

Imazethapyr Aqueous Photolysis, Reaction Quantum Yield, and Hydroxyl Radical Rate Constant

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The recent introduction of imidazolinone-tolerant rice varieties allow imazethapyr to be used in commercial rice. Little is known about imazethapyr photodegradation in the rice field. Laboratory studies were conducted to determine the direct and indirect photolysis rates for imazethapyr and to evaluate the photolysis of imazethapyr in three rice paddy waters. The reaction quantum yield (ϕ_1) for imazethapyr was determined to be 0.023 ± 0.002 , while the hydroxyl radical rate constant (k_{OH}^1) was $2.8 \times 10^{13} \text{ M}^{-1} \text{ h}^{-1}$. These results show that imazethapyr is susceptible to both direct and indirect photolysis reactions in water. The results also show that imazethapyr photolysis in paddy water will be affected by turbidity because of its impact on the availability of sunlight to drive direct and indirect photolysis reactions.

INTRODUCTION

Imazethapyr {5-ethyl-2-(4-isopropyl-4-methyl-5-oxo-4,5-dihydroimidazol-1*H*-2-yl)nicotinic acid} (**Figure 1**) is an imidazolinone herbicide used to control broadleaf weeds and annual grasses in soybean and peanut (*I*). The recent introduction of imidazolinone-tolerant rice varieties allows it to also be used to control red rice and other weeds in commercial rice. Because the use of imazethapyr in commercial rice is relatively new, less is known about its environmental behavior in flooded rice culture. Imazethapyr is a weak organic acid ($\text{p}K_{a1} = 2.1$ and $\text{p}K_{a2} = 3.9$), having a water solubility of 1420 mg L^{-1} (pH 7 and 25 °C) and vapor pressure $< 0.013 \text{ mPa}$ (60 °C) (*I*). The primary dissipation mechanism of imazethapyr in the environment is through microbial degradation (2). Imazethapyr has a half-life of 53–122 days in aerobic field soil (3, 4). Imazethapyr loss from hydrolysis is minimal, with virtually none observed at pH 5 or 7 and only minimal degradation occurring at pH 9 ($t_{1/2} \approx 9.6$ months at 25 °C) (5). Under anaerobic conditions, no significant imazethapyr degradation occurred during a 2-month period when incubated in a variety of soils and sediment (5). Soil residues of imazethapyr can injure succeeding crops (6–9).

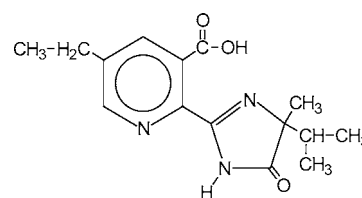


Figure 1. Imazethapyr chemical structure.

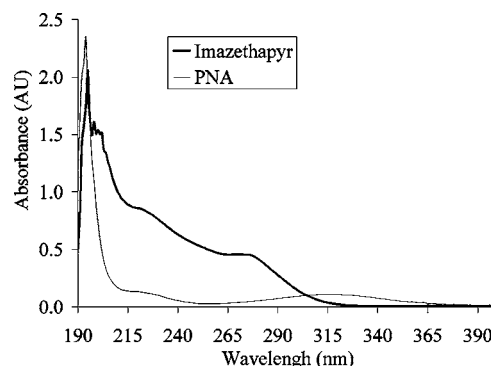


Figure 2. Light absorbance by the herbicide imazethapyr and by the chemical actinometer *p*-nitroanisole (PNA).

Photolysis is an important dissipation mechanism for certain other pesticides used in rice production (10). Imazethapyr has the potential to be degraded by direct photolysis because it absorbs light above 290 nm (**Figure 2**). Imazethapyr undergoes

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aqueous photolysis with half-lives ranging from 44 h (pH 5) to 57 h (pH 9) (5). Because imazethapyr is weakly absorbed to soil (1) and is hydrolytically stable in water and under anaerobic aquatic conditions (5), photolytic mechanisms could play an important role in imazethapyr dissipation in rice paddies.

The rate of direct photolysis is determined by light intensity and the extent of light absorption and reaction quantum yield of the molecule (11, 12). The reaction quantum yield (ϕ) is used to estimate direct photolysis rates under different use scenarios (13) and, therefore, is an important environmental parameter for photolabile compounds such as imazethapyr (14). Schwarzenbach et al. (15) defines reaction quantum yield as

$$\phi = \frac{\text{number of molecules transformed}}{\text{number of photons absorbed because of the presence of the molecule}} \quad (1)$$

Indirect photolysis is another important contributor to pesticide degradation in rice paddies (16, 17). Singlet oxygen, alkylperoxy radicals, triplet-state chemical species, and hydroxyl radicals are highly reactive chemical species present in natural waters that act as intermediates in indirect photolytic reactions (17). The hydroxyl radical ($\cdot\text{OH}$) is the most reactive species toward a wide variety of organic compounds (18) and can be formed in surface water by several mechanisms, including the photolysis of nitrate or dissolved organic carbon, and by reactions between H_2O_2 with Fe^{II} (15). Inclusion of hydroxyl radical reactions in environmental models such as EXAMS often improves correlations between the observed and predicted behaviors of pesticides in natural waters (10, 16).

The reaction quantum yield and hydroxyl rate constant for imazethapyr have not been reported in the literature but are necessary to fully evaluate its environmental fate in aquatic systems such as rice paddies. For these reasons, laboratory experiments were conducted to determine the (1) photodegradation rates in three natural rice paddy waters, (2) reaction quantum yield, and (3) hydroxyl radical rate constant for imazethapyr.

MATERIALS AND METHODS

Materials. Imazethapyr (99% purity) and 2,4-D (99% purity) were obtained from Chem Service, Inc. (West Chester, PA). Acetonitrile, acetophenone, Acrodiscs 13-mm GHP syringe filters, borosilicate vials (1 mL), catalase, high-purity HPLC-grade water, hydrogen peroxide (30%), K_2HPO_4 , *p*-nitroanisole (PNA), and pyridine (PYR) were obtained from Burgoon (Galveston, TX). High-performance liquid chromatography/diode array detector (HPLC/DAD) and the columns were obtained from Waters (Milford, MA). The spectrophotometer was obtained from Beckman Coulter, Inc. (Fullerton, CA). Cuvettes used for molar absorptivity and formic acid were obtained from Fisher (Pittsburgh, PA). Lamps for simulating sunlight were obtained from Kelsun Distributors, Inc. (Bellevue, WA).

Simulated Sunlight Equipment. Two 100 W UV lamps (F72T12/VHO 5.0 Midday sun) were used to simulate the UV portion of sunlight emission (16). The lamps were placed in a growth chamber where the temperature was kept constant at 25 ± 1 °C.

Imazethapyr Photolysis in Rice Paddy Water. Paddy water samples were collected 2–3 weeks prior to study initiation from rice fields located in Beaumont, TX (BM), Clarksdale, MS (CD), and Eagle Lake, TX (EL) and stored at 4 °C until use. Analyses performed on the waters included elemental analysis, total dissolved salts, hardness, conductivity, alkalinity, and pH. Buffered deionized water (pH 7.0) was included as a control.

A Beckman DU-640 spectrophotometer and a 10-mm Suprasil 300 quartz cuvette were used to determine the absorbance of each water source to check for possible light attenuation. The absorbance was measured between 290 and 800 nm using the spectrophotometer

Table 1. Water Samples pH and Absorbance and Imazethapyr Photolysis Rate Constant and Half-Life ($t_{1/2}$)

| water sources ^a | pH | absorbance ^b (% of control) | rate constant, k ($\text{M}^{-1} \text{h}^{-1}$) | $t_{1/2}$ | |
|----------------------------|-----|-------------------------------------------|---------------------------------------------------------|----------------------------------|-------------------------------|
| | | | | noncorrected ^c (h) | corrected ^d (h) |
| deionized water | 7.0 | | -0.296 a ^e | 2.3 | 3.3 |
| Eagle Lake | 7.3 | 0 | -0.247 a | 2.8 | 4.0 |
| Beaumont | 8.0 | 207 | -0.194 b | 3.6 | 5.1 |
| Clarksdale | 8.2 | 314 | -0.191 b | 3.6 | 5.1 |

^a Water sources: deionized (pH 7.0), Eagle Lake rice paddy (pH 7.3), Beaumont rice paddy (pH 8.0), and Clarksdale rice paddy (pH 8.2). ^b The percentage of the absorbance was observed in the control (deionized water); the absorbance was measured on selected wavelengths between 290 and 400 nm. ^c Noncorrected values, values determined with UV-light exposure. ^d Corrected for sunlight equivalent based on the light emission of unobstructed midday sunlight at College Station on March 27, 2005 and corrected for the effect of a cylindrical vial (15). ^e Means within a column followed by different letters are significantly different at $p \leq 0.05$.

described above. Absorbance was also determined for imazethapyr in deionized water solution (pH 7.0) to compare with the paddy water absorbance. Only pH and light absorbance correlated well with imazethapyr photolysis rates. Values for pH and light absorbance for each water sample are shown in **Table 1**.

Water samples were fortified with imazethapyr at $15 \mu\text{g mL}^{-1}$ (approximately $1 \times$ field rate), placed into 1-mL borosilicate glass vials, capped, and subjected to irradiation by UV lamps at a distance of 12-cm beneath the light source for periods of 0, 1, 2, 6, 12, 24, 48, 72, and 96 h. A dark control for each exposure time was included to check for chemical hydrolysis. After irradiation, the samples were filtered using Acrodisc syringe filters to remove particulates prior to chromatographic analysis. Filtration reduced imazethapyr recovery by $<1\%$ (data not shown).

After exposure and filtration, imazethapyr was quantified by HPLC equipped with a DAD. A Waters Symmetryshield RP8 3.5- μm particle size 2.1×150 -mm column with a mobile phase of 39% deionized water, 1% formic acid, and 60% acetonitrile was used for chemical analysis. Isocratic elution at 0.3 mL min^{-1} was performed, and imazethapyr was detected at a wavelength of 245 nm. On the basis of the water samples collected from the field locations, the limit of quantitation (LOQ) was estimated to be $1.3 \mu\text{g mL}^{-1}$.

The natural log of the remaining imazethapyr concentration [$\ln(C/C_0)$] was calculated, and the first-order plots were constructed. Photolysis half-life values were calculated using the equation

$$t_{1/2} = \frac{\ln(2)}{k_p} \quad (2)$$

where k_p is the absolute value of the slope and first-order rate constant for imazethapyr. Photolysis half-lives were corrected for the sunlight equivalent using mid-day sunlight measured in College Station, TX on March 27, 2005. This date represents the optimal date for planting rice in the Houston rice area (from March 15 to April 21). A correction for cylindrical test-tube effect was also performed (15).

A natural sunlight correction factor taking into account differences between our simulated sunlight conditions and natural sunlight was calculated as follows:

$$\text{natural sunlight correction factor} = \frac{\sum_{290 \text{ nm}}^{400 \text{ nm}} I(\text{natural})}{\sum_{290 \text{ nm}}^{400 \text{ nm}} I(\text{simulated})} \quad (3)$$

by summing the natural sunlight intensities from 290 to 400 nm that were measured at noon on a cloud-free day (March 27, 2005) at College Station, TX and dividing by simulated sunlight intensities summed over the same wavelength.

The experiment was conducted as a randomized block design with three replications. Imazethapyr first-order rate constant data were subjected to analysis of variance and Fisher's protected LSD test at $p \leq 0.05$.

Imazethapyr Reaction Quantum Yield (ϕ). The reaction quantum yield of imazethapyr (ϕ) was estimated using chemical actinometry (19), where ϕ is estimated by a comparison with an actinometer having a known reaction quantum yield. The chemical actinometer system used was the PNA/PYR system developed by Dulin and Mill (20).

The molar absorptivity of imazethapyr (7.85×10^{-5} M in buffer at pH 7.0) and PNA (1×10^{-5} M in high-purity water) was measured by spectrophotometry, as described earlier. The blank for imazethapyr was phosphate buffer at pH 7, while the blank for PNA was high-purity water. Absorbance was measured between 300 and 400 nm, and absorptivity was calculated for each wavelength using the Beer-Lambert law

$$\epsilon = \frac{A}{bc} \quad (4)$$

where ϵ is molar absorptivity in $M^{-1} \text{ cm}^{-1}$, A is absorbance at wavelength λ , b is the cell path length (in centimeters), and c is the molar concentration of imazethapyr or PNA. The maximum calculated molar absorptivity of PNA ($\epsilon_{314 \text{ nm}} = 10\,835 \text{ M}^{-1} \text{ cm}^{-1}$) was within 2% of reported values ($\epsilon_{314 \text{ nm}} = 10\,965 \text{ M}^{-1} \text{ cm}^{-1}$) (20). For imazethapyr, the maximum molar absorptivity occurred at 224 nm and was calculated as $\epsilon_{224 \text{ nm}} = 5898 \text{ M}^{-1} \text{ cm}^{-1}$. Molar absorptivities for both imazethapyr and PNA were used to calculate the reaction quantum yield as described below.

Using discrete samples for each compound, imazethapyr (7.85×10^{-5} M in buffer at pH 7.0) and PNA (1×10^{-5} M) were simultaneously exposed to the UV light source. In pilot studies, PNA was treated with various concentrations of pyridine (0.2, 0.1, 0.05, 0.005, 0.0025, and 0.0005 M) to regulate the PNA degradation rate so that it would closely match that of imazethapyr. The experiment was performed as described for the imazethapyr photolysis study, with regards to the light source, exposure time, temperature, and experimental design.

The reaction quantum yield was calculated using the equation

$$\phi_I = \phi_{\text{PNA}} \left[\frac{k_I \sum I_\lambda \epsilon_{\lambda \text{ PNA}}}{k_{\text{PNA}} \sum I_\lambda \epsilon_{\lambda I}} \right] \quad (5)$$

where ϕ_{PNA} is the reaction quantum yield for PNA, k_I and k_{PNA} are the first-order rate constants for imazethapyr and PNA, respectively, I_λ is the irradiance at wavelength λ (watts m^{-2}), and $\epsilon_{\lambda I}$ and $\epsilon_{\lambda \text{ PNA}}$ are the molar absorptivity ($\text{M}^{-1} \text{ cm}^{-1}$) at each wavelength λ for imazethapyr and PNA, respectively. The reaction quantum yield of the PNA actinometer was calculated using the PYR molar concentration and the equations described by Dulin and Mill (20)

$$\phi_{\text{PNA}} = 0.00028 + 0.44[\text{PYR}] \quad (6)$$

The PYR concentration that regulated the PNA degradation rate to best match the degradation rate of imazethapyr was 0.0005 M. Therefore, the calculated reaction quantum yield for PNA was $\phi_{\text{PNA}} = 0.0005$.

Imazethapyr Hydroxyl Radical Rate Constant ($k_{\text{OH}^\bullet}^I$). The hydroxyl radical rate constant for imazethapyr was determined by the method of Armbrust (16). For this experiment, the herbicide 2,4-D was included as a benchmark to compare with other literature results. Equimolar concentrations of herbicide (either imazethapyr or 2,4-D) and acetophenone at 0.02 mM were dissolved in high-purity water and transferred into clear borosilicate glass vials with no other cosolvents. Hydrogen peroxide was dissolved in each vial to generate hydroxyl radicals through the photolytic cleavage of hydrogen peroxide. Prior to light irradiation, an aqueous hydrogen peroxide solution was added to generate final concentrations of 0.5, 1, 3, 5, 10, and 20 mM. Additional controls included (1) herbicide plus acetophenone (no peroxide) in amber vials, (2) herbicide plus acetophenone plus 20 mM peroxide in amber vials, and (3) herbicide plus acetophenone in clear vials. The vials were capped and placed 12 cm beneath the light source

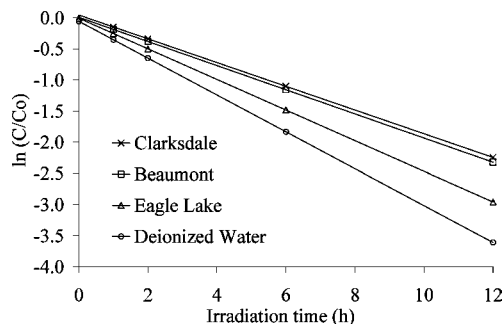


Figure 3. First-order rate plots for degradation of $15 \mu\text{g mL}^{-1}$ imazethapyr in deionized water and water collected from rice paddies at Eagle Lake, TX, Beaumont, TX, and Clarksdale, MS. Fitted equations for imazethapyr in each water source were (Clarksdale) $y = 0.043 - 0.191x$ ($R^2 = 0.96$), (Beaumont) $y = 0.007 - 0.194x$ ($R^2 = 0.98$), (Eagle Lake) $y = -0.007 - 0.247x$ ($R^2 = 0.95$), and (deionized water) $y = -0.058 - 0.296x$ ($R^2 = 0.98$).

and irradiated for 10 min. After irradiation, the excess hydroxyl radicals were quenched with $15 \mu\text{L}$ of $500 \mu\text{g mL}^{-1}$ catalase solution (phosphate buffer at pH 7.0) as reported by Armbrust (16). A $150\text{-}\mu\text{L}$ volume of acetonitrile and formic acid was added to the vials prior to analysis to make the samples more compatible with the mobile phase.

Acetophenone, 2,4-D, and imazethapyr were quantified by HPLC with an isocratic mobile phase consisting of 60% deionized water, 39% acetonitrile, and 1% formic acid using a 0.3 mL min^{-1} flow rate. Detection wavelengths were 245 nm for both imazethapyr and acetophenone and 281 nm for 2,4-D. The experiment was conducted as a randomized block design with four replications.

The hydroxyl radical rate constant was determined for each herbicide using competitive kinetics (21) and was calculated using the equation

$$k_{\text{OH}^\bullet}^M = \frac{\ln([M]_0/\ln[M]_\infty)}{\ln([C]_0/\ln[C]_\infty)} k_{\text{OH}^\bullet}^C \quad (7)$$

where $k_{\text{OH}^\bullet}^M$ and $k_{\text{OH}^\bullet}^C$ are the rate constants for the herbicide and the reference compound (acetophenone), respectively.

RESULTS AND DISCUSSION

Photolysis Rate Constant Determination in Rice Paddy Waters. Imazethapyr degradation in dark controls was $<1\%$, and therefore, corrections for dark reactions were not performed. Linear regression analysis of the natural log of the concentration remaining/initial concentrations (C/C_0) against time (in hours) for each water source is shown in **Figure 3**. The first-order rate kinetics and half-lives are shown in **Table 1**.

Although half-lives were relatively short for imazethapyr, in comparison to other herbicides, in all water sources, analysis of variance showed differences in imazethapyr half-life between water sources. Significant faster photodegradation of imazethapyr was observed in deionized water and Eagle Lake paddy water. Slower photolysis was observed in the paddy waters of Beaumont and Clarksdale. Half-life values found in this experiment are similar to the value found by Curran et al. (22) for imazethapyr photolysis in distilled water (4 h). These results demonstrated that imazethapyr has a relatively short aqueous photolysis half-life in rice paddy water.

In rice paddies, several factors may affect photolysis. Adsorption to colloids may affect photolysis of imazethapyr applied pre-emergence. Chemicals adsorbed within colloidal spaces or sequestered in organic matter may be protected from light. Imazethapyr photolysis was faster in moist soil and sandy soil compared to silty clay loam soils (3). Greater adsorption and

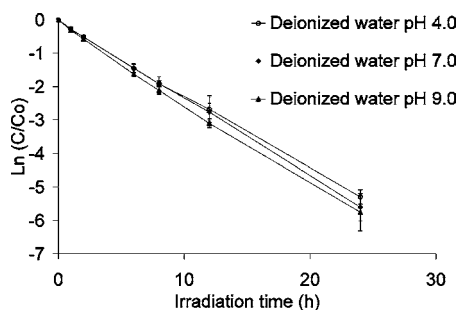


Figure 4. Effect of pH on the aqueous photolysis of imazethapyr (error bars represents 95% confidence intervals).

reduced herbicide availability may reduce photolysis rates (3). Another factor that may affect the photolysis rate is the depth of water (23). As the water column becomes deeper, the UV intensity becomes lower (24). For example, the reported photolytic half-lives for the compound ammonium dinitramide (ADN) for a summertime irradiation ranged from 6 min at the surface to 15 years at a depth of 2 m (23). Another factor that may be important in controlling imazethapyr photolysis is the movement of the herbicide deeper in the soil profile. Light penetration is minimal in soil depths greater than >1 mm in the profile (25). Flushing the rice field to incorporate imazethapyr may reduce its dissipation by photolysis. Therefore, longer photolytic half-lives in the field are not unreasonable for imazethapyr.

Faster degradation of imazethapyr observed in deionized water and Eagle Lake paddy water may have been due to the low turbidity that allowed more light penetration (Table 1). Conversely, the Beaumont and Clarksdale paddy waters were more turbid. It is apparent that Beaumont and Clarksdale paddy waters absorb more light compared to deionized water and Eagle Lake paddy water. The largest absorbance was observed around the same wavelengths where imazethapyr effectively absorbs (data not shown). Therefore, light attenuation may have caused photolysis differences between water samples. It is known that humic acids in water delay photodegradation of imazethapyr by light attenuation (26). Dissolved inorganic substances may hinder degradation as a result of light attenuation or accelerate degradation because of mediation of indirect photoprocesses (27).

The Pearson's correlation (0.955) between half-life and water pH was significant at $\alpha = 0.05$. This relatively high correlation suggested that pH significantly affected the degradation of imazethapyr in these natural waters. However, an experiment testing three deionized water pH (4, 7, and 9) showed that imazethapyr photolysis was not dependent upon water pH (Figure 4). The high correlation found in the first experiment likely occurred because there was a positive correlation between turbidity and pH within the rice paddy water sources (data not shown).

However, in a field situation, pH may affect imazethapyr photolysis. Because pH has been documented as affecting soil adsorption (29–31), with low pH values promoting imazethapyr adsorption (30–33) and reducing the herbicide availability and consequently photolysis rate (28), we suspect that, in rice fields, this pH effect on adsorption should be noticed only during the first few weeks of flooding. After this period, regardless of the original pH before flooding, the soil pH should approach neutrality (34). The change in pH upon flooding may take up to several weeks, depending upon the soil characteristics, organic matter levels, microbial population, temperature, and other soil chemical properties (34).

Table 2. Measured and Previously Reported Hydroxyl Radical Rate Constants for Imazethapyr and 2,4-D

| chemical | rate constant k_{OH}^M ($M^{-1} h^{-1}$) | |
|-------------|----------------------------------------------|--------------------------------------------------------|
| | measured ^a | reported |
| imazethapyr | $2.8 \times 10^{13} \pm 0.44 \times 10^{13}$ | 1.8×10^{13} (21) |
| 2,4-D | $3.5 \times 10^{13} \pm 0.91 \times 10^{13}$ | 5.8×10^{12} (17) 8.4×10^{12} (16) |

^a The competitor (acetophenone) hydroxyl radical rate constant used to calculate the measured rate constant was $2.1 \times 10^{13} M^{-1} h^{-1}$ (21).

Reaction Quantum Yield (ϕ) Determinations. The measured molar absorptivities and UV-irradiance values were used to calculate the reaction quantum yield for imazethapyr, resulting in a value of $\phi_I = 0.023 \pm 0.002$ ($n = 4$). This value is similar in magnitude to those reported for other pesticides (14, 35), which are often ≤ 0.1 . This value indicates that approximately 2% of the absorbed light energy actually goes toward disrupting chemical bonds in imazethapyr.

Hydroxyl Radical Rate Constant (k_{OH}^I) Determinations. During the 10-min study duration, losses because of direct photolysis and chemical hydrolysis were <1, <1, and 1% for acetophenone, imazethapyr, and 2,4-D, respectively. The losses because of the reaction with hydrogen peroxide in the absence of light were <1, 3, and 2% for acetophenone, imazethapyr, and 2,4-D, respectively. Therefore, corrections for these losses were not necessary. The measured hydroxyl radical rate constant for 2,4-D herbicide was $3.5 \times 10^{13} M^{-1} h^{-1}$ and was within 80% of literature values (Table 2). The hydroxyl radical rate constant for imazethapyr was calculated to be $2.8 \times 10^{13} M^{-1} h^{-1}$. The magnitude of this value is similar to those reported for other pesticides (16) and indicates that imazethapyr reacts with hydroxyl radicals at nearly diffusion-controlled rates.

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Received for review September 8, 2005. Revised manuscript received January 12, 2006. Accepted January 13, 2006. The authors would like to thank the Universidade Federal de Santa Maria for the student's salary and CAPES/Brazil for the student's fellowship.

JF052214B