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Rate Constants for the Gas-Phase Reactions of OH Radicals with Dimethyl Phosphonate over the Temperature Range of 278−351 K and for a Series of Other Organophosphorus Compounds at ∼280 K

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Rate constants for the gas-phase reactions of OH radicals with dimethyl phosphonate [DMHP; $(CH_3O)_2P(O)H$] were measured over the temperature range of 278−351 K at atmospheric pressure of air using a relative rate method with 4-methyl-2-pentanone as the reference compound. The Arrhenius expression obtained was $1.01 \times 10^{-12}\ e^{(474 \pm 159)/T}$ cm^3 molecule^{-1} s^{-1}, where the indicated error is two least-squares standard deviations and does not include uncertainties in the rate constants for the reference compound. Rate constants for the gas-phase reactions of OH radicals with dimethyl methylphosphonate [DMMP, $(CH_3O)_2P(O)CH_3$], dimethyl ethylphosphonate [DMEP, $(CH_3O)_2P(O)C_2H_5$], 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, $(C_2H_5O)_3PO$] were also measured at 278 and/or 283 K for comparison with a previous study (Aschmann, S. M.; Long, W. D.; Atkinson, R. *J. Phys. Chem. A*, 2006, *110*, 7393). With the experimental procedures employed, experiments conducted at temperatures below the dew point where a water film was present on the outside of the Teflon reaction chamber resulted in measured rate constants which were significantly higher than those expected from the extrapolation of rate data obtained at temperatures (283−348 K) above the dew point. Using rate constants measured at ≥283 K, the resulting Arrhenius expressions (in cm^3 molecule^{-1} s^{-1} units) are $6.25 \times 10^{-14}\ e^{(1538 \pm 112)/T}$ for DMMP (283−348 K), $9.03 \times 10^{-14}\ e^{(1539 \pm 27)/T}$ for DMEP (283−348 K), $4.35 \times 10^{-13}\ e^{(1444 \pm 148)/T}$ for DEMP (283−348 K), $4.08 \times 10^{-13}\ e^{(1485 \pm 328)/T}$ for DEEP (283−348 K), and $4.07 \times 10^{-13}\ e^{(1448 \pm 145)/T}$ for TEP (283−347 K), where the indicated errors are as above. Aerosol formation at 296 ± 2 K from the reactions of OH radicals with these organophosphorus compounds was relatively minor, with aerosol yields of ≤8% in all cases.

Introduction

Organophosphorus compounds are widely used as pesticides.[1] These compounds and their precursors may be released into the atmosphere where they can undergo chemical reactions with OH radicals, NO_3 radicals,and O_3.[2] To date, rate constants for the gas-phase reactions of a number of simple organophosphorus compounds of structures $(RO)_nP(O)(SR)_{3-n}$, $(RO)_nP(S)(SR)_{3-n}$, $(RO)_2P(O)X$, and $(RO)_2P(S)X$ (where R = CH_3 or C_2H_5 and X = H, CH_3, C_2H_5,and $OCH{=}Cl_2$) with OH radicals, NO_3 radicals,and O_3 have been measured at room temperature.[3–13] For these chemicals, reaction with the OH radical is calculated to be the dominant atmospheric loss process.[4,8,10,13]

Recently, we reported temperature-dependent rate constants for the reactions of OH radicals with dimethyl methylphosphonate [DMMP, $(CH_3O)_2P(O)CH_3$], dimethyl ethylphosphonate [DMEP, $(CH_3O)_2P(O)C_2H_5$], 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, $(C_2H_5O)_3PO$] over the temperature range of 278−348 K.[12] At temperatures ≥ 296 K, all exhibited strong negative temperature dependencies, with values of B in $k = Ae^{-B/T}$ of $B \sim -1440$ K. The measured rate constants at 278 ± 2 K were significantly higher than those expected from the Arrhenius expressions derived using the ≥296 K rate data, and the experimental data at 278 ± 2 K were also significantly more scattered than data at higher temperatures.[12]In this work, we have used a relative rate method to measure rate constants for the gas-phase reaction of OH radicals with dimethyl phosphonate [DMHP; $(CH_3O)_2P(O)H$] over the temperature range of 278−351 K and have reinvestigated the kinetics of the OH radical reactions with DMMP, DMEP, DEMP, DEEP, and TEP at 278 and/or 283 K. In addition, aerosol formation from the OH radical-initiated reactions of these organophosphorus compounds was measured at 296 ± 2 K.

Experimental Methods

The majority of the experiments were carried out using a ∼5000 L volume Teflon bag inserted inside of a 5870 L Teflon-coated chamber, with irradiation provided by a 24 kW xenon arc lamp filtered through a 6 mm thick Pyrex pane to remove wavelengths < 300 nm.[12,13] This 5870 L volume chamber was fitted with a heating/cooling system, allowing its temperature to be maintained to within ±1 K over the range of 278−348 K for the present study. Additional experiments were conducted at 296 ± 2 K and 735 Torr of total pressure of dry purified air in a ∼7000 L volume Teflon chamber[8,10,13] equipped with two parallel banks of blacklamps for irradiation. Both chambers were provided with Teflon-coated fans to ensure rapid mixing of reactants during their introduction into the chamber. Temperatures of the gas mixtures inside of the chambers were measured

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by thermocouples, and in all experiments, the temperature rise due to the intermittent irradiations was ≤2 K.

Rate Constant Measurements. Rate constants for the reactions of OH radicals with DMHP, DMMP, DMEP, DEMP, DEEP, and TEP were measured using a relative rate technique in which the concentrations of the organophosphorus compound and a reference compound (whose OH radical reaction rate constant is reliably known) were measured in the presence of OH radicals.[8,10,12,13] Providing that the only loss processes for the organophosphorus compound and the reference compound were by reaction with OH radicals

$$\text{OH} + \text{organophosphorus compound} \rightarrow \text{products} \quad (1)$$

$$\text{OH} + \text{reference compound} \rightarrow \text{products} \quad (2)$$

then

$$\ln\left(\frac{[\text{organophosphorus}]_{t_0}}{[\text{organophosphorus}]_t}\right) = \frac{k_1}{k_2}\left[\ln\left(\frac{[\text{reference compound}]_{t_0}}{[\text{reference compound}]_t}\right)\right] \quad \text{(I)}$$

where $[\text{organophosphorus}]_{t_0}$ and $[\text{reference compound}]_{t_0}$ are the concentrations of the organophosphorus compound and reference compound, respectively, at time t_0, $[\text{organophosphorus}]_t$ and $[\text{reference compound}]_t$ are the corresponding concentrations at time t, 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.[8,10,12,13] The initial reactant concentrations (molecule cm^{-3}) were CH_3ONO, ~2.4 × 10^{14}; NO, ~2.4 × 10^{14}; and organophosphorus compound and reference compound, ~2.4 × 10^{13} each. The reference compounds used were 4-methyl-2-pentanone for experiments with DMHP, 4-methyl-2-pentanone and di-*n*-butyl ether for experiments with DMMP and DMEP, and α-pinene for experiments with DEMP, DEEP, and TEP. As in previous studies,[8,10,12,13] in each experiment the reactant mixture was irradiated for three periods with GC-FID analyses after each irradiation period (and with replicate GC-FID analyses prior to the initial irradiation period and after the third irradiation period). Hence, four data points were obtained per experiment, and unless noted otherwise, three experiments were carried out at each temperature. The total irradiation times were up to 60 min in the ~7000 L Teflon chamber and up to 105 min in the ~5000 L Teflon bag.

The concentrations of 4-methyl-2-pentanone, di-*n*-butyl ether, α-pinene, DMHP, DMMP, DMEP, DEMP, DEEP, and TEP were measured during the experiments by gas chromatography with flame ionization detection (GC-FID).[8,10,12] Gas samples of 100 cm^3 volume were collected from the chamber onto Tenax-TA solid adsorbent (maintained at room temperature), with subsequent thermal desorption at ~205 °C onto a 30 m DB-1701 megabore column initially held at 0 °C and then temperature programmed to 200 at 8 °C min^{-1}. On the basis of replicate analyses in Teflon chambers in the dark, the analytical uncertainties for the organophosphorus compounds and the reference compounds used were typically ≤3%.

Aerosol Formation Measurements. Irradiations of $CH_3ONO-NO-$organophosphorus compound−air and $CH_3ONO-NO-$organophosphorus compound−reference compound−air were carried out at 296 ± 2 K in the ~7000 L Teflon chamber, with the organophosphorus compound and reference compound being monitored by GC-FID as described above and with the aerosol number density and size distribution being measured during the experiments using a TSI 3936L72 scanning mobility particle sizer (SMPS). The initial reactant concentrations were similar to those used for the kinetic experiments (see above).

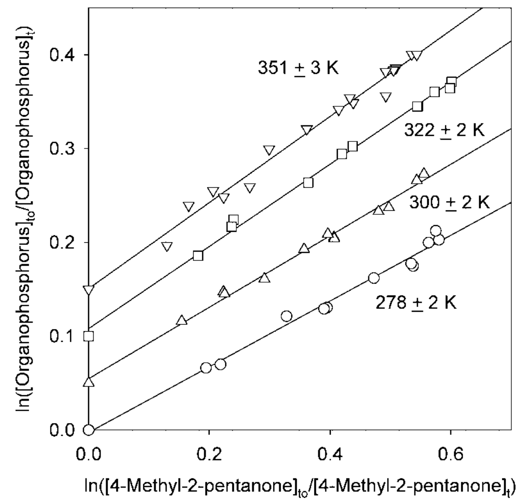

Figure 1. Plots of equation I for the reaction of OH radicals with dimethyl phosphonate (DMHP) at 278 ± 2, 300 ± 2, 322 ± 2, and 351 ± 3 K with 4-methyl-2-pentanone as the reference compound. The DMHP data at 300, 322, and 351 K have been displaced vertically by 0.05, 0.10, and 0.15 units, respectively, for clarity.

Chemicals. The chemicals used (and their stated purities) were diethyl methylphosphonate (97%), dimethyl methylphosphonate (97%), di-*n*-butyl ether (99+%), dimethyl phosphonate (the catalog name is dimethyl phosphite) (98%), 4-methyl-2-pentanone (99+%), α-pinene (99+%), and triethyl phosphate (99+%), Aldrich Chemical Co.; dimethyl ethylphosphonate (98%), Cerilliant Corporation; diethyl ethylphosphonate (98%), Lancaster; and NO (≥99.0%), Matheson Gas Products. Methyl nitrite was prepared as described by Taylor et al.[14] and stored under vacuum at 77 K.

Results and Discussion

In all experiments, replicate GC-FID analyses prior to irradiation and after the final irradiation period showed no evidence for dark losses of the organophosphorus compounds or the reference compounds, with the replicate post-reaction analyses agreeing to within 3% for DMHP, DMMP, DMEP, DEMP, DEEP, and TEP and to within 2% for the reference compounds 4-methyl-2-pentanone, di-*n*-butyl ether, and α-pinene (and hence being within the analytical uncertainties).

Rate Constants for the Reaction of OH Radicals with DMHP. Irradiations of $CH_3ONO-NO-$DMHP−4-methyl-2-pentanone (the reference compound)−air mixtures were carried out in the ~7000 L Teflon chamber at 296 ± 2 K and in the ~5000 L Teflon bag at four temperatures over the range of 278−351 K. The experimental data obtained in the ~5000 L Teflon bag are plotted in accordance with eq I in Figure 1, and the rate constant ratios k_1/k_2 obtained from least-squares analyses of the data obtained in both chambers are given in Table 1. These rate constant ratios are placed on an absolute basis using a rate constant for the reaction of OH radicals with 4-methyl-2-pentanone of k_2(4-methyl-2-pentanone) = 7.88 × 10^{-13} $e^{829/T}$ cm^3 molecule^{-1} s^{-1}. This Arrhenius expression was obtained from a least-squares analysis of the absolute rate constants of Le Calvé et al.[15] over the temperature range of 253−372 K and the room temperature relative rate constants of Cox et al.,[16]

TABLE 1: Rate Constant Ratios k_1/k_2 and Rate Constants k_1 Measured in Our Present and Previous Work for the Reaction of OH Radicals with Dimethyl Phosphonate (DMHP), with 4-Methyl-2-pentanone As the Reference Compound unless Noted Otherwise

temperature (K)	chamber[a]	k_1/k_2[b]	$10^{12} \times k_1$[c] (cm^3 molecule^{-1} s^{-1})	reference
278 ± 2	A	0.350 ± 0.025	5.44 ± 0.39	this work
296 ± 2	B	[d]	4.83 ± 0.25	10
296 ± 2	B	0.411 ± 0.033	5.33 ± 0.43	this work
298 ± 2	C	[e]	5.01 ± 0.17	7
300 ± 2	A	0.381 ± 0.020	4.76 ± 0.25	this work
322 ± 2	A	0.438 ± 0.016	4.53 ± 0.17	this work
351 ± 3	A	0.459 ± 0.029	3.84 ± 0.25	this work

[a] A = ~5000 L Teflon bag inside of the 5870 L evacuable chamber; B = ~7000 L Teflon chamber; C = 5870 L evacuable, Teflon-coated 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(4-methyl-2-pentanone) = 7.88×10^{-13} $e^{829/T}$ cm^3 molecule^{-1} s^{-1} (see text), unless noted otherwise. The indicated errors are the two least-squares standard deviations and do not include the uncertainties in the rate constants k_2. [d] With *n*-octane as the reference compound. Rate constant ratio of $k_1/k_2 = 0.598 \pm 0.030$ placed on an absolute basis by use of k_2(*n*-octane) = 8.07×10^{-12} cm^3 molecule^{-1} s^{-1} at 296 K.[2] [e] With dimethyl ether as the reference compound. Rate constant ratio of $k_1/k_2 = 1.79 \pm 0.06$ placed on an absolute basis by use of k_2(dimethyl ether) = 2.80×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K.[2]

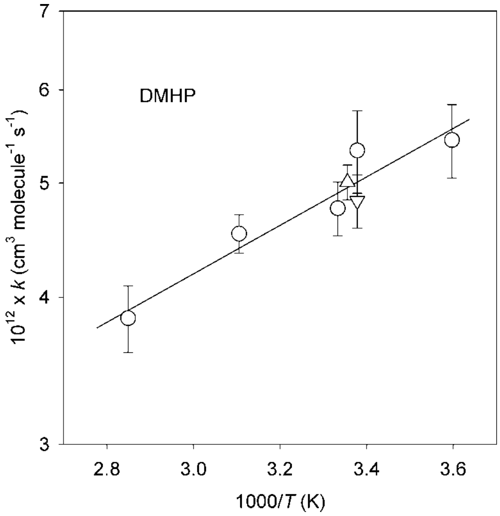

Figure 2. Arrhenius plot of rate constants for the reaction of OH radicals with dimethyl phosphonate (DMHP). Rate constants are from ○, ~5000 L Teflon bag inside of the evacuable chamber, relative to 4-methyl-2-pentanone; △, 5870 L evacuable chamber, relative to dimethyl ether;[7] ▽, ~7000 L Teflon chamber, relative to *n*-octane.[10] The solid line is our recommended Arrhenius fit (see Table 2 and text).

Atkinson et al.,[17] and O'Rji and Stone[18] (the relative rate data being re-evaluated to be consistent with recent recommendations[2] for the reference compounds used). The resulting rate constants k_1 are given in Table 1 together with the previous relative rate measurements from our laboratory.[7,10]

Table 1 shows that within the experimental uncertainties, the rate constants measured here at room temperature agree well with our previous rate constants[7,10] obtained using dimethyl ether[7] and *n*-octane[10] as the reference compounds. The rate constants from our present and previous studies[7,10] are plotted in Arrhenius form in Figure 2. Within the experimental uncertainties, the rate data fit an Arrhenius expression over the complete temperature range studied (278−351 K) and show no evidence for higher measured rate constants at 278 ± 2 K compared to predictions from the ≥296 K data, as observed for DMMP, DMEP, DEMP, DEEP, and TEP.[12] This is despite the fact that water condensation on the outside of the ~5000 L Teflon bag occurred during the experiments at 278 ± 2 K.

A least-squares fit of the rate constants at 278−351 K measured relative to that for 4-methyl-2-pentanone results in k_1(DMHP) = 1.02×10^{-12} $e^{(474 \pm 159)/T}$ cm^3 molecule^{-1} s^{-1}, where the indicated error is two least-squares standard deviations. Using this temperature dependence to correct the rate constants measured at 296 K and 300 K to 298 K leads to an average 298 K rate constant of 4.97×10^{-12} cm^3 molecule^{-1} s^{-1} (Table 2). Combination of this 298 K rate constant with the above temperature dependence leads to the recommended Arrhenius parameters given in Table 2 (note that the pre-exponential factor changes by only 1% from that obtained using only data relative to 4-methyl-2-pentanone).

Rate Constant Measurements for DMMP, DMEP, DEMP, DEEP, and TEP. A series of irradiations of CH_3ONO−NO−DMMP−DMEP−4-methyl-2-pentanone−air and CH_3ONO−NO−DMMP−DMEP−di-*n*-butyl ether−air mixtures and a single CH_3ONO−NO−DEMP−TEP−α-pinene−air irradiation were carried out in the ~5000 L Teflon bag at 278 ± 2 K to repeat our previous measurements[12] at this temperature. As noted in the Introduction and evident from Table 3, our previously measured rate constants for the reactions of OH radicals with DMMP, DMEP, DEMP, DEEP, and TEP at 278 ± 2 K[12] were significantly higher than those predicted from an Arrhenius extrapolation of rate constants measured at temperatures ≥ 296 K. In our previous study,[12] the chamber system was cooled to 278 K overnight, and water condensation was observed on the outside of the ~4500 L volume Teflon bag. In the present study, the chamber system was cooled to 278 K immediately prior to the start of the experiments, and the chamber was at 278 K for <2 h prior to the start of the experiment. Additionally, dry pure air was slowly flowed into the evacuable chamber to minimize water condensation.

The rate constants obtained are given in Table 3 together with our previous measurements[12] and rate constants predicted from extrapolation of the Arrhenius expressions[12] derived using data at ≥296 K. The rate constants for DMMP and DMEP measured in the present work at 278 ± 2 K are somewhat lower than our previous rate constants[12] at this temperature, by 15−20% and 7−13%, respectively, but are still 10−20% higher than the rate constants predicted from the higher-temperature data. Rate constants for the DEMP and TEP reactions at 278 ± 2 K, obtained from a single experiment, agreed within the experimental uncertainties with our previous measurements[12] (Table 3). While we attempted to avoid water condensation in these experiments, it still occurred, although to a lesser extent than that in our previous[12] study.

Since it appeared that water condensation on the outside of the chamber walls may contribute to the higher measured rate

TABLE 2: Arrhenius Parameters, $k_1 = Ae^{-B/T}$, and 298 K Rate Constants for the Reactions of OH Radicals with Dimethyl Phosphonate (DMHP), Dimethyl Methylphosphonate (DMMP), Dimethyl Ethylphosphonate (DMEP), Diethyl Methylphosphonate (DEMP), Diethyl Ethylphosphonate (DEEP), and Triethyl Phosphate (TEP)

organophosphorus	A (cm^3 molecule^{-1} s^{-1})	B (K)[a]	$10^{12} \times k_1$ (298 K)[b] (cm^3 molecule^{-1} s^{-1})
$(CH_3O)_2P(O)H$ (DMHP)	1.01×10^{-12}	-474 ± 159	4.97
$(CH_3O)_2P(O)CH_3$ (DMMP)	6.25×10^{-14}	-1538 ± 112	10.9[c]
$(CH_3O)_2P(O)C_2H_5$ (DMEP)	9.03×10^{-14}	-1539 ± 27	15.8[c]
$(C_2H_5O)_2P(O)CH_3$ (DEMP)	4.35×10^{-13}	-1444 ± 148	55.3
$(C_2H_5O)_2P(O)C_2H_5$ (DEEP)	4.08×10^{-13}	-1485 ± 328	59.5
$(C_2H_5O)_3PO$ (TEP)	4.07×10^{-13}	-1448 ± 145	52.5

[a] Indicated errors are two least-squares standard deviations. Estimated overall errors in B are ±300 K, except for DEEP, where the estimated error in B is ±400 K, and are based on a ±12% (±15% for DEEP) overall uncertainty in the rate constants (see footnote b) at the extremes of the temperature range covered, rounded up to the next 100 K. [b] Average from rate constants at 296 K and 300 K to 298 K listed in Tables 1 and 5, correcting the rate constants at 296 and 300−298 K using the temperature dependence listed in this table. Estimated overall uncertainties are ±12%, except for DEEP, where the estimated overall uncertainty is ±15%. [c] See also text.

TABLE 3: Rate Constants k_1 Measured for the Reactions of OH Radicals with Dimethyl Methylphosphonate (DMMP), Dimethyl Ethylphosphonate (DMEP), Diethyl Methylphosphonate (DEMP), Diethyl Ethylphosphonate (DEEP), and Triethyl Phosphate (TEP) at 278 ± 2 K

	$10^{11} \times k_1$ (cm^3 molecule^{-1} s^{-1})			
organophosphorus	≥296 K data[a]	measured[b]	reference compound	reference
DMMP	1.6 (1.6)	2.28 ± 0.15	di-*n*-butyl ether	12
		1.83 ± 0.14	4-methyl-2-pentanone	this work
		1.92 ± 0.21	di-*n*-butyl ether	this work
DMEP	2.3 (2.3)	2.91 ± 0.22	di-*n*-butyl ether	12
		2.54 ± 0.16	4-methyl-2-pentanone	this work
		2.71 ± 0.18	di-*n*-butyl ether	this work
DEMP	7.9 (7.8)	9.52 ± 1.22	α-pinene	12
		9.70 ± 0.59[c]	α-pinene	this work
DEEP	8.0 (8.5)	9.17 ± 1.05	α-pinene	12
TEP	7.3 (7.4)	9.35 ± 1.11	α-pinene	12
		8.83 ± 0.70[c]	α-pinene	this work

[a] Rate constant calculated at 278 K from the Arrhenius expressions previously derived from rate constants measured over the temperature range of 296−348 K.[12] Values in parentheses are from the presently derived Arrhenius parameters given in Table 2. [b] Rate constant ratios placed on an absolute basis using rate constants (cm^3 molecule^{-1} s^{-1}) at 278 K of k_2(4-methyl-2-pentanone) = 1.55×10^{-11} (see text), k_2(di-*n*-butyl ether) = 3.20×10^{-11},[19] and k_2(α-pinene) = 5.81×10^{-11}.[2] Indicated errors are two least-squares standard deviations and do not include uncertainties in the values of k_2, which are expected to be ∼±10%. [c] From a single experiment.

constants for these reactions than those predicted from the ≥296 K data, we carried out all further experiments for the DMMP, DMEP, DEMP, DEEP, and TEP reactions at 283 ± 2 K, at or above the local dew point, which was ∼280 K. This procedure avoided water condensation during the experiments. The data obtained at 283 ± 2 K are plotted in accordance with eq I in Figures 3 (DMMP and DMEP reactions) and 4 (DEMP, DEEP, and TEP reactions). The experimental data for DEEP exhibited more scatter than did the corresponding data for DEMP or TEP (Figure 4), consistent with our previous room-temperature study[8] and with the greater scatter of the room-temperature rate constants for DEEP than those for DEMP or TEP.[12] The rate constant ratios k_1/k_2 obtained by least-squares analyses of these data and the rate constants k_1 derived are given in Table 4, together with the reference compounds used and their rate constants k_2. The measured rate constants at 283 ± 2 K are lower than those at 278 ± 2 K, by 8% for DEEP and by 16−33% for DMMP, DMEP, DEMP, and TEP. On the basis of the previously measured temperature dependencies at ≥296 K, the rate constants at 283 K would be expected to be 10% lower than those at 278 K. Apart from the DEEP reaction, the rate constants at 283 K are hence significantly lower than those at 278 K based on the temperature dependencies derived from the ≥296 K data.

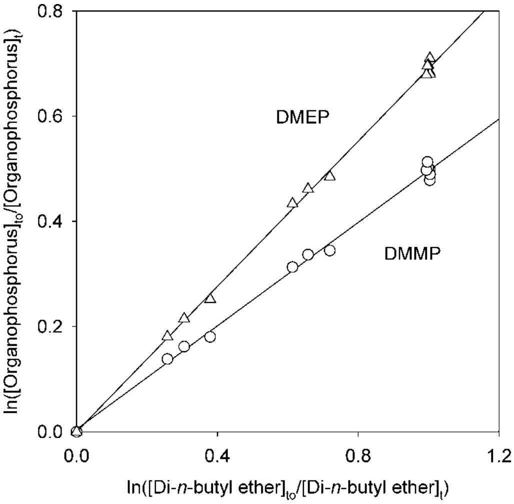

Figure 3. Plots of equation I for the reactions of OH radicals with dimethyl methylphosphonate (DMMP) and dimethyl ethylphosphonate (DMEP) at 283 ± 2 K, with di-*n*-butyl ether as the reference compound.

The rate constants for DMMP, DMEP, DEMP, DEEP, and TEP from the present study at 283 ± 2 K and those from our previous studies at ≥296 K[5,8,10,12] are given in Table 5 and are plotted in Arrhenius form in Figures 5 (DMMP and DMEP) and 6 (DEMP, DEEP, and TEP). Least-squares analyses of the rate constants for DMMP and DMEP obtained relative to di-*n*-butyl ether and of the rate constants for DEMP, DEEP, and TEP obtained relative to α-pinene lead to the values of B in $k_1 = Ae^{-B/T}$ given in Table 2. The pre-exponential factors, A, were (cm^3 molecule^{-1} s^{-1}) 6.52×10^{-14} for DMMP, 9.23×10^{-14}

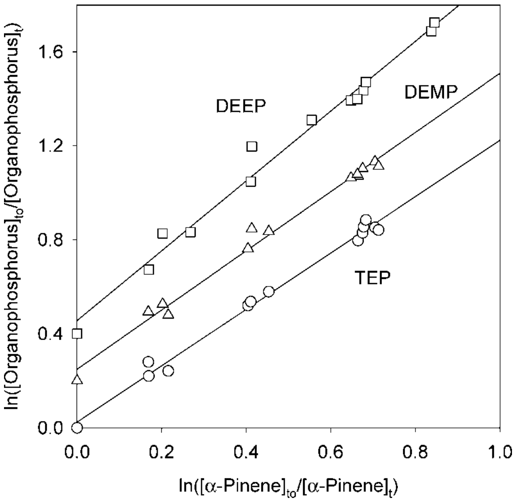

Figure 4. Plots of equation I for the reactions of OH radicals with triethyl phosphate (TEP), diethyl methylphosphonate (DEMP), and diethyl ethylphosphonate (DEEP) at 283 ± 2 K, with α-pinene as the reference compound. The data for DEMP and DEEP have been displaced vertically by 0.20 and 0.40 units, respectively, for clarity.

TABLE 4: Rate Constant Ratios k_1/k_2 and Rate Constants k_1 (cm^3 molecule^{-1} s^{-1}) Measured for the Reactions of OH Radicals with Dimethyl Methylphosphonate (DMMP), Dimethyl Ethylphosphonate (DMEP), Diethyl Methylphosphonate (DEMP), Diethyl Ethylphosphonate (DEEP), and Triethyl Phosphate (TEP) at 283 ± 2 K

organophosphorus	reference compound	k_1/k_2[a]	$10^{11} \times k_1$[b]
DMMP	di-*n*-butyl ether	0.492 ± 0.019	1.52 ± 0.06
DMEP	di-*n*-butyl ether	0.691 ± 0.017	2.13 ± 0.06
DEMP	α-pinene	1.26 ± 0.09	7.12 ± 0.51
DEEP	α-pinene	1.49 ± 0.12	8.42 ± 0.68
TEP	α-pinene	1.20 ± 0.08	6.78 ± 0.46

[a] Indicated errors are two least-squares standard deviations. [b] Placed on an absolute basis by use of rate constants at 283 K of k_2(di-*n*-butyl ether) = 3.08×10^{-11} cm^3 molecule^{-1} s^{-1} [19] and k_2(α-pinene) = 5.65×10^{-11} cm^3 molecule^{-1} s^{-1}.[2] 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%.

for DMEP, 4.35×10^{-13} for DEMP, 4.13×10^{-13} for DEEP, and 4.03×10^{-13} for TEP. The temperature dependencies, *B*, were used to correct rate constants measured at 296[5,8,10] to 298 K. For DEMP, DEEP, and TEP, the average of the 298 K rate constants was then combined with the temperature dependence determined using the rate constants measured relative to α-pinene to obtain the Arrhenius parameters given in Table 2. The final values of the pre-exponential factors, *A*, given in Table 2 are within 1.3% of those derived using only the rate constants relative to α-pinene.

For the DMMP and DMEP reactions, DMMP and DMEP were both present in the reactant mixtures used here and in our previous[12] study. Hence, rate constant ratios $k(\mathrm{OH} + \mathrm{DMEP})/k(\mathrm{OH} + \mathrm{DMMP})$ are also available (Table 6), and these are independent of temperature, with a weighted average of 1.41 ± 0.03, where the indicated error is two standard deviations (the unweighted average is 1.41 ± 0.05). The averages of the 298 K rate constants measured relative to di-*n*-butyl ether and *n*-decane[10] (the latter corrected from 296 K, as noted above) are 1.06×10^{-11} cm^3 molecule^{-1} s^{-1} for DMMP and 1.62×10^{-11} cm^3 molecule^{-1} s^{-1} for DMEP, with $k(\mathrm{OH} + \mathrm{DMEP})/k(\mathrm{OH} + \mathrm{DMMP}) = 1.53$. The 298 K rate constants for DMMP and DMEP were then adjusted equally in opposite directions

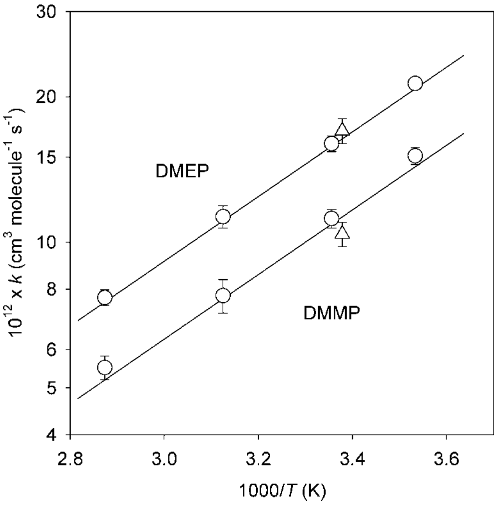

Figure 5. Arrhenius plots of rate constants for the reactions of OH radicals with dimethyl methylphosphonate (DMMP) and dimethyl ethylphosphonate (DMEP). Rate constants are from ○, ∼4500 or ∼5000 L Teflon bag inside of the evacuable chamber, relative to di-*n*-butyl ether (this work and ref 12); and △ ∼7000 L Teflon chamber, relative to *n*-decane.[10] The solid lines are our recommended Arrhenius fits (see Table 2 and text).

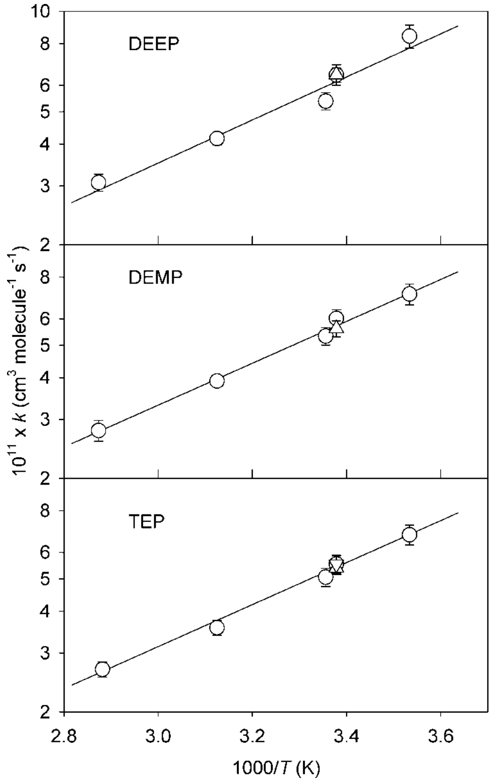

Figure 6. Arrhenius plots of rate constants for the reactions of OH radicals with diethyl methylphosphonate (DEMP), diethyl ethylphosphonate (DEEP), and triethyl phosphate (TEP). Rate constants are from ○, ∼4500 or ∼5000 L Teflon bag inside of the evacuable chamber and ∼7000 L Teflon chamber (296 ± 2 K), relative to α-pinene (this work and refs 8 and 12); △, ∼7000 L Teflon chamber, relative to 1,3,5-trimethylbenzene;[8] and ▽, ∼6400 L Teflon chamber, relative to propene (TEP only).[5] The solid lines are our recommended Arrhenius fits (see Table 2 and text).

to be consistent with the directly measured rate constant ratio $k(\mathrm{OH} + \mathrm{DMEP})/k(\mathrm{OH} + \mathrm{DMMP})$, and our "best-fit" 298 K rate constants and Arrhenius parameters are given in Table 2, with $k(\mathrm{OH} + \mathrm{DMEP})/k(\mathrm{OH} + \mathrm{DMMP}) = 1.45$. The final values

TABLE 5: Rate Constants k_1 Measured in the Present and Previous Work from This Laboratory[5,8,10,12] for the Reactions of OH Radicals with Dimethyl Methylphosphonate (DMMP), Dimethyl Ethylphosphonate (DMEP), Diethyl Methylphosphonate (DEMP), Diethyl Ethylphosphonate (DEEP), and Triethyl Phosphate (TEP) over the Temperature Range of 283−348 K

	$10^{12} \times k_1$ (cm^3 molecule^{-1} s^{-1})[a]				
temperature (K)	DMMP[b]	DMEP[b]	DEMP[c]	DEEP[c]	TEP[c]
283 ± 2	15.2 ± 0.6	21.3 ± 0.6	71.2 ± 5.1	84.2 ± 6.8	67.8 ± 4.6
296 ± 2	10.4 ± 0.6[d]	17.0 ± 1.0[d]			55.3 ± 3.5[e]
296 ± 2			60.2 ± 3.7	64.4 ± 3.2	55.4 ± 3.2
296 ± 2			56.1 ± 3.1[f]	64.6 ± 4.6[f]	53.9 ± 2.4[f]
298 ± 1					50.6 ± 3.2
298 ± 2	11.2 ± 0.5	16.0 ± 0.6	53.3 ± 3.2	53.8 ± 3.2	
320 ± 2	7.76 ± 0.62	11.3 ± 0.6	39.1 ± 1.3	41.6 ± 1.8	35.7 ± 1.8
347 ± 2					26.8 ± 1.4
348 ± 2	5.51 ± 0.31	7.69 ± 0.29	27.8 ± 2.0	30.7 ± 1.8	

[a] Indicated errors are two least-squares standard deviations in the rate constant ratios k_1/k_2 and do not include uncertainties in the rate constant k_2, which are expected to be ~±10%. [b] Relative to di-*n*-butyl ether, unless noted otherwise, and placed on an absolute basis using k_2(di-*n*-butyl ether) = $6.29 \times 10^{-18}\ T^2\ e^{1164/T}$ cm^3 molecule^{-1} s^{-1}.[19] [c] Relative to α-pinene, unless noted otherwise, and placed on an absolute basis using k_2(α-pinene) = $1.21 \times 10^{-11}\ e^{436/T}$ cm^3 molecule^{-1} s^{-1}.[2] [d] Relative to *n*-decane[10] and placed on an absolute basis using a rate constant of k_2(*n*-decane) = 1.09×10^{-11} cm^3 molecule^{-1} s^{-1} at 296 K.[2] [e] Relative to propene[5] and placed on an absolute basis using k_2(propene) = 2.66×10^{-11} cm^3 molecule^{-1} s^{-1} at 296 K.[2] [f] Relative to 1,3,5-trimethylbenzene[8] and placed on an absolute basis by use of k_2(1,3,5-trimethylbenzene) = 5.67×10^{-11} cm^3 molecule^{-1} s^{-1} at 296 K.[2]

TABLE 6: Directly Measured Rate Constant Ratios k_1/k_2 for DMEP versus DMMP, DEEP versus DEMP, TEP versus DEMP, and TEP versus DEEP in ~4500−7000 L Volume Teflon Chambers

test compound	reference compound	temperature (K)	k_1/k_2[a]	reference
DMEP	DMMP	283 ± 2	1.40 ± 0.04	this work
DMEP	DMMP	298 ± 2	1.42 ± 0.03	12
DMEP	DMMP	320 ± 2	1.44 ± 0.07	12
DMEP	DMMP	348 ± 2	1.39 ± 0.05	12
DEEP	DEMP	283 ± 2	1.13 ± 0.10[b]	this work
DEEP	DEMP	296 ± 2	1.09 ± 0.04	8
DEEP	DEMP	298 ± 2	1.04 ± 0.03	12
DEEP	DEMP	320 ± 2	1.06 ± 0.02	12
DEEP	DEMP	348 ± 2	1.10 ± 0.03	12
TEP	DEMP	283 ± 2	0.920 ± 0.016	this work
TEP	DEMP	296 ± 2	0.958 ± 0.012	8
TEP	DEEP	283 ± 2	0.828 ± 0.007[b]	this work
TEP	DEEP	296 ± 2	0.866 ± 0.026	8

[a] Indicated errors are two least-squares standard deviations. [b] From a single experiment.

of the pre-exponential factors, *A*, given in Table 2 are 4% lower for DMMP and 2% lower for DMEP than those derived using only rate constants relative to di-*n*-butyl ether.

The Arrhenius expressions given in Table 2 are shown as the solid lines in Figures 5 and 6. Within the experimental uncertainties, the values of *B* in $k = Ae^{-B/T}$ for DMMP, DMEP, DEMP, DEEP, and TEP are all similar, with an average value of $B = -1490 \pm 100$ K, where the uncertainty is two standard deviations. In contrast, the temperature dependence of the DMHP reaction is significantly less negative, with $B = -474 \pm 159$ K. On the basis of the magnitude of the rate constants for the reactions of OH radicals with DMMP, DMEP, DEMP, DEEP, and TEP, the highly negative values of *B*, and the significant deuterium isotope effect for DMMP compared to that for DMMP-d_9,[10] we previously suggested that these reactions proceed by initial complex formation followed by decomposition involving C−H bond breakage.[12] For example, for the DMMP reaction

$$OH + (CH_3O)_2P(O)CH_3 \leftrightarrow [HO{-}(CH_3O)_2P(O)CH_3] \rightarrow H_2O + CH_3OP(O)(CH_3)OC^{\bullet}H_2 \quad (3)$$

with back-decomposition of the [HO−(CH$_3$O)$_2$P(O)CH$_3$] complex to reactants having a higher barrier than that for decomposition via C−H bond cleavage to H_2O + $CH_3OP(O)(CH_3)OC^{\bullet}H_2$ or to other products in order to account for the negative temperature dependence.[12] The significantly less negative temperature dependence for DMHP compared to that for DMMP, DMEP, DEMP, DEEP, and TEP then indicates that the heights of the two barriers for decomposition of the HO−DMHP complex are more similar than those in the case for the DMMP, DMEP, DEMP, DEEP, and TEP reactions. Previous product studies[7,10] of the OH + DMHP reaction suggest that reaction occurs by initial H-atom abstraction from both of the CH_3O groups and from the P−H bond,[7,10] with the latter possibly accounting for ~15% of the overall reaction.[7]

In a number of experiments (both in this work and previously), DEMP and DEEP were both present in the same reactant mixture, and direct measurements of the rate constant ratio *k*(OH + DEEP)/*k*(OH + DEMP) were obtained over the temperature range of 283−348 K (Table 6). Consistent with the similar temperature dependencies derived for the DEMP and DEEP reactions (Table 2), direct measurements of *k*(OH + DEEP)/*k*(OH + DEMP) show that, within the experimental uncertainties, this rate constant ratio is independent of temperature, with a weighted average of 1.07 ± 0.03, where the indicated error is two standard deviations. Rate constant ratios *k*(OH + TEP)/*k*(OH + DEMP) and *k*(OH + TEP)/*k*(OH + DEEP) are also available at 283 ± 2 and 296 ± 2 K (Table 6); for both rate constant ratios, the values at the two temperatures agree to within 5%. The present Arrhenius parameters given in Table 2 are virtually identical to those obtained previously from rate data at ≥296 K, with our present and previous[12] values of *B* being within 70 K apart from DEEP, where the present value of *B* is 140 K more negative than that reported previously.[12]

Our data suggest that at temperatures below the dew point where water condensation on the outside of the Teflon bag occurred (~280 K in this case), the measured rate constants are higher than those expected from the Arrhenius expressions derived using higher-temperature data. This effect was most evident for DMMP, DMEP, DEMP, and TEP, being smaller and almost not observable within the experimental uncertainties for DEEP, and was not observed for DMHP. Replicate analyses after the irradiation periods in experiments at 278 K suggested that this was not due to a dark decay of the organophosphorus compounds. Since water is known to permeate through Teflon,[20] this may lead to a thin film of water on the inside of the Teflon chamber at temperatures below the dew point. The observed absence of a dark decay of the organophosphorus compounds at 278 K suggests that a light-induced wall loss process may then occur. However, at this point this is merely a possibility, and the atmospheric implications of these observations, if any, are presently unknown. Note that we have previously shown that at 296 ± 2 K, gaseous water vapor has no effect on the rate constants for the reactions of OH radicals with DEMP, DEEP, or TEP, over the relative humidity range of ∼5−50%.[8]

Aerosol Formation. Aerosol formation was measured during $CH_3ONO-NO-$air irradiations of each organophosphorus compound, as well as of some mixtures, carried out in the ∼7000 L Teflon chamber at 296 ± 2 K. The initial reactant concentrations and experimental procedures were as in the kinetic experiments, and the fraction of the initially present organophosphorus compound reacted by the end of the experiment was 20% for DMHP, 34% for DMMP, and 40−43% for DMEP, DEMP, DEEP, and TEP. The aerosol number and size distribution were measured during the experiments using a TSI 393672L scanning mobility particle sizer (SMPS). The aerosol loadings prior to beginning the irradiations and with all of the reactants present in the chamber were ≤ 2 μg m^{-3} (and <1 μg m^{-3} for all but the DMHP experiment). The SMPS data showed that in all experiments, new particle formation occurred during the first irradiation period, with the increase in aerosol mass during the second and third irradiation periods due to the growth of existing particles. As generally observed,[21] the aerosol yield, defined as (aerosol formed/organophosphorus compound reacted), increased with the amount of aerosol present (or correspondingly, with the extent of reaction). Assuming that the aerosol had the same density as the organophosphorus reactant, the aerosol yields at the end of the reactions, defined as {(aerosol formed, corrected for wall losses)/(organophosphorus compound reacted)}, were 3% for DMHP, 1% for DMMP, 6% for DMEP, 2% for DEMP, 4% for DEEP, and 6% for TEP. The aerosol yield during the last portion of the reaction (i.e., Δ(aerosol)/Δ(organophosphorus compound) between the end of the second and third irradiation periods) were 5% for DMHP, 2% for DMMP, 8% for DMEP, 3% for DEMP, 6% for DEEP, and 7% for TEP. In the irradiations of mixtures, some of which contained the reference compounds, within the experimental uncertainties, the aerosol formed was the sum of the aerosol yields of the individual reactants. Hence, aerosol formation from the organophosphorus compounds studied here at the initial concentrations employed here was relatively minor, being ≤8% in all cases.

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