Monitoring Metal Sulfide Growth in the Gas Phase using FT-ICR MS

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Results
Cationic Metal Sulfide Clusters

Reactivity of specific metal clusters was monitored as a function of reaction time.
Both cluster size and degree of hydration were found to be important factors in metal cluster reactivity with H₂S(g).

Hydrolysis is not observed: solvent molecules only slow the reactions with H₂S(g).

Background

Research has shown that metal clusters are vital to environmental processes such as mineral formation and biochemical systems involved in respiration, photosynthesis and nitrogen fixation. The transition between dissolved species and nanoparticle state is only recently described for Fe(II) and Zn(II). Systems is it possible to have clusters of different stoichiometries condense, forming larger species, before nanoparticle formation. Previously, our group used LEED-TFTS to characterize single layer CO adsorption and H₂S adsorption. This work seeks to understand the chemical processes involved in the formation of aqueous nanoparticles by monitoring the formation of such metal clusters in the gas phase using FT-ICR MS.

Particles from field samples are modeled by growing clusters in laboratory solutions in the case of Fe(II), Cu, Zn and Ag. The kinetics of growth of the clusters are followed by observing loss of size of monomeric metal and sulfide both present in micrometer concentrations by voltammetry and absorption spectroscopy. Binding constants are also measured by these methods. The spectroscopic and voltammetric measurements indicate the ratio of metal to sulfur in the various clusters, but not the stoichiometry of the actual clusters which are generally electrochemically and spectrally more stable. Our research group has been using LEED/FTICR MS as an analytical tool to probe these inherently difficult samples. In order to investigate the nucleation and particle growth of metal clusters in aqueous systems, we have developed a method to model these systems by monitoring gas phase reactions of metal cations with H₂S(g).

Experimental

Experiments were done using a Bruker Apex Ettal FT-ICR MS (T7) which has been modified to allow reaction gases to be induced into the ICR cell region using a variable leak valve (Vana). All ions were produced by EI and were exposed to H₂S(g) pressure (4kPa-90mbar) for various reaction times before reaction and detection of the reaction products. The mass accuracy capability of FT-ICR MS allows for the proper stoichiometric characterization of resulting metal sulfide clusters.

Cationic Metal clusters were mass selected and accumulated (1.5s) in the source region of the instrument. Analysis of the 207m/z parent ion required a large isolation window (50m/z) to maintain strong signal intensity allowing for simultaneous analysis of 225m/z 4m.

No mass selection was necessary in negative ion mode. Anionic clusters were accumulated for up to 1.5s in the source region before transfer to the ICR cell for analysis.

All samples were prepared from a 10mm Cel(NO₃)₂-4H₂O aqueous stock solution. ESII samples were then diluted to 0.6mM in 50/50 water/methanol.

Conclusions

• Reactions of H₂S with electrophilic cationic nitrate clusters in the gas phase produce a number of sulfur containing clusters.
• Electrospray produced positive ions of the type [Cel(NO₃)₂(H₂O)₃(CH₂O)]⁺ that react with H₂S(g) to form [Cel(SH)₂(H₂O)₃(CH₂O)]⁺ suggesting that solvent acts as a reactant in the H₂S reaction suggesting that gas phase reactions reflect processes in solution.
• Negative ions produced by electrospray were of the type [Cel(NO₃)₃]⁻ which reacted sequentially with H₂S(g) producing ions of the type [Cel(NO₃)₃H₂S]⁻ but no Cel(II) was detected.
• Reactions increase from n=1 to n=3 then decrease for n=4 and n=5 is unreactive. The reaction sequence in n=3 and 4 lead to terminal species that do not react any further.
• The gas phase results suggest that precipitation of Cel in condensed phase may proceed through a variety of molecular clusters involving increasing numbers of cationic ions and both nitrate and sulfide anions.