Impact of pyruvic acid photolysis on acetaldehyde and peroxo radical formation in the boreal forest: theoretical calculations and model results

Philipp G. Eger\textsuperscript{1}, Luc Vereecken\textsuperscript{2}, Rolf Sander\textsuperscript{1}, Jan Schuladen\textsuperscript{1}, Nicolas Sobanski\textsuperscript{1}, Horst Fischer\textsuperscript{1}, Einar Karu\textsuperscript{1}, Jonathan Williams\textsuperscript{1}, Ville Vakkari\textsuperscript{3,4}, Tuukka Petäjä\textsuperscript{5}, Jos Lelieveld\textsuperscript{1}, Andrea Pozzer\textsuperscript{1}, and John N. Crowley\textsuperscript{1}

\textsuperscript{1}Atmospheric Chemistry Department, Max-Planck-Institute for Chemistry, 55128 Mainz, Germany  
\textsuperscript{2}Institute for Energy and Climate Research: IEK-8, Forschungszentrum Juelich, 52425 Juelich, Germany  
\textsuperscript{3}Atmospheric Composition Unit, Finnish Meteorological Institute, 00101 Helsinki, Finland  
\textsuperscript{4}Atmospheric Chemistry Research Group, Chemical Resource Beneficiation, North-West University, Potchefstroom, South Africa  
\textsuperscript{5}Institute for Atmospheric and Earth System Research (INAR)/Physics, Faculty of Science, University of Helsinki, Helsinki, Finland

Correspondence: John N. Crowley (john.crowley@mpic.de)

Received: 18 September 2020 – Discussion started: 20 October 2020  
Revised: 1 September 2021 – Accepted: 7 September 2021 – Published: 28 September 2021

Abstract. Based on the first measurements of gas-phase pyruvic acid (CH$_3$C(O)C(O)OH) in the boreal forest, we derive effective emission rates of pyruvic acid and compare them with monoterpene emission rates over the diel cycle. Using a data-constrained box model, we determine the impact of pyruvic acid photolysis on the formation of acetaldehyde (CH$_3$CHO) and the peroxy radicals CH$_3$C(O)O$_2$ and HO$_2$ during an autumn campaign in the boreal forest.

The results are dependent on the quantum yield ($\phi$) and mechanism of the photodissociation of pyruvic acid and the fate of a likely major product, methylhydroxy carbene (CH$_3$COH). With the box model, we investigate two different scenarios in which we follow the present IUPAC (IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, 2021) recommendations with $\phi = 0.2$ (at 1 bar of air), and the main photolysis products (60\%) are acetaldehyde + CO$_2$ with 35\% C–C bond fission to form HOCO and CH$_3$CO (scenario A). In the second scenario (B), the formation of vibrationally hot CH$_3$COH (and CO$_2$) represents the main dissociation pathway at longer wavelengths (75\%) with a $\sim 25\%$ contribution from C–C bond fission to form HOCO and CH$_3$CO (at shorter wavelengths). In scenario 2 we vary $\phi$ between 0.2 and 1 and, based on the results of our theoretical calculations, allow the thermalized CH$_3$COH to react with O$_2$ (forming peroxy radicals) and to undergo acid-catalyzed isomerization to CH$_3$CHO.

When constraining the pyruvic acid to measured mixing ratios and independent of the model scenario, we find that the photolysis of pyruvic acid is the dominant source of CH$_3$CHO with a contribution between $\sim 70\%$ and 90\% to the total production rate. We find that the photolysis of pyruvic acid is also a major source of the acetylperoxy radical, with contributions varying between $\sim 20\%$ and 60\% dependent on the choice of $\phi$ and the products formed. HO$_2$ production rates are also enhanced, mainly via the formation of CH$_3$O$_2$. The elevated production rates of CH$_3$C(O)O$_2$ and HO$_2$ and concentration of CH$_3$CHO result in significant increases in the modelled mixing ratios of CH$_3$C(O)OOH, CH$_3$OOH, HCHO, and H$_2$O$_2$.

1 Introduction

Organic acids play a crucial role in tropospheric chemistry, impacting secondary organic aerosol formation, air quality, and climate (Kanakidou et al., 2005; Hallquist et al., 2009). Pyruvic acid (CH$_3$C(O)C(O)OH), an organic acid that is central in plant metabolism as part of the Krebs cycle...
peracetic acid, and formaldehyde (HCHO). Products can have a significant impact on tropospheric chemistry, and the major ones are expected to be acetaldehyde, HO\textsubscript{2}, and CH\textsubscript{3}C(O)O\textsubscript{2} (more details are presented in Sect. 1.1). These products can have a significant impact on tropospheric chemistry, e.g. via the formation of peroxyacetyl nitrate (PAN), peracetic acid, and formaldehyde (HCHO).

Global models have recently revealed discrepancies between simulated and measured acetaldehyde concentrations (Millet et al., 2010; Wang et al., 2019; Wang et al., 2020). Wang et al. (2020) reported CH\textsubscript{3}CHO mixing ratios that were up to a factor of 10 higher than predicted by a global chemistry-transport model (EMAC) in the marine boundary layer around the Arabian Peninsula, implying missing sources of CH\textsubscript{3}CHO in remote and polluted regions. Wang et al. (2019) also found that models systematically underestimate CH\textsubscript{3}CHO compared to observations, implying a missing source of acetaldehyde in the remote troposphere. This finding was supported by the simultaneous measurement of peracetic acid (which is formed, for example, via the degradation of acetaldehyde in remote environments) with the organic aerosol source of CH\textsubscript{3}CHO also being insufficient to explain the results. Instead, Wang et al. (2019) suggested that CH\textsubscript{3}CHO arises from the degradation of gas-phase organic compounds. Pyruvic acid, among other organic acids in the gas and aerosol phase, might be one of the compounds that can be converted to acetaldehyde in the remote troposphere, and its integration into global models might contribute to resolve discrepancies, especially in forested regions.

Generally, field measurements as well as modelling and laboratory-based kinetic studies on pyruvic acid are limited, and its impact on atmospheric chemistry is still poorly understood. In this study we highlight the potential role of pyruvic acid in the boreal forest, one of the largest terrestrial biomes on Earth. For this, we use data from a measurement campaign in 2016 (IBAIRN, Influence of Biosphere–Atmosphere Interactions on the Reactive Nitrogen budget).

The photolysis of pyruvic acid: quantum yields and products

Because its reaction with OH is slow (k\textsubscript{OH+pyruvic acid} = 1.2 × 10\textsuperscript{−13} cm\textsuperscript{3} molecule\textsuperscript{−1} s\textsuperscript{−1} at 298 K; Mellouki and Mu, 2003), photolysis and dry deposition are the dominant loss terms for gas-phase pyruvic acid. Heterogeneous uptake to atmospheric aerosols is also calculated to be inefficient during the IBAIRN campaign in the boreal forest (see below), where particle surface area densities were of the order of 2 × 10\textsuperscript{−7} cm\textsuperscript{2} cm\textsuperscript{−3}, and the particles contained a large organic fraction (Liebmann et al., 2019) that is likely to reduce the uptake coefficient compared to that measured for pure aqueous particles (γ = 0.06; Eugene et al. 2018).

The photodissociation of pyruvic acid at actinic wavelengths is not well understood. According to the most recent IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation (2021) evaluation, which considers experimental data until 2017, the three thermodynamically accessible photolysis channels are
IUPAC recommends a photodissociation quantum yield (\(\phi\)) of 0.2 at 1 bar pressure (i.e., for boundary layer conditions), with branching ratios of 0.6, 0.05, and 0.35 for Reaction (R1), (R2), and (R3), respectively, which implicitly assumes that the initially formed carbene (CH\(_3\)COH) immediately isomerizes to acetaldehyde. The radical products of Reaction (R3) (CH\(_3\)CO and HOCO) react rapidly in air to form peroxy radicals (Reactions R4 and R5).

\[
\begin{align*}
\text{CH}_3\text{C}(\text{O})(\text{O})\text{OH} + hv &\rightarrow \text{CH}_3\text{CHO} + \text{CO}_2 \quad \text{(R1)} \\
&\rightarrow \text{CH}_3\text{C}(\text{O})\text{OH} + \text{CO} \quad \text{(R2)} \\
&\rightarrow \text{CH}_3\text{CO} + \text{HOCO}. \quad \text{(R3)} \\
\text{CH}_3\text{CO} + \text{O}_2 + M &\rightarrow \text{CH}_3\text{C}(\text{O})\text{O}_2 + M \quad \text{(R4)} \\
\text{HOCO} + \text{O}_2 &\rightarrow \text{HO}_2 + \text{CO}_2 \quad \text{(R5)} \\
\end{align*}
\]

The formation of methyldihyroxy carbene (CH\(_3\)COH) as an intermediate in pyruvic acid photolysis has been postulated for many years (Vesley and Leemakers, 1964; Yamamoto and Back, 1985). Schreiner et al. (2011) observed isomerization of singlet CH\(_3\)COH to acetaldehyde in an Ar matrix at 11 K, their high-level theoretical analysis revealed high barriers for isomerization, where H-atom tunnelling through the energy barrier led to a lifetime of about 1 h at 11 K, which favoured the formation of acetaldehyde over that of vinyl alcohol. Only very recently has CH\(_3\)COH been detected experimentally as a product of pyruvic acid photolysis in the gas-phase (Samanta et al., 2021) and its unimolecular isomerization to both CH\(_3\)CHO and CH\(_2\)=CHOH confirmed to be efficient at the experimental pressure of a few millibars (mbar) of helium. Indeed, Samanta et al. (2021) show that, at a photolysis wavelength of 351 nm (close to the maximum cross-section of pyruvic acid) formation of an energy-rich carbene (CH\(_3\)COH*) and CO\(_2\) (Reaction R6) is essentially the only product channel operating. CH\(_3\)CHO and CH\(_2\)=CHOH were formed subsequently (at \(\approx 2:1\) ratio favouring CH\(_3\)CHO) in the unimolecular isomerization of CH\(_3\)COH* (Reactions R7 and R8).

\[
\begin{align*}
\text{CH}_3\text{C}(\text{O})(\text{O})\text{OH} + hv &\rightarrow \text{CH}_3\text{COH}* + \text{CO}_2 \quad \text{(R6)} \\
\text{CH}_3\text{COH}* &\rightarrow \text{CH}_3\text{CHO} \quad \text{(R7)} \\
&\rightarrow \text{CH}_2=\text{CHOH} \quad \text{(R8)} \\
\end{align*}
\]

Samanta et al. (2021) suggest that, at ambient pressures, a significant fraction of the energized, nascent carbene will be deactivated by collisions with air (Reaction R9) and the thermalized carbene (CH\(_3\)COH), which can no longer rapidly overcome the barriers to isomerization, may react with oxygen or water vapour (Reed Harris et al., 2016, 2017b; Eger et al., 2020; Samanta et al., 2021) (Reactions R10 and R11).

\[
\begin{align*}
\text{CH}_3\text{COH} + M &\rightarrow \text{CH}_3\text{COH} + M \quad \text{(R9)} \\
\text{CH}_3\text{COH} + \text{O}_2 &\rightarrow \text{CH}_3\text{C}(\text{O}) + \text{HO}_2 \quad \text{(R10)} \\
\text{CH}_3\text{COH} + \text{H}_2\text{O} &\rightarrow \text{CH}_3\text{CH(\text{OH})}_2 \quad \text{(R11)} \\
\end{align*}
\]

As summarized by IUPAC, there have been many experimental studies deriving primary photodissociation quantum yields and product yields following the photolysis of pyruvic acid. The studies which were carried out at atmospherically relevant wavelengths (i.e., within the \(\approx 300–400\) nm absorption band) are listed in Table S1 in the Supplement. The experiments were carried out at different pressures of various bath gases and at different wavelengths and at different concentrations of pyruvic acid, all of which appear to play a role in determining the products formed. Table S1 shows that CO\(_2\) is formed at a yield of close to 100%, whereas the yield of CH\(_3\)CHO is highly variable. CH\(_2\)=CHOH has been detected both at a few torr of helium (Samanta et al., 2021) and at 1 bar of air (Calvert et al., 2011). Other end products observed during the photolysis of pyruvic acid in 1 bar of air include acetic acid (Calvert et al., 2011; Reed Harris et al., 2016, 2017b) and PAN (Grosjean, 1983; Berges and Warneck, 1992) when NO\(_2\) was present, which together provide evidence for the formation of the acetyl peroxy radical (CH\(_3\)C(O)O\(_2\)) and thus CH\(_3\)CO, for example, in Reactions (R3) and (R4) when sunlight or solar-simulating light sources are used. Secondary products (resulting, for example, from the further reactions of CH\(_3\)CHO) such as HCHO and CH\(_3\)OH have also been observed at pressures close to 1 bar (Grosjean, 1983; Calvert et al., 2011; Reed Harris et al., 2016; Reed Harris et al., 2017a). While the Norrish type 1 process (\(\text{C}=\text{O}\) bond fission) forming CH\(_3\)CO and HOCO appears to be unimportant at 351 nm (Samanta et al., 2021), it may be favoured at wavelengths \(< 340\) nm (Chang et al., 2014). This is illustrated in Fig. 1 where we present the wavelength-resolved photolysis rate constants across the UV absorption spectrum of pyruvic acid (assuming an overall photolysis quantum yield of 1, and absorption cross-sections recommended by IUPAC). The wavelength-resolved actinic flux was calculated for the IBAIRN measurement site on the 13 September 2016 using the Tropospheric Ultraviolet and Visible Radiation model (TUV; https://www.acom.ucar.edu/Models/TUV/Interactive_TUV/, last access: 1 September 2020). Integration of the \(J\) values at wavelengths \(< 340\) nm indicates that (at local noon) \(\approx 25\%\) of pyruvic acid dissociation occurs at these shorter wavelengths.

## 2 Methods

The goal of this study is to evaluate the impact of pyruvic acid on acetaldehyde and radical formation rates in the boreal forest using a data-constrained, chemical box model. For this purpose we make use of experimental data from a field study, which was performed in the Finnish boreal forest at
the Station for Measuring Ecosystem-Atmosphere Relations II (SMEAR II) in Hyytiälä (61.846° N, 24.295° E; 180 m above sea level; see Hari and Kulmala, 2005), an area that is characterized by large emission rates of biogenics (mainly monoterpenes) and low-NO\textsubscript{x} concentrations (Rinne et al., 2000; Williams et al., 2011; Aalto et al., 2015; Fischer et al., 2021).

The variability in the reported photodissociation quantum yield and product distributions (see discussion above) suggests that pyruvic acid photodissociation is not yet fully understood. In addition, the fate of the potentially dominant carbene product (Samanta et al., 2021) is unknown. Therefore, in order to better constrain the fate of CH\textsubscript{3}CHO in the atmosphere, quantum chemical calculations were undertaken to characterize its likely atmospheric reactions, for which experimental data do not exist.

2.1 The IBAIRN campaign

The IBAIRN campaign took place in September 2016, during the summer–autumn transition, and was characterized by frequent temperature inversions near ground level during nighttime (Liebmann et al., 2018a), which led to the accumulation of nocturnally emitted trace gases from vegetation. A detailed description of the campaign and the instruments deployed can be found elsewhere (Liebmann et al., 2018a; Eger et al., 2020). A summary (with details of detection limit, etc.) is provided in Table S2. Briefly, pyruvic acid was measured by a chemical ionization quadrupole mass spectrometer (Eger et al., 2020), the sum of monoterpenes (henceforth referred to as MT) was measured by a PTR-ToF-MS, and single MTs were monitored by a GC-AED (Liebmann et al., 2018a). Despite some discrepancies related to instrument location and inhomogeneity in terpene emissions within the forest, both instruments were in reasonably good agreement throughout the campaign. Since a high temporal resolution is preferable for our simulation, we have used the PTR-ToF-MS dataset. NO and NO\textsubscript{2} were measured by a chemiluminescence detector and a cavity ring-down spectrometer (Sobanski et al., 2016; Liebmann et al., 2018b), ozone was measured by optical absorption, and CO was measured by quantum-cascade-laser absorption spectroscopy (Eger et al., 2020). Formic and acetic acid as well as methyl ethyl ketone (MEK) and methyl vinyl ketone (MVK) were taken from the continuous PTR-MS measurements at the site at heights between 42 and 336 m. Photolysis rate coefficients were derived using actinic flux measurements from a spectral radiometer (METCON GmbH) (METCON GmbH) and evaluated cross sections and quantum yields (Burkholder et al., 2015). Mixing layer (MXL) heights were derived by combining in situ measurements made by a scanning Doppler lidar (Hellén et al., 2018) with results from the ECMWF ERA-Interim reanalysis (Dee et al., 2011), with a spatial resolution of ~80 km. Since the lidar was unable to resolve MXL heights < 60 m (as regularly experienced during nocturnal inversions), all values below this threshold have been set to 60 m, representing an upper limit.

2.2 Theoretical analysis of the fate of singlet methylhydroxy carbene, CH\textsubscript{3}COH

We investigated the reactions of CH\textsubscript{3}COH theoretically under atmospheric conditions, examining its unimolecular reactions and bimolecular reactions with O\textsubscript{2}, H\textsubscript{2}O, and HCO(O)OH, where the latter is representative of carbonyl acids. The reaction with pyruvic acid itself is also briefly explored. The rovibrational characteristics and energetics of all critical points on the potential energy surface were characterized at the CCSD(T)/aug-cc-pVTZ//M06-2X-D3/aug-cc-pVTZ level of theory with a wavenumber scaling factor of 0.971 (Zhao and Truhlar, 2008; Dunning, 1989; Purvis and Bartlett, 1982; Grimmel et al., 2011; Database of Frequency Scale Factors for Electronic Model Chemistries (Version 4); Alecu et al., 2010). This method compares favourably with the more rigorous focal point analysis of Schreiner et al. (2011), with energy differences in the singlet state unimolecular chemistry of less than 0.7 kcal mol\textsuperscript{-1}, indicating that the method is reliable for kinetic predictions under atmospheric temperatures. Where necessary, broken-symmetry SCF (self-consistent field) calculations were used to describe singlet biradicals (Noodleman, 1981), and IRC (intrinsic reaction coordinate) calculations were used to verify the pathways. For reactants, products, and transition states, we exhaustively characterized all conformers; for complexes we only characterized those directly connecting to a transition state. All quantum chemical calculations were performed using the Gaussian-16 program suite (Frisch et al., 2016).

The quantum chemical data were then used to calculate high-pressure rate coefficients for reactions over a saddle point using multi-conformer transition state theory (MC-TST) calculations (Vereecken and Peeters, 2003), under a rigid rotor harmonic oscillator approximation. Tunnelling corrections are performed assuming an asymmetric Eckart barrier (Eckart, 1930; Johnston and Heicklen, 1962). Most reactions have high energy barriers, and the presence of pre- and post-reaction complexes has a negligible influence on the reaction rate. For barrierless reactions, typically complexation reactions, we assume the reaction rate is close to the collision limit unless indicated otherwise.

2.3 Box model

We have used the CAABA/MECCA atmospheric chemistry box model to numerically simulate the impact of pyruvic acid photolysis on the formation of radicals and CH\textsubscript{3}CHO over the diel cycle during the IBAIRN campaign. Our study is based on model version 4.4.2, with updated reactions related to pyruvic acid in which two different scenarios were investigated (see Sect. 3.3) in order to examine the sensitivity of
the model output to, for example, photoysis quantum yields and products.

The chemical mechanism used in this study contains 600 gas-phase species and 2000 gas-phase reactions and photoysis steps. In addition to the basic ozone, HO3 and NO3 chemistry, the mechanism contains the detailed “Mainz Organic Mechanism” (MOM) for non-methane hydrocarbons (NMHC), isoprene, terpenes, and aromatics. MOM is derived from a reduced version of the Master Chemical Mechanism (MCM). Full details about CAABA/MECCA and MOM are available in Sander et al. (2019). Photoysis reactions are calculated for a latitude of 62° N. A complete reaction scheme and source of rate coefficients can be found in the data archive (see Data availability section).

Several parameters (temperature, pressure, relative humidity) and trace-gas concentrations (pyruvic acid, O3, NO, NO2, PAN, CO, MTs, formic and acetic acid, methyl ethyl ketone (MEK), and methyl vinyl ketone, MVK) as well as the photoysis rate constants of various trace gases were constrained to values measured during the IBAIRN campaign.

Based on the GC-AED measurements, the MTs were split into α-pinenes (49 %), β-pinene (13 %), Δ-carene (27 %), and camphene (8 %). Limonene is not included in the standard chemical mechanism of CAABA/MECCA, but as its contribution to the MTs during IBAIRN was only 3 % it was treated as Δ-carene (increasing the Δ-carene contribution to 30 %).

The atmospheric methane mixing ratio was set to a constant value of 1.8 ppmv. Non-methane alkanes, the degradation of which represents 30–45 % of the acetaldehyde source globally (Millet et al., 2010), were constrained to 1000 pptv of ethane, 250 pptv of propane, and 150 pptv of n-butane, as found in similar environments in Finland (Hakola et al., 2006; Hellén et al., 2015). The mixing ratio of PAN, which is generally the most abundant of the peroxy acetyl nitrates (PANs), was calculated from a measurement of the sum of peroxy nitrates, whereby [PAN] = 0.9 × Σ[PNs] (estimation based on observations by, for example, Shepson et al., 1992b; Roberts et al., 2004; Roiger et al., 2011). The model-generated, averaged OH concentration through the diel cycle was in good agreement (within 20 %) with that calculated from the correlation of ground-level OH measurements with UVB radiation intensity at the Hyvittälä site (with [OH] = 5.62 × 105 [UVB]0.62 molecules cm−3 when UVB is in units of W m−2; Petäjä et al., 2009; Hellén et al., 2015), but showed more variability resulting from changes in NO mixing ratios and the conversion of HO2 to OH.

3 Results and discussion

In the following, we analyse in situ measurements of pyruvic acid to derive emission rates, present the results of the theoretical calculations of the fate of CH3CHO, and discuss the box-model output for the IBAIRN campaign with a focus on pyruvic acid emission rates and its impact on acetaldehyde and radical chemistry in the boundary layer of the boreal forest.

3.1 Pyruvic acid emission rate relative to monoterpenes during IBAIRN

In order to derive the pyruvic acid emission rate (Epyr) during IBAIRN, we assume that only photoysis and dry deposition contribute significantly to its overall loss rate and that pyruvic acid is in steady state. The latter assumption is reasonable as its mean lifetime was (2 ± 0.5) h. Due to a homogeneous fetch at the measurement site, we can neglect transport processes, and Epyr is defined by Eq. (1), where [pyr]ss is the measured mixing ratio, Jpyr is the photoysis rate constant of pyruvic acid, kdep is the first-order loss rate constant for its dry deposition, and hMXL is the well-mixed boundary layer height.

\[
E_{pyr} = [pyr]_{ss}(J_{pyr} + k_{dep})h_{MXL}
\] (1)

Epyr is effectively an emission rate normalized to the MXL height (hMXL). As the photoysis is a substantial fraction of the overall losses of CH3C(O)C(O)OH, the choice of quantum yield \( \phi \) directly impacts the calculated emission rate.

The deposition rate of pyruvic acid was calculated from

\[
k_{dep} = \frac{v_{dep} \cdot h_{MXL}}{1 + \frac{v_{dep}}{v_{max}}} \]

for the day and a maximum of

\[
k_{dep} = \frac{v_{dep} \cdot h_{MXL}}{1 + \frac{v_{dep}}{v_{max}}} \]

for the night (Shepson et al., 1992a), with the transition following the diel variation in the mixing layer height hMXL (see Fig. S1 in the Supplement). Further, as pyruvic acid and H2O2 have similar solubilities, we assumed that their deposition velocities are equal, so that vdep = 8.4 cm s−1 during the day and vdep = 0.8 cm s−1 during the night, as derived by Crowley et al. (2018) for the same site. This resulted in a minimum dry-deposition loss rate constant of

\[
k_{dep} = 0.9 \times 10^{-4} \text{s}^{-1} \]

during the day and a maximum of

\[
k_{dep} = 1.8 \times 10^{-4} \text{s}^{-1} \]

during the night.

The same calculation is performed for the MTs (Epyr) over the same period (and thus for the same MXL height). We note that hMXL controls not only the value of kdep, but also directly affects the mixing ratios of both MTs and pyruvic acid for a given emission rate. The relative emission rate \((E_{pyr}/E_{MT})\) can be calculated from Eq. (2), where terms in square brackets are concentrations.

\[
\frac{E_{pyr}}{E_{MT}} = \frac{[pyr]_{ss}(J_{pyr} + k_{dep})}{[MT]_{ss}(k_{OH}[OH] + k_{NO3}[NO_3] + k_{O_3}[O_3])}
\] (2)

In the denominator, kOH, kNO3, and kO3 are rate coefficients for reaction of MTs with OH, NO3, and O3, respectively. As we do not have GC data at high time resolution, an effective rate coefficient for loss of the monoterpenes was derived from the mean MT composition as measured by GC-AED (49 % α-pinene, 13 % β-pinene, 27 % carene (sum of 2-carene and 3-carene), 3 % d-limonene, and 8 % camphene) and the corresponding rate coefficients (Perring et al., 2013;
which are presented in Fig. 2. A plot showing the variability of the MT and pyruvic acid mixing ratios over the same period was previously reported (see Fig. 3 of Eger et al., 2020).

During September, the emission rate of pyruvic acid ($E_{\text{pyr}}$) reaches its maximum a few hours after solar noon when the temperature peaks, similar to $E_{\text{MT}}$. However, the amplitude of the day-to-night difference in $E_{\text{pyr}}$ is a factor of $\sim 3$ smaller than observed for $E_{\text{MT}}$. This could indicate that pyruvic acid emissions are less temperature-dependent than MT emissions (see below) and that other environmental factors may additionally play a role at this time of year.

The emission rates of the MTs derived as described above show a large day–night variation with values a factor of $\sim 20$ larger around noontime compared to midnight. This is significantly larger than the expected variation (factor of 2–3) based on the average noon-to-midnight temperature difference of 10 K and the parameterization of Guenther et al. (1993), whereby $E_{\text{MT}} \propto \exp(\beta(T - 297 K))$ with $\beta = 0.1 K^{-1}$ (which is in line with the empirical value of $\beta = 0.12 K^{-1}$ that was derived for this site in September by Hellén et al., 2018). One potential reason for this discrepancy may be emissions in autumn from fresh leaf litter that significantly contribute to the observed mixing ratios (Hellén et al., 2018) although the assumption of evenly distributed sources and a well-mixed boundary layer is not necessarily valid during the night, especially during strong temperature inversions.

Figure S3 shows that the daytime emission of pyruvic acid relative to MT ($E_{\text{pyr}}/E_{\text{MT}}$) varies by a factor of $\sim 2$, depending on the chosen scenario, whereas the nighttime emission ratio is only dependent on the deposition velocity of pyruvic acid. For further analysis we adopt a quantum yield of 0.2, as presently preferred by IUPAC. On average, ($E_{\text{pyr}}/E_{\text{MT}}$) $\sim 0.6$, with a minimum value of $\sim 0.3$ in the evening and a maximum value of $\sim 1$ in the early morning, indicating elevated pyruvic acid emissions relative to MT at night. To derive a $T$-dependent expression from the diurnal profile of the emission factor, we fit an exponential function to the plot of temperature versus $E_{\text{pyr}}/E_{\text{MT}}$ (Fig. S4), yielding

$$E_{\text{pyr}} = 0.28 + 3.17 \cdot \exp \left( \frac{273 - T}{4.24} \right) \cdot E_{\text{MT}}.$$  

We note that (like the values of $E_{\text{pyr}}$) the temperature dependence derived is strongly influenced by the diel variation of the MXL height and thus carries significant uncertainty and may not be transferable to other locations or even times of the year.

As our measurements of pyruvic acid are the first to have been made in the boreal forest, we cannot compare our relative emission ratio ($E_{\text{pyr}}/E_{\text{MT}}$) with previous measurements in a similar environment. Instead, where possible, we derive the emission ratio from measurements of MTs, isoprene, and pyruvic acid in warmer climates.

Jardine et al. (2010b) performed measurements in an enclosed (glass dome) tropical forest biome at Biosphere 2 in

![Figure 2. Diel variation of the (MXL height-corrected) emission rates of pyruvic acid ($E_{\text{pyr}}$, scenario B) and monoterpenes ($E_{\text{MT}}$) along with $J_{\text{pyr}}$ (yellow shaded), $T$, and $h_{\text{MXL}}$ for the IBAIRN campaign.](image-url)
Table 1. Emission rate of pyruvic acid ($E_{pyr}$) relative to isoprene ($E_{iso}$) and MT ($E_{MT}$).

| Reference          | Location                 | Plant species          | ($E_{pyr}/E_{iso}$) | ($E_{pyr}/E_{MT}$) |
|--------------------|---------------------------|------------------------|---------------------|--------------------|
| This study         | Hyytiälä, Finland         | Boreal forest          | ~20                 | 0.62               |
| Talbot et al. (1990)| Manaus, Brazil            | Tropical forest        | 0.003               | –                  |
| Jardine et al. (2010b) | Biosphere 2, Arizona, US | Tropical biome         | 0.17                | 4                  |
| Jardine et al. (2010b) | Biosphere 2, Arizona, US | Mango tree             | 0.05                | 1.7                |
| Jardine et al. (2010a) | Biosphere 2, Arizona, US | Creosote bush          | 0.05                | 0.07               |

Arizona, US, where they found maximum mixing ratios of 120 ppbv isoprene, 6 ppbv MTs, and 15 ppbv pyruvic acid. As the glass dome absorbed actinic wavelengths and prevented active photochemistry, the chemical loss processes for pyruvic acid, isoprene, and MT (including photolysis and reactions with OH, O$_3$, and NO$_3$) are negligible. Initially disregarding the deposition of isoprene and MT, we derive lower limits of ($E_{pyr}/E_{iso}$) ~ 0.17 and ($E_{pyr}/E_{MT}$) ~ 4 (see Table 1). However, due to the presence of large concentrations of isoprene-consuming microbes in the soil of Biosphere 2, the isoprene loss rate via deposition may be enhanced, which will decrease the effective emission ratio ($E_{pyr}/E_{iso}$). In addition, branch enclosure studies were performed on a Mangifera indica (mango) tree within Biosphere 2, yielding mean fluxes (in nmol m$^{-2}$ s$^{-1}$) of 3.2 for isoprene, 0.09 for MT, and 0.15 for pyruvic acid. Pyruvic acid emissions peaked during the day when temperature and photosynthetically active radiation (PAR) were highest and correlated very well with isoprene emissions and (to a certain extent) with MT emissions. Assuming that a mango tree is representative of the tropical vegetation, we derive an emission ratio of ($E_{pyr}/E_{iso}$) ~ 0.05 and ($E_{pyr}/E_{MT}$) ~ 1.7 (see Table 1), which is consistent with our estimations for the IBAIRN campaign. However, given that Talbot et al. (1990) observed great variability in pyruvic acid emission fluxes among five different tree species during measurements in the tropical Ducke Forest Reserve close to Manaus, Brazil, this agreement may, to some extent, be coincidental. Talbot et al. (1990) also reported a mean emission flux (derived from enclosure experiments) relative to isoprene of ($E_{pyr}/E_{iso}$) ~ 0.003, which is about 1 order of magnitude smaller than in the study of Jardine et al. (2010b). In a further branch enclosure study by Jardine et al. (2010a) emissions from a creosote bush (Larrea divaricata), which is typically found in US drylands, were investigated. Average noontime branch emission rates (in µg C gdw$^{-1}$ h$^{-1}$) of 7.5, 10.4, and 0.2 for isoprene, MT, and pyruvic acid resulted in relative emission ratios of ($E_{pyr}/E_{iso}$) ~ 0.05 and ($E_{pyr}/E_{MT}$) ~ 0.07 for this mixed isoprene–MT-emitting species.

The comparison with the few datasets available in the literature indicates that the variability of the emission factors ($E_{pyr}/E_{MT}$) and ($E_{pyr}/E_{iso}$) among different plant species and different environments is large. In addition, a lack of pyruvic acid measurements over different seasons in the boreal forest means that we cannot exclude that the value we derive is biased by emissions (e.g. from ground-level, decaying plant litter in September) that are particular to this season and environment. The emission rates we derive are therefore relevant for the autumnal boreal forest but require validation before being extended to other regions and seasons with confidence.

3.2 Theoretical calculations on the fate of CH$_3$COH

Singlet methylhydroxy carbene, CH$_3$COH, is best characterized as having an sp$^2$-hybridized central carbon, bearing an in-plane lone pair in an sp$^2$ orbital and an empty p orbital perpendicular to the CCO plane. The lone pairs of the hydroxy O atom back-donate into the empty p orbital, such that the most favourable geometry has the hydroxy–H atom in the CCO plane. The orientation of the terminal OH group has a large impact on the energy, with 3 kcal mol$^{-1}$ energy difference between the syn- and anti-conformers. Due to the interaction between the hydroxy O atom and the carbene functionality, internal rotation of the OH group has a very high barrier, 24 kcal mol$^{-1}$. Concomitantly, syn/anti-interconversion is very slow, with predicted rate coefficients at 300 K of less than 10$^{-2}$ s$^{-1}$. Under atmospheric conditions, thermalized syn- and anti-CH$_3$COH are thus best considered as separate species, with possibly distinct chemistry. No information is available on the relative yield of these conformers from pyruvic acid photolysis.

3.2.1 Unimolecular reactions of CH$_3$COH

Both syn- and anti-CH$_3$COH can isomerize to vinyl alcohol over high barriers ≥ 24 kcal mol$^{-1}$ (see Fig. 3). Anti-CH$_3$COH has an additional pathway for isomerization to acetaldehyde, with a barrier of 23 kcal mol$^{-1}$. Due to these high barriers, the thermal rate of isomerization is comparatively slow, with a 300 K rate coefficient of $\leq 4 \times 10^{-4}$ s$^{-1}$ (see Table 2). As already discussed by Schreiner et al. (2011), formation of CH$_2$CHO from anti-CH$_3$COH is most favourable at low temperatures, owing to a thinner energy barrier and hence faster tunnelling. At temperatures above 260 K, we find that formation of CH$_2$=CHOH from anti-CH$_3$COH becomes dominant, with a $\sim 3.5 : 1$ ratio of CH$_2$=CHOH to CH$_3$CHO at room temperature.
Table 2. Theory-predicted high-pressure rate coefficients for reaction of singlet CH$_3$COH.

| Reactants                  | Products                          | $k$(298 K)      | $A$               | $n$  | $E_a$ |
|----------------------------|-----------------------------------|----------------|--------------------|------|-------|
| syn-CH$_3$COH + O$_2$      | CH$_3$C(OH)O$_2^*$                | $2.2 \times 10^{-20}$ | $5.74 \times 10^{-22}$ | 3.05 | 4092  |
| anti-CH$_3$COH + O$_2$     | CH$_3$C(OH)OO$^*$                 | $6.6 \times 10^{-21}$ | $1.71 \times 10^{-22}$ | 2.97 | 3960  |
| syn-CH$_3$COH + H$_2$O     | CH$_3$CH(OH)$_2$                  | $1.9 \times 10^{-20}$ | $1.57 \times 10^{-55}$ | 13.56 | -1049 |
| anti-CH$_3$COH + H$_2$O    | CH$_3$CH(OH)$_2$                  | $5.7 \times 10^{-21}$ | $1.09 \times 10^{-61}$ | 15.61 | -1443 |
| syn-CH$_3$COH              | anti-CH$_3$COH                    | $8.9 \times 10^{-3}$  | $7.86 \times 10^{-20}$ | 10.77 | 6598  |
|                            | CH$_3$=CHOH                       | $1.9 \times 10^{-4}$  | $3.62 \times 10^{-91}$ | 34.20 | -1444 |
| anti-CH$_3$COH             | syn-CH$_3$COH                     | $2.8 \times 10^{-5}$  | $6.55 \times 10^{-20}$ | 10.71 | 8137  |
|                            | CH$_3$=CHOH                       | $9.2 \times 10^{-5}$  | $2.02 \times 10^{-14}$ | 40.40 | -6660 |
|                            | CH$_3$C(=O)H                     | $3.4 \times 10^{-4}$  | $1.26 \times 10^{-81}$ | 30.96 | -563  |
| CH$_3$=CHOH + HC$_3$OOH    | CH$_3$C(=O)H + HC$_3$OOH         | $2.9 \times 10^{-18}$ | $1.82 \times 10^{-76}$ | 19.88 | -6192 |
| CH$_3$C(=O)H + HC$_3$OOH   | CH$_3$=CHOH + HC$_3$OOH           | $8.1 \times 10^{-27}$ | $1.09 \times 10^{-78}$ | 20.59 | -633  |

Calculations were performed at the CCSD(T)/M06-2X-D3 with MC-TST level of theory. Rate coefficients are given at 298 K (s$^{-1}$ or cm$^3$ molecule$^{-1}$ s$^{-1}$). Temperature-dependent rate coefficients can be calculated using the parameters of a Kooij expression $k(200-450 \text{K}) = A \times (T/K)^n \times \exp(-E_a/T)$ with $A$ given per second (s$^{-1}$) or cubic centimetres per molecule per second (cm$^3$ molecule$^{-1}$ s$^{-1}$) and $E_a$ in kelvin (K).

Figure 3. Zero point energy (ZPE)-corrected potential energy surface for unimolecular reactions of singlet CH$_3$COH at the CCSD(T)/M06-2X-D3 level of theory.

Given the low predicted thermal rate coefficients, it seems unlikely that the experimentally observed acetaldehyde and vinyl alcohol in pyruvic acid photolysis are formed from isomerization of thermalized CH$_3$COH. The energy distribution of energized, nascent carbenes would be rather broad as the available energy upon pyruvic acid photodissociation is distributed over all fragments and their relative motion, and the isomerization yield would then be pressure-dependent. The CH$_3$CHO and CH$_2$=CHOH isomers formed would have enough energy to undergo keto-enol tautomerization, but given the high barrier exceeding 55 kcal mol$^{-1}$, it is more probable they will instead be stabilized by collisional energy loss.

3.2.2 Reaction of CH$_3$COH with O$_2$

Under atmospheric conditions, the reaction with O$_2$ is potentially an important loss process for CH$_3$COH (Reed Harris et al., 2016, 2017a; Eger et al., 2020). The potential energy surface is shown in Fig. 4. Contrary to radicals, which react with O$_2$ by (near-)barrierless radical recombination, the singlet CH$_3$COH carbene does not have an unpaired electron and the reaction proceeds mostly by association of its out-of-plane empty p orbital with a lone electron pair in O$_2$, re-
quiring orbital rearrangement to a triplet C’O’O’ moiety with a sp³-hybridized central carbon. This unfavourable process has high barriers, > 9 kcal mol⁻¹, and concomitantly low rate coefficients, $k(298 \text{K}) \sim 10^{-20}$ cm³ molecule⁻¹ s⁻¹ (see Table 2). The rate coefficient is however highly uncertain, owing to an uncertainty (∼1 to 2 kcal mol⁻¹) on the barrier height.

The decomposition of the CH₃C’(OH)OO’ triplet diradical intermediate, forming CH₃C’=O + HO₂, is reminiscent of the chemistry of α-OH alkyl radicals with unpaired electrons and should occur rapidly owing to the sufficiently high energy content of the peroxyl-alkyl diradical (Hermons et al., 2005, 2004; Dillon et al., 2012; Olivella et al., 2001; Dibble, 2002). Note that this chemistry is very distinct from that of the singlet CH₃C(OH)OO Criegee intermediate. The acyl radical product is expected to recombine rapidly with a second O₂ molecule, forming acyloxy radicals, CH₃C(=O)OO’. Alternatively, the triplet CH₃C’(OH)OO’ intermediate can react with a second O₂ molecule by a barrierless recombination reaction (Fig. 4), forming the diperoxyl singlet diradical CH₃C(OH)(OO’)OO’, which in turn can eliminate HO₂, similar to other α-OH peroxyl radicals, forming the acyloxy radicals directly. This second O₂ addition is sufficiently exothermic to allow for formation of peracetic acid with a singlet O₂ molecule, but this process has a rather large barrier of ∼24 kcal mol⁻¹ and is expected to be a minor contributor, leaving CH₃C(O)O₂ + HO₂ as the likely dominant products of the overall reaction of CH₃COH with oxygen molecules.

3.2.3 Reactions of CH₃COH with carboxylic acids

Samanta et al. (2021) observed loss of CH₃COH via reaction with pyruvic acid, which may indicate that its fate in the atmosphere may also be (partially) controlled by similar reactions. To theoretically investigate the reaction of CH₃COH with carboxylic acids, we used formic acid in the calculations. Not only is formic acid an abundant organic acid in the atmospheric boundary layer, but also its reactivity is related to the properties of the –C(=O)OH moiety, and the results are transferable to other oxoacids, including pyruvic acid, which was present in high concentrations in most laboratory investigations.

As shown in Fig. 5, CH₃COH forms strong complexes with HC(O)OH, with 11 kcal mol⁻¹ stability. From this complex, an addition process occurs that is best described as the transfer of the acidic H⁺ atom to the carbene lone pair on the CH₃COH central carbon, with simultaneous association of one of the negatively charged lone electron pair of the carbonyl oxygen to the carbene vacant p orbital, forming a 1-hydroxyethyl ester (CH₃CH(OH)OC(O)H). Due to the concerted association of the two carbene orbitals with suitable partners in the carboxylic moiety, this process has a very low barrier ($\leq 1$ kcal mol⁻¹). This mechanism is feasible due to the size of the –C(O)OH group and the possibility of shifting the double bond to the other oxygen atom upon H-atom loss. For the anti-CH₃COH carbene, we also found that an in-plane approach of the carboxylic acid towards the COH moiety in methyleneoxy carbene can simultaneously transfer the acidic H atom to the carbene carbon while the carbene hydroxy H atom is transferred to the carbonyl oxygen in the acid, reforming the HC(O)OH co-reactant. This catalysis reaction converts anti-CH₃COH to acetaldehyde, CH₃CHO, without an energy barrier. Both adduct formation and the catalysis reaction should proceed with rate coefficients near the collision limit.

Carboxylic acids can also catalyse keto-enol tautomerization, possibly helping the isomerization between CH₃CHO and CH₂=CH₂OH by reducing the effective barrier by over 50 kcal mol⁻¹ though the thermal reaction remains slow (see Table 2). The only reaction of CH₃CHO that has been investigated experimentally to date is that with pyruvic acid (Samanta et al., 2021), which we also examine theoretically in the Supplement. Note that the large rate coefficient for CH₃COH with organic acids calculated here would imply that reaction of thermalized CH₃COH with pyruvic acid would overwhelm any other bimolecular CH₃COH reaction in their work and most of the experiments listed in Table S1.

3.2.4 Reactions of CH₃COH with H₂O

Based on the reactivity of small carbenes towards closed-shell molecules, Samanta et al. (2021) suggested that reaction with H₂O might be an important loss process of the CH₃COH carbene intermediate. We have characterized the insertion reaction of CH₃COH in the H₂O molecule and found very high barriers, ≥ 11 kcal mol⁻¹, with very low rate coefficients $\sim 10^{-20}$ cm³ molecule⁻¹ s⁻¹ (see Fig. 5 and Table 2). The reaction is significantly slower than with carboxylic acid as the smaller H₂O molecule is unable to simultaneously reach both carbene orbitals in a favourable geometry. The reaction of H₂O with CH₃COH is best described as a shift of an H⁺ atom to the carbene lone pair orbital, followed
by migration of the water HO⁻ moiety to the vacant carbene orbital to form a bond with a lone electron pair. The reaction is further hindered by the back-donation of the CH₂COH oxygen atom into the vacant carbene orbital, partially filling the vacant carbene orbital and reducing the reactivity of the carbene functionality. We therefore propose that CH₂COH will be significantly less reactive towards closed shell species than the CH²⁺ and CH²⁻ carbenes which are known to exhibit very fast insertion and cyclo-addition reactions (Vereecken et al., 1998; Goulay et al., 2009; Douglas et al., 2019; Jasper et al., 2007; Gannon et al., 2010).

3.2.5 Summary of theoretical calculations: the fate of thermalized CH₂COH in 1 bar of air

The theoretical analysis of the fate of CH₂COH carbene intermediates formed in PA photolysis indicates that the acetaldehyde formation observed in many experiments could be the result of a fast catalysis reaction of CH₂COH with pyruvic acid, which under typical experimental conditions dominates over competing reactions, such as with O₂, by several orders of magnitude. This conclusion is consistent with the experimental observations of Reed Harris et al. (2017a), who report a reduction in the acetaldehyde yield when low pyruvic acid concentrations are used and an increase in the formation of acetic acid (which can be formed in the reaction of CH₃C(O)O₂ radicals with HO₂). In the atmospheric boundary layer atmosphere, where the concentrations of organic acids may lie between 10¹⁰ and 10¹¹ molecule cm⁻³ (Millet et al., 2015) and that of O₂ is close to 5 × 10¹⁸ molecule cm⁻³, the reactions of CH₂COH with organic acids and O₂ are competitive, whereas reaction of CH₂COH with water is minor. Table 2 lists the predicted rate coefficients for these reactions.

3.3 Box-model results: contribution of pyruvic acid to acetaldehyde and radical formation

To account for the large variability in photodissociation quantum yields and product yields reported in the literature (see above), we modelled two scenarios, A and B:

- **Scenario A.** In this scenario we used pyruvic acid cross-sections, quantum yields, and product yields according to the IUPAC recommendations with a photodissociation quantum yield (ϕ) of 0.2 at 1 bar pressure and branching ratios of 0.6, 0.05, and 0.35 for Reactions (R1), (R2), and (R3) as listed in Sect. 1.1.

- **Scenario B.** Here we use the same absorption cross-sections as scenario A but build on the recent observations of (Samanta et al., 2021) and the theoretical work presented in Sect. 3.2, which considers the formation and fate of an excited CH₂COH molecule (+ CO₂). In scenario B, we consider the effects of using photodissociation quantum yields of 0.2, 0.5, and 1 (scenarios B₀.₂, B₀.₅, and B₁, respectively). Photolysis at wavelengths < 340 nm was considered to generate CH₃CO + HO, whereas photolysis at wavelengths > 340 nm was assumed to form CO₂ + energy rich CH₂COH⁺, which undergoes the reactions outlined in Sect. 1. Assuming a quantum yield that is independent of wavelength results in 25 % of pyruvic acid photolysis at noon taking place at wavelengths < 340 nm and 75 % at wavelengths > 340 nm. In the model, we assume that this ratio does not change (i.e. we neglect wavelength-dependent variations in the relative actinic flux through the diel cycle). The values of 25 % and 75 % listed above roughly correspond to the relative importance of peroxy radical formation (via Reactions R3, R4, and R5) at the shorter wavelengths compared to CH₂COH + CO₂ formation (Reaction R6) at the longer wavelengths. Some experimental data indicate that addition of O₂ can reduce the CH₂COH yield in favour of formation of, for example, acetic acid. For this reason we use a rate coefficient for reaction of CH₂COH with O₂ that is competitive with the reaction between CH₂COH and organic acids. This is a factor of ~10 larger than the value obtained theoretically, but we consider this value still within the uncertainty (~1 to 2 kcal mol⁻¹ on the barrier height) of our current theoretical results as the peculiar wavefunction of CH₂COH may require even higher levels of theory to be described accurately.

In the box model, in addition to reaction with O₂, the thermalized carbene also reacts with formic and acetic acids to form acetaldehyde:

\[
\text{CH}_2\text{COH} + \text{HCOOH} \rightarrow \text{CH}_3\text{CHO} + \text{HCOOH} \quad \text{(R12)}
\]

\[
\text{CH}_2\text{COH} + \text{CH}_3\text{C(O)OH} \rightarrow \text{CH}_3\text{CHO} + \text{CH}_3\text{C(O)OH} \quad \text{(R13)}
\]

with a rate coefficient of \(5 \times 10^{-11} \text{ cm}^3\text{ molecule}^{-1}\text{s}^{-1}\).

We assumed that (at 1 bar) 70 % of CH₃COH⁺ was quenched to CH₃COH, 20 % isomerized to CH₃CHO, and 10 % isomerized to CH₂=CHOH in order to reproduce the CH₃CHO-to-CH₂=CHOH ratio reported by Samanta et al. (2021). A summary reaction scheme for the photodissociation of pyruvic acid and the fate of the initial products is given in the SI.

3.3.1 CH₃CHO formation

The modelled formation of CH₃CHO from pyruvic acid photolysis through the diel cycle when considering scenario A is displayed as a stacked plot of contributing reactions in Fig. 6. Immediately apparent from this figure is the dominance of pyruvic acid photolysis compared to all other processes. Under scenario A, even with the low quantum yield (ϕ = 0.2) recommended by IUPAC, pyruvic acid photolysis contributes > 80 % to the overall CH₃CHO production term, with a maximum of ~15 % (at noon) arising from reactions...
of the ethylperoxy radical, formed in the reaction of OH with ethane (7.5 %) and butane (3.75 %) and in the photolysis of CH$_3$C(O)C$_2$H$_5$ (3.75 %).

Under scenario B, pyruvic acid photolysis still dominates the formation of CH$_3$CHO, with a noontime contribution of 91 %, 86 %, and 71 % when quantum yields of 1, 0.5, and 0.2 are considered. Of the pyruvic acid contribution, 45 % of the CH$_3$CHO arises via isomerization of the initially formed, energized carbene (blue), while the remaining 55 % results from reactions of the thermalized carbene with formic (orange) and acetic (green) acids, the concentrations of which were constrained by observations. The modelled, noontime mixing ratio of CH$_3$CHO varies from 400 pptv (scenario B$_{1.0}$) to 160 pptv (scenario B$_{0.2}$). In the legend, the first term is the equation tag used by CAABA/MECCA for the reaction. LC4H9O2 is the peroxy radical formed in the reaction of OH with butane. A full listing of the reactions can be downloaded (see Data availability section).

### 3.3.2 CH$_3$C(O)O$_2$ formation

The CH$_3$C(O)O$_2$ radical is formed in a termolecular reaction between the CH$_3$CO radical and O$_2$. Figure 7 displays the main photochemical reactions that lead to the formation of CH$_3$CO in our model. The spikes in the simulated production rates are connected to spikes in the diel average NO mixing ratio at the site. In analysing the data, we therefore consider not only the contributions at noon (when NO mixing ratios were large), but also at 10:30 when NO mixing ratios were comparably low.

Under scenario A, where $\varphi = 0.2$ and the yield of the CH$_3$CO radical is 0.35, the contribution of pyruvic acid photolysis to the overall production rate at 12:00 and 10:30 is about 23 % and 16 %, respectively, roughly equally divided into a direct contribution (J43018) and an indirect contribution (G42008a) arising via enhanced CH$_3$CHO levels. The main contributors to the formation of CH$_3$CO are reactions initiated by the degradation of isoprene and MTs (in the legend of Fig. 7: BIACETO2, C511O2, C716O2, CO23C4CHO, CO235C6CHO), which involve reactions of peroxy radicals with NO.

Under scenario B$_1$, the photolysis of pyruvic acid becomes significantly more important, contributing a total of 63 % of the total production rate for CH$_3$CO at 10:30 and 42 % at 12:00. When considering scenarios B$_{0.5}$ and B$_{0.2}$ the contributions of pyruvic acid photolysis are reduced to 46 % (29 %) and 29 % (17 %), respectively, where the numbers in parentheses are for the “high-NO$_x$” situation. Generally, the reaction of the thermalized carbene with O$_2$ (G42099), the direct photolysis at wavelengths $< 340$ nm (J43018), and the indirect enhancement in CH$_3$CO formation via the enhanced levels of CH$_3$CHO (G42008a) contribute roughly equally to the formation of CH$_3$CO resulting from pyruvic acid photolysis.
Figure 7. Modelled rates of CH$_3$CO formation (in pptv s$^{-1}$) through the diel cycle from photolysis of pyruvic acid (blue, orange, and green) and other photochemical processes during IBAIRN. (a) Scenario A (IUPAC). (b) Scenario B$_1$. (c) Scenario B$_{0.5}$. (e) Scenario B$_{0.2}$. In the legend, the first term is the equation tag used by CAABA/MECCA for the reaction. A full listing of the reactions can be downloaded (see Data availability section).

Figure 8. Modelled rates of HO$_2$ formation (in pptv s$^{-1}$) through the diel cycle from photolysis of pyruvic acid (blue, orange, and green) and other photochemical processes during IBAIRN. (a) Scenario A (IUPAC). (b) Scenario B$_1$. (c) Scenario B$_{0.5}$. (d) Scenario B$_{0.2}$. In the legend, the first term is the MCM designation for the reaction. A full listing of the reactions can be downloaded (see Data availability section).
ysis. The modelled mixing ratio of the CH$_3$C(O)O$_2$ radical at noon increases by a factor of $\sim 1.5$ when comparing scenario B$_1$ with the quantum yields for pyruvic acid photodissociation set to zero.

3.3.3 HO$_2$ formation

In Fig. 8, we plot the nine most important model pathways to HO$_2$ production through the diel cycle. The dominant modelled production terms for HO$_2$ involve HCHO (photolysis HCHO and reaction with OH, G4108, J41001b), the reaction of methoxy radicals (G4118, whereby CH$_3$O is generated mainly in the reaction of CH$_3$O$_2$ radicals with NO), and the reaction of OH with CO. The direct contribution of pyruvic acid photolysis to HO$_2$ formation (via its photolysis (J43018) and through the reaction of CH$_3$COH with O$_2$, G42099) is $\sim 10\%$ under scenario B$_1$ under low-NO$_x$ conditions (i.e. at 10:30). Under all other scenarios it is lower, with values (in percent) of $< 1$ (scenario A at both 10:30 and 02:00), $\sim 6$ (scenario B$_1$ at 12:00), $\sim 5$ and $\sim 3.5$ (scenario B$_{0.5}$ at 10:30 and 12:00, respectively), and $\sim 1.5$ and $< 1$ (scenario B$_{0.2}$ at 10:30 and 12:00, respectively). However, although the direct impact of pyruvic acid photolysis is weak, it has a significant indirect effect via the enhanced formation of CH$_3$C(O)O$_2$ radicals (directly via Reactions R3 + R4 and R10 and indirectly via CH$_3$CHO formation), which, in the presence of O$_2$, reacts with NO to form CH$_3$O$_2$. Enhanced production rates of CH$_3$O$_2$ result in enhanced production rates of CH$_3$O and HCHO and thus HO$_2$.

$$\text{CH}_3\text{C(O)}\text{O}_2 + \text{NO}(+\text{O}_2) \rightarrow \text{CH}_3\text{O}_2 + \text{NO}_2 + \text{CO}_2 \quad (R14)$$

$$\text{CH}_3\text{O}_2 + \text{NO} \rightarrow \text{CH}_3\text{O} + \text{NO}_2 \quad (R15)$$

$$\text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{HCHO} + \text{HO}_2 \quad (R16)$$

$$\text{HCHO} + h\nu(+\text{O}_2) \rightarrow 2\text{HO}_2 + \text{CO} \quad (R17)$$

The model simulations have shown that the photolysis of pyruvic acid at the levels observed during the IBAIRN campaign has a potentially significant effect on both CH$_3$CHO mixing ratios and production rates of HO$_2$ and CH$_3$C(O)O$_2$ radicals, the latter being especially enhanced under low-NO$_x$ conditions. The enhanced production rates and concentrations of CH$_3$C(O)O$_2$ and HO$_2$ also result in significant increases in the modelled mixing ratios of several trace gases that are formed from these radicals. Comparing scenario B$_1$ to the case in which the pyruvic acid photodissociation quantum yield ($\varphi$) is set to zero results in an increase by factors of 2.2, 2.0, and 1.6 for CH$_3$C(O)OOH, CH$_3$OOH, and H$_2$O$_2$, respectively (see Fig. S6). HCHO mixing ratios are enhanced by a factor of 1.2. Vinyl alcohol mixing ratios of up to 40 pptv were generated in scenario B$_1$. Clearly, the photolysis of pyruvic acid can potentially impact strongly on the concentrations of, for example, C1 and C2 carbonyl compounds and peroxides in the boreal environment.

4 Conclusions

We have combined measurements of pyruvic acid in an autumn campaign in the boreal forest (IBAIRN) with theoretical calculations designed to characterize the fate of the methylhydroxy carbene radical (CH$_3$COH, the major product of pyruvic acid photodissociation) with a box-modelling study. We investigated the impact of pyruvic acid photolysis on the rates of production of acetaldehyde (CH$_3$CHO) and the peroxy radicals CH$_3$C(O)O$_2$ and HO$_2$. The theoretical study revealed unexpected features of CH$_3$COH chemistry, including slow reactions of thermalized carbene with H$_2$O but an efficient acid-catalysed conversion to CH$_3$CHO in the presence of organic acids such as HC(O)OH. The reaction of CH$_3$COH with O$_2$ is slow but will contribute to its fate (and thus the formation of CH$_3$C(O)O$_2$ and HO$_2$) in the lower atmosphere where O$_2$ concentrations are high if the rate constant used (elevated by an order of magnitude compared to the theoretical value) is correct.

In our box model, the photolysis of pyruvic acid was parameterized as presently recommended by IUPAC (whereby the main products are CH$_3$CHO and CO$_2$) and also using a more detailed mechanism in which the formation and fate of CH$_3$COH was considered and in which the quantum yield was varied. In all scenarios, we find that the photolysis of pyruvic acid was the dominant source of CH$_3$CHO during IBAIRN and that its instantaneous contribution to the daytime formation of CH$_3$C(O)O$_2$ varied between 16% and 63%, dependent on the assumed scenario and also on the NO concentration. Pyruvic acid photodissociation results in a significant increase in the mixing ratios of several carbonyl compounds and peroxides in the boreal environment.

The results of our modelling study are strongly dependent on the chosen quantum yields and photodissociation mechanism. To reduce the uncertainty in the role of pyruvic acid photolysis, there is an urgent need for further experimental and theoretical work on the photochemistry of pyruvic acid and on the fate of methylhydroxy carbene under atmospheric conditions. In addition, further measurements of pyruvic acid mixing ratios and of its deposition velocity in different environments are required to better constrain its abundance and lifetime and thus the impact of its photolysis. Enclosure studies would be helpful to investigate the dependence of pyruvic acid emission rates on different plant types and environmental conditions.

Data availability. The Max Planck Institute data used for the IBAIRN analysis and the reaction scheme used in the box model are archived at https://doi.org/10.5281/zenodo.3254828 (Crowley and Fischer, 2019).

Supplement. The supplement related to this article is available online at: https://doi.org/10.5194/acp-21-14333-2021-supplement.
Author contributions. PGE was responsible for the pyruvic acid measurement during IBAIRN. PGE and JNC, with contributions from JL, wrote the manuscript. LV conducted the theoretical calculation on the fate of methylhydroxycarbene, RS and AP did the box modelling, and NS was responsible for the CRDS measurements of NO2 and PANs during IBAIRN. JS was responsible for the O3 and J value measurements during IBAIRN. HF was responsible for the NO and CO measurements during IBAIRN. EK and JW were responsible for the MT measurements during IBAIRN. VV was responsible for the mixing layer height measurements during IBAIRN. TP was responsible for the SMEAR II observations and infrastructure. All authors contributed to the paper.

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

Disclaimer. Publisher’s note: Copernicus Publications remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Acknowledgements. We thank the technical staff of SMEAR II station for the excellent support during IBAIRN.

Financial support. This research has been supported by the ENVRIplus (grant no. 654182). We are grateful to ENVRIplus for partial financial support of the IBAIRN campaign.

The article processing charges for this open-access publication were covered by the Max Planck Society.

Review statement. This paper was edited by Gabriele Stiller and reviewed by two anonymous referees.

References

Aalto, J., Porcar-Castell, A., Atherton, J., Kolari, P., Pohja, T., Hari, P., Nikinmaa, E., Petaja, T., and Back, J.: Onset of photosynthesis in spring speeds up monoterpane synthesis and leads to emission bursts, Plant Cell Environ., 38, 2299–2312, https://doi.org/10.1111/pce.12550, 2015.

Alecu, I. M., Zheng, J. J., Zhao, Y., and Truhlar, D. G.: Computational thermochemistry: scale factor databases and scale factors for vibrational frequencies obtained from electronic model chemistries, J. Chem. Theor. Comput., 6, 2872–2887, https://doi.org/10.1021/ct100326h, 2010.

Andreae, M. O., Talbot, R. W., and Li, S. M.: Atmospheric measurements of pyruvic and formic acid, J. Geophys. Res.-Atmos., 92, 6635–6641, https://doi.org/10.1029/JD092iD06p06635, 1987.

Berges, M. G. M. and Warneck, P.: Product quantum yields for the 350 nm photodecomposition of pyruvic-acid in air, Ber. Bunsen Phys. Chem., 96, 413–416, https://doi.org/10.1002/bbpc.19920960334, 1992.

Burkholder, J. B., Sander, S. P., Abbatt, J., Barker, J. R., Huie, R. E., Kolb, C. E., Kurylo, M. J., Orkin, V. L., Wilmouth, D. M., and Wine, P. H.: Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation No. 18, JPL Publication 15-10, Jet Propulsion Laboratory, Pasadena, available at: http://jpldataeval.jpl.nasa.gov (last access: September 2020), 2015.

Calvert, J. G., Mellouki, A., Pilling, M. J., and Wallington, T. J.: The Mechanisms of Atmospheric Oxidation of the Oxygenates, Oxford Univ. Press, New York, 2011.

Chang, X.-P., Fang, Q., and Cui, G.: Mechanistic photodecarboxylation of pyruvic acid: Excited-state proton transfer and three-state intersection, J. Chem. Phys., 141, 154311, https://doi.org/10.1063/1.4898085, 2014.

Crowley, J. N. and Fischer, H.: IBAIRN data (Boreal forest, Hyryläi Sept. 2016) Max-Planck-Institut, Mainz [data set], Zenodo, https://doi.org/10.5281/zenodo.3254828, 2019.

Crowley, J. N., Pouvesle, N., Phillips, G. J., Axinte, R., Fischer, H., Petajä, T., Nölscher, A., Williams, J., Hens, K., Harder, H., Martinez-Harder, M., Novelli, A., Kubistin, D., Bohn, B., and Lelieveld, J.: Insights into HO3 and RO2 chemistry in the boreal forest via measurement of peroxyacetic acid, peroxyacetic nitric anhydride (PAN) and hydrogen peroxide, Atmos. Chem. Phys., 18, 13457–13479, https://doi.org/10.5194/acp-18-13457-2018, 2018.

Dee, D. P., Uppala, S. M., Simmons, A. J., Berrisford, P., Poli, P., Kobayashi, S., Andrae, U., Balsmaseda, M. A., Balsamo, G., Bauer, P., Bechtold, P., Beljaars, A. C. M., van de Berg, L., Bidlot, J., Bormann, N., Delso, C., Dragni, R., Fuentes, M., Geer, A. J., Haimberger, L., Healy, S. B., Hersbach, H., Holm, E. V., Isaksen, L., Källberg, P., Köhler, M., Matricardi, M., McNally, A. P., Monge-Sanz, B. M., Morcrette, J.-J., Park, B.-K., Peube, C., de Rosnay, P., Tavolato, C., Thépaut, J.-N., and Vitart, F.: The ERA-Interim reanalysis: configuration and performance of the data assimilation system, Q. Roy. Meteorol. Soc., 137, 553–597, https://doi.org/10.1002/qj.828, 2011.

Dibble, T. S.: Mechanism and dynamics of the CH2O + O2 reaction, Chem. Phys. Lett., 355, 193–200, https://doi.org/10.1016/S0009-2614(02)00211-7, 2002.

Dillon, T. J., Pozzer, A., Vereecken, L., Crowley, J. N., and Lelieveld, J.: Does acetone react with HO2 in the upper-troposphere?, Atmos. Chem. Phys., 12, 1339–1351, https://doi.org/10.5194/acp-12-1339-2012, 2012.

Douglas, K. M., Blitz, M. A., Feng, W. H., Heard, D. E., Plane, J. M. C., Rashid, H., and Seakins, P. W.: Low temperature studies of the rate coefficients and branching ratios of reactive loss vs quenching for the reactions of (CH2)2-C1 with C2H6, C2H4, C2H2, Icarus, 321, 752–766, https://doi.org/10.1016/j.icarus.2018.12.027, 2019.

Dunning, T. H.: Gaussian-basis sets for use in correlated molecular calculations. I. the atoms boron through neon and hydrogen, J. Chem. Phys., 90, 1007–1023, https://doi.org/10.1063/1.456153, 1989.

Eckart, C.: The penetration of a potential barrier by electrons, Phys. Rev., 35, 1303–1309, https://doi.org/10.1103/PhysRev.35.1303, 1930.

Eger, P. G., Schuladen, J., Sobanski, N., Fischer, H., Karu, E., Williams, J., Riva, M., Zha, Q., Ehn, M., Quéléver, L. L. J., Schallhart, S., Lelieveld, J., and Crowley, J. N.: Pyruvic acid in the boreal forest: gas-phase mixing ratios and impact
Gannon, K. L., Blitz, M. A., Liang, C. H., Pilling, M. J., Seakins, Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Fischer, L., Breitenlechner, M., Canaval, E., Scholz, W., Striednig, Fischer, H., Axinte, R., Bozem, H., Crowley, J. N., Ernest, C., Gilge, S., Hafermann, S., Harder, H., Hens, K., Janssen, R. H. H., Königstedt, R., Kubistin, D., Mallik, C., Martinez, M., Novelli, A., Parchatka, U., Plass-Dülmer, C., Pozzer, A., Regelin, E., Reiffs, A., Schmidt, T., Schuladen, J., and Lelieveld, J.: Diurnal variability, photochemical production and loss processes of hydrogen peroxide in the boundary layer over Europe. Atmos. Chem. Phys., 19, 11953–11968, https://doi.org/10.5194/acp-19-11953-2019, 2019.

Fischer, L., Breitenlechner, M., Canaval, E., Schoz, W., Striednig, M., Graus, M., Karl, T. G., Petäjä, T., Kulmala, M., and Hansel, A.: First Eddy Covariance Flux Measurements of Semi Volatile Organic Compounds with the PTR3-TOF-MS. Atmos. Meas. Tech. Discuss. [preprint], https://doi.org/10.5194/amt-2021-117, in review, 2021.

Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Scalmani, G., Barone, V., Mennucci, B., Petersson, G. A., Nakatsuji, H., Li, X., Caricato, M., Mareniich, A. V., Bloino, J., Janesko, B. G., Gomperts, R., Mennucci, B., Hratchian, H. P., Ortiz, J. V., Izmaylov, A. F., Sonnenberg, J. L., Williams-Young, D., Ding, F., Lipparrini, F., Egidi, F., Goings, J., Peng, B., Petrone, A., Henderson, T., Ransinghe, D., Zakrzewski, V. G., Gao, J., Rega, N., Zheng, G., Liang, W., Hada, M., Eara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Itao, O., Nakai, H., Vreven, T., Throssell, K., Møllegaard, J., Peralta, I. E., Ogliaro, F., Bearpark, M. J., Heyd, J. J., Brothers, E. N., Kudin, K. N., Staroverov, V. V., Keith, T. A., Kobayashi, R., Normand, J., Raghavachari, K., Rendell, A. P., Burant, J. C., Iyengar, S. S., Tomasi, J., Cossi, M., Millam, J. M., Klene, M., Adamo, C., Cammi, R., Ochterski, J. W., Martin, R. L., Morokuma, K., Farkas, O., Foresman, J. B., and Fox, D. J.: Gaussian 16, Revision B.01, Gaussian Inc., Wallington, CT, 2016.

Gannon, K. L., Blitz, M. A., Liang, C. H., Pilling, M. J., Seakins, P. W., and Glowacki, D. R.: Temperature Dependent Kinetics (195–798 K) and H Atom Yields (298–498 K) from Reactions of (CH\textsubscript{2})\textsubscript{3}–C\textsubscript{1} with Acetylene, Ethene, and Propene, J. Phys. Chem. A, 114, 9413–9424, https://doi.org/10.1021/jp102276j, 2010.

Gaona-Colman, E., Blanco, M. B., Barnes, I., Wiesen, P., and Teruel, M. A.: OH- and O-3-initiated atmospheric degradation of camphene: temperature dependent rate coefficients, product yields and mechanisms, RSC Adv., 7, 2733–2744, https://doi.org/10.1039/c6ra26656h, 2017.

Goulay, F., Trevitt, A. J., Meloni, G., Selby, T. M., Osborn, D. L., Taatjes, C. A., Vereecken, L., and Leone, S. R.: Cyclic Versus Linear Isomers Produced by Reaction of the Methylidyne Radical (CH) with Small Unsaturated Hydrocarbons, J. Am. Chem. Soc., 131, 993–1005, https://doi.org/10.1021/ja804200w, 2009.

Grimme, S., Ehrlich, S., and Goerigk, L.: Effect of the Damping Function in Dispersion Corrected Density Functional Theory, J. Comput. Chem., 32, 1456–1465, https://doi.org/10.1002/jcc.21759, 2011.

Grosjean, D.: Atmospheric reactions of pyruvic acid. Atmos. Environ., 17, 2379–2382, https://doi.org/10.1016/0004-6981(83)90242-1, 1983.

Grosjean, D.: Atmospheric reactions of ortho cresol: gas phase and aerosol products. Atmos. Environ., 18, 1641–1652, https://doi.org/10.1016/0004-6981(84)90386-X, 1984.

Grosjean, D., Williams, E. L., and Grosjean, E.: Atmospheric chemistry of isoprene and of its carbonyl products, Environ. Sci. Technol., 27, 830–840, https://doi.org/10.1021/es00042a004, 1993.

Guenther, A. B., Zimmerman, P. R., Harley, P. C., Monson, R. K., and Fall, R.: Isoprene and monoterpene emission rate variability - model evaluations and sensitivity analyses, J. Geophys. Res.-Atmos., 98, 12609–12617, https://doi.org/10.1029/93jd00527, 1993.

Hakola, H., Hellén, H., and Laurila, T.: Ten years of light hydrocarbons (C\textsubscript{2}–C\textsubscript{6}) concentration measurements in background air in Finland. Atmos. Environ., 40, 3621–3630, https://doi.org/10.1016/j.atmosenv.2005.08.019, 2006.

Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeyss, M., Dommen, J., Donahue, N. M., George, C., Goldman, A. H., Hamilton, J. F., Herrmann, H., Hoffmann, T., Inumaya, J., Yang, M., Jenkins, M. E., Jimenez, J. L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, Th. F., Monod, A., Prévôt, A. S. H., Seinfeld, J. H., Surratt, J. D., Szmielinski, R., and Wildt, J.: The formation, properties and impact of secondary organic aerosol: current and emerging issues, Atmos. Chem. Phys., 9, 5155–5236, https://doi.org/10.5194/acp-9-5155-2009, 2009.

Hari, P. and Kulmala, M.: Station for Measuring Ecosystem–Atmosphere Relations (SMEAR II), Boreal Environ. Res., 10, 315–322, https://doi.org/10.1007/s10533-007-5603-8_9, 2005.

Helas, G., Bingemer, H., and Andreea, M. O.: Organic acids over equatorial Africa: Results from DECAFE 88, J. Geophys. Res.-Atmos., 97, 6187–6193, https://doi.org/10.1029/91jd01438, 1992.

Hellén, H., Kouznetsovet, R., Anttila, P., and Hakola, H.: Increasing influence of easterly air masses on NMHC concentrations at the Pallas-Sodankylä GAW station, Boreal Environ. Res., 20, 542–552, 2015.

Hellén, H., Praplan, A. P., Pykkä, T., Yliivinkka, I., Vakkari, V., Bäck, J., Petäjä, T., Kulmala, M., and Hakola, H.: Long-term measurements of volatile organic compounds highlight the importance of sesquiterpenes for the atmospheric chemistry of a boreal forest, Atmos. Chem. Phys., 18, 13839–13863, https://doi.org/10.5194/acp-18-13839-2018, 2018.

Hermans, I., Nguyen, T. L., Jacobs, P. A., and Peeters, J.: Tropopause chemistry revisited: HO\textsubscript{2}-initiated oxidation as an efficient acetone sink, J. Am. Chem. Soc., 126, 9908–9909, https://doi.org/10.1021/ja0467317, 2004.

Hermans, I., Muller, J. F., Nguyen, T. L., Jacobs, P. A., and Peeters, J.: Kinetics of alpha-hydroxy-alkylperoxyl radicals in oxidation processes. HO\textsubscript{2} center dot-initiated oxidation of ketones/alkydehydes near the tropopause, J. Phys. Chem. A, 109, 4303–4311, 2005.

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R. A., Crowley, J. N., Herrmann, H., Jenkin, M. E., McNeil, V. F., Mellouki, A., Rossi, M. J., Troe, J., and Wallington, T. J.): Evaluated kinetic and photochemical data
for atmospheric availability, available at: http://iupac.pole-ether.fr/index.html, last access: June 2021.

Jacob, D. J. and Wofsy, S. C.: Photochemistry of biogenic emissions over the Amazon forest, J. Geophys. Res.-Atmos., 93, 1477–1486, https://doi.org/10.1029/JD093iD02p01477, 1988.

Jardine, K., Abrell, L., Kurc, S. A., Huxman, T., Ortega, J., and Guenther, A.: Volatile organic compound emissions from Larrea tridentata (creosotebush), Atmos. Chem. Phys., 10, 12191–12206, https://doi.org/10.5194/acp-10-12191-2010, 2010a.

Jardine, K. J., Sommer, E. D., Saleska, S. R., Huxman, T. E., Harley, P. C., and Abrell, L.: Gas Phase Measurements of Pyruvic Acid and Its Volatile Metabolites, Environ. Sci. Technol., 44, 2454–2460, https://doi.org/10.1021/es093544p, 2010b.

Jasper, A. W., Klippenstein, S. J., and Harding, L. B.: Secondary Kinetics of Methanol Decomposition: Theoretical Rate Coefficients for 3CH2 + OH, 3CH2 + CH2, and 3CH2 + CH3, J. Phys. Chem. A, 111, 8699–8707, https://doi.org/10.1021/jp0736950, 2007.

Johnston, H. S. and Heicklen, J.: Tunnelling corrections for unsymmetrical eckart potential energy barriers, J. Phys. Chem., 66, 532–533, https://doi.org/10.1021/j100809a040, 1962.

Kanakidou, M., Seinfeld, J. H., Pandis, S. N., Barnes, I., Dentener, F. J., Facchini, M. C., Van Dingenen, R., Ervens, B., Nenes, A., Nielsen, C. J., Swietlicki, E., Putaud, J. P., Balkanski, Y., Fuzzi, S., Horth, J., Moortgat, G. K., Winterhalter, R., Myhre, C. E. L., Tsigaridis, K., Vignati, E., Stephanou, E. G., and Wilson, J.: Organic aerosol and global climate modelling: a review, Atmos. Chem. Phys., 5, 1053–1123, https://doi.org/10.5194/acp-5-1053-2005, 2005.

Liebmann, J., Karu, E., Sobanski, N., Schuladen, J., Ehn, M., Schallhart, S., Quéléver, L., Hellen, H., Hakola, H., Hoffmann, T., Williams, J., Fischer, H., Lelieveld, J., and Crowley, J. N.: Direct measurement of NO3 radical reactivity in a boreal forest, Atmos. Chem. Phys., 18, 3799–3815, https://doi.org/10.5194/acp-18-3799-2018, 2018a.

Liebmann, J. M., Muller, J. B. A., Kubistin, D., Claude, A., Holla, R., Plass-Dülmer, C., Lelieveld, J., and Crowley, J. N.: Direct measurements of NO2 reactivity in and above the boundary layer of a mountaintop site: identification of reactive trace gases and comparison with OH reactivity, Atmos. Chem. Phys., 18, 12045–12059, https://doi.org/10.5194/acp-18-12045-2018, 2018b.

Liebmann, J., Sobanski, N., Schuladen, J., Karu, E., Hellen, H., Hakola, H., Zha, Q., Ehn, M., Riva, M., Heikkinen, L., Williams, J., Fischer, H., Lelieveld, J., and Crowley, J. N.: Alkyl nitrate reactivity in the boreal forest: formation via the NO3-, OH- and O3-induced oxidation of biogenic volatile organic compounds and ambient lifetimes, Atmos. Chem. Phys., 19, 10391–10403, https://doi.org/10.5194/acp-19-10391-2019, 2019.

Mellouki, A. and Mu, Y.: On the atmospheric degradation of pyruvic acid in the gas phase, J. Photoch. Photobio. A, 157, 295–300, https://doi.org/10.1016/S0166-4919(03)00070-4, 2003.

Millet, D. B., Guenther, A., Siegel, D. A., Nelson, N. B., Singh, H. B., de Gouw, J. A., Warneke, C., Williams, J., Eerdekens, G., Sinha, V., Karl, T., Flocke, F., Apel, E., Riemer, D. D., Palmer, P. I., and Barkley, M.: Global atmospheric budget of acetaldehyde: 3-D model analysis and constraints from in-situ and satellite observations, Atmos. Chem. Phys., 10, 3405–3425, https://doi.org/10.5194/acp-10-3405-2010, 2010.
Rinne, J., Hakola, H., Laurila, T., and Rannik, Ü.: Canopy scale monoterpenes emissions of *Pinus sylvestris* dominated forests, Atmos. Environ., 34, 1099–1107, https://doi.org/10.1016/S1352-2310(99)00335-0, 2000.

Roberts, J. M., Flocke, F., Chen, G., de Gouw, J., Holloway, J. S., Hübner, G., Neuman, J. A., Nicks Jr., D. K., Nowak, J. B., Parrish, D. D., Ryerson, T. B., Suarez, D. T., Warneke, C., and Fehsenfeld, F. C.: Measurement of peroxycarboxylic nitric anhydrides (PANs) during the ITCT 2K2 aircraft intensive experiment, J. Geophys. Res.-Atmos., 109, D23S21, https://doi.org/10.1029/2004jd004960, 2004.

Roiger, A., Aufmhoff, H., Stock, P., Arnold, F., and Schlager, H.: An aircraft-borne chemical ionization – ion trap mass spectrometer (CI-ITMS) for fast PAN and PPN measurements, Atmos. Meas. Tech., 4, 173–188, https://doi.org/10.5194amt-4-173-2011, 2011.

Samanta, B. R., Fernando, R., Rösch, D., Reisler, H., and Osborn, D. L.: Primary photodissociation mechanisms of pyruvic acid on S1: observation of methylhydroxycarbene and its chemical reaction in the gas phase, Phys. Chem. Chem. Phys., 23, 4107–4119, https://doi.org/10.1039/D0CP00424F, 2021.

Sander, R., Baumgaertner, A., Cabrera-Perez, D., Frank, F., Grosov, M., Groß, J.–U., Harder, H., Huijnen, V., Jöckel, P., Karydis, V. A., Niemeyer, K. E., Pozzer, A., Riede, H., Schultz, M. G., Taraborrelli, D., and Tauer, S.: The community atmospheric chemistry box model CAABA/MECCA-4.0, Geosci. Model Dev., 12, 1365–1385, https://doi.org/10.5194/gmd-12-1365-2019, 2019.

Schreiner, P. R., Reisenauer, H. P., Ley, D., Gerbig, D., Wu, C. H., and Allen, W. D.: Methylhydroxycarbene: Tunneling control of a chemical reaction, Science, 332, 1300–1303, https://doi.org/10.1126/science.1203761, 2011.

Shepok, P. B., Bottenheim, J. W., Hastie, D. R., and Venkatram, A.: Determination of the relative ozone and PAN deposition velocities at night, Geophys. Res. Lett., 19, 1121–1124, https://doi.org/10.1029/92gl01118, 1992a.

Shepok, P. B., Hastie, D. R., So, K. W., and Schiff, H. I.: Relationships between PAN, PPN and O3 at urban and rural sites in Ontario, Atmos. Environ. A-Gen., 26, 1259–1270, https://doi.org/10.1016/0001-276X(92)90387-z, 1992b.

Sobanski, N., Schuladen, J., Schuster, G., Lelieveld, J., and Crowley, J. N.: A five-channel cavity ring-down spectrometer for the detection of NO2, NO3, N2O5, total peroxy nitrates and total alkyl nitrates, Atmos. Meas. Tech., 9, 5103–5118, https://doi.org/10.5194amt-9-5103-2016, 2016.

Stefan, M. I. and Bolton, J. R.: Reinvestigation of the acetone degradation mechanism in dilute aqueous solution by the UV/H2O2 process, Environ. Sci. Technol., 33, 870–873, https://doi.org/10.1021/es9808548, 1999.

Talbot, R., Andreae, M., Berressem, H., Jacob, D. J., and Beecher, K.: Sources and sinks of formic, acetic, and pyruvic acids over Central Amazonia: 2. Wet season, J. Geophys. Res.-Atmos., 95, 16799–16811, https://doi.org/10.1029JD95iD10p16799, 1990.

Vereecken, L. and Pierfoot, K., and Peeters, J.: B3LYP-DFT characterization of the potential energy surface of the CH(X2Π)+C2H2 reaction, J. Chem. Phys., 108, 1068–1080, https://doi.org/10.1063/1.475345, 1998.

Wesley, G. F. and Leermakers, P. A.: Photochemistry of alpha-keto acids + alpha-keto esters. 3. Photolysis of pyruvic acid in vapor phase, J. Phys. Chem., 68, 2364–2366, https://doi.org/10.1021/j100790a507, 1964.

Walker, D.: Pyruvate carboxylation and plant metabolism, Biol. Rev., 37, 215–254, https://doi.org/10.1111/j.1469-185x.1962.tb01161.x, 1962.

Wang, N., Edtbauer, A., Stönnner, C., Pozzer, A., Bourtsoukidis, E., Ernle, L., Dienhart, D., Hottmann, B., Fischer, H., Schuladen, J., Crowley, J. N., Paris, J.-D., Lelieveld, J., and Williams, J.: Measurements of carbonyl compounds around the Arabian Peninsula: overview and model comparison, Atmos. Chem. Phys., 20, 10807–10829, https://doi.org/10.5194/acp-20-10807-2020, 2020.

Wang, S. Y., Hornbrook, R. S., Hills, A., Emmons, L. K., Tilmes, S., Lamarque, J. F., Jimenez, J. L., Campuzano-Jost, P., Nault, E. A., Crounse, J. D., Wennberg, P. O., Kim, M., Allen, H., Ryerson, T. B., Thompson, C. R., Pfeil, J., Moore, F., Nance, D., Hall, B., Elkins, J., Tanner, D., Huey, L. G., Hall, S. R., Ullmann, K., Orlando, J. J., Tyndall, G. S., Flocke, F. M., Ray, E., Hanisco, T. F., Wolfe, G. M., St Clair, J., Commare, R., Duabre, B., Barletta, B., Blake, D. R., Weinzierl, B., Dollner, M., Conley, A., Vitt, F., Wofty, S. C., Riemer, D. D., and Apel, E. C.: Atmospheric acetaldehyde: importance of air-sea exchange and a missing source in the remote troposphere, Geophys. Res. Lett., 46, 5601–5613, https://doi.org/10.1029/2019gl082034, 2019.

Williams, J., Crowley, J., Fischer, H., Harder, H., Martinez, M., Petjäi, T., Rinne, J., Bäck, J., Boy, M., Dal Maso, M., Hakala, J., Kajos, M., Keronen, P., Rantala, P., Aalto, J., Aaltonen, H., Paatero, J., Vesala, T., Hakola, H., Levula, J., Pohja, T., Herrmann, F., Auld, J., Mesarchaki, E., Song, W., Yassaa, N., Nölscher, A., Johnson, A. M. C., Custer, T., Sinha, V., Thieser, J., Poulvesle, N., Taraborrelli, D., Tang, M. J., Bozem, H., Hosaynali-Beygi, Z., Axinte, R., Oswald, R., Novelli, A., Kumbist, D., Hens, K., Javed, U., Trawny, K., Breitenberger, C., Hilgado, P. J., Ebben, C. J., Geiger, F. M., Corrigan, A. L., Russell, L. M., Ouwersloot, H. G., Vilà-Guerau de Arellano, J., Ganzelvo, L., Vogel, A., Beck, M., Bayerle, A., Kampf, C. J., Bertelmann, M., Köllner, K., Hoffmann, T., Valverde, J., Vogel, A., Soufli, D., Hens, K., Trawny, K., Breitenberger, C., Hilgado, P. J., Ebben, C. J., Geiger, F. M., Corrigan, A. L., Russell, L. M., Ouwersloot, H. G., Vilà-Guerau de Arellano, J., Ganzelvo, L., Vogel, A., Beck, M., Bayerle, A., Kampf, C. J., Bertelmann, M., Köllner, K., Hoffmann, T., Valverde, J., González, D., Riekkola, M.-L., Kulmala, M., and Lelieveld, J.: The summertime boreal forest field measurement intensive (HUMPPA-COPEC-2010): an overview of meteorological and chemical influences, Atmos. Chem. Phys., 11, 10599–10618, https://doi.org/10.5194/acp-11-10599-2011, 2011.

Yamamoto, S. and Back, R. A.: The photolysis and thermal-decomposition of pyruvic-acid in the gas-phase, Can. J. Chem., 63, 549–554, https://doi.org/10.1139/v85-089, 1985.

Zhao, Y. and Truhlar, D. G.: The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals, Theor. Chem. Account., 120, 215–241, https://doi.org/10.1007/s00214-007-0310-x, 2008.