16. Abstract
The technique of Pulsed Laser Photolysis - long path laser absorption is employed to study the kinetics of the reaction \( \text{CH}_3\text{O}_2 + \text{NO}_2 \rightarrow \text{CH}_3\text{O}_2\text{NO}_2 + \text{N}_2 \) and the reaction \( \text{OH} + \text{HNO}_3 \rightarrow \text{NO}_3 + \text{H}_2\text{O} \). The first reaction was measured over the temperature range 253-353K by following the reactant \( \text{CH}_3\text{O}_2 \), while the second reaction was investigated at 298 and 251K by monitoring the product \( \text{NO}_3 \). At all temperatures, \( k_1 \) is found to monotonically increase with increasing \( \text{N}_2 \) pressure over the range 76-722 Torr, indicating that reaction occurs predominantly by addition. The dependence of \( k_1 \) on \( \text{N}_2 \) pressure shows that the reaction is in the fall-off region between second and third order kinetics. These results are compared with previous results and their atmospheric implications are discussed. The value of \( k_2 \) obtained agrees well with our previous measurements (Wine, et al., J.G.R., 86, 1105, 1981). In addition, the yield of \( \text{NO}_3 \) in reaction (2) was directly measured to be near unity at both 298 and 251K. Chapters (1) and (2) describe the studies of \( k_1 \) and \( k_2 \), respectively.
Abstract

The technique of Pulsed Laser Photolysis - long path laser absorption is employed to study the kinetics of the reaction \( \text{CH}_3\text{O}_2 + \text{NO}_2 \rightarrow \text{CH}_3\text{O}_2\text{NO}_2 + \text{N}_2 \) and the reaction \( \text{OH} + \text{HNO}_3 \rightarrow \text{NO}_3 + \text{H}_2\text{O} \). The first reaction was measured over the temperature range 253-353K by following the reactant \( \text{CH}_3\text{O}_2 \), while the second reaction was investigated at 298 and 291K by monitoring the product \( \text{NO}_3 \). At all temperatures, \( k_1 \) is found to monotonically increase with increasing \( \text{N}_2 \) pressure over the range 76-722 Torr, indicating that reaction occurs predominantly by addition. The dependence of \( k_1 \) on \( \text{N}_2 \) pressure shows that the reaction is in the fall-off region between second and third order kinetics. These results are compared with previous results and their atmospheric implications are discussed. The value of \( k_2 \) obtained agrees well with our previous measurements, (Hine, et al., J.G.R., 86, 1105, 1981). In addition, the yield of \( \text{NO}_3 \) in reaction (2) was directly measured to be near unity at both 298 and 291K. Chapters (1) and (2) describe the studies of \( k_1 \) and \( k_2 \), respectively.
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Introduction

The methylperoxy radical is an important intermediate in reaction sequences through which hydrocarbons are oxidized in both atmospheric and combustion processes. In combustion systems the fate of peroxy radicals is predominantly governed by their reactions with other radicals, while in the atmosphere, and particularly in the polluted troposphere, it is expected that reactions with stable molecules will be important.

The major species which can react with CH$_3$O$_2$ in the atmosphere include HO$_2$, NO, NO$_2$, SO$_2$, and O$_3$. The rate constant for the reaction of CH$_3$O$_2$ with NO has been recently measured using direct kinetic techniques and found to be nearly as fast as the reaction of HO$_2$ with NO. Therefore, in a polluted atmosphere where NO$_x$ concentrations are high, methyl peroxy radicals are expected to react mostly with NO$_x$ species. For the subject reaction of the present investigation,

$$\text{CH}_3\text{O}_2 + \text{NO} + \text{N}_2 \xrightarrow{k_1} \text{CH}_3\text{O}_2\text{NO}_2 + \text{N}_2$$

(1)

to effectively compete with the reaction of CH$_3$O$_2$ with NO,

$$\text{CH}_3\text{O}_2 + \text{NO} \xrightarrow{k_2} \text{CH}_3\text{O} + \text{NO}_2$$

(2)

the value of $k_1$ should be of similar magnitude as that of $k_2$. If Reaction (1) were a significant path for CH$_3$O$_2$ removal, NO$_2$ production (and the subsequent O$_3$ generation) would be reduced.

Until recently most rate coefficients for CH$_3$O$_2$ radical reactions were obtained by steady state competitive experiments. In the past few years direct measurement techniques such as discharge flow-mass spectrometry, flash photolysis-ultraviolet absorption, and molecular
modulation-UV absorption spectroscopy have been adopted for CH₃O₂ radical studies.

To date three direct measurements of $k_1$ have been carried out. Cox and Tyndall⁹ utilized the molecular modulation-UV absorption technique and obtained a value of $k_1$ which was essentially independent of bath gas pressure. The flash photolysis-UV absorption method has been employed by Adachi and Basco,¹⁰ and Sander and Watson² to measure $k_1$. Adachi and Basco's results are in agreement with those of Cox and Tyndall. However, unlike the previous two measurements, Sander and Watson found Reaction (1) to be pressure dependent. These investigators carried out their experiments under secondary reaction free conditions using a very sensitive probe for CH₃O₂ radicals. Hence, their results appear to be more reliable.

There are no previous measurements of $k_i$ as a function of temperature. In the present study, $k_1$ was measured as a function of N₂ diluent gas pressure and temperature using the recently developed technique of pulsed laser photolysis-long path laser absorption. Due to the monochromaticity of the photolysis laser, and the resultant photolysis specificity, all unwanted photofragments were essentially eliminated, while the high intensity of the CW 257 nm probing laser beam enabled measurement of very low concentrations of CH₃O₂. Under these secondary reaction free conditions, our measured value of $k_1$ was found to be pressure dependent in excellent agreement with Sander and Watson. Also, as to be expected for an addition reaction, $k_1$ was found to increase with decreasing temperature.
The technique of pulsed laser photolysis-laser induced fluorescence was originally proposed to be employed in the study of Reaction (1). CH₃O₂ radicals were to be produced using either 355 nm photolysis of Cl₂/CH₄/O₂ mixtures or UV photolysis of azomethane. To follow the course of the reaction either NO₂ reactant in excess CH₃O₂ or CH₂O product in excess NO₂ were to be monitored using laser induced fluorescence.

There were two developments which excluded carrying out laser induced fluorescence detection of CH₂O to map out the course of Reaction (1): a) we could not obtain the expected 10 mW of UV laser output in the intracavity Ar⁺ laser pumped tunable dye laser (in fact, we succeeded in obtaining only 20 µW!), and b) in some recent studies it was shown that Reaction (1) proceeds predominantly through an addition mechanism; therefore, the CH₂O product yield is very low, and an unrealistically high detection sensitivity for CH₂O would be needed. For these reasons, we abandoned the idea of monitoring CH₂O.

The second approach of following the NO₂ decay in excess CH₃O₂ was pursued when the first approach failed. The primary requirement for this experiment was the creation of a uniform known concentration of CH₃O₂ by laser photolysis. We have succeeded in obtaining a spatially uniform, 'top hat' profiled laser beam using a segmented aperture optical integrator. With this added capability, we can produce CH₃O₂ radicals in excess over NO₂. Our capability to detect NO₂ via laser induced fluorescence (pumped by the 488 nm output of an argon ion laser) is well developed and has been used in the study of the reaction of CH₃O₂ with NO. However, when we tried to monitor NO₂ in excess CH₃O₂, we found the decay of NO₂ to be non-exponential. The decay rates decreased with time due to the disproportionation reaction.
\[ \text{CH}_3\text{O}_2 + \text{CH}_3\text{O}_2 \rightarrow \text{Products} \quad (a) \]

The rate coefficient for Reaction (a) is reasonably well known.\(^2\) A simple calculation shows that unless Reaction (1) is very fast, i.e., is \(\approx 1 \times 10^{-11} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}\), the \(\text{CH}_3\text{O}_2\) concentration would decrease by more than 10\% by the time the \(\text{NO}_2\) concentration dropped to \(1/e\) times its original value. Therefore, it was evident that even though we could measure \(k_1\) at low temperatures and high pressures the required range of pressures and temperatures could not be covered.

Upon realizing that our originally proposed methods would be either inapplicable or of limited use, we decided to develop the laser photolysis-long path laser absorption technique. This effort was very successful and we completed the measurement of \(k_1\) as a function of temperature and pressure, as discussed below.
PULSED LASER PHOTOLYSIS-LONG PATH LASER ABSORPTION KINETICS
STUDY OF THE REACTION OF METHYLPEROXY RADICALS WITH NO₂
Experimental

A schematic diagram of the apparatus used to study Reaction (1) is shown in Figure 1. A jacketed reactor with an internal volume of ~1 l and a length of 107 cm was constructed out of pyrex. The cell was maintained at a constant temperature by circulating either methanol (253-298 K) or ethylene glycol (298-353 K) from a temperature controlled circulator through the outer jacket. It was found that the temperature was uniform to within 2°C throughout the length of the cell. On both ends of the reactor two 1/8" thick, 2" diameter quartz (Suprasil 1) plates were attached using O-ring seals and metal clamps. The reactants were pre-mixed in a mixing chamber and slowly flowed through the reactor. At the outlet of the reactor, the pressure in the system was measured using an absolute one-turn Bourdon gauge (Wallace and Tiernan Model FA160-N%) before the gas mixture was pumped out.

Azomethane/N₂ and NO₂/N₂ mixtures were prepared in 12l bulbs on a gas handling system. The bulbs were connected to the mixing chamber using teflon tubing and stainless steel ultra-torr fittings. The rates of flow of the azomethane/N₂ mixture, NO₂/N₂ mixture, N₂, and O₂ into the mixing chamber were controlled by stainless steel needle valves and measured by calibrated mass flow transducers. The tubes leading into the mixing chamber had radial outlets to turbulently mix the gases. The concentration of each component in the reaction mixture was determined from measurements of appropriate mass flow rates and the total pressure. The concentration of NO₂ in the NO₂/diluent mixture was checked (before and after each set of experiments) by simultaneous measurements of the total pressure (of the mixture) and NO₂ absorption
Figure 1. A Schematic Diagram of Pulsed Laser Photolysis-Long Path Laser Absorption Apparatus.
at 366 nm. The measurements were carried out using an Hg pen-ray lamp as the light source, a 70 cm absorption cell, and a bandpass filter-photo-multiplier detector combination. The absorption cross section used to determine $[\text{INO}_2]$, $5.75 \times 10^{-16}$ cm$^2$, has been previously measured in our laboratory and agrees well with the literature value. The azomethane concentration was occasionally checked by a method identical to that for NO$_2$; the absorption cross section of azomethane was measured to be $1.13 \times 10^{-20}$ cm$^2$ at 366 nm, which is slightly higher than the published value, but in agreement with other recent measurements.

Azomethane was prepared as described in Appendix I. NO$_2$, obtained from Matheson Gas Products, had a stated purity of 99.5%, and was purified by mixing it with UHP O$_2$ to convert all NO to NO$_2$, and subsequently subjecting it to freeze-pump-thaw cycles to remove O$_2$. NO$_2$ and O$_2$ were Matheson grade and had stated purity levels of 99.9995% and 99.99%, respectively; these gases were used as supplied.

An ArF excimer laser, the photolysis light source, was housed in an adjoining room, approximately 2 meters from the front window of the reactor. We found this spatial separation to be essential if a uniform beam was to be obtained. (Operation of the laser under slightly fluorine-rich conditions also helped to make the beam more diffuse.) The beam was approximately 2 cm x 7 cm by the time it reached the reactor. The laser beam was transmitted through a custom made dielectric mirror, DM and traveled through the reactor impinging on the MgF$_2$ coated aluminum mirror M, where a fraction of the beam was reflected back into the reactor. Both mirrors DM and M, were mounted on precision mirror mounts with vernier control to enable very fine adjustments. (DM was specially coated for us by Acton Research Corp. to have ~ 85% transmission at 193 nm and ~ 95% reflectivity at 257 nm.)
The doubled CW 257 nm UV beam was generated as described in Appendix II. This beam was diverted into the reactor using mirror \( M \), so as to traverse the volume photolyzed by the ArF laser beam. By adjusting Mirrors \( D \) and \( M \), the CW UV beam was multipassed 8 times through the reactor to obtain a path length of \( \sim 860 \) cm. The 8th pass was diverted away from the reactor by a small aluminum mirror \( M_2 \), passed through a methanol cell and a 257 nm bandpass filter, and detected by a quartz envelope 1P28 (RCA) photomultiplier tube. (It was necessary to use a methanol filter to prevent the 193 nm laser pulse from being detected by the PM tube.) The output of the PM tube was amplified and stored in a signal averager (Tracor-Northern 1500) operating in the analog mode and triggered 150 \( \mu \)sec after the photolysis pulse. (We could not obtain a usable signal in the first 150 \( \mu \)sec due to interference from fluorescence induced by the 193 nm beam.) The PM tube was operated at \( \sim 600 \) V to have a resistor bridge current of \( \sim 1 \) mA. The anode current was always kept below 1 \( \mu \)A by using suitable neutral density filters to reduce the intensity of the 257 nm beam. To increase the signal-to-noise ratio of the decay curves, 16 to 64 flashes were averaged. The pulse rate of the photolysis laser (0.03 to 0.01 Hz) was such that the contents of the reactor was replaced between consecutive photolysis pulses. This was necessary in order to sweep out the products (which also absorb the probing beam) and use identical gas mixtures for each flash. In preliminary experiments it was established that as long as the cell was swept out between flashes either the laser repetition rate or the flow rate of the mixture through the reactor did not affect the measured value of \( k_1 \). The intensity of the transmitted 257 nm beam before photolysis was higher than that obtained when all \( \text{CH}_3\text{O}_2 \) had reacted. This residual absorption has been observed by both Cox and
Tyndall, and Sander and Watson, and is attributed to the absorption by 
CH₃O₂NO₂, the product of Reaction (1). Sander and Watson have shown 
that the absorption of the analyzing beam by a reaction product which is 
stoichiometrically coupled to the monitored reactant species by a single 
reaction (as it is in the present case) does not affect the kinetic data 
that is obtained. In addition, they point out that the proper I₀ value 
that should be used in the data analysis is the intensity of the 257 nm 
beam when all CH₃O₂ has reacted, and not the value obtained when CH₃O₂NO₂ 
is absent. It is worth noting that since the intensity of the probing 
beam was high, the signal-to-noise was excellent and we could easily work 
with less than 3% initial absorption and still follow the decay of CH₃O₂ 
down to ~ 4 1/e times!
Results

Reaction (1) was studied as a function of the pressure of the bath gas N\textsubscript{2} and temperature (at 298K, 76-722 torr; at 353K, 330-696 torr; at 253K, 109-510 torr). As pointed out earlier, all experiments were carried under pseudo-first order conditions with [NO\textsubscript{2}] > [CH\textsubscript{3}O\textsubscript{2}]. Figure 2 shows typical decays of [CH\textsubscript{3}O\textsubscript{2}] as a function of time; the decays are exponential and thus confirm the presence of pseudo-first order conditions. The decay of [CH\textsubscript{3}O\textsubscript{2}] was usually followed, for 3 \(1/e\) times. The pseudo-first order rate constant, \(k_1\) (\(\equiv\) slope of \(\ln[\text{CH}_3\text{O}_2]\) vs. t plots) was measured for various values of [NO\textsubscript{2}] at each temperature and N\textsubscript{2} pressure. \(k_1\) was then plotted against [NO\textsubscript{2}]; the slope of this line gave \(k_2\). Figure 3 shows one such plot. It should be pointed out that the fitting procedure we employed (a linear least squares analysis) did not force the \(k_1\) vs. [NO\textsubscript{2}] line to a zero intercept; in our system, it is possible to have a non-zero intercept since the entire volume of the reactor was not subjected to the photolysis. The intercepts in all our experiments were small relative to the measured \(k_1\) values.

Table I lists the individual values of \(k_1\) along with all the pertinent experimental conditions. The quoted errors for \(k_1\), calculated from the slope of \(k_1\) vs. [NO\textsubscript{2}] plots, are \(2\sigma\) and reflect the precision of the measurement. The absolute accuracy of the measured values of \(k_1\), is expected to be \(\sim 20\%\) which includes the error in the [NO\textsubscript{2}] measurement.

Table II lists the values of \(k_1\) obtained at various N\textsubscript{2} pressures and temperatures. Figure 4 shows a plot of \(k_1\) as a function N\textsubscript{2} number density at three different temperatures. The solid lines drawn through these points are visual best fits.
Figure 2. Temporal Profiles in the Presence of Varying Amounts of NO$_2$. The concentration of NO$_2$ for each decay curve is shown next to the least squares lines drawn through the experimental points.
\[
\text{CH}_3\text{O}_2^+ + \text{NO}_2^+ + \text{N}_2 \rightarrow \text{CH}_3\text{O}_2\text{NO}_2^+ + \text{N}_2
\]

(519 ± 2) Torr N\textsubscript{2}

298K

\[
(3.36 \pm 0.32) \times 10^{12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}
\]

\[
\left[\text{NO}_2\right] \times 10^{15} \text{ molecules cm}^{-3}
\]

Figure 3. Plot of Pseudo-First Order Rate Constants vs. NO\textsubscript{2} Concentration at 298K and 519 Torr of N\textsubscript{2}. 

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Table I. Rate Constant Data for the Reaction of CH$_3$O$_2$ with NO$_2$.

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<th>Temperature K</th>
<th>Pressure torr</th>
<th>[Azomethane] $10^{15}$ cm$^{-3}$</th>
<th>[O$_2$] $10^{17}$ cm$^{-3}$</th>
<th>[CH$_3$O$_2$]$^a$ $10^{14}$ cm$^{-3}$</th>
<th>[NO$_2$] $10^{14}$ cm$^{-3}$</th>
<th>$k_1$, $10^{12}$s$^{-1}$ cm$^3$ molecule$^{-1}$</th>
<th>$k_1 \times 10^{12}$b cm$^3$ molecule$^{-1}$s$^{-1}$</th>
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<td>k₁ x 10¹⁺b cm³ molecule⁻¹s⁻¹</td>
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<td>2.22</td>
<td>1.32</td>
<td></td>
<td>5.66</td>
<td>2.29</td>
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</tr>
<tr>
<td></td>
<td>0.61</td>
<td>2.22</td>
<td>1.54</td>
<td></td>
<td>7.89</td>
<td>3.29</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.64</td>
<td>2.21</td>
<td>1.60</td>
<td></td>
<td>9.96</td>
<td>3.89</td>
<td>(3.85±0.30)</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>$N_2$ Pressure (torr)</td>
<td>[Azomethane] $10^{15}$ cm$^{-3}$</td>
<td>[O$_2$] $10^{17}$ cm$^{-3}$</td>
<td>[CH$_3$O$_2$]$_a$ $10^{13}$ cm$^{-3}$</td>
<td>[NO$_2$] $10^{14}$ cm$^{-3}$</td>
<td>$k_1$ x $10^{12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>---------------</td>
<td>----------------------</td>
<td>---------------------------------</td>
<td>--------------------------</td>
<td>----------------------------</td>
<td>------------------------</td>
<td>-----------------------------</td>
<td></td>
</tr>
<tr>
<td>253</td>
<td>503±3</td>
<td>0.60</td>
<td>4.59</td>
<td>1.80</td>
<td>3.00</td>
<td>1.66</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.78</td>
<td>5.36</td>
<td>1.30</td>
<td>4.34</td>
<td>2.16</td>
<td></td>
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<tr>
<td></td>
<td>0.63</td>
<td>4.56</td>
<td>2.55</td>
<td>6.55</td>
<td>3.01</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>0.62</td>
<td>4.59</td>
<td>2.59</td>
<td>8.52</td>
<td>4.05</td>
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<tr>
<td>519</td>
<td>1.11</td>
<td>5.22</td>
<td>2.2</td>
<td>5.85</td>
<td>2.60</td>
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<td></td>
<td>0.99</td>
<td>5.21</td>
<td>2.6</td>
<td>11.20</td>
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<tr>
<td></td>
<td>0.88</td>
<td>5.21</td>
<td>2.0</td>
<td>18.15</td>
<td>9.72</td>
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</tr>
<tr>
<td></td>
<td>1.10</td>
<td>5.22</td>
<td>2.1</td>
<td>23.8</td>
<td>13.20</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a) The initial concentration of CH$_3$O$_2$, [CH$_3$O$_2$]$_o$, was calculated by back-extrapolating the decay curve for 150 µsec, (the delay between photolysis and initiation of signal acquisition.)

b) The quoted errors are 2σ and represent the precision of the measurements.
Table II. Rate Constants for the Reaction of CH₂O₂ with NO₂ as a Function of Temperature and N₂ Pressure.

<table>
<thead>
<tr>
<th>Temperature K</th>
<th>Pressure Torr</th>
<th>Number Density $10^{19}$ molecules cm⁻³</th>
<th>$k_3 \times 10^{12}$ cm³ molecule⁻¹ s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>295</td>
<td>76</td>
<td>0.246</td>
<td>1.36 ± 0.23</td>
</tr>
<tr>
<td>157</td>
<td>0.509</td>
<td>1.90 ± 0.32</td>
<td></td>
</tr>
<tr>
<td>258</td>
<td>0.836</td>
<td>2.60 ± 0.56</td>
<td></td>
</tr>
<tr>
<td>352</td>
<td>1.141</td>
<td>2.82 ± 0.28</td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>1.620</td>
<td>3.25 ± 0.50</td>
<td></td>
</tr>
<tr>
<td>519</td>
<td>1.682</td>
<td>3.36 ± 0.32</td>
<td></td>
</tr>
<tr>
<td>722</td>
<td>2.339</td>
<td>4.12 ± 0.38</td>
<td></td>
</tr>
<tr>
<td>353</td>
<td>330</td>
<td>0.903</td>
<td>1.19 ± 0.15</td>
</tr>
<tr>
<td>354</td>
<td>0.966</td>
<td>1.35 ± 0.21</td>
<td></td>
</tr>
<tr>
<td>511</td>
<td>1.398</td>
<td>1.71 ± 0.10</td>
<td></td>
</tr>
<tr>
<td>696</td>
<td>1.904</td>
<td>1.93 ± 0.20</td>
<td></td>
</tr>
<tr>
<td>253</td>
<td>109</td>
<td>0.416</td>
<td>2.50 ± 0.34</td>
</tr>
<tr>
<td>250</td>
<td>0.954</td>
<td>3.85 ± 0.30</td>
<td></td>
</tr>
<tr>
<td>503</td>
<td>1.920</td>
<td>5.10 ± 0.50</td>
<td></td>
</tr>
<tr>
<td>519</td>
<td>1.981</td>
<td>5.8 ± 1.0</td>
<td></td>
</tr>
</tbody>
</table>
Figure 4. Plots of $k_1$ vs. $N_2$ Number Density. The lines drawn through the points are visual best fits.
There are two possible chemical complications that can arise in our experiments: (a) production of $O_3$ due to reaction of $O(^3P)$ (formed by either $O_2$ or $NO_2$ photolysis) with $O_2$ and (b) production of $NO$ and its subsequent reaction with $CH_3O_2$. Photolysis of $O_2$ under the most unfavorable conditions, i.e., high $[O_2](\sim 5 \times 10^{17} \text{ cm}^{-3})$ and high photolysis laser energy ($\sim 10 \text{ mJ/cm}^2$), would produce $\sim 1 \times 10^{13} O(^3P) \text{ cm}^{-2}$. (The absorption cross section for $O_2$ at 193 nm is $\sim 1 \times 10^{-21} \text{ cm}^2$.13) Similarly, photolysis of $NO_2$ would lead to $\sim 1 \times 10^{12} O(^3P) \text{ cm}^{-3}$. (The absorption cross section for $NO_2$ at 193 nm is $\sim 6 \times 10^{-19} \text{ cm}^2$.15.) Any $O(^3D)$ that is formed via photolysis would be quenched to $O(^3P)$ in less than 0.1 $\mu\text{sec}$ by $N_2$.16 The photolytically produced $O(^3P)$ would then react with either $O_2$ or $NO_2$,

$$O(^3P) + O_2 + M \xrightarrow{k_s} O_3 + M$$

(4)

$$O(^3P) + NO_2 \xrightarrow{k_s} NO + O_2$$

(5)

The fraction of $O(^3P)$ that would lead to $O_3$ formation would, of course, depend on the ratio of $k_s[O_2][M]$ to $k_s[NO_2]$. Under the extreme conditions of low temperature (where $k_s$ is large) and low $NO_2$, we would produce $\sim 4 \times 10^{12} O_3 \text{ cm}^{-3}$. In our experiment, then, we would obtain $\sim 3\%$ absorption of 257 nm radiation due to $O_3$. However, the $O_3$ formation does not affect measurement of the $CH_3O_2$ decay since all $O_3$ is formed within 100 $\mu\text{sec}$ (99% completion) after the laser flash, and, therefore simply changes the value of $I_0$. The concentration of $O_3$ formed is too low to have any effect on the kinetics of the measured rate of $CH_3O_2$ decay. This conclusion was checked by increasing the photolysis energy by a factor of 4 while keeping $[CH_3O_2]_0$ constant (by decreasing [azomethane] by a factor
of 4); the measured decay rates were, within experimental error, unaffected.

The amount of NO that is produced via NO₂ photolysis would be at most 1.2% when 10 mJ/cm² is used for photolysis and all O(³P) that is produced reacts with NO₂ to produce NO. NO would of course, react with CH₃O₂ to produce CH₃O and NO₂,

\[
\text{CH₃O₂ + NO} \xrightarrow{k_2} \text{CH₃O + NO₂ . (2)}
\]

The rate constant for Reaction (2) is known to be \( \approx 8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1} \). Since the measured values of \( k_2 \) vary from 1.19 to \( 5.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1} \), the contribution of Reaction (2) could never be greater than 8% (i.e., at high temperature and low pressures). Again, this possibility was discarded as inconsequential by the observation that the measured rate constant was independent of photolysis energy.

CH₃O formed in Reaction (2) would react with NO₂ to give CH₃ONO₂.

\[
\text{CH₃O + NO₂} \rightarrow \text{CH₃ONO₂ . (6)}
\]

Formation of CH₃ONO₂ would not affect the measured rate constant since CH₃ONO₂ does not regenerate CH₃O₂, does not strongly absorb 257 nm radiation, and its concentration is too low to effectively remove CH₃O₂ via reaction. (The absorption cross section for CH₃ONO₂ is \( \approx 4 \times 10^{-18} \text{ cm}^2 \) at 257 nm.\(^{17}\))

In addition to the two photolysis related problems that were discussed above, it is possible that our measured rate constants are incorrect if the thermal decomposition of the CH₃O₂NO₂ product leads to CH₃O₂ production on the same time scale as the measured CH₃O₂ decay,
Reaction (7) would, of course, be most severe at higher temperatures. The rate constant for Reaction (7) is not known. However, it cannot be very different from that of HNO$_2$ decomposition leading to HO$_2$ and NO$_2$ production, which has been measured. Using this rate constant, the fastest rate for Reaction (7) at 353K, would be $\sim 20 \text{s}^{-1}$. This rate is negligible when compared to the [CH$_3$O$_2$] decay rates of 699-8837 $\text{s}^{-1}$ that were measured at 353K. Experimentally, if Reaction (7) was important, we would have observed non-exponential [CH$_3$O$_2$] decays and more importantly, a non-linear dependence of $k_i$ on [NO$_2$]. We found the [CH$_3$O$_2$] to decay exponentially for at least 3 1/e times and $k_i$ vs [NO$_2$] plots were linear. Therefore, Reaction (7) could not have been significant under our experimental conditions.
Discussion

There are three separate direct measurements of $k_1$ at 298K. Cox and Tyndall\textsuperscript{9} measured $k_1$ to be $(1.2 \pm 0.3) \times 10^{-12}$ cm$^3$molecule$^{-1}$s$^{-1}$ at 500 torr of Ar + CH$_4$, and $k_1 = (1.6 \pm 0.3) \times 10^{-12}$ cm$^3$molecule$^{-1}$s$^{-1}$ at 540 torr N$_2$, using the molecular modulation technique. This pressure independent value of $k_1$ is in good agreement with those obtained by Adachi and Basco\textsuperscript{10} who measured $k_1$ to be $(1.53 \pm 0.07) \times 10^{-12}$ cm$^3$molecule$^{-1}$s$^{-1}$ independent of pressure (between 53 and 580 torr Ar) using the method of flash photolysis-kinetic spectroscopy. This pressure independent behavior has been interpreted to mean that Reaction (1) is at its high pressure limit above ~50 torr of Ar. Sander and Watson,\textsuperscript{2} however, found $k_1$ to vary from $(1.5 \pm 0.10) \times 10^{-12}$ cm$^3$molecule$^{-1}$s$^{-1}$ at 50 torr N$_2$ to $(3.94 \pm 0.17) \times 10^{-12}$ cm$^3$molecule$^{-1}$s$^{-1}$ at 700 torr of N$_2$ at 298K. Moreover, the value of $k_1$ was observed to be dependent on the nature of the bath gas, i.e., He, N$_2$, or SF$_6$. This type of pressure dependent behavior is typical of an addition reaction. Sander and Watson’s data also shows that Reaction (1) is in the “fall-off” regime, i.e., between second and third order, in pressure range of 50 to 700 torr of He, N$_2$, and SF$_6$. It should also be pointed out that the lower pressure values of $k_1$ obtained by Sander and Watson agree reasonably well with $k_1$ values of both Cox and Tyndall, and Adachi and Basco.

As seen from Table III, our measured values of $k_1$ are in excellent agreement with those of Sander and Watson; this argues very heavily for $k_1$ being pressure dependent. Sander and Watson have pointed out that the possible reason for the discrepancy between their values at higher pressures and those of Cox and Tyndall, is the long residence time of the gas mixtures and depletion of NO$_2$ along the length of the cell in
Table III. Comparison of Our Results With Previous Data at 298K.

<table>
<thead>
<tr>
<th>Pressure (torr)</th>
<th>Diluent</th>
<th>This Work $k_1$, $10^{12} \times \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$</th>
<th>Sander and Watson Ref (2)</th>
<th>Cox and Tyndall Ref (9)</th>
<th>Adachi and Basco Ref (10)</th>
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</thead>
<tbody>
<tr>
<td>50</td>
<td>N\textsubscript{2}</td>
<td>1.36±0.23</td>
<td>1.15±0.10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>76</td>
<td>N\textsubscript{2}</td>
<td>1.90±0.32</td>
<td>1.58±0.15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>N\textsubscript{2}</td>
<td>2.60±0.56</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>157</td>
<td>N\textsubscript{2}</td>
<td>2.82±0.28</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>225</td>
<td>N\textsubscript{2}</td>
<td>3.25±0.50</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>258</td>
<td>N\textsubscript{2}</td>
<td>3.35±0.32</td>
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</tr>
<tr>
<td>350</td>
<td>N\textsubscript{2}</td>
<td>3.94±0.17</td>
<td>2.98±0.23</td>
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</tr>
<tr>
<td>352</td>
<td>N\textsubscript{2}</td>
<td>4.12±0.38</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>N\textsubscript{2}</td>
<td>4.12±0.38</td>
<td>3.67±0.21</td>
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</tr>
<tr>
<td>519</td>
<td>N\textsubscript{2}</td>
<td>4.12±0.38</td>
<td>3.35±0.32</td>
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<td></td>
</tr>
<tr>
<td>540</td>
<td>N\textsubscript{2}</td>
<td>4.12±0.38</td>
<td>1.6±0.3</td>
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</tr>
<tr>
<td>700</td>
<td>N\textsubscript{2}</td>
<td>4.12±0.38</td>
<td>3.94±0.17</td>
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</tr>
<tr>
<td>722</td>
<td>N\textsubscript{2}</td>
<td>4.12±0.38</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>4.12±0.38</td>
<td>1.2±0.3</td>
<td></td>
<td>1.53±0.07</td>
</tr>
</tbody>
</table>

*The preferred value reported by Watson and Sander is the average value $\approx k_1/[\text{NO}_2]$. 
the molecular modulation apparatus. In Adachi and Basco's experiments, the concentrations of reactants used were extremely large. This should have led to many secondary reaction complications. Also, their \( \text{CH}_3\text{O}_2 \) radical detection scheme was quite insensitive. Furthermore, as the authors pointed out, they would have to make a large correction to their high flash energy results due to the participation of Reaction (6), if \( k_6 = 8 \times 10^{-12} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1} \). To date, three separate direct measurements of \( k_6 \) have been carried out which yield a value of \( k_6 = (8 \pm 2) \times 10^{-12} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1} \). Even though Adachi and Basco carried out a separate set of experiments using low flash energies and obtained values of \( k_6 \) (supposedly in the absence of secondary reaction complications) in agreement with their previous measurements, their results have to be considered suspect. They had very large concentrations of free radicals even in their low flash energy experiments which could lead to erroneous results. We believe that at 298K, the data obtained by Sander and Watson and in the present investigation are devoid of secondary reaction complications and hence should be used for atmospheric modeling studies.

There are no previous determinations of the temperature dependence of \( k_1 \). Our results are consistent with what is to be expected for an addition reaction which goes through an energy-rich complex. The strong temperature dependence of the measured values of \( k_1 \) suggests that \( k_{1\infty} \) is likely to be \( > 1 \times 10^{-11} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1} \) at 253K. At 600 Torr, for example, the apparent "activation energy" for Reaction (6) is \( \sim -1.6 \text{ Kcal/mole} \).

For atmospheric modelling purposes it is convenient to obtain an analytical expression which best describes the temperature and pressure dependence of \( k_1 \). Sander and Watson have fit their data for \( k_1 \) at 298K.
to the following semi-empirical equation which is based on Troe's formulation of RRKM theory:\textsuperscript{19}

\[
k([M],T) = \frac{k_c(T)[M]}{1 + k_c(T)[M]/k_c(T)} F_c \left\{ 1 + \left[ \log_{10}(k_c(T)/k_c(T)) \right]^2 \right\}^{-1}
\]

In Equation (I), \(k_c(k_c)\) are the rate constants in the low (high) pressure limits and \(F_c\) is a parameter which relates the energy dependence of the rate constant for activated complex decomposition to the shape of the \(k\) vs \([M]\) curve. They obtain \(k_c(298) = (2.33 \pm 0.8) \times 10^{-30}\) cm\(^6\) molecule\(^{-1}\) sec\(^{-1}\), \(k_c = (7.0 \pm 1.0) \times 10^{-12}\) cm\(^3\) molecule\(^{-1}\) sec\(^{-1}\) and \(F_c = 0.4\).

Because Sander and Watson's data base at 298K is much larger than ours and because our results are in excellent agreement with theirs, we have fit our temperature dependent data by trial and error with the constraint that \(k_c(298), k_c,\) and \(F_c\) must fall within the error limits given by Sander and Watson. The best fit to the data is obtained for (Figure 4)

\[
k_c(T) = 2.2 \times 10^{-90} \left( \frac{T}{298} \right)^{2.5} \text{ cm}^6\text{molecule}^{-2}\text{sec}^{-1}
\]

\[
k_c(T) = 7 \times 10^{-12} \left( \frac{T}{298} \right)^{-3.5} \text{ cm}^3\text{molecule}^{-1}\text{sec}^{-1}
\]

\(F_c = 0.4\).

Our results suggest that Reaction (1) could contribute significantly towards removal of CH\(_3\)O\(_2\) and NO\(_2\) in the presence of high concentrations of NO\(_x\) (such as those encountered in urban smog) if CH\(_3\)O\(_2\)NO\(_2\) is thermally stable.
References


Acknowledgements

We would like to thank Drs. S.P. Sander and R.T. Watson for very helpful discussions throughout this work. We would also like to thank Mr. A.O. Langford for discussions which steered us towards utilization of colinear photolysis and probing laser beams.

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Chapter 2

A STUDY OF OH REACTION WITH HNO$_3$:
KINETICS AND NO$_3$ YIELD
INTRODUCTION

Nitric acid, HNO$_3$, is an important reservoir for both HO$_x$ and NO$_x$ species in the stratosphere where it is principally formed via the combination reaction of NO$_2$ with OH,

$$\text{OH} + \text{NO}_2 + \text{M} \xrightarrow{k_1} \text{HNO}_3 + \text{M}. \quad (1)$$

HNO$_3$ is removed from the stratosphere via solar photolysis as well as reaction with OH,

$$\text{OH} + \text{HNO}_3 \xrightarrow{k_2} \text{products}. \quad (2)$$

Recently, we measured $k_2$ and found it to be faster than previously believed.$^{2-5}$ In addition, $k_2$ was found to exhibit a negative temperature dependence which is unusual for a biomolecular reaction. Even though it is known that NO$_3$ is formed in reaction (2) at 298 K$^6$ and it has been generally assumed that NO$_3$ and H$_2$O are the only products of reaction (2), we suggested the possibility of reaction (2) proceeding through multiple pathways leading to different sets of products,$^1$ i.e.,

$$\text{OH} + \text{HNO}_3 \xrightarrow{k_{2a}} \text{H}_2\text{O} + \text{NO}_3 \quad (2a)$$

$$\text{OH} + \text{HNO}_3 \xrightarrow{k_{2b}} \text{H}_2\text{O}_2 + \text{NO}_2 \quad (2b)$$

$$\text{OH} + \text{HNO}_3 \xrightarrow{k_{2c}} \text{Addition Product} \quad (2c)$$

It was further implied that the branching ratios, i.e., $k_{2a}/k_2$ and $k_{2b}/k_2$ could vary with temperature, thereby explaining the unusual temperature dependence.
In stratospheric model calculations it was found that the estimated ozone concentration changes due to anthropogenic emissions were sensitive to not only the new value of $k_2$ but also the identity of the reaction products. Therefore, we carried out the experiments reported here to measure the yield of $NO_3$ in reaction (2) as well as to remeasure $k_2$ by a different experimental technique. The rate coefficient was measured by monitoring the temporal profile of $NO_3$ formed from reaction (2) following the production of OH by laser photolysis of HNO$_3$. By measuring the amount of $NO_3$ produced from a known (calculated) concentration of OH, the yield of $NO_3$ and hence the branching ratio, $k_{2a}/k_2$, was also determined.

While the work reported here was in progress, three other groups have studied reaction (2). Nelson et.al. measured $k_2$ at 298 K using flash photolysis-resonance fluorescence technique to be $(8.2 \pm 1.8) \times 10^{-14}$ cm$^3$molecule$^{-1}$s$^{-1}$ and using flash photolysis-laser absorption technique to be $(10.6 \pm 3.4) \times 10^{-14}$ cm$^3$molecule$^{-1}$s$^{-1}$. In addition, they also found the $NO_3$ free radical to be a major product of reaction (2). Kurylo et.al. and Margitan and Watson have also studied reaction (2) using the flash photolysis-resonance fluorescence technique. Their results are in reasonably good agreement with our previous measurements both in terms of the observation of a negative temperature dependence and the value of $k_2$ at 298 K (and other temperatures).

**EXPERIMENTAL**

The experimental approach used in the present investigation of reaction (2) was to create OH via pulsed laser photolysis of HNO$_3$, and to subsequently monitor the temporal concentration profile of the $NO_3$ reaction product using the long path laser absorption technique. Even if $NO_3$ is a minor product, as long as it is formed directly from reaction (2), the temporal profile
will reflect the rate of reaction (2). The ratio of [NO₃] formed to initial [OH] is a direct measure of the branching ratio for NO₃ formation, \( k_{2a}/k_2 \).

A schematic diagram of the apparatus is shown in Figure 1. A jacketed pyrex cell \( \sim 5 \) cm in diameter and \( \sim 45 \) cm long was maintained at a fixed temperature using an ethylene glycol-water mixture circulated from a thermostated reservoir. HNO₃ mixed with a large amount of an inert gas (N₂, Ar or SF₆) was passed into the reactor and then into a (76 cm long) absorption cell. The concentration of HNO₃ in this mixture was directly measured in the absorption cell at 298 K using the 228.8 nm Cd line. The 228.8 nm line was isolated from the neighboring 214 nm line using a 0.25 m monochromator and detected by a photomultiplier tube (RCA 4837). The current output of the photomultiplier was constantly monitored using an electrometer. Before each run the cell was flushed with the diluent gas and \( I_0 \), the incident light intensity, recorded. Then, the HNO₃/diluent gas mixture was introduced and \( I \), the transmitted light intensity, measured. At the end of the run, \( I_0 \) was again measured to check for drifts in light intensity during the experiment. The HNO₃ concentration was calculated using an absorption cross section of \( 6.32 \times 10^{-20} \) cm² at 228.8 nm.⁹,¹¹ The pressure in the system was measured at the exit of the reactor using a capacitance manometer. The flow rates of all gases were monitored using calibrated mass flow meters.

A pulsed KrF excimer laser (248 nm) was used as the photolysis light source. It was placed \( \sim 2 \) m from the reactor to ensure a spatially uniform beam. The laser beam entered the reactor through mirror \( M_2 \) and exited through \( M_1 \) where its energy could be monitored. The cw 662 nm laser beam used for NO₃ concentration measurement was generated by pumping a tunable ring dye laser with the all-lines output of an argon ion laser. The line
Figure 1. Schematic Diagram of the Laser Photolysis-Long Path Laser Absorption Apparatus.
width of the dye laser output was measured with a etalon to
be \( \sim 2 \times 10^{-3} \) nm. The probe beam was multi-pass through the reactor using
mirrors \( M_1 \) and \( M_2 \) to obtain a path length of 4.5 to 9 m (Mirrors \( M_1 \) and \( M_2 \)
were specially coated to transmit 86% at 248 nm and reflect 99.5% at
660 nm). The probe beam emerged from the cell, passed through a red filter
and a set of collimators and illuminated a diffuser attached to the entrance
slit of a 0.25 m monochromator. A red-sensitive photomultiplier tube
(Hamamatsu R928P) was used at the exit slit for light detection. The
photomultiplier was wired so as to have a response time of less than 1 \( \mu \)sec
and the resistor bridge current was always much greater (\( \sim 1000 \) times) than
the anode current. The photomultiplier response was found to be linear over
a wide range of light intensity. The red filter prevented the detection of
the photolysis beam while the combination of apertures, the diffuser, and
the monochromator ensured that only the probe beam was detected (i.e., any
fluorescence induced by photolysis laser and room light did not interfere
with the measured probe beam intensity). The wavelength of the probe beam
was periodically checked using a 0.75 nm monochromator operating in the
second order. The monochromator was calibrated against known standards
and the wavelength was accurate to 0.1 nm.

The diluent gases used in this study were obtained from Matheson Gas Products and had the following stated purities: \( \text{Ar} \geq 99.995\%, \text{SF}_6 \geq 99.99\%
and \( \text{N}_2 \geq 99.9995\% \). They were used without further purification. \( \text{HNO}_3 \) was
prepared by reacting concentration \( \text{H}_2\text{SO}_4 \) with \( \text{NaNO}_3 \) under vacuum at \( \sim 290 \) K
and collecting the vapor at 77 K. It was then purified by trap-to-trap
distillation (273-77 K) with only the middle fraction being kept. The pure
\( \text{HNO}_3 \) was stored in the dark at 77 K.
In a typical kinetics experiment \( \sim 10^{16} - 10^{17} \text{ HNO}_3 \text{ cm}^{-3} \) in 20-100 torr diluent gas (N\(_2\), Ar, or SF\(_6\)) was flowed through the cell with a linear velocity of \( \sim 3 \text{ cm/sec} \). The signal averager (working in the peak height analysis mode), which monitored the probe beam intensity, was pretriggered \( \sim 1 \text{ msec} \) before the photolysis laser beam entered the reactor. Pretriggering allowed the measurement of \( I_0 \), the intensity of the 662 nm beam in the absence of NO\(_3\). The photolysis laser beam (248 nm, \( \sim 5 \text{ mJ cm}^{-2} \)) photodissociated HNO\(_3\) to produce OH,

\[
\text{HNO}_3 \xrightarrow{\text{hv}, \lambda=248 \text{nm}} \text{OH} + \text{NO}_2. \tag{3}
\]

OH then reacted with HNO\(_3\) to produce NO\(_3\);

\[
\text{OH} + \text{HNO}_3 \xrightarrow{k_{2a}} \text{H}_2\text{O} + \text{NO}_3. \tag{2a}
\]

The probe beam intensity was attenuated due to absorption by NO\(_3\) and was measured in real time. This intensity-time profile was converted to an \([\text{NO}_3]\) time profile using the relationship \( \ln (I/I_0) = [\text{NO}_3]_0 \alpha \) (where \( \alpha \) is absorption cross section of NO\(_3\) at 662 nm, and \( \alpha \) is the path length). One such profile obtained by averaging 32 flashes is shown in Figure 2. In general, 16-100 flashes (repetition rate .03 Hz) were averaged to obtain the NO\(_3\) temporal profile. In the absence of any NO\(_3\) loss, which was indeed the case when the reactor was completely replenished between photolysis laser flashes, the temporal profile of \([\text{NO}_3]\) is given by the relationship,

\[
[\text{NO}_3] = \frac{k_{2a}}{k_2} [\text{OH}]_0 \left(1 - e^{-k_2[H\text{NO}_3]t}\right)
\]
Figure 2. Temporal Profile of $\text{NO}_3$ Concentration Following the Photolysis of $\text{HNO}_3$ at 248 nm.
where \([\text{NO}_3]\) is concentration of \(\text{NO}_3\) at time \(t\), \([\text{OH}]_0\) is the initial \([\text{OH}]\), and \([\text{HNO}_3]\) is the constant measured concentration of \(\text{HNO}_3\). A plot of

\[
\ln([\text{NO}_3]_t - [\text{NO}_3]) \text{ vs. time yields a straight line, such as the one shown in Figure 3; the slope of the line gives } k'_2 \left(= k_2' \text{[HNO}_3]\right).\]

Note that to obtain \(k'_2\) neither \(c\) nor \(e\) needs to be known. \(k'_2\) was measured at various concentrations of \(\text{HNO}_3\); a plot of \(k'_2\) vs. \([\text{HNO}_3]\) yields a straight line whose slope is \(k_2\) (see Figure 4). (In most experiments, the \([\text{NO}_3]\) time profile was fitted using an iterative computer program to the expression

\[
[\text{NO}_3]_t = \frac{k'_2}{k'_d - k'_2} [\text{OH}]_0 \left(k_{2a} / k_2\right) (e^{-k'_2 t} - e^{-k'_d t})
\]

The value of \(k'_2\) thus obtained was identical to the slopes of \(\ln([\text{NO}_3]_t - [\text{NO}_3])\) vs. \(t\) plots since \(k_d\), the first order rate constant for \(\text{NO}_3\) loss, was usually \(~20 \text{ s}^{-1}\) while \(k'_2\) ranged from \(3000 \text{ s}^{-1}\) to \(20,000 \text{ s}^{-1}\).

Experiments carried out to measure the yield of \(\text{NO}_3\) in reaction (2) were very similar to the kinetics runs. Careful attention was given to ensure reproducibility in photolysis laser energy and beam quality. Unlike the kinetics runs only 10 flashes were averaged. The laser energy density was measured before and after the run using a calibrated energy monitor. In preliminary experiments it was determined that the energy density was constant to within 10% over the whole length of the cell. The transmission of the mirror \(M_2\) and cell windows were directly determined by measuring the attenuation of the 248 nm laser beam. As in the kinetics runs the concentration of \(\text{HNO}_3\) was constantly monitored. The maximum in absorption due to \(\text{NO}_3\) was measured for various concentrations of \(\text{HNO}_3\) and laser energies. Since, there was no loss of \(\text{NO}_3\) in the time scale of the experiment, the maximum absorbance gave the net concentration of \(\text{NO}_3\) produced. The initial
Figure 3. First Order NO$_3$ Growth Plot; Slope of the Line Gives $k'$. 

$3710 \pm 155$
Figure 4. Plot of \( k' \) vs. \( \text{HNO}_3 \) Concentration. Slope gives the rate coefficient.
concentration of photolytically produced OH, \([\text{OH}]_0\), was calculated using the equation,

\[
[\text{OH}]_0 = P \times [\text{HNO}_3] \times \sigma_{\text{HNO}_3}^{248} \times \phi
\]

where \(P\) = photon flux at 248 nm in photons/cm\(^2\), \([\text{HNO}_3]\) is the measured \(\text{HNO}_3\) concentration, \(\sigma_{\text{HNO}_3}^{248}\) is the absorption cross section of \(\text{HNO}_3\) at 248 nm taken to be \(2.01 \times 10^{-20}\) cm\(^2\)/molecule,
\(^{10,11}\) and \(\phi\) is the quantum yield of OH in \(\text{HNO}_3\) photolysis at 248 nm and taken to be unity.\(^{12}\) (This equation is valid since the system is optically thin at 248 nm.) The concentration of \(\text{NO}_3\) produced was calculated using the relation,

\[
[\text{NO}_3]_{\text{max}} = \frac{1}{\sigma_{\text{NO}_3}^{662}} \ln\left(\frac{I_o}{I_m}\right)
\]

where \(I_o\) and \(I_m\) are measured intensities of 662 nm beam in the absence and the presence (at maximum) of \(\text{NO}_3\), \(\sigma_{\text{NO}_3}^{662}\) is the absorption cross section for \(\text{NO}_3\) at 662 nm taken to be \(1.70 \times 10^{-17}\) cm\(^2\),\(^{13,14,15}\) and \(L\) is the path length. The ratio \([\text{NO}_3]_{\text{max}}/[\text{OH}]_0\) gives the yield of \(\text{NO}_3\) in reaction (2).

RESULTS AND DISCUSSION

Some initial tests were performed to ensure that the absorption at 662 nm was indeed due to \(\text{NO}_3\). When the laser was tuned off the band no absorption was measured. When tuned on to the side of the band, an absorption that is to be expected (within 20%) based on the reported cross sections was measured.\(^{13-15}\) In addition, it was verified that \(\text{NO}_2\) and \(\text{HNO}_3\) were not contributing to the measured attenuation. Therefore, it is clear that \(\text{NO}_3\) was indeed the transient that was measured.
Kinetic Studies

All experiments were carried out under pseudo-first order conditions with HNO$_3$ in very large excess ($10^3 < [\text{HNO}_3]/[\text{OH}]_0 < 5 \times 10^4$). In preliminary experiments it was determined that a variation of 10 in $[\text{HNO}_3]/[\text{OH}]_0$ ratio at a fixed $[\text{HNO}_3]$ did not affect the measured rate coefficients. Also, as long as the contents of the reactor were completely replaced between consecutive photolysis laser flashes, the NO$_3$ concentration reached a maximum and its subsequent decay rate was very small. The position of the absorption cell (i.e., in front or back of the reaction with respect to the direction of gas flow) did not have any effect on the measured rate coefficient. As seen from Figure 3, the decay of $[\text{OH}]$ as reflected by the $[\text{NO}_3]$ rise is exponential and the dependence of $k_2(= k_2[\text{HNO}_3])$ on $[\text{HNO}_3]$ is linear. These observations in conjunction with the invariance of $k_2$ to changes in $[\text{OH}]_0$, i.e., photolysis laser energy, demonstrate that chemical complications did not effect the measured value of $k_2$.

One systematic error which can produce the observed negative temperature dependence of $k_2$ is the occurrence of reaction (2) due to the presence of NO$_2$ in the HNO$_3$ sample or in the reactor. Concentrations of NO$_2$ in our HNO$_3$ samples were unmeasurably low. (NO$_2$ concentration was measured using long path absorption of 366 nm.) (Note that one needs $\sim 20\%$ NO$_2$ in the sample to see the observed increase with decrease in temperature while the upper limit for measured NO$_2$ was 0.5$\%$.) In addition, we checked for the presence of reaction (1) by taking advantage of the fact that $k_1$ is strongly dependent on both pressure and the identity of the third body. As seen from Table I, the pressure and identity of the third body did not effect the measured value of $k_2$. It is easy to show that if reaction (1) was indeed important substantial differences in measured values of $k_2$ would have been observed.
Table I

\[ k_2 \times 10^{13}, \text{cm}^3\text{molecule}^{-1}\text{s}^{-1} \]

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>Diluent</th>
<th>298</th>
<th>251</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ar, 50 torr</td>
<td>1.25</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>N\textsubscript{2}, 50 torr</td>
<td>-----</td>
<td>1.94</td>
</tr>
<tr>
<td></td>
<td>SF\textsubscript{6}, 60 torr</td>
<td>1.39</td>
<td>0.28</td>
</tr>
</tbody>
</table>
Figure 5 shows the Arrhenius plot for reaction (2). As seen from this figure, the present measurements yield $k_2$ values which are in excellent agreement with our previous measurements. (We could not measure $k_2$ at temperatures much lower than 251 K because the vapor pressure of HNO$_3$ is very low and hence sufficient concentrations of HNO$_3$ could not be introduced into the cell to perform the measurement. It should be noted that the concentrations of HNO$_3$ needed in the current method are ~20 times larger than those required in our previous flash photolysis-resonance fluorescence experiments.) Discrepancies between our values of $k_2$ and other previous (pre 1980) measurements have already been described. Hence no discussion of these discrepancies needs to be presented here.

Of the three recent measurements of $k_2$ at 298 K, only the results of Nelson et al.\textsuperscript{7} seen to be different from our measured value of $k_2$. Their value of $k_2$ measured using the flash photolysis-laser absorption technique, $(1.0 \pm 3.4) \times 10^{-14}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, falls within the lower limits of the $k_2$ values of our two studies, $(12.5 \pm 2.8) \times 10^{-14}$ and $(13.2 \pm 3.0) \times 10^{-14}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. However, their $k_2$ value obtained using a technique very similar to our previous study yields the lowest value of $k_2$ reported since 1980. There are no obvious reasons as to why Nelson et al.'s results disagree with $k_2$ values reported by Kurylo et al.,\textsuperscript{8} $1.38 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, Margitan and Watson,\textsuperscript{9} $1.1 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, and our two measurements.

The temperature dependencies observed by Kurylo et al.\textsuperscript{8} and Margitan and Watson\textsuperscript{9} are very similar to that observed by us previously. However, both these studies tend to support a non-Arrhenius behavior of $k_2$, $k_2$ not decreasing with increases in temperature at $T > 298$ K. Kurylo et al. have fit their low temperature (i.e., $T < 298$ K) data to an Arrhenius form,
Figure 5. Arrhenius Plot of $k_1$. Open Circles Obtained by Monitoring NO$_3$. Close Circles from our Previous Study (Wine et al., JGR, 86, 1105 (1981)).
\[ k_2 = (1.05 \pm 0.20) \times 10^{-14} \exp\left(\frac{-760 \pm 50}{T}\right) \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}, \]

which is nearly identical to that reported by us previously. Margitan and Watson have chosen not to report an Arrhenius expression since they observe a slight change in \( k_2 \) when pressure is changed from 20-100 torr at 238 K. They believe that the pressure dependence of \( k_2 \) is real since there was insufficient amount of NO\(_2\) in their system for reaction (1) to be responsible for this observation.

**NO\(_3\) Yield in Reaction 2**

As in the case of kinetics experiments the yield measurements were carried out under pseudo-first order conditions. The ratio of the NO\(_3\) yield to the initial OH concentration \([\text{NO}_3]/[\text{OH}]_0\), was measured. At 298 K the average of 7 runs yield \([\text{NO}_3]/[\text{OH}]_0\) to be \((0.98 \pm 0.20)\) and an average of 5 runs at 251 K yield the ratio to be \((1.17 \pm 0.19)\). The quoted errors are \(2\sigma\) and refer to the precision only. A propagation of error calculation was carried out to estimate systematic errors. The major source of systematic errors are inaccuracies in photolysis photon flux measurements and in the absorption cross sections for NO\(_3\) at 662 nm and HNO\(_3\) at 248 and 228.8 nm. The yields are calculated to be \(0.97 \pm 0.35\) at 298 K and \(1.17 \pm 0.34\) at 251 K. (These errors represent \(2\sigma\) values.) The lower limits for NO\(_3\) yields are, therefore, 0.62 and 0.83 at 298 K and 251 K, respectively.

The yield measurements demonstrate clearly that NO\(_3\) is the major, if not the only, product of reaction (2) (i.e., \(k_{2a}/k_2\) is close to unity). This result is not surprising and confirms the previous assumption regarding the reaction pathway. Even though the yields at 298 K and 251 K are, within quoted errors, identical, a possible source of discrepancy between the two
measurements needs to be pointed out. It has been assumed that the NO$_3$ absorption cross section at 662 nm, $\sigma_{NO_3}^{662}$, is temperature independent—an assumption that is not proven. Any such temperature dependence will directly effect the measured value. The second possible source of error is the absorption cross section of HNO$_3$ at 248 nm being temperature dependent. We have shown that there were no secondary chemistry problems. In this regard, it should be noted that secondary chemistry (which should be due to either secondary reaction which consume OH or NO$_3$) would tend to reduce the yields, but the measured yields are around the theoretical maximum. It should be pointed out that our measured value of NO$_3$ yield is in good agreement with the results of Nelson et.al.

CONCLUSIONS

The results of the present study confirm our previous value of $k_2$ at 298 K as well as the temperature dependence of $k_2$. Two other flash photolysis studies, by Kurylo et.al.\textsuperscript{8} and Margitan and Watson,\textsuperscript{9} also are in good agreement with our previous results as well as the present values of $k_2$. However, the results of Nelson et.al.\textsuperscript{7} at 298 K do not agree with these four studies. The yield measurements demonstrate that reaction (2a) is the major pathway and is in agreement with results of Nelson et.al. Thus the atmospheric calculation presented earlier\textsuperscript{1} assuming NO$_3$ to be the only product can be considered preferable over the other alternative. The maximum affects on perturbation calculations due to the new values of $k_2$ seems most reasonable.

Finally, it should be pointed that there could, eventually, be a good agreement between various measurements thereby increasing our confidence in atmospheric chemistry calculations. However, until a good feasible explanation of the origin of the unusual temperature dependence of $k_2$ is
available, reaction (2) will not be well understood and a certain level of caution (skepticism?) should be exercised in applying these results to atmospheric calculations.
References


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APPENDIX I

Preparation of Azomethane

The apparatus used for preparation of azomethane is shown in Figure 1a. The method we used is a slightly modified version of the Renaud and Leitch preparation procedure.

Ten grams of Sym-1,2-dimethylhydrazinedihydrochloride (obtained from Aldrich Chemical Co.) was slowly added to 25 ml of 6N NaOH contained in a 250 ml Erlenmeyer flask. The flask was cooled in an ice bath and the contents vigorously stirred using a magnetic stirrer. When 10 gm of Sym-1,2-dimethylhydrazinedihydrochloride was added, ~ 3 ml of 6N NaOH was mixed with this solution to dissolve any remaining solid. This solution was transferred to the dropping funnel.

35 grams of mercury (II) oxide was mixed with 50 ml of distilled water in the three-necked 500 ml flat-bottom flask. The three-necked flask was connected on one side to a helium tank and another side to a cold finger. The cold finger, maintained at 0°C with crushed ice, was connected to two glass traps in series. Both traps were cleaned by flaming them under vacuum.

Before starting the addition of the solution present in the dropping funnel to the three-necked flask, the assembled system was flushed with He for at least one hour to remove all traces of air present in the assembly. The first trap was maintained at 193K (dry ice-chloroethylene slush) and the second at ~ 163K (ethanol cooled with liquid N2). The solution in the dropping funnel was added in drops to the slurry of mercuric oxide which was slowly stirred with a magnetic stirrer. The addition was completed in ~ 45 minutes and He allowed to flow for another
Figure 1a. Apparatus for the Preparation of Azomethane.
20 minutes to sweep out any remaining azomethane into the traps. (The flow rate of helium was \( \sim 20 \text{ ml/min.} \))

The traps were disconnected from the assembly and cooled to 77K with liquid \( \text{N}_2 \) to pump out \( \text{He} \) before transferring the contents to a bulb. The cold finger of the bulb was then maintained at 197K and azomethane distilled into a storage vessel maintained at 77K. The first and the last fractions were discarded. The vapor pressure of azomethane at 197K is \( \sim 7 \text{ torr} \) while that of \( \text{H}_2\text{O} \) is less than \( 1 \times 10^{-3} \text{ torr} \) which enabled us to separate the two.

All preparation and handling of azomethane was carried out in the dark or under red lights to avoid photolysis. The azomethane was stored at 197K.
APPENDIX II

Generation of the 257 nm CW UV Laser Beam

A schematic diagram of the setup is shown in Figure 2a. A Lexel model 95 Argon ion laser was operated on the 514 nm line. The output of this laser was checked to ensure that the laser was operating in TEM_{cc} mode. The Gaussian beam was focused using a 10 cm focal length quartz plano convex lens to obtain a tight beam waist with a confocal parameter of 10 cm. (The focal length at 514 nm of the lens was accurately measured using the cat's eye technique) The position of the lens was adjusted to locate the beam waist in the middle of a 50 mm long (10 mm x 10 mm on the side) ADP crystal (Inrad Corp.) which was housed in a gold plated copper block. This copper block was in snug contact with a gold plated pedestal which was backed by a Peltier thermoelectric cooler. The Peltier cooler itself was backed by a heater block which, in turn, was cooled by circulating water at a constant temperature (+ 2 °C) from a temperature controlled five gallon water bath heated by a fish tank heater. By adjusting the rate of water flow and the temperature of the heater block (which was controlled by a proportional heater) the temperature of the ADP crystal could be maintained at -10 °C with a precision of ± 0.1 °C. We found that the doubled 257 nm output was a maximum at this temperature.

The 257 nm beam was diverging as it exited the crystal; this beam was rendered parallel by a second lens (~/ 15 cm focal length at 257 nm). The collinear 257 nm and 514 nm beams were dispersed by a prism and the 514 nm beam stopped by a block. The entire assembly was housed inside a box to prevent dust from getting in and 514 nm light from scattering out.
Figure 2a. Details of the Second Harmonic Generation Set Up.
With an input energy of 1 W at 514 nm, we could routinely obtain
\( \sim 50 \mu\text{W} \) of 257 nm, which was more than adequate to carry out our experiments.