Part 1—Introduction and Description of Cavity Ringdown Spectrometer

Chapter 1—Introduction

Atmospheric Chemistry

The earth's atmosphere has been described as a complex photochemical reactor, yet the vast majority of the earth's atmosphere consists of closed shell species (all electrons paired). Over 99% of the atmosphere consists of N_2, O_2, and Ar. Other major closed shell species include CO_2, Ne, He, Kr, H_2, and N_2O.[1-3] In the troposphere, these species are chemically inert, and will not undergo any chemical reactions.

The complexity of earth's chemistry comes from the presence of trace species. These chemical species have abundances on the order of parts per million (ppm), parts per billion (ppb), or parts per trillion (ppt). The most reactive of these species are open shell radicals (at least one unpaired electron). These species include ozone (O_3), reactive hydrogen (HO_x, defined as OH and HO_2), reactive nitrogen (NO_x, defined as NO, NO_2, and NO_3), and various organic species (alkanes, alkenes, carbonyls, radicals).[1-3] The chemical reactions amongst all of these species directly determine local air quality and global climate change.

Of particular interest to the Los Angeles community is the chemistry governing smog formation. Smog consists of anthropogenic aerosols combined with elevated levels of toxic gases, such as O_3. Although stratospheric ozone is considered "good ozone" due to its ability to block ultraviolet radiation from penetrating through the atmosphere, tropospheric ozone is considered "bad ozone" due to its adverse health effects on humans. Exposure to elevated concentrations of ozone can lead to a decrease in lung function, aggravation of asthma, throat irritation and cough, chest pain and shortness of breath, inflammation of lung tissue, and higher susceptibility to respiratory infection.[4] Recent studies have also shown that long-term exposure to ozone can lead to fatal cardiovascular or pulmonary conditions.[4] The EPA recommends that to maintain good air quality, O_3 levels stay below 75 ppb, and should not exceed this limit for more than three days per year.[2, 5] Although the air quality in Los Angeles has drastically improved in the last 30 years, the ozone levels still regularly exceed this limit. Figure 1.1 shows ozone levels in the Los Angeles basin from the last 30 years.[5] In 2008, the ozone level in the Los Angeles basin exceeded the federal standard (75 ppm) for 120 days, posing a very serious health risk.

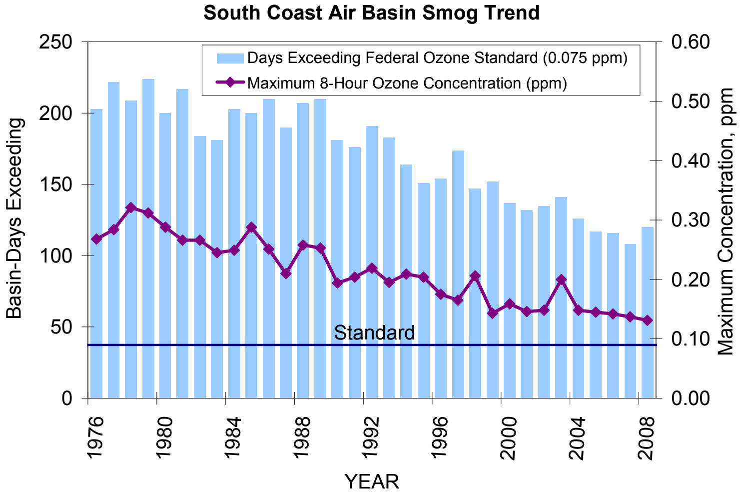


Figure 1.1. Days per year that ozone concentrations in the Los Angeles basin have exceeded the federal standard of 75 ppb, from 1976 to 2008. The number of days with excessive ozone has decreased over the last 30 years. However, even as recently as 2008, ozone levels exceeded the federal standard for 1/3 of the year. Reprinted with permission from South Coast Air Quality Management District, Copyright 2012.[5]

A better understanding of the complex chemistry behind ozone formation will allow us to refine our air quality regulations to reduce smog. The main source of ozone in the troposphere is from a series of reactions beginning with either CO or CH_4.[2] The net reactions are:

$$CO + 2\ O_2 \rightarrow CO_2 + O_3 \tag{1.1}$$

$$CH_4 + 10\ O_2 \rightarrow CO_2 + H_2O + 5\ O_3 + 2\ OH \tag{1.2}$$

CO, O_2, and CH_4 are all unreactive closed shell species. Without a catalyst, Reactions 1.1 and 1.2 will never occur. The mechanism for Reaction 1.1 (shown in Reactions 1.3–1.6) reveals that HO_x and NO_x are the catalysts to ozone formation.[2] **We therefore expect any other atmospheric reaction involving HO_x and NO_x to affect ozone and smog formation.** HO_x and NO_x concentrations can be significantly increased due to industrial and automotive emissions. Studying chemical reactions involving HO_x and NO_x will allow us to determine the best approaches to reducing tropospheric ozone concentrations.

$$CO + OH \rightarrow H\bullet + CO_2 \tag{1.3}$$

$$H\bullet + O_2 \overset{+M}{\rightarrow} HO_2 \tag{1.4}$$

$$HO_2 + NO \rightarrow OH + NO_2 \tag{1.5}$$

$$NO_2 + h\nu + O_2 \rightarrow NO + O_3 \tag{1.6}$$

There are three main approaches to studying atmospheric chemistry. Laboratory studies focus on the basic physical chemistry of atmospheric molecules. These studies measure spectroscopy, kinetics, and dynamics of the individual reactions that take place in the atmosphere. Field studies focus on applying the results of laboratory studies to detection of chemicals in the atmosphere. These studies show us how reactions proceed under actual atmospheric conditions. Modeling studies use the results of the laboratory and field studies to simulate the earth's atmosphere. The atmospheric models allow us to predict the future of the atmosphere for different anthropogenic emissions, allowing us to develop appropriate climate policies. Results from the field and modeling studies can often indicate basic reactions that are either missing or have clearly incorrect rate constants, suggesting new laboratory studies to be undertaken. All three types of studies are important, and each method relies on the other two to generate meaningful results.

The experiments described in this thesis consist of basic physical chemistry experiments and electronic structure calculations on radical reactions of atmospheric interest. **We focus on direct spectroscopic detection of each chemical reaction's primary products.** In contrast to our methods, many laboratory studies use end-product analysis and kinetics modeling to back out the rate constants of interest. By utilizing a direct detection method, our kinetics results have minimal reliance on other reactions' rate constants, and are thus subject to lower uncertainties than end-product studies. The experimental technique that we employ is infrared cavity ringdown spectroscopy (IR-CRDS), a sensitive method that utilizes an optical cavity to obtain infrared spectra for absorptions on the order of ppm.[6-11] A major advantage to using IR-CRDS is that radical concentrations can be kept low, preventing appreciable amounts of secondary chemistry from occurring. The principles of IR-CRDS and details of our experimental apparatus are described in the remainder of Part 1 of this thesis (Chapter 2).

The interpretation of CRD spectra can be difficult. Our goal is to make accurate kinetics measurements for use in atmospheric models. However, individual peaks must be assigned to chemical species with confidence before it is possible to make kinetics measurements. Some spectroscopic peaks lack structure, making it difficult to *a priori* unambiguously assign the peak to a molecule. Additionally, many peaks will appear in similar spectral regions, further complicating assignment of the spectrum. **To aid in interpreting the spectra, we perform electronic structure calculations to simulate**

spectroscopy and kinetics results. These calculations give us further insight into the chemical physics that governs our experiments. By combining the electronic structure calculations with a kinetics study, we can compare our experimental measurements to simulation, and further refine our understanding of the chemical system being studied.

Specific Chemical Systems of Interest

The work described in this thesis examines three chemical systems of atmospheric interest using a combination of experimental and theoretical techniques. The chemical systems and techniques used are

- Peroxynitrous acid (HOONO)—electronic structure calculations to interpret previous spectroscopic experiments on the branching ratio of $OH + NO_2$
- $HO_2 + HCHO$—CRDS detection of the OH stretch and $\widetilde{A}-\widetilde{X}$ transitions of the primary product, hydroxymethylperoxy (HMP, $HOCH_2OO$•); electronic structure calculations to model the spectroscopic bands and evaluate appropriate computational methods for hydroxyalkylperoxy systems; kinetics experiments and modeling to show that the existing chemical mechanism is incomplete
- Alkoxy radicals (RO•)—electronic structure calculations to determine how the chemical structure of alkoxy radicals affects the OH stretch spectrum; electronic structure calculations and kinetics modeling to interpret the "*n*-butoxy low $[O_2]$ isomerization anomaly" observed in previous experiments; reanalysis of previously obtained relative kinetics data, CRDS detection of the OH stretch and $\widetilde{A}-\widetilde{X}$ transitions of the alkoxy isomerization products HOR• and HOROO•

A brief description of each chemical system is given below. More detailed descriptions of the chemical systems and experiments can be found in the individual chapters of this thesis.

Torsion-Torsion Coupling in Peroxynitrous Acid (HOONO)

The reaction of OH with NO_2 can go through one of two pathways: formation of HOONO (Reaction 1.7), or formation of nitric acid ($HONO_2$, Reaction 1.8).[12]

$$OH + NO_2 \rightleftharpoons HOONO \tag{1.7}$$

$$OH + NO_2 \rightarrow HONO_2 \tag{1.8}$$

The energy diagram for this chemical system is shown in Figure 1.2. HOONO is a weakly bound molecule (D_0 = 19.6 kcal mol^{-1}) and will rapidly dissociate back to OH and NO_2, therefore acting as a temporary reservoir for HO_x and NO_x.[12] In contrast, nitric acid is strongly bound (D_0 = 47.2 kcal mol^{-1}) and acts as a permanent reservoir for HO_x and NO_x. It is therefore important to determine the branching ratio k_{HOONO}/k_{HONO2}, in order to accurately ascertain how these reactions will affect the ozone budget.

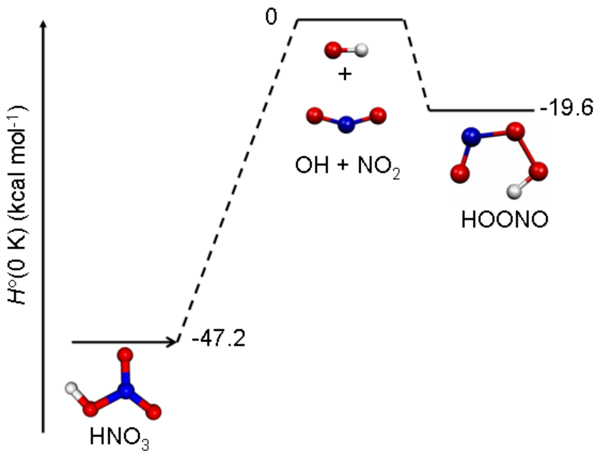


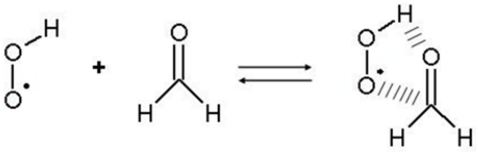
Figure 1.2. Potential energy surface for OH + NO_2. From Mollner et al.[12] Reprinted with permission from AAAS

The existence of a HOONO pathway has been postulated for 30 years.[13] However, direct detection of HOONO in the gas phase[14, 15] and kinetics measurements[12] have only been performed recently. Both experiments have measured the OH stretch spectra for HOONO and $HONO_2$, making use of the ratio of the integrated absorbances of each band and theoretical absorption cross sections[16] to determine the branching ratio k_{HOONO}/k_{HONO2}. However, this simple procedure ignores the possibility of sequence band formation within the OH stretch spectrum. Torsionally excited HOONO has a higher OH stretch frequency than ground state HOONO. We expect that the thermal population of torsional modes will create a set of OH stretch "sequence bands." Some of these bands will fall under other peaks, and will therefore be missing from a simple integration of the observed HOONO band. In order to obtain an accurate branching ratio, a correction factor must be applied to the CRDS results to account for the unobserved intensity in the sequence bands.

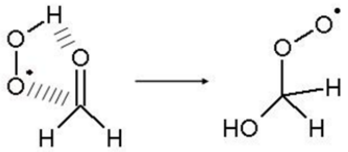
Part 2 of this thesis (Chapter 3) describes a 3-dimensional potential energy surface used to model the sequence band formation in HOONO. Analysis of the potential energy surface shows us that the two torsional motions of HOONO are coupled by the internal hydrogen bond. Both torsions contribute to the formation of sequence bands. The energy levels generated from the potential energy surface show us how much OH stretch intensity is shifted out of the main HOONO peak, and give us a correction factor to apply to the experimentally determined k_{HOONO}/k_{HONO2}.

HO_2 + HCHO: Spectroscopy, Kinetics, and Electronic Structure of $HOCH_2OO\bullet$

The reaction of hydroperoxy radical (HO_2) with carbonyl compounds has been proposed as a major sink for carbonyl compounds in the upper troposphere/lower stratosphere (UTLS).[17] The reaction of HO_2 with formaldehyde (HCHO) is the simplest of these reactions. The reactions proceeds through a hydrogen bound intermediate (Reaction 1.9) before isomerizing into a hydroxyalkylperoxy product (Reaction 1.10).



(1.9)



(1.10)

Ab initio calculations have shown that reaction of HO_2 + HCHO will proceed at room temperature.[18-20] A potential energy diagram for HO_2 + HCHO is shown in Figure 1.3.[18] There is no activation barrier to Reaction 1.9. The activation barrier to Reaction 1.10 is lower than dissociation back to HO_2 + HCHO.[18, 19, 21] The combination of these two factors indicates that the isomerization reaction will occur in the atmosphere, and that Reaction 1.9 should have an increased rate at reduced temperatures. In contrast, it is currently unknown whether the reaction of HO_2 with larger carbonyls (acetaldehyde, acetone) will form isomerization product, because the barrier to isomerization may or may not be higher than dissociation back to products.[19, 22, 23]

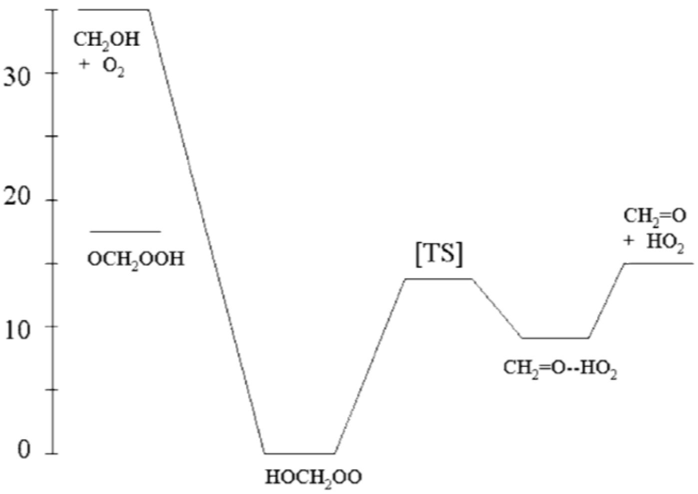


Figure 1.3. Potential energy surface for HO_2 + HCHO. Reprinted from Dibble (2002) with permission from Elsevier.[18]

Previous experiments have measured the kinetics of HO_2 + HCHO by FTIR spectra of the end-products,[24] or via the $\tilde{B}-\tilde{X}$ band of the direct reaction product, hydroxymethylperoxy ($HOCH_2OO$•, or HMP).[25, 26] Despite these measurements, considerable uncertainty still exists in the activation energy (±80%, 2σ).[27] One source of this uncertainty is interference from other species (HO_2, CH_3O_2) within the structureless $\tilde{B}-\tilde{X}$ spectrum of HMP. Detection of this intermediate by other spectroscopic transitions (free from interferences from other chemical species and structured to provide validation of the spectral assignment) could lead to improved kinetic rate constants and give rise to the possibility of studying reactions of HO_2 with larger carbonyls.

Part 3 of this thesis (Chapters 4–6) describes experimental and theoretical work on the spectroscopy and kinetics of HMP. We used CRDS to make the first detection of the OH stretch vibrational spectrum and the $\tilde{A}-\tilde{X}$ electronic spectrum. We performed quantum chemical calculations to verify the assignment of the spectroscopic bands to HMP, assess coupling between the HOCO and OOCO torsional motions, and to show which levels of theory are appropriate for use in further studies of hydroxyalkylperoxy radicals. The kinetics data that we obtain from these spectroscopic bands are in excellent agreement with the existing kinetics model. This indicates that the rate constants and secondary chemistry from previous studies are well modeled.

Alkoxy (RO•) Isomerization: Spectroscopy, Kinetics, and Electronic Structure of Primary Products

Alkoxy radicals (RO•) are an important intermediate in the reactions of volatile organic compounds. The oxidation of alkanes (RH) in the presence of NO_x, leads to atmospheric alkoxy formation (Reactions 1.11–1.13). Once formed, these radicals can undergo decomposition (Reaction 1.14), isomerization and subsequent reaction with O_2 (Reactions 1.15 and 1.16), or direct reaction with O_2 (Reaction 1.17). Because HO_x and NO_x are produced and consumed, these reactions directly impact ozone chemistry.

$$\mathrm{RH + OH \longrightarrow R\bullet + H_2O} \tag{1.11}$$

$$\mathrm{R\bullet + O_2 \xrightarrow{M} RO_2\bullet} \tag{1.12}$$

$$\mathrm{RO_2\bullet + NO \longrightarrow RO\bullet + NO_2} \tag{1.13}$$

$$\mathrm{RO\bullet \xrightarrow{decomp} R' + R''{=}O} \tag{1.14}$$

$$\mathrm{RO\bullet \xrightarrow{isom} HOR\bullet} \tag{1.15}$$

$$\mathrm{HOR\bullet + O_2 \longrightarrow HOROO\bullet} \tag{1.16}$$

$$\mathrm{RO\bullet \xrightarrow{O_2} HO_2\bullet + RHO} \tag{1.17}$$

Previous experiments have determined the relative rate $k_{\mathrm{isom}}/k_{\mathrm{O2}}$, typically by end-product analysis.[28] In contrast, previous work in the Okumura group has used CRDS to measure the OH stretch of the primary isomerization products, HOR• or HOROO•.[29, 30] CRDS of the primary products should yield a value of $k_{\mathrm{isom}}/k_{\mathrm{O2}}$ with lower uncertainty than an end-product study because secondary chemistry does not affect the CRDS experiment. However, numerous issues plagued the previous CRDS experiment. First, gas concentrations and scaling of absorbances to [RO•] were not done properly. Second, the spectra previously reported also were taken at times where secondary chemistry affected the experiment, and are therefore not "clean" spectra of HOR• or HOROO•. Third, anomalous behavior in the relative kinetics data is observed at low [O_2] (less than 1 torr); the yield of isomerization product increases as [O_2] is increased. Finally, the effects of alkoxy decomposition, recombination with NO, and prompt processes were not considered in deriving $k_{\mathrm{isom}}/k_{\mathrm{O2}}$, a problem common to all alkoxy studies in the past 30 years.[28]

Part 4 of this thesis (Chapters 7–10) describe experimental and theoretical work on the spectroscopy and relative kinetics of alkoxy isomerization. We used CRDS to make the first detection of the $\tilde{A}-\tilde{X}$ band of δ-HOC_4H_8OO•, the isomerization product of *n*-butoxy. We also report the first clean OH stretch spectra of δ-HOC_4H_8•, δ-HOC_4H_8OO•, δ-HOC_5H_{10}•, and δ-$HOC_5H_{10}OO$•, the isomerization products of *n*-butoxy and 2-pentoxy. The results of our electronic structure calculations show clear differences in the OH stretch absorption cross sections of HOR• and HOROO•, and clear patterns for how the relative locations of the hydroxyl and peroxy groups affect the OH stretch intensity. We also reanalyzed the previously acquired relative kinetics data to correct for calculation errors and to show that decomposition, recombination with NO, and prompt processes clearly affect the derived value of $k_{\mathrm{isom}}/k_{\mathrm{O2}}$.