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Direct Measurements and Kinetic Studies of Reaction Intermediates in the Ozonolysis of Alkenes Using Cavity Ring-Down Spectroscopy

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Campos-Pineda, Mixtli

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Direct Measurements and Kinetic Studies of Reaction Intermediates in the Ozonolysis of Alkenes Using Cavity Ring-Down Spectroscopy

A Dissertation submitted in partial satisfaction of the requirements for the degree of

Doctor of Philosophy

in

Chemistry

by

Mixtli Campos-Pineda

December 2017

Dissertation Committee:
Dr. Jingsong Zhang, Chairperson
Dr. Yadong Yin
Dr. Christopher Bardeen
The Dissertation of Mixtli Campos-Pineda is approved:

Committee Chairperson

University of California, Riverside
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ABSTRACT OF THE DISSERTATION

Direct Measurements and Kinetic Studies of Reaction Intermediates in the Ozonolysis of Alkenes Using Cavity Ring-Down Spectroscopy

by

Mixtli Campos-Pineda

Doctor of Philosophy, Graduate Program in Chemistry
University of California, Riverside, December 2017
Dr. Jingsong Zhang, Chairperson

As our understanding of the different physical and chemical aspects of tropospheric processes increases, complex reaction mechanisms are developed and tested in local, regional, and global atmospheric models. These complex mechanisms give rise to nonlinear dynamical processes that depend not only on the additive effects of the reactions that comprise them. In addition to studying kinetics of elementary reactions and unimolecular processes, it is necessary to study mechanisms as a whole. This work utilizes a flow reactor and cavity ring-down spectroscopy (CRDS) to study the mechanism of ozonolysis of various alkenes in real time. The use of a flow reactor as a cavity for CRDS measurements allows the simulation of concentration profiles of analytes at different reactor segments by modelling the plug-flow behaviour as a series of continuously-stirred tank reactors (CSTRs). Experimental measurements are used to validate ozonolysis mechanisms used for these simulations. Informed by kinetic modelling, direct measurements of formaldehyde oxide (CH$_2$OO) produced in situ from ozonolysis of ethene and direct measurements of vinoxy radicals (·CH$_2$CHO) from
ozonolysis of 2-butenes are carried out under various reaction conditions. New insights on the mechanisms of ozonolysis of ethene and 2-butenes are obtained by comparing measurements of these reaction intermediates and formaldehyde with simulations from mechanisms containing current kinetic information of elementary reactions, pointing out to the importance of existing and new reaction pathways. Yields of the fraction of stabilized carbonyl oxides produced from ozonolysis of several alkenes are also measured at low pressures, and nascent yields are determined by extrapolation to the zero-pressure limit, providing benchmarks for theoretical and master equation calculations.
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1 Introduction

1.1 Chemistry of the troposphere

The troposphere is the lowest layer of the atmosphere and comprises the first 10 – 15 km from the Earth’s surface.\(^1\) In this region, rapid heat transfer from the surface and rotational mixing play an important role, producing most of the meteorological phenomena observed as weather. Anthropogenic and biogenic emissions of both reactive and relatively inert species then mix in the nitrogen and oxygen rich troposphere and lead to a plethora of chemical reactions, turning the troposphere into a giant chemical reactor. Furthermore, emission of particles along with gas-phase compounds and aerosols add to the complexity of the chemical system, as heterogeneous reactions become available. In a similar manner, convective and laminar flows, as well as diffusion, result in different mixing regimes and add more dimensions to the reaction kinetics in the gas-phase.

Tropospheric chemistry depends on mixing and transport, and species with different lifetimes will react in different stages in the troposphere or, in the case of compounds with long lifetimes such as CFCs, outside of it. A significant part of tropospheric chemistry involves, then, transient species that produce more stable compounds via different chemical processes.\(^2,3\) A great amount of research has provided information of these reactions.\(^4,5\) Studies describing primary pollutant emissions, transport, health effects, and concentrations of species in the clean and polluted atmosphere have improved our understanding of the troposphere at the local, regional,
and global scales. Chemical processes have been described historically by two different pollution regimes: particle and aerosol driven (“London” smog) and photochemically driven (“Los Angeles” smog). While these two regimes occur to different degrees in a given location, these two historical examples represent two distinct aspects of tropospheric chemistry. The “London” smog scenario, so called due to the heavy smog observed in the mornings in places with heavy industry and first studied in London in the seventeenth century, involves particle phase chemistry of black and brown carbon (e.g. soot), as well as acidic aerosols and sulfur dioxide. On the other hand, “Los Angeles” smog refers to a phenomenon first studied in the Los Angeles area in the late 1940s, where pollution occurred under high actinic flux conditions and high daily temperatures. The cause of this pollution was attributed to photochemistry of volatile organic compounds (VOCs) and oxides of nitrogen (NOx), producing ozone and several of the species now recognized as indicators of tropospheric pollution: CO, NO2, HCHO, HCOOH, HNO3, OH radicals, etc. The importance of VOC chemistry was shown, and a big part of the field of atmospheric chemistry is now dedicated to understanding the different chemical processes involving volatile organic compounds. Oxidation is an important depletion pathway and is done by species such as OH radicals, organic radicals (RO2·, ·CH2CHO, etc.), NO3, and O3. In addition, species that produce these oxidants (such as HO2·) also affect this depletion process. In the case of alkenes, oxidation is one of the main depletion pathways in the troposphere and ozonolysis is one of the main oxidation process for alkenes.
1.2 Ozonolysis of alkenes

In the troposphere, ozonolysis of alkenes is of particular importance for several reasons: it provides a depletion pathway for unsaturated VOCs that does not require sunlight, produces OH radical in significant amounts, produces oxidized organic compounds, which can be further oxidized to form highly oxidized molecules (HOMs) and ultimately produce secondary organic aerosol (SOA).\textsuperscript{13–15} While, the rate of ozonolysis can vary greatly depending on the alkene, with rate constants spanning a range of order of magnitude from $1.6 \times 10^{-18}$ cm$^3$/molecule$\cdot$s in the case of ethene to $1.1 \times 10^{-15}$ cm$^3$/molecule$\cdot$s for 2,3-dimethyl-2-butene, some biogenic and anthropogenic olefins are produced in significant quantities and have relatively fast rate constants, as is the case for α-pinene, β-pinene, and isoprene, which have rate constants of $8.5 \times 10^{-17}$ cm$^3$/molecule$\cdot$s, $1.6 \times 10^{-17}$ cm$^3$/molecule$\cdot$s, and $1.4 \times 10^{-17}$ cm$^3$/molecule$\cdot$s, respectively.\textsuperscript{3,4,16} The mechanism of ozonolysis, first proposed in the liquid phase by Rudolf Criegee,\textsuperscript{17} involves the 1,3-dipolar cycloaddition of ozone to the olefinic bond in order to create a trioxolane, also known as primary ozonide (POZ).\textsuperscript{18} The ozonolysis reactions is very exothermic and the POZ is formed with high internal energy and will break into carbonyl and a carbonyl oxide product.\textsuperscript{15,18–21} It has been theoretically shown that, for some alkenes, the POZ can be formed with different geometries, each one with different energies and with different energy barriers, leading to different energy distribution and branching ratios of the products.\textsuperscript{22} If the olefin is endocyclic, the scission of the POZ will lead with a highly energetic molecule with carbonyl and carbonyl oxide groups, the high internal energy resulting in extremely low lifetimes and virtually no collisional stabilization.\textsuperscript{23} For
acyclic or exocyclic olefins, the scission of the POZ leads to a distribution of the internal energy between the carbonyl and the carbonyl oxide and, whereas the carbonyl is relatively stable in the troposphere, the broad energy distribution of the carbonyl oxide will allow it to undergo several processes.\textsuperscript{19,24} Carbonyl oxides, also known as Criegee intermediates (CIs), with internal energies above or near the barrier for decomposition or isomerization, will rapidly undergo these unimolecular processes and, thus, have short lifetime in the troposphere.\textsuperscript{21} These are known as “hot” or “excited” CIs and will ultimate produce several radicals, such as \textit{\textbullet}OH, and different carbonyls with high internal energies (e.g. “hot” HCOOH).\textsuperscript{19,25–27} CIs produced with internal energies below the barrier for decomposition or isomerization, will have long enough lifetimes in the troposphere to also participate in bimolecular reactions, they are known as “stabilized” Criegee intermediates (sCIs). These sCIs will oxidize species in the atmosphere and produce NO$_3$, SO$_3$, carbonyls, as well as secondary ozonides (SOZs), which are trioxolanes formed by the addition of the carbonyl oxide to a carbonyl group.\textsuperscript{28–32} These SOZs can decompose and form other carbonyls, break into a single HOM, or form clusters and grow into SOAs.\textsuperscript{25,33,34}

1.3 Criegee intermediates

Given that the carbonyl coproducts are relatively stable, the importance of the ozonolysis reaction lies in the fate of the Criegee intermediates. CIs have been the subject of a significant amount of studies, the first regarding its structure.\textsuperscript{19,20} Originally believed to behave as a biradical, it is now understood that it has significant zwitterionic
character. Several groups have studied the energetics and geometries of the van der Waals adduct, the transition state, and the POZ formed from the 1,3 dipolar cycloaddition of ozone to the double bond. Rathman et al. showed that certain alkenes will form more than one POZ conformer, with different energies and different barriers for decomposition. Furthermore, the calculation of these energies provides information regarding the total energy to be distributed between the carbonyl and the carbonyl oxide, and work by Olzmann et al., Kroll et al., and others use this energy information in a master equation to calculate the branching ratio between “hot” and “stabilized” CI. Some experimental work on determination of these branching ratios has been done for alkenes such as, 2,3-dimethyl-2-butene, ethene, and trans-2-butene by doing zero-pressure extrapolation of sCI yield data for pressures ranging from 100 – 1000 Torr. Ambient pressure yields of sClIs provides important mechanistic information regarding the fraction of CI produced by ozonolysis that can undergo bimolecular reactions.

Ozonolysis of symmetric alkenes will only produce one species of carbonyl oxide. For example, ethene ozonolysis will only produce formaldehyde oxide (CH$_2$OO). If the alkene is asymmetric, more than one species of carbonyl oxide will be produced. Propene ozonolysis, as an example, will produce both formaldehyde and acetaldehyde oxide. Furthermore, CIs that have $\alpha$-hydrogens can isomerize into vinylhydroperoxide (VHP) by hydrogen migration into the negative oxygen, which will most likely decompose into a vinoxy radical and OH. If the CI formed also has hydrogen bonded to the carbonyl groups (e.g. CH$_3$CHOO), it can exist in syn or anti conformations. Syn
conformers have the negative oxygen on the same side as the α-hydrogen, while anti conformers have it on the opposite side. The syn-CIs will isomerize into VHP and decompose to vinoxy radical and OH, while the anti-CIs will have other decomposition processes, such as isomerization into dioxirane and “hot” acid, with subsequent decomposition into reactive fragments.\textsuperscript{38,42,44} It has been shown that the interconversion barrier for syn and anti conformers prevent isomerization of syn-CI into anti-CI and vice-versa.\textsuperscript{38,45} Therefore, these two conformers undergo distinct unimolecular processes that result in different products, and information on their branching ratios is valuable.\textsuperscript{22,44} The syn-CI conformers have received particular attention in the literature because they undergo isomerization into VHP and decomposition into a vinoxy radical, which is highly reactive with oxygen and produces carbonyl, bicarbonyl, HOMs, and additional \textsuperscript{-OH}.\textsuperscript{26,43,46,47} For example, the simplest species of vinoxy radicals, \textsuperscript{-CH\textsubscript{2}CHO}, can produce OH radicals as well as HOOCHCHO, glyoxal, and formaldehyde.\textsuperscript{48,49} On the other hand, the anti-CI conformer has fewer decomposition channels, and there is some work suggesting that isomerization to dioxirane is the main decomposition pathway for anti-CI conformers.\textsuperscript{38,44,50} The high internal energy of the CI allows it to undergo conversion into a “hot” acid that can generate more oxidizing species or contribute to SOA formation. Stabilization of these CIs is also important in the atmosphere, as it will limit the extent of these unimolecular decomposition processes occur. Lester and collaborators argue that decomposition processes account for most of the depletion of sCIs.\textsuperscript{47,51} However, as the concentrations of species that react with sCIs (e.g NO\textsubscript{2}, SO\textsubscript{2})
can vary in the clean and polluted troposphere and given that the role of these species in tropospheric chemistry is vital, these reactions are of great interest.\textsuperscript{52}

1.4 Synthesis of stabilized Criegee intermediates

While the general mechanism of ozonolysis is fairly well understood, the complexity of the tropospheric composition provides additional unknowns in the relation of ozonolysis and the fate of atmospheric compounds of interest, such as NO\textsubscript{2}, SO\textsubscript{2}, HNO\textsubscript{3}, etc. Due to their short lifetime, direct measurements of CIs were only possible until recently. Welz and coworkers have developed a method to produce stabilized CIs by photodissociation of diodoalkane and subsequent reaction of the iodoalkyl radical with oxygen.\textsuperscript{53} Characterization of the RCHOO formed from these reactions using tunable synchrotron photoionization showed it to be the carbonyl oxide isomer. As these CIs are formed with low internal energy, they have much longer lifetimes and can be produced in concentrations high enough to study their kinetics. Additional work by other research groups has exploited this technique to obtain UV action spectra,\textsuperscript{54–56} UV absorption spectra,\textsuperscript{57–60} and IR spectra\textsuperscript{61} of several CIs. The measurement of the UV spectra of CH\textsubscript{2}OO showed that it has high absorption cross-section in the wavelength region between 300 – 400 nm, corresponding to the $\tilde{B}(1\text{A}') \leftarrow \tilde{X}(1\text{A}')$ transition,\textsuperscript{57} and allowed for the possibility of measuring kinetics of CIs with optical methods.\textsuperscript{58,62} Several groups have explored, then, the reactions of sCIs with atmospherically relevant species, of particular importance being the reactions of CIs, with NO\textsubscript{2}, SO\textsubscript{2}, HNO\textsubscript{3}, H\textsubscript{2}O, (H\textsubscript{2}O)\textsubscript{2}.\textsuperscript{57,62–65} It has been found, in general, that some of these reactions are orders of
magnitude faster than previously thought,\textsuperscript{29,66} and further work has suggested that the role of these reactions and their products in the atmosphere might be more critical than currently proposed.\textsuperscript{67–69} In addition, comparison of measured rates with ones obtained from theoretical calculations provides benchmark for assessing the accuracy of different methods. Additionally, the availability of accurate rate constants will lead to improved mechanisms for modelling.

1.5 From dynamics, to kinetics, to reaction mechanisms

Experimental techniques used to study ozonolysis of alkenes vary according to the reaction system studied\textsuperscript{1}. Studies of dynamics of unimolecular processes are generally informed by previous theoretical work,\textsuperscript{18,22,24} and depend on careful excitation of a single species in order to determine unimolecular decomposition constants and comparing data with results from theories such as Rice-Ramsperger-Kassel-Marcus (RRKM),\textsuperscript{51} or by isotopic labelling of species and observation of the decomposition products.\textsuperscript{44,70} Determinations of rate constants for ozonolysis of several olefins have been done by several groups using the pseudo-first order method.\textsuperscript{3,4} This information permits the assessment of the effect of ozonolysis against other oxidation processes, and to consider ozonolysis of several species explicitly in atmospheric mechanisms.\textsuperscript{10,13} Some reaction systems have been studied at the same time and the reaction rate constants have obtained using the method of relative rates.\textsuperscript{71,72} By measuring relative rates, many studies have been able to provide rate constant information of reactions involving transient species such as OH and HO\textsubscript{2} radicals.\textsuperscript{3} However, these measurements assume a mechanism to be
complete which, if not the case, can lead to inaccurate results. As a consequence, reported rate constants can be found in the literature with differences of orders of magnitude. The last step in complexity when studying kinetics of ozonolysis is to test a mechanism of several primary and secondary reactions against measurements of reaction intermediates and end of reaction products. While complex mechanisms have been mostly used for regional or global geographical models, it has also been applied to chamber and laboratory controlled experiments. Naturally, a mechanism includes theoretical and experimental findings from kinetics of elementary reactions and from dynamics of decomposition processes, and research is continuously done all the way from the elementary level to the evaluation of complex mechanisms.

1.6 Experimental techniques

Measuring a complex mixture of gas-phase species in situ presents an analytical challenge in the study of atmospheric reactions. Depending on the kinetic or mechanistic study, some analytic techniques have advantages over others. In general, techniques that are used to study atmospheric chemistry offer high sensitivity, ability to sample or trap products with short lifetimes (or to observe their reactions in situ), and capacity to sample gas-phase analytes. Spectroscopic techniques are widely used to study dynamics, kinetics, and mechanism of ozonolysis of alkenes. Work on dynamics is done by using small flow reactors in order to achieve short reaction timescales and observing products using optical or mass spectrometry. The study of the tunneling and unimolecular decomposition of syn-CH₃CHOO using a capillary flow reactor and supersonic expansion
with IR measurements,\textsuperscript{51} or the study of the formation of OH radicals from syn- and anti-CIs using laser induced fluorescence (LIF) are examples of this type of experiments.\textsuperscript{77} These experiments provide benchmarks for theoretical work,\textsuperscript{22} as theoretical calculations have been done by several groups at different levels of theory to provide information on the potential energy surface of different ozonolysis reactions at different stages in the mechanism.\textsuperscript{15,18,19,78} These calculations are then used in master equation calculations to obtain information such as yields and branching ratios of species such as CIs or OH radicals, or to obtain information on decomposition dynamics using RRKM theory.\textsuperscript{23,24} Theoretical calculations are also used to provide rate constants for reactions in the mechanism of ozonolysis.\textsuperscript{68,69} Experimental techniques for determination of rate constants use continuous flow,\textsuperscript{29,48} stropped-flow,\textsuperscript{79} and tank reactor\textsuperscript{33} schemes coupled with various detection techniques. As these measurements involve elementary reaction kinetics, and ozonolysis mechanisms involve several reaction steps, a lot of research can be found in the literature.\textsuperscript{3,4,10} Using broadband multi-pass transient absorption spectroscopy with a slow-flow reactor, Leonid Sheps\textsuperscript{57} showed the first UV absorption spectrum of CH$_2$OO and determined the rate constant of its reaction with SO$_2$. The same detection method was used in a stainless steel flow cell by Foreman et al.\textsuperscript{62} to determine rate constants of the reaction of CH$_2$OO with HCl and HNO$_3$. As further example, Zhu and Johnston\textsuperscript{48} showed that cavity ring-down spectroscopy can be used to measure the yields and relative rates of the reaction of ·CH$_2$CHO with oxygen. As the number of elementary reactions increases, the reactors used are usually continuous flow reactors with detection techniques that can measure several species at the same time. Copeland et
al.\textsuperscript{75,76} used a flow tube and photoelectron spectroscopy to fit mechanisms of ozonolysis of ethene, 2,3-dimethyl-2-butene, and 2-methylpropene to observed products. Fenske et al.\textsuperscript{42} used a flow cell reactor and FTIR in a multireflection long path cell to measure rate constants of CH\textsubscript{3}CHOO and CH\textsubscript{3}CHO by fitting an ozonolysis mechanism of 2-butene. Examples of chamber studies and field measurements can be found in the works of Newland et al.,\textsuperscript{71} and Novelli et al.,\textsuperscript{67} respectively.

1.7 Optical cavities and CRDS

The use of optical cavities in analytical chemistry begun with the work of O’Keefe and Deacon.\textsuperscript{80} By taking advantage of the theory of Fabry-Perot resonators, the effective optical path of a light pulse in a glass cavity could be in the kilometer range. These long paths could only be achieved before by placing mirrors kilometers apart, a technique known as differential optical absorption spectroscopy (DOAS).\textsuperscript{81} Optical cavities can then measure the absorption of light by molecules in a greatly increased path length either by measuring the change in the intensity of light, as is the case for cavity enhanced absorption spectroscopy (CEAS), or by measuring the rate of decay of a light pulse after several passes through the optical cavity, as is the case for cavity ring-down spectroscopy (CRDS).\textsuperscript{82} Optical cavities were readily used for atmospheric measurements,\textsuperscript{83} and various studies of the chemical compositions in the atmosphere has been done using either CEAS or CRDS instruments.\textsuperscript{84–86}

Cavity ring-down spectroscopy relies in the use of high reflectivity mirrors in a cavity to increase the effective path length of the light pulse.\textsuperscript{82} Figure 1.1 shows a
schematic of a CRDS apparatus. The small amount of light transmitted after each pass of
the light through the cavity is captured by a detector. The n-th transmitted pulse will have
an intensity described by:

\[ I_n = I_0 R^{2n} e^{-2n\alpha d} \]

where \( I_n \) is the intensity of the n-th pass of the light pulse, \( I_0 \) is the initial intensity of the
pulse detected, \( R \) is the mirror reflectivity, \( \alpha \) is the absorption coefficient and \( d \) is the
sample length. If the cavity has a length \( L \), the time when the n-th pulse is measured is \( t = n \times 2L/c \) (where \( c \) is the speed of light) and the intensity can be described as:

\[ I(t) = I_0 e^{\frac{tc}{L(LR-\alpha d)}} \]

This expression can then be simplified to:

\[ I(t) = I_0 e^{-\frac{t}{\tau}}, \text{ where} \]

\[ \tau = \frac{L}{c(1 - R + \alpha d)} \]

given that \( \ln R = (R - 1) \), as the value of \( R \) is small. If there is no sample, losses can be
attributed to the mirror and scattering and incorporated into \( R \):

\[ \tau_0 = \frac{L}{c(1 - R)} \]

The absorption coefficient is then measured by the difference of the decay times with and
without absorbent species:

\[ \frac{1}{\tau} - \frac{1}{\tau_0} = \frac{c}{L} (1 - R + \alpha d) - \frac{c}{L} (1 - R) \]

\[ \frac{1}{\tau} - \frac{1}{\tau_0} = \alpha \frac{dc}{L} \]
\[ \alpha = \frac{L}{d} \Delta \left( \frac{1}{\tau} \right) = \sigma N \]

where N is the number density and \( \sigma \) is the absorption cross-section. As the optical cavity’s sensitivity is proportional to the length of the sample, a CRDS instrument with good sensitivity will have enough length to be used as a flow reactor, cavities with a sample length of 1 meter can detect number densities as low as \( 10^7 \) molecules/cm\(^3\), making CRDS optimal for atmospheric measurements.

1.8 Dissertation work

The work presented here investigates important aspects of the ozonolysis reaction of some alkenes. First, we use a flow reactor to measure average steady-state concentrations of CH\(_2\)OO produced from ozonolysis of ethene. The direct measurement of formaldehyde oxide produced from the ozonolysis reaction of ethene has never been published before. Measurements of the average steady-state concentrations of formaldehyde oxide are performed at different reaction times and under different reactant initial concentrations. Using a mechanism of ozonolysis of ethene, we assess the depletion processes of CH\(_2\)OO at short timescales and provide upper limits to the rate constants of the reaction of formaldehyde oxide with ethene and ozone. The need for further work in the determination of rate constants of the reaction of formaldehyde oxide and formaldehyde is also discussed.

Second, we use a new technique involving direct measurement of SO\(_2\) consumption during ozonolysis of cis-2-butene, trans-2-butene, 2-methyl-2-butene, 2,3-dimethyl-2-butene, cyclopentene, and cyclohexene in order to determine the yield of stabilized
Criegee intermediates at low pressures. The nascent yield is then determined by extrapolation and compared among the alkenes studied. The utility of these measurements is twofold, it provides benchmarks for master equation calculations which allows for a better understanding of the dynamics of the decomposition of the POZ, and provides low pressure information to study the behaviour of the yield of sCIs as pressure increases.

Finally, realizing that decomposition is also an important pathway of sCI depletion, we look into a key radical and product from the decomposition of CH$_3$CHOO, the vinoxy radical. By measuring the average steady-state concentrations of ·CH$_2$CHO and HCHO produced by ozonolysis of cis- and trans-2-butene under different reaction conditions, we can obtain information regarding the yield ratio of vinoxy radical between the two alkenes and compare with known yield ratios of OH radicals. This information allows us to determine the proportion of OH radical produced from isomerization and decomposition of syn-CH$_3$CHOO, allows us to evaluate a model of the mechanism of ozonolysis of 2-butenes, and provides us with further insights of the different decomposition pathways.
1.9 Figures

Figure 1.1. Schematic of the cavity-ringdown apparatus. A light source S emits a pulse that goes into a cavity of length L enclosed by two high-reflectivity mirrors with reflectivity R. The transmitted light after going through the cavity once will reach a detector D, resulting in a measurement of intensity $I_0$. Light reflected into the cavity will suffer losses due to scattering and absorption if along the sample distance $d$. At the $n$-th round trip the pulse will have an intensity $I_n$. 
1.10 References


2 Direct measurement of CH$_2$OO produced by ozonolysis of ethene.

2.1 Abstract

Criegee intermediates are carbonyl oxides produced by scission of a primary ozonide produced by ozonolysis of alkenes. These intermediates are produced with a broad distribution of internal energy and can decompose, isomerize, or undergo bimolecular reactions. Their importance lies in the role of these processes in tropospheric chemistry, as they produce oxidized species that can lead to the formation of highly oxidized molecules (HOMs) and secondary organic aerosols (SOAs), as well as organic radicals and hydroxy radical (-OH). The simplest Criegee intermediate, CH$_2$OO, produced from ethene ozonolysis was measured directly and in real time using cavity ring-down spectroscopy (CRDS) in a flow cell reactor. A section of the absorption spectrum of the $\tilde{\text{B}}(^1\text{A}^\prime) \leftarrow \tilde{\text{X}}(^1\text{A}^\prime)$ transition of CH$_2$OO was measured in the wavelength range of 370 – 390 nm and compared with a reference UV spectrum of CH$_2$OO produced by the reaction of iodomethyl with oxygen, showing excellent agreement. Sulfur dioxide was used as a scavenger to further confirm that the measured absorption belonged to formaldehyde oxide. Direct measurements of CH$_2$OO and HCHO produced under different reaction times and reactant conditions allowed for testing some rates of bimolecular reactions of CH$_2$OO in an ozonolysis mechanism against experimental data for the first time. Kinetic modelling showed that, even if CH$_2$OO production was low at short reaction times, the low concentration of reaction products minimizes secondary reactions and results in
increased steady-state concentrations of CH$_2$OO. At the short reaction times (< 600 ms), the most significant depletion pathways of formaldehyde oxide were found to be the reactions with ozone, ethene, and formaldehyde. The upper limit of the rate of the CH$_2$OO + O$_3$ reaction was found to be ~5x10$^{-13}$ cm$^3$/molecule∙s and the rate of the CH$_2$OO + C$_2$H$_4$ reaction ~5x10$^{-15}$ cm$^3$/molecule∙s. Formaldehyde was found to be an important depletion pathway of CH$_2$OO but could not be accurately simulated with the ozonolysis mechanism employed. This points out to the necessity of further studies regarding the CH$_2$OO + HCHO reaction.

2.2 Introduction

Ozonolysis of olefins plays an important role in the troposphere as it is one of the main oxidation processes of unsaturated volatile organic carbons (VOCs). Furthermore, the products of ozonolysis ultimately lead to production of highly oxidized molecules (HOMs), secondary organic aerosols (SOAs), carbonyl products, organic radicals and ·OH. Ozonolysis of alkenes was described first in the liquid phase by Rudolph Criegee, and involves a 1,3 dipolar cycloaddition of ozone to the olefinic bond, through a van der Waals complex, in order to form a primary ozonide (POZ). The zero-point energy of the POZ is generally much lower than the energy of the reaction and this exothermicity results in a highly energetic POZ that rapidly decomposes into a carbonyl and a carbonyl oxide (in the case of endocyclic alkenes, in a molecule with a terminal carbonyl and a terminal carbonyl oxide). As the POZ breaks, the carbonyl and the carbonyl oxide, also known as Criegee intermediate (CI) are left with a broad internal
energy distribution\textsuperscript{10}. Whereas the carbonyl product is relatively stable, the CI can undergo several reaction pathways. The fraction of CI with high internal energies will have short lifetimes and readily isomerizes or decomposes. However, a fraction of the CI can be produced with relatively low internal energy, allowing it to have long enough lifetimes to undergo bimolecular reactions in addition to the decomposition pathways.\textsuperscript{10,11} This fraction of CI is called the “stabilized” Criegee intermediate (sCI) and its importance in tropospheric chemistry has made it the object of many studies.\textsuperscript{12–16}

Previously, insights on CI chemistry were obtained by observing end reaction products, branching ratios, and relative rates.\textsuperscript{17,18} However, a recently developed technique by Welz and coworkers allowed for the direct production of sCI by photolysis of diodoalkane and reaction of the produced iodoalkyl with oxygen.\textsuperscript{19} The ability to produce sCI in situ was seized by several research groups in order to measure UV\textsuperscript{20–22} and IR\textsuperscript{23} spectra, and to assess kinetics of sCIs,\textsuperscript{24,25} whose reaction rate constants often had order-of-magnitude differences in the literature.\textsuperscript{26} Of particular importance are those reactions involving atmospherically relevant species such as NO\textsubscript{2}, SO\textsubscript{2}, H\textsubscript{2}O, (H\textsubscript{2}O)\textsubscript{2}, etc., now with studies measuring rate constants with better accuracy.\textsuperscript{19,24,27–29} Furthermore, recent work has also pointed out the importance of unimolecular decomposition processes and shed light on tunneling from sCI into unimolecular decomposition products.\textsuperscript{30,31} More accurate information of rate constants of bimolecular reactions of sCIs is important for explicit atmospheric models such as the Master Chemical Mechanism (MCM),\textsuperscript{26,32} on the other hand, the study of unimolecular processes involving sCIs can provide further insights on the energetics of the CI decomposition pathways.
Nevertheless, the complexity of the mechanism of ozonolysis leads to secondary reactions that still require further study. The importance of reactions of CI and carbonyls, carboxylic acids, olefins, etc. lies in their concentrations in different environments, where they can potentially act as the main depletion pathways of sCIs. Kinetic information of these secondary processes becomes important to provide a better understanding of the ozonolysis reaction in the troposphere. Therefore, it is necessary to study the ozonolysis reaction itself, monitoring the products of interest and comparing experimental measurements with a model mechanism that contains accurate pathways and rate constants. In this work, we measure HCHO and CH$_2$OO directly from ozonolysis of ethene under different reaction times and reactant concentrations in order to assess the importance of some depletion processes at short timescales.

2.3 Experimental Method

A flow cell was used as a plug flow reactor to carry out the ozonolysis reaction under different conditions. Ethene (95%, Matheson Tri Gas) and nitrogen (UHP, Airgas) were mixed in a manifold and exposed to an ozone/oxygen mixture at the reactor inlet. The reaction then proceeded along the cavity. Linear flow velocities were measured to be in the range of 30 – 60 cm/s, the flow cell diameter was 2.54 cm and the reactor length was 59 cm (see Figure 2.1). Dimensionless flow parameters were calculated for the reactor and are summarized in Table 2.1.

The reaction cell also had the role of optical cavity, and the average concentration of the species of interest was measured using cavity ring-down spectroscopy (CRDS).
Originally used to test high-reflectivity mirrors, CRDS was developed into an analytic
technique by O’Keefe and Deacon\textsuperscript{34} and is now widely used to measure gas-phase
analytes.\textsuperscript{35–38} It relies in a single light pulse passing multiple times through a sample in a
cavity enclosed by two high-reflectivity mirrors. A small fraction of the pulse gets
transmitted into a detector and the rate of decay of the intensity of the transmitted light
corresponds to the concentration of the absorbing species following the equation:

\begin{equation}
\sum_i \sigma_i(\lambda)N_i + f(\lambda) = \frac{L}{\ell \cdot c} \left( \frac{1}{\tau} - \frac{1}{\tau_0} \right)
\end{equation}

where \(\sigma_i(\lambda)\) is the absorption cross section of the \(i\)-th species at wavelength \(\lambda\), \(N_i\) is its
number density, \(f(\lambda)\) is a parametric function introduced to account for broad extinction
contributions from background and unidentified species, \(1/\tau_0\) is the decay rate of the
empty cell, \(1/\tau\) is that of the cell with the sample, \(\ell\) is the length of the sample in the cell
(59 cm in our flow reactor), \(L\) is the length of the cell (100 cm), and \(c\) is the speed of
light. A Nd:YAG laser (Surelite 2, Continuum) generated a 10 Hz pulse at 532 nm that
pumped a tunable dye laser (Lambda-Physik). The laser dyes used, and their outputs,
were as follows: Styryl 8 in MeOH and DMSO was used to produce a tunable output in
the range of 750 – 780 nm, DCM in MeOH was used to produce a tunable output in the
range of 640 – 650 nm, and Pyridine 1 in MeOH was used for an output in the 670 – 690
nm range. A frequency doubling unit (Autotracker III, Inrad) was used to produce the
High-reflectivity mirrors (>99.9\%, Layertec GmbH, 3 pairs with maximum reflectivity at
395, 330, and 360 nm, respectively) were used to obtain ring-down times from 7 – 20
microseconds. The limit of detection of CI based on the reference absorption cross-section from Foreman et al.\textsuperscript{39} in the MPI-Mainz UV database\textsuperscript{40} was estimated to be 2x10\textsuperscript{10} molecule/cm\textsuperscript{3} in our system. Flows were measured and controlled with calibrated mass flow controllers (GFC17, Aalborg). Reactant concentrations were varied from 8x10\textsuperscript{14} – 1.7x10\textsuperscript{15} molecule/cm\textsuperscript{3} for ozone and from 5x10\textsuperscript{16} – 1x10\textsuperscript{17} molecule/cm\textsuperscript{3} for ethene.

Production of CH\textsubscript{2}OO in the ozonolysis reaction of ethene is slow, as the rate constant of the ozonolysis reaction is 1.6x10\textsuperscript{-18} cm\textsuperscript{3}/molecule\cdot s. On the other hand, several fast depletion processes of CH\textsubscript{2}OO occur, namely the reactions of CH\textsubscript{2}OO with ethene, ozone, formaldehyde, etc. The steady-state concentration of CH\textsubscript{2}OO can be calculated using the appropriate expression:

\[
[\text{CI}] = \frac{k_{oz}[\text{C}_2\text{H}_4][\text{O}_3]}{k_{\text{CI+Ozone}}[\text{O}_3] + k_{\text{CI+Alkene}}[\text{C}_2\text{H}_4] + k_{\text{CI+HCHO}}[\text{HCHO}] + k_d + \cdots}
\]

Under experimental ozone and ethene concentrations, the steady-state concentration of CH\textsubscript{2}OO was estimated to be \sim 4x10\textsuperscript{10} molecule/cm\textsuperscript{3}. This concentration is orders of magnitude lower than the amount of CI generated by photolysis of diiodomethane and reaction with oxygen.\textsuperscript{39} In order to increase this steady-state concentrations, therefore, the depletion processes were inhibited by reducing reaction time and the formation of products. A mechanism of ozonolysis of ethene was constructed based on the work of Copeland et al.\textsuperscript{41} and incorporating new kinetic data from the literature.\textsuperscript{24,28,29,31} Table 2.2 shows the mechanism used to model the ozonolysis reaction. These reactions are translated into a system of ordinary differential equations (ODEs) and integrated using a Bulirsh-Stoer method by the software package KINTECUS.\textsuperscript{42} As the dimensionless
parameters shown in Table 2.1 comply with the criteria by Cutler et al.\textsuperscript{43} and Lee et al.\textsuperscript{44} for non-Poiseuille flow, the reactor was assumed to behave reasonably close to a plug-flow reactor, and modelled as a series of continuously-stirred tank reactors (CSTRs) in tandem, where the output of the previous CSTR becomes the input of a new CSTR along the flow cell. A total of 10 CSTRs were used to simulate a concentration profile along the flow cell. The use of additional segments showed convergence in the concentration profiles and, thus, only ten segments were used to facilitate simulations. A concentration profile of CH\textsubscript{2}OO along the flow cell at different reaction times is shown in Figure 2.2.

2.4 Results and Discussion

The simulated concentration profile indicates that short reaction times will have higher average steady-state concentrations of CH\textsubscript{2}OO. Using a reaction time of \~600 ms with an initial ozone concentration of 1.7x10\textsuperscript{15} molecule/cm\textsuperscript{3} and an initial ethene concentration of 1x10\textsuperscript{17} molecule/cm\textsuperscript{3}, an average CH\textsubscript{2}OO concentration of 1x10\textsuperscript{11} molecule/cm\textsuperscript{3} was measured in the reaction cell. These concentrations were high enough for an absorption spectrum to be measured and for kinetic experiments to be conducted with direct monitoring of CH\textsubscript{2}OO from the ozonolysis reaction of ethene for the first time. Figure 2.3 shows an absorption cross-section, calculated from the measured change in decay time $\Delta(1/\tau) = (1/\tau) - (1/\tau_0)$ scaled to the CH\textsubscript{2}OO absorption spectrum by Foreman et al. in the range of 370 – 390 nm. The concentration of CH\textsubscript{2}OO can be determined from this scaling, according to Equation 1. In this region and under the reaction conditions, only CH\textsubscript{2}OO has distinct features with enough intensity to be above
the limit of detection. Formaldehyde was not produced in high enough concentration at the short reaction times to affect the decay rate. However, when reaction time was increased by a factor of 5, features from the $^3A_2 \leftrightarrow X^1A_1$ transition of formaldehyde$^{45}$ can be identified (see Figure 2.4). This is a confirmation that the reaction time is short enough to prevent a high production of reaction products along the reaction cell. While the production of CH$_2$OO is small at short reaction times, the depletion processes are minimized and the average concentration of CH$_2$OO is high in comparison with long reaction times (see Figure 2.5). As reaction time increases, albeit CH$_2$OO production increases, the secondary depletion processes become increasingly dominant, reducing the average concentration of CI in the reaction cell.

Further confirmation that the features observed belong to CH$_2$OO was obtained by adding SO$_2$ to the C$_2$H$_4$+N$_2$ manifold in order to scavenge the CH$_2$OO (the rate constant of the CH$_2$OO + SO$_2$ reaction is $3 \times 10^{-11}$ cm$^3$/molecule·s). The concentration of SO$_2$ used was $3 \times 10^{14}$ molecule/cm$^3$, more than a hundredfold the steady-state concentration of CH$_2$OO. Figure 2.6 shows the change in decay time for the ozonolysis reaction with and without sulfur dioxide. With addition of SO$_2$, the features attributed to CH$_2$OO vanish and only the spectrum of sulfur dioxide remains. This is a strong indication that the features observed in fact belong to CH$_2$OO.

Having direct measurements of CH$_2$OO from ozonolysis of ethene allows us to probe different reaction conditions in order to better understand the role of the depletion processes of CH$_2$OO. Reaction time was gradually increased and the average steady state concentration of CH$_2$OO was measured. Figure 2.7 shows the CH$_2$OO concentrations at
different reaction times for different ethene and ozone concentrations. Comparison with the kinetic model shows reasonable agreement with some observations. Whereas the rates constants of unimolecular decomposition and self-reaction of CH$_2$OO are fairly well established,$^{29,31}$ the reaction rate constant of CH$_2$OO with ethene (k=7.0x10$^{-16}$ cm$^3$/molecule·s), measured by Buras et al.$^{28}$ as well, is suggested to be considered as a lower limit. Furthermore, the rates of reaction of CH$_2$OO with ozone (k=1.0x10$^{-13}$ cm$^3$/molecule·s) and with HCHO (k=1.0x10$^{-12}$ cm$^3$/molecule·s) have been obtained by fitting an ozonolysis mechanism to reaction products and by determination of relative rates and branching ratios (see Copeland et al.$^{41}$), and have not been studied directly using CH$_2$OO from diiodomethane photolysis. The reactions of CH$_2$OO with ozone, ethene, and formaldehyde, therefore, form a set of parameters that can be adjusted in a range to fit the experimental data. As our experimental conditions minimize secondary reactions, only the coproduct of ozonolysis (formaldehyde) and the reactants (ozone and ethene), will have a significant contribution to depletion of formaldehyde oxide, besides the self-reaction and unimolecular decomposition. Direct measurements of CH$_2$OO under different reaction conditions allowed us to establish upper limits for the reaction rate constants of formaldehyde oxide with ethene (k < 5x10$^{-15}$ cm$^3$/molecule·s) and ozone (k < 5x10$^{-13}$ cm$^3$/molecule·s), this is consistent with work by Copeland et al.$^{41}$ and Buras et al.$^{28}$ Vereecken and coworkers$^{46}$ have calculated the rate constant of the reaction of CH$_2$OO with ozone to be 1.0x10$^{-12}$ cm$^3$/molecule·s and with ethene to be 6.24x10$^{-14}$ to 5.61x10$^{-15}$ cm$^3$/molecule·s with accuracy increasing at higher levels of theory, indicating that precise calculation of energy barriers is needed for an accurate calculation of rate
constants. In addition, an increase in the slope of the plots when either ozone or ethene concentration is doubled shows that, while there is more CH\textsubscript{2}OO production, its depletion is faster, as the O\textsubscript{3} + CH\textsubscript{2}OO or the C\textsubscript{2}H\textsubscript{4} + CH\textsubscript{2}OO reaction rate is increased. However, doubling the amount of ozone doesn’t show as much steady-state CH\textsubscript{2}OO concentration as when the amount of alkene is doubled, indicating that the reaction of the CI with ozone is higher than the reaction with ethene, making the depletion of CI by ozone more significant, which is consistent with our assessment of the rate constants for these reactions and with the data found in the literature.

The consumption of ozone and production of formaldehyde were measured in the 338 - 342 nm range in order to determine the reaction time. Unless formaldehyde depletion processes occur with rates much faster than the sum of the rates of the HCHO + CH\textsubscript{2}OO reactions, at the short reaction times there should be no significant HCHO depletion. Furthermore, data in the literature indicates that, even at long reaction times, the yield of HCHO from ethene ozonolysis remains > 90%. Ozone consumption was monitored in the wavelength range of 322 - 325 nm as well, albeit with somewhat high uncertainty (± 10%). No measurable consumption of ozone was observed. Figure 2.8 shows that formaldehyde production increased at longer reaction times but overall remains low proving, in addition to the low ozone consumption, that the reaction times are short. However, the model overpredicts the concentration of HCHO by a factor of 3 – 4, indicating that further work is needed to assess the extent of depletion and production of formaldehyde by secondary reactions and points out to the need of further work in determination of rate constants of the different HCHO + CH\textsubscript{2}OO reactions.
2.5 Conclusions

Formaldehyde oxide produced by ozonolysis of ethene was directly measured using cavity ring-down spectroscopy. Measurements of average steady-state concentrations of CH$_2$OO and HCHO under several ozone and ethene concentrations are compared with a simulation of an ozonolysis mechanism to provide insights on CH$_2$OO depletion processes. Measurements of CH$_2$OO concentrations at different reaction times and initial reactant concentrations allowed for a qualitative assessment of loss processes at the first stages of the ozonolysis reaction. The use of flow reactors and laboratory scale conditions, provides additional control on mixing and reaction conditions, allows the assessment of the known secondary reactions in an ozonolysis mechanism, offering an intermediate step between determination of individual rate constants and application of reaction mechanisms in chamber studies.
2.6 Figures

Figure 2.1. Schematic of the flow reactor used for ethene ozonolysis experiments. Ethene was mixed with nitrogen as buffer gas (SO₂ added only for scavenging). The ethene mixture reacted with ozone in oxygen from an ozone generator from the reactor inlet throughout the cell. The reactor was also used as a cavity for CRDS measurements.
Figure 2.2. Concentration profile of formaldehyde oxide along the reactor at different reaction times. The segments of the flow cell were modelled as CSTRs and the whole reactor is modelled as CSTRs in tandem.
Figure 2.3. Absorption cross-section of the 370 – 390 nm section of the $\tilde{B}(1A') \leftarrow \tilde{X}(1A')$ transition of CH$_2$OO calculated from the measured decay rates $\Delta[1/\tau]$ of the ethene ozonolysis reactions. Determination of the cross-section by scaling the ringdown decay rates to cross-section data from Foreman et al.$^{39}$
Figure 2.4. Measured decay rate of the light pulse in the ethene ozonolysis reaction at long reaction time (> 2 s). Spectrum corresponds to a $^3\text{A}_2 \leftrightarrow X^1\text{A}_1$ transition of formaldehyde.$^{45}$
Figure 2.5. Simulated average concentration of ozone, formaldehyde, and formaldehyde oxide in the reactor at different reaction times. The initial rise in CH$_2$OO concentration corresponds to an increase in the overall rate of ozonolysis at a timescale where the depletion processes are still minimized. The decrease in CH$_2$OO concentration at longer times indicates an increasing prominence of secondary reactions.
Figure 2.6. Measurements of the decay rate of light in the ozonolysis reaction of ethene with the presence and absence of SO\textsubscript{2} (used as a scavenger). Change in decay rate due to CH\textsubscript{2}OO absorption is not present during experiments with the scavenger. Reference spectra obtained from the MPI-Mainz UV/VIS Spectral Atlas.$^{40}$
Figure 2.7. Average steady-state concentrations of CH$_2$OO at different flow rates under different reaction conditions. Open squares correspond to simulated average steady-state concentrations.

- $[C_2H_4] = 5 \times 10^{16}$, $[O_3] = 1.7 \times 10^{15}$
- $[C_2H_4] = 1 \times 10^{17}$, $[O_3] = 1.7 \times 10^{15}$
- $[C_2H_4] = 1 \times 10^{17}$, $[O_3] = 8 \times 10^{14}$
Figure 2.8. Average steady-state concentrations of CH$_2$OO at different flow rates under different reaction conditions.
2.7 Tables

Table 2.1. Flow parameters of the reactor under experimental conditions. Da and Pe are the Damköhler and Peclet numbers, respectively.

<table>
<thead>
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<th>Characteristic Time</th>
<th>Value</th>
<th>Description</th>
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<tr>
<td>$t_{ck}$</td>
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<td>Chemical reaction</td>
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<tr>
<td>$t_{sd,R}$</td>
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<td>Radial species diffusion</td>
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<tr>
<td>$t_{fc,R}$</td>
<td>0.06</td>
<td>Radial forced convection</td>
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<tr>
<td>$t_{fc,L}$</td>
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<td>Axial forced convection</td>
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<table>
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<tr>
<td>$t_{fc,R}/t_{sd,R}$</td>
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<tr>
<td>$t_{ck}/t_{fc,L}$</td>
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</table>

<table>
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<tr>
<td>$t_{sd,R}/t_{fc,L}$</td>
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<tr>
<td>$t_{sd,R}/t_{ck}$</td>
</tr>
<tr>
<td>$t_{fc,R}/t_{fc,L}$</td>
</tr>
</tbody>
</table>

*Criteria from Cutler et al.43 and references therein.
Table 2.2. Mechanism of ozonolysis of ethene used to model steady-state concentrations along the reactor. Modelling was done by dividing the PFR into CSTRs in tandem. Rate constants are from Copeland et al.\textsuperscript{41} unless otherwise specified.

<table>
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<th>#</th>
<th>Reaction</th>
<th>$k$ (cm$^3$/molecule·s)</th>
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<tbody>
<tr>
<td>1'</td>
<td>C$_2$H$_4$+O$_3$ $\rightarrow$ H$_2$CO+0.2H$_2$COO+0.8HCHOO</td>
<td>1.60E-18</td>
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<td>HCHOO $\rightarrow$ CO$_2$+H$_2$</td>
<td>8.00E+03*</td>
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<tr>
<td>3</td>
<td>HCHOO $\rightarrow$ CO+H$_2$O</td>
<td>2.00E+04*</td>
</tr>
<tr>
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<td>HCHOO $\rightarrow$ H+HCO$_2$</td>
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<tr>
<td>5</td>
<td>HCHOO $\rightarrow$ HCOOH</td>
<td>7.00E+02*</td>
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<tr>
<td>6</td>
<td>HCO$_2$ $\rightarrow$ H+CO$_2$</td>
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<td>H+O$_3$ $\rightarrow$ OH+O$_2$</td>
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</tr>
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<tr>
<td>24</td>
<td>H$_2$COO+HCOOH $\rightarrow$ P</td>
<td>1.10E-10$^d$</td>
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*Unimolecular reaction rates in s$^{-1}$. $^a$The distinction of stabilized CH$_2$OO (denoted by H$_2$COO) and “hot” CH$_3$OO (denoted by HCHOO) is done with a stabilized yield from Hatakeyama et al.\textsuperscript{11}$^b$The reaction of CI with ethene form Buras et al.\textsuperscript{28}$^c$Unimolecular decomposition and self-reaction of CI from Chhantyal-Pun et al.\textsuperscript{31}$^d$Rate constant from Huang et al. and references therein.\textsuperscript{26}$^e$Rate constant of CI and formic acid from Welz et al.\textsuperscript{24}
2.8 References


3 Low-pressure yields of stabilized Criegee intermediates produced from ozonolysis of a series of alkenes.

3.1 Abstract
Cavity ring-down spectroscopy (CRDS) and chemical titration with sulfur dioxide (SO₂) were used to indirectly measure the yields of stabilized Criegee intermediates (sCIs) produced from ozonolysis of cis-2-butene, trans-2-butene, 2-methyl-2-butene, 2,3-dimethyl-2-butene, cyclopentene, and cyclohexene at low pressures in the range of 2-60 Torr. The yield of stabilized sCI, acetaldehyde oxide (CH₃CHOO), from cis-2-butene ozonolysis decreased with decreasing pressure and reached 0.05 ± 0.04 at the zero-pressure limit. In the case of trans-2-butene, the yield of sCI was found to decrease with decreasing pressure and reach zero at the zero-pressure limit. The nonsymmetric alkene 2-methyl-2-butene produced two stabilized sCIs, CH₃CHOO and acetone oxide ((CH₃)₂COO), and their total yield decreased with decreasing pressure and reached 0.01 ± 0.03 at the zero-pressure limit. For 2,3-dimethyl-2-butene, the sCI yield also decreased with decreasing pressure but reached a minimum of 12 ± 5% at the zero-pressure limit. For cyclopentene and cyclohexene, the sCI yields were essentially constant near zero, as expected from endocyclic alkenes. The zero-pressure yields of sCI, corresponding to the nascent fraction of CI formed with internal energy below the barriers of dissociation/isomerization, of various alkenes are compared.
3.2 Introduction

In the troposphere, ozonolysis is a significant depletion pathway of unsaturated volatile organic carbons.\textsuperscript{1} Ozonolysis of alkenes is involved in the production of OH radicals and highly oxidized organic molecules (HOMs) that ultimately form secondary organic aerosol.\textsuperscript{2} This reaction involves a 1,3 dipolar cycloaddition of ozone to the olefinic bond, forming a primary ozonide (POZ). As the reaction is highly exothermic, the POZ breaks into a carbonyl and a carbonyl oxide, a biradical known as Criegee intermediate (CI), with broad internal energy distributions.\textsuperscript{3} Although the carbonyl product is relatively stable, the carbonyl oxide biradical can undergo rapid unimolecular decomposition, as well as bimolecular reactions. Unimolecular decomposition pathways involve isomerization into conformers such as vinylhydroperoxide, dioxirane, and carboxylic acid or ester, with a subsequent decomposition into products such as OH radicals. If the internal energy distribution is broad, a fraction of CIs could be produced with relatively low internal energies (below their isomerization/dissociation energy barriers) and have long enough lifetimes to also undergo bimolecular reactions. These are known as “stabilized” Criegee intermediates (sCIs) and their reactions have been studied by several groups, sometimes with significant differences in their rate constants.\textsuperscript{4}

A technique involving photolysis of diodoalkene and subsequent reaction with oxygen to produce stable CIs was developed and used by Weltz and coworkers\textsuperscript{5}, and has permitted direct characterization of sCIs in the gas phase. In recent years, several research groups have used this method to produce sCIs in order to study their spectroscopy, unimolecular decomposition rates, and reaction kinetics with
atmospherically relevant species.\textsuperscript{5–12} In the troposphere, however, the stabilized CI is a fraction of the total CI produced, and the decomposition pathways of the “hot” Criegee intermediates must also be considered. Furthermore, the energy distribution of the formed CI from ozonolysis is of theoretical interest.\textsuperscript{3} Therefore, it is necessary to determine the yields of sCIs and, by balance, the yields of “hot” Cls produced from the ozonolysis reactions. Several groups have used chemical titration to study the yields of sCIs at different pressures.\textsuperscript{13–18} Chemical titration relies on the use of a scavenger to react and capture sCI before it can undergo unimolecular or other bimolecular processes. The appearance of a product of the reaction of sCI with the scavenger, or the consumption of the scavenger, is monitored and related to the sCI production and, thus, to the sCI yield. Hexafluoroacetone has been used to scavenge sCI and the formation of a secondary ozonide has been monitored.\textsuperscript{16} Similarly, SO\textsubscript{2} has been used to scavenge sCI due to their fast reaction and the production of H\textsubscript{2}SO\textsubscript{4}\textsuperscript{13,14,17,18} has been used for the sCI yield measurements.

In this work, we utilized a new method for indirect determination of the yields of sCIs at low pressures by measuring SO\textsubscript{2} consumption using cavity ring-down spectroscopy (CRDS). The ozonolysis reactions were performed in a flow cell at short residence time to allow for rapid titration of sCIs and to reduce the extent of secondary reactions. As we measured SO\textsubscript{2} consumption, there was no need to monitor H\textsubscript{2}SO\textsubscript{4} that formed after the initial sCI + SO\textsubscript{2} reaction, rendering our method more direct and better suited for low pressure measurements. The method was tested by comparing measured yields at low pressures with available information for trans-2-butene and 2,3-dimethyl-2-
butene. Branching ratios of the stabilized carbonyl oxides (sCIs) formed from the ozonolysis of cis-2-butene, trans-2-butene, 2-methyl-2-butene, 2,3-dimethyl-2-butene, cyclopentene, and cyclohexene were obtained at low pressures and the yields of nascent sCIs at zero-pressure limit were determined.

3.3 Experimental Method

Determination of the concentrations of reactants and main products was carried out using CRDS. In CRDS, the analyte occupies a cell enclosed by high reflectivity mirrors and the rate of decay of a laser pulse is measured\textsuperscript{19,20}. The difference between the rate of decay of the analyte versus and empty cell corresponds to the number density of the analyte in the system according to the following equation:

$$\sum_i \sigma(\lambda)_i N_i + f(\lambda) = \frac{L}{l \cdot c} \left( \frac{1}{\tau} - \frac{1}{\tau_0} \right)$$

where $1/\tau_0$ is the decay rate of the empty cell, $1/\tau$ is that of the cell with the analyte, $l$ is the length of the analyte in the cell, $L$ is the length of the cell, $c$ is the speed of light, $\sigma(\lambda)_i$ is the absorption cross section of the $i$-th species at wavelength $\lambda$, and $N_i$ is its number density. The parameter $f(\lambda)$ is introduced in order to account for unidentified broad extinction contribution at varying wavelengths.

The reaction cell and instrument setup are shown in Figure 3.1. A Nd:YAG (Continuum Surelite II) laser with an output wavelength of 532 nm pumped a dye laser (Lambda-Physik ScanMate), whose output was frequency-doubled using an harmonic generator (Inrad Autotracker III). The laser pulse from the harmonic generator went into
an optical cavity enclosed by two high reflectivity mirrors centered at 330 nm with a reflectivity of 99.9% (Los Gatos Research). A photomultiplier tube (PMT) was used to detect the light output from the cavity and the intensity decay. The reaction cell was maintained at a set pressure, and the gas residence time was controlled by regulating total flow and pumping speed. The mirrors were protected by two purge lines carrying a small flow of 15 mL/min of N₂ in order to preserve their high reflectivity and avoid contamination. A gas mixture of alkene, nitrogen and scavenger (SO₂) was prepared in a manifold and mixed with ozone at the cell inlet. The reaction cell behaved as a plug-flow reactor and the ozonolysis reaction reached steady state rapidly under the pressure and flow conditions used. At steady state, the concentration gradient of the reactants and products along the reaction cell remain constant over time. Thus, the average composition of the analyte can be monitored by the optical absorption of the sample at several wavelengths. Number density calculations were done by fitting reference cross sections of the reactants and main stable products in Equation 1 (Carbonyl oxide CIs were not included as their steady state concentrations were very low). The reference cross sections were obtained from The MPI-Mainz UV/VIS Spectral Atlas of Gaseous Molecules of Atmospheric Interest. Determination of the initial concentration of ozone and sulfur dioxide was done by replacing either of the corresponding species and alkene with nitrogen and fitting the decay rates to the reference absorption cross sections. Figure 3.2 shows experimental measurements of initial O₃ and SO₂ concentrations in the flow cell, as well as representative spectra of an ozonolysis experiment and sCl measurement with SO₂ titration.
For these experiments, pressure ranged from 2-60 Torr and flow rates ranged from 100-2000 mL/min to maintain the residence time in the reactor from 3-5 seconds. The laser wavelength ranged from 318-325 nm for the ozonolysis experiments. The concentration of alkene was kept in excess at ~3x10^{16} molecules/cm^3 with respect to ozone, whose initial concentration was set to ~4x10^{14} and ~7x10^{14} molecules/cm^3 for trans-2-butene and 2,3-dimethyl-2-butene ozonolysis, respectively. For cis-2-butene, 2-methyl-2-butene, cyclopentene and cyclohexene, the initial concentrations of O_3 and SO_2 for the reactions studied in this work were set at 2x10^{14} and 4x10^{14} molecules cm^{-3}, respectively. These conditions ensured that ozone was the limiting reagent and that all of it was consumed during the experiments.

The sCI yield at a set pressure was determined indirectly by measuring the difference in the SO_2 number density before and during the ozonolysis reaction in the reaction cell. At high initial SO_2 concentrations, it can be assumed that all the sCIs were titrated due to the fast reaction of sCI with SO_2. However, an excessive amount of SO_2 in the reactor can hinder our ability to measure its change in concentration and, in addition, could promote the formation of secondary products and aerosol. In order to test the minimum amount of SO_2 required to efficiently titrate each sCI, several initial concentrations of SO_2 were added to the reactor and the amount of consumed SO_2 was measured. Figure 3.3 shows the consumption of SO_2 (∆SO_2) with respect to its initial concentration, where the maximum consumption was reached at high initial concentrations of SO_2. It is noted that the uncertainty in the measurements increased at high SO_2 concentrations. As mentioned above, excessive amounts of SO_2 can lead to a
significant reduction of the decay time, resulting in less precise measurements of $\Delta(1/\tau)$. The solid line shows a fit to further illustrate the plateau in the SO$_2$ consumption when the initial SO$_2$ concentration was about twice as high as the initial ozone. Special care was taken to ensure that all experiments were carried out in this regime.

The yield of sCI for a certain alkene ozonolysis reaction can be calculated by:

$$Y_{sCI} = \frac{\Delta[SO_2]}{\Delta[O_3]}$$  \hspace{1cm} (2)

where $\Delta[O_3]$ and $\Delta[SO_2]$ are the concentrations of consumed ozone and consumed sulfur dioxide, respectively. The concentration of consumed ozone was determined by measuring the amount of ozone in the reactor before and during the reaction (O$_3$ detection limit was determined to be $\sim$2x10$^{13}$ molecules/cm$^3$).

Interference in the SO$_2$ consumption measurements from the reaction with OH radical was avoided by using an excess amount of alkene which, given that the rate coefficient of the OH + alkene reaction (6.4x10$^{-11}$ and 1.2x10$^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for trans-2-butene and TME, respectively) is much larger than that of the OH + SO$_2$ reaction in the gas phase (3x10$^{-14}$ - 4x10$^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ in the 4-60 Torr range), effectively scavenged all the OH radicals from the reaction cell and prevented consumption of SO$_2$ by the OH + SO$_2$ reaction. Measurements of SO$_2$ in the presence and absence of ozone and oxygen showed no measurable difference in its spectral features. Therefore, the reactions of SO$_2$ with ozone and oxygen were considered to be unimportant under the experimental conditions. In addition, work by Kurtén et al., Vereecken et al., and more recently by Kuwata et al. showed that conversion of SO$_2$ to SO$_3$, and thus
removal of SO\textsubscript{2}, in the sCI + SO\textsubscript{2} reaction is the predominant pathway. As measurement bias from SO\textsubscript{2} resulting from the isomerization channel of the sCI + SO\textsubscript{2} reaction is not significant, the maximum consumption of SO\textsubscript{2} can be quantitatively related to the consumption of sCI.

3.4 Results and Discussion

3.4.1 \textit{trans}-2-Butene

The yield of stabilized acetaldehyde oxide produced from the ozonolysis of \textit{trans}-2-butene at different pressures is shown in Figure 3.4. Measurements were done in 2 Torr intervals from 2-14 Torr. There was a relatively large uncertainty in the sCI yield measurements in the ozonolysis of \textit{trans}-2-butene. This was the consequence of the relatively slow rate constant (k=2.1x10\textsuperscript{-16} cm\textsuperscript{3} molecule\textsuperscript{-1} s\textsuperscript{-1}) of the reaction of \textit{trans}-2-butene with ozone, which limited the extent of the reaction and necessitated a slightly longer residence time in the flow reactor (4-5 s). The limited extent of reaction increased the uncertainty in the sCI measurements, and the longer residence time tended to build up more background from the secondary reactions, which hindered the higher pressure measurements. Our measured yield of sCI in the \textit{trans}-2-butene ozonolysis reaction decreases with decreasing pressure in the 2-14 Torr range; the measurement at 2 Torr shows no presence of sCI. A linear fitting of our data is added to indicate this trend. There was only one other study of the yield of acetaldehyde oxide in \textit{trans}-2-butene ozonolysis by Hatakeyama et al.;\textsuperscript{17} the pressure dependence of the yield of acetaldehyde
oxide was measured by the SO$_2$ titration and production of H$_2$SO$_4$ in the pressure range of 10-760 Torr, and the sCI yield was found to decrease with decreasing pressure. The high pressure data by Hatakeyama et al. were fitted linearly and extrapolated to the low pressure limit (shown in Figure 4), where the yield was found to approach zero, although with less precision than the high pressure measurements. Both our results and those by Hatakeyama et al. converge on a zero yield of sCI at the zero-pressure limit; both also agree with the trend of decreasing sCI yield with decreasing pressure in the low pressure region. At pressures above 10 Torr, our sCI values tend to be higher than those by Hatakeyama et al., albeit it is not possible to accurately determine the extent of the disagreement.

3.4.2 2,3-Dimethyl-2-Butene

The yield of stabilized acetone oxide produced from the ozonolysis of 2,3-dimethyl-2-butene at different pressures is shown in Figure 3.5. The relatively fast reaction rate of ozonolysis (k=1.1x10$^{-15}$ cm$^3$ molecule$^{-1}$ s$^{-1}$) allows for increased precision. The sCI values in this study are in the range of 0.1 to 0.3 in the pressure region of 4-60 Torr and decrease with the decreasing pressure. The yield of sCI obtained at 4 Torr, the lowest pressure in our work, is 14 ± 6% and a linear extrapolation of our measurements in the range of 4-60 Torr shows a zero-pressure limit yield of 12 ± 5%. The previous studies monitoring SOZ formation by Drozd et al.$^{16}$ and measuring H$_2$SO$_4$ formation by Hakala et al.$^{13}$ have determined the yield of acetone oxide at higher pressures from 40-900 Torr, with a low pressure limit extrapolation resulting in a yield of
sCI of approximately 15% (extrapolation in Figure 3.5 was obtained from digitized figures of the corresponding references). Hakala et al. noticed that their sCI yields measured via H$_2$SO$_4$ formation in the pressure range of 40-900 Torr$^{13}$ were lower than those via SOZ formation with the HFA reaction by Drozd et al.$^{16}$ and Hakala et al. attributed the difference between the sCI yields from the H$_2$SO$_4$ and SOZ measurements possibly to uncertainty in measuring SOZ formation by FTIR spectroscopy and to secondary chemistry.$^{13}$ Our measurements overlap with these two previous studies in the pressure region of ~35-60 Torr. Our sCI yields at 35-60 Torr are higher than but within the uncertainty of those by Drozd et al.$^{16}$ Our yields are higher than the 40-60 Torr measurements of Hakala et al.$^{13}$ although they noted that their measurements at the lowest pressures (50 and 60 Torr) might be biased low. Hakala et al. also noted that the zero-pressure yield of sCI could be as low as 10% if these points at 50 and 60 Torr were included in their extrapolation, as their sCI yield at 50 Torr was 12.7 ± 6%. It should be pointed out, furthermore, that in the 4-60 Torr region the slope of our data is larger than those extrapolated from the high pressure data by Drozd et al. and Hakala et al. A modest fall-off behavior has been suggested by Hakala et al., as they noticed that in the low pressure region of 45-100 Torr their data did not follow the linear trend from the higher pressure. It is plausible that our data may continue with a different trend (smaller slope) in the higher pressure region. Nevertheless, our experiments provide confirmation of a nascent yield of sCI around 12% by using a technique that is best suited for low pressure measurements.
The comparison in Figure 3.5 shows that the sCl yields from our SO$_2$ scavenger, Hakala et al.'s H$_2$SO$_4$ formation, and Drozd et al.'s HFA SOZ measurements have discrepancies at relatively higher pressures but seem to converge at the zero-pressure limit. This could be an indication of pressure-dependent chemistry, especially for the sCl + SO$_2$ reaction, as both our experiment and that by Hakala et al. depend on the SO$_2$ scavenging. As previously noted, several computational studies have determined that oxidation SO$_2$ to SO$_3$ is the main pathway for the sCl + SO$_2$ reaction.$^{23-25}$ However, Kuwata et al. noticed that further exploration of the intermediate heteroozonide (HOZ) formed by the sCl + SO$_2$ reaction need be done, as a stabilized HOZ could further react with other atmospheric species.$^{25}$ This is significant, as recent work by Huang et al.$^{26}$ showed that the rate coefficient for the sCl + SO$_2$ reaction had a strong pressure dependence. It might, then, be plausible that at relatively higher pressures stabilization of the HOZ and subsequent reactions of the stabilized HOZ may depress the H$_2$SO$_4$ production in the sCl yield measurements, and furthermore, if the stabilized HOZ reacts significantly with SO$_2$ it could increase the SO$_2$ consumption in the sCl yield measurements. However, the behavior of the SO$_2$-Cl adduct needs to be studied further in order to determine its impact on the sCl determinations. Another consideration in comparing our work with that by Hakala et al. is the effect of water in the reaction system. In the measurements of sCl yield via H$_2$SO$_4$ formation by Hakala et al.,$^{13}$ 500 times of SO$_2$ and 5500 times of H$_2$O than the limiting reagent (~0.1 ppm alkene) were introduced to facilitate the H$_2$SO$_4$ formation, while no water was added in our experiment, except for possibly a small amount of H$_2$O product from the ozonolysis
reaction. The measurements of sCI and SO$_2$ might be affected by water if it is able to effectively scavenge sCI or react with SO$_2$. In our system, given that the amount of ozone (the limiting reagent) was ~15-30 ppm, the amount of water produced (if any) was expected to much smaller, and thus in our study water or water dimer could not compete with SO$_2$ as the sCI scavenger ($k=1.5\times10^{-16}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ and $k<1.3\times10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for water and water dimer, respectively). Reaction of water and SO$_2$ can be assumed to be insignificant due to the small amount of water in our system. Furthermore, the fact that SO$_2$ and water of high concentrations were added and coexisted in the H$_2$SO$_4$ formation and sCI yield measurements indicated the relative slowness of the SO$_2$ and H$_2$O reaction.

3.4.3 cis-2-Butene

Figure 3.6 shows the yield of acetaldehyde oxide (CH$_3$CHOO) from cis-2-butene ozonolysis. In the pressure range of 4–16 Torr, the sCI yield decreased with decreasing pressure. The trend is guided with a linear fit with an extrapolation to a sCI yield of 0.05 ± 0.04 at the zero-pressure limit. No distinction has been made between syn and anti conformers. No other work has explored the low pressure yields of sCI from ozonolysis of cis-2-butene. However, the previous study by Hatakeyama et al. and our findings on the yield of acetaldehyde oxide from ozonolysis of trans-2-butene showed a decrease of the sCI yield to zero at the zero-pressure limit. Our current findings show a similar trend for the cis-2-butene ozonolysis, albeit with a slightly higher yield. Both the previous studies on trans-2-butene and the current work on cis-2-butene indicate that the
acetaldehyde oxide can be stabilized with increasing pressure. Hatakeyama et al. found the yield of sCI from the trans-2-butene ozonolysis to be ~0.2 at 1 atm pressure, and our work on the sCI yield from trans-2-butene ozonolysis showed that the pressure-dependent yield had an increasing trend with increasing pressure, a trend which should flatten as the sCI yield reached a value around 0.2 at higher pressure of 1 atm. Figure 3 shows that the yield of sCI from cis-2-butene ozonolysis also increased with pressure and might be above 0.2 at 1 atm. Previous studies on the cis-2-butene ozonolysis determined the CH$_3$CHO yield of 0.18 and 0.43, respectively, at 1 atm pressure. The difference in the sCI yields between trans- and cis-2-butene can be partially due to measurement uncertainty and could require further work. The difference could also be due to different branching ratios of syn- and anti-CH$_3$CHO and their nascent internal energies from the trans-2-butene and cis-2-butene ozonolysis reactions. The theoretical work did indicate different branching ratios of syn- and anti-CH$_3$CHO in these two systems (0.75 syn-CH$_3$CHO for trans-2-butene and 0.28 for cis-2-butene).

3.4.4 2-Methyl-2-Butene

As 2-methyl-2-butene is an asymmetric alkene, its ozonolysis produces both acetaldehyde oxide and acetone oxide ((CH$_3$)$_2$COO), and the yield of sCI shown in Figure 3.7 corresponds to the sum of stabilized CH$_3$CHO and (CH$_3$)$_2$COO. The trend from 4–18 Torr shows decreasing total yield of sCIs with decreasing pressure and an extrapolation to the zero-pressure limit shows a nascent yield of total sCI of 0.01 ± 0.03. Given that the previous work on 2,3-dimethyl-2-butene have shown a nascent yield of
stabilized acetone oxide of approximately 0.12\textsuperscript{13,16} and that on \textit{trans}-2-butene ozonolysis a nascent yield of stabilized acetaldehyde oxide of zero,\textsuperscript{17} as well the nascent yield of stabilized acetaldehyde oxide of 0.05 in the \textit{cis}-2-butene ozonolysis from this work, the observed low yield of nascent sCIs found from 2-methyl-2-butene ozonolysis might be more due to the stabilized acetaldehyde oxide. The yield of acetone oxide from 2,3-dimethyl-2-butene at 1 atm has been measured to be \textasciitilde 0.4,\textsuperscript{13,14} while that of acetaldehyde oxide from \textit{trans}-2-butene ozonolysis was \textasciitilde 0.2 at 1 atm\textsuperscript{17} and that from \textit{cis}-2-butene ozonolysis was 0.18 or 0.43 at 1 atm pressure;\textsuperscript{27,28} it is expected the trend of total sCI yield from 2-methyl-2-butene ozonolysis to continue increasing slightly at higher pressure and level off in the range of 0.2 to 0.4 at 1 atm.

3.4.5 Cyclopentene and Cyclohexene

Figure 3.8 and Figure 3.9 show the low pressure yields of sCI produced by ozonolysis of cyclopentene and cyclohexene, respectively. The uncertainties regarding the sCI yield from cyclohexene are greater due to the lower rate constant (k=1.4x10\textsuperscript{-16} cm\textsuperscript{3}/molecule\cdot s for cyclohexene and k=8.1x10\textsuperscript{-16} cm\textsuperscript{3}/molecule\cdot s for cyclopentene). Nevertheless, both systems show essentially no sCI production at the low-pressure range of 5 – 20 Torr. The extrapolation to the zero-pressure limit for both cyclopentene and cyclohexene shows essentially no nascent sCI production as well. Hatakeyama et al. showed that the yield of sCI in the ozonolysis reaction of cyclopentene and cyclohexene at 1 atm pressure were 0.05 \textpm 0.01 and 0.03 \textpm 0.02, respectively.\textsuperscript{17} Donahue et al. have studied the yield of sCI produced by ozonolysis of cyclohexene in the pressure range of \textasciitilde
550 to 700 Torr and found that the yield of sCI near the atmospheric pressure was zero.\textsuperscript{30} This is to be expected for endocyclic alkenes, as the breaking of the POZ produces a single molecule with both a carbonyl and a carbonyl oxide, as well as high internal energy, resulting in a CI with very short lifetime that cannot be readily stabilized and, thus, decomposes at all pressures. Our low pressure yields of sCIs from these two endocyclic alkenes is consistent with data reported by Hatakeyama et al.\textsuperscript{17} and Donahue et al.,\textsuperscript{30} and with the expected extremely short lifetimes of CI produced from the endocyclic alkenes.

Figure 3.10 shows a summary of the nascent yields of sCI from ozonolysis of olefins according to their number of carbons and structure. Several factors, such as the nascent product internal energy distribution of CI and the isomerization/decomposition energy barrier of CI, determine the nascent yield of sCI in the ozonolysis of alkene. As the ozonolysis reaction has a large exothermicity, the specific structure and reaction mechanism of the alkene would determine the excess energy disposal among the products and thus the internal energy distribution of the nascent CI. The more ways the excess energy can be partitioned between the carbonyl and CI fragments, the lower internal energy the nascent CI product could contain and potentially the higher yield of the nascent sCI. For example, for acyclic and exocyclic alkenes, their POZs decompose into separated carbonyl and CI fragments, and the excess energy is partitioned into many modes of the fragments (translational, vibrational, and rotational); the larger alkene could allow more vibrational modes for internal energy partition. The energy barrier for CI isomerization and decomposition also influences the nascent yield of sCI; the higher the
energy barrier, the larger the fraction of CI could be produced with internal energy below the barrier and thus as sCI. These factors also influence how efficiently the CI can be stabilized by collisions and thus the pressure dependence of the sCI yield.

The nascent sCI yields of endocyclic olefins are zero because the CIs produced have high internal energies, as the ring scission of the POZ leads to a single molecule (CI) with both carbonyl and carbonyl oxide, and, consequently with short lifetime and undergoing very fast dissociation. Because of these, the CIs from endocyclic alkenes cannot be efficiently stabilized and thus the sCI yields are zero from the low pressure to the atmospheric pressure.

For acyclic olefins, however, the reaction mechanism involves initial splitting of POZ into the carbonyl and carbonyl oxide fragments and thus a broad internal energy distribution in CI, and sCI can be produced and it can also be further pressure stabilized. The experimental nascent sCI yields from the acyclic alkenes (Figure 3.10), as well as the pressure dependences of the sCIs, are consistent with this reaction mechanism. For the acyclic olefins studied so far, there is a significant variation in the nascent yield of sCI (from approximately zero to 0.2), and there is no straightforward correlation with the size of the olefin (number of carbons). It should also be noted that overall the nascent sCI yields of these acyclic olefins are significantly smaller than unity, underscoring the large excess energy in the ozonolysis reactions and the significant amount of internal energy in the nascent CI fragments. Hatakeyama et al. found the nascent yield of CH₂OO from ozonolysis of ethene to be ~0.2.¹⁸ Although ethene is the smallest alkene in size, it has a higher sCI yield. The sCI yields of trans-2-butene and cis-2-butene are in the low range
of 0.00-0.05, and that of 2-methyl-2-butene is in the same range with a slightly increased molecular size. A significant increase in the nascent sCI yield is observed in 2,3-dimethyl-2-butene (~0.12) with a further increase in the molecular size. The CI product of ethene, formaldehyde oxide, has a theoretical isomerization energy barrier of 18.2-19.1 kcal/mol to dioxirane and 30.8-31.8 kcal/mol to hydroperoxide. The isomerization energy barrier of acetaldehyde oxide to vinylhydroperoxide was calculated to be 17.1 kcal/mol and that of acetone oxide to be 14.8-16.2 kcal/mol. The higher sCI in ethene could be due to the higher isomerization energy barrier of CH₂OO, as well as its nascent energy distribution from the ethene ozonolysis. The theoretical studies estimated that the nascent sCI yield in ethene was 0.2 in an earlier work or 0.36 in a recent report. This comparison of the nascent yield of formaldehyde oxide highlights the importance of experimental measurements to help theoretical work. For the ozonolysis of acyclic C₄-C₆ acyclic alkenes, the nascent yield of sCI in 2,3-dimethyl-2-butene is higher, despite of the lower isomerization barrier of acetone oxide; it seems that the increased molecular size may start to have an effect on the partitioning of excess energy and the internal energy distribution of CI. The early theoretical study estimated that the nascent sCI yield in 2,3-dimethyl-2-butene was ~0.04, and this underestimation in comparison with the experimental value again highlights the importance of experimental measurements to validate the theoretical work. Our experimental results add to those in the literature and help the computational and theoretical work.
3.5 Conclusions

Indirect determination of the yield of stabilized acetaldehyde oxide and acetone oxide were carried out at low pressures using chemical titration of the sCIs with the SO₂ scavenger. In contrast with the previous work, SO₂ consumption instead of H₂SO₄ formation was monitored in order to determine the low pressure sCI yields. Furthermore, the low pressure measurements can provide more accurate zero-pressure extrapolation of the sCI yield that may have different pressure dependence at higher pressures (e.g., a falloff behavior). The yields of stabilized Criegee intermediates produced from ozonolysis of cis-2-butene, trans-2-butene, 2-methyl-2-butene, 2,3-dimethyl-2-butene, cyclopentene, and cyclohexene were determined at low pressures. The pressure dependences of the sCI yields were in accordance to expectation from the previous work and consistent with the upper limits set by high pressure measurements. The nascent yields of sCIs of acyclic alkenes vary with the number of carbons, without a straightforward trend. The nascent sCI yields of endocyclic alkenes are essentially zero. These data allow for more insights on the nascent yields of sCIs and provide benchmarks for theoretical calculations.
3.6 Figures

Figure 3.1. Schematic of the reaction cell used for alkene ozonolysis. The corresponding alkene and SO\textsubscript{2} were mixed with nitrogen. Ozone was generated in situ and reacted with the alkene/SO\textsubscript{2} mixture at the inlet. Pressure was monitored using a digital pressure gauge and residence time was determined by measuring the time it took to fill and empty the reaction cell. Purge lines were set up to protect mirrors from contamination. FM: flow meter; PMT: photomultiplier tube.
Figure 3.2. Representative spectra of experimental measurements of initial and final concentrations of O$_3$ and SO$_2$. $\Delta(1/\tau) = (1/\tau - 1/\tau_0)$. Spectra were fitted with reference cross sections.$^{21}$ No ozone features were observed during the ozonolysis experiments, indicating its complete consumption.
Figure 3.3. SO$_2$ consumption in the 2,3-dimethyl-2-butene ozonolysis reaction at different initial SO$_2$ concentrations at a total pressure of 12 Torr. [SO$_2$]/[O$_3$]$_i$ is the ratio of initial [SO$_2$] with respect of ozone and represents the proportion of excess SO$_2$ in the reaction cell. ∆[SO$_2$]/∆[O$_3$] is the ratio of consumed SO$_2$ with respect to the amount of ozone consumed in the reaction and represents the amount of sCl scavenged. At high [SO$_2$]/[O$_3$]$_i$, the amount of sCl scavenged reached a maximum plateau, corresponding to complete titration of sCl and the yield of sCl. Error bars represent one standard deviation of repeated measurements.

In this work: 
\[ \Delta[O_3] = [O_3]_i \]
Figure 3.4. Yield of acetaldehyde oxide in the ozonolysis of trans-2-butene at different pressures. In the case of trans-2-butene, experiments were carried out only from 2-14 Torr due to the rapid extinction of the ring-down time, presumably by aerosol and secondary products. The solid line is a linear fit of the data in this study. Extrapolated data from Hatakeyama et al.\textsuperscript{17} are included for comparison (dashed line). Error bars represent one standard deviation of repeated measurements.
Figure 3.5. Yield of acetone oxide from ozonolysis of 2,3-dimethyl-2-butene at different pressures. Experiments were conducted from 4 to 60 Torr. The solid line is a linear fitting of the data in this study, and it is used as a simple illustration of the pressure-dependent sCI yield. The yield data from Drozd et al.\textsuperscript{16} and Hakala et al.,\textsuperscript{13} with their lowest pressure points around 40 Torr, are included for comparison (dashed and dotted lines are their respective extrapolations). Error bars represent one standard deviation of repeated measurements.
Figure 3.6. Yield of acetaldehyde oxide from ozonolysis of cis-2-butene at different pressures. The dashed line is a linear fit of the data with an extrapolation to the zero-pressure limit. Error bars represent one standard deviation of measurements at each pressure.
Figure 3.7. Total yield of acetaldehyde oxide and acetone oxide produced from ozonolysis of 2-methyl-2-butene at different pressures. The dashed line is a linear fit of the data with an extrapolation to the zero-pressure limit. Error bars represent one standard deviation of measurements at each pressure.
Figure 3.8. Yield of sCI produced from ozonolysis of cyclopentene at different pressures. The dashed line is a linear fit of the data with an extrapolation to the zero-pressure limit. Error bars represent one standard deviation of measurements at each pressure.
Figure 3.9. Yield of sCI produced from ozonolysis of cyclohexene at different pressures. The dashed line is a linear fit of the data with an extrapolation to the zero-pressure limit. Error bars represent one standard deviation of measurements at each pressure.
Figure 3.10. Nascent (zero-pressure) yield of sCI (total sCI in the case of 2-methyl-2-butene) produced from ozonolysis of different olefins according to the carbon number and the structure. The yield of CH$_2$OO from ethene ozonolysis was reported from Hatakeyama et al.$^{18}$ The solid circles represent acyclic olefins and solid squares for endocyclic olefins.
3.7 References


Direct measurement of vinoxy radicals and formaldehyde produced from ozonolysis of 2-butenes

4.1 Abstract
Tropospheric ozonolysis of alkenes plays an important role in the atmosphere due to their production of highly oxidized species and organic radicals via reactions and decomposition of the Criegee intermediate. In the case of Criegee intermediates with α-carbons, the isomerization and subsequent decomposition of the Criegee intermediate leads to the production of ·OH radicals. For cis- and trans-2-butene, the ozonolysis reaction leads to production of syn- and anti-CH$_3$CHOO, and the syn conformer isomerizes into a vinylhydroperoxide that in turn decomposes into ·OH radical and ·CH$_2$CHO, also known as vinoxy radical. Vinoxy radicals react rapidly with tropospheric oxygen, further producing ·OH as well as formaldehyde (HCHO) and glyoxal (CHOCHO). Using cavity ring-down spectroscopy in a flow reactor with multi- and single-inlet configurations, the concentrations of ·CH$_2$CHO and HCHO were monitored under various conditions and compared to a reaction mechanism. The ratio of average steady-state concentrations of vinoxy radicals from cis-2-butene with respect to trans-2-butene was found to be approximately 0.6, in good agreement with the yield ratio of OH radicals from ozonolysis of these two alkenes. On the other hand, the yield ratio of HCHO was close to unity, indicating that it was produced from additional reaction pathways not involving the vinoxy radical.
4.2 Introduction

One of the most important roles that ozonolysis of olefins plays in the troposphere is the production of OH radicals,\textsuperscript{1–3} in particular during nighttime, as this process does not require sunlight.\textsuperscript{1,4} In the case of 2-butenes, and similarly for alkenes that produce Criegee intermediates with $\alpha$-hydrogens, the production of OH radicals is done via isomerization of the acetaldehyde oxide zwitterion into a vinylhydroperoxide (VHP) by H-atom migration.\textsuperscript{5,6} The vinylhydroperoxide has a short lifetime and it rapidly decomposes into $\cdot$CH$_2$CHO, also known as vinoxy radical, and $\cdot$OH. Figure 4.1 shows a schematic of the mechanism of $\cdot$OH formation. The Criegee intermediate produced from 2-butene ozonolysis can have two different conformations, depending on the proximity of the negatively charged oxygen to the $\alpha$-hydrogen, the conformer closest to it being the syn-CH$_3$CHOO and the one with the opposite orientation being the anti-CH$_3$CHOO (see Figure 4.1). Computational work by Kuwata et al.\textsuperscript{7} showed that the barrier of isomerization of syn-CH$_3$CHOO into VHP is roughly 6.5 kcal/mol lower than the barrier of isomerization into dioxirane. On the other hand, the barrier of isomerization of the anti conformer into dioxirane is roughly 15.2 kcal/mol lower than the barrier of isomerization into VHP. Therefore, the VHP is only formed from the syn-CH$_3$CHOO, as the anti conformer will form dioxirane. The VHP decomposes into $\cdot$OH and $\cdot$CH$_2$CHO, which reacts with oxygen to produce additional OH radicals, as well as HCHO and CHOCHO.\textsuperscript{8}

Ozonolysis of 2-butenes has been extensively studied, and the yields of several of its products have been measured.\textsuperscript{9–13} By monitoring the formation of products using
certain scavengers, yields of organic radicals and ·OH have also been determined.\textsuperscript{2,14–17} Computational works have studied several steps of the ozonolysis of 2-butenes, from the formation of ·OH radicals, to the dissociation pathways of the vinoxy radical.\textsuperscript{7,18–22} Gutbrod et al. and Kuwata et al. have shown that the energy barrier of isomerization of syn-CH\textsubscript{3}CHOO into VHP is significantly lower than the barrier of isomerization into dioxirane and, therefore, decomposition of syn-CH\textsubscript{3}CHOO via dioxirane is not significant,\textsuperscript{7,23} and it has been shown that the barrier for syn and anti interconversion is high, usually higher than 20 kcal/mol.\textsuperscript{7,21,24} Therefore, the syn and anti conformers of acetaldehyde oxide will undergo distinct processes with different product yields and branching ratios. Furthermore, studies on the fraction of CH\textsubscript{3}CHOO that is formed with relatively low internal energies and survives long enough to undergo bimolecular reactions, the stabilized Criegee intermediates, have provided insights on the impact of bimolecular reactions on the unimolecular decomposition processes.\textsuperscript{25,26} The ability to produce CH\textsubscript{3}CHOO via photolysis of diiodoethane and reaction of iodoethyl with oxygen\textsuperscript{27} has been exploited by several groups in order to assess the kinetics of bimolecular reactions of both syn and anti conformers.\textsuperscript{28,29} In addition, some have studied the decomposition pathways of CH\textsubscript{3}CHOO into vinoxy and OH radicals, assessed the effect of tunneling, providing unimolecular decomposition rates and providing experimental data to compare with theoretical calculations.\textsuperscript{30–32}

Given the assumption that most of the OH radical is produced via decomposition of syn-CH\textsubscript{3}CHOO, it is possible to obtain information of the branching ratio between syn and anti conformers for OH radical yield measurements. This ratio has been found to be
different for ozonolysis of cis-2-butene and ozonolysis of trans-2-butene, both by theoretical calculations and by measurements of the ·OH yields. It has been found both experimentally and theoretically that cis alkenes show preference for anti-CH₂CHOO production.¹⁹,³³ It is expected that some OH radical production will occur from isomerization and decomposition of the anti conformer, but their contribution is expected to be low, as the dioxirane/”hot” ester channel requires additional decomposition processes to produce them.³³ In this work, we measure ·CH₂CHO and HCHO directly from the ozonolysis of 2-butenes under various reaction conditions using cavity ring-down spectroscopy (CRDS) in a flow reactor with multi- and single-inlet configurations and compare the experimental measurements with simulations of steady-state concentrations using a mechanism of ozonolysis in order to provide new insights on branching ratios of syn-CH₂CHOO from cis- and trans-2-butene ozonolysis and formaldehyde reaction pathways.

4.3 Experimental Method

Cavity-ring down spectroscopy was used to measure average steady-state concentrations of HCHO and ·CH₂CHO in a wavelength range of 340 – 350 nm. The high reflectivity mirrors used had an operational wavelength range of 340 – 370 nm (99.95%, Layertec GmbH). The cavity also played the role of a flow cell with two different configurations, a single-inlet flow cell where a O₃/O₂/N₂ mixture reacted at the reactor inlet with a C₄H₈/N₂ mixture from a manifold, and a multi-inlet flow cell where a fraction of the O₃/O₂/N₂ mixture was exposed to the alkene mixture at different inlets.
along the flow cell. Figure 4.2 shows a schematic of both cell configurations. Flows were controlled using both flow meters (GFM17, Aalborg) with an attached pin valve (Swagelok), and using mass flow controllers (GFC17, Aalborg). The reaction times are set relatively long (1 – 2 s) to ensure that the reaction went to completion, and the reactions were carried out at a low pressure of 15 Torr to prevent significant stabilization of the acetaldehyde oxide. The ozonolysis reactions of cis- and trans-2-butene were carried out at the ozone concentration range of 4x10^{15} - 1x10^{16} molecule/cm^3 and with different oxygen additions to the C_4H_8/N_2 mixture ranging from 5x10^{15} - 3x10^{16} molecule/cm^3. Ozone was produced using a corona-discharge ozone generator (Welsbach Ozone Systems) from an oxygen flow (>95%, Airgas) and adsorbed in silica gel at ~ -70°C using an acetone/CO_2 bath, the temperature of the trap was changed to ~ -40°C using an acetonitrile/CO_2 bath during the experiments. Figure 4.3 shows a schematic of the O_3/O_2/N_2 mixture and the C_4H_8/N_2 mixture manifolds. The alkene was kept in excess at 1x10^{17} molecule/cm^3.

The mechanism of ozonolysis of 2-butene is summarized in Figure 4.4. The flow cell was assumed to behave as a plug flow reactor and was modelled as a series of CSTRs using the kinetic package Kintecus. In the case of the multi-inlet flow cell, the modelled segments were set to coincide with the inlets along the reactor in order to account for the additional O_3/O_2/N_2 flowed into the system. The concentrations of ·CH_2CHO and HCHO were measured from the ring-down decay rates by considering only the contributions of both species according to the following equation:
\[
\left( \frac{1}{\tau(\lambda)} - \frac{1}{\tau_0(\lambda)} \right) = \frac{dc}{L} \left( \sigma_{\text{vinoxy}}(\lambda) N_{\text{vinoxy}} + \sigma_{\text{form}}(\lambda) N_{\text{form}} + f(\lambda) \right)
\]

The number densities of vinoxy radical and formaldehyde were obtained by fitting reference absorption cross-sections of \( \cdot \text{CH}_2\text{CHO} \) and HCHO (see Figure 4.5) using single value decomposition (SVD) of the canonical form of this equation, thus, \( f(\lambda) \) becomes a polynomial function. Figure 4.6 shows an example of the spectra measured and a SVD fit.

4.4 Results and Discussion

4.4.1 Multi-inlet flow cell

Figure 4.7 shows the concentrations of vinoxy radical and formaldehyde from \textit{cis}- and \textit{trans}-2-butene at different concentrations of oxygen added to the \textit{C}_4\text{H}_8/\text{N}_2\) mixture. While the model follows the trend for \( \cdot \text{CH}_2\text{CHO} \) under different oxygen additions, it does not replicate the behavior of formaldehyde. Furthermore, two issues arise from multi-inlet flow cell measurements: one experimental and one due to the model applied. Determination of the amount of oxygen in the reactor also proved to be experimentally difficult, as the concentration of oxygen from the trap cannot be accurately determined and is only known to be comparatively low at each segment inlet and only the oxygen concentration added can be measured. In the case of the model, it can be observed that it fails to describe the concentration of formaldehyde for \textit{trans}-2-butene ozonolysis. A ratio of the steady-state concentration of \( \cdot \text{CH}_2\text{CHO} \), and HCHO, for \textit{cis}-2-butene with respect
to trans-2-butene can be calculated. These ratios were approximately 0.6 and 1 for \( \cdot \text{CH}_2\text{CHO} \) and HCHO, respectively.

4.4.2 Single-inlet flow cell

As single-inlet experiments did not distribute the O\(_3\)/O\(_2\)/N\(_2\) mixture along the reactor (it was added entirely at the first reactor inlet), ozone concentration was easier to measure but the oxygen concentration from the ozone trap was difficult to quantify and can only be said to be high enough to scavenge most of the \( \cdot \text{CH}_2\text{CHO} \). Nevertheless, the absorption cross-section of \( \cdot \text{CH}_2\text{CHO} \) is high enough to allow for the measurement of the small average steady-state concentrations in the reaction cell. Figure 4.8 shows the \( \cdot \text{CH}_2\text{CHO} \) concentrations at different initial ozone concentrations for cis- and trans-2-butene ozonolysis. The ratio of these steady-state concentrations was determined to be approximately 0.6. This ratio is consistent with the measurements from the multi-inlet flow cell, and with the reported yield of OH radical for cis-2-butene (0.36), and trans-2-butene (0.6) ozonolysis.\(^{16}\) This is indication that the vinoxy radical, and by extension syn-CH\(_3\)CHOO, is closely related to OH radical production. Therefore, most OH radical is produced from the decomposition of the syn conformer of acetaldehyde oxide. In addition, since \( \cdot \text{CH}_2\text{CHO} \) reacts with oxygen to produce additional OH radicals, the yield of vinoxy radical and, by extension, the yield of syn-CH\(_3\)CHOO (\( \alpha \) and \( \beta \) in Figure 4.1) must be lower than 0.36 and 0.6 for cis- and trans-2-butene ozonolysis, respectively.

Figure 4.9 shows the concentrations of HCHO for cis- and trans-2-butene ozonolysis at different initial ozone conditions. The ratio of the steady-state
concentrations is essentially unity. Given that the mechanism previously shown produces formaldehyde mostly from the reaction of vinoxy radical and oxygen, it cannot account for this behavior and was modified to include an additional HCHO production pathway that is not dependent on vinoxy radical chemistry. Some examples of such pathways have been proposed by Martinez & Herron\textsuperscript{35} and by Kuwata et al.,\textsuperscript{22} the former involving isomerization of the anti conformer of acetaldehyde oxide into a “hot” ester, and decomposition into formaldehyde, the latter involving a rearrangement of the VHP into hydroxyacetaldehyde with a subsequent decomposition into formaldehyde (See Figure 4.10). In the mechanism used for simulating the ozonolysis reaction, a non-specific HCHO formation pathway from anti-CH\textsubscript{3}CHOO decomposition was included to explain the experimental results.

4.4.3 Mechanism of ozonolysis of 2-butene

Table 4.1 and Table 4.2 show the detailed mechanism for trans- and cis-2-butene ozonolysis, respectively. As the reaction products are the same, so are all of the secondary reactions, and the distinction comes from the branching ratios of the different conformers of acetaldehyde oxide and the difference in the rate constant of the ozonolysis reaction. However, it was assumed that the internal energy content of syn- and anti-CH\textsubscript{3}CHO from trans- and cis-2-butene was similar and, thus their subsequent reactions. Nevertheless, several aspects that require further work have been found by using experimental measurements to validate the mechanism of ozonolysis. As covered in Chapter 2, stabilization of the Criegee intermediate at 15 Torr is ~10% and ~15% for
trans- and cis-2-butene, therefore, the effect of the bimolecular reactions of acetaldehyde oxide is not considered to be very significant. Furthermore, the stabilized acetaldehyde oxide is expected to react rapidly with the reactants and reaction products. However, currently there is no much data on the reactions of CH₃CHOO and the rate constants of its reaction with ozone, 2-butene, and formaldehyde were assumed to be sufficiently similar to those of CH₂OO. Similarly to the case of CH₂OO from ethene ozonolysis, it is expected that acetaldehyde oxide will be depleted by the reactants and acetaldehyde. Fenske et al.³⁶ have reported the rate of the reaction of CH₃CHOO with CH₃CHO to be 1.10x10⁻¹² cm³/molecule·s and, thus, acetaldehyde is an important scavenger of the Criegee intermediate. Fang et al.³⁰ reported the unimolecular isomerization rate of stabilized syn-CH₃CHOO to be 166 s⁻¹, producing vinoxy radicals and OH, but not in a significant amount as the yield of stabilized acetaldehyde oxide is small. Reaction of the stabilized Criegee intermediate with the vinoxy radical was set to be fast (k=1.00x10⁻¹¹ cm³/molecule·s) but does not play a significant role under the reaction conditions as oxygen effectively scavenged the vinoxy radical.

The steady-state concentration of vinoxy radical is expected to be low, as there are many depletion processes. The depletion processes for vinoxy radicals in the ozonolysis mechanism used were its reaction with oxygen, OH radical, and acetaldehyde oxide. Of these reactions, only the reaction with oxygen has a measured rate constant. However, OH is scavenged by the alkene (k=6.40x10⁻¹¹ cm³/molecule·s) rapidly and the concentration of acetaldehyde oxide is expected to be small, as mentioned above. The pressure-adjusted overall rate constant for the reaction of oxygen with the vinoxy radical
is $1.05 \times 10^{-13}$ cm$^3$/molecule·s, and the high oxygen concentrations ensured that oxygen effectively scavenged the vinoxy radical. Although the yield of CHOCHO has been reported by Zhu and Johnston to be $0.15 \pm 0.05$, and Lorenz et al. have reported that the combined yield of CHOCHO and HCHO is $\sim 0.2$, we found that experimental measurements best agree with a HCHO yield of 0.18 from the reaction of vinoxy radical with oxygen. Further studies on glyoxal and formaldehyde production from this reaction would provide more information on these yields.

The yield of HCHO from anti-CH$_3$CHOO decomposition was set to be the same as the yield of HCHO from the reaction of vinoxy radical and oxygen. That the yields of HCHO are the same for the reaction pathways of both acetaldehyde oxide conformers is the consequence of cis- and trans-2-butene ozonolysis having the same yield of HCHO but different syn- and anti-CH$_3$CHOO branching ratios, and that the yields of the syn and anti conformers for a given 2-butene should add to unity. While the production of HCHO from the anti conformer was chosen for the kinetic model, there is currently no way to determine the source of HCHO that is not produced from the reaction of the vinoxy radical and oxygen and further work is necessary to determine these reactions.

The yield of vinoxy radical, as mentioned above, is known to be less than the yield of OH radical, as OH radicals are coproducts of formaldehyde and glyoxal produced from the reaction of vinoxy radical with oxygen. The OH yield from ·CH$_2$CHO and oxygen will be the sum of the yields of HCHO and CHOCHO, e.g. 0.24 in our kinetic model. From these constraints on the model, the values for the yield of syn-CH$_3$CHOO from ozonolysis of trans- and cis-2-butene ($\alpha$ and $\beta$ in Figure 4.1) were found to be $\sim 0.5$ and
~0.3 respectively. However, these values depend on the yields of HCHO and CHOCHO, as well as on an accurate determination of oxygen in the reactor, and can only be considered to be rough estimates. Nevertheless, this points to the necessity of further work on the relative rates of the different pathways of the reaction of the vinoxy radical with oxygen, as well as further work on the improvement of the reaction system for accurate oxygen measurements. Furthermore, as can be observed from the simulations in Figure 4.8 and Figure 4.9, the kinetic model was in good agreement with the experimental results. Constraints from measured rate constants and from the various information of branching ratios and yields allowed us to use our experimental results to provide estimates of rate constants and branching ratios.

4.5 Conclusions

Direct measurements of \( \cdot \text{CH}_2\text{CHO} \) and HCHO produced from ozonolysis of \( \text{cis} \)- and \( \text{trans} \)-2-butene were done under different ozone and oxygen concentrations. A multi-inlet flow cell was used with limited success to assess the role of oxygen on the steady-state concentration of \( \cdot \text{CH}_2\text{CHO} \) but proved difficult to accurately assess the concentrations of ozone at each reaction segment and the behavior of the reaction system. Nevertheless, the multi- and single-inlet experiments led to interesting results. Measurements of the ratio of steady-state concentrations of \( \cdot \text{CH}_2\text{CHO} \) for \( \text{cis} \)-2-butene with respect to \( \text{trans} \)-2-butene ozonolysis are in agreement with the yield ratio of OH radicals reported in the literature for these reactions. This supports the assumption that OH radicals are produced principally from isomerization of syn-CH₃CHOO into
vinylhydroperoxide and its decomposition into vinoxy and OH radicals. Measurements of HCHO show equal production from cis- and trans-2-butene ozonolysis, suggesting the existence of a HCHO production pathway equally as important as the production of HCHO from -CH₂CHO + O₂. While further work is needed to identify the HCHO production channel, this work provides new insights on the different parts of the mechanism of ozonolysis of 2-butenes.
4.6 Figures

Figure 4.1. Mechanism of OH radical formation from ozonolysis of 2-butenes via isomerization of syn-CH$_3$CHOO into vinylhydroperoxide (VHP) and decomposition into vinoxy and OH radicals. The symbols $\alpha$ and $\beta$ are used to indicate the yields of syn-CH$_3$CHOO for *trans*- and *cis*-2-butene, respectively.
Figure 4.2. Design of multi- and single-inlet flow cells used in cis- and trans-2-butene ozonolysis experiments.
Figure 4.3. Design of the ozone trap with a flow manifold for multi-inlet reactor experiments, in the case of single-inlet experiments, flow after the flow meter (FM) goes directly to the reactor inlet and it was not divided among segments. The alkene and nitrogen flow manifold was the same for both single- and multi-inlet experiments.
Figure 4.4. Mechanism of ozonolysis of 2-butene. Yields are shown in blue, rate constants are shown in red. Rates obtained from refs 6,8,38.
Figure 4.5. Reference spectra used for the determination of the number densities of vinoxy radical and formaldehyde. The spectra for vinoxy radical and formaldehyde were obtained from Wang and Zhang\textsuperscript{39} and Cantrell et al.,\textsuperscript{40} respectively.
Figure 4.6. Single value decomposition (SVD) fit of experimental spectra. The ·CH$_2$CHO and HCHO features show at 347.25 and 347.75 nm, respectively.
Figure 4.7. Average steady-state concentrations of CH$_2$CHO and HCHO in the ozonolysis of cis- and trans-2-butene in a multi-inlet flow cell. Measurements in black, simulated concentrations using an ozonolysis mechanism in red.
Figure 4.8. Average steady-state concentrations of ·CH₂CHO in the ozonolysis of *cis*- and *trans*-2-butene in a single-inlet flow cell. Measurements in black, simulated concentrations using an ozonolysis mechanism in red.
Figure 4.9. Average steady-state concentrations of HCHO in the ozonolysis of *cis*- and *trans*-2-butene in a single-inlet flow cell. Measurements in black, simulated concentrations using an ozonolysis mechanism with an additional HCHO production process from anti-CH$_3$CHOO in red.
Figure 4.10. Possible HCHO formation channels. A “hot” ester channel has been proposed by Martinez and Herron\textsuperscript{35} that involves the migration of a methyl group to form an ester with high internal energy. Kuwata et al.\textsuperscript{22} propose a OH migration in VHP in order to form hydroxyacetaldehyde, with eventual production of formaldehyde.
Table 4.1. Mechanism of ozonolysis of trans-2-butene used to simulate the concentration profile in the single-inlet flow cell and calculate average steady-state concentrations.

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<th>#</th>
<th>Reaction</th>
<th>Branching ratio</th>
<th>k (cm³/molecules·s)</th>
<th>Reference</th>
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<td>$\text{C}_4\text{H}_6+\text{O}_3 \rightarrow \text{CH}_3\text{CHO}$</td>
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<td>$\rightarrow 0.5\text{CH}_2\text{CHO} + 0.5\text{OH}$</td>
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<td>$\rightarrow 0.05\text{CH}_2\text{CO} + 0.05\text{H}_2\text{O}$</td>
<td>0.05</td>
<td>-</td>
<td>15</td>
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<td>$\rightarrow 0.07\text{CH}_3\text{OH}$</td>
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<td>-</td>
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<td></td>
<td>$\rightarrow P$</td>
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<td>Mass balance</td>
</tr>
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<td>6.00E-15⁺</td>
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</tr>
<tr>
<td>3</td>
<td>$\text{CH}_2\text{CHO} + \text{O}_2 \rightarrow \text{HCHO} + \text{CO} + \text{OH}$</td>
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<td>1.80E-14⁺</td>
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<tr>
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<td>7.60E-14⁺</td>
<td>See text</td>
</tr>
<tr>
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<td>-</td>
<td>10⁺</td>
<td>Wall loss</td>
</tr>
<tr>
<td>6</td>
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<td>166⁺</td>
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<td>1.10E-12</td>
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<td>8</td>
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<td>2.60E-14</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>$\text{CH}_3\text{CHO} + \text{CH}_3\text{CHO} \rightarrow \text{H}_2\text{O} + \text{HCHO} + \text{HCHO} + \text{H}_2\text{C}_2$</td>
<td>-</td>
<td>3.60E-15</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>$\text{CH}_3\text{CHO} + \text{O}_3 \rightarrow \text{CH}_3\text{CHO} + \text{O}_2 + \text{O}_2$</td>
<td>-</td>
<td>1.00E-13</td>
<td>See text</td>
</tr>
<tr>
<td>11</td>
<td>$\text{CH}_3\text{CHO} + \text{H}_2\text{O} \rightarrow P$</td>
<td>-</td>
<td>5.40E-17</td>
<td>43</td>
</tr>
<tr>
<td>12</td>
<td>$\text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2$</td>
<td>-</td>
<td>1.60E-12</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>Reaction</td>
<td>Rate Constant (M$^{-1}$ s$^{-1}$)</td>
<td>Rate Constant (cm$^3$ molecule$^{-1}$ s$^{-1}$)</td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>--------------------------------------------------------------------------</td>
<td>------------------------------------</td>
<td>-----------------------------------------------</td>
<td>---</td>
</tr>
<tr>
<td>13</td>
<td>OH + C$_4$H$_8$ → C$_4$H$_8$OH</td>
<td>-</td>
<td>6.40E-11</td>
<td>36</td>
</tr>
<tr>
<td>14</td>
<td>CH$_3$OH + OH → 0.85CH$_2$OH + 0.85H$_2$O</td>
<td>0.85</td>
<td>9.10E-13</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td>→ 0.15CH$_3$O + 0.15H$_2$O</td>
<td>0.15</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>15</td>
<td>CH$_2$OH + O$_2$ → H$_2$CO + HO$_2$</td>
<td>-</td>
<td>9.10E-12</td>
<td>44</td>
</tr>
<tr>
<td>16</td>
<td>HCHO + OH → HCO + H$_2$O</td>
<td>-</td>
<td>1.60E-11</td>
<td>36</td>
</tr>
<tr>
<td>17</td>
<td>OH + CH$_2$CHO → P</td>
<td>-</td>
<td>1.00E-11</td>
<td>See text</td>
</tr>
<tr>
<td>18</td>
<td>CH$_3$CHO + OH → 0.05CH$_2$CHO + 0.05H$_2$O</td>
<td>0.05</td>
<td>1.53E-11</td>
<td>45,46</td>
</tr>
<tr>
<td></td>
<td>→ 0.95H$_2$O + 0.95CH$_3$CO</td>
<td>0.95</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>19</td>
<td>CH$_3$CHO → P</td>
<td>-</td>
<td>10*</td>
<td>Wall loss</td>
</tr>
<tr>
<td>20</td>
<td>CH$_3$CHO + C$_4$H$_8$ → P</td>
<td>-</td>
<td>1.00E-15</td>
<td>See text</td>
</tr>
<tr>
<td>21</td>
<td>CH$_3$CHO + HCHO → P</td>
<td>-</td>
<td>1.00E-12</td>
<td>See text</td>
</tr>
<tr>
<td>22</td>
<td>CH$_3$CHO + CH$_2$CHO → P</td>
<td>-</td>
<td>1.00E-11</td>
<td>See text</td>
</tr>
</tbody>
</table>

Rate constants represent the overall rate for a numbered reaction. *Unimolecular rate constants in 1/s. †Rates obtained from the branching ratios of the overall rate constant adjusted for pressure according to the IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation (http://iupac.pole-ether.fr).
Table 4.2. Mechanism of ozonolysis of cis-2-butene used to simulate the concentration profile in the single-inlet flow cell and calculate average steady-state concentrations.

<table>
<thead>
<tr>
<th>#</th>
<th>Reaction</th>
<th>Branching ratio</th>
<th>$k$ (cm$^3$/molecule$\cdot$s)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$C_4H_8 + O_3 \rightarrow CH_3CHO$</td>
<td>1</td>
<td>1.30E-16</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>$\rightarrow 0.15 CH_3CHO$OO</td>
<td>0.1</td>
<td>-</td>
<td>See text</td>
</tr>
<tr>
<td></td>
<td>$\rightarrow 0.3 CH_3CHO + 0.3 OH$</td>
<td>0.3</td>
<td>-</td>
<td>See text</td>
</tr>
<tr>
<td></td>
<td>$\rightarrow 0.05 CH_2CO + 0.05 H_2O$</td>
<td>0.05</td>
<td>-</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>$\rightarrow 0.07 CH_3OH$</td>
<td>0.07</td>
<td>-</td>
<td>41,42</td>
</tr>
<tr>
<td></td>
<td>$\rightarrow 0.18 HCHO$</td>
<td>0.18</td>
<td>-</td>
<td>See text</td>
</tr>
<tr>
<td></td>
<td>$\rightarrow P$</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>$CH_2CHO + O_2 \rightarrow CHOCHO + OH$</td>
<td>0.06</td>
<td>6.00E-15$^1$</td>
<td>See text</td>
</tr>
<tr>
<td>3</td>
<td>$CH_2CHO + O_2 \rightarrow HCHO + CO + OH$</td>
<td>0.18</td>
<td>1.80E-14$^1$</td>
<td>See text</td>
</tr>
<tr>
<td>4</td>
<td>$CH_2CHO + O_2 \rightarrow OOCH_2CHO$</td>
<td>0.76</td>
<td>7.60E-14$^1$</td>
<td>See text</td>
</tr>
<tr>
<td>5</td>
<td>$CH_3CHOO \rightarrow P$</td>
<td>-</td>
<td>10$^*$</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>$CH_3CHOO \rightarrow P$</td>
<td>-</td>
<td>166$^*$</td>
<td>30</td>
</tr>
<tr>
<td>7</td>
<td>$CH_3CHO + CH_3CHO \rightarrow SOZ$</td>
<td>-</td>
<td>1.10E-12</td>
<td>36</td>
</tr>
<tr>
<td>8</td>
<td>$CH_3CHO + CH_3CHO \rightarrow CH_3COOH + CH_3CHO$</td>
<td>-</td>
<td>2.60E-14</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>$CH_3CHO + CH_3CHO \rightarrow H_2O + HCHO + HCHO + H_2C_2$</td>
<td>-</td>
<td>3.60E-15</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>$CH_3CHO + O_3 \rightarrow CH_3CHO + O_2 + O_2$</td>
<td>-</td>
<td>1.00E-13</td>
<td>See text</td>
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<td>1.60E-12</td>
<td>36</td>
</tr>
<tr>
<td>13</td>
<td>$OH + C_4H_8 \rightarrow C_4H_8OH$</td>
<td>-</td>
<td>6.40E-11</td>
<td>36</td>
</tr>
<tr>
<td>Reaction</td>
<td>Equation</td>
<td>Rate Constant</td>
<td>Product</td>
<td>Reaction</td>
</tr>
<tr>
<td>----------</td>
<td>----------</td>
<td>---------------</td>
<td>---------</td>
<td>----------</td>
</tr>
<tr>
<td>14</td>
<td>CH₃OH + OH → 0.85CH₃OH + 0.85H₂O</td>
<td>0.85</td>
<td>9.10E-13</td>
<td>44</td>
</tr>
<tr>
<td>15</td>
<td>CH₂OH + O₂ → H₂CO + HO₂</td>
<td>-</td>
<td>9.10E-12</td>
<td>44</td>
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<td>16</td>
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<td>19</td>
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<td>1.00E-12</td>
<td>See text</td>
</tr>
<tr>
<td>20</td>
<td>CH₃CHOO + CH₃CHOO → P</td>
<td>-</td>
<td>1.00E-11</td>
<td>See text</td>
</tr>
</tbody>
</table>

Rate constants represent the overall rate for a numbered reaction. *Unimolecular rate constants in 1/s. †Rates obtained from the branching ratios of the overall rate constant adjusted for pressure according to the IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation (http://iupac.pole-ether.fr).
4.8 References


5 Conclusions

The mechanism of ozonolysis of alkenes comprises several reaction and decomposition pathways that require continuing research, as they have a significant effect in atmospheric chemistry. By using a flow reactor and cavity ring-down spectroscopy (CRDS), Criegee intermediates, vinoxy radicals, and formaldehyde were measured, and their role in various interesting parts of the mechanism of ozonolysis were studied. The flow reactor was determined to behave as a plug-flow reactor (PFR) and modeled as a series of continuously-stirred tank reactors (CSTRs). This allowed a kinetic modelling of the ozonolysis mechanism to better describe the concentration profiles of the reaction products along the cell and, thus, the simulated average steady-state concentrations.

Direct measurements of CH$_2$OO produced from ethene ozonolysis were performed in the flow reactor. A high resolution absorption spectrum in the wavelength range of 375 – 390 nm was obtained. The capacity to measure formaldehyde oxide directly from the ozonolysis reaction allowed us to compare the average steady-state concentrations under different reaction conditions, and assess loss processes at short timescales. The concentrations of CH$_2$OO and HCHO were monitored at different reaction times under “high” (1x10$^{17}$ molecule/cm$^3$) and “low” (5x10$^{16}$ molecule/cm$^3$) concentrations of ethene, as well as “high” (1.7x10$^{15}$ molecule/cm$^3$) and “low” (8x10$^{14}$ molecule/cm$^3$) concentrations of ozone. The results indicate that, at the short reaction times (< 600 ms) studied, only the direct reactions C$_2$H$_4$ + O$_3$, CH$_2$OO + O$_3$, and CH$_2$OO + C$_2$H$_4$ are affected by the change in reactant concentration. Furthermore, depletion of CH$_2$OO is hindered more by reducing the concentration of ozone than by reducing the concentration...
of ethene, indicating that $k_{\text{ethene}+\text{Cl}} < k_{\text{ozone}+\text{Cl}}$. Upper limits for rate constants were found to be $k_{\text{ethene}+\text{Cl}} \leq 1 \times 10^{-15}$ cm$^3$/molecule·s and $k_{\text{ozone}+\text{Cl}} \leq 3 \times 10^{-13}$ cm$^3$/molecule·s. More work is needed to completely elucidate the role of HCHO as a scavenger, but it was found to be significant to CH$_2$OO depletion.

Indirect measurements of the yield of stabilized Criegee intermediates produced by ozonolysis of $cis$- and $trans$-2-butene, 2-methyl-2-butene, 2,3-dimethyl-2-butene, cyclopentene and cyclohexene were performed by using SO$_2$ as a scavenger and monitoring the change in SO$_2$ concentration with respect to a change in the ozone concentration. The ozonolysis reaction was carried out at low pressures and the zero-pressure yield was obtained for all sCIs studied by extrapolation of the low pressure data. It was found for acyclic alkenes that the nascent yields of sCIs are near zero for all but 2,3-dimethyl-2-butene. However, there is a trend of stabilization as pressure increases and the number of carbons increases. For the endocyclic alkenes cyclopentene and cyclohexene, the sCI yield at low pressure is essentially zero and, thus, so is their nascent sCI yield. This information is of great use for master equation calculations at the zero-pressure limit, as it provides benchmarks for the theory. That the yield of stabilized of stabilized formaldehyde oxide has been shown to be much higher (0.2) than the alkenes studied opens new questions and possibilities of research into the energetics of CH$_2$OO.

Finally, ·CH$_2$CHO and HCHO produced by ozonolysis of $cis$- and $trans$-2-butene were monitored directly in single- and multi-inlet flow cells. Multi-inlet flow cell measurements showed that reactors with staggered inlets can be used to probe early reaction processes but otherwise had limited success. Measurements of ·CH$_2$CHO and
HCHO from broth single- and multi-inlet reactor configurations showed that, while the ratio of \( \cdot \text{CH}_2\text{CHO} \) produced from \textit{cis}-2-butene with respect to \textit{trans}-2-butene was around 0.6, the ratio of produced HCHO was essentially 1. The ratio of the average steady-state concentration of \( \cdot \text{CH}_2\text{CHO} \) is very close to the yield ratio of OH radical produced from \textit{cis}- and \textit{trans}-2-butene and is consistent with the assumption that OH is mainly produced from syn-\text{CH}_3\text{CHOO} decomposition. That the ratio of HCHO is close to 1 indicates additional processes producing HCHO. A process forming HCHO from anti-\text{CH}_3\text{CHOO} was introduced to an ozonolysis mechanism and used to simulate both \( \cdot \text{CH}_2\text{CHO} \) and HCHO under different initial ozone concentrations with good agreement.

Overall, three aspects of the ozonolysis reaction of alkenes were explored, the formation and some primary depletion processes of CH\(_2\text{OO}\), the low-pressure and nascent yields of sCIs, and the formation of \( \cdot \text{CH}_2\text{CHO} \) from syn-\text{CH}_3\text{CHOO} and the possibility of additional HCHO production channels from anti-\text{CH}_3\text{CHOO}. The use of CRDS in a PFR showed that there is a lot yet to understand from the mechanism of ozonolysis and further work is required to fully incorporate these reactions in models of tropospheric chemistry.