Measuring the Kinetics between Aldehydes and Peroxides

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Aerosols

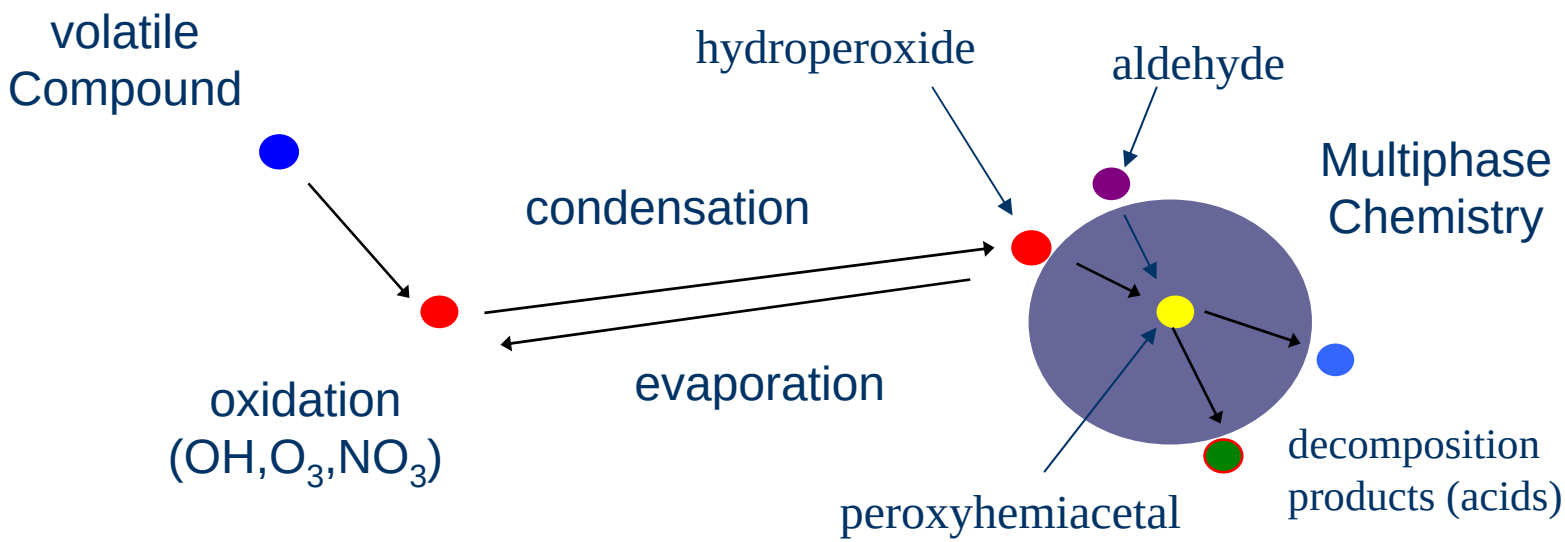
- An aerosol is a suspension of particles in a gas
- Play an important role in climate and atmospheric chemistry
- Influence global climate by scattering and absorbing sunlight and provide condensation nuclei for cloud droplets
- Participate in heterogeneous chemical reactions and have adverse effects on human health

Primary versus Secondary Aerosol Formation

- Primary particles are directly emitted into the atmosphere



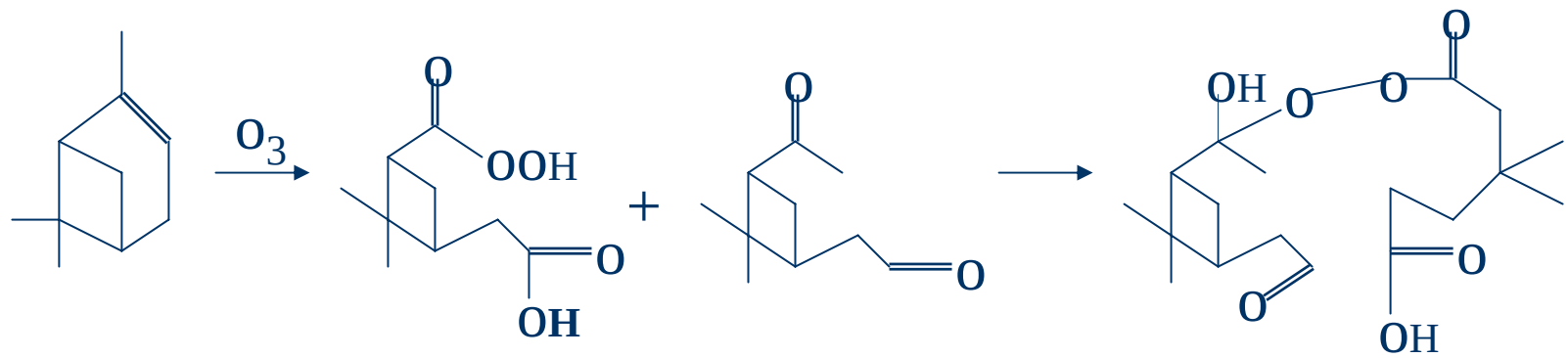

Secondary Aerosol Formation



Secondary organic aerosol is formed in the atmosphere through gas-to-particle conversion process

Formation of Peroxyhemiacetals

- Monoterpenes are atmospherically abundant alkenes that can react with O_3 to form hydroperoxides and aldehydes
- Hydroperoxides and aldehydes can react in particles to produce secondary organic aerosol

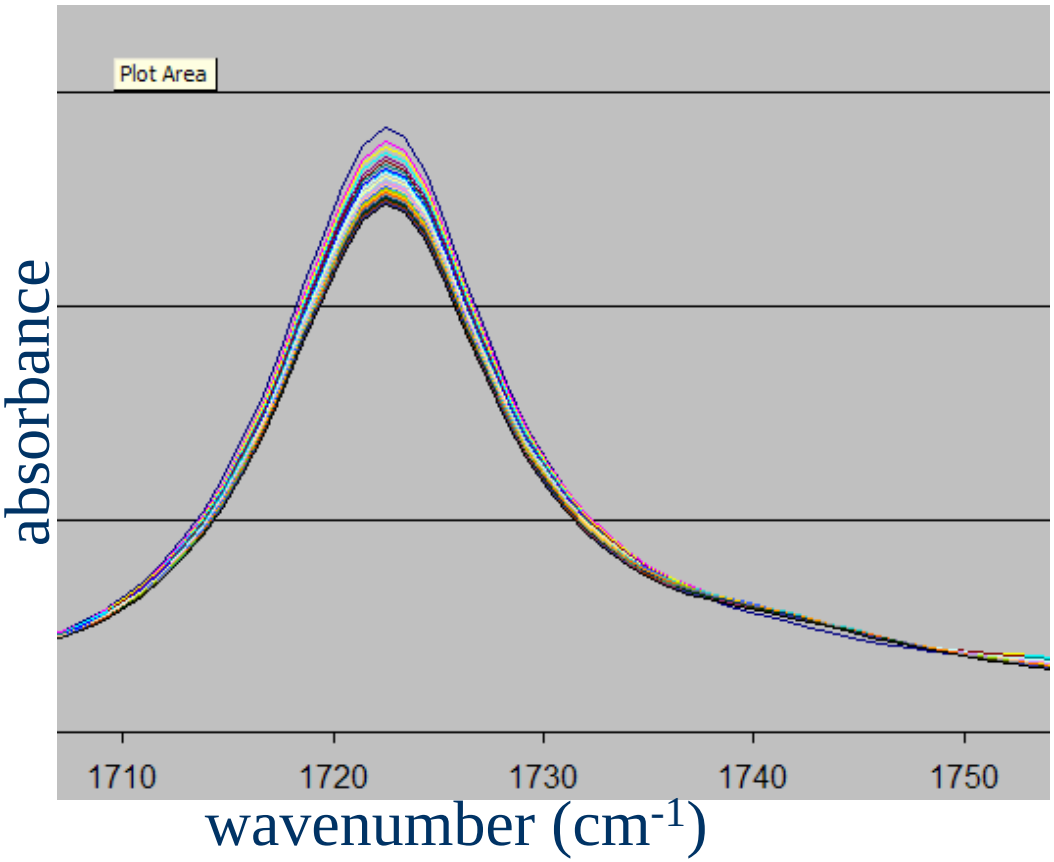


✂-pinene hydroperoxide aldehyde peroxyhemiacetal

Measuring the Kinetics

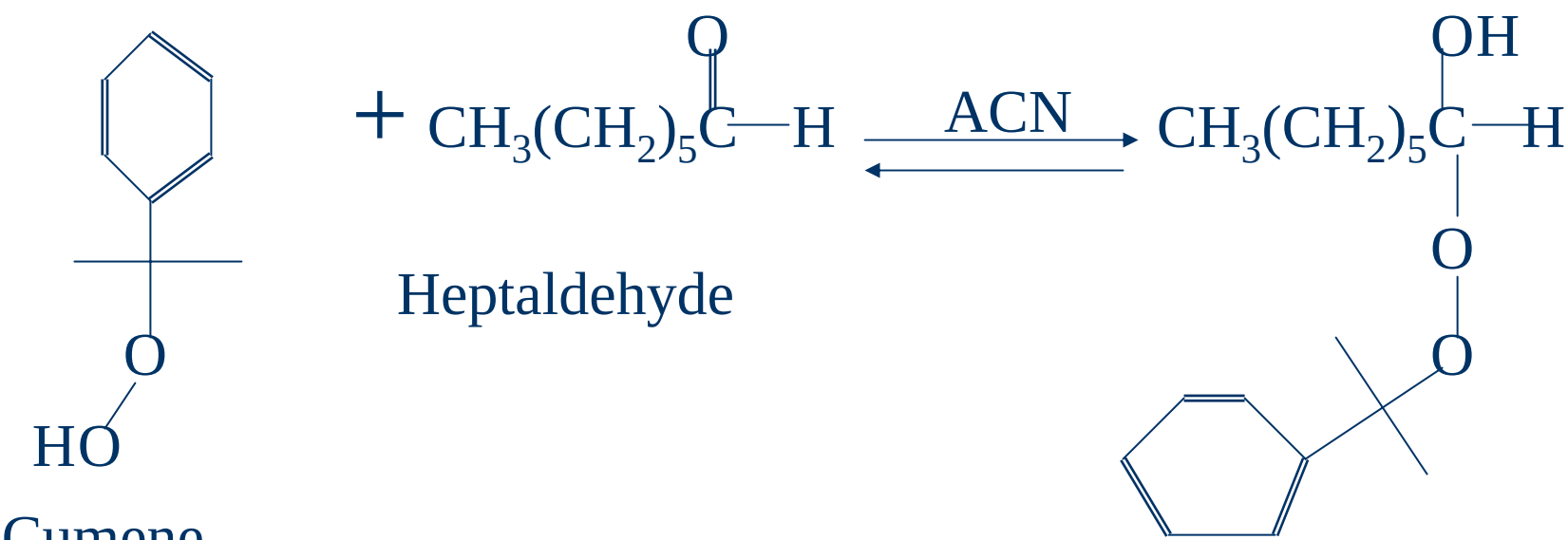
- Need to know rates of peroxyhemiacetal reactions to evaluate atmospheric importance
- Ran reactions in a cell using infrared spectrometer to monitor reactants and products
- Used changes in carbonyl or hydroperoxide peak in IR spectra to determine reaction rate

Monitoring the Reaction



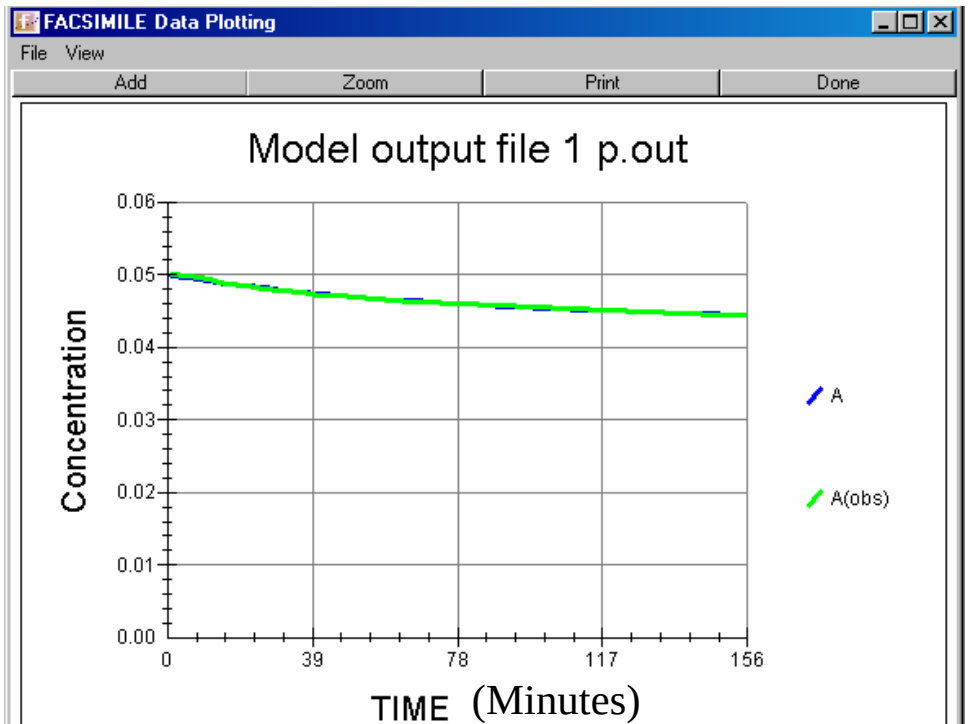
- Reaction of 0.05M heptaldehyde with 0.05M cumene hydroperoxide in acetonitrile solution over two hours

Measuring the Kinetics



Kinetics Analysis

- Using FACSIMILE program, found the rate constant for the forward and backward reaction



$k_1 = 3.2 \times 10^{-2}\ M^{-1}min^{-1}$

$k_2 = 9.6 \times 10^{-3}\ M^{-1}min^{-1}$

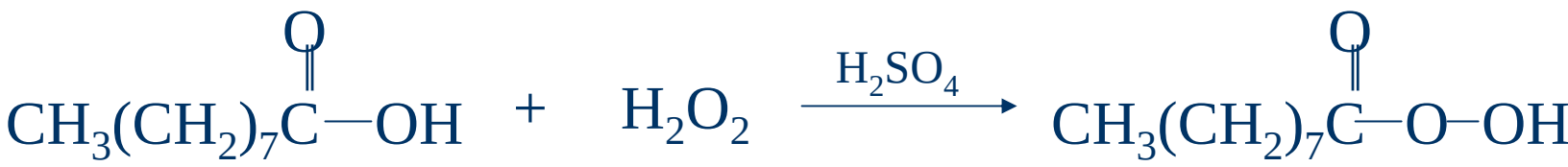
Kinetics of Selected Reactions

- Performed experiments using different aldehydes, hydroperoxides, and solvents

Aldehyde	Peroxides	Solvent	K_1
Acetaldehyde	Cumene Hydroperoxide	Carbon Tetrachloride	5.7×10^{-1}
Acetaldehyde	Pernonanoic Acid	Acetonitrile	6.4×10^{-2}
Acetaldehyde	Pernonanoic Acid	Carbon Tetrachloride	7.2×10^{-1}
Heptaldehyde	Cumene Hydroperoxide	Acetonitrile	3.2×10^{-2}
Heptaldehyde	Cumene Hydroperoxide	Carbon Tetrachloride	1.0
Heptaldehyde	Pernonanoic Acid	Acetonitrile	7.1×10^{-2}
Heptaldehyde	Pernonanoic Acid	Carbon Tetrachloride	3.6×10^{-1}

Note: Pernonanoic acid was synthesize in the lab (95% pure)

Synthesis of Pernonanoic Acid



Nonanoic Acid

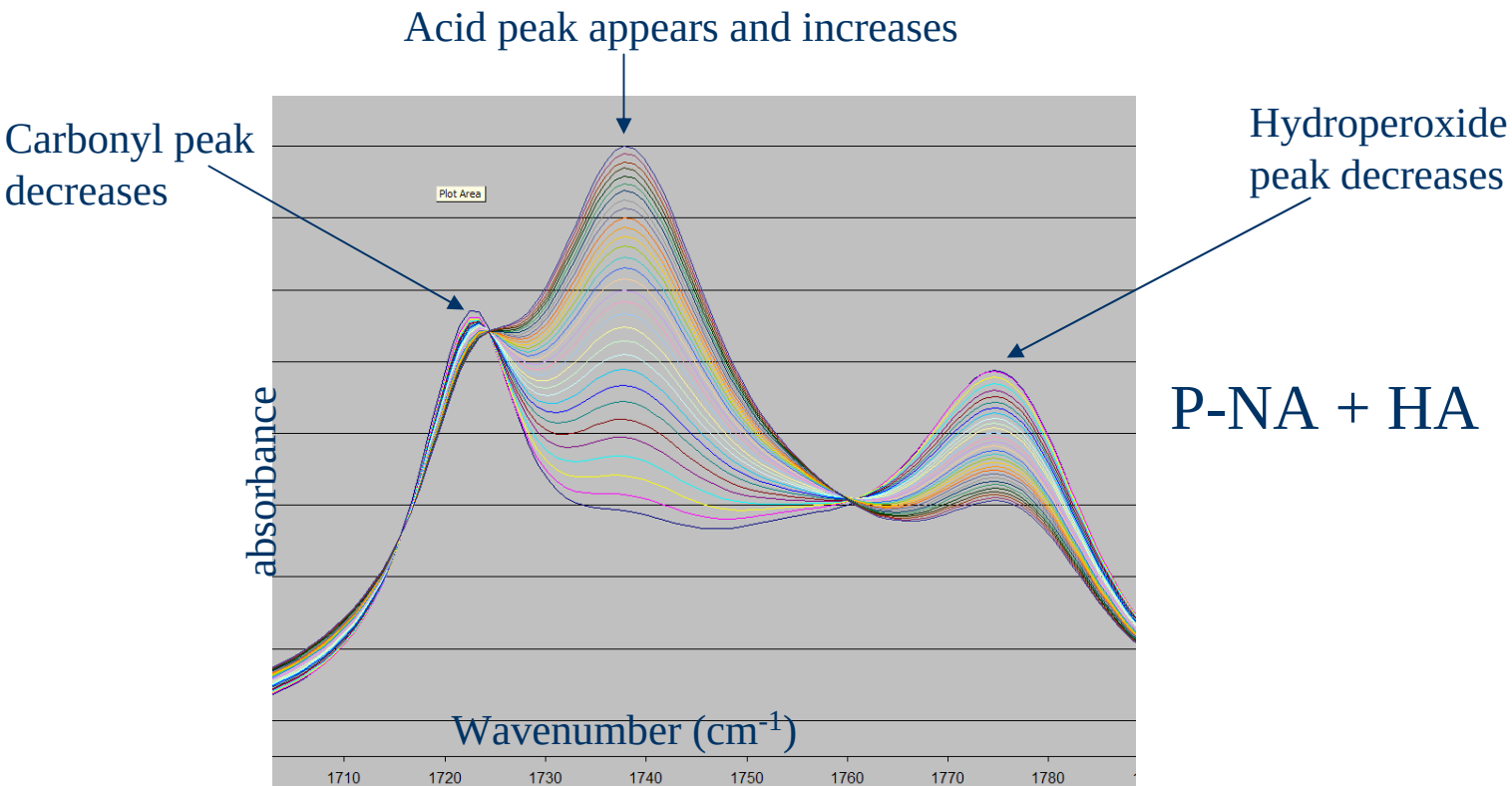
Hydrogen Peroxide

Pernonanoic Acid

Peroxide analysis showed that product was about 95 % pure

Monitoring the Reaction

- Pernonanoic acid reaction spectrum is different from the cumene hydroperoxide spectrum



Kinetics Interpretation

Cumene hydroperoxide: $A + B \rightleftharpoons C$ (equilibrium is reached)

Pernonanoic acid: $A + B \rightleftharpoons C \rightarrow D$ (decomposition of products to acids)

Future Research

- Need to do peroxide analyses of the final product of the pernonanoic reaction with aldehydes to find out the amount of peroxide that remains
- Use different solvents to run the reactions to simulate atmospheric conditions
- Use the kinetic rate constants to model the reaction of hydroperoxides and aldehydes in the atmosphere

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