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Kinetic and Product Study of the Gas-Phase Reactions of OH Radicals, NO_3 Radicals, and O_3 with $(C_2H_5O)_2P(S)CH_3$ and $(C_2H_5O)_3PS$

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Rate constants for the reactions of OH radicals and NO_3 radicals with *O,O*-diethyl methylphosphonothioate [$(C_2H_5O)_2P(S)CH_3$; DEMPT] and *O,O,O*-triethyl phosphorothioate [$(C_2H_5O)_3PS$; TEPT] have been measured using relative rate methods at atmospheric pressure of air over the temperature range 296−348 K for the OH radical reactions and at 296 ± 2 K for the NO_3 radical reactions. At 296 ± 2 K, the rate constants obtained for the OH radical reactions (in units of 10^{-11} cm^3 molecule^{-1} s^{-1}) were 20.4 ± 0.8 and 7.92 ± 0.27 for DEMPT and TEPT, respectively, and those for the NO_3 radical reactions (in units of 10^{-15} cm^3 molecule^{-1} s^{-1}) were 2.01 ± 0.20 and 1.03 ± 0.10, respectively. Upper limits to the rate constants for the reactions of O_3 with DEMPT and TEPT of $<6 \times 10^{-20}$ cm^3 molecule^{-1} s^{-1} were determined in each case. Rate constants for the OH radical reactions, measured relative to $k(\mathrm{OH} + \alpha\text{-pinene}) = 1.21 \times 10^{-11}\, e^{436/T}$ cm^3 molecule^{-1} s^{-1}, resulted in the Arrhenius expressions $k(\mathrm{OH} + \mathrm{DEMPT}) = 1.08 \times 10^{-11}\, e^{(871\pm25)/T}$ cm^3 molecule^{-1} s^{-1} and $k(\mathrm{OH} + \mathrm{TEPT}) = 8.21 \times 10^{-13}\, e^{(1353\pm49)/T}$ cm^3 molecule^{-1} s^{-1} over the temperature range 296−348 K, where the indicated errors are two least-squares standard deviations and do not include the uncertainties in the reference rate constant. Diethyl methylphosphonate was identified and quantified from the OH radical and NO_3 radical reactions with DEMPT, with formation yields of 21 ± 4%, independent of temperature, from the OH radical reaction and 62 ± 11% from the NO_3 radical reaction at 296 ± 2 K. Similarly, triethyl phosphate was identified and quantified from the OH radical and NO_3 radical reactions with TEPT, with formation yields of 56 ± 9%, independent of temperature, from the OH radical reaction and 78 ± 15% from the NO_3 radical reaction at 296 ± 2 K.

Introduction

Volatile organic compounds emitted into the troposphere can undergo photolysis (at wavelengths >290 nm), react with OH radicals, react with NO_3 radicals, and react with O_3.[1] Alkyl and aryl phosphates [$(RO)_3PO$], phosphonates [$(RO)_2P(O)R$], phosphorothioates [$(RO)_xP(SR)_{3-x}S$], and phosphonothioates [$(RO)_2P(S)R$], where R = alkyl or aryl, are used as plasticizers, flame retardants, fire-resistant fluids and lubricants, and pesticides.[2,3] These compounds and their precursors may be released into the atmosphere, where they can undergo transport and chemical transformations. The kinetics of the atmospheric reactions of a number of simple "model" alkyl phosphates, alkyl phosphorothioates, and alkyl phosphonates of structure $(RO)_nP(O)(SR)_{3-n}$, $(RO)_nP(S)(SR)_{3-n}$, and $(RO)_2P(O)X$ (R = CH_3 or C_2H_5 and X = H, CH_3, C_2H_5, or $OCH{=}CCl_2$) have been studied.[4−13] For the alkyl phosphates, phosphonates, and phosphorothioates studied to date, reaction with the OH radical is the dominant atmospheric loss process.[5,9,11]

The only alkyl phosphorothioates or phosphonothioates containing a P═S bond studied to date are $(CH_3O)_3PS$ and $(CH_3O)_2P(S)SCH_3$.[5,14] In addition to the measurement of rate constants for the reactions of $(CH_3O)_3PS$ and $(CH_3O)_2P(S)SCH_3$ with OH radicals, NO_3 radicals, and O_3,[5] the formation yields of $(CH_3O)_3PO$ and $(CH_3O)_2P(O)SCH_3$ from the OH radical initiated reactions of $(CH_3O)_3PS$ and $(CH_3O)_2P(S)SCH_3$, respectively, were determined.[14]

In this work we have extended our recent studies of the atmospheric chemistry of a number of alkyl phosphates and phosphonates[9,11,13] to the measurement of rate constants for the gas-phase reactions of OH radicals, NO_3 radicals, and O_3 with *O,O*-diethyl methylphosphonothioate [DEMPT; $(C_2H_5O)_2P(S)CH_3$] and *O,O,O*-triethyl phosphorothioate [TEPT; $(C_2H_5O)_3PS$] at 296 ± 2 K. Rate constants for the OH radical reaction were also measured up to 348 K and, because diethyl methylphosphonate [DEMP; $(C_2H_5O)_2P(O)CH_3$] and triethyl phosphate [TEP; $(C_2H_5O)_3PO$] were observed as reaction products from the OH and NO_3 radical initiated reactions of DEMPT and TEPT, respectively, their formation yields were also measured.

Experimental Methods

Experiments were carried out in two chamber systems. A series of experiments was conducted at 296 ± 2 K and 735 Torr total pressure of dry purified air in a ∼7000 L volume Teflon chamber, equipped with two parallel banks of blacklamps for irradiation.[9,11] Temperature-dependent experiments were carried out using a ∼4500 L volume Teflon "bag" inserted inside a 5870 L Teflon-coated chamber,[13] with irradiation provided by a 24-kW xenon arc lamp filtered through a 6 mm thick Pyrex pane to remove wavelengths <300 nm. The 5870 L volume Teflon-coated evacuable chamber is fitted with a heating/cooling system, allowing its temperature to be maintained to within ±1

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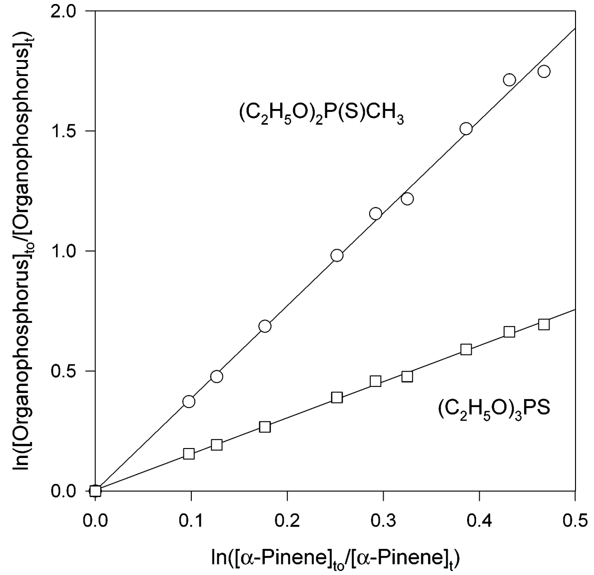

Figure 1. Plots of eq I for reactions of OH radicals with *O,O*-diethyl methylphosphonothioate (DEMPT) and *O,O,O*-triethyl phosphorothioate (TEPT) at 296 ± 2 K in the ~7000 L Teflon chamber, with α-pinene as the reference compound.

K over the range 299−348 K for the present study. Both chambers were provided with Teflon-coated fan(s) to ensure rapid mixing of reactants during their introduction into the chamber. Temperatures of the gas mixtures inside the chambers were measured by thermocouples. For the experiments carried out in the evacuable chamber, the gas temperature within the Teflon bag was within ±1 K of the set-point temperature of the chamber heating/cooling system controller. In all experiments in both chambers, the temperature rise during the intermittent irradiations was always <2 K.

Kinetic Studies. Rate constants for the reactions of OH and NO_3 radicals with DEMPT and TEPT were measured using relative rate techniques in which the concentrations of DEMPT and TEPT and a reference compound (whose OH radical or NO_3 radical reaction rate constant is reliably known) were measured in the presence of OH or NO_3 radicals.[5,6,8,9,11,13]

$$\left.\begin{matrix} OH \\ NO_3 \end{matrix}\right\} + \text{organophosphorus compound} \rightarrow \text{products} \quad (1)$$

$$\left.\begin{matrix} OH \\ NO_3 \end{matrix}\right\} + \text{reference compound} \rightarrow \text{products} \quad (2)$$

Providing that the organophosphorus compound and the reference compound reacted only with OH radicals or NO_3 radicals, then,

$$\ln\left(\frac{[\text{organophosphorus}]_{t_o}}{[\text{organophosphorus}]_t}\right) - D_t = \frac{k_1}{k_2}\ln\left(\frac{[\text{reference compound}]_{t_o}}{[\text{reference compound}]_t}\right) - D_t \quad \text{(I)}$$

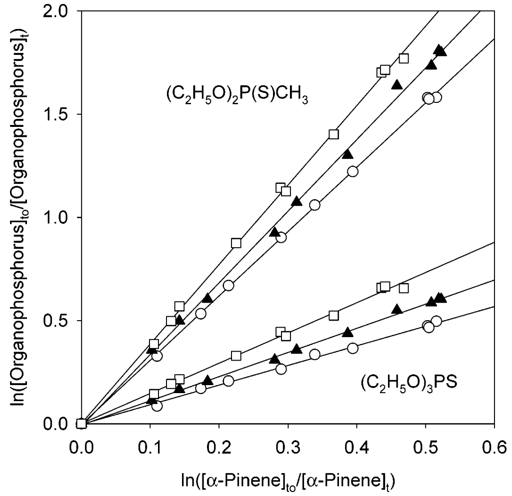

Figure 2. Plots of eq I for reactions of OH radicals with *O,O*-diethyl methylphosphonothioate (DEMPT) and *O,O,O*-triethyl phosphorothioate (TEPT) at 299 ± 2 K (□), 321 ± 2 K (▲), and 348 ± 3K (○) in the ~4500 L Teflon bag, with α-pinene as the reference compound.

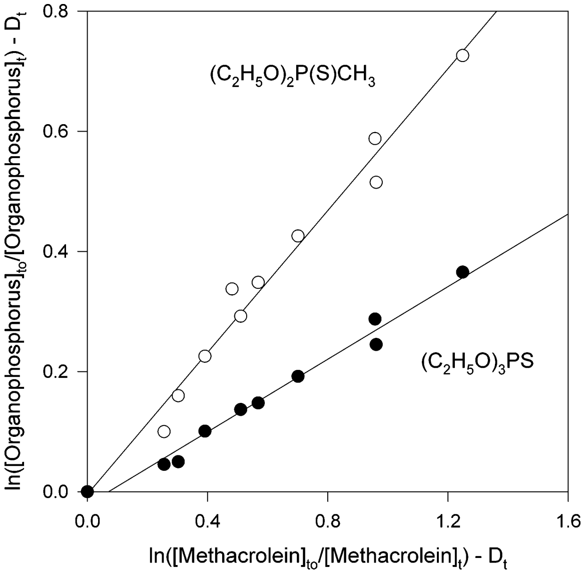

Figure 3. Plots of eq I for reactions of NO_3 radicals with *O,O*-diethyl methylphosphonothioate (DEMPT) and *O,O,O*-triethyl phosphorothioate (TEPT) at 296 ± 2 K (~7000 L Teflon chamber), with methacrolein as the reference compound.

where $[\text{organophosphorus}]_{t_o}$ and $[\text{reference compound}]_{t_o}$ are the concentrations of DEMPT or TEPT and reference compound, respectively, at time t_o, $[\text{organophosphorus}]_t$ and $[\text{reference compound}]_t$ are the corresponding concentrations at time t, D_t is a factor to account for dilution caused by any additions to the chamber during the experiments ($D_t = 0$ for the OH radical reactions and $D_t = 0.0026$ per N_2O_5 addition to the ~7000 L Teflon chamber in the NO_3 radical reactions), and k_1 and k_2 are the rate constants for reactions 1 and 2, respectively.

Hydroxyl radicals were generated in the presence of NO by the photolysis of methyl nitrite in air at wavelengths >300 nm.[5,8,9,11,13] The initial reactant concentrations (molecules cm^{-3}) were as follows: CH_3ONO, $\sim 2.4 \times 10^{14}$; NO, $\sim 2.4 \times 10^{14}$; DEMPT $(0.70-2.91) \times 10^{13}$; TEPT, $(1.94-2.62) \times 10^{13}$; and α-pinene (the reference compound), $\sim 2.4 \times 10^{13}$. Irradiations were carried out in the ~7000 L Teflon chamber at 20% of the maximum light intensity for up to 7 min, and in the ~4500 L Teflon bag for up to 17 min. Experiments were also conducted to investigate the importance of dark decay and photolysis of $\sim 2.4 \times 10^{13}$ molecules cm^{-3} of DEMPT and TEPT in the ~7000 L Teflon chamber. For the photolysis experiment, 1.4×10^{16} molecules cm^{-3} of cyclohexane was also added to the chamber to scavenge any OH radicals formed, and the reactant mixture was irradiated for a total of 60 min at 20% maximum

TABLE 1: Rate Constant Ratios k_1/k_2 and Rate Constants k_1 (cm^3 molecule^{-1} s^{-1}) for the Reactions of OH Radicals with *O,O*-Diethyl Methylphosphonothioate (DEMPT) and *O,O,O*-Triethyl Phosphorothioate (TEPT), with α-Pinene as the Reference Compound

		DEMPT		TEPT	
T (K)	chamber[a]	k_1/k_2[b]	$10^{11} \times k_1$[c]	k_1/k_2[b]	$10^{11} \times k_1$[c]
296 ± 2	A	3.86 ± 0.14	20.4 ± 0.8	1.50 ± 0.05	7.92 ± 0.27
299 ± 2	B	3.85 ± 0.09	20.0 ± 0.5	1.47 ± 0.07	7.65 ± 0.37
321 ± 2	B	3.47 ± 0.10	16.3 ± 0.5	1.17 ± 0.04	5.51 ± 0.19
348 ± 3	B	3.12 ± 0.05	13.2 ± 0.3	0.951 ± 0.042	4.03 ± 0.18

[a] A = ~7000 L Teflon chamber; B = ~4500 L Teflon bag inside 5870 L evacuable chamber. [b] Indicated errors are two least-squares standard deviations. [c] Placed on an absolute basis by use of the rate constant expression k_2(α-pinene) = 1.21×10^{-11} $e^{436/T}$ cm^3 molecule^{-1} s^{-1}.[1] The indicated errors are the two least-squares standard deviations and do not include the uncertainties in the rate constants k_2, which are likely to be ~ ±10%.[13]

TABLE 2: Rate Constant Ratios k_1/k_2 and Rate Constants k_1 (cm^3 molecule^{-1} s^{-1}) for the Reactions of NO_3 Radicals with $(C_2H_5O)_2P(S)CH_3$ and $(C_2H_5O)_3PS$ at 296 ± 2 K, with Methacrolein as the Reference Compound

organophosphorus compound	k_1/k_2[a]	$10^{15} \times k_1$[b] (cm^3 molecule^{-1} s^{-1})
$(C_2H_5O)_2P(S)CH_3$ (DEMPT)	0.591 ± 0.057	2.01 ± 0.20
$(C_2H_5O)_3PS$ (TEPT)	0.302 ± 0.029	1.03 ± 0.10

[a] Using methacrolein as the reference compound. The indicated errors are two least-squares standard deviations. [b] Placed on an absolute basis by use of a rate constant of k_2(methacrolein) = 3.4×10^{-15} cm^3 molecule^{-1} s^{-1} at 296 K.[1,16]

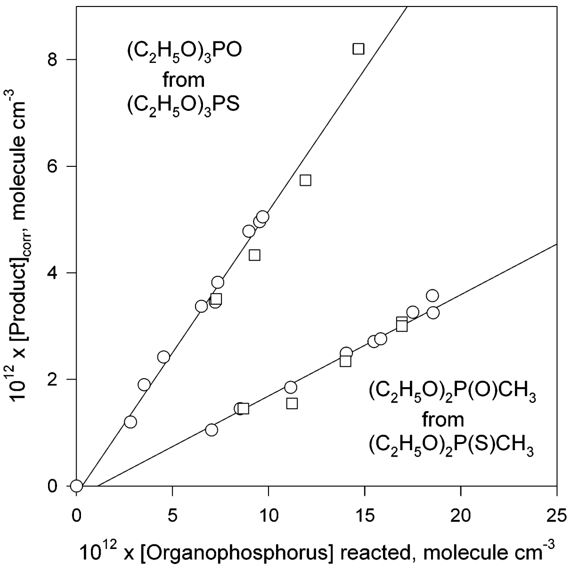

Figure 4. Plots of amounts of diethyl methylphosphonate (DEMP) and triethyl phosphate (TEP) formed, corrected for secondary reactions with OH radicals (see text), against amounts of DEMPT and TEPT reacted, respectively, with OH radicals at 296 ± 2 K in the ~7000 L Teflon chamber. (○) Data from irradiated CH_3ONO−NO−DEMPT−TEPT−α-pinene−air mixtures; (□) data from irradiated CH_3ONO−NO−DEMPT−air and CH_3ONO−NO−TEPT−air mixtures.

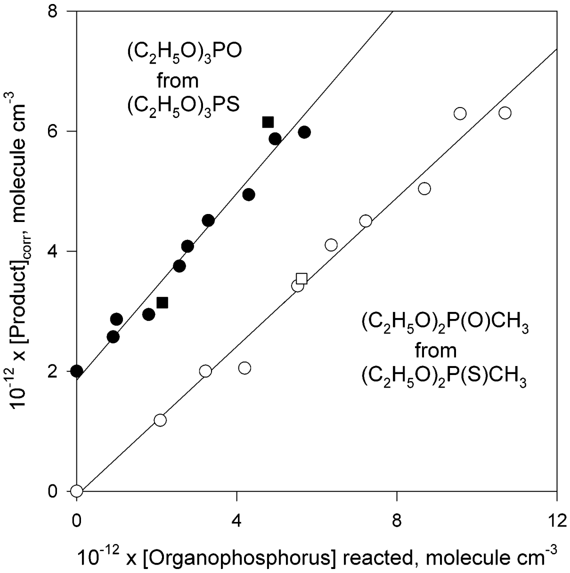

Figure 5. Plots of amounts of diethyl methylphosphonate (DEMP) and triethyl phosphate (TEP) formed, corrected for secondary reactions with NO_3 radicals (see text), against amounts of DEMPT and TEPT reacted, respectively, with NO_3 radicals at 296 ± 2 K in the ~7000 L Teflon chamber. (○, ●) Data from reacting N_2O_5−NO_3−NO_2−DEMPT−TEPT−methacrolein−air mixtures; (□, ■) data from reacting N_2O_5−NO_3−NO_2−DEMPT−methacrolein−air and N_2O_5−NO_3−NO_2−TEPT−air mixtures. The data for $(C_2H_5O)_3PO$ (TEP) have been displaced vertically by 2.0×10^{12} molecules cm^{-3} for clarity.

light intensity (the light intensity and spectral distribution as used in the OH radical rate constant determinations) with analyses after each 15 min of irradiation.

Nitrate radicals were produced from the thermal decomposition of N_2O_5,[15] and NO_2 was also included in the reactant mixtures. The initial reactant concentrations (molecules cm^{-3}) were as follows: DEMPT, (1.96−2.16) × 10^{13}; TEPT, (1.86−1.98) × 10^{13}; methacrolein (the reference compound), ~2.4 × 10^{13}; and NO_2, (2.4−4.8) × 10^{13}. Two additions of N_2O_5 (each addition corresponding to (1.1−1.3) × 10^{14} molecules cm^{-3} of N_2O_5 in the chamber) were made to the chamber during an experiment.

The concentrations of the organophosphorus compounds and the reference compounds were measured during the experiments by gas chromatography with flame ionization detection (GC-FID). Gas samples of 100 cm^3 volume were collected from the chamber onto Tenax-TA solid adsorbent, with subsequent thermal desorption at ~250 °C onto a 30 m DB-5 megabore column initially held at 0 °C for 2 min and then temperature programmed to 200 °C at 8 °C min^{-1}. This GC column and temperature program provided separation of DEMP from DEMPT and of TEP from TEPT. Based on replicate analyses in the chamber in the dark, the analytical uncertainties for DEMPT, TEPT, and the reference compounds used were typically ≤3%.

The rate constants, or upper limits thereof, for the reactions of DEMPT and TEPT with O_3 were determined by monitoring the decay of DEMPT and TEPT in the presence of a known concentration of O_3,[9,11] with cyclohexane being present to scavenge any OH radicals formed. Assuming that under these

TABLE 3: Molar Formation Yields of $(C_2H_5O)_2P(O)CH_3$ (DEMP) and $(C_2H_5O)_3PO$ (TEP) from the Reactions of OH Radicals with $(C_2H_5O)_2P(S)CH_3$ (DEMPT) and $(C_2H_5O)_3PS$ (TEPT), Respectively

reactant	product	*T* (K)	molar yield[a]
$(C_2H_5O)_2P(S)CH_3$	$(C_2H_5O)_2P(O)CH_3$	296 ± 2	0.19 ± 0.04
		299 ± 2	0.22 ± 0.05
		321 ± 2	0.23 ± 0.04
		348 ± 3	0.24 ± 0.08
$(C_2H_5O)_3PS$	$(C_2H_5O)_3PO$	296 ± 2	0.53 ± 0.09
		299 ± 2	0.59 ± 0.10
		321 ± 2	0.57 ± 0.09
		348 ± 3	0.45 ± 0.14

[a] Indicated errors are two least-squares standard deviations of the slopes of the plots such as those shown in Figure 4 combined with estimated uncertainties in the GC-FID calibration factors for DEMPT, TEPT, DEMP, and TEP of ±10% each.

conditions the only loss process for DEMPT and TEPT is by reaction with O_3, then

$$\ln([\text{organophosphorus}]_{t_o}/[\text{organophosphorus}]_t) - D_t = k_3[O_3](t - t_o) \quad \text{(II)}$$

where $[\text{organophosphorus}]_{t_o}$ and $[\text{organophosphorus}]_t$ are the concentrations of DEMPT or TEPT at times t_o and t, respectively, D_t (=0.0026) is the small amount of dilution caused by the initial addition of O_3 to the ~7000 L Teflon chamber, and k_3 is the rate constant for reaction 3.

$$O_3 + \text{organophosphorus compound} \rightarrow \text{products} \quad (3)$$

The initial reactant concentrations (molecules cm^{-3}) were as follows: DEMPT and TEPT, ~2.4×10^{13} each; O_3, 3.48×10^{13}; and cyclohexane, 1.4×10^{16}. O_3 concentrations were measured during the 4.0 h duration reaction by ultraviolet absorption using a Dasibi Model 1003-AH ozone analyzer, and the concentrations of DEMPT and TEPT were measured by GC-FID as described above.

Formation of $(C_2H_5O)_2P(O)CH_3$ and $(C_2H_5O)_3PO$ from the OH Radical Reactions. Products of the reactions of OH radicals with DEMPT and TEPT were investigated using GC-FID analyses. In addition to data from the kinetic experiments discussed above, irradiations of two CH_3ONO−NO−DEMPT−air and two CH_3ONO−NO−TEPT−air mixtures were carried out at 296 ± 2 K, with initial reactant concentrations similar to those used in the kinetic experiments and with analyses by GC-FID and combined gas chromatography−mass spectrometry (GC−MS). For the GC−MS analyses, 100 cm^3 gas samples were collected from the chamber onto Tenax-TA solid adsorbent, with subsequent thermal desorption onto a 60 m DB-5MS capillary column in a Hewlett-Packard (HP) 5890 GC interfaced to a HP 5971A mass selective detector operated in the scanning mode. The GC column was initially held at −25 °C for 10 min and then temperature programmed at 8 °C min^{-1} to 300 °C.

Formation of $(C_2H_5O)_2P(O)CH_3$ and $(C_2H_5O)_3PO$ from the NO_3 Radical Reactions. Products of the reactions of NO_3 radicals with DEMPT and TEPT were investigated at 296 ± 2 K in the ~7000 L Teflon chamber using GC-FID analyses, including data from the kinetic experiments. GC−MS analyses were also carried out during one DEMPT and one TEPT reaction for product identification. The initial reactant concentrations (molecules cm^{-3}) were as follows: DEMPT and/or TEPT, $(1.84−2.16) \times 10^{13}$, methacrolein (when present), ~2.4×10^{13}; and NO_2, $(2.4−4.8) \times 10^{13}$. Two additions of N_2O_5 (each addition corresponding to $(1.1−1.6) \times 10^{14}$ molecules cm^{-3} N_2O_5 in the chamber) were made to the chamber during an experiment.

Chemicals. The chemicals used, and their stated purities, were as follows: diethyl methylphosphonate (97%), *O*,*O*-diethyl methylphosphonothioate (97%), α-pinene (99+%), methacrolein (95%), and triethyl phosphate (99+%), Aldrich Chemical Co.; *O*,*O*,*O*-triethyl phosphorothioate, Chem Service; and NO (≥99.0%), Matheson Gas Products. Methyl nitrite and N_2O_5 were prepared and stored as described previously,[8,9,11] and O_3 in O_2 diluent was generated using a Welsbach T-408 ozone generator. NO_2 was prepared as needed by reacting NO with an excess of O_2.

Results

Photolysis and Dark Reactions. No decays (<5%) of gas-phase DEMPT or TEPT were observed in the ~7000 L Teflon chamber either in the dark over a period of 4.8 h or during photolysis (60 min irradiation at the same light intensity and spectral distribution as used in the OH radical rate constant determinations, with a total duration of the experiment of 3.6 h). These data show that dark decay and photolysis of DEMPT and TEPT were of no importance in the irradiated CH_3ONO−NO−DEMPT−TEPT−air mixtures used to determine the OH radical reaction rate constants. Replicate analyses of the reactant mixtures in the ~4500 L Teflon bag prior to initiating the reactions also showed no evidence for dark decay of DEMPT or TEPT (nor of continued formation of DEMP or TEP, respectively, after introduction of DEMPT or TEPT into the chamber; see below).

Rate Constants for Reactions with OH Radicals and NO_3 Radicals. CH_3ONO−NO−DEMPT−TEPT−α-pinene−air irradiations and reactions of N_2O_5−NO_3−NO_2−DEMPT−TEPT−methacrolein−air and N_2O_5−NO_3−NO_2−DEMPT−methacrolein−air mixtures were carried out in the ~7000 L Teflon chamber at 296 ± 2 K, and CH_3ONO−NO−DEMPT−TEPT−α-pinene−air irradiations were carried out in the ~4500 L Teflon bag inside the 5870 L evacuable chamber at 299 ± 2, 321 ± 2, and 348 ± 3 K. The data obtained are plotted in accordance with eq I in Figures 1 and 2 (OH radical reactions) and Figure 3 (NO_3 radical reactions). Least-squares analyses of these data lead to the rate constant ratios k_1/k_2 given in Tables 1 (OH radical reactions) and 2 (NO_3 radical reactions). These rate constant ratios k_1/k_2 are placed on an absolute basis by use of recommended rate constants of $k_2 = 1.21 \times 10^{-11}\, e^{436/T}$ cm^3 $molecule^{-1}$ s^{-1} for the reaction of OH radicals with α-pinene[1] and $k_2 = 3.4 \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1} at 296 K for the reactions of NO_3 radicals with methacrolein.[1,16] The resulting rate constants k_1 for the reactions of OH radicals and NO_3 radicals with DEMPT and TEPT are given in Tables 1 and 2, respectively.

Rate Constants for Reactions with O_3. No decays (<5%) of gas-phase DEMPT or TEPT were measured in the ~7000 L Teflon chamber in the presence of 3.48×10^{13} molecules cm^{-3} O_3 over a reaction period of 240 min. Use of an upper limit of 5% for the amount of DEMPT or TEPT reacted over this time period results in upper limits to the rate constants for reaction of O_3 with DEMPT and TEPT of $k_3 < 6 \times 10^{-20}$ cm^3 $molecule^{-1}$ s^{-1} at 296 ± 2 K.

Products of the Reactions with OH Radicals and NO_3 Radicals by Gas Chromatography. GC-FID and GC−MS analyses of irradiated CH_3ONO−NO−DEMPT−air and CH_3ONO−NO−TEPT−air mixtures and of reacted N_2O_5−NO_2−DEMPT−methacrolein−air and N_2O_5−NO_2−TEPT−air mix-

TABLE 4: Formation Yields of $(C_2H_5O)_2P(O)CH_3$ (DEMP) and $(C_2H_5O)_3PO$ (TEP) from the Reactions of NO_3 Radicals with $(C_2H_5O)_2P(S)CH_3$ (DEMPT) and $(C_2H_5O)_3PS$ (TEPT), Respectively, at 296 ± 2 K

organophosphorus compound	product	molar yield[a]
$(C_2H_5O)_2P(S)CH_3$ (DEMPT)	$(C_2H_5O)_2P(S)CH_3$ (DEMP)	0.62 ± 0.11
$(C_2H_5O)_3PS$ (TEPT)	$(C_2H_5O)_3PO$ (TEP)	0.78 ± 0.15

[a] Indicated errors are two least-squares standard deviations of the slopes of the plots shown in Figure 5 combined with estimated uncertainties in the GC-FID calibration factors for DEMPT, TEPT, DEMP, and TEP of ±10% each.

TABLE 5: Room Temperature Rate Constants (cm^3 $molecule^{-1}$ s^{-1}) for the Gas-Phase Reactions of Selected Organophosphorus Compounds with OH and NO_3 Radicals

organophosphorus compound	$10^{12} \times k(OH)^a$	$10^{16} \times k(NO_3)^a$	reference
$(CH_3O)_3PO$	6.92 ± 0.09		Tuazon et al.[4]
$(CH_3O)_2P(O)SCH_3$	8.64 ± 0.63	<11	Goodman et al.[5]
$(CH_3S)_2P(O)OCH_3$	8.92 ± 0.70	≤24	Goodman et al.[5]
$(CH_3O)_3PS$	69.0 ± 3.8	<160	Goodman et al.[5]
$(CH_3O)_2P(S)SCH_3$	55.4 ± 1.7	<280	Goodman et al.[5]
$(C_2H_5O)_3PO$ (TEP)	51.7^b	2.4 ± 1.4	Aschmann et al.[9,13]
$(C_2H_5O)_2P(O)CH_3$ (DEMP)	55.6^b	3.7 ± 1.1	Aschmann et al.[9,13]
$(C_2H_5O)_2P(O)C_2H_5$	57.8^b	3.4 ± 1.4	Aschmann et al.[9,13]
$(C_2H_5O)_3PS$ (TEPT)	76.9^b	10.3 ± 1.0	this work
$(C_2H_5O)_2P(S)CH_3$ (DEMPT)	201^b	20.1 ± 2.0	this work

[a] Relative rate measurements. Placed on an absolute basis using the most recent recommendations for the reference compounds used.[1] [b] Calculated from Arrhenius expressions.

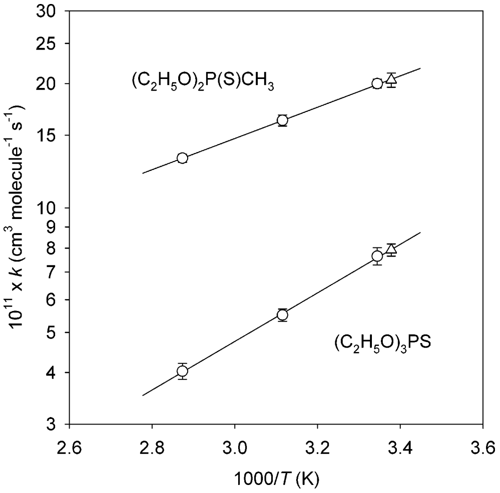

Figure 6. Arrhenius plot of rate constants for reactions of OH radicals with *O,O*-diethyl methylphosphonothioate (DEMPT) and *O,O,O*-triethyl phosphorothioate (TEPT). Rate constants are from experiments carried out in (○) ~4500 L Teflon bag inside evacuable chamber (299−348 K) and (△) ~7000 L Teflon chamber at 296 ± 2 K. The indicated error bars are two least-squares standard deviations (Table 1) and do not include the uncertainties in the rate constants for α-pinene, the reference compound in all cases.

tures showed the formation of DEMP from the DEMPT reactions and of TEP from the TEPT reactions. DEMP and TEP were present prior to the irradiations, with the initially present DEMP and TEP concentrations, relative to those of DEMPT and TEPT, respectively, depending on the reaction system, chamber, and temperature. The respective initial DEMP/DEMPT and TEP/TEPT ratios in the $CH_3ONO-NO-DEMPT-TEPT-\alpha\text{-pinene}-air$ mixtures were 0.4−1.3% and nondetectable at 296 ± 2 K, 0.9−2.5% and ≤1.2% at 299 ± 2 K, 6.5−8.0% and 3.7−5.4% at 321 ± 2 K, and 7.2−30% and 3.1−11% at 348 ± 3 K. Relative to DEMPT and TEPT, there was initially 8.4−9.3% DEMP in the $CH_3ONO-NO-DEMPT-air$ mixtures and 0.6−0.8% TEP in the $CH_3ONO-NO-TEPT-air$ mixtures, all at 296 ± 2 K. The respective initial DEMP/DEMPT and TEP/TEPT ratios in the $N_2O_5-NO_3-NO_2-DEMPT-TEPT-methacrolein-air$ mixtures were 2.2−4.1% and 1.4−2.5%, with 7.9% DEMP in the $N_2O_5-NO_3-NO_2-DEMPT-methacrolein-air$ mixture and 0.6% TEP in the $N_2O_5-NO_3-NO_2-TEPT-air$ mixture.

DEMP and TEP also react with OH and NO_3 radicals,[9,13] and the measured concentrations of DEMP and TEP in these OH and NO_3 radical initiated reactions were corrected for secondary reactions with OH or NO_3 radicals[17] and for the amounts initially present. The OH radical reaction rate constants used to calculate these corrections were calculated from the Arrhenius expressions obtained here for DEMPT and TEPT and previously[13] for DEMP and TEP, and the rate constants used for the NO_3 radical reactions were those measured here and previously.[9] The multiplicative correction factors to take into account these secondary reactions increase with the rate constant ratio $k(OH/NO_3 + product)/k(OH/NO_3 + reactant)$ and with the extent of reaction,[17] and were ≤1.40 for formation of DEMP from the OH + DEMPT reactions, ≤1.67 for formation of TEP from the OH + TEPT reactions, ≤1.08 for formation of DEMP from the NO_3 + DEMPT reactions, and ≤1.05 for formation of TEP from the NO_3 + TEPT reactions. Plots of the amounts of DEMP and TEP formed, corrected for secondary reactions and initially present DEMP and TEP, against the amounts of DEMPT and TEPT reacted, respectively, are shown in Figure 4 for the OH radical reactions at 296 ± 2 K and in Figure 5 for the NO_3 radical reactions. Good straight-line plots are observed, and the data obtained from experiments containing only DEMPT or TEPT are indistinguishable from those obtained from experiments in which both DEMPT and TEPT were present. The formation yields of DEMP from the DEMPT reactions and of TEP from the TEPT reactions, obtained by least-squares analyses of the experimental data, are given in Tables 3 (OH radical reactions) and 4 (NO_3 radical reactions). As evident from Table 3, the uncertainties in the DEMP and TEP formation yields from the OH radical initiated reaction increase at the higher temperatures because of the presence of higher fractions of initial DEMP or TEP in the reactant mixtures at higher temperatures. Within the overall experimental uncertainties (and within the two least-squares standard deviations of the slopes of plots such as those shown in Figure 4), the DEMP and TEP formation yields from the OH radical initiated reactions of DEMPT and TEPT, respectively, are independent of temperature over the range 296−348 K. The weighted averages [weighted by $(1/\text{standard deviation})^2$] are 21 ± 4% for formation of DEMP

TABLE 6: Arrhenius Parameters, $k = Ae^{-B/T}$, for the Reactions of OH Radicals with *O,O*-Diethyl Methylphosphonothioate (DEMPT) and *O,O,O*-Triethyl Phosphorothioate (TEPT), and Literature Data for Diethyl Methylphosphonate (DEMP) and Triethyl Phosphate (TEP)

reactant	A (cm^3 molecule^{-1} s^{-1})[a]	B[a,b] (K)	$10^{11} \times k$(298 K)[c] (cm^3 molecule^{-1} s^{-1})
$(C_2H_5O)_2P(S)CH_3$ (DEMPT)[d]	1.08×10^{-11}	-871 ± 25	20.1
$(C_2H_5O)_3PS$ (TEPT)[d]	8.21×10^{-13}	-1353 ± 49	7.69
$(C_2H_5O)_2P(O)CH_3$ (DEMP)[e]	4.20×10^{-13}	-1456 ± 227	5.56
$(C_2H_5O)_3PO$ (TEP)[e]	4.29×10^{-13}	-1428 ± 219	5.17

[a] From least-squares analysis of rate constants measured relative to those for α-pinene, using k_2(α-pinene) = $1.21 \times 10^{-11}\, e^{436/T}$ cm^3 molecule^{-1} s^{-1}.[1] [b] Indicated errors are two least-squares standard deviations. Estimated overall uncertainties in B are ±400 K. [c] Calculated from Arrhenius expression. Estimated overall uncertainties are ±12%. [d] This work. [e] From Aschmann et al.[13]

from DEMPT and 56 ± 9% for formation of TEP from TEPT, where the indicated errors are two weighted standard deviations combined with estimated overall uncertainties in the GC-FID response factors for DEMP, DEMPT, TEP, and TEPT of ±10% each.

Discussion

The rate constants measured here for the reactions of OH radicals, NO_3 radicals, and O_3 with DEMPT and TEPT are the first reported for these compounds. The observed lack of reaction with O_3 is consistent with previous data for the reactions of O_3 with $(CH_3O)_3PS$ and $(CH_3O)_2P(S)SCH_3$.[5] As shown in Table 5, the room temperature rate constants measured here for the reactions of NO_3 radicals with DEMPT and TEPT are higher by factors of 6 and 4 than those for the reactions of NO_3 radicals with DEMP and TEP, respectively,[9] and are consistent with the upper limits to the room temperature rate constants previously measured for $(CH_3O)_3PS$ and $(CH_3O)_2P(S)SCH_3$.[5] The increased reactivity of DEMPT and TEPT compared to DEMP and TEP toward reaction with the NO_3 radical suggests that reaction at the P=S bond is important, consistent with the observed formation of DEMP from DEMPT and of TEP from TEPT in 62 ± 11% and 78 ± 15% yields, respectively, at 296 ± 2 K (Table 4).

At room temperature, DEMPT and TEPT are also more reactive toward the OH radical than are DEMP and TEP by factors of 3.6 and 1.5, respectively (Table 5), and this is consistent with the increased reactivity of $(CH_3O)_3PS$ and $(CH_3O)_2P(S)SCH_3$ compared to $(CH_3O)_3PO$, $(CH_3O)_2P(O)SCH_3$, and $(CH_3S)_2P(O)OCH_3$ (Table 5). This increase in OH radical reaction rate constants in compounds containing P=S bonds compared to the corresponding compounds containing P=O bonds indicates a reaction pathway involving the P=S bond,[5] and this is confirmed by the formation of DEMP from DEMPT (in 21 ± 4% yield, independent of temperature over the range 296−348 K), TEP from TEPT (in 56 ± 9% yield, independent of temperature over the range 296−348 K), $(CH_3O)_3PO$ from $(CH_3O)_3PS$ (in 28 ± 4% yield at 296 ± 2 K),[14] and $(CH_3O)_2P(O)SCH_3$ from $(CH_3O)_2P(S)SCH_3$ (in 13 ± 5% yield at 296 ± 2 K).[14] Interestingly, the partial rate constants at room temperature for the formation of DEMP from DEMPT [$(4.1 \pm 0.7) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}] and of TEP from TEPT [$(4.3 \pm 0.6) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}] are essentially identical, suggesting that interaction of the OH radical with the P=S group occurs at the same rate in both DEMPT and TEPT.

The OH radical reaction rate constants measured here (Table 1) are plotted in Arrhenius form in Figure 6. Good straight-line plots are observed, and least-squares analyses leads to the Arrhenius parameters listed in Table 6, which show that the values of B in $k = Ae^{-B/T}$ for DEMPT and TEPT are highly negative. Furthermore, the value of B for TEPT is similar to those for DEMP and TEP (and dimethyl methylphosphonate, dimethyl ethylphosphonate, and diethyl ethylphosphonate).[13] Analogous to the corresponding reactions of OH radicals with TEP, DEMP, and other alkyl phosphonates, the magnitude of the rate constants for the OH radical reactions with DEMPT and TEPT (Tables 1 and 6) and the highly negative values of B suggest that these reactions proceed by initial complex formation (possibly a hydrogen-bonded complex), followed by decomposition to either reactants or products. For example, for TEPT

$$OH + (C_2H_5O)_3PS \leftrightarrow [HO{-}(C_2H_5O)_3PS] \rightarrow \text{products} \qquad (4)$$

with back-decomposition of the $[HO{-}(C_2H_5O)_3PS]$ complex to reactants having a higher barrier than decomposition(s) to products to account for the negative temperature dependence.[18]

The formation of DEMP from DEMPT and of TEP from TEPT in less than 100% yields shows that other products are formed from both the OH radical and NO_3 radical reactions. The identification of products from the OH radical-initiated reactions using in situ atmospheric pressure ionization mass spectrometry and Fourier transform infrared spectroscopy will be reported elsewhere,[19] with the possible reaction mechanisms also being presented and discussed.[19]

Atmospheric Implications. As evident from the rate constants measured in this work for $(C_2H_5O)_3PS$ and $(C_2H_5O)_2P(S)CH_3$ and previously for $(CH_3O)_3PS$ and $(CH_3O)_2P(S)SCH_3$,[5] the alkyl phosphorothioates and phosphonothioates containing a P=S bond are highly reactive toward OH radicals, but react only slowly with NO_3 radicals and O_3. Combining the rate constants measured here for $(C_2H_5O)_3PS$ and $(C_2H_5O)_2P(S)CH_3$ with an average 12-h daytime concentration of OH radicals of 2.0×10^6 molecules cm^{-3},[20] an average 12-h nighttime concentration of NO_3 radicals of 5×10^8 molecules cm^{-3},[21] and a 24-h average concentration of O_3 of 7×10^{11} molecules cm^{-3},[22] leads to calculated lifetimes due to reactions with OH radicals, NO_3 radicals, and O_3 of 0.7−1.8 h, 23−45 days, and >275 days, respectively. In the gas phase, therefore, these compounds will have short atmospheric lifetimes due to reaction with OH radicals, with these reactions forming, in part, the corresponding oxon. Ambient measurements of parathion and methyl parathion and their oxon derivatives paraoxon and methyl paraoxon appear to be consistent with these expectations,[23−25] although oxidation of parathion and methyl parathion on surfaces cannot be ruled out.[19]

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References and Notes

(1) Atkinson, R.; Arey, J. *Chem. Rev.* **2003**, *103*, 4605.

(2) Toy, A. D.; Walsh, E. N. *Phosphorus Compounds in Everyday Living*; American Chemical Society: Washington, DC, 1987.

(3) *The Pesticide Manual*, 9th ed.; Worthing, C. R., Hance, R. J., Eds.; British Crop Protection Council: Farnham, U.K., 1991.

(4) Tuazon, E. C.; Atkinson, R.; Aschmann, S. M.; Arey, J.; Winer, A. M.; Pitts, J. N., Jr. *Environ. Sci. Technol.* **1986**, *20*, 1043.

(5) Goodman, M. A.; Aschmann, S. M.; Atkinson, R.; Winer, A. M. *Arch. Environ. Contam. Toxicol.* **1988**, *17*, 281.

(6) Atkinson, R.; Aschmann, S. M.; Goodman, M. A.; Winer, A. M. *Int. J. Chem. Kinet.* **1988**, *20*, 273.

(7) Kleindienst, T. E.; Smith, D. F. *Chemical Degradation in the Atmosphere*, Final Report on *The Atmospheric Chemistry of Three Important Volatile Chemical Precursors* to Applied Research Associates, Inc.; U.S. Air Force Contract No. F08635-93-C-0020; Armstrong Laboratory Environics Directorate, Tyndall AFB, FL, Sept 1996.

(8) Martin, P.; Tuazon, E. C.; Atkinson, R.; Maughan, A. D. *J. Phys. Chem. A* **2002**, *106*, 1542.

(9) Aschmann, S. M.; Tuazon, E. C.; Atkinson, R. *J. Phys. Chem. A* **2005**, *109*, 2282.

(10) Sun, F.; Zhu, T.: Shang, J.; Han, L. *Int. J. Chem. Kinet.* **2005**, *37*, 755.

(11) Aschmann, S. M.; Tuazon, E. C.; Atkinson, R. *J. Phys. Chem. A* **2005**, *109*, 11828.

(12) Feigenbrugel, V.; Le Person, A.; Le Calvé, S.; Mellouki, A.; Muñoz, A.; Wirtz, K. *Environ. Sci. Technol.* **2006**, *40*, 850.

(13) Aschmann, S. M.; Long, W. D.; Atkinson, R. *J. Phys. Chem. A* **2006**, *110*, 7393.

(14) Atkinson, R.; Aschmann, S. M.; Arey, J.; McElroy, P. A.; Winer, A. M. *Environ. Sci. Technol.* **1989**, *23*, 243.

(15) Atkinson, R.; Plum, C. N.; Carter, W. P. L.; Winer, A. M.; Pitts, J. N., Jr. *J. Phys. Chem.* **1984**, *88*, 1210.

(16) IUPAC. http://www.iupac-kinetic.ch.cam.ac.uk/ (2006).

(17) Atkinson, R.; Aschmann, S. M.; Carter, W. P. L.; Winer, A. M.; Pitts, J. N., Jr. *J. Phys. Chem.* **1982**, *86*, 4563.

(18) Donahue, N. M. *Chem. Rev.* **2003**, *103*, 4593.

(19) Tuazon, E. C.; Aschmann, S. M.; Atkinson, R. Unpublished data; to be submitted for publication.

(20) Prinn, R. G.; Huang, J.; Weiss, R. F.; Cunnold, D. M.; Fraser, P. J.; Simmonds, P. G.; McCulloch, A.; Harth, C.; Salameh, P.; O'Doherty, S.; Wang, R. H. J.; Porter, L.; Miller, B. R. *Science* **2001**, *292*, 1882.

(21) Atkinson, R. *J. Phys. Chem. Ref. Data* **1991**, *20*, 459.

(22) Logan, J. A. *J. Geophys. Res.* **1985**, *90*, 10463.

(23) Woodrow, J. E.; Seiber, J. N.; Crosby, D. G.; Moilanen, K. W.; Soderquist, C. J.; Mourer, C. *Arch. Environ. Contam. Toxicol.* **1977**, *6*, 175.

(24) Woodrow, J. E.; Crosby, D. G.; Mast, T.; Moilanen, K. W.; Seiber, J. N. *J. Agric. Food Chem.* **1978**, *26*, 1312.

(25) Seiber, J. N.; McChesney, M. M.; Woodrow, J. E. *Environ. Toxicol. Chem.* **1989**, *8*, 577.