Kinetic Investigations of NOx Chemistry Pertaining to the Global Nitrogen Cycle

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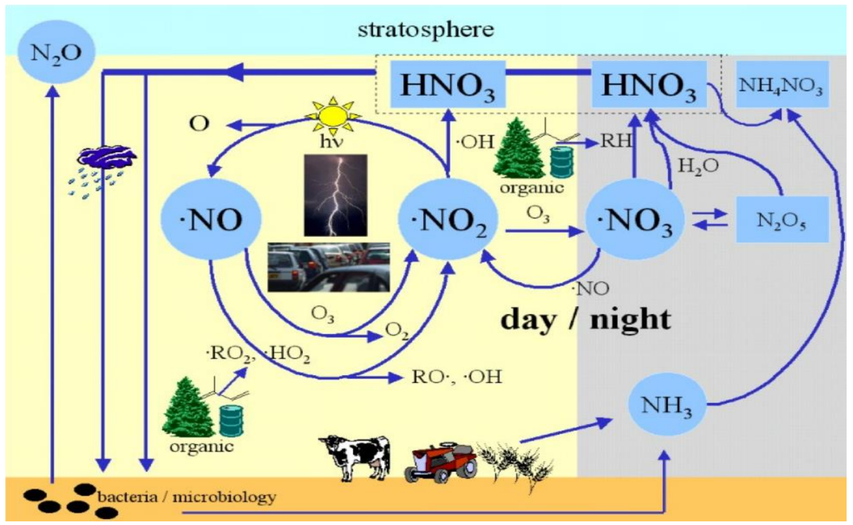
Abstract

Nitrogen containing compounds (NOx compounds) are of central importance to the global nitrogen cycle and the reactions in which they participate significantly impact many atmospheric processes and even influence global climate change. Despite this, the kinetic properties of many of the NOx reaction pathways remain incompletely understood. Of particular interest is nitrous acid (HNO_2) and the multitude of atmospheric reactions in which it participates. Specifically, the rate of decomposition of HNO_2 under atmospheric conditions and in aerosol particles is largely unknown. This project aims to detail the kinetic processes involved in the decomposition of aqueous HNO_2 using UV-Vis and Raman spectroscopy. We show that the decomposition of HNO_2 occurs via first order reaction kinetics, but with a varying rate constant that is dependent on the initial HNO_2 concentration in solution. This result implies the decomposition proceeds through two different mechanisms – one at high concentrations (≥ 500mM) of HNO_2 and one at low concentrations (≤ 10 mM). The measured rate constants for the high and low concentration regimes were found to be 0.035 min^{-1} and 0.0029 min^{-1} respectively..

Environmental Impacts

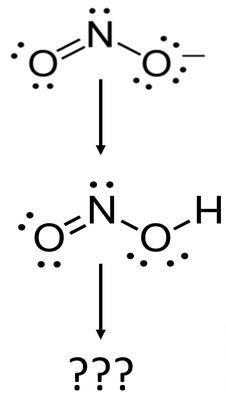


The global nitrogen cycle is critical to many environmental processes and has far reaching impacts for our environment:

- Many NOx species in the atmosphere are released by humans
- NOx species have been implicated in ozonolysis, contributing to the depletion of our ozone layer.
- The reactions that can occur are dependent on the time of day

Nitrous acid can react to form a multitude of NOx compounds shown on the figure above, thereby significantly impacting the entire global nitrogen cycle.

Experimental method



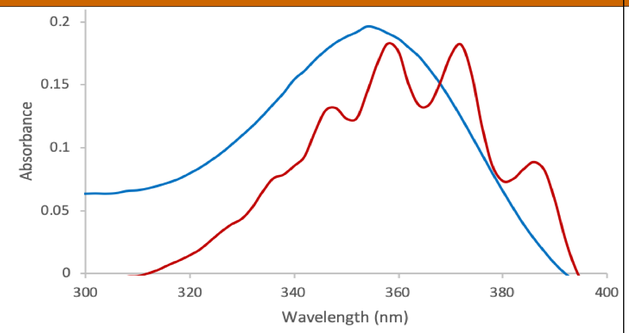


Figure 1: UV-Vis spectra of NO_2^- (blue) and HNO_2 (red). The HNO_2 feature can be monitored to measure the decomposition rate, and any additional features that appear in the spectrum as the reaction progresses can provide insight into the identity of the products formed.

Results

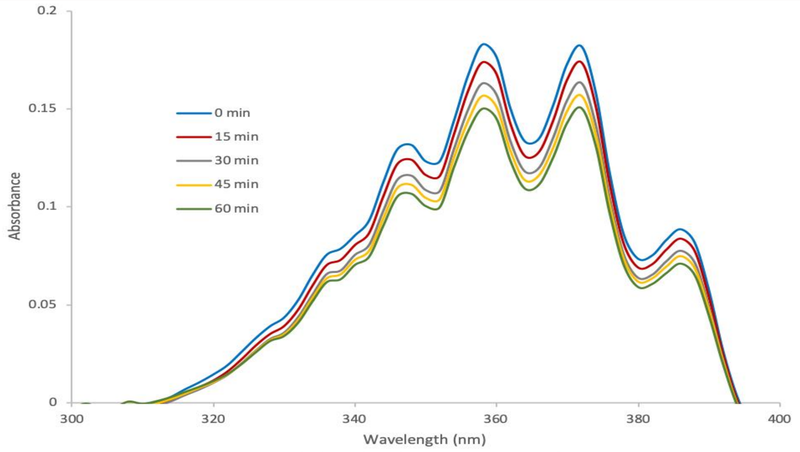


Figure 2: A comparison of the absorbance intensity of 10 mM aqueous HNO_2 throughout a 60 minute experiment at 15 minute time intervals. The decrease in absorbance indicates the decomposition of HNO_2 over time.

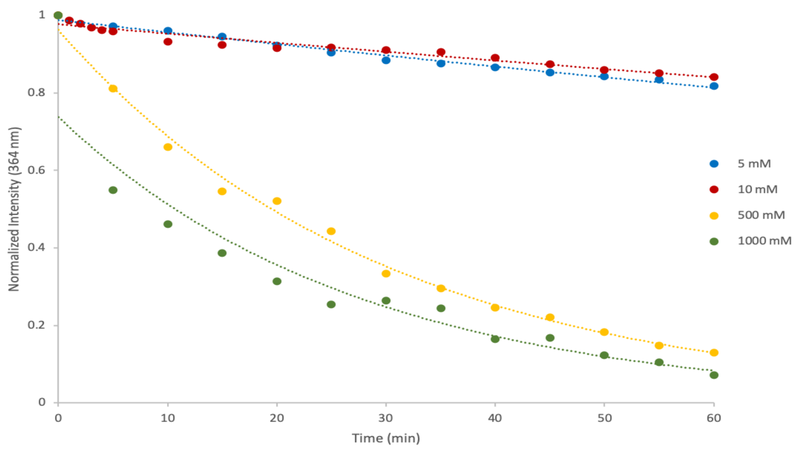


Figure 3: The exponential decay curves for HNO_2 at multiple concentrations is shown. This plot shows the difference in rate of decomposition depending on the concentration of HNO_2 present at the start of the reaction. At higher concentrations the decomposition of HNO_2 is much faster than the decomposition at lower concentrations.

Results (cont.)

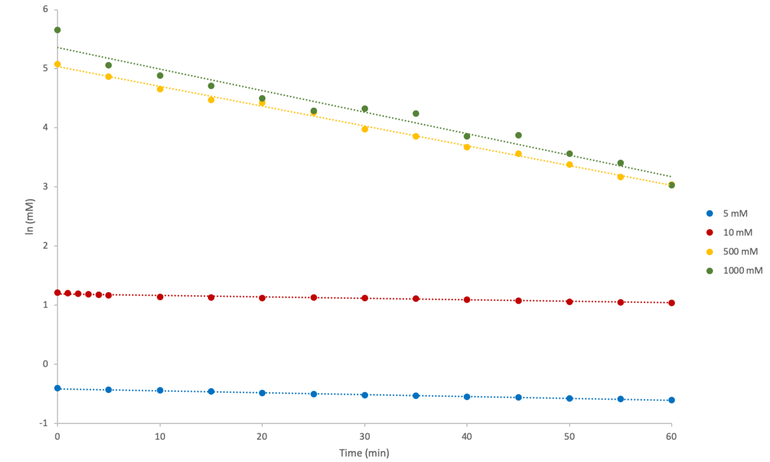


Figure 4: A natural log function of the concentration that remains of HNO_2 at every time point. This natural log plot yields a straight line meaning that the decomposition of HNO_2 occurs via first order kinetics. The integrated rate law for a first order reaction is given by: $ln[A]= -kt+ln[A]_0$. The rate constant, k, is the slope of the line that is fit to the graph above and should be the same at all concentrations. Based off the slopes in the low and high concentration regimes the rate constants have been found to be 0.0029 min^{-1} and 0.035 min^{-1} respectively.

Conclusion and Future Directions

- Surprisingly, the rate constant for the reaction is determined to be dependent on the initial HNO_2 concentration, indicating the reaction proceeds via *entirely different mechanisms* at high and low concentrations.
  - High concentration regime: k = 0.035 min^{-1}
  - Low concentration regime: k = 0.0029 min^{-1}
- Future studies will aim to elucidate the specific molecular mechanisms that describe the reaction at the different concentration regimes.
- The turnover point (where the reaction switches from one mechanism to the other) remains to be determined
- The reaction will be tested under atmospheric conditions (e.g. presence of CO_2, UV exposure, etc.)

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