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Photodegradation of Flumorph in Aqueous Solutions and Natural Water under Abiotic Conditions

Ji Ye Hu,*,† Chang Liu,† Xue Zhang,† Dong Mei Qin,‡ and Chang-Ling Liu§

†School of Applied Science, University of Science and Technology Beijing, Beijing 100083, China, ‡Institute for the Control of Agrochemicals, Ministry of Agriculture, Beijing 100026, China, and §Shenyang Research Institute of Chemical Industry, Shenyang 110021, China

Flumorph is an oomycete fungicide that is now used extensively in China (Hu, J. Y.; Liu, C.; Yan, H. Degradation of flumorph in soils, aqueous buffer solutions, and natural waters. *J. Agric. Food Chem. 2008*, **56**, 8574−8579). The photodegradation of flumorph in aqueous solutions and natural water have been assessed under natural and controlled conditions in this work. The kinetics of photodecomposition of flumorph was determined using the high-performance liquid chromatography (HPLC)−diode array detector (DAD), and the identification of photoproducts was carried out with HPLC−mass spectrometry (MS) [electrospray ionization (ESI) positive mode]. The rate of photodecomposition of flumorph in aqueous solutions and natural water followed first-order kinetics in both UV radiation and natural sunlight, and the *Z* isomer of flumorph could convert to the *E* isomer. The degradation rates were faster under UV light than sunlight, with the half-lives ($t_{1/2} = \ln 2/k$) of 36.5−64.2 min and 36.3−73.1 days, respectively. One major photoproduct was detected in UV light and tentatively identified according to HPLC−MS spectral information as (*E* or *Z*)-3-(3, 4-dimethoxyphenyl)-3-(4-fluorophenyl)-2-acrylamide. Photosensitizers, such as H_2O_2 and riboflavin, could enhance photolysis of flumorph in natural sunlight. The results obtained indicated that photoreaction was an important dissipation pathway of flumorph in natural water systems.

KEYWORDS: Flumorph; photodegradation; photoproducts; aquatic

INTRODUCTION

Pesticides enter into natural water bodies by direct application and by leaching from soil and vegetation. Many of these chemicals present in aqueous media can undergo photochemical transformation with sunlight via direct or indirect photoreaction. In the surface layers of aquatic systems, photochemical reactions can play a dominant role in the conversion and degradation of pesticides. To assess the role of these processes on the behavior and fate of pesticides in natural water systems, photochemical studies in aqueous solution over a wide range of environmental conditions are needed (*2*).

Flumorph [(*E*,*Z*)-3-(3,4-dimethoxyphenyl)-3-(4-fluorophenyl)-1-morpholinopropenone] has two isomers (*E* and *Z*), which have both good fungicide activities against *Peronospora* and *Phytophthora* at a dose of 100−200 g of active ingredient (a.i.) ha^{-1}. It is widely used for some plants, such as cucumber, tomato, grape, potato, etc. Because flumorph is used extensively in China, investigations to understand its environmental behavior are important. Our previous work has shown that flumorph is quite stable in aqueous buffer solutions and natural waters, with no degradation occurring under dark conditions (*1*). There is no information available in the literature about flumorph photodegradation, and its photoproducts and kinetics in aqueous solutions and natural water have not been fully characterized. In this project, the degradation kinetics and the main photoproducts in aqueous solutions in controlled and natural conditions were

Table 1. *cis*−*trans* Isomers of Flumorph Conversion and Degradation under UV Light

double-distilled water							
time (min)	0	5	10	15	20	100	190
E (mg L^{-1})	5.00	4.54	4.20	3.83	3.54	1.68	0.11
Z (mg L^{-1})	5.00	5.40	5.30	5.00	4.95	1.76	0.12
pH 9 buffer solution							
time (min)	0	5	10	20	40	100	190
E (mg L^{-1})	5.00	4.46	4.22	3.72	3.47	0.77	ND[a]
Z (mg L^{-1})	5.00	5.50	4.95	4.72	3.77	0.84	ND
pH 7.4 buffer solution							
time (min)	0	10	20	100	190	240	300
E (mg L^{-1})	5.00	4.22	3.85	2.61	0.83	0.28	0.11
Z (mg L^{-1})	5.00	5.02	4.95	2.95	0.91	0.30	0.13
pH 4.5 buffer solution							
time (min)	0	10	20	100	160	190	240	300
E (mg L^{-1})	5.00	3.93	3.47	2.61	1.57	0.99	0.38	0.14
Z (mg L^{-1})	5.00	5.05	4.95	3.01	1.75	1.19	0.46	0.16

[a] ND = not detected.

*To whom correspondence should be addressed: School of Applied Science, University of Science and Technology Beijing, Beijing 100083, China. E-mail: jiyehu@sas.ustb.edu.cn.

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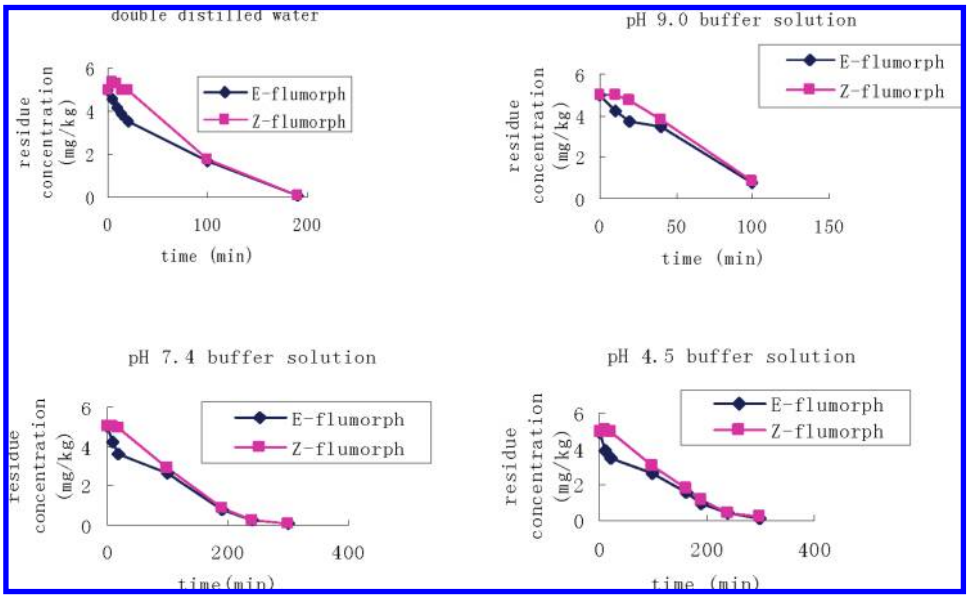

Figure 1. *E* and *Z* isomer conversion and degradation under UV light.

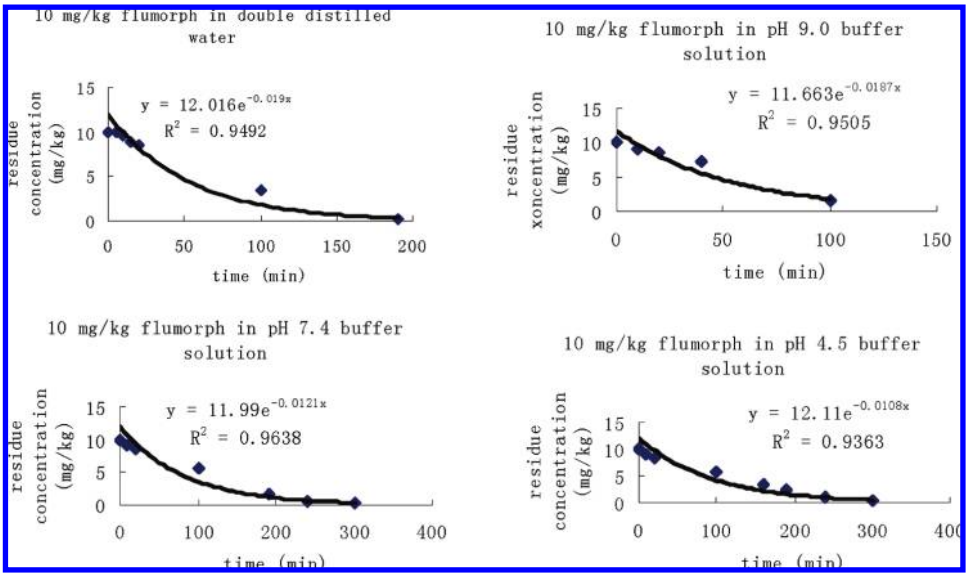

Figure 2. Flumorph (the total amount of *E* and *Z* isomers) photodegradation followed the first-order kinetics in distilled water and buffer solutions.

Table 2. Photodegradation Kinetic Parameters: Rate Constants (k), Correlation Coefficients (R^2), and Half-Lives ($t_{1/2}$) of Flumorph (*E* plus *Z*) in Distilled Water and Buffer Solutions under UV Light

			buffer solutions								
distilled water			pH 4.5			pH 7.4			pH 9.0		
k ($\times 10^2$) (min^{-1})	$t_{1/2}$ (min)	R^2	k ($\times 10^2$) (min^{-1})	$t_{1/2}$ (min^{-1})	R^2	k ($\times 10^2$) (min^{-1})	$t_{1/2}$ (min)	R^2	k ($\times 10^2$) (min^{-1})	$t_{1/2}$ (min)	R^2
1.90	36.5	0.95	1.08	64.2	0.94	1.21	57.3	0.96	1.87	37.1	0.95

evaluated using the high-performance liquid chromatography (HPLC)−diode array detector (DAD) and HPLC−mass spectrometry (MS). Moreover, experiments with different photosensitizers under sunlight were carried out to gain information about the photocatalytic degradation of flumorph. Photochemical investigations in this context may contribute to a better understanding of pesticide behavior in the environment.

MATERIALS AND METHODS

Chemicals. Flumorph standard (purity, 99.5%; $Z/E \approx 1{:}1$) was obtained from the Shenyang Research Institute of Chemical Industry, China. Water for HPLC was double-distilled. HPLC-grade methanol was procured from Dikma Ltd. (China). SPE columns were Dikma Ltd. preparation products (C-18, 500 mg, 3 mL). Riboflavin and H_2O_2 used as photosensitizers in the experiment were analytical-grade. KCl, HCl, KH_2PO_4, Na_2HPO_4, $NH_3 \cdot H_2O$, and NaOH of analytical grade were used for buffer preparation.

Buffer Solutions. Three buffer solutions (pH at 4.5 ± 0.1, 7.4 ± 0.1, and 9.2 ± 0.1) were used to study the aqueous degradation of flumorph. The procedures followed for their preparation according to ref *3*.

Natural Water. To study the influence of natural water constituents on photodegradation, lake water was collected from Guishui Lake located in the suburb of Beijing, China. Natural water was sampled by dipping a clean stainless-steel can into the top the 1 m of water until the can was full. Samples were subsampled prior to beginning the experiment for measurements of dissolved total organic carbon (TOC), total suspended solids

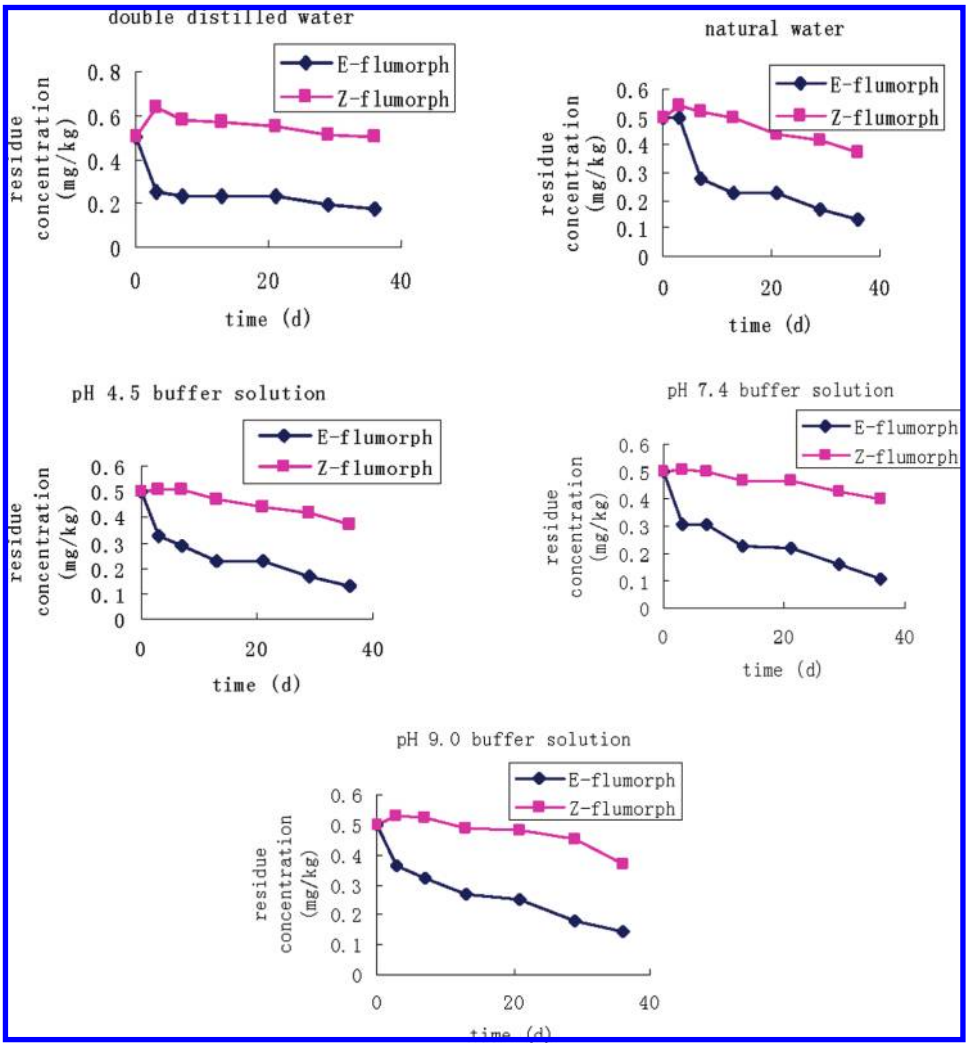

Figure 3. *E* and *Z* isomer conversion and degradation under natural sunlight.

Table 3. Photodegradation Kinetic Parameters: Rate Constants (k), Correlation Coefficients (R^2), and Half-Lives ($t_{1/2}$) of Flumorph (*E* plus *Z*) in Natural Water, Distilled Water, and Buffer Solutions under Solar Light

						buffer solutions								
natural water			distilled water			pH 4.5			pH 7.4			pH 9.2		
k ($\times 10^2$) (day^{-1})	$t_{1/2}$ (day)	R^2	k ($\times 10^2$) (day^{-1})	$t_{1/2}$ (day)	R^2	k ($\times 10^2$) (day^{-1})	$t_{1/2}$ (day)	R^2	k ($\times 10^2$) (day^{-1})	$t_{1/2}$ (day)	R^2	k ($\times 10^2$) (day^{-1})	$t_{1/2}$ (day)	R^2
1.91	36.3	0.95	0.95	73.1	0.89	1.66	41.8	0.95	1.59	43.6	0.94	1.63	42.5	0.96

(TSS), pH, and electrical conductivity (EC). Data are as follows: TOC, 24.5 mg L^{-1}; TSS, 20.1 mg mL^{-1}; pH, 7.9; EC, 1.98 mS cm^{-1}.

To avoid microbial degradation, buffer solutions and natural water were sterilized by filtration and all glass apparatuses were sterilized by autoclaving for 20 min at 121 °C. Aseptic techniques were adopted throughout the study to maintain sterility.

HPLC and HPLC−MS Conditions. A HPLC (Shimadzu LC-20A) equipped with an analytical column (250×4.6 mm inner diameter, 5 μm ODS) was attached to a DAD. The chromatographic conditions used for the analysis of flumorph residues were as follows: the mobile phase was methanol/water (70:30, v/v), with a total flow of 0.8 mL min^{-1}. The injection volume was 20 μL. Detection was performed at 242 nm (*4*). Under these conditions, the retention time of flumorph was about 7.5 min for the *E* isomer and 8.4 min for the *Z* isomer. All measurements were carried out at room temperature.

For HPLC−MS analysis, UPLC−MS/MS (Waters, Acquity-TQD) and Acquity UPLC BEH C-18 column (1.7 μm, 2.1 × 50 mm) were employed. Acquisition parameters were as follows: ESI^+ full-scan mode, 70−450; cone voltage, 45 V; capillary voltage, 3 kV; source temperature, 120 °C; desolvation temperature, 350 °C; desolvation gas, N_2, at 600 L h^{-1}.

Photodegradation Equipment. Photolysis experiments for the aqueous solutions were carried out in an XPA (II) photolysis reactor made in Nanjing, China, equipped with a Philips HPK 150 W high-pressure mercury lamp, with a prominent emission band around 250−400 nm. The lamp was jacketed with a water-cooled Pyrex filter. The tap water cooling circuit maintained the temperature at 30−35 °C.

Sunlight conditions: Photolysis under sunlight was conducted from March to May, 2009, in Beijing, China. The sunlight intensity at 300−400 nm wavelength was 400, 2009, and 365 mW cm^{-2} at the beginning, middle, and end of the day, respectively.

Kinetics of Photodegradation and Photoproduct Identification. For UV light, kinetic studies of photodegradation were performed with a high-pressure mercury lamp (HPK 150 W) in water-cooled quartz housing. Samples were placed in a quartz glass cuvette. The concentration of the pesticide flumorph in aqueous solutions (buffer solutions and distilled water) was 10 mg L^{-1} to facilitate the identification of intermediate products. At specific time intervals (2 min), samples of 2 mL were withdrawn from the reactor and analyzed after direct injection for HPLC or HPLC−MS. Each series of photodegradation experiments

Table 4. Influence of Riboflavin and H_2O_2 on the Photodegradation of Flumorph under Sunlight[a]

							buffer solutions								
	natural water			distilled water			pH 4.5			pH 7.4			pH 9.2		
photosensitizers	k ($\times 10^2$) (day^{-1})	$t_{1/2}$ (day)	R^2	k ($\times 10^2$) (day^{-1})	$t_{1/2}$ (day)	R^2	k ($\times 10^2$) (day^{-1})	$t_{1/2}$ (day)	R^2	k ($\times 10^2$) (day^{-1})	$t_{1/2}$ (day)	R^2	k ($\times 10^2$) (day^{-1})	$t_{1/2}$ (day)	R^2
H_2O_2	291.6	0.24	0.94	1441.9	0.048	0.93	1302.2	0.053	0.94	371.14	0.19	0.99	115.42	0.6	0.97
riboflavin	36.41	1.90	0.99	137.25	0.51	0.99	4.21	16.46	0.99	3.78	18.34	0.99	179.87	0.39	0.99
blank	2.92	23.74	0.98	3.68	18.83	0.99	4.05	17.11	0.99	2.43	28.52	0.98	2.77	25.02	0.99

[a] H_2O_2, 1 mg L^{-1}; riboflavin, 1 mg L^{-1}.

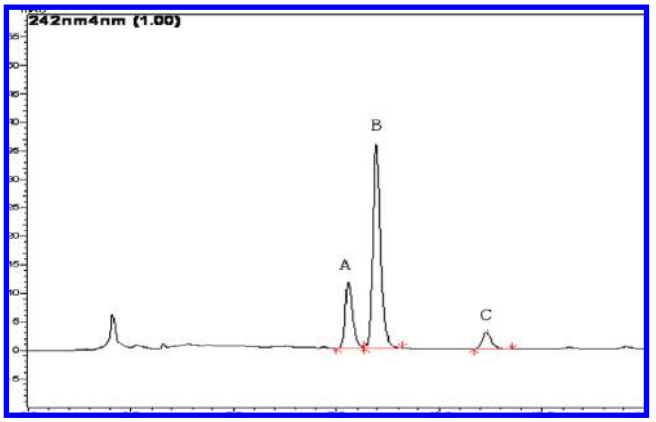

Figure 4. HPLC chromatogram of one product (C) and parent pesticides *E*-flumorph (A) and *Z*-flumorph (B).

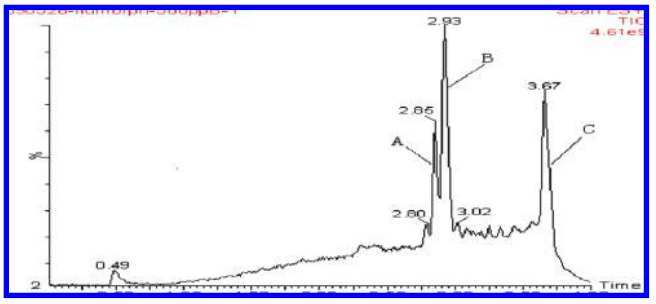

Figure 5. TIC of the LC−MS chromatogram.

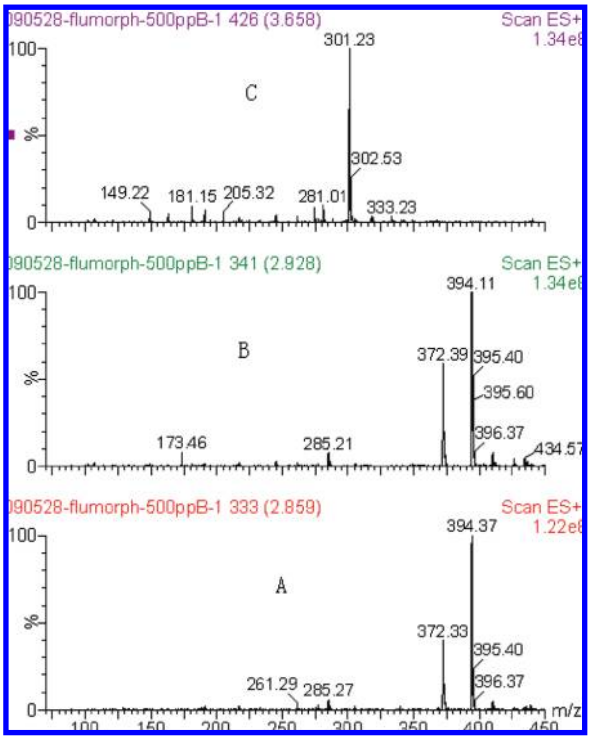

Figure 6. LC−MS spectrum of the flumorph (A and B) and photoproduct (C).

was conducted in three replicates and accompanied by dark reaction controls.

For the sunlight experiment, the initial concentration of flumorph in aqueous solutions (buffer solutions and natural water) was 1 mg L^{-1}, being close to the natural environmental conditions. Samples (5 mL) were drawn out from each bottle at 0, 3, 7, 13, 21, 29, and 36 days. Samples were treated followed the solid-phase extraction (SPE) (C-18) sample preparation procedure below: A SPE method has been developed to allow for purification and low-concentration experiment. C-18 cartridges (3 mL, 500 mg) were conditioned with methanol (5 mL), followed by distilled water (5 mL). Immediately after, the sample solutions (5 mL) was removed and passed through the cartridge at a flow rate of approximately 1 mL min^{-1}. After loading, the analytes were eluted with methanol (2 mL). The eluate was dried under a gentle stream of nitrogen. The residue was reconstituted in the mobile phase (1 mL) for HPLC analysis.

Different kinds of photosensitizers, such as riboflavin and H_2O_2, were added to samples to evaluate their behavior as possible photocatalysts and their effect on the photolysis of pesticides under natural sunlight. These compounds were used in the concentration of 1 mg L^{-1} with the initial concentration of the pesticides fixed at 1 mg L^{-1}.

RESULTS AND DISCUSSION

Kinetics Studies. Previous hydrolysis experiments in our laboratory revealed that flumorph was quite stable in aqueous buffer solutions and natural waters in the dark (*1*). This also means that the hydrolytic processes of flumorph during the course of the photolysis experiment can be ignored.

Negligible degradation was also observed in the dark at 25 ± 2 °C in this project. Under UV light, in both buffer solutions and distilled water, the *E* isomer could convert to the *Z* isomer, especially at earlier irradiation time, and then both degraded rapidly (**Figure 1** and **Table 1**). This course that the *E* isomer of flumorph converted to the *Z* isomer was called photoisomerization (*5*). Its molecular behavior in which structural change between isomers occurs is caused by photoexcitation.

The kinetics of flumorph (the total amount of *E* and *Z* isomers) followed an apparent first-order degradation model (**Figure 2**). **Table 2** lists the values of k and the linear regression coefficients for the first-order kinetics of the photodegradation of flumorph. According to these values, the appropriate first-order relationship appears to fit well. The half-lives could be determined from the equation: $t_{1/2} = \ln 2/k$. The investigated pesticide was sufficiently degraded in aqueous solutions under UV light. The half-lives ranged from 36.5 to 64.2 min for flumorph in the examined waters (distilled water and buffer solutions). The pH influence of the environmental medium on the photodegradation rate had been observed and followed pH 9.2 > 7.4 > 4.5.

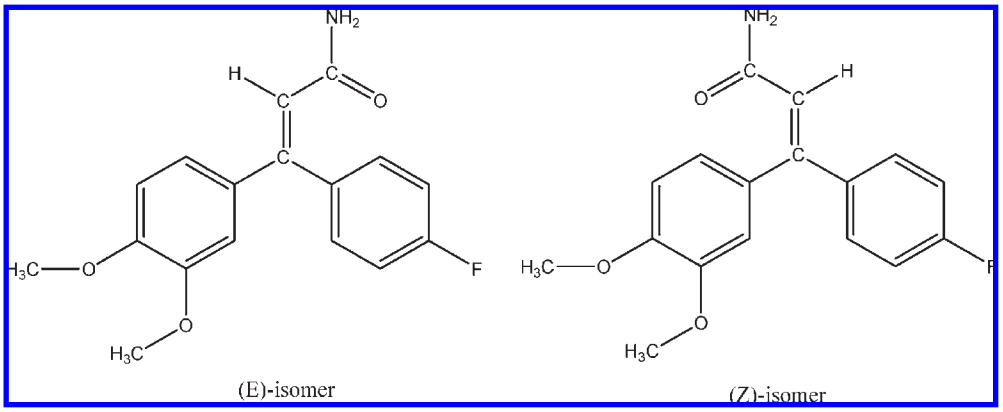

Figure 7. Chemical structure of the photoproduct C (*E* or *Z* isomer).

Under exposure to sunlight, flumorph degraded relative slowly compared to UV light in distilled water and buffer solution samples. **Figure 3** illustrates the conversion of the *E* to *Z* isomer, and **Table 3** lists the photodecomposition parameters of flumorph (the total amount of *E* and *Z* isomers) under sunlight.

The indirect photolysis of pesticide residues was obtained by means of riboflavin and H_2O_2 additions on the samples. Indirect photolysis (sunlight with H_2O_2 or riboflavin) of the tested pesticide also follows first-order kinetics. Riboflavin and H_2O_2 accelerated flumorph photolysis in sunlight, with half-lives ranging from 0.048 to 18.34 days. The values of the rate constants, regression coefficients, and half-lives are listed in **Table 4**. The reason for this behavior is a radical mechanism. These photosensitizers have broad absorption bands in the UV−vis range and can photogenerate hydroxyl radicals ($^{\bullet}OH$), which can quickly react with aromatic and unsaturated bonds of organic compounds. They are the main responsible agent that attack the pesticide molecules and start their breakage (*6*, *7*).

Our previous work reported that flumorph is quite stable in aqueous buffer solutions and natural waters, with no degradation occurring under various conditions in the dark. From the data obtained in this project, photolysis may be the main degradation pathway in the aqueous medium of the environment. Moreover, because the photosensitizers exist extensively in the aqueous environment, flumorph photolysis can be accelerated.

Photoproduct Identification. Special attention was paid to the photoproducts. Aqueous solutions of flumorph were irradiated under UV light, and samples were taken at regular time intervals. One photoproduct has been always found at any time intervals besides flumorph in the HPLC chromatogram (Figure **4**). A is *E*-flumorph; B is *Z*-flumorph; and C is the photoproduct. In the dark, no additional peak was detected besides the parent pesticides A and B.

From the total ion chromatogram (TIC) of liquid chromatography (LC)−MS, the photoproduct C has also been observed (**Figure 5**).

The degradation product C was tentatively identified by studying their mass spectra (**Figure 6**).

Photoproduct C is identified as (*E* or *Z*)-3-(3,4-dimethoxyphenyl)-3-(4-fluorophenyl)-2-acrylamide (**Figure 7**), according to its mass spectrum, with an ion peak at *m*/*z* 301 $[M + 1]^+$. The ion peaks of parent flumorph are $[M + H]^+ = 372$ and $[M + Na]^+ = 394$. C has a conjugated system, and it is quite stable.

Results obtained in this study demonstrated that the dark decomposition of flumorph in aqueous solution is negligible with respect to the photochemical decomposition. The *E* isomer could convert to the *Z* isomer, especially at earlier irradiation time, and then both degraded rapidly. The rate of flumorph (*E* and *Z* isomers) photodecomposition of aqueous solutions followed first-order kinetics.

In the case of the used photosensitizers, such as riboflavin and H_2O_2, a synergistic effect is observed. One major photoproduct is detected in UV light and tentatively identified according to HPLC−MS spectral information as (*E* or *Z*)-3-(3,4-dimethoxyphenyl)-3-(4-fluorophenyl)-2-acrylamide. From the data obtained in this project, photolysis may be the main degradation pathway in the aqueous medium of the environment.

ACKNOWLEDGMENT

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