INVESTIGATIONS OF THE HETEROGENEOUS REACTION BETWEEN AMMONIA AND SULFURIC ACID AEROSOLS

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The Earth is surrounded by a blanket of air about 120km thick, which we call the atmosphere. Its composition is primarily that of gas, but water droplets and particulate phase species also represent important constituents.

Particulate Matter (PM) is the general term used for a mixture of solid particles and liquid droplets in our atmosphere. Sulfuric acid aerosol is formed by the oxidation of SO2 in gas/aqueous/aerosol phase.

Soluble trace gases such as Ammonia, NH3, are produced from agricultural sources and represents a significant atmospheric pollutant in Ireland.

The preferred form of sulfuric acid in the aerosol phase is ammonium sulfate (NH4)2SO4. Each sulfuric acid molecule is looking for two ammonia molecules (neutralization). If there is not enough ammonia present, sulfuric acid exists either as H2SO4(aq) or NH4HSO4.

AMMONIA (100ppm standard; NH3/N2, diluted to pH range: admission to flow tube via a 6mm diameter movable glass injector.

AEROSOL FLOW-REACTOR is made of glass, ID: 81mm, maximal reactive length: 7.8mm. Operated at room temperature and atmospheric pressure.

AEROSOL GENERATION: H2SO4, aerosol generated by passing a flow (200-500 sccm) of air over hot sulfuric acid (>2g, T=130°C).

HIGH H2SO4, aerosol generated by acid (~2g, T=130°C).

RESULTS: FTIR

\[ H_2SO_4 \]

\( \text{WET: 35}\% \text{rh} \)

\( \text{DRY: 1.5}\% \text{rh} \)

\( \text{NH}_3 \text{ vs } \text{NH}_4^+ \) @ various [H2SO4]

FTIR

\( \text{Wet/dry } H_2SO_4 \text{ yields the same dissociation products, bisulfate ion } 1180cm^{-1}, \text{1035cm}^{-1} \text{ and } 890cm^{-1} \text{ } H_2SO_4 \rightarrow H^+ + HSO_4^- \)

\( \text{Low } [H_2SO_4] \text{ the major "dry" particle } (NH_4)_2SO_4/H_2SO_4 \text{. Varying the humidity yields } (NH_4)_2SO_4/H_2SO_4/H_2O \text{ particle} \)

\( \text{At higher } H_2SO_4 \text{ concentrations and low } [NH_3], \text{ ammonium bisulfate is formed as seen from the FTIR both wet and dry} \)

\( \text{Varying } [NH_3], \text{ the composition of the particles was changed from } NH_3HNO_3/H_2SO_4 \text{ to } NH_3HNO_3/(NH_4)_2SO_4/H_2SO_4 \text{ to predominantly } (NH_4)_2SO_4/H_2SO_4 \text{. } NH_3HNO_3 \text{ is visible at } 968cm^{-1} \)

\( \text{At high } [H_2SO_4] \text{ wet/dry, the only product observed is } NH_3HNO_3 \)

NO3 Monitor

\( \text{Low } [H_2SO_4] \text{ wet/dry, increase of } N_2 \text{ does not affect the } [NH_4^+] \)

\( \text{High } [H_2SO_4] \text{ wet/dry, } [NH_4^+] \text{ ion increases proportionally with increase in } NH_3 \)

SMPS

\( \text{Low } [H_2SO_4], \text{ dry particles are mainly small, with diameter of 21nm, addition of } H_2O _2 \text{ we see a shift in particle diameter to 206nm} \)

\( \text{High } [H_2SO_4], \text{ there is a slight shift in particle diameter from 57nm (dry) to 64nm (wet)} \)

\( \text{NH}_4HSO_4 \text{ particle diameter: 185nm; } (NH_4)_2SO_4 \text{ particle diameter: 71nm} \)

Conclusion

Our investigations into the reaction between NH3 and H2SO4 aerosols, have shown that the main products formed are: NH4HSO4 and (NH4)2SO4; their relative importance depend on both concentration and humidity.

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