

Reactivity of Certain Organophosphorus Insecticides toward Hydroxyl Radicals at Elevated Air Temperatures

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Methods were developed to determine OH reaction rates for medium-weight organophosphorus pesticides in the gas phase. A 57-L chamber was constructed that utilized xenon arc irradiation (>290 nm) to photolyze the OH precursor, methyl nitrite. Experiments were performed at elevated temperatures ranging from 60 to 80 °C to minimize wall sorption. Solid-phase microextraction (SPME) sampling of the gas phase was employed to assess the simultaneous rate of loss of the pesticides in relation to the rate of loss of two reference substances with known OH rate constants. An internal gas-phase standard (hexachlorobenzene), relatively stable to hydroxyl radicals, was used to assess other processes, which included dilution and wall sorption. The relative reaction rates of the organophosphorus insecticides, diazinon and chlorpyrifos, when compared to reference compounds, were unaffected by various air temperatures between 60 and 80 °C. Although both insecticides were expected to react at similar rates on the basis of structural activity model predictions, diazinon reacted 3 times more rapidly than chlorpyrifos and gave estimated environmental OH half-lives of 0.5 and 1.4 h, respectively. The degree of sorption onto the chamber walls was minimal and similar for each of the compounds examined. Experimental gas-phase determinations at elevated temperatures may provide important information that can be used when in the assessment of the potential of airborne pesticide risks to nontarget and ecologically sensitive areas.

Keywords: Gas phase; hydroxyl radical; organophosphorus insecticide; SPME

INTRODUCTION

Oxidations mediated by the hydroxyl (OH) radical are a major tropospheric process leading to the degradation of organophosphorus (OPs) insecticides. The importance of OH for removing airborne OPs is supported by studies conducted at ambient temperature in large vessels on volatile phosphoro and phosphorothio homologues, which show oxidation reaction rates to be rapid, with atmospheric lifetimes ranging from minutes to days (Atkinson et al., 1989; Winer and Anderson, 1990). Volatile pesticide analogues containing thiophosphoryl (P=S) bonds have also been shown to be rapidly oxidized to their corresponding oxon analogues under experimental conditions at ambient air temperature (Atkinson, 1989; Goodman, 1988). The reactivity of OH with the more complicated OP insecticides (i.e., chlorpyrifos, diazinon) has not been established, primarily due to the experimental difficulty in working with these compounds in the gas phase. The vapor pressures for the majority of OPs are sufficiently low that they will sorb out from the gas phase to the walls of reaction vessels at ambient air temperatures.

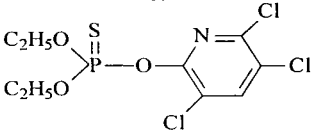
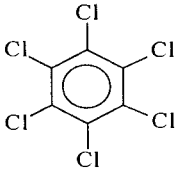
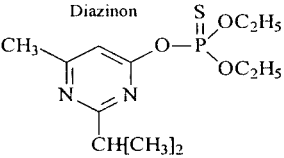
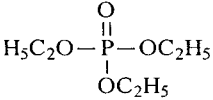
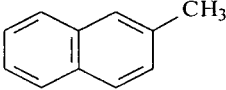
To acquire rate constant information for OPs, our laboratory has taken an approach that measures the gas-phase disappearance of a reactive chemical relative to that of a well-characterized reactive reference substance at elevated air temperatures. Relative rate measurements comparing a reference compound with a well-characterized OH reaction rate constant to a reactive test substance have been previously used at ambient temperatures to determine OH rate constants

for gas-phase reactions (Atkinson, 1986, 1989; Goodman, 1988; Kwok et al., 1992, 1995). Moreover, relative rate measurements at elevated gas temperatures have also been recently employed to acquire oxidation rate constants for semivolatile to low-volatility halogenated aromatics (Anderson and Hites, 1995; Brubaker and Hites, 1998). In these elevated-temperature studies, a mercury UV lamp generated OH radicals via photolysis of ozone or hydrogen peroxide in a small volume reaction cell at elevated gas temperatures.

Because many OPs may rapidly photodecompose at a high-energy wavelength of 254 nm, in the present study, we used filtered xenon arc irradiation (>290 nm) to generate OH radicals by photolyzing gaseous methyl nitrite within a 57-L reaction chamber filled with purified air at atmospheric pressure. To trace the relative rate of loss of our two candidate compounds, diazinon and chlorpyrifos, two reference substances of similar reported OH reaction rates, triethyl phosphate and 2-methylnaphthalene (Meylan and Howard, 1996a), were used. Hexachlorobenzene was used as an internal stable tracer to monitor other loss pathways because it is comparatively stable in the gas phase under the thermal, photochemical, and oxidative conditions of these experiments. Because temperature can potentially influence observed reaction rates of both reference and test substances, separate rate measurements were performed ranging from 60 to 80 °C at 5 °C increments. Due to the need to extract multiple timed-interval samples, gas-phase sampling was performed using solid-phase microextraction (SPME) techniques. SPME avoids disturbing the established gas-phase equilibrium and minimizes loss of sensitivity caused by chamber dilution from repetitive gas-volume sampling. To determine the potential effects of wall sorption on observed OH radical

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Table 1. Physicochemical 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>Diazinon</p>  <p><i>o,o</i>-diethyl <i>o</i>-2-isopropyl-6-methylpyrimidin-4-yl phosphorothioate</p>	25°C : 60°C : 0.729 Pa 70°C : 1.83 Pa 80°C : 4.37 Pa	λ max = 246 nm weakly absorbs > 290 nm to 312 nm
<p>triethyl phosphate</p> 	25°C : 8.80 Pa	absorbs < 290 nm
<p>2-methyl naphthalene</p> 	25°C : 3.71 Pa	λ max = 262 nm weakly absorbs > 290 nm to 315 nm

^a Estimated elevated vapor pressure values for hexachlorobenzene, diazinon, 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). Vapor pressures (at 25 °C) for triethyl phosphate and 2-methylnaphthalene are model estimations from the Meylan and Howard (1996b).

reactivity, evaluations were performed in the dark to estimate wall effects for each of the test, reference and tracer compounds. Separate xenon arc irradiations (in the absence of methyl nitrite) were also conducted over the 2-h experimental time frame to determine the significance of photolysis for all test and reference substances.

MATERIALS AND METHODS

Chemicals. Technical chlorpyrifos was obtained from the Dow AgroSciences Corp., Indianapolis, IN. Technical diazinon and hexachlorobenzene were purchased from ChemServe, West Chester, PA, and Aldrich Chemical Co., Milwaukee, WI, respectively. The molecular structures, estimated elevated vapor pressures, and UV–vis gas-phase absorbance maxima and minima for test, reference, and tracer compounds are presented in Table 1. The elevated temperature vapor pressure values for diazinon and chlorpyrifos may be subject to some uncertainty because they were linearly extrapolated from lower temperature vapor pressure data. The gas-phase spectral information reported for all substances in Table 1 was determined using a remote flow cell linked by fiber optics to a rapid-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 et al., 1995; Bornhop et al., 1991).

Table 2. Calculated and Experimental Reaction Rate Constants for Test, Reference, and Tracer Compounds

substance	calcd OH rate constant (10 ⁻¹²), cm ³ /molecule-s	previously reported exptl OH rate constant (10 ⁻¹²), cm ³ /molecule-s
cyclohexane	8.48	7.49 ^a
toluene	5.23	5.96 ^a
triethyl phosphate	57.9 ^a	55.3 ^b
2-methylnaphthalene	56.5 ^a	53.0 ^a
hexachlorobenzene	0.017 ^a	0.027 ^c
diazinon	96.6 ^a	
chlorpyrifos	91.7 ^a	

^a Meylan and Howard, 1996a. ^b Atkinson et al., 1989. ^c Anderson and Hites, 1995.

The two reference substances (triethyl phosphate and 2-methylnaphthalene) were selected on the basis of their similar reported calculated and experimental OH reactivities and vapor pressures (Table 2). The calculated and experimental rate constants for these reference compounds were within 2× the calculated rate constants for diazinon and chlorpyrifos, thus making them suitable for relative rate measurement assessments (OECD, 1992). Hexachlorobenzene was selected as an internal tracer for determining OH reaction rates for the test substances and reference compounds. Hexachlorobenzene does not absorb wavelengths above 280 nm in the gas phase and therefore should not undergo photolysis under

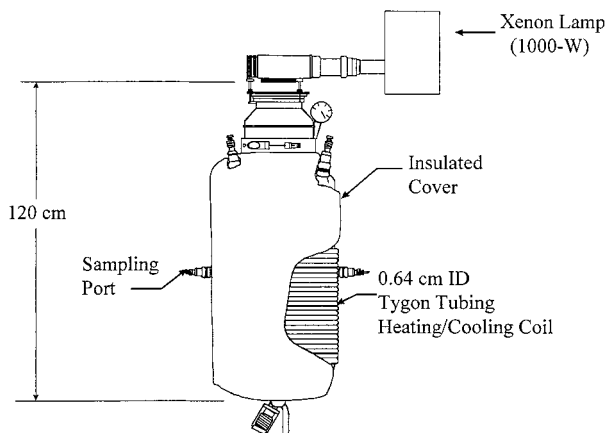
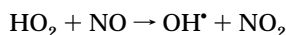
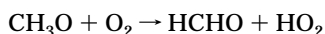
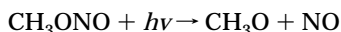


Figure 1. 57-L atmospheric chemical oxidation chamber.

experimental conditions. A recent gas-phase chemical oxidative study by Anderson and Hites (1995) also confirms that this substance is comparatively stable toward OH under tropospheric conditions (experimental rate constant = 2.7×10^{-14} $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at room temperature). Furthermore, the vapor pressure of hexachlorobenzene is intermediate to the vapor pressures of the reactive test substances under examination, making this substance a suitable stable tracer chemical.

Methyl nitrite was prepared according to methods outlined in Rook (1982) with certain modifications. A 500-mL round-bottom flask was charged with 100-mL of Nanopure water and 25 mL of reagent grade methanol. The solution was purged for 15 min using high-purity helium. Methyl nitrite was generated by dropwise addition of a 1:1 solution of concentrated sulfuric acid/nitrosyl sulfuric acid to the sparged water/methanol solution at room temperature. The oxygen-free helium stream carried the gaseous reaction product first through a 10% NaOH solution and then through anhydrous CaCl_2 into a trap cooled to -70°C using a dry ice/acetone slurry. Methyl nitrite was transferred into the reaction chamber using a gastight Hamilton syringe. The residual pale green product was then stored in liquid nitrogen to minimize decomposition.

Chamber System. The 57-L volume reaction chamber was designed to elevate air temperature in a controlled manner from 25 to 80°C (Figure 1). A more complete description of the reaction chamber and xenon arc light source is explained in Hebert et al. (2000). All chamber studies were performed using high-purity-grade air. After the purified air had been heated to the desired temperature, molar equivalent concentrations of gaseous test, reference, and tracer compounds (each at 1 ppm_v) were vaporized into the chamber. This was achieved by first creating a vacuum by pumping out some of the purified air from within the chamber. The gaseous mixture was allowed to reach equilibrium at the respective elevated temperatures at atmospheric pressure before the methyl nitrite was introduced at a concentration of ~ 10 ppm_v. Hydroxyl radicals were generated by the gas-phase photolysis of methyl nitrite at wavelengths >290 nm using xenon arc irradiation after the methods of Atkinson and co-workers (Atkinson, 1989; Goodman, 1988; Kwok, 1992; Kwok et al., 1995)



NO was added to the reaction mixture to avoid the formation of O_3 and NO_3 radicals. After the vessel had been dosed with the OH radical precursor, the xenon arc lamp was illuminated over the 2-h experimental time frame. Under these conditions, sufficient methyl nitrite was present to generate OH for ~ 100 min.

Gas-phase-sampling methods, which used SPME, were employed. SPME allows for the simultaneous sampling of test, reference, and tracer substances exclusively in the gas phase without the need for extracting air from the laboratory chamber. A microfiber coated with a bonded $100\text{-}\mu\text{m}$ polysiloxane phase was inserted into the chamber's side-port through a leak-proof septum. After exposure of the fiber for a 60-s time interval, the fiber was removed and immediately desorbed directly into a hot GC injection port (250°C), and the gas-phase constituents were quantified by mass selective detection (MSD). For the semivolatile ($<10^{-3}$ Torr) reference, test, and tracer compounds under examination, collection onto the SPME fiber was observed to be quantitative in separate dark controlled studies at all temperatures ($60\text{--}80^\circ\text{C}$). Variation among repetitive injections of tested semivolatile compounds at each of these temperatures was found to be $<15\%$.

Preliminary Wall Sorption Assessments. Before the oxidation phase of this study was performed, assessments to characterize wall sorption of the test, reference, and tracer compounds were performed at 60 and 80°C according to procedures outlined by Hebert et al. (2000). In these proportional dilution experiments, the percent of gas for each substance remaining after each dilution was compared to the ideal behavior of a gas that does not interact on the chamber surface to determine percent gas-wall concentrations. This repetitive dilution approach allowed for a reasonable estimate of sorption onto the chamber wall over the elevated temperature range for test, reference, and tracer substances.

Preliminary Photochemical Assessments. A series of photolysis evaluations were performed at 60, 70, and 80°C to determine if direct photolysis contributes to the loss of the compounds being examined. For each air temperature, the test substance solution (in benzene) was flash-volatilized under dark conditions into the 57-L photoreaction chamber as described above. Once equilibrium was established, the solar simulator was turned on. The gas-phase constituents were sampled by SPME at 15-min intervals for 2 h. Photolysis rates were determined by comparing integrated area ratios of the test substances to that of the photochemically stable tracer, hexachlorobenzene, using the first-order expression (Woodrow, 1978)

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

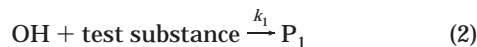
where R = test substance (mol)/tracer (mol).

This method assumes that the test substances and tracer will have similar gas-phase mobilities. Differences from the time-zero ratios between the test compounds and tracer over the experimental time frame of 2 h should reflect loss by direct photolysis.

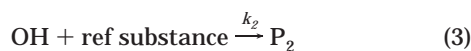
Gas Chromatography. A Hewlett-Packard 5790A gas chromatograph mass selective detector and a Hewlett-Packard 9133 data acquisition system (Pascal operating system) equipped with a Hewlett-Packard 5790 gas chromatograph were employed to assess gas-phase constituents. The GC column was a $30 \text{ m} \times 0.32 \text{ mm i.d.} \times 0.25 \mu\text{m}$ film DB-5 (5% phenyl, 95% methyl silicone, J&W Corp., Folsom, CA) column. GC operating conditions were as follows: 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 70°C . The initial temperature was held for 2 min before a temperature ramp at 40°C/min to 280°C was initiated with a final hold time of 2 min. The mass spectrometer was used in the EI mode, and the ionization energy was 70 eV. Data acquisition was performed in full-scan mode from 50 to 350 mass units. Under these conditions, triethyl phosphate, 2-methylnaphthalene, hexachlorobenzene, diazinon, and chlorpyrifos gave respective retention times of ca. 4.5, 5, 6.2, 7, and 7.8 min. The nominal limits of quantitation (LOQ) using SPME assessments over a 60-s exposure period were ca. 0.5 ng for diazinon and chlorpyrifos, 0.2 ng for hexachlorobenzene, 1.3 ng for triethyl phosphate, and 0.7 ng for 2-methylnaphthalene.

Relative Rate Assessment of Test Substance Reactivity. The relative loss over time of a test substance (R_{test}) with

unknown k_{OH} can be determined in the presence of a reference compound (R_{ref}) with known k_{OH} when $[OH]$ is not constant (Atkinson, 1986; Finlayson-Pitts and Pitts, 1986) as follows:



$$\text{and } -d[R_{test}]/dt = k_1[OH][R_{test}]$$



and $-d[R_{ref}]/dt = k_2[OH][\text{ref substance}]$. And by rearrangement

$$-d[R_{test}]/[R_{test}] = k_1[OH] dt \quad (4)$$

$$-d[R_{ref}]/[R_{ref}] = k_2[OH] dt \quad (5)$$

Rearranging to eliminate $[OH]$ and integrating from $t = 0$ when the initial concentrations are $[R_{test}]_0$ and $[R_{ref}]_0$, respectively, to time t when the concentrations are $[R_{test}]_t$ and $[R_{ref}]_t$ yielding

$$\ln \frac{[R_{test}]_0}{[R_{test}]_t} = \frac{k_1}{k_2} \ln \frac{[R_{ref}]_0}{[R_{ref}]_t} \quad (6)$$

where the ratio (R) is that of the test or reference substances to the tracer concentration. These ratios were determined at time zero and at 15-min sampling intervals (t) through 2 h (end of study). Because the OH rate constant of the reference compound (k_2) is known and the concentration of the test and reference compounds can be experimentally determined, the OH reaction rate constant for the test substance can be estimated by this approach.

Validation of System Comparing Reference Substance Reactivity Rates. Verification of reactions rates was performed by comparing the competitive reaction of cyclohexane to toluene (each at 2 ppm_v) in the presence of OH radicals (10 ppm_v). The competitive reaction of these substances has previously been evaluated in elevated-temperature systems (Anderson and Hites, 1995). Comparing experimental rate constants in our system to both calculated and experimental rate constants should provide a means for validating our procedures. OH reaction rate constants for the test substance, toluene, were determined by multiplying the ratio ($k_{test\ substance}/k_{ref}$) by the known rate constants (k_{ref}) of the reference compound cyclohexane for each experimental temperature. The rate constant at 60 and 80 °C was determined from the temperature-dependent cyclohexane rate expression recommended by Atkinson (1989b) where

$$k_{cyclohexane} = 2.66 \times 10^{-17} T^2 e^{(344+95)/T} \text{ cm}^3 \text{ s}^{-1} \quad (7)$$

The uncertainty in this rate constant is estimated to be $\pm 25\%$. Consequently, the derived toluene rate constant from the ratio (k_1/k_2) of eq 5 will be affected by the underlying uncertainty in the reference rate constant.

RESULTS AND DISCUSSION

Preliminary Wall Sorption Assessments. Elevating air temperatures from 60 to 80 °C within the chamber greatly enhances the ratio of gas-phase to wall concentrations, especially for the lower volatility compounds under examination. At ambient chamber air temperatures these substances exist appreciably on the chamber walls. Figures 2 and 3 show the results from sequential 20-L dilutions of gas-phase constituents 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 figures. Besides the simultaneous examination of test, reference, and tracer candidates,

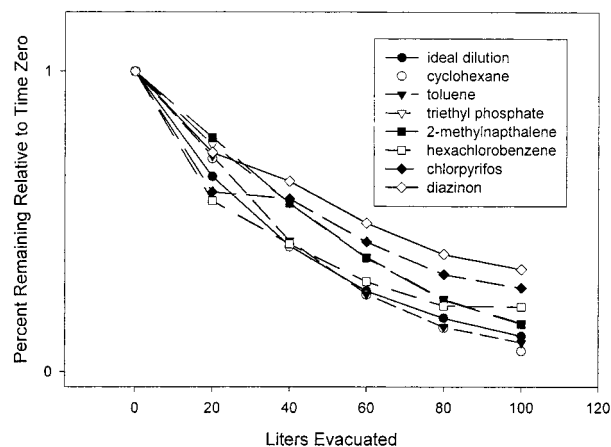


Figure 2. Results from repetitive 20-L dilutions of gas-phase constituents from the 57-L chamber conducted at 60 °C.

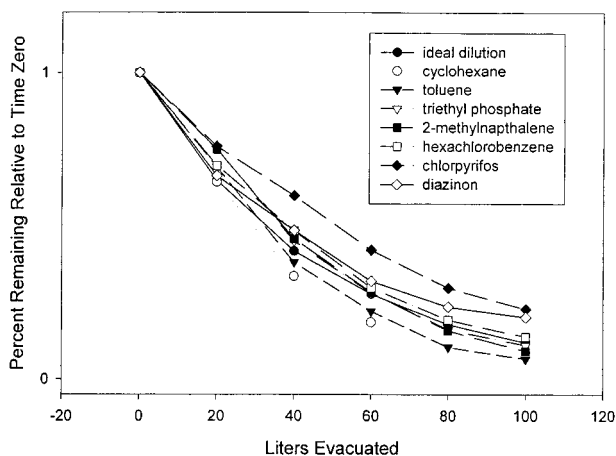


Figure 3. Results from repetitive 20-L dilutions of gas-phase constituents from the 57-L chamber conducted at 80 °C.

cyclohexane and toluene were also introduced into the chamber at these elevated air temperatures. Both cyclohexane and toluene were 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 both the lower and higher temperatures, gaseous triethyl phosphate and 2-methylnaphthalene were diluted from the chamber at nearly similar rates (Figures 2 and 3). Gas-phase concentrations for both of these reference substances were estimated to be near 100% at 60 and 80 °C. Hexachlorobenzene behaved in a fashion similar to that of the reference compounds but had a slightly greater rate of sorption on the chamber walls at the tested temperatures with ca. 90 and 98%, respectively, being in the gas phase at the lower and higher air temperatures. Chlorpyrifos and diazinon have still lower vapor pressures and were found to sorb out of the gas phase at a slightly greater rate than hexachlorobenzene. Although having a greater vapor pressure, diazinon showed a slightly greater rate of being retained on the wall than chlorpyrifos. At 60 °C, gas-phase concentrations for diazinon and chlorpyrifos were estimated to be ca. 78 and 82%, respectively, and 89 and 92% at 80 °C. Although these chamber studies are slightly complicated by sorption, the above assessment indicates that diazinon, chlorpyrifos, reference, and internal tracer substances will principally exist in the gas phase.

Preliminary Photochemical Assessments. Direct photochemical loss of chlorpyrifos and diazinon was

Table 3. Gas-Phase Reaction Rate Constants for Chlorpyrifos and Diazinon Taken at 5 °C Increments from 60 to 80 °C Using Triethyl Phosphate as Reference

temp (°C)	test substance	k_1/k_2^a	est rate constant, $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$	est half-life (1.5×10^6 molecules cm^{-3} OH), h
60	chlorpyrifos	1.38 ± 0.71^b	76×10^{-12}	1.7
65	chlorpyrifos	0.95 ± 0.34	53×10^{-12}	2.4
70	chlorpyrifos	1.59 ± 0.39	88×10^{-12}	1.5
75	chlorpyrifos	1.03 ± 0.43	56×10^{-12}	2.3
80	chlorpyrifos	1.61 ± 0.46	89×10^{-12}	1.4
			mean = 72.4 ± 17	mean = 1.9 ± 0.5
60	diazinon	3.62 ± 0.62	200×10^{-12}	0.6
65	diazinon	3.98 ± 0.34	220×10^{-12}	0.6
70	diazinon	4.35 ± 0.31	241×10^{-12}	0.5
75	diazinon	8.00 ± 0.16	442×10^{-12}	0.3
80	diazinon	3.69 ± 0.33	204×10^{-12}	0.6
			mean = 261 ± 102	mean = 0.52 ± 0.13

^a Triethyl phosphate experimental OH reactivity rate constant (k_2) = $55.3 \times 10^{-12} \text{ cm}^3 \text{mol}^{-1} \text{s}^{-1}$ (Meylan and Howard, 1996a). ^b Indicated errors are 1 least-squares standard deviation.

<10% during the 2-h irradiation at all temperatures. For all temperatures, the proportional disappearance of test and reference substances relative to that of the photochemically stable tracer, hexachlorobenzene, in irradiated experiments was no greater than 10% over the 2-h experimental time frame. Of the analytes, chlorpyrifos showed the greater rate of photolysis with ~8% loss over the 2-h irradiation interval. Less than 5% photodegradation at all temperatures was observed for 2-methylnaphthalene and diazinon. Triethyl phosphate was found to be stable under both light and dark conditions. The rates of photolysis for chlorpyrifos are comparable to those reported in Hebert et al. (2000) under similar experimental conditions. 2-Methylnaphthalene does absorb radiant energy in the mid-UVB range above 290 nm (Table 1) but was found to be stable within the experimental time frame.

System Validation. The competitive OH reactivity of toluene (test substance) to cyclohexane (reference substance) at elevated temperatures was found to provide reasonable estimates of rates to both calculated and experimental OH values of Anderson and Hites (1995). In high-purity air, the estimated rate constant for OH reaction with toluene at 60 °C was $4.7 \times 10^{-12} \text{ cm}^3 \text{s}^{-1}$ compared to the calculated rate constant of $4.59 \times 10^{-12} \text{ cm}^3 \text{s}^{-1}$ from eq 6. The loss of toluene compared favorably to the predicted value and was also found to fall within 10% of the experimentally observed rate constants reported by Anderson and Hites at 60 °C. Toluene and cyclohexane were well-behaved at 60 °C, but lower SPME collection efficiency was observed from the gas phase for these analytes at 80 °C, which led to lower analyte sensitivity and greater variability. At this higher temperature, too few reliable data points could be collected for establishing a meaningful rate constant. Although collection of semivolatile ($<10^{-3}$ Torr) reference, test, and tracer compounds onto the SPME fiber was observed to be both sensitive and quantitative in separate dark controlled studies at all temperatures, for moderately volatile substances such as cyclohexane and toluene, the higher elevated air temperatures may represent an upper limit at which SPME sampling techniques can be effectively used in these chamber studies.

Relative Rate Assessment. Table 3 and Figures 4 and 5 present our experimental results. Both chlorpyrifos and diazinon are structurally similar, and calculated rate constants for these two organophosphorus compounds are similar (Table 2). Chlorpyrifos was

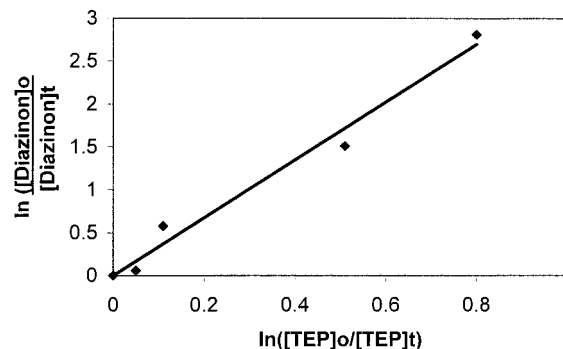


Figure 4. Competitive OH reactivity of diazinon (test substance) to triethyl phosphate (reference substance) at 75 °C.

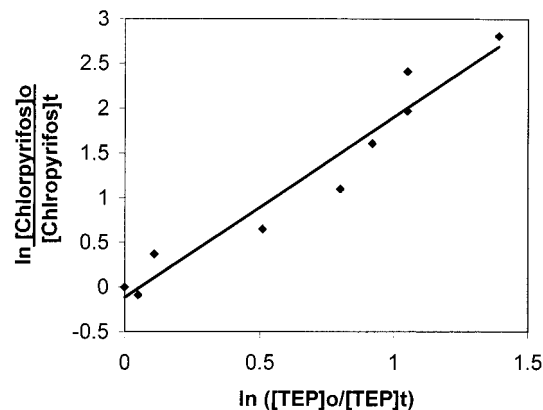


Figure 5. Competitive OH reactivity of chlorpyrifos (test substance) to triethyl phosphate (reference substance) at 75 °C.

reactive with an observed experimental OH reactivity very similar to what was predicted by the atmospheric oxidation program (AOP) model (Meylan and Howard, 1996a). The AOP calculated half-life for this substance was 1.4 h compared to our experimental determinations ranging from 1.4 to 2.4 h over the elevated temperatures under examination (using 1.5×10^6 OH molecules cm^{-3} for half-life calculations). Diazinon, however, was found to react at a rate appreciably higher than predicted (>2–3-fold) with an experimental half-life ranging from 0.3 to 0.6 h when compared to the AOP calculated half-life of 1.3 h. The chlorpyrifos and diazinon data sets did not show strong temperature-dependent rate behavior at the temperatures examined (60–80 °C). We could not, however, plot temperature-dependent relationships for either OP insecticide because temperature-dependent

rate constant relationships (similar to eq 6) are not available for either of these reference compounds. Triethyl phosphate and 2-methylnaphthalene OH reactivity rates were, however, referenced to cyclohexane, which exhibits very limited temperature dependence over the temperature range under examination (eq 6). For each of the above reference substances, the relative rate ratios did not appreciably change from 60 to 80 °C. This observation indicates that these semivolatile reference compounds appear to have low temperature-dependent behavior over the examined temperature range and can therefore be useful for assessing test compounds with similar volatilities and OH reactivities.

The difference in the simultaneous loss of diazinon to chlorpyrifos over all temperatures was substantial. The difference in reactivity was not due to wall sorption because both compounds behaved similarly in the gas phase (Figures 2 and 3). The discrepancy in rate constants between calculated and experimental data for these structurally similar substances suggests that other interactions not explained in the empirical structural activity model may be operating. The AOP model incorporates experimental information for >600 volatile organic compounds and is generally reliable in estimation power within a factor of 2 (Meylan and Howard, 1993). The estimation power for multifunctional semivolatile to low-volatility multifunctional insecticides may, however, be considerably less. In their studies on a series of OH reactions for dimethyl phosphoroamidates and dimethyl phosphorothioamidates, Goodman et al. (1988) found that electronic effects between structural units may have been responsible for discrepancies up to a factor of 3 between measured and calculated rate constants. In their assessment, the loss in estimation power may well represent "the inherent uncertainties for more complex chemicals containing multiple substituent groups". Although Brubaker and Hites (1998) found excellent agreement between experimental and calculated rate constants for tetrachlorinated dibenzo-*p*-dioxins, Kwok et al. (1995) observed discrepancies of 2.5 and 8 between measured and calculated rate constants for dibenzo-*p*-dioxin and dibenzofuran, respectively. Although OH radical reaction rate constants have been successfully generated to extend Atkinson's structure-activity database for certain thiocarbamates and chlorinated aromatics (Kwok et al., 1992; Anderson and Hites, 1995; Brubaker and Hites, 1998), the results of this and other recent studies suggest that further experimental work will be important to assess OH reaction rates for the more complex chemistries that comprise the majority of high-use urban and agricultural pesticides.

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