40 ml quartz tube filled with 20 ml of a thiamethoxam aqueous solution (50 mg/l). This system was placed inside a home-built reactor and submitted to the continuous radiation from a UV lamp (maximum emission at 254 nm, 15 W, Philips TUV G5T8). Aliquots (100 µl) were taken at intervals of 10 min and kept protected from light in a refrigerator at 4 °C prior to the GC-MS analyses.

Degradation procedures

Photolysis experiments were carried out in a 500 ml glass beaker. An aqueous solution of thiamethoxam (200 ml; 50 mg/l) was continuously irradiated by using the same system (reactor and UV lamp) as described in the preceding section. Aliquots (20 ml) were taken after reaction times of 1, 2, 3, and 4 h. All the samples were kept protected from light in a refrigerator at 4 °C prior to the ESI(+)-MS analyses.

Analytical methods

Total organic carbon (TOC) analyses were carried out in a TOC 5000 A (Shimadzu, Minnesota, USA) instrument at 680 °C using a platinum catalyst to promote the organics' mineralization.

ESI-MS and ESI-MS/MS analyses were conducted in a high-resolution hybrid quadrupole (Q) and orthogonal time-of-flight (TOF) mass spectrometer (Q-Tof, Micromass, UK) with a constant nebulizer temperature of 50 °C. The ESI source and the mass spectrometer operated in the positive ion mode, and the cone and extractor potentials were set to 40 and 10 V, respectively, with a scan range of m/z 50–1000. Samples were directly infused into the ESI source by using a micro syringe pump at flow rates of 10 µl/min. MS/MS experiments were carried out by mass selection of a specific ion in Q1 and then submitted to collision-induced dissociation (CID) with argon in the collision chamber. The product ion MS analysis was accomplished by the orthogonal TOF analyzer.

GC-NCI/MS (gas chromatography coupled with MS operating in the negative chemical ionization mode) analyses were carried out in a Trace GC Ultra-Polaris Q (Thermo Electron, CA, USA) instrument equipped with a crossbond-5% diphenyl-95% dimethyl polysiloxane capillary column (30 m length × 0.25 mm i.d.). Helium was used as the carrier gas at a flow rate of 1 ml/min. Prior to the injection, the aqueous samples (100 µl) were evaporated to dryness at room temperature and recomposed to a final volume of 100 µl with dichloromethane. The resulting samples were then stored in amber vials and kept in a refrigerator at 4 °C to prevent further degradation. For analyses, 1 µl of these samples was injected using the splitless mode. The temperature program was as follows: 100 °C for 2 min, 10 °C/min up to 180 °C (10 min), 12 °C/min up to 250 °C (1 min). The transfer-line temperature was set at 275 °C. The injector and MS ion source temperatures were kept at 100 °C and 275 °C, respectively. The MS ion source was operated in the negative chemical ionization (NCI) mode, using methane as the reagent gas at a flow rate of 1 ml/min. NCI mass spectra were monitored from m/z of 50 to 400.

RESULTS AND DISCUSSION

First, the real efficiency of UV radiation in promoting the degradation of thiamethoxam (**1**) in aqueous medium was verified. The experiments were conducted in a quartz tube (quartz does not absorb UV radiation) and, thus, a fast and remarkable thiamethoxam (**1**) degradation was accomplished. GC-MS analyses (see Experimental Section for more details) were performed to monitor the changes in the thiamethoxam (**1**) peak area as a function of irradiation time. These data were thus used to estimate the half-life for such a process. Most importantly, these GC-MS analyses were not able to detect the presence of any degradation product.

The other set of experiments, aiming to detect possible intermediates in solution via direct infusion ESI(+)-MS analyses, were suitably conducted in a glass flask (glass strongly absorbs UV light). As a result, the degradation

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rate of thiamethoxam (**1**) was observed to be much slower than in the experiments conducted in a quartz tube. On the other hand, ESI(+)-MS monitoring revealed that both sets of experiments produced identical results, i.e. the same type of final products (as will be shown later in this paper).

Degradation kinetics: determination of the half-life for the degradation of thiamethoxam

Control experiments showed that UV radiation is essential to induce the degradation of thiamethoxam (**1**). In fact, this compound stays indefinitely stable in aqueous solution when protected from UV light. Figure 1 displays the plot of the relative concentration of thiamethoxam (**1**) solutions (C_t/C_o; C_t and C_o are the thiamethoxam concentration at t and 0 time, respectively) as a function of the UV irradiation time. These concentration values were calculated based on the linear response ($R^2 = 0.9997$) of the calibration curve, i.e. the concentration of reference solutions of thiamethoxam (**1**) *versus* the corresponding GC peak areas (not shown). An analysis of Fig. 1 reveals that under these experimental conditions the half-life for the decomposition of thiamethoxam (**1**) was *ca* 10 min, and that this compound was almost completely degraded (*ca* 96%) after a reaction time of 30 min. However, the TOC content remained practically constant during this time, thereby indicating that thiamethoxam was not mineralized (i.e. converted to H_2O, CO_2, and other small molecules) but converted to other heavier degradation products.

ESI-MS monitoring and ESI-MS/MS structural elucidation

Thiamethoxam (**1**) and its photodegradation products (as will be subsequently shown in this paper) are in equilibrium with their protonated forms in aqueous solution. ESI was able to gently transfer these ionic and unstable species to the gas phase with a little excess of internal energy. To obtain information regarding their structures, these ions were subsequently mass-selected and fragmented upon collision-induced dissociation (CID). As will be discussed later in this paper, these structures, and, therefore, the reaction pathways for the photodegradation of **1**, were proposed on the basis of only on the ESI-MS and ESI-MS/MS data but also taking into account some fundamental and well-known concepts on the reactivity of organic molecules. These concepts were then used to suggest plausible transformations that (**1**) and its degradation products can undergo in aqueous solution under the influence of a UV irradiation source.

Figure 2(a) displays the ESI(+)-MS of an aqueous solution of pure thiamethoxam (**1**), which shows the major presence of the ions of m/z 292/294 $[\mathbf{1} + H]^+$ as well as other minor ions of 314/316 $[\mathbf{1} + Na]^+$ and 330/332 $[\mathbf{1} + K]^+$. Note that the isotopic patterns of such ions are consistent with the presence of both chlorine and sulfur atoms in their structures. The mass-selection and fragmentation upon CID of the ion of m/z 292 yielded a set of fragment ions arising mainly from the losses of NO_2 (m/z 246/248) and $NO_2 + Cl$ (m/z 211) (data not shown).

After an irradiation time of 2 h in a reaction conducted in a glass flask (see Experimental Section for more details), the ESI(+)-MS (Fig. 2(b)) showed the presence of the ions of

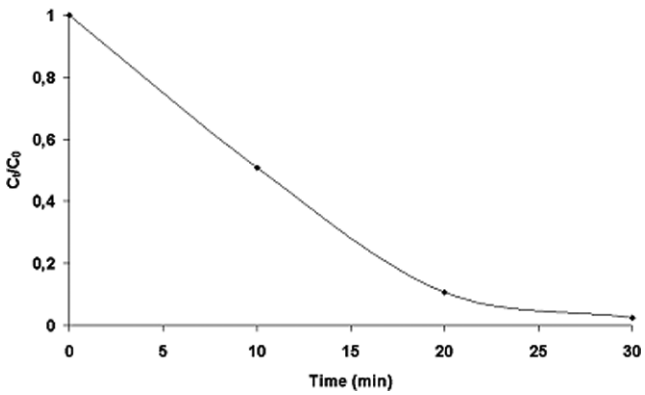

Figure 1. Plot of the thiamethoxam concentration as a function of the UV irradiation time.

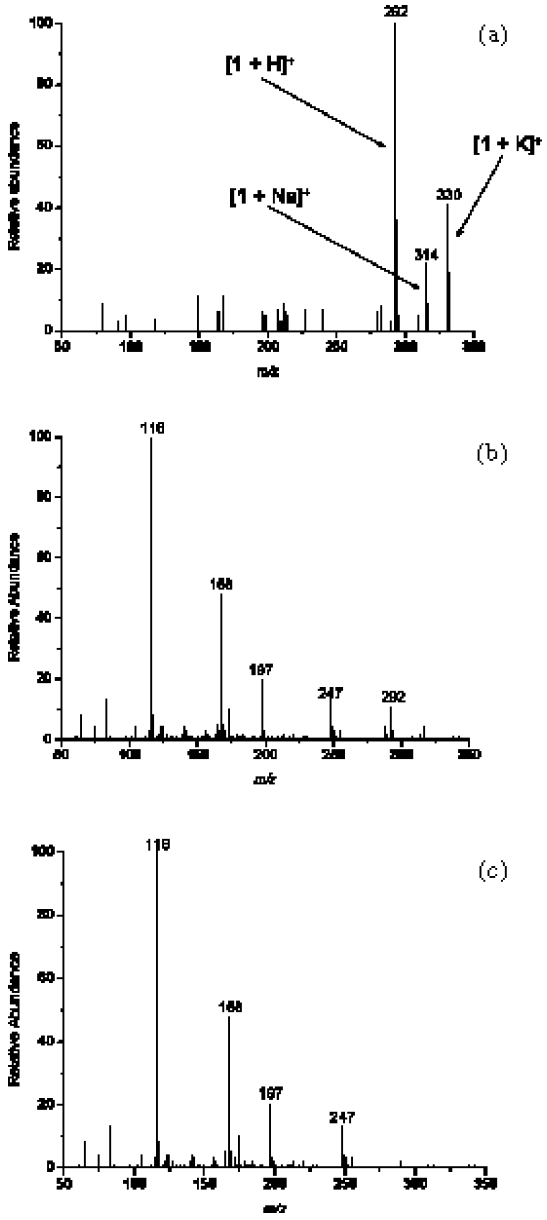

Figure 2. ESI(+)-MS of an aqueous solution of thiamethoxam after different UV irradiation times: (a) initial solution; (b) 2 h; (c) 4 h.

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m/z 247/249, 197, 168, and 116. The mass-selection and CID of the ion of m/z 247 showed the fragment ions of m/z 217, 188, 174, 161, and 132 (ESI(+)-MS/MS shown in Fig. 3). On the basis of these data, the structure $[\mathbf{2}+\mathrm{H}]^+$ was proposed for this ion, which fits well with the fragmentation pattern observed in Fig. 3 (Scheme 2). Note that the isotope pattern of this ion also indicates the presence of one chlorine atom in its structure.

Similarly, the fragmentation patterns of the ions of m/z 197, 168, and 116 (Table 1) were also used to propose them as logical structures. Thus, the structures of the ion of m/z 197 ($[\mathbf{7}+\mathrm{H}]^+$) and its fragments formed upon CID are shown in Scheme 3. Furthermore, Scheme 4 displays the structures of the fragment ions formed upon the dissociation of the precursor ions $[\mathbf{8}+\mathrm{H}]^+$ (m/z 168) and $[\mathbf{4}+\mathrm{H}]^+$ (m/z 116). Note that the isotope patterns of ions $[\mathbf{4}+\mathrm{H}]^+$, $[\mathbf{7}+\mathrm{H}]^+$, and $[\mathbf{8}+\mathrm{H}]^+$ clearly indicate that such ions do not possess chlorine in their structures.

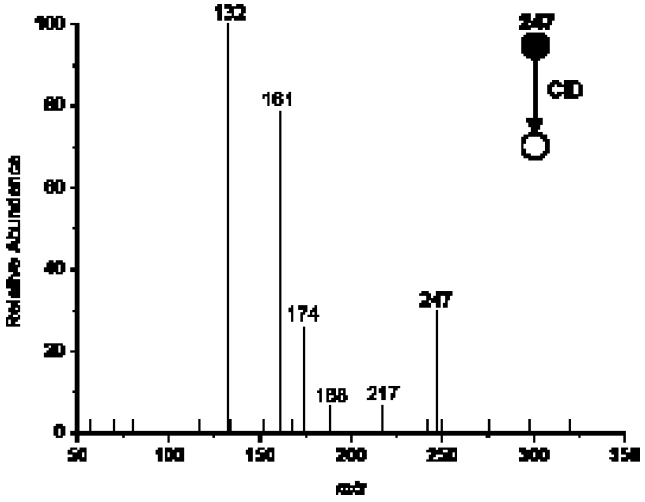
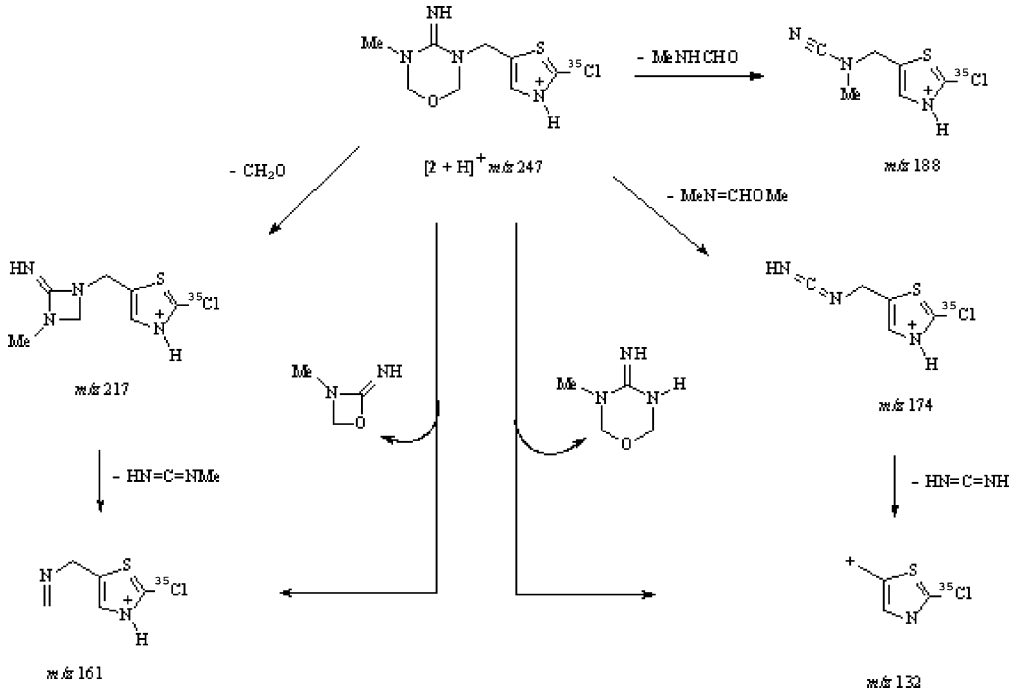


Figure 3. ESI(+)-MS/MS of the ion of *m/z* 247 (proposed to be $[\mathbf{2}+\mathrm{H}]^+$).

After an irradiation time of 4 h, the $[\mathbf{1}+\mathrm{H}]^+$, $[\mathbf{1}+\mathrm{Na}]^+$, and $[\mathbf{1}+\mathrm{K}]^+$ ions practically disappeared in the ESI(+)-MS (Fig. 2(c)), thus indicating that thiamethoxam was almost completely consumed. The relative intensities of the $[\mathbf{2}+\mathrm{H}]^+$, $[\mathbf{4}+\mathrm{H}]^+$, $[\mathbf{7}+\mathrm{H}]^+$, and $[\mathbf{8}+\mathrm{H}]^+$ ions, however, stayed practically constant, thus indicating that their neutral counterparts (i.e. compounds **2**, **4**, **7,** and **8**) were not degraded subsequently in solution. On the basis of these results and assumptions, a reaction route for the photodegradation of thiamethoxam in aqueous solution is shown in Scheme 5. The initial step involves a nucleophilic attack of H_2O on the nitrogen of the nitro group of **1** followed by the release of HNO_3 to form the imine **2**. In fact, compound **2** has previously been detected and identified as a by-product in the photodegradation of thiamethoxam.[21] The conversion of **2** to the intermediate **3** (its protonated form of m/z 229 was not detected in the ESI(+)-MS shown in Fig. 2) is proposed to occur via a fast nucleophilic substitution of the Cl atom, connected at the thiazolic ring of **2**, by the

Table 1. Main fragments arising from the dissociation of the ions $[\mathbf{4}+\mathrm{H}]^+$, $[\mathbf{7}+\mathrm{H}]^+$, and $[\mathbf{8}+\mathrm{H}]^+$ detected in the ESI(+)-MS of an aqueous solution of thiamethoxam exposed to a continuous UV light irradiation

Precursor ion (m/z)	Fragment ions (relative abundance %)
$[4+\mathrm{H}]^+$ (116)	86 (100), 87 (9)
$[7+\mathrm{H}]^+$ (197)	81 (76), 99 (44), 110 (76), 117 (44), 124 (100), 154 (18)
$[8+\mathrm{H}]^+$ (168)	110 (4), 138 (100)



Scheme 2. Proposed fragmentation pathways for the CID of the ion $[\mathbf{2}+\mathrm{H}]^+$ of *m/z* 247.

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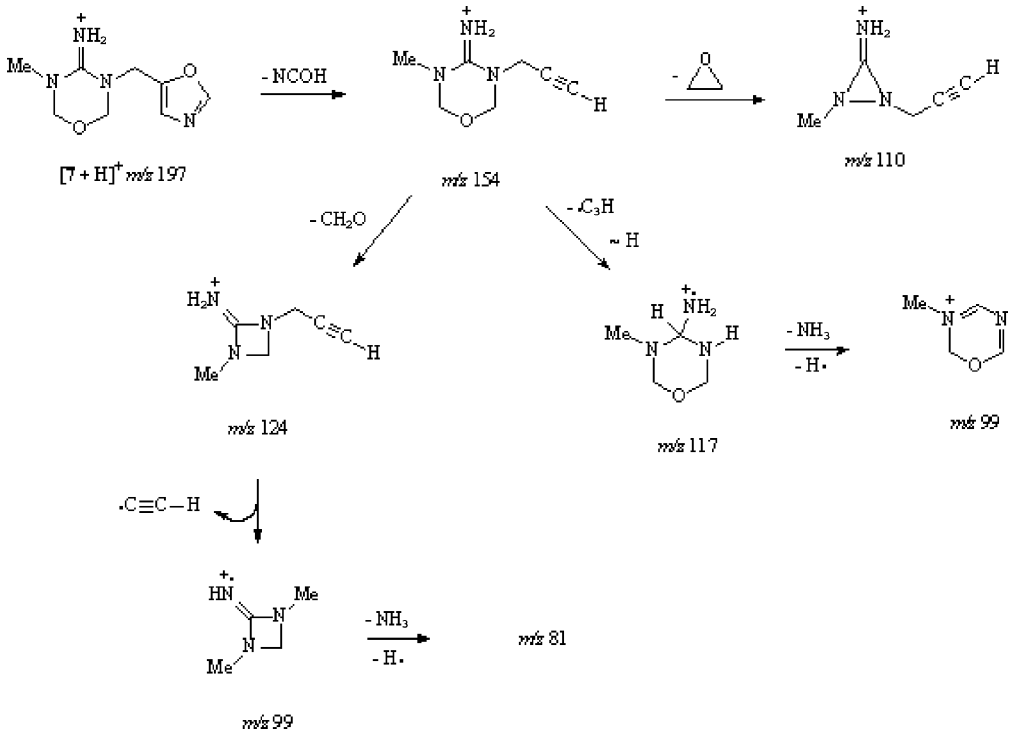
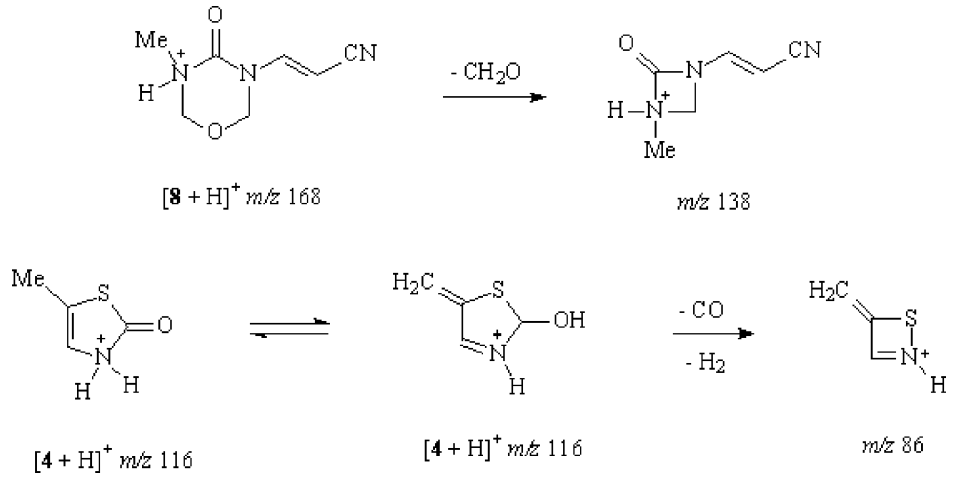


Scheme 3. Proposed fragmentation pathways for the CID of the ion $[\mathbf{7} + H]^+$ of *m/z* 197.



Scheme 4. Fragment ions formed upon the dissociation of the precursor ions $[\mathbf{8} + H]^+$ (*m/z* 168) and $[\mathbf{4} + H]^+$ (*m/z* 116).

OH group. The degradation products **4** (5-methyl-2(3*H*)-thiazolone) and **5** (whose protonated form of *m/z* 114 was not detected in the ESI(+)-MS shown in Fig. 2) are suggested to be formed as a result of the photolytic decomposition of **3**. Simultaneously, the extrusion of the sulfur atom of **3** can generate the azetidinone **6**, which can easily undergo a rearrangement to yield the quite stable oxazine **7**. Finally, the hydrolysis of the imine group and the breakdown of the oxazol ring of **7**, via an extrusion of CO followed by the release of H_2, are suggested to originate compound **8**. It is important to mention that several examples in the literature have established the synthetic usefulness of the photolytic extrusion of sulfur[22] and CO[23,24] to yield ring-contracted products. It must also be said that the structures of the intermediates **2–8** were not suggested in a random way: note that in all the structures proposed there is no violation of the original atoms' connectivity present in the thiamethoxam molecule.

Compounds **3** and **5**, although not being detected in their protonated form in the ESI(+)-MS (Fig. 2), were proposed to be formed under these reaction conditions. Their high instability and reactivity, however, supposedly prevented their detection. It must be said, in addition, that the proposal of other isomeric structures for the ions of *m/z* 247/249, 197, 168, and 116 (Fig. 2) is also feasible and this possibility cannot be entirely ignored.

To verify whether the proposed degradation products (**2–8**) were really formed in solution and not a result of an in-source process, the same set of reactions were monitored by using another mass spectrometer, with an ion trap mass analyzer. Very similar profiles (not shown) were obtained, thereby indicating that the ions detected in

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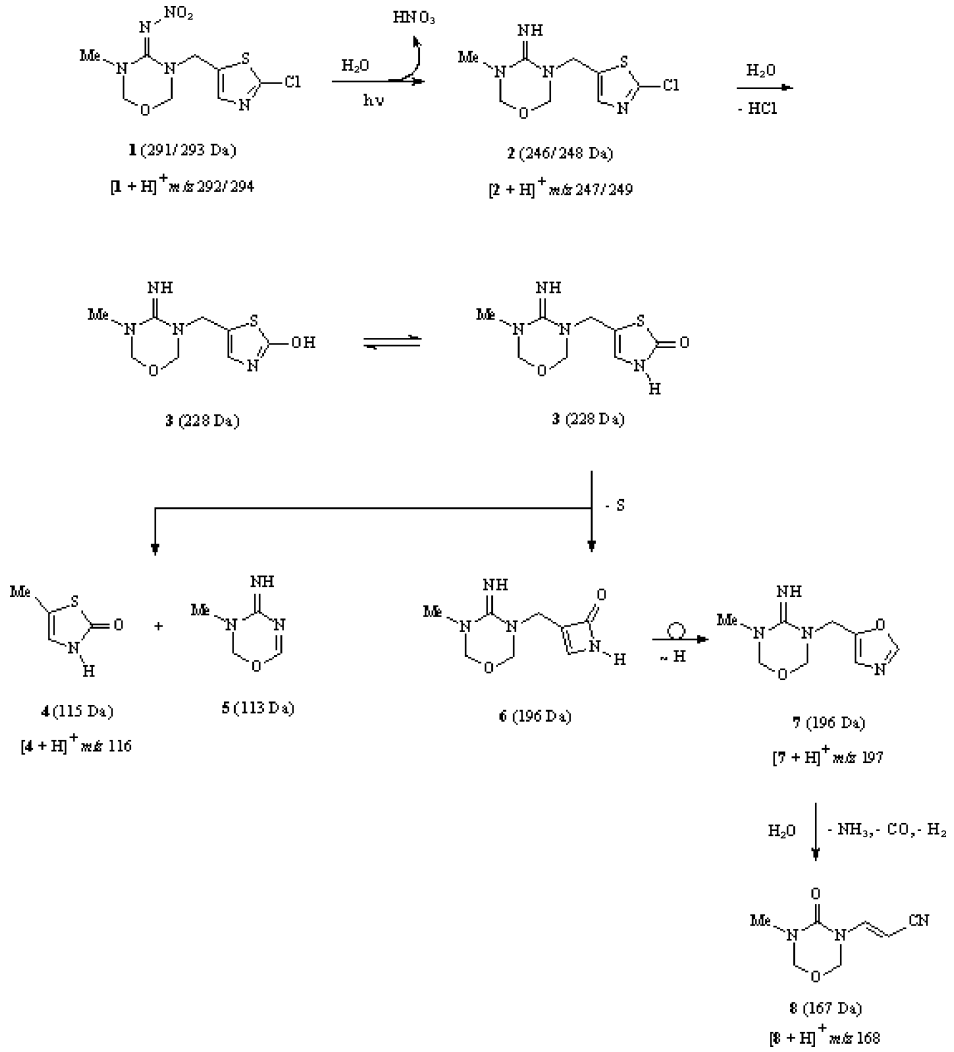
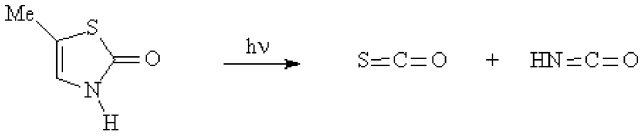


Scheme 5. Possible route for the photolytic degradation of thiamethoxam (**1**) via the formation of products **2–8**.

the ESI(+)-MS were really a result of a process taking place in solution.

Finally, exact mass measurements show good agreement between the theoretical and experimental m/z values for ions $[\mathbf{2} + H]^+$ (chemical composition: $C_8H_{12}ClN_4OS$; theoretical: 247.0420; experimental: 247.0425; difference: 2 ppm); $[\mathbf{4} + H]^+$ (chemical composition: C_4H_6NOS; theoretical: 116.0170; experimental: 116.0167; difference: 3 ppm); $[\mathbf{7} + H]^+$ (chemical composition: $C_8H_{13}N_4O_2$; theoretical: 197.1039; experimental: 197.1050; difference: 6 ppm); $[\mathbf{8} + H]^+$ (chemical composition: $C_7H_{10}N_3O_2$; theoretical: 168.0773; experimental: 168.0782; difference: 5 ppm).

In a previous work, Schwartz and coworkers[21] investigated the formation of volatile products from the photolysis of thiamethoxam in aqueous solution. In this paper, an aqueous solution of thiamethoxam was exposed to artificial sunlight for photoperiods of 12 h over 30 days. The volatile fractions of the irradiated samples were collected, derivatized, and analyzed by GC-MS. These fractions were proposed to be a mixture of carbonyl sulfide (S=C=O) and isocyanic acid (HN=C=O). Note that such volatile compounds can be envisaged to be formed via the decomposition of compound **4**, as shown in Scheme 6.



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Scheme 6. Formation of the volatile products carbonyl sulfide (S=C=O) and isocyanic acid (HN=C=O) from the decomposition of compound **4**.

CONCLUSIONS

The use of ESI(+)-MS to monitor the photodegradation of thiamethoxam in aqueous solution allowed the detection of a number of ions whose structures were suggested based on their ESI(+)-MS/MS data as well as on the exact mass measurements. Furthermore, taking into account a plausible reactivity of the thiamethoxam molecule exposed to UV radiation in aqueous solution, a possible route for its photodegradation was also proposed. This study demonstrates the advantageous features of direct-infusion ESI-MS for the interception of transient reaction intermediates, such as compounds **2–8**. Such a methodology can certainly be applied to monitor other environmentally relevant processes. The

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definitive confirmation of the chemical structures of these compounds could be accomplished by the attainment of the fragmentation pattern of the authentic ions. However, this was not done since the compounds **2–8** are not commercially available. Finally, the present study points to the need of an investigation of the hazard to the environment and living organisms of the novel degradation products herein detected.

Acknowledgements

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