Atmospheric Aqueous Phase Chemistry of Mercury

In rain and cloud droplets
In deliquesced aerosols

Oxidation
Reduction
Complexation
Photolytic reactions

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Air – Droplet Exchange

Determined by Henry's Law constants.
Oxidised Hg compounds are much more soluble than elemental Hg.
If elemental Hg entering droplets is oxidised then aqueous phase chemistry removes elemental Hg from the air,
alternatively,
if oxidised Hg compounds are reduced in the aqueous phase then the presence of droplets will increase the amount of elemental Hg in the air

Complexation

Oxidised Hg in the aqueous phase can form a variety of complexes:

$HgSO_3$, $Hg(SO_3)_2^{2-}$
$HgCl_x^{2-x}$, $HgBr_x^{2-x}$
$Hg(OH)_2$, HgOHX (X=Br, Cl)

Oxidation

$$Hg^0 + O_3 \rightarrow HgO$$

$$HgO + H^+ \rightarrow Hg^{2+} + OH^-$$

$$Hg^0 + HOCl/OCl^- \rightarrow Hg^{2+} + Cl^- + OH^-$$

$$Hg^0 + HOBr/OBr^- \rightarrow Hg^{2+} + Br^- + OH^-$$

$$Hg^0 + OH^\bullet \rightarrow \underline{\mathbf{Hg^+}} + OH^-$$

Reduction

$$HgSO_3 \rightarrow Hg^0 + SO_3^{2-}$$
$$Hg(OH)_2 + h\nu \rightarrow Hg^0 + \text{products}$$
$$Hg^{II} + HO_2/O_2^- \rightarrow \underline{\mathbf{Hg^+}} + \text{products}$$

But just how important is aqueous phase reduction in the atmosphere.
The answer varies from,

VERY, QUITE, not really, to irrelevent,
depending on who you are and what you do!

Hg^{+} in the Aqueous Phase

$$Hg^{+} + OH^{\bullet} \rightarrow Hg^{2+} + OH^{-}$$

$$Hg^{+} + O_2/HO_2^{-} \rightarrow Hg^{0} + O_2 + (H^{+})$$

$$Hg^{+} + O_2 \rightarrow Hg^{2+} + O_2^{-}$$

very fast, and therefore oxidation to Hg^{2+} by OH can be considered as a one step reaction, with the rate limiting step the initial oxidation to Hg^{+} .... and

$Hg^{2+} + HO_2$

..... and the reduction of Hg^{2+} to Hg does not occur because the Hg^{+} formed by the reaction of Hg^{2+} and HO_2 is rapidly re-oxidised to Hg^{2+} by O_2.

This would mean that there is no known reduction pathway for RGM in either the gas or aqueous phases!

This makes life extremely difficult for modellers.

To Conclude

- Tony will be available for questions and answers at each coffee break and lunch hour every day this week …….