KINETIC INVESTIGATION OF THE GAS PHASE ATOMIC SULFUR
AND NITROGEN DIOXIDE REACTION

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Thesis Prepared for the Degree of
MASTER OF SCIENCE

UNIVERSITY OF NORTH TEXAS
May 2011

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Thompson, Kristopher Michael, *Kinetic Investigation of the Gas Phase Atomic Sulfur and Nitrogen Dioxide Reaction*, Master of Science (Chemistry - Physical Chemistry), May 2011, 70 pp., 9 tables, 14 illustrations, references, 64 titles.

The kinetics of the reaction of atomic sulfur and nitrogen dioxide have been investigated over the temperature range 298 to 650 K and pressures from 14 - 405 mbar using the laser flash photolysis - resonance fluorescence technique. The overall bimolecular rate expression

$$k(T) = (1.88 \pm 0.49) \times 10^{-11} \exp\left(\frac{-4.14 \pm 0.10 \text{ kJ mol}^{-1}}{RT}\right) \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

is derived.

Ab initio calculations were performed at the CCSD(T)/CBS level of theory and a potential energy surface has been derived. RRKM theory calculations were performed on the system. It is found that an initially formed SNO₂ is vibrationally excited and the rate of collisional stabilization is slower than the rate of dissociation to SO + NO products by a factor of 100 - 1000, under the experimental conditions.
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Kristopher Michael Thompson
I would like to express my genuine thankfulness to my major professor Dr. Paul Marshall for his guidance in my education. I have had the privilege of his instruction as an undergraduate and as a graduate student, and I am extremely grateful for his wealth of knowledge in chemistry. His patience, encouragement and generosity have been invaluable.

I would like to thank the members of the research group for all their help with the experiment. I am very grateful for the guidance and advice of Dr. Yide Gao in the usage of the reactor, instruments and his help with computational and theoretical techniques. I want to thank Dr. Ionut (John) Alecu for all his computational advice and support, as well as members of Dr. Angela Wilson's research group. I also want to thank Sean Ayling and Adrian Guillory for their help in data acquisition.

I am very thankful and fortunate for support from my wife Michelle and my family for their continuous encouragement and moral support which made all this possible.

Finally I would like to thank the Department of Chemistry at the University of North Texas and the Robert A. Welch Foundation (Grant B-1174) for financial support. I would also like to thank the National Science Foundation (Grant CTS-0113605) for its support of the research group.
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Atmospheric chemistry is the study of the effect of human activity, natural biogenic and geogenic emissions on the atmosphere. This includes the effects of pollution, ozone layer, greenhouse gases, aerosols, and water vapor. In the 13th century European countries began to use coal as a major source of fuel for heating homes and in industry.¹ Concern for the air environment began in the 17th century. High-sulfur coal burning in London caused significant pollution of the air, water, and noticeable acid rain. Infant mortality rates were very high in large cities at that time.² In the mid-20th century, the air quality was of growing concern due to killer smogs, which were comprised of heavy low lying fog and high concentrations of pollutants. Thousands of deaths occurred due to the high amount of SO₂ (1.3 ppm) and particulate matter (4.5 mg m⁻³). These events lead to Britain passing a clean air act, which aimed to control smoke pollution by creating smoke free zones and moved power stations to rural areas. This significantly reduced deaths in the following years. These heavily concentrated sulfur smogs are called London smog or sulfur smog.³⁻⁶

Another type of air pollution is caused by use of gasoline combustion engines. This is known as photochemical smog, which was first noticed in Los Angeles in the mid 1940s. Various plants and vegetable crops were being injured around the city and lead to many investigations focusing on air pollution. The main pollutants discovered were NO₂,
ozone, and olefins. This is most commonly called Los Angeles smog. It was determined that the cause was automobile exhaust, low humidity, and intense sunlight. These issues lead to the formation of the Air Pollution Foundation. Research supported by the foundation lead to the classification of two types of pollutants. Primary pollutants are emitted directly from the source, and secondary pollutants, are formed in the atmosphere by normal atmospheric compounds and primary compound interactions.

The role of sulfur atoms and sulfur molecules is important in combustion and atmospheric chemistry, especially in relation to the environmental SO\textsubscript{x} and NO\textsubscript{x} issues. The major source of these pollutants in the atmosphere is from industrial emissions and motor emissions. Fossil fuels, mainly oil and coal, contain sulfur and nitrogen molecules that have a role in the combustion cycle. The need to understand how species of SO\textsubscript{x} and NO\textsubscript{x} are formed in combustion is crucial in resolving environmental pollution issues.

During combustion sulfur is released into the gas phase as simple molecules and oxidizes rapidly into sulfur oxides where they are thermodynamically favored. Most of the gas phase sulfur is SO\textsubscript{2} even in reducing conditions. An even more undesirable species of sulfur is SO\textsubscript{3}, which may be formed by direct recombination of SO\textsubscript{2} and O, and is thermodynamically favorable at temperatures lower than 1000 K. Trace quantities of sulfur might also have an impact on catalytic cycles. These species of SO\textsubscript{x} may have an effect on combustion radical pools by increasing the amount of chain carriers and propagation reactions and decreasing the termination reactions. It has also been found that under fuel lean conditions SO\textsubscript{2} catalyzes the recombination of chain carriers.
There are many uncertainties in sulfur and nitrogen interactions. Laboratory flame studies have shown that sulfur may enhance or reduce other pollutants in combustion. Exhaust gas NO$_x$ concentration is affected by the amount of sulfur in the fuel, the sulfur and nitrogen ratio, the mixing conditions and the richness of the fuel. Methane-air flames doped with either SO$_2$ or H$_2$S have shown that sulfur inhibits the formation of NO$_x$ in exhaust gas and suggests that desulfurization of certain fuels could lead to increased NO$_x$ emissions.\textsuperscript{12} In fuel rich conditions the enhancement and inhibition of NO depends on the ratio of sulfur and nitrogen in the fuel.\textsuperscript{13} Fuels that contain both sulfur and nitrogen produced higher NO emissions than fuel containing only nitrogen.\textsuperscript{14} Fuel sulfur decreased NO$_x$ levels and increased N$_2$ levels in hydrogen deficient flames but have the opposite effect in fuel rich flames.\textsuperscript{15} It has also been found that sulfur inhibits the ability of NO to be reduced to NH$_3$ and CN and is dependent on the fuel richness.\textsuperscript{16,17} More recent studies show that there is an initial increase of NO in combustion but an increased NO decay after combustion that depends on the amount of sulfur present.\textsuperscript{11}
1.1 References


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CHAPTER 2

EXPERIMENTAL METHOD

2.1 Background

In 1967 Norrish and Porter won the Nobel Prize for Chemistry for the flash photolysis technique they developed in 1949. The great advantage of this technique is the elimination of pressure and mixing limitations experienced by other flow systems and the wide range of reaction time scale.¹ Reactions with rates from $10^0$ to $10^{-6}$ seconds can easily be studied. This is a well-proven method for direct investigation of rates of elementary reactions that are usually steps of a larger mechanism.

In flash photolysis, reactants are premixed and flowed into the reactor at a controlled temperature and pressure. The reacting species are initially inert to each other. An intense burst of light in the ultraviolet or visible region alters one of the reactants, called the precursor, by creating a radical or an excited species. The concentration of the precursor can then be monitored with respect to time as it reacts with the other reactant. One requirement for this method is the flash pulse must be faster than the reaction for detection to occur. Typical time scales for flash photolysis are from milliseconds to microseconds. This method has become more sophisticated with the advancements in laser and optics technology. Reactions in the nanosecond and picosecond range can now be explored.² Another advantage to using lasers is the well defined range of wavelength and high repetition pulse rate.
Many detection methods can be used with flash photolysis, and resonance fluorescence is the method used in this investigation. Atomic species are detected in the vacuum UV through absorption of radiation in resonance with an excited electronic state. The emission lifetime of the excited state is shorter than quenching and the atom returns to the ground state through fluorescence and emits a photon. The microwave flow lamp produces the photons and directs them into the reactor where they have the exact energy as the atomic species produced by the precursor molecule. The atoms get excited to the same electronic state and emit photons isotropically upon relaxation to the ground state. The scattered photons are detected by a photomultiplier tube. Counts of photons versus time are accumulated in a multichannel scaler analyzer. The intensity of the fluorescence is proportional to the radical concentration, and when a least squares fit analysis is performed, the relation between concentration and time is acquired.

2.2 Gas Preparation

Gas mixtures were prepared using a borosilicate glass, vacuum line and bulb, gas handling system. This type of glass has a low expansion coefficient and makes it resistant to thermal shock. The system, as well as the reactor, is evacuated overnight to remove contaminants. Using a combination of mechanical and diffusion pumps, the pressure was reduced to $10^{-4}$ torr inside the handling system.

$\text{NO}_2$ (99.5%, Matheson) was separated from high boiling point impurities by several freeze-pump-thaw cycles with a liquid nitrogen/acetone slush at 178 K. Low boiling point impurities were removed by several freeze-pump-thaw cycles with liquid
nitrogen at 77 K. NO$_2$ was further purified by several distillations at 178 K, where the middle 80% was trapped. CS$_2$ (99%, Sigma Aldrich) was distilled with two freeze-pump-thaw cycles at 77 K. Argon (99.9999%, Air Liquide) was used with no further purification.

Mixtures of CS$_2$ vapor diluted in argon were prepared manometrically into glass bulbs. The partial pressure and the amount of the vapor are dependent on the overall concentration desired for the reaction. Mixtures of NO$_2$ were prepared at room temperature to minimize the presence of the N$_2$O$_4$ dimer. The dimer concentration must be very low to minimize the error in the NO$_2$ concentration and any role for N$_2$O$_4$ in the kinetics.

At 298 K the equilibrium constant, $K_{eq}$ for the dissociation of the N$_2$O$_4$ dimer is equal to 0.1426.$^{3,4}$ When making the mixture, the partial pressure of NO$_2$ is equal to 1.2 torr. Using equation 2.1, where $P^0$ is the standard pressure of 750.7 torr, the partial pressure of N$_2$O$_4$ is 0.014 torr for the mixture. The percentage of N$_2$O$_4$ in the NO$_2$ is equal to 1.2. Upon further dilutions the presence of the N$_2$O$_4$ dimer becomes significantly less. The low-pressure rate constant ($k_0$) for the conversion of N$_2$O$_4$ into 2 NO$_2$ is 6.1 x 10$^{-15}$ [Ar] s$^{-1}$. The smallest concentration of argon used is 3.35 x 10$^{17}$ molecule cm$^{-3}$, which yields a half life of 3.4 x 10$^{-4}$ s, which is on a shorter time scale than the shortest residence time of 0.34 s. This would be the worst case scenario, so higher argon concentrations would produce smaller half lives.

$$\text{N}_2\text{O}_4 \leftrightarrow 2 \text{NO}_2$$

$$K_{eq} = \frac{(P_{\text{NO}_2}/P^0)^2}{(P_{\text{N}_2\text{O}_4}/P^0)} \quad (2.1)$$
Pressure for the system was measured using an absolute pressure transducer (MKS Instruments Type 622). Gas mixtures were prepared several hours prior to experimentation to make sure mixing was complete. During the experiment the precursor, reactant and bath gas are introduced into a manifold on the gas preparation line, which in turn combines them to allow for even mixing before they are sent to the reactor. The flow of gases is controlled by mass flow controllers (MKS Instruments Type 1159B) by measuring the amount of heat transfer from a heated tube to the flowing gas inside the tube. The flow is proportional to the voltage necessary to maintain a constant temperature profile. Since the mass flow rate is controlled and not volume, the pressure and temperature have no effect on the measured flow rate. From the manufacturer the accuracy of the flow controllers is within one percent and the resolution is within 0.1 percent over the full range of the controller.

Calibration of the flow controllers was performed for argon using a Teledyne Hastings-Raydist bubble meter (HBM-1-A). This is done by accurately measuring the time it takes the controller to flow a certain volume of gas and converting to standard conditions. The outlet port of the flow controller is connected to the bubble meter and the displacement of a soap bubble up a graduated cylinder is timed. Laboratory conditions must be converted to the manufacturer's standard conditions (760 torr and 293 K) in order to compare with the factory settings and the calculation is shown in equation 2.2.

\[
\text{Mass Flow} = \frac{\text{volume}}{\text{time}} \times \frac{(P - P_v)}{760} \times \frac{293}{(273 + T)}
\]  

(2.2)

Local pressure \(P\) (from a barometer, in torr), temperature \(T\) (in °C), and water vapor corrections \(P_v\) (tabulated) are made for the calibration measurements.
Five measured flow settings are used and ten measurements per flow setting are averaged and graphed against the displayed flow of the controllers. The equation obtained from the linear regression of the graph is used to derive the actual flow in the concentration calculations and the uncertainties of the slope and the intercept of the graph are used in the random error calculation for the concentration.

2.3 Reactor

The apparatus used for the reaction is a three way cross of stainless steel tubes with an intersection volume of about 8 cm$^3$. All tubes are identical to each other and intersect so all are perpendicular, as shown in Figure 2.1. The inner diameter is 2.2 cm and the tubes extend 11 cm from the intersection. Nichrome resistance wire is threaded through ceramic beads, and wrapped around the reactor center and extend for 4 cm of the tubes for a controlled heat source. Copper tube water jackets are also wrapped around the tube ends to protect the optics and gas fittings. The reactor is thermally insulated and encased in a box constructed from alumina boards (Zircar Products ZAL-50). All ends are sealed with quartz windows and the system is vacuum tested.

Each of the six reactor arms has its own function. The excimer laser (MPB PSX-100) fires through a telescopic expander and into the reactor window with a beam area of 7 x 8 mm$^2$ and continues through the reaction intersection and passes through the opposite window. The laser is filled with F$_2$ 0.19%, Ar 5.0%, neon balance, (Spectra Gases) and the output wavelength is 193 nm.
CS$_2$ is photolyzed by the excimer laser into CS and S.$^6$

$$\text{CS}_2 + h\nu \rightarrow \text{CS}_2^* \left( ^1\text{B}_2 \right) \rightarrow \text{CS} \left( ^1\Sigma^+ \right) + \text{S} \left( ^3\text{P} \right)$$

$$\text{CS} \left( ^1\Sigma^+ \right) + \text{S} \left( ^1\text{D} \right)$$

S $\left( ^1\text{D} \right) + \text{Ar} \rightarrow \text{S} \left( ^3\text{P} \right) + \text{Ar}$

The precursor absorbs energy from the excimer laser and gets promoted to an excited state where dissociation occurs. The majority of the atomic sulfur generated is in the triplet ground state (75%). The rest is in the singlet excited state (25%); upon collisions with the argon bath gas it relaxes to the triplet ground state with a quenching rate.
constant of $1.4 \times 10^{-11} \text{ cm}^3 \text{ atom}^{-1} \text{ s}^{-1}$. Given that the average [Ar] is $2.4 \times 10^{18} \text{ cm}^{-3}$ molecule, the quenching time is less than 1 μs, and so the excited singlet does not affect the experiment.

The microwave discharge lamp is attached to another arm and is perpendicular to the laser. The flow lamp is produced from 0.01% H$_2$S diluted with Ar, flowing at a low pressure of 150 mtorr through a microwave discharge (2.45 GHz) operated at 30-50 watts. Quartz optics is used to cut off any light below 160 nm.

$$
\text{H}_2\text{S} \rightarrow \text{S} \rightarrow \text{S}^* \rightarrow \text{S} + h\nu
$$

Sulfur $^3\text{S}_0 \rightarrow ^3\text{P (4s-3p)}$ 180.7 nm

Resonance fluorescence results from excitation of sulfur atoms. A photon is absorbed, causing an electron to jump to a higher level from which, after a delay, it falls back to its original level, emitting a photon having the same energy as the one absorbed. The emission is directed into the reaction chamber to excite unreacted sulfur radicals.

$$
h\nu + \text{S} \rightarrow \text{S}^* \rightarrow \text{S} + h\nu \rightarrow \text{PMT}
$$

These radicals get excited and then relax and emit photons isotropically into the photomultiplier tube (PMT). The PMT is perpendicular to the laser and the resonance lamp so there is minimal background signal from either. The other arms of the reactor contain a gas inlet that is opposite the resonance lamp, an exhaust that is connected back to the gas preparation line and exhaust gases pass through a cold trap of liquid nitrogen before being pumped to vent. The last arm contains a sheathed thermocouple.
(Type K, chromel/alumel) that is used for controlling and detecting the temperature inside the reactor. During experiments this is moved slightly out of the reaction zone. Thermocouple corrections arising from heat transfer to or from the walls of the reactor have been previously determined and contribute a ± 2.0 % uncertainty. A second thermocouple is placed outside the reactor next to the heating system. The temperature controller uses this to adjust the current through the nichrome heating wire and stabilizes the reactor temperature.

2.4 Detection

The solar-blind ultra violet PMT (Hamamatsu R212) measures the intensity of the emitted photons and is connected to a preamplifier/discriminator. This filters out weak signal from the PMT that arises from thermal electron emission inside the PMT and improves the signal to noise ratio. Signals from the discriminator are amplified and sent to the multi channel scalar, and recorded and analyzed on a computer. A digital delay pulse generator precisely times all the instruments. The excimer laser must be triggered after the multichannel scaler to record the background signal that is produced from the scattered photons from the resonance lamp.

2.5 Experimental Results

The reaction of atomic sulfur and nitrogen dioxide is a second order bimolecular process. The reaction rate depends on the concentration of the two reactants. The overall loss of sulfur with respect to time is expressed as the rate.
\[
S + \text{NO}_2 \rightarrow \text{Products} \quad k_1 \quad (2.3)
\]

Rate = \frac{d[S]}{dt} = -k_1 [S][\text{NO}_2] \quad (2.4)

Sulfur can also be lost through diffusion and secondary reactions with photolyzed fragments.

\[
S \rightarrow \text{loss} \quad k' \quad (2.5)
\]

Taking equations 2.4 and 2.5, a new rate expression is derived.

\[
\frac{d[S]}{dt} = -k_1 [S][\text{NO}_2] - k'[S] \quad (2.6)
\]

Flooding of the system is used to simplify the second order rate expression into a pseudo first order expression that only relies on one species concentration. In flooding, one of the reactants is much larger than the other and is essentially constant. In this experiment sulfur atoms react with excess NO\textsubscript{2}.

\[
[S] \ll [\text{NO}_2] \quad (2.7)
\]

The concentration of atomic sulfur from the CS\textsubscript{2} mixture was at least 100 times less than the NO\textsubscript{2} concentration to ensure pseudo first order conditions throughout the experiment. Since the NO\textsubscript{2} concentration is at least 100 times larger than sulfur, it is essentially constant and can be expressed in the pseudo first order rate constant along with the diffusion rate constant.

\[
\frac{d[S]}{dt} = -(k_1[\text{NO}_2] + k')[S] \quad (2.8)
\]
\[ k_{ps1} = (k_1 \ [NO_2] + k') \] (2.9)

\[ \frac{d[S]}{dt} = -k_{ps1} \ [S] \] (2.10)

The fluorescence signal intensity is proportional to the concentration. The pseudo first order rate constant and the uncertainty can be obtained from the non-linear least-squares fitting of the exponential decay of the signal intensity over time, shown in Figure 2.2.\textsuperscript{10,11}

Signal intensity can be expressed in the following equation.

\[ [S] = [S]_0 \ \exp (-k_{ps1} \ t) \] (2.11)

\[ I \propto [S] \] (2.12)

\[ I = [S]_0 \ C \ \exp (-k_{ps1} \ t) + B \] (2.13)

The values of \([S]_0\), \(C\) and \(B\) are constants, where \(B\) is the background signal from the continuous emission from the microwave flow lamp and \(C\) is the proportionality constant.

The concentration of nitrogen dioxide is calculated using partial pressures and the ideal gas law.

\[ P \ (NO_2) = P \ (NO_2)_{\text{bulb}} / P \ (\text{total})_{\text{bulb}} \times \frac{\text{Flow} \ (NO_2)}{\text{Flow} \ (\text{total})} \times \frac{P \ (\text{total})_{\text{system}}}{RT} \] (2.14)

\[ a_{\text{bulb}} = P \ (NO_2)_{\text{bulb}} / P \ (\text{total})_{\text{bulb}} \] (2.15)

\[ [NO_2] = a_{\text{bulb}} \times \frac{\text{Flow} \ (NO_2)}{\text{Flow} \ (\text{total})} \times \frac{P \ (\text{total})_{\text{system}}}{RT} \] (2.16)
Figure 2.2  Exponential decay of the signal intensity.

Combining equations 2.14 and 2.15 yield 2.16, where $a_{\text{bulb}}$ is the mole fraction of NO$_2$, and R is the gas constant ($9.66 \times 10^{18}$ torr cm$^3$ molecule$^{-1}$ K$^{-1}$). Each of the parameters in the equation is independent of each other and have their own uncertainty that contribute to the overall error in the nitrogen dioxide concentration. The uncertainty is calculated using equation 2.17.

$$\sigma_{[\text{NO}_2]} = [\text{NO}_2] \times \left\{ \sum \left( \frac{\sigma_x}{x} \right)^2 \right\}^{1/2}$$  \hspace{1cm} (2.17)
The $x$ is equal to the different parameters in the equation, for example the error in temperature is divided by the temperature, squared, added to the other parameters and the square root is taken. This number is multiplied by the concentration and yields the error.

Five successive NO$_2$ concentrations are used to obtain $k_{ps1}$ values, with the lowest being zero. A plot of $k_{ps1}$ versus [NO$_2$] analyzed with a weighted linear least square fitting, produces $k_1$ from the slope and $k'$ from the intercept and the uncertainty involved, as seen in Figure 2.3.

![Figure 2.3](image_url)  
Figure 2.3  
Pseudo first order rate versus nitrogen dioxide concentration.
The initial atomic sulfur concentration is determined using equation 2.18 and 2.19, which are based on the Beer-Lambert law.\(^1,6\)

\[
[S] = I_0 - \{I_0 \times \exp(-\sigma [\text{CS}_2])\}
\]

\[
I_0 = \frac{\lambda \times c \times h}{2} \times \left[\frac{F \times (0.83)}{A \times 1000}\right]
\]

In these equations \(\sigma\) is the absorption cross section of \(\text{CS}_2\) (1.3x10\(^{-16}\) cm\(^2\))\(^12\), \(\lambda\) is the wavelength of the laser pulse (193 nm), \(F\) is the flash energy of the laser pulse, \(A\) is the area of the laser pulse (0.6 cm\(^2\)), and 0.83 is the power of the pulse in the reaction zone after passing through the window. The concentration of sulfur is not critical to the second order rate calculations, but it needs to be determined to make sure pseudo first order conditions are retained through the experiment. Atomic oxygen concentrations are calculated in the same way as sulfur, with the absorption cross section of \(\text{NO}_2\) (4.6 x 10\(^{-19}\) cm\(^2\))\(^13\). The oxygen concentration was kept below sulfur by a factor of at least 10\(^2\) so the atomic oxygen concentration does not influence the reaction rate.

Experimental parameters must be varied in order to rule out any secondary chemistry that might affect the second order rate constant for the reaction. The flash energy is varied to check for the possibility of photolysis fragments and/or reaction products participating in the loss of sulfur radicals. A working range of 0.02 - 0.09 mJ was used where the secondary rate constant was found to be unchanged. The time the reactants spent together before the reaction is initiated is called residence time. The residence time was varied in the range 0.34 - 2.98 s to make sure there was no thermal decomposition or mixing effects that influence the rate constant.
The $[S]_0$ was varied over $1.3 \times 10^{11} - 6.5 \times 10^{11}$ molecule cm$^{-3}$ to determine if there were any secondary reactions with the precursor and photolyzed fragments.

Two of the most important variables are pressure and temperature. With effect of an increase in pressure, the stabilization occurs through collisions with a third body, the bath gas, and rate of the collisions increases with an increase in bath gas concentration. The dependence of the rate constant on temperature is given by the Arrhenius equation.

$$k = A \exp \left(\frac{-E_a}{RT}\right)$$ \hspace{1cm} (2.20)

In 1889, Svante Arrhenius derived this empirical expression from numerous experimental rate measurements that were dependant on temperature.\textsuperscript{14} In this equation, $A$ is the Arrhenius parameter and describes the collision frequency, and $E_a$ is the energy of activation which is similar to the barrier that reactants must overcome to be converted into products. Equation 2.20 can be expressed linearly by taking the natural logarithm of both sides and gives equation 2.21.

$$\ln k = - \frac{E_a}{R} \left(\frac{1}{T}\right) + \ln A$$ \hspace{1cm} (2.21)

A plot of $\ln k$ versus $(1/T)$ will yield a straight line, in most cases, with a slope equaling $-\frac{E_a}{R}$ and the intercept $\ln A$. A negative slope will indicate a positive activation energy consistent with the reactants overcoming a barrier to products. A positive slope will indicate a negative activation energy and the process is barrierless. In these types of reactions the reactants most likely form an adduct or an intermediate species.\textsuperscript{2}

Thirty two measurements over the temperature range 292 - 656 K are summarized in Table 2.1. By varying the reaction conditions it was determined the reaction is
unaffected by secondary chemistry, mixing effects, and thermal decomposition over the temperature range. The second order rate constants were within \( \pm 1\sigma \). Experimental results indicated there was no dependence of the rate on argon bath gas density and a comparison is shown in Figure 2.4. A weighted linear least squares analysis of the \( k_1 \), Figure 2.5.\(^{15}\) The overall bimolecular rate expression derived from the Arrhenius plot is given by equation 2.22, where the uncertainty is \( 2\sigma \).

\[
k(t) = (1.9 \pm 0.5) \times 10^{-11} \exp\left(-\frac{4.1 \pm 0.1 \text{ kJ mol}^{-1}}{RT}\right) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (2.22)
\]

The uncertainty in the Arrhenius parameter and the activation energy are calculated from the covariance given from the straight line fitting. For each data pair \( (1/T, \ln k) \), it is an assumption that all of the error comes from \( \ln k \). The fitting program From these fittings, a larger intercept relates to a more positive slope, and a smaller intercept relates to a more negative slope, therefore the errors in the slope and intercept change together, hence correlation. The uncertainty in the overall rate constant depends on the correlation of the two variables. This can be calculated using equation 2.23.\(^{16}\)

\[
\text{Var} (\ln k) = \sigma (\ln A)^2 + \frac{2}{T} \text{ Cov}(\ln A, -E_a/R) + \left(1/T^2\right) \sigma (-E_a/R)^2 \quad (2.23)
\]

The \( 2\sigma \) statistical uncertainty is 2\% to 4\%, with the smallest error in the middle of the graph. A 2\% allowance for systematic error is included with the variance in quadrature to yield the 95\% confidence limit of about 5\%.
Figure 2.4  Comparison of the second order rate constant with the argon bath gas density.
Figure 2.5  Arrhenius plot for the $S + NO_2$ rate constant.
Table 2.1 Summary of measurements for the rate constant $k_1$.

<p>| $T$ (K) | $\tau_{\text{res}}$ (s) | $F$ (mJ) | $P$ (mbar) | [CS$_2$] / $10^{13}$ molecule cm$^{-3}$ | [$S_0$] / $10^{11}$ molecule cm$^{-3}$ | [NO$<em>2$]$</em>{\text{max}}$ / $10^{13}$ molecule cm$^{-3}$ | [O]$_0$ / $10^9$ molecule cm$^{-3}$ | $k_1$ / $10^{-11}$ molecule$^{-1}$ cm$^3$ s$^{-1}$ |
|---------|----------------|---------|----------|---------------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| 292     | 2.54           | 0.040   | 134      | 3.05                            | 2.24                        | 2.43 ± 0.12                  | 0.63                        | 10.59 ± 0.63                |
| 293     | 1.18           | 0.072   | 27       | 1.81                            | 2.28                        | 2.19 ± 0.53                  | 0.98                        | 9.51 ± 2.31                 |
| 293     | 2.05           | 0.087   | 67       | 3.89                            | 6.11                        | 7.20 ± 0.60                  | 4.01                        | 10.38 ± 1.03                |
| 294     | 0.65           | 0.044   | 67       | 5.37                            | 4.12                        | 7.20 ± 0.19                  | 1.96                        | 9.85 ± 0.36                 |
| 294     | 0.65           | 0.030   | 14       | 9.09                            | 4.74                        | 5.09 ± 0.28                  | 0.95                        | 9.67 ± 0.59                 |
| 295     | 0.61           | 0.038   | 14       | 2.66                            | 1.77                        | 3.49 ± 0.21                  | 0.82                        | 9.86 ± 0.65                 |
| 419     | 0.61           | 0.030   | 27       | 5.75                            | 3.01                        | 3.82 ± 0.25                  | 0.71                        | 6.65 ± 0.54                 |
| 419     | 3.44           | 0.042   | 133      | 4.52                            | 6.30                        | 15.60 ± 0.20                 | 4.06                        | 6.31 ± 0.45                 |
| 423     | 2.25           | 0.050   | 269      | 8.11                            | 3.94                        | 4.91 ± 0.22                  | 1.52                        | 6.58 ± 0.34                 |
| 423     | 1.09           | 0.040   | 136      | 8.03                            | 5.65                        | 3.47 ± 0.28                  | 0.86                        | 6.49 ± 0.45                 |
| 424     | 1.12           | 0.030   | 68       | 3.02                            | 4.19                        | 8.03 ± 0.13                  | 1.49                        | 5.80 ± 0.27                 |
| 425     | 1.80           | 0.056   | 271      | 1.69                            | 2.95                        | 4.92 ± 0.13                  | 1.71                        | 6.14 ± 0.22                 |
| 427     | 0.82           | 0.086   | 27       | 7.26                            | 2.54                        | 4.80 ± 0.39                  | 2.56                        | 6.00 ± 0.26                 |
| 431     | 2.81           | 0.051   | 135      | 5.59                            | 6.45                        | 11.20 ± 0.43                 | 3.54                        | 6.33 ± 0.42                 |
| 434     | 2.06           | 0.055   | 68       | 6.58                            | 5.36                        | 12.10 ± 0.39                 | 4.12                        | 6.44 ± 0.53                 |
| 545     | 2.96           | 0.020   | 400      | 2.03                            | 2.29                        | 15.00 ± 0.28                 | 1.86                        | 4.42 ± 0.28                 |
| 547     | 1.39           | 0.064   | 136      | 2.03                            | 2.27                        | 7.95 ± 0.13                  | 3.15                        | 4.65 ± 0.38                 |
| 549     | 1.14           | 0.052   | 134      | 2.34                            | 1.82                        | 3.79 ± 0.20                  | 1.22                        | 4.70 ± 0.23                 |
| 549     | 1.74           | 0.052   | 405      | 1.39                            | 2.13                        | 5.83 ± 0.07                  | 1.88                        | 4.57 ± 0.20                 |
| 553     | 0.34           | 0.060   | 27       | 4.40                            | 1.46                        | 2.65 ± 0.30                  | 0.99                        | 4.83 ± 0.22                 |
| 553     | 1.40           | 0.039   | 139      | 7.14                            | 2.99                        | 11.40 ± 0.48                 | 2.75                        | 4.80 ± 0.29                 |
| 553     | 1.94           | 0.039   | 268      | 2.62                            | 4.85                        | 18.40 ± 0.19                 | 4.44                        | 4.84 ± 0.18                 |
| 553     | 0.83           | 0.035   | 67       | 1.52                            | 1.60                        | 6.76 ± 0.14                  | 1.47                        | 4.77 ± 0.22                 |</p>
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2.6 References


CHAPTER 3

THEORETICAL INVESTIGATION

3.1 Introduction

Computational chemistry is quickly emerging as a main field of theoretical chemistry. Mathematical methods and quantum mechanics are used to explore chemical processes. There are many advantages in using computational chemistry for studying combustion and atmospheric chemistry, especially since reactions are in the gas phase. Reactions that are too difficult or dangerous to explore in the laboratory can be safely done using computers. Modeling a reaction computationally can give foresight into proposing mechanisms and experimental conditions. A theoretical investigation can also reinforce experimental results or can eliminate certain reaction pathways.

Potential energy reaction pathways are constructed from reactants, products, local minima, transition states and barrier heights. High precision quantum mechanical electronic structure methods are needed to develop the potential energy surface (PES) of a reaction. These calculations yield accurate geometries, frequencies and energies of the PES species. Analyzing the PES with transition state theory (TST) or Rice, Ramsperger, Kassel, and Marcus (RRKM) theory can give rate constants.

The level of theory and basis set selection depends on the type and size of the molecule. Considerations must be made for open/closed shell systems. Spin
state and symmetry have a major effect on the energy of the system. The electron correlation whether restricted or unrestricted must be accounted for. Most importantly the right combination must be used for the least computational cost and the highest accuracy.

3.2 Density Functional Theory

Harmonic vibrational frequencies and optimized geometries were determined using the Becke three-parameter hybrid functional \(^1\) combined with the Lee, Yang and Parr correlation density functional theory method \(^2\) (B3LYP) using the 6-311G(d,p) \(^3\) basis set. The Pople-style basis set is a triple split valence basis that uses six primitive Gaussian type orbitals (PGTO) for the core orbitals and a triple contraction of the valence orbitals that are split into three, one and one PGTOs. (d,p) is added to improve the accuracy of the calculation and represents an added p-type polarization function for hydrogen atoms and an added d-type polarization function for all other atoms. The vibrational frequencies have been scaled by 0.990 to account for anharmonicity. \(^4\)

3.3 Ab Initio Theory

The QCISD\(^5\) and CCSD(T)\(^6-10\) methods have been used to explore the species of the potential energy surface (PES). These are two ab initio electronic structure theories that utilize multi-configurational wavefunctions and take into account electron correlation. Both of these methods begin with a single reference Hartree-Fock approximation and perform single and double excitations of the electrons. The quadratic configuration interaction singles and doubles (QCISD) theory is derived
from configuration interaction (CI) and adds higher order terms to make it size consistent and size extensive for the single and double excitations.

The CCSD(T) method is based on coupled cluster (CC), which includes all corrections, singles and doubles, to the reference wave function of a different type to infinite order. In this method single and double excitations are performed with an added perturbative triples contribution describing the coupling between singles and triples.

3.4 Correlation Consistent Basis Sets

The correlation consistent (cc) basis sets developed by Dunning et al.\textsuperscript{11-13} recover correlation energy of the valence electrons by adding functions of similar energy regardless of type. For example, the contribution from a second p-function is similar to the contribution from a first s-function. This systematic increase of primitive functions and contracted functions of the basis sets yields the acronymic naming of the basis sets, correlation consistent polarized (cc-p), valence(V), \( n \), zeta(Z), where \( n \) is the level of order (triple and quadruple).

Special modifications, designed for second and third row atoms, to these basis sets are used for the calculations. The cc-pV\((n + d)\)Z basis sets add extra polarization functions and the cc-pwVnZ basis sets properly treat the effects of core valence correlation where the core is weighted more heavily than the valence electrons.\textsuperscript{14}

The progressive enlargement of the basis sets allows the extrapolation to the complete basis set (CBS) limit and performing calculations in this fashion minimizes
the errors at each level. At the CBS limit the only error involved is fundamentally from the method used and the basis set error is essentially removed. A two point extrapolation is given by equation 3.1\textsuperscript{15}.

\[
E^\infty = \frac{(E_X X^3 - E_Y Y^3)}{(X^3 - Y^3)}
\]  

(3.1)

\(E_X\) represents the energy calculated with the triple zeta basis set and \(E_Y\) is the energy from the quadruple zeta calculation.

3.5 Computational Methodology

Initial stationary points on the PES are explored using B3LYP/6-311G(d,p) level of theory, where the geometries and frequencies are optimized. Approximate transition states are found by a series of relaxed and progressive scans of bond lengths and angles. These saddle points are optimized. Verification that a transition state truly connects the two minima on the PES is done using an intrinsic reaction coordinate pathway calculation (IRC) and a visual evaluation of the imaginary frequency.

All the species are then reoptimized at the QCISD/6-311G(d,p) level of theory starting from the B3LYP/6-311G(d,p) optimized geometries to get more accurate geometries and frequencies and all zero point energies are scaled and recorded. All calculations done at the two levels above are performed using the *Gaussian 03* program suite.\textsuperscript{16}

The optimized geometries from the QCISD/6-311G(d,p) calculations are used for the CCSD(T) calculations to get accurate energies. The triple zeta and quadruple zeta basis sets are used to obtain the energies needed for the CBS extrapolation. To
remove the possibility of spin contamination, a spin-restricted open-shell Hartree-Fock (ROHF) wavefunction is used for reference in an unrestricted CCSD(T) calculation. The spatial components of the $\alpha$ and $\beta$ orbitals are the same in the ROHF wavefunction, which eliminates the spin contamination found in spin-unrestricted Hartree-Fock (UHF) calculations involving doublet and higher spin states.

Core-valence corrections were performed at the CCSD(T)/cc-pwVTZ level using the difference between the frozen-core and the all-electron correlation energies. Mass velocity and Darwin scalar relativistic effects have been calculated using CISD/cc-pwVTZ theory for the kinetic energy of the electrons near the sulfur nucleus. The zero point energy of each molecule was calculated with the QCISD/6-311G(d,p) theory and scaled by 0.955 to account for anharmonicity. These corrections have been included into the CBS energy of all species investigated on the PES. All the CCSD(T) and CISD(T) calculations were performed using Molpro 06 program suite.17

3.6 Computational Results

Stationary points on the S + NO$_2$ potential energy surface with optimized geometries at the QCISD/6-311G(d,p) level theory are shown in Figures 3.1 and 3.2. Relative energies are shown in the potential energy diagram in Figure 3.3. The spin state, Cartesian coordinates, rotational constants and frequencies at the QCISD/6-311G(d,p) level of theory are shown in Tables 3.1 and 3.2. The electronic energies for the stationary points including scaled zero point, scalar relativistic and core-valence effects, and extrapolated to the complete basis set limit are shown in
Table 3.3. As a test, comparison of the calculated enthalpies and the experimental enthalpies was made for the $S + NO_2 \rightarrow SO + NO$ reaction. From the NIST - JANAF tables$^{18}$, the $\Delta H_0$ value from experiment is $-215.9 \pm 1.6$ kJ mol$^{-1}$ and the computed value is $-213.2$ kJ mol$^{-1}$. There is a difference of 2.7 kJ mol$^{-1}$, which is within a typical "chemical accuracy" of 1 kcal mol$^{-1}$.

At the B3LYP/6-311G(d,p) level of theory, geometry optimizations were performed to look for any low-lying species on a quartet surface. All enthalpies are at 0 K and include ZPE. It was found that the quartet state of the SNO$_2$ adduct is 306.6 kJ mol$^{-1}$ above the doublet state, the quartet state of TS-1 is 104.0 kJ mol$^{-1}$ above the doublet state and there is no bound quartet state for SONO. All these enthalpies are very high and a quartet potential energy surface would not affect the interpretation of the experiments. For this reason no further investigation of quartet states at a higher level of theory was performed.

The potential energy diagram is shown in Figure 3.3. It may be seen that atomic sulfur can react with nitrogen dioxide through three channels. Sulfur can react at the nitrogen atom without going through a barrier and a stable adduct is formed. Dissociation of the adduct proceeds through TS-1 and the SONO-trans species is formed. Dissociation of the trans species proceeds through TS-4 to SO and NO. Sulfur reacts at the oxygen atom through two different channels. In the first pathway reactants pass over a barrier, TS-2, and form SONO-trans which dissociates through TS-4 to SO and NO. In the second pathway reactants pass over the TS-3 barrier and form SO and NO directly.
Calculations were performed for species from a reaction of SO and NO to form c-OSNO and t-OSNO. As SO and NO approach each other there are two different pathways. Going through TS-6 reactants form c-OSNO and going through TS-7 reactants form t-OSNO. There is also a transition state, TS-8, connecting the cis and the trans structures of OSNO, where instead of a rotation about the S - N bond there is a bending of the O - N - S angle. The barrier to rotation of the S - N bond from the cis to trans(TS-9) was calculated at 161.7 kJ mol\(^{-1}\) relative to SO + NO and the enthalpy for the angle bend transition state (TS-8) was calculated at 0.3 kJ mol\(^{-1}\). The angle bending is symmetry forbidden: TS-8 has a symmetry of A' and it connects two minima with symmetry A''. Even though it is symmetry forbidden, it is energetically favorable for isomerization. Structures for each species are shown in Figure 3.4 and the potential energy diagram is shown in Figure 3.5. Cartesian coordinates, rotational constants and frequencies at the QCISD/6-311G(d,p) level theory are shown in Table 3.4. Single point energies at the CCSD(T)/CBS level theory are given in Table 3.5.

Calculations were also performed to explore a pathway on a different PES at the CCSD(T)/CBS level theory. A reaction of the SNO\(_2\) adduct with NO\(_2\) to form O\(_2\)NSNO\(_2\) was found to be barrierless. This species then goes through a transition state, TS-5, and becomes O\(_2\)NSONO, which dissociates to NO\(_2\) and SONO without a barrier. The resulting PES is shown in Figure 3.6. Species on the PES of the SNO\(_2\) adduct reacting with an additional NO\(_2\) calculated at the QCISD/6-311G(d,p) level theory are shown in Table 3.6, and the Cartesian coordinates, rotational constants and frequencies are shown in Table 3.7. It appears that the addition of NO\(_2\) catalyzes the
$\text{SNO}_2$ to SONO reaction and may explain the lack of pressure dependence and the negative activation energy by going under the TS-1 barrier.
Figure 3.1 Minima on PES, all species are planar. Distances in $10^{-10}$ m, angles in degrees.
Figure 3.2 Transition states on the PES, all planar except for TS1.

Distances in $10^{-10}$ m, angles in degrees.
Figure 3.3  Potential energy diagram showing relative enthalpy at 0 K.
Table 3.1  Minima on the SNO₂ potential energy surface, analyzed at the QCISD/6-311G(d,p) level of theory.

<table>
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<tr>
<th>Species</th>
<th>State</th>
<th>Cartesian Coordinates (Å)</th>
<th>Rotational Constants (GHz)</th>
<th>Scaled frequencies (cm⁻¹)</th>
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<td>NO₂</td>
<td>^2A₁</td>
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<td>242.6568</td>
<td>738</td>
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<td>^2B₂</td>
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<td></td>
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Table 3.2  Transition states on the SNO$_2$ potential energy surface, analyzed at the QCISD/6-311G(d,p) level of theory.

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<td>181 1250</td>
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<td>2.147824 0.355013 0.000000</td>
<td>2.78110</td>
<td>656 1602</td>
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<td>N</td>
<td>1.019797 0.023445 0.000000</td>
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<td>TS-4 $^2$A''</td>
<td>S</td>
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<td>572i 439</td>
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<tr>
<td></td>
<td>O</td>
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<td>86 851</td>
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<tr>
<td></td>
<td>O</td>
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<td></td>
<td>N</td>
<td>1.064973 -0.846513 0.000000</td>
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<td></td>
</tr>
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Table 3.3  Component energies (hartrees) of stationary points on the SNO$_2$ PES. Scalar relativistic energy calculated at CISD/cc-pwVTZ level of theory. Core-valence correction calculated at CCSD(T)/cc-pwVTZ level of theory. Scaled zero point energy calculated at QCISD/6-311G(d,p) level of theory.

<table>
<thead>
<tr>
<th>Species</th>
<th>CCSD(T)/cc-pV(T+d)Z</th>
<th>CCSD(T)/cc-pV(Q+d)Z</th>
<th>CCSD(T)/CBS Limit</th>
<th>$E_{\text{Relativistic}}$</th>
<th>$E_{\text{Core}}$</th>
<th>ZPE</th>
<th>$E_{\text{Total}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>-397.654382</td>
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<td>-397.677544</td>
<td>-1.077452</td>
<td>-0.295605</td>
<td>0.000000</td>
<td>-398.459391</td>
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<tr>
<td>NO$_2$</td>
<td>-204.800372</td>
<td>-204.862773</td>
<td>-204.908309</td>
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<td>-603.409567</td>
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<td>NO</td>
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<td>-129.754538</td>
<td>-129.781885</td>
<td>-0.081138</td>
<td>-0.103054</td>
<td>0.004030</td>
<td>-129.769969</td>
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<tr>
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<td>-472.855584</td>
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<td>-0.348758</td>
<td>0.002471</td>
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<td>0.008977</td>
<td>-603.345514</td>
</tr>
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<td>TS-2</td>
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<td>TS-4</td>
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<td>-602.649381</td>
<td>-1.210190</td>
<td>-0.451413</td>
<td>0.007599</td>
<td>-603.408158</td>
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</table>
Figure 3.4  Species on SO + NO PES. Distances in $10^{-10}$ m, angles in degrees.
Figure 3.5  
SO + NO potential energy diagram showing relative enthalpy at 0 K
Table 3.4  Species on the SO + NO potential energy surface, analyzed at the QCISD/6-311G(d,p) level of theory.

<table>
<thead>
<tr>
<th>Species</th>
<th>State</th>
<th>Cartesian Coordinates (Å)</th>
<th>Rotational Constants (GHz)</th>
<th>Scaled frequencies (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>c-OSNO</td>
<td>(2^A^\text{a})</td>
<td>N  -0.936178  -0.532069  0.000000</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>O  -0.627389  -1.708476  0.000000</td>
<td>4.9025</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>S  0.000000   0.813606  0.000000</td>
<td>3.9287</td>
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<tr>
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<td>O  1.446546   0.546825  0.000000</td>
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</tr>
<tr>
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<td>N  -0.205683  -0.963425  0.000000</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>O  -1.252626  -1.578623  0.000000</td>
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<td>274</td>
</tr>
<tr>
<td></td>
<td></td>
<td>S  0.000000   0.696681  0.000000</td>
<td>3.9287</td>
<td>438</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O  1.432598   1.028259  0.000000</td>
<td></td>
<td>1455</td>
</tr>
<tr>
<td>TS-6</td>
<td>(2^A^\text{a})</td>
<td>S  0.000000   1.004162  0.000000</td>
<td>15.1206</td>
<td>267i</td>
</tr>
<tr>
<td></td>
<td></td>
<td>N  -1.134808  -0.785526  0.000000</td>
<td>4.9565</td>
<td>205</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O  1.355460   0.324392  0.000000</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>O  -0.362503  -1.645381  0.000000</td>
<td></td>
<td>1851</td>
</tr>
<tr>
<td>TS-7</td>
<td>(2^A^\text{a})</td>
<td>S  0.000000   0.860788  0.000000</td>
<td>25.7855</td>
<td>310i</td>
</tr>
<tr>
<td></td>
<td></td>
<td>N  -0.215494  -1.256214  0.000000</td>
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<td></td>
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<td>O  -1.323602  -1.601932  0.000000</td>
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<tr>
<td>---</td>
<td>---</td>
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<td>---</td>
<td>---</td>
</tr>
<tr>
<td>TS-8</td>
<td>$^2A'$</td>
<td>N</td>
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<td>O</td>
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<td>TS-9</td>
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<td>0.078806</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>-2.551467</td>
<td>0.134123</td>
<td>-0.403237</td>
</tr>
<tr>
<td></td>
<td>S</td>
<td>1.070037</td>
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</tr>
<tr>
<td></td>
<td>O</td>
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<td>0.676474</td>
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</table>
Table 3.5  Component energies (hartrees) of stationary points on the SO + NO PES. Scalar relativistic energy calculated at CISD/cc-pwVTZ level of theory. Core-valence correction calculated at CCSD(T)/cc-pwVTZ level of theory. Scaled zero point energy calculated at QCISD/6-311G(d,p) level of theory.

<table>
<thead>
<tr>
<th>Species</th>
<th>CCSD(T)/cc-pV(T+d)Z</th>
<th>CCSD(T)/cc-pV(Q+d)Z</th>
<th>CCSD(T)/CBS Limit</th>
<th>$E_{\text{Relativistic}}$</th>
<th>$E_{\text{Core}}$</th>
<th>ZPE</th>
<th>$E_{\text{Total}}$</th>
</tr>
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<tbody>
<tr>
<td>c-OSNO</td>
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<td>-602.679154</td>
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<td>0.009511</td>
<td>-603.437422</td>
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<td>t-OSNO</td>
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<tr>
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<tr>
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<td>0.007530</td>
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</table>
Figure 3.6 Potential energy diagram of the SNO₂ adduct reacting with a second NO₂ molecule. Relative enthalpy at 0 K.
Figure 3.7 Species on the PES of the SNO$_2$ adduct reacting with a second NO$_2$ molecule. Distances in 10$^{-10}$ m, angles in degrees.
Table 3.6  S(NO$_2$)$_2$ potential energy surface, analyzed at the QCISD/6-311G(d,p) level theory.

<table>
<thead>
<tr>
<th>Species</th>
<th>State</th>
<th>N</th>
<th>O</th>
<th>S</th>
<th>Rotational Constants (GHz)</th>
<th>Scaled frequencies (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_2$NSNO$_2$</td>
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<tr>
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<tr>
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<td></td>
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<td>0.974931</td>
<td>1.2458</td>
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</tr>
<tr>
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<td></td>
<td>5.1883</td>
<td>1.6054</td>
<td>0.974931</td>
<td>1.2458</td>
<td>180</td>
</tr>
<tr>
<td></td>
<td></td>
<td>24</td>
<td>71</td>
<td>180</td>
<td>180</td>
<td>636</td>
</tr>
<tr>
<td></td>
<td></td>
<td>666</td>
<td>811</td>
<td>855</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TS-5</td>
<td>$^1$A'</td>
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<td>1.6054</td>
<td>0.974931</td>
<td>1.2458</td>
<td>180</td>
</tr>
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<td>71</td>
<td>180</td>
<td>180</td>
<td>636</td>
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<td>666</td>
<td>811</td>
<td>855</td>
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<td>5.1883</td>
<td>1.6054</td>
<td>0.974931</td>
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<td>180</td>
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<td>636</td>
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<td>855</td>
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<tr>
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49
Table 3.7  Component energies (hartrees) of the species on the S(NO$_2$)$_2$ PES. Scalar relativistic energy calculated at CISD/cc-pwVTZ level of theory. Core-valence correction calculated at CCSD(T)/cc-pwVTZ level of theory. Scaled zero point energy calculated at QCISD/6-311G(d,p) level of theory.

<table>
<thead>
<tr>
<th>Species</th>
<th>CCSD(T)/cc-pV(T+d)Z</th>
<th>CCSD(T)/cc-pV(Q+d)Z</th>
<th>CCSD(T)/CBS Limit</th>
<th>$E_{\text{Relativistic}}$</th>
<th>$E_{\text{Core}}$</th>
<th>ZPE</th>
<th>$E_{\text{Total}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_2$NSNO$_2$</td>
<td>-807.350221</td>
<td>-807.495952</td>
<td>-807.602296</td>
<td>-1.342611</td>
<td>0.608445</td>
<td>0.023776</td>
<td>-808.312686</td>
</tr>
<tr>
<td>TS-5</td>
<td>-807.348207</td>
<td>-807.493718</td>
<td>-807.599901</td>
<td>-1.342615</td>
<td>0.607908</td>
<td>0.021628</td>
<td>-808.312980</td>
</tr>
<tr>
<td>O$_2$NSONO</td>
<td>-807.369000</td>
<td>-807.514506</td>
<td>-807.620685</td>
<td>-1.342627</td>
<td>0.607921</td>
<td>0.022297</td>
<td>-808.333094</td>
</tr>
</tbody>
</table>
3.7 RRKM Theory

RRKM theory was developed by Rice, Ramsperger, Kassel, and Marcus, and can approximate the rate of reaction for systems with energized species formed from collisions.19-22 This theory relies on the assumption that all reactions pass through a transition state and that intramolecular vibrational distribution happens rapidly compared to the reaction timescale. When the energized molecule is formed it can be collisionally stabilized by the bath gas M or go to products by dissociation or isomerization.

\[
\begin{align*}
A + M & \rightarrow A^* + M \\
A^* + M & \rightarrow A + M \\
A^* & \rightarrow \text{Products}
\end{align*}
\]

Each of these processes can be analyzed based on the internal energy, the density of the rovibrational states and the number of rovibrational channels of the system. The potential energy surface suggests that there is adduct formation in the system and the adduct can be analyzed using RRKM theory to predict its unimolecular rate constant via the fundamental relation shown in equation 3.2.22

\[
k(E) = \frac{W^2(E-E_0)}{\hbar \rho(E)}
\]  

\[
(3.2)
\]

\(\rho(E)\) is the density of states of the adduct and shown in equation 3.3. The number of vibrational frequencies is represented by \(s\) and the zero point energy is \(E_z\). \(E\) is the critical energy of the unimolecular reaction and \(E_0\) is the internal energy of the
species. The pathway being explored, dissociation of SNO$_2$ to products, is shown in Figure 3.6.

\[ \rho (E) = \frac{[E + a(E) E_z]^{s-1}}{(s-1)! \Pi h\nu_i} \]  
\hspace{1cm} (3.3)

The correction factor derived by Whitten and Rabinovich is shown in equations 3.4 - 3.7.$^{23}$

\[ a = 1 - \beta \omega \]  
\hspace{1cm} (3.4)

\[ \beta \approx (s-1) \sum \nu_i^2 / \{s (\sum \nu_i)^2\} \]  
\hspace{1cm} (3.5)

\[ \log \omega \approx -1.0506(E / E_z)^{0.25} \text{ at } (E > E_z) \]  
\hspace{1cm} (3.6)

\[ \omega^{-1} \approx 5(E / E_z) + 2.73(E / E_z)^{0.5} + 3.51 \text{ at } (E < E_z) \]  
\hspace{1cm} (3.7)

\( W^{\dagger}(E-E_0) \) is the sum of states of the transition state where \( s \) represents the number of frequencies there minus the imaginary frequency, i.e. 5, and is obtained via equation 3.8.

\[ W^{\dagger}(E-E_0) = \frac{(E-E_0) + a (E_z)}{s! \Pi h\nu_i} \]  
\hspace{1cm} (3.8)

The \( W^{\dagger}(0) \) from the Whitten-Rabinovich equation can be incorrect by several orders of magnitude as \( E \to E_0 \). Troe added 1 to this result to force \( W^{\dagger}(E) \) for \( E=0 \) to the correct limiting value of 1.$^{24}$ The modified value interpolates between the correct value at \( E_0 \) and the smooth range at \( E \). The corresponding rate constant is shown in equation 3.9. The energies used in the analysis are from the \textit{ab initio} calculations and these and the correction factors are listed in Table 3.6.

\[ k(E) \approx \frac{1}{h\rho (E)} + \frac{W^{\dagger}(E-E_0)}{\{h\rho(E)\}} \]  
\hspace{1cm} (3.9)
The average collision energy for adduct formation of 1.5 RT at 300 K is equal to 3.7 kJ mol\(^{-1}\).\(^{25}\) With a well depth of 152.2 kJ mol\(^{-1}\), the typical energized molecule energy is equal to 155.9 kJ mol\(^{-1}\), which is 6.2 kJ mol\(^{-1}\) above the threshold energy of 149.7 kJ mol\(^{-1}\) for the dissociation to products. The energy specific rate constant for dissociation to products \(k(E)\) was determined as \(8.54 \times 10^9\) s\(^{-1}\).

Figure 3.8 Reaction pathway used in the RRKM analysis for S-NO\(_2\) \(\rightarrow\) products.
Table 3.8 Values used in the RRKM analysis of the S + NO₂ → products reaction.

<table>
<thead>
<tr>
<th></th>
<th>Energy kJ mol⁻¹</th>
<th>Zero point energy kJ mol⁻¹</th>
<th>s</th>
<th>β</th>
<th>ω</th>
<th>a</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>W²(E-E₀)</td>
<td>6.2</td>
<td>23.58</td>
<td>5</td>
<td>0.236</td>
<td>0.161</td>
<td>0.962</td>
<td>17.49</td>
</tr>
<tr>
<td>ρ (E)</td>
<td>155.9</td>
<td>29.36</td>
<td>6</td>
<td>0.179</td>
<td>0.0254</td>
<td>0.995</td>
<td>5.43 mol J⁻¹</td>
</tr>
</tbody>
</table>
3.8 References


4.1 Discussion

The present rate constants are in agreement within a factor of 1.5 with a previous atomic resonance fluorescence experiment performed in a low pressure flow tube from 296 - 410 K by Clyne et al.\textsuperscript{1} The prior work over a smaller temperature range indicated an approximately zero activation energy. The comparison is shown in Figure 4.1. The positive slope of the Arrhenius plot of the averaged data from new measurements indicates a negative activation energy. This negative energy of activation suggests a barrierless reaction and thus rules out the pathways through TS-2 and TS-3. A frozen matrix experiment has been performed on the system by Bahou et al.,\textsuperscript{2} where samples of OCS/NO\textsubscript{2}/M (M=N\textsubscript{2} or Ar) were irradiated at 248 nm and the major products produced and identified were c-OSNO and t-OSNO. CS\textsubscript{2}/NO\textsubscript{2}/Ar samples were irradiated at 193 nm and no reaction product was observed, only cyclic CS\textsubscript{2} and CS were identified. A previous computational study has been performed at the B3LYP/cc-pVTZ level theory by Chen et al.\textsuperscript{3} These two groups worked in collaboration and come to the same conclusions. The theoretical study predicted the major product to be SNO\textsubscript{2} due to barrierless formation. The absence of a barrier is in agreement with our calculations. There is a difference in the energies of the stationary points by 10 - 30 kJ mol\textsuperscript{-1}; this is to be expected due to our higher level of theory.
These two groups concluded that irradiation of OCS yields predominately excited state singlet sulfur that reacts with the oxygen of NO₂ and proceeds through TS-2 and goes on the form SO and NO. These then go on to recombine and produce c-OSNO and t-OSNO. From our own calculations of the SO + NO reaction the S-N binding energies of the cis and trans isomers of OSNO are small (31 and 17 kJ mol⁻¹ as seen in Figure 3.5 on pg. 40). Interestingly, the S-N bond lengths of c-OSNO and t-OSNO are ca. 0.1 Å shorter than the stronger S-N bond in SNO₂ (151 kJ mol⁻¹), and the stretching frequencies in the cis and the trans species are more than 100 cm⁻¹ higher than the S-NO₂ stretching frequency of 436 cm⁻¹. The OSNO isomers were detected in the frozen matrix² but at elevated temperatures they would not exist. Bahou et al.² concluded CS₂ and NO₂ may form van der Waals complexes and have a geometric constraint for reaction; also there could be destruction of any products formed from irradiation with 193 nm light.

The lack of dependence of the rate constant on bath gas density in our experiments suggests that there is no adduct being formed as the final product. The reaction of another NO₂ molecule with the SNO₂ adduct was investigated to try and explain the lack of bath gas density dependence.

\[ S + NO₂ + NO₂ \rightarrow SNO₂ + NO₂ \rightarrow S(NO₂)₂ \rightarrow \text{Products} \]

This mechanism could explain the lack of adduct formation in the frozen matrix experiments where there is a dense environment and close proximity of the reactants, however this process could not work in the gas phase.
In the gas phase the rate would depend on the formation of the energized adduct, the dissociation to reactants and product formation. The adduct steady state equation for gas phase reaction is shown in equation 4.1.

\[
S + NO_2 \rightarrow SNO_2^* \quad k_1 \\
SNO_2^* + NO_2 \rightarrow \text{Products} \quad k_2
\]

\[
d[SNO_2^*]/dt = k_1 [S] [NO_2] - k_{-1} [SNO_2^*] - k_2 [SNO_2^*] [NO_2] = 0 \quad (4.1)
\]

From this the reaction rate is derived and shown in equation 4.2.

\[
\text{Rate} = k_1 k_2 [S] [NO_2]^2 / \{k_{-1} + k_2 [NO_2]\} \quad (4.2)
\]

There are two limiting cases. From the rate expression, if the back reaction (k_{-1}) was negligible the reaction would be second order, and the rate of reaction is simply the rate of the first step, k_1 [S] [NO_2]. If k_2 [NO_2] \ll k_{-1} then the reaction of the energized adduct with an additional NO_2 molecule would give a third order rate. The likely magnitude of k_{-1} was investigated.

The partition functions for S, NO_2 and SNO_2 were used in equation 4.3 to obtain the equilibrium constant.\(^4\)

\[
K_c (T) = (Q_{\text{Products}} / Q_{\text{Reactants}}) \exp (- \Delta H_0 / RT) \quad (4.3)
\]

The high-pressure limit was calculated for k_{-1} (shown as k_{\text{dissociation}} in Fig. 3.6 on pg. 43) via the relation \(K_c = k_1 / k_{-1}\) and k_1 is a typical collision rate constant of \(1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\).\(^5\) The Arrhenius A-factor for k_{-1} over the temperature range 298 - 2000 K for S + NO_2 ⇌ SNO_2 is \(2.16 \times 10^{15} \text{ s}^{-1}\).
The energy-specific rate constant $k_1(E)$ was calculated via an Inverse Laplace Transform method, where the Arrhenius pre-exponential factor for the high pressure limit ($A_\infty$) and the threshold energy ($E_0$) are used and shown in equation 4.4.6

$$k(E) = A_\infty \frac{\rho(E-E_0)}{\rho(E)} \quad (4.4)$$

The density of states ($\rho$) is calculated with the method described in section 3.7. The energy specific rate for the reverse reaction is $k_{-1}(E) = 3.36 \times 10^{11} \text{ s}^{-1}$. This is about 40 times larger than the result for the RRKM energy specific reaction rate $k(E) = 8.54 \times 10^9 \text{ s}^{-1}$ for $\text{SNO}_2 \rightarrow \text{SO} + \text{NO}$. This shows that roughly one out of 40 collisions goes to products and the back reaction has a major influence on the mechanism. With reference to eq. 4.2, a maximum plausible values of $k_2[\text{NO}_2]$ is $8.54 \times 10^9 \text{ s}^{-1}$ and therefore $k_{-1} \gg k_2[\text{NO}_2]$. In the context of the mechanism shown at the bottom of p. 49, the rate would be third order and shown in equation 4.5.

$$\text{Rate} = k_1 k_2 [S] [\text{NO}_2]^2 / k_{-1} \quad (4.5)$$

Third order kinetics are not seen in the gas phase experiments so reaction with a second NO$_2$ molecule may be ruled out.

RRKM theoretical analysis was performed to help explain the experimental results. The density of states for the SNO$_2$ adduct and the sum of states for TS-1 was calculated and the energy specific rate constant was determined as $8.54 \times 10^9 \text{ s}^{-1}$. This value is 700 times faster than the rate constant for stabilization, $1.15 \times 10^7 \text{ s}^{-1}$, and suggests that the pressure-dependent rate of adduct stabilization is much slower than
its dissociation rate. When the SNO$_2$ adduct is formed it is in a vibrationally excited state that quickly dissociates to products. Although stabilization of the adduct is thermodynamically favorable, dissociation to products is kinetically favorable and dominates the reaction. This explains the lack of pressure dependence of the rate constant.
Figure 4.1 Arrhenius plot for the $S + NO_2$ rate constant and comparison with previous experiment from the literature.\textsuperscript{1}
4.2 Conclusions

The kinetics of the reaction of atomic sulfur and nitrogen dioxide has been investigated over 298 to 650 K using the laser flash photolysis - resonance fluorescence technique. The reaction was found to have a negative activation energy and the rate constant is independent of pressure over the range 14 - 405 mbar. *ab initio* calculations were performed at the CCSD(T)/CBS level of theory and predict initial adduct formation in accord with the negative activation energy from experiment. Additional *ab initio* calculations were performed on another possible potential energy surface where the SNO₂ adduct reacts with an additional NO₂ molecule. RRKM theory calculations were performed on the system. It is found that the adduct is formed in a vibrationally excited state and the rate of collisional stabilization is slower than the rate of dissociation to products via the transition state by a factor of 100 - 1000. This explains the lack of observed pressure dependence of the rate constant.
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