THE CHEMISTRY OF HO\textsubscript{2}NO\textsubscript{2} AND THE PHOTOCHEMISTRY OF THE HO\textsubscript{x}-NO\textsubscript{x}-CO\textsubscript{x} SYSTEM

David Littlejohn
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THE CHEMISTRY OF $\text{HO}_2\text{NO}_2$ AND THE PHOTOCHEMISTRY OF THE $\text{HO}_x\text{NO}_x\text{CO}_x$ SYSTEM

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TABLE OF CONTENTS

I. Introduction ................................................. 1
   A. Peroxynitric Acid ........................................ 2
   B. Alternate Methods of Producing HNO$_4$ ................. 9
   C. The Reaction of HNO$_4$ with OH ....................... 12
   D. Ozone in the Troposphere .............................. 15

II. Experimental .............................................. 23
   A. Methods .................................................. 23
      1. Expansions ............................................ 23
      2. Static Cell Photolysis ................................ 25
      3. Flowing Photolysis ................................... 26
      4. Numerical Simulation of Chemical Systems ........ 29
   B. Apparatus .............................................. 30
      1. Reaction Cell and Temperature Control ............. 30
      2. Optical System ....................................... 32
      3. Detectors ............................................ 34
      4. Electronics .......................................... 36
      5. Photolytic Light Sources ........................... 39
   C. Gases and Flow System .................................. 45
III. Absorption Cross Sections ........................................... 51
   A. Infrared Cross Sections ........................................... 51
   B. Visible Cross Sections ............................................. 77
   C. Ultraviolet Cross Sections ....................................... 79
IV. The Reaction of \( \text{N}_2\text{O}_5 + \text{H}_2\text{O}_2 \) .................................. 84
   A. Experimental Procedures and Data ............................... 84
      1. Reactant Decomposition and Flow-in ......................... 84
      2. Expansion Methodology ...................................... 90
      3. Investigation of Complicating Factors in the
         \( \text{H}_2\text{O}_2 - \text{N}_2\text{O}_5 \) System ........................ 92
      4. Products and Reactant Concentration Dependence on
         \( \text{H}_2\text{O}_2 + \text{N}_2\text{O}_5 \) ................................ 99
   B. Results and Discussion ........................................... 132
      1. Other Reactions in the \( \text{H}_2\text{O}_2 - \text{N}_2\text{O}_5 \) System .... 132
      2. Analysis of the Reaction of \( \text{N}_2\text{O}_5 \) with \( \text{H}_2\text{O}_2 \) .... 138
V. The Reaction of \( \text{OH} + \text{HNO}_4 \) .................................. 158
   A. Experimental Procedures and Data ............................... 158
      1. Reaction system for the Investigation of ................. 158
         \( \text{OH} + \text{HNO}_4 \) ........................................ 158
      2. Experimental Technique ...................................... 164
      3. Actinometry .................................................. 168
   B. Results and Discussion ........................................... 170
VI. The Photochemistry of the \( \text{HO}_x - \text{NO}_x - \text{CO}_x \) System ........ 196
   A. Experimental Procedures and Data ............................... 196
   B. Results and Discussion ........................................... 205
Acknowledgments .................................................. 214
Appendix A: Photomultiplier Tube Gating ................. 215
Appendix B: Pressure Broadening of Rotational Lines in
Infrared Spectra ............................................... 218
Appendix C: Reaction Sets for Numerical Modeling of Chemical
Systems ......................................................... 223
Bibliography ....................................................... 232
THE CHEMISTRY OF HO\textsubscript{2}NO\textsubscript{2} AND THE PHOTOCHEMISTRY AND KINETICS OF THE HO\textsubscript{x} - NO\textsubscript{x} - CO\textsubscript{x} SYSTEM

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ABSTRACT

The objectives of this work were: (1) to investigate formation and destruction reactions of peroxynitric acid, HO\textsubscript{2}NO\textsubscript{2} and (2) to study the photochemistry and kinetics of the HO\textsubscript{x} - NO\textsubscript{x} - CO\textsubscript{x} system were also studied. Investigations were done using infrared spectroscopy to observe the behavior of species involved with the reactions of interest.

Several techniques were used, including expansion of reactants into an evacuated cell, static cell decays under constant illumination, and periodic photolysis of flow systems. Infrared absorption cross sections were obtained for CO, CO\textsubscript{2}, NO, NO\textsubscript{2}, N\textsubscript{2}O\textsubscript{5}, HNO\textsubscript{3}, H\textsubscript{2}O\textsubscript{2}, and H\textsubscript{2}O. The spectroscopic measurements were used to derive kinetic information on the systems under study.

The reaction of H\textsubscript{2}O\textsubscript{2} with N\textsubscript{2}O\textsubscript{5} has previously been studied only in the liquid phase.\textsuperscript{6,7} This study investigated the reaction of gaseous H\textsubscript{2}O\textsubscript{2} and N\textsubscript{2}O\textsubscript{5} in the temperature range of 253 K to 283 K and a pressure range of 10 torr to 80 torr. The reaction occurred primarily heterogeneously in the apparatus in which it was studied. The upper limit for the bimolecular reaction giving the products
$H_2O_2 + N_2O_5 \rightarrow HNO_4 + HNO_3$

determined to be $k_d < 1 \times 10^{-18} \text{cm}^3 \text{molecule}^{-1} \text{second}^{-1}$.

The reaction of $H_2O_2$ with two other species was also examined.

$H_2O_2 + NO \rightarrow \text{products}$

$H_2O_2 + HNO_3 \rightarrow \text{products}$

Both reactions proceed by primarily heterogeneous pathways and appear to be fairly slow in the temperature range of 263 K to 283 K. The upper limit for the bimolecular rate constant for both reactions is $< 1 \times 10^{-19}$ cm$^3$ molecule$^{-1}$ second$^{-1}$.

The decomposition products of HNO$_4$, HO$_2$ and NO$_2$, may react by two pathways:

$HO_2 + NO_2 + M \rightarrow HNO_4 + M$

- $d$

$HO_2 + NO_2 \rightarrow HONO + O_2$

This study found the ratio $k_e/k_d < 0.05$ at 263 K and 30 torr. Using the equation for $k_d$ given by Graham et al., an upper limit for $k_e < 5 \times 10^{-14}$ cm$^3$ molecule$^{-1}$ second$^{-1}$ was obtained.
The products of the reaction of OH with HNO₄ were determined to be

\[ \text{OH} + \text{HNO}_4 \rightarrow \text{H}_2\text{O} + \text{NO}_2 + \text{O}_2 \]

and the rate constant for the reaction was found to be \( k_f = 2.9 \pm 1.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ second}^{-1} \) over the temperature range of 263 K to 283 K.

The decay profiles of species in the static cell photolysis of NO₂, H₂O₂ and CO in 0.1 and 1.0 atmosphere of O₂ were observed and compared with numerical simulations.

The appearance of O₃ after the initiation of photolysis of the system was observed. A chemical reaction cycle has been proposed as a source of O₃ in the troposphere; \(^{54,111}\)

\[ \begin{align*}
\text{OH} + \text{CO} & \rightarrow \text{H} + \text{CO}_2 \\
\text{H} + \text{O}_2 & \rightarrow \text{HO}_2 \\
\text{HO}_2 + \text{NO} & \rightarrow \text{OH} + \text{NO}_2 \\
\text{NO}_2 + \text{hv} & \rightarrow \text{NO} + \text{O} \\
\text{O} + \text{O}_2 & \rightarrow \text{O}_3 \\
\text{net:} \quad \text{CO} + 2\text{O}_2 & \rightarrow \text{CO}_2 + \text{O}_3
\end{align*} \]

Numerical simulations indicate that this cycle was not responsible for the generation of the ozone observed.
1

I. INTRODUCTION

In the past few decades, there has been growing interest and concern regarding chemical processes in the atmosphere. Initially, this interest was limited to chemistry in the troposphere, but more recently interest has spread to the stratosphere as well. In the atmosphere, the chemistry of peroxynitric acid is presently of particular interest. The chemistry associated with its formation and decomposition is still not completely understood. One currently known method of formation of peroxynitric acid is

\[
M \quad \text{HO}_2 + \text{NO}_2 \rightarrow \text{HNO}_4. \quad (1)
\]

\[
M \quad \text{HNO}_4 \rightarrow \text{HO}_2 + \text{NO}_2 \quad (-1)
\]

The reverse reaction is responsible for its destruction. A reaction that may compete with (1) for consumption of \( \text{HO}_2 \) and \( \text{NO}_2 \) is

\[
\text{HO}_2 + \text{NO}_2 \rightarrow \text{HONO} + \text{O}_2. \quad (2)
\]

Other reactions may also be responsible for the formation and decomposition of peroxynitric acid. One reaction of particular importance is

\[
\text{OH} + \text{HNO}_4 \rightarrow \text{products} \quad . \quad (3)
\]
Work has been done to investigate the formation and destruction processes of peroxynitric acid.

In the troposphere, it has been noted recently\(^5\) that there is an apparent hemispheric asymmetry in the global distribution of the measured concentration of ozone. Non-chemical mechanisms for creating this asymmetry have been investigated previously and appear not to be responsible for the hemisphere variation of the ozone concentration. Research was performed to study a possible chemical mechanism that could account for the observed asymmetry.

One of the objectives of this research was to study the formation and destruction reactions of H\(_2\)O\(_4\), particularly formation by the gas phase reaction of H\(_2\)O\(_2\) and N\(_2\)O\(_5\), and destruction by attack of OH radical. Another objective was to investigate the photochemistry and kinetics of the H\(_X\)-NO\(_X\)-CO\(_X\) system by observing the response of species to photolytic light in a mixture of H\(_2\)O\(_2\), NO\(_2\), CO and O\(_2\).

A. Peroxynitric Acid

Initial investigations of the chemistry associated with HO\(_2\)NO\(_2\) began shortly after the turn of the century. Early investigations of its formation and behavior in solution were done by D'Ans and Friederich,\(^6\) and somewhat later by Schwarz.\(^7\) They investigated the reactions of H\(_2\)O\(_2\) and N\(_2\)O\(_5\) and H\(_2\)O\(_2\) with HNO\(_3\) at low temperatures. The first reaction was reported to be very vigorous. The reaction product (presumably HNO\(_4\)) is very unstable and explosively decomposes at 243K. HNO\(_4\) was found to be stable in room temperature aqueous solutions at concentrations between 20 and 70 percent.
In recent years, a resurgence in interest in HNO₄ occurred when the possibility of its existence in the atmosphere was postulated. The radicals HO₂ and NO₂ are very important in the chemical balance of trace species in both the troposphere and the stratosphere. Initially it was believed that they only reacted in a radical disproportionation reaction

\[ \text{HO}_2 + \text{NO}_2 \rightarrow \text{HONO} + \text{O}_2 \]  

(2)

It was noted by Simonaitis and Heicklen that HNO₄ could exist in equilibrium with HO₂ and NO₂

\[ \text{HO}_2 + \text{NO}_2 \rightarrow \text{HNO}_4 \]  

(1, -1)

Their measurements indicated a lifetime of HNO₄ on the order of 50 seconds at room temperature.

Niki et al. were the first to determine the infrared absorption of HNO₄ with a Fourier transform infrared spectrometer in a mixture of Cl₂, H₂ and NO₂ photolyzed by black lamps. The absorption spectrum was confirmed by Hanst and Gay, who used a mixture of Cl₂, NO₂ and H₂CO in a similar system to that used by Niki.

Levine et al. investigated the kinetics of HO₂ + NO₂ reactions in a mixture of HONO, CO, NO₂ and NO in synthetic air at 700 torr pressure. Along with reactions (1) and (2), they studied

\[ \text{HO}_2 + \text{NO} \rightarrow \text{HO} + \text{NO}_2 \]  

(4)
They obtained values for the ratios of the three reactions. Their results indicated that \( k_2/k_1 \approx 0.7 \pm 0.4 \), \( k_2/k_4 \approx 0.043 \pm 0.02 \) and \( k_1/k_4 \approx 0.058 \pm 0.02 \). They suggested that HNO_4 may be important in the chemistry of polluted air.

Simonaitis and Heicklen\(^1\) photolyzed a mixture of N_2O, H_2, O_2, NO and NO_2 at 213.9 nm and reported that (1) was the only reaction of H_2O and NO_2 that was observed. They obtained a value of \( 6 \times 10^{17} \exp(-26,000 \text{ mole}^{-1} \text{ cal/RT}) \text{sec}^{-1} \) for the unimolecular decomposition of HNO_4.

Graham, Winer and Pitts\(^4\) prepared HNO_4 with relatively low amounts of impurities and investigated the unimolecular decomposition of HNO_4 as a function of temperature. HNO_4 was mixed with excess NO, which scavenges H_2O by reaction (3). They obtained a value of \( k_{-1} = 1.4 \times 10^{14} \exp(-2,700\pm500/RT)\text{sec}^{-1} \). From this they calculated thermal decomposition lifetimes of HNO_4 at one atmosphere total pressure of 12 sec at 298 K, 5 min at 273 K and 1 month 220 K. They reported the ratio of \( k_2/k_1 < 0.001 \).

Baldwin et al.\(^14\) estimated the entropy of HNO_4 to be 71.6 eu. This value was obtained by correcting the measured value of the entropy for MeONO_2 for internal rotation. This estimate was then used to calculate a high pressure A factor of \( \log_{10}A = 15.9 \text{ sec}^{-1} \) for reaction (-1). They estimated an activation energy for reaction (-1) to be in the range of 23–25 kcal/mole from modeling smog chamber experiments of n-butane photo-oxidation.
Jesson et al. obtained ultraviolet absorption cross sections of HNO₄ in an aqueous solution at wavelengths between 300 and 360 nm. These values, along with measured rate constants for reactions (1) and (4), and estimates of the rate constants for

\[ \text{HNO}_4 + \text{Cl} \rightarrow \text{HCl} + \text{O}_2 + \text{NO}_2 \]  

(5)

\[ \text{HNO}_4 + \text{O} \rightarrow \text{OH} + \text{O}_2 + \text{NO}_2 \]  

(6)

\[ \text{HNO}_4 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_2 + \text{NO}_2 \]  

(7)

were used in a one-dimensional numerical model of atmospheric chemistry and transport to estimate the effect of HNO₄ on the atmosphere. They concluded that maximum concentrations of 1 to 3 ppb could exist in the stratosphere, but that more information on the kinetics and photochemistry of HNO₄ were needed.

Howard¹⁶ used laser magnetic resonance to directly study the reaction of H₂O + NO₂ in the pressure range of 0.5 to 3 torr. His measurements indicated \( k_2/k_1 < 0.15 \). He determined the M gas dependence of the reaction for M = He, N₂, O₂, NO₂ at 300 K.

Baldwin and Golden¹⁷ used more recent results and RRKM theory to predict a revised value of logio of the high pressure A factor = 16.4 sec⁻¹ at 300 K for reaction (-1).

Graham, Winer and Pitts¹⁸ investigated the pressure and temperature dependence of the unimolecular decomposition of HNO₄. They obtained a
rate constant for reaction (-1) in the second-order regime of $5.2 \times 10^{-6}$ exp(-19900 ± 500/RT) cm$^3$ molec$^{-1}$ sec$^{-1}$ for N$_2$ pressures up to ~7 torr. For 278 K, the limiting first-order high pressure value of reaction (-1) was estimated to be ~0.018 sec$^{-1}$. They obtained a $K_{\text{equil}} = k_{-1}/k_1$ of $8.1 \times 10^{10}$ molec cm$^{-3}$ using their results with those obtained by Howard. They developed empirical expressions for the rate constants of reactions (1) and (-1).

$$k_1,N_2 = 7.3 \times 10^{-33}\exp(2000/RT) \times [M]/(1+4.86 \times 10^{-12}[M]^{0.61}) \text{ cm}^3\text{molec}^{-1}\text{sec}^{-1}$$

$$k_{-1},N_2 = 5.2 \times 10^{-6}\exp(-19900/RT) \times [M]/(1+4.86 \times 10^{-12}[M]^{0.61})\text{sec}^{-1}$$

The relative M gas efficiencies from their results are $[N_2] = 1$ and $[O_2] = 0.83 \pm 0.12$.

Uselman et al.\cite{19} made another investigation of the kinetics of the unimolecular decomposition of HNO$_4$ in a mixture of Cl$_2$, H$_2$ and NO$_2$ in synthetic air at 700 torr total pressure. From their measurements of $K_{\text{equil}}$ for reactions (1) and (-1) over the temperature range of 293.3 to 301.4 K, they obtained values of $\Delta H^o = 23.8 \pm 2.7$ kcal/mole and $\Delta S^o = 40.5 \pm 8.8$ eu for reaction (-1). Using the entropy estimate of Baldwin et al.\cite{14}, they estimate $\Delta H^o_{f298}$(HNO$_4$) $\approx$ -10.8 kcal/mole.

More recently, Graham, Winer and Pitts\cite{20} have determined infrared and ultraviolet cross-sections for HNO$_4$. From their ultraviolet cross sections and the solar flux intensities of Leighton,\cite{1} they obtain a HNO$_4$ lifetime of about 3 hours in the troposphere. Molina and Molina\cite{21}
have obtained UV cross sections of HNO₄ that are considerably lower than those obtained by Graham et al. at longer wavelengths. From their values, they obtain a HNO₄ lifetime in the lower atmosphere of ~30 hours. Cox and Patrick have made measurements of HNO₄ UV cross sections that are somewhat higher than the measurements made by others. A comparison of the measured UV cross sections for HNO₄ is shown in Fig. 1.

Cox and Patrick also studied the kinetics of formation of HNO₄ from HO₂ + NO₂ in a modulation system. They obtain values of \( k_{-1} = 1.5 \pm 0.5 \times 10^{-12} \text{ cm}^3 \text{molec}^{-1} \text{sec}^{-1} \) for the second-order limit and \( k_{-1} = 2.5 \pm 0.5 \times 10^{-31} \text{ cm}^6 \text{molec}^{-2} \text{sec}^{-1} \) in the third-order limit. They derive a value for the unimolecular decomposition of HNO₄ of \( k_1 = 1.2 + 1.0/-0.6 \times 10^{15} \text{exp}(-21900\pm340/RT)\text{sec}^{-1} \). From this they obtain an entropy for HNO₄ of \( S^0 = 76.2 \text{ eu} \), with the assumption that the activation energy for formation is zero.

Barker et al. have investigated the reaction of several species with HNO₄. The products of the reactions were not determined. The reactions studied and the rate constants obtained are as follows:

\[
0 + \text{HNO}_4 \rightarrow \text{products} \quad k_7 = 7.5 \pm 3.4 \times 10^{12} \text{exp}(-2600\pm130/T)\text{cm}^3\text{molec}^{-1}\text{sec}^{-1} \quad (6)
\]

\[
\text{OH} + \text{HNO}_4 \rightarrow \text{products} \quad k_8 \leq 3.5 \times 10^{-12} \text{cm}^3\text{molec}^{-1}\text{sec}^{-1} \quad \text{for} \quad T = 275-297 \text{ K} \quad (3)
\]

\[
\text{O}_3 + \text{HNO}_4 \rightarrow \text{products} \quad k_9 \leq 5 \times 10^{-20} \text{cm}^3\text{molec}^{-1}\text{sec}^{-1} \quad T = 278 \text{ K} \quad (7)
\]

\[
\text{H} + \text{HNO}_4 \rightarrow \text{products} \quad k \approx 2.7 \pm 0.4 \times 10^{-14} \text{cm}^3\text{molec}^{-1}\text{sec}^{-1} \quad T > 250 \text{ K} \quad (8)
\]
Fig. 1. UV absorption spectrum of HNO₄
Graham et al.\textsuperscript{18} obtain an upper limit of $3 \times 10^{-12}$ cm$^3$ molec$^{-1}$ sec$^{-1}$ for $k_8$, which does not disagree with these results. Table 1 summarizes the literature values for the HO$_2$-NO$_2$-HNO$_4$ system.

Further work needs to be done to better understand the chemical behavior of HNO$_4$. Part of the present research was done to provide more information on this system.

B. Alternate Methods of Producing HNO$_4$

To date, all studies have considered formation of HNO$_4$ in the gas phase only by reaction (1). In solution, several methods of preparation exist. D'Ans and Freiderich\textsuperscript{6} and Schwarz\textsuperscript{7} prepared aqueous solutions of HNO$_4$ by reacting HNO$_3$ with H$_2$O$_2$. They also prepared HNO$_4$ by the reaction of N$_2$O$_5$ with H$_2$O$_2$ at low temperatures. Since then, Barker and coworkers\textsuperscript{2} have devised other techniques, as well as using the ones established by earlier workers. The three techniques they have used are:

1) Slowly adding 0.9g of 90 percent H$_2$O$_2$ to 2g of 70 percent HNO$_3$ at 0°C,

2) Very slowly adding 0.4g NO$_2$BF$_4$ powder to 2g of 90 percent H$_2$O$_2$ at 0°C with vigorous stirring,

3) Slowly adding 0.2g NO$_2$BF$_4$ powder to 0.1g of 90 percent H$_2$O$_2$ in 1g CH$_3$CN (acetonitrile) at 0°C.

It should be noted here that NO$_2$BF$_4$ is hygroscopic and preparations utilizing this compound should be done in an atmosphere free of water vapor.

It was decided to investigate the possibility of forming HNO$_4$ by reacting H$_2$O$_2$ with N$_2$O$_5$ and HNO$_3$ in the gas phase. Two other reactions that should be considered in analyzing the results of the above reactions
<table>
<thead>
<tr>
<th>Reference</th>
<th>k₁</th>
<th>k₋₁</th>
<th>k₂</th>
<th>k₂/k₁</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>----</td>
<td>----</td>
<td>~ 3 × 10⁻¹⁷</td>
<td>----</td>
</tr>
<tr>
<td>25</td>
<td>1.97 × 10⁻³¹</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>12</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>0.7 ± 0.4</td>
</tr>
<tr>
<td>16</td>
<td>1.0 ± 0.25 × 10⁻³¹ (M = He)</td>
<td>----</td>
<td>&lt; 3 × 10⁻¹⁵</td>
<td>&lt; 0.15</td>
</tr>
<tr>
<td></td>
<td>2.1 ± 0.52 × 10⁻³¹ (M = N₂)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.5 ± 0.38 × 10⁻³¹ (M = O₂)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.6 ± 3.0 × 10⁻³¹ (M = NO₂)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>----</td>
<td>1.4 × 10¹⁴ exp(-20700/RT)</td>
<td>----</td>
<td>&lt; 0.001</td>
</tr>
<tr>
<td>13</td>
<td>----</td>
<td>6 × 10¹⁷ exp(-26000/RT)</td>
<td>----</td>
<td>(small)</td>
</tr>
<tr>
<td>18</td>
<td>7.3 × 10³³ exp(2000/RT) × [M]eff</td>
<td>5.2 × 10⁻⁶ exp(-9900/RT) × [M]eff</td>
<td>&lt; 5 × 10⁻¹⁶</td>
<td>----</td>
</tr>
</tbody>
</table>

\[
[M]_{\text{eff}} = \left( \frac{[M]}{(1+4.86 \times 10^{-12} \times [M]^{0.61})} \right) \quad \text{rel. eff.: N}_2 = 1.0, \text{ O}_2 = 0.83 \pm 0.2
\]

22 | 1.5 ± 0.5 × 10⁻¹² (2nd order limit) | ---- | ---- | ---- |
|   | 2.5 ± 0.5 × 10⁻³¹ (3rd order limit) | ---- | ---- | ---- |

\[ \text{M} \]

\[ \text{H}_2 + \text{N}_2 \rightarrow \text{HNO}_3 \] (1)

\[ \text{HNO}_3 + \text{H} + \text{NO} \] (1)

\[ \text{H}_2 + \text{NO}_2 \rightarrow \text{HONO} + \text{O}_2 \] (2)

\[ \text{H}_2 + \text{NO}_2 \rightarrow \text{HONO} + \text{O}_2 \] (2)
are those of \( \text{H}_2\text{O}_2 \) with \( \text{NO}_2 \) and \( \text{N}_2\text{O}_5 \) with \( i\text{H}_2\text{O} \). Some of the possible products of these reactions and the enthalpies of reaction are listed below.

\[
\begin{align*}
\text{H}_2\text{O}_2 + \text{N}_2\text{O}_5 &\rightarrow \text{HNO}_3 + \text{HONO} + \text{O}_2 & \Delta H = -21.5 \text{ kcal/mole} \\
&\rightarrow \text{HNO}_3 + \text{HNO}_4 & -13.2 \text{ kcal/mole} \\
&\rightarrow \text{HNO}_3 + \text{HO}_2 + \text{NO}_2 & + 6.0 \text{ kcal/mole} \\
&\rightarrow \text{H}_2\text{O} + \text{NO}_3 + \text{NO}_3 & + 6.1 \text{ kcal/mole} \\
\end{align*}
\]

\[
\begin{align*}
\text{H}_2\text{O}_2 + \text{HNO}_3 &\rightarrow \text{H}_2\text{O} + \text{HONO} + \text{O}_2 & \Delta H = -12.0 \text{ kcal/mole} \\
&\rightarrow \text{H}_2\text{O} + \text{HNO}_4 & - 3.7 \text{ kcal/mole} \\
\end{align*}
\]

\[
\begin{align*}
\text{H}_2\text{O}_2 + \text{NO}_2 &\rightarrow \text{NO}_3 + \text{NO}_3 + \text{H}_2\text{O} & \Delta H = -16.1 \text{ kcal/mole} \\
&\rightarrow \text{HNO}_3 + \text{OH} & 1.7 \text{ kcal/mole} \\
\end{align*}
\]

\[
\begin{align*}
\text{H}_2\text{O}_2 + 2\text{NO}_2 &\rightarrow \text{HNO}_3 + \text{HNO}_3 & \Delta H = -47.8 \text{ kcal/mole} \\
\end{align*}
\]

\[
\begin{align*}
\text{H}_2\text{O}_2 + \text{N}_2\text{O}_4 &\rightarrow \text{HNO}_3 + \text{HNO}_3 & \Delta H = -34.2 \text{ kcal/mole} \\
\end{align*}
\]

\[
\begin{align*}
\text{N}_2\text{O}_5 + \text{H}_2\text{O} &\rightarrow \text{HNO}_3 + \text{HNO}_3 & \Delta H = -9.5 \text{ kcal/mole} \\
\end{align*}
\]

The enthalphy of formation for \( \text{HNO}_4 \) was that determined by Uselman et al., which is uncertain by several kcal/mole.
These reactions are of potential importance in tropospheric and stratospheric chemistry. This research is directed toward determining values of the rate constants and products for these reactions.

C. The Reaction of HNO_4 with OH

The reaction of OH with HNO_4 is of considerable potential importance in atmospheric chemistry. The atmospheric lifetimes of a number of HO_x and NO_x species could be influenced by this reaction. It provides an alternate mechanism for the OH and HO_2 by the following reactions.

\[
\begin{align*}
M + \text{HO}_2 + \text{NO}_2 & \rightarrow \text{HNO}_4 & (1) \\
\text{OH} + \text{HNO}_4 & \rightarrow \text{H}_2\text{O} + \text{NO}_2 + \text{O}_2 & (3) \\
\text{net: OH} + \text{HO}_2 & \rightarrow \text{H}_2\text{O} + \text{O}_2 & (13)
\end{align*}
\]

If reaction (3) is fast, it could significantly affect the lifetimes of OH, HO_2 and HNO_4 in the atmosphere.

No definite experimental values for this reaction have been published. In a review of atmospherically important reaction rate constants, Baulch et al. \cite{26} assume the reaction occurs by hydrogen atom abstraction. Considering the rate constant for OH + HNO_3, they suggest a value of \(1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ second}^{-1}\) for the reaction, with the uncertainty of at least an order of magnitude.

Graham et al. suggest an approximate upper limit of \(3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ second}^{-1}\) for the rate constant of OH + HNO_4. They arrived at this value from observing the concentrations of various species during
the unimolecular decomposition of HNO₄ in the presence of NO with and without added n-butane. The n-butane is an effective scavenger of OH by the reaction:

\[ n - C_4H_{10} + OH \rightarrow \text{products}, \quad k = 2.5 \times 10^{-12} \text{ cm}^3 \text{molec}^{-1} \text{sec}^{-1}. \]  \hspace{1cm} (14)

The OH is produced by the reaction

\[ \text{NO} + \text{HO}_2 \rightarrow \text{HO} + \text{NO}_2. \]  \hspace{1cm} (15)

They observed no detectable change in the unimolecular decomposition rate of HNO₄ when n-butane was added. A significant reduction of HNO₃ formed by the reaction

\[ \text{OH} + \text{NO}_2 \rightarrow \text{HNO}_3 \]  \hspace{1cm} (16)

was observed.

Barker et al.²³ investigated the reaction of OH with HNO₄ using a flow tube-mass spectrometer system. OH radicals were produced by the reaction

\[ \text{H} + \text{NO}_2 \rightarrow \text{OH} + \text{NO}. \]  \hspace{1cm} (17)

HNO₄ was produced by reacting NO₂BF₄ with H₂O₂ and the evolved vapor was flowed into the flow tube. HNO₄ was monitored using the m/e = 46 peak in
the mass spectrometer and OH was monitored by resonance fluorescence. Their experiments were done with HNO₄ concentration in excess of the OH concentration, so that pseudo-first order kinetics occurred. The experimental condition that was varied was either the time the reactants were allowed to mix before sampling or the concentration of one of the reactants. Varying the mixing time gave a value of $3.7 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ second$^{-1}$ for the rate constant of reaction (3). Varying the concentration of HNO₄ with a flow tube temperature of 298K gave a value of $3.3 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ second$^{-1}$ for (3). Similar experiments at 275K gave values of either $3.4 \times 10^{-12}$ or $5.4 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ second$^{-1}$ for (3). The apparent rate constant would alternate between the two values at 275K. Their attempts to eliminate the variation in the rate constant at 275K were unsuccessful. They speculate that the observed rate is the sum of homogeneous and heterogeneous rates and that the slower value of the rate constant observed is likely to be near to the value of the homogeneous component. They conclude, however, that their experimental results indicate an upper limit for the rate constant of reaction (3) of $k_3 \leq 3.5 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ second$^{-1}$.

The values for the bimolecular rate constants for hydrogen abstraction vary widely, ranging from less than $10^{-14}$ cm$^3$ molecule$^{-1}$ second$^{-1}$ to greater than $10^{-11}$ cm$^3$ molecule$^{-1}$ second$^{-1}$. The best reaction models for reaction (3) would be reactions of OH with peroxy compounds. The reactions of OH with H₂O₂ has a rate constant$^{27}$ of $1.6 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ second$^{-1}$ and the reaction of OH with HO₂ has a rate
constant of about $3.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ second}^{-1}$. The reactions of OH with other oxyacids of nitrogen are

\begin{align*}
\text{OH} + \text{HONO} &\rightarrow \text{H}_2\text{O} + \text{NO}_2 \quad k = 6.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ second}^{-1} \quad (18) \\
\text{OH} + \text{HN0}_3 &\rightarrow \text{H}_2\text{O} + \text{NO}_3 \quad k = 8.5 \times 10^{-14} \\ \\
\end{align*}

Since HNO\textsubscript{4} is less stable than HNO\textsubscript{3} and the H atom to be abstracted is part of a peroxy group, it would be expected that the rate constant for OH + HNO\textsubscript{4} to be somewhat faster than the reaction rate constant for OH + HNO\textsubscript{3}. It would be expected to be considerably slower than the reaction of OH + HO\textsubscript{2}. Thus, the expected range for the rate constant $10^{-11}$ to $10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ second}^{-1}$ is fairly wide. Since rate constants at the extremes of this range will have greatly differing effects on atmospheric chemistry, the experimental determination of the value for this reaction is needed to generate better models of the chemistry of the atmosphere.

D. Ozone in the Troposphere

The concentration of ozone in the troposphere is of interest for a variety of reasons. Reactions of ozone with a number of trace species in the troposphere are important in determining their lifetimes, as well as that of ozone. Its concentration is important in modeling the chemistry of the troposphere.
Knowledge of background levels of ozone in "clean air" is needed as a reference for studying the effect of anthropogenic pollutants in the atmosphere. In addition, it is important in understanding the transport mechanisms in the troposphere and the processes that exchange air between the stratosphere and the troposphere.

For over a decade, there has been considerable controversy over the role of ozone in tropospheric chemistry and photochemistry, as well as the relative importance of ozone sources and sinks. Much of the controversy was centered on whether ozone was an inert species in the troposphere that originated in the stratosphere, or if it was photochemically active in the troposphere. Many of the early studies were hampered by uncertainty in potentially important rate constants and uncertainty and variability of atmospheric measurements of important trace species. Local variations in trace species' concentrations made it difficult to determine mean values of the concentrations.

The traditional view was that ozone diffused down from the stratosphere into the troposphere. Ozone is produced in the stratosphere by photolysis of molecular oxygen, generating oxygen atoms which eventually react with other oxygen molecules to generate ozone.

\[
\begin{align*}
0_2 + h\nu &\rightarrow O(^3P) + O(^3P) \quad 175 \text{ nm} < \lambda < 242 \text{ nm} \\
0_2 + h\nu &\rightarrow O(^3P) + O(^1D) \quad 133 \text{ nm} < \lambda < 175 \text{ nm} \\
M \quad O(^1D) &\rightarrow O(^3P) \\
M \quad O(^3P) + O_2 &\rightarrow O_3
\end{align*}
\]
Because of the large column of $O_2$ above it, essentially no ultraviolet sunlight with wavelengths shorter than 200 nm is transmitted to the troposphere. Hence, there is no ozone production in the troposphere by the mechanism that operates in the stratosphere. The concentration of ozone reaches a maximum at 18 to 25 km. This appears to support the concept that the source for tropospheric ozone is the stratosphere and the major sink is destruction at the earth's surface.

A photochemical alternative to this was proposed whereby ozone was generated by cycles such as

$$2NO + O_2 \rightarrow 2NO_2$$
$$2(NO_2 + hv \rightarrow NO + O)$$
$$2(O + O_2 + M \rightarrow O_3 + M)$$

net: $3O_2 + 2hv \rightarrow 2O_3$.

Destruction of ozone could occur by cycles such as

$$NO + O_3 \rightarrow NO_2 + O_2$$
$$O_3 + hv \rightarrow O_2 + O$$
$$NO_2 + O \rightarrow NO + 3O_2$$

net: $2O_3 + hv + 3O_2$.

This is discussed in more detail by Johnston and Podolske\textsuperscript{12}.

This alternative suggested that transport from the stratosphere and destruction at the earth's surface were not the major source and sink for tropospheric ozone.
Hemispheric asymmetries in experimental measurements of ozone, CO and CH₄ have been noted. It is difficult to explain the ozone asymmetry by purely meteorological effects, suggesting photochemistry may influence ozone concentrations.

It now appears that stratosphere-troposphere air exchange, transport, and photochemistry are all important in determining ozone concentration in the troposphere. Any model that attempts to duplicate the behavior of ozone should include both photochemistry and transport mechanisms. Considerable uncertainty still exists in both these areas, however.

The most recent models of the tropospheric behavior of ozone indicate a significant fraction of the tropospheric ozone originating from the stratosphere is photochemically destroyed by

\[
O_3 + h\nu \rightarrow O_2 + O(^{1}D) \quad \lambda < 320 \text{ nm}
\]

\[
O(^{1}D) + H_2O \rightarrow OH + OH
\]

net: \[
O_3 + H_2O \rightarrow O_2 + OH + OH
\]  

Other chemical sinks exist, such as

\[
NO_2 + O_3 \rightarrow NO_3 + O_2
\]

\[
NO_2 + NO_3 \rightarrow NO + NO_2 + O_2
\]

\[
NO + O_3 \rightarrow NO_2 + O_2
\]

net: \[
O_3 + O_3 \rightarrow O_2 + O_2 + O_2
\]
and

\[
\begin{align*}
\HO_2 + O_3 & \rightarrow \text{OH} + O_2 + O_2 \\
\text{OH} + O_3 & \rightarrow \HO_2 + O_2 \\
\text{net: } O_3 + O_3 & \rightarrow O_2 + O_2 + O_2
\end{align*}
\]

(25)

but these are considered less important than the photochemical sink of reaction set (23).

Two series of reactions involving the oxidation of CO and CH\textsubscript{4} have been proposed as mechanisms for the production of ozone.\textsuperscript{51} These reaction schemes are catalytic in the sense that they regenerate intermediates consumed in the reactions. The CO oxidation system is

\[
\begin{align*}
\text{CO} + \text{OH} & \rightarrow \text{CO}_2 + H \\
\text{H} + O_2 & \rightarrow \text{HO}_2 \\
\text{HO}_2 + \text{NO} & \rightarrow \text{NO}_2 + \text{OH} \\
\text{NO}_2 + \text{hv} & \rightarrow \text{NO} + \text{O} \\
\text{O} + O_2 & \rightarrow O_3 \\
\text{net: } \text{CO} + 2O_2 & \rightarrow \text{CO}_2 + O_3
\end{align*}
\]

(26)

The CH\textsubscript{4} oxidation scheme is similar but somewhat more complicated.
\[
\begin{align*}
\text{CH}_4 + \text{OH} & \rightarrow \text{H}_2\text{O} + \text{CH}_3 \\
\text{CH}_3 + \text{O}_2 & \rightarrow \text{CH}_3\text{O}_2 \\
\text{CH}_3\text{O}_2 + \text{NO} & \rightarrow \text{CH}_3\text{O} + \text{NO}_2 \\
\text{NO}_2 + \text{hv} & \rightarrow \text{NO} + \text{O} \\
\text{M} + \text{O} + \text{O}_2 & \rightarrow \text{O}_3 \\
\text{CH}_3\text{O} + \text{O}_2 & \rightarrow \text{H}_2\text{CO} + \text{HO}_2 \\
\text{HO}_2 + \text{NO} & \rightarrow \text{NO}_2 + \text{OH} \\
\text{NO}_2 + \text{hv} & \rightarrow \text{NO} + \text{O} \\
\text{M} + \text{O} + \text{O}_2 & \rightarrow \text{O}_3 \\
\text{H}_2\text{CO} + \text{hv} & \rightarrow \text{CO} + \text{H}_2
\end{align*}
\]

net: \( \text{CH}_4 + 4\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{CO} + \text{H}_2 + 2\text{O}_3 \)

Similar systems can be devised for higher hydrocarbons, although the number of reactions increases considerably. For these systems to be of importance in the troposphere, each of the reactions involving an intermediate must be the dominant mechanism for consumption of that intermediate. If it is only a minor process, then the chain will terminate and it will not be important in ozone generation. In the case of the simpler CO oxidation system, Fishman et al.\textsuperscript{56} and Johnston and Podolske\textsuperscript{112} point out that if reaction (4) is slow, a reaction system to destroy ozone can occur.
OH + OH → H + CO₂
H + O₂ → HO₂ + M
HO₂ + O₃ → O₂ + O₂ + OH
net: CO + O₃ → CO₂ + O₂

For this system, the reactions in (26) are generally regarded as the major pathways for the intermediates involved. The critical reaction in this system is reaction (4). It competes with

HO₂ + O₃ → O₂ + O₂ + OH  (29)

and

HO₂ + HO₂ → H₂O₂ + O₂  (30)

for the HO₂ radical. A recent measurement of the rate constant for reaction (4) by Howard and Evenson⁵⁷ indicates it is fast compared to (29) and (30). The other factor in the competition between reactions is the atmospheric concentrations of NO, O₃ and HO₂. There is still considerable uncertainty in the NO and HO₂ profiles in the atmosphere.⁵⁸ It does appear that there is sufficient NO present to make reaction (4) the dominant pathway for HO₂ in some regions of the troposphere, and consequently the CO oxidation cycle is important as a source of tropospheric O₃.
The oxidation cycles for methane and higher hydrocarbons are more complicated and many of the reactions have not been thoroughly investigated. The validity of the concept that this system can generate ozone in the troposphere cannot be confirmed without more laboratory investigations of the kinetics and more atmospheric measurements.

With the low atmospheric concentrations of the species involved in these cycles, observation of ozone generation in the atmosphere is extremely difficult. It is a large-scale, low-level effect. Long term, simultaneous observations of CO, NO, NO₂ and O₃ are needed. Careful laboratory investigations of the photochemistry and kinetics in systems where ozone generating cycles may occur are needed. It is to this end that part of the present research is directed.
A. Methods

Different techniques were utilized for each of the experimental studies that were done in this research. However, all techniques are based on determining concentrations of various species by conventional infrared absorption spectroscopy. A following section will discuss the methods involved in determining infrared cross-sections.

1. Expansions

To investigate the kinetics and reaction products of the following reactions

\[ \text{N}_2\text{O}_5 + \text{H}_2\text{O}_2 \rightarrow \text{products} \]
\[ \text{HNO}_3 + \text{H}_2\text{O}_2 \rightarrow \text{products} \]
\[ \text{NO}_2 + \text{H}_2\text{O}_2 \rightarrow \text{products} \]
\[ \text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{products} \]
\[ \text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow \text{products}, \]

a technique is needed in which one can quantitatively observe the conversion of reactants into products. For this research, this was satisfied by expanding the reactants into the cell from two bulbs, each containing one reactant. Following expansion into the cell, the decay of reactants and the buildup of intermediates and products can be observed.
The possible products of these reactions were outlined in the previous section. In the case of the reaction of \( \text{N}_2\text{O}_5 \) with \( \text{H}_2\text{O}_2 \), two of the product sets, those of \( \text{HNO}_4 + \text{HNO}_3 \) and \( \text{HO}_2 + \text{NO}_2 + \text{HNO}_3 \), can give similar results because of the equilibrium between \( \text{HNO}_4 \) and \( \text{HO}_2 + \text{NO}_2 \). The actual products can be determined in this situation by the addition of nitric oxide to the reactants and carrier gas. At low temperatures, the equilibrium between \( \text{HNO}_4 \) and \( \text{HO}_2 + \text{NO}_2 \) is slow. Consequently, if the products are \( \text{HO}_2 + \text{NO}_2 + \text{HNO}_3 \), the added NO can scavenge most of the \( \text{HO}_2 \) by reaction (4) before it reacts with \( \text{NO}_2 \) to produce \( \text{HNO}_4 \). If the products are \( \text{HNO}_4 + \text{HNO}_3 \), the \( \text{HNO}_4 \) will decompose slowly, so that it will exist in significant amounts during the observation period. In all other cases, the reaction products can be determined by their characteristic infrared absorptions.

Kinetic information can be derived from the rate of decay of reactants or rate of buildup of products. In most cases, the rate of flow-in of the reactants will have to be taken into consideration. The flow-in of an inert specie will follow the behavior

\[
\frac{[x]_t}{[x]} = (1 - e^{-t/t_0})
\]  

(32)

where \( t_0 \) is a time constant characteristic of the flow system used, and \([x]\) is the ultimate concentration of \( x \).

Several heterogeneous reactions must be taken into consideration when \( \text{H}_2\text{O}_2 \), \( \text{N}_2\text{O}_5 \) and \( \text{HNO}_4 \) are present.\textsuperscript{59-62} These include
In certain situations, these reactions can be dominant loss processes for the species involved.

2. Static Cell Photolysis

The study of the CO oxidation cycle listed in equation (26) was conducted by flowing the reactants $\text{H}_2\text{O}_2$, $\text{NO}_2$ and CO in $\text{O}_2$ carrier gas into the cell. After concentrations of these compounds reached steady-state, the flow was stopped. To initiate the cycle, the photolytic lamps, with output in the near ultraviolet region of the spectrum, were activated and maintained at a constant illumination level. The ultraviolet light photolyzed $\text{NO}_2$ and $\text{H}_2\text{O}_2$ to generate the absent intermediates in the CO oxidation cycle.

$$\text{NO}_2 + \text{hv} \rightarrow \text{NO} + \text{O}^3\text{P}$$

$$\text{H}_2\text{O}_2 + \text{hv} \rightarrow \text{OH} + \text{OH}$$

In order to adequately characterize the kinetics of the reaction system, the behavior of a number of species had to be observed. Since the apparatus was a conventional infrared spectrometer system, each species had to be observed separately. One set of operating conditions was maintained until all species of interest had been observed.
For the low pressure investigations, a similar procedure was used. Once steady state flow conditions were achieved, the cell was rapidly pumped down to the desired pressure. The photolytic lamps were turned on and data were collected on the species under observation. As before, the procedure was repeated until all species had been observed.

In this system, the possible occurrence of several heterogeneous reactions should be noted. Three that have been mentioned previously are

\[
\begin{align*}
H_2O_2 &\rightarrow H_2O + \frac{1}{2}O_2 \\
N_2O_5 + H_2O &\rightarrow HNO_3 + HNO_3 \\
H_2O_2 + 2NO_2 &\rightarrow HNO_3 + HNO_3.
\end{align*}
\]

The first and last reactions represent a significant loss mechanism for \( H_2O_2 \). The last reaction may be responsible for the presence of \( HNO_3 \) in the absence of photolytic light.

Because of the complexity of this system, meaningful analytic rate expressions are difficult or impossible to generate. There are over 15 species of significance present during photolysis. To adequately describe the photochemistry and kinetics of the system, a set of over 60 reactions is needed. To accurately analyze a reaction set this size, numerical techniques are needed. Solutions for the chemical behavior of all species of interest can be generated in this manner.

3. Flowing Photolysis

An investigation of the reaction of OH with \( HNO_4 \) was performed by flowing \( N_2O_5 \) and \( H_2O_2 \) in \( N_2 \) carrier gas into the cell to generate \( HNO_4 \).
Black lamps were used as the photolytic light source. The lamps were turned on and off periodically at a very low frequency. This induced a concentration fluctuation in species affected by photolysis or by the photolytic products. NO$_2$ is present as the decomposition product of N$_2$O$_5$ and HNO$_4$. With black lamps as the photolytic light source, NO$_2$ is the only species that has a significant photolysis rate in the system,

$$\text{NO}_2 + h\nu \rightarrow \text{NO} + O(3P)$$  \hspace{1cm} (36)

The O atoms are likely to react with NO$_2$ to produce more NO,

$$\text{NO}_2 + O \rightarrow \text{NO} + O_2$$  \hspace{1cm} (37)

The NO can then react with HO$_2$ generated by HNO$_4$ decomposition to produce OH,

$$\text{HNO}_4 \rightarrow \text{HO}_2 + \text{NO}_2$$  \hspace{1cm} (-1)

$$\text{NO} + \text{HO}_2 \rightarrow \text{OH} + \text{NO}_2$$  \hspace{1cm} (4)

Thus, the OH concentration variation will be closely coupled to the lamp flashing rate. There will be competition among the following reactions for the consumption of OH.
The relative rates of these reactions can be determined by observing the behavior of various species associated with these reactions. Since the rate constant for reactions (16), (19) and (38) are known, the rate constant for reaction (3) can be obtained by comparing it to one of the known reactions.

As with the other systems studied in this investigation, the occurrence of heterogeneous reactions is a possibility that must be considered. However, most heterogeneous reactions should not be affected by the photolytic light. The occurrence of these reactions should have an insignificant effect on the concentration variations created by the photolytic light, and they should not have to be considered in the analysis.

The results obtained from the experiments can be analyzed by using them in an analytical expression that adequately describes the kinetics of the system. They can also be compared with computer simulations of the kinetics and photochemistry to determine how well the known reactions describe the chemical system.
4. **Numerical Simulation of Chemical Systems**

Since the chemical systems being investigated are complex in terms of both the number of reactions and the number of species, exact analytical expressions often cannot be developed. To be able to predict the behavior of a complex chemical system, numerical techniques must be utilized. The set of chemical reactions that are important in determining the behavior of the system can be written as a system of ordinary differential equations. Generally, the ordinary differential equations will have widely varying time constants, and consequently are known as "stiff" systems. Conventional numerical integration techniques have a tendency to exhibit instability and inaccuracy when used on stiff systems. Recently, several techniques for solving stiff systems have been developed. They are available as computer subroutines to provide a basis for a program to predict the time dependent behavior of a chemical system. One of the most powerful techniques devised to analyze stiff systems is that developed by C. W. Gear. A version that has been modified by Hindmarsh is the basis for the CHEMK chemical kinetics program used in this research.

To simulate the expansion experiments, the flow-in rates of the reactants, and the reactions and reaction rate constants considered to be of importance are used as inputs into the program. Estimated rate constants are used where rate constants have not been established for reactions. The first order or second order equivalent rate constants are used to simulate heterogeneous reactions where necessary.
The output from the program provides a time dependent profile of all of the species involved in the reactions, as well as periodic rate information. This can be compared with experimentally determined profiles to gain an understanding of the chemical behavior of the system.

Simulations of the static cell photolysis experiments were done by inputting the initial concentrations of the reactants, the set of reactions and rates needed to describe the system, and the light intensity. The photodecomposition rates of various species in the system were determined by either experimental observation of the decay of the isolated specie in the presence of the photolytic light, or by the calculation of the "j" value, which is the product of light intensity, cross section and quantum yield integrated over the wavelength region of interest.

Comparison of the experimental profiles with the numerical predictions can give insight into the chemistry of the system and assist in the selection of experimental conditions that will be the most informative.

B. Apparatus

1. Reaction Cell and Temperature Control

The reaction cell used in these investigations consists of a quartz cylinder 28.0 cm inside diameter (28.9 cm outside diameter) by 102.0 cm long, whose ends are enclosed in nickel-plated stainless steel end caps. The cell is sealed by double silicone o-rings at each end of the cylinder. The end caps are maintained at a fixed separation by four Kovar
beams. Three mirrors and mounted in the end caps in a White cell configuration with a base pathlength of 1 meter. The optical pathlength of the cell may be varied externally by a fine adjustment screw. Usable path lengths vary from 4 to 32 meters. The volume of the cell is 63.0 liters, as determined by expansions from bulbs with calibrated volumes. This provides a surface to volume ratio of 0.175 cm⁻¹, when the surface of the mirror mounts is included.

The entire apparatus and optical system is mounted on a Newport Research Corporation vibration damping table. The cell framework is isolated from the metal surface of the table by nylon pads and 5 cm thick high density closed cell neoprene foam. Thermal isolation from the laboratory environment is provided by 20 cm of rigid polyurethane foam backed by 5 cm of aluminum foil backed fiberglass on all sides and on top of the cell.

Cooling within the insulating box is provided by a finned radiator mounted above the cell framework. Coolant is circulated through the radiator continuously. For temperatures above 280 K, pressurized chilled water is used as a coolant. For lower temperatures, methanol chilled by a Neslab LT9 low temperature refrigerator is flowed through an elevated 22 liter accumulator and into the radiator above the cell. Methanol flow is maintained by a combination of siphoning action and gravity.

Temperature control is maintained by resistive heating wire wrapped around the radiator. The current through the wire is regulated by a proportional temperature controller utilizing a precision thermistor as a temperature sensing element. A 50 liter/second muffin fan actively
circulates the air around the cell for even temperature distribution. The temperature distribution inside the insulating box is monitored by a conventional alcohol thermometer as well as four iron-constantan thermo-couples. Three of these are distributed around the cell, while the fourth is placed in a sealed stainless steel tube which extends 30 cm into the cell. The maximum temperature differential indicated within the insulating box is 0.5 K.

A schematic diagram of the apparatus is indicated in Fig. 2. The reaction cell can be pumped out by a large capacity mechanical roughing pump for high pressures, or a liquid nitrogen trapped oil diffusion pump for low pressures. The cell can be evacuated to less than $10^{-3}$ torr.

2. Optical System

All optics external to the cell are enclosed within a plexiglass housing. The housing and the monochromator are purged with a steady flow of dry nitrogen to minimize absorption of infrared light by water vapor and carbon dioxide. The light sources used are an Infrared Industries regulated 2 mm by 12 mm cylindrical Nernst glower for work in the infrared domain and a General Electric No. 1142 tungsten bulb with a current regulated power supply for work in the visible domain. Selection of the light source is done by a mirror. The Nernst glower is operated at 1700K, as measured by an optical pyrometer. The tungsten bulb was operated at 12.6 V and 1.44 A. Light from either source is chopped at 400 Hz by American Time Products tuning fork choppers driven by regulated power supplies. The light is then directed on a collection mirror which
Fig. 2. Schematic diagram of apparatus used in experiments.
focuses the light through the entrance windows and into the cell. There are two windows for both the entrance and exit light paths. The outer window is KBr and is sealed to one end of a Pyrex tube. The inner window and the other end of the tube are mounted in one of the cell end caps with silicone o-rings. The Pyrex tube contains a packet of desiccant and is evacuated to prevent damage to the windows by water vapor and to reduce thermal conduction from the cooled end cap during low temperature experiments. The inner windows were CaF$_2$ for early experiments and BaF$_2$ for more recent experiments. The light exiting the cell is focused by another collection mirror onto the entrance slit of the monochromator.

The internal mirrors are coated with gold over a chromium undercoat. This was followed by a 2000 Å MgF$_2$ overcoat to prevent coating degradation by chemical attack, particularly from H$_2$O$_2$. Thinner overcoats on gold or aluminum were found to be susceptible to chemical attack. The optical system is designed to underfill the internal mirrors and the second collection mirror and overfill the monochromator entrance slit to minimize vibration induced light fluctuations. The McPherson one meter monochromator can be used with 75 line/mm, 150 line/mm, 300 line/mm and 600 line/mm gratings with 12 μm, 6 μm, 3.5 μm and 1.6 μm blaze wavelengths, respectively.

3. **Detectors**

A variety of detectors were available for use in this work. They are listed in Table 2 with typical bias voltages used and their useful
Table 2

Detectors

<table>
<thead>
<tr>
<th>Detector</th>
<th>Bias</th>
<th>Wavelength Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>RCA 1P28B S-5 photomultiplier tube</td>
<td>-700 to -1250v</td>
<td>200 to 700 nm</td>
</tr>
<tr>
<td>RCA 4832 GaAs photomultiplier tube</td>
<td>-500 to -1200v</td>
<td>200 to 900 nm</td>
</tr>
<tr>
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<td>400 to 1200 nm</td>
</tr>
<tr>
<td>Rofin 7460 Ge photodiode</td>
<td>0 to -15v</td>
<td>600 to 1900 nm</td>
</tr>
<tr>
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<td>+300 to +400v</td>
<td>1 to 3.5 μm</td>
</tr>
<tr>
<td>SBRC ITO PbS detector¹</td>
<td>+300 to +400v</td>
<td>1 to 4.0 μm</td>
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<tr>
<td>SBRC InSb photovoltaic detector²</td>
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<td>2 to 5.5 μm</td>
</tr>
<tr>
<td>SBRC HgCdTe photoconductive detector²</td>
<td>+1v</td>
<td>4 to 15 μm</td>
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<tr>
<td>SBRC Ge:Cu photoconductive detector³</td>
<td>+135v</td>
<td>4 to 30 μm</td>
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</tbody>
</table>

Notes
1. Operated at dry ice temperature.
2. Operated at liquid nitrogen temperature.
3. Operated at liquid helium temperature.
wavelength ranges. Much of the work was done using the HgCdTe detector. The housing of this detector allows it to be used with either the McPherson monochromator, or a circular variable filter (CVF), which acts as a low resolution monochromator. The housing is illustrated in Fig. 3. The CVF consists of two germanium half discs which support a thin dielectric film whose thickness increases radially around the disc. The wavelength transmitted by the CVF varies linearly with angle around it. One half disc covers the wavelength range of 3.1 to 6.2 μm and has a peak transmission of 25 to 45 percent. The other half disc covers the wavelength range of 6.0 to 12.1 μm and has a peak transmittance of greater than 40 percent. The CVF is positioned by a 200 step/revolution stepping motor driven by a controller that determines the direction of rotation and the stepping rate. The transmission curve of the CVF at one position and at positions two steps adjacent to it are shown in Fig. 4. The CVF has a resolution of about 1 percent. Because of the spectral overlap problems that existed in the experiments that were done, the CVF was unsuitable for use as a monochromator and was not used.

4. Electronics

A variety of preamplifiers were used in these experiments. The Ge:Cu infrared detector signal was amplified by an op amp preamplifier which has been discussed elsewhere. 67 A Princeton Applied Research Corporation CR-4A low noise amplifier with selectable gain and bandwidth was used in conjunction with the HgCdTe infrared detector. The power
Fig. 3. Infrared detector and CVF housing
Fig. 4. CVF transmission of three positions separated by two steps
supply of the amplifier was modified to improve stability and reduce the 60 Hz ripple. The InSb detector was used with an A210 matched preampifier from Santa Barbara Research Corporation. The photomultiplier tubes were used with a FET input op amp shown in Fig. 5.

Signals from the preamplifiers mentioned above and signals from the PbS (both ATO and ITO), Si and Ge detector were fed into a Princeton Applied Research Corporation Model 124 lock-in amplifier with a Model 116 low noise, high impedance differential reamplifier. The lock-in amplifier amplifies and rectifies the 400 Hz signal and provides a dc voltage output whose level is proportional to the light intensity incident on the detector.

The dc signal from the lock-in amplifier is monitored with a digital voltmeter and recorded with a Fabritek 1074 hardwired signal averager. The analog signal is fed through a RC filter and is digitized by a 12 bit ADC. The digitized signal is stored at selectable intervals as 18 bit words in quadrants of the 4k of memory available. The data can be manipulated using a PDP 8/2 computer which is interfaced to the Fabritek. The data can be stored on paper tape or be transferred to a PDP 8/e computer via an interprocesser buffer for storage on magnetic tape. Signals can be displayed on an oscilloscope or be plotted on a X-Y recorder.

5. Photolytic Light Sources

Two types of photolysis lamps were utilized in these investigations. 30 watt General Electric G30T8 low pressure mercury germicidal
Fig. 5. Schematic diagram of PMT preamplifier circuit
lamps were used to provide photolytic light consisting of ultraviolet mercury emission lines. 30 watt General Electric G30T8-BL black lamps provided broadband ultraviolet light in the near ultraviolet region. Four lamps are located symmetrically around the axis of the cell at a distance of 8 cm from the exterior cell surface. Sheets of Alzak high reflectivity aluminum surround the cell on three sides to increase uniformity of the light distribution. Six volt transformers are used to heat the lamp electrodes to a red glow to assist in turning the lamps on. Further assistance is provided by a Tesla coil discharge applied to wires connected to the center of the lamps.

The lamps can be powered by either of two lamp driver systems. One is a 700 volt regulated power supply utilizing "brute force" techniques to regulate the lamp current with large ballast resistors. The power supply can switch the lamps on and off electronically in response to a low frequency reference square wave.

The other lamp driver uses more sophisticated methods to control the current to the lamps. The power dissipated by the lamps is easily controllable and the lamp's output can be modulated in a variety of waveforms about a dc level. The schematic diagram of this lamp driver is illustrated in Fig. 6. The lamps can be driven at current levels from 0.04 to 0.7A per lamp and the lamp current can be modulated up to 90 percent.

Lamp output is monitored with an EG and G UV100B ultraviolet enhanced silicon photodiode. Since a silicon photodiode is most sensitive to visible and near infrared radiation, the radiation it receives must be
filtered. A 254 nm interference filter with 12 percent peak transmittance and 15 nm FWHM bandwidth is used in conjunction with the germicidal lamps. A Schott UG-5 glass filter, which has broadband transmission between 300 and 400 nm, is used with the black lamps. The current from the photodiode is fed into a LH0042 op amp acting as a photodiode follower with feedback resistance switchable between 100 kΩ and 1MΩ. The knee frequency of the amplifier response is well above that of the lamp modulation system. The maximum photodiode current generated with this system is within its linear response region. The output voltage is monitored on a digital voltmeter and recorded on a X-Y recorder. The photodiode is located inside the temperature-controlled box and its output increases approximately 7 percent from 300 to 250K.

Spectral distribution of the emission from the photolytic lamps was determined by directing the light from the lamps through an American Time Products 400 Hz tuning fork chopper into a McPherson Model 218 0.3 meter monochromator with a RCA 1P28B photomultiplier tube. The amplified 400 Hz signal from the PMT was rectified by the PAR Model 124 lock-in amplifier and recorded in the Fabritek. The emission in the 290 to 460 nm region of the black lamps is shown in Fig. 7. The spectrum has been approximately corrected for variation of PMT response and variation of grating efficiency with wavelength. The mercury emission lines superimposed on the broadband emission of the phosphor can be seen in the figure. The 577 - 579 nm lines and the 546 nm line are present, but are not shown in the spectrum. Their intensity is comparable to that of the 436 nm line.
The G30T8 germicidal lamps were fitted with cylindrical gaseous chlorine filters. These consist of a sealed double-wall concentric quartz jacket filled with an atmosphere of chlorine. The lamps were inserted inside the filters. The chlorine ultraviolet absorption spectrum is such that it selectively absorbs light in the 300 to 400 nm region. This allows near ultraviolet mercury lines to be attenuated with relatively little effect on the 254 nm line, and the longer wavelength mercury lines are only weakly apparent. The spectral distribution is in good agreement with that given by the manufacturer.

C. Gases and Flow System

The carrier gases used in these studies were supplied by the Lawrence Berkeley Laboratory. High dry grade nitrogen was flowed through a Matheson moisture and particulate filter and through a column containing P₂O₅ before use. High dry grade oxygen was passed through a column containing copper turnings at 700K and a column of 5 percent palladium on an alumina substrate at 600K to convert hydrocarbon impurities to CO₂ and H₂O. The flow as then passed through ascarite and P₂O₅ columns to remove the CO₂ and H₂O, respectively. The oxygen is then flowed through a silica gel packed U-tube maintained at 196K with a dry ice-isopropanol bath for further drying. The gas supplier gives the following specifications for maximum impurity concentrations:
Carbon monoxide from Matheson Company of 99.9 percent purity was passed through a silica gel trap maintained at 142K with a liquid nitrogen n-pentane slush bath for purification. An impurity, apparently a metal carbonyl, stained the silica gel a light brown color after extended use.

Carbon dioxide of 99.9 percent purity from Pacific Oxygen Company was checked for impurities using infrared spectroscopy. None were found in concentrations that would significantly affect results. The gas was used only for making cross section determinations of CO₂.

Distilled water of 99.9 percent purity was degassed and vacuum distilled, discarding the initial and final fractions. It was then used without further purification. Hydrogen peroxide of 98 percent purity was obtained from the Becco Chemical Division of FMC Corporation and used without further purification. The major impurity was H₂O₂.

Nitric oxide of 99.0 percent purity from the Matheson Company was passed through a silica gel trap maintained at 196K by a dry ice-isopropanol slush bath. The major impurity was NO₂, which was trapped as N₂O₃. It was then used without further purification.
Nitrogen dioxide of 99.5 percent purity from the Matheson Company was collected at 196K and purified by vacuum distillation and stored under an atmosphere of oxygen to oxidize any remaining NO to NO₂. The oxygen was then pumped off and two further vacuum transfers were done. The remaining white solid was stored at 196K.

Preparation of dinitrogen pentoxide was performed by the technique of Schott and Davidson. Oxygen coming from the purification line was divided into two flows. One flow was directed into an Ozone Research and Equipment Company ozonator, which generated a flow of approximately 5 percent ozone in oxygen. The other stream passed through a regulating needle valve and flowmeter and was bubbled through a bulb with liquid NO₂ and N₂O₄ which was maintained at 274K. The two flows were recombined, where NO₂ and O₃ react to form N₂O₅. The heat of reaction heats the tubing just beyond the mixing region to about 305K. The flow carrying NO₂ is regulated so there is an excess of ozone in the mixing region, indicated by the oxidation of natural rubber. The flow passes through a previously evacuated Pyrex saturator. The saturator is cooled to 196K in a dry ice-isopropanol slush bath after the mix has flowed through it for about 15 minutes. This is to allow HNO₃ formed by the contact of N₂O₅ with the interior walls of the saturator to be transported out of the vessel.

N₂O₅ is collected until all the NO₂ in the bubbler has been consumed. Residual O₂ and O₃ are then pumped off the needle-shaped white crystals in the saturator. The N₂O₅ is then stored at 196K. Less than 1 percent NO₂ is present in the N₂O₅, as determined by
infrared absorption. HNO$_3$ is present at levels of about 10-15 percent. It is apparently formed by a heterogeneous reaction of N$_2$O$_5$ with water on the interior surfaces of the gas handling system. The system was not designed to be bakeable; so, the total removal of water was not possible.

The gas handling manifold was constructed of Pyrex. All stopcocks on the system were Kontes high vacuum stopcocks with teflon bores and Viton o-rings, which were greased with small amounts of Apiezon Type N grease. Gas lines to the manifold were connected with stainless steel Ultra-Torr fittings or stainless steel Swagelock fittings with teflon ferrules. A liquid nitrogen trapped glass oil diffusion pump was used to evacuate the system.

Hastings thermocouple vacuum gauges were used to monitor the pressure on the low side of the diffusion pumps. For measuring pressures in the 0-100 torr range, a MKS Instruments Baratron Model 220-246-100 capacitance manometer was used. For higher pressure measurements, a Texas Instruments Model 145 quartz Bourdon precision pressure gauge and a MKS Instruments Baratron Model 310 BHS-100 capacitance manometer were used. Comparison of pressure readings on the three instruments showed excellent agreement.

The flow rates of gases used during the flow experiments were monitored with either Fisher and Porter Corporation or Manostat Company flowmeters. The flowmeters were calibrated by timing the period needed for a gas flow through a flowmeter to fill a calibrated volume.
In some flow experiments, gases are flowed into the cell through two Pyrex disperser tubes. Each tube has fine holes on alternate sides at 2.5 cm intervals along its length. The diameter of the holes is such that the pressure drop across the holes is large compared to the pressure drop along the tube. These tubes create turbulent mixing within the cell and provide an even distribution of gases. The gases are exhausted through a port in one end of the cell.

Other flow experiments were done by mixing the gases prior to entry into the cell and flowing them in through one disperser tube. The gases were exhausted through the other disperser tube.

In the flow experiments involving NO₂, H₂O₂ and CO, the carrier gas was split into two flows. One flow passed through a regulating needle valve and a flowmeter and then was bubbled through liquid NO₂ and N₂O₄ before going into the cell. Another flow of carrier gas was passed through a regulating valve and a flowmeter before going through a temperature regulated saturator containing H₂O₂. A flow of CO passed through a regulating needle valve and a flowmeter and was mixed with the other flows. When a more dilute mixture of reactants was desired, a third flow of pure carrier gas was added and monitored with a flowmeter. The pressure drop across the cell and the flow system was dependent on flow rate. It was generally less than five torr at one atmosphere total pressure.

In the flowing photolysis experiments, the flow of nitrogen carrier gas was split into three streams. All three flows passed through regulating valves and flowmeters. Two of the flows passed through tempera-
ture controlled saturators containing either H\textsubscript{2}O\textsubscript{2} or N\textsubscript{2}O\textsubscript{5}. These flows were mixed with the third flow and directed into the cell through one of the disperser tubes. At the flow rates used in these experiments, the pressure drop was about 7 torr across the flow system and the cell.

In the expansion experiments, the reactants were jetted into the evacuated cell from pressurized bulbs. Each bulb was connected to one of the disperser tubes, preventing mixing of the reactants outside of the cell. Each bulb was filled with the desired pressure of the reactant and then filled with carrier gas. The total pressure in the bulbs was controlled so that the pressure-volume products of the two bulbs were equal. The stopcocks sealing the bulbs from the cell were opened simultaneously, so that both reactants would enter the cell at the same time.

The flow behavior of the gases can be described by

\[
\text{fraction of gas in cell at time } t = (1 - \exp(-t/t_0)) \quad (39)
\]

where \( t_0 \) is a time constant characteristic of a particular expansion system. The time constant for the system used in these experiments was about 4.3 seconds.
III. ABSORPTION CROSS SECTIONS

A. Infrared Cross Sections

The experimental apparatus described previously was employed as a single beam spectrometer to determine absorption cross sections. The regulated Nernst glower proved to be a very stable source of infrared radiation. Very little change was observed in its output over the course of several hours, and any change was generally fairly constant throughout the spectral region of interest.

Absorption cross sections were determined by recording $I_0(\lambda)$ and then recording $I(\lambda)$. The cross section, $\sigma$, was determined by calculating $\sigma$ as

$$\sigma(\lambda) = \frac{\ln(I_0(\lambda)/I(\lambda))}{n\ell}$$

(40)

where $n$ is the concentration in molecules/cm$^3$ and $\ell$ is the optical pathlength in cm. If necessary, baselines of the absorption spectra were adjusted linearly to zero in spectral regions where no absorption occurred.

All absorption cross sections determined in this study were measured with the 150 line/mm grating and with 2 mm entrance and exit slits on the monochromator. The resulting resolution was 0.013 $\mu$m in first order (4-12 $\mu$m) and 0.0065 $\mu$m in second order (2.4-4 $\mu$m). Spectra were obtained by scanning the monochromator at 0.16 $\mu$m/minute for all species except $\text{H}_2\text{O}_2$ and $\text{O}_3$, which were done at 0.40 $\mu$m/minute. The signals were
digitized and recorded at 0.4 second intervals and with a 0.4 second time constant. In all cases the spectral region scanned during one time constant was less than or equal to 0.1 times the resolution determined by the slits. The optical path length used in all measurements was 800 cm. The faster scan rates were used for H$_2$O$_2$ and O$_3$ because of their significant heterogeneous decay rates.

The wide range of conditions involved in these experiments necessitated the measurement of absorption cross sections as a function of total pressure, temperature, and concentration of the absorbing specie. Measurements were made at temperatures of 263K, 293K and 313K, and at pressure of 0.1 and 1 atmosphere. Many species displayed a marked absorption dependence on all three variables, presumably due to broadening of rotational lines. This is addressed in more detail in Appendix B.

The Beers law formulation of

\[ \text{OD} = \sigma n \lambda \]  

(41)

where OD is the optical density and \( \sigma \) is the cross section at the wavelength of interest was modified to accommodate the species that exhibited a dependence on concentration. It was rewritten as

\[ n = \text{OD}^{\alpha} / \sigma \lambda \quad \text{or} \quad n = \text{OD}^{\alpha} 10^8 \]  

(42)
where $\alpha$ is the correction factor for non-Beers law behavior. In the measurements made in these studies, $\alpha$ ranged from 1 to more than 2.

This expression was further modified into

$$n = 10(\alpha \log(OD) + \beta)$$

where $\beta = -\log (\sigma \lambda)$, for computer analysis of decay curves. The $\alpha$ and $\beta$ coefficients for each species observed are tabulated in Table 3, for the three temperatures and two pressures used in these studies. The one exception to this formulation is the cross section for NO$_2$ at 6.258 $\mu$m. The cross sections determined by Connell were in good agreement with those determined in this investigation, and were used in the same formulation.

Another factor that had been taken into consideration was that of spectral overlap. In conditions where there are a number of species present, a number of absorption bands may overlap and cannot be used for concentration determinations without deconvolution. Fig. 8 schematically illustrates the absorption bands and their approximate strengths. This figure is not necessarily complete and the locations and strengths are only approximate. Overlap problems are particularly severe with the nitrogen oxides and oxyacids of nitrogen. Spectral regions to monitor concentrations of species were chosen where little or no overlap problems existed.

Cross sections for NO$_2$ at 3.428 $\mu$m were measured by expanding a measured pressure of purified NO$_2$ from a 1081 cm$^3$ bulb into the
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<th>T = 293K</th>
<th>T = 313K</th>
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<td>$\alpha$</td>
<td>$\beta$</td>
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<td>3.428</td>
<td>1.04±0.02</td>
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<td>3.428</td>
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Note 1: There was no change in cross section with pressure or concentration.

Note 2: The change in cross section with concentration was not fitted to the $\alpha$, $\beta$ format.
Fig. 8. Infrared absorptions of species involved in these studies.
evacuated cell, and then filling the cell to 0.1 or 1 atmosphere total pressure with nitrogen. Low pressures were measured with the MKS Baratron and higher pressures were measured with the TI Bourdon gauge. Corrections were made for the dimerization of NO₂ into N₂O₄, using the results of Verhoek and Daniels,⁷¹ when determining NO₂ concentrations in the bulb and in the cell. NO₂ illustrated a significant cross section dependence on concentration as well as pressure and temperature. The NO₂ absorption at 3.428 μm was free of interference from absorptions by other species. A representative absorption spectrum at 0.1 and 1 atmosphere total pressure is shown in Fig. 9, which was taken at 313K.

The NO₂ cross sections of 6.258 μm were obtained in a similar manner. Measurements were made at 1 atmosphere total pressure only. The wavelength at which NO₂ is monitored occurs at an absorption minimum between the P and R branches of a H₂O absorption. At one atmosphere, the absorption cross section of H₂O is less than 10⁻³ times that of the NO₂ cross section. In most cases, H₂O will have an insignificant effect on the optical density obtained at this wavelength. A typical absorption spectrum is shown in Fig. 10.

CO₂ cross section determinations were made at 4.238 μm at 263K and 293K, and at 4.239 μm at 313K. Mixtures of CO₂ and N₂ were prepared in a 1081 cm³ bulb in ratios of 1:50 to 1:100. Fractions of these mixtures were expanded into the evacuated cell, and nitrogen was added to the desired pressure. Because of the large cross section of CO₂, the double dilution method was used to obtain reasonable optical
Fig. 10. NO\textsubscript{2} absorption spectrum at 0.1 and 1.0 atmosphere pressure.
densities for the cross section determinations. Fig. 11 illustrates a typical absorption spectrum of CO$_2$ at 313K for 0.1 and 1 atmosphere total pressure.

Cross section for CO were measured at 4.609 $\mu$m at 263K, 4.610 $\mu$m at 292K, and 4.607 $\mu$m at 313K. The rotational lines in the absorption band were partially resolved and the monitoring wavelength was shifted to match the largest peak. Purified samples of CO were expanded into the evacuated cell. Expanded pressures were measured with the MKS Baratron gauge, and nitrogen was added to either 0.1 or 1 atmosphere total pressure. The CO absorption band at 313K is shown in Fig. 12 for 0.1 and 1 atmosphere.

NO cross sections were obtained at 5.242 $\mu$m for 263K and 313K and at 5.246 $\mu$m for 293K. The methods used in their determination were similar to those used to determine the CO cross sections. Care had to be taken to avoid the presence of O$_2$ which would oxidize the NO to NO$_2$ and give abnormally high apparent cross sections. The rotational lines of NO were partially resolved, as indicated in Fig. 13, which illustrates the absorption band at 0.1 and 1 atmosphere total pressure at a temperature of 313K. The irregularities of the long wavelength end of the spectrum are due to the roll-off of the detector spectral response.

The NO$_2$, CO$_2$, CO and NO cross section determinations were done largely with the InSb detector. All other cross section measurements were done at longer wavelengths. The HgCdTe detector was used for these measurements. H$_2$O has a broad infrared absorption that extends from below 5 $\mu$m to above 8 $\mu$m. The pattern of rotational lines is complex,
Fig. 11. CO$_2$ spectrum at 0.1 and 1.0 atmosphere pressure
Fig. 12. Absorption spectrum of CO at 0.1 and 1.0 atmosphere pressure
Fig. 13. Absorption spectrum of NO at 0.1 and 1.0 atmosphere pressure.
but the lines are widely spaced. The line at 6.634 μm was used for cross section determinations at all temperatures. It is one of the strongest lines in the spectrum at the resolution used for these measurements. It was necessary to make baseline correction at a considerably different wavelength from that used for the cross section determination because of the broad absorption. To do this a reference measurement was made and the monochromator was then rapidly slewed to the absorbing region, where standard measurements were done. For the measurements, purified H₂O in liquid form was evaporated directly into the evacuated cell to the desired pressure. At 263K, the H₂O pressure had to be maintained below two torr to prevent condensation within the cell. At higher temperatures, this was not a problem. The restriction of low H₂O pressures at 263K made accurate determination of the α and β factors difficult. A spectrum of H₂O in the region of measurement at 313K is shown in Fig. 14 at 0.1 and 1 atmosphere total pressure.

Because H₂O₂ and O₃ exhibit heterogeneous decomposition at the temperature range in which these experiments were done, the techniques previously used were not useful in determining their cross sections. Previous cross section measurements had been done by Giguere⁷² with H₂O₂ and by McCaa and Shaw⁷³ with O₃, but these were not applicable to these studies. It is difficult to make concentration determinations from pressure measurements because it is unknown what fraction of the pressure of the gas expanded into the cell is due to the decomposition products.
Since the ultraviolet cross sections of $\text{H}_2\text{O}_2^{21,74,75}$ and $\text{O}_3^{76,77}$ are well known, it was decided to utilize them in concentration determination for the infrared cross section measurements. The measurements were done using a flow system in which the compound to be measured and the carrier gas were flowed in the disperser tubes of the cell and out the exhaust port at the end of the cell. The flow out of the cell was directed through a 98 cm long, 2.5 cm diameter Pyrex tube with 2 mm thick CaF$_2$ windows. Light from a deuterium lamp was chopped at 400 Hz by a tuning fork chopper and then focused through the cell with an off-axis spherical mirror of 21 cm focal length. The light passing through the cell was directed into a McPherson 218 0.3 meter monochromator with a 2400 line/mm grating. The dispersed light was detected by a 1P28 photomultiplier tube operating at -800 volts. The output signal was amplified and fed into a lock-in amplifier constructed by the Chemistry Department electronics shop. The output from the lock-in amplifier was directed to a digital voltmeter and a recorder for monitoring. The system is shown in Fig. 15.

The flow into the monitoring cell can be quickly switched between the flow out of the cell and the flow of pure carrier gas. This allowed rapid sequential determination of I and $I_0$ to determine the concentration of the absorbing species. The regulated deuterium lamp exhibits good short term stability and some slow long term drift. $\text{H}_2\text{O}_2$ was monitored at 200 nm, near the short wavelength limit of the operating system. Nitrogen was used as a carrier gas since oxygen has a significant absorption at this wavelength. $\text{O}_3$ was monitored at 300 nm, which
Fig. 15 Ultraviolet monitor used for determining $\text{H}_2\text{O}_2$ and $\text{O}_3$ concentrations
allowed use of oxygen as a carrier gas. The large ozone absorption cross section at shorter wavelengths caused excessively high light absorption at the concentrations of interest.

This system provided real-time detection of \( \text{H}_2\text{O}_2 \) and \( \text{O}_3 \) and was simple to use. It is considered highly superior to titration techniques in this application.

To determine \( \text{H}_2\text{O}_2 \) infrared absorption cross sections, nitrogen carrier gas was flowed through a temperature-controlled saturator containing \( \text{H}_2\text{O}_2 \). The flow passed through the cell and through the UV monitor. Concentration determinations were made before and after each run. For low pressure measurements, a concentration measurement was made and the cell was quickly pumped down to the desired pressure and an infrared scan was done. The \( \text{H}_2\text{O}_2 \) decomposition was then monitored and used to correct the low pressure measurement. A spectrum of \( \text{H}_2\text{O}_2 \) at 313K and 1 atmosphere pressure is shown in Fig. 16. Two peaks due to \( \text{H}_2\text{O} \), a decomposition product, can be seen at the short wavelength end of the spectrum. Cross section measurements were made at the Q branch (at 7.896 \( \mu \text{m} \)) and on the P branch (at 8.040 and 8.264 \( \mu \text{m} \)) to minimize interference by \( \text{H}_2\text{O} \) lines. Accurate low pressure measurements were difficult to obtain because of the low vapor pressure of \( \text{H}_2\text{O}_2 \), particularly at low temperatures.

\( \text{O}_3 \) cross section measurements were performed by passing an ozone-oxygen flow from the ozonator into the cell and the UV monitor. Ozone concentration was controlled by regulating the power of the discharge in the ozonator. For lower levels of ozone than were obtainable directly
Fig. 16 $H_2O_2$ absorption spectrum at 1.0 atmosphere pressure
from the ozonator, the ozone-oxygen mixture was diluted with more oxygen. The concentration was determined before and after each infrared scan at 1 atmosphere. The technique used for low pressure H$_2$O$_2$ cross section measurements was also used for low pressure O$_3$ cross section measurements. It was found that the O$_3$ decomposition was slow enough that corrections were not needed. Early measurements were made with CaF$_2$ windows on the cell, which have an absorption cutoff near 10 μm. Hence, cross section determinations were made on the R branch. Fig. 17 illustrates the O$_3$ absorption band at 313K and 1 atmosphere total pressure.

The cross sections for N$_2$O$_5$ and HNO$_3$ have been previously determined by Connell, Graham, and Harker, using systems similar to the one used in these experiments. To confirm these measurements, the technique similar to that of Connell was used.

N$_2$O$_5$ was flowed into a 3.06 liter bulb and then purified oxygen carrier gas was added to the desired pressure. This mixture was expanded into the vacuated cell and the absorbing region was scanned. Cross sections obtained by Graham were used to determine the amount of HNO$_3$ present and the concentration of N$_2$O$_5$ was obtained. The N$_2$O$_5$ absorption cross sections are shown in Fig. 18 for 263K and 16 torr total pressure and are in good agreement with the previously determined values of Connell, Graham and Harker. The N$_2$O$_5$ cross section appears to be independent of pressure for < 10 torr to 1 atmosphere total pressure and independent of concentration from < 1 x 10$^{14}$ molecules/cm$^3$ to > 2 x 10$^{15}$ molecules/cm$^3$. 
Fig. 17 O₃ absorption spectrum at 1.0 atmosphere pressure
HNO₃ cross sections were checked by filling a 3.06 liter bulb with N₂O₅ to the desired pressure and then adding excess H₂O vapor. Carrier gas was then added to the bulb and the mixture was expanded into cell. The absorbing region was scanned and the cross section determined from the initial pressure of N₂O₅ used. This technique produced somewhat variable HNO₃ concentrations after expansion due to the tendency of HNO₃ to adhere to cell surfaces and to the heterogeneous nature of the conversion of N₂O₅ to HNO₃. The results, while somewhat uncertain, are in agreement with those obtained by Connell, Graham and Harker. Fig. 19 shows the HNO₃ absorption band at 273K and 39 torr total pressure.

Absolute cross sections for HNO₄ were not determined. The values determined by Graham et al. using a Fourier transform spectrometer were used in these studies. A comparison of the relative peak heights of the Q branches determined in these studies was in good agreement with the published values. An R branch of HNO₄ used by Graham et al. was used in monitoring HNO₄ in these experiments because the cross section is independent of pressure, temperature, concentration, and resolution effects over a fairly wide range. There is also freedom from overlapping absorptions in this region. A cross section of 5.6 x 10⁻¹⁹ cm³/molecule at 12.315 μm was used. Fig. 20 illustrates the HNO₄ absorptions in the 7 to 8.5 μm region after other absorptions due to HNO₃ and H₂O₂ have been subtracted. The 7.2 to 7.4 μm region is somewhat noisy due to a dip in reflectivity of the mirrors in this region. Fig. 21 shows the longer wavelength HNO₄ absorption, which
Fig. 20. HNO₄ absorption spectrum at 1.0 atmosphere pressure
Fig. 21. Absorption spectrum of HNO$_3$ and HNO$_4$. 
includes the R branch used in monitoring concentrations. The 11.0 to 11.5 μm HNO₃ absorption is also illustrated on this figure. The HNO₃ concentration is roughly twice that of HNO₄.

The cross sections for HONO used for this work were obtained from published sources.⁸⁰,⁸¹,⁸² HONO has two isomeric structures, that of cis-HONO and trans-HONO. The trans form is about 0.5 kcal/mole more stable than the cis form, and the barrier to internal rotation is about 12 kcal/mole. The cis form has a strong absorption in the 11 to 12 μm region and the trans form absorbs at slightly longer wavelengths in the 12 to 13 μm region. The Q branches are at 11.72 μm and at 12.61 μm. While somewhat uncertain, the absorption cross sections appear to be approximately 1.0 x 10⁻¹⁸ cm²/molecule for both Q branches at 298K. The pressure, temperature and resolution dependence of the cross sections at these wavelengths is not known.

It was noticed in the determination of infrared cross sections that Q branches of absorptions tend to exhibit markedly different characteristics than the P and R branches. The P and R branches of an absorption generally exhibited similar response to temperature, pressure and resolution variations. In many cases, the Q branch response would be markedly different from that of the P and R branch response. For this reason, P and R branch absorptions were often chosen for monitoring concentrations over Q branch absorptions.
B. Visible Cross Sections

NO$_2$, NO$_3$ and O$_3$ have absorption bands in the visible region of the spectrum. In photolysis experiments, visible light from the black lamps, particularly the 546 nm mercury line, can photolyze or excite these species. Visible photolysis of NO$_3$ is particularly important, since no ultraviolet absorptions are known. The visible absorptions are also potentially useful for monitoring concentrations of these species in chemical systems.

Of these three components, NO$_3$ and O$_3$ are photolyzed throughout most of the visible region. The absorption cross sections for these molecules determined by Graham$^{78}$ are shown in Fig. 22. The thermodynamic cutoff for photolytic production of NO$_2$ and O($^3$P) is 580 nm. The primary quantum yield for production of NO$_2$ and O($^3$P) at wavelengths shorter than 580 nm is about 0.85 and the quantum yield for the production of NO and O$_2$ is about 0.15$^{78,113}$. NO$_2$ has a thermodynamic cutoff for photolytic production of NO and O($^3$P) at 398 nm. However, a small pressure-dependent quantum yield for production of O($^3$P) atoms extends to 440 nm$^{83}$.

Since the absorption bands of the three compounds overlap, it would be difficult to monitor a particular species when the others are present. The NO$_3$ absorption band appears to end around 710 nm. The absorption bands of NO$_2$ and O$_3$ which extend into the near infrared were investigated as possible concentration monitoring regions.

Ozone was prepared by flowing a purified oxygen stream through the ozonator. The flow containing oxygen and ozone was passed through the
Fig. 22. Visible absorption bands of NO₃ and O₃.
cell at one atmosphere total pressure. When the ozone concentration inside the cell had stabilized, scans were made from 500 to 900 nm, using a IP28 PMT and a silicon photodiode. Ozone cross section determinations by Graham 78 574.7 and 602.5 nm were used to calibrate the absorption curve. The spectrum obtained is shown in Fig. 23. The absorption appears to terminate at about 840 nm.

$\text{NO}_2$ spectra were obtained by filling the cell with purified $\text{NO}_2$ to the desired pressure and scanning the region of interest with a RCA 4832 PMT and silicon photodiode. The spectra were found to be independent of pressure from 10 torr to 1 atmosphere at the resolution at which the spectra were taken. The spectra obtained are illustrated in Fig. 24. The left-hand spectrum was obtained with the PMT and the right-hand spectrum was obtained with the silicon photodiode. The spectra are in good qualitative agreement with those of Gillispie and Khan,84 who provide a theoretical interpretation of the structure.

C. Ultraviolet Cross Sections

Ultraviolet absorption cross sections are needed in the interpretation of the photolysis experiments. Since the cross sections for the molecules of interest are generally well-known, there was no attempt made to obtain new values. The spectra for $\text{NO}_2$, $\text{N}_2\text{O}_5$, $\text{O}_3$, $\text{HONO}_3$, and $\text{H}_2\text{O}_2$ are shown in Fig. 25. The spectrum of $\text{HONO}_4$ was shown previously in Fig. 1.

The cross sections were used to obtain j-values by numerically integrating the cross section–lamp emission product over wavelength at
Fig. 23. Absorption spectrum of O₃ in the visible and near-infrared region.
Fig. 24 Absorption spectrum of NO₂ in the near infrared region
Fig. 25. UV absorption spectra of NO₂, O₃, N₂O₅, H₂O₂ and HNO₃.
1 nm intervals. The spectrum of HONO was omitted for the sake of clarity. Cox and Derwent\textsuperscript{88} report it to have diffuse bands between 310 and 380 nm and a strong broad absorption centered about 215 nm. With the exception of HNO\textsubscript{4}, the photolysis products have been determined for these compounds. Since HNO\textsubscript{4} does not exist in large concentrations in the static photolysis system, the photolysis products were not of importance. In the flowing photolysis system, the overlap between the black lamp output and the HNO\textsubscript{4} absorption spectrum was small, so the photolysis rate was small and not important.
CHAPTER IV. THE REACTION OF N₂O₅ + H₂O₂

A. Experimental Procedures and Data

1. Reactant Decomposition and Flow-in

The experiments were performed by expanding the reactants and the carrier gas from two bulbs into the evacuated cell. Prior to expansion a bulb was filled to the desired pressure with a reactant, and purified carrier gas was then added. There are separate lines connecting the bulbs to the disperser tubes in the cell; so, the reactants did not mix until they flowed into the cell. This was done to prevent the occurrence of any reaction between the reactants before flowing into the cell. A previous worker, Peter Connell, has shown that the turbulent jetting of the reactants from disperser tubes in the cell provides adequate mixing of the reactants by comparison of this technique with a method where the reactants were mixed prior to expansion into the cell.

A 3.06 liter Pyrex bulb was used for holding N₂O₅, HNO₃ and NO₂ when they were used as reactants. A 5.33 liter Pyrex bulb was used for holding H₂O₂ and H₂O when they were used as reactants. The carrier gas pressure in each bulb was adjusted so the pressure-volume product of the two bulbs were approximately the same. The stopcocks on the bulbs were opened simultaneously, allowing the reactants and the carrier gas to enter the cell at the same time. The temperature of the bulbs and the Pyrex lines connecting them to the cell was 295 ± 2K.
The reactants $H_2O_2$ and $N_2O_5$ were stored in evacuated, temperature controlled Pyrex containers prior to use. The $H_2O_2$ was stored in an ethylene glycol bath at 295K. Although significant heterogeneous decomposition occurred by the process

$$H_2O_2 \xrightarrow{\text{surface}} H_2O + \frac{1}{2}O_2 \quad (44)$$

at this temperature, lower temperatures did not provide sufficient $H_2O_2$ vapor pressure for these experiments. Prior to filling the 5.33 liter bulb with $H_2O_2$, the saturator was pumped on to remove the decomposition products, both of which have much higher vapor pressures than $H_2O_2$ at 295K.\textsuperscript{89,90}

The $N_2O_5$ saturator was kept at 273K in an ice-water bath. Decomposition by the processes

$$N_2O_5 \rightarrow NO_2 + NO_3 \quad (45)$$
$$NO_2 + NO_3 \rightarrow NO + NO_2 + O_2$$
$$NO + NO_3 \rightarrow NO_2 + NO_2$$

occurred more rapidly at higher temperatures. $HNO_3$ was present with $N_2O_5$ due to its formation in the process of preparing $N_2O_5$. The ratio of vapor pressure of $HNO_3$ to the vapor pressure of $N_2O_5$ is lower at higher temperatures. The temperature used was a compromise between minimizing $N_2O_5$ decomposition and minimizing the fraction of $HNO_3$ present. The $N_2O_5$ saturator was pumped on periodically to
remove the \( \text{NO}_2 \) and \( \text{O}_2 \) decomposition products. In between series of experiments, the \( \text{N}_2\text{O}_5 \) container was stored in a dry ice-isopropanol slush bath.

The vapor pressure\(^{91}\) of \( \text{H}_2\text{O}_2 \), \( \text{H}_2\text{O} \), \( \text{N}_2\text{O}_5 \), \( \text{NO}_2 \) and \( \text{HNO}_3 \) are tabulated in Table 4 at various temperatures of interest.

To minimize the heterogeneous decomposition of the reactants, the walls of the bulbs used in the expansions were conditioned by exposing them to the reactants for an extended period before experiments were done. After sufficient exposure to \( \text{N}_2\text{O}_5 \), heterogeneous production of \( \text{HNO}_3 \) in the 3.06 liter bulb was insignificant. The decomposition by the series of reactions in (45) was determined by observing the pressure increase in the 3.06 liter bulb and the manifold to which it was attached using the Baratron pressure gauge. The net reaction for decomposition is

\[
\text{N}_2\text{O}_5 \rightarrow 2\text{NO}_2 + \frac{1}{2} \text{O}_2 .
\] (46)

Thus the change in pressure will be proportional to 1.5 times the amount of \( \text{N}_2\text{O}_5 \) decomposed. The rate of decomposition was found to be approximately 15 percent/hour, less than the decomposition rate of \( \text{H}_2\text{O}_2 \). Therefore, the 3.06 liter bulb was filled before the 5.33 liter bulb. Since the \( \text{N}_2\text{O}_5 \) was in the bulb for less than ten minutes, the amount of decomposition was considered unimportant.

Although \( \text{H}_2\text{O}_2 \) decomposition in the 5.33 liter bulb remained significant after conditioning, it appeared to be fairly reproducible.
Table 4

Vapor Pressures of Compounds Used in Expansion Experiments

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>H$_2$O$_2$</th>
<th>H$_2$O</th>
<th>N$_2$O$_5$</th>
<th>HNO$_3$</th>
<th>NO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>293K</td>
<td>1.52</td>
<td>17.5</td>
<td>284</td>
<td>46.8</td>
<td>560</td>
</tr>
<tr>
<td>283K</td>
<td>0.76</td>
<td>9.2</td>
<td>124</td>
<td>27.0</td>
<td>317</td>
</tr>
<tr>
<td>273K</td>
<td>0.76</td>
<td>4.6</td>
<td>50.7</td>
<td>14.9</td>
<td>172</td>
</tr>
<tr>
<td>263K</td>
<td>0.16</td>
<td>1.95</td>
<td>19.4</td>
<td>7.9</td>
<td>88.8</td>
</tr>
<tr>
<td>253K</td>
<td>0.07</td>
<td>0.78</td>
<td>6.9</td>
<td>4.0</td>
<td>43.6</td>
</tr>
<tr>
<td>196K</td>
<td></td>
<td></td>
<td></td>
<td>0.02</td>
<td>0.05</td>
</tr>
</tbody>
</table>

(from CRC Handbook of Chemistry and Physics, 1970-71)
The pressure increase due to $\text{H}_2\text{O}_2$ decomposition was monitored in the same manner that the $\text{N}_2\text{O}_5$ decomposition was monitored. The decomposition reaction indicates that the change in pressure will be proportional to $0.5$ times the amount of $\text{H}_2\text{O}_2$ decomposed. The experimentally determined decay profile is shown in Fig. 26. The error bars indicate the maximum variation observed in the decays. Since the rate of decomposition was fairly reproducible on short time scales, the expansion of the reactants into the cell was always done four minutes after filling the bulb with $\text{H}_2\text{O}_2$.

The concentrations of the reactants in the bulbs at the time of expansion must be known to analyze the kinetic results. From the ratio of the vapor pressures of $\text{N}_2\text{O}_5$ and $\text{HNO}_3$, it is expected that $\text{HNO}_3$ should be about 23 percent of the total amount of gas in the bulb. This is in good agreement with infrared absorption measurements made immediately following expansion of $\text{N}_2\text{O}_5$ into the cell. This technique gave values of 20-25 percent $\text{HNO}_3$.

The relative amounts of $\text{H}_2\text{O}_2$ and $\text{H}_2\text{O}$ in the 5.33 liter bulb at the time of expansion were determined from the rate of $\text{H}_2\text{O}_2$ decomposition obtained by pressure measurements. This could not be confirmed by infrared measurements because of the continued heterogeneous decomposition of $\text{H}_2\text{O}_2$ in the cell. The initial fraction of $\text{H}_2\text{O}_2$ in the bulb was determined by assuming that the pressure increase observed one hour after the addition of $\text{H}_2\text{O}_2$ to the bulb represented complete decomposition of $\text{H}_2\text{O}_2$. From this value and the observed rate of decomposition (Fig. 26), it was determined that $40 \pm 5$ per cent of the gas admitted to the bulb was $\text{H}_2\text{O}_2$ at the time of expansion.
Fig. 26  Rate of $\text{H}_2\text{O}_2$ decomposition in bulb used in expansion experiments
When H$_2$O and NO$_2$ were used as reactants, they were prepared in the same manner as that for the cross section measurements. NO$_2$ was corrected for N$_2$O$_4$, both in the bulb and in the cell. When HNO$_3$ was used as a reactant, it was prepared by the heterogeneous reaction of N$_2$O$_5$ with excess H$_2$O. No N$_2$O$_5$ was observed in spectra obtained of the expanded mixture. The concentration of HNO$_3$ obtained is somewhat uncertain due to the tendency of HNO$_3$ to adhere to wall surfaces.

2. Expansion methodology

The rate at which the reactants and carrier gas flow into the cell must be known accurately to interpret the kinetics that occur when the reactants initially mix. The fraction of the gas that has flowed into the cell at a time $t$ after expansion is equal to $(1 - \exp(-t/t_0))$, where $t_0$ is the time constant for the flow system, determined by the conductance of the tubing connecting the bulbs of the cell. The time constant was determined by connecting the Baratron pressure gauge to a port on the cell and feeding the gauge output into the Fabritek signal averager. The bulbs were filled with carrier gas and expanded into the cell. A typical output trace is shown in Fig. 27a (upper curve).

The accuracy of this technique was checked by monitoring the buildup of N$_2$O$_5$ in the cell by infrared absorption. The bulbs were filled with N$_2$O$_5$ and O$_2$ carrier gas and expanded into the evacuated cell. A typical profile is shown in Fig. 27b (lower curve). The time constant obtained in this manner was in good agreement with that obtained by the first method. The average value obtained was $t_0 = 4.3 \pm 0.3$ seconds.
Fig. 27. Rate of expansion of gases into cell
Upper - pressure measurement
Lower - absorption measurement
Kinetic information for a reaction system can be obtained by observing the decay of reactants and build-up of products following expansion of the reactants into the cell. The design of the apparatus allows only one wavelength to be monitored at a time. In order to observe all the species of interest in a reaction system, a number of expansions had to be performed under similar conditions. It was found that the concentrations of the reactants and the pressure of the carrier gas in the bulbs were reproducible to ± 5 percent.

In addition to monitoring one wavelength during an expansion, scans were made following an expansion to detect any new absorptions. Expansions and scans were done at a number of pressures and temperatures to observe the effects of these variables on the reaction system. The concentrations of the reactants were varied to determine their effect on the reaction kinetics.

3. Investigation of Complicating Factors in the \( \text{H}_2\text{O}_2-\text{N}_2\text{O}_5 \) System

Some of the complicating factors in these investigations were the heterogeneous decompositions of \( \text{N}_2\text{O}_5 \) into \( \text{HNO}_3 \) and \( \text{H}_2\text{O}_2 \) into \( \text{H}_2\text{O} \) and \( \text{O}_2 \). Being heterogeneous, there were some variations in these rates from run to run. Also, the tendency of \( \text{HNO}_3 \) to adhere to surfaces, particularly at low temperatures, makes it difficult to obtain quantitative information on its production or destruction.

The species monitored in the expansion experiments and the wavelengths used to monitor them are listed below.
The wavelength at which NO₂ is monitored is free of interfering absorptions, as are the wavelengths for NO and H₂O. The 7.158 µm absorption of HNO₄ does not overlap with absorption bands of other species in the system, but is located at a reflection minimum of the mirrors in the cell. This wavelength was used to monitor HNO₄ in initial experiments when CaF₂ windows on the cell prevented use of wavelengths longer than 10 µm. 7.400 µm was used to observe HNO₃ to avoid overlap problems with HNO₄. The cross section at this wavelength is low enough that excessively high optical densities are not incurred at high HNO₃ concentrations. The optical density at this wavelength was corrected for the weak absorption due to N₂O₅. N₂O₅ was observed at 7.960 µm to avoid overlap problems with HNO₃ and to obtain a reasonable cross section. H₂O₂ does absorb weakly here, but the optical density obtained was not corrected since the contribution was generally less than 5 percent.
H₂O₂ could not be successfully monitored by infrared absorption in this system. The strongest absorptions were overlapped by one or more absorption bands of other species which had considerably larger cross sections than H₂O₂. The only band free of interfering absorptions was at 3.8 µm, which had a cross section of less than 10⁻²¹ cm² molecule⁻¹ under the conditions of the experiments. This is too small to be of use in these experiments.

A slight shift in baseline would occasionally occur with the pressure increase caused by the expansion of gases into the cell. A wavelength free of any absorptions near the monitoring wavelength was used as a reference to correct for this shift, if it occurred.

Both of the reactants heterogeneously decompose after expansion into the cell. The approximate rates of the reactions were needed to analyze the experimental observations. The decomposition rate of H₂O₂ in the cell was determined at all temperatures of 263K, 273K and 283K by expanding H₂O₂ and O₂ carrier gas into the cell. The H₂O₂ decay was observed at 8.040 µm. The first order decay rate ranged between 2 x 10⁻³ and 2 x 10⁻⁴ sec⁻¹, depending on cell conditioning. The rates appeared to increase with a decrease in temperature, presumably due to the greater tendency of H₂O₂ to adhere to cell surfaces at low temperatures.

The decomposition of N₂O₅ is regarded as being primarily heterogeneous. Morris and Niki⁵⁹ reported a first order decay rate of 6–8 x 10⁻⁴ sec⁻¹ with a 67 liter Pyrex cell. Connell⁶⁷ reported a variation in first order rate of 1 x 10⁻³ to 7 x 10⁻⁵ sec⁻¹ with the cell used in these experiments. The values obtained under the condi-
tions used for these experiments ranged from about $5 \times 10^{-4}$ sec$^{-1}$ to less than $1 \times 10^{-4}$ sec$^{-1}$ after the cell was well conditioned. The presence of $H_2O_2$ deconditioned the cell walls, and the larger value is the best estimate for the decomposition rate that occurred during experiments.

The reaction of $N_2O_5$ with $H_2O$ must be taken into consideration, since $H_2O$ is present in significant quantities with $H_2O_2$. Morris and Niki investigated this reaction and reported that it occurs both heterogeneously and in the gas phase. They gave an upper limit of $1.3 \times 10^{-20}$ cm$^3$/molecule-second for the homogeneous rate constant.

This reaction was investigated by expanding $H_2O$ and $N_2O_5$ into the cell and observing the decay of $N_2O_5$. Fig. 28 illustrates a semilog plot of four $N_2O_5$ profiles in the presence of excess $H_2O$. The decays of $N_2O_5$ should obey pseudo-first order kinetics under these conditions. The initial concentrations of the reactants and the approximate first order decay rate for $N_2O_5$ are listed below.

<table>
<thead>
<tr>
<th>Run</th>
<th>$[N_2O_5]$</th>
<th>$[H_2O]$</th>
<th>$k$ (sec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>$5.6 \times 10^{14}$</td>
<td>$1.7 \times 10^{16}$</td>
<td>$7.6 \times 10^{-3}$</td>
</tr>
<tr>
<td>B</td>
<td>$7.3 \times 10^{14}$</td>
<td>$9.7 \times 10^{15}$</td>
<td>$5.0 \times 10^{-3}$</td>
</tr>
<tr>
<td>C</td>
<td>$7.3 \times 10^{14}$</td>
<td>$9.5 \times 10^{15}$</td>
<td>$5.0 \times 10^{-3}$</td>
</tr>
<tr>
<td>D</td>
<td>$8.8 \times 10^{14}$</td>
<td>$5.5 \times 10^{15}$</td>
<td>$6.0 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

D'Ans and Friederick and Schwarz used the reaction of $H_2O_2$ with $HNO_3$ in solution to generate $HNO_4$. This reaction system was investigated by expanding $HNO_3$ and $H_2O_2$ into the evacuated cell. $H_2O_2$ was monitored at 8.040 μm, where there is a minimum in the $HNO_3$ absorption.
Fig. 28. Decay profiles of N$_2$O$_5$ in the presence of H$_2$O

Curve A: [N$_2$O$_5$] = 5.6 x 10$^{14}$ molecules/cm$^3$

[H$_2$O] = 1.7 x 10$^{15}$

Curve B: [N$_2$O$_5$] = 7.3 x 10$^{14}$

[H$_2$O] = 9.7 x 10$^{15}$

Curve C: [N$_2$O$_5$] = 7.3 x 10$^{14}$

[H$_2$O] = 9.5 x 10$^{15}$

Curve D: [N$_2$O$_5$] = 8.8 x 10$^{14}$

[H$_2$O] = 5.5 x 10$^{15}$
bands. The $H_2O_2$ decay rates were within the range of those obtained with $H_2O_2$ alone. The $HNO_3$ first order decay rates were $1$ to $5 \times 10^{-4}$ second$^{-1}$, and were less than or equal to the observed $H_2O_2$ decay rate. When a series of expansions were done in succession, the decay rate for $HNO_3$ decreased with each run. There were no detectable absorptions by $HNO_4$ or HONO, which are possible products of the reaction of $HNO_3$ with $H_2O_2$.

The reaction of $NO_2$ with $H_2O$ and $H_2O_2$ should be considered since $NO_2$ will be formed by the decomposition of $N_2O_5$. Kaiser and Wu$^{92}$ and McKinnon et al.$^{60}$ have investigated the reaction of $NO_2$ with $H_2O$,

$$2NO_2 + H_2O \rightarrow HNO_3 + HONO$$

The gas phase rate constants given by refs. 60 and 92 are $k_f \approx 1 \times 10^{-37}$ cm$^6$/molecule$^2$-second and $k_r \approx 1.5 \times 10^{-17}$ cm$^3$/molecule-second.

The reaction apparently proceeds more rapidly heterogeneously. The reaction of $H_2O_2$ with $NO_2$ can proceed in a similar fashion

$$2NO_2 + H_2O_2 \rightarrow 2HNO_3$$

Gray et al.$^{62}$ investigated the reaction of $NO_2$ with $H_2O_2$ and concluded it was primarily heterogeneous. The reaction was investigated by expanding $H_2O_2$ and $NO_2$ into the cell. The $H_2O_2$ decay rates were within the limits obtained with $H_2O_2$ alone. There was no decay of $NO_2$ observed within the limits of experimental uncertainty. Scans
taken 200 seconds after expansion indicated the presence of approximately 1 x 10^{14} \text{molecules/cm}^3 of HNO_3 and < 5 \times 10^{13} \text{molecules/cm}^3 of HNO_2.

When HNO_4 is formed in a chemical system, a major loss mechanism is that of heterogeneous decomposition. To obtain approximate values for this mode of decay, HNO_4 was synthesized by the techniques developed by Barker et al.\textsuperscript{23} so that its decay could be observed without large concentrations of other species present. The gases evolved from the mixture were flowed into the cell to determine the concentration of HNO_4 obtainable. However, no HNO_4 was detected. It appears that all the HNO_4 in the flow decomposed on the tubing walls before entering the cell. The HNO_4 heterogeneous decomposition rates used in this study were obtained from its decay in the presence of significant concentrations of other species, which introduced some uncertainty to the value.

4. Products and Reactant Concentration Dependence of H_2O_2+\text{N}_2\text{O}_5

\text{N}_2\text{O}_5 and H_2O_2 were expanded with O_2 carrier gas into the evacuated cell, as described previously. The decay of \text{N}_2\text{O}_5 was more rapid than the decay that occurred in the \text{N}_2\text{O}_5-H_2O system. Scans were made after expansion to determine which species were present.

Fig. 29 illustrates a typical scan obtained following the expansion of H_2O_2 and \text{N}_2\text{O}_5. The scan was taken 200 seconds after expansion with a cell temperature of 263K. The noise in the spectrum between 7.2 and 7.3 \text{\mu}m is due the reflection minimum in the cell mirrors. The 7.0-7.3 \text{\mu}m absorption band is due to HNO_4. HNO_3 and HNO_4 absorptions
Fig. 29. Absorption spectrum of products of the reaction of H₂O₂ with N₂O₅.
overlap in the 7.4 to 7.8 \mu m region. Subtracting absorptions due to HNO_3, N_2O_5 and H_2O_2 from this figure yielded the spectrum shown in Fig. 19. No absorption due to HONO was observed.

Initial work was done with CaF_2 windows on the cell, which limited infrared transmission to wavelengths shorter than 10 \mu m. These were replaced with BaF_2 windows to allow observation of the HNO_4 band between 12 and 13 \mu m (Fig. 20). This absorption is free of interference by other species and has a larger cross section than the 7.1 to 7.3 \mu m band. No HONO was observed in this region.

The presence of HNO_4 indicated the products of the reaction of H_2O_2 with N_2O_5 with one of the following sets.

\[ H_2O_2 + N_2O_5 \rightarrow HNO_4 + HNO_3 \]

\[ \rightarrow HO_2 + NO_2 + HNO_3 \]

HO_2 and NO_2 can quickly combine to form HNO_4. To discriminate between the product sets, a small amount of NO was added to the cell prior to expansion.

NO scavenges HO_2 by reaction (4), the rate of which is more than an order of magnitude faster than the rate for reaction (1) given by Graham et al.\(^{18}\) If the primary products of H_2O_2 and N_2O_5 are HNO_3, HO_2 and NO_2, the HNO_4 concentration will exist at observable levels when NO is present. If HNO_4 is formed directly, the HO_2 formed by HNO_4 decomposition will react with NO. This will reduce the HNO_4 concentration somewhat, but the concentration will still be observable.
Approximately 0.3 torr of NO was added to the cell prior to the expansion of \(H_2O_2\) and \(N_2O_5\). Such a low pressure does not significantly interfere with the expansion of gases. The process was repeated three times so that the profiles of \(HNO_4\), \(HNO_3\) and \(N_2O_5\) could be observed. The profiles are tabulated in Table 5. The profiles without NO are listed in Table 6.

The dependence of \(HNO_4\) concentration on each of the reactants was determined by independently varying the concentrations of \(N_2O_5\) and \(H_2O_2\). These expansions were done at a cell temperature of 263K, and at final pressures of 33 and 66 torr. The \(HNO_4\) profiles are shown in Figs. 30-33. For the runs in Fig. 30, the initial \(H_2O_2\) concentration was held constant at \(1.8 \times 10^{15}\) molecules/cm\(^3\) while the \(N_2O_5\) concentration was varied from \(3.6 \times 10^{15}\) molecules/cm\(^3\) (curve A) to \(2.1 \times 10^{14}\) molecules/cm\(^3\) (curve G). Similarly, in Fig. 31, the initial \(H_2O_2\) concentration was \(1.8 \times 10^{15}\) molecules/cm\(^3\) and the initial \(N_2O_5\) concentration was varied from \(8.9 \times 10^{15}\) molecules/cm\(^3\) (curve A) to \(8.7 \times 10^{14}\) molecules/cm\(^3\) (curve E).

The runs shown in Fig. 32 were done with an initial \(N_2O_5\) concentration of \(1.3 \times 10^{15}\) molecules/cm\(^3\) and the \(H_2O_2\) concentration was varied from \(1.8 \times 10^{15}\) molecules/cm\(^3\) (curve A) to \(2.1 \times 10^{14}\) molecules/cm\(^3\) (curve F). The \(N_2O_5\) concentration was \(4.1 \times 10^{15}\) molecules/cm\(^3\) for the runs shown in Fig. 33, and the \(H_2O_2\) concentration was again varied from \(1.8 \times 10^{15}\) molecules/cm\(^3\) (curve A) to \(2.1 \times 10^{14}\) molecules/cm\(^3\) (curve E).
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Fig. 30  HNO₄ profiles following expansion of N₂O₅ and H₂O₂

\[ [H₂O₂] = 1.8 \times 10^{15} \]

Curve A:  \[ [N₂O₅] = 3.6 \times 10^{15} \text{ molecules/cm}^3 \]
Curve B:  \[ [N₂O₅] = 2.5 \times 10^{15} \]
Curve C:  \[ [N₂O₅] = 1.5 \times 10^{15} \]
Curve D:  \[ [N₂O₅] = 1.1 \times 10^{15} \]
Curve E:  \[ [N₂O₅] = 8.0 \times 10^{14} \]
Curve F:  \[ [N₂O₅] = 4.0 \times 10^{14} \]
Curve G:  \[ [N₂O₅] = 2.1 \times 10^{14} \]
Fig. 31  HNO₄ profiles following expansion of N₂O₅ and H₂O₂

[H₂O₂] = 1.8 x 10¹⁵ molecules/cm³ for all curves

Curve A: [N₂O₅] = 8.9 x 10¹⁵ molecules/cm³
Curve B: [N₂O₅] = 5.6 x 10¹⁵ " "
Curve C: [N₂O₅] = 3.6 x 10¹⁵ " "
Curve D: [N₂O₅] = 1.8 x 10¹⁵ " "
Curve E: [N₂O₅] = 8.7 x 10¹⁴ " "
Fig. 32  HNO₄ profiles following expansion of N₂O₅ and H₂O₂.  

\([\text{N}_2\text{O}_5] = 1.3 \times 10^{15} \text{ molecules/cm}^3\) for all curves.

Curve A:  \([\text{H}_2\text{O}_2] = 1.8 \times 10^{15} \text{ molecules/cm}^3\)
Curve B:  \([\text{H}_2\text{O}_2] = 1.3 \times 10^{15} \text{ " "}\)
Curve C:  \([\text{H}_2\text{O}_2] = 9.5 \times 10^{14} \text{ " "}\)
Curve D:  \([\text{H}_2\text{O}_2] = 6.9 \times 10^{14} \text{ " "}\)
Curve E:  \([\text{H}_2\text{O}_2] = 3.3 \times 10^{14} \text{ " "}\)
Curve F:  \([\text{H}_2\text{O}_2] = 2.1 \times 10^{14} \text{ " "}\)
Fig. 33  HNO₄ profiles following expansion of N₂O₅ and H₂O₂

[N₂O₅] = 4.1 x 10^{15} molecules/cm³ for all curves

Curve A: [H₂O₂] = 1.8 x 10^{15} molecules/cm³
Curve B: [H₂O₂] = 1.0 x 10^{15} '' ''
Curve C: [H₂O₂] = 6.3 x 10^{14} '' ''
Curve D: [H₂O₂] = 3.6 x 10^{14} '' ''
Curve E: [H₂O₂] = 2.1 x 10^{14} '' ''
The diagram shows the concentration of $\text{HO}_2\text{NO}_2$ over time under conditions of $\text{H}_2\text{O}_2$ dependence, 66 torr, and 263 K. The concentration is expressed as $10^4$ molecules/cm$^3$. The curves are labeled A, B, C, D, and E, each representing different conditions or time points. The x-axis represents time in seconds, ranging from 0 to 160, and the y-axis represents concentration. The diagram is labeled as Fig. 33.
The effects of temperature and pressure on the product profile were investigated. Expansions were done with a cell temperature of 253 K, 263 K, 273 K and 283 K. In most cases, the concentration profiles of \( \text{HNO}_4 \), \( \text{N}_2\text{O}_5 \), \( \text{HNO}_3 \) and \( \text{NO}_2 \) were observed. In some cases, \( \text{H}_2\text{O} \) was also observed. The cross sections of \( \text{NO}_2 \) and \( \text{H}_2\text{O} \) at temperatures where they had not been determined were obtained by interpolating from the 293 K and 263 K values. Since \( \text{NO}_2 \) was generally present in low concentrations and the 0.1 atmosphere cross section is small, there is considerable uncertainty in the concentration. \( \text{H}_2\text{O} \) was present in fairly large concentrations, but the low cross section made it difficult to obtain accurate values of its concentration.

\( \text{HNO}_4 \) was the only species monitored during the expansions done at 253 K. The expanded pressures of \( \text{H}_2\text{O}_2 \) approached 70 percent of the extrapolated \( \text{H}_2\text{O}_2 \) vapor pressure at 253 K. It was noted that \( \text{HNO}_4 \) was generated by expansion of \( \text{N}_2\text{O}_5 \) alone into the evacuated cell when the preceding expansion contained \( \text{H}_2\text{O}_2 \). Apparently, \( \text{H}_2\text{O}_2 \) exhibits a strong tendency to adsorb to surfaces under these conditions, or else a significant amount of condensation occurs. The \( \text{H}_2\text{O}_2 \) could be removed by pumping on the cell for several hours or by adding \( \text{N}_2\text{O}_5 \) to react with it. The \( \text{HNO}_4 \) profiles obtained are illustrated in Fig. 34. The initial \( \text{H}_2\text{O}_2 \) and \( \text{N}_2\text{O}_5 \) concentrations for each curve are listed below in units of molecules/cm\(^3\).
Fig. 34  HNO₄ profiles following expansion of N₂O₅ and H₂O₂ at 253 K

[H₂O₂] = 1.8 x 10¹⁵ molecules/cm³ for all curves

Curve A:  [N₂O₅] = 3.5 x 10¹⁴ molecules/cm³
Curve B:  [N₂O₅] = 2.9 x 10¹⁴  "  "
Curve C:  [N₂O₅] = 5.6 x 10¹⁴  "  "
The expanded pressure was 33 torr for these runs.

The problem of $\text{H}_2\text{O}_2$ adhering to the cell surfaces was not observed at 263K or higher temperatures. Sample runs at 263K, 273K, and 283K are illustrated in Figs. 35-37 and tabulated in Tables 7-9, respectively.

The initial $\text{H}_2\text{O}_2$ and $\text{N}_2\text{O}_5$ concentrations for these expansions are as follows, in units of molecules/cm$^3$:

\[
\begin{align*}
\text{263K} & \quad [\text{H}_2\text{O}_2] = 1.8 \times 10^{15} \quad [\text{N}_2\text{O}_5] = 9.3 \times 10^{14} \\
\text{273K} & \quad = 1.8 \times 10^{15} \quad 5.6 \times 10^{14} \\
\text{283K} & \quad = 1.8 \times 10^{15} \quad 5.6 \times 10^{14}
\end{align*}
\]

Runs were done at each temperature under several sets of conditions, to obtain a good understanding of the kinetics.

The pressure dependence of the $\text{HNO}_4$ profiles was examined under two different initial concentrations of $\text{N}_2\text{O}_5$ and $\text{H}_2\text{O}_2$. The $\text{HNO}_4$ profiles are illustrated in Figs. 38 and 39 and tabulated in Tables 10 and 11. The initial concentrations of $\text{H}_2\text{O}_2$ and in molecules/cm$^3$ are listed below.
Fig. 35  Concentration profiles of HNO$_3$, HNO$_4$, N$_2$O$_5$ and NO$_2$

following expansion of N$_2$O$_5$ and H$_2$O$_2$ at 263 K

\[[N_2O_5] = 9.3 \times 10^{14} \text{ molecules/cm}^3\]

\[[H_2O_2] = 1.8 \times 10^{15} \ " "\]
Fig. 36  Concentration profiles of HNO$_3$, HNO$_4$, N$_2$O$_5$, NO$_2$ and H$_2$O following expansion of N$_2$O$_5$ and H$_2$O$_2$ at 273 K

\[ [N$_2$O$_5] = 5.6 \times 10^{14} \text{ molecules/cm}^3 \]

\[ [H$_2$O$_2] = 1.8 \times 10^{15} \quad " \quad " \]
Fig. 37  Concentration profiles of HNO$_3$, HNO$_4$, N$_2$O$_5$, NO$_2$ and H$_2$O following expansion of N$_2$O$_5$ and H$_2$O$_2$ at 283 K

[$N_2O_5$] = $5.6 \times 10^{14}$ molecules/cm$^3$

[$H_2O_2$] = $1.8 \times 10^{14}$
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Fig. 38  HNO₄ profiles following the expansion of H₂O₂ and N₂O₅ at different pressures

\[ [\text{N}_2\text{O}_5] = 1.1 \times 10^{15} \text{ molecules/cm}^3 \]

\[ [\text{H}_2\text{O}_2] = 2.1 \times 10^{14} \]
Fig. 39  HNO₄ profiles following the expansion of H₂O₂ and N₂O₅ at different pressures

\[
[N₂O₅] = 3.5 \times 10^{15} \text{ molecules/cm}^3 \\
[H₂O₂] = 1.8 \times 10^{15} \quad " \quad "
\]
TABLE 10

Temp. = 263K

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Press           66 torr  40 torr  19 torr
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Run I \([\text{H}_2\text{O}_2] = 2.1 \times 10^{14}\) \([\text{N}_2\text{O}_5] = 1.1 \times 10^{15}\)

Run II \(= 1.8 \times 10^{15}\) \(= 3.5 \times 10^{15}\)

Both runs were done at 263K.

The effect of cell volume and surface-to-volume ratio were investigated by inserting sealed Pyrex tubing into the cell. Thirty-two 0.9 cm diameter tubes 85 cm long were loosely stacked in the cell and kept separated by Pyrex rods. This added 7600 cm\(^2\) surface area, increasing the surface area of the cell by 70 percent. The surface-to-volume ratio of the cell was increased to 0.303 cm\(^{-1}\).

Expansions were done immediately preceding and following the insertion of the tubes to observe the effect of added surface. The expansions were done with a cell temperature of 283K. Three HNO\(_4\) profiles are shown in Fig. 40. Curve A was obtained without the extra surface, and curves B and C were obtained after the extra surface had been added. The initial concentrations were \(1.8 \times 10^{15}\) molecules/cm\(^3\) for \(\text{H}_2\text{O}_2\) and \(2.7 \times 10^{15}\) molecules/cm\(^3\) for \(\text{N}_2\text{O}_5\) in all three runs.

B. Results and Discussion

1. Other Reactions in the \(\text{N}_2\text{O}_5-\text{H}_2\text{O}_2\) System

The presence of contaminants and decomposition products in the samples of \(\text{H}_2\text{O}_2\) and \(\text{N}_2\text{O}_5\) mixed together in these experiments complicate the kinetics of the system. The contaminating species can react with \(\text{H}_2\text{O}_2\) or \(\text{N}_2\text{O}_5\) and make the reaction between them
Fig. 40  HNO₄ profiles following expansion of H₂O₂ and N₂O₅

Curve A  - cell in standard configuration
Curves B, C - cell with additional surface area

\[ [N₂O₅] = 2.7 \times 10^{15} \text{ molecules/cm}^3 \]
\[ [H₂O₂] = 1.8 \times 10^{15} \]
difficult to observe. The major contaminants are H₂O and HNO₃, as well as some NO₂.

Reactions involving these species, as well as the heterogeneous decomposition of the reactants in the cell, were investigated to determine their effect on the kinetics.

The reaction of H₂O with N₂O₅ has been investigated by Morris and Niki. It was investigated in this system to see whether it occurred primarily homogeneously or heterogeneously. Typical curves of N₂O₅ decay in the presence of H₂O at 263K are shown in Fig. 28. The curves exhibit some curvature, which is more pronounced at longer time scales. The average slopes of the lines did not correlate well with either of the initial reactant concentrations or with the product of the concentrations. It was concluded that the reaction is primarily heterogeneous in this system. This conclusion is in agreement with other studies. However, a significant amount of N₂O₅ is lost in this manner.

The possibility of a reaction between H₂O₂ and HNO₃ was investigated. The H₂O₂ decomposition rate was the same as that of H₂O₂ alone. The HNO₃ disappearance rate decreased with succeeding runs, suggesting a heterogeneous process was occurring. There was an absence of absorption by any of the likely products of the reaction of H₂O₂ with HNO₃ in scans taken following their expansion.

HNO₃ exhibits a tendency to absorb or adhere to a surface, and this could explain the disappearance of HNO₃. Morris and Niki
noted a slow, long term loss of HNO₃ from the gas phase with an estimated first order loss rate of $10^{-4}$ second⁻¹. The values obtained in this system, which has a similar surface-to-volume ratio to that of ref. 59, were in the range of 0.8 to $5 \times 10^{-4}$ second⁻¹. From these results, it appears that the reaction between H₂O₂ and HNO₃ in the gas phase is very small, if it occurs at all. The upper limit for the rate constant for this reaction was determined to be $1 \times 10^{-19}$ cm³/molecule-second.

NO₂ will be formed in the H₂O₂-N₂O₅ system by the decomposition of N₂O₅ and HNO₄. H₂O will be formed by the decomposition of H₂O₂. The reaction between H₂O and NO₂ has been investigated by refs. 60 and 92. The concentrations of HNO₃ and HONO observed after the expansion of H₂O₂ and NO₂ into the cell were well in excess of the amounts that would be produced by the gas phase reaction of NO₂ and H₂O if the values for the rate constant in ref. 60 are correct.

HONO exists in cis and trans forms only, the trans form was monitored following the expansion of H₂O₂ and NO₂. From the equilibrium constants given by Altshuller,⁹⁴ the cis form should be present in somewhat lower concentrations than the trans form, indicating a total HONO concentration of $5-7 \times 10^{13}$ molecules/cm³, somewhat less than that of the HNO₃ observed. At the time of expansion, H₂O was present at levels approximately 50 percent higher than H₂O₂ due to the decomposition of H₂O₂ in the bulb prior to expansion. The majority of the HONO was apparently formed heterogeneously by
An equilibrium exists between HONO and $H_2O$, $NO_2$ and $NO$,

$$2HONO \rightarrow H_2O + NO_2 + NO$$  \hspace{1cm} (52)$$

If HONO was present at levels of $\sim 7 \times 10^{13}$ molecules/cm$^3$, NO would exist at levels of $\sim 1 \times 10^{15}$ molecules/cm$^3$ if the system was in equilibrium. While the absorption band of NO was not monitored, the conversion of this much $NO_2$ into NO would have been observed when $NO_2$ was monitored. HONO was apparently not equilibrated with the products in (52) at the time of observation.

Since HNO$_3$ tends to adhere to the cell walls, the amount of HNO$_3$ generated was presumably present in larger concentrations than observed and was present in excess of the HONO concentration. The difference could be due to loss of HONO through the equilibrium process into $H_2O$, $NO_2$ and $NO$. Alternatively, some HNO$_3$ could have been produced by the reaction of $H_2O_2$ with $NO_2$ or $N_2O_4$. The $N_2O_4$ concentration was about 1 percent of the $NO_2$ concentration in the runs where this was investigated. In either case, the reaction is slow and is not important in the system under study. The upper limit for the rate constant for the reaction of $H_2O_2$ with $NO_2$ in the gas phase is $< 1 \times 10^{-19}$ cm$^3$/molecule-second. No information was obtained on whether the reaction occurred by a heterogeneous pathway.
Kaiser and Wu\textsuperscript{92} investigated the possibility of a reaction of 
HNO\textsubscript{3} with NO\textsubscript{2} and H\textsubscript{2}O and did not observed any noticeable reaction. Consequently, these reactions were not investigated in this system.

2. Analysis of the reaction of \textit{N}_2\textit{O}_5 with H\textsubscript{2}O\textsubscript{2} Scans taken after the expansion of H\textsubscript{2}O\textsubscript{2} and N\textsubscript{2}O\textsubscript{5} into the cell indicated the presence of HNO\textsubscript{4} and the absence, within detectable limits, of HONO. The detection limit for HONO is less than 3 x 10\textsuperscript{13} molecules/cm\textsuperscript{3}. HNO\textsubscript{4} could be formed directly by the reaction of N\textsubscript{2}O\textsubscript{5} with H\textsubscript{2}O\textsubscript{2} or indirectly from the recombination of H\textsubscript{O}\textsubscript{2} and NO\textsubscript{2}. Tests were made to determine the reaction product set by adding \~0.3 torr of NO to the cell prior to the expansion of the reactants. NO scavenges H\textsubscript{O}\textsubscript{2} by reaction (4), which is more rapid than the reaction of H\textsubscript{O}\textsubscript{2} with NO\textsubscript{2} to form HNO\textsubscript{4} under the experimental conditions of 0.1 atmosphere pressure and 273K.

If the products of the reaction of H\textsubscript{2}O\textsubscript{2} and N\textsubscript{2}O\textsubscript{5} were H\textsubscript{O}\textsubscript{2} + NO\textsubscript{2} + HNO\textsubscript{3}, the HNO\textsubscript{4} concentration would not rise to detectable limits. If the products were HNO\textsubscript{4} and HNO\textsubscript{3}, HNO\textsubscript{4} would be present at levels somewhat reduced from that without NO. This is due to loss of HNO\textsubscript{4} by dissociation into NO\textsubscript{2} and H\textsubscript{O}2, which would react with NO. The experimental observations were in good agreement with those predicted for the reaction products of HNO\textsubscript{4} and HNO\textsubscript{3}. This product set was \textgreater 90 percent of all product channels.

If the reaction occurs in the gas phase, it may proceed though an complex re-arrangement because of the geometry of the molecules.
Electron diffraction studies\(^9\) of \(\text{N}_2\text{O}_5\) indicated a central angle of \(95 \pm 3^\circ\) and an \(\text{O}--\text{N}--\text{O}\) angle of the end nitro groups of \(134 \pm 9^\circ\). The central \(\text{N}--\text{O}\) distance of \(1.46\text{\AA}\) and the end \(\text{N}--\text{O}\) distance of \(1.21\text{\AA}\) were obtained. \(\text{H}_2\text{O}_2\) has \(\text{C}_2\) symmetry and an \(\text{H}--\text{O}--\text{O}\) angle of \(102^\circ\). The \(\text{O}--\text{O}\) distance is \(1.48\text{\AA}\) and the \(\text{O}--\text{H}\) distance is \(0.98\text{\AA}\).\(^7\) The rearrangement of these molecules into \(\text{HNO}_3\) and \(\text{HNO}_4\) would be fairly complex.

The rate expression for the \(\text{HNO}_4\) buildup and decay in the cell will be:

\[ \frac{d[\text{HNO}_4]}{dt} = k_7[\text{H}_2\text{O}_2][\text{N}_2\text{O}_5] - k_8[\text{HNO}_4] + k_9[\text{H}_2\text{O}_2][\text{NO}_2] - k_{11}[\text{HNO}_4] \]  

(53)

using the numbering system in Appendix C. The concentrations of \(\text{H}_2\text{O}_2\) and \(\text{N}_2\text{O}_5\) during expansion will be described by the flow-in equation

\[ [x] = [x]_0 (1 - \exp(-t/t_0)) \]  

(32)

where \([x]_0\) is the final concentration in the cell if species \(x\) is inert. The value for \(t_0\) is 4.3 seconds for the expansion system used. For approximately ten seconds following the start of expansion, this equation is adequate for describing the flow-in of the reactants \([\text{H}_2\text{O}_2]\) and \([\text{N}_2\text{O}_5]\) can be determined from the reactant concentrations in the bulbs at the time of expansion. Also the reactions affecting \(\text{HNO}_4\) other than (7) will be small and

\[ \frac{d[\text{HNO}_4]}{dt} = k_7[\text{H}_2\text{O}_2][\text{N}_2\text{O}_5] (1 - \exp(-t/4.3))^2 \]  

(54)
The build-up of HNO\(_4\) can be obtained by integrating the above equation

\[
[HNO_4]_t \approx k_7[H_2O_2] [N_2O_5].
\]

\[
[t+8.6 \exp(-t/4.3) - 2.15 \exp(-2t/4.3) - 6.45] \quad (55)
\]

The bimolecular rate constant for reaction (7) can be obtained by the HNO\(_4\) build-up and the concentrations of the reactants in the bulbs.

The effect of independent variation of reactant concentrations on the HNO\(_4\) profile observed can be determined from the results used to generate Figs. 30-33. The ratios of the N\(_2\)O\(_5\) and H\(_2\)O\(_2\) initial concentrations, along with the ratios of the HNO\(_4\) concentrations at 20 and 40 seconds after expansion and at maximum, relative to the minimum values are listed in Table 12. The ratios for the HNO\(_4\) concentrations are generally less than those of the reactants because of reactions which compete with reaction (7). A low value of [HNO\(_4\)] obtained in run G of Fig. 30 is probably the cause of the \(t = 20\) second [HNO\(_4\)] ratios being higher than the [N\(_2\)O\(_5\)] ratios.

The time of occurrence of the maximum HNO\(_4\) concentration is usually longer than 40 seconds. It can be seen from Table 12 that the [HNO\(_4\)] ratios approach the ratios of [N\(_2\)O\(_5\)] as the time of observation approaches the time of expansion. From Table 12, it is apparent that [HNO\(_4\)] ratios approach the [H\(_2\)O\(_2\)] ratios as time increases following expansion.
### TABLE 12

#### From Fig. 30

<table>
<thead>
<tr>
<th>Run</th>
<th>([N_2O_5]_{t=0})</th>
<th>([HNO_4]_{t=20sec})</th>
<th>([HNO_4]_{t=40sec})</th>
<th>([HNO_4]_{\text{max}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>A/G</td>
<td>16.9</td>
<td>19.5</td>
<td>8.2</td>
<td>4.7</td>
</tr>
<tr>
<td>B/G</td>
<td>11.9</td>
<td>17.4</td>
<td>7.9</td>
<td>4.4</td>
</tr>
<tr>
<td>C/G</td>
<td>6.9</td>
<td>11.9</td>
<td>6.5</td>
<td>4.1</td>
</tr>
<tr>
<td>D/G</td>
<td>5.0</td>
<td>9.1</td>
<td>5.3</td>
<td>4.0</td>
</tr>
<tr>
<td>E/G</td>
<td>3.8</td>
<td>6.0</td>
<td>3.8</td>
<td>3.4</td>
</tr>
<tr>
<td>F/G</td>
<td>1.9</td>
<td>2.8</td>
<td>2.2</td>
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<tr>
<td>G/G</td>
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</tbody>
</table>

#### From Fig. 31

<table>
<thead>
<tr>
<th>Run</th>
<th>([N_2O_5]_{t=0})</th>
<th>([HNO_4]_{t=20sec})</th>
<th>([HNO_4]_{t=40sec})</th>
<th>([HNO_4]_{\text{max}})</th>
</tr>
</thead>
<tbody>
<tr>
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<td>5.0</td>
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<tr>
<td>B/E</td>
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<td>3.8</td>
<td>2.5</td>
<td>1.6</td>
</tr>
<tr>
<td>C/E</td>
<td>4.2</td>
<td>2.9</td>
<td>2.2</td>
<td>1.4</td>
</tr>
<tr>
<td>D/E</td>
<td>2.1</td>
<td>1.9</td>
<td>1.6</td>
<td>1.2</td>
</tr>
<tr>
<td>E/E</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

#### From Fig. 32

<table>
<thead>
<tr>
<th>Run</th>
<th>([N_2O_5]_{t=0})</th>
<th>([HNO_4]_{t=20sec})</th>
<th>([HNO_4]_{t=40sec})</th>
<th>([HNO_4]_{\text{max}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>A/F</td>
<td>8.8</td>
<td>2.2</td>
<td>2.3</td>
<td>2.3</td>
</tr>
<tr>
<td>B/F</td>
<td>6.5</td>
<td>2.3</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>C/F</td>
<td>4.6</td>
<td>2.1</td>
<td>2.3</td>
<td>2.3</td>
</tr>
<tr>
<td>D/F</td>
<td>3.4</td>
<td>1.9</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>E/F</td>
<td>1.6</td>
<td>1.1</td>
<td>1.2</td>
<td>1.2</td>
</tr>
<tr>
<td>F/F</td>
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<td>1.0</td>
</tr>
</tbody>
</table>

#### From Fig. 33

<table>
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<th>Run</th>
<th>([N_2O_5]_{t=0})</th>
<th>([HNO_4]_{t=20sec})</th>
<th>([HNO_4]_{t=40sec})</th>
<th>([HNO_4]_{\text{max}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>A/E</td>
<td>8.8</td>
<td>3.2</td>
<td>3.4</td>
<td>3.9</td>
</tr>
<tr>
<td>B/E</td>
<td>5.0</td>
<td>3.1</td>
<td>3.2</td>
<td>3.6</td>
</tr>
<tr>
<td>C/E</td>
<td>3.0</td>
<td>2.1</td>
<td>2.2</td>
<td>2.4</td>
</tr>
<tr>
<td>D/E</td>
<td>1.9</td>
<td>1.6</td>
<td>1.6</td>
<td>1.6</td>
</tr>
<tr>
<td>E/E</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>
Computer simulations were done of the HNO$_4$ dependence on reactants using a simplified version of the reaction scheme shown in Appendix C. Reactions 2, 3, 6, 7, 20, 21 and 22 were used. These simulations indicated that the [HNO$_4$] ratios should approach the ratios of either reactant at times near to the time of expansion. This disagrees with what was observed when the H$_2$O$_2$ variation was tested.

The experimentally observed effects of pressure on the HNO$_4$ profiles were shown in the previous section. The most apparent effect is that the final HNO$_4$ concentration is larger at higher pressures. The total pressure of the system will affect the rate constants for unimolecular decomposition of N$_2$O$_5$ and HNO$_4$, but will not affect the equilibrium of these species with their decomposition products. The pressure will also affect the rate of diffusion to the walls, where heterogeneous reactions may occur. The pressure dependence of the heterogeneous decomposition of N$_2$O$_5$, H$_2$O$_2$ and HNO$_4$ is unknown. The time for a molecule to diffuse a given distance at 19 torr will be about one-third of the diffusion time at 66 torr.

Computer simulations were made of the effect of pressure on the reaction system using the complete set of reactions in Appendix C. The only significant effect of pressure in the simulation was a ~25 percent decrease in the concentration of NO$_2$ as the pressure doubled from 34 to 68 torr at 263 K. This suggests the effects observed are due to heterogeneous processes.

The experimental profiles of the spectra observed at 263 K, 273 K and 283 K were simulated using the CHEMK chemical kinetics program and
the reaction set in Appendix C. The rate constant for reaction (7) was varied to provide the best fit with the experimental data. There was some difficulty in obtaining a good fit because of the variability of the heterogeneous decomposition rates of $N_2O_5$, $H_2O_2$ and $HNO_4$. Typical simulation profiles along with the experimental profiles are shown in Figs. 41-43 for cell temperatures of 263K, 273K and 283K, respectively. The upper curves are those obtained from the computer simulations. The most prominent disagreement between experimental and simulated curves occurred with $H_2O$ and $NO_2$. The experimental curves of these compounds were the most uncertain because of the weak absorption by these species. The experimental $NO_2$ profiles indicate that some $NO_2$ was present with the $N_2O_5$ at the time of expansion. The build-up of $NO_2$ occurs largely in the first 20 seconds after expansion. The rate of change during later periods is much lower. This factor was not included in the simulations. There was some variation in the best rate constant for reaction (7) to fit the experimental data at each temperature, and the rate constants tended to be higher at lower temperatures. This is in contradiction to what would be expected for a gas phase bimolecular reaction. The rate constants used for simulations in Figs. 41-43 were 0.8, 1.0 and $0.3 \times 10^{-17} \text{cm}^3/\text{molecule-second}$, respectively.

Another unusual feature found was that the calculated $HNO_4$ concentration generally would initially be lower than the experimental values. The initial observed build-up $HNO_4$ for several runs is shown in Fig. 44. The temperatures and $[H_2O_2]$ $[N_2O_5]$ product corresponding to the curves are listed below.
Fig. 41  Simulated (upper) and experimental (lower) profiles of a 263 K expansion
Fig. 42 Simulated (upper) and experimental (lower) profiles of a 273 K expansion.
Fig. 43 Simulated (upper) and experimental (lower) profiles of a 283 K expansion
Fig. 44  HNO₄ profiles immediately following expansion of H₂O₂ and N₂O₅ into the cell

<table>
<thead>
<tr>
<th>Curve</th>
<th>Temperature</th>
<th>([N_2O_5] \times [H_2O_2])</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>263 K</td>
<td>(7.4 \times 10^{30}) molecules²/cm⁶</td>
</tr>
<tr>
<td>B</td>
<td>263 K</td>
<td>(2.2 \times 10^{30}) &quot; &quot; &quot;</td>
</tr>
<tr>
<td>C</td>
<td>273 K</td>
<td>(3.2 \times 10^{30}) &quot; &quot; &quot;</td>
</tr>
<tr>
<td>D</td>
<td>273 K</td>
<td>(7.4 \times 10^{30}) &quot; &quot; &quot;</td>
</tr>
<tr>
<td>E</td>
<td>273 K</td>
<td>(1.1 \times 10^{30}) &quot; &quot; &quot;</td>
</tr>
<tr>
<td>F</td>
<td>273 K</td>
<td>(4.1 \times 10^{30}) &quot; &quot; &quot;</td>
</tr>
<tr>
<td>G</td>
<td>283 K</td>
<td>(7.4 \times 10^{30}) &quot; &quot; &quot;</td>
</tr>
<tr>
<td>H</td>
<td>283 K</td>
<td>(1.1 \times 10^{30}) &quot; &quot; &quot;</td>
</tr>
</tbody>
</table>
Fig. 44

Graph showing the concentration of $\text{HO}_2\text{NO}_2$ as a function of time (seconds). The concentration is given in units of $10^{14}$ molecules/cm$^3$. The graph compares different conditions labeled A through H.
<table>
<thead>
<tr>
<th>A</th>
<th>263K</th>
<th>$7.4 \times 10^{-30}$ molecules$^2$/cm$^6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>263K</td>
<td>$2.2 \times 10^{-30}$</td>
</tr>
<tr>
<td>C</td>
<td>273K</td>
<td>$3.2 \times 10^{-30}$</td>
</tr>
<tr>
<td>D</td>
<td>273K</td>
<td>$7.4 \times 10^{-30}$</td>
</tr>
<tr>
<td>E</td>
<td>273K</td>
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<tr>
<td>F</td>
<td>273K</td>
<td>$4.1 \times 10^{-30}$</td>
</tr>
<tr>
<td>G</td>
<td>283K</td>
<td>$7.4 \times 10^{-30}$</td>
</tr>
<tr>
<td>H</td>
<td>283K</td>
<td>$1.1 \times 10^{-30}$</td>
</tr>
</tbody>
</table>

Many of the curves exhibit a marked change in slope between 10 and 15 seconds. From equation (55), the HNO$_4$ concentration at a given time will depend on the rate constant and the product $[H_2O_2][N_2O_5]$. From the curves and the values of $[H_2O_2][N_2O_5]$ listed, the unusual temperature dependence can be seen.

The HNO$_4$ profiles obtained from computer simulation, equation (55) and experiment are compared in Fig. 45. Curve A is experimentally obtained. Curves C and E are calculated from equation (55) using $k_7 = 5 \times 10^{-18}$ and $1 \times 10^{-17}$ cm$^3$/molecule-second, respectively. Curves B and D are from computer simulation using $k_7 = 5 \times 10^{-18}$ and $1 \times 10^{-17}$ cm$^3$/molecule-second, respectively. Curve F is the build up of the total gas concentration in the cell divided by 3500. The curves obtained by computer simulation and equation (55) are in good agreement during the period initially following expansion. The other reactions involving HNO$_4$ become important after several seconds and cause the deviation between the curves.
Fig. 45  Calculated and observed concentration profiles following expansion

Curve A - HNO₄, experimental

Curve B - HNO₄, computer simulation
  \[ k_7 = 5 \times 10^{-18} \text{ cm}^3/\text{molecule-second} \]

Curve C - HNO₄, calculated from eqn. (55)
  \[ k_7 = 1 \times 10^{-17} \text{ cm}^3/\text{molecule-second} \]

Curve D - HNO₄, computer simulation
  \[ k_7 = 5 \times 10^{-18} \text{ cm}^3/\text{molecule-second} \]

Curve E - HNO₄, calculated from eq. (55)
  \[ k_7 = 1 \times 10^{-17} \text{ cm}^3/\text{molecule-second} \]

Curve F - total pressure divided by 3500, experimental
Fig. 45
The experimental curve is in poor agreement with all of the calculated curves. It is unlikely that the observed behavior is due to the reactants not cooling until several seconds after expansion. The process of expansion should provide significant cooling and the gases should be adequately prechilled by the lines before mixing. It is also unlikely that heterogeneous decomposition is responsible for the lack of agreement. The computer simulation includes a first order decomposition of HNO₄ (k = 1 x 10⁻³ second⁻¹) which is used to simulate a heterogeneous decomposition. The rate would have to be much larger to be responsible for the observed behavior. Such a large rate is inconsistent with the behavior of HNO₄ at longer time periods. An estimate of the heterogeneous rate constant can be obtained from the experiments in which NO was present with the reactants. The difference in HNO₄ concentrations in the expansion with and without NO is due to the decomposition of HNO₄ into HO₂ and NO₂. The HO₂ reacts with NO and cannot reform HNO₄. The unimolecular decomposition accounts for part of the loss and the rest is due to heterogeneous decomposition. From computer simulations of these expansions, it is estimated that the HNO₄ heterogeneous rate is 5 x 10⁻³ second⁻¹ or less. This is in the same range as that observed for H₂O₂ and N₂O₅.
It is unlikely that the observed behavior of the HNO₄ build-up is due to HNO₄ reacting with another species in the system. The species present were substantially the same as those present in systems used by other workers who observed no anomalous behavior.

The observed concentrations of HNO₄ following expansion of H₂O₂ and N₂O₅ was used to obtain a value for the rate constant for reaction (7) using equation (55). The results are listed in Table 13 for the runs listed in Tables 7-9 for one to fifteen seconds after expansion. For times shorter than ~10 seconds, there should be < 10 percent error in the calculated rate constant due to complicating reactions. All of the HNO₄ profiles exhibit a decrease in apparent rate constant of reaction (7) with time. The range of rate constants calculated varies widely and does not exhibit any trend with temperature. This type of behavior is highly unlikely in a gas phase bimolecular reaction.

The possibility of reaction (7) occurring by a heterogeneous pathway was investigated by observing the decay of N₂O₅ after expansion into the cell with H₂O₂. Semilog plots of the decay of N₂O₅ are shown in Fig. 46. The solid lines are experimental observations and the dashed line was obtained from a computer simulation. The N₂O₅ concentration was several times lower than that of H₂O₂ in all observations shown. Curvature occurred in the simulated result because N₂O₅ is involved in a number of reactions. The experimental decays exhibit variable decay behavior that is indicative of a heterogeneous reaction. The reaction of N₂O₅ with H₂O₂ is its major loss mechanism.
TABLE 13

<table>
<thead>
<tr>
<th>Time (seconds)</th>
<th>([\text{H}_2\text{O}_2][\text{N}_2\text{O}_5]) = 2.0 \times 10^{30} \text{molecules}^2/\text{cm}^6</th>
<th>\text{[HNO}_4\text{]} \text{molecules/cm}^3</th>
<th>k_g(\text{eff}) \text{cm}^3/\text{molecule-second}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
<td>5.1 \times 10^{-17}</td>
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</tr>
<tr>
<td>3</td>
<td>3.0 \times 10^{13}</td>
<td>5.1 \times 10^{-17}</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>7.2 \times 10^{13}</td>
<td>3.5 \times 10^{-17}</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>1.2 \times 10^{14}</td>
<td>2.8 \times 10^{-17}</td>
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</tr>
<tr>
<td>9</td>
<td>1.7 \times 10^{14}</td>
<td>2.4 \times 10^{-17}</td>
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</tr>
<tr>
<td>11</td>
<td>2.2 \times 10^{14}</td>
<td>2.1 \times 10^{-17}</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>2.6 \times 10^{14}</td>
<td>1.9 \times 10^{-17}</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>2.8 \times 10^{14}</td>
<td>1.6 \times 10^{-17}</td>
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</tr>
</tbody>
</table>

<table>
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<tr>
<th>Time (seconds)</th>
<th>([\text{H}_2\text{O}_2][\text{N}_2\text{O}_5]) = 1.15 \times 10^{30} \text{molecules}^2/\text{cm}^6</th>
<th>\text{[HNO}_4\text{]} \text{molecules/cm}^3</th>
<th>k_g(\text{eff}) \text{cm}^3/\text{molecule-second}</th>
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</thead>
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<tr>
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<td>3</td>
<td>1.9 \times 10^{13}</td>
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<td>3.8 \times 10^{13}</td>
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<td>5.4 \times 10^{13}</td>
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<td>8.6 \times 10^{13}</td>
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<td>1.1 \times 10^{14}</td>
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</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time (seconds)</th>
<th>([\text{H}_2\text{O}_2][\text{N}_2\text{O}_5]) = 1.1 \times 10^{30} \text{molecules}^2/\text{cm}^6</th>
<th>\text{[HNO}_4\text{]} \text{molecules/cm}^3</th>
<th>k_g(\text{eff}) \text{cm}^3/\text{molecule-second}</th>
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</thead>
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</tr>
<tr>
<td>3</td>
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<td>9</td>
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<td>11</td>
<td>6.0 \times 10^{13}</td>
<td>1.0 \times 10^{-17}</td>
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<td>13</td>
<td>7.3 \times 10^{13}</td>
<td>9.5 \times 10^{-18}</td>
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<tr>
<td>15</td>
<td>7.1 \times 10^{13}</td>
<td>7.4 \times 10^{-18}</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 46 Experimental and simulated $\text{N}_2\text{O}_5$ profiles after expansion
The data taken with the additional surface in the cell were somewhat noisy but indicate that the HNO₄ decay rate is larger when more surface is present. The increased surface did not increase the apparent rate of reaction (7) suggesting that the reaction may be occurring primarily on the metal end caps. An alternative explanation is that there is increased heterogeneous decomposition of the reactants, preventing an increase in the products of reaction (7).

The results of the investigation of the reaction of H₂O₂ and N₂O₅ indicate the reaction forms primarily HNO₃ and HNO₄ as reaction products. The reaction is predominantly heterogeneous in the reaction system used to study it. The evidence for this comes from the reactant concentration effects, the temperature and pressure dependence and the characteristics of the initial build-up of HNO₄. The unusual behavior of the HNO₄ dependence on H₂O₂ concentration is not what would be expected from a homogeneous reaction. The increasing apparent rate constant with decreasing temperature also suggests a heterogeneous mechanism. The H₂O₂ heterogeneous decay exhibits an increase in rate at lower temperatures. Both reactions could be related to the tendency of H₂O₂ to adhere to surfaces at low temperatures. The appearance of HNO₄ when N₂O₅ was expanded into an evacuated cell previously exposed to H₂O₂ at 253K supports this contention.

The variable behavior of the initial build-up of HNO₄ and the variability of the N₂O₅ decay in the presence of excess H₂O₂ also indicate the occurrence of a heterogeneous process. The results of expansions with extra surface in the cell do not disagree with this.
With the exception of the production of HNO₄, the chemistry of the H₂O₂-N₂O₅ system was adequately modeled by computer simulation, indicating the kinetics of the system are reasonably well-known.

Some further information that can be obtained from these studies is related to the relative rates of reactions (1) and (2). The HNO₄ formed by the reaction of H₂O₂ and N₂O₅ will undergo unimolecular, and possibly heterogeneous, decomposition to form HO₂ and NO₂. These species can react to form either of the products in (1) or (2).

Levine et al.¹² obtained a ratio of k₂/k₁ of 0.7 ± 0.4 at 1 atmosphere total pressure and at 298K. Graham et al.⁴ obtained k₂/k₁ < 0.001 at 1 atmosphere and at temperatures from 254 to 283K. Howard¹⁶ obtained an upper limit for k₂ of 3 x 10⁻¹⁵ cm³/molecule-second and a ratio of k₂/k₁ < 0.15 at 3 torr and 298K.

Scans through the regions where HONO absorbs following expansion of H₂O₂ and N₂O₅ indicated no detectable absorption by HONO with a detection sensitivity of < 3 x 10⁻¹³ molecules/cm³. These expansions were done at 263K and final pressures of 30 to 70 torr. From computer simulations, the upper limit for k₂ is 5 x 10⁻¹⁴ cm²/molecule-second. Using the equation of Graham et al.⁴ for k₁, an upper limit of k₂/k₁ < 0.05 is obtained for 263K and 30 torr.
A. Experimental Procedures and Data

1. Reaction System for the Investigation of OH + HNO₄

Any chemical system used to investigate the reaction of OH with HNO₄ will be complicated. All useful methods of preparation of HNO₄ in the gas phase contain impurities, and not all methods are capable of generating HNO₄ concentrations large enough to be easily observed using infrared techniques. HNO₄, as well as some of the impurities, undergo heterogeneous reactions, ruling out the use of a static system for this study.

Not all of the preparation methods are capable of generating steady flows of HNO₄. The preparation used is the reaction of N₂O₅ with H₂O₂, which is primarily heterogeneous in the apparatus used. Attempts were made to use the preparative method for HNO₄ developed by the group at SRI. Flowing the evolved gases into the cell yielded little or no HNO₄, as determined by infrared absorption. Any attempt to increase the amount of evolved HNO₄ from the preparation would produce violent bubbling, culminating in a pressure explosion. This technique was abandoned in favor of the H₂O₂–N₂O₅ preparation method.

Stable flows of H₂O₂ and N₂O₅ were produced by passing "high dry" grade nitrogen through temperature-controlled saturators containing N₂O₅ and H₂O₂. The nitrogen was passed through a silica gel trap immersed in an isopropanol–dry ice slush bath prior to entry into the N₂O₅ saturator.
$N_2O_5$ saturator to minimize production of $HNO_3$ by the heterogeneous reaction of $N_2O_5$ with $H_2O$ in the carrier gas. The flows of $H_2O_2$ and $N_2O_5$ were mixed outside the cell. The combined flows were flowed through one of disperser tubes into the cell. Nitrogen was added at the mixing region to dilute the concentrations of the reactants and to generate the desired flow rate. The flow passed out of the cell through the other disperser tube and was exhausted into a fume hood. The flow rates were monitored with calibrated flow meters.

$HNO_4$ concentrations in excess of $2 \times 10^{15}$ molecules/cm$^3$ were generated in this way. Higher concentrations probably could have been generated by increasing the concentrations of the reactants, although no attempt was made to do so. The $HNO_4$ concentrations appeared to be quite stable with time, with less than 5 percent variation over a period of several hours. The major impurities, besides the unreacted reactants, were $HNO_3$, $H_2O$ and $NO_2$. $HNO_3$ is produced by the reaction of $H_2O_2$ and $N_2O_5$, as well as being an impurity in $N_2O_5$ and a product of the primarily heterogeneous reaction of $H_2O$ and $N_2O_5$. $H_2O$ is a product of the heterogeneous decomposition of $H_2O_2$. $NO_2$ is a decomposition product of $N_2O_5$ and $HNO_4$.

$OH$ was generated by a multi-step process initiated by the photolysis of $NO_2$.

\[
NO_2 + h\nu \rightarrow NO + O
\]
\[
O + NO_2 \rightarrow NO_3 + O_2
\]
\[
2x(HNO_4 + M \rightarrow HO_2 + NO_2 + M)
\]
\[
2x(NO + HO_2 \rightarrow OH + NO_2)
\]

net: $2HNO_4 + h\nu \rightarrow 2OH + 2NO_2 + O_2$
Black lamps were used as the light source for photolysis. The output of the lamps (Fig. 7) provides good overlap with the near UV NO₂ absorption band. The other compounds absorb only weakly in this region, minimizing the effect of interference by their photolysis products.

To minimize the effect of heterogeneous reactions on the kinetics of the system, the black lamps were turned on and off periodically to induce periodic changes in the concentrations of the intermediates such as NO, O and OH. The fluctuations in the intermediates will induce changes in the concentrations of the reactants and products which can be observed by infrared absorption. The technique of molecular modulation⁹⁸ is based on this concept.

In the absence of interfering reactions, the reactions that will occur following the reactions in (56) will depend on the competition for OH by various species in the system. If OH + NO₂ + M is faster than other OH reactions and NO₂ is present in large amounts,

\[
2\text{HNO}_4 + \text{hv} \rightarrow 2\text{OH} + 2\text{NO}_2 + \text{O}_2 \\
2\times (\text{OH} + \text{NO} + \text{M} \rightarrow \text{HNO}_3 + \text{M})
\]

net: \[2\text{HNO}_4 + \text{hv} \rightarrow 2\text{HNO}_3 + \text{O}_2\] (57a)

will occur. If almost all of the OH is consumed by reaction with HNO₄, then the following scheme will occur.

\[
2\text{HNO}_4 + \text{hv} \rightarrow 2\text{OH} + 2\text{NO}_2 + \text{O}_2 \\
2\times (\text{OH} + \text{HNO}_4 \rightarrow \text{H}_2\text{O} + \text{NO}_2 + \text{O}_2)
\]

net: \[4\text{HNO}_4 + \text{hv} \rightarrow 4\text{NO}_2 + 2\text{H}_2\text{O} + 3\text{O}_2\] (57b)
These extreme cases indicate the effect of the relative rates of reaction of \( \text{OH} \) with \( \text{NO}_2 \) and \( \text{HNO}_4 \).

If \( \text{OH} \) reacts primarily with \( \text{NO}_2 \), considerable amounts of \( \text{HNO}_3 \) should be generated. The quantum yield for \( \text{HNO}_4 \) destruction should be two, and the concentration of \( \text{NO}_2 \) should not change as the lamps are turned on and off.

If \( \text{OH} \) reacts primarily with \( \text{HNO}_4 \), no \( \text{HNO}_3 \) should be generated. The quantum yield for \( \text{HNO}_4 \) destruction should be twice as high as in the previous situation. Production of \( \text{NO}_2 \) would occur while the lamps are on, and the amount of \( \text{NO}_2 \) produced should equal the amount of \( \text{HNO}_4 \) destroyed.

The actual situation is likely to be intermediate between these two extremes. The relative amounts of \( \text{HNO}_3 \) and \( \text{NO}_2 \) produced should provide an indication of the rate of \( \text{OH} + \text{HNO}_4 \) relative to the rate of \( \text{OH} + \text{NO}_2 + \text{M} \).

The presence of \( \text{N}_2\text{O}_5 \) and \( \text{H}_2\text{O}_2 \) will complicate the chemistry, as they can generate reaction cycles that consume \( \text{NO}_2 \) but do not involve \( \text{HNO}_4 \).
\[
\begin{align*}
\text{NO}_2 + h\nu & \rightarrow \text{NO} + O \\
0 + \text{NO}_2 & \rightarrow \text{NO} + O_2 \\
2x(\text{N}_2\text{O}_5 & \rightarrow \text{NO}_2 + \text{NO}_3) \\
2x(\text{NO} + \text{NO}_3 & \rightarrow \text{NO}_2 + \text{NO}_2)
\end{align*}
\]

net: \(2\text{N}_2\text{O}_5 + h\nu \rightarrow 4\text{NO}_2 + O_2\)

\[
\begin{align*}
\text{NO}_2 + h\nu & \rightarrow \text{NO} + O \\
0 + \text{NO}_2 & \rightarrow \text{NO} + O_2 \\
2x(\text{NO} + \text{HO}_2 & \rightarrow \text{HO} + \text{NO}_2) \\
2x(\text{OH} + \text{H}_2\text{O}_2 & \rightarrow \text{H}_2\text{O} + \text{HO}_2)
\end{align*}
\]

net: \(2\text{H}_2\text{O}_2 + h\nu \rightarrow 2\text{H}_2\text{O} + O_2\)

The chemistry of the system becomes more complicated as these cycles are taken into consideration. The important gas phase reactions for this system are listed in Table 14. The number of OH radicals produced per photon will be reduced due to the reactions competing for the consumption of oxygen atoms and NO. Once OH is produced it may react with either \(\text{NO}_2, \text{HNO}_4, \text{H}_2\text{O}_2\) or \(\text{HNO}_3\). The branching that occurs here will have an effect on the amplitudes of the concentration fluctuations observed as the lamps are turned on and off.

There are a number of heterogeneous reactions that occur in the system. \(\text{HNO}_4\) and \(\text{H}_2\text{O}_2\) decompose on the cell walls. A number of the heterogeneous reactions discussed previously and elsewhere\(^{59-62,92}\)
<table>
<thead>
<tr>
<th></th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>OH + HNO₄ → H₂O + NO₂ + O₂</td>
</tr>
<tr>
<td>2</td>
<td>NO + NO₂ → NO + O</td>
</tr>
<tr>
<td>3</td>
<td>NO + NO → NO₃</td>
</tr>
<tr>
<td>4</td>
<td>NO + NO → NO₂</td>
</tr>
<tr>
<td>5</td>
<td>NO + HO₂ → HO + NO₂</td>
</tr>
<tr>
<td>6</td>
<td>NO + NO₃ → NO₂ + NO₂</td>
</tr>
<tr>
<td>7f,7r</td>
<td>N₂O₅ → NO₂ + NO₃</td>
</tr>
<tr>
<td>8f,8r</td>
<td>HNO₄ → HO₂ + NO₂</td>
</tr>
<tr>
<td>9</td>
<td>NO₂ + NO₃ → NO + NO₂ + O₂</td>
</tr>
<tr>
<td>10</td>
<td>HO₂ + HO₂ → H₂O₂ + O₂</td>
</tr>
<tr>
<td>11</td>
<td>OH + NO₂ → HNO₃</td>
</tr>
<tr>
<td>12</td>
<td>OH + HNO₄ → H₂O + NO₂ + O₂</td>
</tr>
<tr>
<td>13</td>
<td>OH + H₂O₂ → H₂O + HO₂</td>
</tr>
<tr>
<td>14</td>
<td>OH + HNO₃ → H₂O + NO₃</td>
</tr>
</tbody>
</table>
could occur in the system as well. With the exception of NO, the concentration of none of the species involved in the reactions varies strongly with the lamp output. The heterogeneous reaction of NO with H$_2$O$_2$ appears to be slow, and consequently is unimportant in this system. The rates of the other heterogeneous reactions should not be strongly affected by presence or absence of the photolytic light. Thus, the observed fluctuations in the concentrations of the species monitored should not be influenced by heterogeneous reactions that may occur.

2. Experimental Technique

There are a number of three body reactions that are of importance in this system. The pressure regime in which the experiments are done will strongly affect the kinetics of the system. At one atmosphere pressure, reaction (3) in Table 14 will compete with reaction (2) in Table 14 for oxygen atoms and reduce the amount of NO produced, as well as generate more NO$_3$. The net effect will be that fewer OH radicals will be produced at one atmosphere pressure than at lower pressures. The reaction rate of reaction (11) (Table 14) is fast at one atmosphere pressure and, in most cases, will be a major loss term for OH in the system. At lower pressures, however, the equilibria between HNO$_4$ $\rightarrow$ NO$_2$ + NO$_2$ and N$_2$O$_5$ $\rightarrow$ NO$_2$ + NO$_3$ will be slower than they would be at one atmosphere.

It was decided to operate at one atmosphere pressure for these experiments. There is less diffusion to the walls, reducing the effect of heterogeneous reactions. The infrared cross sections of NO$_2$, H$_2$O$_2$ and H$_2$O are larger at one atmosphere, making these species
easier to monitor. The flows of the reactants and carrier gas are easier to control and stabilize at one atmosphere than at lower pressures. The \( \text{HNO}_4 \) and \( \text{N}_2\text{O}_5 \) equilibria will be faster, making the equilibria more useful for predicting \( \text{HO}_2 \) and \( \text{NO}_2 \) concentrations.

The experiments were done at 263 K, 273 K and 283 K. Limitations on the temperature range that could be studied were imposed by the black lamps and by the kinetics of the system. The output of the lamps decreases with temperature. The amplitudes of the fluctuations induced by the lamps is proportional to the lamp output, and below 263 K, the fluctuations would be difficult to detect and would require extensive averaging. At temperatures above 283 K, the ratio of \( \text{NO}_2 \) to \( \text{HNO}_4 \) becomes large enough that virtually all of the \( \text{OH} \) will react with \( \text{NO}_2 \). The \( \text{NO}_2 \) concentration must be kept low enough such that not all the \( \text{OH} \) will react by reaction (11) (Table 14). It must be large enough to generate a detectable signal when the lamps are turned on and off. The amplitude of the fluctuations induced by the lamps will be proportional to the amount of \( \text{NO}_2 \), as well as the light intensity.

The experiments were performed by producing stable flows of \( \text{N}_2\text{O}_5 \), \( \text{H}_2\text{O}_2 \), and \( \text{N}_2 \) carrier gas through the cell. The concentrations of \( \text{HNO}_3 \), \( \text{HNO}_4 \), \( \text{H}_2\text{O}_2 \), \( \text{H}_2\text{O} \), \( \text{N}_2\text{O}_5 \) and \( \text{NO}_2 \) were monitored first without and then with the photolytic lamps turned on. If necessary, the flow rates were adjusted so there was sufficient \( \text{HNO}_4 \) present and that the \( \text{NO}_2/\text{HNO}_4 \) ratio was not too large. In addition, neither of the reactants could be in large excess because they would dominate the chemistry by the cycles mentioned above.
Once the desired flow had been obtained, the lamps were turned on and off periodically by a stable low frequency square wave source driving the lamp flasher. Early experiments were done using molecular modulation techniques to obtain phase and amplitude information for each species observed. With lamp flashing frequencies in the range of 0.06 to 1.0 Hz, the amplitudes were too small to be observed without excessively long averaging periods, with the exception of NO\textsubscript{2}. The technique was abandoned in favor of directly observing the optical density fluctuation of each species as the lamps were turned on and off at a very low frequency.

These experiments were done by flowing the reactants and carrier gas through the cell with the lamps flashing with a period of 480 seconds. At this frequency, concentrations changed sufficiently to be observed by conventional infrared spectroscopy. After the concentrations had stabilized, each species of interest was observed in sequence. The monochromator was set to a wavelength on an absorption band of the molecule to be monitored. The transmitted light intensity was converted to voltage and fed into the Fabritek signal averager for storage. The signal was monitored for eight lamp flashing cycles. The process was repeated for all the compounds to be observed. The wavelengths to monitor concentrations are as follows:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Wavelength (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO\textsubscript{2}</td>
<td>6.258</td>
</tr>
<tr>
<td>H\textsubscript{2}O</td>
<td>6.634</td>
</tr>
<tr>
<td>HNO\textsubscript{3}</td>
<td>7.400</td>
</tr>
</tbody>
</table>
The transmitted light intensities are recorded before and after each experiment with the cell evacuated and filled with one atmosphere of carrier gas. These values are used to calculate the optical density at each wavelength. The wavelengths at which \( \text{H}_2\text{O}_2 \) and \( \text{N}_2\text{O}_5 \) were monitored overlapped with other absorptions. \( \text{H}_2\text{O}_2 \) was monitored on its Q branch, which overlapped with HNO\(_3\), \( \text{N}_2\text{O}_5 \) and HNO\(_4\). The wavelength at which \( \text{N}_2\text{O}_5 \) was monitored contains an absorption due to \( \text{H}_2\text{O}_2 \). The cross sections of \( \text{N}_2\text{O}_5 \), HNO\(_3\) and HNO\(_4\) at 7.896 \( \mu \text{m} \) were determined relative to the wavelengths at which they were monitored. The contribution due to HNO\(_3\) and HNO\(_4\) was subtracted from the observed optical density at 7.896 \( \mu \text{m} \). The resulting curve was stored. The contribution to this curve by \( \text{N}_2\text{O}_5 \) was fairly small; so, the uncorrected 8.040 \( \mu \text{m} \) curve was used to subtract out the \( \text{N}_2\text{O}_5 \) contribution. The 7.896 \( \mu \text{m} \) curve was then used to correct the 8.040 \( \mu \text{m} \) curve. The corrected 8.040 \( \mu \text{m} \) represents only \( \text{N}_2\text{O}_5 \) and was used to make the final correction to the 7.896 \( \mu \text{m} \) curve which was stored earlier.

The optical density curves are summed over the eight lamp periods to reduce noise and eliminate small random fluctuations in concentrations. The optical density curves are converted into concentrations by using the cross sections determined earlier. Cross sections for the curves obtained at 273 K and 283 K were obtained by interpolating between the values obtained at 263 K and 293 K. A least squares linear regression program is used to obtain slopes of the curves for each quarter and half of the lamp period. In a few cases, the curve exhibited a net upward or downward slope due to a small increase or
decrease in concentration during the course of the run. This was corrected for by adjusting the net slope of the curve to zero. The rate of change of the curves was small, ranging from somewhat larger than $10^{11}$ molecules/cm$^3$-second to less than $10^9$ molecules/cm$^3$-second. The concentrations of the species observed were in the range of about $10^{13}$ to $10^{15}$ molecules/cm$^3$.

3. Actinometry

The light intensity produced by the black lamps must be known accurately in order to analyze the observed behavior of the species in the reaction system. The light intensity will directly affect the amount of NO generated and consequently it will be related to the amount of OH produced. The emitted light will primarily photolyze NO$_2$, although the long wavelength tails of the UV absorptions of N$_2$O$_5$, H$_2$O$_2$, HNO$_4$ and HNO$_3$ overlap slightly with the black lamp output.

The light intensities were determined by photolyzing NO$_2$ in one atmosphere of N$_2$ at 283 K, 273 K and 263 K, and observing the decay of NO$_2$ at 6.258 μm. Three types of measurements were made. In the first two measurements, a bulb was filled with a measured pressure of NO$_2$ and then expanded into the evacuated cell. Nitrogen was added to one atmosphere pressure. In the first type of measurement, the NO$_2$ profile was recorded in the Fabritek signal averager while the lamps were on at a constant current. In the second type of measurement, the lamps were turned on and off with a period of 480 seconds while the NO$_2$ profile was recorded in the Fabritek.
The third type of measurement involved flowing NO\textsubscript{2} in one atmosphere of nitrogen while the lamps were turned on and off periodically. The fluctuation in NO\textsubscript{2} concentration was again monitored with the Fabritek. The NO\textsubscript{2} profile was analyzed in the same manner as the profiles obtained from the H\textsubscript{2}O\textsubscript{2}-N\textsubscript{2}O\textsubscript{5} flow experiments.

The observed decays were analyzed by comparing them with computer simulations with different light intensities using the CHEMK kinetics computer program. An average near-UV cross section of 4.8 \times 10^{-19} \text{ cm}^2/\text{molecule} was used for NO\textsubscript{2} in the simulations. This was derived from the product of the corrected lamp spectrum and the NO\textsubscript{2} UV absorption spectrum at one nm intervals, which were then summed for \( \lambda = 290 \) to 460 nm and divided by the integrated lamp spectrum. Any error in the value of the average NO\textsubscript{2} cross section will be compensated by the calculated light intensity, since the product of the cross section and the light intensity determines the number of molecules photolyzed.

Similar calculations were done for N\textsubscript{2}O\textsubscript{5}, H\textsubscript{2}O\textsubscript{2}, HNO\textsubscript{4} and HNO\textsubscript{3} to determine how significant the photolysis of these species was. The photolysis rates of all of these compounds were less than 0.5 percent of the photolysis rate of NO\textsubscript{2}.

The light intensities derived from the second and third types of measurements were in good agreement, being within 10 percent of each other. The light intensity obtained from the first type of measurement was somewhat higher. This was due to the type of source activating the lamp driver. A lower current was supplied by the very low
frequency generator than that supplied for the dc experiments. Thus, the lamps had greater output during the dc runs.

There was a tendency for the lamp intensity to decrease slightly during the course of an experiment. During the four minute period for lamps were on, the drift in the output was generally less than ±3 percent of the average. The lamps do exhibit an initial output spike when first turned on.

Since the second and third types of actinometry measurements more closely simulate the experimental conditions, the light intensity values obtained from these runs were used in the analysis of the results. The light intensities at each temperature were:

- 263 K: $0.5 \times 10^{15}$ photons/cm$^2$-second
- 273 K: $1.0 \times 10^{15}$
- 283 K: $2.5 \times 10^{15}$

B. Results and Discussion

The observed concentration profiles of NO$_2$, HNO$_4$, HNO$_3$, N$_2$O$_5$, and H$_2$O$_2$ provide a basis with which the rate constant for the reaction of OH with HNO$_4$ can be determined. The profiles can also provide information on the products of this reaction. Typical experimental profiles of the observed species are illustrated in Fig. 47 (from run F). NO$_2$ and HNO$_4$ generally had the largest fluctuations in concentration. The lamps were on during the first half of the run, and off during the second half of the run. The run shown was done at 283 K.
Fig. 47 Concentration profiles during one lamp cycle, starting when the lamps are turned on.
The concentrations of \( \text{NO}_2 \), \( \text{HNO}_4 \), \( \text{HNO}_3 \), \( \text{H}_2\text{O}_2 \) and \( \text{N}_2\text{O}_5 \) for the seven runs used in the analysis are listed in Table 15. The average slopes of the concentration profiles for the half cycle during which the lamps were on were obtained by a linear regression program run in the PDP-8/L minicomputer interfaced to the Fabritek. The experimentally derived slopes for all the runs are listed in Table 16 with the standard deviations from the least square fit analysis. Actual uncertainties may be larger in some cases. This is due to errors in the correction for spectral overlap, and correction for drift in concentration during a run.

To be able to develop a value for the rate constant of the reaction of \( \text{OH} \) with \( \text{HNO}_4 \), a method must be devised to analyze the slopes in terms of the rate constant. Analytic expressions for the chemical system are difficult to generate because of its complexity and the large fluctuations in concentrations of the intermediates, particularly \( \text{NO}, \text{O}, \text{and OH} \). Use of the steady-state approximation is unlikely to be valid for these three intermediates.

Another difficulty is the occurrence of heterogeneous reactions in the system. These reactions can affect the concentrations of a number of the observed species. The use of light modulated at a low frequency should reduce their influence, since the heterogeneous rates should not be influenced by the presence or absence of light. An exception to this are heterogeneous reactions involving \( \text{NO} \), since the NO concentration is closely coupled to the light output.
<table>
<thead>
<tr>
<th></th>
<th>NO₂</th>
<th>HNO₄</th>
<th>HNO₃</th>
<th>H₂O₂</th>
<th>N₂O₅</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>263K</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Run A</td>
<td>1.6 x 10¹⁴</td>
<td>1.8 x 10¹⁵</td>
<td>3.0 x 10¹⁵</td>
<td>7.2 x 10¹⁴</td>
<td>5.5 x 10¹³</td>
</tr>
<tr>
<td>Run B</td>
<td>1.7 x 10¹⁴</td>
<td>1.5 x 10¹⁵</td>
<td>2.7 x 10¹⁵</td>
<td>1.0 x 10¹⁵</td>
<td>1.7 x 10¹⁴</td>
</tr>
<tr>
<td>Run C</td>
<td>9.3 x 10¹³</td>
<td>7.0 x 10¹⁴</td>
<td>1.4 x 10¹⁵</td>
<td>2.4 x 10¹⁵</td>
<td>6.4 x 10¹³</td>
</tr>
<tr>
<td>Run D</td>
<td>1.7 x 10¹⁴</td>
<td>7.9 x 10¹⁴</td>
<td>1.5 x 10¹⁵</td>
<td>5.3 x 10¹⁴</td>
<td>1.2 x 10¹⁴</td>
</tr>
<tr>
<td><strong>273K</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Run E</td>
<td>1.6 x 10¹⁴</td>
<td>8.1 x 10¹⁴</td>
<td>1.7 x 10¹⁵</td>
<td>2.4 x 10¹⁵</td>
<td>1.6 x 10¹⁴</td>
</tr>
<tr>
<td>Run F</td>
<td>6.0 x 10¹⁴</td>
<td>1.0 x 10¹⁵</td>
<td>2.7 x 10¹⁵</td>
<td>2.1 x 10¹⁴</td>
<td>4.2 x 10¹⁴</td>
</tr>
<tr>
<td>Run G</td>
<td>3.5 x 10¹⁴</td>
<td>6.0 x 10¹⁴</td>
<td>1.6 x 10¹⁵</td>
<td>4.8 x 10¹⁴</td>
<td>1.4 x 10¹⁴</td>
</tr>
</tbody>
</table>

TABLE 15

Concentrations in molecules/cm³
### Table 1a

Slopes in units of molecules/cm³-second

<table>
<thead>
<tr>
<th></th>
<th>NO₂</th>
<th>HNO₄</th>
<th>HNO</th>
<th>H₂O₂</th>
<th>N₂O₅</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>263K</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Run A</td>
<td>2.9 ± 0.4 x 10¹⁰</td>
<td>-3.8 ± 0.6 x 10¹⁰</td>
<td>-1.3 ± 1.3 x 10⁹</td>
<td>-3.5 ± 2.0 x 10⁹</td>
<td>1.5 ± 1.0 x 10⁹</td>
</tr>
<tr>
<td><strong>273K</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Run B</td>
<td>7.9 ± 0.2 x 10¹⁰</td>
<td>-7.6 ± 0.5 x 10¹⁰</td>
<td>1.0 ± 1.0 x 10¹⁰</td>
<td>-2.0 ± 0.5 x 10¹⁰</td>
<td>-0.5 ± 4.0 x 10⁹</td>
</tr>
<tr>
<td>Run C</td>
<td>2.7 ± 0.2 x 10¹⁰</td>
<td>-4.3 ± 0.5 x 10¹⁰</td>
<td>-3.5 ± 5.0 x 10¹⁰</td>
<td>-4.8 ± 0.5 x 10¹⁰</td>
<td>-2.5 ± 2.0 x 10⁹</td>
</tr>
<tr>
<td>Run D</td>
<td>6.5 ± 0.6 x 10¹⁰</td>
<td>-7.6 ± 0.8 x 10¹⁰</td>
<td>-2.2 ± 2.0 x 10¹⁰</td>
<td>4.3 ± 4.0 x 10⁹</td>
<td>-4.5 ± 2.0 x 10⁹</td>
</tr>
<tr>
<td><strong>283K</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Run D</td>
<td>1.6 ± 0.1 x 10¹¹</td>
<td>-1.6 ± 0.2 x 10¹¹</td>
<td>2.5 ± 2.5 x 10¹⁰</td>
<td>-1.0 ± 0.2 x 10¹⁰</td>
<td>-9.0 ± 0.4 x 10¹⁰</td>
</tr>
<tr>
<td>Run F</td>
<td>6.6 ± 0.2 x 10¹¹</td>
<td>-4.7 ± 0.2 x 10¹¹</td>
<td>4.4 ± 1.0 x 10¹⁰</td>
<td>-3.4 ± 0.2 x 10¹⁰</td>
<td>-1.6 ± 0.2 x 10¹¹</td>
</tr>
<tr>
<td>Run G</td>
<td>3.6 ± 0.2 x 10¹¹</td>
<td>-3.0 ± 0.2 x 10¹¹</td>
<td>5.0 ± 2.0 x 10¹⁰</td>
<td>-5.7 ± 0.4 x 10¹⁰</td>
<td>-7.9 ± 0.2 x 10¹⁰</td>
</tr>
</tbody>
</table>
An alternative to deriving an analytic expression for the rate constant can be developed by tracing the destruction channels for intermediates after they are produced. A fairly simple mechanism can be developed, although the assumptions used to generate it may not be entirely valid.

The initial step of the system is the photolysis of NO₂, reaction 1 in Table 14. The O atom will react primarily with NO₂ to form the products NO + O₂ (reaction 2) or NO₃ (reaction 3). The relative rates of these reactions are known for one atmosphere pressure. The NO produced here will react with either HO₂ or NO₃. The HO₂ can be considered to come from the decomposition of HNO₄. The NO₃ can be considered to come from either reaction 3 or from N₂O₅ decomposition. The equilibrium constants for HNO₄ and N₂O₅ can be used to predict the relative concentrations of NO₃ and HO₂ from the observed concentrations of N₂O₅, HNO₄ and NO₂. These values, in turn can be used to calculate the relative rates of reactions (5) and (6) in Table 14, which determines the fraction of NO converted to OH.

If the assumptions made so far are valid, the number of OH radicals produced per photon absorbed can be determined, as well as the amount of formation or destruction of NO₂, HNO₄ and N₂O₅. The OH produced will be consumed by reactions (11)-(14) in Table 14. With the exception of reaction (12), the rate constants for these reactions are known. The relative rates of consumption of OH by these reactions will have an effect on the rate of change in concentration of NO₂, HNO₃, HNO₄ and H₂O₂. If the rate constant for OH + HNO₄ is small, most
of the OH will react with NO₂ and H₂O₂. NO₂ production will be small, HNO₃ production large, and HNO₄ destruction small when the lights are on. If the rate constant is large, HNO₄ can effectively compete with NO₂ and H₂O₂ for OH. This will increase NO₂ production, decrease HNO₃ production, and increase HNO₄ destruction during illumination of the system.

This simplified mechanism ignores a number of somewhat slower reactions, the flow-in and flow-out of all the species involved and assumes that HO₂ and NO₃ remain in equilibrium with NO₂, and HNO₄ and N₂O₅, respectively. It does qualitatively illustrate the behavior of the system and its dependence on the rate constant of OH with HNO₄. The use of the equilibria of reactions (8) and (9) in Table 14 to determine HO₂ and NO₃ concentrations is not likely to be valid at low temperatures, where the forward and reverse rates will be slow. The flow out of intermediates can be an important factor in the determination of their concentration. This is particularly true for NO.

Since the observed rates of change of concentrations when the lamps are on are in the range of 10⁻⁴ to 10⁻⁶ of the total concentration per second, fairly small production or destruction terms can significantly affect the observed result. To be able to quantitatively predict the rate of change of the observed species, and consequently obtain a value of the rate constant for reaction (12) in Table 14, a method is needed to accurately determine the behavior of all of the important species in the chemical system. The CHEM/K chemical kinetics computer program described previously was used for this purpose.
The list of reactions and rate constants used for modeling the chemical system used in this study is included in Appendix C. Inputs into the program included temperature, light intensity and lamp flashing period. The flow-in rates of $\text{NO}_2$, $\text{HNO}_4$, $\text{HNO}_3$, $\text{H}_2\text{O}_2$ and $\text{N}_2\text{O}_5$ were adjusted until the calculated concentrations agreed with the observed values. The flow-in rates help to correct for any unknown reactions not included in the reaction set. A reaction producing a species can be replaced by a flow-in term for that species if the reaction proceeds at a steady rate. A number of heterogeneous reactions may occur in this system and their occurrence can be compensated for by the flow terms. The program was run for a sufficient number of simulated lamp cycles such that there was little or no change in the concentration of any species from cycle to cycle. The final cycle of the output was used to determine the rate of change in concentrations during the period the lamps were on and the period when the lamps were off.

Programs were run to simulate each experimental run. The flow rates were adjusted using a value of $1.0 \times 10^{-12}$ cm$^3$/molecule-second for the rate constant of reaction (12) in Table 14. Programs were then run with this rate constant assigned values ranging from $2 \times 10^{-13}$ to $2 \times 10^{-11}$ cm$^3$/molecule-second without further adjustment in the flow rates. There was some variation of the concentrations of several species with the rate constant of $\text{OH} + \text{HNO}_4$. NO$_2$ was the species most strongly affected by this rate constant. These changes in concentration did not significantly affect the calculated rate of change of concentrations. Concentration profiles for NO$_2$, HNO$_4$, HNO$_3$, H$_2$O$_2$
and N₂O₅ are shown for a typical simulation in Fig. 48. The simulation done was of the experimental run shown in Fig. 47. The rate constant for the reaction of OH + HNO₄ used was 2 x 10¹² cm³/molecule-second.

The rate of change, or slope, of a concentration during a half cycle was determined by calculating the slope from the concentrations computed at various times during the half cycle and averaging them. In situations where either the concentration or slope did not change by large amounts during the half cycle, the initial and final concentrations were used to determine the slope. Slopes from the simulations were obtained for NO₂, HNO₄, HNO₃, H₂O₂ and N₂O₅, which are the same species for which the experimental values of the slopes were obtained. The experimentally determined slopes and the slopes from the simulations were then compared to determine which value of the rate constant for the reaction of OH + HNO₄ used in the simulations provided the best agreement. The slopes from the computer simulation for NO₂ and HNO₄ during the half cycle when the lamps were on are plotted against the rate constant used for OH + HNO₄ in Figs. 49-55 for experimental runs A through G. The experimentally determined slopes for NO₂ and HNO₄ are superimposed on the curves. The error bars indicate one standard deviation uncertainty in the experimental values.

Typical curves for calculated slopes of HNO₃, H₂O₂ and N₂O₅ vs. OH + HNO₄ rate constant are shown in Fig. 56 along with the experimental values from run C, the run being simulated. The calculated slopes of HNO₃, H₂O₂ and N₂O₅ usually do not exhibit a very strong dependence on the rate constant of the reaction of OH with HNO₄.
Fig. 48 Calculated concentration profiles during one cycle, starting when the lamps are turned on.
Fig. 49 Comparison of calculated and experimental slopes - Run A
Fig. 50 Comparison of calculated and experimental slopes - Run B
Fig. 52 Comparison of calculated and experimental slopes - Run D.
Fig. 53 Comparison of calculated and experimental slopes - Run E
Fig. 54  Comparison of calculated and experimental slopes - Run F
Fig. 55 Comparison of calculated and experimental slopes - Run G
Fig. 56 Comparison of experimental and calculated slopes for HNO₃, H₂O₂ and N₂O₅.
In general, the experimentally determined values of the slopes of HNO$_3$, H$_2$O$_2$ and N$_2$O$_5$ did not agree well with the calculated values.

There are a number of possible causes for the discrepancies between calculated and experimental values for HNO$_3$, H$_2$O$_2$ and N$_2$O$_5$. The HNO$_3$ slopes were generally small and the total HNO$_3$ concentration was large. The optical system exhibits a transmission minimum in the region that HNO$_3$ is monitored, possibly due to the overcoating on the mirrors in the cell. This resulted in a fairly small signal with which HNO$_3$ was monitored. The HNO$_3$ profiles usually exhibited a net change in concentration, even after the cycles were averaged. As a result, most of the runs required a correction to eliminate this. The concentration of nitric acid tended to be the most variable of the species monitored. It also has a tendency to adhere to the cell walls, increasing the possibility of its involvement in heterogeneous reactions. N$_2$O$_5$ also absorbs weakly at the wavelength at which HNO$_3$ was monitored, and corrections had to be made when this absorption was significant. These factors created considerable undertainty in the HNO$_3$ profile and made it unreliable as an indicator for the rate constant for OH + HNO$_4$.

H$_2$O$_2$ and N$_2$O$_5$ are both somewhat unstable and decompose heterogeneously. Their heterogeneous decomposition rates are variable and are dependent on the conditioning of the cell surfaces. Since it was not possible to observe all the species simultaneously, the heterogeneous decomposition rates could be different at the time of observation of different species. However, these rates should not contribute significantly to the observed slopes, unless a variable intermediate such as NO is involved in the decomposition mechanism.
The wavelengths used to monitor $H_2O_2$ and $N_2O_5$ overlap with other species. Absorption bands for $H_2O_2$ and $N_2O_5$ that are free of interfering absorptions are either too weak to be of use or are outside the spectral range of the optical system. The interfering absorptions were approximately corrected for by subtracting their estimated optical density contribution from the total optical density obtained at the monitoring wavelength. For $H_2O_2$, this involved making corrections for HNO$_4$, HNO$_3$ and $N_2O_5$. The wavelength used to monitor $N_2O_5$ has an interfering absorption by $H_2O_2$. This required first correcting for the HNO$_3$ and HNO$_4$ absorptions and then making iterative corrections for $N_2O_5$ and $H_2O_2$. The accuracy of the corrections is not as high as would be desirable. The correction for HNO$_3$ introduces a significant amount of noise into the curves. The temperature, pressure and concentration dependence of the cross sections of the interfering species at these wavelengths is unknown, and this introduces uncertainty to the corrections.

These factors make the reliability of the data obtained for changes in $H_2O_2$, $N_2O_5$ and HNO$_3$ low. In a number of runs, the slopes obtained for these species are small, contributing to the uncertainty. The poor agreement between the experimental data and the simulations supports the contention that the $H_2O_2$, $N_2O_5$ and HNO$_3$ results are not very reliable. The uncertainty and the potential error in the experimental data and the insensitivity of the slopes from the simulations to the rate constant for $OH + HNO_4$ supported the decision not to use them in the rate constant determination.
The data obtained from the observation of NO$_2$ and HNO$_4$ should be relatively free from the problems associated with H$_2$O$_2$, N$_2$O$_5$ and HNO$_3$. The slopes of both NO$_2$ and HNO$_4$ were reasonably large for all the runs. The simulations indicated that both species are fairly sensitive to the OH + HNO$_4$ rate constant.

The values for the rate constant for the slopes of HNO$_4$ and NO$_2$ from each run were obtained from the rate constant value at which the curve from the simulations agreed with the experimental determination, as indicated in Figs. 49–55. The uncertainties for these values of the rate constant were obtained by determining at which point on the experimental slope, increased or decreased by its uncertainty, would intersect the slope. The values were averaged to give an uncertainty for each rate constant determination. The mean of the values of the rate constant was obtained by weighted averaging, where the values were weighted by the inverse of their uncertainties. Weighted means were obtained for the points from the HNO$_4$ slopes, the NO$_2$ slopes and both slopes combined. The values for the rate constant of the reaction of OH with HNO$_4$ are:

<table>
<thead>
<tr>
<th>Data Type</th>
<th>Rate Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNO$_4$ data</td>
<td>$1.9 \pm 0.3 \times 10^{-12}$ cm$^3$/molecule-second</td>
</tr>
<tr>
<td>NO$_2$ data</td>
<td>$5.0 \pm 0.3 \times 10^{-12}$ &quot; &quot;</td>
</tr>
<tr>
<td>Combined data</td>
<td>$3.4 \pm 0.2 \times 10^{-12}$ &quot; &quot;</td>
</tr>
</tbody>
</table>
There is some discrepancy between the result from the HNO₄ data and the result of the NO₂ data. Part of this is due to the high values for the NO₂ data obtained in runs F and G.

There are several sources of error that should be considered. The photolytic light intensity must be well known to accurately simulate the experimental run. An error of 20 percent in the light intensity used in the simulation can shift the slope vs. rate constant curve sufficiently to cause as much as a 50 percent error in the value obtained for the rate constant. The lamps were monitored continuously during the experiments with a UV photodiode-Schott UG-5 filter combination. The lamps exhibited some fluctuation during each cycle, but this was less than ± 3 percent of the average value. There was a small decrease in light intensity during the course of the experiments. This was generally less than 5 percent. Every effort was made to have identical settings for each run. The light intensity variation, as indicated by the lamp monitor, was less than 5 percent from run to run at a given temperature.

Heterogeneous reactions, particularly those involving intermediates, could influence the observed chemistry. The heterogeneous oxidation of NO into NO₂ could significantly increase the NO₂ slopes in the system. Other possibilities are heterogeneous reactions of NO with HNO₃ or H₂O₂.

\[
\begin{align*}
\text{NO} + \text{HNO}_3 & \rightarrow \text{HONO} + \text{NO}_2 \\
\text{NO} + \text{H}_2\text{O}_2 & \rightarrow \text{HONO} + \text{OH}
\end{align*}
\]
These reactions could have an effect on the slopes of the species observed if their rates were large enough. The most significant effect of these reactions would be to reduce the amount of NO available to form OH. NO concentrations were generally below that observable by infrared spectroscopy in the apparatus used, since very long path lengths were not obtainable. Observation of NO concentrations would provide a check of the possibility of other reactions of NO.

Errors in the computer simulation of the chemistry could come from an inadequate reaction set or incorrect rate constants. A considerably larger reaction set, which included a number of reactions considered to be of marginal importance, was tested and was found to give essentially the same results as the reaction set listed in Appendix C. Most of the rate constants for the reactions used in the reaction set are well known. The slopes generated by the program are not very sensitive to the flow rates, and the flow rate uncertainty is less than 10 percent. Heterogeneous or unknown reactions that have not been included in the reaction set of the simulation could be responsible for generating curves that produce an apparent discrepancy between the HNO₄ and NO₂ results.

The reactions that affect the HNO₄ profile are

\[ \text{HNO}_4 + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{NO}_2 + \text{O}_2 \]
The NO₂ profile is affected by a large number of reactions. Consequently, the results obtained from the HNO₄ are considered to be a better indicator of the rate constant for OH + HNO₄ than those obtained from NO₂. By weighting the HNO₄ data twice as much as the NO₂ data, a value of

\[ k(\text{OH} + \text{HNO}_4) = 2.9 \pm 1.0 \times 10^{-12} \text{ cm}^3/\text{molecule-second} \]

is obtained. The uncertainty given is obtained from taking all known sources of error into consideration. This value is in agreement with the upper limits for the rate constant given by Graham et al.¹⁸ and Barker et al.²³

The value does not disagree with rate constant for other OH hydrogen abstraction reactions. A few of the reactions are listed below with the \( \Delta H^* \) and rate constant for each.

<table>
<thead>
<tr>
<th>reaction</th>
<th>( \Delta H^* ) (kcal/mole)</th>
<th>rate constant (cm³/molecule-second)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2 )</td>
<td>-67.6</td>
<td>3.5 \times 10^{-11}</td>
</tr>
<tr>
<td>( \text{OH} + \text{HNO}_2 \rightarrow \text{H}_2\text{O} + \text{NO}_2 )</td>
<td>-40.2</td>
<td>6.6 \times 10^{-12}</td>
</tr>
<tr>
<td>( \text{OH} + \text{HNO}_4 \rightarrow \text{H}_2\text{O} + \text{NO}_2 + \text{O}_2 )</td>
<td>-48.4</td>
<td>2.9 \times 10^{-12}</td>
</tr>
<tr>
<td>( \text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2 )</td>
<td>-34.0</td>
<td>1.6 \times 10^{-12}</td>
</tr>
<tr>
<td>( \text{OH} + \text{HNO}_3 \rightarrow \text{H}_2\text{O} + \text{NO}_3 )</td>
<td>-17.8</td>
<td>8.5 \times 10^{-14}</td>
</tr>
</tbody>
</table>
The products of the reaction OH with HNO$_3$ have been recently identified in this laboratory as H$_2$O and NO$_3$.\textsuperscript{99}

This study also indicates that the products of the reaction of OH with HNO$_4$ are H$_2$O + NO$_2$ + O$_2$. Simulations which used a product set of either HO$_2$ + HNO$_3$ or H$_2$O$_2$ + NO$_3$ gave NO$_2$ slopes an order of magnitude below that obtained with a product set of H$_2$O + NO$_2$ + O$_2$. NO$_2$ slopes of such a small magnitude cannot be reconciled with the experimental results.

Several attempts were made to observe HONO in the system. HONO concentrations were below $-3 \times 10^{13}$ molecules/cm$^3$, the approximate detection limit in the system. HONO concentrations were expected to be low because it would be photolyzed by the photolytic light and the reactions producing it are fairly slow. As a result, the upper limit for the rate constant for the reaction

\[
\text{HO}_2 + \text{NO}_2 \rightarrow \text{HONO} + \text{O}_2
\]

obtained from the experiments involving expansion of H$_2$O$_2$ and N$_2$O$_5$ could not be improved.
A. Experimental Procedures and Data

The experiments described here were designed to simulate the ozone generation cycle shown in (21). They were performed at total pressures of 0.1 and 1.0 atmosphere at three temperatures: 263 K, 293 K and 313 K. NO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub> and CO were flowed into the cell in O<sub>2</sub> carrier gas. When the photolytic lamps were turned on, the intermediates involved in the cycle were generated.

The gases were flowed with the photolytic lamps off. The gases were mixed outside the cell and flowed through both disperser tubes. The flow was exhausted through the large port at one end of the cell. The flows were measured and maintained at a fixed flow rate using calibrated flow meters. The flows were regulated to give reasonable optical densities of the species of interest. After flowing for 30 minutes, the signals were measured at wavelengths where the species of interest absorb. The flow was then stopped. The monochromator was set at a wavelength to observe the decay profile of a particular species and the lamps were turned on. The signal was stored in the Fabritek signal averager. The lamps were turned off after 30 minutes and the signals were again measured at wavelengths of interest. This was done to get the concentrations of the species before and after photolysis. The wavelengths and the species observed are listed below.
The flow was then restored at the same flow levels. This process was repeated until the decay profiles of all the species listed above had been obtained. No data were collected during the first photolysis run, because the concentrations of a number of species had not attained stable levels.

This process was varied somewhat for the experiments done at 0.1 atmosphere pressure. The flow was started and allowed to continue for 30 minutes, at the end of which the transmitted light intensity at the eight wavelengths listed was observed. The flow was then stopped and the cell was rapidly evacuated to 75 torr. Observation was begun at one wavelength, and the photolytic lamps were turned on. At the end of 30 minutes, the lamps were turned off and the transmitted light intensities at the wavelengths of interest were observed. The cell was then filled with O₂ carrier gas to one atmosphere and the flows were restarted. As with the one atmosphere experiments, the process was repeated until all desired species had been observed. The first run was not used to allow concentrations to stabilize.

The light intensities to be used as references for the observations made before, during and after photolysis were obtained before and after each set of photolysis runs. Early experiments were hampered by excessive change in the transmitted light intensity over

<table>
<thead>
<tr>
<th>Wavelength (μm)</th>
<th>Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.428</td>
<td>NO₂</td>
</tr>
<tr>
<td>4.238</td>
<td>CO₂</td>
</tr>
<tr>
<td>4.609</td>
<td>CO</td>
</tr>
<tr>
<td>5.244</td>
<td>NO</td>
</tr>
<tr>
<td>6.634</td>
<td>H₂O</td>
</tr>
<tr>
<td>7.400</td>
<td>HNO₃</td>
</tr>
<tr>
<td>8.040</td>
<td>H₂O₂</td>
</tr>
<tr>
<td>9.477</td>
<td>O₃</td>
</tr>
</tbody>
</table>
the course of a set of runs. This was caused by the degradation of the mirror coatings by H$_2$O$_2$ and HNO$_3$. A sufficiently thick (2000 Å) overcoat of MgF$_2$ on the mirrors prevented the occurrence of this in later experiments. The reference light intensities were obtained with the cell evacuated and at 0.1 and 1.0 atmosphere total pressure. There were generally some changes in the reference light level with pressure.

The measurements at the wavelengths of interest that were made before and after each run were used to determine the concentrations of the listed species before and after each photolysis run. The concentrations were averaged over the set of runs done to characterize the chemistry of each condition. The decay profiles obtained were adjusted to agree with the initial values of the average concentrations when necessary. The initial average concentrations were used as inputs for computer simulations of the kinetics. The averaged initial concentrations for the runs are listed in Table 17.

Separate observations were made of ozone in the system, since it was present in very low concentrations. The CaF$_2$ windows used in early experiments were replaced with BaF$_2$ windows for increased transmission in the 10 μm region. The spectrometer path length was increased to 32 meters to provide increased sensitivity. The runs were performed at 293 K and one atmosphere pressure. The techniques described previously to obtain decay profiles were also used here. The monochromator was set at 9.478 μm and data were collected by the Fabritek. The lamps were turned on 30 seconds after data collection
TABLE 17

Initial Concentrations for HO\textsubscript{x}-NO\textsubscript{x}-CO\textsubscript{x} Runs

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Pressure</th>
<th>NO\textsubscript{2}</th>
<th>NO</th>
<th>CO\textsubscript{2}</th>
<th>CO</th>
<th>H\textsubscript{2}O</th>
<th>H\textsubscript{2}O\textsubscript{2}</th>
<th>HNO\textsubscript{3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>313K, 1 ATM</td>
<td></td>
<td>8.6E15</td>
<td>7.1E12</td>
<td>3.4E13</td>
<td>9.3E15</td>
<td>2.9E15</td>
<td>1.0E15</td>
<td>1.7E15</td>
</tr>
<tr>
<td>313K, 0.1 ATM</td>
<td></td>
<td>7.9E14</td>
<td>1.8E13</td>
<td>2.1E13</td>
<td>6.7E14</td>
<td>7.8E14</td>
<td>1.3E14</td>
<td>1.6E14</td>
</tr>
<tr>
<td>293K, 1 ATM</td>
<td></td>
<td>6.3E15</td>
<td>3.7E13</td>
<td>5.0E13</td>
<td>1.1E16</td>
<td>9.9E15</td>
<td>2.9E15</td>
<td>6.3E15</td>
</tr>
<tr>
<td>293K, 0.1 ATM</td>
<td></td>
<td>5.2E14</td>
<td>6.3E12</td>
<td>7.1E12</td>
<td>9.4E14</td>
<td>7.9E14</td>
<td>2.2E14</td>
<td>4.5E14</td>
</tr>
<tr>
<td>263K, 1 ATM</td>
<td></td>
<td>1.1E16</td>
<td>1.8E13</td>
<td>4.2E13</td>
<td>1.1E16</td>
<td>4.8E15</td>
<td>4.0E14</td>
<td>4.9E15</td>
</tr>
<tr>
<td>263K, 0.1 ATM</td>
<td></td>
<td>6.9E14</td>
<td>6.2E12</td>
<td>3.7E13</td>
<td>1.3E15</td>
<td>4.0E14</td>
<td>2.0E13</td>
<td>3.8E14</td>
</tr>
</tbody>
</table>
was begun. Seventy seconds after the lamps were turned on, data collection was stopped and the spectral region from 8.96 to 10.32 μm was scanned. This procedure was repeated five times, with concentrations allowed to stabilize by flowing the reactants for 30 minutes between runs. The five 9.478 μm observations and the five scans were averaged to reduce noise.

The sum of the scans is shown in Fig. 57. The ozone absorption band from cross-section measurements is indicated by the dashed line. The noise in the trace is due to the weakness of the analytical light, caused by the large number of reflections needed to obtain the necessary path length. The optical density shown converts into an ozone concentration of about 0.5 to 2 x 10^{13} molecules/cm^2.

The sum of the observations made at 9.478 μm were analyzed using a linear regression program to obtain slopes and intercepts before and after the lamps were turned on. From the start of the scan to the time the lamps were turned on, the slope of the summed optical density was 

\[-3.6 \pm 2.3 \times 10^{-4} \text{ second}^{-1}\]

and the intercept was \[0.020 \pm 0.004\].

From the time the lamps were turned on to the time the scan was completed, the slope was \[4.2 \pm 0.6 \times 10^{-4} \text{ second}^{-1}\], and the intercept was \[0.006 \pm 0.004\].

The photolytic light source for these experiments consisted of two 30 watt germicidal lamps and two 30 watt black lamps. This combination was used to allow sufficient photolysis of both NO₂ and H₂O₂. The lamps were monitored with a UV enhanced photodiode and a Schott UG-5 filter. The monitor was more sensitive to the output from the black
Fig. 57 Sum of scans made after activation of the photolytic lights
lamps than the 254 nm output from the germicidal lamps. The lamp behavior typically observed by the monitor is illustrated in Fig. 58. Some fluctuations, amounting to less than ±3 percent of the mean value, occurred in the first 5 minutes after the lamps were turned on. The output was stable from that time on until the end of the run.

Actinometry was performed to determine the lamp output of both the germicidal and the black lamps at the three temperatures used in the experiments. The photolysis rate of \( \text{H}_2\text{O}_2 \) by the black lamps was determined to be less than 0.5 percent of the photolysis by the germicidal lamps. Consequently, \( \text{H}_2\text{O}_2 \) photolysis was used to obtain the light intensities of the 254 nm output of the germicidal lamps.

\( \text{H}_2\text{O}_2 \) was flowed through the cell with \( \text{N}_2 \) carrier gas until the desired concentration was obtained, as observed with the 8.040 \( \mu \)m \( \text{H}_2\text{O}_2 \) absorption. The flow was stopped, and the decay of \( \text{H}_2\text{O}_2 \) in the dark was observed. The lamps were turned on and the decay rate of \( \text{H}_2\text{O}_2 \) was observed after the intermediates had built up to steady state concentrations. The lamps were turned off and the dark decay of \( \text{H}_2\text{O}_2 \) was again recorded. \( \text{H}_2\text{O}_2 \) has an overall quantum yield of two in this system.

\[
\text{H}_2\text{O}_2 + h\nu \rightarrow \text{HO} + \text{HO}
\]
\[
\text{HO} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2
\]
\[
\text{HO} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2
\]

net \( 2 \text{H}_2\text{O}_2 + h\nu \rightarrow 2 \text{H}_2\text{O} + \text{O}_2 \)
Fig. 58  Photolytic lamp output with time, as observed by the photodiode monitor
The photolysis rate was obtained by subtracting the average of the dark decays from the rate observed with the lights on. The light intensities obtained were:

\[
\begin{align*}
I(254 \text{ nm, } 313 \text{ K}) &= 4.8 \times 10^{15} \text{ photons/cm}^2\text{-second} \\
I(254 \text{ nm, } 293 \text{ K}) &= 4.0 \times 10^{15} \text{ photons/cm}^2\text{-second} \\
I(254 \text{ nm, } 263 \text{ K}) &= 2.2 \times 10^{15} \text{ photons/cm}^2\text{-second}
\end{align*}
\] (59)

The light intensities for the black lamps were obtained by disconnecting the two germicidal lamps from the lamp driver and photolyzing NO\textsubscript{2}. A 1081 cm\textsuperscript{3} bulb was filled with a measured pressure of NO\textsubscript{2}. This was expanded into the cell, which was then filled with one atmosphere of N\textsubscript{2}. The black lamps were turned on and the NO\textsubscript{2} decay was monitored at 3.428 µm. The quantum yield for NO\textsubscript{2} will be between one and two under these conditions. The decays were analyzed using a quantum yield\textsuperscript{67} of 1.67. They were also analyzed by computer simulation to take into consideration the formation of species such as NO\textsubscript{3} and N\textsubscript{2}O\textsubscript{5}. The black lamp light intensities obtained were:

\[
\begin{align*}
I(313 \text{ K}) &= 4.3 \times 10^{15} \text{ photons/cm}^2\text{-second} \\
I(293 \text{ K}) &= 3.1 \times 10^{15} \text{ photons/cm}^2\text{-second} \\
I(263 \text{ K}) &= 1.0 \times 10^{15} \text{ photons/cm}^2\text{-second}
\end{align*}
\]

The light intensities obtained were used in the analysis of the decays and in computer simulation of the experiments.
B. Results and Discussion

The kinetics and photochemistry of the \( \text{H}_2\text{O}_2 - \text{NO}_2 - \text{CO} \) system was investigated because of their importance to the chemistry of trace species in the troposphere. Fishman and Crutzen\textsuperscript{51} and Heicklen et al.\textsuperscript{111} have proposed a photolytic cycle for the generation of ozone in the troposphere.

\[
\begin{align*}
\text{CO} + \text{HO} & \rightarrow \text{CO}_2 + \text{H} \\
\text{H} + \text{O}_2 & \rightarrow \text{HO}_2 \\
\text{HO}_2 + \text{NO} & \rightarrow \text{HO} + \text{NO}_2 \\
\text{NO}_2 + \text{hv} & \rightarrow \text{NO} + \text{O} \\
\text{O} + \text{O}_2 & \rightarrow \text{O}_3 \\
\text{net: CO} + 2\text{O}_2 & \rightarrow \text{CO}_2 + 2\text{O}_2
\end{align*}
\]

For this cycle to make an important contribution to the tropospheric ozone budget, each of the reactions listed must be the dominant pathway for the reaction of the reactants involved.

The compounds used in these experiments were maintained at concentration levels in the range of \( 10^{13} \) to \( 10^{16} \) molecules/cm\(^3\). These levels were much higher than those present in unpolluted regions of the troposphere, but were necessitated by the limited sensitivity of the spectrometer system. This factor produced considerably different kinetics than those occurring in the atmosphere. Another difference was the presence of the cell walls, on which heterogeneous reactions could occur. Heterogeneous reactions had to be considered in the
analysis of the decay profiles. This is particularly true of $H_2O_2$, which is known to be involved in a number of heterogeneous reactions.

The large number of species and the large number of reactions that occur make this system difficult to analyze. The CHEMK computer program, described previously, was used to simulate the kinetics of the experimental runs. The reactions and rate constants used are listed in Appendix C. The experimentally derived initial concentrations and light intensities were used as inputs for the program. The final concentrations from experiment and theory are compared in Table 18. The initial concentrations in both cases are those listed in Table 17. While there is reasonable agreement between the experimental and calculated results for the one atmosphere runs, there is generally poor agreement between the experimental and calculated results for the 0.1 atmosphere runs. This appears to be largely due to difficulties in obtaining reproducible concentrations at 0.1 atmosphere and monitoring them accurately. Experimental and calculated profiles for the one atmosphere and 0.1 atmosphere runs at 293 K are compared in Figs. 59 and 60, respectively.

The poor agreement between experimental and calculated results could be due to a number of factors. The rapid evacuation of the cell could cause cooling of the gases and condensation of species such as $H_2O$, $H_2O_2$ and $HNO_3$. These could slowly evaporate during the run and give misleading results. The light intensity transmitted through the cell varies slightly with cell pressure and the effect is
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<td>6.3E13</td>
</tr>
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Fig. 59  Comparison of experimental (lower) and calculated (upper) concentration profiles at 293 K and 1.0 atmosphere pressure.
Fig. 60 Comparison of experimental (lower) and calculated (upper) concentration profiles at 293 K and 0.1 atmosphere pressure.
not entirely reproducible. Since the concentrations of most species and their corresponding absorptions are small under these conditions, small shifts in the baseline can have a significant effect. The cross sections at 0.1 atmosphere are generally small and somewhat uncertain at low concentrations. There was considerable run-to-run fluctuation in the concentrations of several species. This was caused in part to the difficulty in re-establishing stable flows of the reactants. It was decided not to use low pressure runs because of these difficulties.

The differences between the experimental and calculated profiles were analyzed to determine the cause of the difference. The runs at 293 K and 313 K have higher HNO₃ concentrations and lower NO and H₂O₂ concentrations than predicted by the simulations. This suggests a heterogeneous reaction of NO or NO₂ with H₂O₂ to form HNO₃. The 263 K experimental run indicates higher NO₂ and H₂O₂ concentrations and lower NO and HNO₃ concentrations than predicted by the simulations. This could be due to the lamps having lower light output than that used in the simulation.

The conversion of CO to CO₂ in the system occurs by the two reactions of CO + HO and CO + O + M. In all runs, the simulations indicate that the CO + HO reaction is much faster than the CO + O + M reaction. Considerable investigation of the CO + HO reaction has been done, but it is still imperfectly understood. The CO and CO₂ profiles agree well in the 293 K and 263 K runs. The 313 K run suggests that the OH + CO rate constant is higher at 313 K than at lower
temperatures. There have been other studies that indicate that the reaction does exhibit such a temperature dependence.\textsuperscript{100}

The observation of the build-up of small amounts of ozone, as indicated in Fig. 57, is consistent with the results of computer simulations. The simulations predict the build-up of ozone to concentrations of $-1 \times 10^{13}$ molecules/cm$^3$ about 10 seconds after the lamps are turned on, and then a slow decay to levels of $-1 \times 10^{11}$ molecules/cm$^3$ at the end of the run. The experimentally observed concentrations were in the range of $-0.5\text{--}2 \times 10^{13}$ molecules/cm$^3$. This was indicated by both the scans and the observations at 9.478 $\mu$m. The uncertainty arises from the noise in the optical density due to the weak signal.

The presence of HONO and HNO$_4$ was not confirmed. The computer simulations predict maximum concentrations that would be only marginally detectable in the system. This suggests rough agreement between the experimental results and simulated results in terms of the HONO and HNO$_4$ chemistry.

The experimental results, in general, appear to confirm the validity of the reaction system used to model the experiments. The major difficulties in the experiments is the occurrence of heterogeneous reactions and the need to perform repeated photolysis runs to observe all the species.

If the computer simulations are accurate models of the gas phase kinetics in the experiments, the reaction rate predictions made by the
simulations can be analyzed to determine which reactions are responsible for the ozone production and whether the CO oxidation cycle is active in the experiments performed.

The simulations indicate that the build-up of ozone is due to the initial photolysis of NO₂ to produce oxygen atoms. These combine with oxygen molecules to form ozone. As the NO produced by photolysis builds up, it reacts with ozone, reducing its concentration.

For the cycle listed in (26) to operate successfully each step in the cycle must be the dominant pathway for the consumption of the intermediates involved. The computer simulations indicate that the CO oxidation cycle was not active in the experiments performed. The reaction rate of HO with CO was small compared to the rate for HO + NO₂ + M to form HNO₃. The rate of H + O₂ + M was the major loss mechanism for hydrogen atoms. The reactions of HO₂ + NO₂ + M and NO + NO₃ were more important in the balance of HO₂ and NO, respectively, than the reaction of HO₂ + NO. NO₂ + hv and O + O₂ + M were major destruction mechanisms for NO₂ and oxygen atoms.

In addition, the CO₂ production rate would be the same as the gross ozone production rate if the cycle were responsible for the ozone generation. The simulations of the experiments indicate that this was not the case.

The operation of the CO oxidation cycle as an ozone production mechanism will be dependent on the concentration balance of a number of trace species. In the troposphere, the concentrations of the HOₓ
and NO\textsubscript{x} species need to be critically balanced for the mechanism to operate. To be able to determine the behavior of ozone in the atmosphere, the general differential equation for ozone concentration must be analyzed in the manner presented by Johnston and Podolske\textsuperscript{112}. The relative importance of the terms in the differential equation will depend on the region of the atmosphere under consideration.

In conclusion, the experimental results cannot confirm the existence of a CO oxidation mechanism that is responsible for ozone production in the atmosphere. The presence of heterogeneous reactions make experimental confirmation difficult. To determine if it does occur in the troposphere, studies need to be made of the concentrations of trace species and accurate knowledge obtained of the temperature and pressure dependence of the rate constants for the reaction involved.
ACKNOWLEDGMENTS

I would like to thank Professor Harold S. Johnston for his guidance and support throughout my graduate career. While allowing a student to develop on his own, he was always available as a sounding board and a source of information and ideas.

The encouragement and assistance of my fellow graduate students has been both helpful and enjoyable. Particular thanks go to Peter Connell, Bill Marinelli, Herb Nelson and Jim Podolske, with whom I have had many stimulating and engaging discussions during my career.

The personnel of the Department of Chemistry and the Lawrence Berkeley Laboratory have been most helpful in their support of this research.

I would particularly like to thank Lisa for her emotional support and understanding.

Special thanks are due to my parents. Their support and encouragement were a source of inspiration.

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APPENDIX A: PHOTOMULTIPLIER TUBE GATING.

In many experimental situations, it is sometimes desirable to observe low level light signals which have been preceded by any intense pulse of light. A photomultiplier tube (PMT) is an excellent device with which to monitor low intensity light. However, it can be easily saturated or possibly damaged when exposed to high light intensity. Recovery from saturation is too slow to monitor signals immediately following the saturating pulse.

A technique that exists to circumvent this problem is that of gating the PMT off during the saturating pulse. There are five general methods of doing this: pulsing the photocathode, pulsing the first dynode, pulsing other dynodes or groups of dynodes, pulsing the high voltage supply, or pulsing a special gating electrode that exists in a few tubes.

There are a number of problems that exist in gating PMT's. Electrical pickup, ringing, afterpulsing and excited photocathode states can make signal measurement after gating difficult. The problems are discussed in more detail elsewhere.

The circuit discussed here has been used successfully with 1P28-class PMT's. A schematic diagram of the modified dynode chain is shown in Fig. A1. The gating technique involves temporarily shorting dynodes 6 and 7 together via Q1 to prevent further amplification of the electron cascade initiated by the intense pulse of light.

A pulse of approximately -5 volts and pulse width between 1 and 10 microseconds from a suitable pulse generator is applied to the pulse
Fig. A1 Photomultiplier tube gating circuit
input immediately preceding the intense pulse of light. The circuit has rise and fall times of less than one microsecond. It has been used to gate a PMT off for periods of 1 to 10 microseconds. The circuit provides an attenuation of 1000 while the pulse is applied. The system is sensitive to the rise and fall times of the input pulse and also to the current capacity of the pulse generator. These parameters need to be optimized to provide maximum performance of the circuit.
APPENDIX B: PRESSURE BROADENING OF ROTATIONAL LINES IN INFRARED SPECTRA

There are a number of factors that must be considered when investigating the effect of broadening of spectral lines by pressure. The spectrometer transmission function, or spectral slit function, will play an important role in the observed effects. For a spectrometer with entrance and exit slit widths of equal width, the slit function will be a triangle if diffraction is neglected. If the entrance and exit slit widths are not equal, the slit function will be trapezoidal in shape. Most spectrometer systems operate with equal entrance and exit slits. The slit function can then be defined as

\[ f(v - v_0) = 1 - \frac{v - v_0}{w} \]

for \( v - v_0 \leq w \) and \( f(v - v_0) = 0 \) elsewhere, where \( v_0 \) is the center frequency and \( w \) is the spectral slit width (FWHM). This is illustrated in Fig. B1.

With an experimental apparatus scanning through a spectral region, the actual response will in general not be triangular. The detector response time and the RC time constant of the amplifier circuitry will act to round the slit function and displace the observed slit function, or instrumental response function, from the actual slit function.
Fig. B1  Slit functions  
(top) Ideal slit function  
(center) experimental slit function, \( \nu' \neq \nu_0 \)  
(bottom) experimental slit function being scanned across a spectral feature
The overlap of the instrumental response function with the spectral features that are being scanned will determine the broadening effects observed. If the response function is much narrower than the spectral features, the broadening will be directly observable. If the response function is wider than the spectral feature, the broadening will not be directly observable. However, information can be obtained on the linewidths indirectly.\(^\text{106}\)

The broadening of rotational lines of infrared absorption bands is largely due to Lorentz broadening. Measurements\(^\text{107}\) have shown the rotational lines of HCl, H\(_2\)O and CO\(_2\) infrared absorptions to have Lorentzian shape and have shown the rotational linewidth to increase in proportion to pressure. Simple Lorentz broadening theory is based on the concept of a sudden change in the radiation emitted or absorbed by an atom or molecule at the time of collision. The assumptions made are that the mean time between collisions is large compared to the collision time, and there is a change of phase or break of the radiation. This causes the radiation to be spread into a series of independent wave-trains, which causes broadening of the line. The Lorentz linewidth,\(^\text{108}\) \(\delta\), can be written as

\[
\delta = \frac{4Np^2\lambda}{\sqrt{\pi}nmRT}
\]
where

\(N\) = Avogadro's number

\(\rho\) = optical collision diameter or cross section

\(p\) = pressure

\(m\) = molecular weight if a pure gas is involved; reduced mass
  if a gas mixture is involved.

\(R\) = the gas constant

\(T\) = temperature
The optical collision diameters may be greater or less than the gas kinetic collision diameters.

To obtain a measure of the transmittance or absorbance that occurs when a slit function is moved across a spectral feature, one must integrate across the frequency region transmitted by the slit.

\[
T = 1 - A = \frac{\exp(-\sigma(v)n\lambda) f(v - v_0) dv}{f(v - v_0) dv}
\]

where
- \( T \) = transmittance
- \( A \) = absorbance
- \( f(v - v_0) \) = slit function
- \( v_1, v_2 \) = limits of slit function
- \( \sigma(v) \) = cross section as a function of \( v \)
- \( n \) = number of absorbers per unit volume
- \( \lambda \) = path length

This integral has been analyzed for a number of situations that exist in spectroscopy, although one cannot derive a general equation valid in all situations. When the simplifying assumptions used are valid or nearly so, the experimental and theoretical agreement is good.

The theoretical interpretation is useful when the absorption band structure is known. Structure from high resolution work can be applied to a lower resolution system if the slit function, or instrument response function, is known. However, without such data, most pressure broadening effects have to be determined empirically.
APPENDIX C: REACTION SETS FOR NUMERICAL MODELING OF CHEMICAL SYSTEMS

The following three tables are lists of the sets of reactions and rate constants used to model the chemistry of the three systems investigated in this research. The simulations were done with the CHEMK chemical kinetics program described in the text. The rate constants are in units of $(\text{cm}^3/\text{molecule})^n \text{ seconds}^{-1}$, where $n = 0$ for unimolecular and heterogeneous reactions, $n = 1$ for bimolecular reactions, and $n = 2$ for termolecular reactions. Activation energies are in K.

The first reaction set is that used to model the expansion of $\text{H}_2\text{O}_2$ and $\text{N}_2\text{O}_5$ into the cell and the kinetics that occur after expansion. The first six reactions are used to describe the flow-in of the reactants and the carrier gas. $X$ is a dummy variable used to implement this process. The effective rate constant for the flow in will depend on the ultimate concentration of the species without reaction and is given by

$$k_{\text{eff}} [A]_0 = \frac{1}{t_0} \frac{[A]}{[X]_0}$$

where $t_0$ is the time constant for the flow system, $[X]_0$ is the initial concentration assigned to the dummy variable and $[A]_0$ is the ultimate concentration of the specie $A$. The flow-out of $X$ is given by $k_{\text{eff}} = 1/t_0$. 
The second reaction set listed below was used in simulations of very low frequency photolysis of flowing H₂O₂ and N₂O₅ in one atmosphere nitrogen carrier gas. The first five reactions are photolysis reactions. The effective cross sections for the species were determined by calculating relative j-values from the absorption spectra for the compounds and the measured emission spectrum of the black lamps. Light intensities obtained from NO₂ photolysis were used as a reference.

The rate constants used for the heterogeneous reactions were assigned values that were typically observed during experiments. The reaction products for heterogeneous HNO₄ decomposition were assumed to be H₂O₂ and NO₂. Supporting evidence for this assumption comes from experiments where H₂O₂ and N₂O₅ were expanded into the cell containing a low pressure of NO. The rates of the flow-in reactions were used to provide agreement between the observed and calculated concentrations of NO₂, H₂O₂, HNO₄, N₂O₅ and H₂O. If a species was inert, its effective flow-in rate constant would be the flow rate times the concentration in the cell divided by the cell volume. The effective flow-out rate constants are simply the flow rate divided by the cell volume. This was 1.9 x 10⁻³ second⁻¹ for all the runs that were done.

The reaction set in the third table was used to model the chemistry in the HOₓ - NOₓ - COₓ system. Since this was a non-flowing system, no flow reactions had to be included.
Two germicidal lamps and two black lamps were used as photolytic light sources for the system. The black lamps have broad output in the near UV and the germicidal lamps have strong output at 254 nm. NO$_2$ and HONO were the only species strongly photolyzed by the black lamps. Photolysis rates of other species were less than 1 percent of their respective photolysis rates at 254 nm and were not included.

The large number of reactions was needed because of the large number of species present, many of which are quite reactive. While the rates of some of the reactions are not very fast, they are important in determining the concentrations of some intermediates.

The heterogeneous reactions (46–49) were assigned values that were typical of the heterogeneous rates in the system. Other heterogeneous reaction may have been occurring in the system. They were not studied in depth and no good estimates could be obtained for them. Consequently, they were not included in the reaction set.
Table C-1
Reactions Used to Model Expansion Experiments

Flow Reactions

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<td>2</td>
<td>$x = x + N_2O_5$</td>
<td>$k_{\text{eff}} x [N_2O_5]$</td>
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<td>3</td>
<td>$x = x + H_2O_2$</td>
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<td>4</td>
<td>$x = x + HNO_3$</td>
<td>$k_{\text{eff}} x [HNO_3]$</td>
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<tr>
<td>5</td>
<td>$x = x + H_2O$</td>
<td>$k_{\text{eff}} x [H_2O]$</td>
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<td>6</td>
<td>$x = 0.23$</td>
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Chemical Reactions

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<td>8</td>
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<td>9</td>
<td>$HO_2 + NO_2 = HNO_4$</td>
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<td>10</td>
<td>$N_2O_5 = NO_2 + NO_3$</td>
<td>$8.1 \times 10^{-12}$</td>
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<td>11</td>
<td>$NO_2 + NO_3 = N_2O_5$</td>
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<td>$NO + NO_3 = NO_2 + NO_2$</td>
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</tr>
<tr>
<td>14</td>
<td>$HO_2 + HO_2 = H_2O_2 + O_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>$HO_2 + NO = OH + NO_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>$OH + H_2O_2 = H_2O + HO_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>$OH + NO_2 + M = HNO_3 + M$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>$OH + HO_2 = H_2O + O_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>$HO_2 + NO + M = HNO_3 + M$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>$H_2O_2 = H_2O$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: 1, 2, 3, 4
Table C-1 (continued)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Chemicals</th>
<th>Equation</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>HNO₄</td>
<td>= HO₂ + NO₂</td>
<td>note 4</td>
</tr>
<tr>
<td>22</td>
<td>N₂O₅</td>
<td>= HNO₃</td>
<td>note 4</td>
</tr>
<tr>
<td>23</td>
<td>H₂O</td>
<td>= HNO₃</td>
<td>note 4</td>
</tr>
</tbody>
</table>

Note 1: This was varied to provide the best fit with experimental data.

Note 2: The empirical expressions given by Ref. 18 were used to calculate the effective rate constant for each pressure and temperature.

Note 3: The expressions developed by Connell were used for these rate constants.

Note 4: These reactions simulate heterogeneous reactions that occur in the cell. Reactions 22 and 23 simulate the heterogeneous reaction of N₂O₅ and H₂O to form 2HNO₃. The effective first order rate constants were variable, depending on temperature and conditioning of the cell. They were generally in the range of 1 x 10⁻² to 1 x 10⁻⁴ second⁻¹ in the H₂O₂-N₂O₅ system.
<table>
<thead>
<tr>
<th>Photolysis Reactions</th>
<th>$\sigma_{\text{eff}}$</th>
<th>Q.Y.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 $\text{NO}_2 + h\nu$ = $\text{NO} + \text{O}$</td>
<td>$4.8 \times 10^{-19}\text{cm}^2$</td>
<td>1.0</td>
</tr>
<tr>
<td>2 $\text{N}_2\text{O}_5 + h\nu$ = $\text{NO}_2 + \text{NO}_2 + \text{O}$</td>
<td>$2.1 \times 10^{-21}\text{cm}^2$</td>
<td>1.0</td>
</tr>
<tr>
<td>3 $\text{H}_2\text{O}_2 + h\nu$ = $\text{OH} + \text{OH}$</td>
<td>$2.9 \times 10^{-22}\text{cm}^2$</td>
<td>1.0</td>
</tr>
<tr>
<td>4 $\text{HNO}_4 + h\nu$ = $\text{HO}_2 + \text{NO}_2$</td>
<td>$2.0 \times 10^{-22}\text{cm}^2$</td>
<td>1.0</td>
</tr>
<tr>
<td>5 $\text{HNO}_3 + h\nu$ = $\text{OH} + \text{NO}_2$</td>
<td>$8.2 \times 10^{-23}\text{cm}^2$</td>
<td>1.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chemical Reactions</th>
<th>A</th>
<th>$E_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 $\text{HNO}_4 + \text{M}$ = $\text{HO}_2 + \text{NO}_4 + \text{M}$</td>
<td></td>
<td>note 1, note 2</td>
</tr>
<tr>
<td>7 $\text{HO}_2 + \text{NO}_2 + \text{M}$ = $\text{HNO}_4 + \text{M}$</td>
<td></td>
<td>note 1, note 2</td>
</tr>
<tr>
<td>8 $\text{N}_2\text{O}_5 + \text{M}$ = $\text{NO}_2 + \text{NO}_3 + \text{M}$</td>
<td></td>
<td>note 1, note 2</td>
</tr>
<tr>
<td>9 $\text{NO}_2 + \text{NO}_3 + \text{M}$ = $\text{N}_2\text{O}_5 + \text{M}$</td>
<td></td>
<td>note 1, note 2</td>
</tr>
<tr>
<td>10 $\text{NO}_2 + \text{NO}_3$</td>
<td>$2.3 \times 10^{-13}$</td>
<td>1000</td>
</tr>
<tr>
<td>11 $\text{NO} + \text{HO}_2$ = $\text{HO} + \text{NO}_2$</td>
<td>$8.1 \times 10^{-12}$</td>
<td>-</td>
</tr>
<tr>
<td>12 $\text{NO} + \text{NO}_3$ = $\text{NO}_2 + \text{NO}_2$</td>
<td>$1.9 \times 10^{-11}$</td>
<td>-</td>
</tr>
<tr>
<td>13 $\text{O} + \text{NO}_2$ = $\text{NO} + \text{O}_2$</td>
<td>$9.3 \times 10^{-12}$</td>
<td>-</td>
</tr>
<tr>
<td>14 $\text{O} + \text{NO}_2 + \text{M}$ = $\text{NO}_3 + \text{M}$</td>
<td>$9.0 \times 10^{-32}$</td>
<td>-</td>
</tr>
<tr>
<td>15 $\text{O} + \text{NO} + \text{M}$ = $\text{NO}_2 + \text{M}$</td>
<td>$1.55 \times 10^{32}$</td>
<td>-384</td>
</tr>
<tr>
<td>16 $\text{OH} + \text{HNO}_4$ = $\text{H}_2\text{O} + \text{NO}_2 + \text{O}_2$</td>
<td></td>
<td>note 3</td>
</tr>
<tr>
<td>17 $\text{OH} + \text{NO}_2 + \text{M}$ = $\text{HNO}_3 + \text{M}$</td>
<td></td>
<td>note 4</td>
</tr>
<tr>
<td>18 $\text{OH} + \text{H}_2\text{O}_2$ = $\text{HO}_2 + \text{H}_2\text{O}$</td>
<td>$1.6 \times 10^{-12}$</td>
<td>-</td>
</tr>
<tr>
<td>19 $\text{OH} + \text{HNO}_3$ = $\text{H}_2\text{O} + \text{NO}_3$</td>
<td>$8.5 \times 10^{-14}$</td>
<td>-</td>
</tr>
<tr>
<td>20 $\text{HO}_2 + \text{HO}_2$ = $\text{H}_2\text{O}_2 + \text{O}_2$</td>
<td>$2.5 \times 10^{-12}$</td>
<td>-</td>
</tr>
<tr>
<td>21 $\text{H}_2\text{O}_2$ = $\text{H}_2\text{O}$</td>
<td>$1 \times 10^{-3}$</td>
<td>-</td>
</tr>
<tr>
<td>22 $\text{HNO}_4$ = $\text{HO}_2 + \text{NO}_2$</td>
<td>$1 \times 10^{-3}$</td>
<td>-</td>
</tr>
<tr>
<td>23a $\text{N}_2\text{O}_5$ = $\text{HNO}_3$</td>
<td>$1 \times 10^{-3}$</td>
<td>-</td>
</tr>
<tr>
<td>23b $\text{H}_2\text{O}$ = $\text{HNO}_3$</td>
<td></td>
<td>note 5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Flow Reactions</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>24 $\text{NO}_2$</td>
<td></td>
<td>note 6</td>
</tr>
<tr>
<td>25 $\text{HNO}_3$</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>26 $\text{N}_2\text{O}_5$</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>27 $\text{HNO}_4$</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>28 $\text{H}_2\text{O}_2$</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>29 $\text{H}_2\text{O}$</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>30 $\text{NO}_2$</td>
<td>$1.9 \times 10^{-3}$</td>
<td>-</td>
</tr>
<tr>
<td>32 $\text{HNO}_3$</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>33 $\text{HNO}_4$</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>34 $\text{H}_2\text{O}_2$</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>35 $\text{H}_2\text{O}$</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>36 $\text{NO}$</td>
<td></td>
<td>-</td>
</tr>
</tbody>
</table>
Table C-2 (continued)

Note 2: Values for these equations were obtained from empirical equations given by Graham et al.\textsuperscript{18} and Connell\textsuperscript{67}.

Note 2: M dependence is included implicitly in the rate constant.

Note 3: This rate constant was varied from $2 \times 10^{-13}$ to $2 \times 10^{-11}$ (cm\textsuperscript{3}/molecule-second) to determine the best fit with experimental data.

Note 4: This reaction exhibits a complicated pressure and temperature dependence. The values for the conditions in which the experiments were done were obtained from JPL Publication 79-27.

Note 5: Reactions 23a and 23b are designed to simulate the heterogeneous reaction of H\textsubscript{2}O and N\textsubscript{2}O\textsubscript{5}. The value for the rate constant of 23b was varied to provide unity stoichiometry for H\textsubscript{2}O and N\textsubscript{2}O\textsubscript{5}.

Note 6: These effective rate constants were used to match the calculated concentrations with those observed for each run.
### TABLE C-3

Reactions Used to Model HO$_x$–NO$_x$–CO$_x$ Photochemistry

<table>
<thead>
<tr>
<th>Reaction</th>
<th>A</th>
<th>$E_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 $O + O_2 + M$ = $O_3 + M$</td>
<td>1.1E-34</td>
<td>-510</td>
</tr>
<tr>
<td>2 $O + O_3$ = $O_2 + O_2$</td>
<td>1.9E-11</td>
<td>2300</td>
</tr>
<tr>
<td>3 $O + NO + M$ = $NO_2 + M$</td>
<td>1.5E-32</td>
<td>-584</td>
</tr>
<tr>
<td>4 $O + NO_2$ = $NO + O_2$</td>
<td>9.3E-12</td>
<td></td>
</tr>
<tr>
<td>5 $O + NO_2 + M$ = $NO_3 + M$</td>
<td>9.0E-32</td>
<td></td>
</tr>
<tr>
<td>6 $O + NO_3$ = $NO_2 + O_2$</td>
<td>1.0E-11</td>
<td></td>
</tr>
<tr>
<td>7 $O + HO_2$ = $HO + O_2$</td>
<td>3.1E-11</td>
<td></td>
</tr>
<tr>
<td>8 $O + H_2O_2$ = $HO + HO_2$</td>
<td>2.8E-12</td>
<td>2125</td>
</tr>
<tr>
<td>9 $O + CO^+ + M$ = $CO_2 + M$</td>
<td>6.5E-33</td>
<td>2180</td>
</tr>
<tr>
<td>10 $O^+ + O_2$ = $O_2 + O$</td>
<td>2.9E-11</td>
<td>-67</td>
</tr>
<tr>
<td>11 $O^+ + O_3$ = $O_2 + O_2$</td>
<td>1.2E-10</td>
<td></td>
</tr>
<tr>
<td>12 $O^+ + O_3$ = $O_2 + O^+ + O$</td>
<td>1.2E-10</td>
<td></td>
</tr>
<tr>
<td>13 $O^+ + NO_2$ = $NO + O_2$</td>
<td>1.0E-10</td>
<td></td>
</tr>
<tr>
<td>14 $O^+ + H_2O$ = $HO + HO$</td>
<td>2.3E-10</td>
<td></td>
</tr>
<tr>
<td>15 $O^+ + H_2O_2$ = $HO + HO_2$</td>
<td>5.2E-10</td>
<td></td>
</tr>
<tr>
<td>16 $O^+ + CO_2$ = $CO_2 + O$</td>
<td>6.8E-11</td>
<td>-117</td>
</tr>
<tr>
<td>17 $O_2 + NO + NO$ = $NO_2 + NO_2$</td>
<td>3.3E-39</td>
<td>-530</td>
</tr>
<tr>
<td>18 $O_2 + H + M$ = $HO_2 + M$</td>
<td>6.7E-33</td>
<td>-290</td>
</tr>
<tr>
<td>19 $O_3 + M$ = $O + O_2 + M$</td>
<td>7.4E-10</td>
<td>11430</td>
</tr>
<tr>
<td>20 $O_3 + NO$ = $NO_2 + O_2$</td>
<td>2.3E-12</td>
<td>1450</td>
</tr>
<tr>
<td>21 $O_3 + NO_2$ = $NO_3 + O_2$</td>
<td>1.2E-13</td>
<td>2450</td>
</tr>
<tr>
<td>22 NO + NO$_2$ + H$_2$O = HONO + HONO</td>
<td>6.0E-38</td>
<td></td>
</tr>
<tr>
<td>23 NO + NO$_3$ = NO$_2$ + NO$_2$</td>
<td>1.9E-11</td>
<td></td>
</tr>
<tr>
<td>24 NO + HO + M = HONO + M</td>
<td>2.0E-32</td>
<td>-1110</td>
</tr>
<tr>
<td>25 NO + HO$_2$ = NO$_2$ + HO</td>
<td>4.0E-12</td>
<td>-225</td>
</tr>
<tr>
<td>26 NO$_2$ + NO$_2$ + M = N$_2$O$_4$ + M</td>
<td>3.0E-35</td>
<td>-1040</td>
</tr>
<tr>
<td>27 NO$_2$ + NO$_3$ = NO$_2$ + NO + O$_2$</td>
<td>2.3E-13</td>
<td>1000</td>
</tr>
<tr>
<td>28 NO$_2$ + NO$_3$(+M) = N$_2$O$_5$(+M)</td>
<td>note 1</td>
<td></td>
</tr>
<tr>
<td>29 NO$_2$ + H = HO + NO</td>
<td>7.1E-10</td>
<td>505</td>
</tr>
<tr>
<td>30 NO$_2$ + HO(+M) = HNO$_3$(+M)</td>
<td>note 2</td>
<td></td>
</tr>
<tr>
<td>31 NO$_2$ + HO$_2$(+M) = HNO$_4$(+M)</td>
<td>note 3</td>
<td></td>
</tr>
<tr>
<td>32 NO$_3$ + NO$_3$ = NO$_2$ + NO$_2$ + O$_2$</td>
<td>8.5E-13</td>
<td>2450</td>
</tr>
<tr>
<td>33 H + H$_2$O$_2$ = H$_2$ + HO$_2$</td>
<td>2.0E-12</td>
<td>1400</td>
</tr>
<tr>
<td>34 H + HO$_2$ = HO + H$_2$O</td>
<td>3.0E-12</td>
<td>1400</td>
</tr>
<tr>
<td>35 HO + HO$_2$ = H$_2$O + O$_2$</td>
<td>3.5E-11</td>
<td></td>
</tr>
<tr>
<td>36 HO + H$_2$O$_2$ = H$_2$O + HO$_2$</td>
<td>1.6E-12</td>
<td></td>
</tr>
<tr>
<td>37 HO + HONO = H$_2$O + NO$_2$</td>
<td>6.6E-12</td>
<td></td>
</tr>
<tr>
<td>38 HO + HNO$_3$ = H$_2$O + NO$_3$</td>
<td>8.5E-14</td>
<td></td>
</tr>
<tr>
<td>39 HO + HNO$_4$ = H$_2$O + NO$_2$ + O$_2$</td>
<td>note 4</td>
<td></td>
</tr>
<tr>
<td>40 HO + CO = H + CO$_2$</td>
<td>2.7E-13</td>
<td></td>
</tr>
<tr>
<td>41 HO$_2$ + HO$_2$ = H$_2$O$_2$ + O$_2$</td>
<td>2.3E-12</td>
<td></td>
</tr>
<tr>
<td>42 HONO + HONO = NO + NO$_2$ + H$_2$O</td>
<td>9.5E-19</td>
<td></td>
</tr>
<tr>
<td>43 HNO$_4$(+M) = HO$_2$ + NO$_2$(+M)</td>
<td>note 3</td>
<td></td>
</tr>
<tr>
<td>44 N$_2$O$_4$ + M = NO$_2$ + NO$_2$ + M</td>
<td>4.2E-7</td>
<td></td>
</tr>
</tbody>
</table>
45 \[ \text{N}_2\text{O}_5 (+\text{M}) = \text{NO}_2 + \text{NO}_3 (+\text{M}) \]  
46 \[ \text{H}_2\text{O}_2 = \text{H}_2\text{O} \]  
47 \[ \text{N}_2\text{O}_5 = \text{HNO}_3 + \text{HNO}_3 \]  
48 \[ \text{H}_2\text{O} + \text{NO}_2 + \text{NO}_2 = \text{HONO} + \text{HNO}_3 \]  
49 \[ \text{H}_2\text{O}_2 + \text{NO}_2 = \text{HNO}_3 + \text{HNO}_3 \]  
50 \[ \text{NO}_2 + \text{hv} \rightarrow \text{NO} + \text{O} \]  
51 \[ \text{HONO} + \text{hv} \rightarrow \text{HO} + \text{NO} \]  
52 \[ \text{H}_2\text{O}_2 + \text{hv} \rightarrow \text{HO} + \text{HO} \]  
53 \[ \text{N}_2\text{O}_5 + \text{hv} \rightarrow \text{NO}_2 + \text{NO}_2 + \text{O} \]  
54 \[ \text{HNO}_3 + \text{hv} \rightarrow \text{HO} + \text{NO}_3 \]  
55 \[ \text{HNO}_4 + \text{hv} \rightarrow \text{HO}_2 + \text{NO}_2 \]  
56 \[ \text{O}_3 + \text{hv} \rightarrow \text{O}_4 + \text{O}_2 \]  
57 \[ \text{O}_3 + \text{hv} \rightarrow \text{O} + \text{O}_2 \]  
58 \[ \text{NO}_2 + \text{hv} \rightarrow \text{NO} + \text{O} \]  
59 \[ \text{HONO} + \text{hv} \rightarrow \text{HO} + \text{NO} \]  
60 \[ \text{NO}_3 + \text{hv} \rightarrow \text{NO}_2 + \text{O} \]  

Note 1: These reactions have a complex pressure and temperature dependence. The values were obtained from formulas in Ref. 67.

Note 2: Rate constant values obtained from formula in JPL Publication 79-27.

Note 3: Rates constant values obtained from formulas in Ref. 18.

Note 4: The value for this rate constant was obtained experimentally.

Note 5: These reactions were designed to simulate heterogeneous reactions. Values used for the rate constants were those typically observed for the heterogeneous reactions involved.

Note 6: The reactions listed here represent photolysis by the black lamps and germicidal lamps. Only NO2 and HONO are significantly photolyzed by the black lamps. The black lamp photolysis rate for all other species is less than 1 percent of their respective germicidal lamp photolysis rate and not included. Reactions 58 and 59 represent the black lamp photolysis of NO2 and HONO, respectively. Reaction 60 represents the photolysis of NO3 by the 546nm mercury line.
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