Condensed Phase Reactions of Carboxynitrates with Alcohols to Form Esters: Measurements of Kinetics and Equilibria

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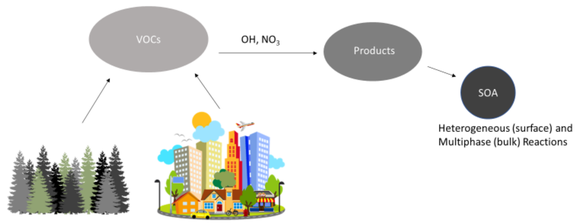
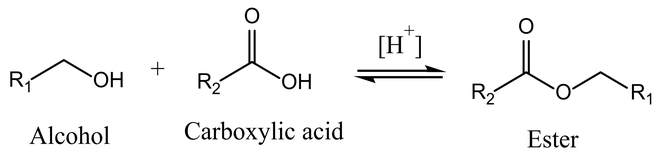
CIRES

Background

SOA Formation



Ester Formation

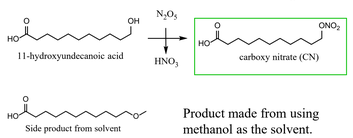


Alcohol Carboxylic acid Ester

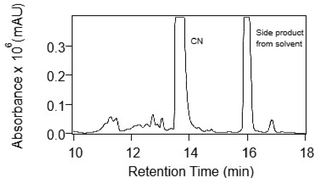
- These reactions can impact the formation, composition, and chemical-physical properties of aerosol.
- While known to occur the kinetics and equilibria are not well established.

Methods

Probe Molecule Synthesis

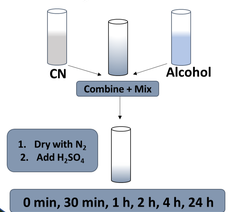


Product made from using methanol as the solvent.

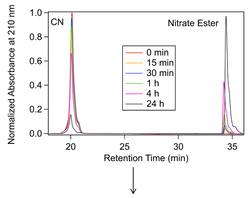


Kinetic Experiments

- CN probe is combined with 1-octanol
- Sulfuric acid is added to investigate acid catalysis



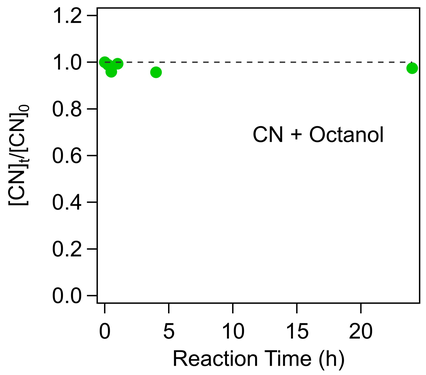
HPLC with DAD allowing for UV-Vis detection



Collect and analyze reactant and products using ESI-ToF-MS and FTIR

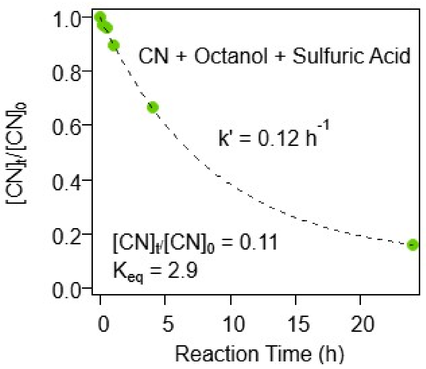
Kinetics and Equilibria

Probe + Alcohol: Single Organic Phase



No ester formation in the absence of sulfuric acid CN probe is stable over the course of 24 h

Probe + Alcohol: Acid Catalyzed Two-Phase



Ester formation starting around 15 min

$k_{f,c} = 0.16\ M^{-2}h^{-1}$

$k_{r,c} = 0.054\ M^{-2}h^{-1}$

Data Analysis

- Excess alcohol for pseudo-first order
- k' is the experimental rate constant
- Can calculate equilibrium constant, and catalyzed forward and reverse rate constants

Fit Equation: $y_0 + A\exp(\frac{-(x-x_0)}{\tau})$ where $y_0 = \frac{[CN]_{eq}}{[CN]_o}$ and $\tau = 1/k'$

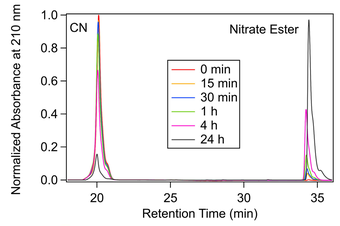
$$k' = k_{f,u}[OH] + k_{r,u} + k_{f,c}[OH][H_2SO_4] + k_{r,c}[H_2SO_4][H_2O]$$

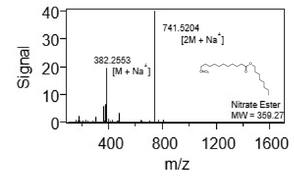
$k_{f,u}$ and $k_{r,u} = 0$

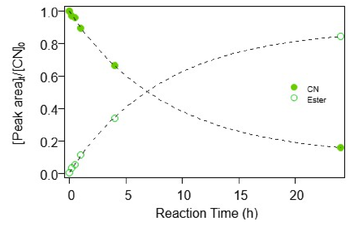
$$K_{eq} = \frac{k_{f,c}}{k_{r,c}} = \frac{\left(\frac{[CN]_o}{[CN]_{eq}} - 1\right) * [H_2O]}{[OH]}$$

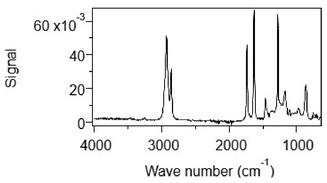
Product Identification

Nitrate Ester Product









- When the probe reacts with octanol, a product peak forms at 35 minutes on the HPLC chromatogram
- Normalized product growth peak area matches probe loss within 1%
- Product is identified by ESI-ToF-MS and FTIR

Conclusions

- Probe molecule allows for measurement of the kinetics and equilibria of ester formation
- Reaction only proceeds with an acid catalyst
- The equilibrium constant is close to the range of values measured previously
- Rate and equilibrium constants can be added to models to better predict transformation of SOA in the atmosphere

	K_{eq}
CN + octanol	2.9
Literature	4-11

Lee, D. G.; Yan, Y.; Chandler D. W. Measurement of Equilibrium Constants for the Formation of Esters from Aliphatic Carboxylic Acids and Alcohols. *Anal. Chem.* **1994**, 66, 32-34.