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Photochemistry of the pesticide azinphos methyl and its model molecule 1,2,3-benzotriazin-4(3*H*)-one in aqueous solutions: Kinetic and analytical studies

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Abstract

The photodegradation of the organophosphorus pesticide azinphos methyl and 1,2,3-benzotriazin-4(3*H*)-one in aqueous solutions with excitation within the wavelength range 254–313 nm was studied. For both compounds, the degradation depended on the excitation wavelength: the quantum yield decreased with decreasing the excitation energy.

The analysis of the irradiated solution of azinphos methyl revealed the presence of several products. 1,2,3-Benzotriazin-4(3*H*)-one was shown to be the major product accounting for roughly 50% of azinphos methyl conversion. Such product led in its turn to an efficient formation of anthralinic acid via the formation of an iminoketene derivative. Detailed mechanisms for the formation of the primary products from both azinphos methyl and 1,2,3-benzotriazin-4(3*H*)-one are proposed and discussed.

Keywords: Organophosphorus; Azinphos methyl; Photolysis; 1,2,3-Benzotriazin-4(3*H*)-one; Iminoketene; Anthranilic acid

1. Introduction

The presence of persistent organic chemicals in groundwater, streams, rivers lakes and waste water effluents may cause serious problems to the environment, human health and to the equilibrium of ecosystems. Among these pollutants, the pesticides represent an important class. The interest in these environmental effects leads to an increase of the research activities toward the development of new treatment methods which could help in an efficient remediation of contaminated waters. Many of these pollutants which are present in aqueous solutions can undergo photochemical transformation with solar light via direct as well as indirect photoreactions. Several pesticides present absorption spectra with an important overlap with that of solar light emission ($\lambda > 295$ nm). They can therefore undergo direct photochemical dissociation in the environment [1–4] permitting the formation of various byproducts. If the pesticide does not absorb the solar light, they may still undergo photochemical transfomation via indirect photoreaction. It is therefore of interest to know to what extent they are degraded via such interesting and low cost processes.

Azinphos methyl (*O*,*O*-diethyl *S*-[(4-oxo-1,2,3-benzotriazin-3(4*H*)-yl) methyl] ester is an insecticide from organophosphorus family which has been used as an alternative to organochlorine compounds for pest control. Such chemicals are included in several lists of pollutants due to their widespread use and high toxicity [5,6]. They have relatively high solubilities in water thus they are transported readily through soils and into ground waters or surfaces waters [5]. Several studies on the degradation of various organophosphorus compounds were undertaken such as photoassisted titanium dioxide mediated degradation [7,8], electrogenerated Fenton's reagent [9], Photo Fenton reaction [10], biodegradation [11], X-ray irradiation [12] and combined degradation using both semiconductors and organic sensitizers [13]. Azinphos methyl is widely and efficienly used to protect apple, peaches, lemon trees and fruits from a variety of insects. Its application on numerous agricultural and vegetable crops, fruits and vegetables is tolerated in several countries [14].

Recent studies on the degradation of azinphos methyl reported the formation of several products, identified using

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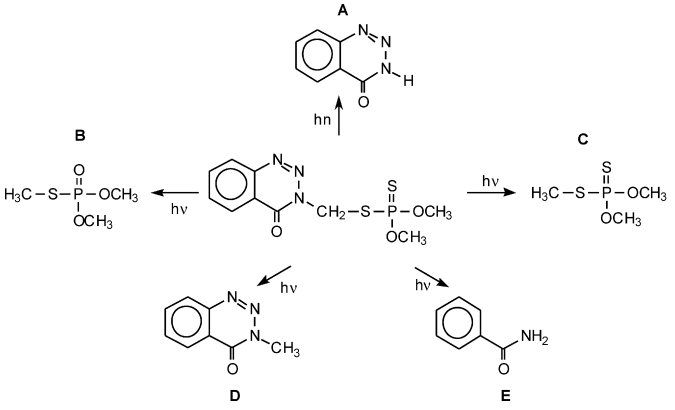
GC–MS analysis [15]. It was clearly reported that the photodecomposition mainly involves the dissociation of the C–S and the N–C bonds. The triazinic products, A and D, are known pollutants present in the environment due to their use as herbicides [16–18]. Within this work, the toxicity measurements of the irradiated solution of azinphos methyl by using acethylcholine esterase thermal lens spectrometer bioassay (AChE-TLS) [19] revealed a 30% decrease of initial AChE activity. Since AChE was not susceptible to the inhibition byproducts E and A, the detected reduced activity of the enzyme was mainly attributed to the formation of the trimethyl phosphate esters B and C but it could also be owing to non detected or secondary photoproducts.



The photodecomposition of azinphos methyl was also shown to occur efficiently on soils and leaf surfaces [20]. The rate of disappearance increased with increasing soil moisture content. From analytical point of view, the noninsecticidal water-soluble photoproducts due to sunlight excitation amounted to roughly 1.4–6.5%. They were identified as to *N*-methylbenzazimide (D), 1,2,3-benzotriazin-4(3*H*)-one (A) and the oxon derivative of azinphos methyl.

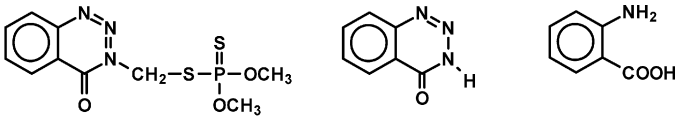
The present study was conducted in order to get a better insight into the photochemical behaviour of azinphos methyl. The specific objective is to elucidate the nature of the main photoproducts formed under UV irradiation which could be important in relation to their persistence in the environment and also to determine the conditions of their formation. The kinetic aspect of azinphos methyl photodegradation is also of great importance in order to elucidate the mechanism of the formation of these products during the irradiation process using both conventional and time resolving techniques.

2. Experimental

2.1. Materials

Azinphos methyl (*O*,*O*-diethyl *S*-[(4-oxo-1,2,3-benzotriazin-3(4*H*)-yl) methyl] ester was purchased from Riedel-de Haën (98.5%). 1,2,3-Benzotriazin-4(3*H*)-one was from Aldrich (98%). Antranilic acid was provided by Fluka (>99.5%). They were all used as received. All other reactants were of the highest grade available. All solutions were prepared with deionised ultrapure water which was purified with Milli-Q device (Millipore) and its purity was controlled by its resistivity.

The following abbreviations were used throughout all the text:



Azinphos-methyl **AZM** | 1,2,3 benzotriazin-4(3H)-one **BZT** | Anthranilic acid **ACA**

2.2. Steady state irradiations

For kinetic as well as analytical purposes, aqueous solutions were irradiated with a parallel beam using a xenon arc lamp (1600 W) equipped with a Schoeffel monochromator. The bandwidth was 10 nm. Solution in a quartz cell (1 cm optical pathlength) was deoxygenated by argon or nitrogen bubbling or oxygenated by oxygen bubbling for 20 min prior to irradiation. Then the cell was closed using a septum. The initial concentration of the solution was checked by HPLC analysis after bubbling. The irradiations at 254 nm were obtained with PHILIPS TUV 6 W lamp delivering a parallel beam. Potassium ferrioxalate was used as a chemical actinometer as reported in the literature [21]. The pH of the solutions was adjusted using dilute solutions of $HClO_4$ or NaOH. For analytical purposes, irradiations were performed in a device equipped with germicide lamps (up to 6) emitting at 254 nm and a 100 ml cylindrical quartz reactor. Similar setup was used for the irradiation at 313 nm. The deaeration of the solution was accomplished by continuous nitrogen bubbling.

2.3. Laser flash photolysis

Transient absorption experiments in the 20 ns to 400 μs time scale were carried out on a nanosecond laser flash photolysis spectrometer from Applied Photophysics (LKS.60). Excitation (λ = 266 nm) was from the fourth harmonic of a Quanta Ray GCR 130-01 Nd:YAG laser (pulse width ≈5 ns), and was used in a right-angle geometry with respect to the monitoring light beam. A 3 cm^3 volume of an argon saturated solution was used in a quartz cell, and was stirred after each flash irradiation. Individual cell samples were used for a maximum of five consecutive experiments. The transient absorbance at preselected wavelength was monitored by a detection system consisting of a pulsed xenon lamp (150 W), monochromator, and a 1P28 photomultiplier. A spectrometer control unit was used for synchronizing the pulsed light source and programmable shutters with the laser output. This also housed the high-voltage power supply for the photomultiplier. The signal from the photomultiplier was digitized by a programmable digital oscilloscope (HP54522A). A 32 bits RISC-processor kinetic spectrometer workstation was used to analyse the digitized signal.

2.4. Analyses

UV–vis spectra were recorded on a Cary 300 scan (Varian) spectrophotometer LC/MS studies were carried out with