Investigating the Peroxy Radical Reactivity via the Organic Iodide Precursor 3-Iodo-1-Propanol

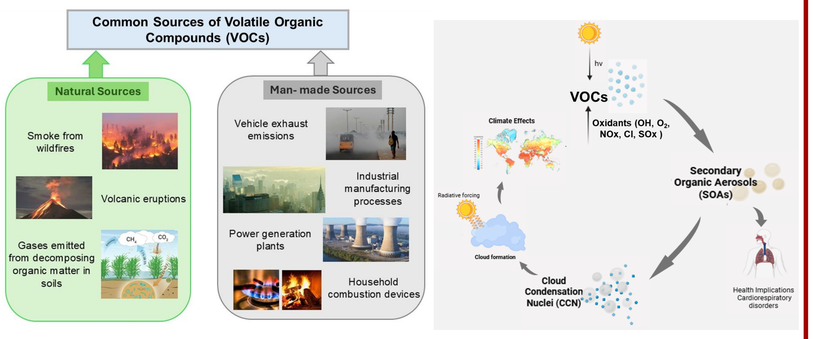
Nathanel Aviges, Lishana Wimalarathne, and Jean C. Rivera-Rios
Department of Chemistry and Chemical Biology, Rutgers University- New Brunswick, NJ

Abstract

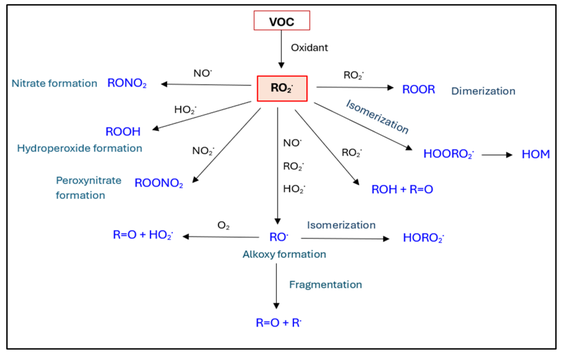
Ozone and hydroxyl radicals are key oxidants in the atmosphere that influence climate by reacting with gases like carbon monoxide, methane, and volatile organic compounds (VOCs). These reactions affect processes such as precipitation, the greenhouse effect, and Earth's albedo. However, measuring hydroxyl radicals, particularly from peroxyl radicals is difficult due to their short lifespans and limitations in current experimental methods. This study focuses on functionalized organic iodide precursor 3-iodo-1-propanol and its reactivity under different atmospheric conditions. The organic iodide precursor was photolyzed in a flow reactor using 254 nm, 300 nm and 350 nm light. The resulting products were monitored and quantified using iodide adduct chemical ionization mass spectrometry (I^--CIMS). The primary isomerization product formed upon photolysis was identified as 4-hydroperoxybutanal (m/Q=217), the major bimolecular photolysis products 3-hydroxypropanal (m/Q=201), 1,3-propanediol (m/Q=203), 3-hydroperoxy-1-propanol (m/Q=219), and the dimer bis(3-hydroxypropyl) peroxide (m/Q=277). The distribution of photolysis products was found to vary significantly with the three wavelengths and the residence time within the system.

Introduction

Atmospheric chemistry studies how substances in our air evolve, including emissions, reactivity, deposition, and transport- with a special focus on VOCs, which play key roles to influence air quality and climate.



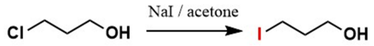
RO_2 Fate Diagram



Peroxy radicals (RO_2) are central to atmospheric oxidation product distributions. A single precursor can form hundreds of species depending on the oxidation conditions.

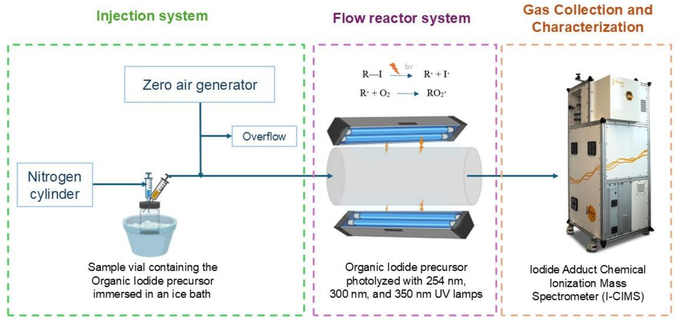
Results and Discussion

Synthesis of 3-Iodo-1-Propanol

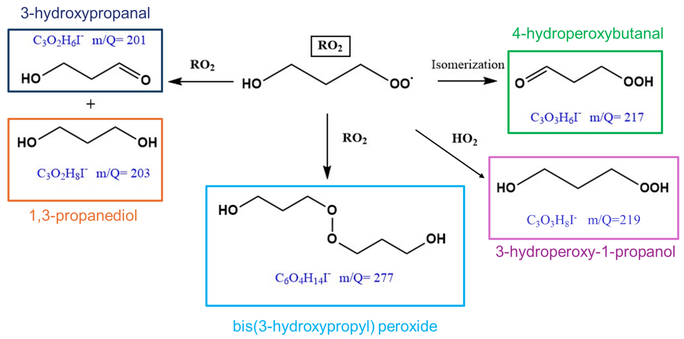


3-iodo-1-propanol was photolyzed under different atmospheric conditions to investigate the photolysis products formed.

Schematics of the Flow Reactor System

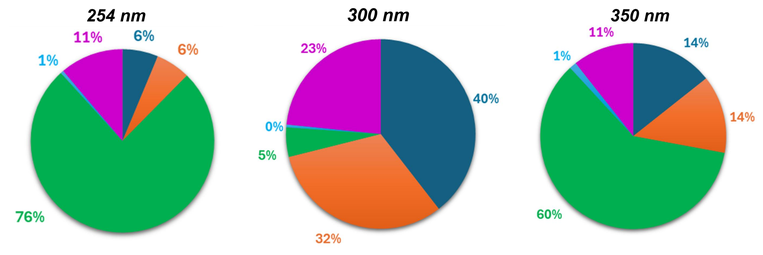


Photolysis Products of the 3-Iodo-1-Propanol

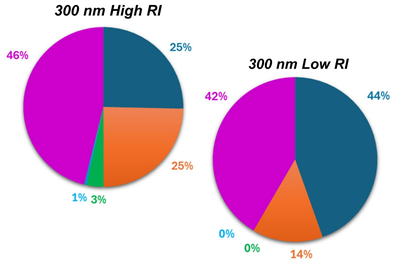


Photolysis Products Distribution

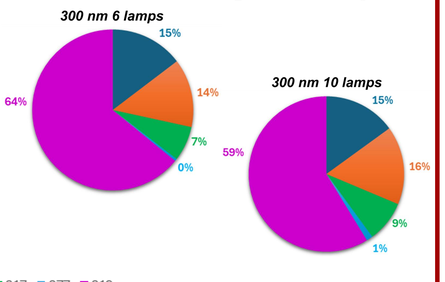
1. Effect of Photolysis Wavelength



2. Effect of Precursor Concentration



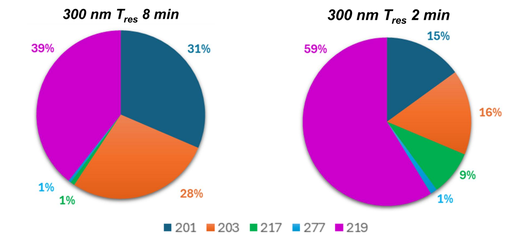
3. Effect of Light intensity



201 203 217 277 219

Results and Discussion

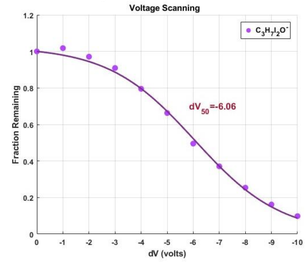
4. Effect of Residence Time



Determining the Sensitivity of the Photolysis Products to the Iodide-CIMS

1. Voltage Scanning Approach

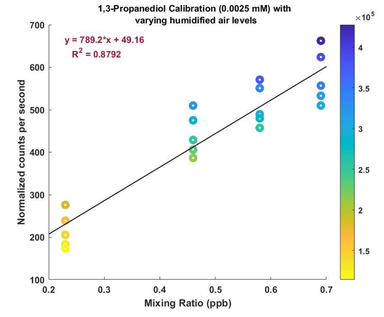
Voltage scanning is used to probe the binding energy of iodide-molecule adducts, allowing the sensitivity of photolysis products to be related to cluster stability.



Photolysis Products	m/Q	dV_{50} (V)
$C_3H_4IO_2^-$	201	-4.30
$C_3H_6IO_2^-$	203	-5.42
$C_3H_8IO_3^-$	217	-6.95
$C_3H_8IO_3^-$	219	-6.07
$C_6H_{14}IO_4^-$	277	-4.63
$C_3H_7I_2O^-$	313	-6.06

2. Calibrating the CIMS

The Iodide-CIMS is calibrated with some identified photolysis products to enable the correlation between signal intensity and product concentration.



Future Directions

- Synthesize and calibrate the Iodide CIMS with 3-hydroperoxy-1-propanol (m/Q=219) to improve product quantification.
- Model the flow reactor system using F0AM box model to simulate reaction kinetics and compare with experimental results.
- Investigating the functional group effects on peroxy radical reactivity using organic iodide precursors 4-iodo-2-butanone and 4-iodo-2-butanol.

Acknowledgement

We gratefully acknowledge the funding support of Rutgers University and the valuable assistance of colleagues in the Rivera-Rios Atmospheric Chemistry group.

References

J. Phys. Chem. A, 2021, 125, 10303–10314
J. Am. Chem. Soc., 2010, 132, 10748–10755
J. Phys. Chem. A, 2021, 125, 9027–9039
J. Phys. Chem. Lett., 2013, 4, 3513–3520