EVALUATION OF A GAS-PHASE ATMOSPHERIC MECHANISM FOR LOW NO\textsubscript{x} CONDITIONS

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- Background and Objectives
- Environmental Chambers Employed
- Chamber Effects Characterization
- Evaluation Results
- Modeling assessment of relative rates of low NO\textsubscript{x} reactions
- Discussion and Conclusions

BACKGROUND

- Ground-level ozone \(O_3\) is formed in complex reactions of emitted VOCs with NO\textsubscript{x} in sunlight
- The mechanisms representing these reactions in models are critical to accurate \(O_3\) control strategy predictions.
- Environmental chamber data provide the best way to test these mechanisms independent of other uncertainties
- However, current mechanisms were evaluated using data with higher NO\textsubscript{x} levels than most current ambient conditions.
- This is a concern because the nature of the oxidation processes change as NO\textsubscript{x} is reduced.
- Opportunities exist for lower NO\textsubscript{x} mechanism evaluation:
  - Existing Low NO\textsubscript{x} data from CSIRO and TVA Chambers
  - Experiments from the new UCR EPA Chamber designed for low NO\textsubscript{x} evaluations are becoming available
OBJECTIVES

• Evaluate the SAPRC-99 mechanism (the most up-to-date and detailed mechanism used by the CARB) for low NO\textsubscript{x} conditions.

• Obtain and characterize existing TVA and CSIRO chamber data for mechanism evaluation.

• Conduct experiments in the new UCR EPA chamber most needed for low NO\textsubscript{x} evaluation.

• Evaluate mechanism using available TVA, CSIRO, and UCR EPA chamber data.

• Investigate modifications to SAPRC-99 to better represent low NO\textsubscript{x} conditions.

• Recommend research needed to improve mechanism performance.

SUMMARY OF ENVIRONMENTAL CHAMBERS USED IN THE LOW NO\textsubscript{x} EVALUATION

<table>
<thead>
<tr>
<th></th>
<th>TVA</th>
<th>CSIRO</th>
<th>UCR EPA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume (m\textsuperscript{3})</td>
<td>28</td>
<td>2 x 20</td>
<td>2 x 85</td>
</tr>
<tr>
<td>Walls</td>
<td></td>
<td>FEP Teflon® Film</td>
<td></td>
</tr>
<tr>
<td>Lighting</td>
<td>Fluorescents</td>
<td>Sunlight</td>
<td>Argon Arc</td>
</tr>
<tr>
<td>Number of Experiments</td>
<td>32 Char, 48 Mech Eval</td>
<td>19 Mixture experiments</td>
<td>36 Char 42 Mech Eval</td>
</tr>
<tr>
<td>Measured Species Used in Evaluation</td>
<td>O\textsubscript{3}, NO, CO, HCHO, PAN, VOCs</td>
<td>O\textsubscript{3}, NO, NO\textsubscript{y}-NO</td>
<td>O\textsubscript{3}, NO, NO\textsubscript{2}, CO, HCHO, PAN, HNO\textsubscript{3}, VOCs</td>
</tr>
</tbody>
</table>
DISCUSSION OF TVA INDOOR CHAMBER

- Experiments conducted by Simonaitis and Bailey of TVA in 1993 through 1995 for low NOx mechanism evaluation
- Steps taken to reduce background by extensive purging between runs
- 3 types of fluorescent lamps used to approximate solar spectrum
- NO2 actinometry results averaged 0.392 min\(^{-1}\)
- Temperature during runs varied from ~295 - 315 °K
- TVA Chamber no longer operational
- Data made available for modeling by Jeffries and Co-workers for an RRWG project
DISCUSSION OF CSIRO OUTDOOR CHAMBER

- Located outdoors in a suburb of Sydney, Australia
- Multiple complex surrogate – NOx experiments conducted by Johnson and co-workers to test and derive parameters for Johnson's parameterized "extent of reaction" model
- Data used from 10 dual chamber surrogate experiments conducted in a collaborative project with Jeffries and co-workers
- Data made available for modeling as part of an RRWG project
- Photolysis rates for modeling derived as follows:
  - NO2 photolysis rates as function of time estimated from TSR data using relationship of Demerjian and Schere
  - Ratios of other photolysis rates to NO2 calculated using Peterson (1977) actinic fluxes as function of time of day
- Other characterization parameters estimated based on characterization results for other chambers
EXAMPLES OF CSIRO TEMPERATURE AND LIGHT CHARACTERIZATION ASSIGNMENTS

Temperature (Experimental and Model Input)

Experimental and Model Fit TSR
(Modeled TSR derived from calculated NO₂ photolysis rates and Demerjian and Schere Relationship)

<table>
<thead>
<tr>
<th>Run 340 P</th>
<th>Run 362 P</th>
<th>Run 342 L</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.2</td>
<td>0.4</td>
</tr>
<tr>
<td>300</td>
<td>480</td>
<td>660</td>
</tr>
</tbody>
</table>

TSR or temperature vs. minutes after midnight

- ▲ Experimental
- --- Model
- - - No HV adj.

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DIAGRAM OF UCR EPA CHAMBER

- 2 Banks of Blacklights
- 200 KW Arc Light
- Two air Handlers are located in the corners on each side of the light (not shown).
- Temperature controlled room flushed with purified air and with reflective material on all inner surfaces
- Access Door
- SEMS (PM) Instrument
- Mixing System
- Under floor of reactors
- Floor Frame
- Movable top frame allows reactors to collapse under pressure control
- Gas sample lines to laboratory below
PICTURES OF UCR EPA CHAMBER

DISCUSSION OF UCR EPA CHAMBER

- Constructed using a $2.9 Million EPA earmark to develop a “Next Generation” chamber for mechanism evaluation
  - Large volume to minimize background and permit PM studies and instrumentation with large sample requirements
  - Indoor chamber for maximum characterization and control
  - Light source simulating sunlight
  - Low background to permit well-characterized experiments at low pollution levels
  - Advanced analytical instrumentation
  - Temperature control to ±1°C in ~5°C - ~50°C range

- Experiments with current configuration began in early 2003:
  - Initial characterization and evaluation runs funded by EPA
  - Very low NOx surrogate experiments run for this project
### DERIVATION OF MAJOR CHAMBER CHARACTERIZATION PARAMETERS

<table>
<thead>
<tr>
<th>Parameter</th>
<th>TVA</th>
<th>CSIRO</th>
<th>UCR EPA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Continuous Radial source (HONO offgasing)</td>
<td>Negligible compared to high HCHO offgasing</td>
<td>T-Dependent rate assumed to be same as SAPRC OTC or 3 x higher</td>
<td>Model char. runs sensitive to HONO offgasing</td>
</tr>
<tr>
<td>NO\textsubscript{x} Offgasing</td>
<td>Model CH\textsubscript{3}CHO - Air runs</td>
<td>Approx. same as radical source</td>
<td>Approx. same as radical source</td>
</tr>
<tr>
<td>HCHO background and offgasing</td>
<td>Model HCHO in CO - NO\textsubscript{x} or NO\textsubscript{x} - air runs</td>
<td>Assumed to be unimportant compared to R.S.</td>
<td>Model HCHO in char. runs w/o HCHO source</td>
</tr>
<tr>
<td>Initial HONO</td>
<td>Model CO - NO\textsubscript{x}, NO\textsubscript{x} - Air, and CH\textsubscript{4} - NO\textsubscript{x} runs</td>
<td>No data – varied in evaluation simulations</td>
<td>Model char. runs sensitive to initial HONO</td>
</tr>
<tr>
<td>O3 Decay</td>
<td>Measured</td>
<td>Estimated</td>
<td>Measured</td>
</tr>
<tr>
<td>Dilution</td>
<td>Derived from tracer data</td>
<td>Estimated to be minor</td>
<td>Believed to be low in most runs</td>
</tr>
</tbody>
</table>

### VALUES OF MAJOR CHAMBER CHARACTERIZATION PARAMETERS

<table>
<thead>
<tr>
<th>Parameter</th>
<th>TVA</th>
<th>CSIRO (varied)</th>
<th>UCR EPA</th>
</tr>
</thead>
<tbody>
<tr>
<td>HONO or NO\textsubscript{2} offgasing / NO\textsubscript{2} photolysis rate ratio</td>
<td>7.2 ppt</td>
<td>Standard: Temp.-dependent fit for OTC (10-100 ppt) High RS: 3 x Std.</td>
<td>Runs 55-80: 5 ppt Runs 81-168: Side A: 8.5 ppt Side B: 12.5 ppt</td>
</tr>
<tr>
<td>HCHO offgasing / NO\textsubscript{x} photolysis rate ratio</td>
<td>HCHO: 45 ppt HCHO precursor: 135 ppt</td>
<td>Assumed to be low compared to other sources</td>
<td>10 ppt</td>
</tr>
<tr>
<td>Initial HONO</td>
<td>0.5 ppb</td>
<td>Standard: ~0 High RS: 2 ppb</td>
<td>0.05 ppb</td>
</tr>
<tr>
<td>O3 Decay</td>
<td>7% /hour</td>
<td>1.3% /hour</td>
<td>1.1% /hour</td>
</tr>
<tr>
<td>Light Intensity</td>
<td>$k_1 = 0.392 \text{ min}^{-1}$</td>
<td>Standard: Deriv’d from TSR data High: 1.15 x Std.</td>
<td>$k_1 = 0.284 \text{ min}^{-1}$</td>
</tr>
</tbody>
</table>
**UCR-EPA HONO INPUT PARAMETER VS. RUN NO.**

- **Rad. Source (Side A)**
- **Rad. Source (Side B)**
- **NOx Source (Side A)**
- **NOx Source (Side B)**
- **Assigned (Side A)**
- **Assigned (Side B)**

**EPA Run Number**

- 0
- 5
- 10
- 15
- 20
- 25
- 50
- 75
- 100
- 125
- 150
- 175

**HONO Input / NO2 Photolysis Rate Ratio (ppt)**

**COMPARISONS OF RADICAL SOURCE PARAMETERS FOR UCR EPA AND PREVIOUS CHAMBERS**

- **ETC**
- **DTC**
- **DTC-3**
- **DTC-10**
- **XTC**
- **CTC1**
- **CTC2**
- **OTC**
- **Fit for OTC**

**Average Temperature (K)**

- 290
- 300
- 310
- 320

**HONO offgasing / NO2 photolysis rate ratio (ppt)**

- 1
- 10
- 100
- 1000
MEASURE OF MODEL PERFORMANCE FOR OZONE

Model performance for simulating both ozone formation and NO oxidation is measured by ability to predict $\Delta([O_3]-[NO])$:

$$\Delta([O_3]-[NO]) = ([O_3]-[NO])_{FINAL} - ([O_3]-[NO])_{INITIAL}$$

This gives a useful measure for both high NO and high O$_3$ conditions.

UCR EPA RUNS AND FITS TO $\Delta([O_3]-[NO])$

<table>
<thead>
<tr>
<th>Run Type</th>
<th>Runs</th>
<th>NO$_x$ Range (ppb)</th>
<th>Average Model Fits</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Bias</td>
</tr>
<tr>
<td>Characterization</td>
<td>32</td>
<td>0 - 200</td>
<td>-2%</td>
</tr>
<tr>
<td>Formaldehyde - NO$_X$</td>
<td>2</td>
<td>8 - 25</td>
<td>-23%</td>
</tr>
<tr>
<td>Formaldehyde - CO - NO$_X$</td>
<td>2</td>
<td>15-20</td>
<td>-10%</td>
</tr>
<tr>
<td>Ethene - NO$_X$</td>
<td>2</td>
<td>10 - 25</td>
<td>-15%</td>
</tr>
<tr>
<td>Propene - NO$_X$</td>
<td>2</td>
<td>5 - 25</td>
<td>16%</td>
</tr>
<tr>
<td>Toluene or m-Xylene - NO$_X$</td>
<td>4</td>
<td>5 - 25</td>
<td>10%</td>
</tr>
<tr>
<td>Aromatic - NO$_X$ + CO</td>
<td>6</td>
<td>5 - 30</td>
<td>-17%</td>
</tr>
<tr>
<td>Ambient Surrogate - NO$_X$</td>
<td>24</td>
<td>2 - 110</td>
<td>-11%</td>
</tr>
</tbody>
</table>
### SUMMARY OF TVA RUNS AND FITS TO $\Delta[O_3]-[NO]$  

<table>
<thead>
<tr>
<th>Run Type</th>
<th>Runs</th>
<th>NOx Range (ppb)</th>
<th>Average Model Fits</th>
<th>Bias</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Characterization</td>
<td>32</td>
<td>0 - 54</td>
<td>1%</td>
<td>15%</td>
<td></td>
</tr>
<tr>
<td>Formaldehyde - NOx</td>
<td>4</td>
<td>39 - 42</td>
<td>-4%</td>
<td>10%</td>
<td></td>
</tr>
<tr>
<td>Isopentane - NOx</td>
<td>1</td>
<td>18</td>
<td>-28%</td>
<td>28%</td>
<td></td>
</tr>
<tr>
<td>Ethene, Propene, or trans-2-Butene - NOx</td>
<td>7</td>
<td>22 - 54</td>
<td>10%</td>
<td>10%</td>
<td></td>
</tr>
<tr>
<td>Toluene or m-Xylene - NOx</td>
<td>5</td>
<td>50 - 266</td>
<td>1%</td>
<td>8%</td>
<td></td>
</tr>
<tr>
<td>Simple Mixture - NOx</td>
<td>23</td>
<td>50 - 100</td>
<td>6%</td>
<td>7%</td>
<td></td>
</tr>
<tr>
<td>Ambient Surrogate - NOx</td>
<td>12</td>
<td>25 - 169</td>
<td>-8%</td>
<td>9%</td>
<td></td>
</tr>
</tbody>
</table>

### CSIRO RUNS AND FITS TO $\Delta[O_3]-[NO]$  

<table>
<thead>
<tr>
<th>Run Type</th>
<th>Runs</th>
<th>NOx Range (ppb)</th>
<th>Average Model Fits</th>
<th>Bias</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ambient Surrogate – NOx</td>
<td>20</td>
<td>17 - 100</td>
<td>-42%</td>
<td>42%</td>
<td></td>
</tr>
<tr>
<td>Standard Char. Model</td>
<td></td>
<td></td>
<td>-26%</td>
<td>27%</td>
<td></td>
</tr>
<tr>
<td>High Radical Source</td>
<td></td>
<td></td>
<td>-33%</td>
<td>33%</td>
<td></td>
</tr>
<tr>
<td>High Light Intensity</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

W. P. L. Carter  5/27/04  Low NOx Mechanism Evaluation
EFFECTS OF ALTERNATIVE CHARACTERIZATION ASSUMPTIONS ON CSIRO SIMULATIONS

\[ \frac{\Delta([O_3]-[NO])}{\text{Experiment} - \text{Model}} \times \frac{1}{\text{Experiment}} \]

\[ \Delta([O_3]-[NO]) \text{ Underprediction error vs. Surrogate / NOx ratio} \]

MODEL BIASES FOR PREDICTION OF $\Delta([O_3]-[NO])$

- All Characterization
- HCHO - NOx
- HCHO - CO - NOx
- Isopentane - NOx (TVA)
- Ethene - NOx
- Propene - NOx
- trans-2-Butene - NOx (TVA)
- Toluene - NOx
- m-Xylene - NOx
- Toluene - CO - NOx (UCR)
- m-Xylene - CO - NOx (UCR)
- Simple Mixes (TVA)
- Surrogate - NOx

UCR EPA
TVA
CSIRO
LOWEST NOx UCR EPA SURROGATE EXPERIMENT
(ROG SURROGATE = 300 PPBC, NOx = 2 PPB)

Concentration (ppm) vs Time (minutes)

MODEL UNDERPREDICTION BIASES FOR
SURROGATE – NOx RUNS VS. ROG/NOx RATIO

ROG / NOx Ratio Relative to ROG / NOx Giving Maximum O3
MODEL UNDERPREDICTION BIASES FOR SURROGATE – NOx RUNS VS. ROG/NOx RATIO

- UCR EPA
- CSIRO
- TVA
- UCR EPA (New Runs)
- MOIR
- - - - - Approximate MIR

ROG / NOx Ratio Relative to ROG / NOx Giving Maximum O3

MODEL UNDERPREDICTION SENSITIVITIES FOR UCR EPA RUNS

- SAPRC-99 (Range gives low and high walls→HONO)
- Reduced OH + NO2

This includes more recent runs carried out for EPA OBM project
COMPARISON OF CB4 AND SAPRC-99 MODEL ERRORS FOR UCR EPA SURROGATE RUNS

This includes more recent runs carried out for EPA OBM project.

COMPARISON OF CURRENT SURROGATE FITS WITH DATA USED IN PREVIOUS EVALUATION
## MODEL PERFORMANCE IN SIMULATING OTHER MEASUREMENTS IN SURROGATE RUNS

<table>
<thead>
<tr>
<th>Compounds</th>
<th>TVA</th>
<th>UCR EPA</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO(_2)</td>
<td>No data (NO(_x)-NO only)</td>
<td>Tends to underpredict consumption following maximum</td>
</tr>
<tr>
<td>PAN</td>
<td>Very significantly underpredicted</td>
<td>Reasonably well simulated in runs where O3 well simulated</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>Tendency to underpredict (depends on offgasing model)</td>
<td>Tendency to underpredict depends on NO(_x) levels</td>
</tr>
<tr>
<td>Reactant VOCs</td>
<td>Generally consistent with data</td>
<td>Tendency to underpredict final consumption rates</td>
</tr>
<tr>
<td>HNO(_3)</td>
<td>No data</td>
<td>Generally consistent with available data ([NO(_x)&gt;50 ppb])</td>
</tr>
</tbody>
</table>

Note: Data for above compounds not available for CSIRO Runs

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## MODEL PERFORMANCE SIMULATING FORMALDEHYDE IN UCR EPA SURROGATE RUNS

Formaldehyde Underprediction bias vs. ROG/NO\(_x\) or NO\(_x\) (experimental - calculated) / experimental \(\Delta[HCHO]\)
MODEL PERFORMANCE SIMULATING PAN IN UCR EPA SURROGATE RUNS

PAN Underprediction bias vs. ROG/NOx or NOx (experimental - calculated) / experimental final PAN

EFFECT OF CO ON AROMATIC - NOx RUNS

Toluene

m-Xylene

EPA077 (~25 ppb NOx)

EPA067 (~20 ppb NOx)

EPA066 (~5 ppb NOx)

Aromatic - NOx experiment

Aromatic - CO - NOx experiment

Aromatic - NOx model

Aromatic - CO - NOx model
EFFECTS OF ADJUSTMENTS TO PARAMETERIZED TOLUENE MECHANISM

ASSESSMENT OF NEED TO MODIFY MECHANISM FOR LOW NOx CONDITIONS

- Lower NOx levels result in increased importance of peroxy + peroxy reactions, which form different organic products that the peroxy + NO reactions that dominate when NOx is higher.
- SAPRC-99 uses an approximate “chemical operator” method for RO₂ reactions that neglects this change in products with NOx.
- Representing RO₂+RO₂ reactions more explicitly requires adding many reactions to the mechanism.
- Process analysis calculations were carried out to assess the relative importance of the different types of competing RO₂ reactions at low NOx.
- The results can then be used to assess priorities for mechanism modifications for more accurate low NOx predictions.
MODEL SIMULATIONS OF PEROXY REACTION INTEGRATED REACTION RATE RATIOS

Ratios of integrated reaction rates vs. NOx inputs relative to NOx giving maximum O3

IMPLICATIONS CONCERNING HOW TO MODIFY MECHANISMS FOR LOW NOx CONDITIONS

- Results of test calculations of integrated peroxy radical reaction rates with three types of low NOx scenarios indicate that:
  - Major low-NOx sink for peroxy radicals is reaction with HO2
  - Maximum importance of Alkyl Peroxy + Acyl Peroxy reaction is ~10%
  - Alkyl peroxy + Alkyl peroxy reactions negligible
- Adding reactions or species to improve representations of organic peroxy + peroxy reactions probably not worthwhile
- Higher priority is improving representation of:
  \[
  \text{RO}_2 + \text{HO}_2 \rightarrow \text{ROOH} + \text{O}_2 \\
  \text{ROOH} + \text{OH} \text{ or h} \nu \rightarrow \text{Products}
  \]
- This requires adding more hydroperoxide species to the mechanism, whose reactions are uncertain.
DISCUSSION AND CONCLUSIONS:

Good News

• Range of conduction where mechanisms have been evaluated has been significantly expanded
  • TVA data of comparable or better quality than previous runs in other chambers, despite formaldehyde contamination
  • CSIRO data proved to be useful in this evaluation, but more characterization information would increase its utility
  • Lower background in UCR EPA chamber permitted useful mechanism evaluation with NOx as low as ~2 ppb and improves precision of evaluation
  • Simulations of lower NOx characterization and most simple VOC – NOx experiments generally satisfactory
  • No apparent mechanism problem simulating very low NOx conditions where maximum O3 formation potentials achieved.
  • Inaccuracies caused by approximate treatment of RO2+RO2 reactions in current mechanism are probably not important

Bad News

• SAPRC-99 mechanism has consistent bias in underpredicting NO oxidation and O3 formation rates at low ROG/NOx ratios
  • Underprediction bias for CB4 even worse
  • Significant problems with current aromatics mechanisms:
    • Ozone increase caused by adding CO “radical amplifier” to aromatic – NOx systems underpredicted by factor of ~2
    • Adjustments to the mechanisms as currently parameterized cannot correct this problem
    • Aromatics mechanism problems may be the cause of the low ROG/NOx underprediction bias, but this is not certain.
  • Improving accuracy of low NOx organic product predictions for requires explicit treatment of uncertain organic hydroxides
RESEARCH NEEDS

• The current parameterized aromatics mechanisms need to be reformulated and made consistent with available data
• The underprediction problem at low ROG/NOₓ needs to be investigated and resolved
• Data are needed on effects of temperature on ozone and other secondary products. (UCR EPA chamber suitable for this)
• Well-characterized, low NOₓ chamber data are needed to develop and test models for secondary PM formation. (UCR EPA chamber also suitable for this)
• SAPRC-99 needs to be updated to be consistent with latest recommendations and made more compatible with SOA models
• A new condensed mechanism, traceable to an updated and evaluated detailed version, needs to be developed to finally replace the out-of-date CB4 mechanism