Elucidation of Fipronil Photodegradation Pathways

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The phenylpyrazole insecticide fipronil (**I**) photolyzes to its desthio product (**II**) in aqueous solution. However, the necessity of an intervening oxidation to a sulfone intermediate (**III**) has not been resolved, and the photodegradation products of **II** have not been identified. Using GC-MS, HPLC−UV/vis, electrospray MS, ^{19}F NMR, and GC-TSD, our objective was to characterize the photodegradation pathways of **I**, which would clarify the role of **III**, identify products of **II**, and explain unbalanced mass accounts in previous studies. Findings showed that **II** is formed directly and photochemically from **I**, confirmed by the greater stability of **III** ($t_{1/2}$ 112 h), and that successive oxidations of **I** to **III** and then a sulfonate (**IV**) comprise a second pathway. Compound **II** underwent photodechlorination, substitution of chlorine by trifluoromethyl, and pyrazole ring cleavage. This work is significant to understanding the photochemistry of novel phenylpyrazole pesticides in the environment.

Keywords: *Fipronil; phenylpyrazole; photodegradation; ^{19}F NMR; mass spectrometry*

INTRODUCTION

Fipronil (5-amino-1-[2,6-dichloro-4-(trifluoromethyl)-phenyl]-4-[(trifluoromethyl)-sulfinyl]-1*H*-pyrazole-3-carbonitrile; **I**) is a novel phenylpyrazole insecticide (Moffat, 1993) that is applied in a number of crops worldwide (Colliot et al., 1992). **I** exhibits high specificity toward insects (Colliot et al., 1992), is effective against insects with resistance or tolerance to pyrethroid, cyclodiene, organophosphorus, and carbamate insecticides (Colliot et al., 1992; Hosie et al., 1995), and acts by blocking the γ-aminobutyric acid-gated chloride channel (Colliot et al., 1992; Moffat, 1993; Hosie et al., 1995; Cole et al., 1993). We were interested in the fate of **I** in California flooded rice fields, particularly its aqueous decomposition under intense summer sunlight (UV intensity up to 1350 μW/cm^2 at 310 nm) (Ngim and Crosby, 1999b).

Recent work by our laboratory (Ngim and Crosby, 1999a) demonstrated rapid dissipation of **I** in rice field water ($t_{1/2}$ 10−125 h) and in deionized water irradiated in a UV photoreactor ($t_{1/2}$ 8.0−9.4 h). In both experiments, **I** was photolyzed principally to its corresponding desthio analogue (**II**), and a mass balance could not be achieved. **II** is considerably more stable to photolysis ($t_{1/2}$ 120−134 h) than is **I** (Ngim and Crosby, 1999a) and exhibits comparable toxicity (Hainzl and Casida, 1996), leading to concerns of environmental persistence and nontarget toxicity. The formation of **II** from **I** involves loss of sulfoxide (SO), possibly through a free-radical mechanism (Hainzl and Casida, 1996; Bobe et al., 1998), and requires that the cyano and amino groups of the pyrazole ring be present (Hainzl and Casida, 1996). However, the pathway by which this reaction occurs is unresolved, as direct SO extrusion was shown by Hainzl and Casida (1996), while a preliminary oxidation to the sulfone (**III**) followed by loss of sulfur dioxide (SO_2) was proposed by Bobe et al. (1998). Furthermore, both studies used solutions of **I** in aqueous methanol which are not representative of natural waters and bring to question whether their findings are relevant to the environment.

Our objective was to elucidate the photodegradation pathways of **I** to determine the importance of **III** in the conversion of **I** to **II**, identify photodegradation products of **II** to explain its dissipation, and reconcile the incomplete mass balance in our previous studies.

MATERIALS AND METHODS

Reagents. Fipronil (99.4% purity; **I**) and its corresponding desthio (99.4%; **II**), sulfone (100.0%, **III**), sulfonate (91.4%; **IV**), sulfide (99.2%), and amide (98.7%) were provided by Rhône-Poulenc Agro (Research Triangle Park, NC). Trifluoromethoxy-acetanilide was purchased from Aldrich (Milwaukee, WI). Organic solvents (Optima grade) were purchased from Fisher Scientific (Pittsburgh, PA), except for d_2-chloroform which was from Stohler (Waltham, MA). HPLC water was from Fisher Scientific, and deionized water was prepared with a Corning Megapure distillery (Dubuque, IA).

Fipronil Photoproduct Determination by GC-MS. Solutions of **I**−**III** (<2 μg/L) were prepared by magnetically stirring the neat chemical in distilled deionized water for 24 h and filtering (0.22 μm) through a 47 mm nylon membrane (MSI; Westboro, MA). Aliquots (1−2 L) were irradiated either in a custom borosilicate glass photoreactor (Crosby and Tang, 1969) fitted with a single 120 cm F40/350BL fluorescent UV lamp (Sylvania-GTE) or in Teflon-capped borosilicate glass roller bottles (Wheaton) placed in a custom photoreactor (Draper and Crosby, 1984) containing six of the UV lamps arranged in cylindrical fashion around the exposed vessel. The maximal lamp energy output is at 360 nm with UV cutoff of 285−290 nm (Draper and Crosby, 1984), but the borosilicate glass construction of either apparatus ensures relevant environmental exposures (≥300 nm); the total radiant energy at the center of the latter reactor is 400 μW/cm^2 (Draper and Crosby, 1984). Experimental trials were run in triplicate with duplicate dark controls.

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Table 1. 70-eV GC-MS Spectra for Fipronil Photopathway Constituents

compound	ions (% relative abundance)
fipronil (**I**)	367(100), 369(73), 213(45), 215(28), 69(27), 77(25), 351(17), 255(16), 353(13), 257(12)
desthio fipronil (**II**)	388(100), 333(99), 77(91), 390(66), 69,(55), 213(48), 335(33), 179(32), 215(32), 143(24), 100(23), 281(23), 369(23), 120(19)
desthio fipronil product (**IIa**)	166(100), 227(99), 228(97), 229(95), 281(90), 61(71), 230(69), 69(59), 283(59), 201(51), 254(43), 88(40), 157(34), 203(32), 256(30), 213(29), 143(28), 215(16)
desthio fipronil product (**IIb**)	354(100), 299(85), 179(64), 77(57), 69(55), 356(40), 75(36), 143(34), 144(33), 142(29), 235(27), 263(27), 335(25)
desthio fipronil product (**IIc**)	363(100), 422(91), 77(57), 69(48), 365(35), 403(31), 247(32), 424(30), 347(29), 143(17), 249(14)
fipronil−sulfone (**III**)	383(100), 213(88), 77(77), 255(73), 385(66), 69(51), 215(51), 257(45), 241(40), 452(22), 178(18), 143(17), 179(17), 454(16)

Solutions were irradiated for two to three half-lives and passed through 6 mL, 1 g C-18 solid-phase extraction (SPE) cartridges (Varian, Harbor City, CA). Cartridges received no more than 500 mL of solution each and were eluted with ethyl acetate (3 mL) by centrifuge. Eluates were combined when appropriate, concentrated to 1 mL with a N_2 evaporator (Organomation Associates, Shrewsbury, MA) and analyzed with a Hewlett-Packard 6890 series gas chromatograph and a model 5972A mass-selective detector (GC-MS) (Wilmington, DE) fitted with a 30 m × 0.25 mm i.d. × 0.25 μm film DB-5 column (J&W Scientific, Folsom, CA) and operated in full scan mode (50−500 *m*/*z*). Instrument conditions included splitless injection, 275 °C injector, 280 °C transfer line, and 150−270 °C at 10 °C/min, and a 23.00 min hold time. The identification of photoproducts was made by comparison to dark controls and authentic standards.

Fipronil Photoproduct Determination by ^{19}F NMR. I was dissolved in 30% aqueous methanol (90 mg/L) contained in Teflon-capped quartz test tubes and irradiated in the six lamp UV photoreactor. Removed samples were spiked with trifluoromethoxyacetanilide internal standard, and an aliquot (0.8 mL) was transferred to a Wilmad 528 PP NMR tube (Buena, NJ) for direct analysis. Additional photolyzate was passed through a 6 mL, 1 g C-18 SPE cartridge (Varian) prior to analysis to verify the presence of **IV**, which is anionic at near-neutral pH and would not sorb to the packing. ^{19}F NMR spectra were obtained on an Omega 500 MHz NMR spectrometer (General Electric) operating at 470.596 MHz with a dedicated 5 mm ^{19}F probe and a specific ^{19}F preamplifier. Products were identified by comparison with authentic standards and dark controls. Instrument parameters were similar to those of a past investigation of the photolytic fate of trifluralin (Mabury and Crosby, 1995).

Furthermore, combined rice field water extracts (from 500 mL of water total) that were previously analyzed by C-18 SPE and gas chromatography with a nitrogen-sensitive thermionic specific detector (GC-TSD) were solvent-exchanged with d_2-chloroform and analyzed against standards to compare the utility of ^{19}F NMR as a quantitative technique.

Sulfonate Determination by HPLC−UV/Vis and Electrospray MS. IV was analyzed in triplicate deionized water solutions of **I** and **III** irradiated in UV light and in duplicate dark controls. Solutions were acidified to pH 2−3 with concentrated HCl and passed slowly (1−2 mL/min) through 1 g, 6 mL C-18 SPE cartridges (Varian), which received no more than 500 mL of photolyzate and were eluted with ethyl acetate and methanol (3 mL each). Eluates pertaining to a given sample were combined, evaporated to dryness under N_2, and reconstituted in 1 mL of methanol. Acidification was intended to protonate the sulfonate group, but analyte loss via amine protonation was also possible. The sulfonate could not be derivatized by methylation or silation, precluding GC analysis.

Eluates were analyzed by an Isco high-performance liquid chromatograph with a UV/visible wavelength detector (HPLC−UV/vis) (model 2360 gradient programmer, model 2350 pump, V^4 variable wavelength detector; Lincoln, NE) fitted with a 5 μm particle diameter, 250 mm × 4.6 mm i.d. Alltima C-18 column and a matching 7.5 mm guard column (Alltech, Deerfield, IL). The instrument conditions included a 1 mL/min flow rate of isocratic methanol/acetic acid (0.005 M in HPLC water) (80:20) and a detector wavelength of 280 nm. The wavelength corresponds to the absorption maximum of **IV**, determined by a Hewlett-Packard model 8451A diode array spectrophotometer (Wilmington, DE).

Eluates producing HPLC chromatograms with a peak matching the retention time of the analytical standard for **IV** were evaporated under N_2, reconstituted in 1 mL of acetonitrile/H_2O (50:50), and analyzed by direct loop injection into a Finnigan MAT model LCQ mass spectrometer (San Jose, CA) operated in negative electrospray ionization mode at full scan (*m*/*z* 50−500). Conditions included an acetonitrile/H_2O (50:50) mobile phase, −4.25 kV spray voltage, 80 units N_2 sheath gas, 20 units N_2 auxiliary gas, 220 °C heated capillary temperature, and 25 V capillary voltage. Confirmation was achieved by the comparison of spectra with that of authentic **IV**.

Sulfone Photolysis Kinetics. Deionized water solutions of **III** (<2 μg/L) were prepared identically to those used for determining the formation of **II**−**IV**. Triplicate aliquots (1 L each) were irradiated for 2−3 $t_{1/2}$ of dissipation in the single-lamp photoreactor maintained at 35.0 ± 1.0 °C by a cooling coil attached to a constant temperature circulator; duplicate dark controls in Teflon-capped amber glass bottles (900 mL) (Kimble-Kontes) were maintained in a water bath for comparison. Samples (25 mL) were periodically passed through 3 mL, 500 mg C-18 SPE cartridges (Varian), which were eluted with ethyl acetate (2 mL). Eluates were concentrated to 1 mL with a N_2 evaporator (Organomation Associates) and analyzed by GC-TSD with a Varian 3300 instrument (Walnut Creek, CA) fitted with a 15 m × 0.32 mm i.d. × 0.28 μm film DB-1701 column (J&W Scientific). Instrument conditions included 250 °C injector, 275 °C detector, 1.00 min initial hold, 100−220 °C at 50 °C/min, 1.00 min hold, 220−245 °C at 10 °C/min, and a 15.00 min final hold.

RESULTS AND DISCUSSION

The identification of photodegradation products by GC-MS, HPLC−UV/vis, electrospray MS, and ^{19}F NMR provided mutually consistent data, producing the pathways for **I** illustrated in Figure 1. GC-MS analyses identified **II** as the principal photoproduct of **I**, which agreed with previous kinetic photolysis studies that produced **II** in about 50% yield (Ngim and Crosby, 1999a). Minor quantities of **III** were also detected, and similar findings in dark controls confirmed that oxidation occurred without UV radiation. This was consistent with our previous findings that combined **III** and fipronil−amide (Figure 2) accounted for <5% of **I** (Ngim and Crosby, 1999a). Furthermore, fipronil−sulfide (Figure 2) irradiated in deionized water produced trace levels of **I** and **II** that were consistent with its oxidation to **I**, which was subsequently converted to **II**. GC-MS ions and relative abundances of **I** and its photopathway constituents are shown in Table 1. The GC-MS total ion chromatogram of photolyzed **II** (Figure 3) showed a number of peaks that were not present in the dark control. Among those photoproducts possibly identified by interpretation of spectra (Table 1) were compounds formed by pyrazole ring degradation (**IIa**; M^+, 281 *m*/*z*), monodechlorination at the phenyl ring

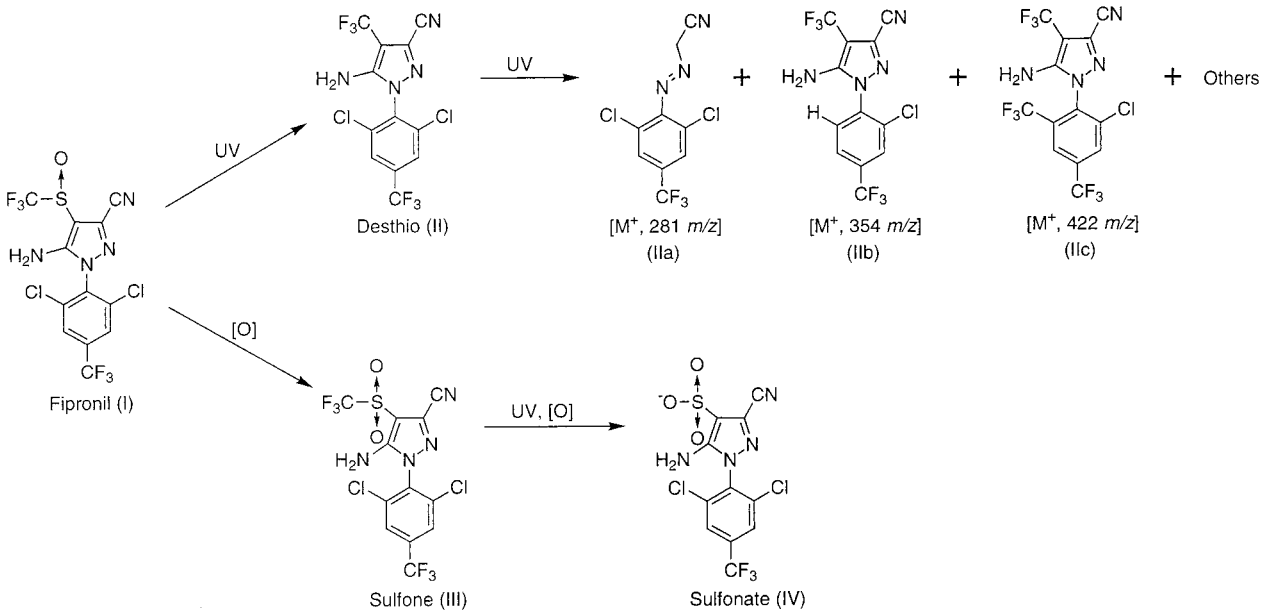

Figure 1. Dual fipronil photodegradation pathways in deionized water.

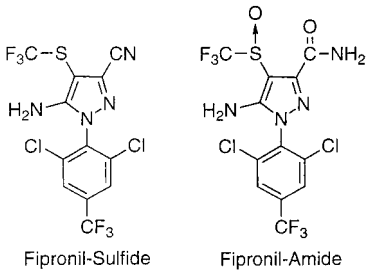

Figure 2. Structures of the corresponding amide and sulfide of fipronil.

(**IIb**; M^+, 354 *m/z*), and replacement of one chlorine with trifluoromethyl (**IIc**; M^+, 422 *m/z*) (Figure 1), and these could at least partially explain the dissipation of **II** in sunlit rice field water and deionized water irradiated by UV light, as well as the incomplete mass balance in previous work (Ngim and Crosby, 1999a). The phenyl ring ions of each were useful in their identification, as 213, 179, and 247 *m/z* corresponded to those of **IIa**−**IIc**, respectively (Table 1). Also, **IIa** was identified by its $[M\text{-}27]^+$ of 254 *m/z* (Table 1), which result from the loss of CNH. Although dechlorinations in pure deionized water are unfavorable, it is possible that **II** itself (or its impurities) could have served as reductants. However, the reduction of fipronil to its sulfide (Figure 2) did not occur in irradiated solutions of **I**. The GC-MS total ion chromatograms of the mixed standard and photolysis extracts of **I** and **II** are illustrated in Figure 3. The photolysis of **III** did not generate **II**.

The results of ^{19}F NMR analyses of **I** irradiated in 30% aqueous methanol complemented those from GC-MS. Both **II** and **III** were detected in directly analyzed samples exposed to UV radiation for 9 h (Figure 4), indicating that the presence of methanol did not affect the formation of photoproducts. The trifluoromethyl group attached or adjacent to the pyrazole ring was particularly useful in product identification, as shifts of −75.324, −57.055, and −80.499 ppm corresponded to **I**−**III**, respectively. By contrast, shifts due to the trifluoromethyl on the chlorinated aromatic ring varied only slightly for **I**−**III** (−63.847 to −63.878 ppm) and

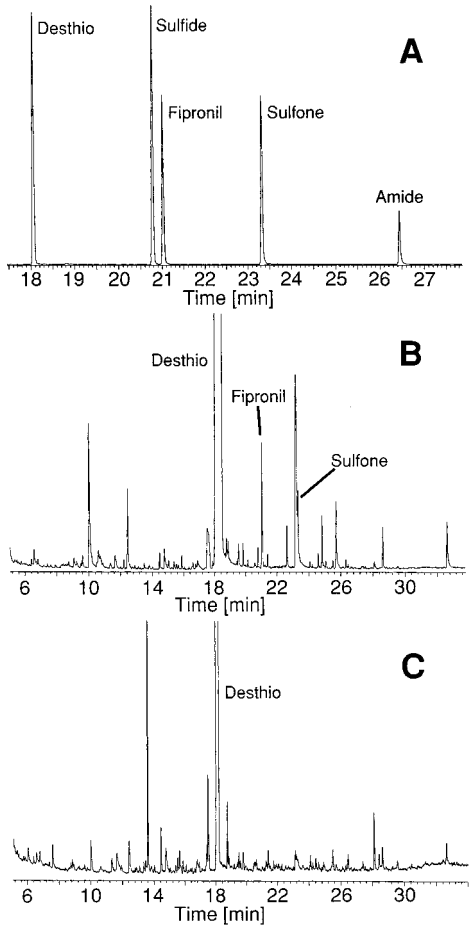

Figure 3. GC-MS total ion chromatograms of a mixed standard (A) and the photolyzates of fipronil (t = 36 h; B) and desthio fipronil (t = 14 days; C). Retention times (min) are as follows: desthio fipronil (18.06), fipronil−sulfide (20.79), fipronil (21.03), fipronil−sulfone (23.337), and fipronil−amide (26.46).

were less diagnostic. Also, subsequent analysis of the photolyzate following a C-18 SPE cleanup revealed a peak (−64.024 ppm) corresponding to the standard for **IV**. By comparison, **II**−**IV** were not detected in dark

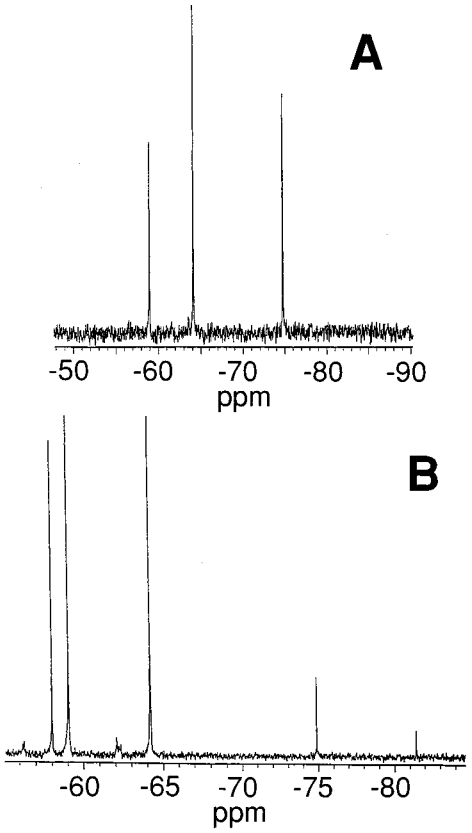

Figure 4. ^{19}F NMR spectra of a fipronil standard (A) and its photolyzate (t = 9 h; B) in 30% aqueous methanol. Chemical shifts (ppm) are as follows: fipronil (−75.324, −63.862), desthio fipronil (−57.055, −63.847), fipronil−sulfone (−80.499, −63.878), trifluoromethoxyacetanilide internal standard (−58.644).

controls, and the absence of **III** may be symptomatic of the lesser sensitivity of ^{19}F NMR relative to GC-MS.

The analysis of combined rice field water extracts by ^{19}F NMR represented 112% of **I** and 99% of **II** that had been previously determined by GC-TSD (2.33 and 0.94 μg/L in water, respectively) (Ngim and Crosby, 1999a). These results were obtained without the harsh conditions of analyses typified by hot injectors in gas chromatography, for example, and resulted in enhanced confidence in sample integrity. The utility of ^{19}F NMR as a selective, sensitive quantitative tool for the analysis of fluorinated agrochemicals was demonstrated, complementing its previous use in characterizing the photodegradation of trifluralin (Mabury and Crosby, 1995).

HPLC−UV/vis and electrospray MS analyses showed that **IV** was formed from **I** and **III**. HPLC−UV/vis chromatograms showed a peak from the irradiated solutions of **I** (t = 36 h) and **III** (t = 14 day) at about 1.8 min that corresponded with that of known **IV**, whereas **IV** was present at only trace levels in the dark controls. The identity of this peak was confirmed by electrospray MS, which produced spectra with percent relative ion abundances for the photolyzates of **I** and **III** (m/z 399.4 (100), 401.2 (78), and 403.2 (16)) that were identical to those of authentic **IV** (Figure 5). **IV** is very likely formed from **I** via **III** (Figure 1), since **III** was determined by GC-MS and ^{19}F NMR to be a product of **I**. The identification of **IV**, along with the possible degradation products of **II** that were previously discussed, could account for the incomplete mass balance

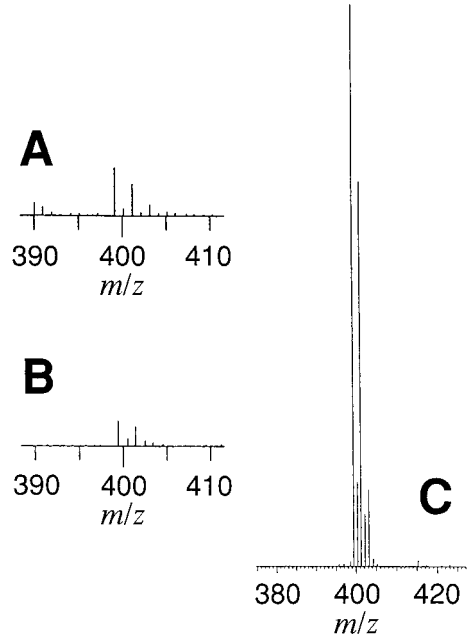

Figure 5. Correlation of negative ionization electrospray MS spectra of the photolyzates of fipronil (A) and fipronil-sulfone (B) with that of authentic fipronil−sulfonate (C; $[M]^+$ 399.4 m/z, $[M+2]^+$ 401.2 m/z, $[M+4]^+$ 403.2 m/z).

for **I** in previous kinetic field and laboratory photolysis experiments.

Since **II** was formed almost instantaneously and in high yield in kinetic photolysis studies of **I** (Ngim and Crosby, 1999a), comparable dissipation of **III** should have occurred with accompanying conversion to **II** if it were indeed an intermediate in the photolysis of **I** to **II**. GC-TSD analyses of photolyzed **III** produced a $t_{1/2}$ of 112 ± 35 h (n = 3) based on pseudo-first-order kinetics (R^2 0.99 ± 0.01) without forming **II**, whereas the dark controls were stable for the duration of the experiment (240 h). As **I** was photolyzed more rapidly than **III** in identical photoreactors ($t_{1/2}$ 9.42 h) (Ngim and Crosby, 1999a), the direct formation of **II** from **I** (Figure 1) previously indicated by GC-MS results was confirmed.

Sulfur extrusion reactions resembling that converting **I** to **II** are known. For instance, the pyrolysis of episulfoxides to SO and alkenes was demonstrated to involve a concerted chelotropic extrusion, a biradical pathway, or sulfenic acid intermediates (Hartzell and Paige, 1966; Hartzell and Paige, 1967; Aalsbersberg and Vollhardt, 1977). Also, sulfones were shown to degrade thermally or photochemically to SO_2 and products consistent with radical coupling reactions (Givens, 1981; Givens et al., 1984; Gould et al., 1984). Bimolecular dethionylations are also possible (Szmant, 1961), but steric effects might hinder the reaction of **I**.

The sulfinyl photoextrusion of **I** appears to be unique, as **II** is not formed from photolyzed analogues lacking the amino or cyano pyrazole ring side chains (Hainzl and Casida, 1996). Direct interaction must occur with the trifluoromethylsulfinyl group, or these substituents stabilize a transition state. Intramolecular H bonding of amino H with the sulfinyl O to form a six-membered arrangement has been proposed (Hainzl and Casida, 1996), but models show that the trifluoromethyl and cyano groups would be sterically unfavorable. Alternatively, the combined electron-withdrawing capabilities

of the cyano and trifluoromethylsulfinyl groups might promote desulfinylation by transition state stabilization.

The free-radical mechanism proposed for the sulfinyl cleavage of **I** in aqueous methanol (Hainzl and Casida, 1996) is consistent with that for arylmethylsulfoxides in benzene (Khait et al., 1981), but neither the potential diffusion of radical species (i.e., $F_3C\bullet$ or $F_3CS(O)\bullet$) nor the presence of excess dissolved oxygen that could react with these radicals support the high yields of **II**. Hainzl and Casida (1996) proposed this mechanism on the basis of the accelerated formation of **II** by HO• in solutions of 1% H_2O_2 in aqueous methanol irradiated by UV light, but we observed that indirect photolysis of **II** in aqueous 0.003% H_2O_2 was significantly enhanced over that in deionized water alone ($t_{1/2}$ 3.76 h vs 120−134 h) (Ngim and Crosby, 1999a). On the basis of these arguments, a concerted SO extrusion mechanism is more plausible.

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