Atmospheric fate of a new polyfluoroalkyl building block, $\text{C}_3\text{F}_7\text{OCHFCF}_2\text{SCH}_2\text{CH}_2\text{OH}$

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*now at York University
Per- and Polyfluoroalkyl Substances (PFAS)

- **PFAS** contain a perfluoroalkyl moiety within the molecule, $-C_nF_{2n}$ or $-C_nF_{2n+1}$
- **Per**fluoroalkyl substances: no H atoms, unless they are associated with a specific functional group
- **Poly**fluoroalkyl substances: at least one carbon with hydrogen atoms bound to it
- 2018 OECD PFAS list: 4700 unique CAS numbers for PFAS in the global market
  - little data on uses, properties, and environmental effects for most PFAS

OECD/UNEP. *Toward a new comprehensive global database of PFAS.* 2018.
PFAS applications
Persistent degradation products

Persistence! 

- Perfluoroalkyl sulfonamido substances
- Fluorotelomer substances

Perfluoroalkane sulfonic acids (PFSAs)
- $n=8$; perfluorooctane sulfonic acid, PFOS

Perfluoroalkyl carboxylic acids (PFCAs)
- $n=7$; perfluorooctanoic acid, PFOA

PFAS phase-outs and replacements

Sulfonylic acids + related chemicals

Carboxylic acids + related chemicals
A novel polyfluorinated surfactant

FESOH
Synthetic intermediate and primary degradation product

diFESOS
Surfactant
Atmospheric oxidation of FESOH

**Objective**: Assess the atmospheric fate of a novel polyfluorinated alcohol, FESOH:

1. Identify transformation products
2. Measure gas-phase kinetics to estimate lifetime
Gas-phase reactions: Experiments at NCAR

Research objectives

1. Measure Cl reaction kinetics
2. Measure OH reaction kinetics
3. Identify gas-phase oxidation products

With John Orlando and Geoff Tyndall, National Center for Atmospheric Research, Boulder, CO, USA
Aqueous reactions: Experiments at York University

Research objective:
To assess the products of \([\text{Cl/OH} + \text{FESOH}]\) reactions upon contact with water, representing aqueous components of the atmosphere
- Offline sampling and analysis with UPLC-MS/MS

With Cora Young and Teles Furlani at York University
**Kinetics of Cl + FESOH**

\[
\ln \left( \frac{[\text{FESOH}]_t}{[\text{FESOH}]_{t_0}} \right) = \left( \frac{k_{\text{FESOH}}}{k_{\text{ref}}} \right) \ln \left( \frac{[\text{ref}]_t}{[\text{ref}]_{t_0}} \right)
\]

- \( k(\text{Cl} + \text{FESOH}) = (1.6 \pm 0.6) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \)
- FTOHs: \( k(\text{Cl} + \text{C}_4\text{F}_9\text{CH}_2\text{CH}_2\text{OH}) = (1.61 \pm 0.49) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \)

“c”: corrected for the wall losses of FESOH

\[ k(\text{OH} + \text{FESOH}) = (4.3 \pm 2.0) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]

- FESOH gas-phase lifetime of 2.6 ± 1.6 days with respect to reaction with OH, assuming \([\text{OH}] = 10^6 \text{ molecule}^1 \text{ cm}^{-3}\)

\[ k(\text{OH} + \text{C}_4\text{F}_9\text{CH}_2\text{CH}_2\text{OH}) = (1.07 \pm 0.22) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]

- FESOH is 4x faster than FTOHs for OH, but the same for Cl reaction: effect of S atom with OH only?

"c": corrected for the wall losses of FESOH

Gas-phase products

- **Primary products**
  - FESOH
  - FESOH + Cl/OH

- **Secondary products**
  - CO₂
  - CO

- **Other products**
  - CO₂
  - CO

FESOH + ...
- Cl
- Cl + NO
- OH (with NO)
**Aqueous phase products (bubbler)**

- Represents fate in aqueous components of the atmosphere
- Only 1 perfluorinated acid – fluorotelomer-based chemicals make a suite of acids\(^1\)
- Terminal gas phase product $\rightarrow$ terminal aqueous phase product liberated 3 HF

Conclusions: Atmospheric oxidation of FESOH

- Shorter OH lifetime than FTOHs
- Defluorination to smaller transformation products
  - Terminal products:
    - Only 1 perfluorinated acid formed

\[
\begin{align*}
\text{Gas-phase} & \quad \rightarrow \quad \text{Aqueous-phase} \\
\text{Only 1 perfluorinated acid formed}
\end{align*}
\]
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Mabury Group, 2019
Cora Young & Teles Furlani, York, 2018
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