THE HETEROGENEOUS INTERACTION OF TRACE GASES ON MINERAL DUST AND SOOT: KINETICS AND MECHANISM

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Abstract

The present thesis work deals with the investigation of the heterogeneous reactions involving nitrate radical (NO$_3$), dinitrogen pentoxide (N$_2$O$_5$) and ozone (O$_3$) on surrogates of atmospheric mineral dust particles characteristic of the troposphere. An additional investigation of heterogeneous reaction of NO$_3$ on flame soot was carried out. The goal is to characterize the kinetics (the uptake coefficient $\gamma$) as well as the reaction products. The obtained results are intended to provide reliable data for numerical modelling studies. The experiments were performed in a very low pressure flow reactor (Knudsen cell reactor), coupled to mass spectrometry (MS) and optical probing (Resonance Enhanced Multiphoton Ionization (REMPI)).

The used mineral dust powder samples were: Kaolinite, CaCO$_3$, natural limestone, Saharan Dust and Arizona Test Dust. Two different types of soot were produced: soot originating from a rich decane flame at a high fuel/oxygen ratio (‘grey’ soot) and soot generated from a lean flame at a low fuel/oxygen ratio (‘black’ soot).

Uptake experiments of NO$_3$ on mineral dust were carried out under continuous molecular flow conditions (steady state) at 298 ± 2 K using the thermal decomposition of N$_2$O$_5$ as a NO$_3$ source. In situ laser detection (REMPI) was employed in addition to beam-sampling electron-impact mass spectrometry in order to specifically detect NO$_2$ and NO in the presence of N$_2$O$_5$, NO$_3$ and HNO$_3$. We found a steady state uptake coefficient $\gamma_{ss}$ ranging from (3.4 ± 1.6) x 10$^{-2}$ for natural limestone to 0.12 ± 0.08 for Saharan Dust with $\gamma_{ss}$ decreasing as [NO$_3$] increased. NO$_3$ adsorbed on mineral dust led to uptake of NO$_2$ in an Eley-Rideal mechanism where usually no uptake is observed in the absence of NO$_3$. The disappearance of NO$_3$ was in part accompanied by the formation of N$_2$O$_5$ and HNO$_3$ in the presence of NO$_2$. NO$_3$ uptake performed on small amounts of Kaolinite and CaCO$_3$ led to formation of some N$_2$O$_5$ according to $\text{NO}_3(\text{ads}) + \text{NO}_2(\text{g}) \rightarrow \text{N}_2\text{O}_5(\text{ads}) \rightarrow \text{N}_2\text{O}_5(\text{g})$.

Slow formation of gas phase HNO$_3$ on Kaolinite, CaCO$_3$, Arizona Test Dust and natural
limestone has also been observed and is clearly related to the presence of adsorbed water involved in the heterogeneous hydrolysis of $N_2O_5^{\text{ads}}$.

Uptake of $N_2O_5$ on mineral dust samples led to $\gamma_{ss}$ values ranging from $(3.5 \pm 1.1) \times 10^{-2}$ for CaCO$_3$ to 0.20 ± 0.05 for Saharan Dust with $\gamma_{ss}$ decreasing as $[N_2O_5]_0$ increased. We have observed delayed production of HNO$_3$ upon uptake of $N_2O_5$ for every investigated sample owing to hydrolysis of $N_2O_5$ with surface-adsorbed H$_2$O. At high and low $[N_2O_5]$ Arizona Test Dust and Kaolinite turned out to be the samples to produce the largest amount of gas phase HNO$_3$ with respect to $N_2O_5$ taken up. In contrast, the yield of HNO$_3$ for Saharan Dust and CaCO$_3$ is lower. On CaCO$_3$ the disappearance of $N_2O_5$ was also accompanied by the formation of CO$_2$. For CaCO$_3$ sample masses ranging from 0.33 to 2.0 g, the yield of CO$_2$ was approximately 42 - 50% with respect to the total number of $N_2O_5$ molecules taken up. The reaction of $N_2O_5$ with mineral dust and the subsequent production of gas phase HNO$_3$ leads to a decrease in $[NO_x]$ which may have a significant effect on global ozone decrease.

The rate of uptake of ozone on various mineral dust substrates was very similar for all the examined substrates. Both initial and steady state uptake coefficients $\gamma_0$ and $\gamma_{ss}$ were found to be similar for all examined substrates. Uptake experiments on cut marble samples have shown that $\gamma_0$ and $\gamma_{ss}$ based on the geometric and total internal (BET) surface area may be over and underestimated between a factor of 50 to 100, respectively. Based on these considerations we proposed initial and steady state uptake coefficients of the order of $10^{-4}$ and $10^{-5}$, respectively. For all uptake experiments on mineral dust surrogates, the disappearance of O$_3$ was accompanied by formation of O$_2$. The different mineral dust surrogates may be more accurately distinguished by their time-dependent relative O$_2$ yield rather than the magnitude of $\gamma$. The heterogeneous reaction of O$_3$ on mineral dust has been found to be non-catalytic and of limited importance in the atmosphere.

Uptake experiments of NO$_3$ on decane flame soot led to a large steady state uptake coefficient $\gamma_{ss}$ of 0.2 ± 0.02 for grey and black soot with $\gamma_{ss}$ decreasing as $[NO_3]$ increased. Adsorbed NO$_3$ led to an uptake of NO$_2$ admitted from the hot NO$_3$ source. On large quantities of grey soot we observed production of HONO (nitrous acid) corresponding to almost 100% of NO$_2$ taken up, whereas no HONO was formed on black soot. The disappearance of NO$_3$ was in part accompanied by the formation of $N_2O_5$ according to reaction: $N_2O_3^{\text{ads}} + NO_2^{\text{ads}} \rightarrow N_2O_5^{\text{ads}} \rightarrow N_2O_5^{\text{g}}$ probably due to the presence of
adsorbed NO$_3$ on the substrate. Subsequently, hydrolysis of N$_2$O$_5^{(ads)}$ with adsorbed H$_2$O led to production of gas phase HNO$_3$. For both grey and black soot we observed production of NO which did not depend of the amount of soot and [NO$_3$]. Decomposition of NO$_3$ and HONO on the soot substrates has been proposed to be responsible of gas phase NO formation.
Versione breve

Il presente lavoro di tesi verte sullo studio di reazioni eterogenee di radicale nitrato (NO₃), pentossido d’azoto (N₂O₅) e ozono (O₃) su surrogati di particelle di polvere minerale atmosferica. Un ulteriore studio è stato svolto sull’interazione eterogenea di NO₃ su fuligine generata da una fiamma. Lo scopo è di caratterizzare la cinetica (tramite il coefficiente di cattura, γ) così come i prodotti di reazione. I risultati ottenuti vogliono costituire una base reale di dati per gli studi di modellizzazione numerica.

Gli esperimenti sono stati eseguiti in un reattore a bassa pressione (il reattore di Knudsen) accoppiato a uno spettrometro di massa (MS) e ad un sistema di rilevamento ottico (Resonance Enhanced Multiphoton Ionization (REMPI)).

I campioni di polvere minerale impiegati sono stati i seguenti: Kaolinite, CaCO₃, natural limestone, Saharan Dust e Arizona Test Dust. Due differenti tipi di fuligine sono stati prodotti: fuligine prodotta da una ricca fiamma alimentata a decano e mantenuta con un elevato rapporto combustibile/ossigeno (‘grey’ soot, fuligine grigia) e fuligine prodotta da una debole fiamma e mantenuta con un basso rapporto combustibile/ossigeno (‘black’ soot, fuligine nera).

Esperimenti di cinetica di cattura di NO₃ su polveri minerali sono stati eseguiti sotto condizioni di regime molecolare stazionario (steady state) a 298 ± 2 K usando la decomposizione termica di N₂O₅ come sorgente di NO₃. Una rivelazione laser (REMPI) in situ è stata impiegata in aggiunta alla spettrometria di massa al fine di rivelare specificatamente NO₂ e NO in presenza di N₂O₅, NO₃ e HNO₃.

Abbiamo trovato coefficienti di cattura stazionaria γₘₜ che vanno da \((3.4 \pm 1.6) \times 10^{-2}\) per natural limestone a 0.12 ± 0.08 per Saharan dust con \(\gammaₘₜ\) decrescente all’aumentare della concentrazione di NO₃. NO₃ adsorbito sulle polveri minerali porta alla cattura di molecole di NO₂ seguendo un meccanismo Eley-Rideal dove usualmente alcuna cattura è osservata nell’assenza di NO₃. La disparsione di NO₃ è stata in parte accompagnata dalla formazione di N₂O₅ e HNO₃ in presenza di NO₂. Esperimenti di
cinetica di cattura di NO\textsubscript{3} eseguiti su piccole quantità di Kaolinite e CaCO\textsubscript{3} hanno portato alla formazione di N\textsubscript{2}O\textsubscript{5} in accordo con la reazione \[ \text{NO}_3(\text{ads}) + \text{NO}_2(\text{g}) \rightarrow \text{N}_2\text{O}_5(\text{ads}) \rightarrow \text{N}_2\text{O}_5(\text{g}) \]. Una lenta formazione di HNO\textsubscript{3} in fase gassosa su Kaolinite, CaCO\textsubscript{3}, Arizona Test Dust e natural limestone è stata anche osservata ed è chiaramente legata alla presenza di acqua adsorbita che a sua volta ha portato all'idrolisi eterogenea di N\textsubscript{2}O\textsubscript{5}.

Esperimenti di cinetica di cattura di N\textsubscript{2}O\textsubscript{5} su campioni di polvere minerale hanno portato a valori di $\gamma_{ss}$ che vanno da $(3.5 \pm 1.1) \times 10^{-2}$ per CaCO\textsubscript{3} a $0.20 \pm 0.05$ per Saharan Dust con $\gamma_{ss}$ decrescente all'aumentare della concentrazione di N\textsubscript{2}O\textsubscript{5}. Abbiamo osservato una ritardata produzione di HNO\textsubscript{3} in seguito alla cattura di N\textsubscript{2}O\textsubscript{5} per ogni campione analizzato dovuto all'idrolisi di N\textsubscript{2}O\textsubscript{5}. Ad alta e bassa concentrazione di N\textsubscript{2}O\textsubscript{5} Arizona Test Dust e Kaolinite si sono rivelati essere i campioni che producono il più grande ammontare di HNO\textsubscript{3} in fase gassosa in rapporto a N\textsubscript{2}O\textsubscript{5} catturato. In contrasto, la quantità di HNO\textsubscript{3} per Saharan Dust e CaCO\textsubscript{3} è risultata essere più bassa. Su CaCO\textsubscript{3} la disparizione di N\textsubscript{2}O\textsubscript{5} è stata anche accompagnata dalla formazione di CO\textsubscript{2}. Per campioni di CaCO\textsubscript{3} aventi massa tra 0.33 e 2.0 g, la produzione di CO\textsubscript{2} è stata all’incirca del 42 – 50 % rispetto al numero totale di molecole di N\textsubscript{2}O\textsubscript{5} catturate. La reazione di N\textsubscript{2}O\textsubscript{5} con polvere minerale e la conseguente produzione di HNO\textsubscript{3} in fase gassosa porta a una diminuzione nella concentrazione di NO\textsubscript{x} che può avere un effetto significante sulla decrescita globale d’ozono.

Il coefficiente di cattura dell’ozono sui vari substrati di polvere minerale è stato misurato molto simile per tutti i campioni esaminati. Sia il coefficiente di cattura iniziale $\gamma_0$ che quello a condizioni stazionarie $\gamma_{ss}$ sono risultati simili per tutti i substrati esaminati. Esperimenti di cinetica di cattura su un campione di marmo hanno mostrato che $\gamma_0$ e $\gamma_{ss}$ calcolati sulla base della superficie geometrica e sulla superficie interna (BET) possono essere sopra e sottostimati di un fattore tra 50 e 100, rispettivamente. Basandosi su queste considerazioni abbiamo proposto un coefficiente di cattura iniziale $\gamma_0$ e stazionario $\gamma_{ss}$ dell’ordine di $10^{-4}$ a $10^{-5}$, rispettivamente. Per tutti gli esperimenti di cinetica di cattura su surrogati di polveri minerali, la disparizione di O\textsubscript{3} è stata accompagnata dalla formazione di O\textsubscript{2}. I differenti surrogati di polveri minerali possono essere piu’ accuratamente distinti dalla loro produzione di O\textsubscript{2} piuttosto che dalla grandezza del coefficiente di cattura $\gamma$. La reazione eterogenea di O\textsubscript{3} su polveri minerali è stata trovata non catalitica e di importanza limitata nell’atmosfera.
Esperimenti di cinetica di cattura di NO₃ su fuligine prodotta da una fiamma di decano hanno riportato un grande coefficiente di cattura stazionario $\gamma_{ss}$ di $0.20 \pm 0.05$ per fuligine grigia e nera con $\gamma_{ss}$ decrescente all’aumentare della concentrazione di NO₃. NO₃ adsorbito ha portato a una cattura di NO₂ ammessa dalla sorgente di NO₃. Su grandi quantità di fuligine grigia abbiamo osservato una produzione di HONO (acido nitroso) corrispondente ad almeno 100% di NO₂ catturato, mentre alcuna quantità di HONO si è formata sulla fuligine nera. La disparizione di NO₃ e’ stata in parte accompagnata dalla formazione di N₂O₅ in accordo con la reazione:

$$\text{NO}_3(\text{ads}) + \text{NO}_2(\text{ads}) \rightarrow \text{N}_2\text{O}_5(\text{ads}) \rightarrow \text{N}_2\text{O}_5(\text{g})$$

probabilmente dovuta alla presenza di NO₃ assorbito sul substrato. Successivamente, idrolisi di N₂O₅(ads) con acqua adsorbita H₂O(ads) ha portato alla produzione di acido nitrico HNO₃ in fase gassosa. Per fuligine grigia e nera abbiamo osservato una produzione di NO che non dipende dalla quantità di fuligine e dalla concentrazione di NO₃. La decomposizione di NO₃ e HONO su substrati di fuligine e’ stata proposta essere responsabile della formazione di NO in fase gassosa.
CHAPTER 1

INTRODUCTION

1.1 The Atmosphere of the Earth

The main constituents of the atmosphere are N\textsubscript{2}, O\textsubscript{2}, H\textsubscript{2}O\textsubscript{(g)} (water vapor), CO\textsubscript{2}, O\textsubscript{3} and suspended particles. In Table 1.1 we report the main constituents of the atmosphere and their lifetimes $\tau$ defined as $\tau = M/F$ where $M$ is the amount of chemical species and $F$ the rate of destruction or generation.

Based on its vertical temperature profile the atmosphere is divided into different regions as displayed in Figure 1.1. The two lowest regions are the troposphere and the stratosphere. The troposphere is the atmospheric layer closest to the Earth’s surface. Its thickness is variable: 7 km below the poles, 18 km below the equator and 13 km in the temperate areas. The troposphere extends from the surface of the Earth up to the tropopause and contains almost all of the atmosphere’s water vapor. Although the troposphere accounts for only a small fraction of the atmosphere’s total height, it contains about 80% of its total mass estimated to be $5.2 \times 10^{18}$ kg. In the troposphere, the temperature decreases almost linearly with height with a rate of 9.7 K km\textsuperscript{-1}. The reason for this progressive decline is the increasing distance from the sun-warmed earth\textsuperscript{1}. At the tropopause, the temperature has fallen to an average of about 217 K (-56°C). As air moves vertically, its temperature changes in response to the local pressure. An air parcel that is transported from the surface to 1 km can decrease in temperature from 5 to 10 K depending on its water content. Because of the strong dependence of the saturation vapor pressure on temperature, this decrease of temperature of a rising parcel can be accompanied by an increase in relative humidity (RH) in the parcel. As a result, upward air motions of a few hundreds of meters can cause the air to reach saturation (RH = 100%) accompanied by the formation of clouds\textsuperscript{1}.
The troposphere can be divided into the *planetary boundary layer*, extending from the Earth’s surface up to about 1 km, and the *free troposphere*, extending from about 1 km to the tropopause.

An important aspect of the atmosphere is the presence of ozone (O₃) in the stratosphere. This plays an important role in the protection of life against solar radiation, particularly, against high energy ultraviolet radiation (UVR) in the region from 290 to 320 nm.

![Temperature-altitude profile of the atmosphere of the Earth.](image)

**Figure 1.1.** Temperature-altitude profile of the atmosphere of the Earth.

<table>
<thead>
<tr>
<th>Gas</th>
<th>%vol</th>
<th>lifetime $\tau$</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂ (Nitrogen)</td>
<td>78</td>
<td>$1.6 \times 10^7$ y</td>
</tr>
<tr>
<td>O₂ (Oxygen)</td>
<td>21</td>
<td>$3-10 \times 10^3$ y</td>
</tr>
<tr>
<td>Ar (Argon)</td>
<td>0.93</td>
<td></td>
</tr>
<tr>
<td>H₂O (Water)</td>
<td>0–4</td>
<td>10 d</td>
</tr>
<tr>
<td>CO₂ (Carbon Dioxide)</td>
<td>$3.3 \times 10^{-2}$</td>
<td>3-4 y</td>
</tr>
<tr>
<td>Ne (Neon)</td>
<td>1.8 $\times 10^{-3}$</td>
<td></td>
</tr>
<tr>
<td>He (Helium)</td>
<td>5.2 $\times 10^{-4}$</td>
<td>10⁶ y</td>
</tr>
<tr>
<td>CH₄ (Methane)</td>
<td>1.7 $\times 10^{-4}$</td>
<td>9 y</td>
</tr>
<tr>
<td>Kr (Krypton)</td>
<td>1.1 $\times 10^4$</td>
<td></td>
</tr>
<tr>
<td>N₂O</td>
<td>5.0 $\times 10^{-5}$</td>
<td></td>
</tr>
<tr>
<td>Xe</td>
<td>8.7 $\times 10^{-6}$</td>
<td></td>
</tr>
<tr>
<td>O₃</td>
<td>1.0 $\times 10^{-6}$</td>
<td>100 d</td>
</tr>
</tbody>
</table>

**Table 1.1.** Main constituents of the atmosphere of the Earth and lifetimes $\tau$ of the main components."
1.2 Atmospheric pollution

Tropospheric air pollution with examples displayed in Tables 1.2 and 1.3 has an impact on scales ranging from local to global. Reactive intermediates in the oxidation of mixtures of volatile organic compounds (VOCs) and oxides of nitrogen (NO\textsubscript{x}) leading to tropospheric O\textsubscript{3} formation play a central role: the hydroxyl radical (OH) during the day; the nitrate radical (NO\textsubscript{3}), at night; and ozone (O\textsubscript{3}), which reacts both during day and night. Halogen atoms may also play a role during the day in the marine boundary layer.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Concentration</th>
<th>Lifetime $\tau$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO\textsubscript{2}</td>
<td>350 ppm</td>
<td>3 – 4 y</td>
</tr>
<tr>
<td>CH\textsubscript{4}</td>
<td>1.7 ppm</td>
<td>9 – 15 y</td>
</tr>
<tr>
<td>N\textsubscript{2}O</td>
<td>310 ppb</td>
<td>120 y</td>
</tr>
<tr>
<td>CFC</td>
<td>100 ppt – 1ppb</td>
<td>&gt; 100 y</td>
</tr>
<tr>
<td>O\textsubscript{3}</td>
<td>$1.0 \times 10^{12}$ cm\textsuperscript{-3} (40 ppb)</td>
<td>100 d</td>
</tr>
<tr>
<td>H\textsubscript{2}O</td>
<td></td>
<td>10 d</td>
</tr>
</tbody>
</table>

Table 1.2. Typical concentrations and lifetimes of the most important greenhouse gases\textsuperscript{3}.

Tropospheric O\textsubscript{3} formation highlights the essential role of solar radiation in atmospheric chemistry. At the Earth’s surface, radiation of wavelength $\lambda \geq 290$ nm (actinic region) is available for inducing photochemical reactions. The complex chemistry involving volatile organic compounds (VOCs) and NO\textsubscript{x} ($\text{NO}_x = \text{NO} + \text{NO}_2$) leads to the formation of NO\textsubscript{3} among many other species and a large variety of additional oxidizing species such as tropospheric O\textsubscript{3} and PAN (CH\textsubscript{3}C(O)OONO\textsubscript{2}). These oxidizing species are referred to as photochemical oxidants.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Concentration</th>
<th>Lifetime $\tau$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO\textsubscript{2}</td>
<td>$2.4 \times 10^{12}$ cm\textsuperscript{-3} (100 ppb)</td>
<td>125 s</td>
</tr>
<tr>
<td>N\textsubscript{2}O\textsubscript{5}</td>
<td>$5.0 \times 10^9$ cm\textsuperscript{-3} (200 ppt)</td>
<td>20 s</td>
</tr>
<tr>
<td>NO\textsubscript{3}</td>
<td>$2.0 \times 10^9$ cm\textsuperscript{-3} (100 ppt)</td>
<td>5 s</td>
</tr>
<tr>
<td>H\textsubscript{NO}	extsubscript{3}</td>
<td>$5.0 \times 10^{10}$ cm\textsuperscript{-3} (2 ppb) polluted</td>
<td>6.3 d</td>
</tr>
<tr>
<td></td>
<td>$2.4 \times 10^9$ (100 ppt) background</td>
<td></td>
</tr>
<tr>
<td>NO\textsubscript{x} = NO + NO\textsubscript{2}</td>
<td>10 – 1000 ppb Urban-suburban</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.2 – 10 ppb Rural</td>
<td>1 d\textsuperscript{4}</td>
</tr>
<tr>
<td></td>
<td>0.02 – 0.08 ppb Tropical forest</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.02 – 0.04 ppb Remote marine</td>
<td></td>
</tr>
</tbody>
</table>

Table 1.3. Typical concentrations and lifetimes of the most important nitrogen-containing pollutants\textsuperscript{5}.
An increase in tropospheric O\textsubscript{3} has been observed globally over the past century\textsuperscript{6,7}. The surface concentrations of O\textsubscript{3} found in remote areas of the world are of the order of approximately 30 to 40 ppb as compared to 10 -15 ppb in pre-industrial times since 1850. This increase has been attributed to an increase in NO\textsubscript{x} emissions associated with the switch to fossil fuels during the industrial period\textsuperscript{8}.

The influx of air containing O\textsubscript{3} from the stratosphere contributes to tropospheric ozone. However, the major source of O\textsubscript{3} is represented by the photolysis of NO\textsubscript{2} ($J_{\text{NO}_2} = 8.0 \times 10^{-3} \text{ s}^{-1}$):

$$\text{NO}_2 + \text{hv} \rightarrow \text{NO} + \text{O}(^3\text{P}) \quad (\lambda < 420 \text{ nm}) \quad (1.1)$$

followed by

$$\text{O}(^3\text{P}) + \text{O}_2 \text{M} \rightarrow \text{O}_3 \quad (1.2)$$

Increased concentrations of O\textsubscript{3} are expected to increase OH concentrations and decreased lifetimes of methane (CH\textsubscript{4}). Because both O\textsubscript{3} and CH\textsubscript{4} are greenhouse gases, this chemistry has obvious implications for global climate change.

Nitrogen oxides (NO + NO\textsubscript{2} = NO\textsubscript{x}) play a major role in ozone production, aerosol formation, and acid deposition. Nearly 50% of NO\textsubscript{x} emissions come from motor vehicles. Although some NO\textsubscript{2} is emitted directly into the atmosphere by combustion processes, most is formed by oxidation of NO with ozone:

$$\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \quad (1.3)$$

Reaction (1.3) proceeds with a rate constant that depends on temperature, while the photolytic rate constant for reaction (1.1) is a function of the actinic flux. Reaction (1.2) is assumed to proceed very fast at atmospheric pressure.

Once NO is converted to NO\textsubscript{2}, a variety of potential reaction paths are available. These include photolysis to form ground-state oxygen atoms, O($^3\text{P}$), which generate O\textsubscript{3} according to equation (1.2) as well as reaction with OH to form nitric acid (HNO\textsubscript{3}) according to:

$$\text{NO}_2 + \text{OH} \text{M} \rightarrow \text{HNO}_3 \quad (1.4)$$
At a sufficiently high concentration of both NO$_2$ and O$_3$, the nitrate radical (NO$_3$) and dinitrogen pentoxide (N$_2$O$_5$) are formed as follows:

\[
\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2 \quad (1.5)
\]

\[
\text{NO}_3 + \text{NO}_2 + \text{M} \rightarrow \text{N}_2\text{O}_5 + \text{M} \quad (1.6)
\]

Like OH, NO$_3$ reacts with organics to initiate their oxidation. NO$_3$ chemistry is important only at night because it photolyzes rapidly during the day at $\lambda = 662$ nm (lifetime = 5 s). NO$_3$ has been detected in both polluted and remote regions and can be considered the driving force in the chemistry at night when the photolytic production of OH shuts down$^{9,10}$.

As discussed by Andreae and Crutzen$^{11}$ and Ravishankara$^{12}$, the formation and subsequent hydrolysis of N$_2$O$_5$ on wet surfaces, including those of aerosol particles out whose surface water has been adsorbed, is believed to be a significant contributor to the formation of nitric acid in the atmosphere on both local and global scales according to:

\[
\text{N}_2\text{O}_5 + \text{H}_2\text{O}_{(\text{ads})} \rightarrow 2\text{HNO}_3 \quad (1.7)
\]

The rate constant of reaction (1.4) is $4.1 \times 10^{-11}$ cm$^3$/molecule s, whereas that one for reaction (1.7) is $1.4 \times 10^{-14}$ cm$^3$/molecule s. Therefore, HNO$_3$ formation mainly occurs by way of reaction (1.4)$^{13}$. HNO$_3$ is renoxified by the following two reactions:

\[
\text{HNO}_3 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{NO}_3 \quad (1.8)
\]

\[
\text{HNO}_3 + \text{hv} \rightarrow \text{OH} + \text{NO}_2 \quad (1.9)
\]

Reaction (1.9) produces NO$_2$ that may be photolysed producing O($^3$P) ultimately leading to O$_3$ in the atmosphere. However, reaction (1.9) is slow even at noontime in the mid-troposphere corresponding to a $J_{\text{HNO}_3}$ value of $7.3 \times 10^{-7}$ s$^{-1}$ and the major removal processes for nitric acid in the troposphere are by dry and wet deposition$^{14}$.

Ozone is a source of hydroxyl radical (OH) according to the following equations:

\[
\text{O}_3 + \text{hv} \rightarrow \text{O}(^1\text{D}) + \text{O}_2 \quad (\lambda < 320 \text{ nm}) \quad (1.10)
\]

\[
\text{O}(^1\text{D}) + \text{H}_2\text{O} \rightarrow 2\text{OH} \quad (1.11)
\]
Another important source of OH in polluted atmospheres comes from reaction of O₃ with terpenes and photolysis of nitrous acid (HONO):

\[ \text{HONO} \ + \ h\nu \rightarrow \ \text{OH} \ + \ \text{NO} \quad (\lambda < 400 \text{ nm}) \]  

(1.13)

OH reacts rapidly with most air pollutants and trace species found in the atmosphere. However, sources of HONO are not well known. It has been measured in very small concentrations in the exhaust of automobiles that do not have emission catalysts \(^{15,16}\), inside automobiles during operation \(^{17}\), and indoors from the emissions of gas stoves \(^{18,19}\). There are also heterogeneous sources of HONO \(^{20,21}\), in particular the following reaction:

\[ 2\text{NO}_2 \ + \ \text{H}_2\text{O} \stackrel{\text{surface}}{\rightarrow} \text{HONO} \ + \ \text{HNO}_3 \]  

(1.14)

However, reaction (1.14) is very slow \((6.0 \times 10^{-6} \text{ m s}^{-1})^{19}\) and so it is of secondary importance for HONO formation.

### 1.3 Heterogeneous chemistry

The planetary atmosphere contains gases together with liquid and solid particles that all affect the terrestrial radiation field and atmospheric chemical composition. One of the most intense areas of current research in atmospheric sciences is the effect of these particles, natural and anthropogenic, on the radiative balance of Earth \(^{12}\). Recently, the importance of heterogeneous chemistry was boosted by the recognition of the crucial role played by the heterogeneous reactions in the dramatic Antarctic ozone hole and the global stratospheric ozone depletion \(^{22}\). However, the analysis of tropospheric heterogeneous chemistry is complicated by two factors: (a) rapid mixing in the troposphere which makes it difficult to attribute a change to a specific process, and (b) the variety of condensed matter and gaseous species that can participate in the reactions.

To calculate a heterogeneous reaction rate in the atmosphere we need to know:

- The surface area.
- The phase of the condensed matter.
- The composition of the bulk (for liquids) and the surface (for solids).
1. Introduction

- The identity and concentrations of the gas-phase species that can undergo heterogeneous reactions, provided it is a first order process.
- The reactive uptake coefficient $\gamma$ on the specific substrate under atmospheric conditions for the reaction.

The simplest way to include heterogeneous reactions in atmospheric models is to represent the loss of a reactant $M$ from the gas phase as a result of reaction to generate a product $Y$ as a first-order process:

$$M \xrightleftharpoons{\text{heterogeneous, } k_{\text{het}}}{\rightarrow} Y$$  \hspace{1cm} (1.15)

where $k_{\text{het}}$ is the rate constant (s$^{-1}$). Such a rate law is often found as the rate of temporal change of the gas-phase concentration of reactant $M$ in the presence of the condensed phase substrate will be first order in many, but not all cases:

$$\frac{d[M]}{dt} = \frac{d[Y]}{dt} = k_{\text{het}}[M]$$  \hspace{1cm} (1.16)

where $t$ is the reaction time and the square brackets indicate concentration. The first-order rate constant for removal of $M$ from the gas phase, $k_{\text{het}}$, contains all the information on the heterogeneous reaction and is given by equation (1.17):

$$k_{\text{het}} = \frac{\bar{c}A\gamma}{4}$$  \hspace{1cm} (1.17)

where $A$ is the surface to volume ratio or surface concentration (cm$^2$ cm$^{-3}$) for reactions in air, $\bar{c}$ is the mean molecular speed of species $M$, and $\gamma$ is the reactive uptake coefficient.

The determination of $\gamma$ based on the measurement of $k_{\text{het}}$ for any given atmospheric condition is one of the most important efforts in current atmospheric heterogeneous research$^{12}$. Among the suspended material in the troposphere, condensed water is likely to be predominant. However, sulphuric acid droplets, sea salt particles, soot, silicates, and organic aerosols also provide media for important transformations via heterogeneous processes.
1.4 Total Aerosol Load and Mineral Dust Aerosols

<table>
<thead>
<tr>
<th>Source</th>
<th>Estimated Flux (Tg yr⁻¹)</th>
<th>Particle Size Categoryᵃ</th>
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</thead>
<tbody>
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<td><strong>Primary</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Natural</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil dust (mineral aerosol)</td>
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<td>Mainly coarse</td>
</tr>
<tr>
<td>Sea salt</td>
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</tr>
<tr>
<td>Volcanic dust</td>
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<td>Coarse</td>
</tr>
<tr>
<td>Biological debris</td>
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<td>Coarse</td>
</tr>
<tr>
<td>Secondary</td>
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<td></td>
</tr>
<tr>
<td>Sulfates from biogenic gases</td>
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<td>Fine</td>
</tr>
<tr>
<td>Sulfates from volcanic SO₂</td>
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<td>Fine</td>
</tr>
<tr>
<td>Organic matter from biogenic VOC</td>
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<td>Fine</td>
</tr>
<tr>
<td>Nitrates from NOₓ</td>
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<td>Fine and coarse</td>
</tr>
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<td><strong>Total natural</strong></td>
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</tr>
<tr>
<td>Industrial dust, etc. (except soot)</td>
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<td>Fine and coarse</td>
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<tr>
<td>Soot</td>
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<tr>
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<td>Sulfates from SO₂</td>
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<td>Biomass burning</td>
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</tr>
<tr>
<td><strong>Total</strong></td>
<td>3600</td>
<td></td>
</tr>
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</table>

ᵃCoarse and fine size categories refer to mean particle diameter above and below 1 μm, respectively. Note: Sulfates and nitrates are assumed to occur as ammonium salts. Flux unit: Tg yr⁻¹ (dry mass). 1 Tg = 10¹² g.

**Table 1.4.** Main sources of aerosol in the atmosphere.

Aerosols are small (sub-micron to several microns) particles in suspension in the atmosphere. They can be in the solid phase or in the liquid phase and originate both from natural and man-made (anthropogenic) sources. Aerosols can be directly emitted as particles (primary aerosols) into the atmosphere by volcanoes, through the effect of wind
lifting dust particles in arid regions, from combustion during biomass burning, from sea spray and from oxidative processes of vegetation. They can also be the result of chemical reactions (secondary aerosols). Table 1.4 summarizes the main sources of aerosols expressed in Tg yr\(^{-1}\). The global atmospheric lifetime (yr) characterizes the time required to turn over the global atmospheric burden. It is defined as the burden (Tg) divided by the mean global sink (Tg/yr) for a gas in steady state (i.e., with unchanging burden).

On a global scale, it is estimated that 10 to 20% of the aerosols can be characterized as anthropogenic. Aerosols represent a reactive surface in the atmosphere for heterogeneous chemical reactions\(^4\). In the atmosphere particles above \(> 2.5 \mu m\) diameter are mainly natural aerosols such as mineral dust and sea salt. It is estimated that \(3.4 \times 10^3 – 1.4 \times 10^4\) Tg of aerosols are emitted annually into the atmosphere. These aerosols come from such different sources as sea-salt, wind-blown soils, fossil fuel combustion, biomass burning, and volcanic-eruptions.

Recent modeling studies estimate yearly emission fluxes of mineral dust between 800 and 1500 Tg yr\(^{-1}\)\(^24\) whipped up from approximately 33% of the global land surface that is arid and therefore may be a potential source region for atmospheric mineral dust aerosol\(^25\). Bauer et al.\(^26\) estimated that the effective area of mineral aerosol is equivalent to 30% of the Earth’s surface of which 10% may be attributed to Africa. Sea salt aerosols are present in the marine boundary layer\(^27\), while desert dust can be transported by storms from Africa across the Atlantic all the way to the east coast of the United States\(^28\).

![Annual mean average column dust (mg m\(^{-2}\))\(^29\).](image)
Figure 1.2 shows the horizontal distribution of the annual load of mineral dust\textsuperscript{29}. The North African dust cloud covers the whole North African continent, travels over the tropical Atlantic and dust loads of approximately 10 mg m\textsuperscript{-2} are found over the coast of the South American continent. High dust loads are predicted over Pakistan, India and east China and downwind of those regions.

Although dust sources are unevenly distributed across the earth, evidence that they have global effects comes from satellite data that deliver optical depth images of dust blowing for instance from the Saharan desert all the way to the south-eastern US\textsuperscript{30} during spring and summer as displayed in Figure 1.3.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure13.png}
\caption{Dust plume from northwest Africa extending out over the Atlantic Ocean. Images courtesy Jeffrey Schmaltz and Jacques Descloitres, MODIS Rapid Response Team, NASA GSFC. An intense African dust storm sent a massive dust plume westward over the Atlantic Ocean March 2, 2003.}
\end{figure}

Atmospheric aerosols can cool or warm the atmosphere directly by absorption and scattering of solar and terrestrial radiation and they can change the optical properties of clouds through modification of the distribution of cloud condensation nuclei (CCN)\textsuperscript{31}. The presence of mineral dust aerosols may also affect the photochemical reaction rates as well\textsuperscript{32-35}. Mineral dust aerosols are recognized to have an important influence on atmospheric composition\textsuperscript{12,36} because they provide reactive surfaces in the atmosphere.
where heterogeneous chemical reactions may take place. Trace gases such as HNO₃ and N₂O₅ contribute to the formation of particulate nitrate on the dust particles by surface processes in the troposphere. These processes represent an important sink for nitrogen oxide species, with decreases of daytime NOₓ levels reaching up to 60% in the presence of dust at a loading of about 1.8-11.5 μg m⁻³ corresponding to a particle surface area of (0.11-0.7) x 10⁻⁶ cm² cm⁻³.

Field observations, laboratory and modeling studies have established the interaction of trace gases with mineral dust aerosol, as schematically represented in Figure 1.4, as well as the quantitative impact of the latter on the composition of the atmosphere. Box, regional and global scale models have shown the importance of dust on both the photochemical rates of oxidant formation as well as the loss of trace gases regarding atmospheric composition.

![Figure 1.4. Simultaneous uptake of trace atmospheric gases on mineral dust.](image_url)

Mineral dust has been found up to a height of 8 km. The atmospheric residence time of mineral dust depends on the meteorological conditions and on the aerosol size. For example particles with a diameter of 100 μm are only found close to the source regions, whereas small particles of 2 μm diameter can stay in the atmosphere for several days and may travel for long distances.

Aerosols can also influence gas phase chemical cycles by absorbing and scattering of sunlight and thus influencing the photochemical reaction rates (J values). Bian and Zender showed the change of Jₒ(¹D) and J_NO₂ for O(¹D) and NO₂, respectively, in a recent model.

The maximum photolytic rate forcing by dust on O₃ and OH, the key tropospheric oxidants, has been found in dust source regions in the boundary layer. Photolysis rate forcing has been shown to produce more O₃ with a global annual perturbation of 0.23%. Dust absorption reduces photochemistry and hence this leads to an increase or decrease of [O₃]
The radiative effect of aerosols is currently one of the most active areas in climate research. Aerosols influence the Earth’s radiative balance directly by scattering incoming shortwave radiation back to space, or indirectly through their influence on cloud properties. The indirect effect is considered to be one of the largest uncertainties in current global climate models. There are several indirect ways in which aerosols influence the radiative balance of the Earth:

- The reflectivity of clouds through the cloud albedo.
- Perturbation of precipitation processes.
- Change of the initial droplet size distributions produced close to cloud base, and subsequent change of the effectiveness of coalescence of atmospheric aerosol particles at a later stage of cloud development through changing of the spread in drop sizes.
- Modification of freezing processes in mixed-phase clouds. Both of these two latter mechanisms (coalescence and freezing) influence precipitation development.

Precipitation is a key component in determining the lifetime and extent of clouds. It also is a key component in the atmospheric energy balance through the redistribution of latent heat. These phenomena are illustrated in Figure 1.5. The left panel represents a clean (background) case with a given cloud albedo, extent, precipitation intensity and dynamic structure.

![Figure 1.5. Schematic representation of the indirect effects of aerosols.](image)

The right panel depicts the case where all of the indirect effects of aerosols act at the same time. In the polluted case, cloud albedo has increased. Precipitation has decreased due to changes in cloud microphysics as well as a weakening in the overall dynamic driving force.
for convection. The rectangle in the middle of Figure 1.5 indicates the expected sign of the indirect effect (increase or decrease) in going from clean to polluted conditions. The first to be recognized was the albedo or “Twomey” effect which is the increase in cloud albedo due to an increase in aerosol concentration. On average, mineral dust contributes more than 60% of total optical depth in dusty regions, 15% in urban regions, and up to 10% in the remote Southern Hemisphere\textsuperscript{48}. For a dynamic forcing that creates a cloud with a given vertical extent and liquid water content, an increase in aerosol concentration going into the cloud can result in the formation of a larger number of smaller droplets and therefore in cloud condensation nuclei (CCN). The end result is in an increase in cloud albedo\textsuperscript{49}. On the whole, however, increasing aerosol concentrations are expected to increase cloud albedo\textsuperscript{50}. The same processes that increase cloud albedo in low-level clouds, and subsequently lead to production of more and smaller droplets, tends to decrease the efficiency with which precipitation is formed. If precipitation is suppressed, water that would have been removed from the atmosphere remains aloft and can be transported to other locations before it is deposited to the surface.

1.5 Mineral dust: field measurements

Suitable locations to study the heterogeneous depletion of gaseous species in the presence of mineral dust are the Mount Cimone research Station (Italy) and Izana observatory (Spain). These stations perform measurements on several significant dust episodes each year and most episodes occur during spring and summer. The Monte Cimone station is located in the Mediterranean region in northern Italy south of the Alps and the Po valley and north of the Mediterranean Sea at 44°12’N and 10°22’E. Owing to its altitude, 2165 m above sea level, air masses reflect European continental background conditions in the free troposphere. This measurement site is located at about 1600 km from the Saharan desert. The Izana observatory is part of the World Meteorological Organization (WMO) Global Atmosphere Watch (GAW) network, and is operated by the Spanish Meteorological Institute. This station is located on a mountain ridge on the island of Tenerife at 2360 m above sea level (a.s.l., 28° 18’ N, 16° 29’ W).

In 2000 a study was initiated on Mineral Dust and Tropospheric Chemistry (MINATROC) in the framework of an EU program on Environment and Climate. This project combines a
study on the molecular level details, field observations and mineral modeling in order to estimate the global significance of heterogeneous reactions on dust. It combines laboratory investigations field measurements and atmospheric chemistry models. In this context the laboratory studies provided mechanistic information on absorption and reaction of atmospheric gases on aerosol surfaces, and the identification of the saturating effect of adsorbed species. The measurement campaign MINATROC took place during 5 weeks in June and July 2000, at Mount Cimone and between 15 July and 15 August 2002 at the Izana observatory. Intensive measurements were carried out between 1 June and 5 July 2000 at Monte Cimone. Aerosols were observed by means of particle sizing instruments, differential mobility analyzer and optical particle counter, LIDAR systems, and impactor measurements. In addition atmospheric trace gases were measured by Hanke, Bonasoni and other personal participating in the MINATROC campaign. Subsequently to this extensive field campaign observations of ozone concentration and PM$_{10}$ (particulate matter less than 10 μm, known as PM$_{10}$) particle size and mass distribution were carried out until December 2000 by Bonasoni et al.. The long term measurements of coarse aerosol particles, in the size range of 1-2 μm in diameter, are shown in Figure 1.6.

Figure 1.6. Time series of aerosol volume concentrations (size bin 1–2 μm diameter) at Mount Cimone in μm$^3$ cm$^{-3}$. (top) Observations by Bonasoni et al. (bottom) Model results.
During the MINATROC field campaign airborne Saharan dust reached Mount Cimone at the beginning of July. During this event the volume concentration of particles of 1-2 μm diameters was 3 μm$^3$ cm$^{-3}$. Trajectory analysis by Bonasoni et al.$^{39}$ showed that all the measured peaks in the coarse aerosol concentrations originate from North Africa. Figure 1.6 compares the observed aerosol concentrations to the model results. Generally, there is good agreement between the observed most prominent dust events and the model simulation, indicating that the model captures dust uplift in the Saharan desert and transport to the Mediterranean region.

As displayed in Figure 1.7, during 3 and 4 July, enhanced coarse aerosol concentrations were observed. The first panel compares measured and model aerosol volume concentrations. The analysis of the aerosol chemical composition$^{52}$ showed that the largest contribution of nitrate was observed in air masses originating from Western Europe, whereas the most dominant submicron aerosol mass was made of soot in air masses originating from Eastern Europe. During the Saharan dust outbreak, Saharan dust and anthropogenic particles seemed to be externally mixed.

Figure 1.7. (top) Time series of aerosol volume concentrations (size bin 1–2 μm) at Mount Cimone in μm$^3$ cm$^{-3}$. The black line shows observations$^{39}$, and the grey line shows model results. (bottom) Time series of ozone, HNO$_3$, and NO$_x$ concentrations in ppb$^v$.$^{39,54,55}$, respectively. The black line is observations, the dark grey line is the model CTR simulation, and the light grey line is the HET simulation.
The episode shown in Figure 1.7, 21 June to 6 July, was influenced during the first days until 23 June, by Eastern European air masses. In the following day the air masses came from Western Europe. Polluted air reached the measurement site at the end of June. This event can clearly be seen in the NOx measurement time series. As displayed in Figure 1.7 (third panel), HNO3 concentrations are lower, that is between 0.2 to 1.2 ppbv, and increase to 2 ppbv before the pollution event. Around 2 July, before the dust event, about 1 ppbv of HNO3 is measured. During the dust event, HNO3 is strongly reduced and very low concentrations are measured. The ozone measurements (Figure 1.7, second panel) show that the low concentrations at 25 and 26 June are related to the arrival of Mediterranean air. The highest pollution levels are observed for air masses spending most of their time in the continental boundary layer over NW Europe and arriving between 27 and 30 June. Ozone decreases by about 20 ppbv and increases immediately after the dust event. Following the models, 80 % of ozone reduction occurring during the dust event can be explained by transport of ozone poor air from desert and 20 % by heterogeneous chemical reactions.

1.6 Mineral dust characterization

In order to make a link between the mineral dust samples used in the present work and the real composition of the mineral dust collected during dust episodes, we want to refer to a recent field campaign. A strong African dust episode affected the Canary Islands from 28 to 31/07/02 and has been characterised at the Izana Observatory (IZO) in the free troposphere (FT), and Sta. Cruz de Tenerife (SCO), in the Marine Boundary Layer (MBL). The IZO station is normally unaffected by local and regional pollution sources in contrast to the SCO station located in the MBL that is most often under the direct influence of local anthropogenic emissions related to traffic and harbour activities. Therefore, using data from IZO it has been possible to characterize the Saharan dust with minor or no interference of other pollutants. Levels of TSP, and PM10, PM 2.5 and PM1 were monitored at IZO by means of an optical particle counter. The mineralogic characterisation of TSP (total suspended particles) was carried out by X-ray diffraction (XRD) analysis using a powder diffractometer.
Semiquantitative concentrations of major mineral phases identified by XRD in TSP samples collected at IZO (top) and at SCO (bottom) are shown in Table 1.5. Quartz is the major mineral phase identified at both sites (23%). As regards clay minerals, the presence of Illite, Paligorskite, Kaolinite and Clinohlore was identified at both sites in similar proportions. The clay minerals accounted for 47% of TSP mass at IZO and 42% at SCO. Calcite was estimated to be present to the extent of 9% of TSP at IZO, and only of 6% at SCO. By contrast, gypsum contents were lower at IZO (3.5%) than at SCO (10%). The presence of Halite (NaCl, related to the marine aerosol) has only been detected at SCO (2%)\textsuperscript{56}.

<table>
<thead>
<tr>
<th>Clay minerals</th>
<th>Izana</th>
<th>Sta. Cruz</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paligorskite</td>
<td>Mg\textsubscript{5}(Si,Al)\textsubscript{10}O\textsubscript{26}(OH)\textsubscript{2}.8H\textsubscript{2}O</td>
<td>10  9</td>
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<tr>
<td>Illite</td>
<td>(KH\textsubscript{3}O)Al\textsubscript{2}Si\textsubscript{4}AlO\textsubscript{10}(OH)\textsubscript{2}</td>
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<tr>
<td>Kaolinite</td>
<td>Al\textsubscript{2}Si\textsubscript{4}O\textsubscript{8}(OH)\textsubscript{4}</td>
<td>14  10</td>
</tr>
<tr>
<td>Clinohlore</td>
<td>(Mg,Fe)\textsubscript{6}(Si,Al)\textsubscript{4}O\textsubscript{10}(OH)\textsubscript{8}</td>
<td>8   9</td>
</tr>
</tbody>
</table>

**Feldspars**

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<th>Mineral</th>
<th>Formula</th>
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<th>Sta. Cruz</th>
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<td>Microcline</td>
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<td>(NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4}</td>
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<td>5</td>
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</tbody>
</table>

**Table 1.5.** Semiquantitative concentrations of major mineral phases identified in TSP in samples collected at Izana and Sta. Cruz. (2002).

SEM images of TSP sampled at IZO and SCO during 29 July 2002 (Figure 1.8) confirmed the results obtained by XRD.

The majority of African dust collected at IZO are made up of clay minerals and quartz (Figure 1.8, a). The clay particles may be grouped into two sub-groups: (a) typical large
(usually $> 10\mu m$) and flat clay mineral crystals (Figure 1.8, c), and (b) small aggregates of micro-crystals (approximately $1\mu m$) of clay minerals (Figure 1.8, c).

**Figure 1.8.** SEM microphotographs of TSP collected on 29th July 2002 at IZO (a–d) and at SCO (e–h). IZO: (a) rounded quartz; (b) large ($>10\mu m$) plate clay particles; (c) aggregates of micro-crystals of clay minerals; (d) silica skeletons of fresh water diatom from the *Melosira* genus, present in lakes or ponds from Northern Africa. SCO: (e) general aspect showing the presence of mineral dust, marine aerosol and *Melosira* genus diatoms, coated with sulphate; (f) spongy carbonaceous particles with sodium chloride crystals from marine aerosol; (g) K/Ca sulphate coating clay aggregates and (h) $<5\mu m$ Ca sulphate particles with crystalline habit$^{56}$. 
The EDAX analysis did not show any compositional difference between these two types of clay particles, both containing Si and Al with minor proportions of Fe, K and Mg. The presence of quartz (SiO₂) and other silicate particles was also very frequent. Similar findings were made in TSP at SCO (Figure 1.8, e) although a high proportion of natural marine aerosols and spongy carbonaceous anthropogenic particles were also present (Figure 1.8, f). Sulphate submicron particles associated with other particles (carbonate, clays) forming aggregates of total diameter 10μm were also observed (Figure1.8, g, h).

1.6 Soot particles

Soot consists of partially burned carbon produced under fuel rich conditions. 90% of soot particles come from the consumption of fossil fuels, particularly Diesel fuel, coal, jet fuel, natural gas and kerosene, as well as the burning of wood and other biomass. Under ideal conditions the combustion of hydrocarbons exclusively leads to carbon dioxide CO₂ and H₂O. Ideal conditions means that the oxygen content of the mixture everywhere is sufficient to oxidize the fuel completely according to equation (1.17):

\[
C_xH_y + (x + y/4)O_2 \rightarrow xCO_2 + y/2H_2O
\]  

(1.17)

Under these conditions the maximum of heat is released and a minimum of chemical energy is available for mechanical work. Practical combustion deviate from ideal conditions; if the local oxygen concentration is not sufficient to oxide the fuel according to equation (1.17) other products of incomplete combustion such as carbon monoxide (CO), hydrocarbons and soot appear. The terms “soot” and black carbon “BC” are often referred to designate carbonaceous particles. Soot is related to primary combustion generated carbonaceous aerosols, whereas BC is used to point out the light-absorbing property of carbonaceous particles. Its reactive surface is likely to be irreversibly affected by O₂ and other species. Therefore, soot may play a special role only if its surface remains active. Soot is formed through different chemical and physics processes such as the formation and growth of large hydrocarbons and their aggregation to particles. In addition, it may serve as cloud nucleation nuclei (CCN) for aerosols, for example, in the wake of aircraft engines.
Soot particles are mainly composed of amorphous carbon or black carbon but may contain a significant quantity (up to 50% of the soot particle mass) of hydrocarbons as a bulk phase or adsorbed on the particle surface\(^{60}\). This organic fraction may play a significant role in the reactivity of soot and may take an active part in the formation of secondary reaction products such as HONO according to equation (1.18):

\[
\text{NO}_2 + [\text{C} - \text{H}]_{\text{red}} \rightarrow \text{HONO} + [\text{C}]_{\text{ox}}
\] (1.18)

Soot aerosols present in polluted atmospheres may have typical sizes of 10 to 50 nm and a lifetime of several days up to tens of days before being precipitated to the ground by rain. Meanwhile, they are strongly suspected to partake actively in physico-chemical reactions with gaseous pollutants such as HNO\(_3\), NO\(_2\) and O\(_3\)\(^{61-64}\) and therefore reduce oxidized species in the atmosphere.

Novakov T. et al.\(^{65}\) presented estimates of black carbon emissions from the United States, United Kingdom, Germany, Soviet Union, India and China for the period from 1875 to the present. These countries are the major producers of coal and diesel fuel, which are the principal black carbon-producing fuels. The concentration of black carbon is variable: 800 ng/m\(^3\) in continental rural regions\(^{66}\), 40 ng/m\(^3\) in the Arctic\(^{67}\) and 20 ng/m\(^3\) in the remote oceanic regions\(^{68,69}\). Black carbon is of special interest because it absorbs sunlight, heats the Earth’s atmosphere, and contributes to global warming that might accelerate the greenhouse effect, unlike most aerosols, which reflect sunlight to space and have a global cooling effect.

Because soot particles are the principal light-absorbing atmospheric aerosol, any analysis or prediction of climate variability must include an accurate inventory of this species. Because both absorbing BC aerosols and reflective aerosols reduce the amount of sunlight reaching the ground it should tend to cause local cooling on the earth’s surface, in contrast to greenhouses gases which trap heat in earth’s atmosphere.

As a very recent example of soot emission a study on the characterization of different types of carbonaceous particles in smoke and its aging behaviour was reported\(^{70,71}\). In that study individual aerosol particles in smoke plumes from biomass fires and in regional hazes in southern Africa were studied using analytical transmission electron microscopy (TEM). Based on these analyses, three distinct types of carbonaceous particles were present in the smoke: organic particles with inorganic (K-salt) intrusion, “tar ball” particles, and soot.
The relative concentrations of organic particles were largest in young smoke, whereas tar balls were dominant in a slightly aged (~1 hour) smoke from a smoldering fire. Further aging caused the accumulation of sulphate on organic soot particles. In addition, large aggregates of calcium-bearing particles were present in the aged smoke samples, and the length of the aggregates ranged from 2 to 15 μm. The calcium-bearing particles were very fine grained, with diameter ranging from 50 to 300 nm, although some were up to 500 nm large (Figure 1.10). These particles included the carbonaceous minerals aragonite and calcite, sulphate (gypsum) and phosphate in the form of apatite.

**Figure 1.9.** TEM image of a typical portion of a sample of young smoke from a flaming fire. Particles are attached to the lacy support film; most particles are carbonaceous (organic) with inorganic K-sulphate inclusions.70
1.7 Motivation for the present work

Despite the published results of field observations and modeling studies, there are only few reports on laboratory experiments that deal with the heterogeneous reactivity of NO$_3$ and N$_2$O$_5$ on mineral dust aerosol surrogates and soot substrates. Only a very recent laboratory study has been performed with N$_2$O$_5$ on Saharan Dust using a combination of Knudsen flow reactors and DRIFTS. We have therefore embarked on a laboratory program to measure some of the heterogeneous reactions involving N$_2$O$_5$ and NO$_3$ as relevant trace atmospheric gases. In the present work, we have used a Knudsen flow reactor in order to investigate the uptake and reaction of O$_3$, NO$_3$ and N$_2$O$_5$ on selected authentic mineral dust samples such as Kaolinite, Saharan Dust from Cape Verde Islands, Arizona test dust and natural limestone as well as on samples of pure CaCO$_3$. Additional work has been carried out on soot samples regarding its heterogeneous interaction with NO$_3$. 

Figure 1.10. TEM images of aggregates of calcium-rich particles. (a) Large aggregates of fine calcium sulfate from a fire from Zambia. (b) Calcium carbonate particles aggregated with tar balls in aged smoke 8 to 38 km downwind of the fire. (c) CaCO$_3$ particles and aragonite crystals.
The present thesis work also reports a kinetic study of the heterogeneous reaction of O₃ on mineral dust surrogates presented as powders. Its specific objective was the investigation of the mechanism of adsorption of ozone on surrogates of mineral dust as well as the kinetics of the heterogeneous reaction including reaction products that are released into the gas phase.

1.8 References


1. Introduction


1. Introduction


1. Introduction


1. Introduction


1. Introduction

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CHAPTER 2

EXPERIMENTAL SETUP

The Knudsen flow reactor has been specifically designed for the study of heterogeneous reactions with detection using mass spectrometry (MS) and \textit{in situ} Resonance Enhanced Multiphoton Ionization (REMPI). The Knudsen reactor has been developed more than thirty five years ago for kinetics measurements. It is a low pressure flow reactor that operates under the molecular flow regime. This technique has been applied to the study of chemical kinetic over a wide variety of systems. In the pressure regime of $P_{\text{tot}} < 10^{-3}$ Torr, gas wall-collisions are strongly favoured over gas phase collisions; the technique is thus ideally suited for the study of heterogeneous chemistry. The gases under study react with the substrate in the absence of limiting gas phase diffusion, and the collision frequency between the gas and the substrate may be determined using gas kinetics\textsuperscript{1}.

2.1 The Knudsen flow reactor

The apparatus is displayed schematically in Figure 2.1.\textsuperscript{2} It consists of a vacuum line (4) from which the gases are admitted into the reactor (1). The Knudsen Cell (1) is the reactor where the gas-surface interaction takes place. The vacuum line is used to store gases and is evacuated by an oil-sealed pump (6). Gas is injected into the reactor either in pulses of milliseconds duration via a solenoid valve (24) (General Valve Corporation, model series 9, IOTA ONE system) or continuously via a capillary backed by a calibrated volume $V_c$ (25) and a needle valve (26). The pressure in the calibrated volume is measured by a Baratron pressure gauge. The molecules that escape from the reactor form an effusive molecular beam that is collected by an electron impact quadrupole mass spectrometer QMS (Balzers QMA 421) (10) placed in the lower part of a differentially pumped vacuum chamber. The Phase
Sensitive Detection (PSD) enables the separation of the MS signal of the sample molecular beam from the background signal owing to secondary interaction of the reactants with the walls of the detection chamber. Therefore, the beam effusing from the reactor is modulated using a tunable chopping wheel (20 – 350 Hz) (9) located just above the ionization zone of the mass spectrometer in the lower differentially pumped chamber. The PDS is then processed by a lock-in amplifier (SRS 830) (11).

**Figure 2.1.** Schematic drawing of the Knudsen cell reactor and view of the REMPI excitation and detection parts, including triggering and signal processing electronics.

1, Knudsen cell reactor; 2, variable potentiometer; 3, sample (N$_2$O$_5$, NO$_3$, O$_3$); 4, gas inlet lines; 5, 6 cm hot glass tube of 0.6 cm diameter externally heated to 530 K using NiCr wire for the gas sample inlet (V = 1.7 cm$^3$); 6, mechanical pump; 7, cryogenic pump; 8, turbo pump; 9, mechanical chopper; 10, quadrupole mass spectrometer; 11, lock-in amplifier; 12, oscilloscope; 13, dry pump; 14, Pyrex cell for REMPI detection; 15, preamplifier; 16, boxcar integrator; 17, oscilloscope; 18, delayed beam triggering; 19, photodiode (FND 100); 20, pulsed Nd:YAG laser; 21, dichroic harmonic separator; 22, PDL (Pulsed Dye laser)-3; 23, mirror; 24, inlet valves; 25, calibrated volume ($V_c$); 26, needle valve; 27, isolation plunger; 28, sample holder; 29, escape orifice.
The main characteristic of the Knudsen flow reactor is that molecules entering into the reactor interact with the whole reactive surface area of the substrate at any given time. The kinetic measurements are performed under dynamic conditions, controlled by the rate of effusion through the escape orifice (29). The change in the orifice size is related to changes in the gas concentration \([M]\) in the reactor as well the first order rate constant of effusion. The molecular flow leaving the reactor during an experiment is controlled by the escape rate constant \(k_{\text{esc}}\). In addition, the experimental rate of a given reaction or its corresponding rate constant is always assessed by comparison to a reference experiment.

<table>
<thead>
<tr>
<th>Definition</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor volume (V)</td>
<td>2000 cm(^3)</td>
</tr>
<tr>
<td>Reactor surface area (A(_R))</td>
<td>1830 cm(^2)</td>
</tr>
<tr>
<td>Sample geometric surface area (A(_s))</td>
<td>19.6 cm(^2) (TEFLON holder), 4.9 cm(^2) (DELRIN holder)</td>
</tr>
<tr>
<td>Orifice diameter (nominal)</td>
<td>1, 4, 8 and 14 mm</td>
</tr>
</tbody>
</table>

**Table 2.1** Characteristic parameters of the Knudsen cell reactor.

An O-ring sealed movable plunger (27) allows the separation of the reactive surface area located in the sample holder (28) from the reactor volume. The change of the MS signal levels upon opening and closing the sample chamber obtains a value of the net uptake coefficient \(\gamma\) which represents the probability that molecules have, within their lifetime in the reactor, to disappear from the gas phase by uptake on the reactive surface. The escape aperture may be varied by fitting a plunger-mounted plate with different orifice sizes. The internal surface of the reactor (made of Pyrex glass and stainless steel) are fully TEFLON\(^\text{®}\) (FEP) coated in order to limit potential interactions between gas phase species and the walls. Under the molecular flow conditions, each molecule that enters the volume of the reactor collides with the walls until it is lost by reaction with a probability \(\gamma\), or leaves the cell through the escape orifice. From gas kinetic theory, the gas-wall collision frequency of the average molecule (per molecule per cm\(^2\)), referred to as \(Z_1\), is calculated from the mean velocity \(\bar{c}\) of the gas-phase molecule and the reactor volume \(V\):

\[
Z_1 = \frac{\bar{c}}{4V} = \sqrt{\frac{8RT}{\pi M}} \cdot \frac{1}{4V} \quad (2.1)
\]
where \( R \) is the gas ideal gas constant, \( T \) the temperature in Kelvin, \( \bar{c} \) the mean molecular speed and \( M \) the molecular mass in kg/mol.

The geometry of the escape orifice limits the probability of back-diffusion of molecules that collide with the walls of the orifice hole (Clausing factor). Thus, after Clausing correction every molecule which crosses the orifice of surface area \( A_H \) leaves the reactor with a probability equal to 1. The condition for \( N \) molecules in the reactor can then be expressed according to:

\[
\frac{-dN(t)}{dt} = 1 \quad (2.2)
\]

Thus the flow \( F_0^M \) of molecules \( M \) leaving the reactor via the orifice with area \( A_H \) is expressed as:

\[
F_0^M = \frac{dN(t)}{dt} = Z_t A_H N(t) \quad (2.3)
\]

where \( N(t) \) is the time dependent total number of molecules inside the reactor. In the absence of any reactive surface the escape rate constant, \( k_{esc} \) \([s^{-1}]\) which characterizes the kinetics of molecular effusion out of the Knudsen reactor, is defined as:

\[
k_{esc} = Z_t A_H \quad (2.4)
\]

The molecular residence time in the gas phase is \( \tau_g = 1/k_{esc} \). It depends on the molecular weight of the gas molecules as well on the area of the escape orifice. The MS signal \( I_0^M \) [Volt] is directly proportional to \( F_0^M \) [molecule s\(^{-1}\)] via a calibration factor following equation (2.5):

\[
F_0^M = I_0^M \cdot C_{cal(M)} \quad (2.5)
\]

where \( C_{cal(M)} \) is a calibration factor for the species \( M \) of interest whose value depends on the MS instrumental parameters.
The experimental value of $k_{esc}$ is assessed by fitting the single exponential decay of the MS signal during a reference experiment either after the source of the molecules entering the reactor has been halted at time $t_0$ or after pulsed injection (Figure 2.3); the rate law of the effusion is first order based on the solution of the differential equation (2.3):

$$N(t) = N(t_0) \cdot e^{-k_{esc}t} \quad (2.6)$$

Table 2.2 reports the characteristic parameter of the Knudsen reactor. We performed experiments according to two protocols characterized by their different procedure. In continuous flow (or steady state) experiments, reactants were introduced at a constant flow. In pulsed valve experiments, we observe the exponential decrease of the gas concentration in the reactor upon injection of a known dose of gas. Both techniques are complementary and provide information on the kinetics and the mass balance of a given reaction.

<table>
<thead>
<tr>
<th>Definition</th>
<th>Theoretical Value</th>
</tr>
</thead>
</table>
| $k_{esc}$ (experimentally determined values for nominal orifice diameters)$^a$ | 0.02$(T/M)^{1/2}$ s$^{-1}$ for 1 mm orifice  
0.25$(T/M)^{1/2}$ s$^{-1}$ for 4 mm orifice  
0.8$(T/M)^{1/2}$ s$^{-1}$ for 8 mm orifice  
1.9$(T/M)^{1/2}$ s$^{-1}$ for 14 mm orifice |
| Collision frequency $\omega$ (nominal) with $A_s$ | $\omega = Z_1 A_s = 1.81(T/M)^{1/2}A_s$ [s$^{-1}$] |

$^a$ T given in K, M in g, $A_s$ in cm$^2$|

Table 2.2. Kinetic parameters of the Knudsen cell. The theoretical value of $k_{esc}$ is calculated according to equation (2.4).

### 2.2 Steady State Experiment

When a continuous flow $F_{in}^M$ of molecules is admitted into the reactor through a capillary inlet, we obtain a constant molecular flow. Once the equilibrium is established in the reactor and in the absence of any reaction, the steady state flow of molecules effusing out of the reactor $F_0^M$ is equal to the flow $F_{in}^M$ (Figure 2.2). When a reactive surface is exposed, the new
steady state molecular flow $F_r^M$ is reduced with respect to $F_0^M$ because of the rate of loss to the substrate. If we exclude the saturation of surface sites during the uptake, $F_r^M$ may be expressed as:

$$F_r^M = F_0^M - \frac{dN_r(t)}{dt} = F_0^M - (\gamma_{ss} \cdot Z_1 A_S) \cdot N_r(t) \quad (2.7)$$

$Z_1 A_S$ is the collision frequency $\omega$ over the total reactive geometric surface with area $A_S$ and $\gamma_{ss}$ is the probability that molecules have, within their lifetime in the reactor, to disappear from the gas phase by uptake on the reactive surface. By multiplying equation (2.7) by $k_{esc}$ the observed pseudo first order rate constant $k_{obs}$ for reaction is derived according to equation (2.8):

$$k_{obs} = (\frac{F_0^M}{F_r^M} - 1) \cdot k_{esc} = \gamma_{obs} \cdot \omega \quad (2.8)$$

Usually, at steady state conditions, $\gamma_{obs}$ is named steady state uptake $\gamma_{ss}$ coefficient.

The MS signal is directly proportional to the flow of molecules leaving the reactor. It drops from $I_0^M$ to $I_r^M$ after exposing a reactive surface. The gases leave the Knudsen reactor through the escape orifice whose diameters (1, 4, 8, 14 mm) determine the residence time ($\tau_g = 1 / k_{esc}$) and molecular concentration at a given flow rate according to:

$$I_{0}^{M} = I_{r}^{M} \cdot C_{(M)} \quad (2.9)$$

where $I_0^M$ is the mass spectrometric signal amplitude (MS) flow of molecules effusing from the reactor and $C_{(M)}$ is the calibration factor for species M of interest that depends on instrumental parameters. Based on the ideal gas law ($PV = nRT$) the MS signal is calibrated in the following manner:
\[
\frac{dN}{dt} = \frac{dP}{dt} \frac{V_c}{RT} N_A = F_M^{in}
\]  

(2.10)

where \( R \) is the ideal gas constant, \( T \) the temperature in Kelvin, \( V_c \) a calibrated volume, \( N_A \) the Avogadro’s number and \( F_M^{in} \) the inlet gas flow. Under the assumption that \( F_M^{o} = F_M^{in} \), that is at steady state, the calibration factor \( C_{cal(M)} \) results:

\[
C_{cal(M)} = \frac{dP \cdot x}{t_0^{M}}
\]

(2.11)

where \( t_0^{M} \) is the MS signal. The concentration \( [M]_{MS} = N/V \) in the reactor is related to the flow of molecules leaving the reactor \( F_0^{M} \) according to equation (2.12):

\[
[M]_{MS} = \frac{F_0^{M}}{k_{esc} \cdot V_{cell}}
\]

(2.12)

**Figure 2.2.** \( \text{N}_2\text{O}_5 \) steady state uptake experiment on a sample of 510 mg of CaCO\(_3\). Curves (a), (b), (c) and (e) correspond to the raw MS signals monitored at m/e 46, m/e 30, m/e 44 and m/e 18, respectively. The MS signal monitored at m/e 63 (curve (d)) corresponds to HNO\(_3\) production. Orifice diameter of 14 mm, \( A_s = 19.6 \text{ cm}^2 \) and \([\text{N}_2\text{O}_5]_0 = (4.0 \pm 1.0) \times 10^{11} \text{ cm}^{-3}\).
The concentration in the reactor may be chosen within the range \((1-1000) \times 10^{10} \text{ cm}^{-3}\) either by adjusting the inlet flow \(F_0^M = F_i^M\) or at a given flow rate changing the orifice size and thus the residence time \(\tau_g\).

### 2.3 Pulsed Valve Experiment

Pulses of reactive gas are admitted into the reactor during the short-opening period of the solenoid valve on the millisecond time scale. In the reactive case, the plunger is lifted and allows the heterogeneous interaction between the gas phase and the surface of interest. The MS probes molecules which have, within their lifetime in the reactor, the possibility to disappear from the gas phase by uptake on the reactive surface with an effective probability \(\gamma_{\text{eff}}\). Equation (2.3) may be written for this case as follow:

\[
\frac{-dN_r(t)}{dt} = (Z_iA_{ri} + \gamma_{\text{eff}}Z_iA_{rs}) \cdot N_r(t) \quad (2.13)
\]

where \(N_r(t)\) is the time dependent number of molecules in the reactor. The solution of equation (2.13) is given by:

\[
N_r(t) = N_0 e^{-(Z_iA_{ri} + \gamma_{\text{eff}}Z_iA_{rs})t} \quad (2.14)
\]

\(N_0\) is the number of molecules injected into the reactor and is experimentally determined by integration of the reference pulse (see Figure 2.3). Typically, pulses have a duration of 5 ms at a dose of \(5.0 \times 10^{15}\) molecules per pulse\(^2\). The “reference pulse” is fired when the sample is still isolated from the gas. We determine the total number of injected molecules per pulse and the value of \(k_{\text{esc}}\), which is obtained by simply fitting the decaying MS signal to a single exponential decay in the absence of reaction. The “reactive pulse” is obtained by repeating the same operation with the plunger lifted. The total observed exponential decay in the presence of a reactive substrate is thus characterized by a new rate constant, \(k_{\text{dec}}\), given by
k_{dec} = \gamma_{eff}Z_1A_s + k_{esc}. By identification of \gamma_{eff}Z_1A_s with the first order reactive rate constant k_{eff}, the uptake coefficient may be derived according to equation (2.15):

\[
\gamma_{eff} = \frac{k_{eff}}{Z_1A_s} = \frac{k_{eff}}{\omega} \quad (2.15)
\]

k_{eff} is obtained by comparing k_{dec} with k_{esc} measured in a reactive and a reference experiment, respectively. The number of collision per surface area at a given gas concentration [M] expressed in cm\(^3\) is \(Z_{11} = \frac{\bar{c}}{4}[M]\) following the kinetic theory of gases. At a given \(\gamma_{eff}\) the total number n of collisions per surface area is given by the following equation (2.16):

\[
n = Z_{11} \cdot \gamma_{eff} = \frac{\bar{c}}{4}[M] \cdot \gamma_{eff} \quad (2.16)
\]

Figure 2.3 shows a pulsed valve measurement performed with ozone (O\(_3\)) on 400 mg of Kaolinite. The two curves represent the reference pulse and the reactive pulse of O\(_3\) on the substrate, respectively. For each reactive pulse we defined the “cumulative dose of O\(_3\) taken up” as the difference of the area between the two curves.

Figure 2.3. Pulsed valve experiment performed in the Knudsen reactor: the reference pulse corresponds to 5.0 \(\times 10^{15}\) molecules of O\(_3\) entering in the reactor, without interacting with the substrate, the reactive pulse corresponds to 5 \(\times 10^{15}\) molecules of O\(_3\) interacting with 400 mg of Kaolinite (\(A_e = 19.5\) cm\(^2\); 14 mm orifice).
2. Experimental Setup

2.4 Optical detection: Resonance Enhanced Multiphoton Ionization (REMPI) of NO₂ and NO in the Knudsen flow reactor

As displayed in Figure 2.1, a Pyrex cell (14) has been added to the main body of the reactor in order to enable in situ REMPI detection. Inside this REMPI cell two electrodes were mounted, each on an electrical feedthrough. The electrodes consist of two polished Cu plates mounted in a cell that is equipped with two quartz windows for the entry and exit of a focused visible laser beam. The dye laser beam is focused by means of a 70 mm (focal length) plano-convex lens in the center of the two plate electrodes which are biased at ± 65 V against ground. REMPI was performed using a Quanta Ray® PDL-3 dye laser (22) pumped by the third harmonic of a Quanta Ray® Nd:YAG (GCR-3) laser (20) at 355 nm which generates visible light in the wavelength range 420 to 520 nm. Two different dyes were used to study REMPI of NO and NO₂: Coumarin 120 (absorption λ\text{max} = 354 \text{ nm}) and Coumarin 307 (absorption λ\text{max} = 395 \text{ nm}) for NO and NO₂, respectively³. Ions and electrons created in the focal volume of the dye laser are collected by the plate electrodes, amplified (15) and, after inversion of one of the signals, added before averaging by a box-car (SRS 250) integrator (16) in order to yield the REMPI signal.

The signal area A\text{REMPI} resulting from the integration for 300 μs under the REMPI signal is proportional to the number of charge carriers initially generated by REMPI and so is directly proportional to the gas concentration [M]\text{REMPI} following equation (2.17):

\[
[M]\text{REMPI} = A\text{REMPI} \cdot C_{(M)\text{REMPI}} \quad (2.17)
\]

where \(C_{(M)\text{REMPI}}\) is a calibration factor that is directly determined from an absolute determination of [M] using a suitably calibrated MS signal for species M. In order to determine this calibration factor we monitored \([M]_{\text{MS}}\) against the integrated REMPI signal \(A_{\text{REMPI}}\) following equation (2.18):

\[
C_{(M)\text{REMPI}} = \frac{[M]_{\text{MS}}}{A_{\text{REMPI}}} \quad (2.18)
\]
Previous studies have already examined the complexity of the REMPI spectrum of NO at ambient temperature. Nitric oxide can be ionized by four photons including both two and three-photon resonances. The two-photon resonances are found to be much more intense than the three-photon ones. Absorption of two more photon promotes the excited state molecule above its ionization potential and the molecule spontaneously ionizes. The excitation process is depicted in Figure 2.4 and corresponds to a [2 + 2] process: two photons at $\lambda_{\text{NO}} = 452.6$ nm resonantly excite NO in the $X^2\Pi \rightarrow A^2\Sigma^+$ band.

![Energy level diagram](image)

**Figure 2.4.** Energy level diagram showing the two-photon resonant, four-photon ionization of nitric oxide via vibrations of the $A^2\Sigma^+$ state. The final four-photon energy in the continuum (shaded region) and the ionization energy (dashed line) are indicated.

Two additional photons at $\lambda_{\text{NO}} = 452.6$ nm are absorbed between the $A^2\Sigma^+$ states and the vibrational Rydberg levels resulting in the ionization of the molecule. The overall process is described by the following reactions:

\[
\text{NO}(X^2\Pi) + 2h\nu_i \rightarrow \text{NO}(A^2\Sigma^+) \quad (2.E1)
\]

\[
\text{NO}(A^2\Sigma^+) + 2h\nu_i \rightarrow \text{NO}^+ + e^- \quad (2.E2)
\]
The REMPI spectrum of NO and the energy of the dye laser (Coumarin 120) near 452 nm is shown in Figure 2.5. The region of major intensity of the REMPI spectrum ranges between 451.2 and 452.4 nm, the most intense narrow peak is at $\lambda_{\text{NO}} = 452.6$ nm.

**Figure 2.5.** REMPI spectrum of NO between 442 and 460 nm (trace (b)) compared with the corresponding gain curve of the laser dye (Coumarin 120, absorption $\lambda_{\text{max}} = 354$ nm used for the ionization process (curve (a)). The sharp peak located at $\lambda_{\text{NO}} = 452.6$ nm has been used to monitor NO (arrow).

In order to ionize NO$_2$ we have used a one color excitation scheme requiring four photons. The nature of the process is revealed by a resonance involving a three-photon transition from the ground state to a vibrational level of a 3s Rydberg state originating near 50000 cm$^{-1}$ \footnote{7,8}. The complete excitation process presented in the diagram displayed in Figure 2.6 corresponds to a [3 + 1] mechanism: one photon at $\lambda_{\text{NO}_2} = 511$ nm resonantly excites NO$_2$ in the band connecting the ground state $X^2\text{A}_1$ to a virtual intermediate state. At our chosen excitation wavelength of 511 nm, the two-photon energy for wavelengths longer than 498.2 nm falls just short of the origin of the 249.1 nm $B^2\text{B}_2$ state in NO$_2$. Both excited state levels, namely $A^2\text{B}_2$ and $A^2\text{B}_1$ of NO$_2$ are not involved in the electronic transition at $\lambda_{\text{NO}_2} = 511$ nm. Therefore, it has to take place via a virtual intermediate level located above $A^2\text{B}_1$. Two additional photons at $\lambda_{\text{NO}_2} = 511$ nm are resonantly absorbed from this virtual state to the four photon excited state via the $E^2\Sigma_u^+$ Rydberg levels\footnote{8}. 
The complete excitation process may be viewed as a \([3 + 1]\) ionization process, with the spectral structure reflecting the resonance at the three-photon level:

\[
\text{NO}_2(X^2A_1) + 3h\nu_2 \rightarrow \text{NO}_2(E^2\Sigma_u^+) \quad (2.E3)
\]

\[
\text{NO}_2(E^2\Sigma_u^+) + h\nu_2 \rightarrow \text{NO}_2^+ + e^- \quad (2.E4)
\]

**Figure 2.6.** Energy level diagram showing the three-photon resonant, four-photon ionization of \text{NO}_2 via vibrations of the \(B^2B_2\) state. The \text{NO}_2 dissociation to yield neutral \text{NO}(X^2\Pi) and \text{O}(^3P) is indicated (dashed arrow). The final four-photon energy in the continuum (shaded region) and the ionization energy (dashed line) are indicated.

The REMPI spectrum of \text{NO}_2 and the energy of the dye laser (Coumarin 307) near 511 nm is shown in Figure 2.7. The high level background below the REMPI signal is due to vibrationally excited \text{NO} produced from \text{NO}_2 dissociation during the excitation/photoionization process. The resulting spectrum is thus the sum of an ionization spectrum for \(2\text{NO}\) overlaid on a continuous ionization spectrum for \text{NO} generated by photodissociation of \text{NO}_2. In this case molecular \text{NO}_2 undergoes a transition to the electronically excited \(B^2B_2\) dissociative state, producing vibrationally excited \text{NO}(X^2\Pi) which then interacts with the laser beam as displayed in Figure 2.7. The fact that we observe a REMPI signal presumably due to \text{NO}^+ above 500 nm shows that two-photon dissociation of \text{NO}_2 must occur below the origin of the \(B^2B_2\) state. Energetically speaking, the only possible pathway is to \text{NO}(X^2\Pi) + O(^3P), and as anticipated, the \text{NO}^+ spectrum is
continuous and unassignable in this region\textsuperscript{8}. An ancillary REMPI experiment has been performed by exciting a flow of pure NO at $\lambda_{NO_2} = 511$ nm. As expected, we did not observe any NO$^+$ REMPI signal which must mean that NO was formed with significant excess energy during NO$_2$ excitation enabling REMPI detection of NO$_2$ at $\lambda_{NO_2} = 511$ nm\textsuperscript{8}.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure27.png}
\caption{REMPI spectrum of NO$_2$ between 500 and 525 nm (trace (b)) compared to the corresponding gain curve of the laser dye (Coumarin 307, absorption $\lambda_{\text{max}} = 395$ nm) used for the ionization process (curve (a)). $\lambda_{NO_2} = 511$ nm was used for detection of NO$_2$ (arrow).}
\end{figure}

In order to examine the kinetics of the rate-limiting step of the REMPI process for NO$_2$ and NO we have studied the dependence of the NO$^+$ ion yield as a function of laser intensity. At the limit of low intensities or small cross sections, that is in the absence of significant saturation, the overall ionization is simply given by the following expression of absorption:\textsuperscript{9}

\begin{equation}
N = \sigma_1 \sigma_\| I^{n+m}
\end{equation}

In this equation $I$ represents the laser intensity, $\sigma_1 I^n$ the transition probability for the n-resonant transitions and $\sigma_\| I^m$ the transition probability for the m ionization photons. $\sigma_1$ and $\sigma_\|$ are the cross-sections for the n-photon transition and m-photon-ionization, respectively. Typical values for NO cross-sections are:

$\sigma_1$ (two photon; NO) = $4.8 \times 10^{-51}$ cm$^4$ s and $\sigma_\|$ (two-photon; NO) = $2.0 \times 10^{-49}$ cm$^4$ s, obtained from the theoretical calculation of the two-photon resonant excitation of NO and of
the two-photon ionization of NO\textsuperscript{10}. For NO\textsubscript{2}, typical values for NO\textsubscript{2} cross-sections are: 
\[ \sigma_1 (\text{three-photon; NO}_2) = 2.6 \times 10^{-82} \text{ cm}^6 \text{ s}^2 \text{ and } \sigma_\text{II} (\text{one-photon; NO}_2) = 2.0 \times 10^{-20} \text{ cm}^2, \]

obtained for the theoretical calculation of the three-photon resonant excitation of NO\textsubscript{2} and the one-photon ionization of NO\textsubscript{2}\textsuperscript{10}.

At moderate laser intensities, the ionization rate is saturated and the overall ionization probability is proportional to:

\[ N = \sigma_1 I^n \]  

(2.E6)

As displayed in Figure 2.8 the measurement of the yield of NO\textsuperscript{+} (\( \lambda_{\text{NO}} = 452.6 \text{ nm} \)) versus laser intensity showed an \( I^2 \) and \( I^{1.7} \) dependence at low and high laser intensities, respectively, whereas NO\textsubscript{2}\textsuperscript{+} (\( \lambda_{\text{NO}_2} = 511 \text{ nm} \)) showed an \( I^{2.9} \) and \( I^{1.9} \) dependence at low and high laser intensities, respectively. Therefore, the NO\textsuperscript{+} and NO\textsubscript{2}\textsuperscript{+} REMPI spectra are controlled by the \( \text{X}^2\Pi \rightarrow \text{A}^2\Sigma^+ \) and \( \text{X}^2\Lambda_1 \rightarrow \text{E}^2\Sigma_u^+ \) transitions in NO and NO\textsubscript{2}, respectively.

**Figure 2.8.** REMPI signal for NO and NO\textsubscript{2} excitation at 452.6 nm and 511 nm, respectively. The full and open circles represent experimental data for NO and NO\textsubscript{2}, respectively. The fit of the data to a power law is shown as the dashed lines.

The conditions chosen for REMPI detection of NO\textsubscript{2} and NO did not show a measurable contribution from the photodissociation of NO\textsubscript{3} which otherwise would have complicated the interpretation of the present results owing to secondary photolysis at \( \lambda_{\text{NO}_2} = 511 \text{ nm} \) and
\(\lambda_{\text{NO}} = 452.6\) nm. Figure 2.9 displays an auxiliary experiment of NO\(_3\) interacting with the DELRIN\(^\text{®}\) support that has been carried out in order to show that the uptake of NO\(_3\) on DELRIN\(^\text{®}\) (\(\gamma_{\text{DELRIN}} = 8.2 \times 10^{-3}\)) and the subsequent decrease of the m/e 62 (NO\(_3^+\)) signal does not affect the REMPI signal for NO\(_2\) present as an impurity from the NO\(_3\) source. Moreover, NO\(_2\) did not show any uptake on DELRIN\(^\text{®}\) under all conditions.

On the other hand, REMPI detection of NO at \(\lambda_{\text{NO}} = 452.6\) nm leads to some two-photon photodissociation of NO\(_2\), if present. In order to prove the photodissociation of NO\(_2\) and subsequent ionization of the product NO under NO REMPI detection conditions, we photoionized a flow of pure NO at \(\lambda_{\text{NO}} = 452.6\) nm. Subsequently, we introduced an additional flow of pure NO\(_2\) identical to [NO] and observed an increase in the NO REMPI signal of approximately (20±5) % of that of the original NO (at 20 mJ/cm\(^2\) power energy). This means that the REMPI detection of NO at \(\lambda_{\text{NO}} = 452.6\) nm will lead to an additional REMPI signal if NO\(_2\) is present at the same time as NO. This secondary photoexcitation/ionization process in NO\(_2\) has been fully accounted for in the present data evaluation.

**Figure 2.9.** Simultaneous measurement of the NO\(_3\) uptake on a DELRIN sample holder using MS at m/e 62 (curve (b)) and the REMPI signal for NO\(_2\) at \(\lambda_{\text{NO}_2} = 511\) nm converted to a MS signal at m/e 46 (curve (a)). [NO\(_3\)] = (7.0 ± 1.0) \(\times 10^{11}\) cm\(^{-3}\) at orifice diameter 8 mm. The constant REMPI NO\(_2\) signal that is equivalent to the displayed MS signal in the presence of the changing NO\(_3\) MS signal, upon NO\(_3\) uptake indicates that NO\(_3\) secondary photolysis at \(\lambda_{\text{NO}_2} = 511\) nm does not contribute to the NO\(_2\) REMPI signal according to NO\(_3\) + h\(\nu\) → NO\(_2\) + O\(^3\)P) under the present experimental conditions.
2.5 Reactants preparations used in the present work

The studies presented in this work required the synthesis of some products which are not commercially available. Therefore, they were synthesised in the laboratory before performing each series of experiments. The purity of the gas samples was checked in the Knudsen reactor by mass spectrometry before their reaction with the substrates.

NO₂ and NO were obtained from Carbagas SA and Matheson Inc., respectively.

HONO was generated in situ by flowing gaseous HNO₃ through a reaction vessel filled with humid KNO₂ (FLUKA puriss. p.a ≥ 98.8%).

Pure HNO₃ was prepared from a mixture of liquid HNO₃ (90%, Fluka AG) and H₂SO₄ (98%, Fluka AG) in a ratio of 1:3 v/v. Subsequently, N₂ was bubbled through the solution under reduced pressure for about 10 minutes in order to rid the solution of trace amounts of NO₂.

N₂O₅ was synthesized by the oxidation of NO₂ with excess ozone. The O₃/O₂ mixture at the outlet of the ozonator (Fisher 502) is passed through a P₂O₅ trap in order to eliminate residual moisture before being mixed with equally dried NO₂. The N₂O₅ is collected in a methanol/dry-ice bath at 195 K and is subsequently analyzed for purity by MS.

NO₃ was generated by thermal decomposition of N₂O₅. This will be described in detail in Chapter 3.

O₃ was prepared in an ozone generator (Fischer 502) in which O₃ is generated by a corona discharge using a flow of pure oxygen at a pressure of 400 mbar. Subsequently O₃ was condensed in a Pyrex trap containing silica gel cooled to 185 K in a methanol bath. Subsequently we let O₃ desorb from silica gel into a darkened storage vessel in order to stock it for some time. Since the absorption spectrum of ozone is well known, it was used to quantitatively determine the concentration of ozone in the sample. A glass absorption cell of 7 cm optical path length and equipped with quartz windows was used for the measurement.
of ozone absorption at 256.3 nm using a cross section $\sigma = 1.15 \times 10^{-17}$ cm$^2$ for the calculation of the concentration at the measured total pressure in the absorption cell$^{12}$. 
2.6 References


2. Experimental Setup
CHAPTER 3

THE HETEROGENEOUS CHEMICAL KINETICS OF NO₃ ON ATMOSPHERIC MINERAL DUST SURROGATES

3.1 Introduction

Atmospheric chemistry is driven by reactions of free radicals owing to their reactivity with many trace gases. In addition to OH, HO₂ and O₃ that exert their oxidizing potential in the atmosphere under photolytic conditions, the nitrate free radical, NO₃, is an important atmospheric oxidizing agent in the nighttime atmosphere whose reactivity with unsaturated biogenic hydrocarbons as well as with aldehydes and ketones is comparable to the reactivity of the hydroxyl free radical in the daytime atmosphere. Together with O₃, nitrate radical represents a significant part of the oxidation potential of the atmosphere at night. Under conditions of the simultaneous presence of NOₓ, O₃ and reactive organic gases in the same air mass, NO₃ is responsible for the nighttime formation of organic peroxy free radicals that are precursors to tropospheric O₃. NO₃ is thereby involved in the rate-limiting step of either H abstraction from or addition to an olefinic double bond.

Specifically, the presence of NO₃ that rapidly undergoes photolysis during the day has several important consequences for tropospheric chemistry. It controls reactive nitrogen, NOₓ, at night by forming N₂O₅ which undergoes heterogeneous hydrolysis to HNO₃, an important daytime reservoir compound for NO₂. The fast radical recombination reaction
between NO$_3$ and NO$_2$ leading to N$_2$O$_5$ is the only known source for HNO$_3$ at nighttime. NO$_3$ also acts as an initiator for the formation of non-photolytic OH free radicals at night through reaction of HO$_2$ with NO, thereby starting oxidation chain reactions of reactive organic gases. Lastly, NO$_3$ may form peroxyacetyl and other organic nitrates that may also act as temporary NO$_x$ reservoirs.\(^2\,^3\)

Atmospheric nighttime concentrations of NO$_3$ reach values of up to $4.0 \times 10^7$ molecule cm$^{-3}$ in the stratosphere\(^4\) and $2.0 \times 10^9$ molecule cm$^{-3}$ in the troposphere\(^5\). Despite these significant concentrations only a few studies of the heterogeneous reactions of the nitrate radical have been performed\(^6\,-^9\), none so far on mineral dust. The present work intends to fill this gap by studying the NO$_3$ uptake on mineral dust and some of its surrogates in order to obtain a value for the uptake coefficient $\gamma$ for NO$_3$ that may be included in global modeling of heterogeneous chemistry on mineral dust aerosols. Together with HNO$_3$ and N$_2$O$_5$, NO$_3$ contributes to the formation of particulate nitrate on the dust particles by surface processes in the troposphere\(^1\)\(^1\).

There is no study at this time that directly proposes the uptake of NO$_3$ on mineral dust surfaces from measurements of the nitrate radical in the lower troposphere despite field measurements that report NO$_3$ concentrations\(^1\)\(^2\) and mixing ratios\(^1\)\(^3\) as a function of meteorological data. Box, regional and global scale models have gauged the importance of dust on both the photochemical rates of oxidant formation as well as the loss of trace gases regarding atmospheric composition\(^1\)\(^1\)\(^,\)\(^1\)\(^4\)-\(^1\)\(^7\). The comparison of the global scale models of Bian and Zender\(^1\)\(^6\) with the one presented by Bauer et al\(^1\)\(^7\) reveals significant quantitative differences of the effect of mineral dust on O$_3$ and several important trace gases such as HNO$_3$, N$_2$O$_5$ and H$_2$O$_2$. However, both studies agree that the direct interaction of O$_3$ with mineral dust is of minor importance, whereas the uptake of its precursor HNO$_3$ is responsible for most of the ozone decrease in the areas affected by dust. It is difficult to quantitatively compare the results of Bian and Zender with Bauer et al. because the uptake coefficient $\gamma$ for HNO$_3$ on global mineral dust is a factor of 100 lower whereas $\gamma$ for NO$_3$ is a factor of 33 larger in the former. The estimated uptake coefficients (guesses) used in the simulations performed by Bauer et al. where $\gamma_{\text{HNO}_3} = 0.1$, $\gamma_{\text{N}_2\text{O}_5} = 3.0 \times 10^{-3}$ (rH = 70%) and $\gamma_{\text{NO}_3} = 3.0 \times 10^{-3}$. On the other hand, Bian and Zender used different estimated values: $\gamma_{\text{HNO}_3} = 1.1 \times 10^{-3}$, $\gamma_{\text{N}_2\text{O}_5} = 1.0 \times 10^{-3}$ and $\gamma_{\text{NO}_3} = 0.1$. This reflects both the uncertainty of past measurements as well as the absence of experimental information that is replaced by
guesswork such as in the case of NO₃. We have therefore embarked on a laboratory program to measure some of the heterogeneous reactions involving NO₃ and N₂O₅ (chapter 4) likely to be important in global mineral dust studies.

3.2.1 Experimental Aspects

Experiments have been performed at 298 ± 2K using the Knudsen flow reactor, described in detail in Chapter 2. In order to unambiguously monitor the concentration of NO, NO₂, NO₃, HNO₃ and N₂O₅, Resonance Enhanced Multiphoton Ionization (REMPI) was employed in situ as part of a multi-diagnostic experimental technique in addition to molecular beam-sampling electron-impact mass spectrometry (MS) coupled to phase-sensitive detection.

The rate constant for the effusive losses $k_{esc}$ is given by the kinetic theory of gases and was routinely measured for each compound. However, owing to the fact that the loss of the NO₃ free radical includes both physical, that is effusion, and chemical wall-loss processes, the usual algebra for the retrieval of $\gamma$ is slightly more complex as explained below. The characteristic parameters and relevant kinetic expressions used in this work are given in Table 2.2.

3.2.2 Sample preparation

The used samples are the following: Kaolinite, poorly ordered (KGa-2, Warren County, Georgia, USA), CaCO₃ (Fluka), natural limestone (Transmat SA, La Sarraz, Switzerland), Arizona Medium Test Dust (Powder Technology Incorporated, Burnsville MN, USA), Saharan Dust collected from deposits on the Cape Verde Islands and Molecular sieve (Fluka). Table 3.1 reports the composition of the main components of the analysed mineral dust. The true density $\rho_t$ of all the examined powder samples was taken from the literature while the bulk density $\rho_b$ was determined from the weight and the volume of the sample. The average particle diameter was determined using SEM, and the Brunauer-Emmett-
Teller (BET) surface area of every sample displayed in Table 3.1 was measured using a Sorptomatic 1900 Carlo Erba (Fisous Instruments).

Two kinds of sample holders were used: one consisted of a TEFLON® coated Pyrex holder having an available sample surface of 19.6 cm², the other consisted of an internal reduction piece made out of DELRIN®, an acetal resin, leading to a sample surface of 4.9 cm². DELRIN® showed a modest reactivity towards uptake of NO₃ resulting in \( \gamma_{\text{DELRIN}} = 8.2 \times 10^{-3} \). We discovered during the study that DELRIN® is less porous for small molecules such as H₂O and less sticky for HNO₃ with respect to TEFLON®. As a consequence, we applied the appropriate corrections to all uptake measurements.

<table>
<thead>
<tr>
<th>Kaolinite¹</th>
<th>CaCO₃²</th>
<th>Natural limestone³</th>
<th>Saharan Dust⁴</th>
<th>Arizona Test Dust⁵</th>
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</thead>
<tbody>
<tr>
<td>Al₂Si₂O₅(OH)₄</td>
<td>CaCO₃ 99.9%</td>
<td>CaCO₃ 97%</td>
<td>SiO₂ 47%</td>
<td>SiO₂ 68-76%</td>
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<td>SiO₂ 44.2%</td>
<td>SiO₂ 1.9%</td>
<td>Al₂O₃ 0.5%</td>
<td>FeO 14.7%</td>
<td>Al₂O₃ 10-15%</td>
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<tr>
<td>TiO₂ 2.17%</td>
<td>Al₂O₃ 37.2%</td>
<td>Fe₂O₃ 0.3%</td>
<td>Al₂O₃ 17.6%</td>
<td>Fe₂O₃ 2.5%</td>
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<tr>
<td>Fe₂O₃ 1.14%</td>
<td>MgO 0.2%</td>
<td>Al₂O₃</td>
<td>MgO 5.1%</td>
<td>Fe₂O₃ 2.5%</td>
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<tr>
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<td>Other elements 0.1%</td>
<td>Na₂O 2.1%</td>
<td>MgO 1-2%</td>
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</tr>
<tr>
<td>MgO 0.04%</td>
<td>CaO 0.04%</td>
<td>K₂O 2.5%</td>
<td>TiO₂ 0.5-1.0%</td>
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<tr>
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<td>TiO₂ 4.5%</td>
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<tr>
<td>Na₂O 0.02%</td>
<td>MgO 2%</td>
<td>K₂O 2-5%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K₂O 0.02%</td>
<td>P₂O₅ 0.6%</td>
<td>Fe₂O₃ 2-4%</td>
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<tr>
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<td>SO₃ 0.3%</td>
<td>CaO 5.0%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F 0.02%</td>
<td>MnO 0.3%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \rho_t = 2.1-2.6 \text{ g/cm}^3 )</td>
<td>( \rho_t = 2.93 \text{ g/cm}^3 )</td>
<td>( \rho_t = 2.7 \text{ g/cm}^3 )</td>
<td>( \rho_t = 2.7 \text{ g/cm}^3 )</td>
<td>( \rho_t = 2.65 \text{ g/cm}^3 )</td>
</tr>
<tr>
<td>( \rho_b = 0.528 \text{ g/cm}^3 )</td>
<td>( \rho_b = 0.96 \text{ g/cm}^3 )</td>
<td>( \rho_b = 1.13 \text{ g/cm}^3 )</td>
<td>( \rho_b = 1.2 \text{ g/cm}^3 )</td>
<td>( \rho_b = 0.6 \text{ g/cm}^3 )</td>
</tr>
<tr>
<td>( d = 1.0 \mu m )</td>
<td>( d = 3.5 \mu m )</td>
<td>-</td>
<td>( d = 0.9 \mu m )</td>
<td>-</td>
</tr>
<tr>
<td>( S_{\text{BET}} = 22.57 \text{ m}^2/\text{g} )</td>
<td>( S_{\text{BET}} = 5.06 \text{ m}^2/\text{g} )</td>
<td>-</td>
<td>( S_{\text{BET}} = 39.6 \text{ m}^2/\text{g} )</td>
<td>-</td>
</tr>
</tbody>
</table>

**Table 3.1.** Composition of mineral dust samples used in this work.

¹C.V. Clemency, Dept. of Geological Sciences, SUNY at Buffalo, Buffalo N.Y.(USA), for the Clay Minerals Society.
²Fluka AG, CH-9471 Buchs (Switzerland).
³Transmat SA, Route de Ferreyres, CH-1315 La Sarraz (Switzerland).
⁵Powder Technology Inc., 1433 Ewing Avenue S. Burnsville, MN 55306, USA.
In order to probe diffusion effects of NO$_3$ inside bulk powders, several additional reference experiments were carried out. Glass optical flats of 19.6 cm$^2$ were sprayed with a mineral dust suspension in methanol or water in order to obtain a sample whose total exposed surface is equal to the sample holder. Typically, 5 – 20 mg of powder can be deposited onto the glass support to full coverage judged by eye and resulting in an average thickness of less than 4 μm. The purpose of these experiments was to obtain samples consisting of a few monolayers ever so poorly characterized in order to probe the mass dependence of NO$_3$ uptake. Most of the experiments have been carried out with gram quantities rather than mg. Uptake experiments have been carried out using mineral dust samples that were pumped for half an hour to less than 10$^{-7}$ Torr at T = 294 K after which no H$_2$O desorption has been observed.

### 3.2.3 NO$_3$ source

NO$_3$ was generated by thermal decomposition of N$_2$O$_5$ inside a 6 cm hot glass tube of 0.6 cm diameter ((5), Figure 2.1, Chapter 2) that was externally heated to 530 K using NiCr wire thereby approaching 100% decomposition of N$_2$O$_5$ under the chosen experimental conditions according to reaction (3.1):

$$\text{N}_2\text{O}_5 \rightarrow \text{NO}_2 + \text{NO}_3$$  \hspace{1cm} (3.1)

The gas phase residence time at ambient temperature of N$_2$O$_5$ in the gas injection line upstream of the NO$_3$ hot source has been calculated to be 5.7 s. N$_2$O$_5$ flow rates were on the order of 10$^{16}$ molecule s$^{-1}$. NO$_3$ was monitored using mass spectrometry at m/e = 62 (NO$_3^+$), HNO$_3$ at m/e = 63 (HNO$_3^+$), NO and NO$_2$ by REMPI detection at λ$_{\text{NO}}$ = 452.6 nm and λ$_{\text{NO}_2}$ = 511 nm, respectively. N$_2$O$_5$ did not have a measurable parent peak under our experimental conditions; the most intense peak was its fragment NO$_2^+$ at m/e 46. Both N$_2$O$_3$ and HNO$_3$ did not show any measurable contribution at m/e 62 in reference experiments such that these two species did not interfere with the MS detection of NO$_3$. In reference experiments of pure N$_2$O$_5$ m/e 62 was 0.01% of m/e 46.
Hydrolysis of N$_2$O$_5$ may occur on internal surfaces of the inlet line before admission into the hot glass 0.6 cm tube generating HNO$_3$ as an impurity on the order of 10 to 15%. HNO$_3$ does not thermally decompose inside the hot glass tube of the NO$_3$ source because we did not observe any change in the MS signal amplitude at m/e 63 when increasing the source temperature to 530 K. In addition, using pure NO$_2$-free HNO$_3$ flowing through the hot NO$_3$ source and using REMPI detection at $\lambda_{NO_2} = 511$ nm no REMPI signal of NO$_2$ from potential heterogeneous decomposition of HNO$_3$ on the hot walls of the source vessel was detected. We attribute this apparent resistance to decomposition to the small HNO$_3$ residence time of approximately 400 $\mu$s in the hot glass tube.

### 3.2.4 Calibration of NO$_3$ and secondary reactions in the NO$_3$ source

The NO$_3$ concentration has been determined by titration with NO according to reaction (3.2) where the end point has been detected by monitoring the additional NO$_2$ at excess NO:

$$\text{NO}_3 + \text{NO} \rightarrow 2\text{NO}_2$$ (3.2)

With a NO concentration of approximately $1.0 \times 10^{12}$ molecule cm$^{-3}$ the reaction is fast enough to convert more than 90% of the NO$_3$ inside the reactor using $k_{(298K)} = 2.6 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. The titration experiment at $T = 298$ K resulted in a yield of $143 \pm 29$% NO$_2$ and $54 \pm 18$% NO$_3$ (error represents one standard deviation) with respect to N$_2$O$_5$ decomposed. The deviation from the expected 100% yield for both NO$_2$ and NO$_3$ indicates a fast secondary decomposition reaction of NO$_3$ into NO$_2$ or NO within the hot glass tube of the source$^{18}$. Both REMPI detection at $\lambda_{NO_2} = 511$ nm (NO$_2$) and MS detection at m/e 62 (NO$_3$) allowed us to verify the mass balance of NO$_3$ with N$_2$O$_5$ and to conclude that the thermal decomposition of N$_2$O$_5$ is complete and that therefore no N$_2$O$_5$ is present in the mixture of NO$_3$ and NO$_2$ coming from the NO$_3$ source.
Possible candidates for products resulting from wall decomposition of NO$_3$ are NO$_2$ and NO according to reactions (3.3) and (3.4):

\[
\begin{align*}
\text{NO}_3 & \rightarrow \text{NO}_2 + \frac{1}{2} \text{O}_2 & \Delta H^0_{\text{r(gas)}} &= -9.1 \text{ kcal/mol} & (3.3) \\
\text{NO}_3 & \rightarrow \text{NO} + \text{O}_2 & \Delta H^0_{\text{r(gas)}} &= +4.6 \text{ kcal/mol} & (3.4)
\end{align*}
\]

In order to find the products of the wall decomposition of NO$_3$ without ambiguity we performed an ancillary experiment taking advantage of simultaneous REMPI detection of NO and NO$_2$ at $\lambda_{\text{NO}} = 452.6$ nm, the primary wavelength for NO detection (Chapter 2). In addition to NO, NO$_2$ is also detected at this wavelength owing to concomitant photolysis of NO$_2$ to NO and subsequent REMPI detection of NO as discussed at the end of chapter 2. As displayed in Figure 3.1, the ion yield for REMPI detection at $\lambda_{\text{NO}} = 452.6$ nm has been plotted as a function of [NO$_2$] originating from a pure NO$_2$ flow (open triangles) together with the ion yield of [NO$_2$] from a mixture of NO$_2$ and NO$_3$ flowing out of the hot NO$_3$ source (filled circles).

![Figure 3.1](image_url)  

**Figure 3.1.** REMPI signal at $\lambda_{\text{NO}} = 452.6$ nm as a function of [NO$_2$] for a pure NO$_2$ flow (open triangles) plotted together with the signal resulting from a mixture of NO$_2$ and NO$_3$ flowing out of the hot NO$_3$ source (filled circles). The point marked with the arrow represents the hypothetical REMPI signal at $\lambda_{\text{NO}} = 452.6$ nm if we have 10% of NO in a mixture of NO$_2$ and NO$_3$ at [NO$_3$] = 2.0 x $10^{12}$ cm$^{-3}$. The absolute concentrations of NO$_2$ and NO$_3$ have been separately determined using REMPI detection at $\lambda_{\text{NO}_2} = 511$ nm and MS at m/e 62, respectively, (orifice diameter = 8 mm).
Both [NO₂] and [NO₃] in the mixture have previously been independently determined by using REMPI detection at \( \lambda_{\text{NO}_2} = 511 \text{ nm} \) for [NO₂] and the MS signal \( I^{62} \) at m/e 62 for [NO₃], respectively. Based on Figure 3.1, we conclude that reaction (3.3) is the reason for the excess of NO₂ over NO₃ (see above) because it shows the complete absence of NO detected at \( \lambda_{\text{NO}} = 452.6 \text{ nm} \). The fact that the REMPI signal of the pure NO₂ reference gas coincides with the mixture flowing out of the NO₃ source leads to the conclusion that NO must be absent from the mixture which excludes reaction (3.4) as a candidate for wall decomposition of NO₃. Figure 3.1 shows the expected REMPI signal of NO₂ containing 10% NO which is 50% larger compared to pure NO₂ owing to the four-fold higher sensitivity of NO vs. NO₂ at \( \lambda_{\text{NO}} = 452.6 \text{ nm} \) as explained in Chapter 2. Figure 3.1 also shows that a 5% impurity of NO in NO₂ may be detected using REMPI. Potential NO that is formed heterogeneously following reaction (3.4) can only be partially titrated via reaction (3.2) because the titration rate is too slow in the absence of an excess of [NO₃]. Based on this slow titration rate NO should therefore be detectable if formed in reaction (3.4). We therefore exclude the heterogeneous decomposition of NO₃ according to reaction (3.4) with high confidence.

We were unable to measure any change in the O₂ signal following reaction (3.3) because molecular oxygen is present as a background gas in the Knudsen flow reactor owing to small leaks (o-ring seals). It was therefore impossible to separate the small expected O₂ contribution due to the NO₃ decomposition from the O₂ background. Molecular oxygen is the expected stable NO₃ decomposition product from both reaction pathways, reactions (3.3) and (3.4).

### 3.2.5 Wall loss of NO₃ in the Knudsen flow reactor

NO₃ itself was also subject to unspecified wall-loss in the Knudsen reactor as the measured rate of loss was consistently higher than the expected or calculated value (see Table 3.2). This indicated that a competing NO₃ loss process with a rate constant \( k_{\text{dec}} \) adds to the expected, that is calculated, rate constant for effusion \( k_{\text{esc}} \) based on the measured effusion rate of non-reactive gases such as N₂, Ar, CO₂ and SF₆. The relative concentration of NO₃
The heterogeneous chemical kinetics of NO$_3$ on atmospheric mineral dust surrogates decreases with decreasing orifice size because it undergoes wall loss with increasing residence time in the Knudsen reactor. Lower signals at smaller orifices, that is, at longer residence time in the reactor, indicate a loss process for NO$_3$. The measured first-order rate of loss given by $k'$ of NO$_3$ at a given escape orifice size of the reactor is based on the observed single-exponential decay of NO$_3$. It may actually be expressed as the sum of two components, namely $k_{esc}$ and $k_{dec}$, representing escape, that is physical, and chemical loss, respectively:

$$k' = k_{esc} + k_{dec} \quad (3.1)$$

The measurement of $k'$ at three different aperture sizes (Table 3.2) enabled the determination of $k_{dec} = 0.6 \pm 0.27$ s$^{-1}$. The additional loss process of NO$_3$ was found to be first order with respect to NO$_3$ and constant over the course of all performed experiments. In this work every measurement of $k_{obs}$ has been performed using $k'$ instead of $k_{esc}$. We determined the observed rate constant $k_{obs}$ by taking $k' = k_{esc}$ (theoretical value) + $k_{dec}$, where $k_{dec} = 0.6 \pm 0.27$ s$^{-1}$, as an effective loss process instead of $k_{esc}$ by itself resulting in the following equation:

$$k_{obs} = \left(\frac{I_0}{I_r} - 1\right) \cdot (k_{esc} + k_{dec}) \quad (3.2)$$

where $I_0^{62(NO_3)}$ and $I_r^{62(NO_3)}$ are MS signal at m/e 62 before and during reaction, respectively.

<table>
<thead>
<tr>
<th>Ø escape orifice (mm)</th>
<th>Calculated $k_{esc}$ (s$^{-1}$)</th>
<th>Measured $k'$ (s$^{-1}$)</th>
<th>$k_{dec}$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>4.15</td>
<td>5.0</td>
<td>0.85</td>
</tr>
<tr>
<td>8</td>
<td>1.74</td>
<td>2.3</td>
<td>0.56</td>
</tr>
<tr>
<td>4</td>
<td>0.54</td>
<td>0.9</td>
<td>0.36</td>
</tr>
</tbody>
</table>

*Table 3.2.* Comparison of calculated rate constant for effusion, $k_{esc}$, and measured loss rate constant of NO$_3$, $k' = k_{esc} + k_{dec}$, in Knudsen flow reactor of differing orifice diameters.
3.2.6 Determination of the uptake coefficient

The net observed uptake coefficient for NO$_3$ is $\gamma_{\text{obs}} = \frac{k_{\text{obs}}}{\omega}$ and is only valid if the rate law for uptake is first order in NO$_3$. In our data analysis, $\gamma_{\text{obs}}$ was calculated using the geometric surface area of the sample holder which will be justified below based on additional reference experiments. In the present work the observed uptake coefficient $\gamma_{\text{obs}}$ became $\gamma_{\text{ss}}$, when the uptake of NO$_3$ monitored at m/e 62 clearly reached steady state at 400 s of exposure time whereas $\gamma_0$ equals $\gamma_{\text{obs}}$ at $t = 0$ s, i.e. immediately after lifting the plunger. Upon increasing the exposure time by a factor of two, $\gamma_{\text{ss}}$ did not change significantly.

Continuous flow uptake experiments were carried out at ambient temperature (298 ± 2 K) under molecular flow conditions. The concentration of NO$_3$ inside the Knudsen reactor was kept constant at $(7.0 \pm 1.0) \times 10^{11}$ and $(4.0 \pm 1.0) \times 10^{12}$ cm$^{-3}$ for low and high [NO$_3$] experiments, respectively. The associated [NO$_2$] determined by REMPI was $(1.7 \pm 1.0) \times 10^{12}$ cm$^{-3}$ for [NO$_3$] = $(7.0 \pm 1.0) \times 10^{11}$ and $(7.3 \pm 2.0) \times 10^{12}$ cm$^{-3}$ for [NO$_3$] = $(4.0 \pm 1.0) \times 10^{12}$. In ancillary experiments, it was found that NO$_2$ only interacted with Saharan Dust whereas all other examined surrogate dust samples did not show any reactivity towards NO$_2$ under the selected experimental conditions.

3.2.7 Product study

The mass spectra of the species involved in the NO$_3$ source share common fragment peaks when using MS detection. The main common fragment and molecular ion peaks for NO$_3$, N$_2$O$_5$, NO$_2$, NO and HNO$_3$ are m/e 46 and 30. The REMPI detection of NO$_2$ allowed us to subtract with great accuracy the contribution of NO$_2$ to the total MS signal $I_{0}^{46}$ at m/e 46 originating from the source.

As indicated above, we observed that the NO$_3$ source contains HNO$_3$ as an impurity that contributes to the total MS signal at m/e 46. Fortunately, at the present experimental conditions HNO$_3$ has a measurable, albeit low intensity, parent peak at m/e 63. In order to evaluate the contribution of HNO$_3$ at m/e 63 and m/e 46, we have analyzed the MS
3. The heterogeneous chemical kinetics of NO$_3$ on atmospheric mineral dust surrogates

spectrum of pure HNO$_3$. The base and parent peak of HNO$_3$ are at m/e 46 (NO$_2^+$) and m/e 63 (HNO$_3^+$), respectively. In addition we did not observe any NO$_2$ impurity in HNO$_3$ following REMPI detection at $\lambda_{\text{NO}_2} = 511$ nm that is specific for NO$_2$.

In the following, the subscript 0 and r will refer to continuous gas uptake experiments in the absence and presence, respectively, of the solid sample.

Using the detailed mass spectrum of pure HNO$_3$ we have accurately determined the effective contribution of HNO$_3$ at m/e 46 by using the measured fragmentation pattern $f = \frac{I_0^{63}(\text{HNO}_3)}{I_0^{46}(\text{HNO}_3)} = 52 \pm 8$. The absolute NO$_2$ concentration $[\text{NO}_2]_{0(\text{REMPI})}$ originating from the NO$_3$ source has been determined by means of REMPI detection according to equation (2.17). In order to calculate its corresponding MS signal contribution $I_0^{46(\text{NO}_2)}$ at m/e 46, we used the following equation:

$$I_0^{46(\text{NO}_2)} \cdot \frac{C_{\text{cal}}(\text{NO}_2)}{C_{\text{esc}}(\text{NO}_2)} = \frac{[\text{NO}_2]_{0(\text{REMPI})} \cdot k_{\text{esc}}(\text{NO}_2) \cdot V_{\text{cell}}}{C_{\text{cal}}(\text{NO}_2)} \quad (3.E3)$$

where $C_{\text{cal}}(\text{NO}_2)$ is the NO$_2$ calibration factor obtained from equation (2.11) for pure NO$_2$ and $k_{\text{esc}}(\text{NO}_2)$ is its effusive loss rate constant. Equation (3.E3) allows one to calculate the fraction of the MS signal at m/e 46 owing to the presence of NO$_2$ using the measured REMPI signal for NO$_2$ to establish its absolute concentration. No molecular species including NO$_3$ other than NO$_2$ gives rise to a REMPI signal at $\lambda_{\text{NO}_2} = 511$ nm.

In the absence of any substrate, $I_0^{46(\text{NO}_2)}$ and $f \cdot I_0^{63(\text{HNO}_3)}$ have been subtracted from the total MS signal $I_0^{46}$ at m/e 46 in order to attribute the remaining signal to the NO$_2^+$ fragment of the electron-impact ionization of NO$_3$ once the absence of undissociated N$_2$O$_5$ from the NO$_3$ source was established:

$$I_0^{46(\text{NO}_3)} = I_0^{46(\text{NO}_2)} - I_0^{46(\text{NO}_2)} \cdot f \cdot I_0^{63(\text{HNO}_3)} \quad (3.E4)$$

When the sample is exposed to the gases from the NO$_3$ source, NO$_3$ is taken up and reacts on the mineral dust surface resulting in a decrease of [NO$_3$] which leads to a concomitant
decrease of the MS signal $I_r^{46}$ at m/e 46. As shown in previous studies on mineral dust\textsuperscript{20}, HNO$_3$, present as an impurity, reacts on the dust surface without formation of volatile products that may contribute to the total MS signal $I_r^{46}$.

We have determined $r = \frac{I_0^{46(NO_3)}}{I_0^{62(NO_3)}} = 9.5 \pm 2.0$ as the ratio of the MS signal $I_0^{46(NO_3)}$ at m/e 46 (NO$_3^+$) and $I_0^{62(NO_3)}$ at m/e 62 (NO$_3^+$) for NO$_3$ free radical in the absence of a reactive substrate. As a result of the exposure of the sample to NO$_3$ we expect two possible reaction products: HNO$_3$ and/or N$_2$O$_5$. Under our experimental conditions HNO$_3$ may possibly be formed at high densities by heterogeneous recombination of NO$_2$ and NO$_3$ to N$_2$O$_5$ and subsequent heterogeneous hydrolysis. HNO$_3$ has in fact been observed at m/e 63 resulting from the interaction of NO$_3$ with excess NO$_2$ under the present experimental conditions. In order to find other possible reaction products contributing to an excess $I_r^{46}_{\text{exc}}$ at MS signal intensity at m/e = 46 not due to HNO$_3$, we have subtracted the following known contributions from the total MS signal $I_r^{46}$: a) $I_r^{46(NO_2)}$ for NO$_2$, b) $r \cdot I_r^{62(NO_3)}$ for NO$_3$, c) $f \cdot I_r^{63(HNO_3)}$ for the possible HNO$_3$ formation during the reaction. The final expression for the residual amplitude $I_r^{46}_{\text{exc}}$ resulted from the following equation:

$$I_r^{46}_{\text{exc}} = I_r^{46} - I_r^{46(NO_2)} - r \cdot I_r^{62(NO_3)} - f \cdot I_r^{63(HNO_3)}$$

(3.E5)

The resulting residual MS signal from equation (3.E5) is related to reaction products owing to the heterogeneous interaction of NO$_3$ with the exposed surface of the sample. It is reasonable to expect that N$_2$O$_5$ may be the only reaction product contributing to m/e 46 as will be discussed below.

It was not possible to quantify the possible formation of NO by REMPI detection at $\lambda_{\text{NO}} = 452.6$ nm because its concentration dropped below our detection limit at the chosen detection conditions. Therefore, in order to estimate a possible excess at m/e 30 ($I_r^{30}_{\text{exc}}$) due to NO formation during the exposure of mineral dust substrates to NO$_3$, we have corrected the total MS at m/e 30 for the contribution of NO$_3$, HNO$_3$, NO$_2$ and N$_2$O$_5$. In all uptake experiments of NO$_3$ with mineral dust substrates $I_r^{30}_{\text{exc}} = 0$. The detailed procedure utilized to determine $I_r^{30}_{\text{exc}}$ has been reported in Chapter 5 for reaction of NO$_3$ on soot.
3.2.8 Experimental uncertainties

The uncertainties for NO$_3$ and HNO$_3$ were determined from the signal to noise ratio of the MS signal at m/e 62 and m/e 63 and were estimated at ± 15 % and ± 20 %. The uncertainties for [NO] and [NO$_2$] were estimated at ± 15 % and ± 10 %, respectively. They have been determined from the signal to noise ratio of the REMPI signal at $\lambda_{\text{NO}} = 452.6$ nm and $\lambda_{\text{NO}_2} = 511$ nm, respectively.

Based on the uncertainty of f (± 8 %) and on a typical uncertainty of ± 10 % of the REMPI signal the resulting overall uncertainty for $I_{0}^{46(\text{NO}_3)}$ is estimated at ± 18 %. On the other hand, the composite uncertainty of $I_{\text{exc}}^{46}$ is evaluated at ± 45 % based on the relative uncertainties of 10, 15 and 20 % for the REMPI signal of NO$_2$ as well as the MS signal contributions of NO$_3$ and HNO$_3$ to m/e 46, respectively. Therefore, N$_2$O$_5$ will be the only species that will be measured at an appreciable uncertainty of ± 45 % owing to the numerous subtracted contributions at m/e 46.

3.3 Uptake of NO$_3$: Results and Discussion

Typical raw data of an uptake experiment of NO$_3$ on 2g of CaCO$_3$ are shown in Figure 3.2a. After a steady flow of NO$_3$ had been established, the isolation plunger is lifted at t = 400 s and the substrate is exposed to the NO$_3$ flow. Because of the uptake of NO$_3$ on CaCO$_3$, the number of molecules effusing through the escape orifice into the MS decreases immediately. In all the performed experiments, NO$_3$ adsorbed on available surface sites gave rise to uptake of NO$_2$ that stems from the thermal decomposition of N$_2$O$_5$ and NO$_3$ (reactions (3.1) and (3.3)). This leads to a net decrease of the REMPI signal for NO$_2$ at $\lambda_{\text{NO}_2} = 511$ nm.
Figure 3.2a. Typical Knudsen reactor experiment for NO$_3$ uptake on a sample of 2g of CaCO$_3$ at [NO$_3$] = (7.0 ± 1.0) x 10$^{11}$ cm$^{-3}$ (orifice diameter = 8 mm, $A_s$ = 19.6 cm$^2$). Curves (a), (b) and (d) correspond to the raw MS signals monitored at m/e 30, m/e 46 and m/e 62, respectively. Curve (c) corresponds to the raw REMPI signal for NO$_2$ detection at $\lambda_{NO_2} = 511$ nm converted to a MS signal at m/e 46.

Figure 3.2b. Typical Knudsen reactor experiment for NO$_3$ uptake on a sample of 2g of CaCO$_3$ at [NO$_3$] = (7.0 ± 1.0) x 10$^{11}$ cm$^{-3}$ (orifice diameter = 14 mm, $A_s$ = 19.6 cm$^2$). Curves (a), (b) and (c) correspond to the raw MS signals monitored at m/e 30, m/e 46 and m/e 62, respectively.
As the exposure time increases, the MS signal at m/e 62 (curve (d), Figure 3.2a) partially recovers, indicating a decrease in the rate of uptake of NO$_3$ presumably owing to a decrease of the number of available surface sites for reaction. This results in an apparent reduction of the uptake coefficient. At $t = 820$ s the sample compartment is sealed by lowering the plunger and the MS signal at m/e 62 returns to its initial value. Figure 3.2b shows analogous results for the largest escape orifice leading to a larger rate of NO$_3$ uptake on solid CaCO$_3$. The lower concentration and the concomitant lower residence time $\tau$ of NO$_3$ in the reactor results in a lower degree of saturation and thus enhanced uptake.

In order to unravel whether or not the effective available surface area is influenced by the internal surface area formed by interstitial voids between individual dust particles, the mass dependence of the NO$_3$ uptake on Kaolinite was measured in the Knudsen flow reactor at ambient temperature and at [NO$_3$] = $(7.0 \pm 1.0) \times 10^{11}$ cm$^{-3}$. The mass of Kaolinite ranged from 5 mg to 1 g and the results are shown in Figure 3.3.

For the experiments performed at masses between 5 and 30 mg we used sprayed samples, whereas for masses between 110 mg and 1 g Kaolinite powder samples were used.

![Figure 3.3](image_url)

**Figure 3.3.** Uptake of NO$_3$ on Kaolinite: dependence of the steady state uptake coefficient $\gamma_{ss}$ on sample mass at [NO$_3$] = $(7.0 \pm 1.0) \times 10^{11}$ cm$^{-3}$ (orifice diameter = 8 mm, $A_s = 19.6$ cm$^2$). The number of nominal layers is reported on the upper abscissa. Full circles: experimental values. Curve (a): fit of the data using the pore diffusion model. Point (b): intersection of the linear and horizontal part of the curve which corresponds to the mass of one nominal layer of Kaolinite (see text).
Table 3.3 reports values of $\gamma_{ss}$ using the geometric surface area of the sample holder that increase linearly with mass at low masses as displayed in Figure 3.3. Samples of mass below 250 mg were considered part of this linear mass-dependent regime beyond which $\gamma_{ss}$ converged to a limiting value of $\gamma_{ss} = 5.5 \times 10^{-2}$ corresponding to $4.5 \times 10^{17}$ molecules of NO$_3$ taken up during a reaction time of 400 s. The significance of this number will be discussed below. Increasing the sample mass beyond 250 mg at the intersection of the linear mass dependence (point (b)) of $\gamma_{ss}$ in Figure 3.3 with the horizontal line, $\gamma_{ss}$ had no effect on $\gamma_{ss}$ as well as the amount of adsorbed NO$_3$ because apparently not the entire internal sample surface area is available for NO$_3$ adsorption. The limiting $\gamma_{ss}$ value represents the maximum amount of NO$_3$ able to interact with Kaolinite powder within the NO$_3$ residence time owing to the inability of NO$_3$ to penetrate into the sample.

<table>
<thead>
<tr>
<th>Mass (g)</th>
<th>$\gamma_{ss}$</th>
<th>Number of nominal layers$^c$</th>
<th>Number of formal layers$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.005$^a$</td>
<td>$(5.0 \pm 2.0) \times 10^{-3}$</td>
<td>0.02</td>
<td>1</td>
</tr>
<tr>
<td>0.013$^a$</td>
<td>$(1.0 \pm 0.5) \times 10^{-2}$</td>
<td>0.05</td>
<td>3</td>
</tr>
<tr>
<td>0.03$^a$</td>
<td>$(1.1 \pm 0.6) \times 10^{-2}$</td>
<td>0.12</td>
<td>6</td>
</tr>
<tr>
<td>0.11$^a$</td>
<td>$(2.9 \pm 1.1) \times 10^{-2}$</td>
<td>0.44</td>
<td>22</td>
</tr>
<tr>
<td>0.25$^b$</td>
<td>$(3.0 \pm 1.1) \times 10^{-2}$</td>
<td>1</td>
<td>50</td>
</tr>
<tr>
<td>0.4$^b$</td>
<td>$(4.8 \pm 1.5) \times 10^{-2}$</td>
<td>1.6</td>
<td>82</td>
</tr>
<tr>
<td>0.7$^b$</td>
<td>$(5.5 \pm 1.5) \times 10^{-2}$</td>
<td>2.8</td>
<td>143</td>
</tr>
<tr>
<td>1.0$^b$</td>
<td>$(5.5 \pm 1.6) \times 10^{-2}$</td>
<td>4</td>
<td>204</td>
</tr>
</tbody>
</table>

$^a$ Sprayed sample. $^b$ Powder sample. $^c$ Calculated for average grain size of 50 $\mu$m. $^d$ Calculated for an average grain size of 1 $\mu$m disclosed by the manufacturer albeit without documentation.

Table 3.3. Summary of uptake experiments with NO$_3$ on Kaolinite as a function of sample mass at [NO$_3$] = $(7.0 \pm 1.0) \times 10^{11}$ cm$^{-3}$, orifice diameter = 8 mm, $A_s = 19.6$ cm$^2$.

In order to determine the number of layers, $N_L$, the total volume of Kaolinite powder was calculated from its true density $\rho_t = 2.3$ g/cm$^3$ and the mass of the sample spread out across the geometric area of the sample holder ($V_{tot} = m/\rho_t$). From the average particle size d and
the measured thickness of the sample $h_{\text{tot}}$ we calculated the number of layers. Therefore, the number of layers has been expressed as 

$$N_L = \frac{h_{\text{tot}}}{d} = \frac{V_{\text{tot}}}{A_s d} = \frac{m}{\rho_s A_s d}.$$

The number of formal layers calculated for an average sample grain diameter of 1.0 $\mu$m is reported in Table 3.3. The typical grain diameter of 1.0 $\mu$m has been obtained from the manufacturer’s undocumented specifications of the used Kaolinite powder. However, most mineral dust powders are porous materials and the microstructure of the dust substrate is composed of clusters of random distribution with interstitial voids between them. Therefore it is more reasonable to take into account a grain size diameter that is much larger than 1.0 $\mu$m as suggested by electron microscopy (SEM) (Figure 3.4) of similar material where characteristic grain diameters are in the tens of $\mu$m (© OMNI Laboratories, Inc, http://www.omnilabs.com/).

Figure 3.3 shows that a mass of 250 mg corresponds to one nominal layer of 50 $\mu$m diameter Kaolinite spread out over the geometric surface of the sample holder (19.6 cm$^2$). Thus, one nominal layer of Kaolinite will contain closely packed spheres of “effective” grain diameter of 50 $\mu$m knowing full well that the sample in reality is multidisperse and structurally heterogeneous. Therefore, the linear mass-dependent portion of $\gamma_{\text{ss}}$ vs. mass corresponds to a sample holder partially covered with 50 $\mu$m diameter Kaolinite particles which is the structural model we adopt in this work.

![Figure 3.4. SEM-image of a Kaolinite powder sample: Authigenic kaolinite plates covering a quartz grain overgrown with authigenic quartz. SEM image of a core sample (© OMNI Laboratories, Inc, http://www.omnilabs.com/).](image-url)
The use of the BET (Brunauer-Emmett-Teller) surface area and the Pore Diffusion Theory (KLM)\(^{21}\) (see appendix) would substantially underestimate the true uptake coefficient based approximately on \(A_s\), the geometric surface area, between a factor of 10\(^2\) to 10\(^3\). The application of the pore diffusion theory results in \(\gamma_{pd} = 1.7 \times 10^{-5}\), using a tortuosity factor \(\tau = 2\) for a grain size of 1 \(\mu\)m (curve (a), Figure 3.3). The assumption that NO\(_3\) interacts with the BET internal surface leads to \(\gamma_{BET} = 2.0 \times 10^{-4}\) in contrast to \(\gamma_{geom} = (5.5 \pm 1.5) \times 10^{-2}\) calculated on the basis of the geometrical surface area of the sample and displayed in Table 3.3. In order to show that this underestimation of \(\gamma\) resulting from the application of the KLM model or the BET surface is excessive we have performed NO\(_3\) and NO\(_2\) uptake experiments on activated molecular sieve particles that consist of macroscopic rods with a certified pore diameter of 3, 5 and 10 \(\AA\).

The strategy of this experiment is to compare \(\gamma_{ss}\) of NO\(_3\) between a microporous material whose average pore diameter enables penetration of the NO\(_3\) probe, and one that does not allow for pore diffusion because of geometrical constraints. In case no large increase of \(\gamma_{ss}\) is observed in going from small to large pore size one must conclude that pore diffusion will not occur to a significant extent during the lifetime of NO\(_3\) in the reactor.

We chose the following molecular sieve particles having micropores of different diameters: K\(_{12}\)[(AlO\(_2\))\(_{12}\)(SiO\(_2\))\(_{12}\)]:\(\cdot\)XH\(_2\)O, with pore diameter of 3 \(\AA\), Ca\(_{12}\)[(AlO\(_2\))\(_{12}\)(SiO\(_2\))\(_{12}\)]:\(\cdot\)XH\(_2\)O, with pore diameter of 5 \(\AA\) and Na\(_{86}\)[(AlO\(_2\))\(_{86}\)(SiO\(_2\))\(_{106}\)]:\(\cdot\)XH\(_2\)O (Fluka) with pore diameter of 10 \(\AA\), and where X represents the equilibrium H\(_2\)O content exclusive of water remaining adsorbed in the molecular pores. In order to rid the sample of adsorbed water, molecular sieves have been activated by pumping and heating to 200°C. For 9 g of molecular sieve which resulted in the complete coverage of the 19.6 cm\(^2\) sample support we estimated an external surface area of 1.6 \(\times\) 10\(^2\) cm\(^2\) leading to 1.8 \(\times\) 10\(^{-3}\) m\(^2\) g\(^{-1}\). The internal surface area for molecular sieves of different diameter has been reported in Table 3.4 and is consistent with a ratio \(r\) of internal to external surface area of 2.5 \(\times\) 10\(^5\), 1.95 \(\times\) 10\(^5\) and 1.4 \(\times\) 10\(^5\), respectively, for the molecular sieve materials listed in Table 3.4. We estimate that NO\(_3\) has a characteristic size of approximately 4.5 \(\AA\) which would lead to a surface density of approximately 5.0 \(\times\) 10\(^{14}\) molecule cm\(^{-2}\). Therefore, uptake of NO\(_3\) on molecular sieve of 3 \(\AA\) pore size should not take place on the internal surface of the pores in contrast to 5 and 10 \(\AA\) molecular sieve where extensive pore diffusion of NO\(_3\) is expected, at a given sufficient interaction time.
3. The heterogeneous chemical kinetics of NO₃ on atmospheric mineral dust surrogates

As displayed in Figure 3.5 and reported in Table 3.4, $\gamma_{ss}$ for the 3 and 5 Å pore size molecular sieve samples were found to be identical within experimental uncertainty. In addition, for molecular sieve particles of nominal 10 Å pore diameter we observed $\gamma_{ss}$ value larger by a factor 1.7 at a residence time of 0.58 s (8 mm orifice) for NO₃. The spread in $\gamma_{ss}$ between the different molecular sieves is only a factor of 1.7, whereas we expected NO₃ to explore the internal microporous structure of the 5 and certainly of the 10 Å molecular aluminosilicate sieve material, both of which are expected to lead to a marked increase in $\gamma_{ss}$.

**Table 3.4.** Summary of the uptake experiments of NO₃ and NO₂ on 9 g of activated molecular sieve particles of different pore size: steady state ($\gamma_{ss}$) uptake coefficients at an orifice diameter = 8 mm and $A_s = 19.6 \text{ cm}^2$.

<table>
<thead>
<tr>
<th>Molecular sieve (nominal pore diameter Å)</th>
<th>$\gamma_{ss}$ [NO₃] = 7.0 x 10¹¹ cm⁻³</th>
<th>$\gamma_{ss}$ [NO₂] = 3.0 x 10¹¹ cm⁻³</th>
<th>BET Surface area (m² g⁻¹)</th>
<th>$r^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>(1.0 ± 0.3) x 10⁻²</td>
<td>(1.2 ± 0.2) x 10⁻³</td>
<td>455</td>
<td>2.5 x 10⁵</td>
</tr>
<tr>
<td>5</td>
<td>(7.8 ± 3.1) x 10⁻³</td>
<td>(7.4 ± 1.3) x 10⁻⁴</td>
<td>333</td>
<td>1.9 x 10⁵</td>
</tr>
<tr>
<td>3</td>
<td>(5.7 ± 2.2) x 10⁻³</td>
<td>(7.1 ± 1.9) x 10⁻⁴</td>
<td>243</td>
<td>1.4 x 10⁵</td>
</tr>
</tbody>
</table>

*a* ratio of internal to external surface area.

**Figure 3.5.** Uptake experiment performed on activated molecular sieve samples: $\gamma_{ss}$ as a function of the certified pore diameter. Triangles: [NO₃] = (7.0 ± 1.0) x 10¹¹ molecule cm⁻³ ($k_{esc} = 1.75 \text{ s}^{-1}$),
3. The heterogeneous chemical kinetics of NO$_3$ on atmospheric mineral dust surrogates

Circles: [NO$_2$] = (6.0 ± 1.0) x 10$^{11}$ molecule cm$^{-3}$ ($k_{sc} = 2.0$ s$^{-1}$). All experiments have been performed at an orifice diameter of 8 mm and a surface sample area $A_s$ of 19.6 cm$^2$

We emphasize that the three microporous materials had identical interstitial voids because ceramic particles of identical dimension have been used in experiments using the same mass for all three types of molecular sieve. Therefore the packing of the molecular sieve was identical for all experiments. We conclude that on the time scale of our experiment NO$_3$ does not explore the internal surface of the pores where pore diffusion is expected on geometrical grounds, namely on the 5 and 10 Å molecular sieves. The same result has been obtained employing the less reactive radical NO$_2$ (Table 3.4) whose extent of pore diffusion is expected to be larger in view of its smaller γ value as displayed in Figure 3.5.

<table>
<thead>
<tr>
<th>Mineral dust sample</th>
<th>Mass (g)</th>
<th>$\gamma_0$ [NO$_3$]$_0$ = (7.0 ±1.0) x 10$^{11}$ cm$^{-3}$</th>
<th>$\gamma_0$ [NO$_3$]$_0$ = (4.0 ±1.0) x 10$^{12}$ cm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO$_3$</td>
<td>2</td>
<td>0.13 ± 0.1</td>
<td>0.14 ± 0.05</td>
</tr>
<tr>
<td>Natural limestone</td>
<td>2</td>
<td>0.12 ± 0.08</td>
<td>0.20 ± 0.07</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>1</td>
<td>0.11 ± 0.08</td>
<td>0.12 ± 0.04</td>
</tr>
<tr>
<td>Saharan Dust</td>
<td>1</td>
<td>0.23 ± 0.2</td>
<td>0.16 ± 0.05</td>
</tr>
<tr>
<td>Arizona Test Dust</td>
<td>2</td>
<td>0.20 ± 0.10</td>
<td>0.14 ± 0.04</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mineral dust sample</th>
<th>Mass (g)</th>
<th>$\gamma_{ss}$ [NO$_3$]$_0$ = (7.0 ±1.0) x 10$^{11}$ cm$^{-3}$</th>
<th>$\gamma_{ss}$ [NO$_3$]$_0$ = (4.0 ±1.0) x 10$^{12}$ cm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO$_3$</td>
<td>2</td>
<td>(6.7 ± 4.0) x 10$^{-2}$</td>
<td>(1.4 ± 0.4) x 10$^{-2}$</td>
</tr>
<tr>
<td>Natural limestone</td>
<td>2</td>
<td>(3.4 ± 1.6) x 10$^{-2}$</td>
<td>(2.2 ± 0.5) x 10$^{-2}$</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>1</td>
<td>0.14 ± 0.02</td>
<td>(5.0 ± 1.4) x 10$^{-2}$</td>
</tr>
<tr>
<td>Saharan Dust</td>
<td>1</td>
<td>0.12 ± 0.08</td>
<td>(6.5 ± 1.2) x 10$^{-2}$</td>
</tr>
<tr>
<td>Arizona Test Dust</td>
<td>2</td>
<td>0.10 ± 0.06</td>
<td>(2.5 ± 0.7) x 10$^{-2}$</td>
</tr>
</tbody>
</table>

Table 3.5. Summary of Uptake Experiments of NO$_3$ on mineral dust samples: initial ($\gamma_0$) and steady state ($\gamma_{ss}$) uptake coefficients at an orifice diameter = 8 mm, $A_s$ = 19.6 cm$^2$.

We take this result as convincing justification to use the geometric surface area in evaluating the gas-surface collision frequency $\omega$ under the constraint of the present experimental condition of low gas-phase residence times. We think that the present conclusion may overestimate the true γ value by up to a factor of two if we approximate the
shape of the ceramic material by a half sphere and assume a closely-packed arrangement. According to Table 3.5 we use Kaolinite as a typical example to extrapolate the kinetics to the other samples because its $\gamma_0$ is smallest compared to the other examined substrates. However, we also note that $\gamma_0$ is almost identical for all investigated samples within experimental uncertainty. Table 3.5 reports all results concerning experiments performed on 1 – 2 g of surrogate mineral dust powder at the high concentration of $[\text{NO}_3] = (4.0 \pm 1.0) \times 10^{12} \text{ cm}^{-3}$. The steady-state uptake coefficients $\gamma_{ss}$ of NO$_3$ range from $(1.4 \pm 0.4) \times 10^{-2}$ for CaCO$_3$ to $(6.5 \pm 1.1) \times 10^{-2}$ for Saharan Dust using the geometric surface area. At the lower concentration of $[\text{NO}_3] = (7.0 \pm 1.0) \times 10^{11} \text{ cm}^{-3}$ we found larger $\gamma_{ss}$ values ranging from $(3.4 \pm 1.6) \times 10^{-2}$ for natural limestone to $(0.12 \pm 0.08)$ for Saharan Dust compared to the experiments at higher $[\text{NO}_3]$. In Table 3.5 we also report the measured $\gamma_0$ values for NO$_3$ on all the samples of mineral dust at low and high values of $[\text{NO}_3]$. For the low value of $[\text{NO}_3] = (7.0 \pm 1.0) \times 10^{11} \text{ cm}^{-3}$ the $\gamma_0$ values range from $0.12 \pm 0.08$ for Kaolinite to $0.23 \pm 0.2$ for Saharan Dust. At the high value of $[\text{NO}_3] = (4.0 \pm 1.0) \times 10^{12} \text{ cm}^{-3}$ the $\gamma_0$ values range from $0.12 \pm 0.04$ for Kaolinite to $0.2 \pm 0.07$ for natural limestone. In comparison, $\gamma_{ss}$ is lower only by a factor of two relative to $\gamma_0$ obtained at the same experimental conditions of low $[\text{NO}_3]$. Table 3.5 shows in general that the values of $\gamma_{ss}$ and $\gamma_0$ are larger for low compared to high values of $[\text{NO}_3]$ which we attribute to partial inhibition of adsorption sites for NO$_3$. We take the small difference between $\gamma_0$ and $\gamma_{ss}$ at both values of $[\text{NO}_3]$ as an additional confirmation for the absence of pore diffusion because $\gamma_0$ should only be minimally affected by pore diffusion and is expected to come close to the true value of the initial uptake coefficient. From Table 3.5 we may conclude that the uptake of NO$_3$ on mineral dust measured at low $[\text{NO}_3]$ is rapid. We propose to take the evidence of the high reactivity of NO$_3$ and the fact that diffusion of NO$_3$ into a porous material, such as molecular sieves, is immeasurably slow at our experimental conditions as an argument to convince the reader of the non-applicability of pore diffusion in the present case$^{21}$. 
Figure 3.6. NO$_3$ on Kaolinite: uptake coefficient $\gamma_{ss}$ of NO$_3$ as a function of [NO$_3$] ($A_s = 19.6$ cm$^2$).

Full circles and squares represent the experimental uptake values obtained at 4 and 8 mm orifice diameter, respectively.

<table>
<thead>
<tr>
<th>[NO$_3$] cm$^{-3}$</th>
<th>$\gamma_{ss}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^a$ 5.0 x 10$^{11}$</td>
<td>(1.7 ± 0.4) x 10$^{-1}$</td>
</tr>
<tr>
<td>$^a$ 6.8 x 10$^{11}$</td>
<td>(1.3 ± 0.3) x 10$^{-1}$</td>
</tr>
<tr>
<td>$^a$ 9.6 x 10$^{11}$</td>
<td>(1.4 ± 0.4) x 10$^{-1}$</td>
</tr>
<tr>
<td>$^a$ 1.1 x 10$^{12}$</td>
<td>(8.9 ± 2.3) x 10$^{-2}$</td>
</tr>
<tr>
<td>$^a$ 1.2 x 10$^{12}$</td>
<td>(1.5 ± 0.4) x 10$^{-1}$</td>
</tr>
<tr>
<td>$^a$ 1.5 x 10$^{12}$</td>
<td>(7.0 ± 1.8) x 10$^{-2}$</td>
</tr>
<tr>
<td>$^a$ 1.8 x 10$^{12}$</td>
<td>(3.5 ± 1.1) x 10$^{-2}$</td>
</tr>
<tr>
<td>$^b$ 3.5 x 10$^{12}$</td>
<td>(2.2 ± 1.3) x 10$^{-2}$</td>
</tr>
<tr>
<td>$^b$ 3.9 x 10$^{12}$</td>
<td>(3.3 ± 2.0) x 10$^{-2}$</td>
</tr>
<tr>
<td>$^a$ 4.4 x 10$^{12}$</td>
<td>(5.0 ± 1.6) x 10$^{-2}$</td>
</tr>
<tr>
<td>$^a$ 4.5 x 10$^{12}$</td>
<td>(5.0 ± 1.6) x 10$^{-2}$</td>
</tr>
<tr>
<td>$^b$ 5.5 x 10$^{12}$</td>
<td>(1.4 ± 1.5) x 10$^{-2}$</td>
</tr>
<tr>
<td>$^b$ 7.3 x 10$^{12}$</td>
<td>(3.0 ± 0.9) x 10$^{-3}$</td>
</tr>
<tr>
<td>$^b$ 9.3 x 10$^{12}$</td>
<td>(2.0 ± 1.0) x 10$^{-2}$</td>
</tr>
</tbody>
</table>

Experiments performed using an escape orifice diameter of: $^a$ 8 mm, $^b$ 4 mm.

Table 3.6. Uptake experiments of NO$_3$ on 1g of Kaolinite: steady state ($\gamma_{ss}$) uptake coefficients ($A_s = 19.6$ cm$^2$).
As already pointed out above, $\gamma_0$ is similar for all samples. However, this is not the case for $\gamma_{ss}$ which reflects the different saturation behavior of the mineral dust samples which is also the reason for the increasing difference between $\gamma_0$ and $\gamma_{ss}$ with increasing [NO$_3$].

Several uptake experiments of NO$_3$ on 1g of Kaolinite powder were carried out at different [NO$_3$] (Table 3.6).

Figure 3.6 displays data for the 8 and 4 mm escape orifice corresponding to a residence time $\tau_g$ of 0.57 s and 2.1 s, respectively, for a variation of [NO$_3$] between $5.5 \times 10^{11}$ and $9.3 \times 10^{12}$ cm$^{-3}$. We observe two limiting values of $\gamma_{ss}$: a) for [NO$_3$] increasing from $5.5 \times 10^{11}$ cm$^{-3}$ to $1.8 \times 10^{12}$ cm$^{-3}$ $\gamma_{ss}$ decreases from $(1.7 \pm 0.4) \times 10^{-1}$ to $(3.5 \pm 1.1) \times 10^{-2}$,

b) for [NO$_3$] between $1.8 \times 10^{12}$ cm$^{-3}$ and $9.3 \times 10^{12}$ cm$^{-3}$ $\gamma_{ss}$ is constant at $(3.2 \pm 1.4) \times 10^{-2}$ within experimental uncertainty and independent of [NO$_3$]. From this series of measurements it is evident that $\gamma_{ss}$ follows a rate law pseudo first order in NO$_3$ at [NO$_3$] > $1.8 \times 10^{12}$ cm$^{-3}$. Conversely, at [NO$_3$] < $1.8 \times 10^{12}$ cm$^{-3}$ the inverse dependence of $\gamma_{ss}$ on [NO$_3$] suggests that the mechanism of NO$_3$ uptake is complex and does not correspond to simple first-order uptake.

A similar dependence has been observed before by Hanisch and Crowley$^{23}$ in their work on ozone decomposition on Saharan dust and by Sullivan and coworkers$^{24}$ in their study of ozone decomposition on fresh alumina films. The reason for this behaviour may be related to the finite number of available surface sites of the substrate that are not completely saturated at low [NO$_3$] resulting therefore in a larger uptake coefficient compared to high [NO$_3$]. It is the interplay between the finite number of adsorption sites and the competitive rates of desorption and surface reaction of NO$_3$ that leads to this typical inhibition behaviour that was also observed for other free radicals interacting with a solid substrate, so for example for NO$_2$ interacting with soot$^{25}$.

Further experiments performed on natural limestone and CaCO$_3$ showed a strong dependence of $\gamma_{ss}$ on the gas residence time at [NO$_3$] = $2.3 \times 10^{12}$ cm$^{-3}$ suggesting that the mechanism of NO$_3$ uptake is complex and does not correspond to a simple first order uptake reaction as already pointed out for Kaolinite. The $\gamma_{ss}$ value decreased from $(5.1 \pm 2.0) \times 10^{-2}$ to $(2.7 \pm 1.1) \times 10^{-2}$ in going from $\tau_g = (1/k_{esc}) = 0.24$ s ($k_{esc} = 4.15$ s$^{-1}$) to $\tau_g = 1.85$ s ($k_{esc} = 0.54$ s$^{-1}$). These observations indicate that the reactivity of NO$_3$ on natural limestone and CaCO$_3$ decreases for long gas residence times $\tau_g$ as the heterogeneous reaction rate not only depends on the gas phase concentration but apparently
also on intermediates whose surface concentration depend on the extent of reaction that scales with $\tau_g$.

### 3.4 Reaction products

In all experiments adsorbed NO$_3$ gave rise to uptake of NO$_2$ that is associated with the NO$_3$ source. It is important to note that NO$_2$ itself did not show any uptake on the mineral dust surrogates, except for Saharan Dust, where $\gamma_{ss} = (3.1 \pm 0.5) \times 10^{-3}$ has been observed for pure NO$_2$ uptake. For 250 mg of Kaolinite we have observed the formation of small amounts of gas phase reaction products such as N$_2$O$_5$ and HNO$_3$. Using equation (3.E5) we have calculated the rate of formation of N$_2$O$_5$ from the increase of the MS signal at m/e 46, $I_{46}^{exe}$, displayed in Figure 3.7 (curve (c)). From the experiment displayed in Figure 3.7 we conclude that for an initial value of $[\text{NO}_3] = (6.5 \pm 1.0) \times 10^{11}$ cm$^{-3}$ and in the presence of $[\text{NO}_2] = (1.2 \pm 1.0) \times 10^{12}$ cm$^{-3}$ (8.8 $\pm$ 2.0) $\times$ 10$^{11}$ molecule cm$^{-3}$ of N$_2$O$_5$ are produced at steady state conditions. The yield of N$_2$O$_5$ following the uptake of NO$_3$ decreased with increasing saturation of Kaolinite which may be explained by the slow deactivation of reactive surface sites and by the complete saturation of the NO$_3$ uptake at the end of the exposure time after the adsorption of 9.5 $\times$ 10$^{17}$ NO$_3$ molecules (Figure 3.7 (curve b)). For the NO$_3$ uptake on 250 mg of Kaolinite we also observed a small contribution of m/e 63, $I_{63}^{exe}$, related to the production of gas phase HNO$_3$ as displayed in Figure 3.7 (curve (d)). At these experimental conditions this corresponds to the production of $(1.2 \pm 1.5) \times 10^{10}$ molecule cm$^{-3}$ of HNO$_3$ at steady state.

As pointed out above, NO$_3$ may be represented by a 4.5 Å diameter sphere with a projected surface area of $1.59 \times 10^{15}$ cm$^2$/molecule which leads to a full surface coverage of $6.3 \times 10^{14}$ molecules cm$^{-2}$. The 250 mg sample has a total surface area of $5.5 \times 10^4$ cm$^2$ based on a BET surface area of 22 m$^2$/g for Kaolinite. This leads to $1.3 \times 10^{16}$ and $3.5 \times 10^{19}$ NO$_3$ forming a monolayer on 250 mg Kaolinite based on the geometric and BET surface area, respectively.
Figure 3.7. Uptake of NO$_3$ on 250 mg of Kaolinite and resulting reaction products at [NO$_3$] = (6.5 ± 1.0) x 10$^{11}$ molecule cm$^{-3}$. Curve (a) represents the raw MS signal at m/e 62 for the NO$_3$ uptake on the DELRIN® sample holder with Kaolinite, the dashed line (curve (b)) indicates $I^{62(NO_3)}_r$ of the NO$_3$ uptake corrected for the DELRIN® contribution. Curve (c) is the calculated MS signal at m/e 46, $I^{46}_{exc}$, corresponding to N$_2$O$_5$ formation. The variable amplitude of curve (c) is the consequence of the large experimental uncertainty. Curve (d) represents the raw MS signal at m/e 63, $I^{63(HNO_3)}_r$, related to the production of gas phase HNO$_3$ (orifice diameter = 8 mm, $A_s = 4.9$ cm$^2$).

The total number of $9.5 \times 10^{17}$ molecules of NO$_3$ taken up on 250 mg of Kaolinite leads to a surface concentration of $\frac{9.5\times10^{17}}{5.5\times10^4} = 1.72\times10^{13}$ molecule cm$^{-2}$ which corresponds to a coverage ($\theta$) of approximately 2.7 % based on the BET surface area.

Next to Kaolinite, samples of 250 mg of CaCO$_3$ have been the only samples to show formation of N$_2$O$_5$ and HNO$_3$ upon uptake of NO$_3$ (see Table 3.7). When the samples begin to saturate, the observed amounts of N$_2$O$_5$ and HNO$_3$ both decrease. In order to understand the reason for the gas phase production of N$_2$O$_5$ and HNO$_3$ we have to remind the reader that all the investigated samples have a non negligible amount of adsorbed water available on the substrate surface. The significant quantity of adsorbed H$_2$O$_{(ads)}$ that still remains on the different mineral dust substrates at our experimental conditions is reported in Table 3.7 and was measured by gravimetric measurements. Adsorbed water may therefore play an important role for the uptake of NO$_3$ on all samples examined in the Knudsen reactor.

Under our experimental conditions the formation of N$_2$O$_5$ may be related to the presence of NO$_2$ effusing from the NO$_3$ source via its reaction with adsorbed NO$_3$ on the mineral dust
substrate. The observed simultaneous uptake for both NO$_3$ and NO$_2$ suggests the formation of N$_2$O$_5$(ads) through the heterogeneous recombination reaction (3.5a):

$$\text{NO}_3\text{(ads)} + \text{NO}_2 \rightarrow \text{N}_2\text{O}_5\text{(ads)} \quad (3.5a)$$

The conversion of NO$_3$ to N$_2$O$_5$ occurs via an Eley-Rideal mechanism where NO$_3$ first adsorbs onto the dust surface as NO$_3$(ads) and subsequently reacts with gas phase NO$_2$. This reaction is the interfacial analogue of the well known gas-phase equilibrium:

$$\text{NO}_2 + \text{NO}_3 + \text{M} \rightleftharpoons \text{N}_2\text{O}_5 + \text{M} \quad (3.5b)$$

whose equilibrium constant is known from recent work$^{26}$. Once N$_2$O$_5$ has been adsorbed, it may desorb into the gas phase:

$$\text{N}_2\text{O}_5\text{(ads)} \rightarrow \text{N}_2\text{O}_5\text{(g)} \quad (3.5c)$$
### Table 3.7 Summary of reaction products during the heterogeneous reaction of NO₃ on 250 mg and 1 g of mineral dust surrogate samples at an orifice diameter of 8mm.

<table>
<thead>
<tr>
<th>Mineral Dust Sample</th>
<th>(^a\gamma_0)</th>
<th>Reaction Products (250 mg)</th>
<th>(^b\gamma_{ss})</th>
<th>Reaction Products (1g)</th>
<th>Adsorbed water</th>
<th>BET surface area (m² g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO₃</td>
<td>(7.9 ± 2.0) x 10⁻²</td>
<td>12% 15%</td>
<td>(1.4 ± 0.8) x 10⁻²</td>
<td>- 17%</td>
<td>4</td>
<td>5.06</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>(2.1 ± 0.5) x 10⁻²</td>
<td>23% 16%</td>
<td>(5.0 ± 1.5) x 10⁻²</td>
<td>- 15%</td>
<td>23</td>
<td>22.57</td>
</tr>
<tr>
<td>Arizona Test Dust</td>
<td>-</td>
<td>-</td>
<td>(2.5 ± 1.0) x 10⁻²</td>
<td>- 20%</td>
<td>-</td>
<td>22</td>
</tr>
<tr>
<td>Saharan Dust</td>
<td>-</td>
<td>-</td>
<td>(6.5 ± 2.0) x 10⁻²</td>
<td>-</td>
<td>20</td>
<td>39.6</td>
</tr>
<tr>
<td>Natural Limestone</td>
<td>-</td>
<td>-</td>
<td>(1.2 ± 0.4) x 10⁻²</td>
<td>- 35%</td>
<td>-</td>
<td>7</td>
</tr>
</tbody>
</table>

\(^a\) Uptake experiment performed at \([\text{NO}_3])_0 = (7.0 ± 1.0) \times 10^{11} \text{ cm}^{-3}\) on 250 mg of sample. \(^b\) Uptake experiment performed at \([\text{NO}_3])_0 = (2.3 ± 1.0) \times 10^{12} \text{ cm}^{-3}\) on 1 g of sample. \(^c\) Saturated sample (250 mg, \(A_s = 4.9 \text{ cm}^2\)). \(^d\) Non-saturated sample (1 g, \(A_s = 19.6 \text{ cm}^2\)). The yield of \(\text{N}_2\text{O}_5\) and \(\text{HNO}_3\) is given as a percentage with respect to the total number of molecules of NO₃ taken up during the same reaction time. Dash (-) indicates a negative result of the experiment.
On the other hand, \( \text{N}_2\text{O}_5(\text{ads}) \) may react with adsorbed water \( \text{H}_2\text{O}(\text{ads}) \) and form gas phase \( \text{HNO}_3 \), part of which may desorb into the gas phase, according to reaction (3.5d):

\[
\text{N}_2\text{O}_5(\text{ads}) + \text{H}_2\text{O}(\text{ads}) \rightarrow 2\text{HNO}_3(\text{g}) \quad (3.5d)
\]

Additional NO\(_3\) uptake experiments have been performed on all mineral dust samples at \([\text{NO}_3] = 2.3 \times 10^{12} \text{ cm}^{-3}\) on 1.0 g of powder (see Table 3.7). Under these conditions we did not succeed in saturating the substrates at practical reaction times as they are apparently able to adsorb large amounts of NO\(_3\). NO\(_3\) uptake gave rise to gas phase HNO\(_3\) formation for CaCO\(_3\), Kaolinite, Arizona Test Dust and natural limestone without any visible trace of desorbing N\(_2\)O\(_5\) from the surface. Figure 3.8 displays raw data of an uptake experiment of NO\(_3\) on 2 g of natural limestone showing the production of gas phase HNO\(_3\) at a yield of 35% with respect to NO\(_3\) taken up on the substrate.

![Figure 3.8. NO\(_3\) uptake on a sample of 2g of natural limestone at \([\text{NO}_3] = (7.0 \pm 1.0) \times 10^{11} \text{ cm}^{-3}\). Curves (a), (b), (d) and (e) correspond to the raw MS signals monitored at m/e 30, 46, 62 and 63 respectively. Curve (c) corresponds to the raw REMPI signal for NO\(_2\) detection at \( \lambda_{\text{NO}_2} = 511 \text{ nm} \) converted to a MS signal at m/e 46 (orifice diameter = 8 mm, \( A_s = 19.6 \text{ cm}^2 \)).](image-url)

Of note is the fact that a small impurity of 0.5 % and 0.3 % of Al\(_2\)O\(_3\) and Fe\(_2\)O\(_3\), respectively, in natural limestone of 97 % (by weight) CaCO\(_3\) has a significant effect on
the formation of HNO₃ as displayed in Table 3.7. The fact that we did not observe gas
phase formation of N₂O₅ upon uptake of NO₃ on samples of 1g, where large quantities of
adsorbed water are present as displayed in Table 3.7, suggests that reaction (3.5d) may be
faster than reaction (3.5c).

In order to probe for the presence of an adsorbed reactive species on the substrate during
NO₃ uptake, experiments using NO and NO₂ were performed on all the examined
substrates immediately after the uptake of known quantities of NO₃. The goal has been to
determine whether or not the adsorbed NO₃ is able to react with NO or NO₂. On 1g of
Arizona Test Dust, uptake of NO on adsorbed NO₃ produced a small amount of NO₂
which has been observed using REMPI at $\lambda_{\text{NO}_2} = 511$ nm (Figure 3.9). On the time scale
of this experiment of approximately 300 s, $1.3 \times 10^{18}$ molecules of NO₃ have been
adsorbed on the substrate. The reaction with an excess of NO in the absence of gas phase
NO₃ during 230 s resulted in a production of $3.2 \times 10^{17}$ molecules of NO₂ which
corresponds to a 12.3% retrieval of adsorbed NO₃. The observed reaction may be viewed
as a titration reaction at the surface of the substrate according to reaction (3.6)²⁷,²⁸:

$$\text{NO} + \text{NO}_3^{\text{(ads)}} \rightarrow 2\text{NO}_2$$  \hspace{1cm} (3.6)

![Figure 3.9. Uptake of NO₃ on Arizona Test Dust ($F_{\text{NO}_2} = 8.0 \times 10^{15} \text{ cm}^3$, escape orifice of
8 mm, $A_s = 19.6 \text{ cm}^2$), curve (a). Curve (b) corresponds to the flow of generated NO₂ following
the reaction with excess NO on the substrate in the absence of gas phase NO₃. The flow of NO₂
has been monitored by the REMPI signal at $\lambda_{\text{NO}_2} = 511$ nm.](image-url)
On Saharan Dust that has previously been exposed to NO$_3$ and NO$_2$ we have observed uptake of NO but no visible trace of gas phase NO$_2$. As discussed above, NO$_2$ shows an uptake on virgin Saharan Dust samples. On exposed CaCO$_3$ and natural limestone samples, however, no NO uptake has been observed, and as a consequence no NO$_2$ gas phase formation. An additional experiment was carried out on 1g of Saharan Dust where NO$_2$ was used as a probe for adsorbed NO$_3$. On 1g of Saharan Dust, uptake of NO$_2$ on adsorbed NO$_3$ produced a small amount of excess NO$_2$ which has been observed using REMPI at \( \lambda_{NO_2} = 511 \) nm (Figure 3.10). On the time scale of this experiment of approximately 400 s, \( 8.0 \times 10^{17} \) molecules of NO$_3$ have been adsorbed on 1g of Saharan Dust. The reaction with an excess of NO$_2$ in the absence of gas phase NO$_3$ during 100 s resulted in a production of \( 1.8 \times 10^{17} \) molecules of NO$_2$ as displayed by the increase in the NO$_2$ signal in Figure 3.10. The observed reaction may be represented by the following reaction (3.7):

\[
NO_2 + NO_3(ads) \rightarrow 2NO_2 + \frac{1}{2}O_2 \quad \Delta H^0_{(gas)} = -9.1 \text{ kcal/mol} \quad (3.7)
\]

Figure 3.10. Uptake of NO$_3$ on Saharan Dust (\( F_{NO_3} = 1.7 \times 10^{16} \) cm$^{-3}$, escape orifice of 8 mm, \( A_s = 19.6 \) cm$^2$), curve (a). Curve (b) corresponds to the flow of generated NO$_2$ following the reaction with excess NO$_2$ on the substrate in the absence of gas phase NO$_3$. The flow of NO$_2$ has been monitored by the REMPI signal at \( \lambda_{NO_2} = 511 \) nm.
The observed NO₂ production corresponds to 22.5 % of adsorbed NO₃. In this case we did not observe any NO production using REMPI detection at $\lambda_{NO} = 452.6$ nm which is probably related to the fact that NO, if formed, may rapidly react with adsorbed NO₃ as discussed above.

For all the mineral dust substrates studied, the uptake of NO₃ on mineral dust was irreversible, at least on timescales used in this work. This was checked in experiments such as NO₃ uptake on Kaolinite where after approximately 7 minutes of exposure, the sample was isolated and the NO₃ flow subsequently turned off. When the isolation plunger was lifted again, no release of NO₃ was observed at m/e 62. Free radical adsorption on solid polar surfaces are known from the literature. For example, recent work has shown the adsorption of CH₃O₂ free radical on KCl surfaces and effective bimolecular reactions with NO₂ and organic molecules whose kinetic parameters revealed a heterogeneous mechanism²⁹.

In summary, we must clearly point out that the uptake of NO₃ on mineral dust is not in any way catalytic in nature. This conclusion is supported by the formation of volatile reaction products such as N₂O₅ and HNO₃ (Table 3.7) as well as by the complete eventual saturation of the NO₃ uptake on small mass samples of mineral dust as displayed in Figure 3.7. The chemical turnover or reaction rate of NO₃ is accompanied by the slow irreversible build-up of non-volatile reaction products leading to the final inhibition or saturation of NO₃ uptake.

3.5 Conclusions and atmospheric implications

We have shown in this work that NO₃ undergoes fast heterogeneous reactions with surrogate substrates of mineral dust aerosol at $T = 298 \pm 2$ K. Ancillary uptake experiments performed with NO₃ on molecular sieve aluminosilicate particles of different nominal pore diameter have led to the conclusion that the pore diffusion correction is not appropriate for the present experimental conditions of relativity short contact times. Therefore, the geometric surface area of the dust sample has been used for the calculation of $\gamma_0$ and $\gamma_{ss}$. The measured uptake coefficient showed different values for high and low [NO₃]. At $[NO₃] = (4.0 \pm 1.0) \times 10^{12}$ cm$^{-3}$ $\gamma_{ss}$ ranged from $(1.4 \pm 0.4) \times 10^{-2}$ for CaCO₃ to
(6.5 ± 1.1) x 10^{-2} for Saharan Dust. At [NO_3] = (7.0 ± 1.0) x 10^{11} \text{ cm}^{-3}, \gamma_{ss} ranged from (3.4 ± 1.6) x 10^{-2} for natural limestone to (0.12 ± 0.08) for Saharan Dust. These values are significantly larger than the ones used in a recent global modeling simulation of heterogeneous chemistry on mineral dust aerosol\textsuperscript{17}, where a $\gamma$ value of $3.0 \times 10^{-3}$ for NO$_3$ has been used. However, the modeling study performed by Bian and Zender\textsuperscript{16} used a $\gamma$ value of 0.1 for NO$_3$. This value is in agreement with the one we obtained by extrapolation of $\gamma$ to vanishing NO$_3$ concentration from our uptake experiments performed on Kaolinite as displayed in Figure 3.6. We therefore have extrapolated the value of $\gamma_{ss}$ for $[\text{NO}_3] < 5.0 \times 10^{11}$ \text{ molecule cm}^{-3}. With tropospheric $[\text{NO}_3]$ at a typical value of $2.0 \times 10^9$ \text{ molecule cm}^{-3}, $\gamma_{ss}$ tends towards values larger than $0.2 \pm 0.03$ according to the results displayed in Figure 3.6.

The present experimental results of $\gamma$ for NO$_3$ seem to be more in agreement with the guess of Bian and Zender\textsuperscript{16} compared to Bauer et al.\textsuperscript{17} and suggests a significant removal of NO$_3$ in areas affected by mineral dust close to ground. This leads to a decrease of the oxidation potential of the atmosphere at night by virtue of the removal of NO$_3$ and the decrease of O$_3$ observed in all model results, albeit to a variable extent. However, the NO$_3$ removal also affects the abundance of HNO$_3$ because the nighttime sources are the heterogeneous hydrolysis of N$_2$O$_5$ and to a minor extent, the reaction of NO$_3$ with HO$_2$, both of which directly depend on NO$_3$\textsuperscript{17}. It is therefore of some importance to obtain reliable values for the kinetics of key free radicals that control in part important precursors such as HNO$_3$ and N$_2$O$_5$.

The specific comparison of the results of Bauer et al.\textsuperscript{17} and Bian and Zender\textsuperscript{16} highlights the importance of key free radicals such as NO$_3$. The latter attribute a large reactivity to NO$_3$ and a small one to HNO$_3$, and vice versa for the former. However, the resulting trend in both models is the same, namely the decrease of O$_3$ through the reactive process of the ozone precursor NO$_3$ or HNO$_3$. The conclusion is that the resulting effect on the traces gas composition is insensitive to the detailed allocation of heterogeneous reactivity, provided the species in question are chemically coupled as for NO$_3$ and HNO$_3$. In summary, this work delivers several messages of potential importance to atmospheric chemistry: a) The uptake coefficient of NO$_3$ on mineral dust aerosol under tropospheric conditions is larger than 0.1 for a selection of surrogate mineral dust materials and does not seem to be affected by the presence of NO$_2$; b) in contrast to the uptake kinetics the observed reaction products HNO$_3$ and N$_2$O$_5$ seem to depend on the presence of NO$_2$ and on the quantity of the available adsorbed H$_2$O; c) a significant part of NO$_3$ that is
disappearing from the gas phase seems to retain its reactivity in the adsorbed state as shown in experiments with NO\textsubscript{2} and NO; d) the uptake of NO\textsubscript{3} on mineral dust is non-catalytic. Despite the open nitrogen mass balance a significant fraction of adsorbed NO\textsubscript{3} is expected to be released as volatile HNO\textsubscript{3} and N\textsubscript{2}O\textsubscript{5} on mineral dust aerosol which is in fact observed in laboratory experiments.

Water is expected to play an important role because of the hydrolysis of N\textsubscript{2}O\textsubscript{5}, even under the present experimental (dry) conditions. Despite our inability to perform experiments at elevated humidity using the Knudsen flow reactor, we believe that H\textsubscript{2}O cannot substantially alter the uptake kinetics of NO\textsubscript{3}. Our laboratory observations also indicate that the reactivity of NO\textsubscript{3} on mineral dust aerosols decreases for long gas residence times $\tau_g$ as the heterogeneous reaction rate not only depends on the gas phase concentration but also on intermediates whose concentration depend on the extent of reaction. Despite the presence of NO\textsubscript{2} this work indicates that interaction with mineral dust may be an important loss process for tropospheric NO\textsubscript{3} whose quantitative consequences will have to be assessed by modeling studies. Therefore, the uptake of NO\textsubscript{3} on mineral dust aerosols may have a much greater influence on the reduction of O\textsubscript{3} as compared to the estimated value of 0.4% of global ozone reduction\textsuperscript{17} for $\gamma_{NO_3} = 3.0 \times 10^{-3}$. The NO\textsubscript{3} loss rate constant ($k_{het}$) due to heterogeneous uptake onto aerosol is given by $k_{het} = \tau^{-1}(NO_3) = \gamma A \bar{v}/4$ where $\gamma$ is the uptake coefficient of NO\textsubscript{3} and is a function of the mineral dust aerosol composition; $A$ is the surface area density of the dust and $\bar{v}$ is the mean molecular speed of NO\textsubscript{3}. Assuming a surface area density of $A = 1.5 \times 10^6$ cm\textsuperscript{2} cm\textsuperscript{-3} for a dust plume\textsuperscript{30} and $\gamma = 0.2$ from our extrapolated value for NO\textsubscript{3} we evaluated a lifetime of 7 min for NO\textsubscript{3}. This value has to be compared to the diurnal photolysis of NO\textsubscript{3}. During the day, NO\textsubscript{3} has a very short lifetime (about 5s) due to its strong absorption in the visible region (662 nm) and its rapid photodissociation, mainly to NO\textsubscript{2} according to NO\textsubscript{3} + hv $\rightarrow$ NO\textsubscript{2} + O(\textsuperscript{3}P). Since this photochemical gas-phase loss process takes place only during the day, NO\textsubscript{3} loss by reaction on dust is important only during the night. Heterogeneous nighttime removal of NO\textsubscript{3} by mineral dust and formation of gas-phase HNO\textsubscript{3} after reacting with gas-phase NO\textsubscript{2} could change the NO\textsubscript{3}/NO\textsubscript{2} ratio during the night and in the presence of dust plumes\textsuperscript{4}. 
3.6 References


3. The heterogeneous chemical kinetics of NO₃ on atmospheric mineral dust surrogates


(18) Seisel, S.; Fluckiger, B.; Caloz, F.; Rossi, M. J.: Heterogeneous reactivity of the nitrate radical: reactions on halogen salt at ambient temperature and on ice in the presence of HX (X = Cl, Br, I) at 190 K, Physical Chemistry Chemical Physics, 1, 2257-2266, (1999).


3. The heterogeneous chemical kinetics of NO$_3$ on atmospheric mineral dust surrogates
3. The heterogeneous chemical kinetics of NO$_3$ on atmospheric mineral dust surrogates
CHAPTER 4

THE HETEROGENEOUS CHEMICAL KINETICS OF N₂O₅ ON CaCO₃ AND OTHER ATMOSPHERIC MINERAL DUST SURROGATES

4.1 Introduction

Dinitrogen pentoxide, N₂O₅, is part of the family of active nitrogen, NOₓ, owing to its equilibrium with NO₂ and NO₃ according to reaction (4.1), which releases photochemically active NO₃ and NO₂ free radicals.

\[ \text{N}_2\text{O}_5 \leftrightarrow \text{NO}_2 + \text{NO}_3 \]  (4.1)

Under atmospheric pressure and 298 K the thermal lifetime of N₂O₅ is approximately 20 s and is a strong function of temperature\(^1\)\(^2\). The observation of the build up of the concentration of nitric acid, HNO₃, in the polluted urban PBL during the night could only be explained by the heterogeneous conversion of N₂O₅ to HNO₃ according to reaction (4.2)\(^3\)^\(^4\)

\[ \text{N}_2\text{O}_5 + \text{H}_2\text{O}_{(ads)} \rightarrow 2\text{HNO}_3 \]  (4.2)

The substrate for the heterogeneous reaction (4.2) has not been unambiguously identified but is thought to be urban H₂O-containing aerosols or humid surfaces on the ground whose purpose is to make available adsorbed H₂O in order to enable reaction (4.2).
Together with HNO3 and NO3, N2O5 contributes to the formation of particulate nitrate on the dust particles by surface processes in the troposphere. These processes represent an important sink for nitrogen oxide species, with decreases of daytime NOy levels reaching up to 60% in the presence of dust at a loading of about 1.8-11.5 μg m⁻³ corresponding to a particle surface area of (0.11-0.7) x 10⁻⁶ cm² cm⁻³. During the nighttime, the gas-to-particle conversions of NO3 and N2O5 dominates the overall nitrate formation accounting for 80% of total particulate nitrate formation, while the heterogeneous hydrolysis of N2O5 leading to HNO3 accounts for only about 20%.

Dentener showed how the interaction of N2O5, O₃ and HO₂ radicals with mineral dust affects the photochemical oxidant cycle, with ozone concentrations decreasing by up to 10% in and nearby the dust source areas. In the modelling simulation performed by Bauer et al. the uptake of N₂O₅ resulted in a reduction of 11% of its mass in the gas phase whereas the simulations of Bian and Zender indicate a global reduction of 2% of N₂O₅ using an uptake coefficient \( \gamma_{N_2O_5} = 10^{-3} \) at a relatively humidity (rh) of 30%.

Despite the published results of field observations and modeling studies, there is only a single laboratory study that deals with the heterogeneous reactivity of N₂O₅ on mineral dust aerosol surrogates, namely the interaction of N₂O₅ on Saharan Dust using a combination of Knudsen reactor and DRIFTS (Diffuse Reflectance Infrared Transmission Spectroscopy).

4.2 Experimental setup and detection

All experiments were performed in the TEFLON® coated Knudsen flow reactor operating in the molecular flow regime. The characteristic parameters and relevant kinetic expressions for steady state and pulsed experiments are reported in Chapter 2 as well as the synthesis of N₂O₅. The mineral dust composition used in this study is reported in Table 3.1. The two kinds of sample holders, TEFLON® coated Pyrex of 19.6 cm² of available sample surface and the internal reduction piece made out of DELRIN® of available surface area of 4.9 cm², did not show any reactivity with N₂O₅ under the present experimental conditions.
Hydrolysis of N$_2$O$_5$ may occur on surfaces of the traps and of the inlet line before admission into the Knudsen flow reactor generating HNO$_3$ as an impurity ranging from 10 to 15% as studied by MS at m/e 63, its molecular ion peak. N$_2$O$_5$ does not have a measurable parent and fragment peak at m/e 108 and 62, respectively, under the present experimental conditions; the most intense peaks are its fragment NO$_2^+$ at m/e 46 followed by the less intense fragment NO$^+$ at m/e 30. However, the HNO$_3$ impurity also contributes to the MS signal at m/e 46 and 30. Under the experimental conditions used HNO$_3$ has a detectable parent peak at m/e 63.

In the following, the subscript 0 and r will refer to continuous gas uptake experiments in the absence and presence, respectively, of the solid sample.

Through a calibrated mass spectrum of pure HNO$_3$ we have accurately determined the effective contribution of HNO$_3$ at m/e 46 and 30 by using the fragmentation pattern expressed as the ratios $f_{46} = \frac{I_{0}^{46(HNO_3)}}{I_{0}^{63(HNO_3)}} = 52 \pm 8$ and $f_{30} = \frac{I_{0}^{30(HNO_3)}}{I_{0}^{63(HNO_3)}} = 33 \pm 4$. In the absence of a substrate, $f_{46} \cdot I_{0}^{63(HNO_3)}$ and $f_{30} \cdot I_{0}^{63(HNO_3)}$ have been subtracted from the total MS signals $I_{0}^{46}$ and $I_{0}^{30}$ at m/e 46 and 30, respectively, in order to assign the remaining MS amplitude to the NO$_2^+$ and NO$^+$ fragments to N$_2$O$_5$: $I_{0}^{46(N_2O_5)} = I_{0}^{46} - f_{46} \cdot I_{0}^{63(HNO_3)}$ and $I_{0}^{30(N_2O_5)} = I_{0}^{30} - f_{30} \cdot I_{0}^{63(HNO_3)}$.

The ratio between the two most intense peaks of N$_2$O$_5$ therefore was $r = \frac{I_{0}^{46(N_2O_5)}}{I_{0}^{30(N_2O_5)}} = 1.4 \pm 0.2$. Mixtures of N$_2$O$_5$ and HNO$_3$ may thus be monitored using MS signal intensities at m/e 46, 30 and 63. However, in order to quantify N$_2$O$_5$ we chose its most intense peak corresponding to its fragment NO$_2^+$ at m/e 46.

### 4.3 Uptake coefficient of N$_2$O$_5$ and identity of reaction products

When N$_2$O$_5$ is exposed to the sample, it is taken up and undergoes a heterogeneous reaction on the mineral dust surface which results in a decrease of the N$_2$O$_5$ concentration that is monitored using the MS signal $I_{r}^{46(N_2O_5)}$. As shown in previous studies on mineral dust, HNO$_3$ that is always present as an impurity, is taken up on the mineral dust surface.
without releasing any product that may contribute to the total MS signal $I_r^{46}$ at m/e 46. We have therefore determined the rate constant $k_{obs}$ for the disappearance of N$_2$O$_5$ following equation (4.E1), assuming that the rate law is first order in N$_2$O$_5$:

$$k_{obs} = \left( \frac{I_0^{46(N_2O_5)}}{I_r^{46(N_2O_5)}} \right) \cdot k_{esc}$$  \hspace{1cm} (4.E1)

where $I_0^{46(N_2O_5)}$ and $I_r^{46(N_2O_5)}$ are the intensities of the NO$_2^+$ fragment of N$_2$O$_5$ before and during heterogeneous reaction, respectively, and $k_{esc}$ is the measured rate constant of effusion for N$_2$O$_5$ out of the flow reactor. In order to determine $I_r^{46(N_2O_5)}$, the raw MS signal at m/e 46 was corrected for HNO$_3$ generated through hydrolysis of N$_2$O$_5$ with water adsorbed on the substrate surface. Production of HNO$_3$ has in fact been observed at m/e 63 in every uptake experiment of N$_2$O$_5$. Figure 4.1 shows the raw MS signal at m/e 63 for a typical uptake experiment of N$_2$O$_5$ on CaCO$_3$. Therefore, we have corrected the MS signal of N$_2$O$_5$ at m/e 46 for the presence of HNO$_3$ according to equation (4.E2) when the sample is exposed to N$_2$O$_5$:

$$I_r^{46(N_2O_5)} = I_r^{46} - f \cdot I_r^{63(HNO_3)}$$ \hspace{1cm} (4.E2)

The ratio $r$, reported above, turned out to be the same before and during the exposure of the mineral dust sample to N$_2$O$_5$. Therefore, $I_r^{46(N_2O_5)}$ exclusively corresponds to N$_2$O$_5$ for this experiment after correction of the MS signal at m/e 46 for the contribution of HNO$_3$ desorbing from the mineral dust substrate.

The net observed uptake coefficient for N$_2$O$_5$, $\gamma_{obs}$, is given by expression (2.8). In our data analysis, $\gamma_{obs}$ was calculated using the geometric surface area of the sample holder as will be justified below. In the following, we evaluate $\gamma_{obs}$ at the initial and steady state values of the uptake rate leading to $\gamma_0$ and $\gamma_{ss}$, respectively.
4.4 Uptake of N$_2$O$_5$ on CaCO$_3$: Results and Discussion

Typical raw data from an uptake experiment of N$_2$O$_5$ on 510 mg of CaCO$_3$ are shown in Figure 4.1 using the 14 mm diameter-orifice. After a steady state flow of N$_2$O$_5$ has been established, the isolation plunger is lifted at $t = 92$ s and the substrate is thus exposed to the N$_2$O$_5$ flow. MS signals of 18 ($\text{H}_2\text{O}^+$), 30 ($\text{NO}^+$), 44 ($\text{CO}_2^+$), 46 ($\text{NO}_2^+$), and 63 ($\text{HNO}_3^+$) were simultaneously monitored during the uptake. Because of the uptake of N$_2$O$_5$ on CaCO$_3$, the number of molecules exiting through the escape orifice into the MS immediately decreases which leads to a decrease of the MS signal $I_t^{46(N_2O_5)}$ at m/e 46.

During the exposure of the sample to N$_2$O$_5$ both HNO$_3$ and CO$_2$ monitored at m/e 63 and 44, respectively, have been observed in the gas phase. As the exposure time increases, the MS signal at m/e 46 partially recovers, indicating a decrease in the rate of uptake that ultimately leads to steady state towards the end of the displayed uptake experiment. At $t = 1150$ s the sample compartment is sealed by lowering the plunger and the MS signal at m/e 46 approximately returns to its initial steady-state value. The slight decrease of $I_t^{46(N_2O_5)}$ over extended periods of time such as displayed if Figure 4.1 can be explained by a slight decrease of the corresponding flow rate into the reactor.

![Figure 4.1. Typical N$_2$O$_5$ uptake experiment on a sample of 510 mg of CaCO$_3$. Curves (a), (b), (c), (d) and (e) correspond to the raw MS signals monitored at m/e 46, m/e 30, m/e 44, m/e 63 and m/e 18, respectively, using an orifice diameter of 14 mm, $A_s = 19.6$ cm$^2$ and [N$_2$O$_5$]$_0 = (4.0 \pm 1.0) \times 10^{11}$ cm$^{-3}$.

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An ancillary experiment was performed in order to estimate the amount of water $H_2O_{(ads)}$ adsorbed on the CaCO$_3$ substrate surface after a given pumping time. In order to limit $H_2O$ desorbing from the Pyrex sample holder it was replaced by a gold-coated all-metal sample holder. In this way most desorbing $H_2O$ may be attributed to the mineral dust sample. Typically, a fresh sample of 1g of CaCO$_3$ was pumped for 30 minutes at $T = 298 \pm 2$ K in the 14 mm-orifice reactor until the MS signal of $H_2O$ at m/e 18 dropped to the background level. Subsequently, the CaCO$_3$ sample was heated up to 470 K and the MS signal at m/e 18 recorded until it reached background as well indicating that no additional water desorbed at that temperature. The MS signal at m/e 18 was integrated in order to calculate the number of adsorbed water molecules $H_2O_{(ads)}$ using the measured BET surface area of 5.06 m$^2$ g$^{-1}$ for CaCO$_3$. A value of approximately $3.0 \times 10^{13}$ molecule cm$^{-2}$ has been found for the surface density of strongly adsorbed $H_2O_{(ads)}$.

When the CaCO$_3$ substrate is exposed to N$_2$O$_5$ at 92 s, we observed rapid formation of $CO_2(g)$ and $H_2O(g)$ as displayed in Figure 4.1 which were either generated in a chemical reaction or desorbing from a precursor state. In order to better understand the uptake of N$_2$O$_5$ on solid CaCO$_3$ powder, we will briefly digress to the description of the chemical nature of a carbonate surface. From experimental and theoretical surface science studies, there is clear evidence that under ambient conditions of pressure, temperature, and relative humidity, the surface of CaCO$_3$ is terminated by OH groups that persist even under ultrahigh vacuum conditions. The OH-terminated surface may be a result of the dissociative adsorption of water according to reaction (4.3):

$$CaCO_3 + H_2O \rightarrow Ca(OH)(HCO_3)$$ \hspace{1cm} (4.3)

In a recent study$^{17}$, the surface chemistry of CaCO$_3$ with trace atmospheric gases such as HNO$_3$, SO$_2$, HCOOH, and CH$_3$COOH was investigated using FTIR absorption spectrometry. This study has pinpointed adsorbed carbonic acid $H_2CO_3$ to be involved in the surface chemistry of CaCO$_3$ and was identified as a stable intermediate species on the CaCO$_3$ surface in the presence of $H_2O$ vapor. The vibrational spectrum of carbonic acid is thought to be characterized by its C=O stretching frequency at 1685 and 1705 cm$^{-1}$.
corresponding to the adsorbed and condensed phase, respectively. In the following, adsorbed $\text{H}_2\text{CO}_3^-$ will occur as a proposed intermediate in several instances.

Dissolution of CaCO$_3$ in the system $\text{H}_2\text{O} - \text{CO}_2 - \text{CaCO}_3$ is controlled by three rate-determining processes: the kinetics of dissolution at the mineral surface, mass transport by diffusion, and the slow kinetics of formation of $\text{H}_2\text{CO}_3$ in reaction (4.4):

\[
\text{CO}_{2(g)} + \text{H}_2\text{O}_{(ads)} \rightleftharpoons \text{H}_2\text{CO}_3_{(ads)} \rightleftharpoons \text{H}^+_{(aq)} + \text{HCO}_3^-_{(aq)} \quad (4.4)
\]

A theoretical model by Buhmann and Dreybrodt\textsuperscript{18} taking these processes into account predicts that, due to the slow kinetics of formation of $\text{H}_2\text{CO}_3$ in reaction (4.4), precipitation rates on the surface of CaCO$_3$ minerals critically depend on the ratio $V/A$ of the volume $V$ of the solution to the surface area $A$ of the mineral in contact with it. They concluded that $\text{H}_2\text{CO}_3$ formation in reaction (4.4) is rate limiting\textsuperscript{19}.

Bicarbonate ion, $\text{HCO}_3^-$, may react with CaCO$_3$ to yield a surface intermediate that is proposed to be the active surface reactant for the heterogeneous reactions discussed below according to the well-known “Karst dissolution” mechanism of CaCO$_3$ by bicarbonate ion\textsuperscript{20}:

\[
\text{CaCO}_3_{(s)} + \text{H}^+_{(ads)} + \text{HCO}_3^-_{(ads)} \rightarrow \text{Ca(OH)}(\text{HCO}_3^-) + \text{CO}_{2(g)} \quad (4.5)
\]

When the CaCO$_3$ sample is exposed to N$_2$O$_5$ the surface intermediate may react as follows:

\[
\text{N}_2\text{O}_5_{(g)} + \text{Ca(OH)}(\text{HCO}_3^-) \rightarrow \text{Ca(NO}_3^-)_{2} + \text{H}_2\text{O}_{(s)} + \text{CO}_{2(g)} \quad (4.6)
\]

and the net reaction resulting from reaction (4.4), (4.5) and (4.6) will be:

\[
\text{N}_2\text{O}_5 + \text{CaCO}_3 \rightarrow \text{Ca(NO}_3^-)_{2} + \text{CO}_{2(g)} \quad (4.7)
\]

It is evident that $\text{H}_2\text{O}_{(g)}$ and $\text{CO}_2$ resulting from reaction (4.6) could be used again to generate additional Ca(OH)(HCO$_3$) according to reactions (4.4) and (4.5) provided
reaction (4.5) is fast enough under flow reaction conditions. In this way H₂O is neither consumed nor generated and may therefore be viewed as a catalytic species. However, we leave evidence that equations (4.4) and (4.5) do not take place under flow reactor conditions.

On the time scale of the uptake experiments reported in Figure 4.1 the calculated ratio CO₂/N₂O₅ of the product yields was 0.42 which is significantly smaller than 1.0 that is stoichiometrically expected according to reaction (4.7) (see Table 4.1). The mass balance between the adsorbed N₂O₅ and the reaction product CO₂ is therefore not closed. If reactions (4.4) and (4.5) were fast and not rate limiting, the CO₂ yield could be 100%. We therefore have to consider another possible pathway for reaction (4.6) that does not result in release of CO₂:

\[
\text{N}_2\text{O}_5 + \text{Ca} (\text{OH})(\text{HCO}_3) \rightarrow \text{Ca} (\text{NO}_3)(\text{HCO}_3) + \text{HNO}_3(g) \quad (4.8)
\]

In this case N₂O₅ may directly be converted into gas phase HNO₃ which is also observed at longer exposure times as displayed in Figure 4.1. Reaction (4.8) may also help explain why the ratio CO₂/N₂O₅ differs from 1.0 as no CO₂ is released from reaction (4.8). In addition, HNO₃ may also react with CaCO₃ as already observed by Hanisch and Crowley, 2001. We routinely measure a yield of 51 % of gas phase H₂O with respect to N₂O₅ consumed which is comparable to the CO₂ yield according to equation (4.6) and results from the uptake of N₂O₅ on samples of different mass of powdered CaCO₃.

<table>
<thead>
<tr>
<th>CaCO₃ Mass in g</th>
<th>γ₀</th>
<th>γ₀₀</th>
<th>Yield of HNO₃ć</th>
<th>Yield of CO₂ć</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.33a</td>
<td>0.16 ± 0.03</td>
<td>(2.0 ± 0.6) x 10⁻²</td>
<td>5.2 %</td>
<td>47.8 %</td>
</tr>
<tr>
<td>0.51a, b</td>
<td>0.2 ± 0.05</td>
<td>(2.2 ± 0.5) x 10⁻²</td>
<td>5.4 %</td>
<td>42.4 %</td>
</tr>
<tr>
<td>0.58a</td>
<td>0.18 ± 0.05</td>
<td>(2.3 ± 0.5) x 10⁻²</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.73a</td>
<td>0.22 ± 0.04</td>
<td>(2.4 ± 0.4) x 10⁻²</td>
<td>5.4 %</td>
<td>50 %</td>
</tr>
<tr>
<td>2a</td>
<td>0.18 ± 0.025</td>
<td>(1.6 ± 1.6) x 10⁻²</td>
<td>5.4 %</td>
<td>50 %</td>
</tr>
</tbody>
</table>

*Uptake measurements performed with a surface sample area Aₛ = 19.6 cm².

b Uptake experiment displayed in Figure 4.1.

c The yield is given as a percentage with respect to the total number of molecules of N₂O₅ taken up during a reaction time of 550 s.

**Table 4.1.** Uptake experiments with N₂O₅ on CaCO₃ as a function of sample mass at [N₂O₅]₀ = (4.0 ± 1.0) x 10¹¹ cm⁻³.
In the wake of the observation of $H_2O$, $CO_2$ and $HNO_3$ we propose that reactions (4.6) and (4.8) compete with each other. $H_2O$ is formed in reaction (4.6) on CaCO$_3$ that is in part preexisting as a surface intermediate Ca(OH)(HCO$_3$) from prior exposure to atmospheric $CO_2$ and $H_2O$ following reactions (4.4) and (4.5).

Owing to the fact that CaCO$_3$ has a specific surface area (BET) of 5.06 m$^2$/g, the 510 mg sample from the experiment displayed in Figure 4.1 has a total surface area of 2.6 x 10$^4$ cm$^2$. N$_2$O$_5$ may be represented as a sphere with a projected surface area of 6.4 x 10$^{-15}$ cm$^2$/molecule or 1.56 x 10$^{14}$ molecules cm$^{-2}$, assuming that N$_2$O$_5$ has a molecular diameter of approximately 9 Å and a density of 2.93 g/cm$^3$. After an exposure time of 1060 s 2.2 x 10$^{18}$ molecules of N$_2$O$_5$ are taken up on 510 mg of CaCO$_3$ leading to a surface concentration of $N_2O_5$ molecule cm$^{-2}$ which corresponds to a coverage ($\theta$) of approximately 54 % based on the BET surface area after a reaction time of 1060 s. After N$_2$O$_5$ reacted on CaCO$_3$ powder for 1060 s the substrate is apparently at steady state as displayed in Figure 4.1. This means that there is a sufficient number of intermediate species Ca(OH)(HCO$_3$) to allow reactions (4.6) and (4.8) to occur. However, once reacted with N$_2$O$_5$, the intermediate species cannot regenerate because reactions (4.4) and (4.5) are too slow under flow reactor conditions. Therefore, we observe an amount of CO$_2(g)$ smaller than the maximum yield of 100 % at steady state conditions. On the other hand, N$_2$O$_5$ may react with adsorbed water $H_2O_{(ads)}$ that still remains on the CaCO$_3$ substrate, thereby forming two molecules of nitric acid as follows:

$$N_2O_5(g) + H_2O_{(ads)} \rightarrow 2HNO_3(g) \quad (4.9)$$

In this case solid CaCO$_3$ is just the support for the reactive adsorbed water $H_2O_{(ads)}$ and is not consumed in the chemical reaction. Initially, $HNO_3_{(g)}$ is physically adsorbed on the surface to result in adsorbed HNO$_3$ which reacts with a surface OH-group and slowly forms surface nitrates and $H_2O$ according to reaction (4.10):

$$SS-OH + HNO_3_{(ads)} \rightarrow S-NO_3 + H_2O_{(ads,g)} \quad (4.10)$$
where SS represents a surface site for physical adsorption. This mechanism has been proposed by Seisel and co-workers\textsuperscript{21} in a DRIFTS study of the heterogeneous reaction of HNO\textsubscript{3} on mineral dust where they observed the presence of free OH-groups located on the surface of mineral dust and the formation of surface nitrates.

The fact that CO\textsubscript{2} is formed immediately after lifting the plunger (Figure 4.1) whereas HNO\textsubscript{3} is formed later on after a time delay clearly indicates that there are two competitive processes occurring during the reaction of N\textsubscript{2}O\textsubscript{5} with CaCO\textsubscript{3}. Immediately after the exposure of the substrate, N\textsubscript{2}O\textsubscript{5} reacts with the intermediate species Ca(OH)(HCO\textsubscript{3}) on the CaCO\textsubscript{3} sample according to reactions (4.6) and (4.8). At the same time heterogeneous hydrolysis of N\textsubscript{2}O\textsubscript{5} may occur due to the presence of H\textsubscript{2}O\textsubscript{(ads)} on the substrate reaction (4.9)). However, the presence of a sufficient quantity of the intermediate formed in reaction (4.5) may make reactions (4.7) and (4.8) predominant at first with respect to reaction (4.9). This explains the initial rapid formation of CO\textsubscript{2(g)} and the absence of any measurable trace of gas phase HNO\textsubscript{3} at t = 92 s in Figure 4.1. Once the surface intermediate starts to be consumed owing to the initial fast reaction with N\textsubscript{2}O\textsubscript{5} the sample starts saturating and reaction (4.9) becomes predominant compared to reactions (4.7) and (4.8) which would explain the delayed formation of HNO\textsubscript{3} displayed in Figure 4.1.

\textbf{Figure 4.2.} Desorption after N\textsubscript{2}O\textsubscript{5} uptake on a sample of 510 mg CaCO\textsubscript{3}. Curves (a) and (b) correspond to the raw MS signals monitored at m/e 44 and m/e 30, respectively, at an orifice diameter of 14 mm and A\textsubscript{s} = 19.6 cm\textsuperscript{2}. 
After having performed the uptake experiment shown in Figure 4.1 on a substrate of CaCO₃, we sealed the sample and halted the inlet flow of N₂O₅ for approximately 10 minutes. Subsequently, we lifted the plunger again and observed small amounts of desorbing CO₂ (curve (a), Figure 4.2) as well as a MS signal at m/e 30 without any measurable MS signal at m/e 46 (curve (b), Figure 4.2). The total yield of desorbed CO₂ only represented 5% of N₂O₅ taken up on the substrate of CaCO₃ during the reaction time of 1058 s. (Figure 4.1). The small intensity of the MS signal at m/e 30 strongly suggests formation of NO as a decomposition product of N₂O₅.

Uptake experiments of N₂O₅ on 0.58 g of CaCO₃ powder were carried out at smaller orifice size, thus increased residence time τ₉ at constant flow of N₂O₅ of 2.3 x 10¹⁵ molecule s⁻¹. The values of γ₀ and γ₉₉ decrease with increasing values of the residence time as displayed in Figure 4.3 and Table 4.2. The strong dependence of γ₉₉ on τ₉ suggests that the mechanism of N₂O₅ uptake is complex and does not correspond to a simple first order uptake reaction. These observations indicate that the reactivity of N₂O₅ on CaCO₃ decreases for long residence times as the heterogeneous reaction rate not only depends on the gas phase concentration but apparently also on intermediates whose surface concentration depend on the extent of reaction that scales with τ₉ akin to an effective second order reaction.

<table>
<thead>
<tr>
<th>Orifice (mm)</th>
<th>γ₀</th>
<th>γ₉₉</th>
<th>τ₉ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>(1.6 ± 0.13) x 10⁻¹</td>
<td>(6.0 ± 1.2) x 10⁻²</td>
<td>0.34</td>
</tr>
<tr>
<td>8</td>
<td>(8.5 ± 0.8) x 10⁻²</td>
<td>(3.0 ± 0.7) x 10⁻²</td>
<td>0.81</td>
</tr>
<tr>
<td>4</td>
<td>(3.4 ± 1.0) x 10⁻²</td>
<td>(1.8 ± 1.1) x 10⁻²</td>
<td>2.72</td>
</tr>
<tr>
<td>1</td>
<td>(1.1 ± 1.0) x 10⁻²</td>
<td>(1.0 ± 1.0) x 10⁻²</td>
<td>30</td>
</tr>
</tbody>
</table>

**Table 4.2.** Relationship between γ₀ and γ₉₉ at different residence times τ₉ (s) of N₂O₅ interacting with 580 mg of CaCO₃ powder for data plotted in Figure 2, surface sample area Aₛ = 19.6 cm²; F₀⁻¹⁵ = 2.3 x 10¹⁵ molecule s⁻¹
4. The heterogeneous chemical kinetics of N$_2$O$_5$ on CaCO$_3$ and other atmospheric mineral dust surrogates

Figure 4.3. Dependence of $\gamma_0$ (full squares) and $\gamma_{ss}$ (open circles) for the uptake of N$_2$O$_5$ on 580 mg CaCO$_3$ powder on orifice size: $A_s$ is 4.9 cm$^2$, $\Gamma_0^{N_2O_5} = 2.3 \times 10^{15}$ molecule s$^{-1}$.

Apparently, the active surface intermediate Ca(OH)(HCO$_3$) cannot regenerate sufficiently fast according to reaction (4.5) so as to maintain the rate limiting reaction (4.6) at higher partial pressure, that is at longer residence time $\tau_g$.

In order to unravel whether or not the effective available surface area for uptake is influenced by the internal surface area formed by interstitial voids between individual dust particles, the mass dependence of the N$_2$O$_5$ uptake on CaCO$_3$ was investigated in the Knudsen flow reactor at ambient temperature and at [N$_2$O$_5$] = (4.0 $\pm$ 1.0) x 10$^{11}$ cm$^{-3}$. The mass of CaCO$_3$ which is a non-porous material ranged from 0.11 g to 1.8 g and the results are shown in Figure 4.4. Table 4.3 reports values of $\gamma_{ss}$ and $\gamma_0$ using the geometric surface area $A_s = 19.6$ cm$^2$. The steady state and initial uptake coefficient $\gamma_{ss}$ and $\gamma_0$, respectively, of N$_2$O$_5$ were found to increase linearly at low masses of CaCO$_3$. Samples below 0.33 g were considered to be part of this linear mass-dependent regime. Increasing the sample mass further had a negligible effect on the amount of adsorbed N$_2$O$_5$ because not the entire sample surface is apparently available for N$_2$O$_5$ adsorption. This maximum value is attributed to the inability of N$_2$O$_5$ to penetrate through all layers of the sample within the residence time of N$_2$O$_5$ in the gas phase, thus resulting in a constant number of molecules taken up despite the increasing sample mass. The limiting $\gamma_{ss}$ value therefore represents the maximum amount of N$_2$O$_5$ able to interact with CaCO$_3$ powder within the N$_2$O$_5$ residence time.
### Table 4.3. Summary of uptake experiments with N₂O₅ on CaCO₃ as a function of sample mass

\([N₂O₅] = (4.0 \pm 1.0) \times 10^{11} \text{ cm}^{-3}\), orifice diameter = 14 mm, \(A_s = 19.6 \text{ cm}^2\).

<table>
<thead>
<tr>
<th>Mass (g)</th>
<th>(\gamma_{ss})</th>
<th>(\gamma_0)</th>
<th>(\gamma_0) (pulsed valve)</th>
<th>(^a)Number of formal layers</th>
<th>(^b)Number of nominal layers</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.11</td>
<td>((8.0 \pm 5.0) \times 10^{-3})</td>
<td>((5.5 \pm 2.0) \times 10^{-2})</td>
<td>((4.7 \pm 1.5) \times 10^{-2})</td>
<td>5</td>
<td>0.3</td>
</tr>
<tr>
<td>0.15</td>
<td>((1.5 \pm 0.5) \times 10^{-2})</td>
<td>((6.4 \pm 3.0) \times 10^{-2})</td>
<td></td>
<td>7</td>
<td>0.5</td>
</tr>
<tr>
<td>0.33</td>
<td>((2.0 \pm 0.6) \times 10^{-2})</td>
<td>0.16 ± 0.03</td>
<td>0.13 ± 0.018</td>
<td>16</td>
<td>1</td>
</tr>
<tr>
<td>0.51</td>
<td>((2.2 \pm 0.5) \times 10^{-2})</td>
<td>0.2 ± 0.02</td>
<td></td>
<td>25</td>
<td>1.5</td>
</tr>
<tr>
<td>0.58</td>
<td>((2.3 \pm 0.5) \times 10^{-2})</td>
<td>0.18 ± 0.02</td>
<td></td>
<td>30</td>
<td>1.8</td>
</tr>
<tr>
<td>0.73</td>
<td>((2.4 \pm 0.5) \times 10^{-2})</td>
<td>0.22 ± 0.02</td>
<td>0.21 ± 0.016</td>
<td>36</td>
<td>2.2</td>
</tr>
<tr>
<td>1.0</td>
<td>((2.7 \pm 0.4) \times 10^{-2})</td>
<td>0.15 ± 0.025</td>
<td></td>
<td>50</td>
<td>3</td>
</tr>
<tr>
<td>1.3</td>
<td>((2.8 \pm 0.5) \times 10^{-2})</td>
<td>0.16 ± 0.024</td>
<td></td>
<td>64</td>
<td>4</td>
</tr>
<tr>
<td>1.6</td>
<td>((2.8 \pm 0.5) \times 10^{-2})</td>
<td>0.15 ± 0.024</td>
<td>0.15 ± 0.015</td>
<td>80</td>
<td>5</td>
</tr>
<tr>
<td>1.8</td>
<td>((2.8 \pm 0.5) \times 10^{-2})</td>
<td>0.17 ± 0.03</td>
<td></td>
<td>90</td>
<td>5.5</td>
</tr>
</tbody>
</table>

[^a]: Effective diameter of 3.5 \(\mu\)m

[^b]: Effective diameter of 57 \(\mu\)m
4. The heterogeneous chemical kinetics of N$_2$O$_5$ on CaCO$_3$ and other atmospheric mineral dust surrogates

Figure 4.4. Dependence of the uptake coefficient $\gamma_0$ (open squares) and $\gamma_{ss}$ (full circles) on sample mass at [N$_2$O$_5$]$_0$ = (4.0 ± 1.0) x $10^{11}$ cm$^{-3}$ at an orifice diameter of 14 mm for the uptake of N$_2$O$_5$ on CaCO$_3$ powder ($A_s = 19.6$ cm$^2$). Full triangles represent pulsed valve experiments carried out at the same experimental conditions. The average particle diameter on the two scales of the abscissa, namely formal and nominal layers, are 57 and 3.5 $\mu$m, respectively.

In order to better define the saturation behaviour of N$_2$O$_5$ on the substrate further uptake experiments were performed on CaCO$_3$ employing a pulsed valve to admit N$_2$O$_5$ into the reactor. The pulsed-valve experiments were carried out by using a solenoid valve, through which the gas was introduced in pulses with a duration of 5 ms and at a dose of 2.5 x $10^{15}$ molecules per pulse$^{22}$ corresponding to [N$_2$O$_5$]$_0$ = 1.3 x $10^{12}$ cm$^{-3}$. The pulsed valve uptake experiments on CaCO$_3$ showed that there is a modest mass-dependence of the measured uptake $\gamma_{obs}$ by approximately a factor of three to four. For a dose of about 2.5 x $10^{15}$ molecules per pulse we observed an unexpected increase of the uptake $\gamma_{obs}$ with increasing mass of CaCO$_3$ as reported for steady state experiments in Table 4.3 and displayed in Figure 4.4. The increase of $\gamma_{obs}$ saturates at large sample mass because the number of layers exceeds the depth of diffusion of gas into the internal voids. For all series of pulses the measurements are identical, within the uncertainty, to those for steady state experiments. In order to convince the reader that the geometric surface area is appropriate, we want to point out that the results obtained from the pulsed valve experiments are virtually identical to the steady state experiments at “zero” time after the
The heterogeneous chemical kinetics of N$_2$O$_5$ on CaCO$_3$ and other atmospheric mineral dust surrogates

start of the uptake experiment reaction (Figure 4.4). It is improbable for the gas to explore the BET surface area of the sample during typical pulse decay.

Similar behavior has been observed in a recent study carried out by Seisel et al.$^{11}$ In that study uptake experiments of N$_2$O$_5$ on Saharan Dust obtained from pulsed and steady state experiments were in good agreement, indicating that the steady state uptake coefficients are not influenced by saturation effects under their experimental conditions.

![SEM-image of CaCO$_3$ powder sample used in this work.](image)

Figure 4.5. SEM-image of CaCO$_3$ powder sample used in this work.

In order to determine the number of layers, the total volume of the powder was calculated from its true density ($\rho_t = 2.93$ g/cm$^3$) and the mass of the sample spread out across the geometric area of the sample holder. The number of formal layers calculated for an average sample grain diameter of 3.5 $\mu$m from the average particle size and the height of the sample is reported in Table 4.3. The typical grain diameter of 3.5 $\mu$m has been obtained from the manufacturer’s specifications of the used CaCO$_3$ powder.

Based on published microscopic images, it is reasonable to take into account a grain size diameter that is larger than 3.5 $\mu$m as suggested by electron microscopy (SEM) displayed in Figure 4.5. Figure 4.4 shows that a mass of 0.33 g corresponds to one nominal layer of 57 $\mu$m diameter CaCO$_3$ spread out over the geometric surface of the sample holder (19.6 cm$^2$). Thus, one nominal layer of CaCO$_3$ will contain 330 mg of closely packed spheres of “effective” grain diameter of 57 $\mu$m knowing full well that the sample in reality is multidisperse and structurally heterogeneous. Therefore, the linear mass-dependent
portion of $\gamma_{ss}$ vs. mass for masses less than 330 mg corresponds to a sample holder that is partially covered with 57 $\mu$m diameter CaCO$_3$ particles.

The use of the BET surface area and the application of the pore diffusion theory$^{23}$ yields $\gamma_{pd,ss} = (7.4 \pm 1.7) \times 10^{-6}$ for steady state experiments using a grain diameter for CaCO$_3$ of 3.5 $\mu$m. This value is lower by a factor of $10^3$ compared to $\gamma_{ss} = (2.8 \pm 0.5) \times 10^{-2}$ and $\gamma_0 = 0.16 \pm 0.02$ which were calculated on the basis of the geometrical surface area of the sample as displayed in Table 4.3. The use of the pore diffusion theory substantially underestimates the true uptake coefficient so that it may be interpreted as a lower limit for $\gamma$ whereas $\gamma_{ss}$ and $\gamma_0$ based on the geometrical surface area may be regarded as an upper limit to the true value of $\gamma$. 
4. The heterogeneous chemical kinetics of N₂O₅ on CaCO₃ and other atmospheric mineral dust surrogates

4.5 Uptake of N₂O₅ on mineral Dust Substrates: Results and Discussion

Table 4.4 reports results on experiments performed on 1g samples of surrogate mineral dust powder at a high initial concentration of [N₂O₅]₀ = (3.8 ± 1.0) x 10¹² cm⁻³. The steady-state uptake coefficients γₚ of N₂O₅ range from (2.2 ± 0.6) x 10⁻³ for natural limestone to (5.9 ± 1.6) x 10⁻² for Saharan Dust using the geometric surface area. At a lower initial concentration of [N₂O₅]₀ = (4.0 ± 1.0) x 10¹¹ cm⁻³ uptake experiments performed on 0.3 g have revealed larger values of γₚ ranging from (3.5 ± 1.1) x 10⁻² for CaCO₃ to 0.2 ± 0.05 for Saharan Dust.

<table>
<thead>
<tr>
<th>Mineral dust sample</th>
<th>aγ₀</th>
<th>aγₚ</th>
<th>aHNO₃</th>
<th>H₂O (ads) [mg g⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolinite</td>
<td>0.14 ± 0.04</td>
<td>(2.2 ± 0.6) x 10⁻²</td>
<td>30 %</td>
<td>23</td>
</tr>
<tr>
<td>Natural Limestone</td>
<td>(1.1 ± 0.3) x 10⁻²</td>
<td>(2.2 ± 0.6) x 10⁻³</td>
<td>18 %</td>
<td>7</td>
</tr>
<tr>
<td>Arizona Test Dust</td>
<td>(6.4 ± 1.9) x 10⁻²</td>
<td>(1.6 ± 0.4) x 10⁻²</td>
<td>72 %</td>
<td>22</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>(3.3 ± 1.0) x 10⁻²</td>
<td>(6.2 ± 1.8) x 10⁻³</td>
<td>5 %</td>
<td>4</td>
</tr>
<tr>
<td>Saharan Dust</td>
<td>(9.0 ± 2.6) x 10⁻²</td>
<td>(5.9 ± 1.6) x 10⁻²</td>
<td>6 %</td>
<td>20</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mineral dust sample</th>
<th>bγ₀</th>
<th>bγₚ</th>
<th>bHNO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolinite</td>
<td>(0.16 ± 0.04)</td>
<td>(2.1 ± 0.6) x 10⁻²</td>
<td>17 %</td>
</tr>
<tr>
<td>Natural Limestone</td>
<td>(0.43 ± 0.13)</td>
<td>(4.3 ± 1.3) x 10⁻²</td>
<td>12 %</td>
</tr>
<tr>
<td>Arizona Test Dust</td>
<td>(0.2 ± 0.06)</td>
<td>(0.11 ± 0.03)</td>
<td>20 %</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>(0.12 ± 0.04)</td>
<td>(2.1 ± 0.6) x 10⁻²</td>
<td>5 %</td>
</tr>
<tr>
<td>Saharan Dust</td>
<td>(0.3 ± 0.08)</td>
<td>0.2 ± 0.05</td>
<td>4 %</td>
</tr>
</tbody>
</table>

Uptake experiments were performed at [N₂O₅]₀ = (3.8 ± 0.5) x 10¹² cm⁻³ using 1g of sample powder for Aₛ = 19.6 cm²; [N₂O₅]₀ = (4.0 ± 1.0) x 10¹¹ cm⁻³ using 300 mg of sample powder for Aₛ = 4.9 cm². The yield of HNO₃ is given as a percentage with respect to the total molecules of N₂O₅ taken up after a given reaction time of 200 s at an orifice diameter of 8 mm.

Table 4.4. Summary of uptake experiments of N₂O₅ on mineral dust samples: initial (γ₀) and steady state (γₚ) uptake coefficients.

We report the observed initial uptake coefficients γ₀ for N₂O₅ on all the samples of mineral dust at low and high values of [N₂O₅]. For a concentration of [N₂O₅]₀ = (3.8 ± 0.5) x 10¹² cm⁻³ the γ₀ values range from (6.4 ± 1.9) x 10⁻³ for Arizona test dust to (9.0 ± 2.6) x 10⁻² for Saharan Dust. At [N₂O₅]₀ = (4.0 ± 1.0) x 10¹¹ cm⁻³ the γ₀ values range from 0.12 ± 0.04 for CaCO₃ to 0.43 ± 0.13 for natural limestone. For samples such as Saharan Dust, CaCO₃ and Arizona Test Dust values of γₚ and γ₀ decrease.
between a factor of 3 and 7 from low to high $[\text{N}_2\text{O}_5]_0$. As indicated in Table 4.4, both the values $\gamma_{ss}$ and $\gamma_0$ for CaCO$_3$ decrease only by a factor 3.5 from low to high $[\text{N}_2\text{O}_5]$. On the other hand a particular case is represented by natural limestone which shows a decrease of $\gamma_{ss}$ and $\gamma_0$ by a factor of 20 and 40, respectively, when increasing $[\text{N}_2\text{O}_5]_0$. CaCO$_3$ showed values of $\gamma_{ss}$ and $\gamma_0$ higher by a factor of 3 with respect to natural limestone at high $[\text{N}_2\text{O}_5]_0$. This difference is reversed by the same amount for low $[\text{N}_2\text{O}_5]_0$ with $\gamma$ of natural limestone being highly sensitive to saturation by $[\text{N}_2\text{O}_5]$. Natural limestone is a sedimentary rock containing 97% CaCO$_3$ by weight and a small percentage of metal oxides (1.9% of SiO$_2$, 0.5% of Al$_2$O$_3$, 0.3% of Fe$_2$O$_3$, and 0.3% of MgO) that may be responsible for the difference in the kinetic properties of CaCO$_3$ and natural limestone in addition to morphological properties. In recent work Krueger and co-workers$^{24}$ showed that dust containing calcium is very reactive with respect to the uptake of nitric acid. However, because of differences in mineralogy of single dust-particles, not all of the calcium-containing particles react similarly. It is important to note that for Kaolinite $\gamma_{ss}$ and $\gamma_0$ are independent of $[\text{N}_2\text{O}_5]_0$ over the investigated range. Typical raw data from an uptake experiment of $\text{N}_2\text{O}_5$ on 1 g of Kaolinite and Saharan Dust are shown in Figures 4.6 and 4.7. In this series of experiments we did not succeed to saturate the samples during the present observation period.

**Figure 4.6.** Typical $\text{N}_2\text{O}_5$ uptake experiment on a sample of 1 g of Kaolinite. Curves (a), (b), (c) and (d) correspond to the raw MS signals monitored at m/e 46, m/e 30, m/e 63 and m/e 18, respectively, using an orifice diameter of 8 mm and $[\text{N}_2\text{O}_5]_0 = (3.8 \pm 0.5) \times 10^{12}$ cm$^{-3}$. 
4. The heterogeneous chemical kinetics of N$_2$O$_5$ on CaCO$_3$ and other atmospheric mineral dust surrogates

Figure 4.7. Typical N$_2$O$_5$ uptake experiment on a sample of 1 g of Saharan Dust. Curves (a), (b), (c) and (d) correspond to the raw MS signals monitored at m/e 46, m/e 30, m/e 63 and m/e 18, respectively, using an orifice diameter of 8 mm and [N$_2$O$_5$]$_0$ = (3.8 ± 0.5) x 10$^{12}$ cm$^{-3}$.

Uptake experiments of N$_2$O$_5$ on 0.2 g of Kaolinite powder were carried out by varying the initial flow of N$_2$O$_5$ into the reactor (Table 4.5). Figure 4.8 displays data for the 8 mm orifice corresponding to a residence time $\tau_g$ of 1.32 s for a variation of [N$_2$O$_5$]$_0$ by a factor 9.5 that is between (4.0 ± 1.0) x 10$^{11}$ cm$^{-3}$ and (3.8 ± 0.5) x 10$^{12}$ cm$^{-3}$. Figure 4.8 shows that both $\gamma_0$ and $\gamma_{ss}$ remain constant at 0.19 ± 0.05 and (2.3 ± 0.6) x 10$^{-2}$, respectively, independent of an increase in [N$_2$O$_5$] and a change of the gas residence time $\tau_g$. From this series of measurements it is evident that $\gamma_{ss}$ follows a pseudo first order rate law in N$_2$O$_5$ in contrast to the other substrates which showed a decreasing trend from low to high [N$_2$O$_5$] (see Figure 4.3 and Table 4.4).

<table>
<thead>
<tr>
<th>[N$_2$O$_5$] molecules cm$^{-3}$</th>
<th>$\gamma_0$</th>
<th>$\gamma_{ss}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^a$(4.0 ± 1.0) x 10$^{11}$</td>
<td>0.16 ± 0.04</td>
<td>(2.1 ± 0.6) x 10$^{-2}$</td>
</tr>
<tr>
<td>$^b$(6.2 ± 1.5) x 10$^{11}$</td>
<td>0.23 ± 0.06</td>
<td>(2.6 ± 0.5) x 10$^{-2}$</td>
</tr>
<tr>
<td>$^a$(9.0 ± 0.5) x 10$^{11}$</td>
<td>0.22 ± 0.06</td>
<td>(2.2 ± 0.5) x 10$^{-2}$</td>
</tr>
<tr>
<td>$^b$(2.1 ± 0.5) x 10$^{12}$</td>
<td>0.18 ± 0.05</td>
<td>(2.4 ± 0.7) x 10$^{-2}$</td>
</tr>
<tr>
<td>$^a$(3.8 ± 0.5) x 10$^{12}$</td>
<td>0.16 ± 0.04</td>
<td>(2.2 ± 0.6) x 10$^{-2}$</td>
</tr>
</tbody>
</table>

$^a$ Orifice diameter = 8 mm; $^b$Orifice diameter = 4 mm.

Table 4.5. Summary of uptake experiments of N$_2$O$_5$ on 200 mg Kaolinite for data plotted in Figure 8: initial ($\gamma_0$) and steady state ($\gamma_{ss}$) uptake coefficients ($A_s = 4.9$ cm$^2$).
In recent work the uptake of \( \text{N}_2\text{O}_5 \) on Saharan Dust was found to be independent of \([\text{N}_2\text{O}_5]\) \(^{11}\). An initial uptake coefficient \( \gamma_0 = (8.0 \pm 0.3) \times 10^{-2} \) was found, whereas the steady state value \( \gamma_{ss} = (1.3 \pm 0.3) \times 10^{-2} \) was lower by a factor of five with respect to the present results at \([\text{N}_2\text{O}_5]_0 = (3.8 \pm 0.5) \times 10^{12} \text{ cm}^{-3} \).

We have observed delayed production of HNO\(_3\) upon uptake of \( \text{N}_2\text{O}_5 \) for every sample investigated. Gas phase HNO\(_3\) formation may be due to the heterogeneous hydrolysis of \( \text{N}_2\text{O}_5 \) according to reaction (4.9). In order to understand the gas phase production of HNO\(_3\) we want to stress that all the investigated samples have a non negligible amount of adsorbed water available on the substrate surface. The quantities of \( \text{H}_2\text{O}_{(ads)} \) that still remain on the different mineral dust substrates at our experimental conditions as reported in Table 4.4 and were measured by gravimetric measurements. The hygroscopic properties of mineral aerosol samples have been examined in recent work\(^{25}\) which showed significant water adsorption on Arizona Test Dust compared to \( \text{CaCO}_3 \).
In Table 4.4 we also report the percentage of gas phase HNO₃ produced with respect to N₂O₅ taken up during a reaction time of 200 s. At [N₂O₅] = (3.8 ± 0.5) x 10^{12} \text{ cm}^{-3}, Arizona Test Dust and Kaolinite turned out to be the samples to produce the largest amount of gas phase HNO₃, that is 72 % and 30 %, respectively, with respect to N₂O₅ taken up. On the other hand, Saharan Dust and CaCO₃ have been the samples with a lower yield of absolute HNO₃ produced, namely 5 % and 6 %, respectively. At [N₂O₅] = (4.0 ± 1.0) x 10^{11} \text{ cm}^{-3} we obtained lower yields of gas phase HNO₃ compared to ten times higher [N₂O₅]. In this case we may correlate the low yield of HNO₃ to the large rate of uptake of N₂O₅ and of HNO₃ on mineral dust. Adsorbed HNO₃ may then form salts such as Ca(NO₃)₂, Fe(NO₃)₃ and surface nitrates as shown in other experimental studies. A recent study on the reactivity of gaseous HNO₃ on atmospheric mineral dust samples reported values for the uptake of HNO₃ on CaCO₃, Saharan Dust and Arizona Test Dust. In that work, a value of γ₀ = 0.11 was determined for Saharan Dust at [HNO₃] = (5.6 ± 0.4) x 10^{11} \text{ cm}^{-3}, 0.14 for CaCO₃ and 6.6 x 10^{-2} for Arizona Test Dust. These results are consistent with the trend of the present yields of HNO₃ measured for nominally the same mineral dust samples. Whenever the uptake coefficient of HNO₃ on the mineral substrates was low such as for Arizona Test Dust and Kaolinite, we find increased amounts of HNO₃ in the gas phase. Conversely, the reverse is true for samples that rapidly take up HNO₃ as for CaCO₃ and Saharan Dust.

4.6 Atmospheric implications

We have shown in this work that N₂O₅ undergoes a heterogeneous reaction with surrogate substrates of mineral dust aerosol at T = 298 ± 2 K. The measured uptake coefficient showed different values for high and low N₂O₅ concentrations with the smallest differences for Saharan Dust. These γ values are generally larger than the ones used in a recent global modeling simulation of heterogeneous chemistry on mineral dust aerosol at dry conditions where γ = 3.0 x 10^{-3} for N₂O₅ has been used. The γ values resulting from
the present measurements are larger by at least a factor of 10. Therefore, the uptake of N₂O₅ on mineral dust aerosols may potentially have a greater influence on the reduction of the global ozone concentration compared to the estimated value of 0.7 %⁹.

The measured uptake coefficient γ of N₂O₅ on sulfuric acid aerosols was reported to lie within the range 0.06-0.12 at a temperature between 230 and 300 K ³⁰. Other measurements reported γ values of 0.05 on aqueous surfaces over a temperature range from 282 to 294 K ³¹. To our knowledge no reaction probabilities of N₂O₅ on mineral aerosol have been determined to date. In a recent numerical modeling study the interaction of N₂O₅ (γ = 0.1), O₃ and HO₂ radicals with dust resulted in a decrease of tropospheric ozone of up to 10% near the dust source areas⁶.

The photolytic rate of NO₃ (J(NO₃) = 0.2 s⁻¹) is too fast to allow its recombination with NO₂ to N₂O₅ during daylight. Therefore, the heterogeneous chemistry of N₂O₅ is important only at night-time. The heterogeneous reaction of N₂O₅ is most effective during the night when rh is at a maximum in the boundary layer. Thus, under these conditions, dust particles are likely to contain significant quantities of adsorbed water and the assumed high values of γ appear to be justified³². In a recent global modeling study γ = 0.02 (rh = 70%) and γ = 3.0 x 10⁻³ (rh = 30%) for humid and dry conditions have been used as upper and lower limits, respectively⁹. The modeling results show that when applying the high value for the uptake coefficient 0.8 % of the global ozone mass is removed by uptake of N₂O₅ on aerosols. The observed reaction products of the heterogeneous reaction of N₂O₅ with mineral dust, mainly HNO₃, may also have an influence on the oxidizing potential of the atmosphere as well as on the atmospheric ozone balance. Previous laboratory work²¹,²⁹,³³ has shown the importance of the reactivity of HNO₃ on mineral dust substrates. In addition, modeling studies have quantitatively shown decreases in ozone concentration close to the area of HNO₃ destruction⁹.

The Saharan dust sample, from Cape Verde (SDCV), that we have used is representative of atmospheric dust aerosol from a mineralogical standpoint. Its composition has been described in the literature³⁴ and closely simulates atmospheric particles of crustal origin³⁵. The clay fraction (< 2 μm) of dust from Cape Verde shows a Kaolinite-Ililite-Chlorite assemblage which is typical for central Saharan Dust. In the free troposphere mineral dust aerosol of a size less than 2 μm have a settling velocity of approximately 50 cm h⁻¹³⁶.
Therefore it can remain in the atmosphere for several days, travel long distances and undergoes heterogeneous reactions with trace gases.

The loss rate constant ($k_{\text{het}}^{\text{M}}$) due to heterogeneous uptake of a gas species $M$ onto small aerosol particles is given by $k_{\text{het}}^{\text{M}} = \gamma \overline{\sigma} A / 4$ if the rate is not limited by diffusion, where $\gamma$ is the uptake coefficient of $M$ and is a function of the mineral dust aerosol composition, $A$ is the surface area density of the dust aerosol and $\overline{\sigma}$ is the mean molecular speed of $M$.

Assuming a surface area density for Saharan Dust of about $1.5 \times 10^{-6}$ cm$^2$ cm$^{-3}$, we estimate $k_{\text{het}}^{\text{N}_2\text{O}_5} = 1.76 \times 10^{-3}$ s$^{-1}$ ($\tau_{\text{het}}^{\text{N}_2\text{O}_5} = 9.5$ min) for N$_2$O$_5$ based on $\gamma = 0.2$ for Saharan dust at $[\text{N}_2\text{O}_5] < (4.0 \pm 1.0) \times 10^{11}$ cm$^{-3}$ (16 ppb). From the difference between the N$_2$O$_5$ formation and loss in the presence of the equilibrium with NO$_3$ we obtain the expression for the N$_2$O$_5$ steady state lifetime given in equation (4.11):

$$\tau_{\text{ss}}^{\text{N}_2\text{O}_5} = \left( k_{\text{het}}^{\text{N}_2\text{O}_5} + \frac{k_{\text{het}}^{\text{NO}_3} k_1(T)}{k_{-1}^{\text{NO}_2}} \right)^{-1}$$ (4.11)

$k_1(T)$ and $k_{-1}$ are the rate constant for thermal decomposition of N$_2$O$_5$ and its inverse at atmospheric pressure according to equilibrium (4.1), respectively. From recent work on the NO$_3$ heterogeneous reaction on mineral dust we have obtained $\gamma = 0.2$ which leads to $k_{\text{het}}^{\text{NO}_3} = 2.4 \times 10^{-3}$ s$^{-1}$ ($\tau_{\text{het}}^{\text{NO}_3} = 7$ min) for NO$_3$ according to expression (4.11).

At $T = 273$ K $k_1(273\text{K}) = 3.1 \times 10^{-3}$ s$^{-1}$ ($\tau = 5$ min) and equilibrium (4.1) is shifted to the left. For $[\text{NO}_2]$ a typical value is 10 ppb in polluted air so that the pseudo first-order recombination rate $k_{-1}[\text{NO}_2]$ is 0.48 s$^{-1}$ and is thus much larger than the rate constant for heterogeneous loss $k_{\text{het}}^{\text{NO}_3} = 2.4 \times 10^{-3}$ s$^{-1}$. Therefore, the second term of expression (4.11) will be negligible and the steady state lifetime $\tau_{\text{ss}}^{\text{N}_2\text{O}_5}$ of N$_2$O$_5$ will be determined by its heterogeneous loss rate constant $k_{\text{het}}^{\text{N}_2\text{O}_5}$.

At $T = 293$ K equilibrium (4.1) is shifted to the right with $k_1(293\text{K}) = 4.6 \times 10^{-2}$ s$^{-1}$ ($\tau = 20$ s) which is an order of magnitude larger than at $T = 273$ K. Therefore, both terms in equation (4.11) will be of comparable magnitude which will decrease the steady state lifetime of N$_2$O$_5$ with respect to 273 K somewhat.
The calculated overall steady state lifetime for N$_2$O$_5$ at 293 K ($\tau_{\text{ss}}^{\text{N}_2\text{O}_5} = 8.5$ min) is significantly larger than the thermal dissociation lifetime ($\tau = 20$ s) of N$_2$O$_5$. At the same surface area concentration for dust aerosol of 1.5 x $10^{-6}$ cm$^2$ cm$^{-3}$, the heterogeneous loss rate $k_{\text{het}}^{\text{hydr}}$ constant due to hydrolysis (reaction 4.9) is $2.25 \times 10^{-4}$ s$^{-1}$ corresponding to a lifetime of 74 min. This means that some N$_2$O$_5$ may be irreversibly converted to HNO$_3$ during the night by hydrolysis. During January 2004, Wood$^{39}$ performed in situ measurement of N$_2$O$_5$ in Contra Costa Country, California, and derived a steady state lifetime for N$_2$O$_5$ that ranged from 5 to 30 min at [N$_2$O$_5$] = 200 ppt (5.0 x $10^9$ cm$^{-3}$) in the temperature range 275 – 285 K which is comparable to $\tau_{\text{ss}}^{\text{N}_2\text{O}_5}$ calculated above. The measured lifetime for N$_2$O$_5$ from the field thus supports the heterogeneous loss rates of NO$_3$ and N$_2$O$_5$ measured in the present work.
4.7 References


4. The heterogeneous chemical kinetics of N₂O₅ on CaCO₃ and other atmospheric mineral dust surrogates


4. The heterogeneous chemical kinetics of N₂O₅ on CaCO₃ and other atmospheric mineral dust surrogates


4. The heterogeneous chemical kinetics of N$_2$O$_5$ on CaCO$_3$ and other atmospheric mineral dust surrogates


4. The heterogeneous chemical kinetics of N₂O₅ on CaCO₃ and other atmospheric mineral dust surrogates
4. The heterogeneous chemical kinetics of N₂O₅ on CaCO₃ and other atmospheric mineral dust surrogates
CHAPTER 5

HIGH REACTIVITY AND CHEMICAL KINETICS OF NO$_3$ ON LABORATORY FLAME SOOT

5.1 Introduction

Soot particles may allow heterogeneous chemical processes which are known to be important for the conversion of atmospheric trace gases like O$_3$ or NO$_x$. Collision rates of radical species like HO$_2$ and NO$_3$ with soot particles may become comparable to the rates of their fastest homogeneous loss processes, indicating the potential oxidizing capacity of the atmosphere. However, in order to quantitatively estimate the importance of heterogeneous processes on soot surfaces we need to improve the experimental data base for a more intimate knowledge of the heterogeneous reaction mechanism.

Previous studies have examined the heterogeneous reaction of NO$_2$ with soot knowing that NO is un-reactive on this substrate. One of the reaction products which results from the interaction of NO$_2$ with soot substrates is HONO. Nevertheless, there must be additional sources of HONO because soot is not sufficient to explain the [HONO] in the atmosphere. HONO is an important trace gas in the atmosphere because it is easily photolysed to produce OH + NO. In this manner, HONO photolysis increases the rate of photo-oxidation processes in the morning.

During daytime, HONO concentrations up to 200 ppt have been measured. However, the HONO/NO$_x$ ratio in the exhaust of modern vehicles is so much smaller that it cannot be responsible for the amounts measured during the night-time in the boundary layer. Heterogeneous formation of HONO resulting from the reaction of NO$_x$ with adsorbed H$_2$O...
or reducing substrates has been studied extensively in the past but it does not explain the HONO concentrations observed in the atmosphere because this reaction is too slow. This probably means that there is an important unknown source of HONO at daytime.

5.2 Experimental setup

A custom-designed co-flow system has been used in order to produce fresh flame soot from decane fuel in a reproducible way (Figure 5.1). It consists of a diffusion flame maintained in a measurable flow of air. In order to regulate the fuel flow feeding the flame by capillary fores, two types of ceramics of different porosity were used. One type of soot has been generated in a lean flame (low fuel/oxygen ratio) and will be referred to as “black” soot, the second has been generated in a rich flame (high fuel/oxygen ratio) and will be referred to as “grey” soot. Table 5.1 displays the characteristic parameters we have used to produce the two types of flame soot. The samples were collected from the burnt gases at 1 cm above the visible flame on ambient temperature Pyrex glass plates of 19.6 cm² surface area. The soot substrates used in this work are meant to adequately represent the chemical and physical characteristics of fresh soot emitted into the atmosphere by combustion sources and suitable for a systematic laboratory study.

Figure 5.1. Schematic diagram of the co-flow system used to produce soot from liquid fuels.
Table 5.1. Characteristic parameters of flame soot used to produce decane soot and general properties.

<table>
<thead>
<tr>
<th>Flame Type (Decane)</th>
<th>Air flow [L min⁻¹]</th>
<th>Fuel duct (pore Ø) [µm]</th>
<th>Soot type</th>
<th>⁸BET surface Area [m² g⁻¹]</th>
<th>³Diameter of soot particle [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rich</td>
<td>1.2-1.4</td>
<td>17-40</td>
<td>“grey”</td>
<td>69</td>
<td>40</td>
</tr>
<tr>
<td>Lean</td>
<td>1.3-1.5</td>
<td>11-16</td>
<td>“black”</td>
<td>218</td>
<td>20</td>
</tr>
</tbody>
</table>

The mass of soot used in these experiments was varied between 1.5 and 20 mg spread out over 19.6 cm². Each sample was pumped for 10 min before performing an uptake experiment. The gas under study, NO₃, was generated by thermal decomposition of N₂O₅ at 530 K following the same procedure reported in Chapter 3. Hydrolysis of N₂O₅ may occur on internal surfaces of the inlet line before admission into the hot glass capillary generating HNO₃ as an impurity on the order of 10 to 15%. However, HNO₃ does not thermally decompose inside the hot glass tube of the NO₃ source because we did not observe any change in the MS signal amplitude at m/e 63 when increasing the source temperature from ambient to 530 K. In order to unambiguously monitor the concentration of NO and NO₂ in situ, Resonance Enhanced Multiphoton Ionization (REMPI) was employed as part of a multi-diagnostic experimental technique in addition to beam-sampling phase-sensitive mass spectrometry (MS). The experimental REMPI set up used is described in Chapter 2. The characterization of NO₃, its calibration and the secondary reactions in the hot NO₃ source are explained in Chapter 3.

We denoted I₀ᴺᴼ³ and Iᵣᴺᴼ³ the MS signal at m/e 62 before and during reaction, respectively, and the observed rate constant k_obs is given by equation (3.E2).

In the present data analysis, the observed uptake coefficient γᵣₒbs (equation 2.8) was calculated using the geometric surface area Aₛ of the sample holder which will be justified below based on suitable reference experiments. In the present chapter the observed uptake coefficient γᵣₒbs became γᵣₛᵣ, the steady state uptake coefficient, once steady state conditions were achieved after an exposure time of 500 s or so; γ₀ is γᵣₒbs at t = 0 s, that is immediately after lifting the plunger.

Continuous flow uptake experiments were carried out at ambient temperature (298 ± 2 K) under molecular flow conditions. The concentration of NO₃ inside the Knudsen reactor
ranged between \((2.7 \pm 0.5) \times 10^{11} \text{ cm}^{-3}\) and \((2.4 \pm 0.5) \times 10^{12} \text{ cm}^{-3}\). The associated \([\text{NO}_2]\) determined by REMPI was \((8.0 \pm 1.0) \times 10^{11} \text{ cm}^{-3}\) for \([\text{NO}_3] = (2.7 \pm 0.5) \times 10^{11} \text{ cm}^{-3}\) and \((6.2 \pm 1.5) \times 10^{12} \text{ cm}^{-3}\) for \([\text{NO}_3] = (2.4 \pm 0.5) \times 10^{12} \text{ cm}^{-3}\).

As shown in Figure 5.2, a large rate of disappearance of NO\(_3\) was observed at m/e 62 (curve (d)). At the same time, initial formation of HONO as a reaction product was observed on grey soot and detected at m/e 47 (HONO\(^+\)) (curve (e)).

![Figure 5.2](image_url)  

**Figure 5.2.** NO\(_3\) uptake on a sample of 10 mg of grey soot at [NO\(_3\)] = \((7.0 \pm 1.0) \times 10^{11} \text{ cm}^{-3}\). Curves (a), (b), (d), (e) and (f) correspond to the raw MS signals monitored at m/e 30, 46, 62, 47 and 63, respectively. Curve (c) corresponds to the raw REMPI signal for NO\(_2\) detection at \(\lambda_{\text{NO}_2} = 511\) nm converted to a MS signal at m/e 46.

### 5.3 Detection of products

The spectra of the species involved in the NO\(_3\) source share common fragment peaks when using MS detection. NO\(_3\) was monitored using mass spectrometry at m/e = 62 (NO\(_3^+\)). The main common fragment and molecular ion peaks for NO\(_3\), N\(_2\)O\(_5\), NO\(_2\), NO and HNO\(_3\) are m/e 46 and 30. The REMPI detection of NO\(_2\) allowed us to subtract with great accuracy the contribution of NO\(_2\) to the total MS signal \(I_0^{46}\) at m/e 46 that originated from the NO\(_3\) source.
As indicated above, the NO₃ source contains HNO₃ as an impurity that contributes to the total MS signal at m/e 46. Fortunately, HNO₃ has a measurable, albeit low intensity, parent peak at m/e 63 at the present experimental conditions.

In order to evaluate the contribution of HNO₃ at m/e 46 and 30 based on the MS amplitude at m/e 63 we have analyzed the MS spectrum of pure HNO₃. The observable peaks of HNO₃ are at m/e 46 (NO₂⁺), m/e 30 (NO⁺) and m/e 63 (HNO₃⁺). NO NO₂ impurity in HNO₃ was observed according to REMPI detection at λₙ₀₂ = 511 nm that is specific for NO₂. Using the detailed mass spectrum of pure HNO₃ we have accurately determined the effective contribution of HNO₃ at m/e 46 and 30 by using the fragmentation pattern expressed as the ratios \( f_{46} = \frac{I_{0}^{46\text{(HNO}_3\text{)}}}{I_{0}^{63\text{(HNO}_3\text{)}}} = 52 \pm 8 \) and \( f_{30} = \frac{I_{0}^{30\text{(HNO}_3\text{)}}}{I_{0}^{63\text{(HNO}_3\text{)}}} = 33 \pm 4 \).

We remind the reader that the absolute NO₂ concentration \([\text{NO}_2]\)₀(REMPI) originating from the NO₃ source has been determined by means of REMPI detection as explained in Chapter 2. We therefore calculated the corresponding MS signal contribution \( I_{0}^{46\text{(NO}_3\text{)}}\) at m/e 46 originating from the NO₃ source according to equation (3.E3). In the following, the subscript 0 and r will refer to continuous gas uptake experiments in the absence and presence, respectively, of the sample.

In the absence of the soot substrate, \( I_{0}^{46\text{(NO}_3\text{)}}\) and \( f_{46} \cdot I_{0}^{63\text{(HNO}_3\text{)}}\) have been subtracted from the total MS signal \( I_{0}^{46}\) at m/e 46 in order to attribute the remaining signal to the NO₂⁺ fragment of the electron-impact ionization of NO₃ once the absence of undissociated N₂O₅ from the NO₃ source was established. The resulting MS signal \( I_{0}^{46\text{(NO}_3\text{)}}\) at m/e 46 is given by equation (3.E4).

When the sample is exposed to the gases from the NO₃ source, NO₃ is taken up and reacts on soot resulting in a decrease of \([\text{NO}_3]\) which leads to a concomitant decrease of the MS signal \( I_{r}^{46}\) at m/e 46. For the following series of experiments we have determined \( r_{46} = \frac{I_{0}^{46\text{(NO}_3\text{)}}}{I_{0}^{62\text{(NO}_3\text{)}}} = 8.5 \pm 1.5 \) as the ratio of the MS signal \( I_{0}^{46\text{(NO}_3\text{)}}\) at m/e 46 (NO₂⁺) and \( I_{0}^{62\text{(NO}_3\text{)}}\), the molecular ion peak at m/e 62 (NO₂⁺) for NO₃ free radical.

As a result of the exposure of the sample to NO₃ in the presence of NO₂, we expect four possible reaction products: HNO₃, N₂O₅, HONO and NO. Under our experimental conditions HNO₃ may possibly be formed at high densities by heterogeneous
recombination of NO\textsubscript{2} and NO\textsubscript{3} to N\textsubscript{2}O\textsubscript{5} and subsequent heterogeneous hydrolysis. In order to find other possible reaction products contributing to excess $I_{\text{exc}}^{46}$ MS signal intensity at m/e = 46 not due to HNO\textsubscript{3}, we have subtracted the following known contributions from the total MS signal $I_{r}^{46}$: a) $I_{r}^{46(\text{NO}_{2})}$ for NO\textsubscript{2}, b) $r_{46} \cdot I_{r}^{62(\text{NO}_{3})}$ for NO\textsubscript{3}, c) $f \cdot I_{r}^{63(\text{HNO}_{3})}$ for the possible HNO\textsubscript{3} formation during the reaction. The final residual amplitude $I_{\text{exc}}^{46}$ was calculated according to equation (3.E5). It is reasonable to expect that N\textsubscript{2}O\textsubscript{5} may be the only reaction product contributing to an excess at m/e 46, as will be discussed below. Therefore, in the following $I_{\text{exc}}^{46}$ will be named $I_{\text{exc}}^{46(\text{N}_{2}\text{O}_{5})}$.

It was not possible to quantify a possible formation of NO by REMPI detection at $\lambda_{\text{NO}} = 452.6$ nm because its concentration dropped below the detection limit given by the chosen experimental conditions. Therefore, in order to establish the amount of NO due to excess at $I_{\text{exc}}^{30}$ MS signal intensity at m/e = 30 during the exposure of soot to NO\textsubscript{3}, we have accurately determined all the possible contributions to the total MS signal $I_{r}^{30}$ at m/e 30.

The major contribution to $I_{r}^{30}$ comes from the mixture of NO\textsubscript{2} and NO\textsubscript{3} originating from the hot NO\textsubscript{3} source given that the amount of HNO\textsubscript{3} and N\textsubscript{2}O\textsubscript{5} in the presence of the sample are small. Using a reference mass spectrum of pure NO\textsubscript{2} we have calculated the effective contribution of NO\textsubscript{2} at m/e 30 by using the fragmentation pattern expressed as the ratio

$$z_{1} = \frac{I_{0}^{\text{NO}_{2}(30)}}{I_{0}^{\text{NO}_{2}(46)}} = 2.0 \pm 0.2 .$$

The ratio of the MS signal $I_{0}^{30(\text{NO}_{3})}$ at m/e 30 (NO\textsuperscript{+}) and $I_{0}^{62(\text{NO}_{3})}$ at m/e 62 (NO\textsubscript{3}\textsuperscript{+}) for NO\textsubscript{3} radical has been defined as follows:

$$r_{30} = \frac{I_{0}^{30(\text{NO}_{3})}}{I_{0}^{62(\text{NO}_{3})}} = \frac{I_{0}^{30} - z_{1} \cdot I_{0}^{46(\text{NO}_{2})} - f_{30} \cdot I_{0}^{63(\text{HNO}_{3})}}{I_{0}^{62(\text{NO}_{3})}} = 6.3 \pm 0.8 ,$$

where $I_{0}^{30}$ is the total MS signal at m/e 30, $z_{1} \cdot I_{0}^{46(\text{NO}_{2})}$ and $f_{30} \cdot I_{0}^{63(\text{HNO}_{3})}$ are the contributions for NO\textsubscript{2} and HNO\textsubscript{3} both at m/e 30, respectively.

As explained above, it is reasonable to expect that N\textsubscript{2}O\textsubscript{5} will be a reaction product of the reaction of NO\textsubscript{3} on soot. However, we have to consider that pure N\textsubscript{2}O\textsubscript{5} has fragment peaks at m/e 46 and 30 which are correlated by the fragmentation pattern expressed as the ratio

$$r_{\text{N}_{2}\text{O}_{5}} = \frac{I_{0}^{46(\text{N}_{2}\text{O}_{5})}}{I_{0}^{30(\text{N}_{2}\text{O}_{5})}} = 1.36 \pm 0.3 .$$
As shown in previous studies on soot\textsuperscript{15}, HNO\textsubscript{3} reacts on the soot surface resulting in the formation of volatile products such as HONO and NO that contribute to the total MS signal \( I_{30} \) at m/e 30. At the present experimental conditions HONO has a measurable, albeit low intensity, parent peak at m/e 47 (HONO\textsuperscript{+}). Therefore, the effective contribution of HONO at m/e 30 has been determined by using its fragmentation pattern expressed as the ratio

\[
h = \frac{I_{30}(\text{HONO})}{I_{47}(\text{HONO})} = 22 \pm 0.5.\]

As already explained above HNO\textsubscript{3} present in the hot NO\textsubscript{3} source also provides a contribution to the MS amplitude at m/e 30.

Finally, during the exposure of soot to NO\textsubscript{3} we have subtracted the following known contributions from the total MS signal \( I_{30} \): 

- a) \( f_{\text{NO}_2} \cdot I_{46}(\text{NO}_2) \) for the contribution of generated \( \text{N}_2\text{O}_5 \),
- b) \( z_1 \cdot I_{46}(\text{NO}_2) \) for the contribution of NO\textsubscript{2} present in the NO\textsubscript{3} source,
- c) \( r_{30} \cdot I_{62}(\text{NO}_3) \) for the contribution of NO\textsubscript{3},
- d) \( h \cdot I_{47}(\text{HONO}) \) for HONO,
- e) \( f_{30} \cdot I_{63}(\text{HNO}_3) \) for HNO\textsubscript{3}.

The final expression for the residual amplitude \( I_{30\text{exc}} \) resulted from the following equation:

\[
I_{30\text{exc}} = I_{30} - \frac{I_{46}(\text{NO}_2)}{r_{\text{NO}_2}} - z_1 \cdot I_{46}(\text{NO}_2) - r_{30} \cdot I_{62}(\text{NO}_3) - h \cdot I_{47}(\text{HONO}) - f_{30} \cdot I_{63}(\text{HNO}_3) \quad (5.1)
\]

The resulting residual MS signal from equations (3.5) and (5.1) is related to the reaction products owing to the heterogeneous interaction of NO\textsubscript{3} with the exposed surface of the sample. It is reasonable to expect that \( \text{N}_2\text{O}_5 \) and NO may be the only reaction product contributing to m/e 46 and 30, respectively, as will be discussed below.

### 5.4.1 NO\textsubscript{3} interaction with grey decane soot

The interaction of NO\textsubscript{3} and decane soot was investigated in a series of uptake experiments performed at different masses of soot and at different [NO\textsubscript{3}]. Figure 5.2, shows a typical uptake experiment of NO\textsubscript{3} on 10 mg of grey soot at [NO\textsubscript{3}] = (7.0 \pm 1.0) \times 10\textsuperscript{11} cm\textsuperscript{-3}. After a steady flow of NO\textsubscript{3} had been established, the isolation plunger was lifted at \( t = 550 \) s and the substrate exposed to the NO\textsubscript{3} flow. Because of the uptake of NO\textsubscript{3} on soot, the number of molecules effusing through the escape orifice into the MS immediately decreases.
At $t = 1050$ s the sample compartment is sealed by lowering the plunger and the MS signal at m/e 62 returns to its initial value. The slight decrease of $I_{62(NO_3)}$ over extended periods of time such as displayed if Figure 5.2 can be explained by a slight decrease of the corresponding flow rate into the reactor. In all of the performed experiments we obtained an uptake of NO$_2$ that stems from the thermal decomposition of N$_2$O$_5$ and NO$_3$ (reaction (3.1)). This led to a net decrease of the REMPI signal for NO$_2$ at $\lambda_{NO_2} = 511$ nm (curve (c), Figure 5.2).

Reference uptake experiments with pure NO$_2$ in the presence of grey soot were performed at $[NO_2] = (2.3 \pm 0.5) \times 10^{12}$ cm$^{-3}$ (Figure 5.3). A large and instantaneous rate of uptake was observed and attained steady-state conditions after 3 minutes of interaction.

The initial and steady-state uptake coefficient resulted in $\gamma_0 = (3.0 \pm 0.6) \times 10^{-2}$ and $\gamma_{ss} = (1.3 \pm 0.2) \times 10^{-3}$, respectively. Simultaneously to the uptake of NO$_2$ a large product peak of HONO appears which shows that the conversion of NO$_2$ into HONO is a fast process (curve (c), Figure 5.3). The observed HONO yields defined as the ratio of the amount of HONO released to the amount of NO$_2$ taken up during the reaction time tended towards $100 \pm 10$% (Figure 5.3).

![Figure 5.3. NO$_2$ uptake on a sample of 10 mg of grey soot at $[NO_2] = (2.3 \pm 0.5) \times 10^{12}$ cm$^{-3}$ (orifice diameter = 8 mm). Curves (a), (b) and (c) correspond to the raw MS signals monitored at m/e 30, 46 and 47, respectively. Curve (c) describes HONO production.](image)

A similar behavior at low $[NO_2]$ has been observed in recent work on the reactivity of NO$_2$ on flame soot$^8$. The present reference experiments clearly showed that NO$_2$ adsorbs on
soot. This is in contrast with reference experiments with NO$_2$ on mineral dust which showed that NO$_2$ does not adsorb on dust substrate except on Saharan dust$^{16}$. In that case NO$_2$ reacted only NO$_3$ adsorbed on the substrate via an Eley-Rideal mechanism.

**Figure 5.4a.** Uptake of NO$_3$ on 10 mg of grey soot and resulting reaction products at [NO$_3$] = (7.0 ± 1.0) x 10$^{11}$ molecule cm$^{-3}$ like in Figure 5.2 (orifice diameter = 8 mm). Curve (a) represents the raw MS signal at m/e 62 for the NO$_3$ uptake on the soot sample. Curve (b) represents the raw MS signal at m/e 47 related to the production of gas phase HONO. Curve (c) represents the corrected MS signal at m/e 30 corresponding to the production of gas phase NO.

During the uptake of NO$_3$ on grey soot the MS signal at m/e 62 (curve (a), Figure 5.4a) partially recovered as the exposure time increases, indicating a decrease in the rate of uptake of NO$_3$, presumably owing to a decrease of the net number of available surface sites for reaction. As a consequence we observed an apparent reduction of the uptake coefficient. As displayed in Figure 5.4a, a large burst of HONO at m/e 47 coincident with the uptake of NO$_3$ has been observed immediately after the exposure of the sample which reaches steady state after 500 s (curve (b), Figure 5.4a). Small amounts of NO have also been observed at the beginning of the reaction and tended to zero at steady-state conditions (curve (c), Figure 5.4a). A fast rate of initial formation of HONO and NO has been observed immediately after exposure of the sample to NO$_3$. The observed HONO formation results from the reduction of NO$_2$ by reducing H atoms in both C – H bonds on the soot according to reactions (5.1a) and (5.1b)$^{17}$:
\[ \text{NO}_2 \rightarrow \text{NO}_2\text{(ads)} \]  
\[ \text{NO}_2\text{(ads)} \text{ or } \text{NO}_2 + \{\text{C} - \text{H}^1\}_\text{red} \rightarrow \text{HONO} + \{\text{C} \}_\text{ox} \]  

The species listed in curved brackets refer to surface adsorbates. \{\text{C} - \text{H}^1\}_\text{red} represents a surface site that reduces NO\(_2\) to HONO and \{\text{C} \}_\text{ox} is the same site after surface oxidation by NO\(_2\) on soot. The interaction of NO\(_2\) with an adsorption site in reaction (5.1a) must be weak; otherwise NO\(_2\) would not be sufficiently mobile to subsequently encounter other surface sites for reaction, (5.1b) in a Langmuir-Hinshelwood mechanism.

**Figure 5.4b.** Uptake of NO\(_3\) on 10 mg of grey soot and resulting reaction products at [NO\(_3\)] = (7.0 ± 1.0) \times 10^{11} \text{ molecule cm}^{-3} \text{ (from experiment displayed in Figure 5.2, orifice diameter = 8 mm)} \text{ Curve (a) represents the raw MS signal at m/e 62 for the NO}_3\text{ uptake on the soot sample. Curve (b) is the calculated MS signal at m/e 46, I}_\text{exc}^{46}, \text{ corresponding to N}_2\text{O}_5\text{ formation. Curve (c) represents the raw MS signal at m/e 63 for the impurity HNO}_3\text{ uptake on soot. Positive flow MS signal at m/e 63 indicated by the hatched area under curve (c) represents the net amount of generated HNO}_3.\text{ For all grey and black soot samples we have observed the formation of small amounts of gas phase N}_2\text{O}_5 which may be related to the uptake of NO}_2\text{ in the presence of adsorbed NO}_3. \text{ It is important to note that NO}_2\text{ itself reacts both on grey and black decane soot. Using relation (3.E5) we have calculated the yield of N}_2\text{O}_5 from the increase of the MS signal at m/e 46, I}_\text{exc}^{46}, \text{ displayed in Figure 5.4b (curve (b)). The yield of N}_2\text{O}_5 following the} \]
uptake of NO$_3$ continuously increases and reaches a steady-state after 500 s. The noise of curve (b) is the consequence of the large experimental uncertainty.

From the experiment displayed in Figure 5.4b we conclude that for an initial value of [NO$_3$] = (7.0 ± 1.0) x 10$^{11}$ cm$^{-3}$ and in the presence of [NO$_2$] = (1.0 ± 0.5) x 10$^{12}$ cm$^{-3}$, (3.1 ± 0.3) x 10$^{12}$ molecule cm$^{-3}$ of N$_2$O$_5$ are produced at steady state conditions. Under our experimental conditions the formation of N$_2$O$_5$ may be related to the presence of NO$_2$ effusing from the NO$_3$ source via its reaction with adsorbed NO$_3$ on the soot substrate. The observed simultaneous uptake for both NO$_3$ and NO$_2$ suggests the formation of N$_2$O$_5$(ads) through the heterogeneous recombination reaction (5.2a):

$$\text{NO}_3\text{(ads)} + \text{NO}_2\text{(ads)} \rightarrow \text{N}_2\text{O}_5\text{(ads)} \quad (5.2a)$$

The conversion of NO$_3$ to N$_2$O$_5$ occurs via a Langmuir-Hinshelwood mechanism where NO$_3$ and NO$_2$ first adsorb onto the soot surface and subsequently react together forming N$_2$O$_5$ which in part leaves the surface. This reaction is the interfacial analogue of the well known gas-phase equilibrium (3.5b).

Once N$_2$O$_5$ has been formed in the adsorbed state, it may desorb into the gas phase.

$$\text{N}_2\text{O}_5\text{(ads)} \rightarrow \text{N}_2\text{O}_5\text{(g)} \quad (5.2b)$$

HNO$_3$, present as an impurity, reacted on the soot substrate as well. This reaction has been studied in recent laboratory work using the same experimental apparatus$^{15}$. As displayed in Figure 5.4b, a large initial uptake of HNO$_3$ was observed at m/e 63 (curve (c)). After a reaction time of 170 s, an excess in the MS signal at m/e 63 corresponding to formation rather than loss of HNO$_3$ was observed. The enhanced rate of formation of HNO$_3$ in the presence of soot means that part of N$_2$O$_5$(ads) formed in reaction (5.2a) undergoes hydrolysis on the surface of soot. HNO$_3$ is then released back into the gas phase according to reaction (3.5d). At these experimental conditions we observe the production of (2.0 ± 0.5) x 10$^{10}$ molecule cm$^{-3}$ of HNO$_3$ at steady state. The yield of HNO$_3$ observed in uptake experiments performed at [NO$_3$] = (2.5 ± 0.5) x 10$^{12}$ cm$^{-3}$ on different amounts of grey and black soot was 1.5-2 % of the total number of NO$_3$ molecules taken up (see Table 5.2).
<table>
<thead>
<tr>
<th>Soot Type</th>
<th>Mass (mg)</th>
<th>NO$_3$(lost) ( \times 10^{18} )</th>
<th>N$_2$O$_5$(g) ( \times 10^{17} )</th>
<th>NO$_2$(lost) ( \times 10^{18} )</th>
<th>NO(g) ( \times 10^{17} )</th>
<th>HNO$_3$(g) ( \times 10^{16} )</th>
<th>HONO(g) ( \times 10^{18} )</th>
<th>Average Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grey soot</td>
<td>5 mg</td>
<td>( (3.2 \pm 0.7) \times 10^{18} )</td>
<td>( (7.0 \pm 1.7) \times 10^{17} )</td>
<td>( 3.2 \pm 0.5 \times 10^{18} )</td>
<td>( 4.8 \pm 0.5 \times 10^{16} )</td>
<td>( 4.8 \pm 0.5 \times 10^{16} )</td>
<td>( 1.6 \pm 0.2 \times 10^{18} )</td>
<td>( (2.5 \pm 0.8) \times 10^{18} )</td>
</tr>
<tr>
<td></td>
<td>10 mg</td>
<td>( (3.3 \pm 0.7) \times 10^{18} )</td>
<td>( (8.5 \pm 1.4) \times 10^{17} )</td>
<td>( 6.5 \pm 1.0 \times 10^{17} )</td>
<td>( 8.0 \pm 0.6 \times 10^{16} )</td>
<td>( 6.8 \pm 0.7 \times 10^{16} )</td>
<td>( 1.6 \pm 0.5 \times 10^{18} )</td>
<td>( 87% )</td>
</tr>
<tr>
<td></td>
<td>20 mg</td>
<td>( (3.3 \pm 0.7) \times 10^{18} )</td>
<td>( (8.4 \pm 1.2) \times 10^{17} )</td>
<td>( 7.0 \pm 1.0 \times 10^{17} )</td>
<td>( 5.3 \pm 0.5 \times 10^{16} )</td>
<td>( 5.3 \pm 0.5 \times 10^{16} )</td>
<td>( 2.5 \pm 0.8 \times 10^{18} )</td>
<td>( 87% )</td>
</tr>
<tr>
<td></td>
<td>average</td>
<td>( (3.3 \pm 0.7) \times 10^{18} )</td>
<td>( (8.5 \pm 1.4) \times 10^{17} )</td>
<td>( 7.0 \pm 1.0 \times 10^{17} )</td>
<td>( 5.3 \pm 0.5 \times 10^{16} )</td>
<td>( 5.3 \pm 0.5 \times 10^{16} )</td>
<td>( 2.5 \pm 0.8 \times 10^{18} )</td>
<td>( 87% )</td>
</tr>
<tr>
<td>Black soot</td>
<td>5 mg</td>
<td>( (3.2 \pm 0.5) \times 10^{18} )</td>
<td>( 1.0 \pm 0.6 \times 10^{18} )</td>
<td>( 2.8 \pm 0.4 \times 10^{18} )</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>( 94% )</td>
</tr>
<tr>
<td></td>
<td>10 mg</td>
<td>( (3.4 \pm 0.8) \times 10^{18} )</td>
<td>( 7.2 \pm 1.2 \times 10^{17} )</td>
<td>( 3.0 \pm 0.6 \times 10^{18} )</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>( 98% )</td>
</tr>
<tr>
<td></td>
<td>20 mg</td>
<td>( (3.5 \pm 0.5) \times 10^{18} )</td>
<td>( 7.0 \pm 1.0 \times 10^{17} )</td>
<td>( 3.0 \pm 0.8 \times 10^{18} )</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>( 98% )</td>
</tr>
<tr>
<td></td>
<td>average</td>
<td>( (3.5 \pm 0.5) \times 10^{18} )</td>
<td>( 7.0 \pm 1.0 \times 10^{17} )</td>
<td>( 3.0 \pm 0.8 \times 10^{18} )</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>( 98% )</td>
</tr>
</tbody>
</table>

*aYield of N$_2$O$_5$, NO and HNO$_3$ given as percentage with respect to the total number of molecules of NO$_3$ taken up on grey and black soot during a reaction time of 500 s.

*bYield of HONO given as a percentage with respect to the total number of molecules of NO$_2$(lost) – N$_2$O$_5$(g) taken up during a reaction time of 500 s.

Dash (-) indicates that no reaction product has been observed.

The average yield is calculated on the basis of the results obtained for 10 and 20 mg of soot because there is no mass dependence as shown from Figures 5.11 and 5.12.

Table 5.2. Summary of the reaction products during the heterogeneous reaction of NO$_3$ on grey soot samples at [NO$_3$]$_0$ = (2.3 ± 0.5) x 10$^{12}$ cm$^{-3}$ and [NO$_2$]$_0$ = (6.0 ± 1.0) x 10$^{12}$ cm$^{-3}$ (orifice diameter = 8 mm).
An increase of gas phase HNO₃ formation in the presence of soot aerosol has been observed in recent experimental work at very low humidities in which NO₂, HNO₃, NO₃/N₂O₅ reacted on soot particles in a large aerosol chamber. In the same study the reaction probability for reaction (3.5d) was assumed to be time independent and resulted in $\gamma = (4.0 \pm 2.0) \times 10^{-5}$.

In Table 5.2 we report the product yields for the NO₃ reaction on three different amounts of grey soot at $[\text{NO}_3] = (2.5 \pm 0.5) \times 10^{12} \text{ cm}^{-3}$. The mass balance reveals that 23-34% of NO₂ taken up on grey soot has been converted into gas phase N₂O₅ according to reactions (5.2a) and (5.2b). The remaining 66-77% of reacted NO₂ equals the yield of HONO produced according to reaction (5.1b) thereby satisfying the NO₂ mass balance for the number of molecules N of NO₂, namely $N(N_2O_5) + N(\text{HONO}) = N(\text{NO}_2)$. This condition summarizes that HONO is exclusively generated from the NO₂ precursor and that N₂O₅ contains one molecule of NO₂. Therefore, we may conclude that NO₃ reacting on grey soot does not generate HONO owing to the closed mass balance of NO₂. The fact that we observe a slow production of NO may not be attributable to the presence of NO₂. Previous work has already shown that HONO is the only gas phase product resulting from the reaction of pure NO₂ with grey soot. Therefore, NO₃ may decompose into NO on the soot substrate according to the following decomposition reaction at the exclusion of NO₂ as a NO precursor:

$$\text{NO}_3 + \text{soot} \rightarrow \text{NO} + \text{products} \quad (5.3)$$

The amount of produced NO has been calculated from the excess MS signal at m/e 30, $I_{30}^{\text{exc}}$ in according to equation (5.12). The yield of NO did not show a significant variation with $[\text{NO}_3]$ and the amount of soot. Table 5.2 displays the fact that NO corresponds to nearly 10-12% of NO₃ taken up on the substrate. In addition, NO is unreactive towards fresh unexposed soot samples, a result obtained in reference experiments for the present soot samples.

In order to explain the trend of the observed product yields in Figures 5.4a and 5.4b we need to analyse the reaction mechanism at the beginning (between t = 62 s and t = 210 s) and at t > 210 s of the uptake process, respectively. At the beginning the fast disappearance of gas phase NO₂ leads to fast HONO production (reaction (5.1b)). At the same time, the fast uptake of NO₃ enhances its decomposition on the substrate resulting in
a fast gas phase production of NO (reaction (5.3)). Consequently, only part of \( \text{NO}_3 \) reacts with \( \text{NO}_2 \) and recombines to \( \text{N}_2\text{O}_5 \) according to reaction (5.2a). At \( t > 210 \) s the number of adsorbed \( \text{NO}_3 \) molecules increases thereby inhibiting the turnover of available surface sites where \( \text{NO}_3 \) decomposition can take place. Therefore, reactions (5.2a) and (5.2b) become predominant with respect to reactions (5.1b) and (5.3) at later reaction time. On the other hand, HONO production is on-going in steady-state by continuous \( \text{NO}_2 \) reaction on grey soot.

We therefore conclude that according to Table 5.2 32 -35 % of \( \text{NO}_3 \) which reacted on grey soot has been converted into \( \text{N}_2\text{O}_5 \) and NO. The remaining amount of \( \text{NO}_3 \) is irreversibly taken up on the substrate, however no saturation for uptake of \( \text{NO}_3 \) has been observed.

### 5.4.2 \( \text{NO}_3 \) interaction with black decane soot

The reaction of \( \text{NO}_3 \) on black soot was examined in the same manner as for grey soot discussed above (Figure 5.5). A fast initial rate of uptake \( \gamma_0 \) has been observed for all experiments performed within a \([\text{NO}_3]\) which ranged between \((2.7 \pm 0.5) \times 10^{11} \) cm\(^{-3}\) and \((2.3 \pm 0.5) \times 10^{12} \) cm\(^{-3}\) as reported in Table 5.2.

**Figure 5.5.** \( \text{NO}_3 \) uptake on a sample of 10 mg of black soot at \([\text{NO}_3] = (7.0 \pm 1.0) \times 10^{11} \) cm\(^{-3}\) (orifice diameter = 8 mm) Curves (a), (b), (d) and (e) correspond to the raw MS signals monitored at m/e 30, 46, 62 and 47, respectively. Curve (c) corresponds to the raw REMPI signal for \( \text{NO}_2 \) detection at \( \lambda_{\text{NO}_2} = 511 \) nm converted to a MS signal at m/e 46.
The amount of produced NO has been calculated from the excess MS signal at m/e 30, \( I_{30}^{ex} \), in accordance to equation (5.1). This signal has been converted into a flow rate using a calibration factor for pure NO and subsequently integrated over the reaction time. From reference uptake experiments with pure NO\(_2\) in the presence of black soot, we observed NO yields, defined as the ratio of the amount of NO released to the amount of NO\(_2\) taken up during the reaction time, tended towards 40 ± 10 % (Figure 5.6). Similar behavior at low [NO\(_2\)] was observed in recent work on the reactivity of NO\(_2\) on flame soot\(^8\).

\[ \text{Figure 5.6. NO}_2 \text{ uptake on a sample of 10 mg of black soot at [NO}_2\] = (2.3 ± 0.5) \times 10^{12} \text{ cm}^{-3} \text{ (orifice diameter = 8 mm). Curves (a), (b) and (c) correspond to the raw MS signals monitored at m/e 30, 46 and 47, respectively. Curve (d) (broken line) is related to NO production.} \]

Figure 5.7 shows the uptake \( \gamma \) of NO\(_3\) on 10 mg of black and grey soot at [NO\(_3\)] = (7.0 ± 1.0) \times 10^{11} \text{ cm}^{-3}. \) The value of \( \gamma_0 \) for black soot is twice that observed for grey soot. At steady state conditions the situation is reversed where \( \gamma_{ss} \) for black soot is smaller by a factor of two with respect to \( \gamma_{ss} \) for grey soot. However, the number on NO\(_3\) molecules taken up on both substrates during the exposure time of 500 s is approximately the same.
As already observed for grey soot, simultaneous uptake of both NO$_3$ and NO$_2$ on black soot suggests the formation of small amounts of gas phase N$_2$O$_5$ according to reactions (5.2a) and (5.2b).

![Figure 5.7. Uptake coefficient $\gamma$ vs. time for NO$_3$ on 10 mg of black (a) and grey (b) soot. [NO$_3$] = (7.0 ± 1.0) x 10$^{11}$ cm$^{-3}$ (orifice diameter = 8 mm).](image)

Figure 5.7 displays the NO product flow generated during uptake of NO$_3$ on 10 mg of black and grey soot at the same experimental conditions. As already discussed NO$_2$ present in the hot NO$_3$ source reacts with black soot to produce mainly NO as exemplified in the interaction with amorphous carbon$^5$. NO$_2$ presumably interacts with black soot resulting in the formation of HONO akin to the reaction on grey soot which to a large extent decomposes into NO according to the following reaction mechanism proposed by Stadler$^8$:

\[
\text{NO}_2 + \{\text{C} - \text{H}\}_\text{red} \rightarrow \text{HONO}_{\text{ads}} + \{\text{C}\}_\text{ox} \quad (5.4a)
\]

\[
2\text{HONO}_{\text{ads}} \rightarrow \text{NO} + \text{NO}_2(\text{ads}) + \text{H}_2\text{O}_{\text{ads}} \quad (5.4b)
\]

The difference in the NO yields between black and grey soot, curves (a) and (b) in Figure 5.8 is clearly related to NO formation according to the reaction mechanism (5.4a) and (5.4b) and may occur in addition to the NO yield originating from the heterogeneous decomposition of NO$_3$ on the substrate according to reaction (5.3) as was the case for grey
soot (Figure 5.8, Table 5.2). Therefore, the separation of NO formation owing to HONO and NO$_3$ decomposition is not possible for the black soot substrate.

![Figure 5.8](image_url)

**Figure 5.8.** NO rate of formation vs. time for NO$_3$ on 10 mg of (a) black and (b) grey soot. [NO$_3$] = (7.0 ± 1.0) x 10$^{11}$ cm$^{-3}$ (orifice diameter = 8 mm).

In recent work performed by Stadler$^8$, black decane soot was exposed to a flow of pure HONO in order to decide whether or not HONO produced on black soot may irreversibly adsorb on the surface or decompose to NO. In that work fast uptake of HONO and production of NO was observed. The total NO product yield at limiting high concentration was 50% with respect to HONO taken up, whereas for [HONO] = (3.7 ± 0.4) x 10$^{11}$ cm$^{-3}$ the total product remaining yield consisted of a 40% NO and 10% NO$_2$. The missing balance of nitrogen was attributed to a reservoir of HONO or reaction product adsorbed on the soot surface. We note that the NO rate of formation resulting from HONO decomposition on black soot is a slow process and is sustained at steady state conditions. On the other hand, the NO rate of formation resulting from NO$_3$ decomposition on grey soot rapidly tends to zero at steady state conditions as shown in Figure 5.8.

Table 5.3 reports the NO yield resulting from the uptake of NO$_3$ an 10 mg of grey and black soot at [NO$_3$] between (2.7 ± 0.5) x 10$^{11}$ cm$^{-3}$ and (2.3 ± 0.5) x 10$^{12}$ cm$^{-3}$. The yield of NO for black soot over an integration period of 500 s was 5 - 8% larger than for grey soot. The calculated NO yield expressed as a percentage with respect to the total number of molecules of NO$_3$ taken up during the same reaction time resulted in a value of (13 ± 3.0)% for grey soot and (20 ± 5.0)% for black soot. The larger value of the NO
yield found for black soot is clearly attributable to HONO decomposition in the aftermath of the uptake of NO$_2$ on black soot. The small difference in the NO yields reported in Table 5.3 suggests that most of HONO remains adsorbed on black soot rather than decompose and form NO.

<table>
<thead>
<tr>
<th>[NO$_3$]$_0$ cm$^{-3}$</th>
<th>NO (grey soot)</th>
<th>NO (black soot)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(2.7 \pm 0.5) \times 10^{11}$</td>
<td>$(1.6 \pm 0.4) \times 10^{17} \ 13%$</td>
<td>$(2.0 \pm 0.5) \times 10^{17} \ 20%$</td>
</tr>
<tr>
<td>$(3.8 \pm 1.8) \times 10^{11}$</td>
<td>$(2.0 \pm 0.6) \times 10^{17} \ 11%$</td>
<td>$(2.6 \pm 0.7) \times 10^{17} \ 19%$</td>
</tr>
<tr>
<td>$(7.0 \pm 1.0) \times 10^{11}$</td>
<td>$(2.6 \pm 0.5) \times 10^{17} \ 9%$</td>
<td>$(4.3 \pm 0.4) \times 10^{17} \ 16%$</td>
</tr>
<tr>
<td>$(1.5 \pm 0.5) \times 10^{12}$</td>
<td>$(3.0 \pm 0.7) \times 10^{17} \ 8%$</td>
<td>$(5.8 \pm 0.8) \times 10^{17} \ 14%$</td>
</tr>
<tr>
<td>$(2.3 \pm 0.5) \times 10^{12}$</td>
<td>$(3.3 \pm 0.4) \times 10^{17} \ 10%$</td>
<td>$(5.1 \pm 0.7) \times 10^{17} \ 15%$</td>
</tr>
</tbody>
</table>

*Yield of NO given as a percentage with respect to the total number of molecules of NO$_3$ taken up during the same reaction time.

**Table 5.3.** Summary of NO yield resulting from the uptake of NO$_3$ with 10 mg of grey and black soot at different [NO$_3$] (orifice diameter = 8 mm).

As reported in Table 5.3, the absolute yield of NO increases by almost a factor of 2 and 2.5 for grey and black soot, respectively at [NO$_3$] > $(7.0 \pm 1.0) \times 10^{11}$ cm$^{-3}$. This surprising result apparently depends on [NO$_3$], thus suggesting that the decomposition of NO$_3$ into NO involves a bimolecular or higher order process on black soot which becomes observable at high surface coverage of NO$_3$. We know from previous work$^8$ that NO cannot originate from NO$_2$ reacting on grey soot. The present work suggests that the calculated NO desorbing form black soot comes from decomposition of adsorbed HONO on the substrate.

### 5.5 Uptake kinetics of NO$_3$ on decane soot

The interaction of NO$_3$ with grey and black decane soot shows that after an initial fast uptake of NO$_3$ there is no saturation of the sample at steady state conditions. Figure 5.9 and Table 5.4 display the values of $\gamma_{ss}$ as a function of [NO$_3$] for grey and black soot. The uncertainties for NO$_3$ uptake experiments were determined from the signal to noise ratio of the MS signal at m/e 62.
After extrapolation of the data we note that for a variation of $[\text{NO}_3]$ between $(2.7 \pm 0.5) \times 10^{11} \text{ cm}^{-3}$ and $(7.0 \pm 1.0) \times 10^{11} \text{ cm}^{-3}$ $\gamma_{ss}$ decreases from $0.2 \pm 0.03$ to $0.11 \pm 0.01$ for both types of soot. Variations of $[\text{NO}_3]$ between $(7.0 \pm 1.0) \times 10^{11} \text{ cm}^{-3}$ and $(2.3 \pm 0.5) \times 10^{12} \text{ cm}^{-3}$ result in a constant value of $\gamma_{ss} = (6.5 \pm 1.5) \times 10^{-2}$, independent of $[\text{NO}_3]$.

![Figure 5.9. Uptake coefficient $\gamma_{ss}$ of NO$_3$ as a function of $[\text{NO}_3]$ (orifice diameter = 8 mm): NO$_3$ on black (triangles) and grey soot (open circles).](image)

<table>
<thead>
<tr>
<th>$[\text{NO}_3]_0 \text{ cm}^{-3}$</th>
<th>$\gamma_0$ (grey soot)</th>
<th>$\gamma_{ss}$ (grey soot)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(2.7 \pm 0.5) \times 10^{11}$</td>
<td>$0.44 \pm 0.05$</td>
<td>$0.2 \pm 0.02$</td>
</tr>
<tr>
<td>$(3.8 \pm 1.8) \times 10^{11}$</td>
<td>$0.35 \pm 0.06$</td>
<td>$0.15 \pm 0.03$</td>
</tr>
<tr>
<td>$(7.0 \pm 1.0) \times 10^{11}$</td>
<td>$0.15 \pm 0.07$</td>
<td>$0.11 \pm 0.02$</td>
</tr>
<tr>
<td>$(1.5 \pm 0.5) \times 10^{12}$</td>
<td>$0.12 \pm 0.05$</td>
<td>$(5.7 \pm 1.3) \times 10^{-2}$</td>
</tr>
<tr>
<td>$(1.8 \pm 0.5) \times 10^{12}$</td>
<td>$0.12 \pm 0.05$</td>
<td>$(6.5 \pm 1.0) \times 10^{-2}$</td>
</tr>
<tr>
<td>$(2.3 \pm 0.5) \times 10^{12}$</td>
<td>$0.12 \pm 0.04$</td>
<td>$(7.2 \pm 1.5) \times 10^{-2}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$[\text{NO}_3]_0 \text{ cm}^{-3}$</th>
<th>$\gamma_0$ (black soot)</th>
<th>$\gamma_{ss}$ (black soot)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(2.7 \pm 0.5) \times 10^{11}$</td>
<td>$0.5 \pm 0.07$</td>
<td>$0.2 \pm 0.03$</td>
</tr>
<tr>
<td>$(5.5 \pm 1.0) \times 10^{11}$</td>
<td>$0.35 \pm 0.08$</td>
<td>$0.17 \pm 0.02$</td>
</tr>
<tr>
<td>$(8.0 \pm 0.5) \times 10^{11}$</td>
<td>$0.3 \pm 0.04$</td>
<td>$(6.7 \pm 1.4) \times 10^{-2}$</td>
</tr>
<tr>
<td>$(1.4 \pm 0.5) \times 10^{12}$</td>
<td>$0.2 \pm 0.05$</td>
<td>$(6.5 \pm 1.5) \times 10^{-2}$</td>
</tr>
<tr>
<td>$(2.3 \pm 0.5) \times 10^{12}$</td>
<td>$0.18 \pm 0.03$</td>
<td>$(4.8 \pm 1.0) \times 10^{-2}$</td>
</tr>
</tbody>
</table>

Table 5.4. Summary of uptake experiments of NO$_3$ on 10 mg grey and black decane soot: initial ($\gamma_0$) and steady state ($\gamma_{ss}$) uptake coefficients (orifice diameter = 8 mm).

From this series of measurements it is evident that $\gamma_{ss}$ follows a rate law pseudo first order in NO$_3$ for $[\text{NO}_3] > (7.0 \pm 1.0) \times 10^{11} \text{ cm}^{-3}$. Conversely, for $[\text{NO}_3] < (7.0 \pm 1.0) \times 10^{11} \text{ cm}^{-3}$
the inverse dependence of \( \gamma_{ss} \) on \([\text{NO}_3]\) suggests that the mechanism of \text{NO}_3\) uptake is complex and does not correspond to a simple first-order uptake. A similar behavior has been observed for the interaction of \text{NO}_3\) with mineral dust substrates such as Kaolinite\(^{16}\) discussed in Chapter 3.

![Figure 5.10. Uptake coefficient \( \gamma_0 \) of \text{NO}_3\) as a function of \([\text{NO}_3]\) (orifice diameter = 8 mm): \text{NO}_3\) on black (full squares) and grey soot (open squares).](image)

If \( \gamma_{ss} \) for black and grey soot seems to follow the same trend as a function of \([\text{NO}_3]\), this is not the case for the value of the initial uptake coefficient \( \gamma_0 \). As shown in Figure 5.10 for \([\text{NO}_3] \geq (7.0 \pm 0.5) \times 10^{11} \text{ cm}^{-3} \) the \( \gamma_0 \) value of \text{NO}_3\) corresponds to a pseudo-first order reaction and \( \gamma_0 \) for black and grey decane soot are almost identical. However, at \([\text{NO}_3] < (1.0 \pm 0.5) \times 10^{11} \text{ cm}^{-3} \) the reactivity as measured by \( \gamma_0 \) of \text{NO}_3\) on black soot is larger with respect to grey soot.
Figures 5.11 and 5.12 display the steady state uptake $\gamma_{ss}$ of NO$_3$ as a function of the mass of grey and black soot (Table 5.5). A linear dependence $\gamma_{ss}$ as a function of the substrate mass is clearly visible for soot masses of up to 7 mg.

We note that for the interaction NO$_3$-soot there is no mass dependence beyond the mass of 7 mg which we interpret as the minimum mass required to form a coherent monolayer of
soot. This value of 7 mg corresponds to a soot loading of $7/19.6 = 0.37$ mg/cm$^2$ and is identical for black soot. In earlier work$^3$ a value for the threshold loading of $0.41 \pm 0.1$ mg/cm$^2$ has been determined. Soot is a porous material and on the time scale of our experiment we do not expect NO$_3$ to explore the internal surface, of the pores as given for instance by the BET surface area as suggested by the present results.

<table>
<thead>
<tr>
<th>Mass (mg)</th>
<th>$\gamma_0$ grey soot</th>
<th>$\gamma_{ss}$ grey soot</th>
<th>$\gamma_0$ black soot</th>
<th>$\gamma_{ss}$ black soot</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>$(7.0 \pm 4.0) \times 10^{-2}$</td>
<td>$(1.8 \pm 1.2) \times 10^{-2}$</td>
<td>$(5.0 \pm 3.5) \times 10^{-2}$</td>
<td>$(1.5 \pm 1.3) \times 10^{-2}$</td>
</tr>
<tr>
<td>3</td>
<td>$0.1 \pm 0.05$</td>
<td>$(3.0 \pm 1.7) \times 10^{-2}$</td>
<td>$(8.0 \pm 3.0) \times 10^{-2}$</td>
<td>$(2.5 \pm 1.3) \times 10^{-2}$</td>
</tr>
<tr>
<td>5</td>
<td>$0.16 \pm 0.035$</td>
<td>$(5.5 \pm 1.6) \times 10^{-2}$</td>
<td>$0.15 \pm 0.035$</td>
<td>$(5.0 \pm 1.5) \times 10^{-2}$</td>
</tr>
<tr>
<td>7</td>
<td>$0.17 \pm 0.035$</td>
<td>$(6.5 \pm 1.6) \times 10^{-2}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>$0.12 \pm 0.030$</td>
<td>$(7.2 \pm 1.2) \times 10^{-2}$</td>
<td>$0.18 \pm 0.03$</td>
<td>$(6.7 \pm 1.4) \times 10^{-2}$</td>
</tr>
<tr>
<td>15</td>
<td>$0.2 \pm 0.032$</td>
<td>$(8.0 \pm 2.0) \times 10^{-2}$</td>
<td>$0.2 \pm 0.03$</td>
<td>$(7.5 \pm 2.3) \times 10^{-2}$</td>
</tr>
<tr>
<td>20</td>
<td>$0.2 \pm 0.032$</td>
<td>$(8.5 \pm 2.0) \times 10^{-2}$</td>
<td>$0.2 \pm 0.03$</td>
<td>$(8.4 \pm 2.0) \times 10^{-2}$</td>
</tr>
</tbody>
</table>

Table 5.5. Summary of uptake experiments with NO$_3$ on grey and black soot as a function of sample mass ([NO$_3$] = $(2.3 \pm 0.5) \times 10^{12}$ cm$^{-3}$, orifice diameter = 8mm).

We conclude that it is not necessary to apply the pore diffusion theory$^{19}$ in the case of NO$_3$ - soot in order to correct $\gamma$ of NO$_3$ for the effect of the pore diffusion of soot. We take this result as justification to use the geometric surface area in evaluating the gas-surface collision frequency $\omega$ under the constraint of the present experimental conditions of low gas-phase residence times for NO$_3$, in part owing to the measured large values of the uptake coefficient $\gamma_{ss}$. The linear mass dependence of $\gamma_0$ and $\gamma_{ss}$ observed below 7 mg for grey and black soot and displayed in Figures 5.11 and 5.12 means that we do not have formed a coherent layer of soot on the sample holder. Beyond 7 mg of soot the initial uptake coefficient $\gamma_0$ is very large and stayed constant, about 0.2, and the molecule of NO$_3$ does not have the time to explore the internal surface area of the substrate. Therefore, as already discussed for N$_2$O$_5$ on mineral dust substrates, we do not think that the application of the pore diffusion theory$^{19}$ may be applied for $\gamma_0$. At steady state conditions we observed that the uptake coefficient $\gamma_{ss}$ follows the same trend as for $\gamma_0$. In that case the application of the pore diffusion theory may be only interpreted as a lower limit for $\gamma$ whereas $\gamma_{ss}$ based on the geometrical surface area may be regarded as an upper limit to the true value of $\gamma$. 
The amount of adsorbed NO₃ for the uptake experiments on grey and black soot turned out to be the same. At \([\text{NO}_3] = (2.3 \pm 0.5) \times 10^{12} \text{ cm}^{-3}\) \((3.3 \pm 0.7) \times 10^{18}\) molecules of NO₃ were adsorbed on 10 mg of soot during a reaction time of 500 s. During this time the samples did not saturate. As discussed in recent work on the interaction of NO₃ on mineral dust, NO₃ may be represented by a 4.5 Å diameter sphere with a projected surface area of \(1.6 \times 10^{-15} \text{ cm}^2/\text{molecule}\) which leads to a full surface coverage of \(6.3 \times 10^{14} \text{ molecules cm}^{-2}\). The 10 mg sample of grey soot has a total surface area of \(6.9 \times 10^3 \text{ cm}^2\) based on a BET surface area of 69 m²/g (see Table 5.1). This leads to \(1.3 \times 10^{16}\) and \(4.3 \times 10^{19}\) molecules NO₃ forming a monolayer on 10 mg of soot based on the geometric and BET surface area, respectively. Therefore, the total number of \(3.3 \times 10^{18}\) molecules of NO₃ taken up on the substrate led to a surface concentration of \(\frac{3.3 \times 10^{18}}{6.9 \times 10^3} = 4.8 \times 10^{14}\) molecule cm² which corresponds to a coverage (θ) of approximately 76% based on the BET surface area.

5.6 Conclusions

Very recently, HONO formation was observed under laboratory conditions when NO₂ was adsorbed on soot particles in the presence of water vapour⁸,¹⁷. It was shown that NO₂ can be reduced on fresh soot particles involving reactive sites, possibly weakly bound hydrogen atoms or other reducing precursors. In addition, the maximum number of NO₂ molecules which can be reduced on the surface of soot particles is limited to less than a monolayer based on the total internal surface such as measured by BET. Therefore, soot cannot be the exclusive source of HONO in the polluted boundary layer¹. However, from the present results it is clear that NO₃ decomposition on grey soot may lead to an additional source of NO at night.

From the present uptake experiments performed on grey and black soot we may extrapolate \(\gamma\) to vanishing NO₃ concentration as displayed in Figures 5.9 and 5.10 and obtain an estimation of \(\gamma_{ss}\) for \([\text{NO}_3] < 7.0 \times 10^{11} \text{ molecule cm}^{-3}\). With tropospheric \([\text{NO}_3]\) at a typical value of \(2.0 \times 10^9 \text{ molecule cm}^{-3}\), \(\gamma_{ss}\) tends towards values larger than 0.3 according to the results displayed in Figure 5.9.
The NO₃ loss rate constant \( k_{\text{het}} \) due to heterogeneous uptake onto aerosols is given by
\[
k_{\text{het}} = \tau^{-1}(\text{NO}_3) = \gamma A \bar{\nu}/4 \]
where \( \gamma \) is the uptake coefficient of NO₃ and is a function of the mineral dust aerosol composition; \( A \) is the surface area density of the dust and \( \bar{\nu} \) is the mean molecular speed of NO₃.

Urban air masses typically contain 10 \( \mu \text{g m}^{-3} \) black carbon aerosols\(^{20} \), which corresponds to an aerosol surface area density of 7.0 x 10\(^{-6} \) cm\(^2\) cm\(^{-3}\) and 2.2 x 10\(^{-5} \) cm\(^2\) cm\(^{-3}\) for grey and black soot, respectively assuming the BET surface area reported in Table 5.1. Using these values and \( \gamma = 0.3 \) from our extrapolated value for NO₃ from figure 5.9 we evaluate a lifetime of 3 min and 1 min for NO₃ on grey and black soot, respectively. As already discussed in Chapter 3, this value has to be compared to the diurnal photolysis of NO₃ in fact during the day NO₃ has a short lifetime of about 5s due to its strong absorption in the visible region (662 nm). Since the photochemical gas-phase loss process of NO₃ only takes place during the day, NO₃ loss by reaction on soot and other aerosol surfaces such as mineral dust\(^{21} \) is important only during the night.

In recent study on soot aerosol\(^{18} \) the uptake of NO₃ on soot yielded an upper limit of \( \gamma \leq 3.0 \times 10^{-4} \) at very low relative humidities (H₂O < 10 ppm), whereas at 50% rh it resulted in an upper limit of \( \gamma \leq 1.0 \times 10^{-3} \). These values are 2 (50% rh) and 3 order of magnitude lower than the \( \gamma \) value of 0.3 that results from the extrapolation for \([\text{NO}_3] < 7.0 \times 10^{11} \) molecule cm\(^{-3}\) in figure 5.9. In that same study\(^{18} \) the impact of soot aerosol surface reactions on the formation of photochemical ozone was investigated in a box model calculation\(^{18} \). The results showed that soot has a minor impact on ozone formation at low \([\text{NO}_3]\), in contrast soot may cause ozone reduction of up to 10% at high \([\text{NO}_3]\). However, we must point out that the nature of the carbonaceous substrate, namely carbon from a spark ignition generator\(^{18} \), is most probably significantly different from flame soot used in the present study.
5.7 Outlook

The large reactivity of NO\textsubscript{3} on grey and black soot and its subsequent reaction with adsorbed NO\textsubscript{2} coming from the hot NO\textsubscript{3} source resulted in rapid production of N\textsubscript{2}O\textsubscript{5}. As reported in Table 5.2, the yield of N\textsubscript{2}O\textsubscript{5} approximately corresponds to 22-25\% of NO\textsubscript{3} taken up on grey and black soot. Reference experiments will be performed in the Knudsen flow reactor in order to measure the reactivity of pure N\textsubscript{2}O\textsubscript{5} on soot. These measurements will allow us to determine the fraction of N\textsubscript{2}O\textsubscript{5} generated as a primary product in reactions (5.2a) and (5.2b) and the fraction released into the gas phase upon uptake of NO\textsubscript{3}. Particular attention will be paid to the detection of potential gas phase products such as NO, NO\textsubscript{2} and HNO\textsubscript{3}. For this purpose we are looking at a new dye laser frequency in order to increase the sensitivity of REMPI detection of NO at $\lambda\textsubscript{NO} = 452.6$ nm and possibly also of NO\textsubscript{2}. 
5.8 References


(6) Rogaski, C. A.; Golden, D. M.; Williams, L. R.: Reactive uptake and hydration experiments on amorphous carbon treated with NO\textsubscript{2}, SO\textsubscript{2}, O\textsubscript{3}, HNO\textsubscript{3}, and H\textsubscript{2}SO\textsubscript{4}, Geophysical Research Letters, 24, 381-384, (1997).


(8) Stadler, D.; Rossi, M. J.: The reactivity of NO\textsubscript{2} and HONO on flame soot at ambient temperature: The influence of combustion conditions, Physical Chemistry Chemical Physics, 2, 5420-5429, (2000).


5. High reactivity and chemical kinetics of NO₃ on laboratory flame soot


The heterogeneous decomposition of ozone on atmospheric mineral dust surrogates at ambient temperature
CHAPTER 6

THE HETEROGENEOUS DECOMPOSITION OF OZONE ON ATMOSPHERIC MINERAL DUST SURROGATES AT AMBIENT TEMPERATURE

6.1 Introduction

Ozone decomposition on mineral dust is a reaction of atmospheric significance that has attracted considerable attention\(^1\text{-}^6\). So far, the mechanism for O\(_3\) destruction on mineral dust is unclear. Recent work has shown that ozone loss can be due to decomposition, catalytic destruction or absorption on mineral oxides\(^7\).

Dentener and co-workers suggested\(^2\) in their modelling studies, that the ozone destruction on mineral aerosol surfaces could lead to a 10\% reduction of O\(_3\) concentration in the dust source areas. This study assumed a reaction probability \(\gamma = 5.0 \times 10^{-5}\) for O\(_3\) on mineral dust surfaces. Recently, Bauer and co-workers\(^8\) have found a decrease of 5\% of the global tropospheric ozone mass in a global modelling study employing an uptake coefficient \(\gamma_{O_3} = 1.0 \times 10^{-5}\) as a best guess. On the other hand, another modelling study which considered the coupling of the photochemical and heterogeneous effects of dust\(^9\), led to a global ozone decrease of 0.7\% assuming \(\gamma_{O_3} = 5.0 \times 10^{-5}\). These significant differences may be caused by differences in the model formulations.

The present chapter reports a kinetic study of the heterogeneous reaction of O\(_3\) on mineral dust surrogates presented as powders; its objective is to investigate the mechanism of adsorption of ozone on surrogates of mineral dust as well as the kinetics of the heterogeneous reaction including reaction products that are released into the gas phase.
6.2 Experimental setup

All experiments were performed in the Knudsen flow reactor operating in the molecular flow regime. The characteristic parameters and relevant kinetics expressions for steady state and pulsed valve experiments are reported in Chapter 2 as well the production of O₃. The mineral dust composition used in this study is reported in Table 3.1. The two kinds of sample holders, TEFLON® coated Pyrex of 19.6 cm² of available sample surface and an internal reduction piece made out of DELRIN® of available surface area of 4.9 cm², did not show any reactivity with O₃ under the present experimental conditions.

According to the UV absorption we estimated that the O₂ impurity in the O₃ sample amounted to 15-28% of the total pressure. Mass m/e 32 was both a marker for the potential reaction product O₂ as well as an important fragment of O₃. In addition, one has to consider that the MS signal S_{32}(t) at m/e 32 will contain the contributions due to the O₂ impurity present in the O₃ sample that amounts to 15-28% of the total pressure according to UV absorption, and due to the small O₂ background already present in the flow reactor.

Ozone has a measurable fragment and a parent peak at m/e 32 (O₂⁻) and m/e 48 (O₃⁻), respectively. In the absence of the sample, one has to consider the contributions to the MS signal S_{32}⁰ at m/e 32 due to the O₂ impurity S_{32}^{imp} in the O₃ sample and to the O₂ background S_{32}^{back} in the flow reactor. We define 

\[ S_{32}^{imp} = \frac{F_{O_{2}}^{imp}}{C_{O_{2}}} \]

where \( F_{O_{2}}^{imp} \) is the O₂ flow relative to the total measured flow \( F_{O_{2}+O_{3}}^{tot} \) and is expressed as

\[ F_{O_{2}}^{imp} = \frac{F_{O_{2}+O_{3}}^{tot} \cdot x}{100} \]

with \( x(\%) \) being the percentage O₂ impurity in the total measured flow \( F_{O_{2}+O_{3}}^{tot} \). The calibration factor \( C_{O_{2}} \) has been determined in separate experiments where the MS signal intensity at m/e 32 was measured as a function of the injected pure O₂ flow. The percentage of O₂ in O₃ is measured in separate calibration experiments using UV absorption as discussed above.

Before exposing the substrate to ozone the corrected MS signal at m/e 32, \( S_{32}^{0} \), is given by equation (6.E1):
Upon lifting the plunger the flow $F_{O_2}(t)$ of oxygen produced by ozone decomposition on the examined substrate has been calculated using the following equation (6.E2):

$$F_{O_2}(t) = \left( S_{32}'(t) - S_{32}^{\text{back}} - S_{32}^{\text{imp}} - R_{32}^{\text{imp}} S_{48}(t) \right) C_{O_2}$$  \hspace{1cm} (6.E2)

where $S_{32}'(t)$ is the raw MS signal at m/e 32 during $O_3$ uptake, $R_{32}^{\text{imp}} = S_{32}^{0} / S_{48}^{0} = 1.7 \pm 0.5$ represents the ratio between the corrected MS signal at m/e 32 and 48 before the exposure of the sample to ozone, $S_{48}(t)$ is the MS signal at m/e 48 during the uptake experiment and $C_{O_2}$ is the calibration factor for oxygen. Equation (6.E2) assumes that molecular oxygen does not react with the sample; a fact that has been established is separate reference experiments. Therefore, $\Delta F_{O_3}(t) = F_{O_2}^{\text{in}}(t) - F_{O_2}^{\text{out}}(t)$ represents the flow or the rate of $O_3$ lost during the uptake experiment that was calculated by calibrating the resulting MS signal at m/e 48.

The parameter of main interest is given by the ratio $r(t) = F_{O_2}(t)/\Delta F_{O_3}(t)$ as a function of time during which the surface is exposed to $O_3$. It is the relative yield of $O_2$ generated per $O_3$ molecule destroyed on the substrate.

### 6.3.1 $O_3$ reaction on poorly ordered Kaolinite

The uptake of ozone on Kaolinite samples taken as a surrogate for mineral dust monitored at m/e 48 was measured at room temperature (RT) with the goal to obtain a quantitative measure of the reaction kinetics as well as the reaction products. The measurements were performed at ozone concentrations in the range $4.0 \times 10^{11}$ to $2.4 \times 10^{12}$ cm$^{-3}$. In the present data analysis, the observed uptake coefficient $\gamma_{\text{obs}}$ (equation 2.8) was calculated using the geometric surface area $A_s$ of the sample holder. The observed uptake coefficient $\gamma_{\text{obs}}$ became $\gamma_{ss}$, the steady state uptake coefficient, once steady state conditions were achieved after an exposure time of 600 s or so; $\gamma_0$ is $\gamma_{\text{obs}}$ at $t = 0$ s, that is immediately after lifting.
the plunger. Figure 6.1 shows a representative uptake experiment of ozone on 0.2 g of Kaolinite spread out on a surface A_s of 4.9 cm^2. Curves (a) and (b) correspond to the raw MS signal monitored at 32 (O_2^+) and m/e 48 (O_3^+), respectively. A constant flow of O_3 that was isolated from the sample by the isolation plunger was initially established. When the flow of O_3 reached a constant level, the isolation plunger was lifted and the initial uptake coefficient γ_0 of ozone on the substrate was obtained. A decrease of the uptake of ozone with exposure time was observed until steady state uptake is reached at t ≥ 800 s. This steady state level is presumably controlled by the competition between the rate of adsorption, heterogeneous reaction and desorption of ozone or its decomposition products.

**Figure 6.1.** Representative Knudsen-Cell experiment for O_3 uptake on 0.2 g sample of Kaolinite. Curves (a) and (b) correspond to raw MS signals monitored at m/e 32 and 48, respectively ([O_3] = (2.7 ± 0.7) x 10^{12} cm^{-3}; 14 mm orifice; surface sample area A_s = 4.9 cm^2).

Uptake experiments of O_3 on Kaolinite powder were systematically carried out by varying the initial concentration of O_3 and its residence time τ_g. For a given orifice size and thus τ_g we observed that k_{ss} was independent of [O_3] within experimental uncertainty. As a case in point we present data for the 14 mm orifice (τ_g = 0.2 s) and for [O_3] ranging between (4.0 ± 0.5) x 10^{11} and (2.4 ± 0.7) x 10^{12} cm^{-3}, leading to k_{ss} = (0.203 ± 0.033) s^{-1}, and a steady state uptake coefficient γ_{ss} = (9.0 ± 1.5) x 10^{-3} (dashed line in Figure 6.2, Table 6.1) based on the geometric surface area of the sample support.
From this series of measurements it is evident that the decomposition reaction of ozone on Kaolinite corresponds to a pseudo first-order rate constant \( k_{ss} \). However, if we decrease the orifice size, thus increase \( \tau_g \) at constant \([O_3] = (2.4 \pm 0.7) \times 10^{12} \text{ cm}^{-3}\) the values of \( k_{ss} \) decrease as displayed in Figure 6.3 and Table 6.2. The strong dependence of \( k_{ss} \) on \( \tau_g \) at a given \([O_3]\) suggests that the mechanism of ozone uptake is complex and does not correspond to a simple first-order rate law for uptake.

**Figure 6.2.** Plot of the pseudo-first order rate constant \( k_{ss} \) for steady state uptake of \( O_3 \) on 0.2 g of Kaolinite versus \( O_3 \) concentration at ambient temperature (14 mm orifice; surface sample area \( A_s = 4.9 \text{ cm}^2 \)).

**Table 6.1.** Results of uptake experiments of \( O_3 \) on 0.2 g (40.8 mg/cm\(^2\)) of Kaolinite at different concentrations and ambient temperature (14 mm orifice; surface sample area \( A_s = 4.9 \text{ cm}^2 \)).
These observations indicate that the reactivity of O\textsubscript{3} on Kaolinite decreases for long residence times $\tau_g$ as the heterogeneous reaction rate not only depends on the gas phase concentration but apparently also on intermediates whose surface concentration depend on the extent of reaction that scales with $\tau_g$. Therefore, the conclusion that the rate law is first order in O\textsubscript{3} based on the results of Figure 6.2 may be erroneous because of the apparent independence of $k_{ss}$ on [O\textsubscript{3}] over a narrow concentration range.

**Figure 6.3.** Plot of $k_{ss}$ of O\textsubscript{3} on 0.2 g of Kaolinite versus orifice size (full circles) at surface sample area $A_s = 4.9$ cm\textsuperscript{2}; ([O\textsubscript{3}] = (2.0 ± 0.5) x 10\textsuperscript{12} cm\textsuperscript{-3}). Open triangles correspond to samples that have been exposed to 4 mbar of O\textsubscript{3} for 16 h off-line.

<table>
<thead>
<tr>
<th>$k_{ss}$ (s\textsuperscript{-1})</th>
<th>$\gamma_{ss}$</th>
<th>Orifice (mm)</th>
<th>$\tau_g$ (s)</th>
<th>#O\textsubscript{3} reacted (Δt~800 s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2.2 ± 0.27) x 10\textsuperscript{-1}</td>
<td>(1.0 ± 0.12) x 10\textsuperscript{-2}</td>
<td>14</td>
<td>0.2</td>
<td>7.4 x 10\textsuperscript{17}</td>
</tr>
<tr>
<td>$^a$(4.8 ± 3.2) x 10\textsuperscript{-2}</td>
<td>(2.2 ± 1.4) x 10\textsuperscript{-3}</td>
<td>14</td>
<td>0.2</td>
<td>-</td>
</tr>
<tr>
<td>(1.5 ± 0.3) x 10\textsuperscript{-1}</td>
<td>(6.7 ± 1.4) x 10\textsuperscript{-3}</td>
<td>8</td>
<td>0.5</td>
<td>3.9 x 10\textsuperscript{17}</td>
</tr>
<tr>
<td>(1.2 ± 0.35) x 10\textsuperscript{-1}</td>
<td>(5.5 ± 1.6) x 10\textsuperscript{-3}</td>
<td>8</td>
<td>0.5</td>
<td>3.2 x 10\textsuperscript{17}</td>
</tr>
<tr>
<td>$^a$(4.3 ± 3.5) x 10\textsuperscript{-2}</td>
<td>(2.0 ± 1.6) x 10\textsuperscript{-3}</td>
<td>8</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>(5.6 ± 3.0) x 10\textsuperscript{-2}</td>
<td>(2.5 ± 1.4) x 10\textsuperscript{-3}</td>
<td>4</td>
<td>2.0</td>
<td>3.0 x 10\textsuperscript{17}</td>
</tr>
</tbody>
</table>

$^a$ after O\textsubscript{3} exposure (16h)

**Table 6.2.** Uptake experiments of O\textsubscript{3} on 0.2 g of Kaolinite for different orifices ($A_s = 4.9$ cm\textsuperscript{2}; [O\textsubscript{3}] = (2.0 ± 0.5) x 10\textsuperscript{12} cm\textsuperscript{-3}; integration time $\Delta t ~ 800$ s).
In order to confirm this hypothesis, further experiments were carried out on samples of Kaolinite by exposing them to a partial pressure of 4 Torr of O₃ during 16h in a separate static vessel. In the following we used the 8 and 14 mm orifices in order to probe the heterogeneous uptake of O₃ and obtained $k_{ss} = (4.3 \pm 3.5) \times 10^{-2}$ and $(4.8 \pm 3.2) \times 10^{-2} \text{ s}^{-1}$ for the 8 and 14 mm orifices, respectively. A similar value, namely $k_{ss} = (5.6 \pm 3.0) \times 10^{-2} \text{ s}^{-1}$, was already found for the 4 mm orifice without preliminary exposure to O₃ as shown in Figure 6.3. It seems that a long exposure of the sample to O₃ deactivates a large fraction of reactive surface sites and leads to values of $\gamma$ that are up to a factor of five smaller than $\gamma_{ss}$ measured at low $\tau_g$ (Figure 6.3). However, a constant “baseline” reactivity persists at steady-state independent of $\tau_g$, after O₃ pre-treatment. Therefore, this "baseline" or residual rate constant for O₃ decomposition is independent of [O₃] following the results displayed in Figure 6.3 as well as of $\tau_g$ used to probe the O₃/Kaolinite interaction (open triangles in Figure 6.3, Table 6.2). Theoretically, the value of $r(t)$ should tend towards 1.5 for the decomposition of O₃ according to the following pseudo-elementary reactions:

\[
O_3 + SS \rightarrow O(SS) + O_2 \quad (6.1)
\]

\[
O_3 + O(SS) \rightarrow O_2 + O_2(SS) \quad (6.2)
\]

where SS and O(SS) are reactive surface sites for O₃ and the atomic oxygen intermediate after O₃ decomposition, respectively. O₂(SS) indicates an adsorbed peroxy species formed in reaction (6.2) through oxidation of the atomic oxygen intermediate O(SS) by O₃. The present measurements do not allow the positive identification of the formation of O(SS) or O₂(SS). However, spectroscopic studies on the decay of O₃ on a manganese oxide substrate by Li and Oyama\textsuperscript{10,11} showed evidence of the formation of a peroxy species akin to O₂(SS) on the substrate surface. The final step in the ozone decomposition reaction may be the thermal decomposition of the peroxide species to form gaseous O₂ according to:

\[
O_2(SS) \rightarrow O_2 + SS \quad (6.3)
\]
Reaction (6.1) is much faster than reactions (6.2) and (6.3), and does not involve the most-abundant reaction intermediate, the peroxide species $O_3(SS)$. Therefore, reactions (6.2) and (6.3) will be rate-limiting and thus measurable. Reactions (6.1) and (6.2) are presumed to be irreversible because we have never detected $O_3$ in desorption using mass spectrometry.

The net is the sum of reactions (6.1), (6.2), and (6.3) and describes the catalytic decomposition of $O_3$ on mineral dust:

$$2O_3 \rightarrow 3O_2$$

(6.4)

This mechanism may explain why transition metal oxides such as manganese oxide, are good catalysts for ozone decomposition.

In the $O_3$ uptake experiment reported in Figure 6.4 $r(t)$ was always less than 1.5 so that catalytic decomposition of $O_3$ may be ruled out.

**Figure 6.4.** The relative yield $r(t)$ during the uptake experiment of $O_3$ on 0.2 g of Kaolinite. Curves (a), (b) and (c) represent plots of $r(t)$ at 14 mm ($\tau_g = 0.2$ s), 8 mm ($\tau_g = 0.5$ s) and 4 mm ($\tau_g = 2.0$ s) orifices, respectively. Curve (d) represents a plot of $r(t)$ at 1 mm for a saturated sample exposed to 4 Torr of $O_3$ during 16 h. ($[O_3] = (2.0 \pm 0.5) \times 10^{12}$ cm$^{-3}$, $A_s = 4.9$ cm$^2$).

At steady state $r(t)$ ranges from 1.0 for a short residence time $\tau_g = 0.2$ s for $O_3$ (curve (a), Figure 6.4), to essentially 0.2 for large residence time $\tau_g = 2.0$ s (curve (c), Figure 6.4).
For the O$_3$-pretreated Kaolinite discussed above, the ratio $r(t)$ hovers at small values so that $r(t) < 0.5$ during the whole duration of the uptake (curve (d), Figure 6.4).

The full mechanism is not as simple as just shown in reactions (6.1), (6.2), (6.3) and (6.4). There is evidence from the inverse dependence of the kinetics on the residence time $\tau_g$ (displayed in Figure 6.3) that suggests that O$_3$ may also bind to the substrate without O$_2$ release. In order to be able to describe this large variation in $r(t)$ the present results suggest a mechanism consisting of four pseudo-elementary reactions for the heterogeneous interaction of O$_3$ with Kaolinite. Initially, O$_3$ collides with a reactive surface site SS on the surface and deposits an O atom (reaction (6.1)). This reaction initiates the heterogeneous decomposition of O$_3$ on chemically reactive surface sites (SS) on the substrate and plays an important role at short residence time $\tau_g$ of O$_3$ leading to $r(t) = 1.0$ (curve (a), Figure 6.4). Two other types of reactions may be proposed where O$_3$ directly reacts with the surface to form a complex without O$_2$ formation according to reactions (6.5) and (6.6):

\[
O_3 + SS \rightarrow \text{adduct} \quad (6.5) \\
O_3 + O(SS) \rightarrow \text{adduct} \quad (6.6)
\]

These reactions are introduced in order to explain the disappearance of O$_3$ without the formation of gas phase O$_2$. Without any detailed knowledge of the surface, the nature and molecular structure of the complex resulting from reaction (6.5) remains obscure. Without any detailed knowledge of the surface, the nature and molecular structure of the complex resulting from reaction (6.5) remains obscure. However, for the adduct resulting from reaction (6.6) a structure may be proposed under the assumption that the solid state reactant resulting from reaction (6.1) is SS$^{5^-} - O^{5^-}$:

![Diagram of SS$^{5^-} - O^{5^-}$]
The heterogeneous decomposition of ozone on atmospheric mineral dust surrogates at ambient temperature

The larger rate of O$_3$ disappearance compared to O$_2$ formation is expected to hold for short residence times of O$_3$ at the beginning of the interaction between O$_3$ and the Kaolinite powder substrate just after having lifted the plunger and leads to $r(t) = 1.0$. The combination of reactions (6.1) and (6.5) or (6.6) enables values of $r \leq 1.0$ because all the measured values of $r(t)$ decrease from 1.0 to a low value of $r(t) \sim 0.2$ at large values of $\tau_g$ and large extents of reaction as shown in Figure 6.4. Considering the data displayed in Figure 6.4 it appears in conclusion that adduct formation, reaction (6.5) or (6.6), is favoured over reaction (6.1) at increasing extents of reaction at constant [O$_3$]. At the beginning of reaction $r(t)$ is close to one and drops to 0.5 at longer reaction times which corresponds to the increasing importance of reaction (6.6) compared to reaction (6.1) (curve (a), Figure 6.4). However, the fact that $r(t)$ drops below 0.5 as displayed in Figure 6.4 (curves (c) and (d)) points to the fact that reaction (6.5) is also occurring at the beginning of the O$_3$ uptake experiment. If reaction (6.5) would exclusively be occurring, $r(t) = 0$ would be obtained.

![Figure 6.5](image-url)

**Figure 6.5.** Dependence of the uptake coefficient $\gamma_0$ (open circles) on sample mass at [O$_3$] = (4.5 ± 1.0) x $10^{11}$ cm$^{-3}$ at an orifice diameter of 14 mm for the uptake of O$_3$ on Kaolinite powder ($A_s = 19.6$ cm$^2$). Full circles display $\gamma_{\text{eff}}$ obtained in pulsed valve experiments carried out under the same experimental conditions.

In order to establish whether or not the effective available surface area is influenced by the internal surface area formed by interstitial voids between individual dust particles, the
mass dependence of the O$_3$ uptake on Kaolinite was measured in the Knudsen flow reactor at ambient temperature and at [O$_3$] = (4.5 ± 1.0) x 10$^{11}$ cm$^{-3}$. The mass of Kaolinite ranged from 0.3 to 4 g and the results are shown in Figures 6.5 and 6.6.

The steady state and initial uptake coefficient $\gamma_{ss}$ and $\gamma_0$, respectively, of O$_3$ were found to linearly increase at low masses of Kaolinite as displayed in Figures 6.5 and 6.6 for $\gamma_0$ (see Table 6.3). Samples below 0.4 g may be considered to be part of this linear mass-dependent regime. Increasing the sample mass further had a negligible effect on the amount of O$_3$ adsorbed because not the entire sample surface is apparently available for O$_3$ adsorption. This maximum value is attributed to the inability of O$_3$ to penetrate through several layers of the sample during the residence time of O$_3$ in the gas phase, thus resulting in a constant number of molecules taken up despite the increasing sample mass.

The fact that we observe an ‘apparent’ mass dependence of $\gamma_0$ from 0 to 0.4 g is interpreted by the fact that we are ‘filling’ a coherent sample layer.

<table>
<thead>
<tr>
<th>Mass (g)</th>
<th>$\gamma_0$</th>
<th>$\gamma_{eff}$</th>
<th>$\gamma_{ss}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>(7.0 ± 2.0) x 10$^{-2}$</td>
<td>(5.2 ± 1.3) x 10$^{-2}$</td>
<td>(8.9 ± 2.7) x 10$^{-3}$</td>
</tr>
<tr>
<td>0.4</td>
<td>(8.0 ± 1.2) x 10$^{-2}$</td>
<td>(5.7 ± 1.0) x 10$^{-2}$</td>
<td>(9.5 ± 2.2) x 10$^{-3}$</td>
</tr>
<tr>
<td>0.75</td>
<td>(8.5 ± 1.5) x 10$^{-2}$</td>
<td>(6.5 ± 1.0) x 10$^{-2}$</td>
<td>(1.44 ± 0.27) x 10$^{-2}$</td>
</tr>
<tr>
<td>1.0</td>
<td>8.4 ± 1.0) x 10$^{-2}$</td>
<td>(7.2 ± 0.9) x 10$^{-2}$</td>
<td>(1.27 ± 0.3) x 10$^{-2}$</td>
</tr>
<tr>
<td>1.5</td>
<td>(8.6 ± 0.8) x 10$^{-2}$</td>
<td>(7.8 ± 0.74) x 10$^{-2}$</td>
<td>(1.62 ± 0.18) x 10$^{-2}$</td>
</tr>
<tr>
<td>2.0</td>
<td>(9.3 ± 0.9) x 10$^{-2}$</td>
<td>(7.8 ± 0.73) x 10$^{-2}$</td>
<td>(1.7 ± 0.20) x 10$^{-2}$</td>
</tr>
<tr>
<td>3.0</td>
<td>(9.2 ± 0.7) x 10$^{-2}$</td>
<td>(7.7 ± 0.73) x 10$^{-2}$</td>
<td>(1.64 ± 0.22) x 10$^{-2}$</td>
</tr>
<tr>
<td>3.5</td>
<td>(8.5 ± 0.7) x 10$^{-2}$</td>
<td>(7.9 ± 0.76) x 10$^{-2}$</td>
<td>(1.67 ± 0.13) x 10$^{-2}$</td>
</tr>
<tr>
<td>4.0</td>
<td>(9.0 ± 0.7) x 10$^{-2}$</td>
<td>(8.0 ± 0.7) x 10$^{-2}$</td>
<td>(1.74 ± 0.13) x 10$^{-2}$</td>
</tr>
</tbody>
</table>

Table 6.3. Measured uptake coefficients $\gamma_{ss}$ of O$_3$ on Kaolinite by using the geometric surface area of the substrate ($A_s= 19.6$ cm$^2$, 14 mm orifice) at [O$_3$] = (4.5 ± 1.0) x 10$^{11}$ cm$^{-3}$.  
Figure 6.6. Dependence of the steady state uptake coefficient $\gamma_{ss}$ on sample mass at $[O_3] = (4.5 \pm 1.0) \times 10^{11}$ cm$^{-3}$ at an orifice diameter of 14 mm for the uptake of O$_3$ on Kaolinite powder ($A_s = 19.6$ cm$^2$). The numerical fit of the data using the pore diffusion model is represented by dashed lines.

In order to better define the saturation behaviour of O$_3$ on the substrate a series of uptake experiments were performed employing a pulsed valve to admit O$_3$ into the reactor. The increase of $\gamma_{eff}$ with the sample saturates at large sample mass and stays constant at $(8.0 \pm 0.7) \times 10^{-2}$ as displayed by the full circles in Figure 6.5. The same behaviour is observed for $\gamma_0$ which stays constant at $(9.0 \pm 0.7) \times 10^{-2}$ at large sample masses. As shown in Figure 6.5, $\gamma_{eff}$ and $\gamma_0$ are identical within experimental uncertainty for all performed experiments.

The results displayed in Figures 6.5 and 6.6 have been plotted as a function of the mass and of the number of layers of Kaolinite. In order to determine the number of layers the total volume of Kaolinite powder was calculated from its true density $\rho_t = 2.3$ g/cm$^3$ and the mass of the sample spread out across the geometric area of the sample holder. From the average particle size and the thickness of the sample we obtain the number of layers. A typical grain diameter of 1.0 $\mu$m has been obtained from the manufacturer’s undocumented specifications of the used Kaolinite powder (Table 3.1). However, most mineral dust powders are porous materials and the microstructure of the dust substrate is composed of clusters of random distribution with interstitial voids between them.
Therefore it is more reasonable to take into account a grain size diameter that is much larger than 1.0 μm as suggested by electron microscopy (SEM) of similar material where characteristic grain diameters are in the tens of μm (© OMNI Laboratories, Inc, http://www.omnilabs.com/).

The plot in Figure 6.5 shows that a mass of 0.4 g corresponds to one nominal layer of ca. 90 μm average diameter particles of Kaolinite spread out over the geometric surface of the sample holder (19.6 cm²). Thus, one nominal layer of Kaolinite will contain closely packed spheres of “effective” grain diameter of 90 μm. Therefore, the linear mass-dependent portion of γss vs. mass in the 0 to 0.4 g range corresponds to a sample holder partially covered with 90 μm diameter Kaolinite particles which is the structural model we adopt in this work. In a recent study on NO3 reaction on mineral dust12 we have obtained similar results for the mass dependence of γ including an “effective” grain diameter of 50 μm for Kaolinite powder.

Figure 6.6 displays steady state uptake experiments performed on the same amount of Kaolinite as in the experiments reported in Figure 6.5. The trend of these measurements is identical to that observed in pulsed valve experiments. Beyond a mass of 0.4 g the steady state value of γss stabilizes at (1.6 ± 0.3) x 10⁻², a factor at 5 less that γ₀. The use of the BET surface area and the application of the pore diffusion (KLM) theory13 yields γpd,ss = (2.7 ± 0.3) x 10⁻⁶. The BET surface area for Kaolinite and other dust samples used in this work is reported in Table 3.1. The theoretical curve in Figure 6.6 has been fitted to the observed steady state uptake coefficient γss as a function of sample mass using a grain diameter for Kaolinite of 1 μm, a surface sample area As = 19.6 cm², as fitting parameters at a fixed orifice diameter of 14 mm and [O₃] = (4.5 ± 1.0) x 10¹¹ cm⁻³.

The use of the BET surface area and the Pore Diffusion Theory substantially underestimate the true uptake coefficient for Kaolinite approximately by a factor of 50 - 100 as well discussed below. The discrepancy to γ based on the geometric surface area As is more than a factor of 10³. Therefore, we propose to regard γpd,ss as a lower limit to the true value of γss. We want to point out that the results obtained from the pulsed valve experiments (γeff) are virtually identical to the results at “zero” time (γ₀) after the start of the uptake reaction as displayed in Figure 6.1. These results reflect the fact that O₃ explores the external surface of the Kaolinite sample at t = 0 and that it is improbable
for the gas to explore the BET surface area of the sample within a time representative of a pulse decay.

An additional series of experiments concerns the thermal cycling behaviour of Kaolinite that had previously been exposed to several Torr of O3 in order to discover stable reaction products that desorb upon heating of the poisoned substrate. For a 1.5 g Kaolinite sample $k_{ss} = 6.3 \times 10^{-2} \text{ s}^{-1}$ corresponding to $\gamma_{ss} = 1.4 \times 10^{-2}$ was measured in the 4 mm diameter flow reactor after pumping the sample for 30 minutes. After exposing Kaolinite to 8 Torr of O3 for 12 h $\gamma_{ss}$ decreased to $9.4 \times 10^{-4}$ in agreement with trends discussed in Figure 6.3. After heating the exposed sample to $80^\circ$C and letting it cool down to ambient temperature $\gamma_{ss}$ increased by roughly an order of magnitude to $8.8 \times 10^{-3}$. During the thermal treatment only desorption of H2O but no O2 was observed. This rejuvenation of the Kaolinite sample is consistent with the thermal decomposition of the surface peroxide species observed by Li and Oyama$^{17,18}$ according to reaction (6.3) which implies an increase of the number of surface sites SS for adsorption of O3 upon thermal decomposition of O2(SS). However, this regeneration of SS only affects the value of $\gamma_{ss}$ and leaves $\gamma_0$ unchanged in contrast to the O3 exposure which also decreases $\gamma_0$ for O3 uptake. We certainly expected to find O2 among the desorbing products but did not observe significant amounts, probably owing to the relatively large background of O2 in the flow reactor. This type of desorption experiments will be performed in the future in a suitably modified Knudsen flow reactor in conjunction with surface-sensitive spectroscopic methods that will contribute towards the understanding of the underlying molecular mechanisms.

6.3.2 Reaction of O3 on CaCO3 and natural limestone

We have performed uptake experiments of O3 on CaCO3 using a sample of 1 g spread out on a surface area A of 4.9 cm$^2$ and a residence time $\tau_g = 0.2$ s corresponding to an orifice of 14 mm. At $[O_3] = (5.3 \pm 0.5) \times 10^{12} \text{ cm}^{-3}$ the ratio between the O2 product yield and the total O3 loss results in $r(t) = 1.4$ and in a measured value of $\gamma_{ss} = (3.6 \pm 1.8) \times 10^{-3}$ and $\gamma_0 = (1.2 \pm 0.3) \times 10^{-2}$ (Table 6.4 and Figure 6.7, curve (a)). At the beginning of the reaction we have obtained $r(t) \leq 1.0$ and at steady state conditions $r(t)$ tends towards 1.5
which corresponds to heterogeneous decomposition using the substrate as a catalyst. An important remark is the “inverse” behavior of \( r(t) \) of \( \text{O}_3 \) on \( \text{CaCO}_3 \) with the extent of reaction (curve (a), Figure 6.7) as opposed to the decrease of \( r(t) \) with reaction time for \( \text{O}_3 \) on Kaolinite (curve (a)-(c), Figure 6.4).

![Figure 6.7](image)

**Figure 6.7.** The relative yield \( r(t) \) during the uptake experiment of \( \text{O}_3 \) on 1 g of \( \text{CaCO}_3 \) (curve (a), orifice = 14 mm), 0.3 g of Saharan Dust (curve (b)), 1 g of natural limestone (curve (c)), and 0.3 g of Arizona Medium Test Dust (curve (d)) ([\( \text{O}_3 \]) = (3.5 \pm 0.5) \times 10^{12} \text{ cm}^{-3}, A_s = 4.9 \text{ cm}^2 \) and 4 mm orifice (\( \tau_g = 2.0 \text{ s} \)).

For comparison purposes we have carried out a systematic study of \( \gamma_{ss} \) as a function of sample mass in order to determine a corrected uptake coefficient \( \gamma_{pd} \) of \( \text{O}_3 \) on \( \text{CaCO}_3 \) powder using the pore diffusion model\(^{13} \). We have used a large sample surface area of \( A_s = 19.6 \text{ cm}^2 \) and an expanded range of sample masses. At steady state \( \gamma_{ss,pd} = (7.8 \pm 0.7) \times 10^{-7} \) with a tortuosity factor \( \tau = 2.0 \) was found for \([\text{O}_3] = (5.3 \pm 0.7) \times 10^{12} \text{ cm}^{-3} \). The fit to the measured values of \( \gamma_{ss} \) resulted in a value of the \( \gamma_{pd} \) that is smaller by a factor of \( 4.6 \times 10^3 \) with respect to the measured value \( \gamma_{ss} \) reported above.
6. The heterogeneous decomposition of ozone on atmospheric mineral dust surrogates at ambient temperature

Figure 6.8. Knudsen-Cell experiment for O₃ uptake on a 2g marble sample of CaCO₃. The curve correspond to raw MS signals monitored at m/e 48 ([O₃] = (2.0 ± 1.2) x 10¹² cm⁻³; 1 mm orifice; surface sample area Aₘ = 19.6 cm²).

In order to assess whether or not the pore diffusion model may yield a lower limit for γ, we have performed a few uptake experiments on a cut marble sample from Carrara (Italy, solid crystalline CaCO₃). In this case we do not expect interstitial diffusion to occur and the projected surface area of the sample that is relevant for uptake is the geometric surface area Aₛ of 19.6 cm². For [O₃] = (2.0 ± 1.2) x 10¹² cm⁻³ and a residence time τ₉ = 28 s (orifice diameter of 1mm) we found γ₀,marble = (2.3 ± 0.4) x 10⁻⁴ and γₛₛ,marble = (3.5 ± 1.6) x 10⁻⁵ as displayed in Figure 6.8. As displayed in Table 6.4 the uptake values γ₀ and γₛₛ calculated on the basis of the geometric surface area Aₛ of the powder sample are overestimated by a factor of 50 and 100, respectively, compared to the uptake values calculated form the reaction of O₃ on marble. On the other hand, the uptake value γₛₛ,pd calculated by applying the pore diffusion theory (KLM) is underestimated by a factor of 50 or so compared to γ₀ and γₛₛ calculated on the basis of the geometric surface area. We therefore take this factor of 50 to 100 which we extend to the remaining mineral dust surrogates as a rough guide as to the estimate the true uptake coefficient for CaCO₃ using the γ values based on Aₛ as a starting point. We stress that γₛₛ,pd and γ₀, γₛₛ based on Aₛ are lower and higher limits to the true values of γ.

Two series of experiments were performed on 1g of natural limestone composed of CaCO₃ (97 %) that contained a small percentage of metal oxides, especially iron and
aluminium oxides (see Table 3.1). As reported in Table 6.4, the values of $\gamma_0$ and $\gamma_{ss}$ measured at low [O$_3$] were larger by a factor of 6 with respect to those high [O$_3$] which is a general trend observed for many mineral dust materials (see Table 6.4). From these measurements it is evident that both $\gamma_0$ and $\gamma_{ss}$ do not follow a rate law pseudo first order in O$_3$ and suggests that the mechanism of O$_3$ uptake is complex.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Orifice (mm)</th>
<th>[O$_3$] (cm$^{-3}$)</th>
<th>$\gamma_0$</th>
<th>$\gamma_{ss}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolinite</td>
<td>14</td>
<td>$(2.4 \pm 0.7) \times 10^{12}$</td>
<td>$(6.3 \pm 0.2) \times 10^{-2}$</td>
<td>$(1.0 \pm 0.2) \times 10^{-2}$</td>
</tr>
<tr>
<td>CaCO$_3$</td>
<td>14</td>
<td>$(5.3 \pm 0.7) \times 10^{12}$</td>
<td>$(1.2 \pm 0.3) \times 10^{-2}$</td>
<td>$(3.6 \pm 0.2) \times 10^{-3}$</td>
</tr>
<tr>
<td>Natural Limestone</td>
<td>4</td>
<td>$(3.0 \pm 0.7) \times 10^{12}$</td>
<td>$(1.3 \pm 0.2) \times 10^{-2}$</td>
<td>$(1.6 \pm 0.5) \times 10^{-3}$</td>
</tr>
<tr>
<td>Saharan Dust</td>
<td>4</td>
<td>$(3.5 \pm 0.7) \times 10^{12}$</td>
<td>$(9.3 \pm 2.6) \times 10^{-2}$</td>
<td>$(6.7 \pm 1.3) \times 10^{-3}$</td>
</tr>
<tr>
<td>Arizona Test Dust</td>
<td>4</td>
<td>$(3.3 \pm 0.7) \times 10^{12}$</td>
<td>$(1.3 \pm 0.6) \times 10^{-2}$</td>
<td>$(2.2 \pm 1.2) \times 10^{-3}$</td>
</tr>
<tr>
<td>Natural Limestone</td>
<td>4</td>
<td>$(2.0 \pm 1.0) \times 10^{13}$</td>
<td>$(2.1 \pm 0.3) \times 10^{-3}$</td>
<td>$(2.4 \pm 0.7) \times 10^{-4}$</td>
</tr>
<tr>
<td>Saharan Dust</td>
<td>4</td>
<td>$(1.0 \pm 0.4) \times 10^{13}$</td>
<td>$(3.7 \pm 1.8) \times 10^{-2}$</td>
<td>$(3.3 \pm 2.5) \times 10^{-3}$</td>
</tr>
<tr>
<td>Arizona Test Dust</td>
<td>4</td>
<td>$(8.0 \pm 1.5) \times 10^{12}$</td>
<td>$(1.3 \pm 0.7) \times 10^{-2}$</td>
<td>$(2.5 \pm 1.2) \times 10^{-3}$</td>
</tr>
</tbody>
</table>

Table 6.4. Summary of the reactive uptake coefficients for various mineral dust surrogates obtained in the present work based on the geometric surface area.

Interestingly, on this substrate the ratio r(t) for ozone uptake and decomposition remains below 0.5 even at a high concentration of ozone and long residence time (Figure 6.7, curve (c)). This kind of sample seems to be an excellent absorber of O$_3$ without extensive decomposition at ambient temperature. Despite the high percentage of CaCO$_3$ in natural limestone the presence of small amounts of metal oxides such as Fe$_2$O$_3$ in excess CaCO$_3$ could be responsible for the suppression of O$_2$ formation.

When we compare $\gamma$ for CaCO$_3$ and natural limestone at roughly the same ozone concentration ([O$_3$] = $(4.0 \pm 1.0) \times 10^{12}$ cm$^{-3}$) we find that the values for $\gamma_0$ are the same
whereas $\gamma_{ss}$ is a factor of 2.5 larger for CaCO$_3$ according to Table 6.4, presumably because of a faster saturation process in natural limestone compared to pure CaCO$_3$.

### 6.4 Reaction of O$_3$ on Saharan Dust and Arizona Medium Test Dust

Two series of experiments were performed on 0.3 g of Saharan Dust using two different ozone concentrations. As reported in Table 6.4, $\gamma_0$ and $\gamma_{ss}$ measured at low [O$_3$] were larger by a factor of 2.5 and 2, respectively, compared to the values at high [O$_3$].

As already observed for natural limestone, $\gamma_0$ and $\gamma_{ss}$ do not follow a rate law pseudo first order in O$_3$ and suggests that the mechanism of O$_3$ uptake is complex. A similar dependence has been observed before by Hanisch and Crowley$^7$ in their work on ozone decomposition on Saharan dust and by Sullivan and coworkers$^{14}$ in their study of ozone decomposition on fresh alumina films. The reason for this behaviour may be related to the finite number of available surface sites of the substrate that are not completely saturated at low [O$_3$] resulting therefore in a larger value of $\gamma$ compared to high [O$_3$].

For steady state uptake performed at [O$_3$] = (3.5 ± 0.5) x 10$^{12}$ cm$^{-3}$ the ratio $r(t)$ has been found to be approximately 0.8 (Figure 6.7, curve (b)), whereas for [O$_3$] = (1.0 ± 0.4) x 10$^{13}$ cm$^{-3}$ it stabilizes around 1.0.

On 0.3 g Arizona Medium Test Dust, we found identical values of $\gamma_0$ and $\gamma_{ss}$ for both values of [O$_3$] as reported in Table 6.4. The ratio $r(t)$ at steady state conditions tends towards a value of approximately 0.4 for both ozone concentrations (Figure 6.7, curve (d)) indicating a significant reactivity for O$_3$ uptake on this substrate and lack of ozone decomposition leading to O$_2$ formation. Both Arizona Test Dust and natural limestone result in a similar $r(t)$ dependence for ozone decomposition, distinctly different from results for Saharan Dust. Saharan Dust contains a significant percentage of metal oxides, with $r(t)$ tending towards values between 0.8 and 1.0 at steady state conditions. If we analyse the chemical composition of the mineral dust examined in this work more carefully, we note that iron oxides such as Fe$_2$O$_3$, FeO and Fe$_3$O$_4$ are present in different percentages: Saharan Dust contains more iron than Natural limestone and Arizona Test.
Dust a fact that may be responsible for the difference in $\gamma$ and $r(t)$ on the different substrates. Specifically, we note that $r(t)$ increases with the amount of iron oxides in the sample which leads to dominant $O_3$ decomposition resulting in $O_2$ in contrast to $O_3$ uptake. This aspect is supported by recent work of Michel et al. who found that the initial reactivity of oxide powders towards ozone followed the order $\alpha$-Fe$_2$O$_3$$\geq$$\alpha$-Al$_2$O$_3$$>$$SiO_2$$>$$Kaolinite$ with the Saharan sand and China loess having lower reactivities more in line with $SiO_2$ and Kaolinite$^{15}$. In this investigation, the initial reactive uptake coefficient $\gamma_0$ of $O_3$ on several mineral oxide powders was measured using a Knudsen reactor leading to $\gamma_0 = (2.0 \pm 0.3) \times 10^{-4}$ for $\alpha$-Fe$_2$O$_3$, $(1.2 \pm 0.4) \times 10^{-4}$ for $\alpha$-Al$_2$O$_3$, $(6.3 \pm 0.9) \times 10^{-5}$ for $SiO_2$ and $(3 \pm 1) \times 10^{-5}$ for Kaolinite. The greater reactivity of the iron oxides is also in agreement with the observations by Suzuki who carried out a laboratory study of $O_3$ reactivity on various mineral oxides$^{6}$. Using a UV absorption monitor, the authors report the relative $O_3$ reactivity of silica, $\alpha$-Fe$_2$O$_3$, Fe$_3$O$_4$, and $\alpha$-Al$_2$O$_3$ in comparison with natural sea sand collected in Japan, which was further separated into an “iron sand” and a “remainder sand” component. The “iron sand” component had a reactivity similar to Fe$_3$O$_4$, a major component in the “iron sand”, that decomposed O$_3$ at a faster rate than the natural sand and the “remainder sand”. This suggests that iron oxide such as Fe$_3$O$_4$ more effectively destroys ozone than the other solid phases present in the sand. It was concluded that iron-containing compounds had a superior ozone decomposition rate than alumina and silica model compounds in agreement with the present kinetic results.

### 6.5 Comparison with literature values

Previous results on the uptake coefficients for $O_3$ uptake on mineral dust obtained by other authors are displayed in Table 6.5 for comparison purposes. $O_3$ uptake on Saharan sand and calcite has been investigated using a fluidized-bed reactor$^{16}$. Although uptake coefficients have not been derived they may be estimated from the data presented employing the BET surface area of the substrate which will lead to a lower limiting value. For Saharan sand the signal reduction obtained in that work corresponds to an initial
uptake coefficient of $\gamma_{0, \text{BET}} = 2.3 \times 10^{-7}$ at $[O_3] = 2.5 \times 10^{12}$ cm$^{-3}$. In a similar manner, the initial uptake coefficient for calcite resulted in a value of $\gamma_{0, \text{BET}} = 4.3 \times 10^{-7}$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\gamma_{0, \text{BET}}$</th>
<th>$\gamma_{\text{ss}, \text{BET}}$</th>
<th>$\gamma_{\text{pd}, \text{ss}}$</th>
<th>$\gamma_{\text{pd}, \text{ss}}$ (this work)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolinite</td>
<td>(3.0 ± 1.0) x 10$^{-5}$ (Michel et al.)$^{15}$</td>
<td>–</td>
<td>–</td>
<td>(2.7 ± 0.3) x 10$^{-6}$</td>
</tr>
<tr>
<td>Saharan sand</td>
<td>(6 ± 2.0) x 10$^{-5}$ (Michel et al.)$^{15}$</td>
<td>6.0 x 10$^{-6}$ (Michel et al.)$^{15}$</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Saharan Dust</td>
<td>2.3 x 10$^{-7}$ (Alebic-Juretic et al.)$^{16}$</td>
<td>–</td>
<td>–</td>
<td>(2.2_{-1.2}^{+1.4}) x 10$^{-6}$ (Hanisch and Crowley)$^{7}$</td>
</tr>
<tr>
<td>CaCO$_3$</td>
<td>4.3 x 10$^{-7}$ (Alebic–Juretic et al.)$^{16}$</td>
<td>–</td>
<td>–</td>
<td>(7.8 ± 0.7) x 10$^{-7}$</td>
</tr>
</tbody>
</table>

Table 6.5. Typical initial and steady-state reactive uptake coefficients for various mineral dust surrogates obtained in previous work.

In recent work performed by Hanisch and Crowley$^{7}$ the heterogeneous reaction of O$_3$ on Saharan Dust has been investigated at ambient temperature (296 K). The conversion efficiencies $r$ for O$_2$ formed presented in that work were 1.0 and 1.3 mole of O$_2$ per O$_3$ destroyed for unheated and heated samples ($T = 450$ K), respectively. In the same work$^{7}$ it was shown that $\gamma$ for the irreversible destruction of O$_3$ on Saharan dust surfaces depended on the O$_3$ concentration leading to $\gamma_{0}^{\text{pd}} = (5.5_{-3.0}^{+4.0}) \times 10^{-5}$ and $\gamma_{\text{ss}}^{\text{pd}} = (2.2_{-1.2}^{+1.4}) \times 10^{-6}$ using the pore-diffusion (KLM) model at $[O_3] = (8.4 \pm 3.4) \times 10^{12}$ cm$^{-3}$. Experiments at $[O_3] = 6.0 \times 10^{12}$ cm$^{-3}$ using Arizona Test Dust and Kaolinite$^{17}$ were performed as well. Only measured values of $\gamma_0$ were reported; for unheated Kaolinite $\gamma_0 = 1.0 \times 10^4$ was close to or below the detection limit whereas $\gamma_0 = 2.0 \times 10^3$ was found for Arizona Test Dust.
In two other recent studies that employed a Knudsen reactor the mass-independent uptake coefficient, $\gamma_{\text{BET}}$, was determined from the observed $\gamma_{\text{obs}}$ values obtained from the linear mass-dependent portion of the plots $\gamma_{\text{obs}}$ versus sample mass according to equation (6.E3):

$$\gamma_{\text{obs}} = \gamma_{\text{BET}} \left( \frac{S_{\text{BET}} m_s}{A_s} \right)$$  \hspace{1cm} (6.E3)

where $m_s$ is the sample mass, $S_{\text{BET}}$ and $A_s$ are the specific BET and geometric surface areas, respectively. For O$_3$ uptake on ground Saharan sand at $[\text{O}_3] = 1.9 \times 10^{11}$ cm$^{-3}$ Michel and co-workers$^{15,18}$ obtained $\gamma_{0,\text{BET}} = (6.0 \pm 2.0) \times 10^{-5}$ whereas at steady state conditions $\gamma_{\text{ss,BET}} = 6.0 \times 10^{-6}$ was found. In comparison, we have found $\gamma_{\text{pd,ss}} = 2.4 \times 10^{-6}$, a value lower by a factor of 2.5 (Table 6.5).

The uptake coefficient, $\gamma_{\text{BET}}$, calculated from the present values of $\gamma_{\text{ss}}$ using the BET surface area resulted in $\gamma_{\text{ss,BET}} = (2.0 \pm 0.6) \times 10^{-6}$ for Kaolinite at $[\text{O}_3] = (4.5 \pm 1.0) \times 10^{11}$ cm$^{-3}$, whereas $\gamma_{\text{ss,BET}} = (8.3 \pm 0.4) \times 10^{-7}$ for CaCO$_3$ at $[\text{O}_3] = (5.3 \pm 0.7) \times 10^{12}$ cm$^{-3}$. These values are identical to those found from the pore diffusion model within experimental uncertainty. However, we would like to reiterate, that these $\gamma$ values are likely lower limits to the true values.

Finally, measurements of O$_3$ deposition velocities ($v_{\text{dep}}$) have been performed on various substrates including Kaolinite sand and CaCO$_3$.$^{19}$ Using these data and the expression $\gamma = 4v_{\text{dep}} / \overline{c}$, Dentener et al.$^{2}$ estimated $\gamma$ values for O$_3$ in the range $10^{-4}$ to $10^{-5}$. This estimate falls far short of the range of the present results for $[\text{O}_3] = (2.0 \pm 0.5) \times 10^{12}$ cm$^{-3}$ if the corresponding steady-state uptake coefficients based on the geometric surface area are used.

6.6 Conclusions

The present data indicate that the reactivity of O$_3$ on Kaolinite decreases with residence time $\tau_g$ and that the heterogeneous reaction rate not only depends on the gas phase concentration of ozone but apparently also on intermediates whose surface concentration depends on the extent of reaction, that is on $\tau_g$. 
Despite the difficulty to detect $O_2$ as a product species from $O_3$ decomposition we report the relative product formation rate as a function of time resulting from the decomposition of $O_3$ on the different substrates by monitoring the ratio $r(t) = F_{O_2}(t)/\Delta F_{O_3}(t)$. There is no simple common mechanism that may explain ozone decomposition on each type of mineral dust substrate which means that no single surrogate material cited above can be representative of “mineral dust” as far as the heterogeneous reaction with ozone is concerned.

We claim that neither $\gamma_0$ nor $\gamma_{ss}$ is a good indicator for $O_3$ reactivity that is able to distinguish between the different substrates because the resulting $\gamma$ values are all very similar for all the examined substrates within a range of $(1.2 \pm 0.3) \times 10^{-2}$ to $(9.3 \pm 2.6) \times 10^{-2}$ for $\gamma_0$ and $(1.6 \pm 0.5) \times 10^{-3}$ to $(1.0 \pm 0.2) \times 10^{-2}$ for $\gamma_{ss}$. The use of values derived from the pore diffusion (KLM) theory and from the BET surface area leads to a lower limit for $O_3$ uptake that underestimates the kinetics of $O_3$ with mineral dust. The uptake values derived from the pore diffusion theory found for Kaolinite and CaCO$_3$ are lower by a factor $3.0 \times 10^3$ with respect to those calculated using the geometric surface area $A_s$ of the sample. We assume that Arizona Test Dust, Saharan Dust and natural limestone will follow the same trend. The uptake experiment performed on crystalline CaCO$_3$ (marble) suggests that the pore diffusion correction of the measured $\gamma$ value will lead to an underestimation of the true value by a factor of $50 - 100$. Therefore, we may conclude that for all mineral dust samples used in this work the uptake value $\gamma$ is of the order of $10^{-5}$. On the other hand, $r(t)$ seems to be a better indicator for the reaction of these surrogates with $O_3$ because it discriminates the different samples to a larger extent compared to the absolute values of $\gamma_0$ or $\gamma_{ss}$ of the various types of substrates.

In order to estimate the effect of ozone uptake on mineral dust we used field measurements of a dust event reported in recent work. At an altitude of 4 km the total aerosol surface area was $1.5 \times 10^6$ cm$^2$ cm$^{-3}$ and $[O_3]$ was 31 ppb ($5.0 \times 10^{11}$ cm$^{-3}$) at 279 K. If we take a $\gamma$ value of $3.5 \times 10^{-5}$ as a lower limit for the uptake of $O_3$ on mineral dust, the lifetime of $O_3$ is 10 days. This lifetime comes quite close to that found in the recent work of Hanisch and Crowley and Sullivan et al. who used a lower limit for $\gamma$ of about $10^{-5}$ and estimated a lifetime ranging between 33 and 55 days for the same aerosol surface area.
In conclusion, the present results show a low reactivity of $O_3$ on mineral dust surrogates as exemplified by experiments on crystalline CaCO$_3$ resulting in $\gamma = 10^{-5}$. This value is larger by a factor of 10 compared to Hanisch and Crowley\textsuperscript{7} and Michel and co-workers\textsuperscript{15} who report $\gamma$ values of the order of $10^{-6}$ using pore diffusion (KLM) theory\textsuperscript{13}.

### 6.7 General conclusions and outlook

Recent modelling studies have been carried out in order to estimate the total decrease of tropospheric trace gases such as HNO$_3$, N$_2$O$_5$, NO$_3$ and O$_3$ in the presence of mineral dust\textsuperscript{8,9}. However, these studies reveal significant differences in model formulation such as dust surface areas, chemistry schemes, trace gas concentrations, and differences in the computation of the heterogeneous removal rates. The present thesis intends to reduce the uncertainties regarding the value of the uptake coefficient $\gamma$ of gas phase species that undergo irreversible reactions on mineral dust surfaces and may play a decisive role in controlling the outcome of these model simulations. Table 6.6 reports the $g$ values used in the work of Bauer et al.\textsuperscript{8} and Bian and Zender\textsuperscript{9}. The last column reports the steady state values $\gamma_{ss}$ that were found from the present experiments on mineral dust surrogates. We propose that these values may be used in future modelling studies for trace gas concentrations lower than $5.0 \times 10^{11}$ cm$^{-3}$. We see from Table 6.6 that the $\gamma$ values found from the present laboratory work are larger by at least two orders of magnitude compared to the estimated values used in the modelling studies\textsuperscript{8,9}. Previous and recent laboratory work has mainly been oriented towards the reactivity of HNO$_3$ and O$_3$ on mineral dust substrates. As reported in Table 6.6, only a single recent study has been performed on the reactivity of N$_2$O$_5$ in a Knudsen flow reactor\textsuperscript{21}. The uptake coefficients found in that work are quite close to those obtained in the present thesis work. However, we think that at tropospheric concentrations of N$_2$O$_5$ $\gamma$ will be much larger than previously believed, especially for the case of Saharan Dust. Such large values for $\gamma$ may have important consequences for the decrease of ozone because NO$_3$ and N$_2$O$_5$ are precursors for HNO$_3$ formation which itself is an important precursor for O$_3$. 
The goal of the present laboratory study has been to understand as well as possible a few isolated heterogeneous reactions of a trace gas interacting with mineral dust. However, we have to consider that real atmospheric conditions at which these heterogeneous reactions take place in the troposphere are different from the used experimental conditions. There are mainly two aspects that may influence the measurement of the “true” (= environmental) value of $\gamma$ at the experimental conditions used in this work:

(a) The choice of the appropriate surface area for mineral dust samples;

(b) The relative humidity at which the present experiments were carried out.

It has already been shown by previous studies that points (a) and (b) presented above may strongly affect the final result. We think that the Knudsen flow reactor is very useful for the understanding of the kinetics of heterogeneous reactions, especially for the determination of the reaction products. However, in order to “reproduce” or simulate real atmospheric conditions it would be preferable to work with aerosols of mineral dust samples generated by dry dispersion. This method has already been employed in recent work performed by Vlasenko et al.$^{23}$ for the investigation of the heterogeneous reaction of HNO$_3$ on Arizona Test Dust$^{22,23}$. In that study, a dry dispersion generation method was used to produce submicron size dust aerosol in a flow tube which was used to measure the kinetics of the heterogeneous reaction of HNO$_3$ with aerosol particles at different values of relative humidity (12% < rh < 73%). This is the first study that applies such a method for the generation of atmospheric mineral dust using a kinetic flow-tube technique. In addition, the reactive surface area of the suspended aerosol particles has been estimated from the measurement of the mobility diameter (SMPS). The results obtained from this experimental work were in agreement with those obtained by Hanisch and Crowley$^{24}$ at very dry conditions typical of the Knudsen reactor (rh < 1%). We think that this is a good starting point for the confirmation of laboratory experiment carried out in a Knudsen flow reactor.

A further potential improvement of the present method may be the probing of aerosol particles by monitoring scattered visible light. This is a simple direct non-invasive experimental method that keeps the probe particles intact and may be complementary to the use of UV light and soft x-ray radiation for the study of aerosol chemistry and physics.
6. The heterogeneous decomposition of ozone on atmospheric mineral dust surrogates at ambient temperature

<table>
<thead>
<tr>
<th></th>
<th>( \gamma_{\text{Bauer et al.}} )</th>
<th>( \gamma_{\text{Bian and Zender}} )</th>
<th>( \gamma_{\text{present work}} )</th>
<th>( \gamma_{\text{recent laboratory work}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNO₃</td>
<td>0.1</td>
<td>1.1 x 10⁻³</td>
<td>-</td>
<td>0.11 (24)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.11 (23)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5.4 x 10⁻² (25)</td>
</tr>
<tr>
<td>NO₃</td>
<td>3.0 x 10⁻³</td>
<td>0.1</td>
<td>0.2</td>
<td>-</td>
</tr>
<tr>
<td>N₂O₅</td>
<td>3.0 x 10⁻³ (rh = 30 %)</td>
<td>1.0 x 10⁻³</td>
<td>0.2</td>
<td>1.3 x 10⁻² (21)</td>
</tr>
<tr>
<td></td>
<td>3.0 x 10⁻³ (rh = 70 %)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O₃</td>
<td>1.0 x 10⁻⁵</td>
<td>5.0 x 10⁻⁵</td>
<td>1.0 x 10⁻⁵</td>
<td>7.0 x 10⁻⁶ (7)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>6.0 x 10⁻⁶ (26)</td>
</tr>
</tbody>
</table>

**Table 6.6.** Typical uptake coefficients on mineral dust of various trace gases used in modeling studies resulting from laboratory studies.
6.8 References


6. The heterogeneous decomposition of ozone on atmospheric mineral dust surrogates at ambient temperature


6. The heterogeneous decomposition of ozone on atmospheric mineral dust surrogates at ambient temperature


Chapter 7

REACTION OF F(2P) WITH HNO3 AS A NITRATE RADICAL SOURCE

7.1 Microwave discharge of F2 for NO3 generation

The uptake experiments performed with NO3 on mineral dust surrogates and laboratory flame soot were carried out using the thermal decomposition of N2O5 as a source for NO3 which was always accompanied by NO2. In the present chapter we want to present an experimental set up to operate a source of NO3 in the absence of NO2. For this purpose we used the reaction of F atoms with HNO3 according to equation (7.1):

\[ F(2P) + HNO_3 \rightarrow HF + NO_3 \]  

Despite its widespread use as a NO3 source, the first room temperature measurement of the rate constant \( k_\text{II} \) for reaction (7.1) has only recently been reported\(^1\) and resulted in a value of \((2.7 \pm 0.5) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) at 298 K.

In order to run reaction (7.1) a discharge flow reactor was coupled to the Knudsen flow reactor. The system is schematically described in Figure 7.1. A microwave discharge cavity (2460 MHz, 20 W) produced F atoms in a sapphire (crystalline Al2O3) tube from a flow of F2 diluted at 4.6 % in helium (MESSER) according to reaction (7.2):

\[ F_2 + \text{energetic radiation} \rightarrow F(2P) \]  

\(^1\) Reference is not provided in the text.
7. Reaction of F(2P) with HNO₃ as a nitrate radical source

Figure 7.1. Experimental set up of the microwave flow discharge fitted to the Knudsen flow reactor.

Figure 7.2. Picture of the experimental set up sketched schematically in Figure 7.1.

The sapphire tube was connected to the Knudsen flow reactor by a capillary made of TEFLON of internal diameter 0.3 mm. The sapphire tube where the microwave discharge took place had a total length of 20 cm and an internal diameter of 0.8 cm. F atoms produced in the discharge
reacted with excess HNO₃ which was introduced 5 cm downstream of the microwave cavity. A flow of pure helium diluted and admitted HNO₃ in the discharge flow reactor. The flow of helium was controlled by a digital flowmeter (BRONKHORST) with a maximum range of 50 ml/min. A distance of 12 cm was allowed for the NO₃ production through reaction (7.1) which was to be completed before sampling of NO₃ across a TEFLON capillary connected to the Knudsen reactor. The pumping rate for helium in the discharge flow reactor has been determined according to expression (7.E1):

\[
S = \frac{F_{\text{He}}}{[\text{He}]}
\]  

A volumetric pumping rate \( S = 56 \text{ cm}^3 \text{ s}^{-1} \) was measured. The helium concentration \([\text{He}]\) was calculated from the measured pressure of helium \( P_{\text{He}} \) in the discharge flow reactor according to expression (7.E2):

\[
[\text{He}] = \frac{P_{\text{He}} N_A}{RT}
\]

where \( R \) is the ideal gas constant, \( T \) the temperature in Kelvin and \( N_A \) Avogadro’s number.

In order to calculate the concentration of \( \text{F}_2 \) diluted in helium in the discharge flow reactor, we used a gas sample of \( \text{F}_2 \) diluted in helium and calculated \([\text{F}_2]\) using expression (7.E1) by considering that \( \text{F}_2 \) was 4.6 % by volume of the total measured \([\text{He}]\). For HNO₃ we proceeded in similar manner by controlling the percentage of its dilution with helium when we adjusted the setting of the digital flowmeter.

As will be explained below, the rate \( k_1 = [\text{F}(^2\text{P})]k_{11} \) of reaction (7.1), resulted in \( 4.6 \times 10^2 \text{ s}^{-1} \), for a typical \([\text{F}(^2\text{P})] = 1.7 \times 10^{13} \text{ molecule cm}^3\). Therefore, the lifetime \( \tau_1 \) for reaction (7.1) is \( 1/k_1 = 2.2 \text{ ms} \). The reacto-diffusive length, \( l(\tau_1) = \sqrt{3D_{\text{He}} \tau_1} \), is a measure of the mean distance across which mixing and reaction (7.1) of the F/HNO₃ mixture takes place. As an approximation of \( D_{\text{He}} \) we chosen the diffusion coefficient of ground state Mg in He, \( D = 340 \pm 27 \text{ cm}^2 \text{ s}^{-1} \) for 1 Torr². Therefore, \( l(\tau_1) \) has been estimated at 1.5 cm. From the dimensions of the microwave discharge flow reactor we may estimate the reacto-diffusive length \( l(t_D) = \sqrt{3D_{\text{He}} t_D} \) using the chosen flow \( F_{\text{He}} \) of helium. For a helium flow \( F_{\text{He}} = 1.4 \times 10^{18} \text{ molecule s}^{-1} \) we calculate \([\text{He}] = 1.3 \times 10^{16} \text{ molecule cm}^{-3} \) for a pumping rate of helium of \( S = 56 \text{ cm}^3 \text{ s}^{-1} \). The relation
between $F_{\text{He}}$ and [He] in the discharge flow reactor is simply given by the following expression (7.E3):

$$F_{\text{He}} = [\text{He}] \cdot A \cdot v \quad (7.E3)$$

where $A$ is the cross section expressed in cm$^2$ of the flow tube in which reaction (7.1) takes place and $v$ is the helium flow speed, expressed in cm s$^{-1}$, that we used in order to calculate the diffusion time $t_D$ of helium in the discharge flow reactor. From expression (7.E3) we found a diffusion time of $t_D = 40$ ms. Therefore, the reacto-diffusive length $l(t_D)$ is calculated as 6.4 cm which is larger that $l(\tau)$ by a factor of four. This means that we have available a long distance (12 cm) over which to allow complete abstraction of H from HNO$_3$ in view of NO$_3$ production. The gas concentrations in the Knudsen reactor were calculated as explained in Chapter 2.

A first experiment consisted of the measurement of the flow of F$_2$ following the discharge. The raw MS signal at m/e 38 displayed in Figure 7.3 (curve (a)) corresponds to the F$_2$ flow into the Knudsen reactor across the inlet capillary. After the flow was established the microwave discharge has been switched on, the inlet flow of F$_2$ decreased by more than 95 % producing a large amount of HF (curve (b), Figure 7.3).

![Figure 7.3](image-url)  

**Figure 7.3.** MS signals at m/e 38 (curve (a)) and 20 ((curve (b) corresponding to F$_2$ and HF, respectively. The decrease of the MS signal at m/e 38 indicates that the microwave discharge has been switched on. The discharge of F$_2$ takes place in the discharge flow reactor upstream of the inlet capillary to Knudsen flow reactor as illustrated in Figure 7.1.
7. Reaction of F(2P) with HNO₃ as a nitrate radical source

7.2 The F + CH₄ Reaction

In order to characterize the source of F atoms and to verify if any important heterogeneous loss of F atoms occurred, preliminary experiments were performed employing methane CH₄ according to reaction (7.3):

\[
\text{CH}_4 + \text{F}(2P) \rightarrow \text{CH}_3 + \text{HF}
\]

The rate constant \( k \) for reaction (7.1) is \( (4.7 \pm 0.5) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) at 298 K. Methane has a fragment at m/e 15 and its molecular ion peak at m/e 16, F(2P) is monitored at m/e 19, and HF at m/e 20. These masses have been detected by using the mass spectrometer that sampled the Knudsen flow reactor.

![Typical mass spectrum for a mixture of F₂ and CH₄ flowing from the discharge flow reactor into the Knudsen flow reactor when the microwave discharge was switched off. The peaks at m/e 38 and 15 correspond to the presence of F₂ and CH₄ respectively.](image)

**Figure 7.4.** Typical mass spectrum for a mixture of F₂ and CH₄ flowing from the discharge flow reactor into the Knudsen flow reactor when the microwave discharge was switched off. The peaks at m/e 38 and 15 correspond to the presence of F₂ and CH₄ respectively.
Figure 7.5. Typical mass spectrum for a mixture of F₂ and CH₄ flowing from the discharge flow reactor into the Knudsen flow reactor when the microwave discharge was switched on. The peak at m/e 38 has disappeared and we note the small increase of peaks at m/e 19 and 20 corresponding to F atoms and HF formation. The decrease of the CH₄ signal and the increase of the C₂H₄ signal indicates a reaction of F atoms with CH₄.

Figures (7.4) and (7.5) display the two mass spectra of methane before and after the reaction with F atoms in the microwave flow discharge system located upstream of the Knudsen flow reactor. Figure 7.5 displays a decrease in the MS signals at m/e 15 and 16 indicating a decrease in methane concentration. Methyl radical, CH₃, resulting from reaction (7.3) is expected to undergo a homogeneous recombination reaction to ethane, C₂H₆, according to reaction (7.4):

\[
\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6 \quad (7.4)
\]

In addition, C₂H₆ (monitored at m/e 30 and 29) may be chemically activated resulting in the formation of C₂H₄ which has mass fragments at m/e 26, 27 and its molecular ion at m/e 28. As displayed in Figure (7.5), the fact that we observe an increase in the MS signal at m/e 28 may be attributed to formation of CO. When we coupled the discharge flow reactor using to the Knudsen flow reactor we measured an increase in the oxygen concentration from 4.2 x 10⁹ to 7.8 x 10⁹ cm⁻³. Therefore, possible leaks in the discharge flow reactor may be responsible for secondary reactions of F atoms with O₂ such as F + O₂ → FO + O.

Table 7.1 reports the concentrations of all reactants in the discharge flow and in the Knudsen reactor for the experiment displayed in Figure 7.5. In Figure 7.5 a slight increase of the MS signals at m/e 19 and 20 corresponding to the production of F atoms and HF, respectively, is
noted. From an initial concentration of \( F_2 \ 1.0 \times 10^{15} \text{ cm}^{-3} \) and considering that the initial flow of \( F_2 \) decreases more than 95\% we should expect a concentration of \( 2.0 \times 10^{15} \text{ F atoms cm}^{-3} \) once that the microwave discharge has been switched on. On the other hand, from the decrease of the MS signal at m/e 16, we measured a decrease of only 13\% of \([\text{CH}_4]_0\) in the discharge flow reactor. If we attribute the decrease of \([\text{CH}_4]_0\) to the reaction with F atoms, according to equation (7.3), then only \( 1.2 \times 10^{15} \text{ F atoms cm}^{-3} \) effectively reacted with \( \text{CH}_4 \). Therefore, it is reasonable to suppose that 60\% of the original production of F atoms reacted with \( \text{CH}_4 \) whereas the other 40\% reacted by forming HF or other reaction products.

<table>
<thead>
<tr>
<th></th>
<th>Discharge flow reactor cm(^{-3})</th>
<th>Knudsen reactor cm(^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{He}])</td>
<td>(2.0 \times 10^{16})</td>
<td>(1.2 \times 10^{13})</td>
</tr>
<tr>
<td>([\text{CH}_4]_0)</td>
<td>(9.5 \times 10^{15})</td>
<td>(6.8 \times 10^{11})</td>
</tr>
<tr>
<td>(\Delta[\text{CH}_4]_0)</td>
<td>(1.2 \times 10^{15})</td>
<td>(8.8 \times 10^{10})</td>
</tr>
<tr>
<td>([\text{F}_2])</td>
<td>(1.0 \times 10^{15})</td>
<td>(1.6 \times 10^{12})</td>
</tr>
<tr>
<td>([\text{F}(^2\text{P})])</td>
<td>(2.0 \times 10^{15})</td>
<td>-</td>
</tr>
<tr>
<td>([\text{O}_2])</td>
<td>(5.5 \times 10^{12})</td>
<td>(7.8 \times 10^9)</td>
</tr>
</tbody>
</table>

**Table 7.1.** Typical concentrations for \( \text{CH}_4 \) and \( \text{F}_2 \) used in the discharge flow reactor and measured using the Knudsen flow reactor a sampling device.

### 7.3 The \( \text{F} + \text{HNO}_3 \) Reaction

A large number of experiments were carried out at 298 K in order to use reaction (7.1) for the generation of \( \text{NO}_3 \) radicals. For the performed experiments we used the following ranges of experimental parameters: total pressure in the discharge flow reactor, 750 – 800 mTorr (mainly helium); \([\text{F}(^2\text{P})]\), \((0.5 – 2.0) \times 10^{13} \text{ cm}^{-3}\) and \([\text{HNO}_3]\), \((1.2 – 6.5) \times 10^{13} \text{ cm}^{-3}\), with initial ratios \([\text{HNO}_3]/[\text{F}]\) ranging from 2 to 8.

Figure 7.6 displays a typical experiment where a steady state flow of \( \text{HNO}_3 \) is mixed with F atoms produced after the microwave discharge has been switched on. The raw MS signal at m/e 63 displayed in Figure 7.6 is proportional to the flow of \( \text{HNO}_3 \) and its decrease when the microwave discharge is switched on. Together with MS detection we use REMPI detection of \( \text{NO}_2 \) at \( \lambda = 511 \text{ nm} \) in order to determine the nature of a possible secondary reaction product.
occuring during NO₃ formation. From the decrease of the MS signal at m/e 63 we measure a decrease of 65 % of the flow of HNO₃ when the microwave discharge is switched on as displayed in Figure 7.6. We attribute this decrease to the reaction of HNO₃ with F atoms according to reaction (7.1). As already stated for the reaction of CH₄ with F atoms, we should expect a concentration of $1.3 \times 10^{15}$ cm$^{-3}$ F atoms after that the microwave discharge has been switched on based on an initial concentration of F$_2$ $6.5 \times 10^{14}$ cm$^{-3}$ (Table 7.2) and considering that the initial flow of F$_2$ decreased by more than 95 %. Therefore, 35 % of the initially generated F atoms reacted by forming HF or other reaction products.

![Figure 7.6](image)

**Figure 7.6.** Typical experiment used to produce NO$_3$ by reaction of HNO$_3$ with F atoms. For $t$ between 0 and 200 s the MS signals at m/e 46 (curve (a)), 30 (curve (b)) and 63 (curve (d)) correspond to HNO$_3$ prior to reacting with F atoms. At $t = 200$ s the microwave discharge is switched on and the MS signal at m/e 63 decrease. At the same time we can record an increase of the REMPI signal (curve (c)) at $\lambda = 511$ nm corresponding to a formation of NO$_2$.

It is reasonable to suppose that the decrease of HNO$_3$ is directly related to the production of F atoms. As the microwave discharge is switched on, an important quantity of NO$_2$ is observed simultaneously with the decrease of the HNO$_3$ flow (Table 7.2). The amount of NO$_2$ has been measured by REMPI detection of NO$_2$ in the Knudsen flow reactor (Chapter 2).
Table 7.2. Typical concentrations for HNO₃ and F₂ used in the discharge flow and in the Knudsen flow reactor in order to produce NO₃.

<table>
<thead>
<tr>
<th></th>
<th>Discharge flow reactor cm⁻³</th>
<th>Knudsen reactor cm⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td>[He]</td>
<td>1.3 x 10¹⁶</td>
<td>4.5 x 10¹⁴</td>
</tr>
<tr>
<td>[HNO₃]₀</td>
<td>2.6 x 10¹³</td>
<td>1.4 x 10¹¹</td>
</tr>
<tr>
<td>Δ[HNO₃]₀</td>
<td>1.7 x 10¹³</td>
<td>9.1 x 10¹⁰</td>
</tr>
<tr>
<td>[F₂]</td>
<td>6.5 x 10¹⁴</td>
<td>2.2 x 10¹²</td>
</tr>
<tr>
<td>[F(²P)]</td>
<td>1.3 x 10¹⁵</td>
<td>-</td>
</tr>
<tr>
<td>[NO₂]</td>
<td>Not measured</td>
<td>2.1 x 10¹¹</td>
</tr>
</tbody>
</table>

7.4 Conclusions

Following these measurements we did not observe a measurable gas phase production of NO₃ that we could detect in the Knudsen flow reactor despite our numerous efforts by changing all the degrees of freedom. The reasons for this unsuccessful attempt at generating NO₃ in the absence of NO₂ result may be:

- The amount of NO₃ is smaller than the detection limit of the MS detection system.
- The number of F atoms may be larger than measured by the decrease of HNO₃ as reported in Table 7.2. We therefore assume that NO₃ formed following reaction (7.1) may react with an excess of F atoms according to equation (7.5):

\[
F(²P) + NO₃ \rightarrow FO + NO₂ \quad (7.5)
\]

The secondary reaction (7.5) was observed to be very fast by Ravishankara and Wine⁴, who used reaction (7.1) as a source of NO₃. They proposed a lower limit of 5.0 x 10⁻¹¹ cm³ molecule⁻¹ s⁻¹ for the rate constant of reaction (7.5) at room temperature. This could explain the possible formation of NO₂ in the experiment displayed in Figure 7.6.

- An additional explanation for the formation of NO₂ may be the secondary thermal decomposition of NO₃ in the discharge flow reactor according to reaction (7.6):
The residence time of NO$_3$ in the discharge flow reactor has been estimated from expression (7.6.3) and resulted in 40 ms. This time is much lower than the lifetime $\tau = 5$ s for NO$_3$\textsuperscript{5}, therefore, we do not think that NO$_3$ decomposes before reaction with F atoms. Owing to the fact that the Knudsen flow reactor operates at pressures of almost 100 times lower than the discharge flow reactor we think that the combination of a Knudsen flow and a discharge flow reactor is a suboptimal experimental means for the production and detection of NO$_3$ following reaction (7.1).
7. Reaction of F(2P) with HNO₃ as a nitrate radical source

7.5 References


(2) Redko, T. P.; Rusinov, I. M.; Blagoev, A. B.: Diffusion of Ground-State (3s² ¹S₀) and Metastable (3s3p ³P₀,₁,₂) Magnesium Atoms in He and Ne, Journal of Physics B-Atomic Molecular and Optical Physics, 26, 107-111, (1993).


7. Reaction of $F(3P)$ with $HNO_3$ as a nitrate radical source
THE PORE DIFFUSION MODEL

When a sample has a non-negligible internal surface such as a porous surface or internal void, we tend to overestimate the uptake coefficient because, in fact, $\omega$ is larger than calculated on the basis of the geometrical surface area. Keyser and co-workers have applied the well known pore diffusion model to heterogeneous reactions of atmospheric relevance by attempting to correct measured uptake coefficients on solid powders. The uptake coefficient $\gamma_{pd}$ resulting from the application of the pore diffusion model is related to the observed uptake coefficient $\gamma_{ss}$ in equation (A.1):

$$\gamma_{ss} = \gamma_{pd} \rho_b S_{BET} (h_e + \eta h_i)$$  \hspace{1cm} (A.1)

where $S_{BET}$ is the specific BET surface area, $h_e$ the height of the first layer, $h_i$ the height of all the internal layers calculated from the total mass $m$ of the sample ($h_i= m/A_s \rho_b - h_e$) and $\rho_b$ is the bulk density of the sample. The total number of layers of the sample, $N_{Layers}$, is given by $N_{Layers} = m/A_s \rho_b d$ where $d$ is the average size of the particle. The effectiveness factor is given by $\eta = \frac{\tanh \Phi}{\Phi}$ with $\Phi$ being the Thiele modulus defined in equation (A.2):

$$\Phi = \frac{m}{\rho_b A_s d} \left(\frac{3 \rho_b}{2 (\rho_i - \rho_b)}\right)^{\frac{3}{2}}$$ \hspace{1cm} (A.2)

The effectiveness factor of a porous solid primarily depends on the relative rates of surface reaction and gas-phase diffusion; it is defined as the ratio of the observed
diffusion-limited reaction rate to the rate that would be observed if diffusion into the bulk of the powder were extremely fast. The effectiveness may also be thought of as the fraction of the internal surface which partakes in the heterogeneous reaction. In porous solids actual diffusive mass transfer can be slower than predicted because within these materials diffusion does neither occur in straight-line paths nor in pores of uniform cross section. To account for this the tortuosity factor $\tau$ is introduced. Although it has its basis in theory, the tortuosity factor remains a fitting parameter in practice because most porous solids are not characterized well enough. For any regular lattice consisting of identical pores $\tau = 3^2$. This result is also obtained for a network of randomly oriented cylindrical pores. If the pore size is distributed, $\tau$ may exceed 3 a little. On the other hand, measurements of the tortuosity factor in a pack of spheres with a narrow particle size distribution gives $\tau < 3^4$. This discrepancy stems, in part, from the assumption that the pores can be regarded as infinitesimally wide in comparison to their length, and therefore leads to the conclusion that molecular diffusion in each pore is unidimensional in a direction parallel to the pore axis. In a short communication Friedman and Seaton (1995) proposed an approximate correction to take into account the finite aspect ratio of the pores. The corrected tortuosity factor became significantly different from $\tau = 3$ except for what are unrealistically low porosities, at least for most porous materials of practical interest. The corrected $\tau$ value should be unity for a medium of very high porosity and should approach the value of 3 for a medium with low porosity.

The analysed powder is characterised by a large distribution of grain diameters, so that the correction factor calculation for this substrate can be carried out only qualitatively. This complication is somewhat avoided because enough powder is present in these experiments so that the correction is calculated for the limit of many grain layers. When $N_{\text{Layers}}$ is large, the correction factor is far more sensitive to the bulk density of the powder than the diameter of the grains. In addition, the value of the correction factor becomes independent of the grain diameter in the limit of large $N_{\text{Layers}}$. 
References


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- High reactivity and chemical kinetics of NO$_3$ on laboratory flame soot, F. Karagulian and M.J. Rossi (in preparation).