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The photo-degradation of mesotrione, a triketone herbicide, in the presence of Cu^{II} ions

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ABSTRACT

The study focuses first on the complexation of Cu^{II} ions with mesotrione. Experimental absorption spectra combined with quantum chemical calculations highlight that Cu^{II} ions bind to the molecule in bidentate mode between O1 and O7 atoms. The calculated electronic transitions of the complex show that three of them are mostly ligand-to-ligand electron transfer while the lowest-energy one involves a ligand-to-metal charge transfer (LMCT). The second aim of this work is to explore the effect of Cu^{II} complexation on the photo-degradation of mesotrione. The kinetics and mechanisms of the reactions are proposed on the basis of the experimental results. The effect of different parameters such as the irradiation wavelength, the oxygen concentration and the pH of the mixture and also the production of reactive species such as hydroxyl radicals is investigated. The photochemical degradation of mesotrione in water arises from the triplet excited state of the molecule and results in a photo-hydrolysis process. For the complex, by exciting mainly in its LMCT absorption band, an electron transfer between copper and mesotrione probably occurs and the mechanism of mesotrione-Cu^{II} photo-degradation differs: in addition to the photo-hydrolysis route, a photo-cyclisation process takes place and the oxidation of the ligand is accompanied by the reduction of Cu^{II} ions.

Introduction

Copper is an essential trace element in water and plays a significant role in metabolism in the human body. It takes an important part in the composition of Bordeaux mixture, which is used to control mildew in agriculture. Up to a certain concentration, copper may pollute the wastewater. As an example, electroplating and smelting industries may be responsible for copper pollution [1].

Mesotrione (2-[4-methylsulfonyl-2-nitrobenzoyl]-1,3-cyclohexanedione) is a selective pre- and post-emergent herbicide for control of broad-leaved and some grass weeds in corn which belongs to the family of triketones (Fig. 1a) [2–4]. It was developed by Syngenta Crop Protection and registered in Europe in 2000 [5,6] in place of atrazine which was prohibited in Europe in 2003. Mesotrione is known to act as inhibitor of an enzyme (*p*-hydroxyphenylpyruvate dioxygenase) localized in the cytoplasm of living cells [5]. It is a moderately persistent substance in soils [7,8] and thus can be leached easily to surface waters [4].

Photo-degradation of pesticides that are potentially exposed to sunlight may play a major role in their environmental fate [9]. The photo-degradation of mesotrione has been undertaken in few studies [10–13], some of them dealing with advanced oxidation processes (AOP) [11,12]. It has been largely reported that the composition of water greatly influences the photo-degradation of pesticides [14]. As an example, the presence of copper can accelerate the degradation of organic molecules in aqueous phase by inducing Fenton-like reactions [15–18] and may inhibit the photo-transformation through a strong chelation with some pesticides [19,20]. As many metal cations, copper(II) may be chelated with organic molecules. To our knowledge, there are only few studies dealing with the complexation by pesticides of metal ions [21,22] and even no data on mesotrione complexation are reported. Thus the first objective of the present study was to investigate the possibility of Cu^{II} ions to bind with mesotrione. In addition, the photochemical mechanisms of copper complexes described in the literature [23–26] highlight the catalytic role of copper in a Cu^{II}–Cu^{I} redox cycle. Such catalytic effect may be based

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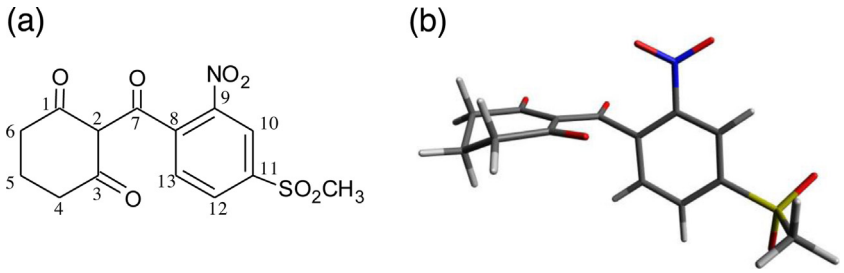

Fig. 1. Structure of mesotrione (a) and optimized geometry for the deprotonated form of mesotrione (D) (b).

on the photo-degradation of the ligand in the coordination sphere of the Cu^{II} metal center and/or on the secondary reactions of the active species produced photochemically from the copper complex [23]. In the case of charge transfer complexes, when the same excited states are involved in the photo-degradation process and in the ligand to metal charge transfer (LMCT) transition, then the Cu^{II} complexes undergo a photo-induced reduction of one copper(II) with the concomitant oxidation of the ligand. Thus, the second aim of this work was to explore the effect of Cu^{II} complexation on the photo-degradation of mesotrione. The kinetics and mechanisms of the reactions are proposed on the basis of the experimental results. The effect of different parameters such as the irradiation wavelength, the oxygen concentration and the pH of the mixture and also the production of reactive species such as hydroxyl radicals was investigated.

1. Materials and methods

1.1. Chemicals

Chemicals were used as received. Anhydrous iron(III) chloride ($FeCl_3$), methanol and acetonitrile (analytical grade for HPLC≥ 99.9%), formic Acid (≥95%), perchloric acid (70%), isopropanol (99.9%), 4-(methylsulfonyl)-2-aminobenzoic acid (AMBA) and 4-(methylsulfonyl)-2-nitrobenzoic acid (MNBA) were purchased from Sigma–Aldrich. Mesotrione (Pestanal), potassium oxalate hydrate ($K_2C_2O_4$, x H_2O) (99%) and copper(II) chloride (95%) were obtained from Fluka, Alfa Aesar and Lancaster, respectively. Experiments were performed in water purified by a Milli-Q device (Millipore).

1.2. Irradiation

Irradiations of mesotrione (40 μM) were performed with different devices. For steady-state irradiation studies and for the identification of photo-products, the experiments were carried out in a pyrex photo-reactor placed in cylindrical stainless steel container. Three fluorescent tubes (DUKE 20W GL20E), presenting a continuous emission in the 275–350 nm range with a maximum centered at 313 nm, were placed around the reactor. For the determination of mesotrione degradation quantum yields, potassium ferrioxalate was used as chemical actinometer [27]. Solutions were irradiated by monochromatic parallels beam using a 1 cm (path length) quartz cell. The light source was a xenon lamp (1000 W) equipped with an Oriel monochromator. The monochromatic irradiations were carried out at different wavelengths (280, 300, 310 and 320 nm). The incident flux measured according to the method described by Calvert and Pitts [27] was in the range (1.0–1.4). 10^{15} photons s^{-1} cm^{-2}.

In order to study the effect of dissolved oxygen concentration, the solutions were deoxygenated by nitrogen bubbling or oxygenated by oxygen bubbling for 20 min prior to irradiation. The pH was adjusted using Jenway 3310 pH-meter to ≥0.1 pH unit by adding $HClO_4$ (0.1 M) or NaOH (0.1 M).

1.3. Analyses

The degradation of mesotrione was monitored by HPLC using a Waters apparatus equipped with a 996-photodiode array detector. The experiments were performed by employing UV detection at 250 and 280 nm. Analytical separation was achieved using a column Agilent Eclipse XDS-C8 column (250 × 4.6 mm, 5 μm). The flow rate was 1.0 mL min^{-1} and the injected volume was 100 μL. A gradient program for the elution was used by employing acidified water (0.05% v/v formic acid) (A) and methanol (B) (Table 1, SI).

LC–MS photoproducts identification was carried out in positive and negative modes with a Waters (Alliance 2695) HPLC system coupled to a Quattro—TOF mass spectrometer equipped with an electrospray ionisation source (ESI) and a photodiode array detector (Waters type 996). Chromatographic separation was obtained using a Phenomenex Synergy Furion RP column C18 (100 × 2 mm, 2.6 μm). The flow rate was 0.2 mL min^{-1} and the injected volume was 3 μL. The elution was accomplished from a mixture of water (acidified with 0.2% v/v acetic acid) (A) and acetonitrile (B) using a gradient mode (Table 2, SI).

The electrospray source parameters in positive mode were: capillary voltage 3.0 kV (2.1 kV in the negative mode), cone voltage 35 V, extraction cone voltage 2 V, source block temperature 100 °C, desolvatation gas temperature 250 °C, ionization energy 20 eV and collision energy 10 eV (7 eV in negative mode).

UV–visible spectra were recorded on a Cary 100 or 300 (Varian) double-beam spectrophotometer, in the 200–700 nm spectral range using quartz cells of 1 cm path length.

1.4. Chemometric methods

The absorption spectra acquired for various metal/ligand molar ratio (R) were analyzed using the Reactlab equilibrium program [28]. This program allows the determination of the number of species that contribute to the spectra using a factor analysis procedure (EFA) [29–31] and of the electronic spectra of each pure species. The Reactlab equilibrium program has also been used to estimate the apparent formation constants (β) of the different complex forms. In order to obtain the best fit between the complexation model and the experimental data, several models of complexes have been envisaged for the refinement of the formation constants. The apparent formation constant $\beta_{x:y}$ ($\beta_{x:y} = [M_xL_y]/([M]^x \times [L]^y)$) results from the equilibrium between the free ligand L and the complex M_xL_y (without taking into account the protonation state of the ligand), where M is the metal cation:

$$xM + yL \rightleftarrows M_xL_y$$