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Temperature-dependent rate coefficients for the reactions of the hydroxyl radical with the atmospheric biogenics isoprene, alpha-pinene and delta-3-carene

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Abstract. Pulsed laser methods for OH generation and detection were used to study atmospheric degradation reactions for three important biogenic gases: OH + isoprene (Reaction R1), OH + α -pinene (Reaction R2) and OH + Δ -3-carene (Reaction R3). Gas-phase rate coefficients were characterized by non-Arrhenius kinetics for all three reactions. For (R1), k_1 (241–356 K) = $(1.93 \pm 0.08) \times 10^{-11} \exp\{(466 \pm 12)/T\} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was determined, with a room temperature value of k_1 (297 K) = $(9.3 \pm 0.4) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of bath-gas pressure (5–200 Torr) and composition (M = N₂ or air). Accuracy and precision were enhanced by online optical monitoring of isoprene, with absolute concentrations obtained via an absorption cross section, $\sigma_{\text{isoprene}} = (1.28 \pm 0.06) \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ at $\lambda = 184.95 \text{ nm}$, determined in this work. These results indicate that significant discrepancies between previous absolute and relative-rate determinations of k_1 result in part from σ values used to derive the isoprene concentration in high-precision absolute determinations.

Similar methods were used to determine rate coefficients (in $10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) for (R2)–(R3): k_2 (238–357 K) = $(1.83 \pm 0.04) \times \exp\{(330 \pm 6)/T\}$ and k_3 (235–357 K) = $(2.48 \pm 0.14) \times \exp\{(357 \pm 17)/T\}$. This is the first temperature-dependent dataset for (R3) and enables the calculation of reliable atmospheric lifetimes with respect to OH removal for e.g. boreal forest springtime conditions. Room temperature values of k_2 (296 K) = $(5.4 \pm 0.2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and k_3 (297 K) = $(8.1 \pm 0.3) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ were independent of bath-gas pressure (7–200 Torr, N₂ or air) and in good agree-

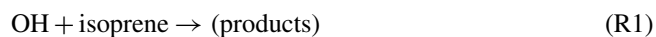
ment with previously reported values. In the course of this work, 184.95 nm absorption cross sections were determined: $\sigma = (1.54 \pm 0.08) \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ for α -pinene and $(2.40 \pm 0.12) \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ for Δ -3-carene.

1 Introduction

Large quantities and varieties of volatile organic compounds (VOC) are released into Earth's atmosphere from vegetation; such biogenic emissions exceed those of anthropogenic origin by a factor of ~ 10 (Goldstein and Galbally, 2007). Isoprene (2-methyl-1,3-butadiene, C₅H₈) contributes about 40 % (Guenther et al., 1995) of this gigaton (10¹⁵ g C) emission of biogenic VOC. The hydroxyl radical, OH, is the primary oxidant in the troposphere, initiating the degradation of most important VOC such as CH₄, isoprene and the monoterpenes (two isoprene units; molecular formula of C₁₀H₁₆). (Atkinson and Arey, 2003). VOC lifetimes are thus constrained by OH, and its abundance is an important test of model reliability.

Much attention was recently focussed on chemistry over tropical forests, as these ecosystems influence Earth's chemistry–climate system as the principal sink for the greenhouse gases CO₂ and CH₄ and source of isoprene and other VOC. Models have traditionally predicted low levels of OH over tropical forests due to its rapid reactions with VOC (notably isoprene; (R1)) and a lack of efficient OH regeneration

mechanisms.



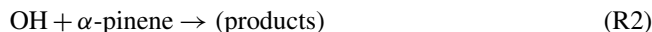
Contrary to these predictions, results from field campaigns have demonstrated that a high OH concentration is maintained (Butler et al., 2008; Lelieveld et al., 2008; Martinez et al., 2010; Stone et al., 2011), with the greatest discrepancies (factor of ≈ 3 to 10) between measured and modelled [OH] being observed where isoprene mixing ratios were large (Kubistin et al., 2010). The representation of photochemistry in models relies almost exclusively on lab-based measurements e.g. of absorption cross sections, quantum yields, rate coefficients and product yields. For (R1), the rate coefficients $k_1(T)$ reported in the literature are characterized by small but significant differences, notably at temperatures away from 298 K. Accordingly, in the work presented in this paper, absolute rate coefficients k_1 (241–356 K) were determined by highly accurate methods at realistic atmospheric temperature conditions.

The largest global contribution to atmospheric terpene emissions is from boreal forests covering Canada, northern Europe and Siberia, together encompassing one-third of Earth's forests. Emissions peak in summer due to strong correlations with temperature and photosynthetic activity. However, similar emission maxima have been observed in the autumn and in late winter/early spring when they are attributed to an increase in photorespiration rate (Back et al., 2005; Hakola et al., 2003). Throughout the year shorter bursts of terpene emission, associated with damage induced by e.g. animals (Heijari et al., 2011), pathogens, storms (Haase et al., 2011) and harvesting, may impact on the local OH budget (Noelscher et al., 2012). Elsewhere, monoterpenes have been detected from other vegetation, notably the forest floor (Hellen et al., 2006) and over active phytoplankton blooms in the Southern Ocean (Yassaa et al., 2008).

Oxidation of terpenes proceeds to a vast number of gas- and condensed-phase products, with consequent production of tropospheric ozone, peroxyacyl nitrates and secondary organic aerosol (Atkinson and Arey, 2003). The product distribution from any given monoterpene depends upon physical conditions of temperature, pressure and humidity, together with the identity of the primary oxidant. Reactions with OH, O₃ and perhaps Cl initiate terpene degradation by day, with NO₃ contributing at night (Ng et al., 2017). The relative importance of these reactions depends on both the availability of the oxidant and the size of the corresponding rate coefficient $k(T)$. These rate coefficients are often reasonably well-established at around ambient temperature, though the database is sparse for terpene reactions for low-temperature conditions ($T < 298$ K) most relevant to high northern latitudes.

Summertime observations in the Finnish boreal forest (Williams et al., 2011) demonstrate that more than half the total terpene concentration measured above the boreal forest

canopy was accounted for by two species: α -pinene (2,6,6-trimethylbicyclo-[3.1.1]hept-2-ene) and Δ -3-carene (3,7,7-trimethylbicyclo[4.1.0]hept-3-ene) (Hakola et al., 2012; Yassaa et al., 2008). Accordingly, this paper describes lab-based experiments to study (R2)–(R3) of OH with these two particularly important biogenic VOC:

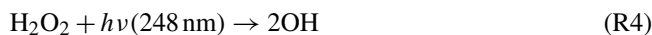


The techniques employed here allowed the first absolute kinetic studies of (R2 and R3) at the temperatures most representative of boreal forests, which can be as low as 253 K during late-autumn and early-spring months throughout which monoterpene emissions persist (Hakola et al., 2012).

2 Experimental

The technique of pulsed laser photolysis (PLP) radical generation coupled to pulsed laser-induced fluorescence (LIF) detection of OH has been used in several absolute kinetic studies of OH + VOC reactions from this laboratory. Details of the apparatus and methods were published previously (Dillon et al., 2012; Karunanandan et al., 2007), and therefore only a brief description is given here.

Experiments were conducted in a 500 cm³ quartz reactor. Cell temperature was controlled by circulating a cryogenic fluid through an outer jacket and monitored with a J-type thermocouple; pressure was monitored using capacitance manometers. Gas flow rates of up to 2000 cm³ min⁻¹ ensured that a fresh gas sample was available for photolysis at each laser pulse. Fluorescence from OH was detected by a photomultiplier tube screened by a 309 nm interference filter and a BG 26 glass cut-off filter. Excitation of the A²Σ($\nu = 1$) ← X²Π($\nu = 0$), Q₁₁(1) transition at 282 nm was achieved using the frequency-doubled emission from a Nd:YAG pumped dye laser. The detection limit at $P = 50$ mbar (air) was found to be $\approx 10^9$ molecule cm⁻³ for a $S/N = 1$ (20 scans). An exciplex laser operating at 248 nm (KrF) was used to initiate radical chemistry via photolysis of H₂O₂ (Reaction R4).



Typically a laser fluence of 12 mJ cm⁻² was used with [H₂O₂] = 1×10^{14} molecules cm⁻³ to generate [OH] $\approx 3 \times 10^{11}$ molecules cm⁻³. Data analysis (see Sect. 3) was considerably simplified by working under pseudo-first-order conditions of [H₂O₂] \gg [OH], even when the concentrations of the organic reactant were low, OH then reacting mainly with H₂O₂.



Time-dependent OH profiles were obtained by recording the LIF signal intensity as the delay time between the photolysis

and the probe lasers was stepped from 0 to a maximum of 15 ms. Accuracy and precision of the rate coefficients determined in this work was further enhanced by online monitoring of the terpenoids isoprene, α -pinene and Δ -3-carene by vacuum ultraviolet (VUV) absorption spectroscopy. In order to achieve this, absorption cross sections, σ , were determined experimentally by recording the attenuation of VUV light by static samples of each terpenoid. Two absorption cells were used with optical path length $l = 30.4$ cm (fitted with heated quartz windows) and $l = 1$ cm. Concentrations were determined by manometric methods, with absolute cell pressure measured to an accuracy of ± 0.01 Torr using a calibrated 10 Torr capacitance manometer. Samples were supplied either undiluted from the headspace above a liquid sample or from a glass storage bulb as a dilute mixture (≈ 1 part in 1000 N_2). These two supply methods had complementary advantages and disadvantages. Use of undiluted samples was more direct but had uncertainties due to the measurement of small sample pressures and the potential for VOC (present at high concentrations) to condense onto the windows of the 1 cm absorption cell (high surface area to volume ratio). These problems were minimized when using dilute VOC at higher pressure in the 30 cm cell (with relatively small surface area to volume ratio) but with the potential for errors associated with sample preparation and storage.

Collimated light from either a low-pressure Hg lamp ($\lambda = 184.95$ nm) or a D₂ lamp (180–260 nm) transmitted the sample and was focussed onto the entrance slit of a 0.5 m monochromator equipped with a grating (300 lines mm^{-1} blazed at 200 nm) and a diode array detector. The volume around the lamp, cell and monochromator was purged with N_2 to minimize absorption by O_2 , O_3 or H_2O . Spectra were recorded at an experimental resolution of 0.4 nm, estimated from full width at half maximum observed for either the $\lambda = 184.95$ nm or 253.65 nm Hg lines, as appropriate. Absorption cross sections were obtained via the Beer–Lambert Law (Eq. 1).

$$I = I_0 \times \exp\{-\sigma l[\text{terpenoid}]\} \quad (1)$$

where I and I_0 are respectively the transmitted and incident light intensity and l is the optical path length.

Online reagent monitoring in kinetic experiments was conducted downstream from the photolysis cell, using an absorption cell ($l = 43.8$ cm) equipped with a low-pressure Hg lamp and a 185 nm interference filter. This set-up was used to measure absolute reagent concentrations via VUV optical absorption at $\lambda = 184.95$ nm. Following the application of small corrections for measured 254 nm stray light intensity ($< 8\%$) and differences in T ($< 30\%$) and P ($< 1\%$) between the cells, [terpenoids] of the order of 10^{12} molecule cm^{-3} could be measured (see Sect. 3.1). A comparison of these optically derived concentrations to approximate manometric measurements was used to confirm that no significant fraction of any of the terpenoids was deposited at the walls in low-temperature experiments.

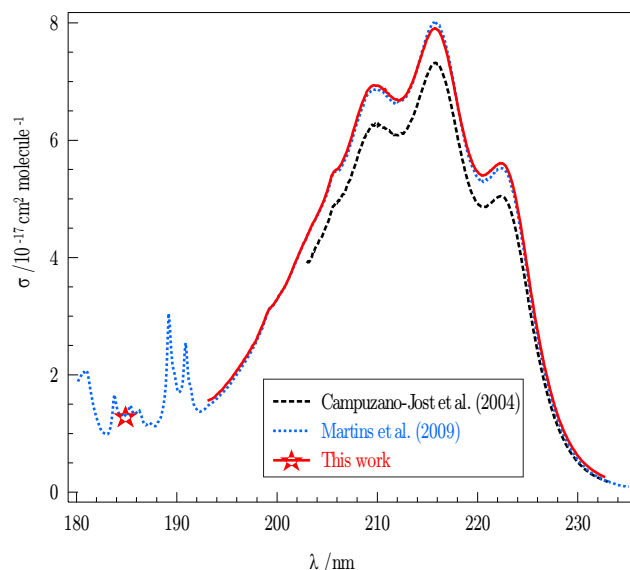


Figure 1. UV absorption spectra for isoprene from this work and from the literature. The red solid line represents data recorded at a resolution of ± 0.4 nm; the red star depicts $\sigma_{\text{isoprene}} = (1.28 \pm 0.02) \times 10^{-17}$ cm^2 molecule $^{-1}$ at 184.95 nm (see Fig. 2) subsequently used to derive absolute concentrations for kinetic experiments. Results from this work agree well with the more extensive, high-resolution dataset from Martins et al. (2009) represented here as a blue dotted line.

The chemicals isoprene (Aldrich 99 %, Sigma-Aldrich), α -pinene (Aldrich, 98 %) and Δ -3-carene (Aldrich, 99 %) were degassed by repeated freeze–pump–thaw cycles at 77 K and diluted in N_2 for storage and supply. H_2O_2 (Roth, 35 % by weight) was concentrated by pumping away water and introduced to the experiment via a bubbler. N_2 and O_2 (Messer 99.999 %) were used without further purification.

3 Results and discussion

Detailed below are determinations of absorption cross sections for the terpenoids isoprene, α -pinene and Δ -3-carene (σ , Sect. 3.1) and temperature-dependent rate coefficients for their reactions with OH: k_1 in Sect. 3.2 and k_2 and k_3 in Sect. 3.3. A discussion of possible systematic uncertainties and a comparison of the results from this work with the existing literature is presented in Sect. 3.4. All other uncertainties quoted throughout are precision only, representing two standard errors.

3.1 Absorption cross sections (σ) for isoprene, α -pinene and Δ -3-carene

Figure 1 displays (as the solid red line) the UV absorption spectrum of isoprene obtained in this work, together with results from two earlier studies. Cross sections were obtained at an experimental resolution of $\delta\lambda \approx 0.4$ nm (the full width

Table 1. UV absorption cross sections for isoprene from this work.

λ (nm) ^a	σ^b	λ (nm)	σ^b	λ (nm)	σ^b	λ (nm)	σ^b
184.95*	1.28	204	4.72	215	7.73	226	2.75
194	1.66	205	5.13	216	7.88	227	1.92
195	1.85	206	5.50	217	7.44	228	1.31
196	2.07	207	5.83	218	6.62	229	0.90
197	2.33	208	6.38	219	5.86	230	0.62
198	2.62	209	6.84	220	5.46	231	0.44
199	3.04	210	6.93	221	5.43	232	0.32
200	3.29	211	6.81	222	5.59	233	0.24
201	3.58	212	6.69	223	5.50	234	0.19
202	3.99	213	6.80	224	4.84		
203	4.36	214	7.23	225	3.78		

^a Data obtained at a resolution of $\Delta\lambda \approx 0.4$ nm, averaged and reported at 1 nm intervals except for * σ at 184.95 nm from high-resolution experiment (see Sect. 3.1 and Fig. 2). ^b σ in units of 10^{-17} cm² molecule⁻¹.

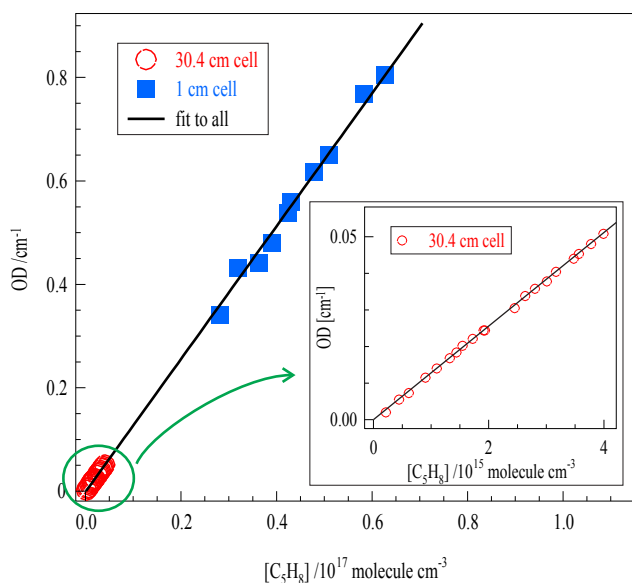


Figure 2. Beer-Lambert plot used to derive the cross section of isoprene at 184.95 nm. An unweighted proportional fit to all the data yields $\sigma_{\text{isoprene}} = (1.28 \pm 0.02) \times 10^{-17}$ cm² molecule⁻¹, represented by the solid black line on both the main plot and insert. This value (also displayed as the red star in Fig. 1) was subsequently used to calculate isoprene concentrations for kinetic experiments.

half maximum of the $\lambda = 253.65$ nm Hg line) in the range of 194–226 nm and are reported in Table 1 at 1 nm intervals. As is evident from Fig. 1, there is excellent agreement ($\leq 1\%$ difference) between the results from this work and the more extensive and higher-resolution ($\delta\lambda \approx 0.075$ nm) dataset from Martins et al. (2009) depicted by the blue dotted line. Campuzano-Jost et al. (2004) reported cross sections (black dashed line in Fig. 1) in the range of 203–233 nm that are on average about 10% smaller. The reasons for this discrepancy are unclear, though it seems unlikely to have resulted from problems with sample purity, which was $>99\%$ in all three studies when supplied. Differences in spectral resolution were also not a likely source of error, since the

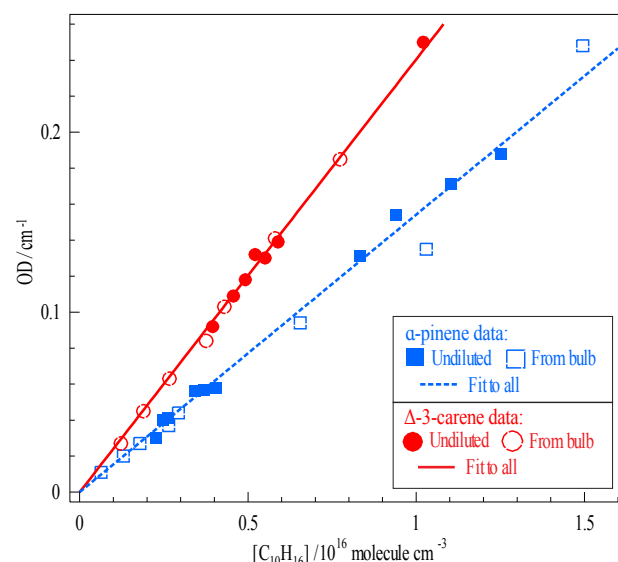


Figure 3. Beer-Lambert plots used to derive 184.95 nm absorption cross sections: $\sigma_{\alpha\text{-pinene}}$ (blue square data points) and $\sigma_{\Delta\text{-3-carene}}$ (red circles). Over a wide range of concentrations, good agreement was observed for data from both undiluted samples and from pre-prepared dilute bulbs (Sect. 2). Unweighted proportional fits with (Eq. 1) yield (in units of 10^{-17} cm² molecule⁻¹) $\sigma_{\alpha\text{-pinene}} = (1.54 \pm 0.05)$ and $\sigma_{\Delta\text{-3-carene}} = (2.40 \pm 0.03)$.

highest-resolution study from Campuzano-Jost et al. (2004) ($\delta\lambda \approx 0.05$ nm) reports the smallest differential cross sections.

Also displayed in Fig. 1, the red star depicts results from this work at $\lambda = 184.95$ nm that used a low-pressure Hg lamp as light source. Figure 2 displays the corresponding plot of $\ln(I_0/I)/l$ vs. [isoprene], which was used to obtain σ_{isoprene} via Eq. (1). Note the good agreement between data obtained across a wide range of concentrations and over different optical path lengths. A proportional fit to all the data yields a value of $\sigma_{\text{isoprene}} = (1.28 \pm 0.02) \times 10^{-17}$ cm² molecule⁻¹ at $\lambda = 184.95$ nm, the wavelength used to derive [isoprene] in subsequent experiments (Sect. 3.2). Evident from Fig. 1 is the good agreement between this discrete value (the red star) and the literature spectrum from Martins et al. (2009), who reported $\sigma_{\text{isoprene}} = 1.29 \times 10^{-17}$ cm² molecule⁻¹. Taking into account potential systematic errors from e.g. manometric measurements and sample purity we estimate an overall uncertainty of $\approx 5\%$, i.e. $\sigma_{\text{isoprene}} = (1.28 \pm 0.06) \times 10^{-17}$ cm² molecule⁻¹.

Figure 3 displays similar plots of $\ln(I_0/I)/l$ vs. [monoterpene] used to obtain (via Eq. 1) 184.95 nm absorption cross sections for α -pinene and Δ -3-carene. A proportional fit to the α -pinene data (blue squares) yields a gradient $\sigma_{\alpha\text{-pinene}} = (1.54 \pm 0.05) \times 10^{-17}$ cm² molecule⁻¹. Confidence in this result was enhanced by noting that over a wide range of concentrations, good agreement and proportionality were observed for data from both undiluted α -pinene samples and

those supplied dilute from a glass bulb (see Sect. 2). Taking into account potential systematic errors we estimate an overall uncertainty of $\approx 5\%$, i.e. $\sigma_{\alpha\text{-pinene}} = (1.54 \pm 0.08) \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ at 184.95 nm. This value is significantly larger than that listed in the UV spectrum (116–250 nm) of Kubala et al. (2009), who report a value of $1.28 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$. The reasons for this $\approx 15\%$ discrepancy are unclear. The Kubala spectrum does display some structure in the region of 175–190 nm, though these features are orders of magnitude coarser than the reported experimental resolution ($\delta\lambda = 0.075 \text{ nm}$) or the narrow-bandwidth ($\delta\lambda < 0.001 \text{ nm}$) Hg-line light source used in this work. In the present study, cross sections at $\lambda = 184.95 \text{ nm}$ were required to convert online optical measurements into absolute $[\alpha\text{-pinene}]$ for rate-coefficient determinations (see Sect. 3.2). As the light source used for $\alpha\text{-pinene}$ monitoring was also a narrow-bandwidth Hg lamp, it is appropriate to use the $\sigma_{\alpha\text{-pinene}}$ value determined in this work.

Similar procedures were followed and a similar quality of data obtained (red circles in Fig. 3) in the determination of $\sigma_{\Delta\text{-3-carene}} = (2.40 \pm 0.03) \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$. There appear to be no previously published values for this parameter. It is significantly larger than $\sigma_{\alpha\text{-pinene}}$ and similar to values reported for other terpenes, e.g. σ (in $10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$) = 2.3 for $\beta\text{-pinene}$ (Kubala et al., 2009) and 4.6 for limonene (Smialek et al., 2012). Assessment of potential systematic errors results in an overall uncertainty of $\approx 5\%$, i.e. $\sigma_{\Delta\text{-3-carene}} = (2.40 \pm 0.12) \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ at $\lambda = 184.95 \text{ nm}$.

3.2 Absolute determinations of k_1 (OH + isoprene)

PLP–LIF studies were carried under pseudo-first-order conditions of $[\text{isoprene}] \gg [\text{OH}]$, such that the OH time profiles, $S(t)$, were described by a simple exponential decay:

$$S(t) = S_0 \exp\{-Bt\} \quad (2)$$

The parameter S_0 describes (in arbitrary units) the LIF signal at $t = 0$ and is proportional to the initial $[\text{OH}]$ produced by the laser pulse (R4). The parameter B is the pseudo-first-order rate coefficient for OH decay (and includes components from both reactive and transport losses). Figure 4 displays typical OH decay profiles recorded in the presence of three different excess $[\text{isoprene}]$, whilst other conditions of $P = 100 \text{ mbar}$ (N_2), $T = 298 \text{ K}$ and $[\text{H}_2\text{O}_2] \approx 1 \times 10^{14} \text{ molecule cm}^{-3}$ were unchanged. The OH decays were exponential over at least 2 orders of magnitude and were fit with Eq. (2) to yield values of B with a high degree of precision (two standard errors were generally less than $\pm 2\%$). Systematic errors from unwanted radical chemistry were unlikely, since isoprene absorbs only weakly at the photolysis wavelength ($\sigma = 1.18 \times 10^{-19} \text{ cm}^2 \text{ molecule}^{-1}$ at 248 nm from Martins et al. 2009), whilst the use of low $[\text{OH}]$ ensured that losses of OH by reaction with itself or with products from (R1) or (R5) could be disregarded in this analysis.

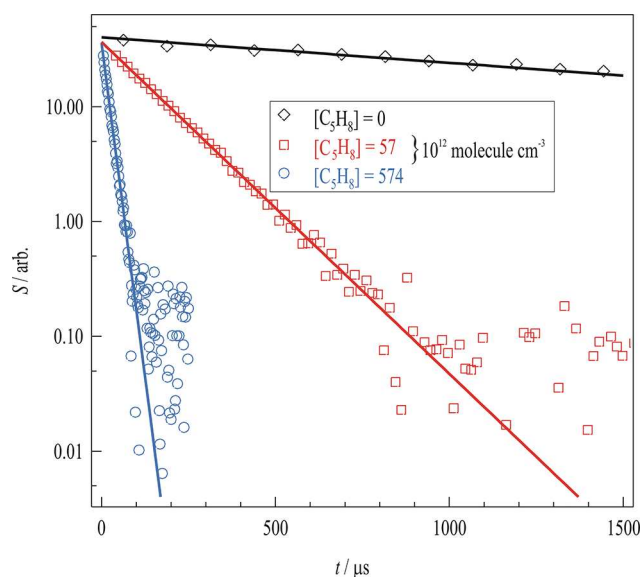


Figure 4. Time-resolved OH LIF signals, S , recorded in the presence of different $[\text{isoprene}]$ used to determine k_1 (298 K). Photolysis Reaction (R5) of $[\text{H}_2\text{O}_2] = 2.3 \times 10^{14} \text{ molecule cm}^{-3}$ was used to generate $[\text{OH}] \approx 5 \times 10^{11} \text{ molecule cm}^{-3}$ in $P = 103 \text{ Torr}$ (N_2). Unweighted fits with Eq. (2) yield first-order rate coefficients B for $[\text{isoprene}] = 0$ (black diamonds) $B = (513 \pm 12) \text{ s}^{-1}$ and $[\text{isoprene}] = 57 \times 10^{12} \text{ molecule cm}^{-3}$ (red squares) $B = (6654 \pm 44) \text{ s}^{-1}$; $[\text{isoprene}] = 574 \times 10^{12} \text{ molecule cm}^{-3}$ (blue circles) $B = (53473 \pm 700) \text{ s}^{-1}$.

Nonetheless, test experiments were conducted using an invariant $[\text{isoprene}] = 3.2 \times 10^{14} \text{ molecule cm}^{-3}$ whilst photolysis laser fluence, and thus radical concentrations, was varied by a factor of 15. No systematic influence was discerned ($< 1\%$ variation in B parameters) from such test experiments conducted both in N_2 and in air, reinforcing confidence in these results.

Figure 5 displays plots of B vs. $[\text{isoprene}]$ at three temperatures, which were fit (Eq. 3) to obtain the bimolecular rate coefficients $k_1(T)$.

$$B = k_1[\text{isoprene}] + k_{\text{loss}} \quad (3)$$

where k_1 is the bimolecular rate coefficient of interest. The term k_{loss} (s^{-1}) accounts for other losses of OH, here dominated by (R5) with the photolysis precursor H_2O_2 , with some small contribution from diffusion and flow out of the reaction zone.

The data display good linearity, with the slopes identified as $k_1(T)$ at three different temperatures and intercept values (around $B = 200 \text{ s}^{-1}$) in line with the predicted loss rate for reaction with H_2O_2 (R5). A mean of six values obtained at room temperature yields k_1 (297 K) = $(9.3 \pm 0.2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Within the experimental uncertainty, the measured rate coefficients were found to be independent of the bath-gas pressure ($3.8 < P / \text{Torr} < 165$) or identity (N_2 or air). Experimental conditions and results of

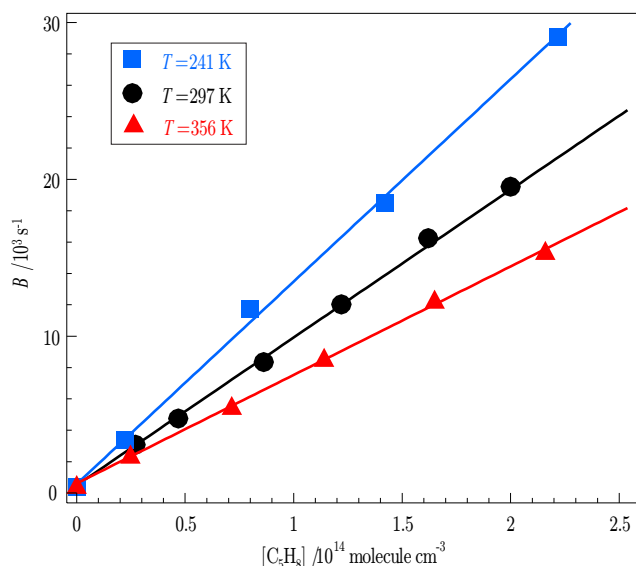


Figure 5. Plots of B parameters vs. associated [isoprene] used to determine k_1 at three different temperatures. Weighted linear fits (Eq. 3) to the data yield (in units of $10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$): k_1 (241 K) = (12.9 ± 0.2) from the blue square data points; k_1 (297 K) = (9.43 ± 0.14) from the black circles and k_1 (356 K) = (6.92 ± 0.13) from the red triangles. Note that error bars on individual data points are too small to be seen here (typically a few hundred on decay rates of several thousand per second).

all such determinations of k_1 are listed in Table 2. Note that the optical derivation of [isoprene] at 184.95 nm means that ratios of $k_1/\sigma_{\text{isoprene}}$ were actually determined and that any subsequent improvements in the database for isoprene cross sections may be used to update the kinetic results from this work. Taking into account potential systematic errors, principally from σ_{isoprene} , and a small (2 to 4 %) uncertainty in carrying out the optical measurements, we estimate a realistic overall error of $\pm 5\%$ or k_1 (297 K) = $(9.3 \pm 0.4) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

The data displayed in Fig. 5 further reveal the “negative” or non-Arrhenius temperature dependence for k_1 , with the largest slopes obtained in experiments conducted at the lowest temperatures (241 K). This trend for $k_1(T)$ is well-established in the literature; results from these previous studies, together the k_1 values from this work (listed in Table 2), are depicted in Fig. 6.

3.2.1 Comparison of k_1 with literature values

The kinetic database for (R1) displays some inconsistencies, with results for k_1 (298 K) from a recent absolute determination by Campuzano-Jost et al. (2004) some 15 % smaller than other values reported, mostly from relative-rate studies (Atkinson et al., 2006b). The ambient temperature results from this work lie in between these two extremes. Absolute determinations of k_1 were generally conducted at lower pres-

Table 2. Summary of rate coefficients k_1 , k_2 and k_3 determined in this work.

T/K	P/Torr^a	[terpene] ^b	n^c	$k/10^{-11} \text{ d}^d$
OH + isoprene \rightarrow (products) (R1)				
241	6.0	22–222	5	12.9 ± 0.2
241	6.1*	22–222	5	13.2 ± 0.3
268	6.7	21–187	6	11.3 ± 0.14
298	3.8	39–287	5	9.20 ± 0.06
297	7.5	27–200	6	9.43 ± 0.14
298	42.9	72–438	8	9.19 ± 0.05
298	71.0	29–223	7	9.12 ± 0.10
298	103	57–574	7	9.20 ± 0.05
298	103*	112–574	5	9.22 ± 0.09
296	165	19–168	7	9.1 ± 0.4
296	165*	19–168	7	9.2 ± 0.4
330	8.1	15–236	6	7.91 ± 0.12
356	9.0	25–216	6	6.92 ± 0.13
OH + α -pinene \rightarrow (products) (R2)				
238	6.0	7–90	7	7.33 ± 0.04
241	211	47–357	6	7.5 ± 0.2
246	96*	13–554	4	7.23 ± 0.10
246	97	131–554	4	6.94 ± 0.05
256	6.5	18–84	6	6.76 ± 0.07
274	7.0	8–30	5	6.12 ± 0.14
296	7.5	5–65	7	5.50 ± 0.08
296	96	43–464	5	5.38 ± 0.06
296	97*	43–464	5	5.25 ± 0.09
296	197	38–420	6	5.39 ± 0.04
323	7.2	19–157	7	5.44 ± 0.08
357	6.9	24–240	7	4.82 ± 0.05
OH + Δ -3-carene \rightarrow (products) (R3)				
235	7.5	4–43	6	11.9 ± 0.3
241	211	13–99	6	11.4 ± 0.3
271	96	44–530	5	9.11 ± 0.13
296	95	42–377	8	8.01 ± 0.13
296	95*	42–377	8	8.08 ± 0.13
298	7.4	8–63	7	8.10 ± 0.10
298	48	9–90	8	8.27 ± 0.08
298	205	34–262	9	8.1 ± 0.2
323	7.1	8–66	6	7.9 ± 0.2
357	6.9	10–99	7	6.92 ± 0.12

^a Bath-gas identity M is N_2 unless marked *, where M is air. ^b Units of [terpene] are $10^{12} \text{ molecules cm}^{-3}$, with values derived from optical measurements using 185 nm σ values determined in this work. ^c n = number of different [terpene] used in determination of k . ^d Units of k are $10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; uncertainties quoted are statistical only (two standard errors) derived from weighted linear fits (see Figs. 5 and 8).

sure than the majority of the relative-rate studies and could therefore yield values that underestimate k_1 (1 bar, 298 K) if the reaction was not at the high-pressure limit under all experimental conditions. However, results from this work revealed no systematic change in k_1 over the range pressure from 3.8 to 165 Torr, in good qualitative agreement with the

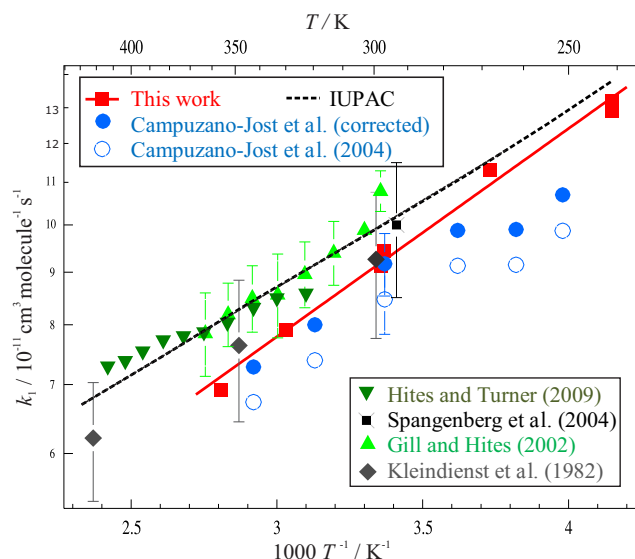


Figure 6. Values of $k_1(T)$ from this work and the literature. A fit of Eq. (4) to our data (red squares) yields $k_1(241\text{--}356\text{ K}) = (1.93 \pm 0.08) \times 10^{-11} \exp\{(466 \pm 12)/T\} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of bath-gas pressure and identity (N_2 or air). Also displayed are the data from Campuzano-Jost et al. (2004) presented as published (open blue circles) and subsequently corrected using isoprene absorption cross sections from Martins et al. (2009) (solid blue circles; see Sect. 3.2.1 for details). Note that error bars were included for all datasets but were commonly smaller than the data markers. The dashed black line represents the current IUPAC recommendation of $k_1(240\text{--}430\text{ K}) = 2.7 \times 10^{-11} \exp(390/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Not displayed for reasons of clarity are the $T < 220\text{ K}$ data points from Spangenberg et al. (2004), results from low-pressure studies of Park et al. (2004) or the many literature results at around $T = 298\text{ K}$ only (see IUPAC).

results from Campuzano-Jost et al. (2004) (50 to 600 Torr, N_2 or air). Results from two studies of $k_1(298\text{ K})$ conducted at lower pressures indicate that the high-pressure limit was close to 3 Torr (He) (Singh and Li, 2007) and 1 Torr (He) (Chuong and Stevens, 2000). In contrast, McGivern et al. (2000) and Park et al. (2004) observed fall-off behaviour for $k_1(298\text{ K})$ over the pressure range $0.5 < P(\text{Ar})/\text{Torr} < 20$, in line with their CVTST/RRKM calculations. Whilst no low-pressure studies of $k_1(P)$ using N_2 or air bath gas are available, the consensus would appear to be that the $k_1(298\text{ K})$ values reported in this work at up to $P = 165\text{ Torr}$ (N_2) and by (Campuzano-Jost et al., 2004) are close to the high-pressure limit, representative of $k_1(760\text{ Torr})$ and thus directly comparable to the relative-rate results in the literature.

The experimental methods used in this work were similar to those employed by Campuzano-Jost et al. (2004), who obtained $k_1(297\text{ K}) = (8.47 \pm 0.59) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, lower than most other determinations and at the lower limit of the range quoted in

the IUPAC (Task Group on Atmospheric Chemical Kinetic Data Evaluation) recommendation. Campuzano-Jost et al. (2004) used a cross section of $8.29 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ at 228.8 nm when determining [isoprene] from optical measurements. The extensive high-resolution dataset from Martins et al. (2009) provides cross sections at both 228.8 and at 184.95 nm (used in this work). If cross sections from Martins et al. (2009) are used to derive [isoprene] for the Campuzano-Jost et al. (2004) results, a value of $k_1(297\text{ K}) = (9.2 \pm 0.7) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ is obtained (see also the filled blue circle data points in Fig. 6), consistent with results from this work. A similar re-evaluation using cross sections from Martins et al. (2009) does not change the rate coefficients from our study.

Evaluation of all ambient temperature literature to date led IUPAC to recommend a room temperature rate coefficient of $k_1(298\text{ K}) = 1.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, slightly larger than the upper limit to our determination, though the two values overlap given that IUPAC quotes an uncertainty of $\Delta \log(k_1) = 0.06$ (i.e. in $10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$): $8.71 < k_1(298\text{ K}) < 10.15$. The results obtained in this work, together with the re-calculation of the results from Campuzano-Jost et al. (2004), could indicate that this evaluation is quoted with an overly conservative uncertainty.

The results from previous studies of $k_1(T)$ together with the IUPAC recommendation and the data from this work (red squares) are presented in Arrhenius format in Fig. 6. All temperature-dependent investigations characterized $k_1(T)$ with a non-Arrhenius temperature dependence, in qualitative agreement with results from this work. However, there are surprisingly few published studies of (R1) over a range of temperatures characteristic of the troposphere, with only Campuzano-Jost et al. (2004) and Park et al. (2004) reporting values of $k_1(T < 298\text{ K})$. As is evident from Fig. 6, the spread of $k_1(T < 298\text{ K})$ is large, around $\pm 30\%$ from the uncorrected values from Campuzano-Jost et al. (2004) to the results from Park et al. (2004) at $T = 279\text{ K}$. IUPAC have completed an extensive evaluation of this literature, together with $k_1(249\text{--}438\text{ K})$ results from Siese et al. (1994) and many published values at $T \approx 298\text{ K}$ (not displayed in Fig. 6 for reasons of clarity). The Arrhenius Eq. (4) was used to parameterize k_1 :

$$k_1(T) = A \exp \left\{ \frac{E}{RT} \right\} \quad (4)$$

with recommended parameters of $k_1(240\text{--}430\text{ K}) = 2.7 \times 10^{-11} \exp\{390/T\} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, with associated uncertainties of $\Delta \log k_1$ of ± 0.06 at 298 K and $\Delta \frac{E}{R}$ of $\pm 100\text{ K}$ to account for the scarcity and spread of $k_1(T)$ data. A weighted fit of Eq. (4) to the data from this work yields $k_1(241\text{--}356\text{ K}) = (1.93 \pm 0.08) \times 10^{-11} \exp\{(466 \pm 12)/T\} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, an adequate parameterization over this limited range of temperature. The good agreement between the experimental results obtained in this work, the corrected values from Campuzano-Jost et al. (2004)

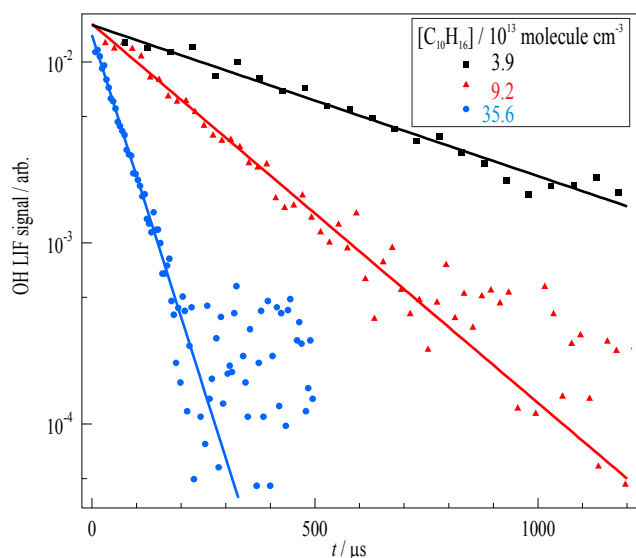


Figure 7. Plot of typical LIF profiles recorded for three α -pinene concentrations, used to determine k_2 (296 K). For all experiments photolysis (R4) at $t=0$ generated $[\text{OH}] \approx 5 \times 10^{11} \text{ molecule cm}^{-3}$ in $P = 97 \text{ Torr}$ (air). Unweighted fits with (Eq. 2) yield B parameters for $[\alpha\text{-pinene}] = 3.9 \times 10^{13} \text{ molecule cm}^{-3}$ (black squares), $B = (1921 \pm 90) \text{ s}^{-1}$; $[\alpha\text{-pinene}] = 9.2 \times 10^{13} \text{ molecule cm}^{-3}$ (red triangles), $B = (4819 \pm 213) \text{ s}^{-1}$ and $[\alpha\text{-pinene}] = 35.6 \times 10^{13} \text{ molecule cm}^{-3}$ (blue circles), $B = (17\,944 \pm 615) \text{ s}^{-1}$.

and the IUPAC recommendation would indicate that the recommended uncertainties could be reduced in any subsequent re-evaluation by IUPAC. Results from Spangenberg et al. (2004), with k_1 (58–300 K) reaching a maximum value of $\sim 3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at around $T = 120 \text{ K}$, demonstrate that large errors could result if the Arrhenius expressions presented here and by IUPAC were extrapolated beyond the temperature range stated.

3.3 Absolute determinations of k_2 and k_3

Figure 7 displays OH LIF profiles recorded in the presence of three different excess α -pinene concentrations, with conditions of $P = 97 \text{ Torr}$ (air), $T = 296 \text{ K}$ and $[\text{H}_2\text{O}_2] \approx 1 \times 10^{14} \text{ molecule cm}^{-3}$ otherwise unchanged. The OH decays were exponential over approximately 2 orders of magnitude and were therefore fit with Eq. (2) to yield B parameters with a high degree of precision ($\pm 5\%$ or less). As with the determinations of k_1 detailed above, systematic errors due to secondary chemistry were considered unlikely, since monoterpenes absorb only weakly at the photolysis wavelength (the 248 nm cross section is $< 1 \times 10^{-20} \text{ cm}^2 \text{ molecule}^{-1}$ (Kubala et al., 2009), resulting in photolysis of $< 1 \times 10^{11} \text{ molecule cm}^{-3}$) of α -pinene. Furthermore, use of small OH concentrations and hence low conversion of α -pinene ensured that perturbations to the LIF profiles by reaction of OH with itself or with the products of

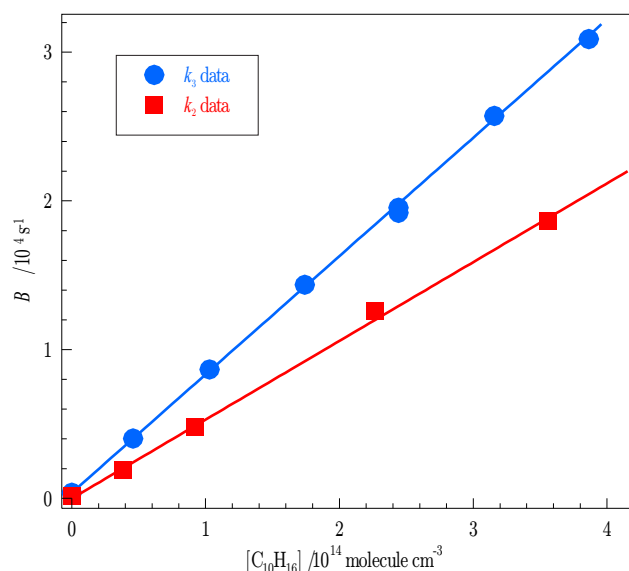


Figure 8. Plots of B parameters derived from Eq. (2) vs. associated $[\alpha\text{-pinene}]$ used to determine k_2 (OH + α -pinene) and k_3 (OH + Δ -3-carene) in conditions of $T = 296 \text{ K}$ and $P = 97 \text{ Torr}$ (air). Weighted linear fits yield (in units of $10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$): k_2 (296 K) = (5.3 ± 0.15) from the red squares and k_3 (296 K) = (8.1 ± 0.1) (blue circles). Note that 2σ statistical errors in B , used to weight these fits, were smaller than the symbols in this plot.

(R2) or (R5) could be disregarded in this analysis. All data for (R2) and (R3) recorded in this work were of similar or superior quality to that presented in Fig. 7, where the presence of the efficient fluorescence quencher O_2 and relatively large bath-gas pressures had a negative impact on LIF signal quality.

The red squares in Fig. 8 represent results from a series of experiments conducted at $P = 97 \text{ Torr}$ (air) and $T = 296 \text{ K}$. Values of B were plotted against $[\alpha\text{-pinene}]$ calculated from its optical extinction at 184.95 nm (see Sect. 2). A weighted linear fit (using statistical errors in B) yields a gradient of k_2 (296 K) = $(5.3 \pm 0.2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The experimental conditions used and results obtained for all determinations of k_2 are listed in Table 1. A mean of the four values obtained at around room temperature yields k_2 (296 K) = $(5.4 \pm 0.2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Within experimental uncertainty, these rate coefficients were independent of the bath-gas pressure ($7 < P/\text{Torr} < 197$) or identity (N_2 or air). This result is in reasonable agreement with a number of experimental and theoretical determinations of k_1 at around ambient temperature, summarized in Table 3.

Experiments conducted at various temperatures revealed a “negative” or non-Arrhenius temperature dependence for k_2 , with the largest values obtained in experiments conducted at the lowest temperatures. This trend for $k_2(T)$ is well-established by four literature datasets (Chuong and Stevens, 2000; Gill and Hites, 2002; Kleindienst et al., 1982; Montenegro et al., 2012) and is commonly observed for other rad-

Table 3. Comparison with literature determinations of k_2 and k_3 at around 298 K.

k^a	T/K	Reference	Techniques used ^b
Absolute determinations of k_2 (OH + α -pinene)			
5.4 ± 0.2^c	296	This work	PLP-LIF
6.09 ± 0.3	300	Davis and Stevens (2005)	DF-LIF
6.08 ± 0.4	300	Chuong et al. (2002)	DF-LIF
6.01 ± 0.82	298	Kleindienst et al. (1982)	FP-RF
Relative-rate determinations of k_2			
5.33 ± 0.79	298	Dash et al. (2014)	GC vs. propene
5.38 ± 0.3	298	Renbaurn-Wolff and Smith (2012)	MS vs. isoprene
5.55 ± 0.97	298	Montenegro et al. (2012)	DF-MS vs. isoprene
5.0 ± 1.1	298	Gill and Hites (2002)	MS vs. 1-butene, 2-methylpropene and trans-2-butene
5.35 ± 0.31	294 ± 1	Atkinson et al. (1986)	GC vs. 2,3-dimethyl-2-butene
5.8 ± 1.7^d	305	Winer et al. (1976)	GC vs. 2-methylpropene
Rate theory for k_2			
4.65	298	Dash et al. (2014)	CVTST
5.1	298	Vereecken et al. (2007)	Estimate using SAR
5.1	300	Fan et al. (2005)	CVTST
12	298	Grosjean and Williams (1992)	Estimate using SAR
Absolute determinations of k_3 (OH + Δ -3-carene)			
8.1 ± 0.3^c	297 ± 1	This work	PLP-LIF
Relative-rate determinations of k_3			
8.7 ± 0.4	294 ± 1	Atkinson et al. (1986)	GC vs. 2,3-dimethyl-2-butene
Rate theory for k_3			
0.506	298	Baptista et al. (2014)	QM calculations
8.51	298	Peeters et al. (2007)	Estimate using SAR
9.1	298	Grosjean and Williams (1992)	Estimate using SAR

^a Units of k_1 are 10^{-11} cm³ molecule⁻¹ s⁻¹. ^b Key to abbreviations: PLP is pulsed laser photolysis, LIF is laser-induced fluorescence, FP is conventional flash photolysis, RF is resonance fluorescence, DF is discharge flow, GC is gas chromatography, MS is mass spectrometry, CVTST is canonical variational transition state theory, and SAR is structure activity relationship.

^c Calculated using σ values from this work. Realistic uncertainty estimate is $\pm 8\%$ for k_1 and k_2 (includes systematic errors in σ and kinetic procedure; see Sect. 3.3). ^d Recalculated using latest k (298 K) = 5.1×10^{-11} cm³ molecule⁻¹ s⁻¹ from IUPAC (Ammann et al., 2016; Atkinson et al., 2006a) for reference reaction OH + isobutene.

ical additions to alkenes. Results from these previous studies, together with the k_2 values from this work (themselves listed in Table 2), are summarized in Table 3 and depicted in Fig. 9.

A similar methodology was followed to determine $k_3(T)$ for the reaction of OH + Δ -3-carene. LIF profiles (not shown) were of a similar quality to those depicted in Fig. 7 and were fit Eq. (2) to obtain B parameters. Optical signals were converted Eq. (1) to absolute [Δ -3-carene] using values of $l = 43.8$ cm and $\sigma_{\Delta\text{-3-carene}} = 2.4 \times 10^{-17}$ cm² molecule⁻¹ as determined in this work (Sect. 3.1). Figure 8 displays (blue circles) a plot of B vs. [Δ -3-carene] for a series of experiments conducted at $T = 296$ K and $P = 96$ Torr (air). The rate coefficient for (R3) is clearly larger than that determined for (R2) above; a weighted linear fit yields a gradient $k_3(296 \text{ K}) = (8.1 \pm 0.1) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹. Exper-

iments were repeated using different bath-gas pressures and in N₂ (see Table 2). No trends in k_3 were observed and a mean of these five results yields $k_3(297 \pm 1) = (8.1 \pm 0.2) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹. Results from all experiments, depicted as black circles in Fig. 9, demonstrate for the first time the non-Arrhenius temperature dependence for $k_3(T)$.

3.3.1 Comparison of k_2 and k_3 with literature values

Table 3 presents a comparison of the ambient temperature values of k_2 and k_3 determined in this work with the available literature. Regarding k_2 , there is excellent agreement between the results of this work and those obtained by the relative-rate technique (Atkinson et al., 1986; Gill and Hites, 2002; Montenegro et al., 2012; Winer et al.,

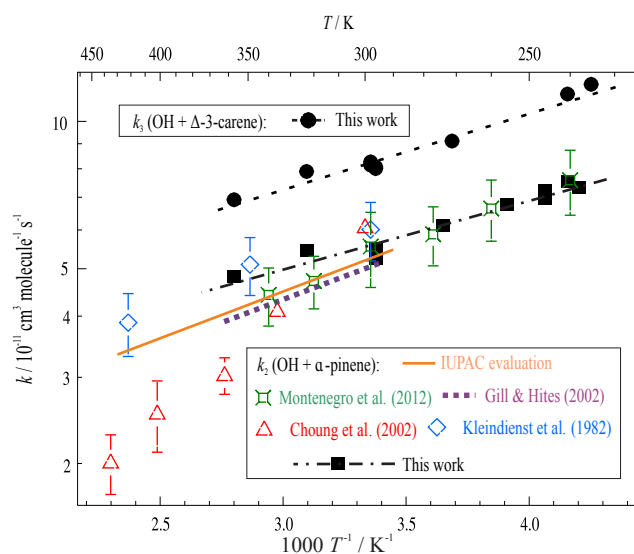


Figure 9. $k_2(T)$ and $k_3(T)$ from this work in Arrhenius format, together with previous experimental results and a $k_2(T)$ literature evaluation. Data from this work were fit with (Eq. 4) to yield k_2 (238–357 K) = $(1.83 \pm 0.04) \times \exp\{(330 \pm 6)/T\}$ (represented by the black dot-dashed line) and k_3 (235–357 K) = $(2.48 \pm 0.14) \times \exp\{(357 \pm 17)/T\}$ (the black dashed line). Not displayed for reasons of clarity are literature datasets containing only ambient temperature k_2 results (these are listed in full in Table 3) and the 44 determinations of k_2 (297–364 K) from Gill and Hites (2002), which are instead represented (purple dotted line) by a fit with (Eq. 4).

1976). The principal source of error in relative-rate determinations often derives from the choice of reference rate coefficient, required to convert an experimentally derived rate-coefficient ratio into an absolute rate coefficient. Confidence may be derived from the fact that five different reference reactions were used across the four published relative-rate (R2) studies. Absolute rate-coefficient determinations do not depend upon literature rates but do require an accurate knowledge of concentrations of the excess reagent (α -pinene or Δ -3-carene). The present dataset used in situ optical absorption spectroscopy to accurately measure $[\alpha\text{-pinene}]$ and subsequently calculate an absolute k_2 (296 K) = $(5.4 \pm 0.2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Any error in $\sigma_{\alpha\text{-pinene}}$ propagates directly into k_2 . Taking into account potential systematic errors, principally the 5% uncertainty in $\sigma_{\alpha\text{-pinene}}$ (Sect. 3.1), a similar uncertainty in carrying out the optical measurements and 2% for sample purity, a total uncertainty of around 8% was calculated, so we calculate k_2 (296 K) = $(5.4 \pm 0.5) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Within combined uncertainties there is reasonable agreement between this result and three previous absolute kinetic studies of (R2) (Chuong et al., 2002; Davis and Stevens, 2005; Kleindienst et al., 1982), all of which relied on manometric determinations of $[\alpha\text{-pinene}]$ to derive k_2 . The IUPAC data evaluation panel currently recommends a value of k_2

(298 K) = $5.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Ammann et al., 2016; Atkinson et al., 2006b), based on results from Atkinson et al. (1986), Gill and Hites (2002) and Kleindienst et al. (1982), with an associated $\Delta \log k_2 = 0.15$ or approximately +40, –30%. A re-evaluation taking into account the data from this work and from the recent (Montenegro et al., 2012) study yields (via a weighted mean) k_2 (298 K) = $5.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; a considerably smaller $\Delta \log(k_2)$ of 0.06 (around $\pm 15\%$) would encompass all experimentally determined ambient temperature k_2 values.

IUPAC (Ammann et al., 2016; Atkinson et al., 2006b) uses the Arrhenius Eq. (4) to parameterize $k_2(T)$. A weighted fit of Eq. (4) to the data from this work yields k_2 (238–357 K) = $(1.83 \pm 0.04) \times 10^{-11} \exp\{(330 \pm 6)/T\} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, represented by the black dot-dashed line in Fig. 9. Where data overlap (290 to 357 K), these $k_2(T)$ lie within the large uncertainty ($\Delta \log k_2 = 0.15$ at 298 K; $\Delta \frac{E}{R} = 200 \text{ K}$) reported by IUPAC for k_2 (290–430 K) = $1.2 \times 10^{-11} \exp\{440/T\} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Ammann et al., 2016; Atkinson et al., 2006b). Represented in Fig. 9 by the solid orange line, this recommendation was based on the results of Gill and Hites (2002) and Kleindienst et al. (1982) and is not in good agreement with the considerably smaller $k_2(T > 350 \text{ K})$ from Chuong et al. (2002). The reasons for this discrepancy are unclear. Chuong suggested that for their experimental conditions of $P = 5 \text{ Torr}$ (He), observed $k(T > 350 \text{ K})$ may not be high-pressure limited values. However, no evidence for such a pressure dependence in k_2 was observed in subsequent relative-rate determinations of $k_2(T = 340 \text{ K}, P = 1 - 5 \text{ Torr He})$ from Montenegro et al. (2012). This discrepancy is not resolved by any results from the present study, as the apparatus did not permit experiments at sufficiently low pressures. The results presented in Table 2 and elsewhere would indicate that the values of k_2 obtained here at $P > 7 \text{ Torr}$ and $T \approx 298 \text{ K}$ were in the high-pressure limit.

The current IUPAC recommendation (Ammann et al., 2016; Atkinson et al., 2006b) does not extend to important atmospheric temperatures lower than 290 K, as no data were available when the evaluation was made. However, there are now two complementary datasets available. The absolute values from this work (see Table 2) and results from the most recent literature dataset (Montenegro et al., 2012) derived by relative-rate methods are in excellent agreement for $T < 298 \text{ K}$ conditions. It is clear from Fig. 9 that these two datasets could provide a basis for IUPAC to extend the recommendation for k_2 to $T < 290 \text{ K}$.

A similar analysis was applied to k_3 , whereby potential systematic errors (5% each for σ_3 and the optical measurements, 1% for sample purity) were combined with the statistical uncertainties listed in Table 2 to yield an overall error estimate of around 8%; hence k_3 (298 K) = $(8.2 \pm 0.6) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The only previous determination of k_3 was from Atkinson et al. (1986), who used

the relative-rate method to obtain $k_3(294\text{ K}) = (8.7 \pm 0.4) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The good agreement between these two datasets, derived by very different experimental methods, is encouraging. It is clear from the data presented in Table 2 and displayed graphically in Fig. 9 that (R3) is characterized by negative or non-Arrhenius $k_3(T)$. A weighted Eq. (4) fit yields $k_3(235\text{--}357\text{ K}) = (2.48 \pm 0.14) \times \exp\{(357 \pm 17)/T\}$, depicted in Fig. 9 as the dashed black line. These results are the first reported for k_3 that were not obtained at room temperature. The non-Arrhenius behaviour observed is common for OH + monoterpene reactions that proceed predominantly by addition of OH to the unsaturated C=C groups, with a smaller contribution ($\sim 10\%$) from direct abstraction of allyl-stabilized hydrogens (Peeters et al., 2001; Vereecken et al., 2007). To a first approximation therefore, (R2) and (R3) should proceed at quite similar rates, as the main reactive site (a methyl substituted endocyclic C=C group) is common to α -pinene and Δ -3-carene. The data listed in Table 2 show that (R2) and (R3) are characterized by rate coefficients broadly consistent with this picture, i.e. non-Arrhenius $k(T)$ values approaching the collision limit of $10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Note that as discussed above, in the reaction conditions employed here, addition of OH to such large (C10) molecules need not be characterized by any discernable pressure dependence. It is somewhat surprising, however, that the results from this work and from Atkinson et al. (1986) clearly demonstrate that OH reacts some 50% faster with Δ -3-carene than with α -pinene. This is unlikely to be due to any enhancement in abstraction rates as Δ -3-carene has fewer allyl hydrogens available than does α -pinene. The observed change in reactivity is presumably due to influence on the C=C reactive site by the different location of the $(\text{CH}_3)_2\text{C}$ substituent in α -pinene and Δ -3-carene. Note that systematic attempts to parameterize k_2 via structure activity relationships have also failed at this level of detail (see e.g. the predicted k_2 and k_3 in Table 3 from Vereecken et al., 2007, and from Grosjean and Williams, 1992).

Finally, it should be reiterated that all k_2 and k_3 values reported in this work were determined via optically derived [monoterpene] and may more formally be considered as ratios such as $k_2(T)/\sigma_{\alpha\text{-pinene}}$ and $k_3(T)/\sigma_{\Delta\text{-3-carene}}$. Currently the database for 184.95 nm cross sections is sparse, consisting of only the results from this work and one other reported value for $\sigma_{\alpha\text{-pinene}}$ from Kubala et al. (2009). Any subsequent improvements in the database for 184.95 nm absorption cross sections for monoterpenes should be used to obtain up to date rate coefficients $k_2(T)$ and $k_3(T)$.

4 Atmospheric implications and conclusions

Breakdown of isoprene, initiated by reaction with the hydroxyl radical, is one of the most important oxidation reactions in the troposphere. The spectroscopic and kinetic results obtained in this work indicate that significant discrepan-

cies between previous absolute and relative determinations of k_1 were most likely the result of using erroneous absorption cross sections to derive [isoprene] in absolute studies. The value of $k_1(297\text{ K}) = (9.3 \pm 0.4) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ reported here is in satisfactory agreement with many previous determinations using different methods and confirms an atmospheric lifetime for isoprene of a few hours in typical rainforest conditions.

Absolute rate coefficients were determined for the gas-phase reactions of OH with two monoterpenes of atmospheric interest: α -pinene (R2) and Δ -3-carene (R3). At around ambient temperature, k_2 and k_3 were large and independent of bath-gas pressure (7–200 Torr) or composition (N_2 or air), indicating that these predominantly addition reactions are approaching their high-pressure limiting rate. The low-temperature rate coefficients derived in this work may be used to calculate atmospheric lifetimes for monoterpenes in realistic boreal forest conditions. Montenegro et al. (2012) used $T = 277\text{ K}$ and $[\text{OH}] = 8.1 \times 10^5 \text{ molecule cm}^{-3}$ to calculate $\tau_2 = \{k_2(T) \times [\text{OH}]\}^{-1} = 5.8\text{ h}$. The values of T and $[\text{OH}]$ used would appear appropriate for daytime boreal forest conditions during a springtime emission event (Back et al., 2005). When using the absolute value of $k_2(277\text{ K})$ from this work, the calculated value of $\tau_2 = 5.8\text{ h}$ is unchanged, a result that significantly enhances confidence in this parameter. We note that similar calculations (using mixing ratios of 30 ppb for O_3 and kinetic data from IUPAC) demonstrate that α -pinene is oxidized by O_3 at a very similar rate. The publication in this work of the first $k_3(T)$ allows the calculation of realistic atmospheric lifetimes for Δ -3-carene with respect to (R3). Using $[\text{OH}] = 8.1 \times 10^5 \text{ molecule cm}^{-3}$ and $k_3(277\text{ K}) = 9.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ from this work, $\tau_3 = 3.8\text{ h}$ was calculated. The corresponding calculation (again using 30 ppb of O_3 and kinetic data from IUPAC) results in a loss rate some 2.5 slower for Δ -3-carene with O_3 . These results demonstrate that the dominant daytime loss process for Δ -3-carene is reaction with OH (R3).

Data availability. The kinetic data are available in tables in the paper; requests to the authors for raw data would be considered on a case-by-case basis depending on proposed usage.

Author contributions. JNC and TJD designed all experiments and planned the overall project; KD conducted the spectroscopic experiments; TJD and CBMG conducted the kinetic experiments; TJD prepared the manuscript with contributions from all authors.

Competing interests. The authors declare that they have no conflict of interest.

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