Measurements of SO$_2$ and HO$_2$NO$_2$ with a Chemical Ionization Mass Spectrometer During INTEX-A

G. Huey, S. Kim, R. Stickel, D. Tanner and INTEX Science Team
Outline

- **SO$_2$ (brief)**
  - Profile
  - Tracing Sources

- **HO$_2$NO$_2$**
  - Properties
  - Steady State Analysis
SO$_2$ Altitude Profile

- Averaged SO$_2$
- Maximum SO$_2$
- Median SO$_2$
HO$_2$NO$_2$

**Formation**

\[ \text{HO}_2 + \text{NO}_2 \rightarrow \text{HO}_2\text{NO}_2 \quad k_1 \]

**Losses**

1) Thermal Decomposition – Strong Function of Temperature

\[ \text{HO}_2\text{NO}_2 \rightarrow \text{HO}_2 + \text{NO}_2 \quad k_{-1} \]

2) Reaction with OH

\[ \text{OH} + \text{HO}_2\text{NO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2 + \text{NO}_2 \quad k_2 \]

3) Photolysis – Both UV and IR (overtone)

\[ \text{HO}_2\text{NO}_2 + \text{hv} \rightarrow \text{HO}_x + \text{NO}_x \]
Altitude Profile of HO$_2$NO$_2$ Lifetime for INTEX - A

Below 7 km lifetime is dominated by thermal decomp. < 3 hours

Above 7 km lifetime is dominated by OH and J 6-8 hours

Graph showing:
- Total Lifetime
- OH Lifetime - Measured OH
- Thermal Lifetime (JPL)
- Photolysis Lifetime w/ overtone
Measured HO$_2$NO$_2$ – INTEX-A

Perritric peaks at ~9 km with average of 77 pptv
Steady State $\text{HO}_2\text{NO}_2$

\[
\begin{bmatrix} \text{HO}_2 \\ \text{NO}_2 \end{bmatrix}_{SS} = \frac{k_1}{k_{-1} + J + k_2} \begin{bmatrix} \text{HO}_2 \\ \text{NO}_2 \\ \text{OH} \end{bmatrix}
\]

SS approximation should be valid at least at lower altitudes.
SS vs. Measured HO$_2$NO$_2$
Measured HO$_x$ – Filtered Data

Correlation driven by higher T, low altitude data
SS – Measured HO$_x$ and T>250 K

Steady State HO$_2$NO$_2$ (pptv) - Measured HO$_x$

- Linear Fit $R^2 = 0.64$
- slope = 0.83
- intercept = -1 pptv
- n = 1436

T > 250 K
Altitude Profile w/ measured HO$_x$

![Altitude Profile with measured HO$_x$](image)

- Altitude (km) on the y-axis
- HO$_2$NO$_2$ (pptv) on the x-axis

Legend:
- Blue line: SS - Measured HO$_x$
- Red line: Median HO$_2$NO$_2$
Correlation w/ Langley 24 hour Model

SS HO$_2$NO$_2$ (pptv) - Langley Model

1:1 Line
Linear Fit $R^2 = 0.67$
slope = 1.17
intercept = 6.5 pptv
n = 2745
SS vs. Measured HO$_2$NO$_2$
Langley Model HO$_x$ – Filtered Data

Fit $R^2 = 0.71$
Slope = 1.25
Intercept = 11 pptv
$n = 2589$
Altitude Profile w/ Langley Model $\text{HO}_x$
Conclusions

- SO$_2$ good marker for coal burning, etc. – need help from transport models to analyze
- Perinitric data is consistent with measured HO$_x$ and NO$_x$ at lower altitudes where thermal decomposition dominates
- At all altitudes HO$_2$NO$_2$ data is consistent with measured NO$_2$ and model HO$_x$.
- HO$_2$NO$_2$ is a good test of photochemistry above 8 km. Depends on both HO$_2$ and OH.
- Other issues to investigate HO$_2$NO$_2$ interaction with cirrus cloud, ratio of HO$_2$NO$_2$ to HNO$_3$ as an indicator of air mass age, HO$_2$NO$_2$ as a marker for ozone production, evaluate magnitude of HO$_2$NO$_2$ as HO$_x$ sink, etc.
Cautions

- J value is not well constrained – Could it be a factor of 2 higher?
- Steady State analysis is certainly imperfect
- All model results based on inferred NO – Impacts HO₂ to OH ratio