Isocyanic acid (HNCO) in MOZART4

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*Showing lots of work from Jim, Patrick and other NOAA types today
Outline

- What is isocyanic acid?
- Where does it come from?
- Why might we be interested?
- How are we modeling it?
- When will I have done more work than this?
What? An organic chemist’s dream…

…every atom once!

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{Methyl isocyanate} \\
\text{N} & = \text{C} = \text{O} \\
\end{align*}
\]

Mildly acidic, \( pK_a = 3.7 \)
Volatil, B.P. = 23.5°C

Other isocyanates…

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{Methyl isocyanate} \\
\text{N} & = \text{C} = \text{O} \\
\end{align*}
\]

\[
\begin{align*}
\text{OCN} & \\
\text{NCO} & \\
\end{align*}
\]

Methylene diphenyl 4,4-diisocyanate (MDI)
(rigid polyurethane manufacture)
Where?

Biomass burning
Domestic coal combustion
Cigarette smoke
Urea catalysis (SCR)
Chemistry (Barnes et al., 2010)
Why? New measurements

NI-PT-CIMS instrument – selective for acids

\[ \text{HA} + \text{CH}_3\text{C(O)O}^- \rightarrow \text{A}^- + \text{CH}_3\text{C(O)OH} \]

Roberts et al. (2008); Veres et al. (2008)

CalNex data (photochem)  Fire lab data

Veres et al. (2010)
Why? Bad for health

Very soluble at physiological pH

> 1 ppbv

Good protein

Bad protein

- Kidney disease
- Inflammation
- Coronary artery disease

Biomass burning

Smoking
Why? Probe fires

Polyamide pyrolysis
Proteins, Nylon, Urea-formaldehyde foam

200 pptv from Boulder fire

Roberts et al. (submitted)
Why? Fires in the Earth system

Past and future occurrences? Increasing biochar production?

Bowman et al., Science (2009)
Why? Expansion of SCR

Diesel engines: urea-SCR de-NO$_X$ system:

\[ \text{H}_2\text{N-C(O)-NH}_2 \rightarrow \text{HNCO + NH}_3 \]  
(pyrolysis)

\[ \text{HNCO + H}_2\text{O} \rightarrow \text{NH}_3 + \text{CO}_2 \]  
(hydrolysis)

\[ 4\text{NH}_3 + 4\text{NO} + \text{O}_2 + \text{Catalyst} \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} + \text{Catalyst} \]

Ideally, no HNCO remains in the exhaust
…But 5-50 ppmv HNCO reported from test engine$^1$

AQ requirements in EU (currently) and CA (by 2013)
…But these can change – i.e. moving target

How? Emissions (January shown)

Currently scaled to HCN (\(f = 0.3^*\))
- biomass burning (FINN)
- biofuel burning (\(\rightarrow\) HCN scaled from anthropogenic CO)

*Observed range: 0.3-0.5 (Roberts et al., submitted)
How? Loss processes

(a) Wet dep in mo_setsox.F90
Allows pH dependence:

\[
\begin{align*}
\text{HNCO(g)} & \rightleftharpoons \text{HNCO(aq)} \\
\text{HNCO(aq)} & \rightleftharpoons \text{NCO}^- + \text{H}_3\text{O}^+
\end{align*}
\]

\[H_{\text{eff}} = H(1 + K_a/[H^+])\]

\[H = 21 \text{ M atm}^{-1}\]

\[K_a = [\text{H}_3\text{O}^+][\text{NCO}^-]/[\text{HNCO}] = 1.2 \times 10^{-4}\]

(b) Dry dep currently like formic acid (HCOO\text{OH})
How? What’s not included?

Gas-phase chemistry, since it’s slow

Ignoring gas-phase sources as well, e.g. amides

\[
\text{HC(O)NH}_2 + X \rightarrow \cdot\text{C(O)NH}_2 \quad \text{or H eject.}
\]

\[
\text{X} = \text{OH, NO}_3, \text{Cl}
\]

\[
\text{HC(O)NH}_2 + X \rightarrow \text{H}_2\text{O} + \text{NCO}
\]

(Another “why?” – pretty easy to model!)
HNCO distribution from January

(a) Surface

(b) Zonal mean

cf. HCN, which has longer lifetime (Randel et al. 2010, Science)
When? After all this…

- Update fire emissions (Christine W)
- Complete test run (what’s the pH distribution?)
- Additional emissions?
  - SCR scenarios?
  - Trash burning emissions?
Summary

• Several HNCO sources
• Likely associated with diseases (tobacco, biofuel…)
• What’s the global distribution?
  • Policy-relevant (SCR expansion, biochar…)
  • Fire emissions (incl. biofuels)