Gas Phase Oxidation of Campholenic Aldehyde and Solution Phase Reactivity of its Epoxide Derivative

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ABSTRACT: The rate constant for the OH reaction with campholenic aldehyde (CA) was measured using the flow tube-chemical ionization mass spectrometry method with a relative rate kinetics technique and was found to be \((6.54 \pm 0.52) \times 10^{-11}\) cm³ molecule⁻¹ s⁻¹ at 100 Torr pressure and 298 K. A mechanism for the formation of the observed products was developed for both NO-free and NO-present conditions. On the basis of measurements of the pressure dependent yields of the products, between 5 and 20% of the CA oxidation at atmospheric pressure is predicted to lead to campholenic aldehyde epoxide (CAE). The aqueous solution reaction rate constants for CAE were determined via NMR spectroscopy and were found to be \((2.241 \pm 0.036) \times 10^{-5}\) s⁻¹ for neutral conditions and \(0.0989 \pm 0.0053 \text{ M}^{-1} \text{s}^{-1}\) for acid-catalyzed conditions at 298 K. The products of the CAE aqueous solution reaction were identified as an isomer of CAE and the aldehyde group hydrated form of this isomer. Unlike the isoprene-derived epoxide, IEPOX, a nucleophilic addition mechanism was not observed. On the basis of the rate constants determined for CA and CAE, it is likely that these species are reactive on atmospherically relevant time scales in the gas and aerosol phases, respectively. The results of the present study largely support a previous supposition that \(\alpha\)-pinene-derived secondary organic aerosol may be influenced by the multiphase processing of various intermediate species, including those with epoxide functionality.

INTRODUCTION
The atmospheric oxidation of biogenic volatile organic compounds (BVOCs) plays a significant role in the production of secondary organic aerosol (SOA), which impacts visibility, human health, and climate forcing. However, the SOA-forming potential of BVOCs remains uncertain: “bottom-up” calculations (using BVOC emission data and parametrized yields) seriously underestimate SOA concentrations in BVOC-dominated environments. It is also the case that the current chemical mechanisms (largely based on laboratory-generated SOA) do not account for the highly oxidized SOA often observed in the ambient atmosphere. These model discrepancies have significant negative implications for the accuracy of air quality and climate predictions. Global annual BVOC emissions are currently estimated to be about 1000 Tg/yr, with isoprene responsible for about 50% and monoterpenes comprising about 15% of the total emissions.

Because of its importance, isoprene-derived SOA has received intense study over the past decade. Because of the contributions of a large number of field and laboratory studies, it is now known that isoprene SOA formation is the result of a relatively complicated series of multigeneration gas phase oxidation events (i.e., the reactions of the products of the initial phase of isoprene oxidation itself) as well as aerosol phase chemical processing. For example, environmental chamber studies of isoprene oxidation under both low and high NO₃ conditions have demonstrated that the multigeneration gas phase oxidation chemistry is dependent on the levels of NO₃. Under low NO₃ conditions, a first generation hydroperoxide oxidation product has been shown to react with OH to form an epoxide (IEPOX), a known SOA precursor species, and to regenerate OH in high yields. Under high NO₃ conditions, the further oxidation of the first generation organonitrate products is an isomer-specific process that can lead to varying levels of NO₂ production (thus restarting the radical chain reaction that leads to tropospheric ozone production) as well as other potential SOA precursor products. Recent work has shown that epoxides and lactones can also be formed from multigeneration oxidation of the high NO₃ organonitrate products. The study of aerosol phase chemical processing of isoprene oxidation products has revealed that SOA properties such as water content, acidity, and inorganic ion content are likely to influence the nature of the chemical reactions which may occur on SOA. In particular, it has been shown that aerosol phase reactions of isoprene-derived epoxides are responsible for a number of species commonly observed on SOA: polyols, organosulfates, oligomers, and other species.

Of the monoterpenes, the SOA-forming ability of \(\alpha\)-pinene has received the most study. Autoxidation, a process by which a single initiating oxidizing reaction can lead to a chain of
Campholenic aldehyde epoxide (CAE) was synthesized by ozonolysis of α-pinene, as Hermann and co-workers have recently proposed that the aldehyde epoxide, as well as isomer-specific reaction products, are used to determine the aqueous reaction rate constant for campholenic aldehyde. In order to determine the OH + campholenic aldehyde rate constant, as well as to determine the details of the overall reaction in either the gas or aerosol phase, depending on their partitioning between the two phases and the kinetics of their potential reactions in the two phases. In particular, this scheme invokes the formation of two different gas phase epoxide precursors, α-pinene oxide and campholenic aldehyde epoxide, and a volatile intermediate, campholenic aldehyde, in order to rationalize the ultimate formation of several highly oxidized, low volatility SOA species. α-Pinene oxide itself has been observed in a number of studies of the oxidation of α-pinene by O3, OH, and NO3. α-Pinene oxide has also been shown to quickly react under neutral aqueous conditions and to produce campholenic aldehyde as a major product. Campholenic aldehyde is a well-known natural product, occurring as a major constituent of such oils as East Indian sandalwood and Valencia orange essence. Organonitrates derived from α-pinene have also been shown to form campholenic aldehyde in aerosol phase reactions. Therefore, previous work suggests a possible role for campholenic aldehyde in the multigeneration, multiphase oxidation of α-pinene, as well as its epoxide, campholenic aldehyde epoxide.

In the present research, two aspects of the proposed gas and aerosol phase mechanism described above are examined. Gas phase experiments, using the flow tube chemical ionization mass spectrometry (FT-CIMS) technique, are performed in order to determine the OH + campholenic aldehyde rate constant, as well as to determine the details of the overall oxidation mechanism. Solution phase experiments, using NMR as the analytical technique, are carried out in order to determine the aqueous reaction rate constant for campholenic aldehyde epoxide, as well as isomer-specific identification of the reaction products.

### EXPERIMENTAL SECTION

#### Synthesis Methods

Campholenic aldehyde (CA) was synthesized according to a previously reported procedure, and campholenic aldehyde epoxide (CAE) was synthesized by adapting a procedure previously described for the epoxidation of para-methoxystyrene. The details of the synthesis methods are reported in the Supporting Information. CA was synthesized to >90% purity (major impurity is likely isopinocamphone). CAE was synthesized to >90% purity (no single impurity was identified).

#### NMR Technique

The various chemical species were identified by using 1H, 13C, 2H−1H correlation spectroscopy (COSY), 13C distortionless enhancement by polarization transfer (DEPT), 1H−13C heteronuclear single-quantum correlation (HSQC), and 1H−13C heteronuclear multiple bond correlation (HMBC) techniques. All spectra were collected using a Varian 400 MHz NMR spectrometer using either or both CDCl3 and D2O solvents (Cambridge Isotope Lab, Inc.).

#### Gas Phase Oxidation Apparatus

The gas phase apparatus is shown in schematic form in Figure 1. The flow tube was operated in a similar fashion to a recent study of the OH reaction with isoprene-derived hydroxynitrates. The main flow tube was 100 cm in length and constructed of Pyrex tubing with 2.2 cm inner diameter. Bulk flow was generated using a large flow of O2 (99.9%, OE Meyer) carrier gas (approximately 15 STP L min−1) injected at the rear of the flow tube. Gases necessary to generate the OH radicals were injected via a side arm 20 cm in length and 1.25 cm inner diameter. Organic compounds were added by flowing helium gas through traps containing the liquid phase of the species, which were placed in temperature controlled water baths near room temperature. Because of the coincident low vapor pressures of the organic compounds and their large OH reaction rate constants, this method led to concentrations of reactants in the flow tube that were kinetically appropriate. The organic compounds entrained in helium gas flow were introduced through a moveable injector with a fan-shaped Teflon device placed at the end to enhance mixing as well as to allow the time of OH reaction to be varied in the flow tube. All gas flow rates were monitored using calibrated mass flow meters. The chemical ionization reagent ion source was placed between the flow tube and the mass spectrometer inlet. Pressure in the flow tube was controlled and varied by adjusting the valve opening of a 31 L s−1 large rotary roughing pump (Leybold, Pittsburgh, PA) located prior to the CIMS inlet. Most of the flow tube gases were removed by this pump, and pressure was monitored using a 0–1000 Torr capacitance manometer. Temperature was measured with Cu-
constant thermocouples and held at a constant 298 ± 2 K for all experiments. For experiments at 100 Torr, the residence time of OH radicals in the flow tube is about 200 ms (as calculated from the total flow rate, the inner diameter of the flow tube, and the length of the flow tube). Therefore, because the organic compounds were introduced downstream from the OH radical source via the moveable injector, the variable OH + organic compound contact times were less than 200 ms. Since the flow tube residence time scales directly with pressure, the residence times at other pressures can be calculated by reference to the 100 Torr residence time stated above. Because of the relatively short residence times, this flow tube approach allows for the observation of some slower reacting intermediate species, which is quite useful for the development of detailed oxidation mechanisms. On the other hand, because product yields are usually defined in terms of stable products, this aspect somewhat complicates the quantitative determination of such stable product yields.

**OH Source.** OH radicals were prepared with two different sources. For both methods, 99.999% helium (OE Meyer) was used to prepare gas mixtures and to drive the precursors quickly through the OH source region. Source 1 involved passing a mixture of carbon tetrafluoride (CF4) in helium through a microwave discharge produced by a Beenakker cavity (Opthos, Frederick, MD) operating at 50 W. The microwave discharge initiated dissociation of CF4 and formation of a fluorine radical reaction R1), which then reacted with water, which was introduced following the microwave discharge source (reaction R2). This leads to the production of OH radicals as follows:

\[ \text{CF}_4 + h\nu \rightarrow xF + \text{CF}_3 \]  
\[ \text{F} + \text{H}_2\text{O} \rightarrow \text{OH} + \text{HF} \]  
\[ \text{R1} \]
\[ \text{R2} \]

The CF4/He mixture was created by combining a 4% CF4 (99.9%, Sigma-Aldrich)/He mixture (0.50 STP mL min⁻¹) with a flow of He (5.0 STP L min⁻¹). H2O was added by flowing 12 STP mL min⁻¹ He through a trap filled with DI water. Source 2 involved passing a mixture of hydrogen (H2) in helium through a microwave discharge produced by aBeenakker cavity operating at 50 W. The microwave discharge initiated dissociation of H2 and the formation of hydrogen atoms reaction R3), which then reacted with NO2 which was introduced following the microwave discharge source (reaction R4). This leads to the production of OH radicals as follows:

\[ \text{H}_2 + h\nu \rightarrow \text{H} + \text{H} \]  
\[ \text{R3} \]

\[ \text{H} + \text{NO}_2 \rightarrow \text{OH} + \text{NO} \]  
\[ \text{R4} \]

The H2/He mixture was created by combining a 3% H2 (99.9%, Sigma-Aldrich)/He mixture (1.00 STP mL min⁻¹) with a flow of He (5.0 STP L min⁻¹). NO2 was introduced into the system by adding a flow of a 4% NO2 (99.5%, Sigma-Aldrich)/He mixture (1.00 STP mL min⁻¹) to a position in the side arm just downstream of the H atom source.

**Chemical Ionization Mass Spectrometry Detection Schemes.** The chemical ionization mass spectrometer, shown in schematic form in Figure 1, is a custom-built instrument (described in detail in Birdsall et al.1) that is based on a commercial dual-polarity quadrupole mass spectrometer (Balzers, Hudson, NH). Two different chemical ionization detection schemes were used. Method 1 involved the use of the proton transfer chemical ionization mass spectrometry (PTR-CIMS) technique, which usually results in the observation of several hydrated protonated ions following proton transfer from \( H^+(\text{H}_2\text{O})_n \) reagent ions:

\[ H^+(\text{H}_2\text{O})_n + M \rightarrow \text{MH}^+(\text{H}_2\text{O})_{n-m} + m(\text{H}_2\text{O}) \]  
\[ \text{R5} \]

H2O impurities in the O2 (99.8%, OE Meyer) that flowed (7.0 STP L min⁻¹) through the ionization source were sufficiently abundant to provide the source of hydrogen necessary for production of reagent ions in reaction R5. For all studies, ion abundances were normalized to the total ion reagent signal (\( H^+(\text{H}_2\text{O})_n \)) of the given study, and it was assumed that the proton transfer process was equally efficient for all detected compounds.

Method 2 involved the use of the iodide chemical ionization mass spectrometry (I-CIMS) technique, which results in the observation of a single ion due to reaction with the \( I^- \) reagent ion:

\[ I^- + M \rightarrow MI^- \]  
\[ \text{R6} \]

\( I^- \) was produced by combining a 1.0 STP mL min⁻¹ flow of a 10% CHI (99%, Sigma-Aldrich) /N2 (99.99%, OE Meyer) mixture with 7.0 STP of 99.99% N2, which was then passed through the ionization source. The chemical ionization reagent ion source included a commercial device (NRD, Grand Island, NY) that consisted of a hollow, cylindrical (69 × 12.7 mm) aluminum body with 10 mCi (3.7 × 10⁸ α particle disintegrations s⁻¹) of ²¹⁰Po coated on the interior walls.

**OH Oxidation Rate Constant Determination Method.** A relative rate constant method similar to a recent study reported by our laboratory12 was used to measure the CA + OH rate constant at 100 Torr pressure and 298 K. In this technique, CA and a competitor with a known rate constant were flowed together through the moveable injector and reacted with the OH radical in the flow tube. The concentrations of the competitors were varied from about 2 × 10¹¹ to 10 × 10¹¹ molecules cm⁻³. While the concentration of CA could not be determined directly, the flow rate through the CA trap was adjusted so that the PTR-CIMS signal was similar to that of the competitors; therefore the CA concentrations were probably also in the same range as those of the competitors. On the basis of previous work with OH Source 1,6 it is estimated that OH concentrations were probably on the order of 1 × 10¹¹ molecules cm⁻³. Assuming that the competitor and CA reacted only with OH radicals under the experimental conditions, the two compounds compete with each other for reaction with OH radicals:

\[ \text{CA} + \text{OH} \rightarrow \text{products} \]  
\[ \text{R7} \]

\[ \text{CA} + \text{OH} \rightarrow \text{products} \]  
\[ \text{R8} \]

The rate laws for CA and the competitor are given by eqs 1 and 2, respectively:

\[ \frac{d[\text{CA}]}{dt} = k_1[\text{CA}][\text{OH}] \]  
\[ \text{R7} \]

\[ \frac{d[\text{competitor}]}{dt} = k_2[\text{competitor}][\text{OH}] \]  
\[ \text{R8} \]

where \( k_1 \) and \( k_2 \) are rate constants for reactions R7 and R8 respectively. By dividing eq 1 by eq 2 and solving the resulting differential equation by separation of variables, it can be shown that
\[
\ln \frac{[CA]_{t,0}}{[CA]_{t,OH}} = \frac{k_s}{k_i} \ln \frac{[\text{competitor}]_{t,0}}{[\text{competitor}]_{t,OH}} 
\]

where \([CA]_{t,0}\) and \([\text{competitor}]_{t,0}\) are the concentrations of CA and the competitor species in the absence of OH radicals at time \(t\), and \([CA]_{t,OH}\) and \([\text{competitor}]_{t,OH}\) are the concentrations of CA and the competitor species in the presence of OH radicals at time \(t\). The relative depletions of CA and the competitor were monitored when the OH source was turned on and off. From the relative depletions, the CA OH radical rate constant \((k_i)\) was determined by plotting \(\ln([CA]_{t,0}/[CA]_{t,OH})\) vs \(\ln([\text{competitor}]_{t,0}/[\text{competitor}]_{t,OH})\) and determining the slope \((k_s/k_i)\). Because the competitor’s OH radical rate constant \((k_s)\) was known, a value for \(k_i\) was determined. The relative rate measurement does not require knowledge of the absolute concentrations of CA and competitor species (rather, relative concentrations—which are assumed to be proportional to the CIMS signal—are required), nor does it require knowledge of the absolute reaction time (which is a fixed quantity in eq 3). Both of these characteristics are important for the present experiments because the vapor pressure (which is needed to calculate the absolute concentrations in the flow tube) of CA is unknown, and the flow tube was operated in the laminar-turbulent flow transition region\(^{16}\) where a straightforward relationship between bulk flow velocity and molecular velocities does not exist (i.e., time of reaction was not known). By operating the flow system in this transition region, the reaction time was increased and more extensive loss of both CA and the competitor species was observed. Different reaction conditions were obtained by varying the time of reaction (injector distance), CA concentration and competitor concentration. CA and the competitors contained either carbonyl or hydroxyl groups (both of which are excellent proton transfer targets) and were detected using PTR-CIMS.

**OH Oxidation Product Study Methods.** In order to explore the mechanism of the OH reaction with CA, both PTR- and I-CIMS methods were used to investigate the reaction products formed. CA was added to the flow system and mass spectra were collected with the OH source on and off. The OH source was controlled by simply switching the applied voltage to the microwave generator on and off. Because of the short flow tube residence times, OH was removed from the system on the order of one second, which allowed the two mass spectra to be collected quickly one after the other. Comparison of these mass spectra revealed which masses corresponded to products of the OH reaction. These masses were quantitatively monitored with the OH source on and off in both low NO\(_x\) (no extra NO added) and high NO\(_x\) (NO added to \(>1 \times 10^{15}\) molecules cm\(^{-3}\)) conditions. NO was added as a 4% NO (98.5%, Sigma-Aldrich)/He mixture. In the low NO\(_x\) experiments, observed products are likely formed from peroxy + peroxy (including hydroperoxy formed from side reactions in the microwave OH radical source) radical interactions, while in the high NO\(_x\) experiments, product formation is most likely from peroxy + NO reactions. Assuming equivalent PTR-CIMS response factors (each of the inferred product species contains a carbonyl functional group and previous work has shown these species have similar PTR rate constants\(^{16}\)), the relative product ratios were determined by comparing the signal from one product to the sum of the product signals. Because of differences in the exothermicity of the PTR reaction for specific chemical compounds, the hydrate distribution of the detected MH\(^+(\text{H}_2\text{O})_n\) ions can help indicate the specific identity of a particular \(m/z\) carrier. For example, ketones have higher proton affinities than their isomeric aldehyde forms\(^{47}\), and are observed to have an ion distribution with fewer highly hydrated ions than aldehydes. Therefore, if standards are available, the hydrate distribution of the detected MH\(^+(\text{H}_2\text{O})_n\) ions can serve as a fingerprint for that particular molecular species in the PTR-CIMS spectrum of the oxidation system. Since I-CIMS methods have been shown to be selective for multifunctional species such as carboxylic acids\(^{48,49}\), I-CIMS spectra were also collected to aid in the association of particular oxidation products with the observed ions. While an authentic campholenic aldehyde epoxide standard was prepared for this study, cyclopentyl acetic acid (97%, Sigma-Aldrich) and glutaraldehyde (70% solution in \(\text{H}_2\text{O}\), Sigma-Aldrich) were used as proxy standards for the potential oxidation products campholenic acid and a ketoaldehyde product, respectively. As shown in Figure 1, standards were added directly to the end of the flow tube to prevent reaction with OH radicals. The pressure dependence of product formation was investigated by varying the pressure in the flow system from 50 to 250 Torr by adjusting the inlet to the roughing pump. Because of the pressure-dependent efficiency of the microwave discharge source, measurements could not be performed at pressures greater than 250 Torr. At the experimental pressures and time scales, it has also been shown that the flow tube acts as a nearly wall-less reactor\(^{46}\), which helps to ensure that the measured relative gas phase concentrations are representative of the true relative product yields. Nonetheless, the flow tube was also coated with halocarbon wax to further reduce gas–wall interactions and care was taken to ensure that product signals were fully equilibrated at each point in the measurement.

**Solution Phase Kinetics Methods.** Kinetics measurements of the aqueous phase reactions of CAE were made by collecting sequential \(^1\)H NMR spectra over the course of the experiment and measuring the loss of CAE. Each measurement was performed in the same manner: 10 \(\mu\)L of CAE was added to a 1 mL aliquot of the desired aqueous solution, and the solution was stirred in a 10 mL beaker. After approximately 1 min of stirring to ensure solution homogeneity, the entire reaction mixture was loaded into an NMR tube, and spectral collection was started. Experiments were performed using a pure \(\text{D}_2\text{O}\) (D 99.9%, Cambridge Isotopes) solution, DCIO\(_4\) (68% in \(\text{D}_2\text{O}\), 99% D, Sigma-Aldrich) solutions of differing acidities, and a solution consisting of 0.02 M D\(_2\)SO\(_4\) (96% in \(\text{D}_2\text{O}\), 99.5% D, Sigma-Aldrich)/1.0 M Na\(_2\)SO\(_4\). A first order decay rate law was found to fit the CAE concentration vs time data, and the first order rate constants were determined for each solution. From the DCIO\(_4\) solution data, the second order acid-catalyzed rate constant was also determined.

**RESULTS AND DISCUSSION**

**OH + Campholenic Aldehyde Rate Constant.** The OH rate constant for CA was obtained via competition experiments using OH generation Source 1 (Source 2 was not used due to its lower OH output). To assess the potential existence of systematic error, relative rate measurements for CA were performed using two competitors with varying, well-measured OH rate constants. The competitors used were allyl alcohol\(^{50–53}\) and 2-methyl-2-propen-1-ol\(^{54}\) with OH rate constants of 4.9 ± 0.1 \(\times 10^{-11}\) (determined from the precision-weighted average of the four literature constants and 9.2 ± 1.3 \(\times 10^{-11}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\), respectively. Using a

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previously described procedure the relative depletion for 2-methyl-2-propen-1-ol was normalized to the depletion of allyl alcohol, and all of the data were used to determine a single value for \( k_2/k_p \). The PTR-CIMS signals from the competitors and CA were monitored with the OH source on and off. The plot of \( \ln \left[ \frac{[\text{CA}]_{\text{OH}}}{[\text{CA}]_{\text{OH off}}} \right] \) vs \( \ln \left[ \frac{[\text{competitor}]_{\text{OH}}}{[\text{competitor}]_{\text{OH off}}} \right] \) is shown in Figure 2. The substantial uncertainty in each data point is due to the fact that relatively large concentrations of CA are needed to drive the OH reaction to occur on the time scale of residence time of the flow tube leading to a relatively small fractional change in the CA concentration and thus relatively low precision in each individual data point. The slope of the best fit line in Figure 2, 1.33 ± 0.11, is equal to the ratio of CA’s OH rate constant to allyl alcohol’s OH rate constant (\( k_2/k_p \)). From allyl alcohol’s weighted average OH rate constant, 4.9 ± 0.1 \( \times 10^{-11} \) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\), the CA + OH rate constant was determined to be 6.54 ± 0.52 \( \times 10^{-11} \) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) (one standard deviation error, which includes contributions from both the relative rate constant uncertainty in \( k_2/k_p \) and uncertainty in the absolute rate constant of allyl alcohol). To the best of our knowledge, this is the first measurement of the OH rate constant for CA. If the OH addition mechanism is assumed to be dominant for CA, OH rate constants similar to those for cyclopentene might be expected. Indeed, previous measurements of the rate constant for the OH + cyclopentene reaction fall in the range from 5.0 to 6.4 \( \times 10^{-11} \) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\), in quite good agreement with the presently determined value for the OH + CA rate constant. Because CA has a methyl group on one of the double bond carbon atoms, its OH rate constant might be more similar to 1-methylcyclohexene, which has been measured to be 9.8 \( \times 10^{-11} \) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\). In this comparison, the presently measured OH + CA rate constant is somewhat smaller than might be expected.

**OH + Campholenic Aldehyde Oxidation Product Identification.** As described in the experimental section, the first stage of the oxidation product identification involved comparing mass spectra taken with the microwave on and off, and then looking for new signals in the “OH source-on” PTR-CIMS spectrum. OH generation Sources 1 and 2 were both used, and it was determined that the product distribution did not depend on the OH source used. Because Source 1 was found to be a somewhat more intense source of OH radicals, all subsequent product studies were performed with this method. Since all of the postulated products contained aldehyde groups, they were all assumed to have equal PTR-CIMS response factors. This allowed direct comparison of the signals to determine the relative molar product yields.

Table 1 shows the relative molar product yields for each important PTR-CIMS signal carrier, as well as an inferred molecular formula and structure. The multiple \( m/z \) values listed for the individual postulated products are due to the existence of differentially hydrated protonated species, \( \text{MH}^+(\text{H}_2\text{O})_n \). In order to support the inferred molecular formulas and structures for the oxidation products of CA, I-CIMS studies were also performed and standards were used to help confirm the identification of the particular species. On the basis of the studies of the OH reactivity of other unsaturated aldehydes, both OH addition to the double bond and OH abstraction of the aldehydic proton may be operative oxidation pathways for CA. OH abstraction of alkenyl hydrogen atoms has also been observed in systems such as cis-2-butene at high temperature. However, Sun and Law have estimated that this mechanism accounts for less than 1% of total OH reaction at 300 K. Therefore, we consider only OH addition and OH abstraction of the aldehydic proton as likely mechanisms for CA oxidation.

Figure 3 shows the proposed oxidation mechanism for CA, with the OH addition pathway shown at top and right and the OH abstraction mechanism shown at left and bottom on the diagram. The experimentally detected species are shown in boxes, along with their molecular formulas, molecular masses, and PTR-CIMS and/or I-CIMS \( m/z \) carriers. In some cases, background signal interference (due to small signals arising from higher order cluster ions of the precursor reactants, a particular problem with the PTR-CIMS method) can make it difficult to distinguish the difference between OH source on

![Figure 2. Relative rate comparison for the measurement of the OH + campholenic aldehyde reaction at 100 Torr with allyl alcohol and 2-methyl-2-propen-1-ol competitors.](Image)

<table>
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<tr>
<th>( m/z )</th>
<th>Relative Molar Yield (%)</th>
<th>Total Molar Yield (%)</th>
<th>Proposed Molecular Formula</th>
<th>Proposed Structure</th>
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and off conditions. For example, both the addition channel hydroxy peroxy radical and its corresponding nitrate product (from NO reaction), were definitively detected with I-CIMS, but not with PTR-CIMS due to such background signal issues, despite the fact that PTR-CIMS should be sensitive to these species.

For the abstraction pathway, both the C10 peroxy radical and the C9 peroxy radical (which forms after a decarboxylation step) would produce m/z signals consistent with those observed with PTR-CIMS methods, as well as m/z signals consistent with the stable final oxidation product, the C9-aldehyde. According to the relative molar yields given in Table 1, the abstraction pathway accounts for 9% of the OH reactivity.
toward CA at 100 Torr. For the addition pathway, the expected C10 hydroxy peroxy radical is observed at a consistent I-CIMS m/z value, and the expected stable final oxidation product produced from the eventual scission of the C–C bond, the C10-ketodialdehyde, was also consistent with observed PTR-CIMS and I-CIMS signals. Because the relatively new literature concerning I-CIMS detection methods does not address the sensitivity of the method to nonacid carbonyl compounds, glutaraldehyde was chosen as a proxy standard for the C10-ketodialdehyde postulated product. While the I-CIMS method was found to have no detectable sensitivity toward the monoaldehyde, CA, the sensitivity was found to be much higher toward the dialdehyde, glutaraldehyde, thus lending support for the association of the I-CIMS 311 m/z carrier to the C10-ketodialdehyde product. According to the relative molar yields given in Table 1, the C10-ketodialdehyde forming pathways accounts for 42% of the OH reactivity toward CA.

A third major oxidation product, postulated to have a molecular formula of C10H16O2 based on PTR-CIMS signals, was found to have a 100 Torr relative molar yield of 26%. Two possible product species were considered as the origin of the PTR-CIMS signals: campholic acid and campholenic aldehyde epoxide (CAE). The OH oxidation of aldehydes can sometimes lead to carboxylic acids through the reaction of the abstraction channel-related peroxy radical with \( \text{HO}_2 \). In order to investigate this possibility, cyclopentyl acetic acid (CPAA) was used as a proxy standard for testing the likelihood of CIMS detection of a campholic acid product. As discussed in the introduction, CAE has been invoked as an intermediate species that may rationalize the existence of certain species in \( \alpha \)-pinene-derived SOA. An authentic CAE sample was prepared to act as a standard for CIMS testing purposes. Figure 4 shows the PTR-CIMS ion distribution pattern for the CPAA, CA, and CAE standards. While the CA and CAE standards showed a similar ion distribution pattern, as would be expected for two species undergoing ionization at the aldehyde group, the CPAA ion distribution was very different, with significant ion abundances at the dehydrated ion \( (M - 17) \), as well as higher hydrates \( (M + 37 \) and \( M + 55 \)). Since the ion distribution for the \( m/z \) 169 and 187-inferred product shown in Table 1 is more typical of an aldehyde ion distribution and does not match the carboxylic acid ion distribution, this data seems to rule out campholic acid as the origin of the \( m/z \) 169 and 187 signals. Furthermore, the \( M + 1 \) to \( M + 19 \) ratio \( (\sim 5:1) \) for the CAE standard in Figure 4 matches the \( m/z \) 169 to \( m/z \) 187 ratio \( (\sim 5:1) \) in Table 1 fairly well. In addition, I-CIMS methods did not detect a C10H16O2-related species, while I-CIMS methods were able to detect the campholic acid proxy CPAA with relatively high sensitivity. The lack of I-CIMS detection is also consistent with CAE as an oxidation product, as the CAE standard was also not detected with I-CIMS methods. Oxygen-containing impurities in the CF4/He and H2/He mixtures used to produce OH could potentially lead to O(3P) radicals, which are known to produce epoxides in high yields from reactions with alkenes. However, the use of O2 as the carrier gas ensures that any O(3P) radicals will be instantaneously converted to O3 before any contact with the CA-containing injector tube flow. Therefore, the PTR-CIMS signals at \( m/z \) 169 and 187 are assigned to CAE and a proposed mechanism for CAE formation is given in Figure 3. Two other PTR-CIMS signals were observed at greater than 5% molar relative yield: a \( m/z \) 167 signal, which was attributed to a C10H15O2 product and a \( m/z \) 183 signal, which was attributed to a C10H14O3 product. The fact that a large majority of the total products likely result from the OH addition pathway is consistent with the observation that the OH + CA rate constant is very similar to the OH + cyclopentene rate constant, which also suggests a relatively minor role for the abstraction channel.

**Pressure Dependence Results.** The pressure-dependent relative molar product yields are given in Figure 5 where the bars represent the one standard deviation error resulting from the averaging of at least 5 individual trials. The abstraction channel product yields of the C9-aldehyde \( (m/z \ 139 + 157 + 175) \), were observed to be relatively constant from 50 to 200 Torr. Because of complications at higher operating pressure, the background signals at 250 Torr prevented a reliable measurement of the C9-aldehyde product yield; therefore, the 200 Torr value was used in the calculation of the relative molar yields at 250 Torr. From 50 to 150 Torr, the CAE \( (m/z \ 169 + 187) \)
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187) yields were observed to decrease and the C10-ketodialdehyde (m/z 185 + 203) yields were observed to increase; above 150 Torr both yields remained relatively constant.

The pressure-dependent product yield behavior was modeled with a Lindemann–Hinshelwood type mechanism (i.e., an energized peroxy radical adduct is the key species, which can revert to reactants, be de-energized by collision, or go on to form products):

$$\text{CA} + \text{OH} + \text{O}_2 \rightarrow \text{CA} + \text{OH} + \text{O}_2^*$$  \hspace{1cm} \text{(R9)}
$$\text{CA} + \text{OH} + \text{O}_2 \rightarrow \text{CA}^* + \text{H}_2\text{O}_2$$  \hspace{1cm} \text{(R10)}
$$\text{CA} + \text{OH} + \text{O}_2 + \text{M} \rightarrow \text{CA} + \text{OH}^* + \text{M}$$  \hspace{1cm} \text{(R11)}
$$\text{CA} + \text{OH} + \text{O}_2 \rightarrow \text{CAE} + \text{HO}_2$$  \hspace{1cm} \text{(R12)}
$$\text{CA} + \text{OH} + \text{O}_2 \rightarrow \text{C10-ketodialdehyde}$$  \hspace{1cm} \text{(R13)}

where (•) represents an energized species. Because reaction R11 is dependent on the number of total gas molecules present (i.e., pressure), and the rate of CAE formation was observed to decrease at higher pressures, it was assumed that CAE was formed from the CA–OH–O2• activated complex. Thus, the addition channel branching point in Figure 6 can be more accurately represented by the two competing reactions, reactions R11 and R12. The pressure-dependent rates of formation can then be defined as follows:

$$\frac{d[\text{C10-ketodialdehyde}]}{dt} = k_{11}[\text{CA} + \text{OH} + \text{O}_2]^*$$  \hspace{1cm} \text{(4)}
$$\frac{d[\text{CAE}]}{dt} = k_{12}[\text{CA} + \text{OH} + \text{O}_2]^*$$  \hspace{1cm} \text{(5)}

where $k_{11}$ and $k_{12}$ are the rate constants of reactions R11 and R12, respectively. Combining these two expressions yields an equation for the rate of total product (TP) formation:

$$\frac{d[\text{TP}]}{dt} = k_{11}[\text{CA} + \text{OH} + \text{O}_2]^* + k_{12}[\text{CA} + \text{OH} + \text{O}_2]^*$$  \hspace{1cm} \text{(6)}

The relative yield of CAE can then be expressed as the CAE rate of formation \text{(eq 5)} over the total product rate of formation \text{(eq 6)}:

$$\frac{d[\text{CAE}]}{d[\text{TP}]} = \frac{\frac{d[\text{CAE}]}{dt}}{\frac{d[\text{TP}]}{dt}} = \frac{k_{11}[\text{CA} + \text{OH} + \text{O}_2]^*}{k_{12}[\text{CA} + \text{OH} + \text{O}_2]^*}$$

Taking the reciprocal of eq 7 yields an expression that is linearly dependent on [M] (and thus pressure):

$$\frac{d[\text{TP}]}{d[\text{CAE}]} = \frac{k_{12} + k_{11}[\text{M}]}{k_{12} + k_{11}[\text{M}] \times \frac{1}{k_{12}}}$$  \hspace{1cm} \text{(8)}

The inverse of the relative yield of CAE vs pressure is plotted in Figure 6. From this plot, it is apparent that the experimental data from 50 to 150 Torr fit the derived Lindemann–Hinshelwood model linear relationship, but the data above 150 Torr do not. The equation for the best fit line to the 50 to 150 Torr data in Figure 6 was determined to be $[(1.58 \pm 0.34) \times 10^{-2}] P \text{ (torr)} + (2.41 \pm 0.36)$. Note that the fitted intercept is not consistent (within the 95% confidence interval) with the theoretical value of 1 given in eq 8, which could be indicative of the inadequacy of the model. When the model intercept is fixed at unity, the best fit slope is $[(2.79 \pm 0.33) \times 10^{-2}]$. If the Lindemann–Hinshelwood model is used to extrapolate the 50–150 Torr experimental data to atmospheric pressure, yields of 7% (intercept = 2.41) and 5% (intercept = unity) at atmosphere pressure are predicted. In previous work on the OH-initiated oxidation of organonitrates derived from isoprene, a similar epoxide + HO2-forming product channel that also showed Lindemann–Hinshelwood pressure-dependent behavior was reported. However, the experimental data seem to indicate that the CAE yield plateaus at about 20% above 150 Torr. Therefore, the experimental data from 150 to 250 Torr suggest that 20% is a reasonable empirical estimate of the atmospheric pressure CAE yield, but this behavior cannot be directly explained from the proposed activated mechanism given here. Therefore, the predicted atmospheric pressure CAE yield is somewhat uncertain and is best reported as likely falling in the range from 5% to 20%.

While a full quantum chemical exploration of the mechanism of the OH-initiated oxidation of campholenic aldehyde is beyond the scope of this work, G2MS-level calculations (the method is described in the Supporting Information) were carried out to confirm that the proposed CAE + HO2-producing channel is thermodynamically feasible. In particular, the energies of CA, OH, O2, the CA–OH adduct, the CA–OH–O2 peroxy radical, CAE, and HO2 were calculated to allow an estimate of the energetics of the proposed oxidation steps. The CA–OH adduct was found to be $-27 \text{ kcal/mol}$ (relative to the reactants CA + OH) and the CAE + HO2 products were found to be $-34 \text{ kcal/mol}$ (relative to the reactants CA + OH + O2). Therefore, if the CA–OH adduct undergoes O2 addition and the resulting peroxy radical remains energized, it is thermodynamically feasible to proceed to the CAE + HO2 products. The stabilized CA–OH–O2 peroxy radical was estimated to be $-55 \text{ kcal/mol}$ (relative to the reactants CA + OH + O2), which confirms that it is not thermodynamically

Figure 6. Lindemann–Hinshelwood mechanism analysis of pressure dependent m/z 169 + 187 (CAE) product yield.
RO2 + H2O reactions can be driven to stable products. The NO radical intermediates that had not reacted via RO2 + RO2 or however, by adding NO to the oxidation system, the peroxy methods due to background issues in the PTR-CIMS method. particularly those that could only be detected by I-CIMS way to estimate the concentration of the peroxy radical species, need to more thoroughly assess the potential oxidation mechanisms.

**NO Dependence Results.** As noted in the Experimental Section, one advantage of the present flow tube technique is the ability to observe intermediate species. However, if the intermediate species are present at comparable concentrations to that of the stable products, the stable product yields will be underestimated. Unfortunately, there is not a straightforward way to estimate the concentration of the peroxy radical species, particularly those that could only be detected by I-CIMS methods due to background issues in the PTR-CIMS method. However, by adding NO to the oxidation system, the peroxy radical intermediates that had not reacted via RO2 + RO2 or RO2 + HO2 reactions can be driven to stable products. The NO dependence of the calculated relative product yields C10−ketodialdehyde (m/z 185 + 203) and CAE (m/z 169 + 187) are plotted in Figure 7. From these data it is clear that the addition of NO leads to larger C10−ketodialdehyde yields, while the CAE yields decrease. Therefore, we conclude that, in the absence of NO, some amount of oxidized CA is in the form of the stabilized hydroxyperoxy radical intermediate, and that NO drives this species exclusively to the C10−ketodialdehyde final product, thus increasing the relative yield of this product and decreasing the yield of the CAE product. Thus, the experimental NO dependence of the product yields is consistent with CAE/C10−ketodialdehyde branching aspect of the overall CA oxidation mechanism given in Figure 3. Since the overall relative yields do not change substantially with NO addition, we can conclude the relative amount of the stabilized hydroxyperoxy intermediate is small compared to the amounts of the C10-ketodialdehyde and the CAE products formed under NO-free conditions. The addition of NO to the oxidation system also led to the formation of two new species. Figure 3 indicates that new PTR-CIMS signals at m/z 186 and 204 were associated with a C9 nitrate product forming via the abstraction channel and a new I-CIMS signal at m/z 358 was associated with a C10 nitrate product forming via the addition channel. The hydroxyperoxy radical associated with the addition channel detected by I-CIMS at m/z 328 is observed to decrease with increasing NO. Because the two organonitrate species were not quantified, the relative yields given in Figure 7 are probably somewhat overestimated. Future work involving the measurement of peroxy + NO rate constants and the nitrate branching ratios for these processes are planned in order to estimate the yields for these reactions.

**Solution Phase Reaction Kinetics for Campholenic Aldehyde Epoxide.** The complete NMR assignments for CAE and its reaction products are provided in the Supporting Information. From a comparison of CAE NMR spectra collected in CDCl3 and D2O, it was apparent that a kinetically fast (i.e., too fast to be observed with the present kinetics technique) equilibrium process was established in water solvent wherein both CAE and a form of CAE for which the aldehyde group had undergone nucleophilic addition of water were present. As the NMR assignments in the Supporting Information show, the hydrated aldehyde group was identified by new 1H and 13C peaks at 5.00 and 91.5 ppm in water solvent that were not present in the chloroform solvent spectra. Using 1H and 13C peak integration ratios, it was determined the equilibrium constant for the aldehyde group hydration of CAE was 1.0.

Further monitoring of CAE in D2O revealed a much slower epoxide ring-opening reaction (kneutral = (2.241 ± 0.036) x 10^-5 s^-1) that resulted in two major products: an isomer of CAE and the aldehyde group hydrated form of this CAE isomer (Keq = 1.8 for this equilibrium process). The Supporting Information gives the full NMR assignments for the observed products, and Figure 8 shows the overall mechanism that rationalizes the observation of all species observed in water solvent. Several multibond correlation NMR experiments (GCOs, GHSMC, and GHMBN) were used to definitively identify the structures of the species. As Figure 8 indicates, the epoxide ring-opening reaction is an unusual isomerization reaction (more typically, epoxide ring-opening reactions in water solvent involve nucleophile addition of water which includes methyl group migration. However, methyl group migrations are not uncommon for reactions which involve carbonation intermediates. Other reaction products, estimated to be at least a factor of...
of 5 less abundant than the major products, could not be definitively identified. The CAE reaction in DCIO₄ solutions was also investigated, and it was found that while the major products formed did not change as compared to reactions in water solvent, the rate of the reaction was determined to be first order in the DCIO₄ concentration. The second order acid-catalyzed rate constant was determined to be $k_{\text{acid}} = 0.0989 \pm 0.0053 \text{ M}^{-1} \text{ s}^{-1}$. In order to investigate the possibility of nucloephilic addition of sulfate to CAE, the CAE reaction in 0.02 M D₂SO₄/1.0 M Na₂SO₄ solution was studied, but no new products were identified.

Previous work has explored aqueous solution reactions for simple epoxides, as well as epoxides that result from the photooxidation of isoprene (IEPOX) and α-pinene (α-PO). Both simple epoxides and IEPOX require acid catalyzed conditions for ring-opening reactions and nucloephilic addition products are exclusively observed. CAE appears to be more similar in reactivity to α-PO, which also undergoes ring-opening reactions under neutral conditions (presumably due to a general acid catalysis mechanism) and is also observed to produce isomerization products. However, the lifetime for α-PO reactions under neutral conditions is less than 5 min, while the lifetime for CAE reaction under the same conditions is 13 h. Furthermore, in addition to isomerization products, α-PO has also been shown to undergo nucloephilic addition of both water and sulfate. In the previous study of α-PO, it was postulated that the relief of the 4 atom ring strain in α-pinene backbone led to mechanisms which rationalized the variety of products formed. By comparison, CAE is characterized by a stable five atom ring, which is apparently unmodified in the mechanism for the formation of the isomerization products. Therefore, the isomerization reactions of α-PO and CAE may be more reasonably rationalized by the types of carbocation intermediates that may form (and isomerize) as compared to those possible for simple epoxides and IEPOX. In their previous work, Kahnt et al. detected an isomer of CAE in the particle phase of CA ozonolysis experiments and deduced an isomerization process during which the epoxide ring opened, a double bond was restored to its original position in CA, and an OH group resulted at the secondary carbon that was part of the epoxide ring in CAE. Figure 8 shows that the CAE isomerization reaction studied in this work actually results in a somewhat different isomer than that proposed by Kahnt et al.

**Atmospheric Implications.** Like most alkenes, CA was found to react quickly with OH (for an average OH concentration of $1 \times 10^9$ molecules cm$^{-3}$, the CA lifetime is only 4.3 h) and is therefore expected to be photochemically active on an atmospherically relevant time scale. The major CA OH addition pathway oxidation product, the C10 ketodialdehyde, is consistent with the observation that many cycloalkanes have been found to undergo C=C bond scission at the double bond site to form dicarbonyl products, and the finding that both OH addition and abstraction (forming the C9 aldehyde) pathways are operative is consistent with previous work for unsaturated aldehydes. The EPA’s prediction tool, EPIS-UITE, was used to predict the vapor pressures of the C9 aldehyde ($9 \times 10^{-4}$ bar) and the C10 ketodialdehyde ($9 \times 10^{-6}$ bar). Using the low volatility organic compound (LVOC) cutoff value of $1 \times 10^{-10}$ bar for compounds likely to be found in the aerosol phase, it appears that neither of these compounds is likely to play a significant role in SOA formation, as both of these species are much too volatile to condense and also probably possess too small Henry’s law coefficients for efficient dissolution in aerosols with high water content. However, the potential for a significant yield of the epoxide CAE under atmospheric conditions indicates that CA oxidation could influence SOA formation along the lines of the mechanism originally proposed by Kahnt et al. While CAE does not react as quickly as α-pinene oxide, its neutral aqueous solution lifetime (13 h) is nonetheless on the order of SOA lifetimes. In addition, because the CAE isomerization reaction is also acid-catalyzed, lower pH aerosol conditions will result in faster reaction. For example, at pH = 0, the predicted CAE lifetime is only 10 s. Therefore, the present work largely confirms the viability of the Kahnt et al. mechanism, which posits that α-pinene-derived SOA can be affected by multiphase chemical processing of various intermediate species, some of which have epoxide functionality and correspondingly facile reactivity in high water content aerosol environments. Figure 9 depicts the postulated mechanism by which α-pinene may undergo multiple gas and aerosol phase reactions to form an aerosol phase compound observed by Kahnt et al.

![Figure 9. Postulated multiphase α-pinene-derived SOA constituent reaction pathway.](image-url)

**CONCLUSION**

The rate constant for the OH reaction with campholenic aldehyde (CA) was measured using the flow tube-chemical ionization mass spectrometry method with a relative rate kinetics technique and was found to be $6.54 \pm 0.52 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 100 Torr pressure and 298 K. A mechanism for the formation of the observed products was developed for both NO-free and NO-present conditions. On the basis of measurements of the pressure dependent yields of the products, between 5 and 20% of the CA oxidation at atmospheric pressure is predicted to lead to campholenic aldehyde epoxide (CAE). The aqueous solution reaction rate constants for CAE were determined via NMR spectroscopy and were found to be $(2.241 \pm 0.036) \times 10^{-18}$ s$^{-1}$ for neutral conditions and $0.0989 \pm 0.0053 \text{ M}^{-1} \text{ s}^{-1}$ for acid-catalyzed conditions at 298 K. The products of the CAE aqueous solution reaction were identified to be an isomer of CAE and the aldehyde group hydrated form of this isomer. Unlike the isoprene-derived epoxide, IEPOX, a nucloephilic addition mechanism was not observed. On the basis of the rate constants determined for CA and CAE, it is likely that these species are reactive on atmospherically relevant time scales in the gas and aerosol phases, respectively. The results of the present study largely support a previous supposition that α-pinene-derived SOA may be influenced by the multiphase...
processing of various intermediate species, including those with epoxide functionality.

**ASSOCIATED CONTENT**

- **Supporting Information**
  The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.6b08642.

  Synthetic methods and NMR assignments for several chemical species and quantum chemical methods (PDF)

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**Notes**

The authors declare no competing financial interest.

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