^{19}F NMR as an Analytical Tool for Fluorinated Agrochemical Research

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^{19}F NMR was utilized to monitor the photodegradation of trifluralin directly in NMR tubes without extraction, cleanup, concentration, or chromatographic separation. Dissipation curves were generated for the parent pesticide and degradation products, and the major products identified by addition of authentic standards were α,α,α-trifluoro-2,6-dinitro-*N*-propyl-*p*-toluidine (**II**), α,α,α-trifluoro-2,6-dinitro-*p*-toluidine (**III**), and 2-ethyl-7-nitro-5-(trifluoromethyl)benzimidazole (**VII**). Numerous peaks were observed in the spectra that may represent labile intermediates not generally observed with other analytical techniques.

Keywords: *^{19}F NMR; trifluralin; photodegradation*

INTRODUCTION

Recent agrochemical development has seen the increasing use of fluorine as a structural component in newly created pesticides; it adds stability, lipophilicity (e.g. CF_3 group), and volatility. Currently, more than 10% of these pesticides listed in the *The Pesticide Manual* (9th ed., The British Crop Protection Council, 1991) contain fluorine, and indications are that this trend is likely to continue.

Given the increasing importance of fluorine in agrochemical design, new methods of analysis are needed to more adequately investigate the influence of this element on environmental fate and disposition. The inherent selectivity and sensitivity afforded by nuclear magnetic resonance (NMR) in the fluorine mode have seldom been utilized in investigations concerning fluorinated pesticides. Earlier attempts suffered primarily from the small NMR magnets available, which required large samples and long analysis times (Mazzola et al., 1984). More recently, Mortimer and Dawson (1991) successfully utilized a 9.4 T magnet with a dedicated ^{19}F 5 mm probe as a residue technique to analyze a number of fluorinated pesticides in a variety of matrices. ^{19}F NMR has also been utilized to identify metabolites of a fluorinated drug (Imirestat) in dog urine (Gilbert et al., 1992) and the monodealkylated trifluralin metabolite in carrots (Mortimer et al., 1994). However, no comparable investigations have been reported for agrochemical degradation under realistic environmental conditions. Naturally occurring fluorinated chemicals are rare, and thus interferences are minimal.

The purpose of this investigation was to evaluate the viability of ^{19}F NMR to directly monitor the aquatic degradation of fluorinated pesticides and the dynamic appearance and loss of their degradation products. Due to the specificity of ^{19}F NMR for fluorine-containing chemicals, little or no cleanup is required. Additionally, larger magnets allowed us to obtain NMR signals, with increased resolution, from degradation products that differ little structurally from the parent pesticide.

Trifluralin (**I**, α,α,α-trifluoro-2,6-dinitro-*N*,*N*-dipropyl-*p*-toluidine) is a fluorinated herbicide heavily used (>1.4 million pounds in 1991) in California to control a variety of grasses and broadleaf weeds. It is known to be photodegraded rapidly to a number of products in water (Leitis and Crosby, 1974) and air (Soderquist et al., 1975). The trifluoromethyl group has proven to be extremely resistant to degradation, with only trace amounts of the corresponding carboxylic acid tentatively identified in soil 3 years after application (Golab et al., 1979). Trifluralin was chosen for this investigation because of its rapid photolysis to degradation products that were available to us as standards.

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EXPERIMENTAL PROCEDURES

Chemicals. Technical grade trifluralin (99.0%) was obtained from ChemService (West Chester, PA); α,α,α-trifluoro-2,6-dinitro-*N*-propyl-*p*-toluidine (**II**), α,α,α-trifluoro-2,6-dinitro-p-toluidine (**III**), and α,α,α-trifluoro-5-nitrotoluene-3,4-diamine (**IV**) were gifts from J. Woodrow (Reno, NV); 2-ethyl-7-nitro-5-(trifluoromethyl)benzimidazole (**VII**), α,α,α-trifluoro-5-nitro-N^4-propyltoluene-3,4-diamine (**V**), and 2,6-dinitro-4-trifluoromethyl-2′,6′-dinitro-4′-[(trifluoromethyl)azo]benzene (**VIII**) were available from previous investigations in this laboratory. Melting points corresponded to literature values, and purity was confirmed by ^{19}F NMR. 4-(trifluoromethoxy)acetanilide (TFMA, 99%) from Aldrich (Milwaukee, WI) was utilized as the internal standard.

NMR Analyses. ^{19}F NMR spectra were obtained on an Omega 500 NMR spectrometer (General Electric) operating at 470.596 MHz with a dedicated 5 mm ^{19}F probe and a specific ^{19}F preamplifier. Chemical shifts were reported relative to $CFCl_3$ (0.000 ppm) or TFMA (−58.500 ppm). Generally, spectra were acquired with a 90° pulse, sweep width of 10 000 Hz, 16K data points, pulse width and delay of 10 μs and 4 s, respectively, line broadening of 1 Hz, and 300 scans for each trifluralin experiment. Relaxation times were measured by using T1 programs from the Omega 500 computer library. Signal to noise ratios (S/N) or peak areas were quantitated using four-point calibration curves.

Photodegradation. Trifluralin was dissolved in 20% aqueous methanol to 88 μg/mL, and 0.8 mL was placed in each Pyrex NMR tube (528 PP, Wilmad); the tubes were situated outdoors in a rack tilted 30° toward the sun (July 1993). A sample tube was retrieved at appropriate time intervals, 100 μL of deuterated methanol added, and the tube placed in the spectrometer for analysis. Pyrex transmits the full spectrum of actinic radiation with some attenuation in intensity, resulting in adequate modeling of reaction pathways; rates of reaction would necessarily be slower in comparison to unfiltered sunlight.

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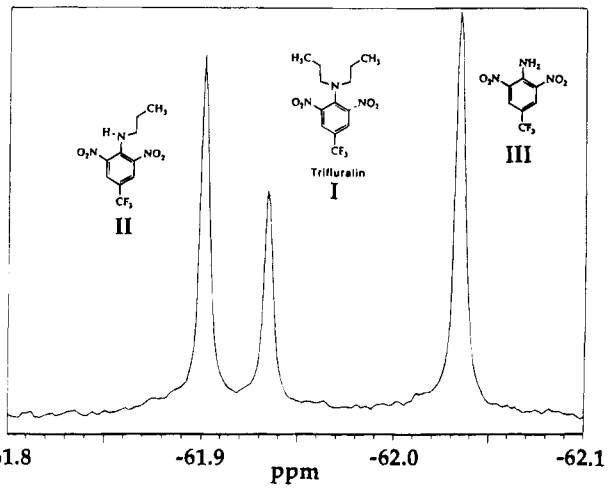

Figure 1. Spectrum of a mixture of **I**–**III** in deuteriochloroform indicating the resolving power of ^{19}F NMR.

Subsequent irradiations of trifluralin were in natural field water (0.45 μm filtered) obtained from a rice field at a more realistic concentration of 100 μg/L. One liter of field water solution, in a large Pyrex fleaker, was placed outside in full July sunlight for 3 h. Water samples, collected at intervals, were extracted three times with methylene chloride, acidified to pH 2, and extracted again three times with methylene chloride. Extracts were combined, reduced in volume on a rotoevaporator, and blown to near dryness under a gentle stream of nitrogen; residues were dissolved in a small amount of deuteriochloroform and subjected to NMR without further cleanup.

Table 1. ^{19}F NMR Signals of Trifluralin and Photoproducts

no.	class	ppm[a,b]
I	tertiary amine (trifluralin)	−63.665
II	secondary amine	−63.605
III	primary amine	−63.734
IV	diamine	−63.698
V	diamine	−62.175
VII	benzimidazole	−61.958
VIII	azobenzene	−64.347

[a] In 20% aqueous methanol. [b] Relative to TFMA at −58.500 ppm.

RESULTS AND DISCUSSION

Resolution. The trifluoromethyl group gives rise to the ^{19}F NMR signal observed for trifluralin. Therefore, structural changes that occur on the molecule will elicit a slight change in the electron density surrounding the trifluoromethyl group, thus producing a unique chemical shift. Figure 1, the total range of which is only 0.3 ppm, demonstrates the resolving capability of a 500 MHz NMR for producing chemically distinct signals for major trifluralin degradation products. Clearly, with only small changes in structure, a significant shift in signal is observed, allowing identification and quantitation. ^{19}F NMR signals for trifluralin and its photodegradation products are listed in Table 1.

Mortimer and Dawson (1991) observed that varying the solvent composition had a significant influence on chemical shift. We observed similar results in methanol/water and chloroform; amino compounds yielded the

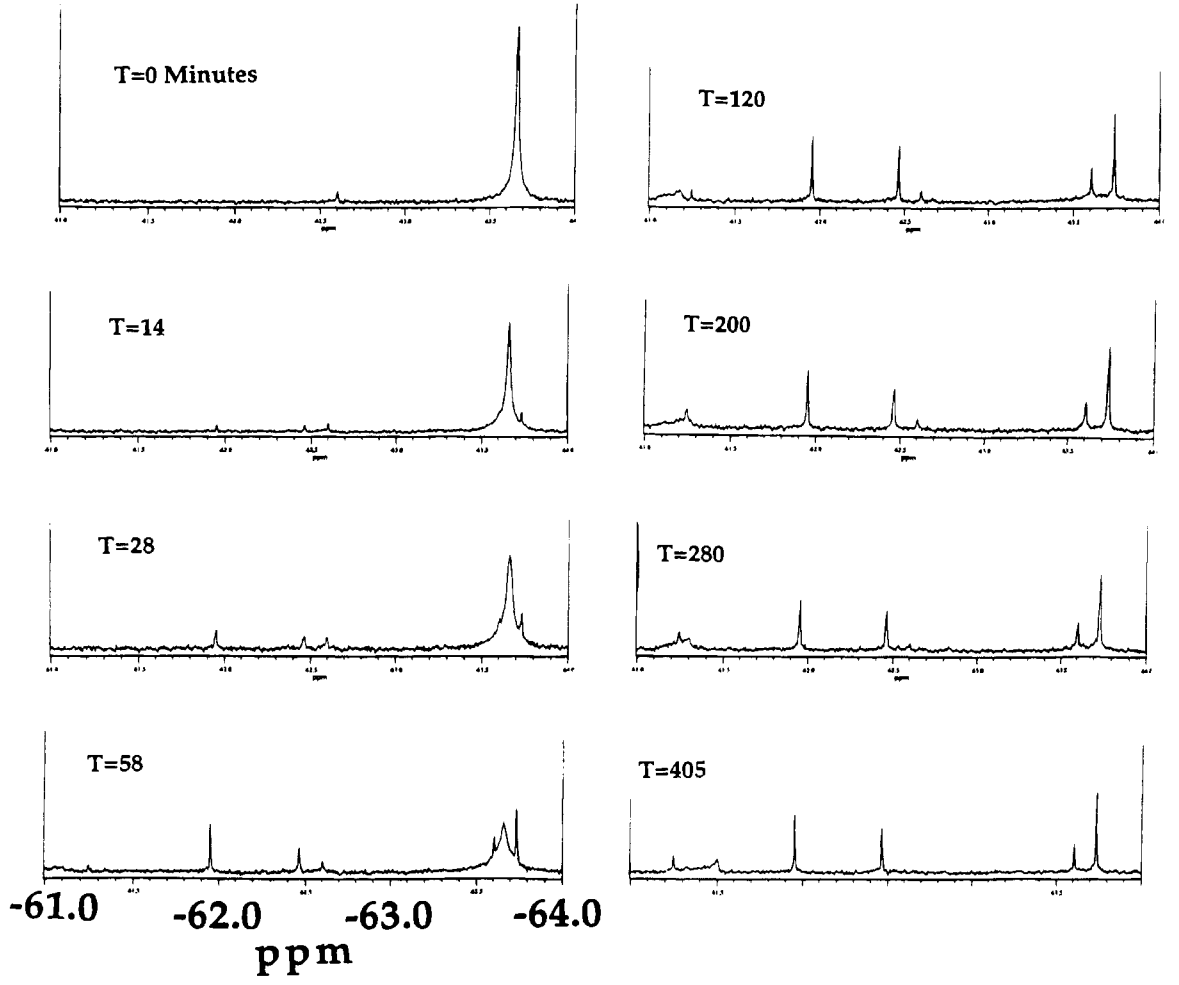

Figure 2. Spectra following sunlight irradiation of 88 mg/L trifluralin in aqueous methanol.

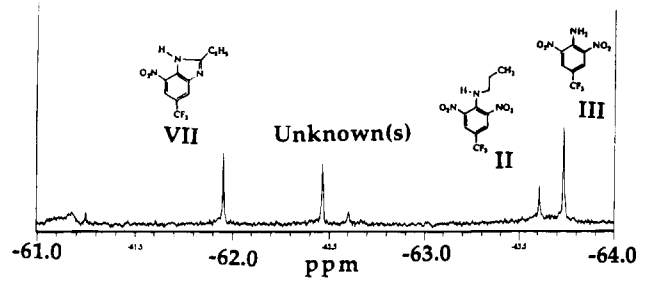

Figure 3. Spectrum of the 120 min sample indicating the identity of photodegradation products. Solvent was 20% aqueous methanol.

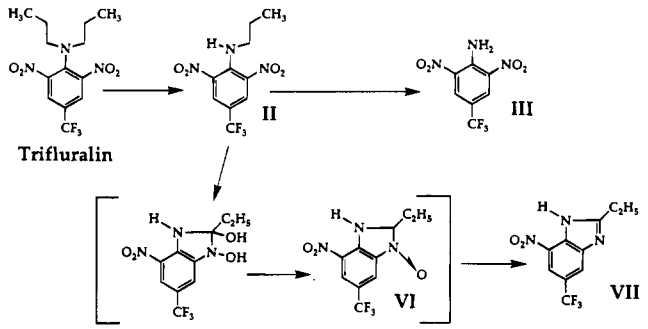

Figure 4. Proposed photodegradation pathway from results observed in this investigation. Parenthetical structures were not identified.

largest variation, presumably due to hydrogen bonding in the polar solvent. Thus, for positive identification of peaks, addition of authentic standard was required.

Quantitation. All of the major degradation products of trifluralin have the same trifluoromethyl group. The relative signal response for each should be linearly related to that for the internal standard (TFMA) that also has a trifluoromethyl group. This was tested by comparing the spectra of four solutions containing different concentrations of equimolar amounts for the internal standard and each of the major degradation products. Results showed that the standard slopes for each, relative to the internal standard, were very similar in S/N or peak area with an average slope ($M \times 10^{-4}$ vs S/N) of 0.031 ± 6%. The limit of detection, defined as 3× background, was approximately 1 mg/L with the scan parameters used, and corresponds to less than 1 μg in the NMR tube.

Trifluralin Photodecomposition. Trifluralin was rapidly degraded under full summer sunlight (2000 μW/cm^2), with an estimated half-life of approximately 30 min. No change was observed in dark controls. Figure 2 indicates the spectra obtained at each time point. After 14 min, the trifluralin peak (−63.665 ppm) had broadened considerably, and small secondary peaks were observed. Subsequent sampling showed the continued broadening and loss of the trifluralin peak; after 120 min, it was completely missing, and peaks for four major products remained. From 120 to 405 min, the spectra did not appreciably change except at −61.0 to −61.5 ppm. Three of the major peaks were identified by fortifying the photoreaction mixture with the corresponding standards; these are indicated on the 120 min spectrum (Figure 3). No available standard produced the peak at −62.469 ppm which might represent one of the intermediates such as **VI** in the formation of the benzimidazole (**VII**). The degradation pathway suggested by these results is shown in Figure 4 and is similar to that reported previously (Leitis and Crosby, 1974; Crosby and Leitis, 1976), with photodecomposition

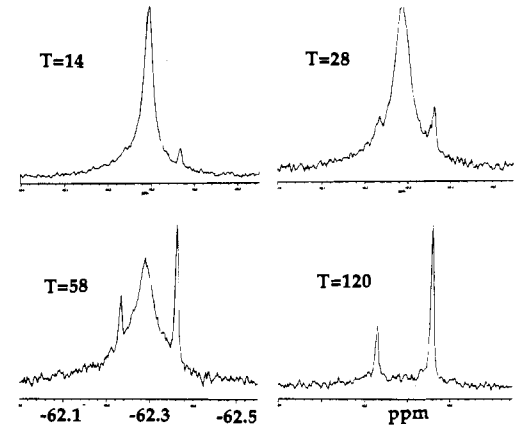

Figure 5. Expansion of the −62.0 to −62.5 ppm region around the trifluralin NMR signal suggesting the presence of numerous structurally similar intermediate degradation products.

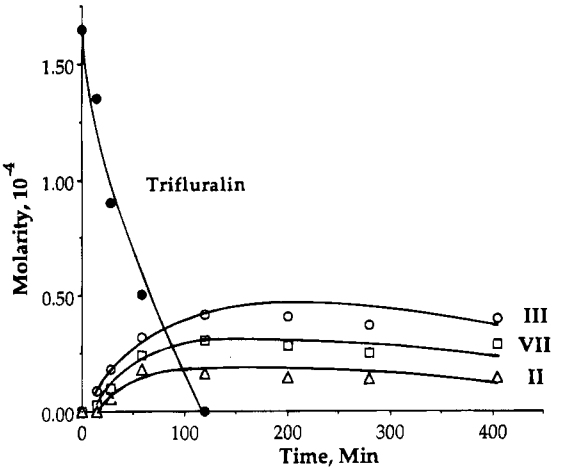

Figure 6. Photolysis rate of trifluralin and appearance and persistence of degradation products.

involving oxidative *N*-dealkylation and cyclization to yield a similar array of products. However, we did not observe formation of the diamino product (**IV**) via the nitro reduction pathway, although it was a major product found in the earlier investigations. Additionally, the proportions of **II** and **III** were significantly greater in the present study.

The only azobenzene standard available was **VIII**, which had a shift significantly upfield on any of the peaks observed in these spectra (Table 1). Numerous other azo or azoxy compounds have been reported from the irradiation of concentrated solutions of trifluralin (Leitis, 1973; Sullivan et al., 1980), and each would have a different chemical shift relative to **VIII**. Without standards, it was impossible to determine whether any of these dimers were formed.

Expansion of the spectral region immediately around trifluralin (Figure 5) illustrates the broadening of the signal. We hypothesize that this broadening indicates the presence of numerous photodegradative intermediates that differ only slightly from the parent herbicide. Such products could be formed during the *N*-dealkylation and may include the hydroperoxide and alcohols. By eliminating the extraction, cleanup, concentration, and other destructive steps, it is reasonable to assume that ^{19}F NMR allows the observation of intermediates that would not normally be seen by other methods.

The rate of trifluralin degradation determined by NMR is shown in Figure 6. It depicts the stability of the photoproducts relative to trifluralin and indicates

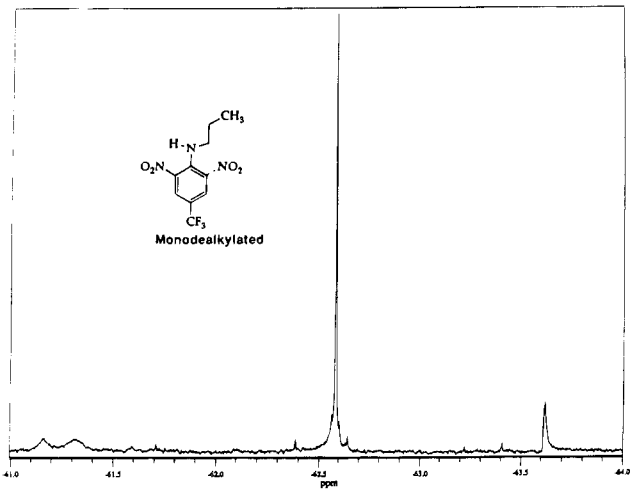

Figure 7. Spectra of trifluralin photodegradation products extracted from field water.

the likelihood that they would be persistent within the sunlit aqueous environment. Attempting to quantify the early time points was difficult due to poor resolution; ultimately, the amounts were determined by peak height from S/N determinations. The identified degradation products represented approximately 15% for the unidentified peak. In the final sample, the total amount of measured signal represented 101% of the original concentration of trifluralin, indicating that all of the degradation products were being detected. However, the average recovery for all samples was 106 ± 13%; the increase is presumably due to difficulty encountered in the computer's accurately determining the area of the broad peaks.

Irradiation in field water more adequately represents the photodegradation reactions that occur in the environment by allowing for indirect or sensitized photolysis. The extract of irradiated field water contained only the monodealkylated product (**II**) in appreciable quantities, and all other peaks represented only minor components (Figure 7). This experiment emphasizes the importance of experimental design in elucidating actual photodegradation pathways important in the real environment.

These results indicate the potential of monitoring qualitatively and quantitatively the dynamic degradation pathways of fluorinated pesticides virtually as they occur in an NMR tube without chromatographic separation. The photodegradation of trifluralin was similar to that observed in previous studies, but without the onerous extraction, cleanup, and concentration steps, resulting in higher confidence in the integrity of the sample.

Quantitation is relatively straightforward, and although confirmation of peak identification is possible, authentic standards generally will be required for comparison. Unlike proton NMR, information obtained from ^{19}F chemical shifts is of only limited value in structural identification. ^{19}F NMR will be an important tool in our continued investigation into fluorinated chemicals and their disposition and fate in the environment.

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