



Reaction kinetics and mechanisms of organosilicon fungicide flusilazole with sulfate and hydroxyl radicals



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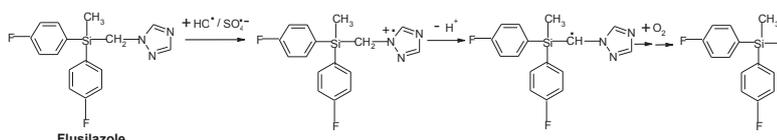
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HIGHLIGHTS

- Flusilazole degradation by photo-Fenton process with solar simulator.
- CG-MS by-products detected show cleavage between silicon and triazole ring.
- A charge transfer reaction mechanism from the fungicide to the radicals is proposed.

GRAPHICAL ABSTRACT



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ABSTRACT

Flusilazole is an organosilane fungicide used for treatments in agriculture and horticulture for control of diseases. The reaction kinetics and mechanism of flusilazole with sulfate and hydroxyl radicals were studied. The rate constant of the radicals with the fungicide were determined by laser flash photolysis of peroxydisulfate and hydrogen peroxide. The results were $2.0 \times 10^9 \text{ s}^{-1} \text{ M}^{-1}$ for the reaction of the fungicide with HO^\bullet and $4.6 \times 10^8 \text{ s}^{-1} \text{ M}^{-1}$ for the same reaction with $\text{SO}_4^{\bullet-}$ radicals. The absorption spectra of organic intermediates detected by laser flash photolysis of $\text{S}_2\text{O}_8^{2-}$ with flusilazole, were identified as α -aminoalkyl and siloxyl radicals and agree very well with those estimated employing the time-dependent density functional theory with explicit account for bulk solvent effects. In the continuous photolysis experiments, performed by photo-Fenton reaction of the fungicide, the main degradation products were: bis(4-fluorophenyl)-hydroxy-methylsilane and the non-toxic silicic acid, diethyl bis(trimethylsilyl) ester, in ten and twenty minutes of reaction, respectively.

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1. Introduction

Advanced oxidation processes (AOPs), like UV/ $\text{S}_2\text{O}_8^{2-}$ and Fenton, have attracted interest for the degradation of organic compounds in wastewater, such as pesticides (Carra et al., 2016;

Navarro et al., 2011). This is especially true in the case of the use of light-induced reactions in water treatments. The photo-assisted Fenton reaction ("photo-Fenton" reaction) typically gives faster rates and a higher degree of mineralization than the thermal reaction and can take the advantage of light in the solar spectral region (Faust and Hoigné, 1990). In photo-Fenton process Fe^{2+} ions are oxidized by H_2O_2 and one equivalent HO^\bullet is produced. The obtained $\text{Fe}(\text{OH})^{2+}$, which is predominant in acidic conditions, act as the light absorbing species that produce another radical while

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the initial Fe^{2+} is regained (Kim and Vogelpohl, 1998). Persulfate reaction mechanism is based on the generation of the strong sulfate radical ($\text{SO}_4^{\cdot-}$). One mole of this reagent can be activated to generate 2 mol of sulfate radical under UV irradiation. The sulfate radical is known to be a very strong oxidant, i.e. $E(\text{SO}_4^{\cdot-}/\text{SO}_4^{2-}) = 2.43 \text{ V vs. NHE}$ (Criquet and Leitner, 2009) for degrading organic contaminants in wastewater (Wang and Liang, 2014; Luo et al., 2017).

Flusilazole is the approved name for 1-[[bis(4-fluorophenyl)methyl]silyl]methyl]-1H-1,2,4-triazole (CAS No. 85509-19-9). It is a triazole family fungicide with a molecular structure shown in Scheme 1. It is a broad-spectrum fungicide, which exhibits curative and preventative activities and is recommended for use in agriculture and horticulture (T. R. Roberts and Hutson, 1990).

Pesticides can easily accumulate in plants, foods, water reservoirs and food chain, which could be triggered by indiscriminate use. Besides, some of them are resistant to the action of sunlight, temperature, water or microorganisms; as a result of this, plant tissue and environmental samples contain high levels of pesticides residues.

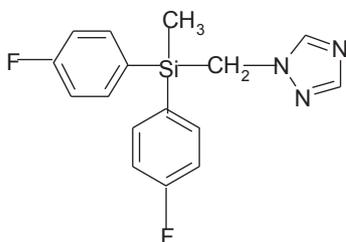
It was suggested that flusilazole is capable of inducing genotoxicity in plants in studies with higher plant models (Ozakca and Silah, 2013). Animal models in vitro and in vivo have been used to investigate the teratogenicity of flusilazole. Some studies reported marked maternal toxicity, growth retardation, and skeletal in rodent models, which contribute to alterations in fetal growth retardation and skeletal development (Farg and Ibrahim, 2007). Besides embryotoxic responses are critically dependent on the timing of exposure during rat embryo development (Dimopoulou et al., 2016).

Photolysis (artificial and natural sunlight) on soil surface and aqueous photodegradation is not an important mode of degradation for flusilazole (T. R. Roberts and Hutson, 1990). Despite flusilazole is a widely used fungicide, documented data on their degradation mechanism and intermediate metabolites is lacking. Differences in chemical reactivity between silicon and carbon compounds influence the degradation and oxidative metabolism of otherwise similar compounds. For instance, organic silicon compounds usually lead to naturally occurring silicates as final product, in sharp contrast with the carbon containing analogous compounds (Griessbach and Lehmann, 1999).

In this context, the aim of the present work is to investigate the kinetics and mechanism of the degradation of flusilazole initiated by HO^{\cdot} and $\text{SO}_4^{\cdot-}$. These radicals have been generated by laser flash photolysis ($\lambda_{\text{exc.}} = 266 \text{ nm}$) of H_2O_2 and $\text{Na}_2\text{S}_2\text{O}_8$, respectively. Also, continuous-irradiation experiments have been performed by photo Fenton reaction of the fungicide and the nature of the primary degradation products formed have been investigated by GC-MS analysis.

2. Experimental

Reagents. Flusilazole (1-((bis(4-fluorophenyl)methyl)silyl)



Scheme 1. Flusilazole.

methyl)-1H-1,2,4-triazole), was purchased from Sigma-Aldrich (Fluka). Sodium peroxodisulfate was obtained from Merck. Ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) 98% was obtained from Fisher Chemical. H_2O_2 30% (w/w) in H_2O was supplied by Sigma-Aldrich. Potassium thiocyanate was from Mallinckrodt.

Distilled water was passed through a Millipore system ($>18 \text{ MX cm}$, $<20 \text{ ppb}$ of organic carbon).

Sample Preparation. Flusilazole (F) saturated aqueous solution was prepared to set up suspensions of lower concentrations by dilution. Oxygen-free and oxygen saturated solutions were obtained by bubbling the samples with argon or oxygen, respectively, for 20–30 min before use.

In continuous photolysis experiments the pH of the solution was adjusted to 3.0 using HCl and the sample was mixed using a magnetic stirrer during the process.

Laser Flash Photolysis (LFP) Experiments. LFP experiments were performed by excitation with the fourth harmonic of a Nd:YAG Litron laser (2 ns fwhm, 2 mJ per pulse at 266 nm). The analyzing light from a 350 W Xe arc lamp was passed through a monochromator (PTI 1695) and detected by a 1P28 PTM photomultiplier. Due to the characteristics LFP detection system used, traces with $\lambda > 650 \text{ nm}$ and $\lambda < 290 \text{ nm}$ could not be detected within the experimental error. A cuvette of 10 mm path length was used for the sample container. Decays typically represented the average of 32 laser shots and were stored in a 500 MHz Siglent digital oscilloscope. Solution absorbance was 0.5 at 266 nm. Reactant concentrations were: $[\text{Na}_2\text{S}_2\text{O}_8] = 1.0\text{--}2.5 \times 10^{-2} \text{ M}$ and flusilazole was in the range $8.49 \times 10^6 \text{ M} - 8.50 \times 10^{-5} \text{ M}$.

Freshly prepared solutions were used in order to avoid thermal reactions of peroxodisulfate and hydrogen peroxide with the substrate.

Bilinear regression analysis. For each experimental condition, several absorbance decay profiles at different detection wavelengths were taken. Absorbance is thus a function of wavelength and time. Taking advantage of the linearity of the absorbance with both, concentrations and absorption coefficients, a bilinear regression analysis was applied to the experimental absorption matrix in order to retrieve information on the minimum number of species and on their relative concentration profiles and absorption spectra (San Román and Gonzalez, 1998).

Time-dependent density functional theory calculations. Time dependent density functional calculations, TD-DFT, has been employed in numerous studies as a useful tool to characterize electronically excited states of a large number of molecules (Dell'Arciprete et al., 2011; Arce et al., 2012). In this work, the hybrid B98 (Schmider and Becke, 1998) density functional combined with the 6-311++G(d,p) basis set, was used to interpret the spectra of the observed transient species. To account for solvent effects, the conductor-like polarizable continuum model, CPCM, was employed using a relative permittivity for H_2O of 78.3553 (Barone and Cossi, 2001). In this way, the interaction between solvent and solute molecules was considered. All calculations have been carried out with the Gaussian 09 package (Frisch et al., 2009). To obtain the theoretical absorption spectrum it is firstly necessary a full optimization of the geometric parameters of the considered ground-state molecule. In all the cases, real frequencies were obtained indicating that molecular structures correspond to stable species. Next, the vertical electronic energies, the associated wavelengths of the band maxima, λ_{max} , and oscillator strengths f were computed at the abovementioned level of theory.

To compare the prediction with experimental data, theoretical bands were approached with individual Gaussian functions characterized with full width values σ (at the 1/e height of the bands) and summed over all relevant electronic transitions (Cobos and Croce, 2010). As Fig. 3 shows, a satisfactory agreement between

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