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# Chlorine-Initiated Oxidation of Hydrocarbons:

Mechanistic Insights from Measurements of Gas- and Particle-Phase Composition

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## Chlorine Chemistry: Fast and Furious

- VOC + ·Cl much faster than VOC + OH
   e.g. 10-100 × for alkanes, 3 × for isoprene
- ·Cl can oxidize functional groups that OH cannot e.g. terminal H on alkane
- • Cl peaks before OH (esp. important in early mornings)
- Higher concentrations of reactive chlorine than previously assumed

-- Underrepresented sources: energy industry, metals processing, trash burning, disinfectant

-- Unrecognized processes: heterogeneous formation from PM chloride Faxon et al., AIChE Journal, 2018

# Very High PM Chloride in New Delhi



High PM chloride can result in high ·Cl through het chemistry

Gani et al., ACPD, 2018

#### Experiments on ·Cl + VOC



#### **Environmental Chamber Experiments**



# Time-of-Flight

## **Chemical Ionization Mass Spectrometer**

- Chemical ionization (soft)
- Time of flight (ToF)
  - Multiple ions at same mass-to-charge ratio (high resolution)
  - Continuous sampling







http://www.aerodyne.com/

#### Isoprene + CI: Multigenerational Chem.



#### Toluene + Cl



#### Toluene + CI: NOx effect



## **Organic Aerosol Composition: Ng Triangle**



Aromatic products on LHS, ring-opened products on RHS of Ng triangle

# Molecular composition of organic aerosol: Filter Inlet for Gases and AEROsols



# Molecular composition of organic aerosol: Filter Inlet for Gases and AEROsols



#### **Organochlorides from Alkanes**



## 2D Thermograms



Chlorine-Octane, High NO<sub>x</sub>



# 2D Thermograms

T<sub>max</sub> increases with m/z

Oligomer and very low volatility compounds

Organic thermal decomposition products

Inorganic thermal decomposition products, e.g. from seed particles. Atmospherically non-volatile compounds

Wang and Hildebrandt Ruiz, ACP, 2018





#### Chlorine- vs OH-Alkane OA



#### OH+Dodecane, High NO<sub>x</sub>



#### Chlorine- vs OH-Alkane OA



#### OH-Dodecane, High NO<sub>x</sub>



#### Chlorine- vs OH-Alkane OA



#### α-pinene + CI: gas and particle-phase products



#### Summary

- Chlorine chemistry is fast and furious; concentrations higher than previously predicted.
- Multigenerational chemistry from Cl+VOC

   → formation of HOM and oligomeric compounds
   → high yields of SOA
- Organochlorides from all precursors (including alkanes), according to FIGAERO-CIMS and ACSM
- Different product distributions from OH vs. Clinitiated chemistry
- Lots of work left to do. Current projects: Isoprene + Cl + NOx α-pinene + Cl Alkanes + Cl, no NOx

# Thank you! Lea's e-mail: <u>lhr@che.utexas.edu</u> Postdoc position available



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