AR226-2702

TORONTO WORKSHOP MATERIALS

September 13-14,2004

Atmospheric Chemistry of Fluorotelomer Alcohols (Part 2)

Robert Waterland

DuPont Engineering Research & Technology, Wilmington, DE

Outline

- What do we know for certain?
  - initial gas phase reaction kinetics
  - photolysis of FTOHs
- What do we know a little about?
  - role of HO_x and NO_x
  - photolysis of fluoroaldehydes
- What's missing that we must know?
  - heterogeneous chemistry
  - competition between HO_x and NO_x
  - hydrates & fluorotelomer olefins

What we know for certain

- FTOH, $C_nF_{2n+1}CH_2CH_2OH$ (n=1,10) are sufficiently volatile to be present in the atmosphere.

  [Stock *et al.*, 2004; Krusic *et al.*, 2004 (submitted)]

- They do not photodissociate in the gas phase.

  [S. Mello *et al.*, in preparation]

- The sole gas phase oxidation product is $C_nF_{2n+1}CH_2CHO$. FTOH lifetime is approx. 11 days:

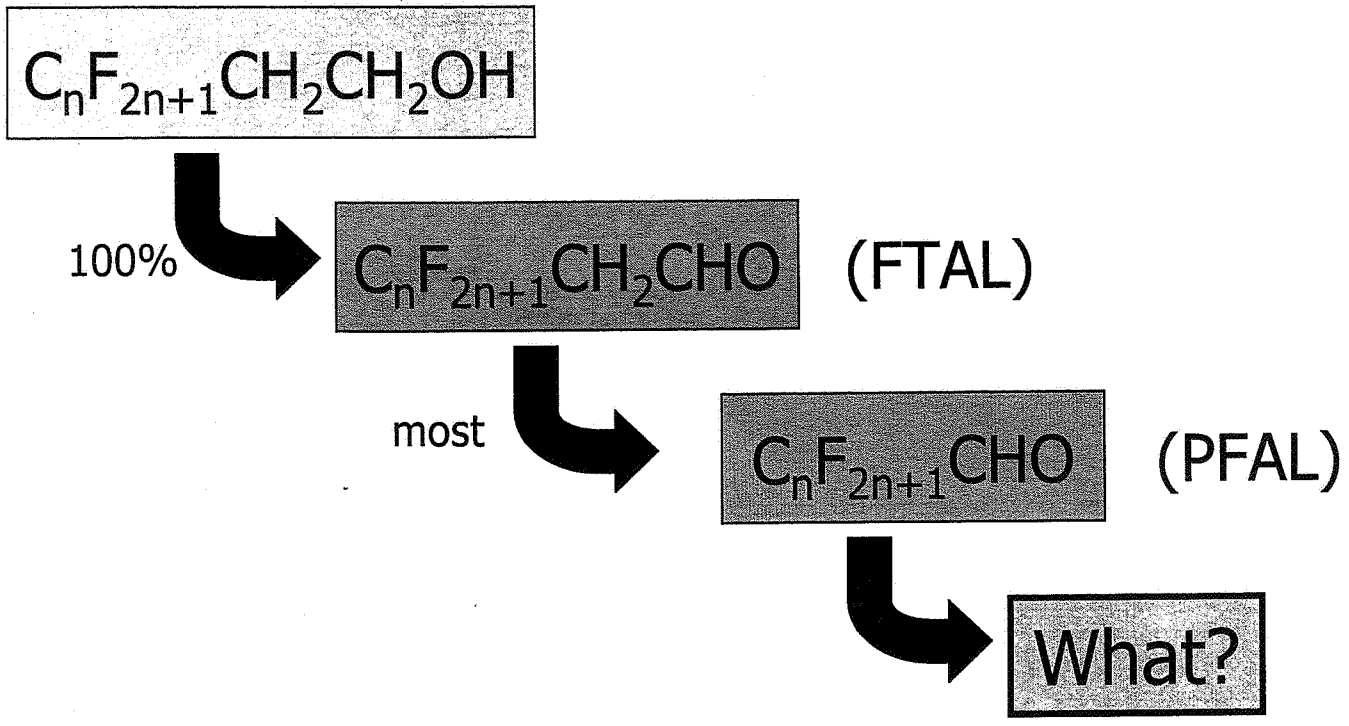
  expect long-range gas-phase transport.

  [Hurley *et al.*, 2004; Le Bras *et al.*, *SETAC* 2004]

- $C_nF_{2n+1}CH_2CHO$ oxidises primarily to $C_nF_{2n+1}CHO$.

  [Hurley *et al.*, 2004; Le Bras *et al.*, *SETAC* 2004]

What we know a little about



A. It depends on what else is around: NO_x and HO_x.

A′. It depends on where you are: urban/suburban or remote.

What we know a little about

A. What else is around: NO_x.
A′. Where you are: urban/suburban.

$C_nF_{2n+1}CHO$

$C_nF_{2n+1}C(O)O_2NO_2$ (FPAN) and mostly CF_2O

But ....
This is based on n=1,2,3,4.
For the higher aldehydes (n>4), yields to FPAN and CF_2O are unknown.

What we know a little about

A. What else is around: HO_x.
A′. Where you are: remote regions.

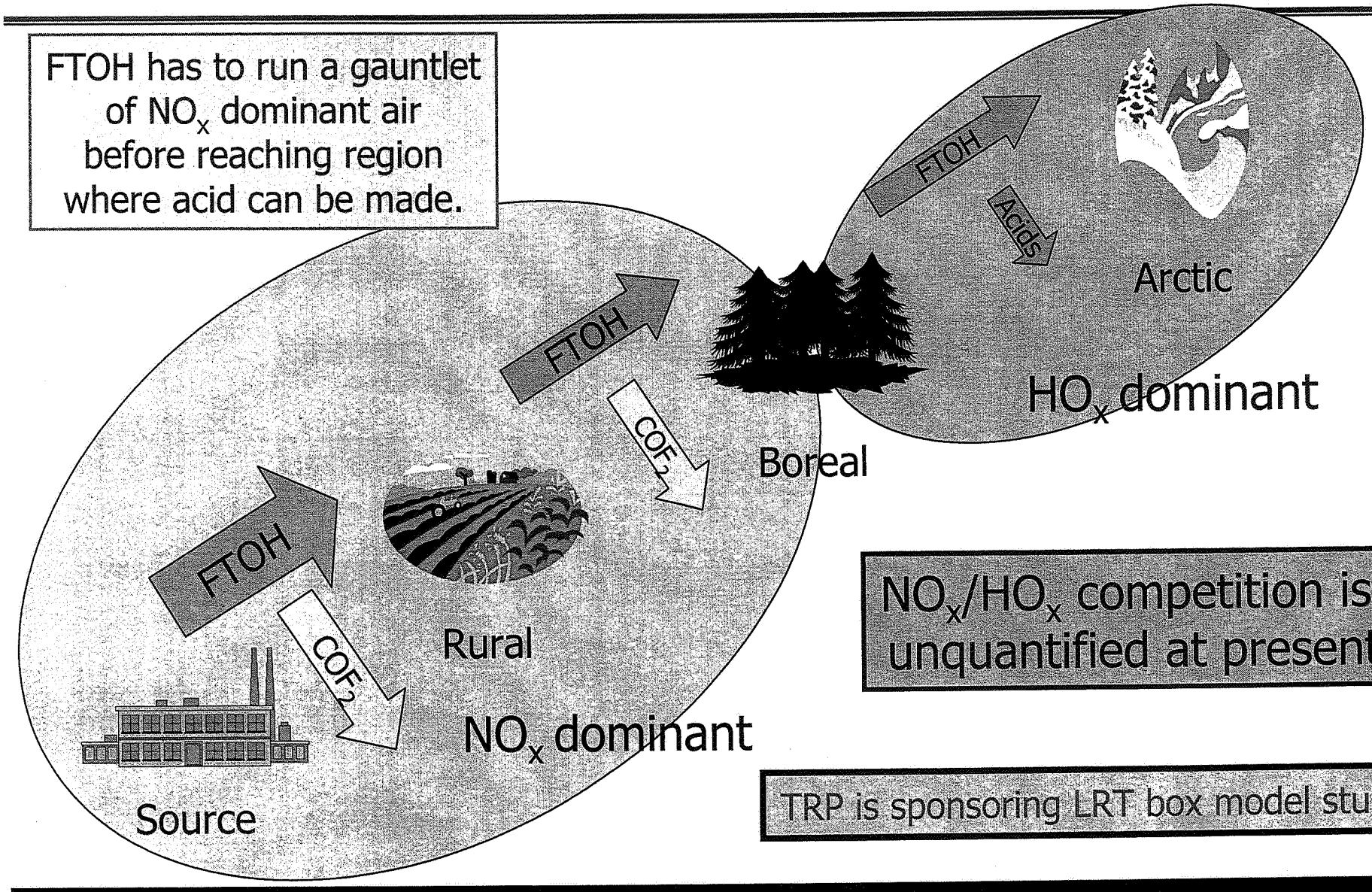
$C_nF_{2n+1}CHO$

Will likely give some $C_nF_{2n+1}C(O)OH$ and O_3

But ....
This is based on n=1,2,3,4 in smog chamber.
For the higher aldehydes (n>4), yields to PFCA and O_3 are unknown.

What we know a little about

FTOH has to run a gauntlet of NO_x dominant air before reaching region where acid can be made.



NO_x/HO_x competition is unquantified at present

TRP is sponsoring LRT box model study

What we know a little about

Competition from photolysis.

Do the fluoroaldehydes photolyze? Competition with chemical pathways?

$$C_nF_{2n+1}CHO + h\nu \longrightarrow \cdot C_nF_{2n+1} + \cdot CHO$$
$$\longrightarrow C_nF_{2n+1}H + CO$$

What is known:

- The fluoroaldehydes absorb in the solar UV.
- They absorb a little more strongly than the normal aldehydes.
- The normal aldehydes photodissociate readily (hours/days).

What we know a little about

Hashikawa *et al.*, J. Fluor. Chem. (in press).

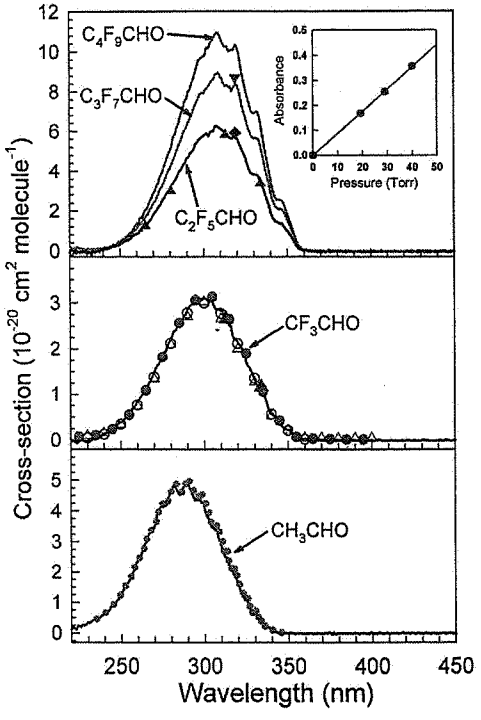


Figure 1

What is known:

Solar UV absorption increases with chain length.

Absorption peak shifted to higher λ vs. normal aldehydes.

Solar flux 1000X higher at peak of C_4F_9CHO vs. CH_3CHO.

What is unknown:

Quantum yields for photodissociation.

For CF_3CHO, photolysis quantum yield at 290-400 nm is 0.02.
For CH_3CHO, at 300nm the quantum yield is ~0.4.

For the higher aldehydes no data exist.

DuPont sponsoring an experimental quantum yield study

What's missing that we must know?

Heterogeneous physical chemistry

Does FTOH sorb to atmospheric aerosol?
If so, what happens to sorbed FTOH?

- water phase (condense/surfactant/separated phase)
- organic phase (condense/surfactant/separated phases)
- graphitic soot & mineral fraction

Virtually nothing known about FTOH sorbing

- Strong indication of tight binding to soils
- **Chemistry completely unknown**

DuPont sponsoring an initial experimental investigation of FTOH sorbing

What's missing that we must know?

Heterogeneous reaction chemistry

What is the chemistry on solid surfaces and liquids?

e.g. Ellis *et al.* [2004] reported ~5% PFCAs yield from FTOH + $^{\bullet}Cl$ (no NO_x)

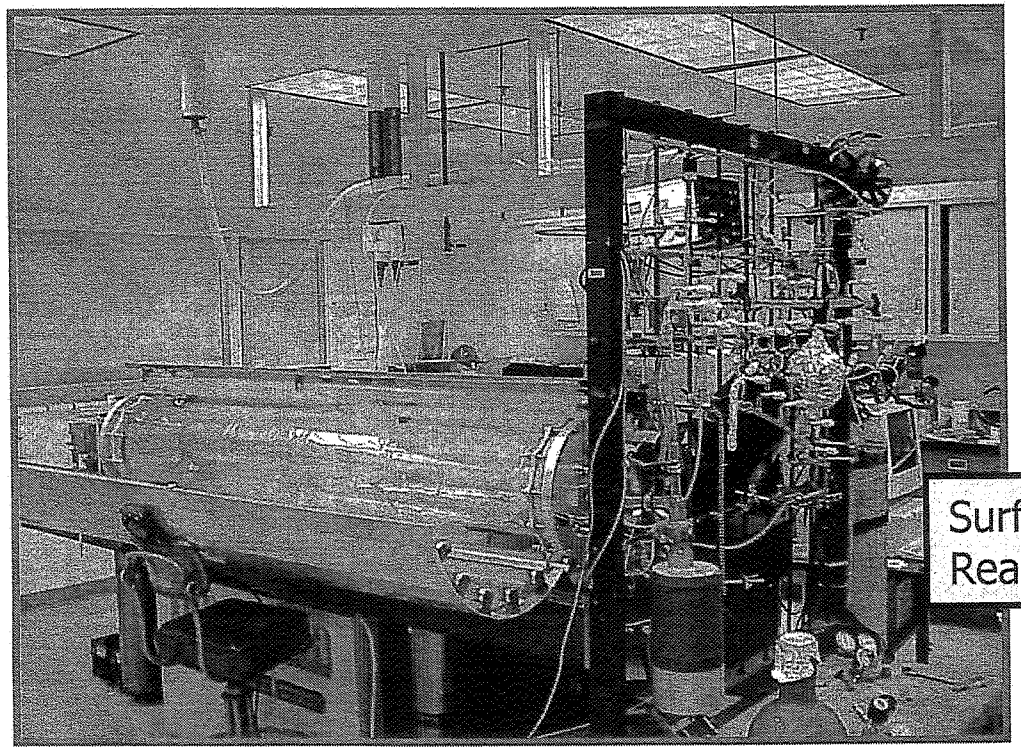
- a suite of lower PFCAs were observed

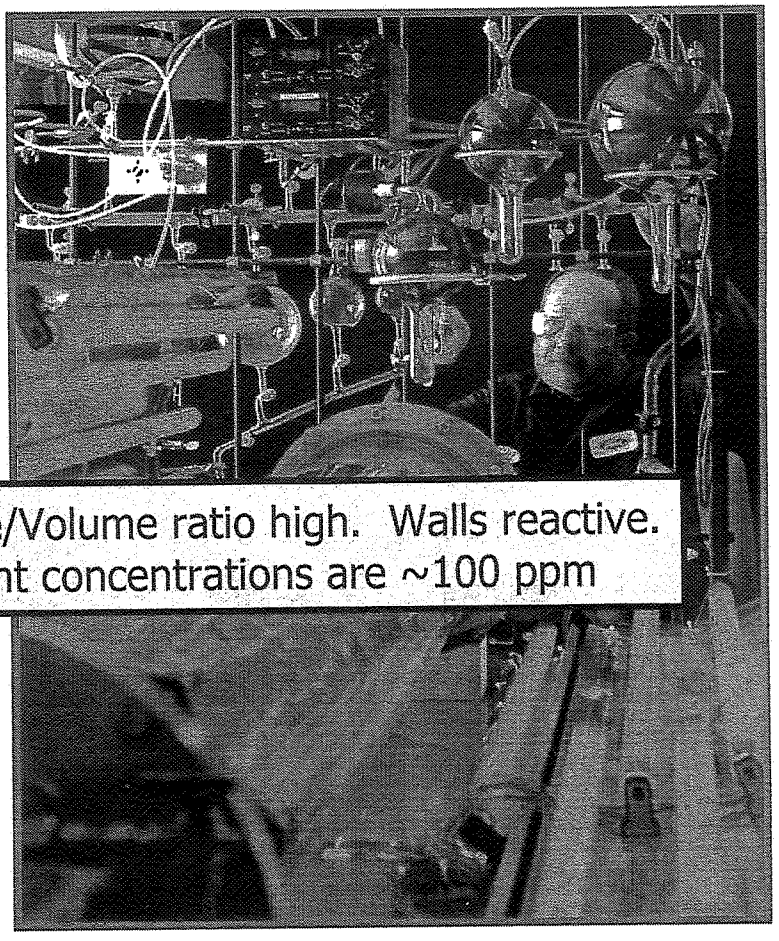
Proposed mechanism is HF elimination from perfluoroalcohols

$$CF_3(CF_2)_{x-1}CF_2OH \longrightarrow CF_3(CF_2)_{x-1}CFO + HF$$

- ***We know this doesn't happen in gas phase***
- So, it must be heterogeneous chemistry (but where?)
- Probably on quartz walls of small smog chamber

Smog Chamber at Ford Motor Co.



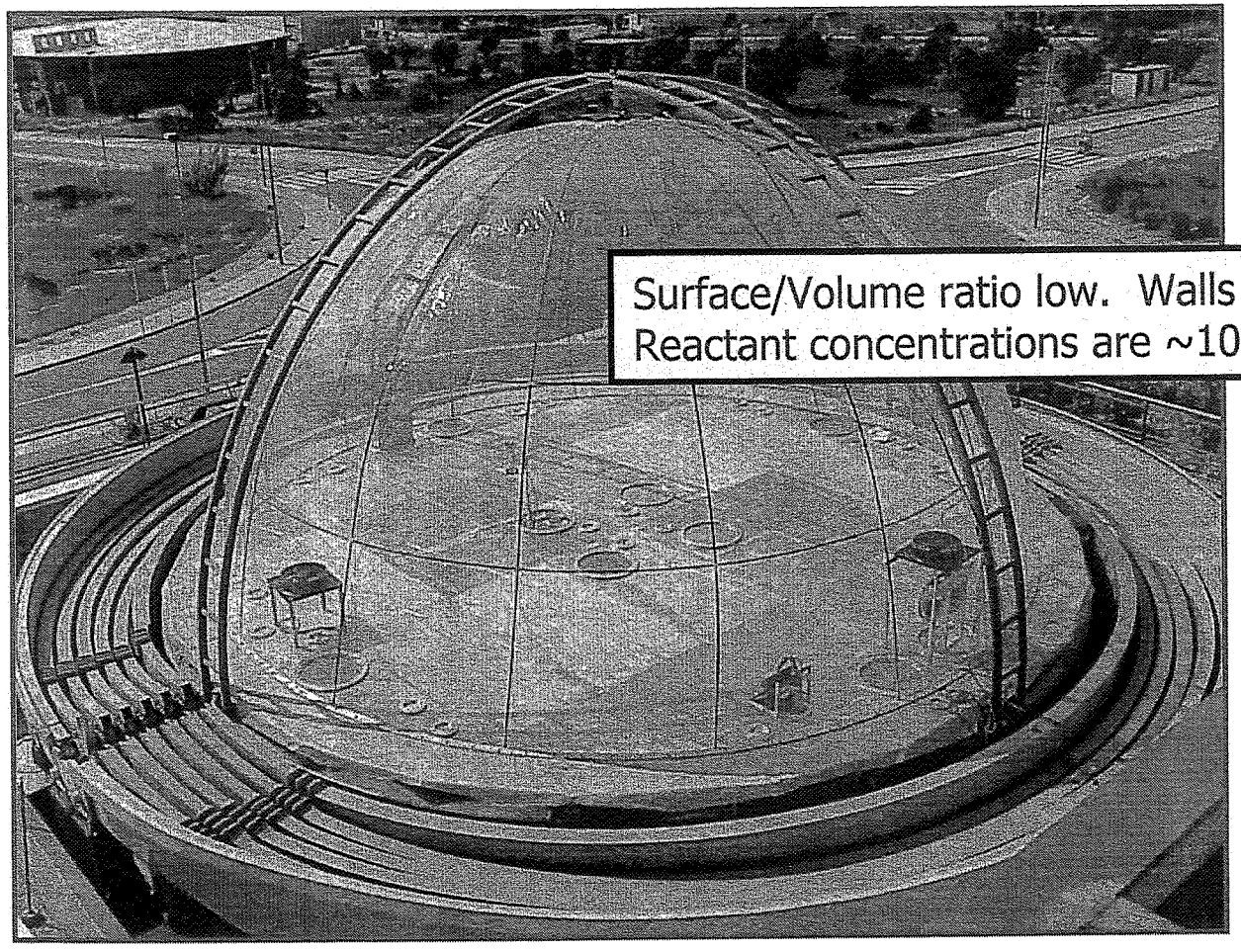


Surface/Volume ratio high. Walls reactive.
Reactant concentrations are ~100 ppm

Photos are courtesy of T. Wallington, Ford.

0.14 m^3 Pyrex chamber, 296 K, 700 Torr

EUPHORE Chamber in Valencia



Surface/Volume ratio low. Walls non-reactive.
Reactant concentrations are ~100 ppb.

204 m^3 Teflon® FEP chamber, 1 atmosphere

What's missing that we must know?

Perfluoroaldehyde hydrates

$$C_nF_{2n+1}CHO \cdot H_2O = C_nF_{2n+1}CH(OH)_2$$

- n=1-4 fluoroaldehydes are commercially available only as hydrates
- Do the n>4 fluoroaldehydes react with water droplets to give hydrates?
- If so, what is the chemistry of these hydrates?

Very little study of hydrates to date

What's missing that we must know?

Telomer B Olefin?

$C_nF_{2n+1}CH=CH_2$ (TBO)

- Residual levels of TBO and FTOH in polymers comparable
- Vapor pressures of TBO and FTOH are comparable
  - 8-2 FTOH = 3 Pa at 21 °C
  - 8-2 TBO = 15 Pa at 25 °C
- TBO much less water soluble (less in water phase?)
  - 8-2 FTOH = 0.130 mg/L (Clariant)
  - 8-2 TBO = 0.001 mg/L (Clariant)
- Little known about TBO chemistry
  - Le Bras (2000) studied $C_nF_{2n+1}CH=CH_2$ (n=4,6) with OH and Cl
  - OH chemistry appears to be similar to FTOHs

More study of Telomer B Olefin Atmospheric Chem needed

Conclusions

- What we know for certain
  - initial gas phase reaction kinetics
- What we know a little about - and need to know more about
  - competition between HO_x and NO_x
  - chemical fate of fluoroaldehydes
  - photolysis of fluoroaldehydes
- What's missing that we must know?
  - sorbing of FTOH to atmospheric aerosol
  - heterogeneous chemistry
  - hydrates & fluorotelomer olefins
  - ...