Can detailed oxidation kinetics studies indicate where reactivity occurs with ice?

Jon Abbatt, University of Toronto

Part 1 – Introduction

Part 2 – Bulk and Surface: Br^-/O_3

Part 3 – Surface Only; SO_2/H_2O_2

Part 4 – Reactant separation: Organic diacids/OH

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Part 3 – Surface Only; SO_2/H_2O_2
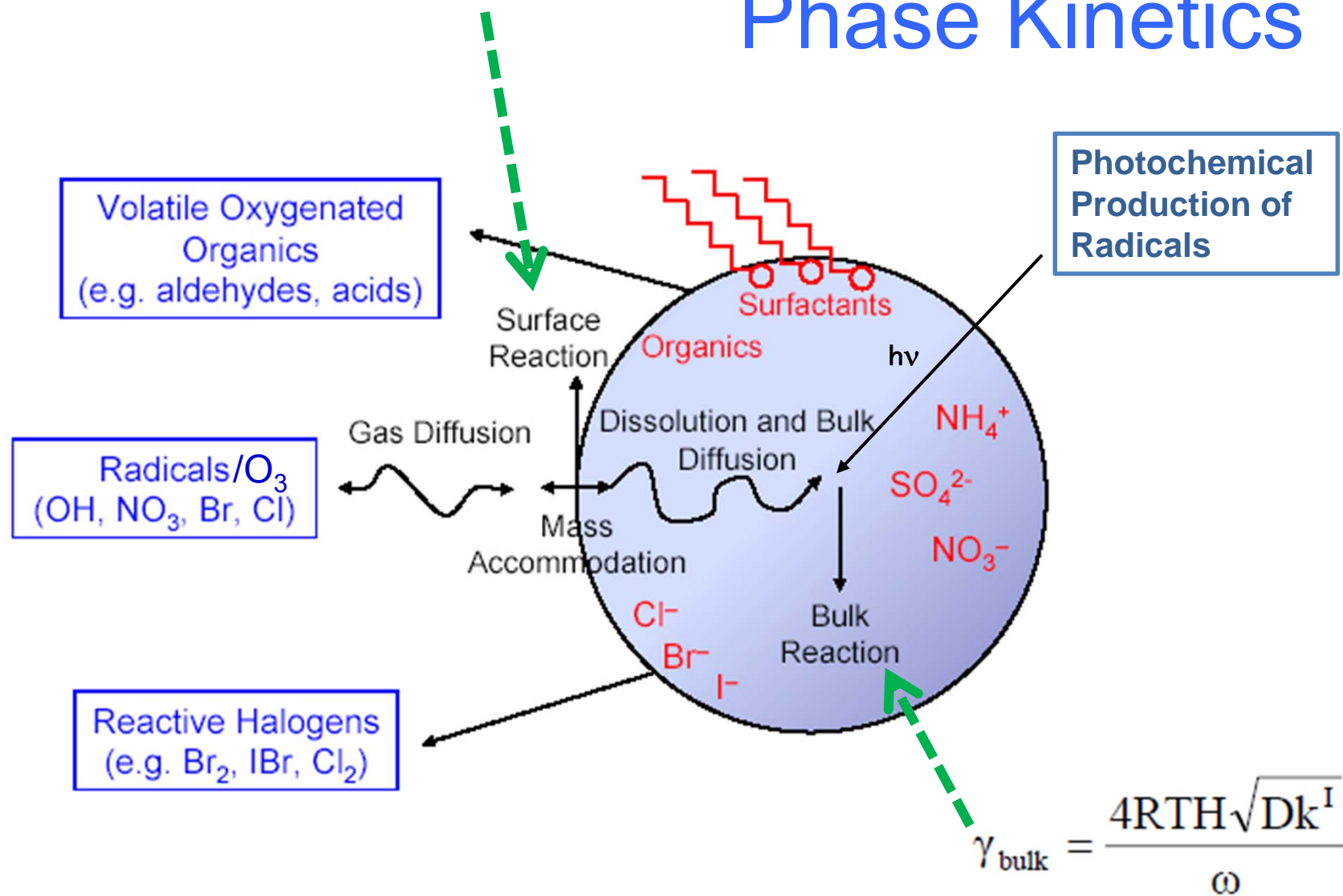
Part 4 – Reactant separation: Organic diacids/OH

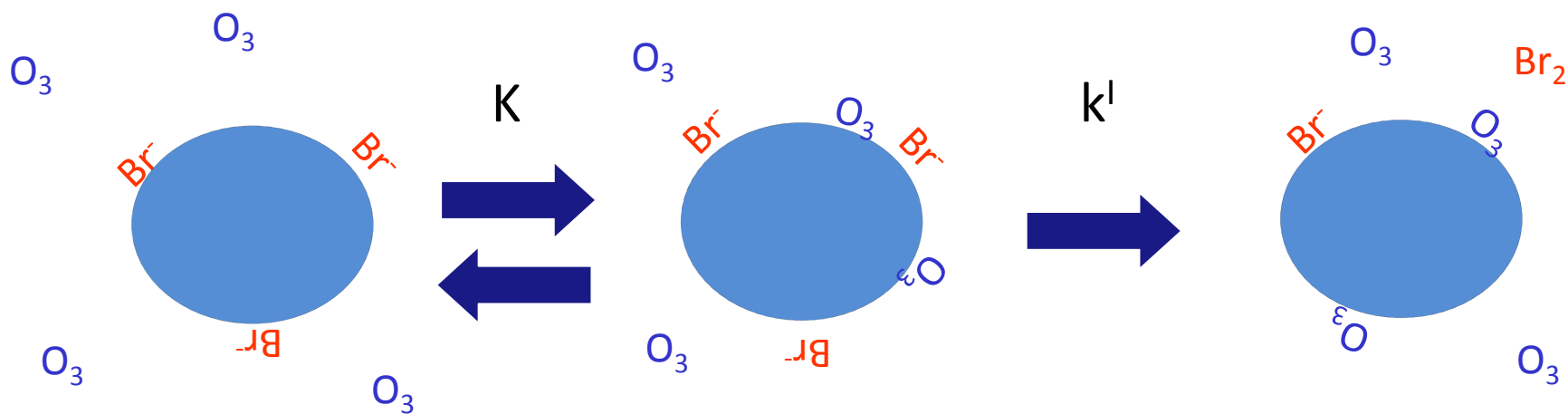Answer: Yes, especially when given the contrast of analogous aqueous phase kinetics.

Thanks to: Sam Clegg, Shawna Gao, Nathan Oldridge

$$\frac{1}{\gamma_{surf}} \approx \frac{1}{\Gamma_s} = \omega\sigma\frac{1+K[O_3]_{gs}}{4Kk_s[Br^-]_s}$$

Surface vs Bulk Phase Kinetics

Volatile Oxygenated Organics (e.g. aldehydes, acids)

Radicals/O_3 (OH, NO_3, Br, Cl)

Reactive Halogens (e.g. Br_2, IBr, Cl_2)

Surfactants

Organics

Surface Reaction

Gas Diffusion

Dissolution and Bulk Diffusion

Mass Accommodation

$h\nu$

NH_4^+

SO_4^{2-}

NO_3^-

Cl^-

Br^-

I^-

Bulk Reaction

Photochemical Production of Radicals

$$\gamma_{bulk} = \frac{4RTH\sqrt{Dk^I}}{\omega}$$

Langmuir—Hinshelwood Mechanism

See: e.g. Poschl et al., 2001

Formation of Br_2 from Exposure of Frozen and Liquid NaCl/NaBr Solutions to O_3

Ice Substrate: Frozen NaCl/NaBr, 253K

Main Points:
- Proceeds via both bulk and surface phase chemistry
- Kinetics provide a quantitative separation of the two
- Chemistry occurs in the brine

Reference: Oldridge and Abbatt, JPC-A, 2011.

Bromine Activation by O_3

• Potential dark initiator of the bromine explosion

• Indications of surface phase chemistry in the aqueous and ice systems: Anastasio and Mozurkewich, 2002; Hunt et al., 2004; Thomas et al., 2006; Clifford and Donaldson, 2007; Wren et al., 2010.

• Br_2 is formed from frozen seawater (Oum et al., 1998)

Issues:

Do the surface- or bulk-phase kinetics dominate on ice substrates?

Is the reaction with brine or with ice?

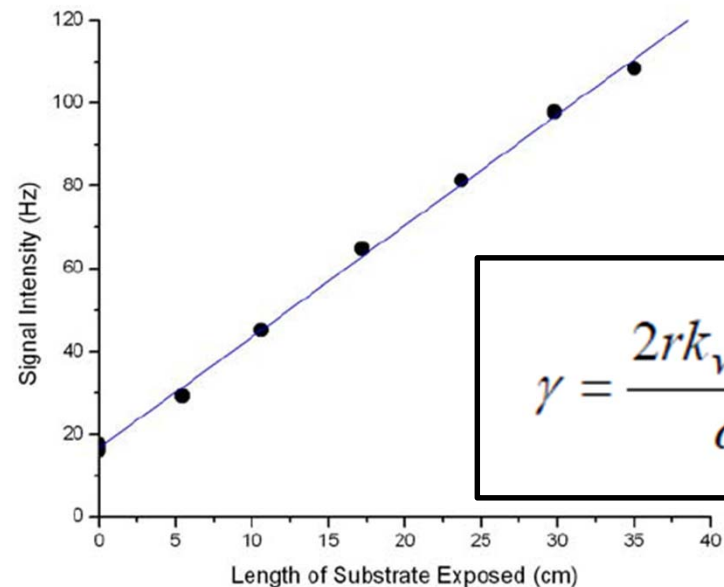# Experimental: Coated-wall Flow Tube and CIMS
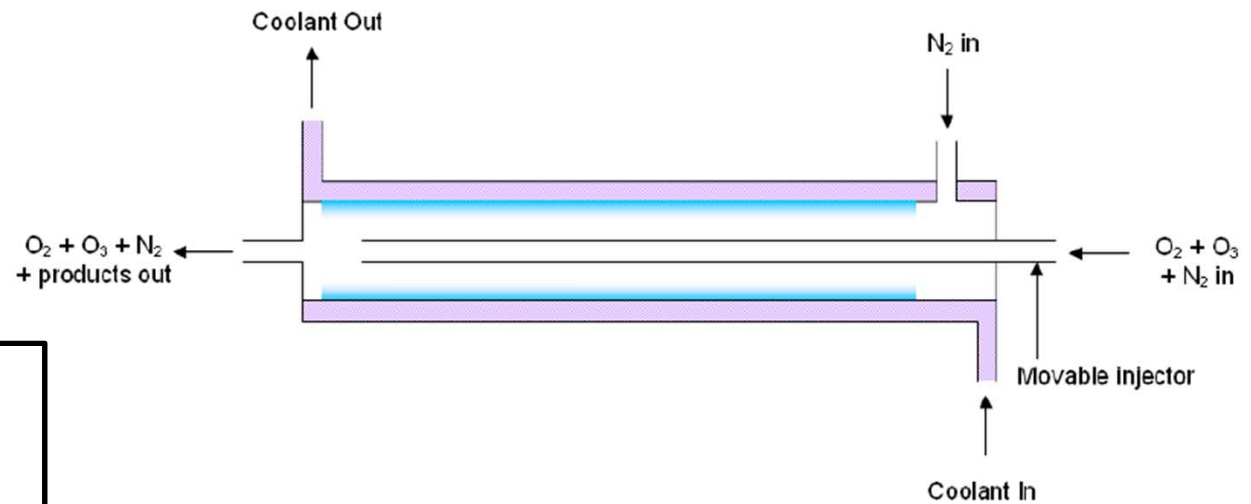
'Frozen Seawater'
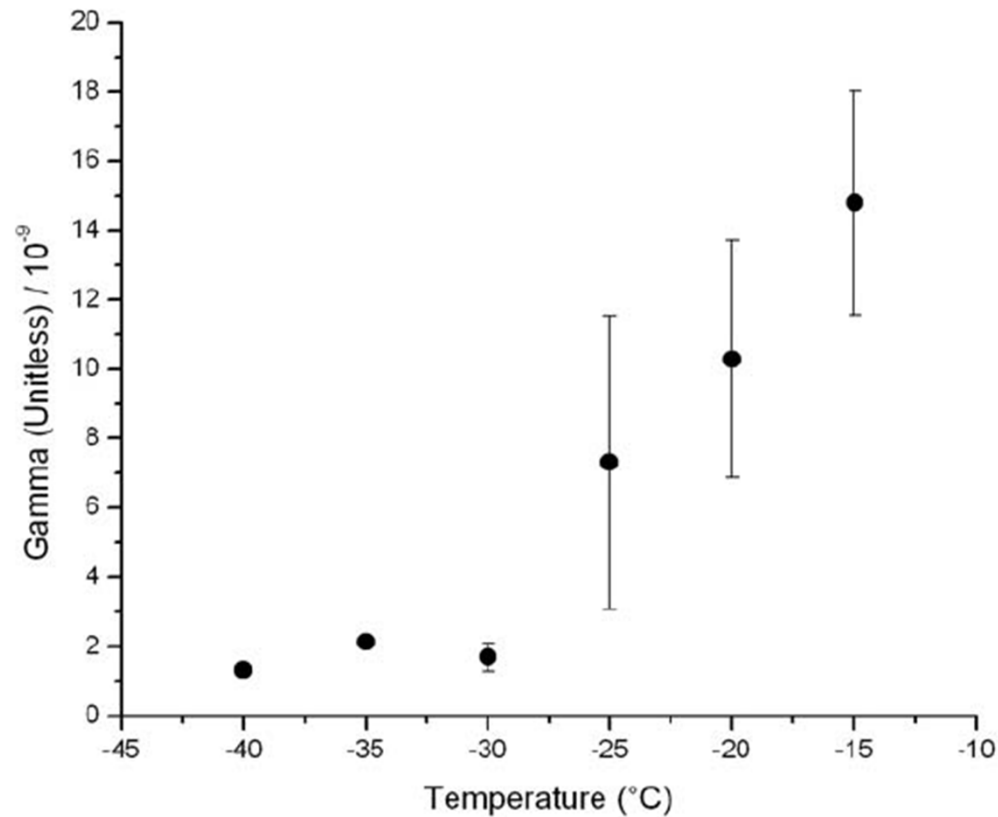- frozen solutions of $NaCl/NaBr/H^+$ that contain ice and brine

CIMS
- I^- and $I^- \cdot H_2O$ reagent ions
- Br_2 detected as IBr_2^-
- 2×10^9 /cm^3 detection limit
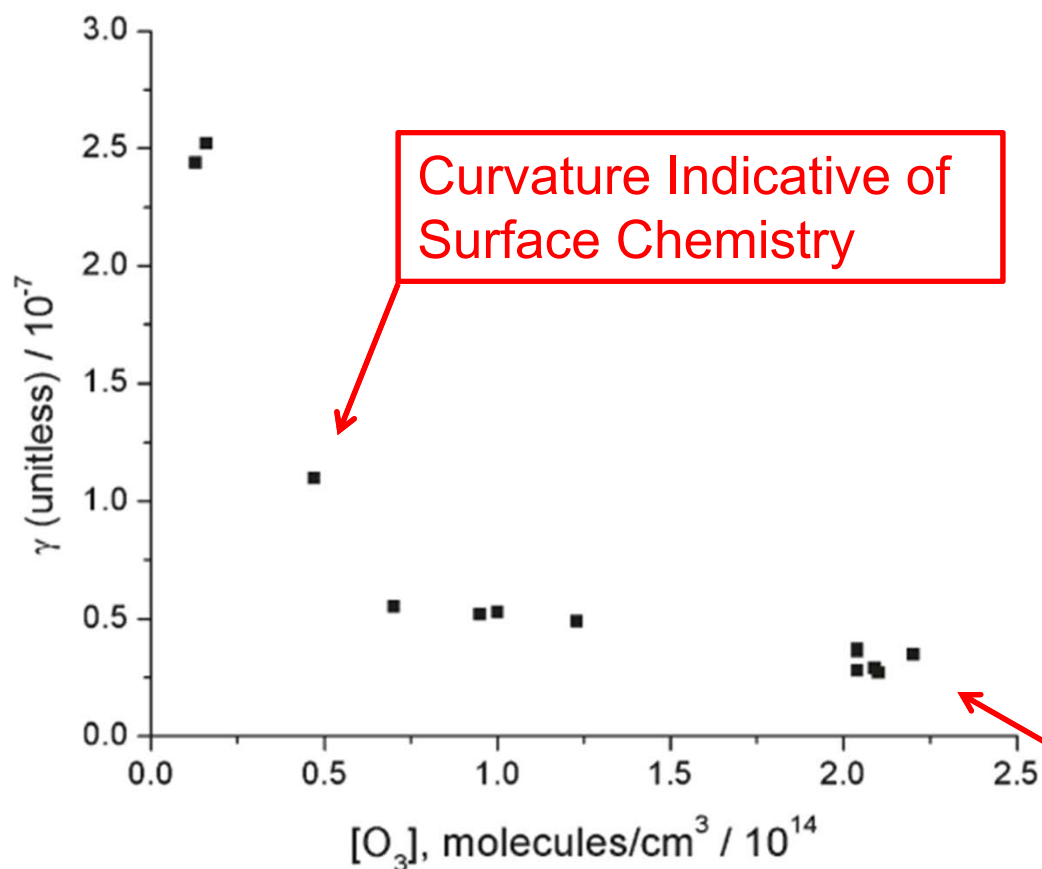
$$\gamma = \frac{2rk_{w,corr}}{\omega}$$

Kinetics on frozen solutions show a strong temperature dependence, probably related to the presence of brine

NaCl 0.5 M, NaBr 8 mM, pH 5.6, $[O_3]$ = 2×10^{14} /cm^3

Results on frozen solutions indicate both bulk- and surface-phase kinetics

Curvature Indicative of Surface Chemistry

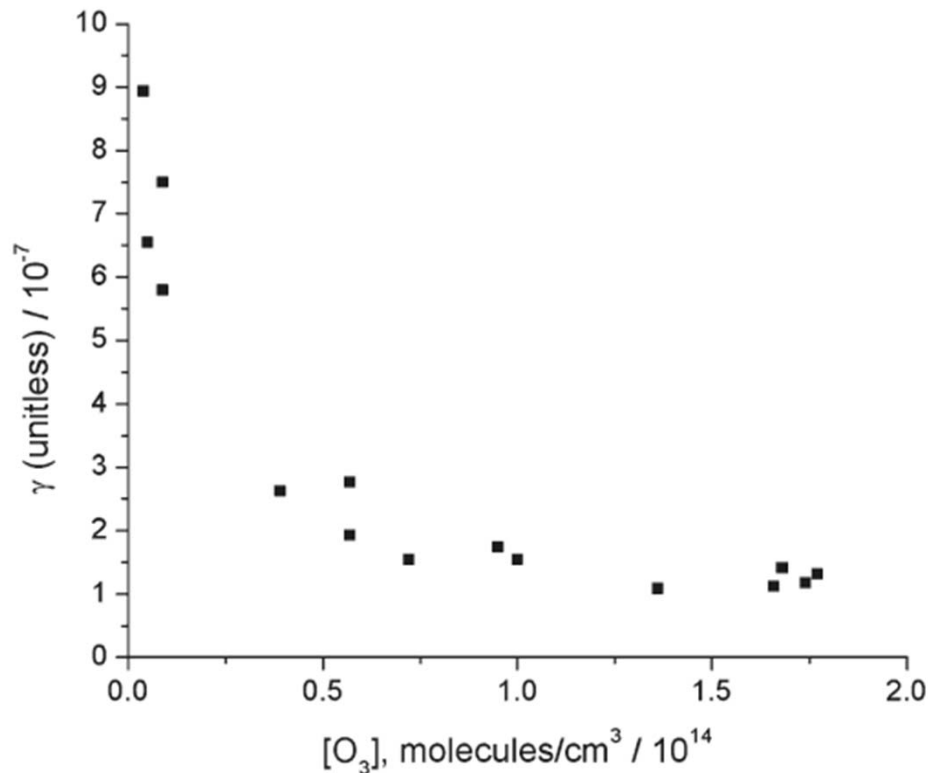Positive Asymptote Indicative of Bulk Phase Chemistry

Langmuir-Hinshelwood Kinetics

$$\frac{1}{\gamma_{surf}} \approx \frac{1}{\Gamma_s} = \omega\sigma \frac{1 + K[O_3]_{gs}}{4Kk_s[Br^-]_s}$$

253 K, NaCl 0.5M
NaBr 8mM,
pH 2, 253 K

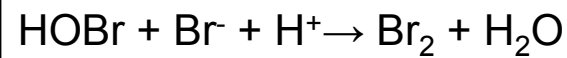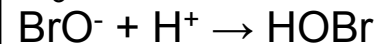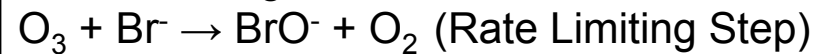Results on liquid solutions have the same dependence on ozone, with the liquid kinetics slightly faster (about 3X)

NaCl 0.5M, NaBr 8mM, pH 2, 273 K

Excellent agreement between the measured bulk uptake coefficient and that calculated using:

$$\gamma_{bulk} = \frac{4RTH\sqrt{Dk^I}}{\omega}$$

and assuming:
$O_3 + Br^- \rightarrow BrO^- + O_2$ (Rate Limiting Step)
$BrO^- + H^+ \rightarrow HOBr$
$HOBr + Br^- + H^+ \rightarrow Br_2 + H_2O$

$\gamma_{Measurement}$ **= 8×10^{-8}**
$\gamma_{Calculation}$ **= 1.1×10^{-7}**

The same mechanism apparently proceeds on both liquid and frozen solutions.

$\Rightarrow$ On the frozen solutions, the reaction probably proceeds via the brine.

Surface- and bulk-phase kinetics proceed **simultaneously**.

Conclusions from the Ozone/Bromide Reaction

- The surface phase reaction is dominant for atmospheric ozone levels

- Bromine activation via this reaction will be positively correlated with temperature

- Efficient activation:

    For $\gamma = 10^{-8}$, 30 ppb of ozone could process a monolayer of Br^- in 1 month, corresponding to about 2 pptv/day into a 500 m high boundary layer
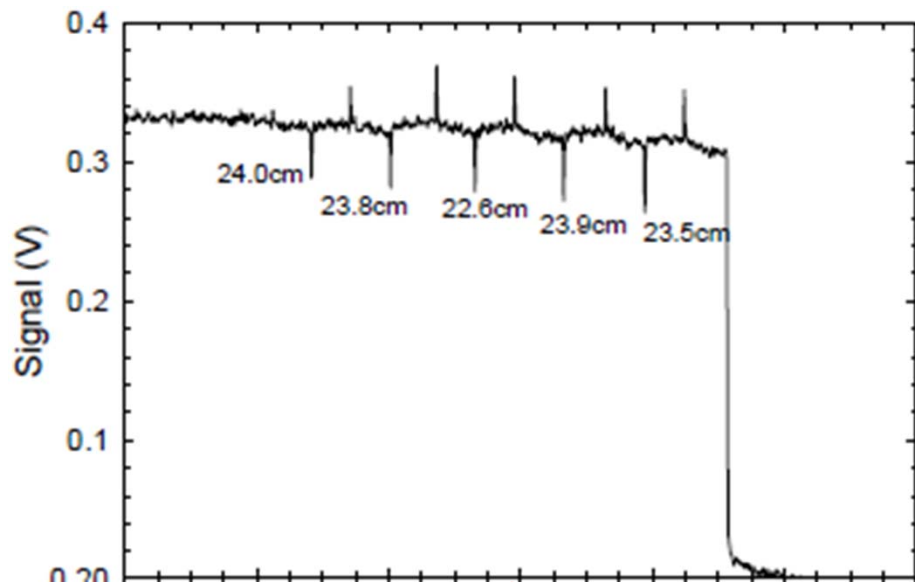
Reactive uptake of SO_2 to ice surfaces containing adsorbed H_2O_2: $SO_{2(g)}$ + $H_2O_{2(g)}$ → $H_2SO_{4(ads)}$
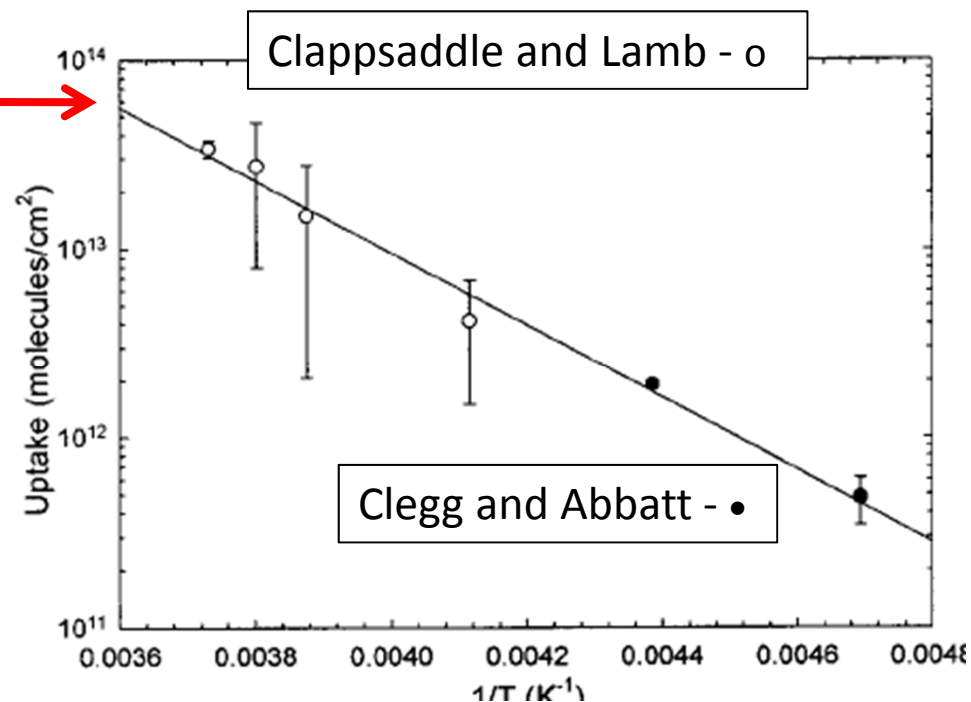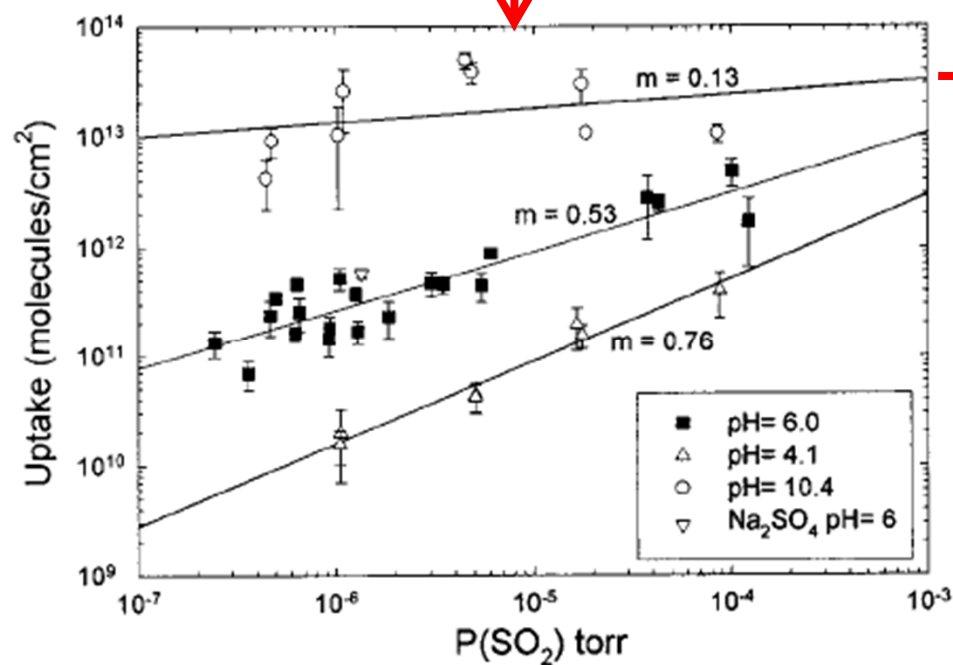
Ice Substrate: Ice, 228 K

Main Points:
• Reaction is relevant to SO_2 dry deposition and SO_2 loss in ice clouds
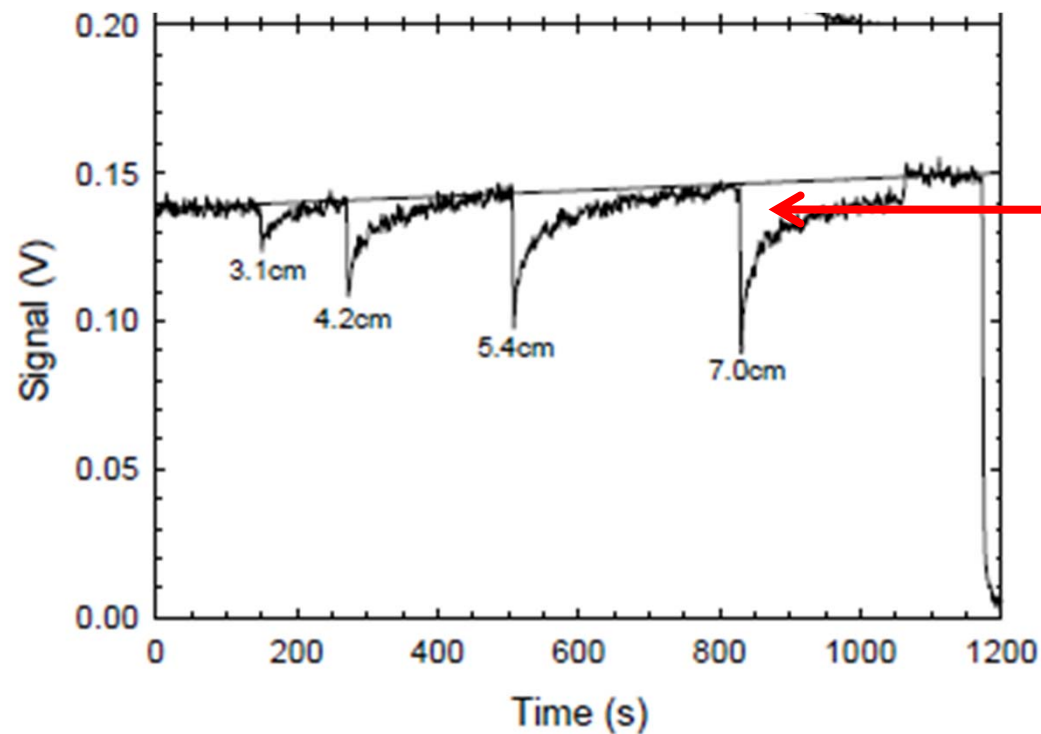• Reaction occurs strictly on the surface

Reference: Clegg and Abbatt, ACP, 2001.

Observations: SO_2 uptake to ice indicates formation of HSO_3^- and an important role for the interaction with water at the surface

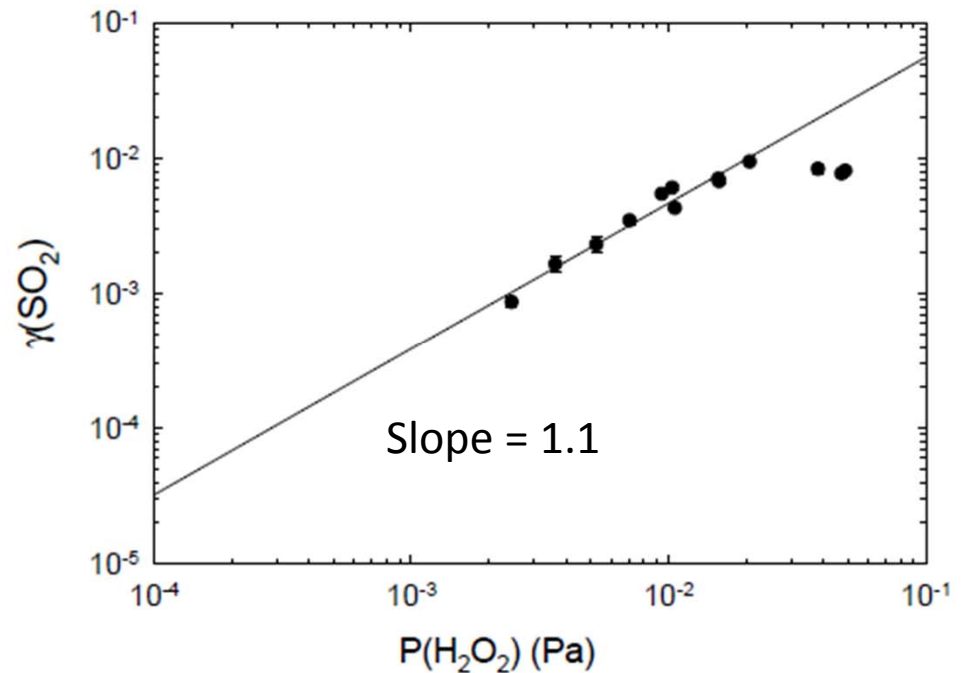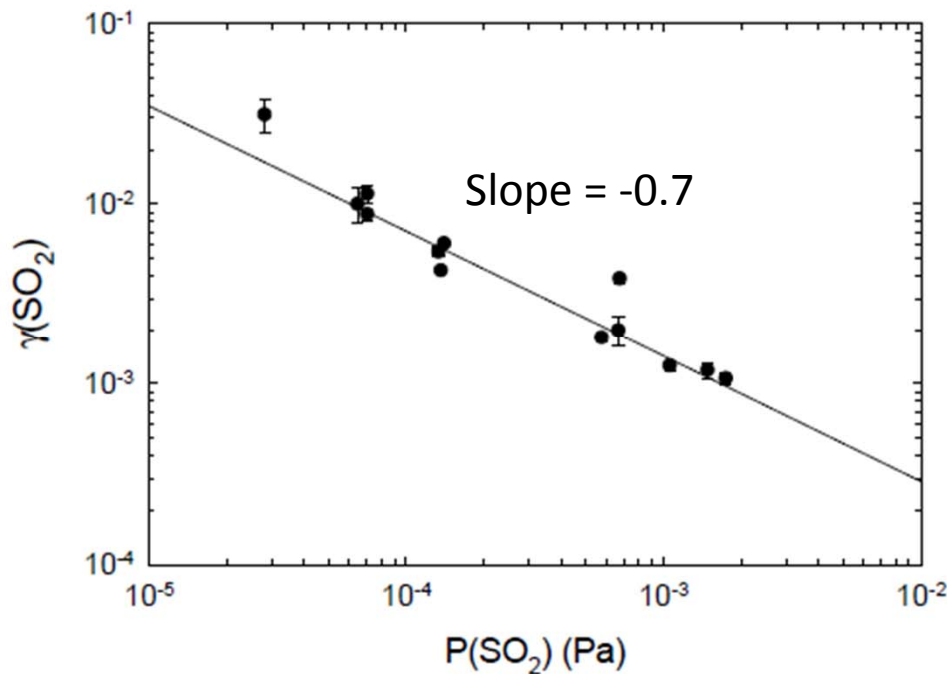Clappsaddle and Lamb - o

Clegg and Abbatt - •

Observations: Enhanced, irreversible SO_2 uptake when H_2O_2 is present

Integration of the amount of lost $SO_2 \approx$ amount of H_2SO_4 formation $\Rightarrow 10^{14} - 10^{15}$ molecules/cm^2

Evidence for chemistry on just the upper monolayer-QLL of the ice films

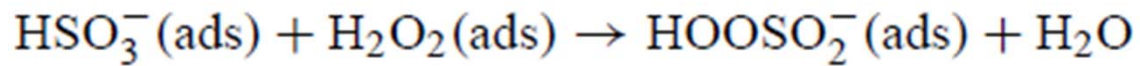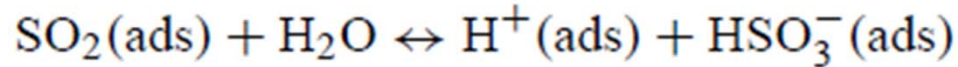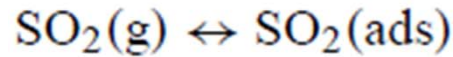# Mechanism: $SO_2 + H_2O_2 \rightarrow H_2SO_4$

$$H_2O_2(g) \leftrightarrow H_2O_2(ads)$$

$$SO_2(g) \leftrightarrow SO_2(ads)$$

$$SO_2(ads) + H_2O \leftrightarrow H^+(ads) + HSO_3^-(ads)$$

$$\boxed{HSO_3^-(ads) + H_2O_2(ads) \rightarrow HOOSO_2^-(ads) + H_2O}$$

$$HOOSO_2^-(ads) + H^+(ads) \rightarrow 2H^+(ads) + SO_4^{2-}(ads)$$

Left plot: $\gamma(SO_2)$ vs $P(SO_2)$ (Pa), Slope = -0.7

Right plot: $\gamma(SO_2)$ vs $P(H_2O_2)$ (Pa), Slope = 1.1
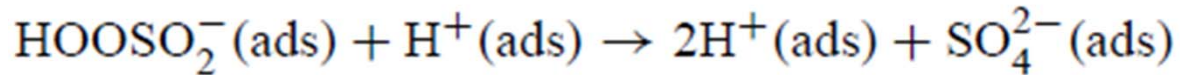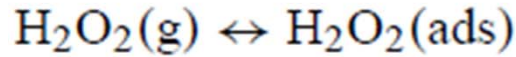
Oxidation of Small Dicarboxylic Acids by Photolytically Generated OH

Ice Substrate: Frozen H_2O/H_2O_2 solutions, 253 K

Main Points:
• Common polar ice components are subject to oxidation to smaller di-acids and CO_2
• Chemistry similar to that in the liquid phase (Yang et al., 2008)
• Reactant solubility/segregation affects the kinetics in ice, and may lead to slow oxidation kinetics in ice

Reference: Gao and Abbatt, JPC-A, submitted.

Organic Diacids/OH: Experimental
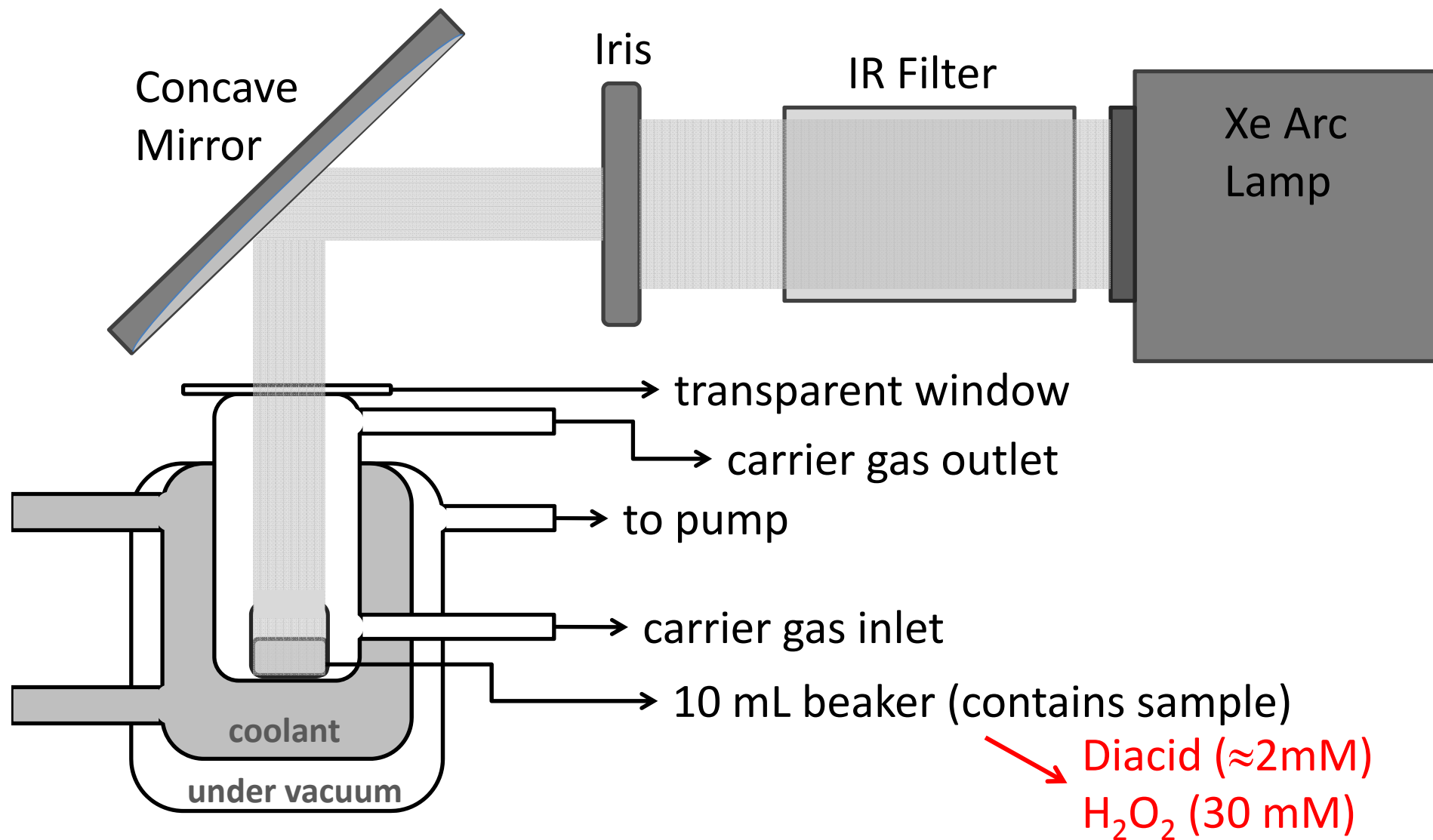
Organic Diacids/OH: Results and Interpretation

	[diacid] (mM)	[H$_2$O$_2$] (mM)	k' (10^{-5} s^{-1})		
			RT	0°C	- 20°C
succinic acid	2.5	30	13±1	11±2	**0.8±0.2**
malonic acid	2.5	30	3.4±0.6	2.2±0.3	1.0±0.1

• Does the OH production rate change between liquid and frozen solutions?
NO: Measurements of the OH production rate using a radical trap show that it is the same in the ice substrates as in liquid solutions.

• Solubility of malonic acid is 20X that of succinic acid

We hypothesize that the succinic acid and the H$_2$O$_2$ phase separate or spatially segregate upon freezing, leading to lower oxidation rates. Is this behavior general?

Conclusions

• Detailed, targeted kinetics studies can provide significant information about the nature of the reaction, much more information than the overall rate

• The results are understandable, driven by <u>how the substrates is prepared</u>:

The **surface reaction** appears to dominate for $O_3 + Br^-$
$\Rightarrow$ Quantitative separation of bulk versus surface chemistry

Aqueous phase processes in "ice" dominate for O_3/Br^-, OH/diacids
$\Rightarrow$ Identification of aqueous phase/brine chemistry

$H_2O_{2(g)} + SO_{2(g)}$ proceeds in the **surface-layer on a pure ice surface**
$\Rightarrow$ Identification of surface phase chemistry

Reactant segregation can lead to slow kinetics with OH/diacids
$\Rightarrow$ Indication of (in)efficient reactant mixing

• Attention should be given to the <u>details of the kinetics,</u> to <u>repeated studies of the same reactions above and below freezing,</u> and to work with <u>real snow/ice samples</u>
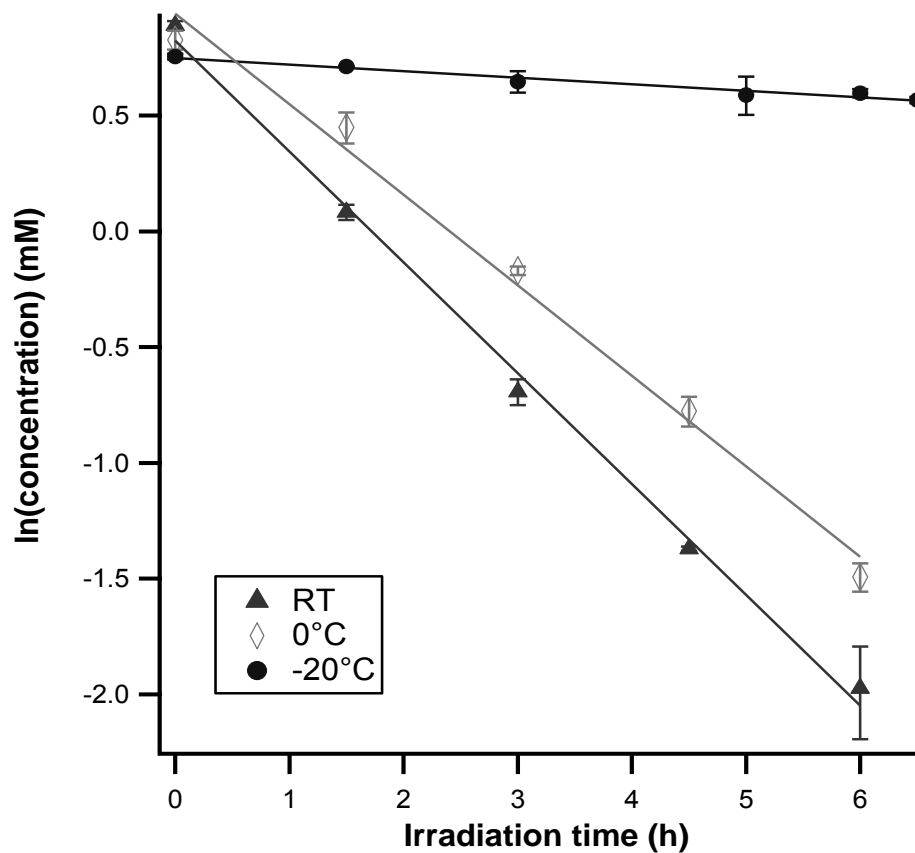
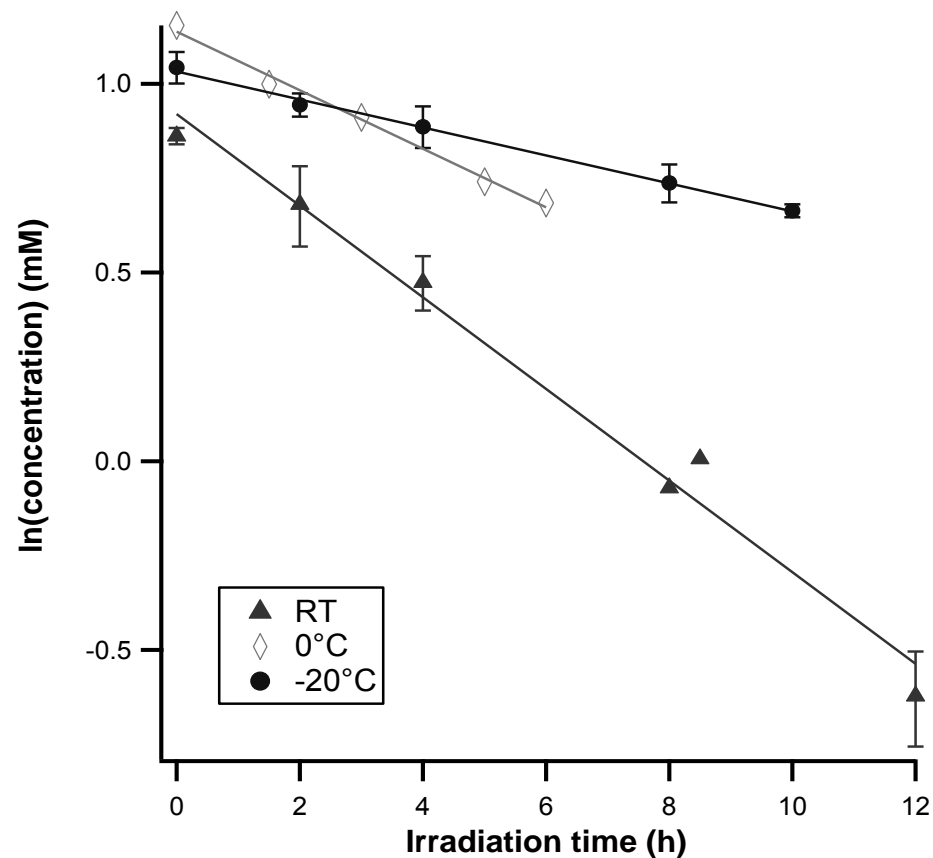Acidity dependence is quite weak in the 'brine' regime (i.e. 253 K), from pH 2 to 7
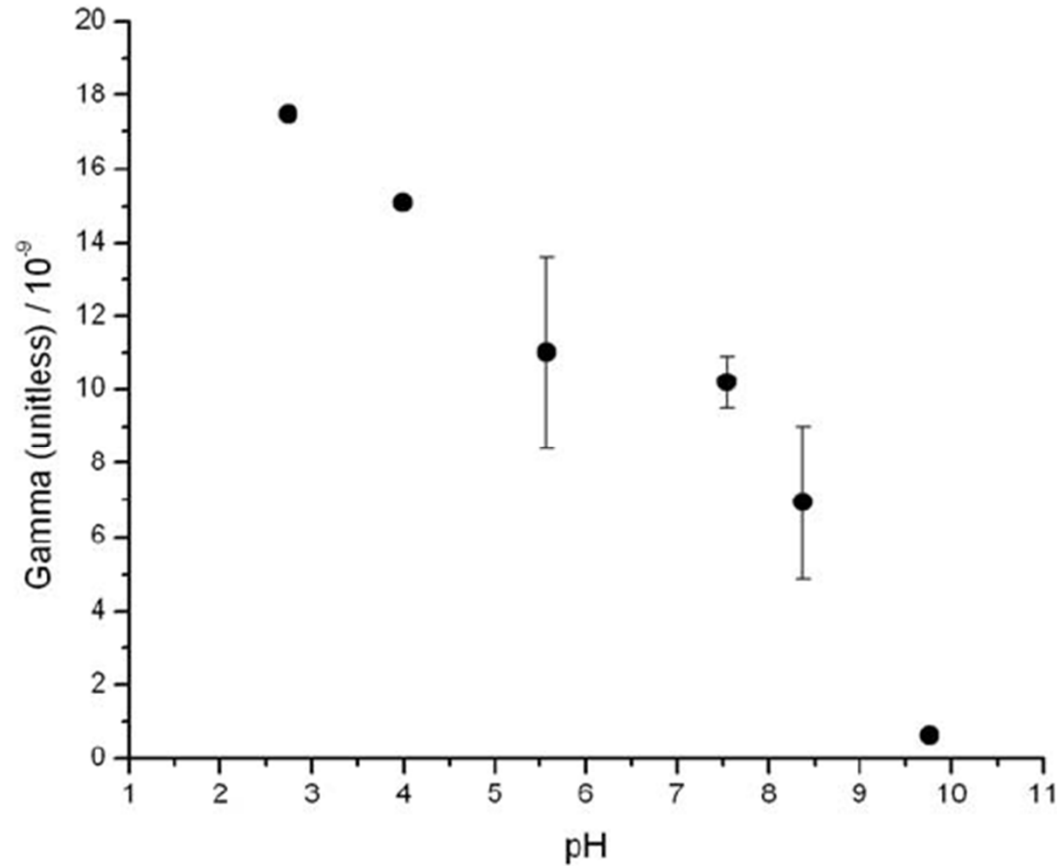
NaCl 0.5 M, NaBr 8 mM, $[O_3] = 2\times10^{14}$ /cm^3 , 253 K

Organic Diacids/OH: Kinetics Results

Succinic Acid
(C4 diacid)

Malonic Acid
(C3 diacid)