

Use of Stable Tracer Studies To Evaluate Pesticide Photolysis at Elevated Temperatures

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New methods were developed to determine photolysis rates of medium-weight pesticides in the gas phase using elevated air temperatures and solid-phase microextraction (SPME). A 57-L glass chamber was constructed that utilized collimated xenon arc irradiation that could heat chamber air to increase the amount of pesticide in the gas phase. Gas-phase photolysis rates were determined at various air temperatures by comparing the rate of loss of each of the tested pesticides to a photochemically stable tracer, hexachlorobenzene. Interval sampling of gas-phase constituents was performed using SPME immediately followed by GC-ECD or GC-MSD analysis. The two pesticides under examination were the dinitroaniline herbicide trifluralin and the organophosphorus insecticide chlorpyrifos. The gas-phase photolysis for trifluralin was found to be rapid with half-lives of 22–24 min corrected for sunlight. These results were comparable to photochemical lifetime estimates from other investigators under sunlight conditions. Elevating temperatures from 60 to 80 °C did not affect photolysis rates, and these rates could be extrapolated to environmental temperatures. From 60 to 80 °C, gas-phase chlorpyrifos photolysis lifetimes were observed to range from 1.4 to 2.2 h corrected for sunlight and will thus be important together with hydroxyl radical reactions for removing this substance from the atmosphere. At these elevated temperatures, pesticides and tracer compounds were found to be substantially in the gas phase, and possible effects on reaction rates from wall interactions were minimized.

Keywords: *Photolysis; pesticide; SPME; atmosphere*

INTRODUCTION

A substantial fraction of aerially applied and ground-applied pesticides can be transferred to the atmosphere and undergo a variety of transformations and transport processes (Pimentel et al., 1986; Glotfelty, 1978; Woodrow et al., 1983). The extensive use of pesticides, especially in agricultural settings, remains a substantial public concern due to hazards associated with exposure to humans and off-site deposition that can affect nontarget ecological communities (National Research Council, 1994; Glotfelty, 1990; Seiber et al., 1995; Drost and Fellers, 1996).

Although the fundamental principles governing the photochemical fate of pesticides are well understood, the ability to quantitatively estimate atmospheric photochemical reaction rates under controlled experimental conditions is elusive. Sorption onto reaction vessel walls complicates interpretation of gas-phase photochemical kinetics. At ambient temperatures, pesticides with low volatilities will tend to interact (primarily sorb) with the vessel walls rather than reside in the gas phase (Miller and Zepp, 1983). Thus, except for compounds with relatively high vapor pressures (>1 Pa), experiments conducted in sealed containers at ambient temperatures generally provide ambiguous information on the kinetics and product distributions of most pesticides. This inability of laboratory assessments to discriminate between gas-phase reactions and artifact wall interactions has also been identified by the U.S. EPA as the major

reason for rejecting industry pesticide registration studies (Edelstein and Spatz, 1994; Hebert and Miller, 1994).

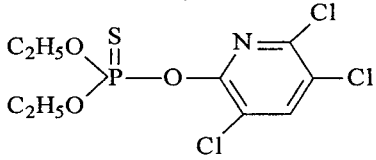
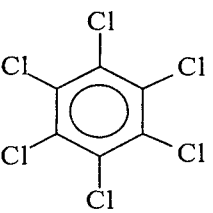
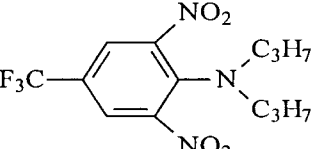
Procedures are presented herein that use elevated temperatures to achieve stable gas-phase concentrations within sealed reaction vessels for estimating photolysis rates. Because temperature can potentially influence observed reaction rates, rate measurements are performed at multiple temperatures. To further minimize sorption effects, the proportional gas-phase disappearance of a reactive chemical relative to that of a photochemically stable tracer of similar volatility and molecular weight is incorporated into the study. This tracer technique, originally designed to measure field pesticide photolysis rates (Woodrow, 1983), has been previously used to estimate photolysis rates of volatile and semivolatile photoreactive pesticides under controlled conditions (Monger and Miller, 1987; Geddes and Miller, 1995; Hebert et al., 1998). Gas-phase sampling techniques using solid-phase microextraction (SPME) were developed to minimize analytical sensitivity issues caused by high-volume sampling (and subsequent dilution) of gas-phase constituents by polystyrene or diphenyl-*p*-phenylene oxide trapping resins.

MATERIALS AND METHODS

Chemicals. Technical chlorpyrifos was obtained from Dow AgroSciences Corp., Indianapolis, IN. Technical trifluralin and hexachlorobenzene were respectively purchased from Chem-Serve, West Chester, PA, and Aldrich Chemical Co., Milwaukee, WI. The physical properties and purities for the above technical materials are presented in Table 1. The ranges in gas-phase absorbance reported in Table 1 were determined using a remote flow cell linked by fiber optics to a rapid-

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Table 1. Physiochemical and Gas-Phase Absorbance Properties of Test and Tracer Compounds^a

Structure	Vapor Pressure	Gas Phase Absorbance
<p>Chlorpyrifos</p>  <p><i>o,o</i>-diethyl <i>o</i>-3,5,6-trichloro-2-pyridyl phosphorothioate</p>	25°C : 3.3 mPa 60°C : 0.67 Pa 70°C : 2.7 Pa 80°C : 9.3 Pa	λ max = 280 nm absorbs >290 nm to 320 nm
<p>Hexachlorobenzene</p> 	25°C : 2.1 mPa 60°C : 1.1 Pa 70°C : 3.1 Pa 80°C : 7.7 Pa	absorbs < 290 nm
<p>Trifluralin</p>  <p>α,α,α-trifluoro-2,6-dinitro-<i>N,N</i>-dipropyl-<i>p</i>-toluidine</p>	25°C : 13.7 mPa	λ max = absorbs strongly in measured range from > 290 nm to 360 nm

^a Estimated elevated vapor pressure values for hexachlorobenzene and chlorpyrifos were calculated using the Clausius–Clapeyron equation from published vapor pressure data at various temperatures by gas saturation and effusion techniques (Kim, 1985).

scanning UV–vis chromatographic detector. This instrument was designed to acquire gas-phase UV spectra for moderate- to low-volatility substances from 200 to 360 nm with a 2.5-nm effective band-pass (Hackett, 1995; Bornhop et al., 1992).

Hexachlorobenzene was selected as a tracer compound for determining gas-phase photolysis rates for the test substances, trifluralin and chlorpyrifos. The gas-phase spectrum of hexachlorobenzene indicated that it does not absorb wavelengths above 280 nm and therefore should not undergo photolysis under experimental conditions (Table 1). Recent gas-phase chemical oxidative studies by Brubaker and Hites (1997) also indicate that this substance will be comparatively nonreactive toward the OH radical under tropospheric conditions. Furthermore, the vapor pressure of hexachlorobenzene is intermediate to the vapor pressures of the photolabile test substances under examination, making this substance a suitable stable tracer candidate.

57-L Photoreaction Chamber. The 57-L-volume borosilicate glass chamber (Figure 1) was designed to minimize incidental light hitting the side walls by applying collimated lighting through the center volume of the vessel and elevate temperature in a controlled manner for assessing photoreaction kinetics for semivolatile to low-volatility substances. Light from the xenon arc lamp was passed through a quartz plate placed onto a Teflon-lined O-ring for an airtight seal on top of the photoreaction chamber. Two sampling ports were located on opposite sides of the chamber. Four additional ports are located on the top chamber lid for air temperature and pressure monitoring. This vessel was water-jacketed by encircling it with 76 m of 0.64-cm Tygon tubing. The chamber was heated using a constant-temperature circulator capable of heating the gaseous volume to 80 °C. To minimize chemical oxidation by ozone, NO (a precursor of OH radical formation), or other airborne oxidants, all chamber studies were performed using purified ultragrade air. After the purified air had been heated to the desired temperature, molar equivalent concentrations of gaseous test compounds were vaporized into the chamber. This was achieved by first creating a partial vacuum by pumping out 20% of the purified air from within the

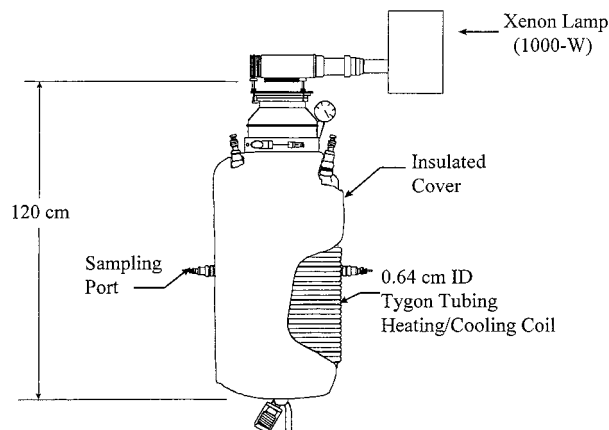


Figure 1. 57-L volume borosilicate glass reaction chamber and collimated xenon arc light source.

chamber. A concentrated solution of test and reference compounds (in benzene) was injected into a heated 250-mL-volume glass volatilization flask attached onto one of the side sampling ports of the chamber. Opening the stopcock allows the flash-volatilized mixture to be passed into the chamber. The gaseous mixture was allowed to reach equilibrium at atmospheric pressure before the experiment was begun.

Solar Simulator. A Kratos SS 1000X solar simulator with collimated xenon arc lighting was used to illuminate the internal air volume of the 57-L reaction chamber (Figure 1). The 7.6-cm output beam has a half-angle divergence of 5°. At a distance of 1 m (the depth of the reaction chamber), the surface irradiance diameter was ~17 cm. This unit was designed by the manufacturer to provide an intensity of 1 sun over a 20-cm-diameter circular target. To verify the collimated light intensity, a fixed-wavelength Spectroline DM-300N UVB ultraviolet meter was used to estimate spatial distribution of 290–310-nm intensity from the top of the chamber to its base, a distance of 1 m. To minimize back-reflection of light at the

anterior end of the chamber, the light was trapped by a darkened surface. The above measurements were then compared to midsummer mid-day noon UVB readings taken at 40° N latitude. The chamber UVB intensity of the collimated beam was found to be equivalent to 0.9 sun, and the irradiated volume was 20% of the total volume of the chamber.

Gas-Phase Sampling. In previous attempts to examine gas-phase reactions of lower volatility organics in chamber experiments, we used Tenax (diphenyl-*p*-phenylene oxide) or XAD polystyrene resins to trap gas-phase analytes. To achieve analytical sensitivity, large sampling volumes were required, which greatly dilute the gaseous concentration especially within laboratory vessels with volumes of ≤ 100 L. To minimize dilution effects, we developed gas-phase-sampling methods using SPME fibers from Supelco Inc., Bellefonte, PA. SPME allows for rapid and sensitive determination of substances exclusively in the gas phase without the need for extracting air from the laboratory chamber, which also minimizes disturbance of chamber equilibrium conditions. A microfiber coated with a bonded 7- μm polysiloxane phase was inserted into the chamber side-port through a septum. After insertion into the chamber, partitioning of gas-phase constituents is quickly established on the fiber coating. After exposure of the fiber for 20 s, the fiber was immediately thermally desorbed into a hot GC injection port (250–275 °C), and the gas-phase constituents were quantified by mass selective detection or by GC-ECD. After chamber gas-phase equilibrium had been established, variability between replicate injections was found to be $<5\%$ when the tracer response was compared to the relative responses of gas-phase test substances. The life span of an SPME fiber under the above experimental conditions was ~ 200 – 220 injections before it was necessary to discard and replace it. The SPME techniques described allow for high sensitivity and rapid and frequent sampling, which are essential in the evaluation of reaction rates for photolabile compounds under laboratory chamber conditions.

Gas Chromatography, GC-ECD System. A Hewlett-Packard 5890 gas chromatograph (GC) with ^{63}Ni electron capture detection was used to determine photochemical reaction rates of trifluralin and chlorpyrifos with hexachlorobenzene as an internal gas-phase standard. The GC column was a 30-m \times 0.32 mm i.d. \times 1 μm film SPB-5 (5% phenyl, 95% methyl silicone, Supelco Inc.) column. GC operating conditions were as follows: The carrier gas was 5% methane in argon at 8 mL/min, and makeup gas flow was set from 40 to 50 mL/min. The injector temperature was set at 275 °C with an initial oven temperature at 90 °C. The initial temperature was held for 4 min before a temperature ramp at 20 °C/min was initiated to 240 °C with a final hold time of 5 min. The electron capture detector temperature was set at 325 °C. Under these conditions, trifluralin, hexachlorobenzene, and chlorpyrifos eluted as single peaks with respective retention times of ca. 11.5, 12, and 14 min, respectively. The nominal detectabilities from all SPME assessments of the 57-L chamber were ~ 50 parts per trillion per volume (ppt_v) for chlorpyrifos and trifluralin and ~ 10 ppt_v for hexachlorobenzene.

Gas Chromatography, GC-MS System. A Hewlett-Packard 5790A gas chromatograph–mass selective detector and Hewlett-Packard 9133 data acquisition system (Pascal operating system) equipped with a Hewlett-Packard 5790 gas chromatograph were employed to assess chlorpyrifos, trifluralin, and hexachlorobenzene. The GC column was a 30 m \times 0.32 mm i.d. \times 0.25 μm film DB-5 (5% phenyl, 95% methyl silicone, J&W Corp., Folsom, CA) column. Helium was used as the carrier at a rate of 0.8 mL/min. The injector temperature was set to 250 °C with an initial oven temperature at 90 °C. The initial temperature was held for 4 min before a temperature ramp at 25 °C/min to 280 °C with a final hold time of 2 min. The mass spectrometer was used in the EI mode, and the ionization energy was 70 eV. For analyte confirmation and sorption evaluations, data acquisition was performed in full-scan mode from 50 to 350 mass units. Under these conditions, trifluralin, hexachlorobenzene, and chlorpyrifos eluted as single peaks with respective retention times of ca. 11, 12, and 14 min. The nominal detectabilities from all SPME assess-

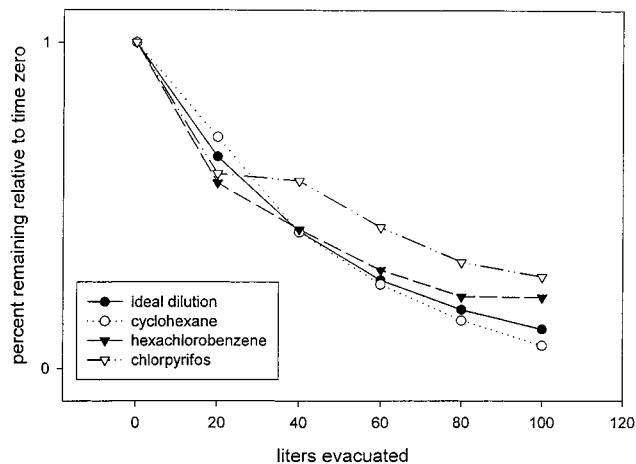


Figure 2. Results from repetitive 20-L dilutions of gas-phase constituents from the 57-L chamber conducted at 60 °C.

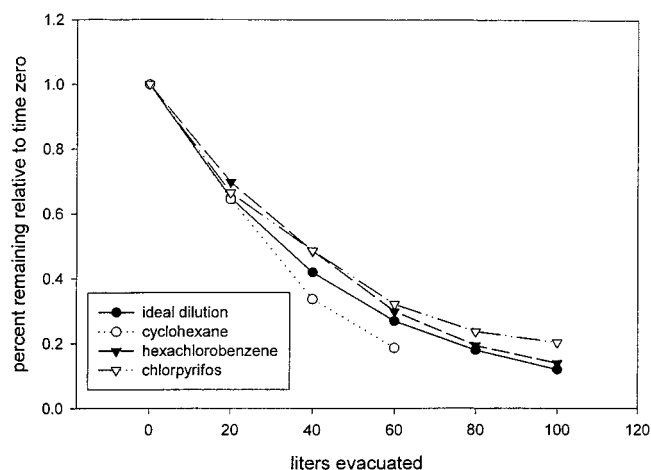


Figure 3. Results from repetitive 20-L dilutions of gas-phase constituents from the 57-L chamber conducted at 80 °C.

ments of the 57-L chamber were ~ 10 ppb_v for chlorpyrifos, ~ 5 ppb_v for trifluralin, and ~ 2 ppb_v for hexachlorobenzene.

Wall Sorption Assessments. To evaluate the significance of wall interactions on gas-phase kinetics, separate assessments to characterize wall sorption were performed at 60 and 80 °C. To estimate the degree of wall sorption, a molar equivalent mixed solution standard of substances ranging in vapor pressure from 1 Pa (cyclohexane, 25 °C) to 2.5 mPa (chlorpyrifos, 25 °C) was flash-volatilized into the 57-L chamber and allowed to equilibrate. Dosing concentrations were well below gas saturation concentrations (3 orders of magnitude) at the elevated temperatures used in this study. After equilibration had been attained, constituents were sampled using SPME and were quantitated by GC-MSD. Twenty liters of the chamber air volume was then removed and allowed to re-equilibrate before SPME sampling. The above procedural sequence was repeated five times, which removed $\sim 92\%$ of the initial gas-phase concentration before termination of the wall sorption experiment. Figures 2 and 3 illustrate the proportional dilution experiment comparing the behavior of an ideal gas (no surface interactions) to the highest and lowest vapor pressure compounds under examination at 60 and 80 °C.

Photolysis Assessments. A series of elevated-temperature photolysis evaluations were performed at 60, 70, and 80 °C. For each air temperature, the test substance solution (in benzene) was flash-volatilized under darkened conditions into the 57-L photoreaction chamber as described above. The time for equilibration was determined by repetitive SPME sampling. Once equilibrium was established (within 30 min), the solar simulator was turned on, illuminating an estimated 20% of the internal volume of the chamber. The gas-phase constituents were sampled by SPME at time zero and at timed

intervals that depended on the reactivity of the test substance. For photoreactive substances, sampling was conducted at 15–20-min intervals with longer intervals for less reactive substances. The maximum irradiation interval was 24 h. The experiment was terminated either after ~24 h or when the test substance/tracer ratio underwent more than four half-lives. Photolysis rate estimations were performed by comparing integrated peak height ratios of the remaining test substance to that of the photochemically stable tracer at each irradiation interval (t) using the first-order expression (Woodrow, 1983)

$$R_t = R_0 e^{-kt} \quad (1)$$

where R = test substance (mol)/tracer (mol).

This method assumes that the test substance and tracer will have similar gas-phase mobilities. Differences in ratios between the parent and tracer over the experimental time frame should reflect loss by photochemical reaction.

The observed total reaction rate constant, k_{total} , was calculated by plotting the natural log of the ratio of test substance to tracer (percent remaining) at each sampling interval against time. The reported observed first-order rates of photolysis (k_{phot} , in h^{-1}) were calculated by subtracting $k_{\text{total}} - k_{\text{dark}}$ to derive k_{phot} , where k_{dark} is the observed rate constant from dark chamber evaluations.

Because the integrated light intensity of the chamber was estimated to 0.9 sun and only 20% of the chamber volume was being irradiated by the collimated lighting, the chamber was corrected for the 82% reduction in total chamber illumination to maximum noontime summer sunlight. An estimate of sunlight half-life was performed as follows:

$$t_{1/2} = (t_{1/2})_{\text{phot}} (\text{sun equivalents}) \times (\% \text{ irradiated chamber volume}) \quad (2)$$

This approach, based on the assumption that the observed rate constant is directly proportional to irradiance, has been used by other investigators to establish half-lives in confined laboratory reaction chamber studies when using collimated light (Woodrow, 1983).

RESULTS

Wall Sorption Assessments. Figures 2 and 3 illustrate the results from repetitive 20-L dilutions of gas-phase chlorpyrifos and hexachlorobenzene from the 57-L chamber conducted at 60 and 80 °C. The gas-phase dilution behavior for an ideal nonsorbing gas is also depicted in these two figures. This iterative dilution approach allows for a reasonable estimate of the extent that wall interaction influences gaseous substances at elevated temperatures. In addition to the examination of chlorpyrifos and hexachlorobenzene, cyclohexane was also introduced at both elevated air temperatures into the chamber. This volatile low-polarity organic was found to principally exist in the gas phase, as expected, and behaved in a nearly ideal manner after being repetitively diluted from the chamber at both temperatures. At 80 °C, gaseous chlorpyrifos and hexachlorobenzene were diluted from the chamber at nearly similar rates. When residual concentrations on the chamber walls were taken into account, approximately 92 and 98% of the respective concentrations for chlorpyrifos and hexachlorobenzene existed in the gas phase. Chlorpyrifos is less volatile and more polar than hexachlorobenzene and was found to sorb out of the gas phase at a slightly greater rate. A slightly greater rate of sorption for these analytes was observed at 60 °C. At this air temperature, approximately 82 and 90% of the respective concentrations for chlorpyrifos and hexachlorobenzene existed in the gas phase. Although these chamber studies are slightly complicated by sorption, the above assessment indicates that semivolatile-

Table 2. Photolysis Rate and Half-Lives from Elevated-Temperature Evaluations within the 57-L Photoreaction Vessel^a

	elevated chamber air temperature		
	60 °C	70 °C	80 °C
trifluralin			
chamber rate	0.33 min^{-1}	0.35 min^{-1}	0.32 min^{-1}
chamber half-life	2.1 h	2.0 h	2.2 h
est environ half-life	23 min	22 min	24 min
chlorpyrifos			
chamber rate	1.3 $\text{e}^{-3} \text{ min}^{-1}$	1.4 $\text{e}^{-3} \text{ min}^{-1}$	9.2 $\text{e}^{-4} \text{ min}^{-1}$
chamber half-life	8.7 h	7.9 h	12.4 h
est environ half-life	1.6 h	1.4 h	2.2 h

^a Environmental half-lives were estimated according to eq 2.

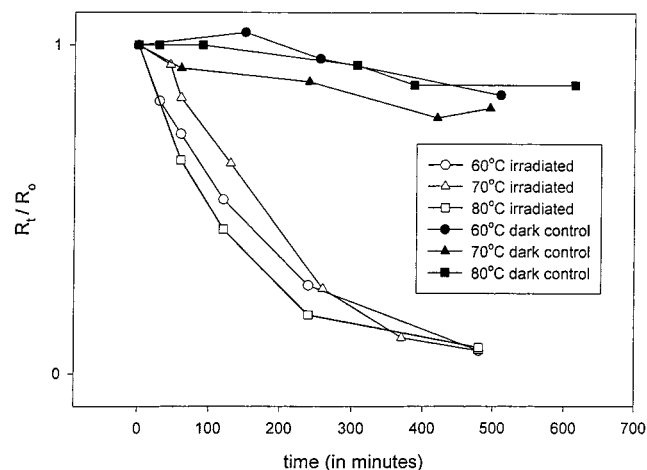


Figure 4. Photochemical and dark control results comparing remaining trifluralin (test) to hexachlorobenzene (tracer) concentrations at 60, 70, and 80 °C using the ratioing approach according to eq 1.

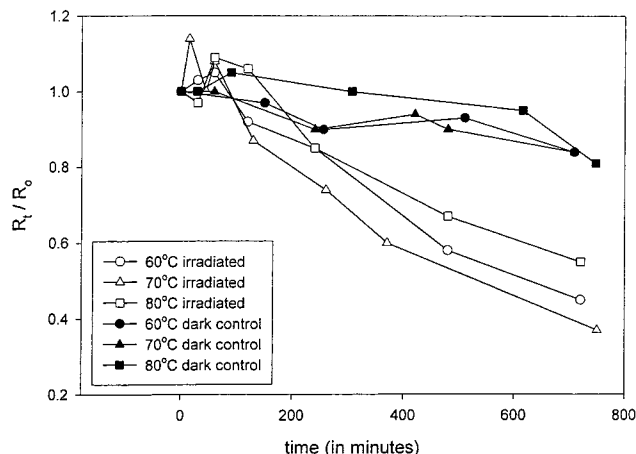
semipolar compounds will predominantly exist in the gas phase at the air temperatures used in this study. Sorption effects are further reduced when ratioing techniques are employed because the rates of sorption for test and tracer compounds were found to be similar.

Trifluralin Photochemical Assessments. The photochemical and dark control results comparing remaining trifluralin to hexachlorobenzene concentrations at 60, 70, and 80 °C using the ratioing approach are presented in Table 2 and Figure 4. For all temperatures, the proportional disappearance of trifluralin to hexachlorobenzene in irradiated experiments was rapid and closely followed first-order loss without any clear trend in temperature dependence. This difference in photochemical loss was plotted as $\ln(R_0/R_t)$ versus time to yield first-order rate constants for photolysis (k_p) and half-life ($t_{1/2}$). The mean chamber irradiated half-life was 2.1 h. The temperature dependence over this limited range was negligible. This observation was not surprising because trifluralin undergoes rapid photolysis and, on the basis of fundamental photochemical principals, temperature should not significantly affect primary photochemical processes. Furthermore, trifluralin has been well-studied under outdoor sunlight conditions (Woodrow et al., 1983; Monger 1987). Data from these field studies conducted at near 40° N latitude also compare favorably with our laboratory results when corrected for the 82% decrease in total chamber illumination to maximum noontime summer sunlight (Table 3).

Chlorpyrifos Photochemical Assessments. Table 2 and Figure 5 present the photochemical results comparing remaining dilute gas-phase chlorpyrifos to

Table 3. Comparison of Experimental Results to Environmental Investigations Conducted under Sunlight

investigator	study conditions	reaction half-life (min)
Woodrow et al. (1979)	field (aerially applied tracer + trifluralin)	21–63
Monger (1988)	outdoor (tracer + trifluralin)	19–74
present work	57-L reaction chamber tracer study	22–24

**Figure 5.** Photochemical and dark control results comparing remaining chlorpyrifos (test) to hexachlorobenzene (tracer) concentrations at 60, 70, and 80 °C using the ratioing approach according to eq 1.

hexachlorobenzene concentrations at 60, 70, and 80 °C. For all temperatures, the proportional disappearance of chlorpyrifos to hexachlorobenzene in irradiated experiments was also observed to proceed rapidly. When the total loss was plotted as $\ln(R_0/R_t)$ versus time, first-order estimated half-lives ranged from 9 to 12 h without any clear trend in rates being affected at higher air temperatures. After correction for dark control losses and chamber illumination, the total rate of reaction of this substance was estimated to range from 1.4 to 2.2 h. The use of high-purity air, free of NO and O₃, was found to minimize artifactual OH radical or other chemical oxidation reactions occurring in the gas phase. To further determine whether OH reactivity was responsible for any observed loss, in one series of experiments conducted at 80 °C, an OH radical scavenger, cyclohexane, was introduced into the chamber at 1000× test substance concentrations. The observed reaction rates for the two separate experimental series were within our estimated experimental error of ±20%. Similar OH radical scavenger studies were also conducted in trifluralin elevated-temperature assessments with no discernible differences in rates being observed. Thermal oxidation was, however, suspected to be responsible for the observed steady loss of chlorpyrifos in the dark controls.

DISCUSSION

These experiments demonstrate that estimates of photolysis rates can be acquired in the gas phase under elevated-temperature conditions. The elevated-temperature evaluations were a compromise, which was necessary to establish stable gas-phase concentrations under laboratory conditions. Because primary photochemical processes are generally unaffected by temperatures, we felt that this method of determining reaction rates was an acceptable alternative approach to the use of testing procedures which are restricted to the more volatile

pesticides due to sorption concerns. The use of elevated temperatures to establish stable gas-phase concentrations has been previously employed in other reaction rate investigations. Atkinson (1988) used elevated temperatures to assess the temperature dependence of hydroxyl radical oxidation rates for semivolatile hydrocarbons. More recently, elevated-temperature studies have been conducted in small-volume reaction cells to determine environmental oxidation rates for semivolatile polychlorinated biphenyls and chlorinated aromatics (Anderson and Hites, 1995; Brubaker and Hites, 1998).

The sorption results from this study indicate that wall effects were evident but had negligible effect on the reaction rates for examined pesticides with vapor pressures ranging from approximately 2 to 14 mPa at 25 °C. Besides vapor pressure, the polar nature of a substance in the gas phase can influence sorption. This may account for the slightly greater wall effect observed at elevated temperatures for chlorpyrifos when compared to the less polar tracer substance hexachlorobenzene. Even at dosing concentrations representing <5% of gas saturation, sorption was discernible at the air temperatures examined. Although the chamber studies were slightly complicated by sorption, it was not likely that wall interactions had an influential effect on reaction rates because both test and tracer compounds were observed to have similar gas-phase mobilities at the lower and higher air temperature limits of the study. Semivolatile substances possessing very high polarity were not examined. For these substances, the effect of sorption on gas-phase kinetics may, in these cases, be of greater significance.

The use of the collimated light assembly for irradiating gas-phase concentrations of trifluralin was found to provide rates similar to those determined in sunlight. Calculations that compensated for the chamber's limited spatial light intensity relative to full-illumination summer sunlight intensities resulted in reaction lifetimes which were similar to previous photochemical tracer evaluations performed under total sunlight illumination by Woodrow (1983) and Monger (1987). The calculated half-life for trifluralin via OH radical is 8 times slower than by direct photolysis (assuming an average tropospheric OH radical concentration of 1.5×10^6 molecules cm⁻³). Trifluralin, however, is one of the few current-use pesticides having a photolysis rate that is expected to greatly exceed atmospheric removal by the OH radical.

Chlorpyrifos has a chromophore that can absorb radiant energy above 290 nm and well into the 300–315-nm wavelength range (Table 1). From our laboratory observations, gas-phase direct photolysis should proceed rapidly with lifetimes being <0.5 day. On the basis of our findings, direct photolysis and chemical oxidations will both be important in transforming this substance in the atmosphere. Using global average OH radical concentrations, the calculated tropospheric second-order half-life of chlorpyrifos is ~1.5 h (Meylan and Howard, 1996), which is similar to our observed direct photolysis half-life for this substance (~1.7 h). It should be noted that daily surface concentrations of OH in temperate regions in the United States are expected to be highly variable, differing by as much as 5 times from the global average concentration (Atkinson, 1988). Due to variations in OH atmospheric concentrations and seasonal sunlight intensities, both removal processes will be important to consider when the atmospheric lifetime of chlorpyrifos is assessed.

The distribution of pesticides among aqueous, particle, and vapor phases in the lower troposphere will influence the importance of gas-phase direct photolysis relative to other physical removal mechanisms such as wet and dry deposition. Chlorpyrifos and trifluralin have reported Henry's constants of 1.75 and 4.03 Pa m³/mol, respectively (Suntio et al., 1988). The *H* values for these substances indicate that photochemical, thermal, or oxidative transformation reactions will occur to a large extent in the gas phase under tropospheric conditions (Majewski and Capel, 1995).

CONCLUSIONS

The recent advancements in SPME have made it possible for us to develop laboratory techniques in laboratory reaction chambers to assess gas-phase photochemical rates for substances with vapor pressures as low as 2 mPa. We have found that stable gas-phase concentrations for these semivolatile substances can be established within a 57-L glass reaction chamber at elevated temperatures. To further minimize the effects of sorption, hexachlorobenzene was used as a photochemically stable tracer to follow the photochemical loss of trifluralin and chlorpyrifos. Neither trifluralin nor chlorpyrifos shows strong temperature dependence in reaction rate at the elevated temperatures under investigation. Although photolysis was the dominant gas-phase process for the observed rapid transformation of trifluralin, photolysis may or may not be the dominant process for gaseous chlorpyrifos. For chlorpyrifos, the relative importance of photolysis to chemical oxidation will largely depend on regional OH radical concentrations occurring at the land surface and seasonal sunlight intensities. Clearly, both degradative processes will be important determinants in the overall tropospheric fate for this substance in the gas phase.

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