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Rate Constants for the Gas-Phase Reactions of the Hydroxyl Radical with Isoprene, α- and β-Pinene, and Limonene as a Function of Temperature

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Rate constants for the gas-phase reactions of the hydroxyl radical with the biogenic hydrocarbons isoprene, α- and β-pinene, and limonene were measured using the relative rate technique over the temperature range 295−364 K and at 760 Torr total pressure. OH was produced by the photolysis of H_2O_2, and helium was the diluent gas. The reactants were detected by on-line mass spectrometry, which resulted in high time resolution allowing for large amounts of data to be collected and used in the determination of the Arrhenius parameters. Many experiments were performed over the temperature range of interest leading to more accurate parameters than previous investigations, which have relied on rate constants measured at three or fewer temperatures. The following Arrhenius expressions have been determined for these reactions (in units of cm^3 $molecule^{-1}$ s^{-1}): isoprene, $2.56^{+0.35}_{-0.31} \times 10^{-11} \exp[(408 \pm 42)/T]$; α-pinene, $1.17^{+0.21}_{-0.18} \times 10^{-11} \exp[(436 \pm 53)/T]$; β-pinene, $1.47^{+0.24}_{-0.21} \times 10^{-11} \exp[(467 \pm 50)/T]$; limonene, $4.20^{+0.59}_{-0.51} \times 10^{-11} \exp[(401 \pm 43)/T]$. The Arrhenius parameters determined here for the reaction of OH with β-pinene are significantly different than the current recommendation, and the parameters given here for limonene are the first to be reported.

Introduction

Global emissions of volatile organic compounds from vegetation have been estimated at 1150 Tg carbon yr^{-1},[1] and over half (54%) of these emissions are isoprene and monoterpenes, such as α- and β-pinene and limonene. Annual natural emissions of terpenes exceed those from anthropogenic sources on a global scale.[1] High emissions, as well as the high atmospheric reactivity of these compounds, give them an important role in the chemistry of the lower troposphere, and their reactions with the hydroxyl radical are a key step in this chemistry.

While there has been increasing interest in the products and the mechanisms of the reaction between OH and monoterpenes,[2−4] the available data on the rate constants for these reactions remain sparse. These data include room-temperature rate constants for α- and β-pinene and limonene[5,6] and temperature-dependent data for α- and β-pinene.[7] To date, there are no temperature-dependent data on the reaction of OH with limonene. In addition, the accuracy of these rate constants has been called into question by recent measurements of OH and HO_2 in the troposphere. Measurements of these two radicals in the lower troposphere indicate that current models generally overpredict OH and HO_2 concentrations by as much as 50%.[8−11] This discrepancy suggests that the current understanding of the chemistry of the lower troposphere is not complete. Uncertainties associated with the OH-initiated oxidation of monoterpenes may be partly responsible for these discrepancies, particularly in rural and remote regions where the chemistry is dominated by natural hydrocarbons.

To verify the accuracy of the rate constants for reactions of these biogenic compounds with OH, we have measured these rate constants for α- and β-pinene and limonene, all as a function of temperature, using the relative rate technique and on-line mass spectrometry. In addition, as a validation of our experimental design, we have also measured the temperature-dependent rate constants for the OH/isoprene reaction. The resulting Arrhenius parameters are reported here.

Experimental Section

The experimental setup was similar to that described in detail elsewhere.[12−17] The present system consists of a 192 cm^3 quartz reaction chamber mounted in a gas chromatographic oven (to allow for temperature control) and sampled by on-line mass spectrometry. Reactions were studied using helium as the diluent gas (99.999% purity, Gas Tech, Inc.) under static conditions at atmospheric pressure.

OH radicals were produced in situ by the photolysis of hydrogen peroxide:

$$H_2O_2 + h\nu\ (\lambda \leq 360\ \text{nm}) \rightarrow 2OH \qquad (1)$$

Hydrogen peroxide vapor was introduced into the reaction chamber by bubbling helium through an aqueous hydrogen peroxide solution (see below). Four 8-W germicidal lamps (General Electric, G8-T5) provided UV radiation centered at 254 nm. The lamps were contained in an aluminum housing attached to the door of the GC oven, and radiation entered the oven through an 18 × 28 cm quartz window.

It is important to note that hydrogen peroxide provides a clean source of OH,[4,18−20] but because of the relatively low absorption cross section of H_2O_2 (6.7×10^{-20} cm^2 $molecule^{-1}$ at 255 nm and 298 K[21]), high concentrations of H_2O_2 and high UV intensity were necessary to generate sufficient OH concentrations in these experiments. To increase the concentration of gaseous hydrogen peroxide entering the chamber, 50% H_2O_2 was preconcentrated by bubbling helium through it for several hours prior to use and continuously throughout the experiments. This was effective because hydrogen peroxide is approximately 10 times less volatile than water. Also, in addition to the high intensity of UV radiation provided by the four lamps, radiation reaching

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TABLE 1: Masses (*m/z* Values) Monitored for Each Reference and Reactant Compound

compound	*m/z* values		
1-butene	56 (M^+)		
2-methylpropene	56 (M^+)		
trans-2-butene	56 (M^+)		
isoprene	67 ($(M-H)^+$)	68 (M^+)	
α-pinene	77 ($C_6H_5^+$)	79 ($C_6H_7^+$)	91 ($C_7H_7^+$)
β-pinene	77 ($C_6H_5^+$)	79 ($C_6H_7^+$)	91 ($C_7H_7^+$)
limonene	67 ($C_5H_7^+$)	68 ($C_5H_8^+$)	93 ($C_7H_9^+$)

TABLE 2: Rate Constants of the Reference Compounds Used in This Study[22]

ref compd	10^{11} *k* (298 K) (cm^3 $molecule^{-1}$ s^{-1})	10^{11}A (cm^3 $molecule^{-1}$ s^{-1})	$-E_a/R$ (K)
1-butene	3.14	0.655	467
2-methylpropene	5.14	0.947	504
trans-2-butene	6.40	1.01	550

TABLE 3: Summary of the Average Measured Rate-Constant Ratios, k_{reac}/k_{ref}, for the Reaction of OH with Isoprene

T (K)	k_{reac}/k_{ref}[a]	*T* (K)	k_{reac}/k_{ref}[a]	*T* (K)	k_{reac}/k_{ref}[a]
298	1.962 ± 0.096	323	1.990 ± 0.146	353	2.078 ± 0.146
303	1.982 ± 0.055	333	1.993 ± 0.186	363	2.068 ± 0.193
313	1.986 ± 0.142	343	2.064 ± 0.154		

[a] Reference compound: 2-methylpropene.

TABLE 4: Summary of the Average Measured Rate-Constant Ratios, k_{reac}/k_{ref}, for the Reaction of OH with α-Pinene

T (K)	k_{reac}/k_{ref}[a]	*T* (K)	k_{reac}/k_{ref}[b]	*T* (K)	k_{reac}/k_{ref}[c]
297	1.584 ± 0.076	295	0.990 ± 0.013	301	0.840 ± 0.028
303	1.551 ± 0.055	298	0.965 ± 0.025	308	0.820 ± 0.020
309	1.568 ± 0.071	303	1.000 ± 0.031	313	0.832 ± 0.039
313	1.574 ± 0.066	308	1.009 ± 0.043	318	0.836 ± 0.031
318	1.565 ± 0.067	313	0.991 ± 0.034	323	0.845 ± 0.032
323	1.595 ± 0.066	318	1.014 ± 0.036	328	0.846 ± 0.024
323	1.538 ± 0.046	323	0.999 ± 0.021	333	0.837 ± 0.031
328	1.560 ± 0.032	328	0.985 ± 0.031	338	0.858 ± 0.027
333	1.524 ± 0.004	333	1.016 ± 0.036	344	0.858 ± 0.026
338	1.587 ± 0.037	338	0.993 ± 0.046	349	0.860 ± 0.014
344	1.616 ± 0.042	344	0.996 ± 0.042	353	0.867 ± 0.027
345	1.548 ± 0.074	348	1.040 ± 0.022	358	0.878 ± 0.014
349	1.565 ± 0.016	353	1.019 ± 0.013	362	0.876 ± 0.032
349	1.542 ± 0.042	359	1.032 ± 0.013		
354	1.588 ± 0.027	364	1.052 ± 0.031		
364	1.594 ± 0.030				

[a] Reference compound: 1-butene. [b] Reference compound: 2-methylpropene. [c] Reference compound: *trans*-2-butene.

TABLE 5: Summary of the Average Measured Rate-Constant Ratios, k_{reac}/k_{ref}, for the Reaction of OH with β-Pinene

T (K)	k_{reac}/k_{ref}[a]	*T* (K)	k_{reac}/k_{ref}[b]	*T* (K)	k_{reac}/k_{ref}[c]
298	2.156 ± 0.049	298	1.329 ± 0.047	299	1.119 ± 0.034
304	2.142 ± 0.036	299	1.345 ± 0.023	299	1.129 ± 0.044
308	2.197 ± 0.048	303	1.379 ± 0.014	304	1.151 ± 0.012
313	2.205 ± 0.057	308	1.371 ± 0.019	309	1.157 ± 0.016
318	2.181 ± 0.053	313	1.376 ± 0.025	314	1.140 ± 0.020
324	2.206 ± 0.061	318	1.361 ± 0.022	318	1.177 ± 0.022
328	2.196 ± 0.056	324	1.390 ± 0.013	323	1.160 ± 0.015
333	2.191 ± 0.087	328	1.366 ± 0.029	328	1.181 ± 0.037
338	2.135 ± 0.095	333	1.402 ± 0.036	334	1.191 ± 0.024
344	2.218 ± 0.109	339	1.363 ± 0.034	339	1.197 ± 0.039
348	2.171 ± 0.109	344	1.348 ± 0.026	344	1.191 ± 0.058
353	2.154 ± 0.118	348	1.365 ± 0.048	349	1.198 ± 0.041
358	2.177 ± 0.098	354	1.366 ± 0.059	353	1.195 ± 0.037
364	2.170 ± 0.137	358	1.355 ± 0.058	358	1.204 ± 0.031
		364	1.397 ± 0.098	362	1.196 ± 0.045

[a] Reference compound: 1-butene. [b] Reference compound: 2-methylpropene. [c] Reference compound: *trans*-2-butene.

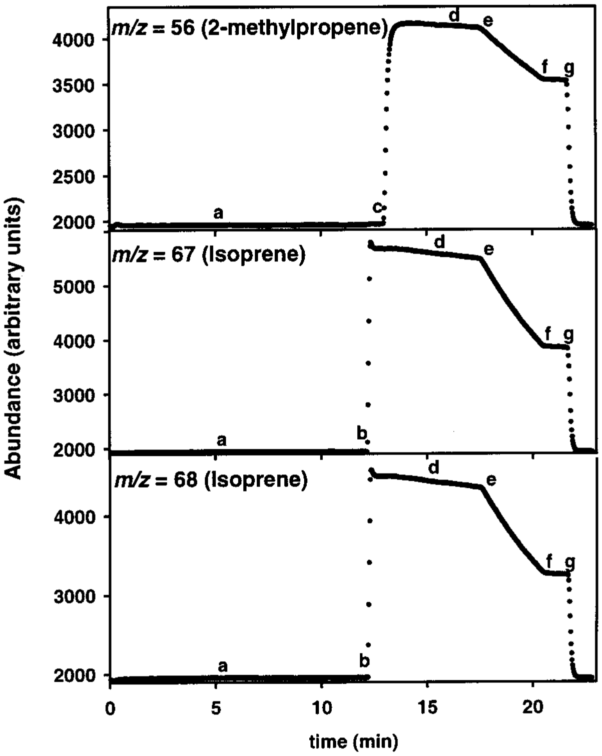

Figure 1. Raw data from the relative rate experiment at 313 K for the reaction of OH with isoprene using 2-methylpropene as the reference compound. He/H_2O_2 is flowed through the chamber for several minutes (a), and then chamber is isolated from all gas flows. At 12.2 min, isoprene is injected (b) followed by injection of 2-methylpropene at 13.0 min (c). After a waiting period (d), the lamps are turned on at 17.6 min (e). At 20.5 min, the lamps are turned off (f), and after 1.0 min, the chamber is flushed with helium (g).

the chamber was maximized by lining the inside of the GC oven with reflective tape and taking care to minimize radiation losses in the lamp housing.

The intensity of UV radiation reaching the center of the reaction chamber was measured using hydrogen peroxide as a chemical actinometer. The H_2O_2 photolysis rate constant, k_p, was measured by monitoring the decrease in ion current at *m/z* 34 before and during irradiation of the chamber filled with H_2O_2 vapor. Our measured value of k_p was 0.041 ± 0.016 s^{-1}. The light intensity was calculated from the following relationship:

$$I = \frac{k_p}{\sigma(\lambda)\phi(\lambda)} \tag{2}$$

where *I* is the light intensity, $\sigma(\lambda)$ is the absorption cross section at wavelength λ (see above), and $\phi(\lambda)$ is the quantum yield at λ (1 at wavelengths >222 nm[21]). The intensity of light reaching the reaction chamber, approximately 25 cm from the light source, was 2.5 ± 1.0 mW cm^{-2}.

OH reaction rate constants were measured by the relative rate technique, which involves measurement of the simultaneous losses of reactant and reference compounds; see reactions 3 and 4:

$$\text{reactant} + \text{OH} \xrightarrow{k_{reac}} \text{products} \tag{3}$$

$$\text{reference} + \text{OH} \xrightarrow{k_{ref}} \text{other products} \tag{4}$$

The relationship between the concentration of the reactant and the reference compound at any time t is given by

$$\ln\left(\frac{[\text{reactant}]_0}{[\text{reactant}]_t}\right) = \frac{k_\text{reac}}{k_\text{ref}} \ln\left(\frac{[\text{reference}]_0}{[\text{reference}]_t}\right) \tag{5}$$

where $[\text{reactant}]_0$ and $[\text{reference}]_0$ are the initial concentrations of the reactant and reference compounds and $[\text{reactant}]_t$ and $[\text{reference}]_t$ are the corresponding concentrations at time t. Clearly, a plot of $\ln([\text{reactant}]_0/[\text{reactant}]_t)$ vs $\ln([\text{reference}]_0/[\text{reference}]_t)$ will have a slope equal to $k_\text{reac}/k_\text{ref}$, and if k_ref is known, k_reac can be calculated.

The reference and reactant compounds were monitored by a Hewlett-Packard 5989A mass spectrometer operating in selected ion monitoring mode and interfaced to the reaction chamber by a 75 cm × 100 μm i.d. deactivated fused silica tube (J&W Scientific, Inc.). The mass spectrometer was set to monitor several masses (m/z values) of the reference and reactant compounds. These m/z values were chosen such that the reference and reactant values did not overlap with each other or with masses from the products of the reaction between OH and the reactant or reference compound.

It is important to note that not all of the products of the reaction between OH and the reactant and reference compounds are known. However, overlap of m/z values used in our experiments could still be avoided by running OH kinetic experiments with the reactant in absence of the reference compound and vice versa while monitoring all of the masses of interest. An increase in the ion current of an m/z value thought to be unique to the reference compound during a reactant-only experiment would indicate that that mass also belongs to a reactant/OH product ion and could not be used. The same would hold for a reference-only experiment. To check for the overlap of masses from the reference compound with the products of OH's reaction with the reference compound or the reactant compound with the products of OH's reaction with the reactant compound, the mass spectrometer was set to monitor m/z values thought to be unique to the compound of interest, and the experiment was performed with the reactant or reference compound (but not both) present in the chamber. Relative rate plots were then generated for all combinations of two m/z values. Because the experiments were performed with only one compound present, the slope of such a plot ($k_\text{ref}/k_\text{reac}$) should equal 1 if the masses were only present in the original compound (not the products). In our experiments, m/z values that gave slopes between 0.95 and 1.05 were used. This condition results in systematic error < 5% for our rate-constant measurements. Using this approach to selecting m/z values resulted in three or four unique m/z values (see Table 1) that we could use to monitor the concentrations of the reactant and reference compounds in each experiment.

Table 2 lists the reference compounds used in this study along with their rate constants as a function of temperature.[22] These compounds were chosen because their rate constants are well-known and because the magnitude of the rate constant satisfied the following condition:

$$0.1 \le \frac{k_\text{reac}[\text{reactant}]_0}{k_\text{ref}[\text{reference}]_0} \le 10 \tag{6}$$

A typical experiment was performed as follows: prior to each experiment, diluent gas was flushed through the reaction chamber for approximately 45 min. The diluent gas was then directed through the hydrogen peroxide solution, and He/H_2O_2 was allowed to flow though the chamber for 10 min. At the onset of an experiment, the reaction chamber was isolated from all gas flows, and the mass spectrometer was set to monitor the m/z values of interest (chosen as described above). The reference and reactant compounds were injected into the chamber, and a waiting period of 3−5 min was allowed to ensure complete mixing and the establishment of a good baseline before irradiation of the chamber. Reactant compounds were injected in a solution of CCl_4, which is essentially nonreactive to OH.[23] Typically, 1−2 μL of a 6 μg/μL solution was injected into the chamber, thus providing reactant compound concentrations ranging from 1×10^{14} to 5×10^{14} molecules cm^{-3}. Reference compounds were stored in 125 cm^3 glass vessels and injected into the chamber with a 25 μL gastight Hamilton syringe to give concentrations approximately equal to that of the reactant compound.

TABLE 6: Summary of the Average Measured Rate-Constant Ratios, $k_\text{reac}/k_\text{ref}$, for the Reaction of OH with Limonene

T (K)	$k_\text{reac}/k_\text{ref}$[a]	T (K)	$k_\text{reac}/k_\text{ref}$[b]	T (K)	$k_\text{reac}/k_\text{ref}$[c]
298	5.082 ± 0.039	298	3.031 ± 0.011	299	2.587 ± 0.010
303	5.262 ± 0.034	303	3.081 ± 0.128	303	2.635 ± 0.016
308	5.161 ± 0.038	308	3.048 ± 0.021	308	2.605 ± 0.015
313	5.158 ± 0.043	313	3.126 ± 0.022	313	2.695 ± 0.018
318	5.167 ± 0.008	318	3.149 ± 0.018	318	2.634 ± 0.018
323	5.264 ± 0.043	323	3.149 ± 0.029	323	2.711 ± 0.024
328	5.206 ± 0.035	328	3.141 ± 0.028	328	2.726 ± 0.030
333	5.174 ± 0.019	333	3.156 ± 0.047	333	2.741 ± 0.032
338	5.202 ± 0.041	338	3.173 ± 0.026	339	2.739 ± 0.033
343	5.280 ± 0.019	343	3.195 ± 0.012	343	2.791 ± 0.019
348	5.292 ± 0.017	348	3.193 ± 0.035	349	2.767 ± 0.037
353	5.351 ± 0.054	353	3.193 ± 0.015	353	2.786 ± 0.059
358	5.384 ± 0.079	358	3.272 ± 0.021	359	2.855 ± 0.056
363	5.358 ± 0.042	363	3.272 ± 0.042		

[a] Reference compound: 1-butene. [b] Reference compound: 2-methylpropene. [c] Reference compound: *trans*-2-butene.

After the waiting period, the UV lamps were turned on, and the reaction was initiated. The reaction was allowed to proceed for about 3 min. After the lamps were turned off, the signal stabilized at a lower level, and after another period, the chamber was flushed with diluent gas. After a small correction for the ventilation rate, the raw data were treated as described previously[12−17] to generate relative rate plots for all combinations of reference and reactant compound masses. A line was fit to each plot, and the slopes were taken and averaged to give the values for $k_\text{reac}/k_\text{ref}$ given below. The experimental sequence is illustrated in Figure 1, which shows the raw data for a kinetic experiment with isoprene using 2-methylpropene as the reference compound.

Chemicals. The chemicals used, their stated purities, and their Chemical Abstracts registry numbers are as follows: hydrogen peroxide (50 wt. % solution in water, 7722-84-1), isoprene (99%, 78-70-5), α-pinene (98%, 80-56-8), β-pinene (99%, 18172-67-3), limonene (97%, 5989-27-5), 2-methylpropene (99%, 115-11-7), 1-butene (99%, 106-98-9), and *trans*-2-butene (99+%, 624-64-6). All of these compounds were obtained from Aldrich Chemicals.

Results and Discussion

The ratios of the reactant to reference rate constants for the reaction of OH with the four reactants are listed, as a function of temperature, in Tables 3 (for isoprene), 4 (for α-pinene), 5-(for β-pinene), and 6 (for limonene). These ratios were obtained by averaging the slopes of the relative rate plots for all combinations of reference and reactant product masses used in

TABLE 7: Summary of All Measurements of k_{alkene}[a]

alkene	temp range (K)	10^{11}A ($\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$)	$-E_a/R$ (K)	$10^{11}\ k_{\mathrm{alkene}}$ (∼298 K)[b] ($\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$)	ref
isoprene	300			7.8	Cox et al.[28]
	299 ± 2			9.98 ± 0.45	Atkinson et al.[24]
	299−422	2.36	409 ± 28	9.31	Kleindienst et al.[7]
	297 ± 2			9.90 ± 0.27	Ohta[25]
	295 ± 1			10.2 ± 0.4	Atkinson and Aschmann[26]
	297			10.1 ± 0.2	Edney et al.[27]
	298			10.1 ± 0.8	Zhang et al.[29]
	295			9.9 ± 0.5	McGivern et al.[30]
	300			11.0 ± 0.4	Chuong and Stevens[31]
	298			8.56 ± 0.26	Campuzano-Jost et al.[32]
	298−363	$2.56^{+0.35}_{-0.31}$	408 ± 42	10.1 ± 1.9	this work
α-pinene	305 ± 2			5.63	Winer et al.[5,c]
	294 ± 1			5.50 ± 0.32	Atkinson et al.[6,c]
	298−422	1.37	446 ± 75	6.12	Kleindienst et al.[7]
	295−364	$1.17^{+0.21}_{-0.18}$	436 ± 53	5.05 ± 1.23	this work
	295−364	$1.12^{+0.18}_{-0.16}$	446 ± 50	5.00 ± 1.13	this work (1-butene and 2-methylpropene only)
β-pinene	305 ± 2			6.57 ± 0.99	Winer et al.[5,c]
	294 ± 1			8.02 ± 0.52	Atkinson et al.[6,c]
	297−423	2.36	358 ± 58	7.85	Kleindienst et al.[7]
	298−364	$1.47^{+0.24}_{-0.21}$	467 ± 50	7.05 ± 1.60	this work
	298−364	$1.40^{+0.14}_{-0.12}$	476 ± 31	6.92 ± 0.97	this work (1-butene and 2-methylpropene only)
limonene	305 ± 2			14.6 ± 2.2	Winer et al.[5,c]
	294 ± 1			17.1 ± 0.5	Atkinson et al.[6,c]
	298−364	$4.20^{+0.59}_{-0.51}$	401 ± 43	16.1 ± 3.1	this work
	298−364	$4.22^{+0.45}_{-0.41}$	395 ± 33	15.9 ± 2.4	this work (1-butene and 2-methylpropene only)

[a] The errors indicated for values from this work represent 95% confidence limits. [b] The values reported here at ∼298 K were calculated on the basis of the Arrhenius parameters reported by the authors when available; in absence of those parameters, the value represents the rate constant reported at the temperature listed in the "temp range" column. [c] From relative rate studies; the values listed here are as reported elsewhere[23] and have been adjusted from the original reported values to reflect more accurate reference compound rate constants.

an experiment. The errors represent the 95% confidence limits of this average. The data for each reaction were fit to the Arrhenius equation, and the resulting parameters are given in Table 7 along with their 95% confidence limits and comparisons to other measurements.

Isoprene. While the experimental approach used here is similar to that used in previous investigations,[12−17] this study is the first in which hydrogen peroxide vapor was used as the OH source. Thus, to validate our approach, temperature-dependent rate constants for the reaction between isoprene and the OH radical were determined using 2-methylpropene as the reference compound. The resulting data are given in Table 3, and the Arrhenius plot is shown in Figure 2. The solid line is the least-squares fit of our data to the Arrhenius expression (the parameters are given in Table 7); the dashed lines represent the 95% confidence limits to the fit. Our result at room temperature is in excellent agreement with those of Atkinson et al.,[24] Ohta,[25] Atkinson and Aschmann,[26] and Edney et al.,[27] and is in good agreement with those of Kleindienst et al.,[7] although our room temperature result is considerably higher than the value reported by Cox et al.[28] Our room-temperature rate constant is also in agreement with recent lower pressure measurements made by Zhang et al. (70−120 Torr), McGivern et al.[30] (20 Torr), and Chuong and Stevens[31] (2−6 Torr), although it is slightly higher than that of Campuzano-Jost et al.[32] (60−600 Torr). In addition, our calculated Arrhenius expression of $k = 2.56^{+0.35}_{-0.31} \times 10^{-11}$ $\exp[(408 \pm 42)/T]$ is in excellent agreement with the current recommendation of $k = 2.54 \times 10^{-11} \exp[410/T]$ of Atkinson.[22] These results indicate that our H_2O_2 approach can be used to determine accurately the rate constants for these reactions.

α-Pinene. The measured rate constants for the reaction of α-pinene with OH are given in Table 4, and the Arrhenius plot is given in Figure 3 along with results from previous investigations. The solid line represents the least-squares fit of our data to the Arrhenius equation; the resulting Arrhenius parameters are given in Table 7. Note that our parameters have been obtained from a fit to all of our data using all three reference compounds. This accounts for relatively higher scatter seen in these data compared with isoprene. Our results at room temperature are in modest agreement with those of Winer et al.[5] and Atkinson et al.[6] Our Arrhenius parameters, $1.17^{+0.21}_{-0.18} \times 10^{-11} \exp[(436 \pm 53)/T]$, are about 15% lower than those reported by Kleindienst et al.,[7] but are in excellent agreement with the current recommendation of $k = 1.21 \times 10^{-11} \exp[444/T]$.[22]

***β*-Pinene.** The measured rate constants for the reaction of OH with β-pinene are given in Table 5 and plotted in Figure 4 along with results from previous investigations. The solid line represents the least-squares fit of our data to the Arrhenius equation; the resulting Arrhenius parameters are given in Table 7. Our results show good agreement with the 305 K measurement of Winer et al.[5] and modest agreement with the room-temperature measurement of Kleindienst et al.[7] Our results, however, are lower than the room-temperature value reported by Atkinson et al.,[6] and our Arrhenius parameters are very different from those reported by Kleindienst et al.[7] In fact, our resulting Arrhenius expression of $k = 1.47^{+0.24}_{-0.21} \times 10^{-11} \exp[(467 \pm 50/T)]$ differs substantially from the current β-pinene recommendation of $2.38 \times 10^{-11} \exp[357/T]$.[22]

A possible explanation for obtaining lower rate constants is that the m/z values used to monitor the reference and reactant products were not unique. If an m/z value belonged to a product ion, it would be formed during the reaction, resulting in an apparent slower decrease of ion signal for that mass value (see parts e and f of Figure 1) and a lower rate-constant ratio (k_{reac}/

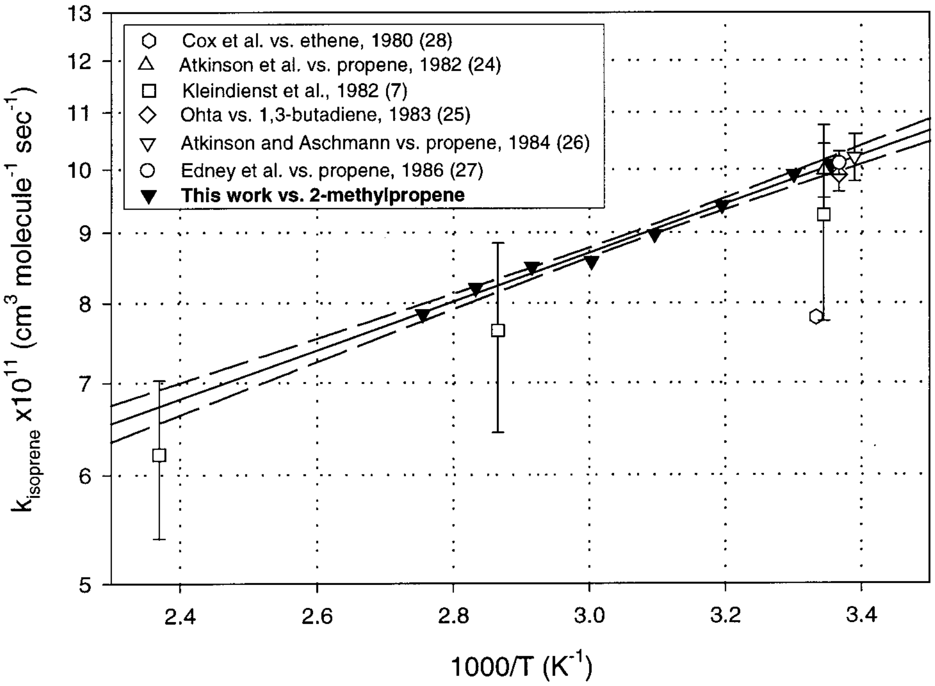

Figure 2. Arrhenius plot showing the measured rate constants for the reaction of OH with isoprene and rate constants from other studies. The solid line is the regression of our measured values; the dashed lines are the 95% confidence limits of the regression.

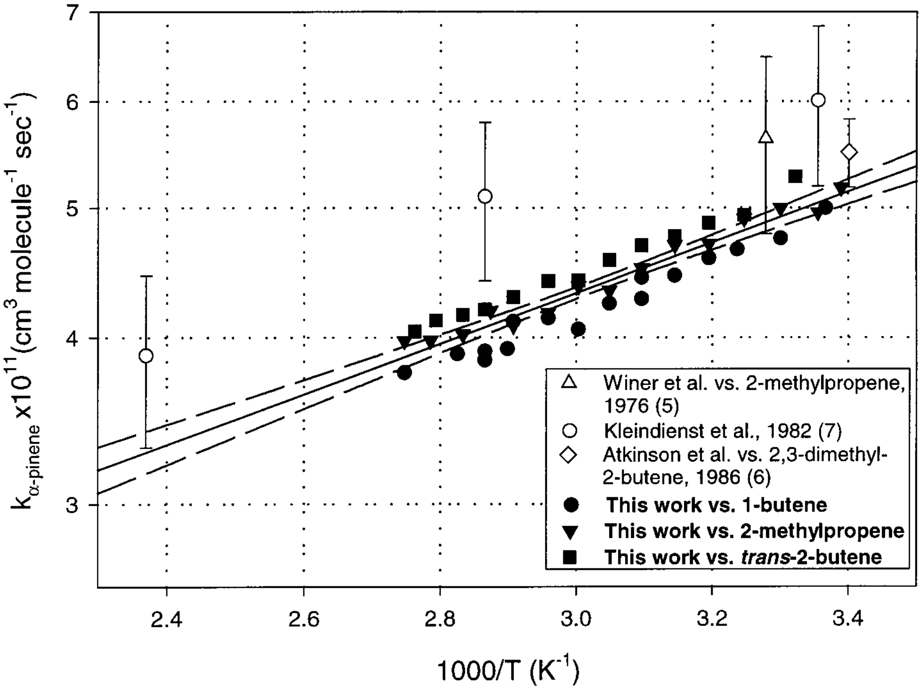

Figure 3. Arrhenius plot showing the measured rate constants for the reaction of OH with α-pinene (for each reference compound) and rate constants from other studies. The solid line is the regression of our measured values; the dashed lines are the 95% confidence limits of the regression.

k_{ref}). However, because we carefully selected the *m*/*z* values used in these experiments to make sure the ions were unique (see above), we are confident that ion overlap is not responsible for the lower rate constants. Although the reason for this discrepancy is not clear, because we obtained our parameters from a large number of measurements (44) and because our system yielded results for isoprene and α-pinene that are consistent with previous measurements, we are confident in the accuracy of the technique for β-pinene.

Limonene. The measured rate constants for the reaction of limonene with OH are given in Table 6 and plotted in Figure 5 along with results from previous investigations. The solid line represents the least-squares fit of our data to the Arrhenius equation; the resulting Arrhenius parameters are given in Table 7. Our results are in modest agreement with the single-temperature results previously reported by Winer et al.[5] and Atkinson et al.[6] To date, no other Arrhenius parameters have been reported for this reaction.

Reference Rate Constants. The rate constants used to determine the Arrhenius parameters reported here were calculated from the slopes of the relative rate plots, which gave k_{reac}/k_{ref} ratios, and from the rate constant for the reference compound, which was calculated from the current Arrhenius parameter recommendations.[22] Because we used a relative method, the

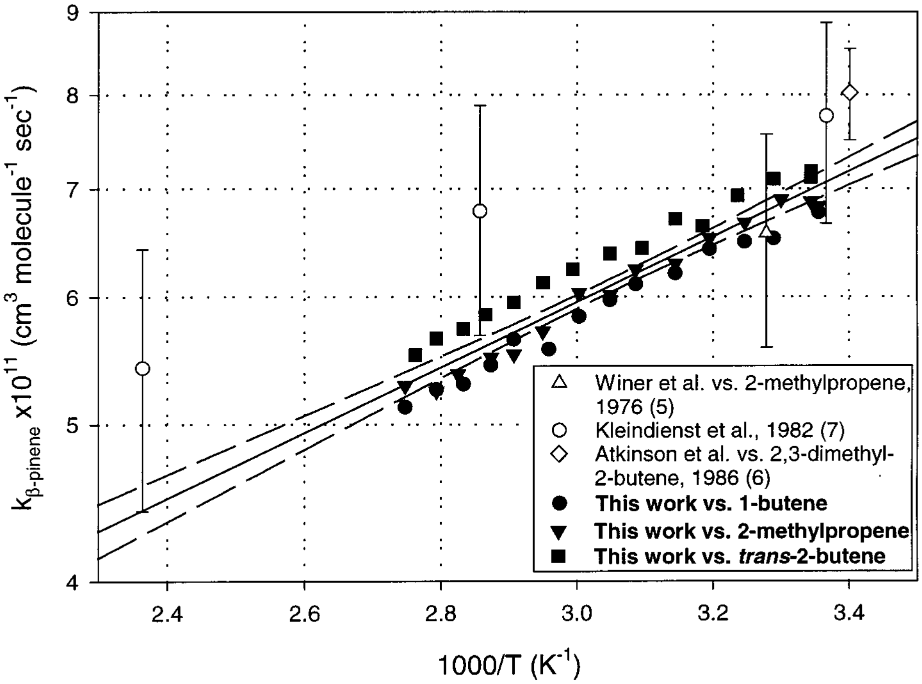

Figure 4. Arrhenius plot showing the measured rate constants for the reaction of OH with β-pinene (for each reference compound) and rate constants from other studies. The solid line is the regression of our measured values; the dashed lines are the 95% confidence limits of the regression.

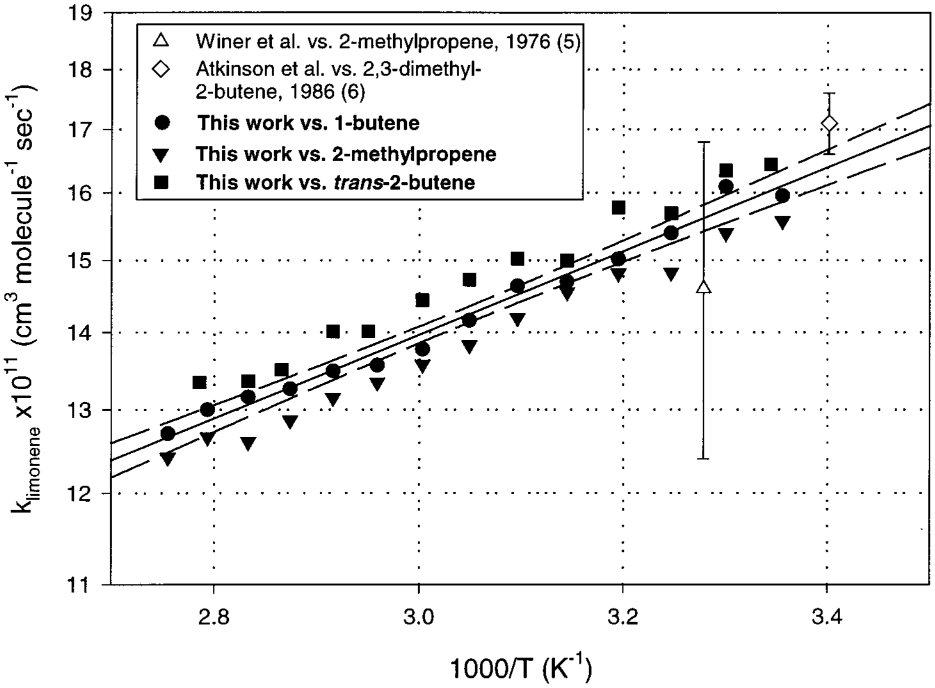

Figure 5. Arrhenius plot showing the measured rate constants for the reaction of OH with limonene (for each reference compound) and rate constants from other studies. The solid line is the regression of our measured values; the dashed lines are the 95% confidence limits of the regression.

accuracy of our results is dependent on the accuracy of the Arrhenius parameters of the reference compounds. For our experiments with α-pinene, β-pinene, and limonene, the reactant rate constants determined using *trans*-2-butene as the reference compound are consistently higher than those obtained using 1-butene or 2-methylpropene (see Figures 3−5). Because 2-methylpropene was used in the isoprene experiments and it gave accurate rate constants, and because there is no systematic difference in the rate constants obtained from 2-methylpropene and 1-butene, this suggests that the currently recommended rate constants for *trans*-2-butene are systematically high by about 5%. To account for this inaccuracy, we have recalculated the Arrhenius parameters for α- and β-pinene and limonene using only 1-butene and 2-methylpropene (see Table 7). While leaving *trans*-2-butene out of the calculations does change the Arrhenius parameters and results in a lower value for the room-temperature rate constant, in all cases the change is <2%, indicating that the inaccuracies in the recommended Arrhenius parameters for *trans*-2-butene are not substantial.

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References and Notes

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