



# Gas-phase and particulate products from the atmospheric degradation of an isoxazole fungicide



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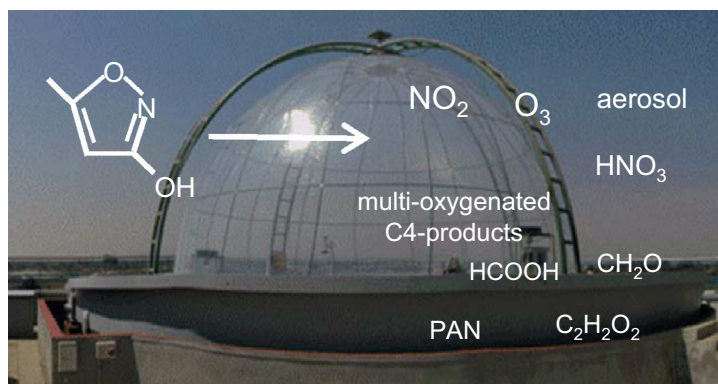
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## HIGHLIGHTS

- Atmospheric OH-reaction study of isoxazoles at a large outdoor simulation chamber.
- Reaction profiles and yields of hymexazol's products were determined.
- Nitrogen derivatives were the main degradation products observed.
- Cleavage products were C4-compounds with 1,3 oxygenated moieties.
- The degradation routes were formulate based on the structurally defined products.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The isoxazole structure is present in several pesticides. However, there is a lack of information about its degradation products after the release to the atmosphere. The main atmospheric reactions of hymexazol (5-methylisoxazol-3-ol), selected as representative model, were investigated at a large outdoor simulation chamber. The predominant products of atmospheric degradations were gaseous nitrogen derivatives (nitric acid, nitrogen dioxide, nitrogen oxide, nitrous acid, and peroxyacetyl nitrate), ozone, and small oxygenated compounds (formic acid, formaldehyde, and methylglyoxal). The aerosol yields were lower than 5%, and an OH rate-dependence was observed in the nucleation, particle growth, and size distribution. Also, the chemical composition of minor multi-oxygenated products was studied for OH-photo-oxidations. More than 20 products were detected in the gas or particulate phase. The most abundant were heterocyclic cleavage products with C4-chain and oxygenated moieties at positions 1 and 3, such as 3,4-dioxobutanoic acid, 3-oxobutanoic acid, and 3-oxobutanal. The suggested reaction pathway is the opening of heterocycle ring by the cleavage of N–O bond and C–N bond, releasing nitrogen oxides.

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## 1. Introduction

The isoxazole structure is a 1,2-azol, five-membered aromatic heterocyclic with an oxygen and a nitrogen. These compounds have

a wide range of applications, including fungicides, insecticides, herbicides and drugs. Examples of approved pesticides in Europe are hymexazol, isoxaben and isoxaflutole. Other compounds are drazoxolon, isouron, isoxathion (not approved), topramezone (pending) or isoxachlortole (not registered in Europe). The release of pesticides based on isoxazole structure to the environment is produced during the manipulation, application and post-application, being the volatilization from the treated surface the most important input into the troposphere (Van den Berg et al., 1999).

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The information about the atmospheric behavior of isoxazoles (as many pesticides and heterocycle compounds) is quite scarce. As other semi-volatile organic compounds (SVOCs) in the atmosphere, isoxazoles are distributed between gas and particle phase (Atkinson et al., 1999). An oxidative degradation is also produced reducing its concentration, but new products are also formed. These secondary pollutants, called residues, include gaseous or condensed compounds with a different atmospheric residence time, and sometimes worse toxicity than the original molecule. However, experimental results about pesticides have been reported only for a lower number of products (Atkinson et al., 1999; Le Person et al., 2007; FOCUS Working Group, 2008). In order to get a comprehensive overview of their atmospheric fate, both their gas and particulate reactivity must be taken in consideration. For that, the use of atmospheric simulation chambers solves some of the difficulties appeared to carry out realistic laboratory studies (Finlayson-Pitts and Pitts, 2000; Feigenbrugel et al., 2006). These full-equipped facilities have allowed the examination of pollutant degradations under atmospheric controlled conditions, such furan, thiophene or pyrrole – aromatic cycles with one heteroatom – (Atkinson et al., 1983, 1984; Bierbach et al., 1992; Cabañas et al., 2004; Gómez-Álvarez et al., 2009) or pesticides (Le Person et al., 2007; Muñoz et al., 2012).

An important isoxazole systemic fungicide is 5-methylisoxazol-3-ol, named hymexazol being used to control diseases caused by soil-borne pathogens and a plant growth stimulant. In the present study, this compound has been selected as model of isoxazole reactivity due to its high input in the atmosphere: relatively high volatility (vapor pressure of 182 mPa at 25 °C) and high use. Since its entry onto the market in the seventies, the number of application has increased – e.g. rice, vegetable, tobacco, tomato, and cucumber crops. In fact, hymexazol is the only registered fungicide that controls both *Aphanomyces* and *Pythium*, and thus is used worldwide as a standard treatment for sugar beet seed (Payne and Williams, 1990).

A previous study performed in our atmospheric chamber was focused on the general description of the hymexazol degradation and the contribution of each atmospheric reaction was compared with other pesticides (Vera et al., 2011). The main aim of the present study is the analysis of its OH-degradation products. Measurements, based on specific instruments and chromatographic techniques, provide information in regard to the composition and the concentration of formed products in the gas phase as well as particulate phase, contributing to the elucidation of the degradation pathway and the evaluation of its environmental impact.

## 2. Experimental section

The experiments were carried out in the EUPHORE photoreactors (Valencia, Spain). These chambers consist of two half spherical fluoropolymeric bags, each one of 200 m<sup>3</sup> with integrated measuring systems for monitoring precursor species, pressure, humidity, temperature, and reaction products (Borrás and Tortajada-Genaro, 2012a). A white-type mirror system (path length of 553.5 m) coupled to a Fourier Transform Infrared spectrometer with MCT detector (NICOLET Magna 550) was used for recording concentrations of major gaseous products. Specific monitors were integrated for measuring NO, NO<sub>2</sub>, NO<sub>x</sub> and O<sub>3</sub>, free of interferences. Aerosol mass concentration was measured with a scanning mobility particle sizer (SMPS).

The chamber set-up or background measurements, see Table 1, were performed filling the photoreactor with air from a purification system. In experiments type A and B, the photoreactor was left

without/with sunlight radiation, to reproduce the same conditions as for ozonolysis and photo-exposed reactions, respectively. In experiment type C, the photoreactor was left in darkness, with an inorganic seeds addition (acidified ammonium sulfate solution of 0.06 M) to establish the aerosol wall losses. Moreover, hymexazol was injected via heated air stream to the closed chamber in order to assure the absence of electrostatic effects with chamber walls. The formation of volatile (background upper limits: O<sub>3</sub> 17 ± 1 µg m<sup>-3</sup>, NO 0.4 ± 0.1 µg m<sup>-3</sup>; NO<sub>2</sub> 5.3 ± 0.5 µg m<sup>-3</sup>; HONO 2.9 ± 0.2 µg m<sup>-3</sup>, HNO<sub>3</sub> 1.3 ± 0.1 µg m<sup>-3</sup>) and particle artifacts (background upper limit: 1 µg m<sup>-3</sup>) were negligible.

The oxidation experiments consisted of the degradation under dry conditions (<2% RH, 295–298 K) in the absence of inorganic seed aerosol (Table 1). Regarding the induced photolysis, cyclohexane was added via sprayer as scavenger of OH radicals. For the ozonolysis, ozone was produced by passing oxygen through a photo-generator (λ = 280–320 nm). For photo-oxidation experiments, hydrogen peroxide was introduced by a sprayer, and HONO was generated by a liquid-phase reaction between a 0.5% NaNO<sub>2</sub> solution and a 30% H<sub>2</sub>SO<sub>4</sub> solution and transferred via a stream of purified air. Later, all the reactants were mixed for 10 min before exposing them to sunlight ( $J_{\text{NO}_2} \approx 7 \times 10^{-3} \text{ s}^{-1}$ ) or kept in darkness for ozone experiment. The onset of aerosol formation (0.01 µg m<sup>-3</sup>, 60 particles cm<sup>-3</sup>) was considered to occur when the first significant particle concentration was registered ( $3\sigma_{\text{background}}$ ). The specific dilution process was determined using SF<sub>6</sub> as a tracer being  $6.5 \times 10^{-6} \text{ s}^{-1}$  the average rate. Finally, the average OH concentrations present in the smog chamber during the photo-oxidation reactions were calculated from the second-order decay of hymexazol ( $k_{\text{OH}} = (4.4 \pm 0.8) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ). The estimated concentration of OH radical was  $2 \times 10^6 \text{ radicals cm}^{-3}$  for experiment in the absence of NO<sub>x</sub> and  $8.8 \times 10^6 \text{ radicals cm}^{-3}$  in the presence of low-NO<sub>x</sub>.

For fingerprint analysis, gaseous products were sampled with C18 cartridges during reaction, under a flow rate of 1 L min<sup>-1</sup> for 0.5 h. Particles were collected at maximum aerosol formation, under a flow rate of 80 L min<sup>-1</sup> for 1 h, on quartz fiber filters that had been pre-baked at 500 °C for 12 h. A blank investigation of cartridges and filters was done to identify possible artifact formation and no compounds or artifacts were observed. The analysis of multi-oxygenated compounds by gas chromatography-mass spectrometry technique was similar to describe in reference (Borrás and Tortajada-Genaro, 2012b). The specific protocol has been included in Supplementary Information.

## 3. Results and discussion

### 3.1. Hymexazol consumption and gaseous products

The first step was a theoretical study of isoxazole molecule reactivity based upon the structure-activity relationship (SAR) methods developed by Kwok and Atkinson (1995). The molecular modeling indicated a low degradation rate by photolysis and ozonolysis reactions but the OH-nucleophilic attack is favored and directed to certain positions with more positive charge density. The kinetic rate constant,  $k_{\text{OH}}$  (cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) for hydrogenated isoxazole ring was  $9.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The theoretical OH kinetic rate constant of other isoxazole rings changed depending on substituents groups. Examples of rate constants are  $6 \times 10^{-12}$ ,  $200 \times 10^{-12}$  and  $204 \times 10^{-12}$  for isoxaflutole, hymexazol and isoxaben – pesticides allowed in Europe – respectively. Then, the atmospheric formation of oxygenated degradation products from isoxazoles is expected to be important.

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