Atmospheric Chemistry of Dimethyl Phosphonate, Dimethyl Methylphosphonate, and Dimethyl Ethylphosphonate

Sara M. Aschmann, Ernesto C. Tuazon, and Roger Atkinson*,†

Air Pollution Research Center, University of California, Riverside, California 92521

Received: September 17, 2005; In Final Form: October 25, 2005

Rate constants for the reactions of OH radicals and NO_3 radicals with dimethyl phosphonate [DMHP, $(CH_3O)_2P(O)H$], dimethyl methylphosphonate [DMMP, $(CH_3O)_2P(O)CH_3$], and dimethyl ethylphosphonate [DMEP, $(CH_3O)_2P(O)C_2H_5$] have been measured at 296 ± 2 K and atmospheric pressure using relative rate methods. The rate constants obtained for the OH radical reactions (in units of 10^{-12} cm^3 $molecule^{-1}$ s^{-1}) were as follows: DMHP, 4.83 ± 0.25; DMMP, 10.4 ± 0.6; and DMEP, 17.0 ± 1.0, with a deuterium isotope effect of $k(OH + DMMP)/k(OH + DMMP\text{-}d_9) = 4.8 \pm 1.2$. The rate constants obtained for the NO_3 radical reactions (in units of 10^{-16} cm^3 $molecule^{-1}$ s^{-1}) were as follows: DMHP, <1.4; DMMP, 2.0 ± 1.0; and DMEP, 3.4 ± 1.4. Upper limits to the rate constants for the O_3 reactions of $<8 \times 10^{-20}$ cm^3 $molecule^{-1}$ s^{-1} for DMHP and $<6 \times 10^{-20}$ cm^3 $molecule^{-1}$ s^{-1} for DMMP and DMEP were determined. Products of the reactions of OH radicals with DMHP, DMMP, and DMEP were investigated in situ using atmospheric pressure ionization mass spectrometry (API-MS) and, for the DMMP and DMEP reactions, Fourier transform infrared (FT-IR) spectroscopy. API-MS analyses showed the formation of products of molecular weight 96 and 126, attributed to $CH_3OP(O)(H)OH$ and $(CH_3O)_2P(O)OH$, respectively, from DMHP; of molecular weight 110, attributed to $CH_3OP(O)(CH_3)OH$, from DMMP; and of molecular weight 124 and 126, attributed to $CH_3OP(O)(C_2H_5)OH$ and $(CH_3O)_2P(O)OH$, respectively, from DMEP. FT-IR analyses showed formation (values given are % molar yields) of the following: from DMMP, CO, 54 ± 6; CO_2, 5 ± 1 in dry air; HCHO, 3.9 ± 0.7; HC(O)OH, <1.4 in dry air; $RONO_2$, ~4; and formate ester, ~8; and from DMEP, CO, 50 ± 7; CO_2, 11 ± 4; CH_3CHO, 18 ± 8; HCHO, <7; HC(O)OH, <6; $RONO_2$, ≤5; and formate ester, 5.0 ± 1.5. Possible reaction mechanisms are discussed.

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 [$(RO)_3PO$] and alkyl phosphonates [$[(RO)_2P(O)R]$, where R = aryl or alkyl], are used as plasticizers, flame retardants, and fire-resistant fluids and lubricants, and organophosphorus compounds of structures $(RO)_{3-x}P(O)R_x$ and $(RO)_{3-x}P(S)R_x$ are widely used as 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 several simple "model" alkyl phosphates, alkyl phosphorothioates, and alkyl phosphonates of structures $(RO)_nP(O)(SR)_{3-n}$, $(RO)_nP(S)(SR)_{3-n}$, and $(RO)_2P(O)X$ (R = CH_3 or C_2H_5 and X = H, CH_3, and C_2H_5) have been studied.[4−9] In this work, we have extended our previous study of the atmospheric chemistry of diethyl methylphosphonate [$(C_2H_5O)_2P(O)CH_3$], diethyl ethylphosphonate [$(C_2H_5O)_2P(O)C_2H_5$], and triethyl phosphate [$(C_2H_5O)_3PO$] to measure rate constants for the gas-phase reactions of OH radicals, NO_3 radicals, and O_3 with dimethyl phosphonate [DMHP, $(CH_3O)_2P(O)H$], dimethyl methylphosphonate [DMMP, $(CH_3O)_2P(O)CH_3$], and dimethyl ethylphosphonate [DMEP, $(CH_3O)_2P(O)C_2H_5$] and investigate the products of the atmospherically dominant OH radical reactions. Additionally, the rate constant for the reaction of OH radicals with fully deuterated dimethyl methylphosphonate [DMMP-d_9, $(CD_3O)_2P(O)CD_3$] was measured.

Experimental Methods

Most experiments were carried out at 296 ± 2 K and 740 Torr total pressure of purified air at ~5% relative humidity in two ~7000 L volume Teflon chambers, each equipped with two parallel banks of black lamps for irradiation and a Teflon-coated fan to ensure rapid mixing of reactants during their introduction into the chamber. One of the Teflon chambers was interfaced to a PE SCIEX API III MS/MS direct air sampling, atmospheric pressure ionization tandem mass spectrometer (API-MS). Experiments utilizing in situ Fourier transform infrared (FT-IR) spectroscopy were carried out at 298 ± 2 K and 740 Torr total pressure of synthetic air (80% N_2 + 20% O_2) in a 5870 L Teflon-coated, evacuable chamber equipped with a multiple reflection optical system interfaced to a Mattson Galaxy 5020 FT-IR spectrometer.[8,9] Irradiation was provided by a 24-kW xenon arc lamp, with the light being filtered through a 6-mm thick Pyrex pane to remove wavelengths <300 nm. IR spectra were recorded with 32 scans per spectrum (corresponding to a 1.2 min averaging time) at a full-width-at-half-maximum resolution of 0.7 cm^{-1} and a path length of 62.9 m.

Kinetic Studies. Rate constants for the reactions of OH and NO_3 radicals with DMHP, DMMP, and DMEP, and for the reaction of OH radicals with DMMP-d_9, were measured using

---

* To whom correspondence should be addressed. E-mail: ratkins@mail.ucr.edu. Tel: (951) 827-4191.

† Also Department of Environmental Sciences and Department of Chemistry.

10.1021/jp055286e CCC: $30.25

relative rate techniques in which the concentrations of the organophosphorus compound 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[5,9]

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

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

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

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

where $[\text{organophosphorus}]_{t_o}$ and $[\text{reference compound}]_{t_o}$ are the concentrations of the organophosphorus compound 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 $D_t = 0.0014$ per N_2O_5 addition to the 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.[5,9] The initial reactant concentrations (molecule cm^{-3}) employed for the OH radical reactions were CH_3ONO, $\sim 2.4 \times 10^{14}$; NO, $\sim 2.4 \times 10^{14}$; and organophosphorus compound and reference compound, $\sim 2.4 \times 10^{13}$ each. The reference compounds used were *n*-octane (DMHP) and *n*-decane (DMMP, DMMP-d_9, and DMEP), and irradiations were carried out at 20% of the maximum light intensity for 10−55 min (DMHP), 10−45 min (DMMP), 10−60 min (DMMP-d_9), and 5−37 min (DMEP). Experiments were also conducted to investigate the importance of dark decay and photolysis of $\sim 2.4 \times 10^{13}$ molecule cm^{-3} of DMHP, DMMP, and DMEP in the chamber, with 3.2×10^{15} molecule cm^{-3} of cyclohexane also being present in the photolysis experiments to scavenge any OH radicals formed.

Nitrate radicals were produced from the thermal decomposition of N_2O_5,[5,9,10] and NO_2 was also included in the reactant mixtures. The initial reactant concentrations (molecule cm^{-3}) were as follows: DMHP, DMMP, or DMEP and methacrolein (the reference compound), $\sim 2.4 \times 10^{13}$ each; and NO_2, $(2.4-4.8) \times 10^{13}$, and two additions of N_2O_5 (each addition corresponding to $(0.9-1.4) \times 10^{14}$ molecule 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). For the analyses of *n*-octane, *n*-decane, methacrolein, DMHP, DMMP, DMMP-d_9, DMEP, and acetaldehyde (see below), 100 cm^3 volume gas samples were collected from the chamber onto Tenax-TA solid adsorbent, with subsequent thermal desorption at ~250 °C onto a 30 m DB-1701 megabore column held at −40 °C or 0 °C and then temperature programmed to 200 °C at 8 °C min^{-1}. On the basis of replicate analyses in the chamber in the dark, the analytical uncertainties for the organophosphorus compounds and the reference compounds used were typically ≤3%.

The rate constants, or upper limits thereof, for the reactions of DMHP, DMMP, and DMEP with O_3 were determined by monitoring the decay of the organophosphorus compound in the presence of a known concentration of O_3,[9] with cyclohexane being present to scavenge any OH radicals formed.[9] Assuming that under these conditions the only loss process for DMHP, DMMP, or DMEP is by reaction with O_3, then

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

where $[\text{organophosphorus}]_{t_o}$ and $[\text{organophosphorus}]_t$ are the concentrations of DMHP, DMMP, or DMEP at times t_o and t, respectively, D_t (= 0.0027) is the small amount of dilution caused by the initial addition of O_3 to the chamber, and k_3 is the rate constant for reaction 3

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

The initial reactant concentrations (molecule cm^{-3}) were as follows: DMHP, DMMP, or DMEP, $\sim 2.4 \times 10^{13}$; O_3, 4.90×10^{13}; and cyclohexane, 3.2×10^{15}. O_3 concentrations were measured during the 5.05 h duration reaction by ultraviolet absorption using a Dasibi Model 1003-AH ozone analyzer, and the concentrations of DMHP, DMMP, and DMEP were measured by GC-FID as described above.

Products of the OH Radical Reactions. Experiments with API-MS Analyses. In these experiments, the chamber contents were sampled through a 25 mm diameter × 75 cm length Pyrex tube at ~20 L min^{-1} directly into the API mass spectrometer source. The operation of the API-MS in the MS (scanning) and MS/MS (with collision activated dissociation (CAD)) modes has been described previously.[11,12] Use of the MS/MS mode with CAD allows the "product ion" or "precursor ion" spectrum of a given ion peak observed in the MS scanning mode to be obtained.[11] Both positive and negative ion modes were used in this work, with the majority of the data obtained being in the negative ion mode. In the positive ion mode, protonated water hydrates ($H_3O^+(H_2O)_n$) generated by the corona discharge in the chamber diluent air were responsible for the protonation of analytes. Ions are drawn by an electric potential from the ion source through the sampling orifice into the mass-analyzing first quadrupole or third quadrupole. Neutral molecules and particles are prevented from entering the orifice by a flow of high-purity nitrogen ("curtain gas"), and as a result of the declustering action of the curtain gas on the hydrated ions, the ions that are mass analyzed are mainly protonated molecular ions ($[M + H]^+$) and their protonated homo- and heterodimers.[11]

In the negative ion mode, negative ions are generated by the negative corona around the discharge needle. The superoxide ion (O_2^-), its hydrates, and O_2 clusters are the major negative ions in the chamber diluent air. Other reagent ions, for example, NO_2^- and NO_3^-, are then formed from reactions between the primary reagent ions and neutral molecules such as NO_2, and instrument tuning and operation were designed to induce cluster formation.[12] The initial concentrations of CH_3ONO and NO, and of DMHP, DMMP, or DMEP, were $\sim 2.4 \times 10^{13}$ molecule cm^{-3} each, and irradiations were carried out for 10 min (DMHP), 5 min (DMMP), and 3 min (DMEP), resulting in ~17% reaction of the initially present DMHP, DMMP, or DMEP.

Experiments with FT-IR Analyses. Irradiations of CH_3ONO (or $(CH_3)_2CHONO$)−NO−air mixtures of DMMP and DMEP were carried out in the evacuable chamber, with analyses by in situ FT-IR spectroscopy. To investigate the formation of HCHO, the photolysis of 2-propyl nitrite[8,9] was used as the OH radical source in certain experiments (photolysis of methyl nitrite forms HCHO, while photolysis of 2-propyl nitrite leads to acetone formation[8,13]). Irradiations were carried out in dry air ($\ll$1% relative humidity (RH)) and (for DMMP) in air with 5% relative humidity. The initial reactant concentrations (in units of 10^{13} molecule cm^{-3}) were as follows: CH_3ONO, 24.6 or $(CH_3)_2CHONO$, 19.7; NO, 24.6; and DMMP, 9.18−11.4 or DMEP, 17.2. The first experiment was carried out with intermittent irradiation of a CH_3ONO−NO−DMMP−air mixture, with individual irradiation periods of 1−13 min each and with IR spectra being recorded during the intervening dark periods. Succeeding experiments were carried out with continuous irradiation. Total irradiation periods ranged from 41 to 84 min.

Chemicals. The chemicals used, and their stated purities, were: *n*-decane (99+%), dimethyl phosphonate (the catalog name is dimethyl phosphite) (98%), dimethyl methylphosphonate (97%), methacrolein (95%), and *n*-octane (99+%), Aldrich Chemical Co.; dimethyl ethylphosphonate (98%), Cerilliant Corporation; and NO ($\geq$99.0%), Matheson Gas Products. A sample of dimethyl methylphosphonate-d_9 was kindly donated by the Midwest Research Institute. Methyl nitrite, 2-propyl nitrite, and N_2O_5 were prepared and stored as described previously,[8,10,13,14] 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 decay of DMMP (<4%) was observed in a ~7000 L Teflon chamber in the dark over a period of 4.0 h, and no decays (<2% for DMHP and <4% for DMMP and DMEP) of gas-phase DMHP, DMMP, or DMEP were observed during 60 min of photolysis using the same light intensity and spectral distribution as used in the OH radical rate constant determinations in the same chamber (the total duration of the photolysis experiment was 3.7 h). These results show that dark losses of DMHP, DMMP, and DMEP to the walls of the Teflon chamber were of negligible importance during all experiments and that any photolysis of DMHP, DMMP, and DMEP over the $\leq$55 min irradiations of CH_3ONO−NO−organophosphorus compound−reference compound−air mixtures was also negligible.

Rate Constants for the Reactions of OH Radicals with DMHP, DMMP, DMMP-*d*$_9$, and DMEP. A series of CH_3ONO−NO−organophosphorus compound−reference compound−air irradiations were carried out in the ~7000 L Teflon chamber, with *n*-octane (DMHP) and *n*-decane (DMMP, DMMP-d_9, and DMEP) as the reference compounds. The data obtained are plotted in accordance with eq I in Figures 1 and 2, and the rate constant ratios k_1/k_2 obtained from least squares analyses of the data are given in Table 1. These rate constant ratios k_1/k_2 are placed on an absolute basis by use of rate constants k_2 for the reactions of OH radicals with *n*-octane and *n*-decane at 296 K of 8.07×10^{-12} cm^3 $molecule^{-1}$ s^{-1} and 1.09×10^{-11} cm^3 $molecule^{-1}$ s^{-1}, respectively,[1] and the resulting rate constants k_1 are given in Table 1. The rate constant ratios determined for the reactions of OH radicals with DMMP and DMMP-d_9 relative to that for *n*-decane (Table 1) lead to the deuterium isotope effect of

$$k(\mathrm{OH} + \mathrm{DMMP})/k(\mathrm{OH} + \mathrm{DMMP}\text{-}d_9) = 4.8 \pm 1.2 \text{ at } 296 \pm 2 \text{ K}$$

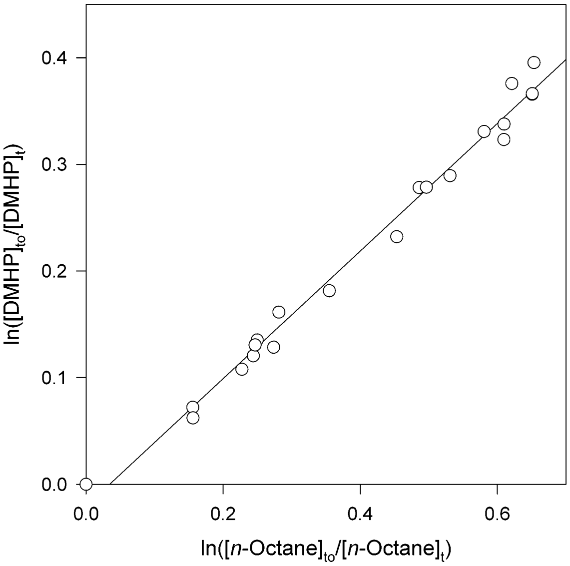

Figure 1. Plot of eq I for the reactions of OH radicals with dimethyl phosphonate (DMHP), with *n*-octane as the reference compound.

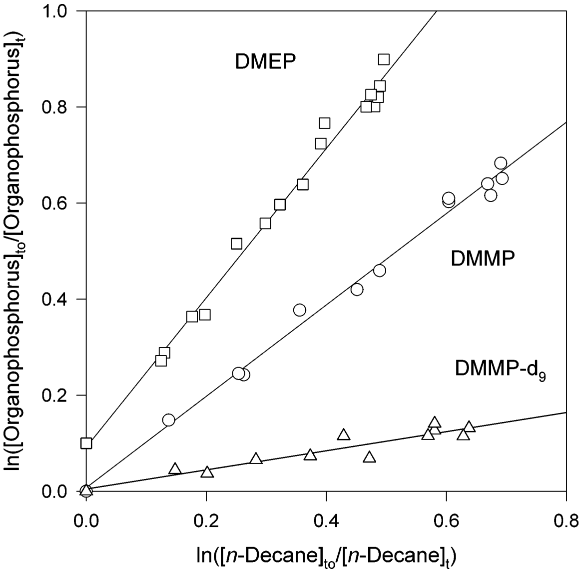

Figure 2. Plots of eq I for the reactions of OH radicals with dimethyl methylphosphonate (DMMP), dimethyl methylphosphonate-d_9 (DMMP-d_9), and dimethyl ethylphosphonate (DMEP), with *n*-decane as the reference compound. The data for DMEP have been displaced vertically by 0.10 units for clarity.

Rate Constants for the Reactions of NO_3 Radicals with DMHP, DMMP, and DMEP. Reactions of N_2O_5−NO_3−NO_2−organophosphorus compound−methacrolein−air mixtures were carried out in the same Teflon chamber as used for the OH radical rate constant determinations. The percentage losses of the organophosphorus compound were significantly less than those of methacrolein, with maximum reactive losses of DMHP, DMMP, and DMEP at the end of the reactions being zero for DMHP (within the analytical uncertainties of ±2−3%), 10% for DMMP, and 17% for DMEP, compared to up to 79% for methacrolein. Least-squares analyses of the data obtained lead to the rate constant ratios k_1/k_2 given in Table 2, where the upper limit rate constant ratio for DMHP assumes an upper limit of 5% reaction of DMHP. These rate constant ratios (or upper limits thereof) are placed on an absolute basis by use of a rate constant at 296 K for the NO_3 radical reaction with methacrolein of 3.4×10^{-15} cm^3 $molecule^{-1}$ s^{-1},[1,15] and the resulting rate constants k_1 are also given in Table 2.

TABLE 1: Rate Constant Ratios k_1/k_2 and Rate Constants k_1 for the Reactions of OH Radicals with DMHP, DMMP, and DMEP at 296 ± 2 K

organophosphorus compound	reference compound	k_1/k_2 [a]	$10^{12} \times k_1$ (cm^3 molecule^{-1} s^{-1})[b]
dimethyl phosphonate (DMHP)	*n*-octane	0.598 ± 0.030	4.83 ± 0.25
dimethyl methylphosphonate (DMMP)	*n*-decane	0.951 ± 0.052	10.4 ± 0.6
dimethyl methylphosphonate-d_9 (DMMP-d_9)	*n*-decane	0.199 ± 0.046	2.17 ± 0.51
dimethyl ethylphosphonate (DMEP)	*n*-decane	1.56 ± 0.09	17.0 ± 1.0

[a] Indicated errors are two least-squares standard deviations. [b] Placed on an absolute basis by use of rate constants at 296 K of k_2(*n*-octane) = 8.07 × 10^{-12} cm^3 molecule^{-1} s^{-1} and k_2(*n*-decane) = 1.09 × 10^{-11} cm^3 molecule^{-1} s^{-1}.[1]

TABLE 2: Rate Constant Ratios k_1/k_2 and Rate Constants k_1 for the Reactions of NO_3 radicals with DMHP, DMMP, and DMEP at 296 ± 2 K

organophosphorus compound	k_1/k_2 [a]	$10^{16} \times k_1$ (cm^3 molecule^{-1} s^{-1})[b]
dimethyl phosphonate (DMHP)	<0.04	<1.4
dimethyl methylphosphonate (DMMP)	0.06 ± 0.03	2.0 ± 1.0
dimethyl ethylphosphonate (DMEP)	0.10 ± 0.04	3.4 ± 1.4

[a] Relative to the reaction of NO_3 radicals with methacrolein. The indicated errors are two least-squares standard deviations. [b] Placed on an absolute basis by use of a rate constant at 296 K of k_2(methacrolein) = 3.4 × 10^{-15} cm^3 molecule^{-1} s^{-1}.[1,15]

Rate Constants for Reactions of O_3 with DMHP, DMMP, and DMEP. No decays of gas-phase DMHP, DMMP, or DMEP were evident in the ~7000 L Teflon chamber in the presence of 4.90 × 10^{13} molecule cm^{-3} of O_3 over a 303 min reaction period. Use of upper limits of 5% for the amounts of DMMP and DMEP reacted and of an upper limit of 7% for the amount of DMHP reacted over this time period results in upper limits to the rate constants for reaction of O_3 with DMHP, DMMP, and DMEP at 296 ± 2 K of

$$k_3(\text{DMHP}) < 8 \times 10^{-20}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

and

$$k_3(\text{DMMP})\ \text{and}\ k_3(\text{DMEP}) < 6 \times 10^{-20}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

The higher upper limit rate constant for DMHP arises because the total spread in the measured DMHP concentrations was 7% during the experiment, although the DMHP concentration at the end of the experiment was within 1% of the DMHP concentration before the addition of O_3.

Products of the Reaction of OH Radicals with DMHP, DMMP, and DMEP by API-MS Analyses. Irradiations of $CH_3ONO-NO-$DMHP, DMMP, or DMEP−air mixtures were carried out in a second ~7000 L Teflon chamber at ~5% relative humidity with analyses by in situ API-MS, using both positive and negative ion modes.

DMHP, $(CH_3O)_2P(O)H$, Reaction. In the positive ion mode, prior to the reaction, ion peaks at 111, 129, 221, and 349 u were observed, these being due to protonated DMHP, a water adduct of protonated DMHP, the protonated DMHP dimer, and a water adduct of the protonated trimer of DMHP, respectively. After the reaction, additional ion peaks at 317, 333, and 347 u were present, and API-MS/MS "product ion" spectra of these showed them to be heterotrimers involving molecular weight 96 and 126 products, with assignments of the following: 317 u, $[\text{DMHP} + \text{DMHP} + 96 + \text{H}]^+$; 333 u, $[\text{DMHP} + 126 + 96 + \text{H}]^+$; and 347 u, $[\text{DMHP} + \text{DMHP} + 126 + \text{H}]^+$. The positive ion API-MS and API-MS/MS spectra were essentially identical to those observed in our previous API-MS study of this reaction using only the positive ion mode for analyses[8] and so is the interpretation.

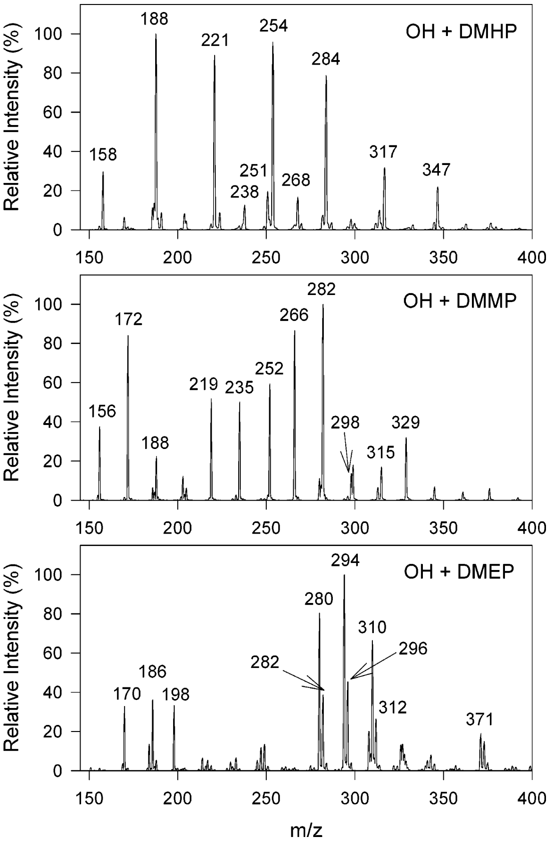

Figure 3. Negative ion API-MS spectra of irradiated $CH_3ONO-NO-$dimethyl phosphonate−air, $CH_3ONO-NO-$dimethyl methylphosphonate−air, and $CH_3ONO-NO-$dimethyl ethylphosphonate−air mixtures after 1 min of irradiation (see text for ion peak assignments).

In the negative ion mode, weak ion peaks were observed prior to reaction which appeared to be due to NO, NO_2, and O_2 adducts of DMHP. After reaction, these ion peaks were very weak, and a series of ion peaks due to reaction products were observed in the API-MS spectra (Figure 3, top panel). API-MS/MS product ion and precursor ion spectra were obtained which indicated that the ion peaks shown in Figure 3 (top) were due to O_2^-, NO_2^-, and NO_3^- adducts of products of molecular weight 96 and 126, with assignments of 158 u, $[126 + O_2]^-$; 188 u, $[126 + NO_3]^-$; 221 u, $[126 + 96 - H]^-$; 238 u, $[96 + 96 + NO_2]^-$; 251 u, $[126 + 126 - H]^-$; 254 u, $[96 + 126 + O_2]^-$; 268 u, $[126 + 96 + NO_2]^-$; 284 u, $[126 + 96 + NO_3]^-$; 317 u, $[126 + 96 + 96 - H]^-$; and 347 u, $[126 + 126 + 96 - H]^-$. Representative examples of the API-MS/MS product ion spectra of the 238 and 268 u ion peaks observed in the API-MS spectra are shown in Figure 4. The API-MS/MS spectra of the 251 u and of the weak 298 u (shown to be $[126 + 126 + NO_2]^-$) ion peaks were identical to those observed when dimethyl phosphate $[(CH_3O)_2P(O)OH]$ was introduced into the clean chamber in the presence of NO_x, indicating that, as

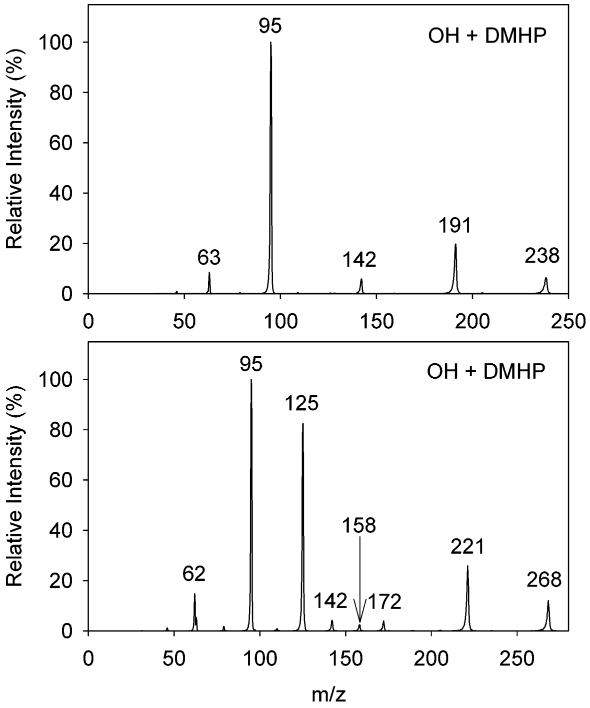

Figure 4. Negative ion API-MS/MS "product ion" spectra of the 238 and 268 u ion peaks present in the API-MS spectra of the reacted DMHP mixture shown in Figure 3. The 238 and 268 u ion peaks are, respectively, attributed to $[96 + 96 + NO_2]^-$ (note the losses of 47 (HNO_2) and 96 u) and $[96 + 126 + NO_2]^-$ (note the losses of 47 (HNO_2), 96, and 126 u).

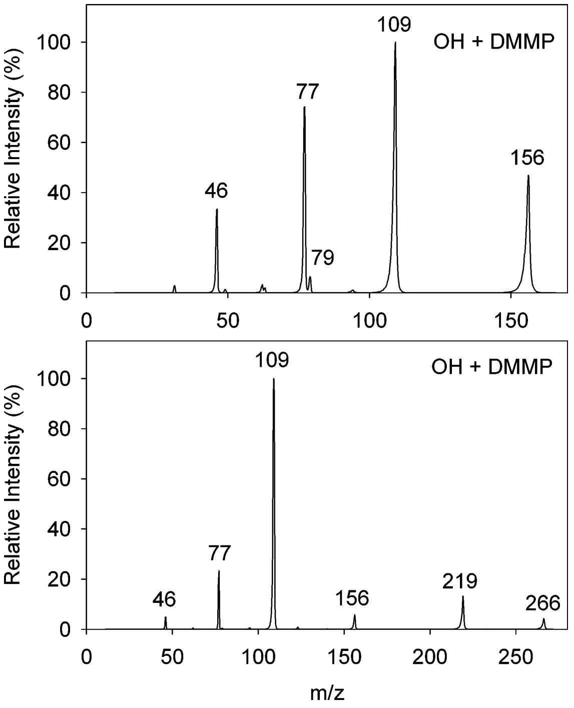

Figure 5. Negative ion API-MS/MS "product ion" spectra of the 156 and 266 u ion peaks present in the API-MS spectra of the reacted DMMP mixture shown in Figure 3. The 156 and 266 u ion peaks are, respectively, attributed to $[110 + NO_2]^-$ (note the loss of 47 u, HNO_2) and $[110 + 110 + NO_2]^-$ (note the losses of 47 (HNO_2) and 110 u).

concluded earlier,[8] dimethyl phosphate is the molecular weight 126 product. Consistent with our previous study,[8] the molecular weight 96 product is attributed to $CH_3OP(O)(H)OH$.

DMMP, $(CH_3O)_2P(O)CH_3$, Reaction. In the positive ion mode, prior to the reaction, ion peaks at 125, 143, 249 (strong), and 391 u were observed, these being due to protonated DMMP, a water adduct of protonated DMMP, the protonated DMMP dimer, and the protonated trimer of DMMP, respectively. After the reaction, additional ion peaks at 345 and 359 u were present, and API-MS/MS "product ion" spectra of these showed them to be heterotrimers involving a molecular weight 110 product, with the assignments: 345 u, $[DMMP + 110 + 110 + H]^+$ and 359 u, $[DMMP + DMMP + 110 + H]^+$.

In the negative ion mode, no ion peaks due to DMMP were observed. After the reaction, ion peaks due to reaction products were observed as shown in Figure 3 (middle panel). API-MS/MS product ion and precursor ion spectra were obtained which indicated that the ion peaks shown in Figure 3 (middle panel) were due to O_2^-, NO_2^-, and NO_3^- adducts of a product of molecular weight 110, with the assignments: 156 u, $[110 + NO_2]^-$; 172 u, $[110 + NO_3]^-$; 188 u, $[110 + NO_2 + O_2]$ and/or $[126 + NO_3]^-$; 219 u, $[110 + 110 - H]^-$ and/or $[110 + NO_2 + HNO_3]^-$; 235 u, $[110 + NO_3 + HNO_3]^-$; 252 u, $[110 + 110 + O_2]^-$; 266 u, $[110 + 110 + NO_2]^-$; 282 u, $[110 + 110 + NO_3]^-$; 298 u, $[110 + 110 + NO_2 + O_2]^-$; 315 u, $[110 + 110 + HO_2 + NO_3]^-$; and 329 u, $[110 + 110 + 110 - H]^-$. Representative examples of the API-MS/MS product ion spectra of the 156 and 266 u ion peaks observed in the API-MS spectra are shown in Figure 5.

The positive and negative ion mode data show that a product of molecular weight 110 is formed, and the negative ion mode data may also be slightly suggestive of a product of molecular weight 126. The product of molecular weight 110 is attributed to $CH_3OP(O)(CH_3)OH$, and the possible molecular weight 126 product would likely be $(CH_3O)_2P(O)OH$ (dimethyl phosphate). However, no ion peak at 251 u ($[126 + 126 - H]^-$) was observed from the OH radical-initiated reaction of DMMP (Figure 3, middle panel), and the API-MS/MS spectrum of the 298 u ion peak differed significantly (having different fragment ions) from the 298 u ion peak of a standard of dimethyl phosphate introduced into the chamber in the presence of NO_x (see above) and from the 298 u ion peak observed in the OH radical-initiated reaction of DMHP reaction (see above). This suggests that the assignment of the 188 u ion peak involving a 110 product is more likely and that the major, if not only, product formed under our experimental conditions (air at ~5% relative humidity) is $CH_3OP(O)(CH_3)OH$.

DMEP, $(CH_3O)_2P(O)C_2H_5$, Reaction. In the positive ion mode, prior to the reaction, ion peaks at 139, 157, 277 (strong), and 291 u were observed, with these being due to protonated DMEP, a water adduct of protonated DMEP, the protonated DMEP dimer, and a protonated heterodimer of DMEP plus a 152 species (this peak being very weak), respectively. After the reaction, an additional weak ion peak at 387 u was present, and API-MS/MS "product ion" spectra showed it to be $[DMEP + 124 + 124 + H]^+$. Hence the positive ion mode indicates the formation of a product of molecular weight 124.

In the negative ion mode, no significant ion peaks due to DMEP were observed. After the reaction, ion peaks due to reaction products were observed as shown in Figure 3 (bottom panel). API-MS/MS product ion and precursor ion spectra of the ion peaks observed in the API-MS spectra were obtained, which indicated that the ion peaks present in the API-MS spectrum shown in Figure 3 (bottom panel) were due to O_2^-, NO_2^-, and NO_3^- adducts of products of molecular weight 124, 126, and 152, with the assignments: 170 u, $[124 + NO_2]^-$; 184 u, $[152 + O_2]^-$; 186 u, $[124 + NO_3]^-$; 198 u, $[152 + NO_2]^-$; 280 u, $[124 + 124 + O_2]^-$; 282 u, $[124 + 126 + O_2]^-$; 294 u, $[124 + 124 + NO_2]^-$; 296 u, $[124 + 126 + NO_2]^-$;

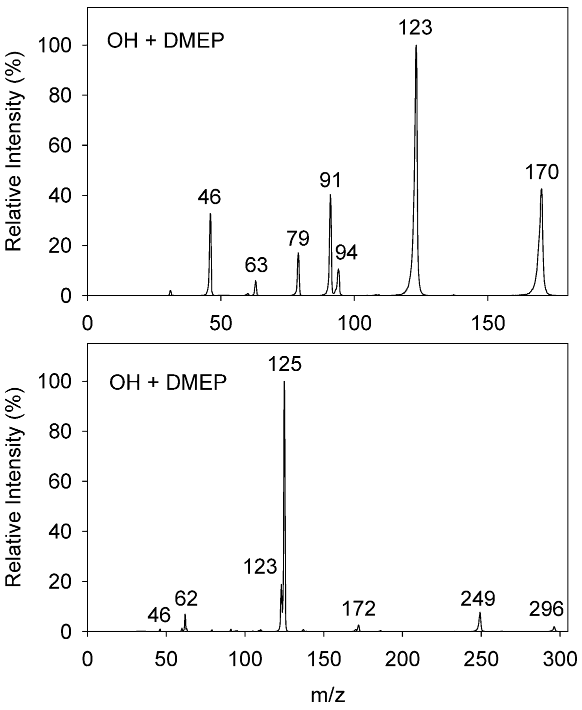

Figure 6. Negative ion API-MS/MS "product ion" spectra of the 170 and 296 u ion peaks present in the API-MS spectra of the reacted DMEP mixture shown in Figure 3. The 170 and 296 u ion peaks are, respectively, attributed to $[124 + NO_2]^-$ (note the loss of 47 u, HNO_2) and $[124 + 126 + NO_2]^-$ (note the losses of 47 (HNO_2) and 124 u).

310 u, $[124 + 124 + NO_3]^-$; 312 u, $[124 + 126 + NO_3]^-$; 371 u, $[124 + 124 + 124 - H]^-$; and 373 u, $[124 + 124 + 126 - H]^-$. Representative examples of the API-MS/MS product ion spectra of the 170 and 296 u ion peaks observed in the API-MS spectra are shown in Figure 6.

The positive and negative ion mode data show that a product of molecular weight 124 is formed, and the negative ion mode data also indicate the formation of a molecular weight 126 product. It is possible that the molecular weight 152 species observed in the negative ion mode after reaction is an impurity in the DMEP sample used, as indicated from the positive ion mode API-MS spectra obtained before and after reaction. The product of molecular weight 124 is attributed to $CH_3OP(O)(C_2H_5)OH$, and the molecular weight 126 product would likely be $(CH_3O)_2P(O)OH$ (dimethyl phosphate). However, no significant ion peaks at 251 u ($[126+126 - H]^-$) or 298 u ($[126 + 126 + NO_2]^-$) were observed from the OH radical-initiated reaction with DMEP (Figure 3, bottom), although the 126 species could well have preferentially formed heterodimers with the more abundant 124 product, as per the assignments given above.

Our API-MS analyses of the OH radical-initiated reactions of DMHP, DMMP, and DMEP indicate the formation of the following products: from DMHP, the molecular weight 126 product $(CH_3O)_2P(O)OH$ and a molecular weight 96 product attributed to $CH_3OP(O)(H)OH$; from DMMP, a molecular weight 110 product attributed to $CH_3OP(O)(CH_3)OH$; and from DMEP, molecular weight 124 and 126 products attributed to $CH_3OP(O)(C_2H_5)OH$ and $(CH_3O)_2P(O)OH$, respectively.

FT-IR and GC-FID Analyses. These experiments were carried out in a 5870 L Teflon-coated evacuable chamber. The quantitative analysis of products and reactants by FT-IR spectroscopy was carried out by a subtractive procedure.[8,9,13] Components were successively subtracted from the spectrum of the mixture using calibrated spectra of the gaseous reactants and known products, which have been recorded previously with the same instrument and identical spectral parameters. As noted above, OH radicals were generated by the photolysis of CH_3ONO or $(CH_3)_2CHONO$ in air, with 2-propyl nitrite being used in experiments to determine the HCHO formation yields (the photolysis of 2-propyl nitrite produces mainly acetone, in contrast to the photolysis of CH_3ONO which generates mainly HCHO). The yield of HCHO from the photolysis of $(CH_3)_2CHONO-NO-$air mixtures was shown in a separate experiment to be 3.0% (uncorrected for any secondary reactions).

TABLE 3: Products Identified and Quantified, and Their Molar Yields, from the OH Radical-Initiated Reactions of DMMP and DMEP

	molar yield (%)[a] from OH radical-initiated reaction of		
	DMMP		DMEP
product	dry air	5% relative humidity	dry air
CO	54 ± 6^b		50 ± 7^b
CO_2	5 ± 1^c	3 ± 1^c	11 ± 4^b
$HCHO^b$	3.9 ± 0.7^b		$<7^{b,d}$
CH_3CHO			18 ± 8^b 17 ± 9 (GC-FID)
HC(O)OH	$<1.4^{b,c}$	$<3.6^c$	$<6^b$
$RONO_2$	$\sim 4^c$		$\leq 5^b$
formate ester	$\sim 8^c$		5.0 ± 1.5^b

[a] FT-IR analyses unless noted otherwise. The cited uncertainties are two least-squares standard deviations combined with estimated uncertainties in the concentrations of DMMP or DMEP, ±5%; CO_2, ±7%;[9] HCHO, ±5%; CH_3CHO, ±7%; and CO, ±7%.[9] [b] From irradiation of $(CH_3)_2CHONO-NO-$air mixtures. [c] From irradiation of $CH_3ONO-NO-$air mixtures. [d] Upper limit because of HCHO formation from the secondary reaction of CH_3CHO with OH radicals.

To analyze the products formed from the reactions of DMMP and DMEP, the products arising from the photolysis of CH_3ONO in the presence of NO (NO_2, HNO_3, HONO, CH_3ONO_2, and HCHO) and from the photolysis of $(CH_3)_2CHONO$ in the presence of NO (NO_2, HNO_3, HONO, $(CH_3)_2CHONO_2$, and $CH_3C(O)CH_3$) were subtracted from the recorded post-irradiation spectra.[8,9,13] The effect of ambient CO_2 on the product CO_2 measurements was minimized by stabilizing the N_2 purge of the FT-IR instrument for a period of at least 90 min prior to the measurements. The CO_2 yields from the photolysis of $CH_3ONO-NO-$air and $(CH_3)_2CHONO-NO-$air mixtures were shown to be ≤1% and ≤2.3%, respectively, and the CO yield from the photolysis of a $(CH_3)_2CHONO-NO-$air mixture was found to be ≤0.9% (all based on the amount of alkyl nitrite consumed). The formation of HCHO, CO, and CO_2 from the photolysis of CH_3ONO or $(CH_3)_2CHONO$ in NO−air mixtures was taken into account in the data analysis, and the measured concentrations of HCHO, CH_3CHO, and CO were corrected for secondary reaction with OH radicals,[16] using the rate constants measured here for DMMP and DMEP and those for HCHO, CH_3CHO, and CO of (in units of 10^{-12} cm^3 molecule^{-1} s^{-1}) 8.5, 15, and 0.23, respectively.[15] The maximum multiplicative correction factors[16] to account for the secondary reaction with OH radicals were 1.63 for HCHO (from a DMMP reaction), 1.37 for CH_3CHO (DMEP reaction), and 1.02 for CO (DMMP reaction). The formation yields of CO, CO_2, HCHO, CH_3CHO (DMEP reaction only), and HC(O)OH determined in the OH radical-initiated reactions of DMMP and DMEP are given in Table 3. Because the reaction of CH_3CHO with OH radicals leads, at least in part, to the formation of HCHO,[1] the observed HCHO yield from DMEP is cited in Table 3 as an upper limit. For CH_3CHO, the formation yield from the DMEP reaction was also measured by GC-FID, as described above for the kinetic experiments, noting that both the GC-FID and in situ FT-IR methods have low sensitivity for CH_3CHO. Within the large

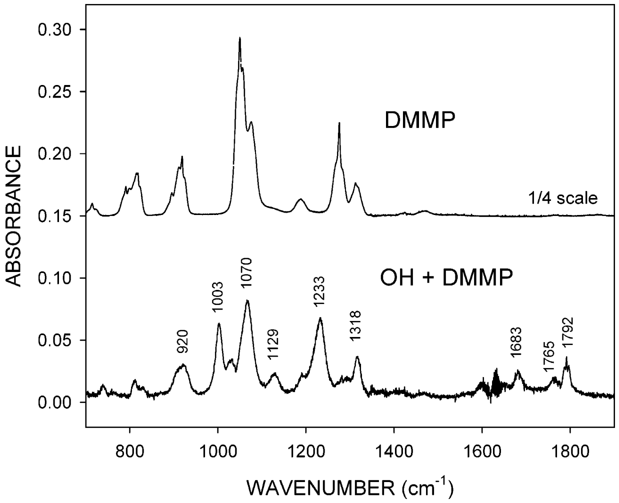

Figure 7. IR spectra from a $CH_3ONO-NO-DMMP-$air ($\ll$1% relative humidity) irradiation experiment: top trace, initial DMMP; bottom trace, residual spectrum depicting the absorption bands of products from DMMP. The CO (2145 cm^{-1}) and CO_2 (2350 cm^{-1}) bands are not shown; see text.

measurement uncertainties, the FT-IR and GC-FID results for CH_3CHO formation are in good agreement (Table 3).

While the identification and quantification of the above low molecular products of DMMP and DMEP are reliable, the identification and measurement of the P-containing products via infrared spectroscopy are presently a problem. Figure 7 shows a spectrum of the initial DMMP (at a concentration of 9.2 × 10^{13} molecule cm^{-3} and at a path length of 62.9 m) together with the residual spectrum due to products arising from DMMP, with the absorptions due to the low molecular products, discussed above, subtracted. The 1233 cm^{-1} band is consistent with the presence of a P=O group (the vapor phase spectra of dimethyl phosphate [$(CH_3O)_2P(O)OH$] and diethyl phosphate [$(C_2H_5O)_2P(O)OH$] show their P=O stretch frequencies to be at 1250 and 1243 cm^{-1}, respectively[8,9]), while the bands at 1070 and 1003 cm^{-1} are in the range associated with P−O−C group(s).[17,18a,19a] The weaker but distinct pair of bands at 1683 and 1318 cm^{-1} are consistent with a product containing the $-ONO_2$ group.[18b,19b] The 1792 and 1129 cm^{-1} bands have the correct positions and relative intensities characteristic of a formate ester, ROCHO[18c,19c] (>P(O)OCHO in the present case), while the weaker 1765 cm^{-1} band could arise from a minor carbonyl product such as >P(O)CHO. On the basis of an average absorption coefficient derived from related compounds measured in this laboratory,[13] the yield of the organic nitrate product, $RONO_2$, is estimated from the band area of the 1683 cm^{-1} absorption as ∼4%. The yield of the organic ester, ROCHO, based on the area of the 1792 cm^{-1} band and an integrated absorption coefficient of $(1.96 \pm 0.03) \times 10^{-17}$ cm molecule^{-1} (average for the corresponding bands of methyl formate, ethyl formate and butyl formate), is estimated as ∼8%.

As for the OH radical-initiated reaction of DMMP, the P-containing products from the reaction of OH radicals with DMEP could not be positively identified. The presence of P=O and P−O−C groups was again indicated by absorption bands in the residual spectrum at 1217 and 1069 cm^{-1}, respectively, with both bands being broad and the latter being overlapped by other bands near 1000 cm^{-1}. The formation of a formate ester, ROCHO, was shown by absorption peaks at 1790 and 1127 cm^{-1} and that of an organic nitrate, $RONO_2$, by peaks at 1684 and 1293 cm^{-1}. Following the yield estimation procedures employed for the DMMP reaction, the yields of the ROCHO and $RONO_2$ products from DMEP were calculated to be 5.0 ± 1.5% and ≤5%, respectively. The upper limit yield of HC(O)OH from the DMEP reaction in dry air ($\ll$1% relative humidity) was determined to be <6%. These product yields are also given in Table 3.

Discussion

The rate constants measured here for the reactions of NO_3 radicals and O_3 with DMHP, DMMP, and DMEP and for the reaction of OH radicals with DMEP are the first reported. The observed lack of reaction with O_3 is consistent with previous data for the reactions of O_3 with trimethyl phosphate [$(CH_3O)_3PO$], *O,O,O*-trimethyl phosphorothioate [$(CH_3O)_3PS$], *O,O,S*-trimethyl phosphorothioate [$(CH_3O)_2P(O)SCH_3$], *O,S,S*-trimethyl phosphorodithioate [$(CH_3S)_2P(O)OCH_3$], *O,O,S*-trimethyl phosphorodithioate [$(CH_3O)_2P(S)SCH_3$], diethyl methylphosphonate [DEMP, $(C_2H_5O)_2P(O)CH_3$], diethyl ethylphosphonate [DEEP, $(C_2H_5O)_2P(O)C_2H_5$], and triethyl phosphate [TEP, $(C_2H_5O)_3PO$].[4,5] The rate constants measured for the reactions of NO_3 radicals with DMMP and DMEP, and the upper limit determined for DMHP, (see Table 2) are of a similar magnitude to those we measured for the corresponding reactions of DEMP, DEEP, and TEP, which were in the range $(2.4-3.7) \times 10^{-16}$ cm^3 molecule^{-1} s^{-1}.[9]

The rate constants measured here for the reactions of OH radicals with DMHP, DMMP, and DMEP are given in Table 4, and those for DMHP and DMMP are compared with the available literature values.[6,7] Our present rate constant for DMHP is in excellent agreement with our previous measurement[6] determined relative to the rate constant for the reaction of OH radicals with dimethyl ether using in situ FT-IR spectroscopy and with the measurement of Kleindienst and Smith[7] relative to the rate constants for the reactions of OH radicals with propane, *n*-butane, and *n*-hexane. However, for the reaction of OH radicals with DMMP, our room-temperature rate constant of 1.04×10^{-11} cm^3 molecule^{-1} s^{-1} is a factor of 1.6 higher than that reported by Kleindienst and Smith,[7] for reasons that are presently not known (a similar discrepancy was observed for the rate constant for the reaction of OH radicals with diethyl methylphosphonate[9]).

Comparison of the present room-temperature OH radical reaction rate constants for DMMP and DMEP (Tables 1 and 4) with those for diethyl methylphosphonate (5.78×10^{-11} cm^3 molecule^{-1} s^{-1})[9] and diethyl ethylphosphonate (6.45×10^{-11} cm^3 molecule^{-1} s^{-1})[9] suggests that the reactions of OH radicals with DMMP, DMEP, DEMP, and DEEP proceed mainly by H-atom abstraction from the OCH_3 or OC_2H_5 groups and similarly for DMHP. That the reaction proceeds by initial H-atom abstraction is supported by the large (considering the magnitude of the overall reaction rate constant) deuterium isotope effect of 4.8 ± 1.2 for DMMP vs DMMP-d_9 measured in this work. Comparison of the rate constants for the reactions of OH radicals with DMMP and DMEP (Tables 1 and 4) at 296 ± 2 K suggests that the replacement of a CH_3 group by a C_2H_5 group bonded directly to the P-atom results in a rate constant increase of $(6.6 \pm 1.2) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. Interestingly, this is essentially identical to the rate constant increase we obtained for the same replacement of a CH_3 group by a C_2H_5 group bonded directly to the P-atom from the corresponding reactions of DEMP and DEEP,[9] of $(5.2 \pm 2.3) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 296 K. This suggests that at least 39 ± 7% of the reaction of OH radicals with DMEP proceeds by H-atom abstraction from the C_2H_5 group bonded directly to the P-atom (the lower limit being because this

TABLE 4: Room Temperature Rate Constants k_1 for the Reactions of OH Radicals with DMHP, DMMP, and DMEP, Compared with Literature Values

	$10^{12} \times k_1$ (cm^3 molecule^{-1} s^{-1})		
organophosphorus compound	this work	literature	reference
dimethyl phosphonate (DMHP)	4.83 ± 0.25	4.94 ± 0.19[a]	Kleindienst and Smith[7]
		5.01 ± 0.17[b]	Martin et al.[9]
dimethyl methylphosphonate (DMMP)	10.4 ± 0.6	6.32 ± 0.29[a]	Kleindienst and Smith[7]
dimethyl ethylphosphonate (DMEP)	17.0 ± 1.0		

[a] At ~298 K, with analyses of the organophosphorus compound and the reference compounds by GC-FID. Relative to rate constants for reactions of OH radicals with propane (DMHP and DMMP), *n*-butane (DMHP), and *n*-hexane (DMHP and DMMP) of 1.14×10^{-12} cm^3 molecule^{-1} s^{-1}, 2.54×10^{-12} cm^3 molecule^{-1} s^{-1}, and 5.61×10^{-12} cm^3 molecule^{-1} s^{-1}, respectively,[7] which are 4.6%, 7.6%, and 7.9% higher, respectively, than more recent recommendations.[1] [b] At 298 ± 2 K, relative to the reaction of OH radicals with dimethyl ether, using a rate constant of k_2(dimethyl ether) = 2.80×10^{-12} cm^3 molecule^{-1} s^{-1}.[15]

calculation assumes that H-atom abstraction from the CH_3 group bonded directly to the P-atom in DMMP is negligible, which may not be the case), and we observe the formation of CH_3CHO from DMEP in 18 ± 8% yield (Table 3). Our API-MS data suggest that there is one major P-containing product, $CH_3OP(O)(CH_3)OH$, from the OH radical-initiated reaction of DMMP, whereas the DMHP and DMEP reactions lead to (at least) two major P-containing products, presumably after reaction at the P−H bond or the CH_3O group in DMHP and at the CH_3O and C_2H_5 groups in DMEP.

The results of the product analysis of the reaction of OH radicals with DMMP, namely, formation yields of the following CO, 54 ± 6%; CO_2, 5 ± 1%; HCHO, 3.9 ± 0.7%; HC(O)OH, <1.4% (in dry air); $RONO_2$, ~4%; and formate ester, ~8%, combined with the expectation that H-atom abstraction from the CH_3O groups is the major reaction pathway in DMMP, can be rationalized by the following reactions

$$OH + (CH_3O)_2P(O)CH_3 \rightarrow H_2O + CH_3OP(O)(CH_3)OC^{\bullet}H_2 \tag{1}$$

$$CH_3OP(O)(CH_3)OC^{\bullet}H_2 + O_2 \rightarrow CH_3OP(O)(CH_3)OCH_2OO^{\bullet} \tag{4}$$

$$CH_3OP(O)(CH_3)OCH_2OO^{\bullet} + NO \rightarrow CH_3OP(O)(CH_3)OCH_2O^{\bullet} + NO_2 \tag{5}$$

$$CH_3OP(O)(CH_3)OCH_2O^{\bullet} + O_2 \rightarrow CH_3OP(O)(CH_3)OCHO + HO_2 \tag{6}$$

$$CH_3OP(O)(CH_3)OCH_2O^{\bullet} \rightarrow CH_3OP(O)(CH_3)OH + HC^{\bullet}O \tag{7}$$

$$HC^{\bullet}O + O_2 \rightarrow CO + HO_2 \tag{8}$$

If CO is formed from reaction 7 followed by reaction 8, then the major P-containing product is the molecular weight 110 product $CH_3OP(O)(CH_3)OH$, consistent with our API-MS analyses. Assuming that the formation of CO is accompanied by $CH_3OP(CH_3)(O)OH$, then 46 ± 6% of other, as yet unidentified, P-containing product(s) must also be formed from the reaction of OH radicals with DMMP. The low yields of HCHO and of the formate ester indicate that decomposition (reaction 9)

$$CH_3OP(O)(CH_3)OCH_2O^{\bullet} \rightarrow CH_3OP(O)(CH_3)O^{\bullet} + HCHO \tag{9}$$

and the reaction of the assumed $CH_3OP(O)(CH_3)OCH_2O^{\bullet}$ intermediate radical with O_2 (reaction 6) are minor and that the major reaction of this radical is by a rearrangement[9] analogous to that observed in esters of structure $RC(O)OCH_2R'$ (reaction 7).[20,21] Our kinetic and products data therefore suggest that the reaction of OH radicals with DMMP is analogous to the OH radical reactions with diethyl methylphosphonate, diethyl ethylphosphonate, and triethyl phosphate, in that formation of the major product involves initial H-atom abstraction from the RO group(s) in $(RO)_{3-x}P(O)R_x$, with the formation of $(RO)_{2-x}P(O)(R)_xOH$.[9]

The products formed from the analogous reactions of DMHP and DMEP would then be the molecular weight 96 product $CH_3OP(O)(H)OH$ from DMHP and the molecular weight 124 product $CH_3OP(O)(C_2H_5)OH$ from DMEP, plus CO in both cases. As noted above, we observed these molecular weight products in the API-MS analyses and we measured a formation yield of CO from the DMEP reaction of 50 ± 7% (Table 3). The additional product of molecular weight 126 observed in the API-MS analyses from the DMEP reaction is attributed to dimethyl phosphate $[(CH_3O)_2P(O)OH]$, suggesting formation after initial H-atom abstraction from the C_2H_5 group, and this is substantiated by the observed formation of CH_3CHO in 18 ± 8% yield. If the formation of CH_3CHO involves initial H-atom abstraction from the C_2H_5 group in DMEP, then one possibility is via decomposition of the alkoxy radical $(CH_3O)_2P(O)CH(O^{\bullet})CH_3$ formed by reactions analogous to 1, 4, and 5 above

$$(CH_3O)_2P(O)CH(O^{\bullet})CH_3 \rightarrow (CH_3O)_2PO + CH_3CHO \tag{10}$$

although the subsequent fate of $(CH_3O)_2PO$ is not presently understood. The sum of the formation yields of CO and CH_3CHO from the DMEP reaction is 68 ± 11%, and this is a lower limit to the contribution from H-atom abstraction from the two CH_3O groups and the C_2H_5 group.

The reaction mechanism leading to the formation of the molecular weight 126 product attributed to dimethyl phosphate observed from DMHP is not known at present, presumably H-atom abstraction occurs from the P−H bond in this case.

Acknowledgment. This work was supported by ENSCO, Inc. While this research has been funded by this agency, the results and content of this publication do not necessarily reflect the views and opinions of the funding agency.

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: Surrey, 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, on Contract No. F08635-93-C-0020; Armstrong Laboratory Environics Directorate: Tyndall AFB, FL, September 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) Atkinson, R.; Plum, C. N.; Carter, W. P. L.; Winer, A. M.; Pitts, J. N., Jr. *J. Phys. Chem*. **1984**, *88*, 1210.

(11) Aschmann, S. M.; Chew, A. A.; Arey, J.; Atkinson, R. *J. Phys. Chem. A* **1997**, *101*, 8042.

(12) Arey, J.; Aschmann, S. M.; Kwok, E. S. C.; Atkinson, R. *J. Phys. Chem. A* **2001**, *105*, 1020.

(13) Aschmann, S. M.; Martin, P.; Tuazon, E. C.; Arey, J.; Atkinson, R. *Environ. Sci. Technol*. **2001**, *35*, 4080.

(14) Taylor, W. D.; Allston, T. D.; Moscato, M. J.; Fazekas, G. B.; Kozlowski, R.; Takacs, G. A. *Int. J. Chem. Kinet*. **1980**, *12*, 231.

(15) IUPAC, http://www.iupac-kinetic.ch.cam.ac.uk/, 2005.

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

(17) Gore, R. C. *Discuss. Faraday Soc*. **1950**, *9*, 138.

(18) Pouchert, C. J. *The Aldrich Library of Infrared Spectra*, 2nd ed.; Aldrich Chemical Co.: Milwaukee, WI, 1975; (a) pp 483−495, (b) pp 207−211, (c) pp 317−324.

(19) Pouchert, C. J. *The Aldrich Library of FT-IR Spectra*, 1st ed.; Aldrich Chemical Co.: Milwaukee, WI, 1989; Vol. 3, (a) pp 837−847, (b) pp 480−481, (c) pp 605−607.

(20) Tuazon, E. C.; Aschmann, S. M.; Atkinson, R.; Carter, W. P. L. *J. Phys. Chem. A* **1998**, *102*, 2316.

(21) Christensen, L. K.; Ball, J. C.; Wallington, T. J. *J. Phys. Chem. A* **2000**, *104*, 345.