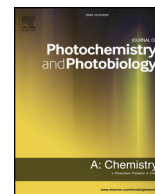




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Light induced degradation of the fungicide Thiophanate-methyl in water: Formation of a sensitizing photoproduct

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ABSTRACT

This work demonstrates that the fungicide thiophanate-methyl generates a sensitizing photoproduct upon irradiation in solar light and explains how the reaction proceeds. The degradation profile of aqueous thiophanate-methyl in simulated solar light showed an autoaccelerated shape indicating the formation of some photodegrading compounds. Among the detected photoproducts, I ($\lambda_{\text{max}} = 340 \text{ nm}$), a quinoxaline derivative generated in the very beginning of the reaction seemed to be the molecule responsible for this autoacceleration. Further experiments were conducted to confirm this hypothesis. The laser flash photolysis ($\lambda_{\text{exc}} = 355 \text{ nm}$) of I generated a transient species reminiscent to the triplet excited state of unsubstituted quinoxaline. The two triplets reacted with the phenolic probe, 2,4,6-trimethylphenol, with $k = 2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. Steady-state irradiations showed that thiophanate-methyl drastically accelerated the photolysis of the probe in an auto-accelerated reaction confirming the production of a sensitizing photoproduct. Moreover, unsubstituted quinoxaline sensitized the degradation of thiophanate-methyl showing that this latter contains labile H atoms. All these data confirmed that I was the sensitizer responsible for the auto-accelerated light induced transformation of thiophanate-methyl. The mechanism of formation of I was studied by quantum calculations. It proceeds through photocyclisation to form a S–S bridge, followed by intra and intermolecular H abstractions and finally departure of HSS. The sensitizing properties of micropollutants photoproducts open a large array of investigations. Our study provides a reliable approach to investigate the overlooked photosensitizing effect of photoproducts during photochemical reactions in water and opens the way to a vast array of research.

1. Introduction

The phototransformation of micropollutants in the environment can result from two types of reactions: those due to solar light absorption by the compound of interest, the so-called direct photolysis, and those due to photoinduced or sensitized reactions involving chromophoric substances. NOM (natural organic matter), nitrate ions and ferric species are examples of natural constituents whose photodegrading effects through their ability to generate various reactive species have been intensively studied [1]. The situation in real waters is however very complex because (i) once the photochemical reactions have been initiated, they can continue due to the secondary oxidant species generated [2] and (ii) the range of possible photoinducers or sensitizers is possibly very large including contaminants themselves. Any contaminant can act as a sensitizer provided it shows the specific photochemical properties required for sensitization. For example, previous

studies have shown that upon solar light irradiation chlorothalonil, an intensively used fungicide, generates a very oxidant triplet excited state with a high yield as well as singlet oxygen [3]. Chlorothalonil is actually able to sensitize the photodegradation of other pesticides on the leaves [4] and could photooxidize other compounds in illuminated surface waters [5]. Sensitizing molecules can be also found among pharmaceutical compounds, for instance those containing a benzophenone-like chromophore known to generate oxidant triplet excited states [6]. Once released in surface waters these compounds could potentially photodegrade other molecules coexisting in the medium and the reactions can continue [7].

During the course of our investigations, we discovered another situation much less described. The sensitization does not occur from the parent contaminant but from one of its photoproducts. This is the case for thiophanate-methyl (TM, dimethyl-4,4'-(ortho-phenylene)bis(3-thioallophanate) (Scheme 1).

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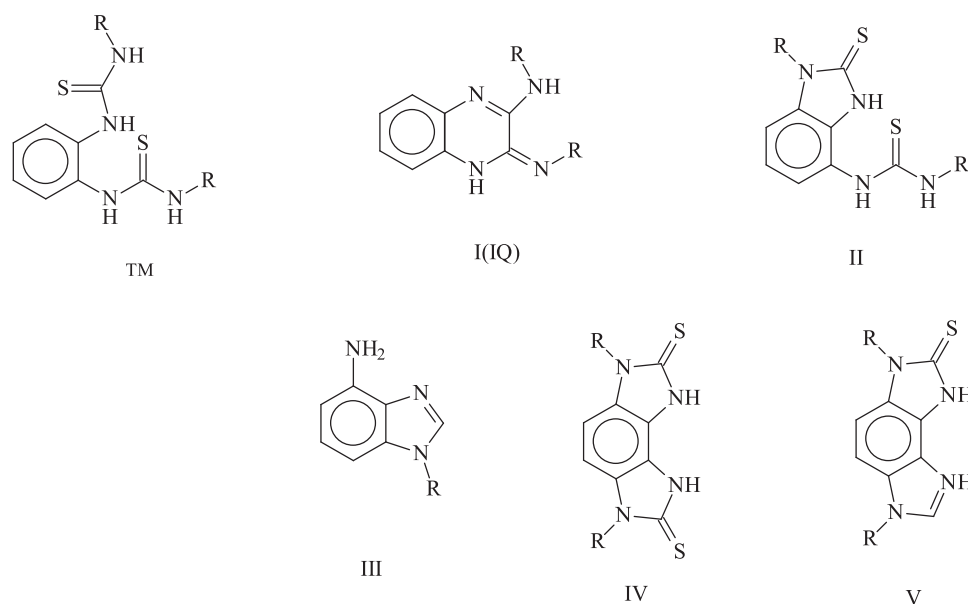
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Scheme 1. Chemical structure of TM, and the main photoproducts of TM reported by Chayata et al. [12]. There are two other structural isomers of I. The specific isomer depicted in this scheme is named IQ below.

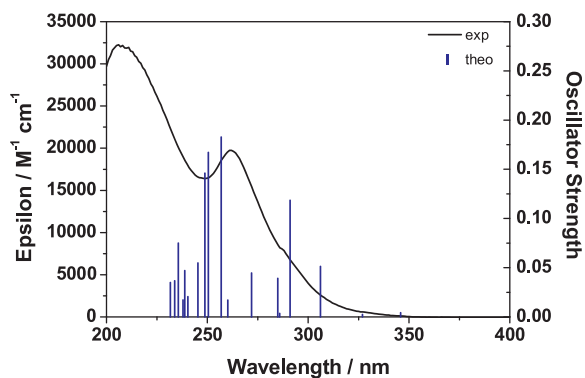


Fig. 1. Experimental absorption spectrum of TM in water (solid line) and theoretical oscillator strengths calculated with TD-DFT at the B3LYP/6-31 + G(d,p) + PCM level (blue lines).

TM is a fungicide, as chlorothalonil, greatly used in Europe for plant diseases on various crops. TM absorbs solar light up to 350 nm (Fig. 1) and was shown to undergo photolysis whatever the studied medium: on glass, filter paper, plant leaves and in water [8–11]. A recent detailed study of the photoproducts generated in water and on the peel of grape and tomatoes was conducted [12]. Nine photoproducts were firmly identified using LC–HR–MS/MS, in particular photoproducts I–V (Scheme 1). Based on their chemical structures, one can conclude that TM undergoes cyclisation with formation of a quinoxaline derivative (I) and substituted benzimidazoles (II–V). To note, compound III which was for long characterized as carbendazim would be actually the isomeric structure shown in Scheme 1 [12]. In some other photoproducts, S atoms are also replaced by O atoms (structures not shown).

To better understand this reaction, the mechanism of TM photolysis was investigated by means of steady-state irradiations and laser-flash photolysis. We demonstrated that the quinoxaline derivative formed as a primary photoproduct shows sensitizing properties and plays a key role in the TM photolysis. Quantum calculations were also performed to explain its formation. Our idea was to develop an approach allowing to demonstrate the sensitizing effect of photoproducts.

2. Material and methods

2.1. Chemicals

Thiophanate-methyl (TM, Pestanal, 99.3%), quinoxaline (99%), 2,4,6-trimethylphenol (99.9%), and *p*-hydroxyphenyl-acetic acid (98%) were purchased from Sigma Aldrich. Catalase from bovine liver, 2000–5000 units mg⁻¹, peroxidase from horse radish and hydrogen peroxide (30%, w/w) were obtained from Sigma-Aldrich. Catalase was stocked at –20 °C while hydrogen peroxide and peroxidase at 4 °C. Water was purified using a reverse osmosis RIOS 5 and Synergy (Millipore) device (resistivity 18 MΩ.cm, DOC < 0.1 mg L⁻¹). The other reagents and solvents were of the best purity available and used as received without further purification. The solubility of TM in water being limited to 26.6 mg L⁻¹, the stock solutions of TM were made in acetonitrile. Final solutions were prepared by adding water to reach water-acetonitrile (98–2%, v/v) as a final solvent composition. Stocks solutions of TM were stored at 4 °C and renewed each two days.

2.2. Irradiations

TM (5 × 10⁻⁵ M) was mainly irradiated in a device equipped with six fluorescent tubes TLAD 15W05 Philips (300–450 nm, Fig. SI-1). A 20 mL capacity Pyrex-glass cylindrical reactor (1.4 cm, i.d.) was used. To accelerate reactions, irradiations were also performed in a device equipped with six fluorescent tubes DUKE GL 20E emitting between 280 and 380 nm (Fig. SI-1). Solutions were deoxygenated by bubbling argon in the solution 15 min prior to the irradiation and during the irradiations. The irradiation of 2,4,6-trimethylphenol (1 × 10⁻⁴ M) in the presence of TM or quinoxaline (5 × 10⁻⁵ M) was made in the polychromatic device 300–450 nm. To investigate the sensitizing effect of the photoproduct I on 2,4,6-trimethylphenol, the following experiments were undertaken. TM (5 × 10⁻⁵ M) was pre-irradiated in the polychromatic device 280–380 nm until a conversion extent of 23% in order to accumulate I. Then 2,4,6-trimethylphenol was added to this solution to reach a final concentration of 10⁻⁴ M. The mother solution of 2,4,6-trimethylphenol was as high as possible to dilute negligibly the pre-irradiated TM solution. The absorbance of the mixture was of 0.210 at 304 nm and of 0.133 at 334 nm. The contribution of I to these absorbances were obtained by measuring the HPLC peaks area. We found that I contributed for 12% and 49% to the absorbances at 304 and

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