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The Heterogeneous Interactions of Organic Molecules with Ice Surfaces at Temperatures of the Upper Troposphere and Lower Stratosphere (UTLS)

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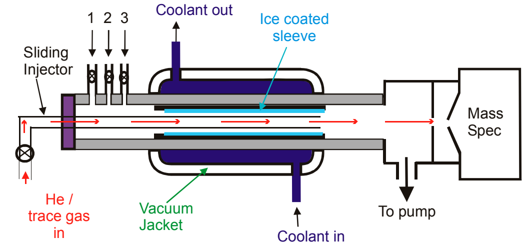
Oxygenated Organics in the UTLS

- **Oxygenated Organic molecules** such as acetic acid are known to be present in the UTLS at mixing ratios of a few hundred pptv (e.g. Chapman et al 1995).
- Concentrations of **Halogenated acid, aldehyde and alcohol** have not been measured in the UTLS. These molecules are expected to have sufficiently long lifetimes to reach the UTLS and their atmospheric load is increasing due to anthropogenic sources.
- Lifetimes in the UTLS are determined by the loss rates. One potential sink is adsorption onto particles and subsequent loss in precipitation. Other major loss processes are reaction with OH and photolysis.
- Cirrus clouds are composed primarily of ice crystals and have global coverage of order 25% thus providing the largest surface area in the UTLS. They have a lifetime of approximately a few days. Because reaction rate scales with surface area, scavenging by cirrus clouds may provide a significant reservoir or sink for organics in the UTLS if a significant proportion of trace gas partitions to the ice surface.
- Any sink that removes a significant proportion of an organic molecule compared with loss due to reaction with OH will affect the HO_x mixing ratio and, as a result, will modify ozone and NO_x ($NO + NO_2$) mixing ratios in the UTLS.

Aims

- Quantify partitioning of a wide range of small oxygenated organics to ice surfaces
- To assess which factors affect partitioning of molecules to the ice surface. Specifically, to address whether experimentally derived partition coefficients can be estimated from other molecular properties e.g. pK_a, bulk phase diagrams
- Identify molecules for which partitioning to the ice surface is likely to be significant, compared to other loss processes, in order to assess which processes need to be included in climate models to more accurately predict HO_x, ozone and NO_x mixing ratios

Experimental



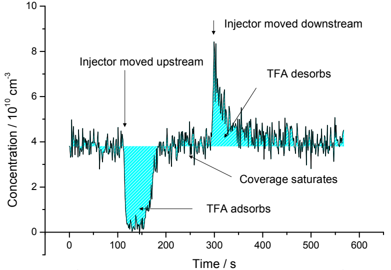
Horizontal Scale x 0.3

1 He
2 He / H2O
3 2nd Reagent

- Experiments are carried out using a coated wall flow tube coupled to a mass spectrometer.
- The ice surface is prepared by inserting wetted Pyrex tube into the flow tube which has been pre-cooled to 258 K. The ice film is then cooled to the experimental temperature.
- Reactant gases are diluted by He in a Pyrex mixing bulb
- Sliding injector admits reactant and controls the exposure time to the ice surface.
- The mass spectrometer measures gas phase trace gas concentration (10^{11} – 10^{14} cm^{-3} or ~1-1000 ppbv) exiting flow tube at pre-calibrated masses. Reductions in gas phase concentration when the injector is withdrawn is interpreted as loss to the surface.

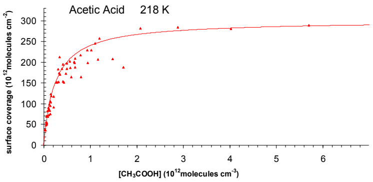
- The uptake trace shows typical interactions of a trace gas with the ice surface
- Surface coverage, N (the number of molecules adsorbed per unit area) for a given partial pressure and temperature, is determined from the integrated area

Uptake of TFA (CF_3COOH) on ice at 208 K



- UTLS organic concentrations are of order 0.1 ppbv. Therefore we need a model to extrapolate surface coverage to UTLS concentrations. The simplest model is the Langmuir Isotherm.

Langmuir Analysis to Estimate Surface Coverage at UTLS concentrations



Assumptions
1. all sites are identical
2. saturation occurs at one monolayer
3. adsorption enthalpy independent of surface coverage

$$A_{(g)} + S \xleftrightarrow{kads\ /\ kdes} A_{(ads)}$$

Single site adsorption isotherm is defined by the equation:

$$\boxed{N_{ads} = \frac{N_{max} K_{eq} c_A}{1 + K_{eq} c_A}}$$

For non-dissociative adsorption of A, on surface site ,S, we can define an equilibrium constant K_{eq}:

$$\boxed{K_{eq} = k_{ads}/k_{des}}$$

k_{ads},k_{des} = adsorption and desorption rate coefficients
N_{ads} = surface coverage, c_A = gas phase concentration

At low concentrations this simplifies to: $\boxed{N_{ads} = N_{max} K_{eq} c_A}$

The partition coefficient $K_{eq}N_{max}$ is used to estimate surface coverage at UT concentrations and compare uptake properties of different molecules

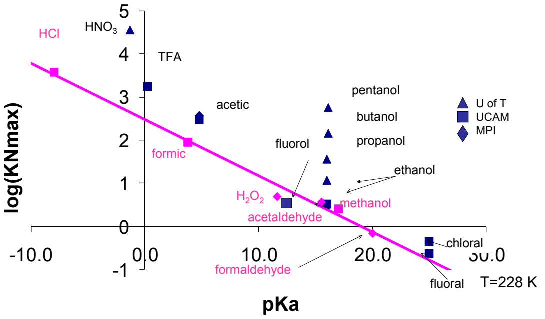
Is Scavenging by Ice Clouds a significant loss process?

Molecule	**Reaction +OH** [a] Singh et al 2005 [b] Sellavag et al 2004a [c] Talukdar et al 2001 [d] Sellavag et al 2004b [e] Dagaukt et al [f] Møgelberg et al 1994	**Photolysis** [g] Atkinson 1994.	**Wet /dry Deposition** [h] Singh et al 2004 [i] Chen et al 2003 [j] Wenger et al 2004 [k] Keene & Galloway 1988, Talbot et al 1988 [l] Wallington et al 1994	**KN_{max} at 228 K / cm^{-1}**	**KN_{max} at 208 K / cm^{-1}**	**Adsorption enthalpy kJ mol^{-1}** (van't Hoff)	**% Scavenging by cirrus Clouds at 228 K and 208 K**
Alcohols							
Ethanol	4 days[a]	N/A	>> 3 days[h]	3.3±0.2	40±2	-50±10	<0.1, 0.2 - 1
Trifluoroethanol	4months[b]	N/A	~ 1 year[i]	3.5±0.1	25±2	-58±5	<0.1, 0.1 – 0.5
Aldehydes							
Cl_3CCHO	10-20days[c]	5-10 days[c]	2-3 days[j]	0.31±0.03	0.46±0.03	-8.2	<0.1
CF_3CCHO	26 days[d]	>27 days[d]	?	0.20±0.03	0.32±0.05	-11.68	<0.1
CH_3CCHO	11 hours[g]	6 days[g]	?	2.6±0.4	?	?	<0.1
Acids							
Formic	20 days[e]	N/A	hours-days[k]	90,	900	-44	0.5 – 2, 5 - 20
Acetic	9-11 days[e]	N/A	hours-days[k]	300,	1080	-52.6	2 – 6.5, 6 - 24
CF_3COOH	10 days[f]	N/A	10-12 days[l]	1800±600	1800±600	~0	1 1 - 44

- Scavenging is insignificant compared other losses for formic acid, all alcohols and aldehydes studied
- Scavenging may be important for acetic acid and is a major loss process for TFA and should be taken account of in modelling TFA concentrations and lifetimes.
- The differences in partition coefficients reflect the difference in the interaction with the ice surface
- One measure of the strength of molecule-water interactions is pK_a

Factors affecting partitioning to the ice surface - pKa

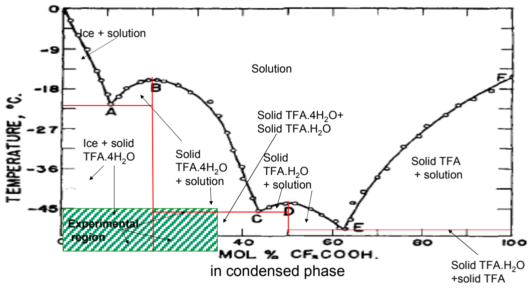
$$\log(KNmax) = -0.14pKa + 2.45$$



- For a wide range of molecules pKa correlates well with partition coefficient (e.g. HCl, formic acid, MeOH, formaldehyde). This suggests that the strength of the interaction of the molecule with the ice surface is a major factor determining partitioning to the ice surface.
- The departure of organic compounds with a longer alkyl chain from this trend suggests other factors are also important. CH_3/CH_2 groups add about 0.7 to log(KN_{Max}) for both acids and alcohols.
- Other molecular properties that show trends with chain length include vapour pressure and surface tension.
- Similar trends are observed at 218 and 208 K

TFA adsorption enthalpy

- TFA is a strong acid and is expected to form strong hydrogen bonds with the ice surface. It has the highest partition coefficient of all molecules studied. However, TFA adsorption enthalpy was estimated to be zero.
- Adsorption enthalpies were calculated from the temperature dependence of the equilibrium constants using van't Hoff plots, which assume that the phase of the system is constant.
- Construction of a phase diagram from the published freezing curve of bulk TFA/H_2O mixtures shows that 3+ phases may exist in our experimental region due to the presence of hydrates.
- Hydrate formation is more common at low temperatures and for molecules that form strong hydrogen bonds. Therefore, it is important to understand the phase diagrams of the molecules studied at UTLS temperatures.



H_2O/TFA Phase diagram constructed from the freezing curve of H.H. Cady & G.H. Cady, JACS, 1954

Conclusions

- Scavenging by ice clouds is only significant for TFA and possibly acetic acid. HOx, NOx and ozone mixing ratios may be better estimated by including scavenging of these molecules by ice clouds.
- pKa is related to the strength of H_2O-molecule interaction. Molecules that form strong interactions with H_2O partition strongly to the ice surface. However, another factor that varies with alkyl chain length is also important.
- Calculation of van't Hoff adsorption enthalpies are only valid within the same phase. It is therefore important to understand the phase diagrams of trace gas/ice at UTLS temperatures.

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