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

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The rate constants for the gas-phase reactions of ozone with the biogenic hydrocarbons isoprene, α- and *β*-pinene, and limonene were measured using the relative rate technique over the temperature range 242−363 K and at 760 Torr total pressure. Helium was the diluent gas, and the reactants were detected by on-line mass spectrometry. The following Arrhenius expressions have been determined for these reactions (in units of $cm^3$ $molecule^{-1}s^{-1}$): isoprene, $(10.9^{+2.70}_{-2.17}) \times 10^{-15} \exp[-(1998 \pm 63)/T]$; α-pinene, $(0.48^{+0.29}_{-0.18}) \times 10^{-15} \exp[-(530 \pm 150)/T]$; *β*-pinene, $(1.74^{+0.46}_{-0.36}) \times 10^{-15} \exp[-(1297 \pm 75)/T]$; and limonene, $(2.95^{+0.77}_{-0.61}) \times 10^{-15} \exp[-(783 \pm 72)/T]$. The Arrhenius parameters determined here for the reactions of ozone with *β*-pinene and limonene are the first to be reported.

## Introduction

Isoprene and various monoterpenes play an important role in the chemistry of the lower troposphere and in the chemistry of the atmospheric boundary layer. These compounds have high global emissions[1] (about $1.2 \times 10^{12}$ kg/yr, mostly from vegetation) and high atmospheric reactivities[2] (the typical atmospheric residence time for these compounds is a few hours). Tropospheric reactions of these compounds with hydroxyl radicals (OH) during daylight hours, with nitrate radicals ($NO_3$) during nighttime hours, and with ozone ($O_3$) throughout the day remove these compounds from the atmosphere. Although reactions of these compounds with OH and $NO_3$ radicals primarily determine their atmospheric residence times, reactions with $O_3$ are also important. For example, reactions of these biogenic hydrocarbons with ozone can be a source of OH radicals at night,[3] and reactions of $O_3$ with some of these biogenic hydrocarbons are potential precursors of secondary organic aerosols.[4] Clearly, the quantitative estimation of these biogenic hydrocarbons' impact on the lower atmosphere requires accurate and precise rate constants for their reactions with $O_3$ at various temperatures of atmosphere interest.

Most kinetic studies of the reactions of $O_3$ with biogenic hydrocarbons have been limited to room-temperature experiments. For example, even though the rate constant for the reaction of $O_3$ with isoprene is well-known at room temperature, there are only three studies of this reaction as a function of temperature,[5−7] and only one of these studies[6] included recommended Arrhenius parameters for this reaction.

In this paper, we will present the results of our rate constant measurements for the reaction of $O_3$ with isoprene, α- and *β*-pinene, and limonene. During the course of this study, we designed and built an experimental system to measure these rate constants based on the relative rate technique with detection of the gas-phase components by on-line mass spectrometry. The Arrhenius parameters determined here for the reactions of ozone with *β*-pinene and limonene are the first to be reported.

## Experimental Section

**Apparatus.** To measure the rate constants for the reaction of $O_3$ with biogenic hydrocarbons, an experimental apparatus based on a relative rate technique was designed and built; see Figure 1 for a schematic diagram of the experimental setup. The principal apparatus component was a cylindrical quartz reactor with a volume of 192 $cm^3$ (5 cm diameter × 10 cm length). The center of the reactor was continuously sampled through a 100-$\mu$m i.d. deactivated fused silica capillary (J&W Scientific Inc.) approximately 60 cm long. This capillary entered the ion source of a mass spectrometer through a septum fitted to a port of the quartz reactor. To allow temperature control of the reactor, it was mounted in a gas chromatographic (GC) oven attached to the mass spectrometer.[8] The temperature was monitored by means of two thermocouples at either end of the reactor.

Reactions were studied using helium as the diluent gas (99.999% purity, Gas Tech Inc.) under static conditions at atmospheric pressure, which was measured by a MKS Baratron manometer. Ozone was produced by flowing $O_2$ (99.998% purity, Gas Tech Inc.) through a 12 kV discharge; the $O_3/O_2$ mixture was stored in a glass vessel (125-$cm^3$ volume), which was fitted with a sampling port plugged by an ozone safe septum.

To prepare the reference/reactant mixture, flows of helium and the reference compound were directed through another 125-$cm^3$ glass vessel for 30 min; see Figure 1. The concentration of the reference compound in this vessel was determined by measuring its flow rate and that of the helium diluent using a calibrated Hewlett-Packard (HP) bubble flow meter. This vessel was isolated, and the reactant compound was injected by an all-glass, gastight Hamilton syringe through a septum. The amount of this injection was such that the concentration of reference and reactant compounds in the gas phase would be about equal to each other. To ensure mixing of the gases, a 60-min waiting period was allowed.

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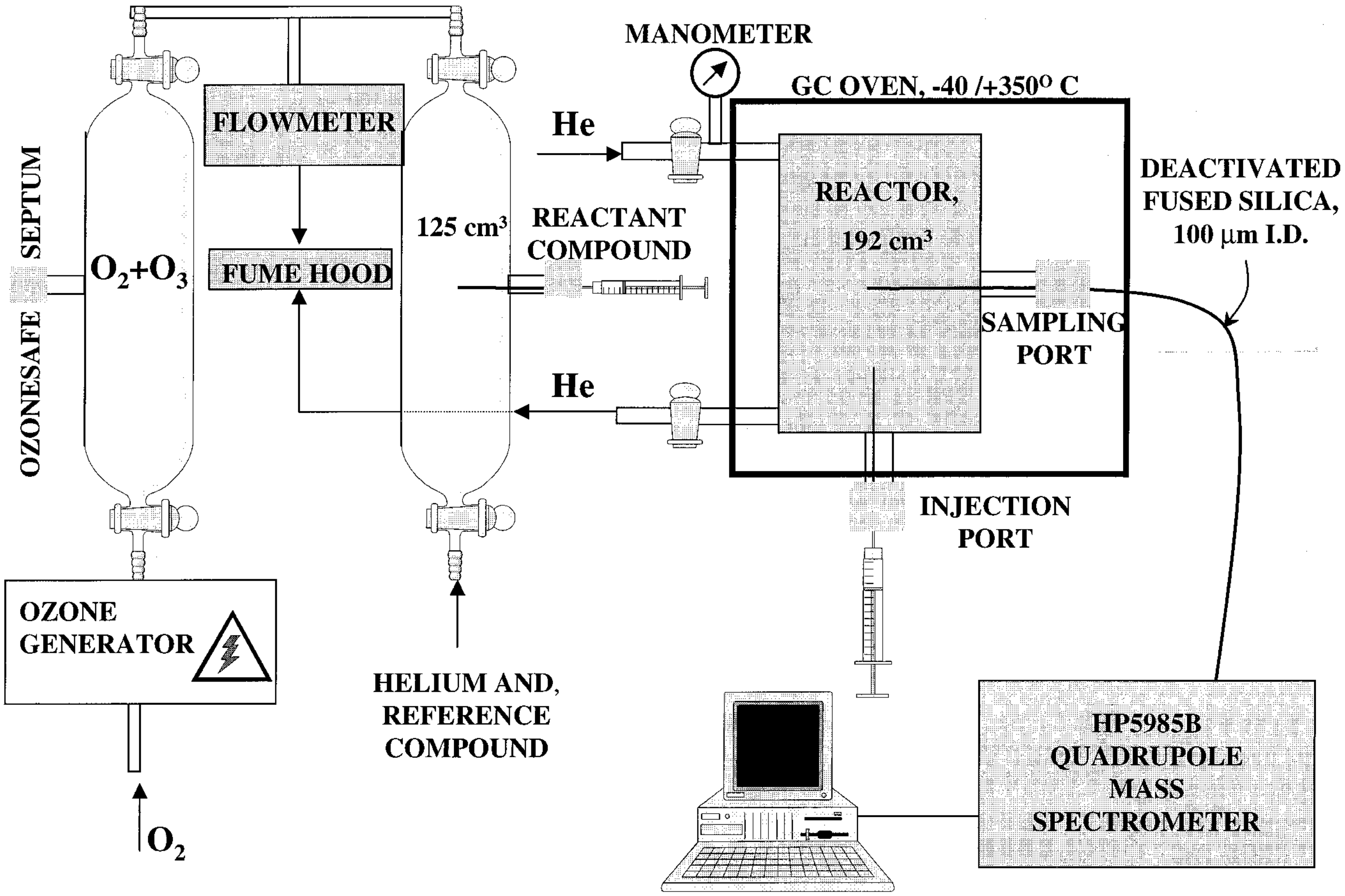

**Figure 1.** Experimental setup for measuring rate constants for the gas-phase reactions of $O_3$ with alkenes using the relative rate technique and with detection of the reference and reactant compounds by on-line mass spectrometry.

**Relative Rate Technique.** The method employed in our investigation involves measurement of the losses of the reactant and reference compounds by reactions 1 and 2

$$O_3 + \text{reactant} \rightarrow \text{products} \qquad (1)$$

$$O_3 + \text{reference} \rightarrow \text{products} \qquad (2)$$

The rate constant for reaction 1 is given by $k_{\text{reac}}$, and the rate constant for reaction 2 is given by $k_{\text{ref}}$. The relationship between the concentration of the reactant and the reference compound is given by

$$\ln\left(\frac{[\text{reactant}]_0}{[\text{reactant}]_t}\right) = \frac{k_{\text{reac}}}{k_{\text{ref}}} \ln\left(\frac{[\text{reactant}]_0}{[\text{reactant}]_t}\right) \qquad (3)$$

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 $\ln([\text{reactant}]_0/[\text{reactant}]_t)$ versus $\ln([\text{reference}]_0/[\text{reference}]_t)$ will have a slope equal to the ratio of the rate constants, $k_{\text{reac}}/k_{\text{ref}}$. Equation 3 is true if there are no other losses of the reactant and reference compounds except for those by reactions 1 and 2. This may not be the case if an alkene is a reactant or reference compound because reactions 1 and 2 have OH radicals as intermediates and because OH reacts rapidly with an alkene, it can cause additional losses of the alkene. For this reason, it is important to select experimental conditions that prevent OH from reacting with the alkene. Thus, we performed our experiments in the presence of an excess of an organic compound that reacts negligibly with $O_3$ but that scavenges any OH radicals generated in the system. The necessary scavenger concentration was given by

$$[\text{scavenger}] = (10-50)[\text{alkene}] \frac{k^{\text{OH}}_{\text{alkene}}}{k^{\text{OH}}_{\text{scavenger}}} \qquad (4)$$

We found that ethanol and acetaldehyde were the best radical scavengers to use for our experiments.

**Detection of Reactants.** The concentrations of the reactant and reference compounds were monitored by on-line, electron-impact mass spectrometry using a quadrupole Hewlett-Packard 5985B mass spectrometer operating in selected ion-monitoring mode. Usually, several masses ($m/z$ values) were employed to monitor the reactant and reference compound concentrations in our experiments. Ion currents of those $m/z$ values have been found to be linear over the range of concentrations used in this work. Our main concern about choosing masses to monitor the concentration of the reactant and reference compounds was to select ones that were unique to a given compound during a kinetic experiment. This means that the selected masses should not: (a) overlap between the reference and reactant compounds; (b) overlap with masses from products of the reaction of ozone with the reactant or reference compounds; (c) overlap with masses from the OH scavenger; and (d) overlap with masses from products of the reaction of OH with the scavenger compound.

We managed to find masses that satisfied all of these conditions in all our experiments, but we should point out that condition *b* was tricky to satisfy because there are numerous products from the reaction of an alkene with $O_3$. Even for the

**TABLE 1: Rate Constants of the Reference Compounds Used in This Study[9]**

| ref compd | $10^{18}k$ (298 K) ($cm^3$ $molecule^{-1}$ $s^{-1}$) | $10^{15}A$ ($cm^3$ $molecule^{-1}$ $s^{-1}$) | $E_a/R$ (K) |
|---|---|---|---|
| 1-butene | 9.64 | 3.36 | 1744 |
| 2-methylpropene | 11.3 | 2.70 | 1632 |
| *cis*-2-butene | 125 | 3.22 | 968 |
| 2,3-dimethyl-1,3-butadiene | 26.5 | 6.90 | 1668 |

reactions of $O_3$ with ethene and propene, the products are not completely known.[9] In general, the procedure was as follows: We first ran the ozone kinetic experiments with the reactant in the absence of a reference compound but in the presence of an OH scavenger. Then we set up the mass spectrometer to monitor as many reactant *m*/*z* values as possible. In this case, we adjusted the sensitivity of the mass spectrometer such that we could measure all *m*/*z* values with a $S/N > 10$ during the reaction of interest. In all cases, we used at least four *m*/*z* values. Then, we calculated the ratio, $k_a/k_b$, for all combinations of any two of monitored *m*/*z* values. Given that all of the monitored *m*/*z* values should be coming from the reactant only (no reference compound was present), all of these rate constant ratios should be equal exactly 1. Thus, all *m*/*z* values that gave a rate constant ratio between 0.95 and 1.05 were used to monitor the concentration of the reactant compound. It is worth mentioning that the systematic errors of the measurements of our rate constants were <5% because this condition was employed in all of our experiments. The same strategy was used for the reference compounds as well. In general, we had three or four unique *m*/*z* values with which to monitor the concentrations of the reactant and reference compounds. These preliminary experiments were repeated at the lowest and highest experimental temperatures to ensure the chosen *m*/*z* values were temperature independent.

**Reference Compounds.** Table 1 gives the rate constants as a function of temperature for the reference compounds used in this study. These reference compounds were chosen because of the accuracy of the rate constants and because the magnitude of the rate constant satisfied the following condition:

$$0.1 \le \frac{k_{\mathrm{reac}}[\mathrm{reactant}]_0}{k_{\mathrm{ref}}[\mathrm{reference}]_0} \le 10 \qquad (5)$$

The *m*/*z* values to be monitored by the on-line mass spectrometer were selected based on their relatively high abundance in the mass spectra of the reference or reactant compounds, on their uniqueness for the two compounds in the reaction chamber (see above), and on a linear response over the concentration ranges used.

**Chemicals.** The chemicals used, their stated purities, and their Chemical Abstracts registry numbers (provided by the author) are as follows: isoprene (99%, 78-70-5), α-pinene (98%, 80-56-8), (+)-β-pinene (98%, 19902-08-0), (1S)-(−)-β-pinene (99%, 18172-67-3), (*R*)-(+)-limonene (97%, 5989-27-5), 2-methylpropene (99%, 115-11-7), *cis*-2-butene (99%, 590-18-1), 1-butene (99%, 106-98-9), 2,3-dimethyl-1,3-butadiene (98%, 513-81-5), acetaldehyde (99.5+%, 75-07-0), and ethyl alcohol (99.5+%, 64-17-5). All of these compounds were obtained from Aldrich Chemicals.

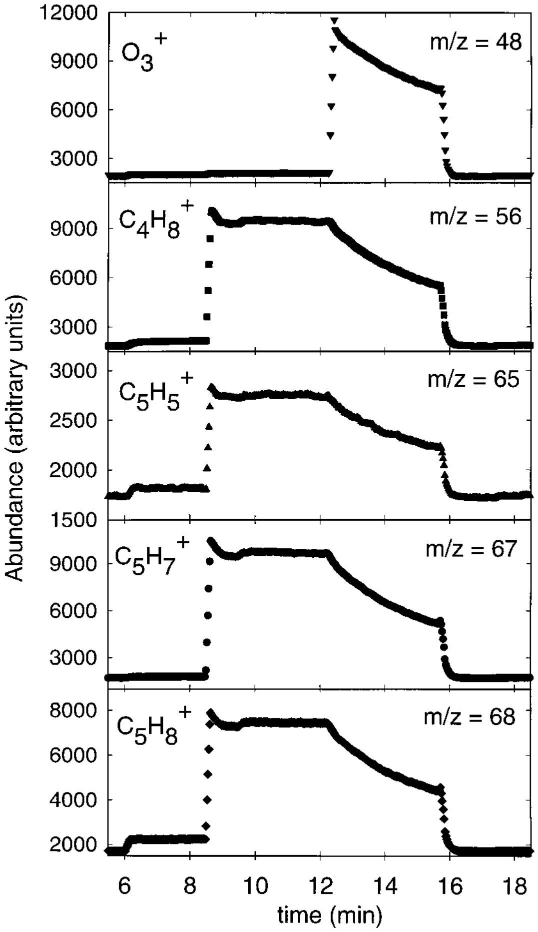

**Figure 2.** Example of raw data from a relative rate experiment for the reaction of $O_3$ with isoprene using 2-methylpropene as the reference compound. The mass spectrometer was set to monitor five *m*/*z* values: *m*/*z* = 48, $O_3$; *m*/*z* = 56, 2-methylpropene; and *m*/*z* = 65, 67, and 68, isoprene.

## Results and Discussion

Figure 2 shows the raw data for a typical kinetic experiment for the reaction of $O_3$ with isoprene using 2-methylpropene as the reference compound. Prior to each experiment, diluent gas was flushed through the reactor for at least 30 min. At the onset of an experiment, the reactor was isolated from all gas flows, and the mass spectrometer was set to monitor five masses (usually with 340 ms dwell time) to establish a signal baseline. In this case, at 6.1 min, 1 μL of acetaldehyde was injected by all-glass syringe such that the scavenger concentration in the reactor was about $(1-5) \times 10^{16}$ molecules/$cm^3$. A waiting period about 2.5 min was allowed to reestablish a signal baseline for all masses.

At 8.6 min, 5−12 μL of the reactant and reference compounds (in helium) were injected together using an all-glass syringe such that the compound concentration in the reactor was about $(2-5) \times 10^{13}$ molecules/$cm^3$; see Figure 2. Note that the mixing period was about 30 s, but the *m*/*z* values for the reactant (at *m*/*z* = 65, 67, and 68) and for the reference compound (at *m*/*z* = 56) were measured for an additional 3.5 min to establish a good baseline before the injection of ozone at 12.3 min. At this time, about 100 μL of an $O_3/O_2$ mixture with about 1% ozone was injected using an all-glass syringe; this initiated the reaction.

As shown in Figure 2, the signal for ozone (at *m*/*z* 48) increases sharply at 12.3 min and then decreases exponentially as the reaction with isoprene continues. The masses monitored for isoprene and 2-methylpropene also decrease exponentially. Data were acquired for about 3.5 min or until the signals for various reactant and reference compound *m*/*z* values had decreased by 2−5 times. In all cases, the duration of a kinetic run exceeded the mixing period of the reactants (30 s in the

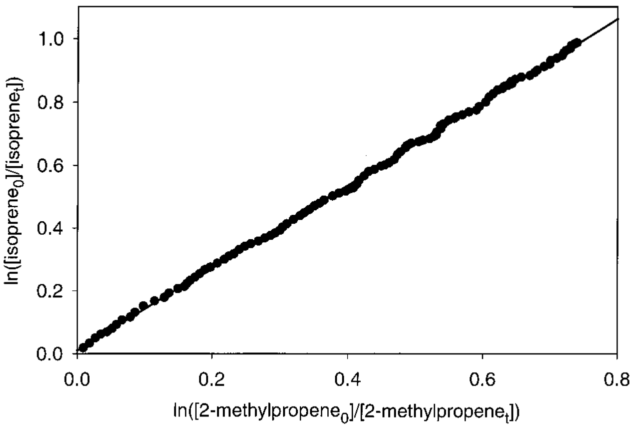

**Figure 3.** Plot of ln([isoprene]$_0$/[isoprene]$_t$) at $m/z = 67$ vs ln([2-methylpropene]$_0$/[2-methylpropene]$_t$) at $m/z = 56$ for the reaction of $O_3$ with isoprene at 298 K. The regression line ($r^2 = 0.9994$; $n = 120$) is shown. The resulting rate constant ratio is 1.315 ± 0.006.

**TABLE 2: Ranges of Depletion Factors**[a]

| | | depletion factor range | |
|---|---|---|---|
| reactant | reference | reactant | reference |
| isoprene | 1-butene | 1.25−2.72 | 1.26−2.56 |
| | 2-methylpropene | 1.79−13.6 | 1.77−8.25 |
| | *cis*−2-butene | 1.14−1.60 | 2.05−25.5 |
| | 2,3-dimethyl-1,3-butadiene | 1.12−1.57 | 1.16−1.84 |
| α-pinene | 1-butene | 2.91−12.8 | 1.10−1.45 |
| | 2-methylpropene | 4.48−24.8 | 1.23−1.90 |
| *β*-pinene | *cis*−2-butene | 1.26−1.75 | 4.57−11.2 |
| | 1-butene | 1.66−1.86 | 1.28−1.29 |
| limonene | *cis*−2-butene | 2.77−4.53 | 2.03−2.59 |
| | 1-butene | 12.9−34.5 | 1.20−1.36 |
| | 2-methylpropene | 8.58−42.5 | 1.17−1.23 |

[a] [reactant]$_0$/[reactant]$_t$ or [reference]$_0$/[reference]$_t$.

above example) by at least a factor of 4. At this time, the reactor was flushed with the diluent gas, and the baseline signal was again monitored to correct for any instrumental drift.

Because we performed our experiments under static conditions, there were small losses of the reactant and reference compounds due to continuous sampling of the reactor through the capillary into the mass spectrometer. The flow rate through the capillary was about 0.03 mL/min, which we calculated using geometric parameters of the capillary and which we experimentally checked by monitoring the pressure inside the isolated reactor as a function of time. Given this flow rate, the volume sampled during a 4 min experiment was only about 0.12 mL. Since this volume only represents 0.06% of the total volume of the reactor, losses of the reactant and reference compounds due to the sampling are negligible. This is born out by the lack of change in the data between 8.5 and 12.3 min; see Figure 2.

The data obtained between 12.3 and 15.7 min, for masses 56, 65, 67, and 68, were treated to generate relative rate plots, an example of which is shown in Figure 3. The slope of this line is the ratio of $k_{\mathrm{reac}}$ to $k_{\mathrm{ref}}$, which in this case is 1.315 ± 0.006. This typical plot demonstrates good linearity and a near zero intercept as required by eq 3. Since a systematic curvature and/or a nonzero intercept in such a plot might indicate a nonozone specific reaction of the reactant and/or the reference compound through secondary reactions, the validity of eq 3 should be tested. This we have done by taking data over a wide range of depletion factors ([reactant]$_0$/[reactant]$_t$), [reference]$_0$/[reference]$_t$) at each temperature. Table 2 lists these depletion factors for each reactant pair for all of our experiments.

The ratio of the reactant to reference rate constants for the reaction of ozone 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). The data for each reaction were fit to the Arrhenius equation, and the resulting parameters are given in Table 7 along with statistically determined 95% confidence intervals. From these rate constant ratios, the rate constants at 298 K and the Arrhenius parameters were deter-

**TABLE 3: Summary of the Average Measured Rate Constant Ratios, $k_{\mathrm{reac}}/k_{\mathrm{ref}}$, for the Reaction of $O_3$ with Isoprene**

| $T$ (K) | no. of expts | $k_{\mathrm{reac}}/k_{\mathrm{ref}}$ | $T$ (K) | no. of expts | $k_{\mathrm{reac}}/k_{\mathrm{ref}}$ |
|---|---|---|---|---|---|
| 242 | 3 | 1.088 ± 0.193[a] | 242 | 4 | 0.057 ± 0.011[b] |
| 257 | 3 | 1.057 ± 0.066[a] | 257 | 5 | 0.063 ± 0.003[b] |
| 273 | 2 | 1.146 ± 0.150[a] | 273 | 3 | 0.081 ± 0.001[b] |
| 288 | 9 | 1.308 ± 0.073[a] | 288 | 3 | 0.108 ± 0.017[b] |
| 298 | 6 | 1.315 ± 0.018[a] | 298 | 6 | 0.119 ± 0.006[b] |
| 310 | 6 | 1.375 ± 0.072[a] | 310 | 2 | 0.136 ± 0.005[b] |
| 324 | 6 | 1.427 ± 0.077[a] | 324 | 5 | 0.173 ± 0.016[b] |
| 257 | 5 | 0.985 ± 0.028[c] | 258 | 1 | 0.435 ± 0.007[d] |
| 273 | 4 | 1.024 ± 0.052[c] | 273 | 1 | 0.469 ± 0.008[d] |
| 288 | 5 | 1.103 ± 0.028[c] | 298 | 8 | 0.507 ± 0.008[d] |
| 298 | 8 | 1.144 ± 0.024[c] | 324 | 1 | 0.553 ± 0.020[d] |
| 310 | 6 | 1.217 ± 0.015[c] | | | |
| 324 | 6 | 1.262 ± 0.017[c] | | | |

[a] Reference compound: 2-methylpropene. [b] Reference compound: *cis*-2-butene. [c] Reference compound: 1-butene. [d] Reference compound: 2,3-dimethyl-1,3-butadiene.

**TABLE 4: Summary of the Average Measured Rate Constant Ratios, $k_{\mathrm{reac}}/k_{\mathrm{ref}}$, for the Reaction of $O_3$ with α-Pinene**

| $T$ (K) | no. of expts | $k_{\mathrm{reac}}/k_{\mathrm{ref}}$[a] | $T$ (K) | no. of expts | $k_{\mathrm{reac}}/k_{\mathrm{ref}}$[b] |
|---|---|---|---|---|---|
| 288 | 3 | 9.475 ± 0.070 | 288 | 5 | 8.515 ± 0.183 |
| 298 | 5 | 9.392 ± 0.081 | 298 | 11 | 7.178 ± 0.294 |
| 310 | 8 | 7.369 ± 0.098 | 310 | 6 | 5.806 ± 0.092 |
| 324 | 3 | 5.619 ± 0.046 | 324 | 7 | 5.158 ± 0.315 |
| 343 | 8 | 5.271 ± 0.256 | 343 | 8 | 4.552 ± 1.107 |
| 363 | 6 | 4.265 ± 0.093 | | | |

[a] Reference compound: 1-butene. [b] Refernce compound: 2-methylpropene.

**TABLE 5: Summary of the Average Measured Rate Constant Ratios, $k_{\mathrm{reac}}/k_{\mathrm{ref}}$, for the Reaction of $O_3$ with *β*-Pinene**

| $T$ (K) | no. of expts | $k_{\mathrm{reac}}/k_{\mathrm{ref}}$[a] | $T$ (K) | no. of expts | $k_{\mathrm{reac}}/k_{\mathrm{ref}}$[b] |
|---|---|---|---|---|---|
| 298 | 6 | 0.179 ± 0.005 | 298 | 3 | 2.255 ± 0.082 |
| 310 | 2 | 0.182 ± 0.003 | | | |
| 324 | 3 | 0.203 ± 0.003 | | | |
| 343 | 7 | 0.208 ± 0.007 | | | |
| 363 | 3 | 0.211 ± 0.007 | | | |

[a] Reference compound: *cis*-2-butene. [b] Reference compound: 1-butene.

**TABLE 6: Summary of the Average Measured Rate Constant Ratios, $k_{\mathrm{reac}}/k_{\mathrm{ref}}$, for the Reaction of $O_3$ with Limonene**

| $T$ (K) | no. of expts | $k_{\mathrm{reac}}/k_{\mathrm{ref}}$[a] | $T$ (K) | no. of expts | $k_{\mathrm{reac}}/k_{\mathrm{ref}}$ |
|---|---|---|---|---|---|
| 298 | 11 | 1.722 ± 0.039 | 298 | 2 | 17.878 ± 0.946[b] |
| 310 | 8 | 1.647 ± 0.063 | 298 | 3 | 22.043 ± 0.821[c] |
| 324 | 3 | 1.619 ± 0.004 | | | |
| 343 | 3 | 1.550 ± 0.003 | | | |
| 363 | 3 | 1.536 ± 0.023 | | | |

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

**TABLE 7: Summary of the Measured Rate Constant Ratios ($k_{reac}/k_{ref}$) and Their Arrhenius Expression**

| reactant compd | ref compd | $k_{reac}/k_{ref}$[a] | $k_{reac}/k_{ref}$ at 298 K[b] |
|---|---|---|---|
| isoprene | 1-butene | $3.69^{+1.30}_{-0.96}\exp[(-306 \pm 87)/T]$ | 1.31± 0.07 |
| | 2-methylpropene | $3.41^{+0.53}_{-0.46}\exp[(-323 \pm 42)/T]$ | 1.14 ± 0.07 |
| | *cis*-2-Butene | $5.02^{+2.68}_{-1.75}\exp[(-1110 \pm 120)/T]$ | 0.12 ± 0.01 |
| | 2,3-dimethyl-1,3-butadiene | $1.37^{+0.38}_{-0.30}\exp[(-295 \pm 72)/T]$ | 0.51 ± 0.03 |
| α-pinene | 1-butene | $0.17^{+0.05}_{-0.04}\exp[(1190 \pm 87)/T]$ | 9.39 ± 0.46 |
| | 2-methylpropene | $0.13^{+0.21}_{-0.08}\exp[(1203 \pm 303)/T]$ | 7.18 ± 0.29 |
| (+)-β-pinene | *cis*-2-butene | $0.51^{+0.15}_{-0.11}\exp[(-308 \pm 84)/T]$ | 0.18 ± 0.01 |
| | 1-butene | | 2.25 ± 0.19 |
| (−)-β-pinene | *cis*-2-butene | | 0.18 ± 0.01 |
| limonene | *cis*-2-butene | $0.88^{+0.24}_{-0.19}\exp[(199 \pm 76)/T]$ | 1.72 ± 0.12 |
| | 1-butene | | 22.04 ± 1.92 |
| | 2-methylpropene | | 17.88 ± 1.84 |

[a] Errors are the 95% confidence limits and do not include estimated systematic errors. [b] Errors include estimated systematic errors.

**TABLE 8: Summary of All Measurements of $k_{alkene}$**

| alkene | temp range (K) | $10^{15}A$ ($cm^3$ molecule$^{-1}$ $s^{-1}$) | $E_a/R$ (K) | $10^{18}k_{alkene}$(at 298 K) ($cm^3$ molecule$^{-1}$ $s^{-1}$) | ref |
|---|---|---|---|---|---|
| isoprene | 295 ± 1 | | | 12.7 | Arnts and Gay[10] |
| | 260−294 | ∼10 | ∼1900 | 17.0[a] | Adeniji et al.[5] |
| | 278−323 | 15.4 | 2139 ± 427 | 11.7[a] | Atkinson et al.[6] |
| | 240−324 | 7.8 ± 1.6 | 1913 ± 139 | 12.8 ± 1.2 | Treacy et al.[7] |
| | 296 ± 2 | | | 12.2 ± 0.3 | Greene and Atkinson[11] |
| | 293 ± 2 | | | 8.95 ± 0.25 | Grosjean et al.[14] |
| | 290.7 ± 2.1 | | | 11.3 ± 3.2 | Grosjean and Grosjean[12] |
| | 296 ± 2 | | | 13.0 | Neeb and Moorgat[13] |
| | **242−324** | $\mathbf{10.9^{+2.70}_{-2.17}}$ | **1998 ± 63** | **13.0 ± 0.8**[b] | **this work** |
| α-pinene | 294 | | | 164 | Ripperton et al.[17] |
| | 298 | | | 330 ± 60 | Japar et al.[18] |
| | 295 ± 1 | | | 145 | Grimsrud et al.[19] |
| | 276−324 | 0.94 | 726 ± 172 | 82[a] | Atkinson et al.[6] |
| | 297 ± 2 | | | 86 ± 13 | Nolting et al.[15] |
| | 296 ± 2 | | | 97.1 ± 10.6 | Atkinson et al.[16] |
| | **288−363** | $\mathbf{0.48^{+0.29}_{-0.18}}$ | **530 ± 150** | **84.1 ± 7.4**[b] | **this work** |
| β-pinene | 294 | | | 65 | Ripperton et al.[17] |
| | 295 ± 1 | | | 36 | Grimsrud et al.[19] |
| | 296 ± 2 | | | 21 ± 5 | Atkinson et al.[6] |
| | 297 ± 2 | | | 14 ± 2 | Nolting et al.[15] |
| | 296 ± 2 | | | 14.8 ± 1.7 | Atkinson et al.[16] |
| | 296 ± 2 | | | 16.7 ± 2.0 | Atkinson et al.[16] |
| | 295 ± 1 | | | 12.2 ± 1.3 | Grosjean et al.[14] |
| | **298−363** | $\mathbf{1.74^{+0.46}_{-0.36}}$ | **1297 ± 75** | **22.2 ± 1.6**[b] | **this work** |
| limonene | 295 ± 1 | | | 640 | Grimsrud et al.[19] |
| | 296 ± 2 | | | 209 ± 22 | Atkinson et al.[16] |
| | 297.3 | | | 350 | Zhang et al.[21] |
| | 296 ± 2 | | | 201 ± 7 | Shu and Atkinson[20] |
| | **298−363** | $\mathbf{2.95^{+0.77}_{-0.61}}$ | **783 ± 72** | **213.2 ± 14.9**[b] | **this work** |

[a] The values reported here at $T = 298$ K were calculated on the basis of Arrhenius parameters reported by other authors when available. [b] Error levels as indicated include estimated systematic errors of 5%.

mined. These values are given in Table 8 along with their 95% confidence limits and comparisons to previous measurements.

**Isoprene.** Figure 4 is an Arrhenius plot of the measured rate constants for the reaction of isoprene with ozone; results from other investigators are also shown. The solid line is the least-squares fit of our data to the Arrhenius equation (these Arrhenius parameters are given in Table 8). Rate constants for this reaction have been given in eight other papers. Our results at room temperature ($1000/T \approx 3.4$) are in good agreement with those of Arnts and Gay,[10] Treacy et al.,[7] Greene and Atkinson,[11] Grosjean and Grosjean,[12] and Neeb and Moorgat.[13] Our rate constants, as a function of temperature, show an Arrhenius dependence that is slightly different than those reported by Atkinson et al.,[6] by Grosjean et al.,[14] and by Adeniji et al.[5]

**α-Pinene.** The measured rate constants for the reaction of α-pinene with ozone are plotted in Arrhenius format in Figure 5 along with their 95% confidence limits and results from previous investigations. The solid line is the least-squares fit of our data to the Arrhenius equation; the resulting Arrhenius parameters are given in Table 8. Our results at room temperature are in excellent agreement with those of Atkinson et al.[6] and Nolting et al.[15] However, our results are about 15% lower than the more recent Atkinson et al.[16] values and significantly lower than those of Ripperton et al.,[17] Japar et al.,[18] and Grimsrud et al.[19] The results of Grimsrud et al.[19] are probably not reliable. As suggested by Atkinson et al.,[16] the cause of these problems is probably the presence of secondary reactions. Only one previous study (Atkinson et al.[6]) included Arrhenius parameter measurements (over the temperature range of 276−324 K); our Arrhenius parameters are somewhat lower than this previous study.

**β-Pinene.** The measured rate constants for the reaction of ozone with β-pinene are plotted in Figure 6 along with their 95% confidence limits and results from previous investigations.

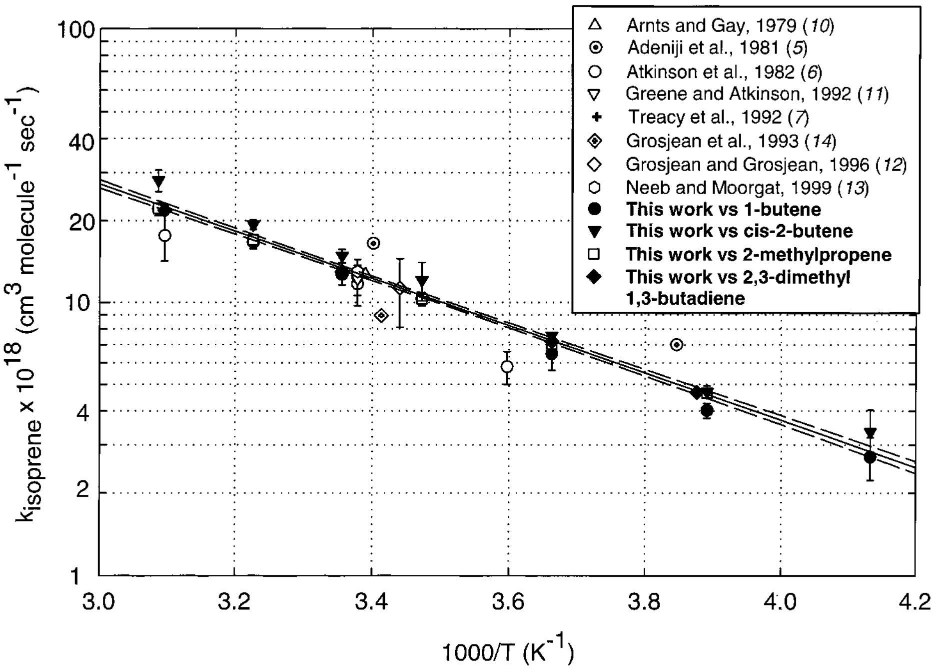

**Figure 4.** Arrhenius plot showing the measured rate constants for the reaction of ozone with isoprene (for each reference compound) and rate constants from other studies. The solid line is the regression of our measured values; the dashed lines are the 95% confidence limits of the regression. The error bars are the 95% confidence limits of our study; these errors do not reflect the uncertainties in the reference rate constants, and they do not include estimated systematic errors.

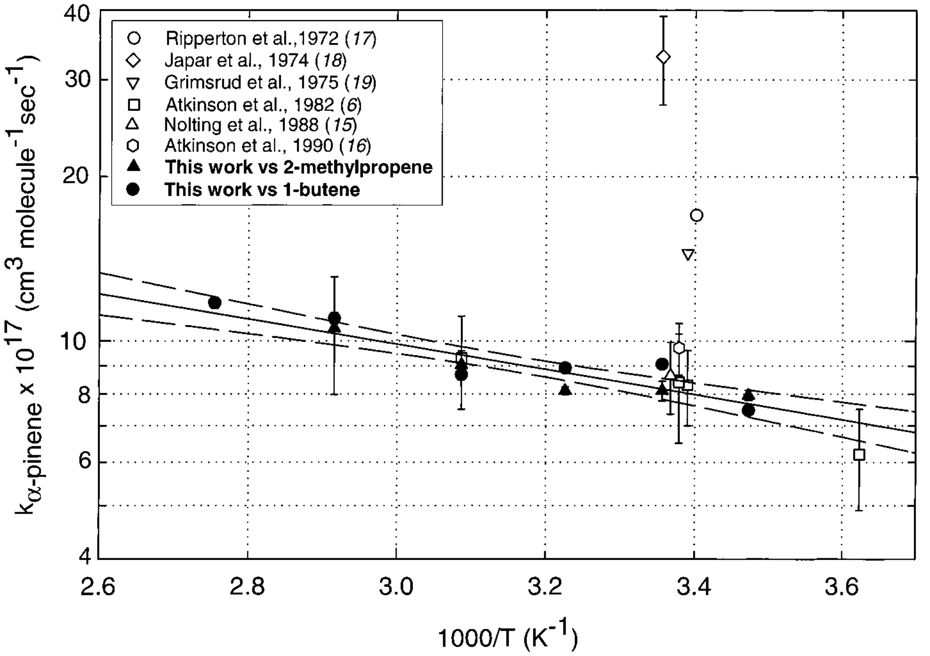

**Figure 5.** Arrhenius plot showing the measured rate constants for the reaction of ozone with α-pinene (for each reference compound) and rate constants from other studies. The solid line is the regression of our measured values; the dashed lines are the 95% confidence limits of the regression. The error bars are the 95% confidence limits of our study; these errors do not reflect the uncertainties in the reference rate constants, and they do not include estimated systematic errors.

The solid line is the best fit of our data to the Arrhenius equation; the resulting Arrhenius parameters are given in Table 8. We performed our measurements using two enantiomers of β-pinene [(+)-β-pinene and (−)-β-pinene] to check if there were any steric effects on the reaction. Previous studies had used a racemic mixture of β-pinene. As expected, we obtained exactly the same ratio of rate constants (see Table 7) for the two enantiomers. Thus, all other rate measurements of this reaction were performed using (+)-β-pinene.

Our rate constant for this reaction at room temperature is in excellent agreement with that of Atkinson et al.[6] But our results are significantly higher than the rate constants reported by Atkinson et al.,[16] Nolting et al.,[15] and Grosjean et al.[14] The reason for this large discrepancy is not clear. But because we paid particular attention to secondary reactions by measuring the reaction rate over a wide range of β-pinene depletion factors (see Table 2), we are confident that our measurements are not complicated by the secondary chemistry as described Atkinson et al.[16] Furthermore, our relative rate plots for this reaction showed good linearity and near nonzero intercepts as required

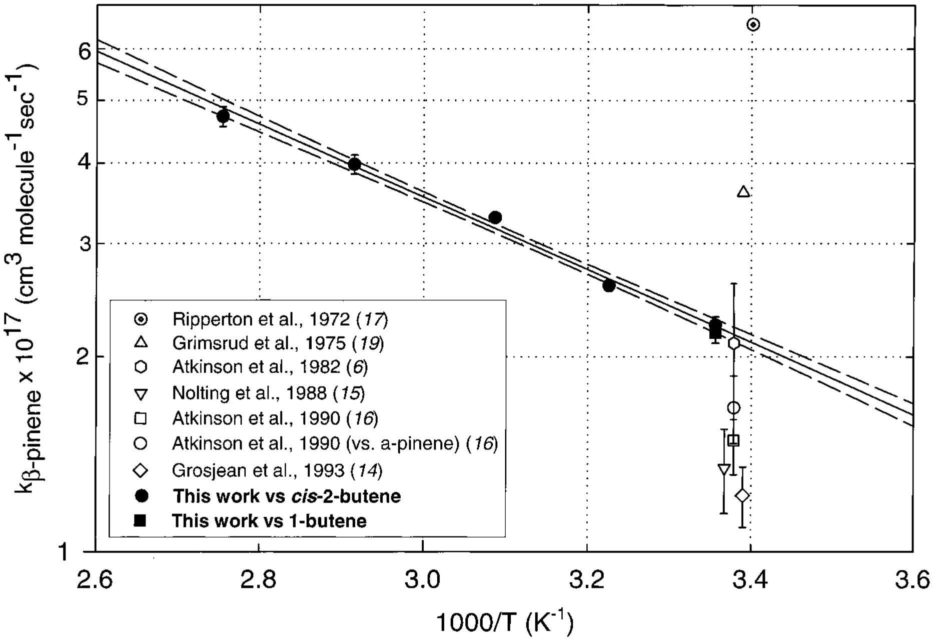

**Figure 6.** Arrhenius plot showing the measured rate constants for the reaction of ozone with β-pinene (for each reference compound) and rate constants from other studies. The solid line is the regression of our measured values; the dashed lines are the 95% confidence limits of the regression. The error bars are the 95% confidence limits of our study; these errors do not reflect the uncertainties in the reference rate constants, and they do not include estimated systematic errors.

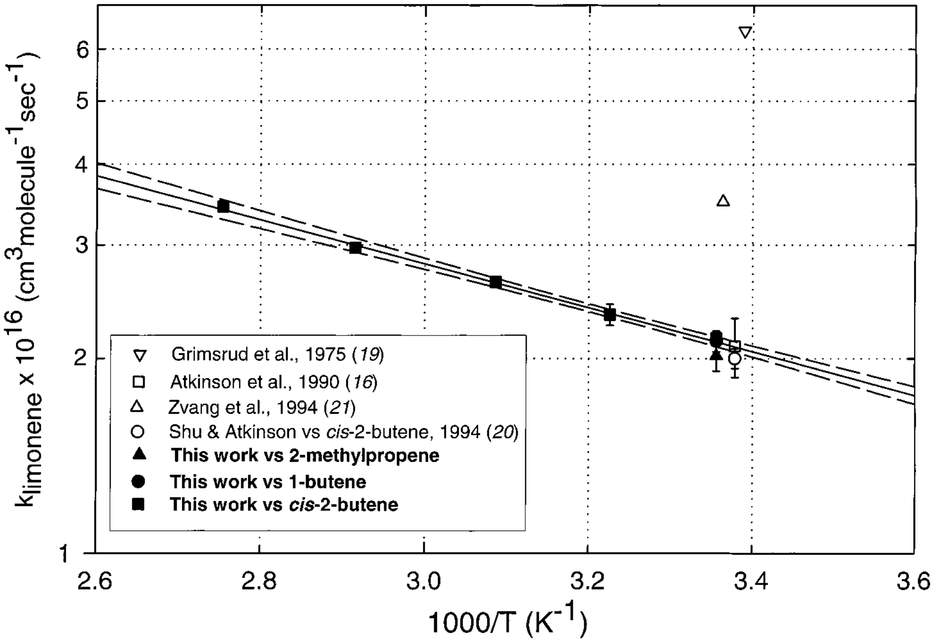

**Figure 7.** Arrhenius plot showing the measured rate constants for the reaction of ozone with limonene (for each reference compound) and rate constants from other studies. The solid line is the regression of our measured values; the dashed lines are the 95% confidence limits of the regression. The error bars are the 95% confidence limits of our study; these errors do not reflect the uncertainties in the reference rate constants, and they do not include estimated systematic errors.

by eq 3. Figure 6 also shows that the results of Ripperton et al.[17] and Grimsrud et al.[19] are significantly higher than our and others studies. To date, no Arrhenius parameters have been reported for the reaction.

**Limonene.** The rate constants measured in this study for the reaction of limonene with ozone are plotted in Figure 7 along with their 95% confidence limits and with results from previous investigations. The solid line is the least-squares fit of our data to the Arrhenius equation; the Arrhenius parameters for this fitted line are given in Table 8. Our rate constant at room temperature is in excellent agreement with that of Atkinson et al.[16] and in good agreement with that of Shu and Atkinson[20] (see Table 8). The rate constants reported by Grimsrud et al.[19] and by Zhang et al.[21] are significantly higher (by at least a factor of 1.7) than our measurements and those of Atkinson et al.[16] and Shi and Atkinson.[20] The reason for this large discrepancy is not entirely clear. To date, no other Arrhenius parameters have been reported for this reaction.

**Relative Atmospheric Residence Times.** We can use our measured rate constants along with some assumed atmospheric ozone concentrations to calculate the residence time of these biogenic hydrocarbons due to this reaction. Seinfeld and Pandis[22] (p 96) suggest that average ozone concentrations are 30 ppb in the remote atmosphere, 85 ppb in the rural atmosphere, and

**TABLE 9: Atmospheric Residence Times (in hours) of Four Biogenic Hydrocarbons Due to Reactions with Ozone Compared to Reactions with the Hydroxyl Radical**

| | remote ozone (at 30 ppb) | rural ozone (at 85 ppb) | urban ozone (at 250 ppb) | hydroxyl (at 9.7 × $10^5$ $cm^{-3}$) |
|---|---|---|---|---|
| isoprene | 26 | 9.3 | 3.2 | 2.8 |
| α-pinene | 4.1 | 1.4 | 0.49 | 5.3 |
| β-pinene | 15 | 5.5 | 1.9 | 3.6 |
| limonene | 1.6 | 0.57 | 0.19 | 1.7 |

250 ppb in the urban atmosphere. Using these values and our rate constants at 298 K, we calculated the residence times due to ozone reactions for the four compounds studied here; the results are given in Table 9. For comparison, we have also calculated the residence time due to reactions with the hydroxyl radical, assuming $[OH] = 9.7 \times 10^5$ $cm^{-3}$ and using published rate constants for these reactions[22] (p. 1306); these results are given in the last column of Table 9. These calculations indicate that isoprene and β-pinene would be lost at about the same rate due to ozone and OH reactions in an urban atmosphere. When the ozone levels are lower, OH reactions predominate for these two compounds. On the other hand, even in a rural atmosphere, α-pinene and limonene would be primarily removed by reactions with ozone, not with OH.

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