Plasma Reactions of $O_n$ High Energy Species – $O$, $O_2(v)$, $O_2(a \: 1\Delta_g)$, and $O_3$

$O_2$ plasma kinetics workshop
Reykjavik
Sep 2016

Albert A. Viggiano
Space Vehicles Directorate
Air Force Research Laboratory
Outline

• Brief introduction to ionospheric chemistry
  — Reasons for energetic oxygen studies

• Techniques for O, O$_2$(v), O$_2$(a $^1\Delta_g$), and O$_3$

• Data examples for each reactant
Summary of Main Ionospheric Chemistry of N and O species

Initiation

Studied at AFRL at high T

Not Studied

Studied at CRYRING
Negative Ion Reactions in the Atmosphere

Numerous places reactive oxygen species are important

For more information on atmospheric ion chemistry
Chem. Rev. 115, 4542–4570 (Feb 2015)
Hypersonic Plasma Effects

- AJAX hypersonic concept vehicle utilizes air plasmas to aid combustion
- Plasma Blackout of $\text{C}^3\text{I}$, GPS Navigation

Combustor Test @ Mach 2
Selected Ion Flow Tube (SIFT) for $O_2(v)$

- T Range 85 - 550 K
- Pressure Range ~0.3 - 1 Torr
- Kinetic energy range 0.01 – 1 eV

Important:

Translational energy distribution is Quasi-Boltzmann
Temperature Range 300-1800 K
Ceramic tube - 1800 K
Quartz tube - 1400 K
Data from HTFA and Drift Tube → Internal Energy Dependence

\[ \text{N}_2^+ + \text{O}_2 \rightarrow \text{O}_2^+ + \text{N}_2 \]

vs. T or KE

900 K limitation miss upturn

More likely vib dependence

Add rotational energy
Most Important Ionospheric Reactions

Changes directions at 900 K
Upturn vs T mostly $N_2 (v \geq 2)$
Previous data missed upturns

Big difference between T and KE
Vibrationally excited $O_2$ important
maybe 10x faster for $v = 2$
N, O Reactions Studied at AFRL by this technique

See: *Adv. in Gas Phase Ion Chem.* vol. 4, p 85-136 (Dec 2001)

\[ O^+ + O_2 \rightarrow O_2^+ + O \ (\leq 1800 \text{ K}) \]

\[ O^+ + N_2 \rightarrow NO^+ + N \ (\leq 1600 \text{ K}) \text{ most important reaction in ionosphere} \]

\[ O^+ + NO \rightarrow NO^+ + O \ (\leq 1400 \text{ K}) \]

\[ O_2^+ + NO \rightarrow NO^+ + O \ (\leq 1400 \text{ K}) \]

\[ N_2^+ + O_2 \rightarrow O_2^+ + N_2 \ (\leq 1800 \text{ K}) \]

\[ N^+ + O_2 \rightarrow NO^+, O_2^+, O^+ \ (\leq 1400 \text{ K}) \text{ also product states of NO} \]

\[ N_n^+ + NO \rightarrow \text{products} \ (\leq 1400 \text{ K}) \]

\[ N_3^+ + O_2 \rightarrow NO^+; NOO^+ \ (\leq 1400 \text{ K}) \]

Chemistry of NOO^+

\[ O_3^+ + N_2, O_2 \rightarrow \text{products} \]
Ionospheric Data
(with E. Mishin, B. Burke)

MISHIN ET AL.: STORMTIME SAPS-RELATED TROUGHS

SAPS wave structure observed by DMSP F14 at 2307 UT on 6 April 2000

Density trough
(n_i - n_i \text{ max}) / n_i \text{ max}

Dependence on electron temperature was not expected
Chemistry Leading to Trough

Vibrational excitation
\[ e(KE) + N_2 \rightarrow N_2(v) \]
\[ e(KE) + O_2 \rightarrow O_2(v) \]

More KE ⇒ more vib.

Atom Transfer
\[ O^+ + N_2(v) \rightarrow NO^+ + N \]

Charge Exchange
\[ O^+ + O_2(v) \rightarrow O_2^+ + O \]

More vib. ⇒ k faster

Uses HTFA data

Our data shows that vibrational excitation leads to faster conversion of atomic species (non-recombining) to diatomic species (recombining)

Dissociative Recombination
\[ NO^+ + e \rightarrow O^+ N \]
\[ O_2^+ + e \rightarrow O^+ O \]

More diatomic ⇒ more recomb.

Determines the ionization balance in the F region
N⁺ + O₂ Chemistry Studied

- Rate constants to 1400 K
  - Rotational and translational energy do little to change rate or products
    - v = 1 goes at $k_{\text{langevin}}$
- Three products formed
  - ~50% O₂⁺ (CT)
  - ~40% NO⁺
  - ~10% O⁺

- All NO⁺ is ground state ($^1\Sigma$) even though NO⁺ ($^3\Sigma$) is exothermic (300- 550 K)
Instruments for ion and electron molecule studies of O$_3$
<table>
<thead>
<tr>
<th>reaction</th>
<th>products</th>
<th>rate constant $k_x (10^{-9} \text{ cm}^3 \text{ s}^{-1})$</th>
<th>branching fractions</th>
<th>$-\Delta H \text{ kJ/mol}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{O}^- + \text{O}_3 \rightarrow$</td>
<td>$\text{O}_3^- + \text{O}$</td>
<td>$1.7; [1.5]$</td>
<td>0.81</td>
<td>63</td>
</tr>
<tr>
<td></td>
<td>$\text{O}_2^- + \text{O}_2$</td>
<td></td>
<td>0.19</td>
<td>294</td>
</tr>
<tr>
<td>$\text{O}_2^- + \text{O}_3 \rightarrow$</td>
<td>$\text{O}_3^- + \text{O}_2$</td>
<td>$1.3; [1.2]$</td>
<td>1.00</td>
<td>160</td>
</tr>
<tr>
<td>$\text{OH}^- + \text{O}_3 \rightarrow$</td>
<td>$\text{O}_3^- + \text{OH}$</td>
<td>$1.4; [1.4]$</td>
<td>0.90</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>$\text{HO}_2^- + \text{O}_2$</td>
<td></td>
<td>0.08</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>$\text{O}_2^- + \text{HO}_2$</td>
<td></td>
<td>0.02</td>
<td>47</td>
</tr>
<tr>
<td>$\text{NO}_2^- + \text{O}_3 \rightarrow$</td>
<td>no reaction</td>
<td>$0.18; [1.1]$</td>
<td>0.99</td>
<td>264</td>
</tr>
<tr>
<td></td>
<td>$\text{NO}_3^- + \text{O}_2$</td>
<td></td>
<td>0.01</td>
<td>-14</td>
</tr>
<tr>
<td>$\text{NO}_3^- + \text{O}_3 \rightarrow$</td>
<td>no reaction</td>
<td>$&lt;0.005; [0.97]$</td>
<td></td>
<td>21</td>
</tr>
<tr>
<td>$\text{CO}_3^- + \text{O}_3 \rightarrow$</td>
<td>no reaction</td>
<td>$&lt;0.001; [0.98]$</td>
<td></td>
<td>98</td>
</tr>
<tr>
<td></td>
<td>$\text{O}_2^- + \text{CO}_2 + \text{O}_2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{CO}_4^- + \text{O}_3 \rightarrow$</td>
<td>$\text{O}_3^- + \text{CO}_2 + \text{O}_2$</td>
<td>$0.46; [0.93]$</td>
<td>0.93</td>
<td>81</td>
</tr>
<tr>
<td></td>
<td>$\text{CO}_3^- + 2\text{O}_2$</td>
<td></td>
<td>0.07</td>
<td>108</td>
</tr>
</tbody>
</table>
FIG. 2. Electron attachment rate coefficient versus temperature. Present results (●) and swarm upper limit of Fehsenfeld et al. [3] (□) are true thermal values. The remaining data are plotted versus electron temperature. The drift tube results of Stelman et al. [4] (dashed line) are derived from a least squares fit of the combined data for 200 and 300 K vibrational temperature ozone reacting with energetic electrons. The electron beam results of Skalny et al. [8] (⊙) and Senn et al. [2] (solid line) were derived by those authors from measurements of the reaction cross section for 300 K vibrational temperature ozone with energetic electrons.

O, N atom reaction technique

Diagram showing a microwave discharge setup with flows of NO and N₂. A graph illustrates ion signal vs. [NO] concentration with markers for O₂⁺, NO⁺, and O₂⁺ with discharge off. The titration point is marked on a line graph.
Positive Ion - Atom Results

\[O_2^+ + N \rightarrow NO^+ + O\]

\[N_2^+ + O \rightarrow NO^+ + N\]

\[
\rightarrow N_2 + O^+
\]

\[\Delta H^0_r(0K) = -96.5 \text{ kcal/mol} \quad (1)\]

\[\Delta H^0_r(0K) = -70.6 \text{ kcal/mol} \quad (2a)\]

\[\Delta H^0_r(0K) = -45.2 \text{ kcal/mol} \quad (2b),\]

\[ \text{Negative Ion - Atom Results} \]

\[ \text{O}_2^- + N \rightarrow \text{NO}_2 + e^-, \quad \Delta_r H^\circ = -4.11 \text{ eV}, \]

\[ \text{NO} + \text{O}^-, \quad \Delta_r H^\circ = -2.39 \text{ eV}, \]

\[ \text{O}_2^- + \text{O} \rightarrow \text{O}_3 + e^-, \quad \Delta_r H^\circ = -0.66 \text{ eV}, \]

\[ \text{O}_2 + \text{O}^-, \quad \Delta_r H^\circ = -1.01 \text{ eV}, \]

\[ \text{O}^- + \text{N} \rightarrow \text{NO} + e^-, \quad \Delta_r H^\circ = -5.09 \text{ eV}, \]

\[ \text{O}^- + \text{O} \rightarrow \text{O}_2 + e^-, \quad \Delta_r H^\circ = -3.71 \text{ eV}. \]

Turbulent Ion Flow Tube

10-760 Torr
300-700 K
Also for very slow rate constants
Limits for $\text{O}_2^+$ with $\text{N}_2$

**Figure 1.** Mass spectrum taken at 35 Torr and 523 K.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$k$ (upper limit)</th>
</tr>
</thead>
<tbody>
<tr>
<td>423</td>
<td>$2 \times 10^{-21}$</td>
</tr>
<tr>
<td>523</td>
<td>$4 \times 10^{-21}$</td>
</tr>
<tr>
<td>623</td>
<td>$1 \times 10^{-20}$</td>
</tr>
</tbody>
</table>

O$_2$(a $^1\Delta_g$) background

- O$_2$(a $^1\Delta_g$) emissions at 1270 nm contribute to the IR airglow\(^1\)
- O$_2$(a $^1\Delta_g$) created in O$_2$ discharges\(^2\)
  - Electron impact on O$_2$
  - O$_2$(b $^1\Sigma_g^+$) collisional quenching by O$_2$
- Affects oxidation chemistry
  - Materials processing\(^3\)
  - Oxygen-iodine lasers\(^4\)

---

$O_2(a \ ^1\Delta_g)$ in Ionosphere D-region

- Reactions controlling e- concentrations in ionosphere influence radiowave propagation$^1$

Brasseur and DeBats, JGR, 91, 4025 (1985)

$^1$Handbook of Geophys. & Space Environ., A.S. Jursa, ed. 1985
Previous Kinetics for $O_2(a \ ^1\Delta_g)$ Reactions

- Large disparity in the literature values of the rate constants for $O^-$ and $O_2^- + O_2(a \ ^1\Delta_g)$

  - $O_2^- + O_2(a \ ^1\Delta_g)$
    - NOAA flowing afterglow (FA)$^{10}$: $2.0 \times 10^{-10}$ cm$^3$ s$^{-1}$
    - Upschulte et al., FA$^{11}$: $2.4 \times 10^{-11}$ cm$^3$ s$^{-1}$

  $^{11}$JPC. 98, 837 (1994)

- $O^- + O_2(a \ ^1\Delta_g)$:
  - NOAA, FA: $3.0 \times 10^{-10}$ cm$^3$ s$^{-1}$
  - Upschulte et al., FA: $3.3 \times 10^{-11}$ cm$^3$ s$^{-1}$
  - Belostostky et al., plasma model: $1.9 \times 10^{-10}$ cm$^3$ s$^{-1}$
  - Stoffels et al., plasma model: $1.3 \times 10^{-10}$ cm$^3$ s$^{-1}$
AFRL Experiments

- Utilize newly designed $O_2(a^1\Delta_g)$ emission detection scheme to re-measure the kinetics for the $O^- + O_2\rightarrow O_2(a^1\Delta_g)$ reactions from 200-700 K

- Calibrate detection setup vs. absolute standard
  - Settle the discrepancy in the literature values

- Expand the studies to other ion-molecule reactions with $O_2(a^1\Delta_g)$

*J. Phys. Chem. A.* 111, 5218-5222 (June 2007)

SIFT with $\text{O}_2(\text{a}^1\Delta_g)$ Detection
Initial experiments

Glass wool: quenches most O atoms from discharge

Typical % of total $\text{O}_2$ concentration in SIFT: 9% $\text{O}_2(\text{a}^1\Delta_g)$, 1% O, <1%$\text{O}_3$
Chemical $O_2(a^1\Delta_g)$ Generation Can Study Temperature Dependencies

$$H_2O_2 + Cl_2 + 2KOH \rightarrow O_2/O_2(a) + 2KCl + 2H_2O$$
\[ \text{O}_2^- + \text{O}_2(a \, ^1\Delta_g) \rightarrow 2\text{O}_2 + e^- \]

Need to account for O, O\textsubscript{3} impurities.
\[ \text{O}_2^- + \text{O}_2(\text{a} \text{ } ^1\Delta_g) \text{ 298 K Results} \]

- \( k = 6.6 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \)
  - 90% of collision rate constant \( \therefore \) very efficient
  - 3x higher than previous highest values

- Upshulte et al. FA experiments
  - Kinetics data showed fast and slow decay
  - Incorrectly assumed slow decay was correct
    - New bi-exponential fit shows fast decay = NOAA value
  - \( \text{O}_2 \) source gas present in FA flow tube
    - Electrons present re-attach to \( \text{O}_2 \) \( \therefore \) lower apparent decay in FA measurements
O\(^-\) + O\(_2\)\((a \, ^1\Delta_g)\) 298 K Results

- \(k = 1.1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}\)
  - 12\% of \(k_{\text{col}}=9.0 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}\)
  - \(2-3x < \) previous values (even more – see T work)

- New charge transfer product channel observed:
  \[
  O^- + O_2(a \, ^1\Delta_g) \rightarrow O_3 + e + 60 \text{ kJ mol}^{-1} \quad <70\%
  \]
  \[
  \rightarrow O_2^- + O + e - 3 \text{ kJ mol}^{-1} \quad >30\%
  \]

- New channel important pathway in low-pressure O\(_2\) discharges where:
  - O\(^-\) is primary ion
  - Three-body O\(_2\)^- formation negligible
Temperature Dependencies
200-700 K

O\(^-\), O\(_2\)^- + O\(_2\) (a\(^1\Delta_g\)) vs. T

Rate Constant (cm\(^3\) s\(^{-1}\))

Temperature (K)
• O\(^{-}\) rate constant at 298 K = 8.6\(\times\)10\(^{-11}\) cm\(^3\) s\(^{-1}\)

• D-region is cold \(\therefore\) O\(^{-}\) rate constants are lower than previously assumed at low temperatures given positive \(T\) dependence

• Increased fraction of O\(^{-}\) converted to O\(_2\)\(^{-}\) at high temperatures increases conversion rate to electrons
  – Additional O\(_2\)\(^{-}\) rapidly converted to e\(^{-}\)
Conclusions

Innovative techniques allow wide range of species studied

New techniques often yield unexpected results
Acknowledgments

In-house
Tom Miller
Skip Williams
Bob Morris
Sue Arnold
Nick Shuman
Shaun Ard
Oscar Martinez
Justin Wiens
Jenny Sanchez

Theory
E. Mishin – atmospheric modeling
Jurgen Troe – statistical modeling

Made possible by long term funding by AFOSR
Molecular Dynamics (Berman)