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# Chiral Stability of Synthetic Pyrethroid Insecticides

WEIPING LIU, SUJIE QIN, AND JIANYING GAN*

Department of Environmental Sciences, University of California, Riverside, California 92521

Synthetic pyrethroids are chiral compounds consisting of multiple stereoisomers. Evaluation of enantioselectivity in environmental fate and ecotoxicity requires analytical methods that preserve stereoisomer integrity during analysis. In this study, we characterized the stability of stereoisomers from four commonly used pyrethroids, *cis*-bifenthrin (*cis*-BF), permethrin (PM), cypermethrin (CP), and cyfluthrin (CF), during gas chromatography (GC) analysis and sample preparation. Stereoisomers of *cis*-BF and PM were found to be stable, but those of CP and CF were unstable, under heat or in water. Isomer conversion occurred only at the αC in CP or CF, causing the analyte stereoisomer to convert to an epimer. At a GC inlet temperature of 260 °C, about 9% conversion occurred for CP and CF. In organic solvents and sterile water, stereoisomers of *cis*-BF and PM were stable, but slow isomer conversion was observed for CP and CF in water at ambient temperature. However, isomer conversion for CP and CF was relatively insignificant (2−3%) when the GC inlet temperature was kept at ≤180 °C or when on-column injection was used. Isomer conversion at the αC in water suggests that abiotic processes may also contribute to enantioselectivity observed in the environment for pyrethroids with the asymmetric αC.

**KEYWORDS: Chiral selectivity; enantioselectivity; isomerization; enantiomerization; chiral pesticides; synthetic pyrethroids**

## INTRODUCTION

Many environmental contaminants are chiral compounds consisting of optical stereoisomers called enantiomers (*1*, *2*). Studies have shown that while enantiomers from the same compound have identical physical−chemical properties, they may exhibit enantioselectivity when interacting with biological systems (*2*). There is evidence suggesting that enantioselectivity occurs with biological activity, in biodegradation by soil or sediment microorganisms, and during bioaccumulation along food chains (*3*−*11*). Therefore, enantioselectivity should be characterized when evaluating environmental behavior and risks of chiral contaminants.

The biggest challenge in determining enantioselectivity is often development of analytical methods that allow separation and identification of enantiomers. Enantiomer separation can only be achieved on chiral selective chromatographic columns. In addition, a few studies have shown that interconversion between stereoisomers may occur due to heat or exposure to polar solvents (*12*−*14*). Isomer conversion has been reported for pyrethroids during photochemical degradation or when exposed to polar solvents (*15*−*17*). As heat is always encountered during analysis on a gas chromatograph (GC) and polar solvents (e.g., methanol, water) are often used in sample preparation, isomer conversion may occur during analysis, resulting in analytical biases. Water-induced isomer conversion is important also because it serves as an alternate route for occurrence of enantioselectivity in the environment.

Synthetic pyrethroids are a class of widely used insecticides, and their use may further increase in the near future as some organophosphate compounds are phased out for certain uses. Most pyrethroids have exceptionally high toxicity to fish and aquatic invertebrates (*18*). Every compound in the synthetic pyrethroid family is chiral, containing 1−3 asymmetric carbons or 2−8 stereoisomers (*19*). Enantiomer pairs form diastereomers that generally differ in physical−chemical properties, which allows diastereomers to be separated on achiral columns. However, separation of enantiomers requires chiral columns. Enantiomers from the same pyrethroid compound are known for their drastic differences in insecticidal activity. For instance, in permethrin (PM) [phenoxybenzyl-(1*SR*)-*cis*,*trans*-3-(2,2-dichlorovinyl)-2,2-dimethyl-cyclopropanecarboxylate], only two of the four stereoisomers have insecticidal activity. In cypermethrin (CP) [(*RS*)-α-cyano-3-phenoxybenzyl-(1*RS*)-*cis*,*trans*-3-(2,2-dichlorovinyl)-1,1-dimethycyclopropanecarboxylate] or cyfluthrin (CF) [(*RS*)-α-cyano-4-fluoro-3-phenoxybenzyl-(1*RS*)-*cis*,*trans*-3-(2,2-dichlorovinyl)-1,1-dimethy-cyclopropanecarboxylate], only two of the eight stereoisomers have biological activity. In recent studies, we found that enantioselectivity was prevalent among pyrethroids in their aquatic toxicity, as well as during their degradation in sediment (*20*, *21*). Therefore, it is important to consider enantioselectivity when evaluating the environmental fate and effects of pyrethroids.

The objective of this study was to investigate the chiral stability of four pyrethroids, (*Z*)-*cis*-bifenthrin (*cis*-BF), PM, CP,

* To whom correspondence should be addressed. Tel: 951-827-2712. Fax: 951-927-3993. E-mail: jgan@ucr.edu.

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and CF, under enhanced heat and in polar solvents. Stereoisomers were isolated by using semipreparative chiral high-performance liquid chromatography (HPLC) methods and were individually examined for their ability to undergo isomer conversion under controlled conditions. The results from this study may be used for establishing conditions under which analytical artifacts and biases are minimized and for understanding mechanisms for the occurrence of enantioselectivity in the environment.

## MATERIALS AND METHODS

**Chemicals.** Analytical standards of racemically mixed *cis*-BF (>96%), CP (>98%), and CF (>98%) were purchased from Chem Service (West Chester, PA). Standards of *R-cis*-BF (>97%), *cis*-PM (>99.3%), and *trans*-PM (>99.0%) were provided by FMC (Princeton, PA). Stock solutions of pesticides were prepared in hexane at 1 mg $mL^{-1}$ and stored at 4 °C. Working solutions were prepared daily by diluting the stock solutions with hexane for HPLC analysis and with acetone−hexane (1:1, v/v) for GC analysis. Other solvents and chemicals used were of analytical or pesticide residue grade.

**Isolation of Stereoisomers by Enantioselective HPLC.** Individual stereoisomers were isolated by using a semipreparative enantioselective HPLC procedure, and the obtained stereoisomers were used in experiments to evaluate chiral stability. To prepare individual stereoisomers, pyrethroid racemates of known quantities were injected into an Agilent 1100 series HPLC (Agilent, Wilmington, DE) and resolved on enantioselective columns, and the fractions corresponding to individual stereoisomers were manually collected. The detailed HPLC methods and configuration assignment for the resolved peaks were reported elsewhere (*21*). In brief, the HPLC was equipped with a variable wavelength UV absorbance detector for quantitative detection and a laser polarimeter detector (PDR-Chiral, Westlake, FL) for identification of optical rotation direction of the separated stereoisomers. Complete separation of stereoisomers for *cis*-BF, *cis*-PM, and *trans*-PM was achieved on a Sumichiral OA-2500-I column (4.6 mm i.d. × 250 mm, Sumika Chemical Analysis Service, Osaka, Japan) using hexane:1,2-dichloroethane (500:1 by volume) as the mobile phase. Complete isomer separation for CP and CF was obtained on two Chirex 00G-3019-DO columns (4.0 mm i.d. × 250 mm, Phenomenex, CA) using hexane:1,2-dichloroethane:ethanol (500:10:0.05, v/v/v) as the mobile phase. The recovered fractions were checked for isomer purity using previously established GC methods (*21*), and highly pure chiral isomers (>99%) were used in the following experiments to evaluate chirality stability.

**GC Experiments.** As multiple heated zones are present in a GC system, thermal conversion of stereoisomers may occur during a GC run. To evaluate the potential for isomer conversion during GC analysis, chiral isomers were individually injected into an Agilent 6890N GC and resolved on an enantioselective capillary column. The GC system was equipped with an electron capture detector (ECD) operating at 310 °C and a BGB-172 chiral column (30 m × 0.25 mm × 0.25 $\mu$m, 20% *tert*-butyldimethylsilyl-$\beta$-cyclodextrin in 15% diphenyl- and 85% dimethylpolysiloxane; BGB Analytik, Adliswil, Switzerland). The flow rate of carrier gas (helium) was 1.5 mL $min^{-1}$. In the final analytical protocol, the column was initially held at 160 °C for 2 min, ramped at 1 °C $min^{-1}$ to 220 °C (first ramp), held at 220 °C for 60 min, ramped at 5 °C $min^{-1}$ to 230 °C (final ramp), and held at 230 °C until complete elution. Retention times were used as the sole criterion for identifying peaks in the GC-ECD chromatograms.

As the GC inlet is the first heated zone that an analyte encounters during analysis, inlet temperature and mode of sample introduction were the two parameters considered in this study. To evaluate the effect of inlet temperature, the temperature in the glass inlet was incrementally increased from 160 to 260 °C, and the individual stereoisomers were introduced through 1.0 $\mu$L injection in the splitless mode (1.0 min holding time). The appearance of peaks with retention time different from the analyte stereoisomer was monitored, and the retention time was matched against other stereoisomers. Peak areas were used to determine the degree of isomer conversion. In a separate experiment, the inlet was fitted with an on-column injection unit, and individual stereoisomers were introduced directly into the column and analyzed under the same conditions, including an inlet temperature of 260 °C. Isomer conversion following on-column injection and inlet injection was compared to evaluate the effect of sample introduction mode on isomer conversion.

**Equilibration Experiments.** The potential for thermal isomer conversion was further studied for individual pyrethroid stereoisomers under controlled conditions. Briefly, a given stereoisomer was prepared at 10 ng $mL^{-1}$ in hexane in a 2 mL glass GC vial, and after the solvent was removed under a stream of nitrogen, the vial was sealed with a Teflon septum cap. The vials were heated in an oven at 200 °C for 50−1000 min. The sample vials were periodically removed from the oven, and after they were cooled to room temperature, the vials were opened and 1.0 mL of hexane was added. The samples were then analyzed by GC-ECD to determine the isomer profile.

Isomer conversion was further evaluated in an experiment in which stereoisomers were extracted from water using a solvent (hexane, ethyl acetate, or dichloromethane) or equilibrated in water for a prolonged time. For the water equilibration experiment, a given stereoisomer in acetone was spiked at 10 ng $mL^{-1}$ in 100 mL of sterile water in glass serum bottles, and the sample bottles were sealed with Teflon septa and aluminum caps. The sample bottles were kept at the room temperature (21 ± 1 °C) in the dark. After 10, 20, 40, 60, and 90 days, the vials were opened and the solution was transferred to a 250 mL separatory funnel, followed by extraction with 50 mL of ethyl acetate for two consecutive times. The organic phase was combined and then passed through 10 g of anhydrous sodium sulfate to remove the residual water. The extract was further evaporated to near dryness on a vacuumed rotary evaporator at 50 °C, and the residues were recovered in 2.0 mL of hexane for analysis on GC.

## RESULTS AND DISCUSSION

**Isomer Conversion during GC Analysis.** Because of its better sensitivity, GC is often preferred over HPLC for analysis of organic compounds at the trace level. However, a GC system contains several heated zones, including the inlet, the column, and the detector. Therefore, thermally induced isomer conversion may lead to artificially biased results during GC analysis. Isomer conversion in a GC detector may be of limited significance, as stereoisomers reaching the detector have already been separated after eluting through the column. Isomer conversion during elution through the column may depend on the oven temperature program and the temperature at which analyte is eluted. Isomer conversion in column is expected to affect only the peak shape by causing peak tailing or peak fronting and does not affect peak profiles or isomer ratios (*14*). However, if isomer conversion occurs in the inlet before the sample is flushed into the column, the peak profile or isomer ratio will deviate from the original value. The deviation is artificial and, if not identified, may lead to biased measurements.

Single stereoisomers of *cis*-BF, *cis*-PM, and *trans*-PM were individually injected and resolved on an enantioselective capillary column, with a splitless inlet temperature of 260 °C. Under the used conditions, no peaks other than the analyte stereoisomer were found for any of the stereoisomers (data not shown). This finding suggests that stereoisomers deriving from the chiral carbons on the cyclopropyl ring (**Figure 1**) are thermally stable, and bond rotation did not occur at the C1 or C3 position. Therefore, when enantioselective GC is used for analyzing pyrethroids with only cyclopropyl chirality, the integrity of peak profiles or isomer ratios is preserved. For pyrethroids (e.g., CP, CF) with three chiral positions, as two of the chiral positions are always related to the substituted cyclopropyl ring, it can be expected that isomer conversion may not occur due to bond rotation at the C1 or C3 position (**Figure 1**).

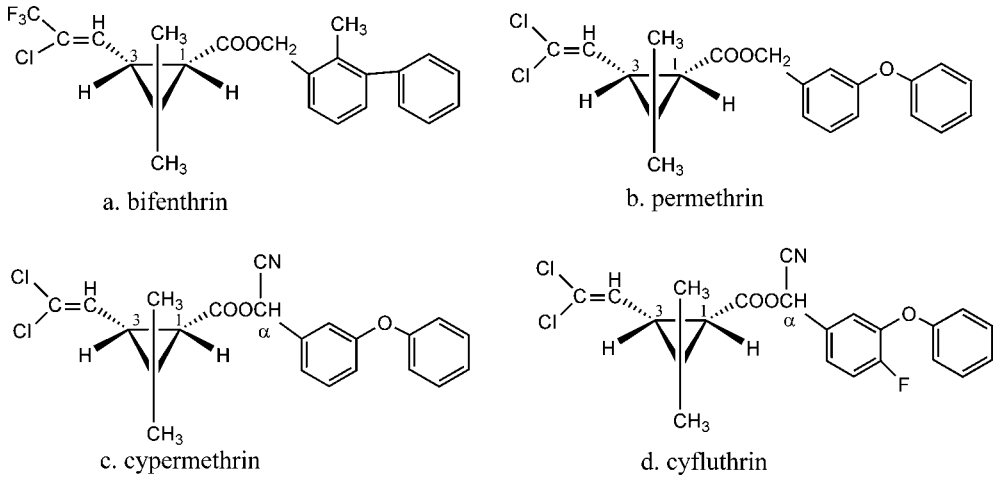


**Figure 1.** Chemical structures of BF, PM, CP, and CF showing chiral positions (labeled with *) in the structure.

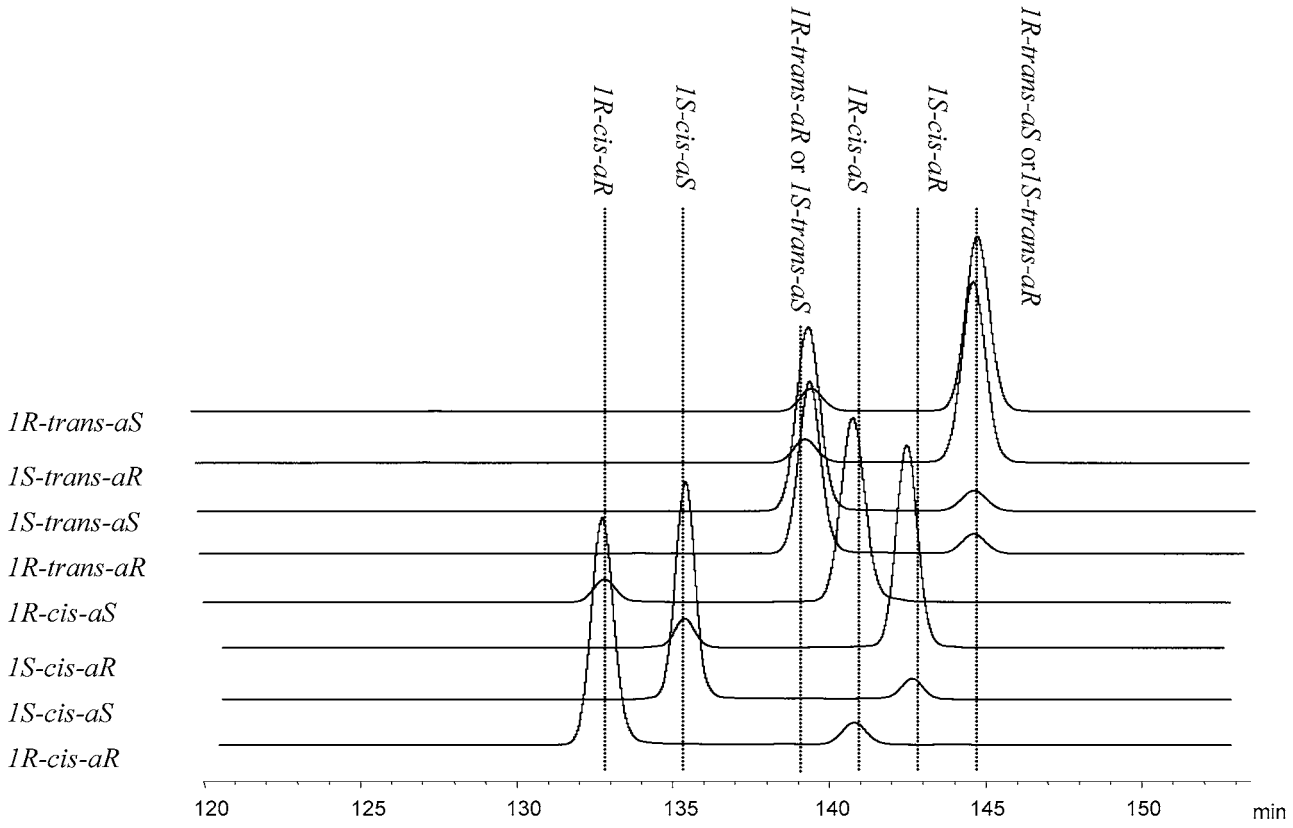


**Figure 2.** Chromatograms of CP stereoisomers when a single stereoisomer was injected into GC at an inlet temperature of 260 °C.

The enantioselective separation and identification of stereoisomers from CP and CF were evaluated in a previous study (*22*). **Figure 2** shows chromatograms when single CP stereoisomers were analyzed on GC at a splitless inlet temperature 260 °C. In each case, in addition to the main peak corresponding to the analyte stereoisomer, a smaller second peak appeared either before or after the analyte stereoisomer. For instance, when 1*R-cis*-α*R* was injected, a small peak was observed after the analyte stereoisomer (**Figure 2**). The retention time of the second peak coincided with that of 1*R-cis*-α*S*. Similarly, a small peak with a retention time equivalent to that of 1*S-cis*-α*R* appeared when 1*S-cis*-α*S* was analyzed under the same conditions (**Figure 2**). The same phenomenon was observed also for 1*R-cis*-α*S* and 1*S-cis*-α*R*, except that the second peak was eluted in front of the analyte stereoisomer. The secondary peaks agreed in retention time with 1*R-cis*-α*R* and 1*S-cis*-α*S*, respectively (**Figure 2**). These observations suggest that isomer conversion consistently occurred at the asymmetric αC for *cis* isomers in CP. Analysis of the four *trans* isomers of CP under the same conditions also consistently gave a primary peak and a smaller secondary peak (**Figure 2**). As the enantiomer pairs from the same trans CP diastereomer were not separated under the given conditions, direct peak assignment was not possible. When 1*S-trans*-α*S* was injected, a second peak with a retention time identical to that of 1*S-trans*-α*R* (or 1*R-trans*-α*S*) was observed. Similarly, when 1*R-trans*-α*R* was injected, a second peak corresponding to 1*R-trans*-α*S* (or 1*S-trans*-α*R*) appeared after the major peak. Assuming that isomer conversion was possible only at the αC, it may be stipulated that 1*S-trans*-α*S* was converted only to 1*S-trans*-α*R* and vice versa. The same

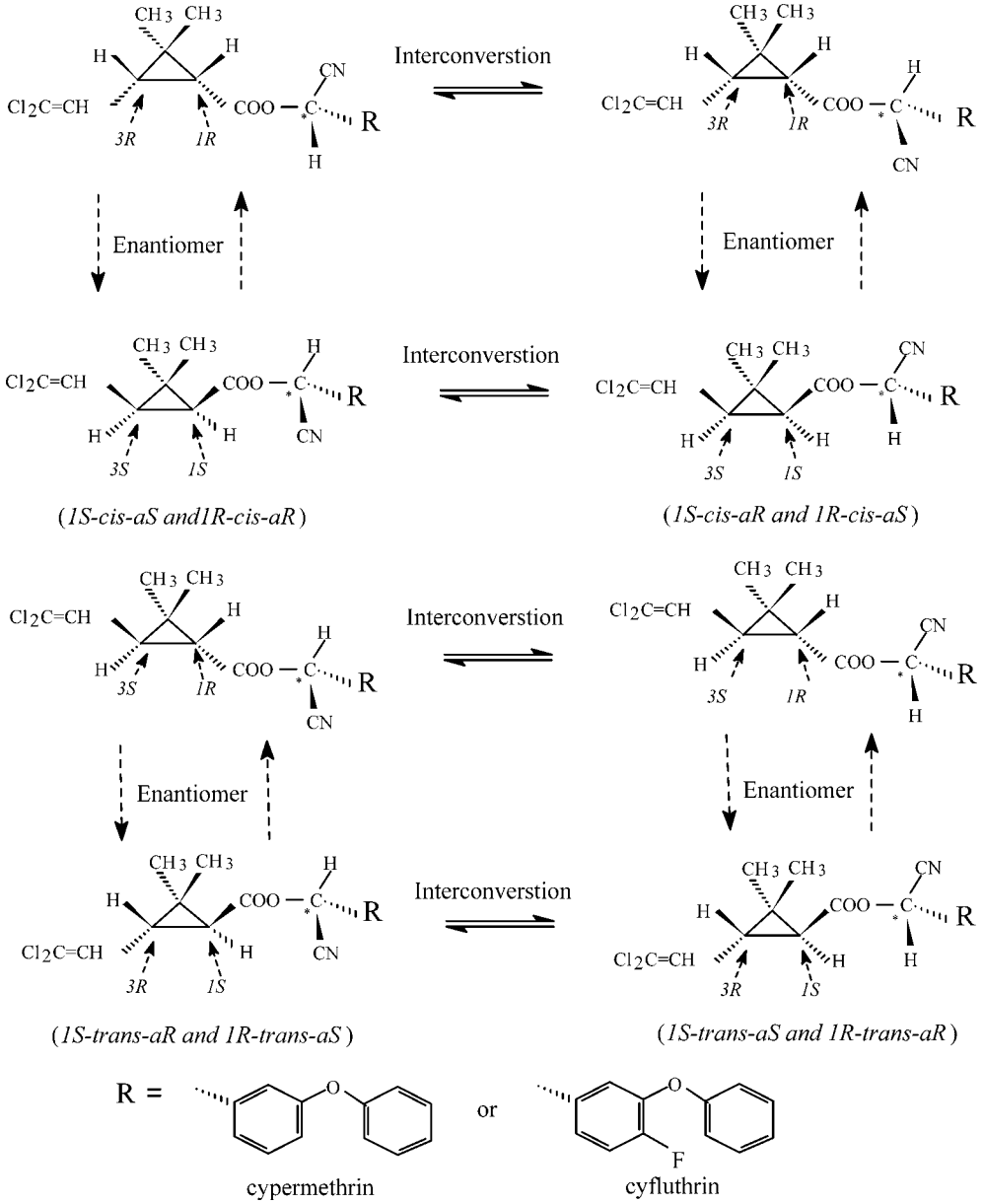


**Figure 3.** Potential isomer conversion pathways for CP and CF stereoisomers.

speculation may be valid also for 1*R-trans*-α*S* and 1*R-trans*-α*R*. Analysis of individual CF stereoisomers under the same conditions showed a very similar behavior as observed for CP stereoisomers.

The conversion pathways for CP and CF stereoisomers may be illustrated schematically in **Figure 3**. Under the used GC conditions, isomer conversion occurred only at the αC. The conversion caused the change of a stereoisomer to an epimer belonging to a different diastereomer, rather than to the corresponding enantiomer in the same diastereomer (**Figure 3**). During the conversion, the chirality on the cyclopropyl ring was not affected, while bonds attached to the asymmetric αC epimerized (**Figure 3**).

When the inlet temperature was 260 °C, the relative peak area of the secondary peak was consistently around 9% for the different stereoisomers (**Figure 2**). When the inlet temperature was gradually decreased, the relative peak area of the formed epimer also decreased, as shown in **Figure 4** for the 1*R-cis*-α*R* isomer of CP and the 1*R-trans*-α*R* isomer of CF. As the inlet temperature was reduced from 260 to 160 °C, the relative peak area of the formed stereoisomer decreased from about 9 to 3%. The effect of inlet temperature implies that inlet temperature may be controlled to minimize isomer conversion during enantioselective analysis of pyrethroids with chirality at the αC. In this study, samples were also introduced directly via on-column injection. The rate of isomer conversion greatly decreased after this modification. The formation of the epimer decreased to only a fraction (22−34%) of that when the sample was introduced through the inlet in the splitless injection mode (**Figure 5**). This validated that the heat in the sample inlet caused isomer conversion for CP and CF stereoisomers. The observation that isomer conversion was not completely eliminated by on-column injection may be attributed to the fact that during on-column injection, the syringe needle was still briefly exposed to the heated inlet before the sample was loaded onto the column. It may be expected that further reduction in isomer conversion may be achieved for CP or CF by combining on-column injection with a lower inlet temperature.

Photochemical isomerization was reported for other pyrethroids in previous studies (*15*, *16*). In the solid phase on glass or silica gel, *cis*−*trans* isomerization was the major reaction for deltamethrin, an enantiopure product with the 1*R-cis*-α*S*

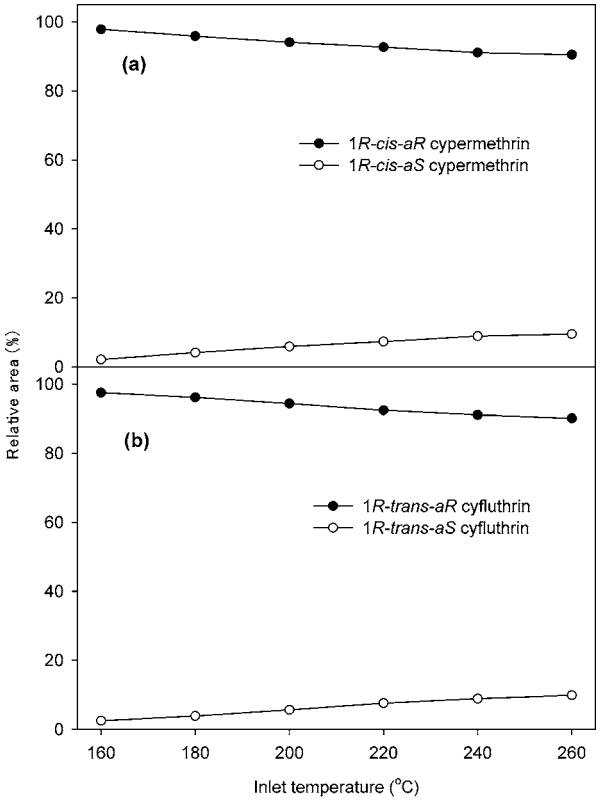


**Figure 4.** Disappearance of the analyte stereoisomer and appearance of the converted epimer as a function of GC inlet temperature. (**a**) 1*R-cis*-α*R*-CP and (**b**) 1*R-trans*-α*R*-CP.

configuration (*15*). After sunlight irradiation as a thin film on glass or in hexane, Maguire (*16*) found that in addition to the formation of 1*S-cis*-α*S*, smaller minor amounts of 1*R-trans*-α*S* and 1*S-trans*-α*S* were also produced. Therefore, isomerization only at the αC position as observed for CP and CF after their exposure to heat suggests that the reaction occurred at the ground state. Thermal isomer inversion has been observed for other chiral compounds in previous studies. Muller et al. (*14*) observed thermal interconversion of metolachlor isomers during GC analysis. Metolachlor has two chiral elements (an asymmetrically substituted carbon and a chiral axis) and consists of four stereoisomers stable at ambient temperature with α*SS*, α*RS*, α*SR*, and α*RR* configurations. At 200 °C, metolachlor stereoisomers were found to rapidly interconvert through internal rotation (atropisomerism) about the chiral axis on the substituted ring, while the chirality at the axis C was stable. The interconversion resulted in the formation of an atropisomer instead of the corresponding enantiomer (*14*). Isomer conversion for metolachlor occurred more rapidly than for CP or CF under similar conditions. About 25−45% of conversion occurred for metolachlor when the inlet temperature was 250−280 °C, but <10% conversion was observed for CP or CF when the inlet temperature was 260 °C in this study.

**Kinetics of Thermal Conversion of Pyrethroid Stereoisomers.** The kinetics for thermal conversion of pyrethroid stereoisomers at the αC position was further evaluated by subjecting individual stereoisomers to thermal treatment at 200 °C. As shown in **Figure 6**, PM stereoisomers were stable even after prolonged equilibration at 200 °C, and no secondary peak was detected. However, 1:1 mixtures of the starting stereoisomer and its converted epimer were eventually obtained for single CP or CF stereoisomers after 1000 min of equilibration (**Figure 6a**,**b**). The kinetics for the disappearance of the starting stereoisomer and appearance of the converted epimer may be described by eq 1 using 1*R-cis*-α*S* as an example:

$$1R\text{-}cis\text{-}\alpha S \underset{k_{-1}}{\overset{k_1}{\leftrightarrow}} 1R\text{-}cis\text{-}\alpha R \quad (1)$$

where $k_{-1}$ represents the rate at which the starting stereoisomer disappears, and $k_1$ is the rate at which the epimer is formed. Assuming that the conversion between a pair of enantiomers is a process of equilibrium, when 1*R-cis*-α*S* (the beginning stereoisomer) is converted to 1*R-cis*-α*R* (the converted stereoisomer), the generated 1*R-cis*-α*R* is also converted back to 1*R-cis*-α*S* at the same rate. If conversion in both directions obeys first-order kinetics, then the following equation can describe the dissipation of 1*R-cis*-α*S*:

$$-\frac{d[S]}{dt} = k_1[S] - k_1[R] \quad (2)$$

where [*S*] is the concentration of 1*R-cis*-α*S* at time *t* and [*R*] is the concentration of 1*R-cis*-α*R* at time *t*. As 1*R-cis*-α*R* is produced from 1*R-cis*-α*S*, the following relationship is valid:

$$-\frac{d[S]}{dt} = k_1[S] - k_1([S]_0 - [S]) \quad (3)$$

where $[S]_0$ is the initial concentration of 1*R-cis*-α*S*. The above differential equation may be solved to give eq 4:

$$[S] = 0.5[S]_0(1 + e^{-2k_1't}) \quad (4)$$

A similar approach may be used to derive the following relationship for describing the production of 1*R-cis*-α*R*:

$$[S] = 0.5[S]_0(1 - e^{-2k_1't}) \quad (5)$$

The measured data were fitted to eqs 4 and 5, and the obtained $k_1$ values were in close agreement with each other for the stereoisomers from the same compound. For CP, the averaged $k_1$ was 0.0961 $h^{-1}$ and the variation between the different stereoisomers was within the experimental error (**Table 1**). The averaged $k_1$ for CF stereoisomers was 0.1082 $h^{-1}$.

**Isomer Conversion in Solvents and Water.** During analysis of organic compounds, most sample preparation methods involve use of various solvents. The most commonly used solvents in analysis of pyrethroids include hexane, ethyl acetate, and dichloromethane. These solvents were used to extract single pyrethroid stereoisomers from water samples. No detectable isomer conversion occurred during solvent extraction at room temperature for any of the tested solvents (data not shown). In a preliminary experiment, no isomerization was observed following storage of selected pyrethroid stereoisomers in hexane for 30 days at room temperature (data not shown).

The stability of pyrethroid stereoisomers was further investigated in water at room temperature (21 ± 1 °C). Stereoisomers of BF and PM were found to be stable, and no isomer conversion occurred. However, as the incubation time increased, a second peak was formed and its relative peak area gradually increased with time for CP or CF stereoisomers (**Figure 7**). The isomer conversion in water consistently followed the same pathways as established for thermal conversion (**Figure 3**). By fitting the measured data to eqs 4 and 5, $k_1$ values for isomer conversion in water were obtained for the different CP or CF stereoisomers (**Table 2**). The averaged $k_1$ was 0.050 $days^{-1}$ for CP stereoisomers and 0.044 $days^{-1}$ for CF stereoisomers. Therefore, for pyrethroids with chirality at the αC position, isomer conversion

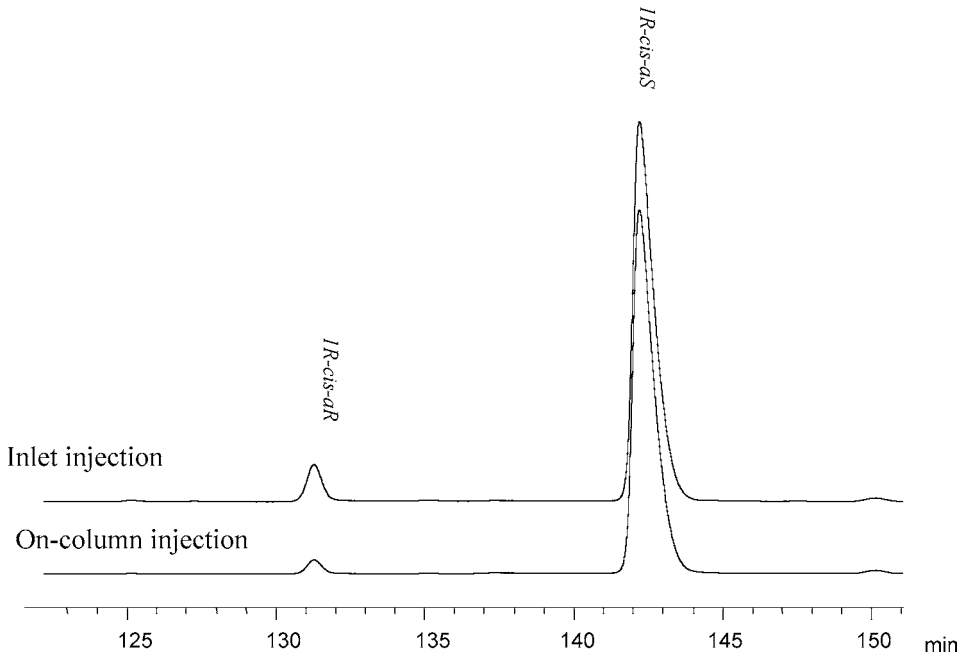


**Figure 5.** GC chromatograms for 1*R-cis*-α*S*-CP following inlet injection and on-column injection.

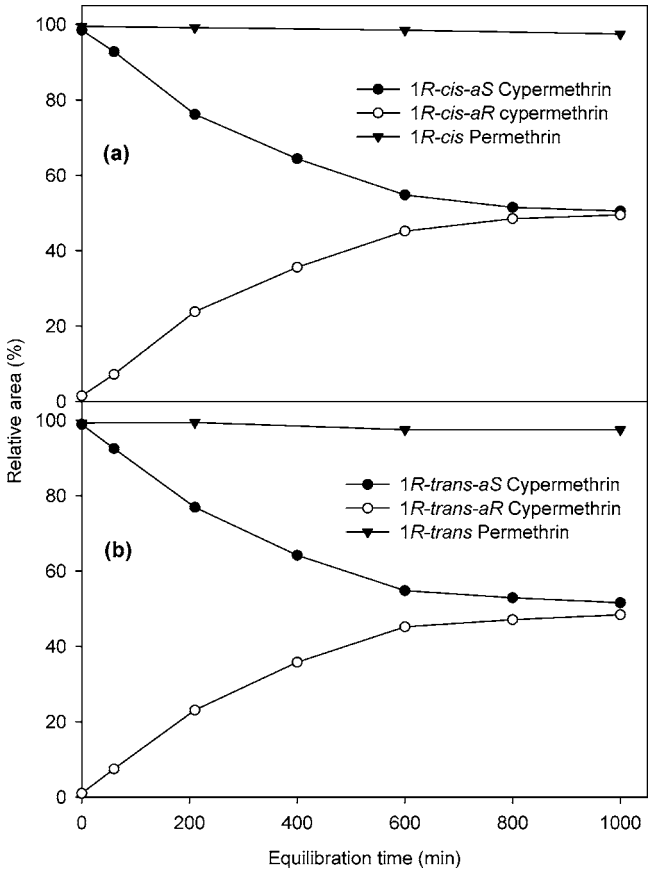


**Figure 6.** Disappearance of the starting stereoisomer and appearance of the converted epimer as a function of time at 200 °C. (**a**) 1*R-cis*-α*S*-CP and 1*R-cis*-PM and (**b**) 1*R-trans*-α*S*-CP and 1*R-trans*-PM.

may be induced by water, and the conversion causes change of a stereoisomer to an epimer.

Leicht et al. (*12*) found that although CF diastereomers were stable in hexane, acetonitrile, or dichloromethane, the same isomers were relatively unstable in methanol or methanol−water mixture. Maguire (*16*) found that in natural water, deltamethrin was subject to cis−trans isomerization yielding 1*S-cis*-α*S* from 1*R-cis*-α*S*. Studying the effect of alcohols on isomerization of deltamethrin exposed to sunlight, Ruzo et al. (*15*) reported formation of 1*R-cis*-α*R* and attributed most of the conversion at the αC to ground state reaction in which the α-proton of deltamethrin exchanged with the solvent. Perschke and Hussain (*17*) further showed that in the dark, isomerization occurred at the αC of deltamethrin in various polar solvents. Therefore, the slow isomerization in water observed for CP and CF in this study likely occurred via a similar ground state pathway as in polar solvents. However, the kinetics observed in this study suggests that it is unlikely that the stability of CP or CF stereoisomers will be significantly affected by water during short time storage or preparation. On the other hand, the water-induced conversion may contribute to occurrence of environmental enantioselectivity for pyrethroids with chirality at the αC position. In previous studies, pronounced enantioselectivity was observed for *cis*-BF and *cis*-PM in sediment and runoff samples as well as during biodegradation by bacteria isolates in solution media (*21*). Observations from this study validate that enantioselective degradation of *cis*-BF or *cis*-PM was likely the result of biotic interactions, rather than abiotic processes. Enantioselective degradation was also observed for CP during its degradation by bacteria strains in aqueous solution and in sediment (*22*). Findings from this study suggest that the enantioselectivity may be attributable to both microbial and chemical processes.

**Table 1.** Kinetic Constant $k_1$ ($h^{-1}$) and Standard Error for the Interconversion of CP and CF Stereoisomers at 200 °C

| | cis | | trans | |
|---|---|---|---|---|
| | 1*R-cis*-α*RS* | 1*S-cis*-α*RS* | 1*R-trans*-α*RS* | 1*S-trans*-α*RS* |
| CP | 0.0961 ± 0.0164 | 0.0954 ± 0.0148 | 0.0942 ± 0.0150 | 0.0985 ± 0.0132 |
| CF | 0.1110 ± 0.0233 | 0.1019 ± 0.0176 | 0.1088 ± 0.0153 | 0.1110 ± 0.0161 |

This study shows that chiral stability in pyrethroids depends on the origin of chirality. For pyrethroids with chirality deriving solely from the cyclopropyl ring, such as *cis*-BF and PM, the chiral configurations were found to be relatively stable. Therefore, the isomer composition for these pyrethroids will be preserved during sample preparation and GC analysis. However,

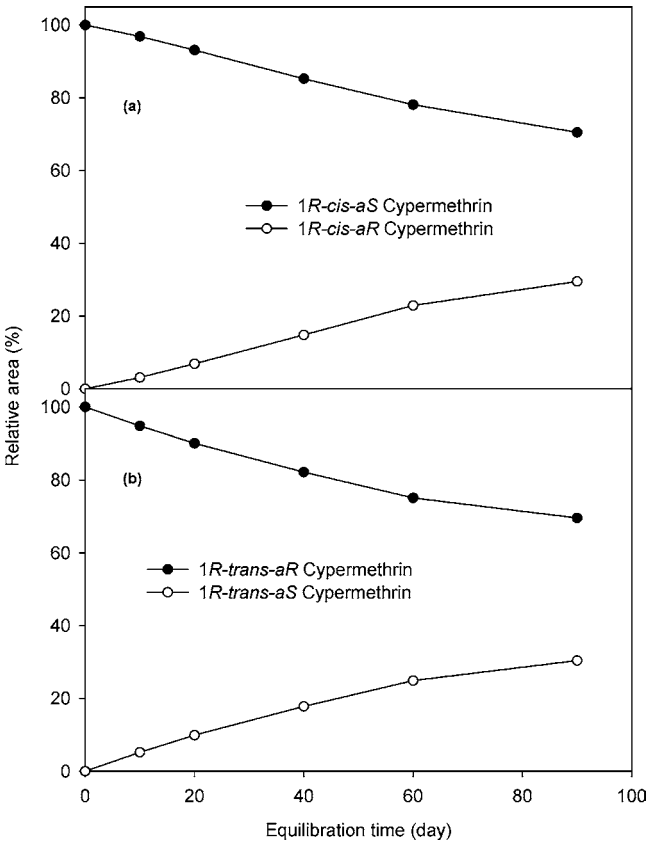


**Figure 7.** Disappearance of the starting stereoisomer and appearance of the converted epimer as a function of time in water at ambient temperature. (**a**) 1*R-cis*-α*S*-CP and (**b**) 1*R-trans*-α*R*-CP.

**Table 2.** Kinetic Constant $k$ (days$^{-1}$) and Standard Error for the Interconversion of CP and CF Stereoisomers in Water at 21 ± 1 °C

| | cis | | trans | |
|---|---|---|---|---|
| | 1*R-cis*-α*RS* | 1*S-cis*-α*RS* | 1*R-trans*-α*RS* | 1*S-trans*-α*RS* |
| CP | 0.0050 ± 0.0005 | 0.0049 ± 0.0008 | 0.0054 ± 0.0007 | 0.0048 ± 0.0008 |
| CF | 0.0043 ± 0.0007 | 0.0044 ± 0.0006 | 0.0047 ± 0.0007 | 0.0043 ± 0.0007 |

for pyrethroids with chirality on the αC, such as CP and CF, isomer conversion may occur at αC position under heat or in water. At an inlet temperature of 260 °C, the thermal conversion caused about 9% of the analyte to convert to an epimer of a different diastereomer. Isomer conversion for CP and CF also occurred in water at a slow rate. As the conversion proceeded at the same rate for all stereoisomers from the same pyrethroid, isomer conversion would affect the analytical outcome only when stereoisomer-enriched samples are analyzed. However, isomer conversion during GC analysis may be effectively minimized by using a lower inlet temperature, on-column injection, or both.

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