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

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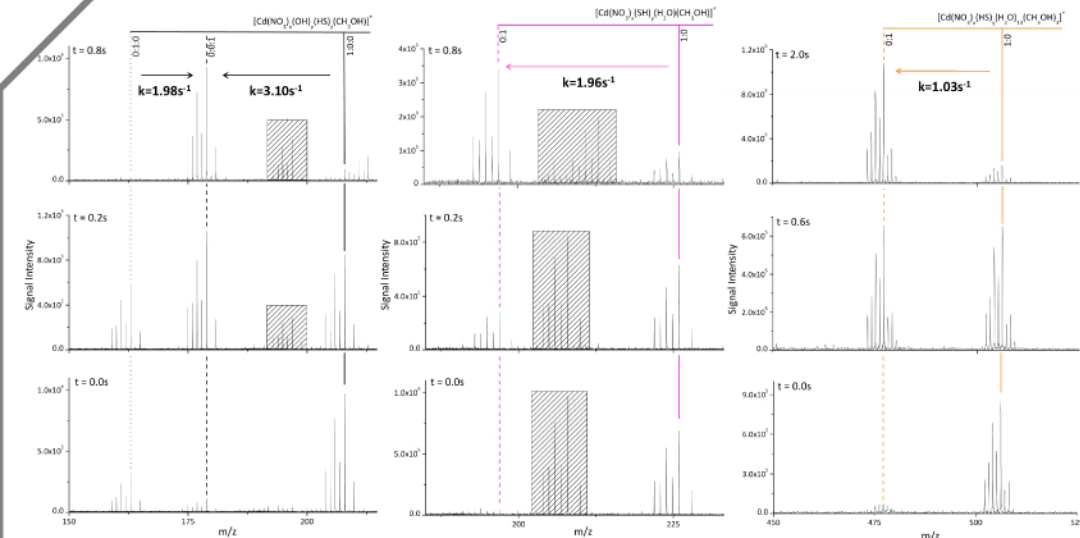[a]University of Delaware, Dep. of Chemistry & Biochemistry, Newark, DE
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Results

Cationic Metal Sulfide Clusters

Figure 1: Mass spectra at reaction times t = 0.0, 0.2, and 0.8s and the calculated rate constants for the gas phase reaction between $[CdNO_3(CH_3OH)]^+$ / $[CdOH(CH_3OH)]^+$ (207 and 162m/z) and $H_2S(g)$ to give $[CdSH(CH_3OH)]^+$ (178m/z).

Figure 2: Mass spectra at reaction times t = 0.0, 0.2, and 0.8s and the calculated rate constant for the gas phase reaction between $[CdNO_3(H_2O)(CH_3OH)]^+$ (225m/z) and $H_2S(g)$ to give $[CdSH(H_2O)(CH_3OH)]^+$ (196m/z).
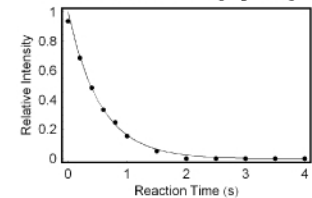
Figure 3: Mass spectra at reaction times t = 0.0, 0.6, and 2.0s and the calculated rate constant for the gas phase reaction between $[CdNO_3(H_2O)_{13}(CH_3OH)_3]^+$ (506m/z) and $H_2S(g)$ to give $[CdSH(H_2O)_{13}(CH_3OH)_3]^+$ (477m/z).
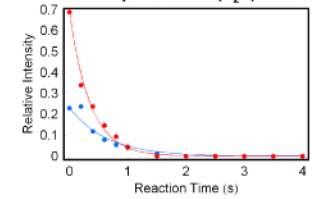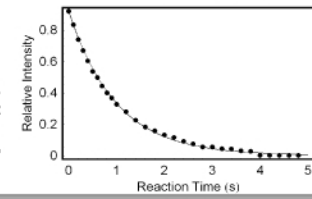
- The reactions observed conform to Scheme I.

- Experimental rate constants were obtained from non-linear fits to the experimental data.

- No loss of solvent molecules is observed as a result of reaction with $H_2S(g)$ for any values of i and j.

- Rate constants tend to decrease with increasing i and j.

Scheme I

$$[Cd(NO_3)(H2O)_i(CH_3OH)_j]^+$$

$$\xrightarrow[-HNO_3]{H_2S}$$

$$[Cd(SH)(H_2O)_i(CH_3OH)_j]^+$$

Anionic Metal Sulfide Clusters

Figure 4: Mass spectra at reaction times t = 0.0, 5.0, and 9.0, 20.0 and 66.0s and the calculated rate constants for the sequential gas phase reactions between $[Cd_2(NO_3)_5]^-$ (535m/z) and $H_2S(g)$.

Figure 5: Mass spectra at reaction times t = 0.0, 5.0, and 9.0, 20.0 and 66.0s and the calculated rate constants for the sequential gas phase reactions between $[Cd_3(NO_3)_7]^-$ (771m/z) and $H_2S(g)$.

Figure 6: Mass spectra at reaction times t = 0.0, 5.0, and 9.0, 20.0 and 66.0s and the calculated rate constants for the sequential gas phase reactions between $[Cd_4(NO_3)_9]^-$ (1007m/z) and $H_2S(g)$.

- Anionic metal clusters show reactivity that varies with cluster size. Mononuclear and pentanuclear metal clusters show no reactivity with $H_2S(g)$ on the time scale of the experiment.

- The rxn sequences are made up of steps that in general conform to Scheme II. The complexes add hydrogen sulfide and lose either one or two molecules of HNO_3 resulting in the introduction of either a –HS or –S moiety. If the loss of the second HNO_3 is slow, then introduction of –S is a sequential process.
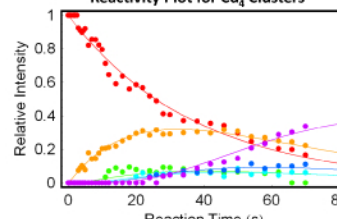
- Experimental data were fit to a simple sequential reaction model and rate constants were derived as shown in the figures.

- Reaction rate increases from Cd to Cd_2 to Cd_3 and decreases from Cd_3 to Cd_4 to Cd_5.

- For Cd_2 reactivity decreases for each of the sequential H_2S reactions.

- The rate constants for sequential reactions for Cd_3 increase until the formation of $Cd_3(NO_3)_4(HS)(S))^-$ which is stable.

- Similarly, the rate constants for sequential reactions for Cd_4 increase until the formation of $Cd_4(NO_3)_4(HS)(S)_2^-$ which is also stable.

Scheme II

$$[Cd_n(NO_3)_{2n+1}]^-$$

$$\xrightarrow[-HNO_3]{H_2S}$$

$$[Cd_n(NO_3)_{2n}SH]^-$$

$$\xrightarrow[-2HNO_3]{H_2S} \quad \xrightarrow[-HNO_3]{H_2S}$$

$$[Cd_n(NO_3)_{2n-1}S]^-$$

Overview

<u>Metal Sulfide clusters</u> were able to be made in the gas phase through ion-molecule reactions within the ICR cell of a FT-MS.

<u>Reactivity of specific metal clusters</u> was monitored as a function of reaction time.

<u>Both cluster size and degree of hydration</u> were found to be important factors in metal cluster reactivity with $H_2S(g)$.

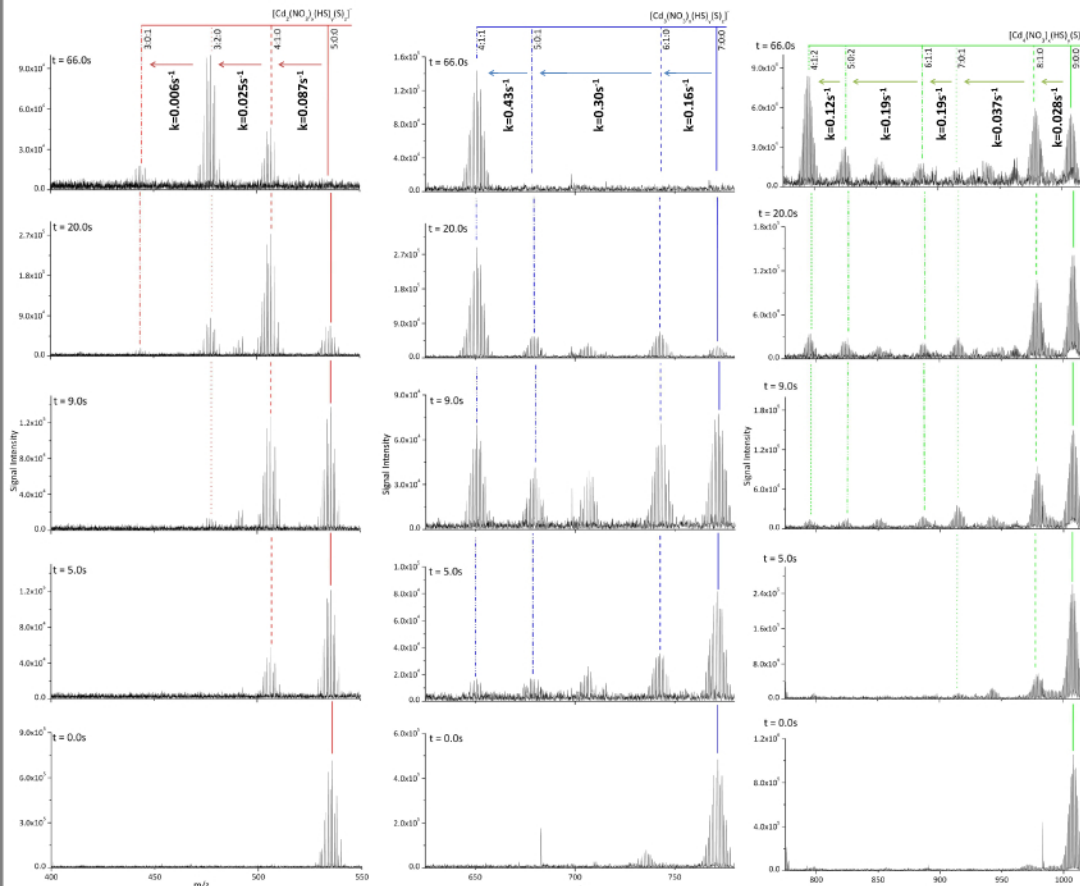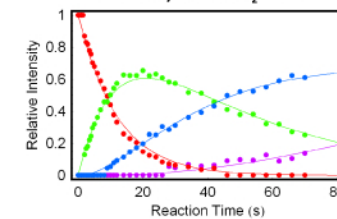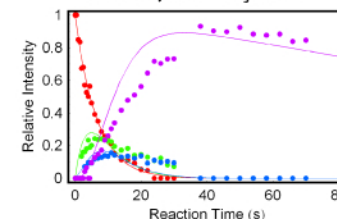<u>Hydrolysis is not observed</u>, solvent molecules only slow the reactions with $H_2S(g)$.

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 nanoparticulate solid has only recently been described for FeS and ZnS systems. It is possible to have clusters of different stoichiometries condense, forming larger species, before nanoparticle formation. Previously, our group used LDI-FTMS to characterized field samples of metal sulfide clusters and ESI-FTMS to characterize laboratory grown cadmium sulfate clusters resulting from oxidation of sulfidic cadmium species. Presented here is a method for understanding the chemical processes involved in the formation of aqueous nanoparticles by monitoring the formation of sulfidic 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, Cu, Zn and Ag. The kinetics of the growth of the clusters are followed by observing loss of monomeric metal and sulfide both present in micromolar concentrations by voltammetry and absorption spectroscopy. Binding constants are also measured by these means. 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 spectroscopically inactive. Our research group has been using ESI FT-ICR 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 environments, we have developed a method to model these systems by monitoring gas phase reactions of metal salts with $H_2S(g)$.

Experimental

Experiments were done using a Bruker Apex Qe FT-ICR MS (7T) which has been modified to allow reaction gases to be introduced into the ICR cell region using a variable leak valve (Varian). All ions were produced by ESI and were exposed to $H_2S(g)$ pressure (4x10-9torr) for various reaction times before excitation 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 ion.

- 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 $Cd(NO_3)_2•4H_2O$ aqueous stock solution. ESI samples were then diluted to 0.5μM in 50/50 water:methanol.

Conclusions

- Reactions of H_2S with electrosprayed cadmium nitrate clusters in the gas phase produce a number of sulfur containing clusters.

- Electrospray produced positive ions of the type $[CdNO_3(H_2O)_i(CH_3OH)_j]^+$ that react with $H_2S(g)$ to form $[CdSH(H_2O)_i(CH_3OH)_j]^+$ suggesting that solvent acts as a observer in the H_2S reaction suggesting that gas phase results reflect processes in solution.

- Negative ions produced by electrospray were of the type $[Cd_n(NO_3)2_{n+1}]^-$ which reacted sequentially with $H_2S(g)$ producing ions of the type $[Cd_n(NO_3)_{2n+1-y-2z}(HS)_y(S)_z]^-$ where y and z are ≤2.

- Reactivity increases from n=1 to n=3 and then decreases for n=4 and n=5 is unreactive. The sequential reactions in n=3 and 4 lead to terminal species that do not react any further.

- The gas phase results suggest that precipitation of CdS in condensed phase may proceed through a variety of molecular clusters involving increasing numbers of cadmium ions and both nitrate and sulfidic anions.