

Chapter 1 – Introduction

1.1 – Scientific Background

Knowledge of gas phase compounds and their chemical reactions are pivotal to our understanding of chemistry. The conditions these molecules are in can vary dramatically, from temperatures as low as 10 K in the depths of the interstellar medium, to more than 1000 K in the combustion of hydrocarbons in engines. The chemistry in these systems is dominated by highly reactive, unstable compounds, leading to fast and complex chemistry occurring. In order to accurately understand these systems, we must be able to observe these unstable species and measure the kinetics of their formation and destruction. While molecular spectra and reaction rate constants of these reactive compounds can be computed with theoretical calculations, they must be benchmarked with experimental measurements to determine their accuracy. To that end, one major focus in experimental gas phase chemistry is to better understand these unstable molecules and their reactions in systems such as atmospheric chemistry and astrochemistry.

1.1a – Atmospheric Chemistry

Understanding Earth's atmosphere and the chemistry behind it has been a major topic in gas phase chemistry since the mid-20th century, when the impact of fossil fuel usage and air pollution resulting from the Industrial Revolution became apparent. The dominant molecule in Earth's atmosphere is N₂ (77% of the atmosphere) followed by O₂ (21%) and argon (1%). The remaining components are largely stable molecules, such as CO₂ and H₂O.

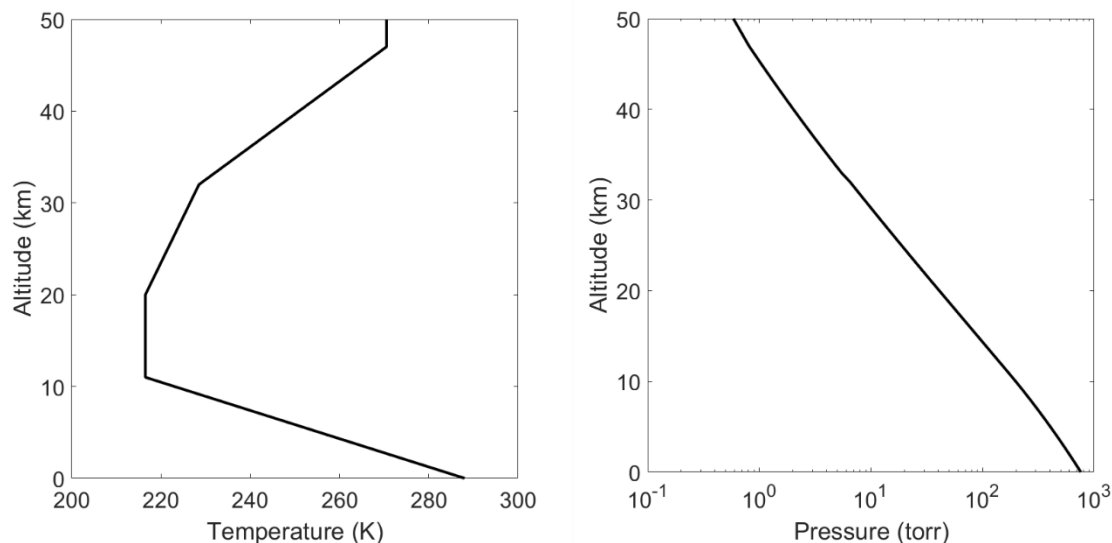
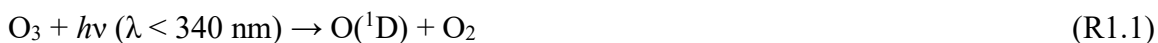


Figure 1.1: The average temperature (left) and pressure (right) profiles of the Earth's lower atmosphere, consisting of the troposphere and stratosphere.

Earth's atmosphere is divided into different regions, the lowest of which are the troposphere (roughly 0 – 18 km), and the stratosphere (roughly 18 – 50 km). The tropopause is the boundary layer between the two and is roughly 11 – 18 km in height. The exact location of the tropopause and the boundary above the stratosphere changes with the longitude and latitude. The average temperatures and pressures within the troposphere, tropopause and stratosphere is shown in Figure 1.1. Much of the reactive chemistry in the troposphere and stratosphere originates from the photolysis of O_3 by short wavelengths of sunlight,¹ which results in the formation of $O(^1D)$



This $O(^1D)$ can subsequently be quenched through collision with a nonreactive partner, such as N_2 , or react with H_2O :



In addition to the OH radical, NO₃ and O₃ are also important oxidizers throughout the atmosphere, particularly during night, when no OH is formed through R1.1-R1.3 due to the lack of sunlight.²

The subsequent chemistry of the OH radical is closely linked to HO₂ chemistry, so for this reason, OH and HO₂ are collectively known as HO_x. There is rapid cycling between the two, through reactions



and



In urban environments, where high pollution leads to the presence of large amounts of NO and NO₂ (collectively known as NO_x), the termolecular reaction of OH is important



These reactions serve as a sink of OH. While HONO can photolyze to reform OH and NO readily, HONO₂ is largely stable, and so R1.9 is an important reservoir of HO_x.³

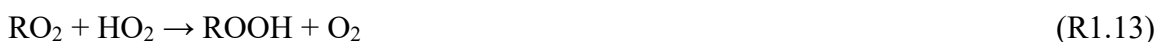
Another important sink for the OH radical is the reaction with hydrocarbons, which are constantly emitted into the atmosphere through both anthropogenic and biogenic sources. Depending on the structure of the hydrocarbon, OH can either abstract a hydrogen, such as in the reaction with CH₄, or add to an unsaturated bond, such as in the reaction with isoprene (C₅H₈, 2-methyl-1,3-butadiene). Both of these mechanisms lead to formation of an alkyl peroxy radical, RO₂



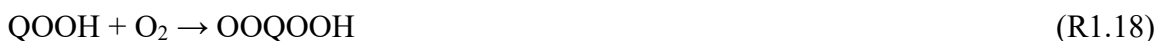
The chemistry of these RO₂ compounds is complex and an active area of study in atmospheric chemistry. In urban areas with high NO_x concentrations, the most common reaction is



where R'CHO is an aldehyde species. Note the reformation of HO_x through R1.12, which leads to additional formation of OH. In low NO_x environments, the most common fates of RO₂ are reactions with HO₂ or other RO₂ molecules.



The two RO₂ reactants in R1.14 – R1.16 may or may not have the same alkyl group. Like in the high NO_x case, many of these reactions lead to the reformation of HO_x, through R1.12 or the photolysis of ROOH to form RO and OH. Recent work on RO₂ radicals in low NO_x environments has also shown that isomerization, through intramolecular hydrogen atom transfers, can play an important role in the formation of highly oxygenated molecules (HOMs).⁴



The subsequent chemistry of the OOQOOH radical leads to the formation of stable HOMs, which are important precursors in secondary organic aerosols (SOAs) due to their low

vapor pressure. Recent work has also suggested that the ROOR accretion products from R1.14 are also important HOMs.⁵

The reaction network of the troposphere and stratosphere is complex, and the reaction rates and product branching ratios must be accurately determined. These parameters are used in widely used atmospheric models and influence policy decisions. While many of these reactions have been well characterized, models are still unable to match field measurements, particularly measurements of the concentration of the OH radical in low NO_x environments.^{1, 6} leading to the need for further refinement and evaluation of the experimental values.

1.1b – Astrochemistry

The interstellar medium (ISM), the diffuse material present in space that is not part of stars or other large celestial bodies, holds about 10 – 15% of the total mass of our galaxy.⁷ This mass consists of both gasses (atoms, molecules, ions and electrons) and solids (dust or ice particles). Despite the diffusivity of the ISM, discrete clouds can form. Molecular clouds are cold, with temperatures of 10 – 20 K and gas densities of 10² – 10⁶ cm⁻³, while atomic clouds can be either cold (50 – 100 K, 20 – 50 cm⁻³) or hot (6 × 10³ – 10⁴ K, 0.2 – 0.5 cm⁻³).⁷ Larger molecular clouds are on the order of tens of parsecs (1 parsec = 3.09 × 10¹⁶ meters) with densities of 10² – 10³ cm⁻³, while smaller molecular clouds are denser, with sizes of tenths of parsecs and densities of 10⁴ – 10⁶ cm⁻³.⁷

The earliest molecules detected in the ISM date to observations made in the late 1930s of small molecules such as CH, CN and CH⁺ with optical spectroscopy.⁷ The advent of radio astronomy, allowing molecules to be detected through their rotational transitions, has allowed for many new discoveries in the ISM. To date, over 200 molecules have been

discovered in the ISM, from small diatomics to compounds as large as C_{60} and C_{70} (though the majority of detected species contain ten atoms or less).⁸ H_2 is by far the most common molecule in the ISM, while CO is the second most abundant, with the CO/ H_2 fraction ranging from $10^{-7} - 10^{-5}$.⁹ As H_2 has no permanent dipole moment, CO is commonly used as a tracer for identifying cold molecular clouds in the ISM. With the advent of new and more sensitive telescopes such as Atacama Large Millimeter/submillimeter Array (ALMA) and the upcoming James Webb Space Telescope, our knowledge of molecules in the ISM and their distribution is rapidly expanding.

The extreme conditions present in the ISM leads to the presence of large amounts of unstable species in the ISM. Radiation from cosmic rays leads to complex ion chemistry, much of which is driven through the ionization of hydrogen, which subsequently leads to the formation of H_3^+ , which subsequently reacts with other atoms and molecules to produce a wide array of cations.¹⁰ Anions are formed through radiative attachment of electrons to neutral atoms and molecules, and subsequent chemical reactions of these anions.¹¹ The low temperature means that unstable compounds are not able to isomerize to more stable isomers, leading to the high abundance of molecules such as HNC.¹²

Many of the molecules detected in the ISM are neutral radicals, from the early discovered molecules such as CH and CN, to molecules as large as C_8H .⁸ While ion chemistry has historically dominated chemical networks for astrochemistry, many reactions between these neutral radicals and neutral closed-shell compounds have been shown to be fast at low temperatures.¹³ The rate constants of many of these neutral-neutral display non-Arrhenius behavior at the low temperatures relevant to the ISM. An extreme example of these non-Arrhenius rate constants is the turn-around displayed by a number of

reactions, where the rate constant reaches a minimum, before becoming faster at lower temperatures. This has been seen in the rate constants of the CN radical with hydrocarbons such as ethane (C_2H_6)¹⁴ and rate constants of OH with oxygenated hydrocarbons such as methanol (CH_3OH)¹⁵⁻¹⁶ and ethanol ($\text{CH}_3\text{CH}_2\text{OH}$)¹⁷⁻²⁰, the latter of which can be seen in Figure 1.2. Therefore, measurements of the rate constants of reactions relevant to the ISM must be studied down to the relevant temperatures and can not necessarily be extrapolated from higher temperature experiments.

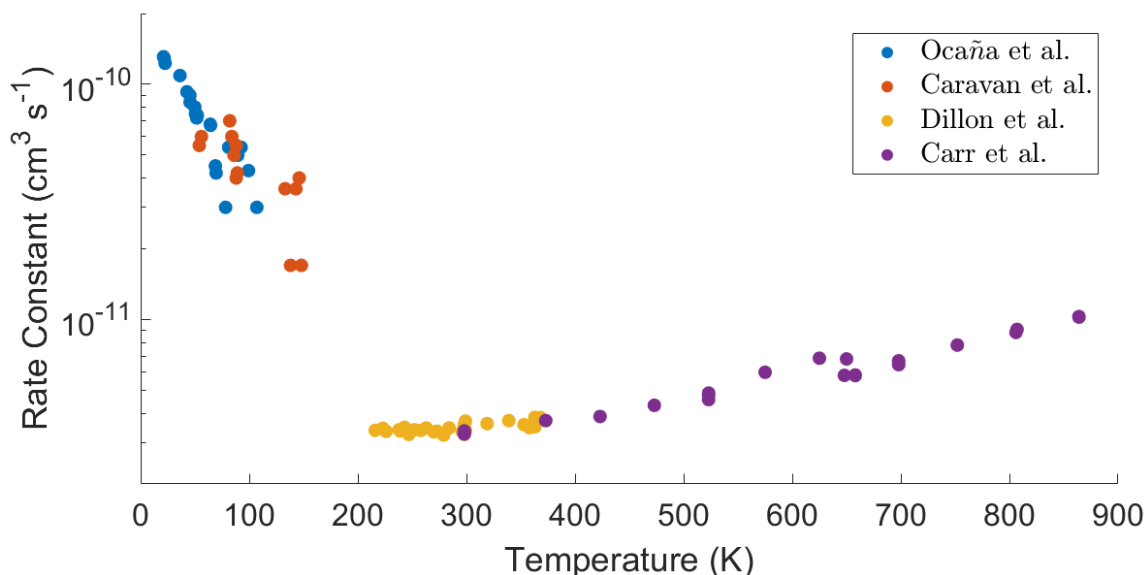


Figure 1.2: The rate constants of the OH + $\text{CH}_3\text{CH}_2\text{OH}$ reaction over the 10 – 900 K range showing the minimum at ~200 K. Data taken from Ocaña et al.,¹⁷ Caravan et al.,¹⁸ Dillon et al.,¹⁹ and Carr et al.²⁰

1.2 – Summary of Thesis Work

This work presented here covers experiments done at Caltech and the University of Rennes 1 to study the temperature-dependent spectroscopy and kinetics of radical reactions with neutral species relevant to atmospheric and astrochemistry. Chapter 2 covers the experimental techniques used throughout this thesis. Chapter 3 discusses mid-infrared cavity ringdown spectroscopy experiments of the temperature- and pressure- dependent

branching ratio of the OH + NO₂ reaction at conditions relevant to atmospheric chemistry. This reaction is critical in determining ozone formation in urban environments, which is a major component of smog. Chapter 4 discusses the rate constants of the reactions of the CN radical with benzene and toluene down to 15 K, as inspired by the 2018 detection of benzonitrile in the ISM.²¹ Chapter 5 focuses on the rate constants of the reaction of OH and CO, two of the most abundant interstellar molecules, down to 30 K, and the unusual temperature dependence of the reaction.

1.3 – References

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