

Solution and surface photochemistry of fenarimol: A comparative study

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Abstract

The photochemistry of the pesticide fenarimol was studied in methanol and on a cellulose surface. The ground state absorption and fluorescence spectra are similar in solution and at the solid/gas interface. Room temperature phosphorescence emission was observed in cellulose. Transient absorption of fenarimol and of its chromophoric units, chlorobenzene and pyrimidine, showed a common absorption band centered at 320 nm in methanol. An absorption band above 350 nm was observed only for fenarimol and was assigned to a recombination intermediate. On cellulose the transient absorption is broader and extends up to 600 nm. The main photodegradation pathway in methanol involves the homolytic cleavage of the bond to the pyrimidyl ring, followed by a fast in-cage recombination of the initially formed pyrimidine and ketyl radicals. On cellulose surfaces, dechlorination is also one of the important photodegradation pathways.

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1. Introduction

Photochemical transformation is one of the main dissipation processes of pesticides under natural conditions [1]. Pesticides normally enter into natural systems mainly by direct application to leaf and soil surfaces. The majority of these compounds are therefore localized at the solid/gas interface [2], indicating that any description of their behavior under environmental conditions requires a detailed study of these compounds in appropriate interfacial model systems.

The fungicide fenarimol (α -(2-chlorophenyl) α -(4-chlorophenyl)-5-pyrimidine-methanol) (see Scheme 1) is commonly used in the form of a spray for treating mildew. Its solution photophysics and photochemistry have been well documented in the literature [3–6].

It was previously found that the photodegradation of this molecule occurs mainly from its lowest excited singlet state, which has (n, π^*) character and is located on the pyrimidine ring [4,5]. The main photodegradation products formed in aqueous

solution under sunlight irradiation were also identified [6]. The product distributions of fenarimol following photodegradation in aqueous solution and under solar irradiation showed the preferential formation of compounds with $m/z = 328$ (A and B), in the initial step of the photolysis process (see Scheme 1). Dechlorination was also found in these aqueous systems (compound C). The homolytic cleavage of the bond to the pyrimidyl ring, with the formation of pyrimidine and ketyl radicals was proposed to be the main primary photoreaction step. Recombination of these radicals would lead to compounds with $m/z = 328$ (A) through pathway 1.

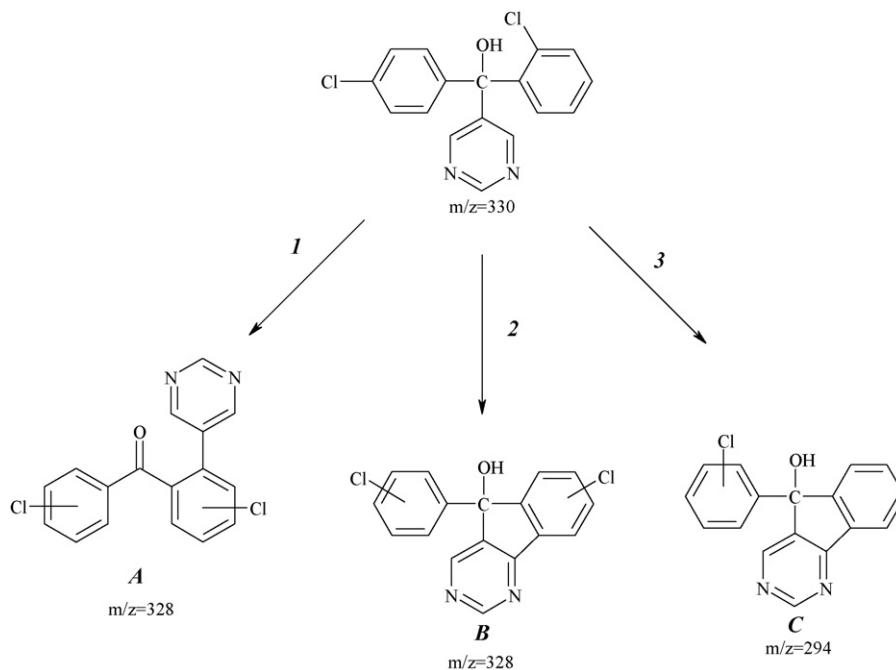
To extend this work, we report a study of the photochemistry of fenarimol in solution and on cellulose surface, performed using laser flash photolysis and chromatographic techniques.

2. Experimental

2.1. Materials

Fenarimol (Riedel-de Haën), cellulose (Fluka), methanol, acetonitrile (Merck Lichrosolv) were used without further treatment. Water was deionized and distilled.

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Scheme 1. Main photoproducts of fenarimol in aqueous solution.

2.2. Preparation of samples on cellulose

Solid powdered samples of fenarimol were prepared as described in previous works [7,8]. The adsorption of the probe was achieved by adding the support to a methanolic solution containing the corresponding amount of fenarimol. The samples were allowed to equilibrate for 12 h and then continuously stirred until all the solvent had evaporated. Final traces of the solvent were removed under reduced pressure ($\sim 10^{-3}$ mbar) at room temperature (~ 1 h). The final concentration of fenarimol was determined by extracting the samples with methanol (a known weight of sample in a known volume of solvent) followed by centrifugation and analysis by HPLC.

2.3. Methods

2.3.1. Diffuse reflectance ground state absorption spectra

Ground state absorption spectra of the solid powdered samples were recorded using a Cintra 40 GCB Scientific Equipment spectrophotometer, with a diffuse reflectance attachment. The measured reflectance, R , was used to calculate the remission function $F(R)$ using the Kubelka-Munk equation.

2.3.2. Diffuse reflectance laser flash photolysis system

Laser flash photolysis experiments were carried out with the fourth harmonic of a Nd:YAG laser (266 nm, 6 ns FWHM, 10–30 mJ/pulse) from B.M. Industries (Thomson-CSF), model Saga 12-10. Transmission geometry was used for solution studies and diffuse reflectance mode for solid samples. A schematic diagram of the system is presented in Ref. [10]. The light arising from the irradiation of the samples by the laser pulse is collected by a collimating beam probe coupled to optical fibers (fused silica) and detected by a gated intensified charge cou-

pled device (ICCD, Oriel model Instaspec V) after passing via a compact fixed imaging spectrograph (Oriel, model FICS 77441). The system can be used either by capturing all light emitted by the sample or in time resolved mode, by the use of a delay box (Stanford Research Systems, Model D6335). The ICCD has high speed gating electronics (2.2 ns) and intensifier, and works in the 200–900 nm wavelength range with appropriate time gates and amplification. Time resolved absorption and emission spectra are available in the nanosecond to second time range. Experiments conducted in solution were made using OD ~ 1 at the excitation wavelength in a 1-cm cell, on air equilibrated and argon purged samples.

For solid samples transient absorption data are reported as percentage of absorption (%Abs.) defined as $100\Delta J_t/J_0 = (1 - J_t/J_0)100$, where J_0 and J_t are the diffuse reflected light before exposure to the laser pulse and at time t after excitation, respectively. For solution samples transient absorption data are reported as ΔOD .

2.3.3. Irradiation, degradation kinetics and product analysis

Photolysis studies were conducted in a system previously used to study photodegradation of pesticides [3,5–9]. The system uses a merry-go-round and an immersion-well photochemical reactor (Applied Photophysics). The 254 nm radiation was obtained using a 16 W low-pressure mercury lamp (Applied Photophysics) without filters and without refrigeration. The solution samples were irradiated at a distance of 5 cm from the lamp housing. The solid samples were irradiated at the same distance after spreading the powder on Petri dishes.

Photolysis was followed by HPLC using a Merck-Hitachi 655A-11 chromatograph equipped with detectors 655A-22 UV and Shimadzu SPD-M6A Photodiode Array. A column

LiChroCART 125 (RP-18, 5 μm) Merck was used and the runs were performed using mixtures water/acetonitrile as the eluent. Analyses were conducted on irradiated and control samples kept in the dark during irradiation.

GC–MS analyses were performed using a Hewlett Packard 5890 Series II gas chromatograph with a 5971 series mass selective detector (E.I. 70 eV). A RTX-20 capillary column with 20 m length and 0.25 mm i.d. (Restek) and a DB-35MS capillary column with 30 m length, 0.25 mm i.d. and 0.25 μm film thickness (J&W Scientific) were used. The initial temperature 70 or 150 $^{\circ}\text{C}$ was maintained during 5 min and then a heating rate of 5 $^{\circ}\text{C}/\text{min}$ was used until a final temperature of 270 $^{\circ}\text{C}$ was reached.

3. Results and discussion

3.1. Ground state diffuse reflectance absorption spectra and time resolved luminescence

The ground state absorption spectrum of fenarimol sorbed on cellulose is similar to that reported in solution (see Fig. 1) [4]. It shows a low intensity absorption shoulder between 280 and 330 nm, assigned to a $n \rightarrow \pi^*$ transition localized on the pyrimidine ring, a medium intensity absorption between 240 and 280 nm, associated with transition of the chlorobenzene and pyrimidine groups, and a high intensity absorption below 240 nm due to a higher $\pi \rightarrow \pi^*$ transition of the chlorobenzene units [4].

Under natural environmental conditions only the solar radiation above 290 nm arrives at the earth surface [1]. Some overlap between the solar spectrum at ground level and the absorption spectrum of fenarimol on cellulose exists, indicating that fenarimol is able to undergo direct photodegradation under natural conditions.

The luminescence of fenarimol in methanol at the pulse end (see Fig. 1, spectrum B) is similar to that reported under stationary conditions [4] and was assigned to fluorescence emission. On cellulose the fluorescence was also detected at the end of the pulse; in addition, an emission band centered at 460 nm was observed 0.5 μs after the laser pulse (Fig. 1, spectrum C).

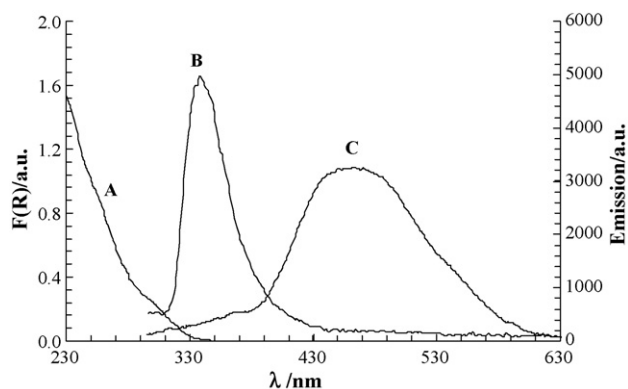


Fig. 1. Ground state absorption spectrum of fenarimol on cellulose ($100 \mu\text{mol g}^{-1}$) (A) and emission spectra of fenarimol in methanol (10^{-4} M, pulse end, 266 nm, 25 mJ/pulse) (B) and on cellulose ($100 \mu\text{mol g}^{-1}$, 0.5 μs , 266 nm, 25 mJ/pulse) (C).

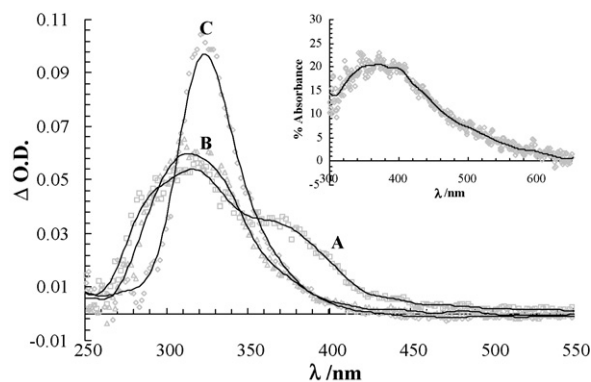


Fig. 2. Transient absorption spectra of fenarimol (A, 1 μs , air equilibrated), chlorobenzene (B, 10 μs , argon purged) and pyrimidine (C, pulse end, argon purged) in methanol (10^{-4} M). The inset shows the transient absorption of fenarimol adsorbed on cellulose ($100 \mu\text{mol g}^{-1}$).

This band was assigned to fenarimol phosphorescence emission by comparison with the reported luminescence data obtained at 77 K [4]. In fact, room temperature phosphorescence has been observed for several compounds on cellulose and is a quite general phenomenon when the adsorption is performed using hydroxylic solvents [10,11]. Under these conditions, the observation of the triplet emission has been explained by the entrapment between the polymer chains, which supplies a rigid environment and protects the probes from molecular oxygen.

3.2. Transient absorption

The transient absorption studies were performed at 266 nm excitation. For comparison purposes similar laser flash photolysis studies were also conducted for pyrimidine and chlorobenzene in methanol. Fig. 2 presents the transient absorption spectra (uncorrected for depletion) obtained for the three compounds.

The transient absorption of chlorobenzene shows a main absorption band at 320 nm. By comparison with the spectra reported in the literature this absorption was assigned to the chlorobenzene triplet state [12]. The decrease of the absorption intensity at 320 nm, in air equilibrated conditions (results not shown), confirm the assignment. Pyrimidine shows a main absorption band at 325 nm, which also increases in argon purged conditions. Based on the behavior in the presence of oxygen and on the published spectra, the observed transient absorption can be assigned to the pyrimidine triplet state [13]. The absorption in this spectral region could also be due to the pyrimidyl radical, a transient formed after hydrogen abstraction by the pyrimidine triplet state [13].

The spectrum obtained for fenarimol shows a main absorption band with a maximum near 315 nm and a shoulder between 350 and 450 nm. The absorption decays in the microsecond time scale but the decay of the main absorption is faster than that of the shoulder, indicating that we have at least two transient species. The comparison of the transient absorption spectra obtained for fenarimol and for its components suggests that the absorption between 350 and 340 nm is due to transients involved in the formation of the final products.

The transient absorption on cellulose is very broad, shows a slight intensity decrease even after 20 ms and extends above 450 nm, giving therefore little insight into the species involved in the photochemical reaction on this surface.

3.3. Photodegradation products and reaction mechanism

The main photodegradation product of fenarimol in methanol and methanol/water mixtures is a compound with $m/z = 328$ (see Fig. 3(a)). The comparison of the mass spectrum with the published data indicated that this compound has the structure of a **A** isomer (see Scheme 1) [6]. The compounds with $m/z = 140$, 190, 250 and 294, identified in previous studies [6], and are minor photodegradation products. We were not able to assign a structure to the product with $m/z = 314$, although it appears to involve loss of an oxygen atom.

Fig. 3(b) shows a comparison of the photoproduct distribution in methanol solution and sorbed on cellulose. The results indicate that the adsorption on cellulose surface strongly modifies the photoproduct distribution. The formation of compounds with $m/z = 294$ increase relative to compound **A**, on going from methanol solution to adsorption on cellulose. The formation of the compound with $m/z = 314$ is also quenched on cellulose and a new product with 33.47 min of retention time appears.

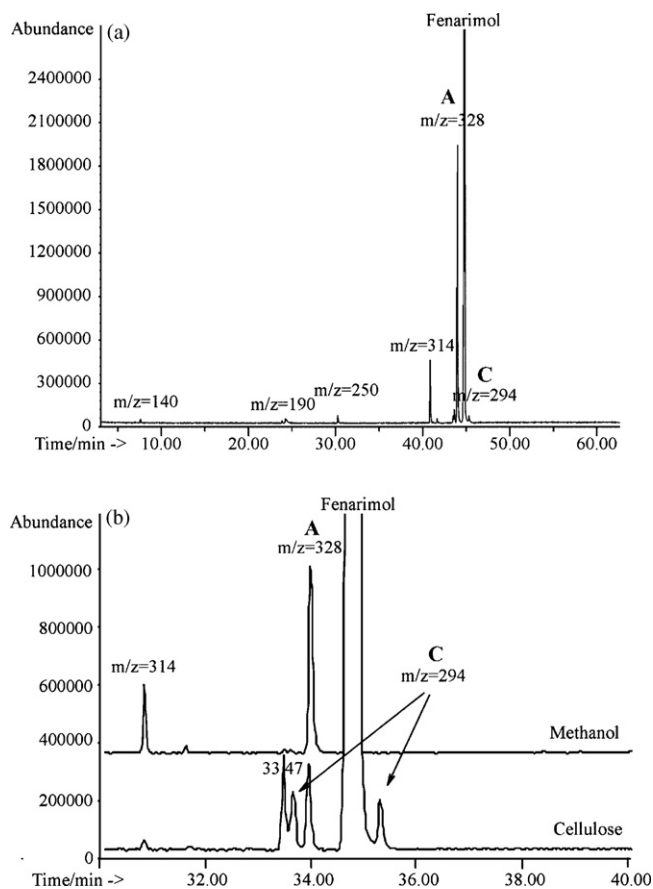
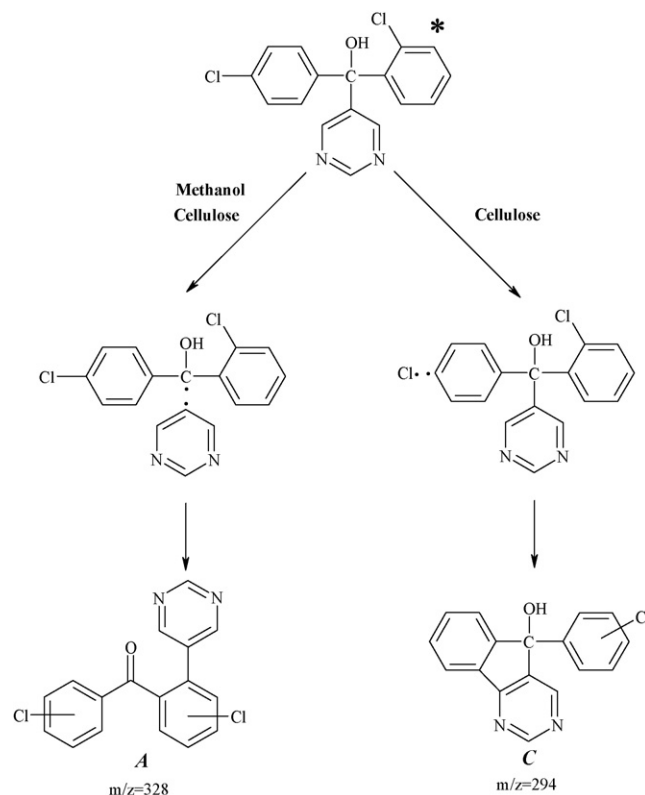


Fig. 3. GC–MS chromatograms of irradiated fenarimol. (a) Methanolic solution irradiated at 254 nm in air equilibrated conditions (initial temperature 70 °C). (b) Comparison of the photoproduct distribution in methanol and on cellulose surface (column DB-35MS, initial temperature 150 °C).



Scheme 2. Main reaction pathways of fenarimol in methanol and on cellulose.

Previous photochemical studies of fenarimol in aqueous solution suggested that the main primary photodegradation step is the homolytic cleavage of the pyrimidine to the carbinol carbon bond. This reaction leads to a chloroketyl radical, a species reported to absorb near 600 nm [14] and therefore easy to detect by flash photolysis. We were not able to detect this radical. However the photoproduct distribution indicates that the major photodegradation product is compound **A** ($m/z = 328$), suggesting therefore the formation of the pyrimidine and ketyl radicals. Fast in-cage recombination of the formed radical pair could prevent us from detecting the ketyl radical within the time resolution of our equipment. The absorption detected between 350 and 450 nm can therefore be due to a recombination intermediate that leads to compound **A** (see Scheme 2).

On cellulose, compound **A** is also formed but the dechlorination of fenarimol becomes one of the major degradation pathways (see Fig. 3(b)). This relative decrease of the recombination pathway should be related to the constraints and lower mobility of the formed radicals, due to the adsorption on solid surface, increasing the rate of the back reaction and lowering the radical movement necessary to form compound **A**.

The photoreduction of chlorophenoxyl pesticides (tridimenol), adsorbed on hydrogen donor surfaces has already been reported [8]. This degradation pathway is very important from the environmental point of view since chloroaromatics are known to be stable to dissipation, under natural conditions. Although lower energy excitation wavelengths are involved under natural conditions, considering the applicability of Kasha's rule for condensed phases and the previous results

obtained under solar radiation [6], the same main photodegradation pathways are expected under environmental conditions.

4. Conclusions

The pesticide fenarimol undergoes direct photodegradation both in methanol and at the cellulose surface. The main photodegradation pathway in methanol involves the homolytic cleavage of the pyrimidine to the carbinol carbon bond. This primary reaction step is followed by fast in-cage recombination of the pyrimidine and ketyl radicals to form an intermediate that leads to a product with $m/z = 328$. On cellulose the dechlorination of fenarimol also occurs. This degradation path involves the cleavage of the C–Cl bond, followed by hydrogen abstraction from the cellulose surface and formation of dechlorinated fenarimol ($m/z = 294$). Fenarimol is expected to undergo both reaction pathways on natural surfaces.

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