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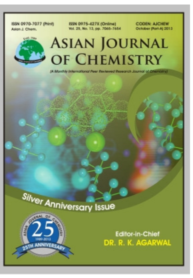

Photochemical Degradation of Bifenthrin in Water Solution

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The mechanism of photochemical degradation of bifenthrin in water solution has been investigated using a laboratory-built photochemical degradation device hyphenated with commercial high performance liquid chromatography and UV-visible photo-spectrometric, fluorescent and mass spectrometric detector. Spectrometric characteristics of bifenthrin and its main degradation products suggest that bifenthrin could be photo-degraded under UV irradiation. The kinetics of the photochemical reaction demonstrates that laboratory-built photochemical degradation is of high efficiency for off-line degradation of interested organics. The photo-degradation reaction of bifenthrin in water solution is approximately the pseudo-first-order reaction. Mass spectrometric results show that bifenthrin is first converted into its space isomerism and then further degraded and converted to the final products under a series of molecular rearrangement, oxidation reduction and de-chlorination reaction.

Key Words: Bifenthrin, Water solution, Photodegradation, Kinetics, Mechanism.

INTRODUCTION

Pyrethroid pesticide is widely used for its efficiency, broad-spectrum and low toxicity[1]. Photo-degradation is the main way to remove pyrethroid pesticides in the environment[2] and the study on the photo-degradation process of pyrethroid pesticide is important to evaluate the environmental safety[1]. Studies have shown[3-6] that photo-degradation reactions of pyrethroid pesticide under different experimental conditions are all approximate the first-order reactions and the reaction rate as well as reaction pathways have a certain relationship with the media. Bifenthrin is one of the mostly used pesticides in recent years and the studies on it were mainly focused on the effects of the light source, photosensitizer, temperature and pH value on its photo-degradation efficiency[7,8]; determination of bifenthrin in environmental samples[9-11]; biological metabolic processes in the body and its toxicological properties[12-15] at home and abroad. However, its degradation in aqueous solution during the reaction is not clear.

These studies report on the spectroscopy and photo-degradation reaction dynamics of bifenthrin pesticides and their degradation products, also identified the photochemical degradation products by mass spectrometry and discussed the photochemical degradation mechanism of bifenthrin in aqueous solution as well as the influencing factors of the degradation kinetics process, by employing the laboratory-built photochemical degradation device[16] and using the high performance liquid chromatography separation as well as its configuration UV-visible spectrophotometer detector, fluorescence spectroscopy and mass spectrometry detector.

EXPERIMENTAL

Agilent 1100 HPLC, equipped with G1315A DAD detector, C18-column, Ion trap mass spectrometry (Trap VL), HPLC software (G2170AA, G2180AA), LC/MSD Trap software (Version 5.3), TES-1332A digital illumination meter.

The laboratory-built photochemical degradation device is mainly made up with UV lamp (Topstar, Xiamen), polytetrafluoroethylene tube (the PTFE, 2.0 m × 0.33 mm ID, Zeus, Corp., USA), light-reflecting wall and the regulating transformers for adjusting the working voltage of the UV lamp (TDGC-3, Xiamen rectifier Factory)[16,17]. Both ends of the PTFE tube in photochemical degradation device are connected with the connectors 1 and 4 of the manual injection valve 7725i (Rheodyne, USA), respectively. When in the position (1) (usually the load position), the pesticides to be degraded were photo-degraded after implantation from the connector 4 of the valve and the valve turned to position (2) from position (1) after the completion of the degradation process. Now, the degradation mixture of pesticides and degradation products were launched from PTFE reaction tube by liquid chromatography single pump (G1310A Isopump, Agilent Technologies, USA), constant volume by volumetric flask after reception. Then, we took certain volume injection to conduct the liquid chromatography separation and studied the spectroscopy and mass spectrometry characteristics of pesticide and its degradation products. The process was shown in Fig. 1.

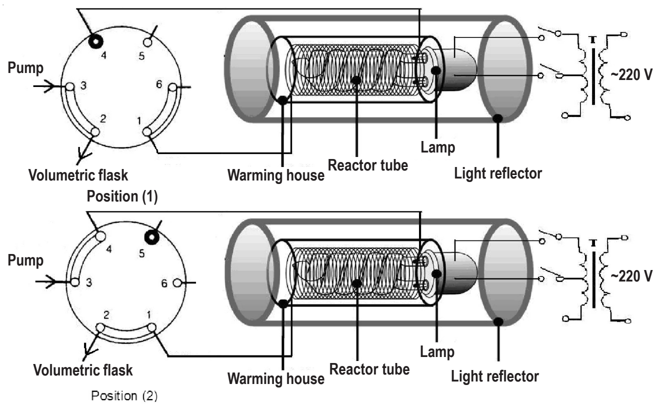

Fig. 1. Schematic diagram of photo-degradation reactor. Position (1): load and irradiation of the pesticide. Position (2): transferring of the photo-degradation products to volumetric flask by isopump driving

Acetonitrile was HPLC grade (Tedia Company, Inc. USA). Water was the ultrapure water (Guangdong Robust Group Co., Ltd). The bifenthrin standard products (1000 mg/L, *n*-hexane) were bought in scientific research and environmental protection monitoring of the Ministry of Agriculture.

General procedure: First, bifenthrin was photo-degraded by employing the device in Fig. 1 and the mixed solution of bifenthrin and its degradation products were collected. Then, the solution was transferred to a volumetric flask, constant volume, 20μL of injection, liquid chromatography separation, detection by UV-visible spectrophotometric device (DAD) and fluorescence spectroscopy detector (FLD). Lastly, the absorption spectra and fluorescence spectra of bifenthrin pesticide parent and the degradation products were studied.

After a known concentration of bifenthrin has been photo-degraded by employing the device in Fig. 1, we did experiments on the study of the influence of illumination time on pesticides maternal concentration as described earlier and then calculated the kinetic parameters of photo-degradation process of bifenthrin.

According to the same steps, we studied on the effects of the intensity of light (lamp voltage), the initial concentration of bifenthtrin**,** water solution salinity, pH value and the coexistent small organic molecules in water solution on pesticide photo-degradation reaction rate.

Detection method: The separation and detection conditions of bifenthrin maternal and photo-degradation products included that the mobile phase was acetonitrile: water = 85:15 (V/V), velocity was 1 mL/min, separation column was Eclipse XDB-C_{18} (5 μm, 4.6 mm × 150 mm, Germany).

The bifenthtrin and its degradation product mixture were determinated by HPLC-MS and the molecular structure was also identified. High performance liquid chromatographic conditions were: mobile phase acetonitrile: water (pH 8 ammonia) = 85:15 (V/V), Agilent ZORBAX Eclipse Plus-C_{18} chromatographic column (3.5 m, 3 mm × 150 mm), a flow rate of 0.3 mL/min, column temperature of 30 ºC, sample volume 20 μL; Agilent Trap VL MSD working conditions were: ESI for the positive ion mode, nebulizer pressure of 40 psi, dryer temperature 350 ºC, drying gas flow rate of 9 L/min, mass scan range 50-1000, the use of the first-stage mass spectrometry for determination.

RESULTS AND DISCUSSION

Spectrometric characteristics of bifenthrin and photo-degradation products: Fig. 2 shows the chromatogram of the photo-degraded bifenthrin and its degradation products after chromatography separation. The results of UV-visible spectrophotometric device and fluorescence spectroscopy device (Fig. 2) show that bifenthrin produces a variety of intermediates after photo-degradation (chromatogram A is bifenthrin and B and C are the main products). With the photo-degradation reaction time lengthening, the concentration of pesticides is getting lower and lower, while the concentration of product B first increases and then decreases and the concentration of product C gradually increase. This indicates that product B is unstable under prolonged light and continues to degrade to other products including product C. In addition, according to the fluorescence chromatogram, we found that there was almost no fluorescence of bifenthrin before irradiation, while with the extension of light, the fluorescence intensity first increased and then decreased. Thus, we presumed that bifenthrin occur the space isomerization phenomena during the light and generate the space isomer with strong fluorescence, which degraded into products B, C in the meanwhile of its generating.

We studied the spectral parameters of bifenthrin and the main photo-degradation products, using the spectral scan function of UV-visible spectrophotometric device and fluorescence spectroscopy device during the chromatographic separation process. The results were shown in Table-1.

TABLE-1
SPECTROMETRIC CHARACTERISTIC OF
BIFENTHRIN AND ITS DEGRADATION PRODUCTS

		Bifenthrin (A)	Product (B)	Product (C)
UV absorbance	λ_{max}	204 /254 nm	204/254 nm	202/246 nm
Fluorescence	λ_{Em}	320 nm	320 nm	343 nm

$^*\lambda_{max}$ is the maximum absorbance wavelength and λ_{Em} is the maximum emission wavelength.

Photo-degradation reaction kinetics parameter of bifenthrin: Fig. 3 is the first-order kinetic simulation curve of photo-degradation reaction of bifenthrin at different initial concentration. The results show that the photo-degradation reaction of bifenthrin is approximate the first-order reaction with the initial concentration of bifenthrin 5, 20, 40 mg/L, the light intensity of 6800 Lux and the reaction temperature 25 ± 1 ºC. With the linear fit of $\ln A/A_0$ and the photo-degradation time (t), the slope of the fitted curve is the photochemical degradation reaction rate constant.

Fig. 4 shows the influence of the intensity of light source on bifenthrin pesticide photo-degradation reaction. The results show that when the intensity of light source varies among 2500-9800 Lux, the photo-degradation reactions of bifenthrin are all approximated to meet the first-order reaction.

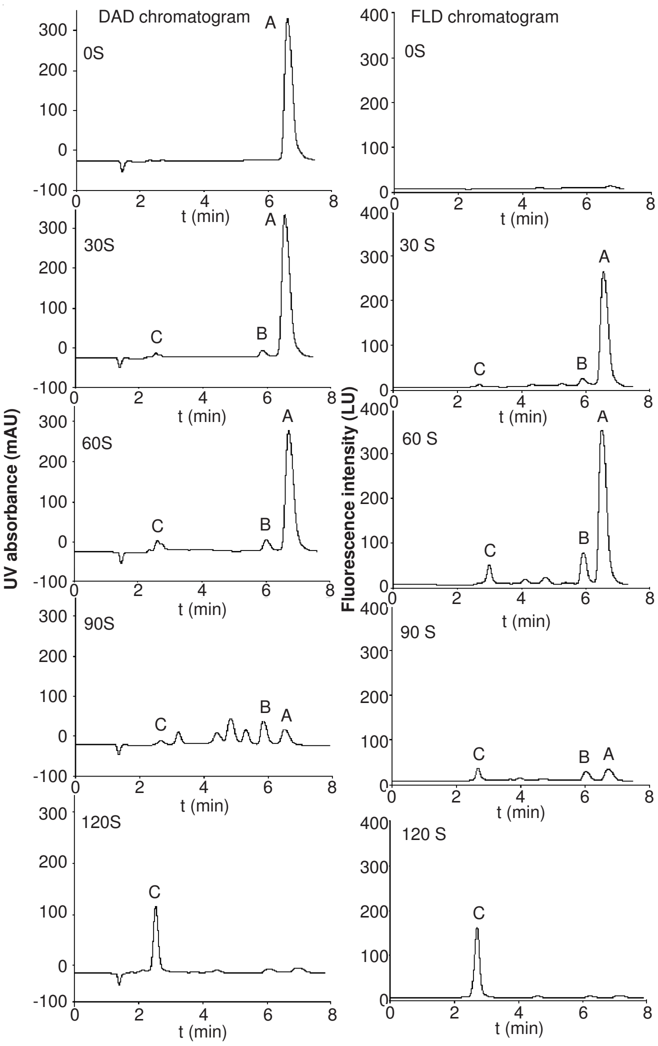

Fig. 2. Chromatograms of bifenthrin and its main photo-degradation products under various irradiation times (A: bifenthrin, B and C are photochemical degradation products)

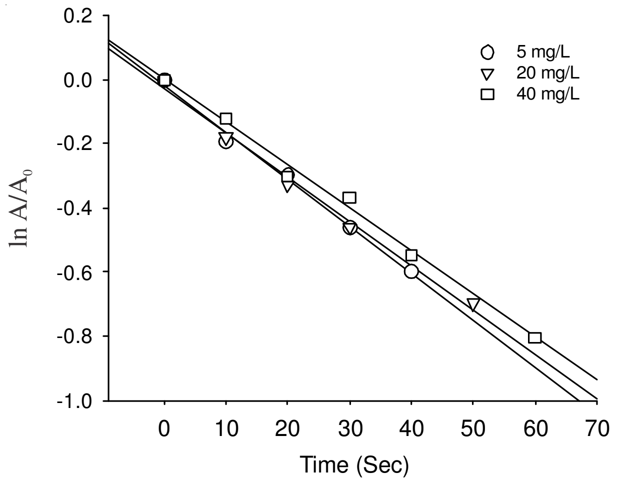

Fig. 3. First-order kinetics simulation curve of bifenthrin under different initial concentrations

With the increase of the intensity of light source, the photochemical degradation reaction rate constant increases, indicating that the intensity of light source is an important factor affecting the photochemical degradation reactions of bifenthrin.

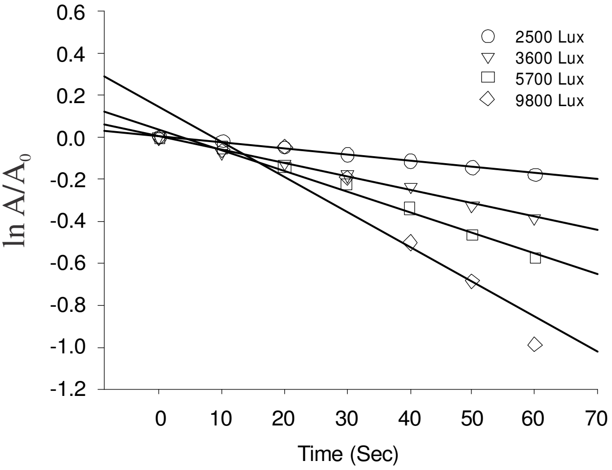

Fig. 4. Effect of illumination intensity on photo-degradation reaction of bifenthrin

The experimental results (Figs. 3 and 4) also show that the influence of the initial concentration of pesticide on photochemical degradation reaction is less, while the intensity of light source is the main factor to control the photochemical degradation reactions. This indicates that the thin layer light degradation reactor of polytetrafluoroethylene (PTFE) used in the experiment is of higher efficiency and fully meets the requirements for the study on the process of photochemical degradation of pesticides.

Influence factors on photochemical degradation reaction: The experiment studied the effects of inorganic salt in aqueous solution (salinity), pH value and small organic molecules on the photo-degradation reaction rate of bifenthrin pesticides. Fig. 5 shows the influence of salinity on the photochemical degradation reactions of bifenthrin pesticide in aqueous solution. The experimental results (Fig. 5) show that the photo-degradation reaction rate of bifenthrin pesticide slows down as the salinity increases. Therefore, considering the experimental results, it is presumed that the photo-degradation rate of bifenthrin in freshwater, estuarine water and seawater will gradually slow down.

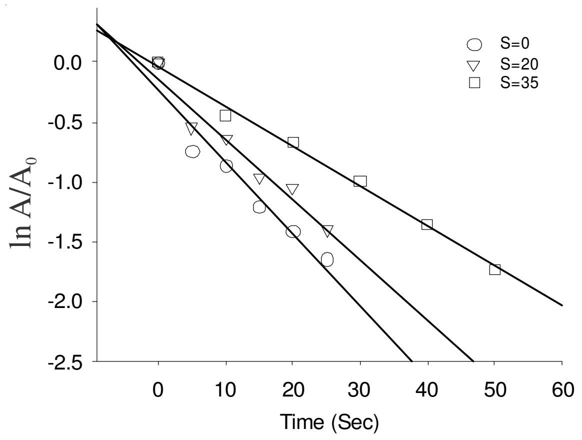

Fig. 5. Effect of salinity on photo-degradation reaction of bifenthrin (S: Salinity)

The effect of pH values on photo-degradation reaction of bifenthrin shown in Fig. 6 indicates that pH value has no effect on the photochemical degradation reaction of pesticides.

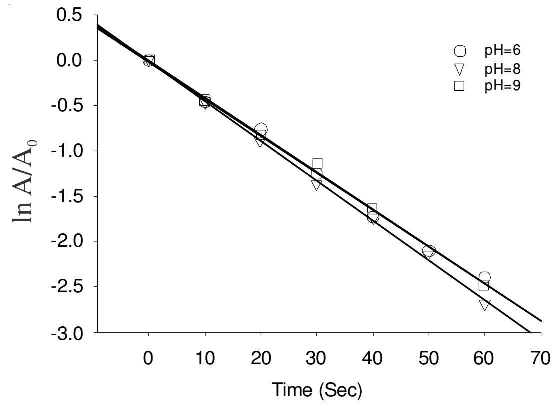

Fig. 6. Effect of pH on photo-degradation reaction of bifenthrin

The influence of the coexistent small organic molecules in aqueous solution on the photo-degradation reaction of bifenthrin pesticide is studied by adding common small organic molecules such as methanol, acetonitrile and *n*-hexane into aqueous solution to form mixed solution. Fig. 7 is the reaction constant fitting curve of the photochemical degradation of bifenthrin in different media, such as water, methanol, acetonitrile, *n*-hexane, *etc*. The experimental results show that photodegradation rate constant of bifenthrin changes from large to small as the solution polarity changes from large to small (from water to *n*-hexane). This indicates that the optical degradation rate of bifenthrin in aqueous solution is the fastest and the presence of a small amount of small organic molecules will reduce the photo-degradation rate constant of bifenthrin, while the degradation rate of bifenthrin is the slowest when in the non-polar organic solvent.

Mass spectrometric identification: Fig. 8 is the first-stage mass spectrum of bifenthrin A and the photo-degradation products B, C. After a careful comparison and analysis of the mass spectra of A and B, we found that the molecular weight and the fragment ions of them were the same, but different in the intensity of each fragment ion. The chromatogram of bifenthrin and the photo-degradation products of bifenthrin shown in Fig. 2 indicated that bifenthrin A and the degradation product B could be completely separated, which showed that there should be a large difference in the molecular structure between them. However, the commonly used XDB-C$_{18}$ column for chromatography does not have the ability of separating space heterogeneous material. Therefore, it is reasonable to speculate that the degradation product B is isomer of bifenthrin after irradiation, ternary ring opening occurred, double bond formed and a rearrangement of the structure.

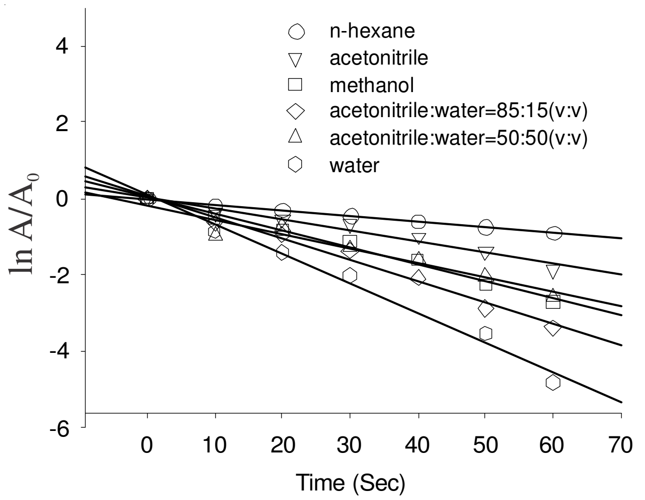

Fig. 7. Effect of small organic molecules on photo-degradation reaction of bifenthrin

After analyzing the mass spectrum of degradation product C, marking the corresponding molecular structure of each

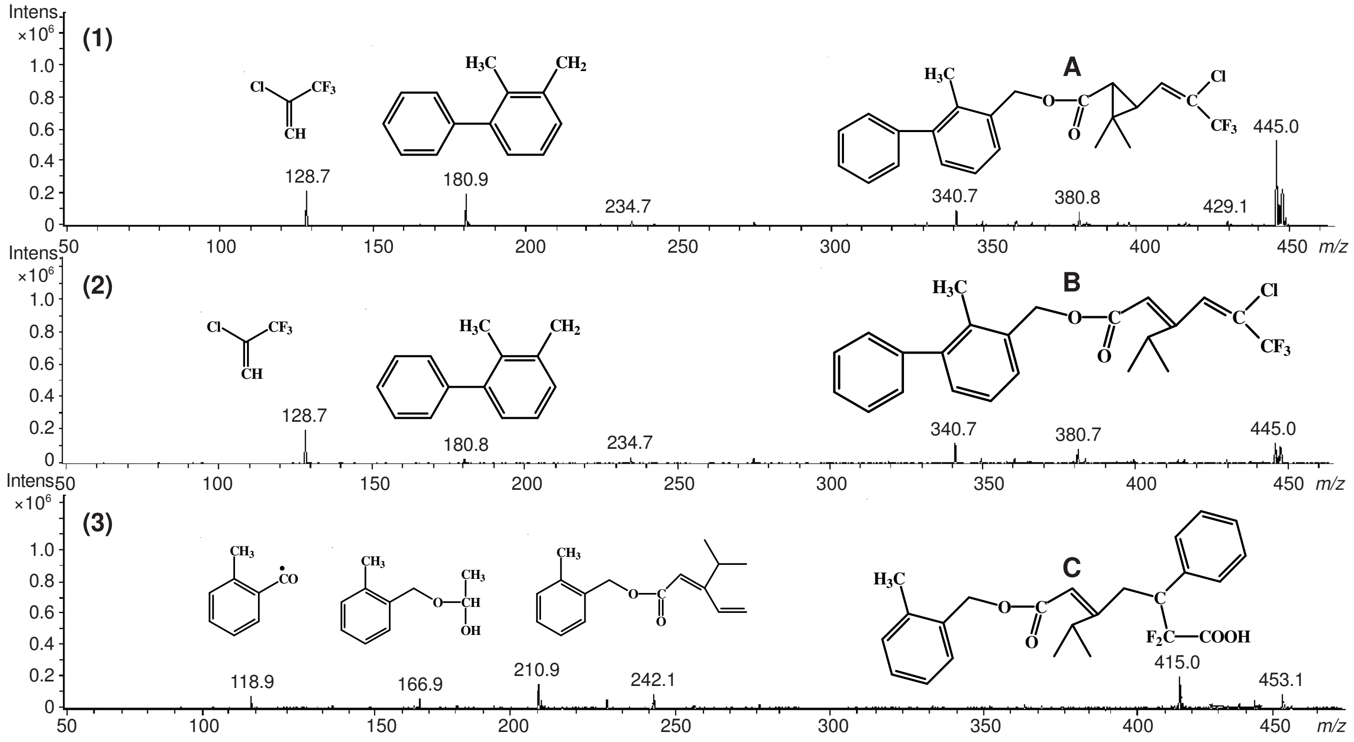

Fig. 8. HPLC-MS spectra of bifenthrin (1) and the photo-degradation products (2) and (3)

fragment ion in the Fig. 8, combining the information in the chromatogram of product C shown in Fig. 2, we can determine that product C has UV absorption, fluorescence emission and meanwhile there is a benzene ring existing. Therefore, we hypothesized that product C is the further degradation product of product B, which generated product C after open loop, de-chlorination and the rearrangement of reaction during the degradation process.

Photo-degradation process of bifenthrin: The existing research results[18,19] show that certain pesticides can occur the isomerization under the light and the ultraviolet rays can induce *cis-trans* isomerization of pesticides, such as permethrin and deltamethrin with cyclopropyl pyrethroid. The photochemical reactions of these pesticides are primarily *cis*- and *trans*-isomer and the tautomeric isomers can occur among various solvents. The order of the isomerization rate in water, ethanol, methanol solvents is water > ethanol > methanol.

According to the literature and in combination with the UV and fluorescence chromatogram of bifenthrin shown in Fig. 2, we find that bifenthrin itself is a weak fluorescent substance and the fluorescence intensity increases after light, but there is no change in the retention time. This indicates that bifenthrin occur space isomerism under ultraviolet irradiation. On that basis, we speculate the photo-degradation process of bifenthrin in aqueous solution as shown in Fig. 9.

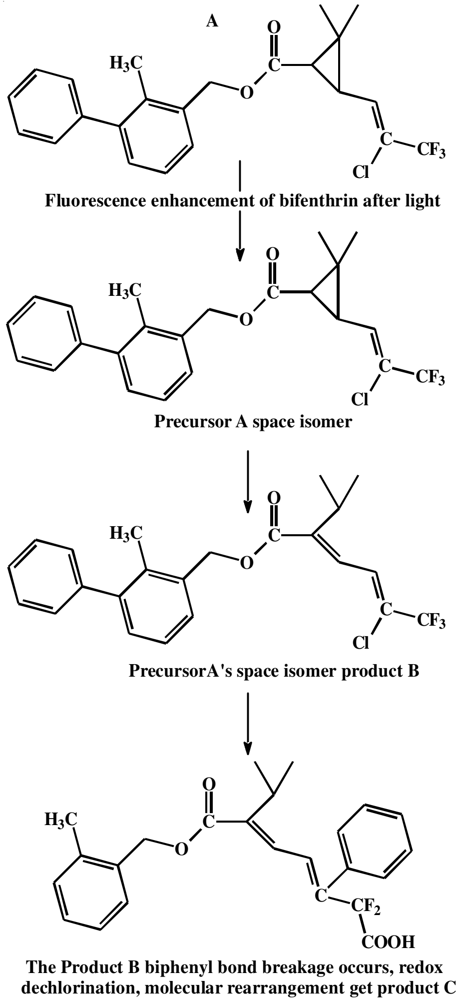

Fig. 9. Photochemical degradation mechanism of bifenthrin in water solution

After the irradiation of bifenthrin in aqueous solution, bifenthrin first occur the spatial isomerism, then, the isomerization products occur ternary ring opening to form a double bond, getting the isomeric product B of the precursor. After the continued light of product B, further biphenyl bond rupture, de-chlorination, redox and molecular rearrangement reactions take place, finally forming the degradation product C.

Conclusion

This paper established the liquid chromatography for separating bifenthrin maternal and the photo-degradation products and proved the feasibility of this method, by studying the photo-degradation reaction constants of bifenthrin in an aqueous solution, identifying the photo-degradation reaction product and speculating the reaction mechanism; adopting the spectroscopy and mass spectrometry studies on the photo-degradation process of bifenthrin pesticide; using UV-visible absorption spectroscopy detector configurated by liquid chromatography, fluorescence detector and mass spectrometry detector. The research method described in this article offers a good application prospect for the photo-degradation process of organic pollutants in terrestrial freshwater and brackish water offshore.

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