Production of Metastable Singlet Oxygen in the Reaction of Nitric Oxide with Active Oxygen

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Review of EOIL Chemistry

O₂/He + NO → O₂(a), O

Discharge Plasma

- e⁻ + O₂ → O₂(a) + e⁻
- e⁻ + O₂ → O + O + e⁻

Ionization

- e⁻ + O₂(a) → losses
- Dilution in He required

- O + NO + M → NO₂ + M
- O + NO₂ → NO + O₂
- O + O₂ + M → O₃ + M
- O + O₃ → O₂ + O₂
- O + O₂(a) + M → products

O + I₂ → IO + I
O + IO → O₂ + I
O₂(a) + I ↔ O₂ + I*
O + I* → O + I

\[
\frac{[I^*]}{[I]} \rightarrow K_{EQ}(T) \frac{[O₂(a)]}{[O₂]}
\]
**I* Loss Mechanisms**

**O + I* Quenching:**
Loss of O$_2$(a)

\[
\ln \left( \frac{[O_2(a)]}{[O_2(a)]_0} \right) = -0.9
\]

Slope = 97 ± 15 s$^{-1}$

k$_Q$ = 1.3x10$^{-11}$ cm$^3$/s at 330 K

Excellent agreement with Emory Univ. results

\[
[I^*]/[I] \text{ is suppressed by unknown chemistry:}
I^* + O_2 \rightarrow I + O_2(X,v) \ ??
\]

Maybe not...

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**Departure from Equilibrium Relationship**

<table>
<thead>
<tr>
<th>P (torr)</th>
<th>O$_2$ (%)</th>
<th>I$_2$ cm$^{-3}$</th>
<th>Power (W)</th>
<th>Rxn Time (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>80%</td>
<td>1.14 (13)</td>
<td>60-120</td>
<td>9.0</td>
</tr>
<tr>
<td>1.5</td>
<td>50%</td>
<td>1.25 (13)</td>
<td>40-120</td>
<td>9.0</td>
</tr>
<tr>
<td>1.5</td>
<td>5.5%</td>
<td>4.7 (12)</td>
<td>70</td>
<td>2.7-7.0</td>
</tr>
<tr>
<td>1.5</td>
<td>5%</td>
<td>5.2 (12)</td>
<td>120</td>
<td>7.6</td>
</tr>
<tr>
<td>1.5</td>
<td>5%</td>
<td>6.0 (12)</td>
<td>70</td>
<td>7.0</td>
</tr>
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</table>

NO$_2$ Added

Gain

Absorption
Sub-Equilibrium Gain

- O + I* quenching does not account for shortfall in [I*]/[I]

- We previously suggested I* loss via
  \[ I^* + O_2 \rightarrow O_2(v) + I \]
  - implies additional O_2(a) loss in absence of O
  - not supported by recent measurements in supersonic flow

- Are there other species in the active-O_2 flow?
  - what is the chemistry of O, O_3, NO in active-O_2?
Production of $O_2(a)$ from $NO_x +$ Active-$O_2$

- Discharge effect: maybe $O^- + NO \rightarrow NO_2 + e^-$
- Experiments at Emory U.: $O + NO_2 \rightarrow O_2(a) + NO$
- NO + precursor species? $O_3$?
  - is there an energetic “dark” species in active-$O_2$ flows?

He:$O_2 = 16:3$ mmole/s, 12.5 torr, 500 W RF

![Graph showing $O_2(a)$ yield vs. $NO, NO_2$ flow rate]
Subsonic Flow Reactor for EOIL Kinetics Experiments

Optical Diagnostics:
- NIR Emission Spectrometer: 0.7 to 1.5 µm, $O_2(a,b)$
- NO-O Chemiluminescence: 580 nm, $O$
- UV Absorption: 254 nm, $O_3$
- Visible Emission Spectrometer: 500 to 800 nm, $O_2^*, O^*, NO_2^*$
Illustration of Optical Setup for O₃ Absorption Diagnostic

- UV lamp: Hg(I) line source, 254 nm
- 20-bit precision on absorbance measurement
- Sensitivity ~ $10^{12}$ molecules/cm³
[O₃] Measurements: 10% O₂/Ar, 3.8 mmoles/s, 300 K

- P dependence is consistent with O + O₂ + M
- O₃ concentrations are much lower than expected
Experimental Conditions

- **O₂/He discharge effluent**: observe kinetic behavior of O₂(a), O, O₃ before and after injection of NO
  - long reaction times, high [NO] to magnify O₂(a) production effect

- Vary pressure and [O₂] to examine reaction order

<table>
<thead>
<tr>
<th>Case A</th>
<th>Case B</th>
<th>Case C</th>
</tr>
</thead>
<tbody>
<tr>
<td>52% O₂ in He</td>
<td>9.6% O₂ in He</td>
<td>9.7% O₂ in He</td>
</tr>
<tr>
<td>10.7 torr</td>
<td>10.1 torr</td>
<td>3.2 torr</td>
</tr>
<tr>
<td>300 K</td>
<td>300 K</td>
<td>300 K</td>
</tr>
<tr>
<td>196 cm/s</td>
<td>229 cm/s</td>
<td>229 cm/s</td>
</tr>
</tbody>
</table>
Baseline Data: Active-\(O_2\) Only

- **O** loss rate, **O\(_3\)** production rate should be larger for \(O + O_2 + M\) mechanism

- **No** loss of \(O_2(a)\) along the main flow tube
  \[
  k(O + O_2(a) + M) < 2 \times 10^{-32} \text{ cm}^6/\text{s}
  \]

A: 52% \(O_2\), 10.7 torr
B: 9.6% \(O_2\), 10.1 torr
C: 9.7% \(O_2\), 3.2 torr
Comparison to Kinetics Models
52% $O_2$/He, 10.7 torr

- $O + O_2 + M \rightarrow O_3 + M$
- $O + O_3 \rightarrow O_2 + O_2$

- $O + O_2 + M \rightarrow O_3(v) + M$
- $O_3(v) + M, O \rightarrow O_3$
- $O_3(v) + O_2(a) \rightarrow O + 2O_2$
- $O + O_2(a) + M \rightarrow O_3^{+} + M$
- $O_3^{+} + M \rightarrow O_3(v) + M$

- $O_3(v) + O_2(a)$ dissociation step can explain large $[O]/[O_3]$
- Too many adjustable parameters
Previous Evidence for Fast $O_2(a) + O_3(v)$

- Loss term for Discharge-Produced $O_3(v)$
- Fast Initial Loss of $O_2(a)$ in $O + O_2$ Mixture

Rawlins et al., JCP 1987

Azyazov et al., LASE 2007
**NO + Active-\(O_2\): 52\% \(O_2\), 10.7 \text{torr}**

- \(O_2(a)\) production increases with [NO] and reaction time
- Removal of O and \(O_3\) are consistent with NO reactions
  
  \[
  O_3 + \text{NO} \rightarrow \text{NO}_2 + O_2 \\
  \text{O} + \text{NO} + \text{M} \rightarrow \text{NO}_2 + \text{M} \\
  \text{O} + \text{NO}_2 \rightarrow \text{NO} + O_2
  \]
**NO + Active-O₂: Pressure Effects**

- **Filled symbols:** zero NO
  - \(\text{O}_2(\text{a})\) and \(\text{O}_3\) are independent of injector position

- **Open symbols:** \([\text{NO}] = 9.2 \times 10^{14} \text{ cm}^{-3}\)
  - \(\text{O}_2(\text{a})\) is produced even when \(\text{O}_3\) is negligible

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**9.6% O₂, 10.1 torr**

**9.7% O₂, 3.2 torr**
\( \text{O}_2(a) \) Production from NO + Active-O\(_2\), 3-10 torr

- **\( \text{O}_2(a) \) production is essentially independent of \( P, [\text{O}_2] \)**
  - sub-linear dependence on NO
  - ground-state \( \text{O}_3 \) is not involved
- **Net \( \text{O}_2(a) \) production rate \( \sim 7 \times 10^{15} \text{ cm}^{-3} \text{ s}^{-1} \) for \( [\text{NO}] \sim 1 \times 10^{15} \text{ cm}^{-3} \)**
Mystery Chemistry: Is There a “Dark” State?

NO + (??) → O₂(a) + (??)

- Reaction requires long-lived metastable species, in steady-state independent of [M]
  - ions, O*, O₂* are rapidly removed prior to the reaction zone
- Note [O][O₂(a)] does not vary much for our conditions
- Speculation: O₃‡, mythical metastable state of O₃?

\[
O + O₂(a) + M \xrightarrow{a} O₃⁺ + M
\]
\[
O₃⁺ + M \xrightarrow{b} \text{products (slow)}
\]
\[
\left[ O₃⁺ \right] = \frac{k_a}{k_b} \left[ O \right][O₂(a)]
\]

Then \( O₃⁺ + NO \xrightarrow{c} NO₂ + O₂(a) \)

- data imply relationship for \( k_a k_c / k_b \sim 3.5 \times 10^{-29} \text{ cm}^6/\text{s} \)
  - If \( k_a \sim 10^{-32} \text{ cm}^6/\text{s} \), \( k_c / k_b \sim 3500 \)
Summary

- Initial examination of $O_2(a)$, $O$, $O_3$ chemistry in $O_2$/He discharge effluent with and without NO addition

  - Active-$O_2$: rates of $O_3$ production and $O$ removal are too slow for conventional $O + O_2 + M$ mechanism
    - suggests $O_3$ dissociation: $O_2(a) + O_3(v)$

- Reaction with NO produces $O_2(a)$
  - precursor unknown, $P$-independent
  - possible connection of energetic precursor with $I^*$ excitation mechanism?

- We don’t understand active-$O_2$ chemistry very well!
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