Chemistry of Inorganic Nitrogen Compounds

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Atmospheric Chemistry
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Required Reading: Finlayson-Pitts and Pitts Chapter 7
Other Possible Reading: Seinfeld and Pandis Chapter 5

Outline

Introduction
• Oxidation of NO to NO₂ and the Leighton Relationship
• Oxidation of NO₂
• Atmospheric Chemistry of HONO
• Reactions of NO₃ and N₂O₅
• Atmospheric Chemistry of HNO₃
• “Missing NOy”
• Ammonia
Bonus Material
Motivation

- Inorganic nitrate compounds intimately involved in important chemical processes in both troposphere and stratosphere
  - $\text{NO}_2$ is key to formation of tropospheric ozone
    - Both in polluted and background troposphere
  - $\text{HNO}_3$ key ingredient in acid rain
  - $\text{NO}_3$ is primary night time oxidant
  - Participate with halogens in $\text{O}_3$ destruction chemistry in stratosphere
    - Regulate chain length of $\text{O}_3$-destroying reactions
- Fascinating chemistry + unresolved issues

Diagram of NOy

- Stable species in circles
- Major pathways denoted by arrows
- Will use this diagram throughout
Definitions

- **NOx = NO + NO$_2$**
  - These are the key nitrogen containing species
  - Rapid interconversion between NO & NO$_2$ in stratosphere and troposphere

- **NOy = NO + NO$_2$ + HNO$_3$ + PAN + HONO + NO$_3$ + 2N$_2$O$_5$ + organic nitrates (RNO$_3$) + particulate nitrate (pNO$_3$) + …**
  - NOx + all of its reservoir species

- **NOz = NOy – NOx**
  - Just the reservoir species

Breaking Down NOy

- **NOx = NO + NO$_2$**
  - Rapid interconversion

- **NOy = NOx + reservoir species**

- **NOz = reservoir species**
Sources and Sinks

- Sources of NOy primarily directly emitted NO + NO₂
  - Combustion sources
    - Mobile – planes, trains and automobiles
    - Stationary - power plants, industrial
  - Natural – Biomass burning, lightning
- Sinks of NOy lost through HNO₃
  - Washout of HNO₃
  - Dry deposition
  - Incorporation into aerosols as nitrate (pNO₃⁻) followed by loss of particles

Typical NOy Concentrations

- Remote areas
  - NOy ~ 1-20 ppb
- Rural areas
  - NOy ~ 1 ppb
- Heavily polluted
  - NOy ~ 0.2-0.5 ppm
- Moderately polluted
  - NOy ~ 0.02-0.2 ppm
- Typical tropospheric
  - O₃ ~ 50 ppb
- Typical
  - OH < 1 ppt
- Mexico City
  - NOy = 0.1-0.4 ppm
- Tropospheric
  - CH₄ = 1.7 ppm
Overall Look at Oxidation

Start with NO and NO₂

Smog chamber experiment to simulate atmospheric oxidation

Over time oxidized to HNO₃ and PAN

Ratio of PAN/HNO₃ depends on initial VOC/NOx ratio

Some HNO₃ lost (in this case to chamber walls)

From Finlayson-Pitts and Pitts

FIGURE 7.1 Cumulative plot of oxidized nitrogen compounds for a typical smog chamber run. Initial concentrations were 4.55 ppmC VOC, 0.21 ppm NO, and 0.23 ppm NO₂ (from Spicer, 1983).

Oxidation of NO to NO₂

- First guess in old days:
  - Reaction 2 NO + O₂ → 2 NO₂ responsible for NO oxidation in polluted urban areas
  - Not the case – too slow at typical [NO]
  - Does occur in power plant plumes with very high [NO]
- Now known: peroxy radicals responsible for NO oxidation
  - NO + HO₂ → OH + NO₂
  - NO + RO₂ → RO + NO₂
- Leighton relationship:
  - Assume hypothetical atmosphere – NO, NO₂ and air (no organics!)
  - Also called “photostationary state”
  - Continued on next slide…
“Photostationary State”

- NO₂ + hv → NO + O \hspace{1cm} (4)
- O + O₂ → O₃ \hspace{1cm} (5)
- O₃ + NO → NO₂ + O₂ \hspace{1cm} (6)

- In steady state:

\[
\frac{[O₃][NO]}{[NO₂]} = \frac{k₄}{k₆}
\]

\[
\frac{k₆[O₃][NO]}{k₄[NO₂]} = 1
\]

Photostationary state often close to reality

FIGURE 7.3 Test of photostationary state in rural Michigan on June 4, 1977, 11:30 to 13:30 hours (adapted from Rüser et al., 1979).

Deviations from photostationary when there are significant organics present

\[
\frac{[NO₂]}{[NO]} = \frac{1}{k₄} \left( k₆[O₃] + k_{HO₂+NO}[HO₂] + \Sigma k_{RO₂+NO}[RO₂] \right)
\]

Deviation from photostationary when there are significant organics present

Oxidation of NO₂

- Daytime = gas phase reaction with OH
  \[ \text{NO}_2 + \text{OH} \xrightarrow{M} \text{HONO}_2 \]

- Lifetime of NO₂ ~ 16 hr
  - At typical [OH] of 2 x 10⁶ molecule cm⁻³
  - Competes with NO₂ photolysis during daytime
    - \( \tau_{\text{photolysis}} \approx 2-3 \text{ minutes} \)
    - Reaction with OH important – converts NOx → NOy

- Recent measurements for rate coefficients
  - Slightly smaller \( k₀ \) & \( k₇ \)
  - \( O₂ \) is ~70% as effective as \( N₂ \) as a quencher
  - See Brown et al., 1999 recommendations and Dransfield et al., 1999
Oxidation of NO\textsubscript{2}

- Nighttime = reactions with O\textsubscript{3} and NO\textsubscript{3}
- \[
    \text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2 \tag{1}
\]
- \[
    \text{NO}_2 + \text{NO}_3 \xrightarrow{M} \text{N}_2\text{O}_5 \tag{2}
\]
- \( k_1 \) relatively small, but [O\textsubscript{3}] often high enough to make it important
  - NO\textsubscript{3} is primary nighttime oxidant of organics
- Several lab studies of \( k_2 \) range of factor of 2 in results
- N\textsubscript{2}O\textsubscript{5} lost via hydrolysis (more in a few slides)
  - Sink of N\textsubscript{2}O\textsubscript{5} = sink of NO\textsubscript{3}

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Oxidation of NO\textsubscript{2}

- Uptake of NO and NO\textsubscript{2} into liquid water (clouds, fogs, etc.) too slow to be important under most atmospheric conditions
- “Heterogeneous” reaction of NO\textsubscript{2} + H\textsubscript{2}O
  \[
  2 \text{NO}_2 + \text{H}_2\text{O} \xrightarrow{\text{surface}} \text{HONO} + \text{HNO}_3
  \]
  - Variety of surfaces show HONO production (e.g. soot)
  - Mechanism still not understood
    - HONO observed but not equivalent HNO\textsubscript{3}
    - Reaction enhanced by light
    - Isotope studies suggest multiple reaction pathways
    - Possible reduction of NO\textsubscript{2} by a surface group
  - Another possible pathway:
    \[
    \text{NO} + \text{NO}_2 + \text{H}_2\text{O} \xrightarrow{\text{surface}} 2 \text{HONO}
    \]
- Reactions of NO\textsubscript{2} with alcohols, organics, sea salt particles, and mineral oxides all discussed, but none are atmospherically important
Atmospheric Chemistry of HONO

- **Importance**
  - Can be major OH source
    - Particularly at sunrise
  - Indoor air pollutant

- **Sources**
  - Heterogeneous reactions of NO₂ (discussed above)
  - OH + NO → M → HONO
    - Hard to build up significant [HONO] during day though, owing to fast photolysis of HONO
  - Surface reactions of HO₂NO₂
  - Small source directly from combustion (autos with no catalytic converter)

Study in Long Beach shows HONO as dominant OH source in early morning and overall 2nd largest source of OH

![Graph showing OH production rates](image)

FIGURE 7.8 Calculated rates of formation of OH radical from photolysis of HONO, O₃, and HCHO at Long Beach, California, on December 10, 1987 (adapted from Wexler and Bertram, 1994).

*From Finlayson-Pitts and Pitts*

Atmospheric Chemistry of HONO

- **Atmospheric fates**
  - Photolysis is major loss
  - Reaction of OH is fast, but not fast enough to compete
  - Uptake of HONO into liquid
    - Oxidation of NO₂⁻ to NO₃⁻
    - Greatly enhanced by freezing
  - Uptake onto ice
    - At T = 180 – 200K, α ≈ 10⁻³
  - Deposition

![Graph showing absorption spectrum](image)

FIGURE 4.14 Absorption spectrum of HONO at 297 K (adapted from Bontemps et al., 1991). Note that the absolute values of the cross sections shown here should be multiplied by 0.805 as recommended by Bontemps et al. (1994).

*From Finlayson-Pitts and Pitts*
HONO as Important OH Source

- Mexico City example (from photochemistry lectures)
- OH production from HONO dominates early morning photochemistry
  - Tails off later in day

Peroxyacetyl Nitrate (PAN)

- Initially unknown product of photooxidation of organic/NO\textsubscript{x} mixtures
  - Called “Compound X”
  - Strong eye irritant
  - Mutagenic & phytotoxic to plants
- Formed from RO\textsubscript{2} + NO\textsubscript{2} reaction
  - Competes with RO\textsubscript{2} + NO reaction
- Loss processes
  - Reverse of formation = thermal decomposition
    - Highly temperature dependent
  - Photolysis
  - Reaction with OH
- Concentrations as high as 70 ppb!
- Rapid vertical mixing leads to long lifetime $\rightarrow$ transport
  - Source of NO\textsubscript{x} to remote areas

\[ \text{O} \quad \| \quad \text{CH}_3\text{COONO}_2 \]

FIGURE 6.19 Calculated first-order loss rates of PAN due to thermal decomposition, OH reaction, and photolysis as a function of altitude (assuming diurnally averaged solar fluxes for 39°N, July 4) (adapted from Takakdar et al., 1995).
PAN Homologs

- General class of compounds = peroxyacyl nitrates
- Formed from different feedstock organics
  - Both natural and anthropogenic
  - PAN is most common of group

\[
\begin{align*}
\text{Peroxypropionyl nitrate (PPN)} & \quad \text{Peroxy-n-butryl nitrate (PnBN)} \\
\text{Peroxybenzoyl nitrate (PBzN)} & \quad \text{Peroxymethacryloyl nitrate (MPAN)}
\end{align*}
\]

Reactions of NO₃

- NO₃ present only at night
  - Very fast daytime photolysis
- Competition between NO₂ & NO
  - NO₃ + NO₂ ↔ N₂O₅
  - NO₃ + NO → 2 NO₂
    - At 1 ppb NO, \( \tau_{NO₃} \approx 2 \) s
    - NO and NO₃ do not coexist
- Reactions with organics
  - Covered in Chapter 6
  - NO₃ = “OH of the night”
- Thermal decomposition
  - Not observed in atm
- Reaction with water
  - Evidence for uptake of NO₃ at high ambient RH
  - Difficult to separate from N₂O₅ uptake

Great review articles on NO₃

FIGURE 7.12 Comparison of measured (Platt et al., 1984) and predicted nitric radical concentrations at Edwards Air Force Base, California, May 23–24, 1982. The dashed line is the model prediction without the unimolecular decomposition of NO₃, and the solid line is that with the decomposition (adapted from Russell et al., 1986).
From Finlayson-Pitts and Pitts

Later chapters cover aqueous phase chemistry of NO₃
Reactions of N\textsubscript{2}O\textsubscript{5}

- Formation from NO\textsubscript{2} + NO\textsubscript{3}
- Loss via hydrolysis
  - N\textsubscript{2}O\textsubscript{5(g)} + H\textsubscript{2}O\textsubscript{(g)} \rightarrow 2\text{HNO}_3\text{(g)}
  - N\textsubscript{2}O\textsubscript{5(g)} + 2\text{H}_2\text{O}\textsubscript{(g)} \rightarrow 2\text{HNO}_3\text{(g)} + \text{H}_2\text{O}\text{(g)}
  - N\textsubscript{2}O\textsubscript{5(g)} + \text{H}_2\text{O}\text{(l)} \rightarrow 2\text{HNO}_3\text{(aq)}
- All three reactions important
- Hydrolysis as much as 90% of HNO\textsubscript{3} production in atmosphere
  - Removal of NO\textsubscript{2} from system results in lower predicted O\textsubscript{3}

- Loss via other reactions
  - Reactions with sea salt
    - Na\textsubscript{X(aq)} + N\textsubscript{2}O\textsubscript{5(g)} \rightarrow \text{XNO}_2\text{(g)} + Na\text{NO}_3\text{(s)}
      - X = Cl, Br, or I
      - Possibly important in marine boundary
  - Reactions with alkenes?

From Finlayson-Pitts and Pitts

Atmospheric Chemistry of HNO\textsubscript{3}

Formation reactions previously discussed:

\[
\begin{align*}
\text{NO}_2 + \text{OH} + \text{M} & \rightarrow \text{HONO}_2 \\
\text{N}_2\text{O}_5\text{(g)} + \text{H}_2\text{O}\text{(g,l)} & \rightarrow 2\text{HNO}_3 \\
\text{NO}_3\text{(aq)} + \text{H}_2\text{O}\text{(l)} & \rightarrow \text{HNO}_3\text{(aq)} + \text{OH}\text{(aq)} \\
\text{NO}_3 + \text{RH} & \rightarrow \text{HNO}_3 + \text{R} \\
\text{HNO}_3\text{(g)} + \text{NH}_3\text{(g)} & \leftrightarrow \text{NH}_4\text{NO}_3\text{(s,aq)} \\
\text{HNO}_3\text{(g)} + \text{NaCl}\text{(s)} & \rightarrow \text{HCl}\text{(g)} + \text{NaNO}_3\text{(s)}
\end{align*}
\]

More discussion on these during aerosol section

- Tropospheric fates
- Fast wet and dry deposition
  - HNO\textsubscript{3} is “sticky”
- Photolysis is slow
- OH rxn relatively slow
  - Interesting kinetics \rightarrow some complex formation
  - Temp dependence of k = positive or negative?
- Reaction with NH\textsubscript{3}
  - Acid – base reaction
  - NH\textsubscript{3}NO\textsubscript{3(s)} formation requires water
  - Equilibrium strongly dependent on temperature
- Reactions with sea salt
  - Possible importance in marine boundary layer
NH₄NO₃ Formation: LA Example

General air motion

NH₃ from agriculture to east of LA

NOx from vehicles in LA produces HNO₃

NH₃ + HNO₃ → NH₄NO₃ enhances particle formation leading to visibility problems in Riverside further inland

“Missing NOy”

- Compare measurement of total NOy with sum of measurements of individual nitrogen containing compounds
  - Shortfall → not all of NOy accounted for
  - See FP&P p.570 - 573
- Problem in numerous field campaigns in past
  - As of FP&P printing in 1999, still very much a mystery

- Measurements by NOAA folks right here in Colorado
- Poor agreement with cleaner westerly winds from mountains
- Better agreement with easterly winds from Boulder/Denver metropolitan area
- Deficit correlated with O₃ indicating photochemical source

From Finlayson-Pitts and Pitts
Alkyl Nitrates

- Missing NOy = alkyl nitrates?
- Mystery possibly solved by Cohen et al. at UC Berkeley
  - Measurements show larger than expected amounts of alkyl nitrates (RNO₃)
  - See Day et al., JGR, 108, 4501, 2003
  - Recent development – jury is still out
- Determined by branching ratio in reaction RO₂ + NO
  - RO₂ + NO → RO + NO₂
  - RO₂ + NO → RONO₂

What do cows, raw sewage, and a brand new Nissan have in common?

Ammonia!
NH₃ is only significant gaseous base in atmosphere

- Sewage and livestock known sources
- Neutralizes atmospheric acids (HNO₃, H₂SO₄, etc.)
- NH₃ contributes to particle growth
- Also lost via dry deposition
- Reaction with OH is slow

Photos courtesy of B. Knighton
NH₃ from Vehicles During Mexico City Field Campaign

- NH₃ correlates with CO₂
- CO₂ is marker for combustion, in this case, from auto
- Thus, NH₃ definitely from vehicles

Proof that signal is truly NH₃, not interference

Can see large plumes of NH₃ while following new truck

Ammonia From Mobile Sources

- Over-functioning catalytic converters reduce nitrogen oxides to ammonia
  - Possibly associated with cars running fuel-rich
- NH₃ from vehicles observed in previous studies
  - LA NH₃ emissions from vehicles estimated as high as emissions from livestock (Fraser and Cass, 1998)
- Observations in Mexico City
  - Higher than expected levels of ambient NH₃ observed
  - Observed correlation with CO₂ plumes directly from exhaust
  - Observed newer cars as highest NH₃ emitters
Real Data from Mexico City

CO = Morning traffic emissions
Late morning boundary layer rise
Evening boundary layer reforms

O₃ = Afternoon photochemistry

Diurnal pattern of what happens in urban area

Mexico City NOx Diurnal Patterns

NO = Morning traffic
Boundary layer + NO + RO₂ → NO₂

NO₂ = Afternoon Photochemistry
Boundary layer reform

CO & O₃ lines in background
Mexico City PAN Diurnal Pattern

NOz levels much less than NOx levels
2003 PAN levels lower than previous (max = 10 ppb)
Indication of changing chemical environment in Mexico City

Figure from E. Dunlea

Data from several groups (Aerodyne Research, RAMA Monitoring network, Penn State, UNAM University)

Mexico City HNO₃ Budget Example

• Data taken during 2003 Mexico City field campaign at La Merced fixed site
• Downtown location near market & traffic corridor
• Data from several groups (Aerodyne Research, RAMA Monitoring network, Penn State, UNAM University)
Early morning
- \( \text{OH} + \text{NO}_2 \rightarrow \text{HNO}_3 \)
- No gas phase
- Low temp, high RH
- HNO\(_3\) partitions to particles

Late morning
- Boundary layer rise \( \rightarrow \) NO\(_2\) decrease
- Temp increase, RH decrease
- HNO\(_3\) repartitioning to gas phase
Afternoon

- Peak in OH
- Now observe gas phase HNO₃ production
- High temp, low RH
- Low pNO₃ formation

**Figure from E. Dunlea**
**Mexico City HNO₃ Budget Example**

- **Production**
  - pNO₃ formation
  - Dry Deposition

- **Production - Loss**
  - Gas phase accumulation

- **Overnight balance into morning**
- **Mid morning**
  - ~10 ppb/hr gas phase HNO₃ “missing”

Currently an unsolved mystery – NOy still a research topic!

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**Summary – What Have We Covered**

- **NOy = NOx + reservoir species**
- **Sources → NO; Sinks → HNO₃**
- **Daytime story = NO ↔ NO₂ interconversion**
  - Photostationary state = good 1st approximation
- **Nighttime story = NO₃ ↔ N₂O₅ interconversion**
- **Details on specific compounds:**
  - NO, NO₂, HONO, NO₃/N₂O₅, HNO₃, PAN
  - Missing NOy
- **Real life examples from Mexico City on NH₃ and HNO₃**
Another NOy Schematic

*FIGURE 5.16* Schematic of NOchemistry.

*From Seinfeld and Pandis*