Introduction

At first glance, freezing a dilute solution of reactants may seem like an excellent way to prevent interesting chemical changes from occurring. However, by creating a “frozen solution” wherein concentrated pockets of unfrozen solution can exist, dramatic increases in rates of reactions and/or alteration of reaction pathways have been observed. Somewhat surprisingly, the extent to which these reactions may be of influence in the chemistry of the cryosphere is relatively unknown.

In this research, the possibility that freezing reactions may produce precursors for the release of ozone destroying halogen atoms is explored. Once released into the troposphere, halogens (particularly bromine) can enter catalytic reaction pathways which destroy ozone, deposit mercury and facilitate the release of even more bromine molecules from snowpack via “bromine explosion” reactions. However, it is still unclear as to how these events are initiated; which is of vital importance to our understanding of these pathways.

One possibility, is that a newly discovered freezing reaction involving halide salts present in seawater may be involved. When dilute solutions of iodide, bromide and an oxidant are frozen together, dibromoiiodide, IBr₂, is shown to be produced. This interhalide may subsequently undergo photolysis to yield bromine and iodobromine atoms. Such reactions may well play an important role in the observed sudden ozone and mercury depletion events observed in the polar tropospheres.

Formation of IBr₂

- 0.05mM I⁻, NO₂⁻ & 0.5mM Br⁻
- pH range 2-3.5
- Frozen to -20°C
- Thawed by variety of methods
- UV-Vis analysis

UV-Vis

- I₂Br⁻ converted to IBr₂⁻ as a result of freezing
- pH dependent conversion suggests H₂ONO⁻ involvement
- Analogous reactions with Cl⁻ instead of Br⁻ show an increased reactivity for Br⁻ over Cl⁻
- Dissolved O₂ necessary for the initial formation of I₂Br⁻

Analysis of Reaction

- More moles dibromoiiodide formed than moles H₂ONO⁻ present
- Appears that nitroacidium ion acting as a catalyst
- H₃O⁺ (pH < 3.6) can be substituted for H₂ONO⁻

Concentration of Species Present Vs. pH

- Concentration of IBr₂⁻ decreases with time when exposed to sunlight
- I₂Br⁻ does not reform
- Loss of active halogen species to gas phase?

Mechanism

- Freezing known to cause a concentrating effect
- Concentrating all reactants evenly x1000 shown to yield IBr₂ without freezing
- Appears that IBr₂⁻ formation is kinetically inhibited unless solution is concentrated
- Freezing removes this restraint

Conclusions

1. Reaction driven by freeze concentration mechanism
2. Similar processes likely to occur in natural environment
3. IBr₂⁻ appears to be a strong candidate as a source of ozone destroying halogen species
4. Oxidant (H₂ONO⁻) can be altered: potential for reaction to occur at more environmentally relevant pHs

Outlook

- Products of decomposition of IBr₂⁻ yet to be identified
- Use of Incoherent Broadband Cavity Enhanced Spectroscopy for analysis
- Decomposition Pathways, quantum yield etc. Need to be verified

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