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# Rate Constants for the Gas-Phase Reactions of OH and O<sub>3</sub> with $\beta$ -Ocimene, $\beta$ -Myrcene, and $\alpha$ - and $\beta$ -Farnesene as a Function of Temperature

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The rate constants for the gas-phase reactions of hydroxyl radicals and ozone with the biogenic hydrocarbons  $\beta$ -ocimene,  $\beta$ -myrcene, and  $\alpha$ - and  $\beta$ -farnesene were measured using the relative rate technique over the temperature ranges 313–423 (for OH) and 298–318 K (for O<sub>3</sub>) at about 1 atm total pressure. The OH radicals were generated by photolysis of H<sub>2</sub>O<sub>2</sub>, and O<sub>3</sub> was produced from the electrolysis of O<sub>2</sub>. Helium was used as the diluent gas. The reactants were detected by online mass spectrometry, which resulted in high time resolution, allowing large amounts of data to be collected and used in the determination of the Arrhenius parameters. The following Arrhenius expressions have been determined for these reactions (in units of cm<sup>3</sup> molecules<sup>−1</sup> s<sup>−1</sup>): for  $\beta$ -ocimene + OH,  $k = (4.35^{+0.78}_{-0.66}) \times 10^{-11} \exp[(579 \pm 59)/T]$ ; for  $\beta$ -ocimene + O<sub>3</sub>,  $k = (3.15^{+1.36}_{-0.95}) \times 10^{-15} \exp[-(626 \pm 110)/T]$ ; for  $\beta$ -myrcene + O<sub>3</sub>,  $k = (2.21^{+0.94}_{-0.66}) \times 10^{-15} \exp[-(520 \pm 109)/T]$ ; for  $\alpha$ -farnesene + OH,  $k_{\text{OH}} = (2.19 \pm 0.11) \times 10^{-10}$  for 323–413 K; for  $\alpha$ -farnesene + O<sub>3</sub>,  $k = (3.52^{+9.09}_{-2.54}) \times 10^{-12} \exp[-(2589 \pm 393)/T]$ ; for  $\beta$ -farnesene + OH,  $k_{\text{OH}} = (2.88 \pm 0.15) \times 10^{-10}$  for 323–423 K; for  $\beta$ -farnesene + O<sub>3</sub>,  $k = (1.81^{+3.46}_{-1.19}) \times 10^{-12} \exp[-(2347 \pm 329)/T]$ . The Arrhenius parameters here are the first to be reported. The reactions of  $\alpha$ - and  $\beta$ -farnesene with OH showed no significant temperature dependence. Atmospheric residence times due to reactions with OH and O<sub>3</sub> were also presented.

## Introduction

It has long been recognized that emissions of biogenic volatile organic compounds (BVOCs) from vegetation can contribute to the production of ozone and secondary aerosols in the troposphere.<sup>1,2</sup> Isoprene (C<sub>5</sub>H<sub>8</sub>) is the most abundant of these biogenic compounds, with an estimated global emission rate of 500 Tg of C year<sup>−1</sup>, but several monoterpenes (C<sub>10</sub>H<sub>16</sub>) and sesquiterpenes (C<sub>15</sub>H<sub>24</sub>) are also important BVOCs. Many of these compounds have relatively high global emission rates and high atmospheric reactivities with OH, NO<sub>3</sub>, and O<sub>3</sub>, suggesting that BVOC lifetimes in the lower troposphere are on the order of a few minutes to a few hours.<sup>3,4</sup> Reaction with OH radicals is a critical step in the atmospheric oxidation of these compounds, and as a result, rate constants have been measured for the gas-phase reactions of OH with a large number of C<sub>5</sub> and C<sub>10</sub> BVOCs. However, there are few rate constant data available for reactions of OH with sesquiterpenes. In addition, reactions of BVOCs with O<sub>3</sub> can be a source of OH radicals both during the day and at night,<sup>5</sup> and reactions of O<sub>3</sub> with some BVOCs are potential precursors of secondary organic aerosol.<sup>6</sup> Therefore, it is useful to determine rate constants for reactions of BVOCs with O<sub>3</sub>. In addition, the rate constants for the BVOC + OH and BVOC + O<sub>3</sub> reactions should be determined as a function of temperature.

The kinetics of the reactions of OH and O<sub>3</sub> with isoprene, the unit structure of monoterpenes, and other major monoterpenes, such as  $\alpha$ - and  $\beta$ -pinene and limonene, have been investigated in our laboratory as a function of temperature.<sup>7,8</sup> However, the OH and O<sub>3</sub> kinetics of ocimene, which has been identified in foliar emission from trees and categorized as “frequently found” monoterpenes, have not been fully investigated.<sup>9</sup> Although there have been some product studies of the

OH- and O<sub>3</sub>-initiated oxidation of ocimene,<sup>10,11</sup> there have been few measurements of the rate constants for these reactions.  $\beta$ -Myrcene is also one of the dominant monoterpene hydrocarbons emitted by major forest species; in fact, it is one of the six most abundant BVOCs.<sup>12</sup> The rate constants for the reaction of  $\beta$ -myrcene with OH have been measured recently in our laboratory using the relative rate technique,<sup>13</sup> but the kinetics of its reaction with O<sub>3</sub> are not known. The sesquiterpene  $\alpha$ -farnesene was identified from branch closure experiments as being emitted by manzanita, white fir, Ceanothus shrubs, and ponderosa pines, and  $\beta$ -farnesene was identified as being emitted by cut and dry ponderosa pine and from silver birch.<sup>14,15</sup> Presumably due to their relatively low vapor pressures, no kinetic experiments have been reported to the reactions of  $\alpha$ - or  $\beta$ -farnesenes. In addition, virtually all of the existing kinetic studies for these reactions have been limited to room-temperature measurements.

This paper reports measurements of the rate constants for the reactions of OH radicals and O<sub>3</sub> with four BVOCs:  $\beta$ -ocimene,  $\beta$ -myrcene, and  $\alpha$ - and  $\beta$ -farnesene as a function of temperature. We used the relative rate technique with detection of the gas-phase components by online mass spectrometry. The Arrhenius parameters determined here for these reactions are the first to be reported.

## Experimental Section

**Chemicals.** The chemicals used, their stated purities, and their Chemical Abstracts registry numbers are as follows:  $\beta$ -ocimene, ~70–75%, 13877-91-3;  $\beta$ -myrcene, ≥90%, 123-35-3;  $\alpha$ -farnesene, 502-61-4;  $\beta$ -farnesene, ≥90%, 18794-84-8; 2-methylpropene, 99%, 115-11-7; *trans*-2-butene, ≥99%, 624-64-6; acetaldehyde, 99.5+%, 75-07-0; hydrogen peroxide, 50 wt % H<sub>2</sub>O, 7722-84-1; carbon tetrachloride, ≥99.5% anhydrous, 56-23-5. All of these compounds were purchased from Sigma-Aldrich Inc. and used without further purification.

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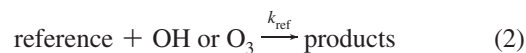
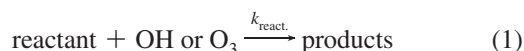
**Apparatus.** The experimental apparatus used to measure the rate constants has been described in detail elsewhere.<sup>7,8,13</sup> Reactions were performed in a 160 cm<sup>3</sup> quartz reaction chamber located in the oven of a Hewlett-Packard 5890 gas chromatograph (for temperature control) and interfaced to a Hewlett-Packard 5989A quadrupole mass spectrometer operated in the electron impact (EI) mode. The center of the chamber was continuously sampled through a 100  $\mu$ m i.d., deactivated fused silica capillary (J&W Scientific Inc., Folsom, CA) approximately 60 cm long.

For the OH reactions, at the onset of an experiment, the reaction chamber was isolated from all gas flows after being flushed with helium (99.999%, Praxair Inc., Indianapolis, IN) for about 30 min, and 20–25  $\mu$ L of a 50% H<sub>2</sub>O<sub>2</sub> aqueous solution was injected. A waiting period of about 3–5 min was then allowed to establish a baseline signal for all masses monitored to correct for any instrumental drift and dark reactions. About 6–10  $\mu$ L of a BVOC solution (in CCl<sub>4</sub> at a concentration of 6  $\mu$ g/ $\mu$ L) and 6–15  $\mu$ L of gas-phase 2-methylpropene (the reference compound) were injected concurrently into the chamber. After a 20 min equilibration time, a 200 W Xe–Hg UV lamp (Hamamatsu Co., Hamamatsu City, Japan) was turned on, initiating the production of OH radicals by the photolysis of H<sub>2</sub>O<sub>2</sub>. The reaction was allowed to proceed for several minutes. The data acquisition rate of the mass spectrometer was set to a dwell time of 200 ms/ion.

For the O<sub>3</sub> reactions, 30  $\mu$ L of gas-phase acetaldehyde was injected with a gastight Hamilton syringe into the chamber; acetaldehyde was used to scavenge OH radicals and thus to avoid additional losses of both the reference and reactant compounds from OH radical reactions. Then about 1–10  $\mu$ L of a BVOC solution (2–6  $\mu$ g/ $\mu$ L in CCl<sub>4</sub>) and 5–10  $\mu$ L of gas-phase *trans*-2-butene (the reference compound) were injected. Ozone was produced by flowing O<sub>2</sub> through an electrolytic generator (1000BT-12, Ozone Solutions, Hull, IA) into the reaction chamber. About 10 min was allowed for mixing and for establishing a baseline before 200  $\mu$ L of an O<sub>3</sub>/O<sub>2</sub> mixture was injected. The data acquisition rate of the mass spectrometer was set to a dwell time of 20 ms/ion, because the BVOC + O<sub>3</sub> reactions were much faster than the BVOC + OH reactions.

**Determination of Rate Constants.** The mass spectrometer was set to monitor masses (*m/z* values) of the reactant and reference compounds. These *m/z* values were selected to avoid overlaps with each other and with masses of potential transformation products. 2-Methylpropene and *trans*-2-butene were monitored at *m/z* 56 (C<sub>4</sub>H<sub>8</sub>), and  $\beta$ -ocimene,  $\beta$ -myrcene, and  $\alpha$ - and  $\beta$ -farnesene were monitored at *m/z* 93 (C<sub>7</sub>H<sub>9</sub>); the electron impact mass spectra of these compounds are shown in Figure S1 of the Supporting Information. The mass of the ion at *m/z* 93 was sufficiently high to be free of interferences from the reference compounds or from products of the OH or O<sub>3</sub> reactions.

During the measurements, the only loss processes in the reaction chamber were reactions with OH or O<sub>3</sub> and physical removal by adsorption onto the reactor walls or by flushing out of the chamber with helium leaks. The rate constants for the reactions of BVOC + OH or BVOC + O<sub>3</sub> were determined by the relative rate technique, which is based on the measurement of the simultaneous losses of the reactant and a reference compound:



where  $k_{\text{react.}}$  is the rate constant of the reactant and  $k_{\text{ref}}$  is the rate constant of the reference compound. The value of the rate constant ratio is determined using the following well-known relationship:

$$\ln\left(\frac{[\text{reactant}]_0}{[\text{reactant}]_t}\right) = \frac{k_{\text{react.}}}{k_{\text{ref}}} \ln\left(\frac{[\text{reference}]_0}{[\text{reference}]_t}\right) \quad (3)$$

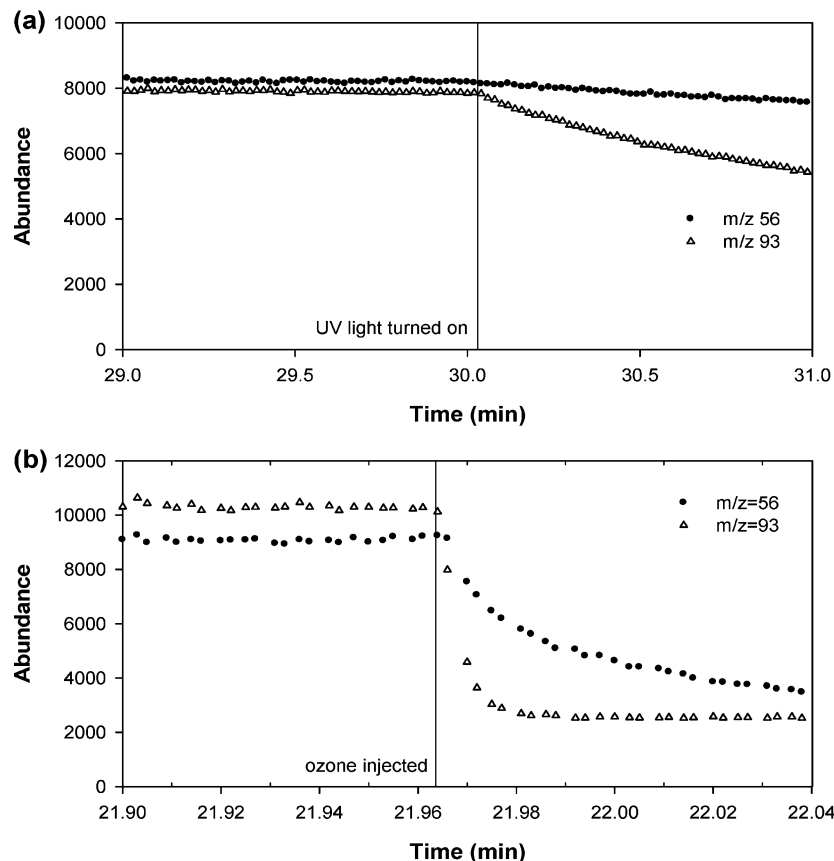
where  $[\text{reactant}]_0$  and  $[\text{reference}]_0$  are the initial concentrations of the reactant and reference compounds and  $[\text{reactant}]_t$  and  $[\text{reference}]_t$  are the corresponding concentrations at time *t*. In our experiments, the signals from the mass spectrometer were assumed to be proportional to the concentrations and were used directly in eq 3. 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  $k_{\text{react.}}/k_{\text{ref}}$ , and if  $k_{\text{ref}}$  is known,  $k_{\text{react.}}$  can be calculated. In our experiments, 2-methylpropene and *trans*-2-butene were used as the reference compounds for the OH and O<sub>3</sub> measurements, respectively. The Arrhenius parameters for the 2-methylpropene + OH reaction are  $A = 0.947 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> and  $E_a/R = -504$  K;<sup>16</sup> these parameters for the *trans*-2-butene + O<sub>3</sub> reaction are  $A = 6.64 \times 10^{-15}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> and  $E_a/R = 1059$  K.<sup>16</sup>

## Results and Discussion

Figure 1 shows the raw data for typical kinetic experiments for the reactions of  $\alpha$ -farnesene + OH (top) and + O<sub>3</sub> (bottom). The ion at *m/z* 93 shows the relative concentration of the farnesene, and the ion at *m/z* 56, for the C<sub>4</sub>H<sub>8</sub> reference compounds. Reactions were initiated by turning on the UV light (in this case at 30.038 min) to produce OH or by injecting O<sub>3</sub> into the reaction chamber (in this case at 21.963 min) after allowing 20–30 min for the components in the reaction chamber to mix. The BVOC rate constants determined in this study were corrected by subtracting baseline and dark decay rates determined before turning on the light or before injecting O<sub>3</sub>. Note that, in the case of the O<sub>3</sub> reaction, most of the reactant was lost within 1200 ms. The resulting signals at each mass were analyzed using eq 3 to generate relative rate plots, examples of which are shown in Figure 2. The slopes of the regression lines are the ratios of  $k_{\text{react.}}$  to  $k_{\text{ref}}$ . These data typically showed good linearity and a near zero intercept.

The average rate constants and their standard errors for the reactions of the four BVOCs with OH radicals and with O<sub>3</sub> are summarized as a function of temperature in Tables S1 ( $\beta$ -ocimene + OH), S2 ( $\alpha$ -farnesene + OH), S3 ( $\beta$ -farnesene + OH), S4 ( $\beta$ -ocimene + O<sub>3</sub>), S5 ( $\beta$ -myrcene + O<sub>3</sub>), S6 ( $\alpha$ -farnesene + O<sub>3</sub>), and S7 ( $\beta$ -farnesene + O<sub>3</sub>) of the Supporting Information. The data for each reaction were fit to the Arrhenius equation, and the resulting parameters (pre-exponential factor *A* and activation energy  $E_a/R$ ) are given in Table 1 along with the rate constants at 298 K. The latter values are compared to a few values from the literature, which are also given in Table 1.

**Reactions with OH.** Figure 3 shows Arrhenius plots of the measured rate constants for the reactions of  $\beta$ -ocimene,  $\beta$ -myrcene, and  $\alpha$ - and  $\beta$ -farnesene with OH radicals and rate constants from other studies. The Arrhenius plot for the  $\beta$ -myrcene + OH reaction shown in Figure 3b is for the rate constants measured previously in our laboratory by Hites and



**Figure 1.** Raw data from the relative rate experiments for the reaction of  $\alpha$ -farnesene with (a) OH and (b)  $O_3$  using 2-methylpropene and *trans*-2-butene, respectively, as the reference compounds.

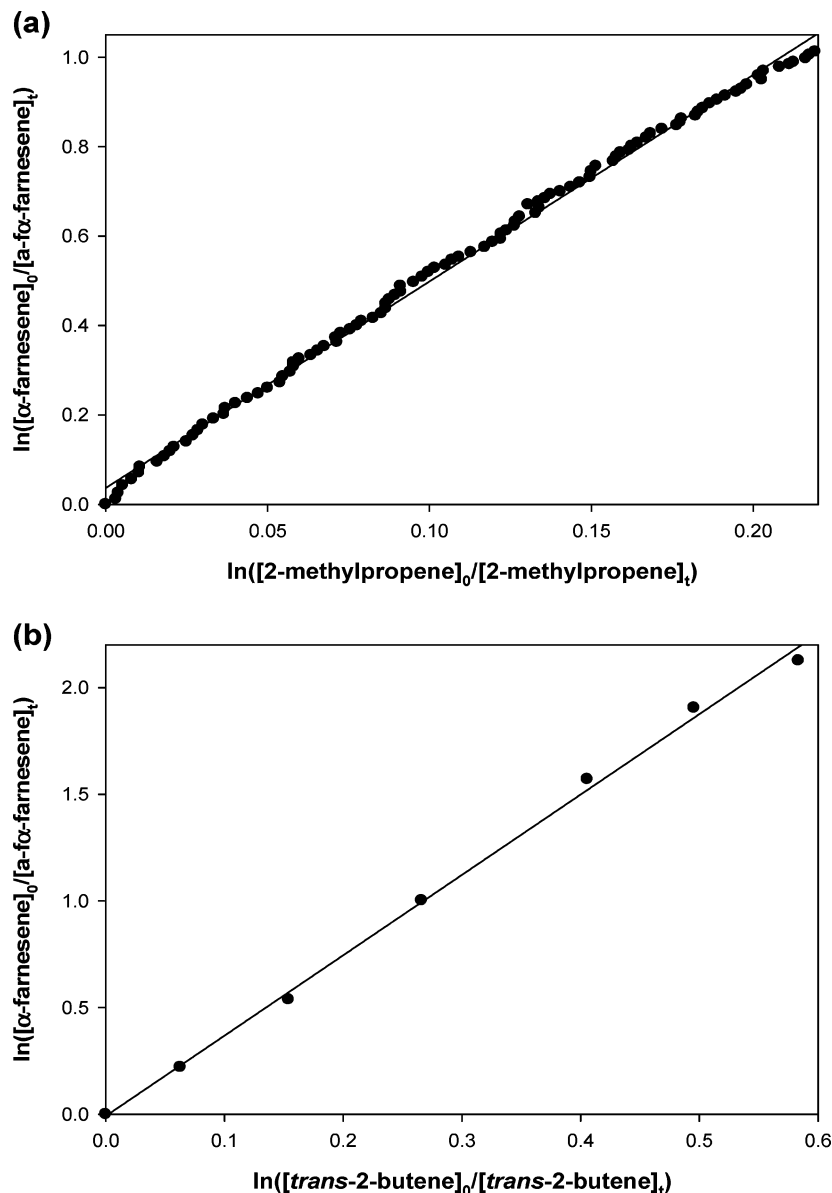
Turner<sup>13</sup> and is replotted here for completeness. In all cases, the solid line is a linear regression of all measured values, and the dashed lines are the 95% confidence limits of the regression.

For the reaction of  $\beta$ -ocimene with OH, the natural logarithms of the measured rate constants are strongly related to the corresponding reciprocal temperatures. Figure 3a shows that our results at room temperature are in good agreement with two other measurements of this rate constant (actually for a mixture of ocimene isomers) in the literature:  $2.50 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 294 K<sup>17</sup> and  $3.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 301 K.<sup>18</sup> Both of these measurements were based on the relative rate method using 2,3-dimethyl-2-butene and 2-methylpropene, respectively, as the reference compounds. The rate constant of  $\beta$ -ocimene at 298 K extrapolated from our Arrhenius relationship [ $(3.03^{+0.44}_{-0.39}) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ] is between these values (Table 1). The slope of the Arrhenius plot for the  $\beta$ -myrcene + OH reaction ( $1071 \pm 82 \text{ K}$ ) is slightly steeper than that of the  $\beta$ -ocimene + OH reaction ( $579 \pm 59 \text{ K}$ ). In other words,  $\beta$ -myrcene reacts with OH faster than  $\beta$ -ocimene at low temperatures ( $<313 \text{ K}$ ) while  $\beta$ -ocimene reacts faster than  $\beta$ -myrcene at high temperatures ( $>313 \text{ K}$ ). We observed a negative temperature dependence for the reaction of  $\beta$ -ocimene with OH, which is similar to other BVOCs reactions with OH.<sup>7,13</sup> The primary mechanism for this reaction is likely to be OH addition, producing an OH-BVOC adduct. Because the rate constant for this reaction is likely to be at its high-pressure limit under the conditions of our experiments, the negative temperature dependence is probably due to the increased rate of the unimolecular dissociation of the collisionally stabilized adduct at high temperature, which was also observed in reactions of aromatic compounds with OH.<sup>19</sup>

Unlike  $\beta$ -ocimene and  $\beta$ -myrcene, there was no significant temperature dependence for either of the farnesene + OH reactions over the temperature range of 313–423 K. In Figure 3c,d, the solid lines represent the mean rate constants of all measurements over the temperature range, and the dashed lines represent the 95% confidence limits of these means; these values are also reported in Table 1. Very few studies have determined the rate constants for the reactions of sesquiterpenes with OH. Experimental rate constants for the cyclic sesquiterpenes  $\alpha$ -cedrene,  $\alpha$ -copaene,  $\beta$ -caryophyllene,  $\alpha$ -humulene, and longifolene at 296 K were reported to be 0.7, 0.9, 2, 2.9, and  $0.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , respectively, using relative rate techniques.<sup>20</sup> However, no experimental data of the farnesene + OH reactions are available except for estimates using the Estimation Programs Interface (EPI) Suite developed by the United States Environmental Protection Agency,<sup>21</sup> and these values are shown in Figure 3c,d and in Table 1. The results of our experiments at 298 K [ $(2.19 \pm 0.11) \times 10^{-10}$  for  $\alpha$ -farnesene and  $(2.88 \pm 0.15) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for  $\beta$ -farnesene] are similar to the estimated values of  $3.19 \times 10^{-10}$  for  $\alpha$ -farnesene and  $2.19 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1}$  for  $\beta$ -farnesene.

**Reactions with  $O_3$ .** Figure 4 shows Arrhenius plots of the measured rate constants for the reactions of  $\beta$ -ocimene,  $\beta$ -myrcene, and  $\alpha$ - and  $\beta$ -farnesene with  $O_3$ ; results from other studies are also included. The solid lines are linear regressions of all measured values, and the dashed lines are the 95% confidence limits of these regressions. Unlike the OH reactions, all of these Arrhenius plots show a positive temperature dependence.

Figure 4a is an Arrhenius plot of the measured rate constants for the reaction of  $\beta$ -ocimene with  $O_3$ . Our result at 298 K is



**Figure 2.** Plots of (a)  $\ln([\alpha\text{-farnesene}]_0/[\alpha\text{-farnesene}]_t)$  at  $m/z = 93$  vs  $\ln([2\text{-methylpropene}]_0/[2\text{-methylpropene}]_t)$  at  $m/z = 56$  for the reaction of OH with  $\alpha$ -farnesene at 323 K along with the regression line ( $r^2 = 0.993$ ;  $n = 103$ ) and (b)  $\ln([\alpha\text{-farnesene}]_0/[\alpha\text{-farnesene}]_t)$  at  $m/z = 93$  vs  $\ln([trans\text{-}2\text{-butene}]_0/[trans\text{-}2\text{-butene}]_t)$  at  $m/z = 56$  for the reaction of O<sub>3</sub> with  $\alpha$ -farnesene at 313 K along with the regression line ( $r^2 = 0.998$ ;  $n = 7$ ).

$3.85 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  is comparable to one such measurement in the literature ( $4.99 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 296 K)<sup>22</sup> but much lower than another such value ( $21.8 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 301 K).<sup>18</sup> The former value was based on the relative rate method using  $\alpha$ -pinene as the reference compound, and the latter one was measured by an absolute rate method. The reason for this latter discrepancy is not clear.

An Arrhenius plot of the measured rate constants for the reaction of  $\beta$ -myrcene with O<sub>3</sub> is shown in Figure 4b, which also includes results from other investigators. The rate constants of the  $\beta$ -myrcene + O<sub>3</sub> reaction are very similar to those of  $\beta$ -ocimene, indicating that the reactions are initiated by the O<sub>3</sub> addition to the double bond with two methyl substituents—the electron-donating effect of the methyl group promotes electrophilic addition.<sup>16,23</sup> Our result at 298 K is  $3.85 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ; there are two other measurements of this rate constant in the literature:  $4.85 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 296 K<sup>22</sup> and  $12.4 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 301 K.<sup>18</sup> The former value was based on the relative rate method using

$\alpha$ -pinene as the reference compound, and the latter one was measured by an absolute rate method. Again our measurements agree well with those of Atkinson et al.<sup>22</sup> but less well with those of Grimsrud et al.<sup>18</sup>

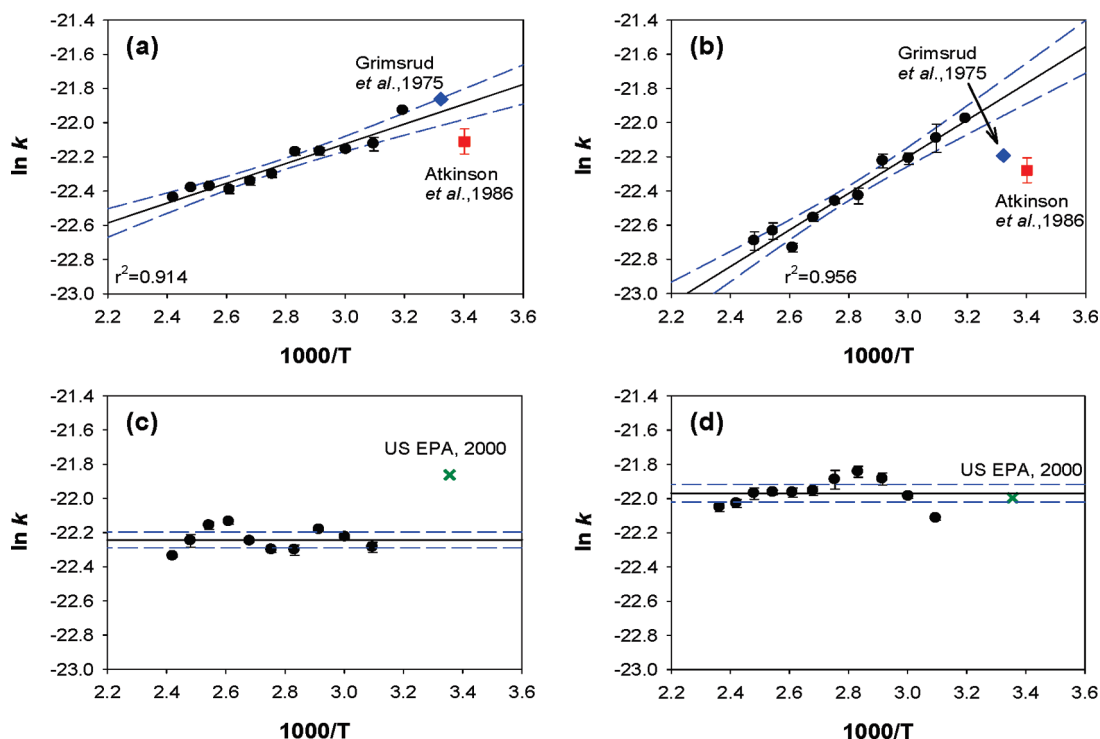
For the reactions of farnesenes with O<sub>3</sub>, Arrhenius plots are shown in Figure 4c,d along with estimated values and a measured rate constant for  $\beta$ -farnesene. Similar to the  $\beta$ -ocimene and  $\beta$ -myrcene pair, the measured rate constants for the two farnesene + O<sub>3</sub> reactions are comparable to each other, indicating that O<sub>3</sub> addition probably occurs at double bonds with two methyl substituents rather than at the terminal conjugated double bonds. The rate constants for the reactions of  $\alpha$ -farnesene and  $\beta$ -farnesene with O<sub>3</sub> at 298 K are  $5.94 \times 10^{-16}$  and  $6.86 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , respectively. The estimated rate constants from the U.S. EPA EPI Suite are  $10.4 \times 10^{-16}$  for  $\alpha$ -farnesene and  $8.74 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for  $\beta$ -farnesene.<sup>21</sup> For the  $\alpha$ -farnesene + O<sub>3</sub> reaction, no experimental data are available in the literature; however, a rate constant of  $4.01 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the  $\beta$ -farnesene reaction with



**TABLE 1: Summary of All Measurements of BVOCs Reactions with OH and O<sub>3</sub>**

BVOC	Structure	Rate constant (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	k (at 298 K) (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )
$\beta$ -ocimene		$k_{\text{OH}} = (4.35^{+0.78}_{-0.66}) \times 10^{-11} \exp[(579 \pm 59)/T]$	$(3.03^{+0.44}_{-0.39}) \times 10^{-10}$
			$(2.50 \pm 0.19) \times 10^{-10}{}^a$
			$3.2 \times 10^{-10}{}^b$
		$k_{\text{O}_3} = (3.15^{+1.36}_{-0.95}) \times 10^{-15} \exp[-(626 \pm 110)/T]$	$(3.85^{+0.30}_{-0.28}) \times 10^{-16}$
$\beta$ -myrcene		$k_{\text{OH}} = (9.19^{+2.38}_{-1.89}) \times 10^{-12} \exp[(1071 \pm 82)/T]{}^d$	$(3.35^{+0.64}_{-0.54}) \times 10^{-10}{}^d$
			$(2.11 \pm 0.16) \times 10^{-10}{}^a$
			$2.3 \times 10^{-10}{}^b$
		$k_{\text{O}_3} = (2.21^{+0.94}_{-0.66}) \times 10^{-15} \exp[-(520 \pm 109)/T]$	$(3.85^{+0.29}_{-0.27}) \times 10^{-16}$
$\alpha$ -farnesene		$k_{\text{OH}} = (2.19 \pm 0.11) \times 10^{-10}$ for 323–413 K	$(2.19 \pm 0.11) \times 10^{-10}$
			$3.19 \times 10^{-10}{}^e$
		$k_{\text{O}_3} = (3.52^{+9.09}_{-2.54}) \times 10^{-12} \exp[-(2589 \pm 393)/T]$	$(5.94^{+1.80}_{-1.38}) \times 10^{-16}$
			$10.4 \times 10^{-16}{}^e$
$\beta$ -farnesene		$k_{\text{OH}} = (2.88 \pm 0.15) \times 10^{-10}$ for 323–423 K	$(2.88 \pm 0.15) \times 10^{-10}$
			$2.84 \times 10^{-10}{}^e$
		$k_{\text{O}_3} = (1.81^{+3.46}_{-1.19}) \times 10^{-12} \exp[-(2347 \pm 329)/T]$	$(6.86^{+1.71}_{-1.37}) \times 10^{-16}$
			$8.74 \times 10^{-16}{}^e$
			$(4.01 \pm 0.17) \times 10^{-16}{}^f$

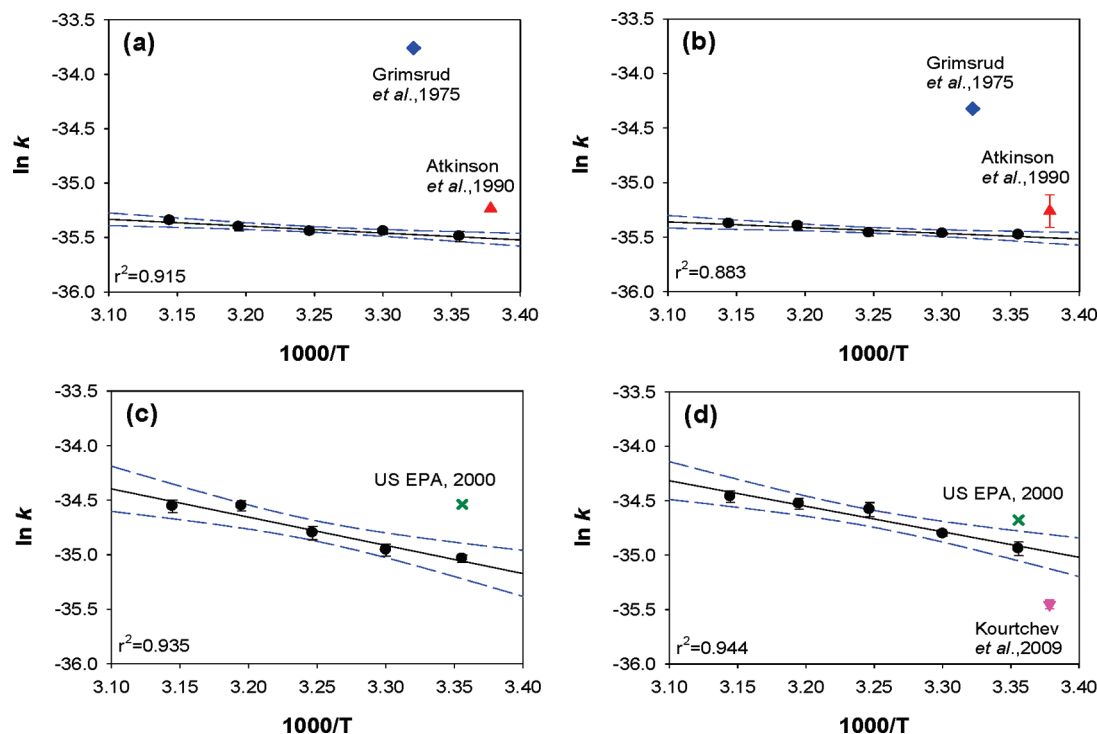
<sup>a</sup> Measured by Atkinson et al. at 294 K.<sup>17</sup> <sup>b</sup> Measured by Grimsrud et al. at 301 K.<sup>18</sup> <sup>c</sup> Measured by Atkinson et al. at 296 K.<sup>22</sup> <sup>d</sup> Hites and Turner.<sup>13</sup> <sup>e</sup> Estimated from U.S. EPA's Estimation Programs Interface Suite (AOPWIN<sup>21</sup>). <sup>f</sup> Measured by Kourtchev et al. at 296 K.<sup>24</sup>



**Figure 3.** Arrhenius plots showing the measured rate constants for the reactions of (a)  $\beta$ -ocimene, (b)  $\beta$ -myrcene (replotted from ref 13), (c)  $\alpha$ -farnesene, and (d)  $\beta$ -farnesene with OH as a function of temperature. The solid line is a linear regression, and the dashed lines are the 95% confidence limits of the regression. For c and d, the solid line indicates the mean rate constant of the measurements in this study, and the dashed lines are the 95% confidence limits of these means.

O<sub>3</sub> at 296 K has been reported recently by Kourtchev et al.<sup>24</sup> The rate constant for  $\beta$ -farnesene obtained at 298 K in this study is between the EPA estimated value and that measured by

Kourtchev et al.<sup>24</sup> Experimental room-temperature rate constants for the reaction of cyclic sesquiterpenes + O<sub>3</sub> are as follows (in units of 10<sup>-16</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>):  $\alpha$ -cedrene, 0.28;



**Figure 4.** Arrhenius plots showing the measured rate constants for the reactions of (a)  $\beta$ -ocimene, (b)  $\beta$ -myrcene, (c)  $\alpha$ -farnesene, and (d)  $\beta$ -farnesene with O<sub>3</sub> as a function of temperature. The solid line is a linear regression, and the dashed lines are the 95% confidence limits of the regression.

**TABLE 2: Atmospheric Residence Times (in hours) of  $\beta$ -Ocimene,  $\beta$ -Myrcene,  $\alpha$ -Farnesene, and  $\beta$ -Farnesene due to Reactions with OH and O<sub>3</sub> at 277 K**

BVOC	OH (at $10^6 \text{ cm}^{-3}$ )	remote O <sub>3</sub> (at 30 ppb)	rural O <sub>3</sub> (at 85 ppb)	urban O <sub>3</sub> (at 250 ppb)
$\beta$ -ocimene	0.79	1.1	0.40	0.14
$\beta$ -myrcene	0.63 <sup>a</sup>	1.1	0.39	0.13
$\alpha$ -farnesene	1.3	1.2	0.43	0.15
$\beta$ -farnesene	0.97	0.97	0.34	0.12

<sup>a</sup> Hites and Turner.<sup>13</sup>

$\alpha$ -copaene, 0.16;  $\beta$ -caryophyllene, 120;  $\alpha$ -humulene, 120; and longifolene <0.07, as determined using relative rate techniques.<sup>25</sup> Compared to most of these cyclic sesquiterpenes, farnesenes exhibit a moderate reactivity toward ozone.

**Relative Atmospheric Residence Time.** We can use our measured rate constants along with assumed OH and O<sub>3</sub> atmospheric concentrations to calculate the atmospheric residence times of these BVOCs at a temperature of 277 K (Table 2). Assuming a global average OH concentration of  $10^6 \text{ cm}^{-3}$ , the atmospheric residence times of  $\beta$ -ocimene,  $\beta$ -myrcene, and  $\alpha$ - and  $\beta$ -farnesene due to the OH reaction are 0.79, 0.63, 1.3, and 0.97 h, respectively. Assuming an average O<sub>3</sub> concentration of 30 ppb, which is typical of a remote location,<sup>26</sup> the atmospheric residence times of these four BVOCs due to the O<sub>3</sub> reaction are 0.97–1.2 h. At an average O<sub>3</sub> concentration of 250 ppb, reflecting high urban conditions,<sup>26</sup> the atmospheric residence times of these four BVOCs with O<sub>3</sub> are 0.12–0.15 h. These calculations indicate that OH reactions predominate for  $\beta$ -ocimene and  $\beta$ -myrcene only when the ozone level is low. Farnesenes would be primarily removed by reactions with ozone, even at remote locations. By way of comparison, isoprene has an atmospheric residence time of 2.8 h due to reaction with OH, 3.2 h due to reactions with O<sub>3</sub> in an urban atmosphere, and 26 h due to O<sub>3</sub> reactions in a remote atmosphere.<sup>8</sup>

## Conclusions

The kinetics of the OH- and O<sub>3</sub>-initiated oxidation of  $\beta$ -ocimene,  $\beta$ -myrcene, and  $\alpha$ - and  $\beta$ -farnesene as a function of temperature were investigated using the relative rate technique with detection by online mass spectrometry. Arrhenius parameters were determined for each BVOC + OH and BVOC + O<sub>3</sub> reaction, and their rate constants at atmospherically relevant temperatures were obtained by the extrapolation of the Arrhenius expression. To date, no other Arrhenius parameters have been reported for these reactions. In addition, there are few experimental data available from the literature against which to compare with our results, even at room temperature. The acyclic monoterpenes,  $\beta$ -ocimene, and  $\beta$ -myrcene, showed similar reactivities with OH and with O<sub>3</sub> compared to the acyclic sesquiterpenes,  $\alpha$ - and  $\beta$ -farnesene, indicating that OH or O<sub>3</sub> addition is the initial step in the oxidative degradation of these compounds and that this reaction occurs at the double bonds with two methyl substituents. The rate constants for the reactions of  $\alpha$ - and  $\beta$ -farnesene with OH radicals are independent of temperature over the range of 313–423 K. For these four compounds, the atmospheric residence times due to OH reactions were calculated to be 0.6–1.3 h compared to about 1 h due to O<sub>3</sub> reactions at remote locations or about 0.1 h at urban locations. This indicates that removal rates of these compounds by OH or O<sub>3</sub> reactions are similar in relatively clean atmospheres but that O<sub>3</sub> reactions dominate in polluted atmospheres.

The results obtained in this study provide additional insights into the role of biogenic emissions in the chemistry of the atmosphere. Further work addressing the reactions of other terpenes with OH and O<sub>3</sub> will help us understand the principle factors that govern their reactivity in the atmosphere.

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**Supporting Information Available:** Tables for the measurements of rate constants for the gas-phase reactions of  $\beta$ -ocimene,  $\beta$ -myrcene, and  $\alpha$ - and  $\beta$ -farnesene with OH and O<sub>3</sub> as a function of temperature and figures of the mass spectra of four BVOCs. This material is available free of charge via the Internet at <http://pubs.acs.org>.

**Note Added after ASAP Publication.** This paper was published ASAP on December 17, 2010. A correction was made in the first paragraph of the Experimental Section. It has come to the authors' attention that the sample of  $\alpha$ -farnesene obtained from Sigma-Aldrich Inc. was a mixture of isomers even though the sample was labeled with the CAS Registry number for  $\alpha$ -farnesene (502-61-4) and labeled with a purity of 99%. The authors thank Ivan Kourtchev at University College Cork for pointing out this problem. The corrected paper was reposted on January 7, 2011.

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