J. Phys. Chem. A **2006,** *110,* 7393−7400

Temperature-Dependent Rate Constants for the Gas-Phase Reactions of OH Radicals with 1,3,5-Trimethylbenzene, Triethyl Phosphate, and a Series of Alkylphosphonates

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Received: March 13, 2006; In Final Form: April 21, 2006

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, $(C_2H_5O)_2P(O)C_2H_5$], triethyl phosphate [TEP, $(C_2H_5O)_3PO$] and 1,3,5-trimethylbenzene have been measured over the temperature range 278−348 K at atmospheric pressure of air using a relative rate method. α-Pinene (for DEMP, DEEP, TEP and 1,3,5-trimethylbenzene) and di-*n*-butyl ether (for DMMP and DMEP) were used as the reference compounds, and rate constants for the reaction of OH radicals with di-*n*-butyl ether were also measured over the same temperature range using α-pinene and *n*-decane as the reference compounds. The Arrhenius expressions obtained for these OH radical reactions (in cm^3 $molecule^{-1}$ s^{-1} units) are $8.00 \times 10^{-14}e^{(1470\pm132)/T}$ for DMMP (296−348 K), $9.76 \times 10^{-14}e^{(1520\pm14)/T}$ for DMEP (296−348 K), $4.20 \times 10^{-13}e^{(1456\pm227)/T}$ for DEMP (296−348 K), $6.46 \times 10^{-13}e^{(1339\pm376)/T}$ for DEEP (296−348 K), $4.29 \times 10^{-13}e^{(1428\pm219)/T}$ for TEP (296−347 K), and $4.40 \times 10^{-12}e^{(738\pm176)/T}$ for 1,3,5-trimethylbenzene (278−347 K), where the indicated errors are two least-squares standard deviations and do not include the uncertainties in the rate constants for the reference compounds. The measured rate constants for di-*n*-butyl ether are in good agreement with literature data over the temperature range studied (278−348 K).

Introduction

Organophosphorus compounds of structure $(RO)_{3-x}P(O)R_x$ and $(RO)_{3-x}P(S)R_x$, where R = alkyl, are widely used as pesticides.[1] These compounds and their precursors may be released into the atmosphere where they can undergo transport and chemical transformations, which for gaseous compounds include 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 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 and $OCH{=}CCl_2$) with OH radicals, NO_3 radicals and O_3 have been measured at room temperature.[3−10] For these organophosphorus compounds, reaction with the OH radical is calculated to be the dominant atmospheric loss process.[4,8,10]

To date, no temperature-dependent rate data exist for the reactions of OH radicals with organophosphorus compounds. Accordingly, in this work we have used a relative rate method to measure 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, $(C_2H_5O)_3PO$] at atmospheric pressure of air over the temperature range 278−348 K. In addition, rate constants for the reactions of OH radicals with 1,3,5-trimethylbenzene and di-*n*-butyl ether have also been measured over the same temperature range, and the yield of acetaldehyde has been measured from the OH radical-initiated reaction of TEP at 347 ± 1 K.

Experimental Methods

Experiments were carried out in three different chamber systems. A limited series of experiments were conducted at 297 ± 1 K and 735 Torr total pressure of dry purified air in a ∼7000 L volume Teflon chamber,[8,10] equipped with two parallel banks of blacklamps for irradiation. Temperature-dependent experiments were initially carried out at 303 and 343−344 K in a 5870 L Teflon-coated, evacuable chamber, with irradiation provided by a 24 kW xenon arc lamp filtered through a 6 mm thick Pyrex pane to remove wavelengths <300 nm.[7,8,10] The majority of the experiments were carried out using a ∼4500 L volume Teflon "bag" inserted inside the 5870 L Teflon-coated chamber, with irradiation again provided by the 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 K over the range 278−348 K for the present study. All three chambers were provided with Teflon-coated fan(s) to ensure rapid mixing of reactants during their introduction into the chamber.

Rate constants for the reactions of OH radicals with DMMP, DMEP, DEMP, DEEP, TEP, 1,3,5-trimethylbenzene and di-*n*-butyl ether were measured using a relative rate technique in which the concentrations of the test compound(s) and a reference compound (whose OH radical reaction rate constant is reliably known) were measured in the presence of OH radicals.[8,10] Providing that the only loss processes for the organophosphorus compound (or test compound) and the reference compound was

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10.1021/jp061542r CCC: $33.50

by reaction with OH radicals,

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

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

then

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

where $[\text{organophosphorus}]_{t_o}$ and $[\text{reference compound}]_{t_o}$ are the concentrations of the organophosphorus (or test) compound and reference compound, respectively, at time t_o, $[\text{organophosphorus}]_t$ 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] The initial reactant concentrations (molecule $\mathrm{cm^{-3}}$) were $\sim(2.4-3.1) \times 10^{14}$ for CH_3ONO, $\sim(2.4-3.1) \times 10^{14}$ for NO and $\sim(2.4-3.1) \times 10^{13}$ for organophosphorus or test compound and reference compound. Irradiations were carried out for up to 27 min (~7000 L Teflon chamber) or 45 min (evacuable chamber, with or without Teflon bag inserted).

The concentrations of α-pinene, 1,3,5-trimethylbenzene, di-*n*-butyl ether, *n*-decane, DMMP, DMEP, DEMP, DEEP and TEP (and acetaldehyde from selected TEP reactions, see below) were measured during the experiments by gas chromatography with flame ionization detection (GC-FID).[8,10] Gas samples of 100 $\mathrm{cm^3}$ volume were collected from the chamber onto Tenax-TA solid adsorbent (maintained at room temperature), with subsequent thermal desorption at ~250 °C onto a 30 m DB-1701 megabore column held at 0 °C or, for analyses involving acetaldehyde, −40 °C, and then temperature programmed to 200 °C at 8 °C $\mathrm{min^{-1}}$. Based on replicate analyses in Teflon chambers in the dark, the analytical uncertainties for the organophosphorus compounds, 1,3,5-trimethylbenzene and the reference compounds used were typically ≤3%.

Temperatures of the gas mixtures inside the chambers were measured by thermocouples. For the experiments carried out in the evacuable chamber, the gas temperature (including that within the Teflon bag when fitted) was within ±1 K of the set-point temperature of the chamber heating/cooling system controller. In all experiments in all three chamber systems, the temperature rise during the intermittent irradiations was always ≤2 K.

The chemicals used, and their stated purities, were acetaldehyde (99.5+%), *n*-decane (99+%), diethyl methylphosphonate (97%), dimethyl methylphosphonate (97%), di-*n*-butyl ether (99+%), α-pinene (99+%), and triethyl phosphate (99+%), (Aldrich Chemical Co.); dimethyl ethylphosphonate (98%) (Cerilliant Corp.); diethyl ethylphosphonate (98%) (Lancaster); 1,3,5-trimethylbenzene (Eastman); and NO (≥99.0%) (Matheson Gas Products). Methyl nitrite was prepared as described by Taylor et al.[11] and stored under vacuum at 77 K.

Results

Irradiations of $CH_3ONO-NO-$organic compound−air mixtures were carried out in one or more of the chamber systems, with the following organic compounds: TEP + 1,3,5-trimethylbenzene + α-pinene, TEP + α-pinene, TEP + di-*n*-butyl ether + α-pinene, 1,3,5-trimethylbenzene + di-*n*-butyl ether + α-pinene, DEMP + 1,3,5-trimethylbenzene + α-pinene, DEEP + 1,3,5-trimethylbenzene + α-pinene, DEMP + di-*n*-butyl ether + α-pinene, DEMP + DEEP + α-pinene, DEEP + di-*n*-butyl ether + α-pinene, di-*n*-butyl ether + α-pinene, DMMP + DMEP + di-*n*-butyl ether, and di-*n*-butyl ether + *n*-decane.

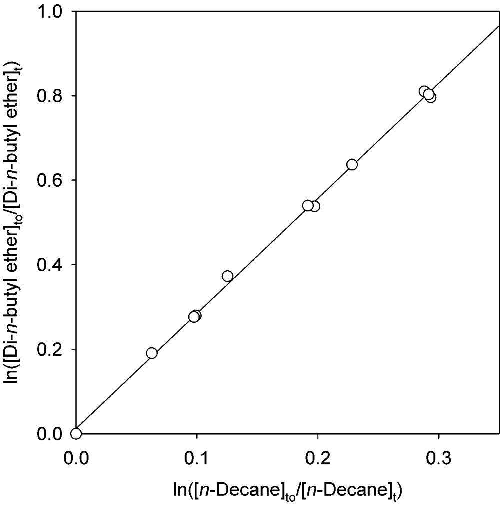

Figure 1. Plot of eq I for the reactions of OH radicals with di-*n*-butyl ether at 297 ± 1 K, with *n*-decane as the reference compound.

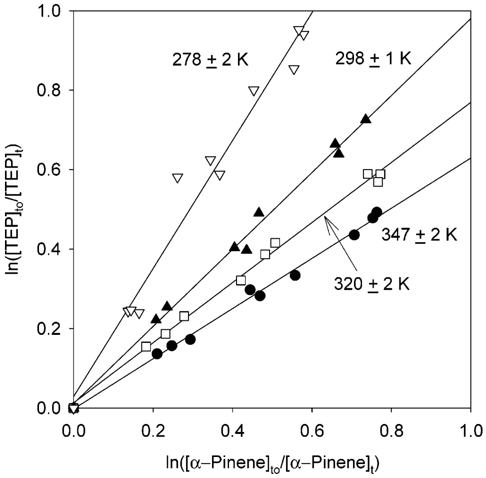

Figure 2. Plots of eq I for the reactions of OH radicals with triethyl phosphate (TEP) at 278 ± 2, 298 ± 1, 320 ± 2 and 347 ± 2 K, with α-pinene as the reference compound.

α-Pinene and di-*n*-butyl ether were used as the reference compounds because rate constants for their OH radical reactions are available as a function of temperature over the temperature range used here (278−348 K),[2,12,13] their OH radical reaction rate constants are of a similar magnitude to those of 1,3,5-trimethylbenzene and the organophosphorus compounds studied here,[2,8,10,12] and they could be analyzed using the same collection and analysis procedure and GC column as employed for 1,3,5-trimethylbenzene and the organophosphorus compounds. Rate constants for the reactions of OH radicals with di-*n*-butyl ether relative to those for α-pinene (over the temperature range 278−348 K)[2] and *n*-decane (at 297 ± 1 K)[2,14] were also measured to check for consistency of the rate constants used for the reference compounds (see below).

Figure 1 shows a plot of eq I for the reaction of OH radicals with di-*n*-butyl ether, with *n*-decane as the reference compound, carried out in the ~7000 L Teflon chamber at 297 ± 1 K (the only set of experiments conducted in that chamber). Figures 2 and 3 show representative plots of eq I for the reactions of OH radicals with TEP and 1,3,5-trimethylbenzene, respectively, with

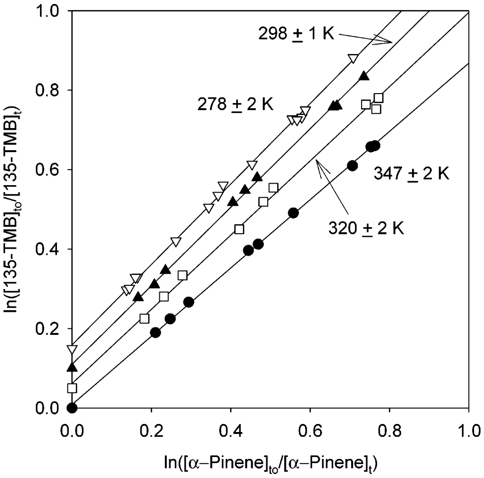

Figure 3. Plots of eq I for the reactions of OH radicals with 1,3,5-trimethylbenzene (135-TMB) at 278 ± 2, 298 ± 1, 320 ± 2 and 347 ± 2 K, with α-pinene as the reference compound. The data for 135-TMB at 320 ± 2, 298 ± 1 and 278 ± 2 K have been displaced vertically by 0.05, 0.10 and 0.15 units, respectively, for clarity.

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 Di-*n*-butyl Ether

temp (K)	chamber[a]	ref compd	k_1/k_2[b]	$10^{11}k_1$ (cm^3 $molecule^{-1}$ s^{-1})[c]
278 ± 2	A	α-pinene	0.507 ± 0.015	2.94 ± 0.09
296 ± 2[d]	B	α-pinene	0.578 ± 0.014[d]	3.05 ± 0.08[d]
297 ± 1	B	*n*-decane	2.72 ± 0.08	2.99 ± 0.09
298 ± 1	A	α-pinene	0.519 ± 0.013	2.71 ± 0.07
303 ± 1	C	α-pinene	0.549 ± 0.007	2.80 ± 0.04
343 ± 1	C	α-pinene	0.517 ± 0.013	2.23 ± 0.06
348 ± 2	A	α-pinene	0.518 ± 0.014	2.19 ± 0.06

[a] A = ~4500 L Teflon bag inside 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 rate constants of k_2(*n*-decane) = 1.10 × 10^{-11} cm^3 $molecule^{-1}$ s^{-1} at 297 K[2,14] and k_2(α-pinene) = 1.21 × 10^{-11} $e^{436/T}$ 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%. [d] From Aschmann et al.[8]

α-pinene as the reference compound at the various temperatures studied in the ~4500 L Teflon bag inserted inside the 5870 L evacuable and thermostated chamber. Plots of the experimental data for DEMP and DEEP using α-pinene as the reference compound and for DMMP and DMEP with di-*n*-butyl ether as the reference compound were analogous to those shown for TEP in Figure 2, in that the data at 278 ± 2 K exhibited significantly more scatter than at ≥298 K. Moreover, at 278 ± 2 K decreases in the measured postreaction TEP and DEEP concentrations of 6% and 11%, respectively, were observed in the dark over a period of 49−55 min from replicate analyses (but not for DMMP or DMEP), suggesting that wall losses of certain of the organophosphorus compounds were occurring after initiation of the reactions. In contrast to this behavior, replicate pre-reaction analyses for all compounds agreed to within ≤3%, as did replicate postreaction analyses for experiments conducted at ≥298 K.

TABLE 2: Rate Constant Ratios k_1/k_2 and Rate Constants k_1 (cm^3 $molecule^{-1}$ s^{-1}) Measured in This Laboratory for the Reactions of OH Radicals with 1,3,5-Trimethylbenzene (135-TMB) and Triethyl Phosphate (TEP), with α-Pinene as the Reference Compound unless Noted Otherwise

		135-TMB		TEP	
temp (K)	chamber[a]	k_1/k_2[b]	$10^{11}k_1$[c]	k_1/k_2[b]	$10^{11}k_1$[c]
278 ± 2	A	1.01 ± 0.03	5.86 ± 0.18	1.61 ± 0.19	9.35 ± 1.11
296 ± 2[d,e]	B[d,e]	*d*	5.75 ± 0.30[d]	*e*	5.53 ± 0.35[e]
296 ± 2[f]	B	1.12 ± 0.02[f]	5.91 ± 0.11[f]	1.05 ± 0.06[f]	5.54 ± 0.32[f]
296 ± 2[f]	B			*f, g*	5.39 ± 0.24
298 ± 1	A	0.989 ± 0.021	5.17 ± 0.11	0.969 ± 0.061	5.06 ± 0.32
303 ± 2	C	1.00 ± 0.03	5.10 ± 0.16	0.805 ± 0.055	*h*
320 ± 2	A	0.934 ± 0.035	4.41 ± 0.17	0.756 ± 0.037	3.57 ± 0.18
344 ± 2	C	0.860 ± 0.026	3.70 ± 0.12	0.523 ± 0.054	*h*
347 ± 2	A	0.859 ± 0.014	3.65 ± 0.06	0.631 ± 0.032	2.68 ± 0.14

[a] A = ~4500 L Teflon bag inside 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(α-pinene) = 1.21 × 10^{-11} $e^{436/T}$ 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%. [d] From Atkinson and Aschmann,[15] in a 6400 L volume Teflon chamber with propene as the reference compound. Rate constant ratio k_1/k_2 = 2.16 ± 0.11 placed on an absolute basis by use of k_2(propene) = 2.66 × 10^{-11} cm^3 $molecule^{-1}$ s^{-1} at 296 K.[2] [e] From Atkinson et al.,[5] in a 6400 L volume Teflon chamber with propene as the reference compound. Rate constant ratio k_1/k_2 = 2.08 ± 0.13 placed on an absolute basis by use of k_2(propene) = 2.66 × 10^{-11} cm^3 $molecule^{-1}$ s^{-1} at 296 K.[2] [f] From Aschmann et al.[8] [g] 1,3,5-Trimethylbenzene was used as the reference compound. The measured rate constant ratio k_1/k_2 = 0.951 ± 0.042 is 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] [h] Because of evidence for wall absorption of TEP (compare with rate constant ratios at similar temperatures obtained in the ~7000 L Teflon chamber and the ~4500 L Teflon bag inserted in the 5870 L evacuable chamber; see also text), rate constants obtained from the rate constant ratios in this chamber system are believed to be erroneously low and therefore are not cited here.

The rate constant ratios k_1/k_2 obtained from least-squares analyses of plots such as those shown in Figures 1−3 are given in Tables 1 (di-*n*-butyl ether), 2 (1,3,5-trimethylbenzene and TEP), 3 (DEMP and DEEP) and 4 (DMMP and DMEP), with the chamber in which the reactions were carried out also being noted. Table 5 also lists rate constant ratios for TEP versus 1,3,5-trimethylbenzene, DMEP versus DMMP and DEEP versus DEMP derived from experiments in which these compounds were present in addition to the reference compound, together with the corresponding rate constant ratios for TEP versus 1,3,5-trimethylbenzene and DEEP versus DEMP obtained in our previous room temperature study.[8] It is immediately obvious from Tables 2 and 3 that the rate constant ratios k_1/k_2 for TEP, DEMP and DEEP obtained in the 5870 L evacuable chamber without a Teflon bag inserted (chamber “C” in Tables 2 and 3) at 303 K and 343−344 K are 15−30% lower than those measured in either the ~7000 L Teflon chamber[8] or the ~4500 L Teflon bag inserted inside the evacuable chamber. In contrast, the rate constant ratios k_1/k_2 for di-*n*-butyl ether and 1,3,5-trimethylbenzene relative to those for α-pinene obtained in the evacuable chamber are in good agreement with rate constant ratios measured using the Teflon chambers (Tables 1 and 2 and Figure 4). The evacuable chamber contains numerous “O”-rings for attachment of flanges, the multiple reflection optical system, and the end-window assemblies, and it is possible that organophosphorus compounds readily absorb into the “O”-ring material.[8]

That rapid initial wall adsorption occurs after introducing TEP into the evacuable chamber, with a subsequent slower wall loss rate, was apparent from our previous room-temperature product study of the OH radical-initiated reaction of TEP.[8] In the present work, additional experiments to investigate wall adsorption/desorption were carried out at 303 and 344 K, with TEP, 1,3,5-trimethylbenzene and α-pinene (~2.4 × 10^{13} molecule cm^{-3} each) being introduced into the evacuable chamber in an atmosphere of pure dry air and three replicate GC-FID analyses

TABLE 3: Rate Constant Ratios k_1/k_2 and Rate Constants k_1 (cm^3 molecule^{-1} s^{-1}) Measured in This Laboratory for the Reactions of OH Radicals with Diethyl Methylphosphonate (DEMP) and Diethyl Ethylphosphonate (DEEP), with α-Pinene as the Reference Compound unless Noted Otherwise

		DEMP		DEEP	
temp (K)	chamber^a	$k_1/k_2{}^b$	$10^{11}k_1{}^c$	$k_1/k_2{}^b$	$10^{11}k_1{}^c$
278 ± 2	A	1.64 ± 0.21	9.52 ± 1.22	1.58 ± 0.18	9.17 ± 1.05
296 ± 2^d	B	1.14 ± 0.07^d	6.02 ± 0.37^d	1.22 ± 0.06^d	6.44 ± 0.32^d
296 ± 2^d	B	*d, e*	5.61 ± 0.31^e	*d, e*	6.46 ± 0.46^e
298 ± 2	A	1.02 ± 0.06	5.33 ± 0.32	1.03 ± 0.06	5.38 ± 0.32
303 ± 2	C	0.872 ± 0.033	*f*	0.856 ± 0.054	*f*
320 ± 2	A	0.827 ± 0.027	3.91 ± 0.13	0.880 ± 0.038	4.16 ± 0.18
343 ± 2	C	0.559 ± 0.029	*f*	0.594 ± 0.054	*f*
348 ± 2	A	0.656 ± 0.047	2.78 ± 0.20	0.726 ± 0.042	3.07 ± 0.18

[a] A = ~4500 L Teflon bag inside 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 k_2(α-pinene) = 1.21 × 10^{-11} e$^{436/T}$ 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%. [d] From Aschmann et al.[8] [e] 1,3,5-Trimethylbenzene was used as the reference compound. The measured rate constant ratios k_1(DEMP)/k_2 = 0.990 ± 0.053 and k_1(DEEP)/k_2 = 1.14 ± 0.08 are 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] [f] Because of evidence for wall absorption of DEMP and DEEP (compare with rate constant ratios at similar temperatures obtained in the ~7000 L Teflon chamber and the ~4500 L Teflon bag inserted in the 5870 L evacuable chamber; see also text), the rate constants derived from the rate constant ratios measured in this chamber system are believed to be erroneously low and therefore are not cited here.

TABLE 4: Rate Constant Ratios k_1/k_2 and Rate Constants k_1 (cm^3 molecule^{-1} s^{-1}) Measured in This Laboratory for the Reactions of OH Radicals with Dimethyl Methylphosphonate (DMMP) and Dimethyl Ethylphosphonate (DMEP), with Di-*n*-butyl Ether as the Reference Compound, unless Noted Otherwise

		DMMP		DMEP	
temp (K)	chamber^a	$k_1/k_2{}^b$	$10^{12}k_1{}^c$	$k_1/k_2{}^b$	$10^{12}k_1{}^c$
278 ± 2	A	0.714 ± 0.045	22.8 ± 1.5	0.909 ± 0.068	29.1 ± 2.2
296 ± 2^d	B	*d*	10.4 ± 0.6^d	*d*	17.0 ± 1.0^d
298 ± 2	A	0.405 ± 0.017	11.2 ± 0.5	0.575 ± 0.021	16.0 ± 0.6
320 ± 2	A	0.317 ± 0.025	7.76 ± 0.62	0.460 ± 0.023	11.3 ± 0.6
348 ± 2	A	0.255 ± 0.014	5.51 ± 0.31	0.356 ± 0.013	7.69 ± 0.29

[a] A = ~4500 L Teflon bag inside 5870 L evacuable chamber; B = ~7000 L Teflon 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(di-*n*-butyl ether) = 6.29 × 10^{-18} T^2 e$^{1164/T}$ cm^3 molecule^{-1} s^{-1}.[12] 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% (see text). [d] From Aschmann et al.[10] *n*-Decane used as the reference compound and the measured rate constant ratios of k_1(DMMP)/k_2 = 0.951 ± 0.052 and k_1(DMEP)/k_2 = 1.56 ± 0.09 are 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.[2,14]

TABLE 5: Rate Constant Ratios k_1/k_2 Measured for TEP versus 1,3,5-Trimethylbenzene, DMEP versus DMMP and DEEP versus DEMP in ~4500−7000 L Volume Teflon Chambers

test compd	ref compd	temp (K)	$k_1/k_2{}^a$	ref
TEP	135-TMB	296 ± 2	0.951 ± 0.042	8
TEP	135-TMB	298 ± 1	0.978 ± 0.061	this work^b
TEP	135-TMB	320 ± 2	0.811 ± 0.016	this work^b
TEP	135-TMB	347 ± 2	0.735 ± 0.039	this work^b
DMEP	DMMP	298 ± 2	1.42 ± 0.03	this work^b
DMEP	DMMP	320 ± 2	1.44 ± 0.07	this work^b
DMEP	DMMP	348 ± 2	1.39 ± 0.05	this work^b
DEEP	DEMP	296 ± 2	1.09 ± 0.04	8
DEEP	DEMP	298 ± 2	1.04 ± 0.03	this work^b
DEEP	DEMP	320 ± 2	1.06 ± 0.02	this work^b
DEEP	DEMP	348 ± 2	1.10 ± 0.03	this work^b

[a] Indicated errors are two least-squares standard deviations. [b] Obtained from CH_3ONO−NO−air irradiations of 1,3,5-trimethylbenzene + TEP + α-pinene, DEMP + DEEP + α-pinene and DMMP + DMEP + di-*n*-butyl ether mixtures.

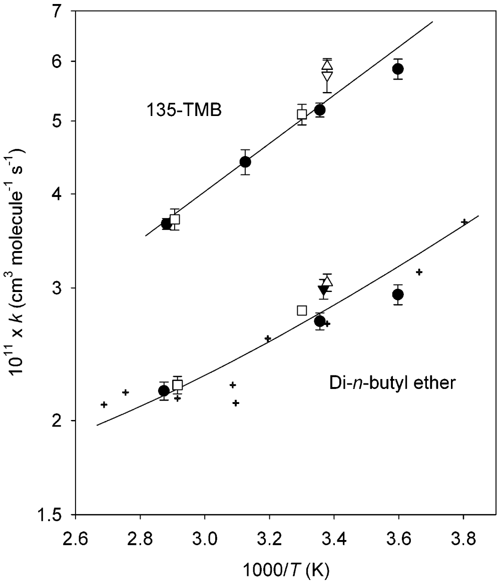

Figure 4. Arrhenius plot of rate constants for the reactions of OH radicals with di-*n*-butyl ether and 1,3,5-trimethylbenzene (135-TMB). Rate constants are from (●) ~4500 L Teflon bag inside evacuable chamber, relative to α-pinene; (□) 5870 L evacuable chamber, relative to α-pinene; (△) ~7000 L Teflon chamber, relative to α-pinene;[8] (▽) ~6400 L Teflon chamber, relative to propene (for 135-TMB);[15] (▼) ~7000 L Teflon chamber, relative to *n*-decane (for di-*n*-butyl ether); and (+) absolute rate constants from Mellouki et al.[12] (263−372 K). The solid lines are, for di-*n*-butyl ether, the Mellouki et al.[12] fit to their data, and for 1,3,5-trimethylbenzene, an Arrhenius fit to our rate constants measured relative to those for α-pinene.

carried out. The chamber was then pumped down from the initial 740−745 Torr to 370−375 Torr and back-filled to 740−745 Torr with pure air, and another three GC-FID analyses were conducted. Though the 1,3,5-trimethylbenzene/α-pinene concentration ratio before and after pump-down and back-filling remained constant at both 303 K (with after/before ratios of 1.01 ± 0.02 and 1.00 ± 0.02 in two experiments) and 344 K (an after/before ratio of 1.00 ± 0.02), the TEP/α-pinene concentration ratio after the pump-down and back-filling increased over the initial concentration ratio by factors of 1.12 ± 0.10 and 1.11 ± 0.08 in the two experiments at 303 K and by a factor of 1.12 ± 0.06 at 344 K, where the indicated errors are all two standard deviations. Assuming these data to be also applicable to a 50% reactive loss, then the rate constant for TEP at 303 and 344 K would have been underestimated by 15−17%. Clearly, reliable data could not be obtained for the organophosphorus compounds using the 5870 L evacuable chamber, and rate constants k_1 are not listed for the TEP, DEMP or DEEP reactions conducted in the evacuable chamber in Tables 2 and 3. All further experiments to determine the temperature dependence of the OH radical reaction rate constants with TEP, DEMP, DEEP, DMMP and DMEP were carried out in a ~4500 L Teflon bag inserted into the evacuable chamber (which therefore served merely as an oven that could be irradiated) and equipped with sampling, injection and thermocouple ports and with a Teflon-coated fan to ensure mixing of the bag contents.

TABLE 6: Arrhenius Parameters, $k = A\ \exp^{-B/T}$, and 298 K Rate Constants for the Reactions of OH Radicals with Dimethyl Methylphosphonate (DMMP), Dimethyl Ethylphosphonate (DMEP), Diethyl Methylphosphonate (DEMP), Diethyl Ethylphosphonate (DEEP), Triethyl Phosphate (TEP) and 1,3,5-Trimethylbenzene (135-TMB)

reactant	A (cm^3 molecule^{-1} s^{-1})	B (K)[a]	$10^{11}k$(298 K) (cm^3 molecule^{-1} s^{-1})	
$(CH_3O)_2P(O)CH_3$ (DMMP)[b]	8.00×10^{-14}	-1470 ± 132	1.11[c]	1.17[d]
$(CH_3O)_2P(O)C_2H_5$ (DMEP)[b]	9.76×10^{-14}	-1520 ± 14	1.60[c]	1.62[d]
$(C_2H_5O)_2P(O)CH_3$ (DEMP)[e]	4.20×10^{-13}	-1456 ± 227	5.56[c]	5.53[d]
$(C_2H_5O)_2P(O)C_2H_5$ (DEEP)[e]	6.46×10^{-13}	-1339 ± 376	5.78[c]	5.96[d]
$(C_2H_5O)_3PO$ (TEP)[e]	4.29×10^{-13}	-1428 ± 219	5.17[c]	5.25[d]
1,3,5-trimethylbenzene[e]	4.40×10^{-12}	-738 ± 176	5.24[c]	5.49[d]

[a] Indicated errors are two least-squares standard deviations. Estimated overall errors in B are ±400 K, except for 1,3,5-trimethylbenzene where the estimated overall error in B is ±300 K. [b] From least-squares analysis of rate constants measured relative to those for di-*n*-butyl ether, using k_2(di-*n*-butyl ether) $= 6.29 \times 10^{-18}T^2e^{1164/T}$ cm^3 molecule^{-1} s^{-1}.[12] [c] Calculated from Arrhenius expression. Estimated overall uncertainties are ±12%, except for DEEP where the estimated overall uncertainty is ±15%. [d] Average from rate constants at 296−303 K listed in Tables 2−4, correcting the rate constants at 296 and 303 K to 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%. [e] 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}.[2]

Acetaldehyde has been shown to be a minor product formed from the reaction of OH radicals with TEP,[8] with a yield of 11 ± 2% at 296 ± 2 K.[8] Consecutive experiments at 296 ± 2 K (∼7000 L Teflon chamber) and at 347 ± 1 K (∼4500 L Teflon bag inside the evacuable chamber) were carried out to investigate acetaldehyde formation at 347 K relative to that at 296 K. After correction for secondary reaction of acetaldehyde with OH radicals (using rate constants for TEP from this work and for acetaldehyde from recent recommendations[2,13]) and relative to a yield at room temperature of 11%,[8] an acetaldehyde formation yield at 347 ± 1 K of 9.5% was obtained.

Discussion

As noted above, Tables 1−4 give the rate constant ratios k_1/k_2, with k_2 being the rate constant for reaction of OH radicals with α-pinene, di-*n*-butyl ether or *n*-decane. These rate constant ratios are placed on an absolute basis by use of rate constants k_2 of k_2(α-pinene) $= 1.21 \times 10^{-11}e^{436/T}$ cm^3 molecule^{-1} s^{-1},[2] k_2(di-*n*-butyl ether) $= 6.29 \times 10^{-18}T^2e^{1164/T}$ cm^3 molecule^{-1} s^{-1},[12] and k_2(*n*-decane) $= 1.10 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 297 K.[2,14] The resulting rate constants k_1 are given in Tables 1-4 and are discussed below. Our rate constants measured at temperatures ≥298 K are relative to either α-pinene or di-*n*-butyl ether (Tables 2−4), whereas those at 296 K included the use of other reference compounds. To avoid introducing errors into the derived temperature dependencies from the use of multiple reference compounds, we have therefore determined Arrhenius parameters using only rate constants measured with α-pinene (for 1,3,5-trimethylbenzene, TEP, DEMP and DEEP) or di-*n*-butyl ether (for DMMP and DMEP) as the reference compound.

Di-*n*-butyl Ether. Figure 4 shows an Arrhenius plot of the absolute rate constants measured by Mellouki et al.[12] over the temperature range 263−372 K for the reaction of OH radicals with di-*n*-butyl ether, together with their three-parameter fit[12] and the present rate constants determined relative to α-pinene and (at 297 ± 1 K) *n*-decane. Our relative rate data agree to within 9% with the Mellouki et al.[12] rate expression. Furthermore, the rate constants obtained here for the reaction of OH radicals with di-*n*-butyl ether at 297−303 K of (2.71−2.99) × 10^{-11} cm^3 molecule^{-1} s^{-1} (Table 1) are in excellent agreement with the other literature room-temperature rate constants (in units of 10^{-11} cm^3 molecule^{-1} s^{-1}) of 2.78 ± 0.36,[16] 2.68 ± 0.32,[17] 2.72 ± 0.02,[18] 2.68 ± 0.12,[18] 3.23 ± 0.10,[19] 2.91 ± 0.15,[19] 3.26 ± 0.25[20] and 3.05 ± 0.08,[8] where relative rate measurements have been reevaluated using the most recent recommendations for the reference compounds used. In addition to the temperature-dependent absolute rate study of Mellouki et al.,[12] Semadeni et al.[19] have measured rate constants for di-*n*-butyl ether relative to those for 2,3-dimethylbutane and diethyl ether over the temperature range 248−353 K. Using recent recommendations for the rate constants for the reactions of OH radicals with 2,3-dimethylbutane and diethyl ether,[2] over the temperature range 260−353 K the rate constants of Semadeni et al.[19] with 2,3-dimethylbutane as the reference compound are within 9% of the Mellouki et al.[12] rate expression except at 353 K where the Semadeni et al.[19] rate constant is 26% higher, and with diethyl ether as the reference compound they are 10 ± 10% higher than the Mellouki et al.[12] rate expression. This good agreement of our rate constants for the reaction of di-*n*-butyl ether, relative to those for α-pinene and *n*-decane, with the available literature data[8,12,16−20] shows that the rate constants we use for the reactions of OH radicals with α-pinene, di-*n*-butyl ether and *n*-decane are self-consistent to better than 10% at room temperature and, for α-pinene and di-*n*-butyl ether, also over the temperature range 278−348 K.

1,3,5-Trimethylbenzene. Figure 4 also shows an Arrhenius plot for the reaction of OH radicals with 1,3,5-trimethylbenzene. As evident from Figure 4 and Table 2, our present 298 ± 2 K rate constant, measured relative to that for α-pinene, is in reasonable agreement with our previous rate constants obtained relative to propene[15] and α-pinene,[8] being ∼10% lower. Our present room-temperature rate constant is also in agreement with other literature data[21−24] and with the recommended 298 K rate constant for trimethylbenzene[2,21] of (5.67 ± 1.14) × 10^{-11} cm^3 molecule^{-1} s^{-1}, which is based on the studies of Atkinson and Aschmann[15] and Kramp and Paulson.[22] Least-squares analysis of the rate constants determined in our present and previous[8] studies relative to those for α-pinene results in the Arrhenius parameters listed in Table 6 and shown as the solid line in Figure 4.

The only other temperature-dependent rate data for the reaction of OH radicals with 1,3,5-trimethylbenzene are the absolute rate constants measured by Bohn et al.[23] over the temperature range 277−341 K at 270−563 Torr of helium diluent using a pulsed laser photolysis-resonance fluorescence technique.[23b] The rate constants of Bohn et al.[23b,24] exhibit Arrhenius behavior over the range 277−320 K with a negative temperature dependence but decrease much more rapidly above 320 K.[23b,24] The rapid decrease in measured rate constants above 320 K[23b,24] is due to back-decomposition of the OH−trimethylbenzene adduct,[23b] which would not occur under our conditions where O_2 and NO_2 reactions with the OH−1,3,5-trimethylbenzene adduct dominate over the back-decom-

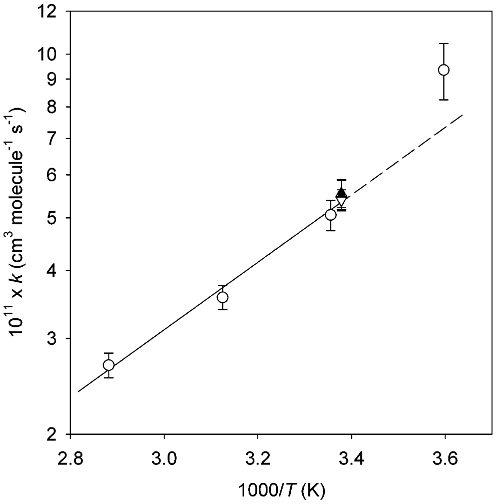

Figure 5. Arrhenius plot of rate constants for the reactions of OH radicals with triethyl phosphate (TEP). Rate constants are from (○) ~4500 L Teflon bag inside evacuable chamber, relative to α-pinene; (△) ~7000 L Teflon chamber, relative to α-pinene;[8] (▽) ~7000 L Teflon chamber, relative to 1,3,5-trimethylbenzene;[8] and (●) ~6400 L Teflon chamber, relative to propene.[5] The solid line is an Arrhenius fit to our rate constants over the temperature range 296−347 K measured relative to those for α-pinene, and the dashed line is an extrapolation of this Arrhenius expression for temperatures <296 K.

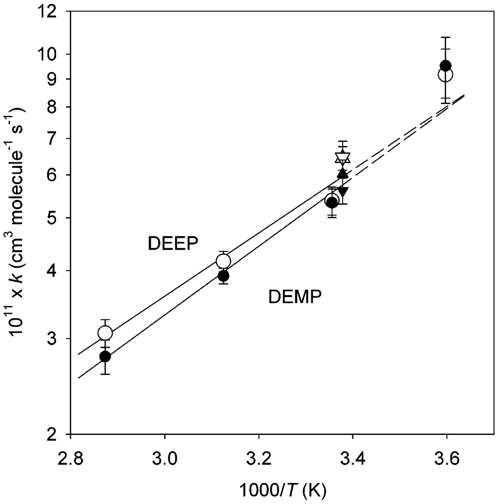

Figure 6. Arrhenius plot of rate constants for the reactions of OH radicals with diethyl methylphosphonate (DEMP) and diethyl ethylphosphonate (DEEP). Rate constants are from (open symbols are for DEEP, filled symbols are for DEMP) (○, ●) ~4500 L Teflon bag inside evacuable chamber, relative to α-pinene; (△, ▲) ~7000 L Teflon chamber, relative to α-pinene;[8] and (▽, ▼) ~7000 L Teflon chamber, relative to 1,3,5-trimethylbenzene.[8] The solid lines are Arrhenius fits to our rate constants over the temperature range 296−348 K measured relative to those for α-pinene, and the dashed lines are extrapolations of these Arrhenius expressions for temperatures <296 K.

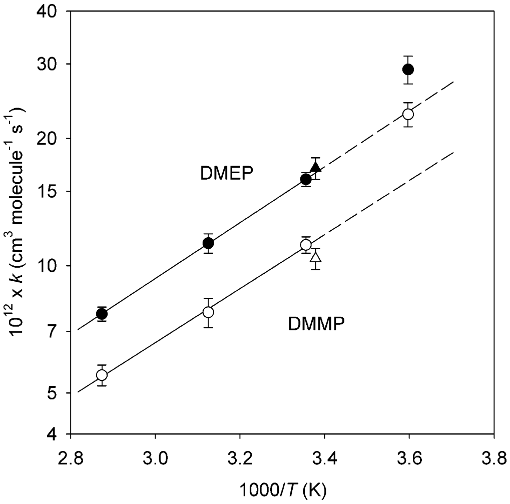

Figure 7. Arrhenius plot of rate constants for the reactions of OH radicals with dimethyl methylphosphonate (DMMP) and dimethyl ethylphosphonate (DMEP). Rate constants are from (open symbols are for DMMP, filled symbols are for DMEP) (○, ●) ~4500 L Teflon bag inside evacuable chamber, relative to di-*n*-butyl ether and (△, ▲) ~7000 L Teflon chamber, relative to *n*-decane.[10] The solid lines are Arrhenius fits to our rate constants over the temperature range 296−348 K measured relative to those for di-*n*-butyl ether, and the dashed lines are extrapolations of these Arrhenius expressions for temperatures <296 K.

position.[2,23b] The rate expression given in Table 5 of Geiger et al.[24] is k(1,3,5-trimethylbenzene) $= (6.3 \times 10^{-12}e^{670/T} - 12e^{-9400/T})$ cm^3 molecule^{-1} s^{-1} for the complete temperature range studied, with the second term accounting for back-decomposition of the OH−trimethylbenzene adduct (note that the only published rate expression is that given in Table 5 of Geiger et al.[24]). Therefore, our rate expression of k(1,3,5-trimethylbenzene) $= 4.40 \times 10^{-12}e^{738/T}$ cm^3 molecule^{-1} s^{-1} can be compared to k(1,3,5-trimethylbenzene) $= 6.3 \times 10^{-12}e^{670/T}$ cm^3 molecule^{-1} s^{-1} from the Bohn et al.[23,24] study. The agreement is good, with our rate constants being uniformly lower by 11−15% over the temperature range 278−320 K than those calculated from the expression k(1,3,5-trimethylbenzene) $= 6.3 \times 10^{-12}e^{670/T}$ cm^3 molecule^{-1} s^{-1}.[24] Our rate constants obtained relative to α-pinene (Table 2 and Figure 4) are equally well fitted by the expression k(1,3,5-trimethylbenzene) $= 5.27 \times 10^{-11}(T/298)^{-(2.73\pm0.53)}$ cm^3 molecule^{-1} s^{-1} over the temperature range 278−347 K, with the Arrhenius expression and the T^{-n} expression giving rate constants that agree to within 1.6% over this temperature range.

TEP, DEMP, DEEP, DMMP and DMEP. The rate constants k for the reactions of OH radicals with TEP, DEMP, DEEP, DMMP and DMEP obtained here and in our previous studies are listed in Tables 2−4 and plotted in Arrhenius form in Figures 5−7. For TEP, DMMP and DMEP, our present room-temperature rate constants measured relative to those for α-pinene (TEP) or di-*n*-butyl ether (DMMP and DMEP) are in good agreement (to within 9% or better) with our previous rate constants measured relative to α-pinene,[8] 1,3,5-trimethylbenzene[8] and propene[5] in the case of TEP and relative to *n*-decane[10] for DMMP and DMEP. Although our present room-temperature rate constant for DEMP relative to that for α-pinene is also in good agreement (to within 5−11%) with our previous rate constants measured relative to α-pinene and 1,3,5-trimethylbenzene,[8] our present 298 ± 2 K rate constant for DEEP is 17% lower that our previous 296 ± 2 K rate constants.[8] This discrepancy is outside of the expected experimental uncertainties and the reason(s) for this difference are not known with any certainty, although it is possible that wall adsorption/desorption in the ~4500 L Teflon bag was occurring to some extent.

At 278 ± 2 K, our rate data for DMMP, DMEP, DEMP, DEEP and TEP all exhibit significantly higher scatter than at the higher temperatures (and this is reflected in the associated two least-squares standard deviations listed in Tables 2−4) and are significantly higher than predicted from extrapolation of the higher temperature, 296−348 K, data (shown as the dashed lines in the Arrhenius plots in Figures 5−7). The reasons for this behavior are not presently known but could include wall losses, partitioning at the lower temperature to aerosol formed from reaction products, and/or reactions at the wall, noting that water condensation on the outer surfaces of the Teflon bag occurred in several of these subambient temperature experiments. Arrhenius parameters for the reactions of OH radicals with DMMP, DMEP, DEMP, DEEP and TEP were obtained from least-squares analyses of the rate constants measured at temperatures ≥296 K relative to those for α-pinene (DEMP, DEEP and TEP, using our present and previous[8] data) or di-*n*-butyl ether (DMMP and DMEP). The resulting Arrhenius parameters are listed in Table 6 and the Arrhenius fits are shown as the solid lines in Figures 5−7. These are the first temperature-dependent data for these reactions to be reported.

Table 5 shows that our present rate constant ratios *k*(TEP)/*k*(1,3,5-trimethylbenzene) and *k*(DEEP)/*k*(DEMP) at 298 ± 2 K are in excellent agreement (within 5%) with the rate constant ratios determined at 296 ± 2 K in our previous room temperature study.[8] Within the experimental uncertainties, the rate constants ratios *k*(DEEP)/*k*(DEMP) and *k*(DMEP)/*k*(DMMP) are both independent of temperature, with values of 1.07 ± 0.06 and 1.42 ± 0.06, respectively, over the temperature range 296−348 K (the uncertainties are two standard deviations), and this is consistent with the very similar Arrhenius activation energies for DEMP and DEEP and for DMMP and DMEP (see Table 6) derived from the rate data relative to α-pinene and listed in Tables 3 and 4.

The Arrhenius expressions given in Table 6 show that 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 $B = -1440 \pm 140$ K, where the uncertainty is two standard deviations. Table 6 also shows that the 298 K rate constants calculated from the Arrhenius expressions agree to within 6% with the average of the measured room-temperature rate constants listed in Tables 2−4, which include rate constants determined relative to reference compounds other than that used to derive the Arrhenius parameters.

The magnitude of the rate constants for these reactions (Tables 2−4), the highly negative values of B, and the previously presented evidence[8,10] that the rate-determining step involves C−H bond breakage (including from the measured deuterium isotope effect of a factor of 4.8 ± 1.2 at 296 ± 2 K for DMMP compared to DMMP-d_9)[10] indicate that these reactions proceed by initial complex formation (possibly a hydrogen-bonded complex) followed by decomposition, and with a major decomposition pathway involving elimination of H_2O.[8,10] For example, for DMMP,

$$\mathrm{OH} + (\mathrm{CH_3O})_2\mathrm{P(O)CH_3} \leftrightarrow [\mathrm{HO}-(\mathrm{CH_3O})_2\mathrm{P(O)CH_3}] \rightarrow \mathrm{H_2O} + \mathrm{CH_3OP(O)(CH_3)OC^{\bullet}H_2} \quad (3)$$

with back-decomposition of the $[\mathrm{HO}-(\mathrm{CH_3O})_2\mathrm{P(O)CH_3}]$ complex to reactants having a higher barrier than decomposition via C−H bond cleavage to $\mathrm{H_2O} + \mathrm{CH_3OP(O)(CH_3)OC^{\bullet}H_2}$ or to other products to account for the negative temperature dependence.[25]

The observation that the acetaldehyde formation yield from the reaction of OH radicals with TEP at 347 K is similar to that at room temperature (9.5% at 347 K compared to 11% at 296 ± 2 K) indicates that the temperature dependence of the pathway leading to acetaldehyde formation (the details of which are not yet known[8]) is similar to the temperature dependence of the overall reaction.

Implications of Our Relative Rate Data for α-Pinene, Di-*n*-Butyl Ether and *n*-Decane. Our relative rate data for di-*n*-butyl ether versus *n*-decane and α-pinene (Table 1 and Figure 4) show that the recommended rate constant for the reaction of OH radicals with α-pinene[2,13] is consistent with the recommended rate constants for the reactions of OH radicals with *n*-decane and, from a number of relative and absolute rate studies, with several other ≥C_4 alkanes.[14] This confirmation of the room-temperature rate constant for α-pinene indicates, again from relative rate studies involving alkenes,[22,26−31] that the recommended[2] room-temperature rate constants for a series of simple alkenes, including propene, 1-butene, 2-methylpropene, *trans*-2-butene, 2,3-dimethyl-2-butene and 1,3-butadiene, are also reliable. In turn, a number of relative rate studies have used propene,[26,29,32] 2-methylpropene,[31] *trans*-2-butene,[33] 2,3-dimethyl-2-butene[30,34−42] and 1,3-butadiene[27] to measure the room-temperature rate constant for the reaction of OH radicals with isoprene (2-methyl-1,3-butadiene). The rate constant for reaction of OH radicals with isoprene resulting from these relative rate studies[26,27,29−42] is $k(\text{isoprene}) = (1.02 \pm 0.07) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 296 ± 3 K (where the uncertainty in the rate constant is two least-squares standard deviations), consistent with the current IUPAC recommendation[13] and with the recommended rate constants for a large number of alkanes and alkenes.[2,14] The ∼15% lower rate constant measured in the recent extensive absolute rate studies of Campuzano-Jost et al.,[43,44] of $(8.47 \pm 0.59) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K,[44] would therefore require a downward revision of many, if not most, OH radical reaction rate constants by ∼15%. Given the general consistency between relative rate studies and absolute rate data for a large number of alkanes, alkenes, aromatic hydrocarbons and oxygenates, such a downward revision of presently recommended OH radical reaction rate constants appears unwarranted and a 298 K rate constant for the reaction of OH radicals with isoprene of $(1.0 \pm 0.1) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} is more likely.

Acknowledgment. This work was supported by ENSCO, Inc. Though 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. R.A. thanks the University of California Agricultural Experiment Station for partial salary support. Drs. Birger Bohn and Cornelius Zetzsch are thanked for kindly providing unpublished data.

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