

MONITORING GAS PHASE ION-MOLECULE REACTIONS OF ENVIRONMENTALLY SIGNIFICANT METAL CLUSTERS WITH HYDROGEN SULFIDE USING FT-ICR MS

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OVERVIEW

Gas phase ion-molecule reactions between metal salt clusters and H₂S result in the formation of a variety of metal sulfide species.

Anionic clusters display <5% reaction efficiency with the exception of [Cd₄(CH₃COO)₆]⁻.

Cationic metal clusters show higher initial reaction efficiencies which decrease significantly with successive -SH substitution.

BACKGROUND

Research has shown that metal clusters are vital to environmental processes such as mineral formation and bioavailability (Wolthers et al., 2003). The transition from dissolved species to nanoparticulate solid is not well understood. Molecular clusters of varying structure and stoichiometry are thought to be important intermediates in the precipitation process (Luther and Rickard, 2005; Rozan et al., 2000). Understanding the properties of these clusters is therefore important. Previously, we have used ESI FT-MS to study the reaction between [Cd₄(NO₃)₂₀]⁺ and H₂S(g) resulting in the substitution of NO₃⁻ with HS⁻ and S²⁻ (ASMS 2008). Our present contribution extends the study of gas phase reactions of H₂S with metal clusters to acetates and environmentally important chlorides.

EXPERIMENTAL

To investigate the formation of metal sulfide clusters in aqueous environments, we have modified a 7T Bruker Apex Qe FT-ICR MS to conduct gas phase ion-molecule reactions of metal clusters with H₂S(g). Clusters are brought into the high vacuum region of the mass spectrometer by ESI of aqueous salt solutions (~0.5 mM). The charged clusters are exposed to elevated pressures of H₂S (4x10⁻⁹ - 9x10⁻⁹ Torr) in the ICR cell for varying reaction times followed by 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.

CONCLUSIONS

Gas phase ion-molecule reactions were observed for the reactions between various metal salts and H₂S.

- ~ Anionic clusters show <5% reaction efficiency.
- ~ Cationic clusters display higher reaction efficiencies than anionic clusters.
- ~ Initial reaction efficiencies decrease with successive -SH substitutions.
- ~ Metal cluster ligands significantly effect reactivity. NO₃ > OH > Cl

Observed reactions provide insight into the initial steps of metal sulfide cluster formation.

Solvated ion pairs could act as models for metals in aquatic environments.

Larger clusters may highlight chemistry taking place in supercritical aquatic systems near hydrothermal vents.

REFERENCES
Luther, George W., I. I.; Rickard, David T. *Journal of Nanoparticle Research*, (2005), 7(4-5), 389-407.
Ridge, Douglas P., Armentrout, Peter (Editor) *The Encyclopedia of Mass Spectrometry Volume 1: Theory and Ion Chemistry* (2003) Elsevier, Chapter 1.
Rozan, T. F., M. E. Lassman, D. P. Ridge, G. W. Luther. *Nature*, (2000), 406, 879-882.
Wolthers, Mariette; Van der Gaast, Sierk J.; Rickard, David. *American Mineralogist*,

RESULTS

Cationic metal clusters show higher reaction efficiencies than the anionic species (See Tables 1 & 2).

Reaction rates vary significantly with successive sulfide addition for cationic clusters (See Table 1 and Figure 1).

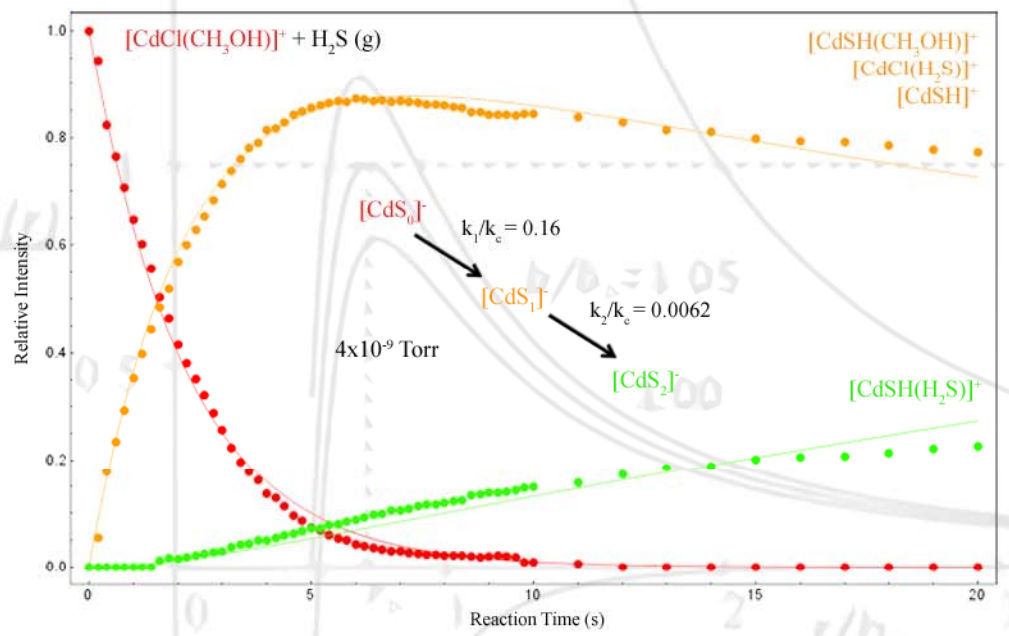


Figure 1: Plot of relative intensity vs. time for the reaction between [CdCl(CH₃OH)]⁺ and H₂S (4x10⁻⁹ Torr) highlighting the experimentally determined reaction efficiencies. Lines represent results for nonlinear regression modeling using the appropriate integrated rate equations.

ANIONIC METAL CLUSTERS

Table 2: Reaction efficiencies for the gas phase ion-molecule reactions between anionic metal clusters and H₂S (g).

Reactant	P (10 ⁻⁹ Torr)	k ₁ /k _c	k ₂ /k _c	k ₃ /k _c	k ₄ /k _c	k ₅ /k _c	k ₆ /k _c	k ₇ /k _c
[Cd(CH ₃ COO) ₂] ⁻	4	0.032	0.034	0.023				
[Cd(CH ₃ COO) ₃] ⁻	9	0.035	0.042	0.030				
[Cd ₂ (CH ₃ COO) ₄] ⁻	4	0.018	0.015	0.010	0.0020			
[Cd ₂ (CH ₃ COO) ₅] ⁻	9	0.019	0.015	0.0095	0.0034			
[Cd ₃ (CH ₃ COO) ₇] ⁻	4	0.015	0.14	0.038	0.011	0.019	0.0073	
[Cd ₃ (CH ₃ COO) ₇] ⁻	9	0.016	0.24	0.061	0.012	0.035	0.0082	
[Cd ₄ (CH ₃ COO) ₉] ⁻	4	0.013	0.034(24)	1.00*	1.00*	1.00*	0.0079	0.0097(15)
[Cd ₄ (CH ₃ COO) ₉] ⁻	9	0.013	0.042(15)	1.00*	1.00*	1.00*	0.0080	0.015
[Cd(NO ₃) ₃] ⁻	4 & 9	No RXN						
[Cd ₂ (NO ₃) ₂] ⁻	4	0.031	0.0069					
[Cd ₃ (NO ₃) ₇] ⁻	4	0.046	0.035	0.00090				
[Cd ₄ (NO ₃) ₉] ⁻	4	0.0094	0.0090	0.017				
[CdCl ₃] ⁻	4 & 9	No RXN						
[Cd ₄ Cl _{2x-1}] ⁻	4 & 9	No RXN						

CATIONIC METAL CLUSTERS

Table 1: Reaction efficiencies for the gas phase ion-molecule reactions between cationic metal clusters and H₂S (g).

Reactant	P (10 ⁻⁹ Torr)	k ₁ /k _c	k ₂ /k _c	k ₃ /k _c	k ₄ /k _c	k ₅ /k _c
[Cd(CH ₃ COO)] ⁺		Not Obs				
[Cd ₂ (CH ₃ COO) ₃] ⁺	4	0.77	0.0033	0.0045		
[Cd ₃ (CH ₃ COO) ₅] ⁺	4	0.923	0.0722	0.0045	0.0013	
[Cd ₃ (CH ₃ COO) ₅] ⁺	9	0.88	0.073	0.0062	0.0066	
[Cd ₄ (CH ₃ COO) ₇] ⁺	9	0.37	0.54	0.28	0.0029	0.0016
[Cd(NO ₃) ₃] ⁺		Not Obs				
[Cd(NO ₃)(CH ₃ OH)] ⁺	4	1.00				
[Cd(OH)] ⁺		Not Obs				
[CdOH(CH ₃ OH)] ⁺	4	0.77				
[CdCl] ⁺		Not Obs				
[CdCl(CH ₃ OH)] ⁺	4	0.16	0.0062			
[ZnCl] ⁺		Not Obs				
[ZnCl(CH ₃ OH)] ⁺	4	0.037				

Gas phase ion-molecule reactions between anionic cadmium clusters and H₂S are <5% efficient except for [Cd₄(CH₃COO)₆]⁻ (See Table 2 and Figure 2).

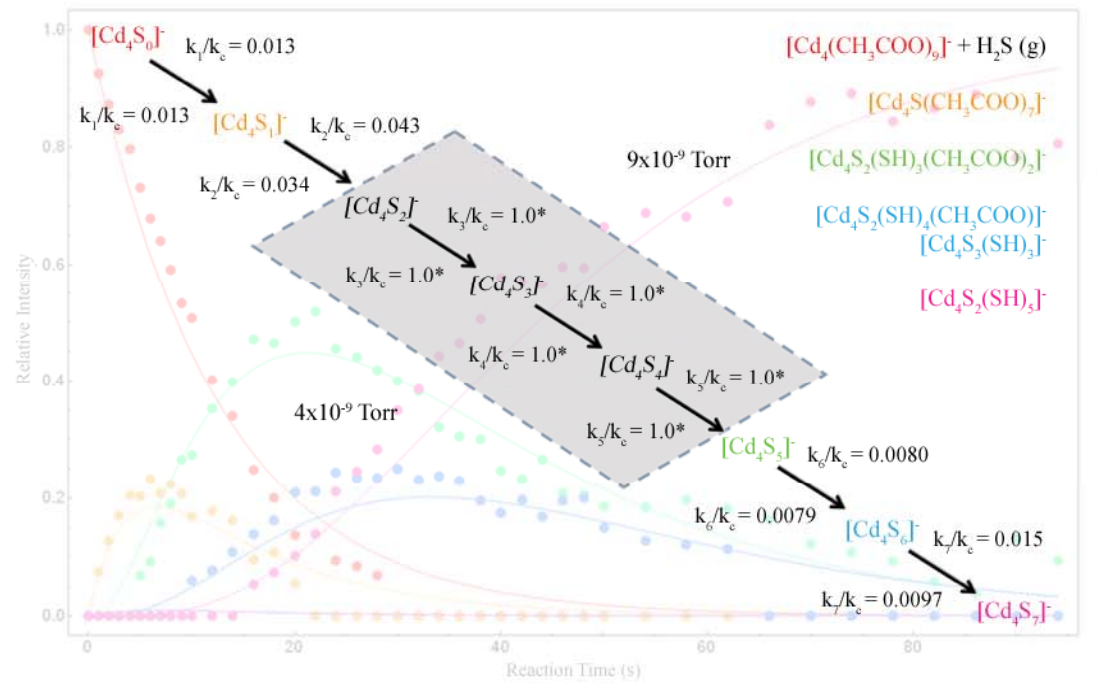
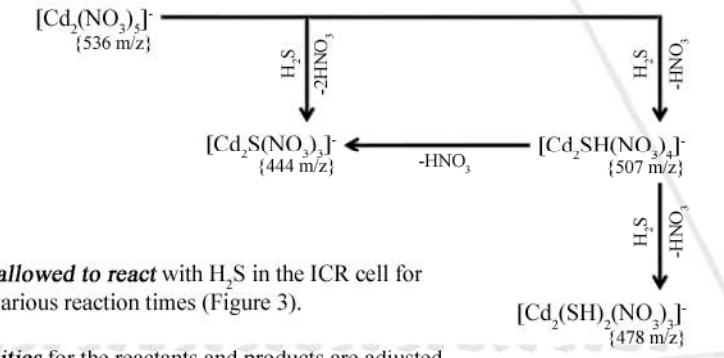


Figure 2: Reaction efficiencies for the sequential steps of the reaction between [Cd₄(CH₃COO)₆]⁻ and H₂S (4x10⁻⁹ Torr and 9x10⁻⁹ Torr). *Clusters with 2, 3, and 4 sulfur atoms are not observed at either pressure, suggesting that k₂, k₃, and k₄ are collision rate limited reaction steps.

DATA ANALYSIS

EXAMPLE REACTION SCHEME

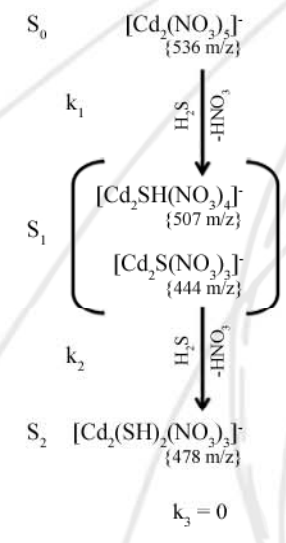


Clusters are allowed to react with H₂S in the ICR cell for various reaction times (Figure 3).

Relative intensities for the reactants and products are adjusted for differences in isotopic distributions.

To allow for comparison, product clusters are grouped into families based on the number of sulfur atoms added.

GROUP BY NUMBER OF SULFUR ATOMS



RATE EQUATION

$$\frac{d[S_0]}{dt} = -k_1[S_0]$$
$$\frac{d[S_1]}{dt} = k_1[S_0] - k_2[S_1]$$
$$\frac{d[S_2]}{dt} = k_2[S_1]$$
$$k_3 = 0$$

INTEGRATED RATE EQUATION

$$S_0 = [A]_0 e^{-k_1 t}$$
$$S_1 = [A]_0 \frac{k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t})$$
$$S_2 = k_1 k_2 \left[\frac{e^{-k_1 t}}{(k_2 - k_1)(k_3 - k_1)} + \frac{e^{-k_2 t}}{(k_1 - k_2)(k_3 - k_2)} + \frac{e^{-k_3 t}}{(k_1 - k_3)(k_2 - k_3)} \right]$$

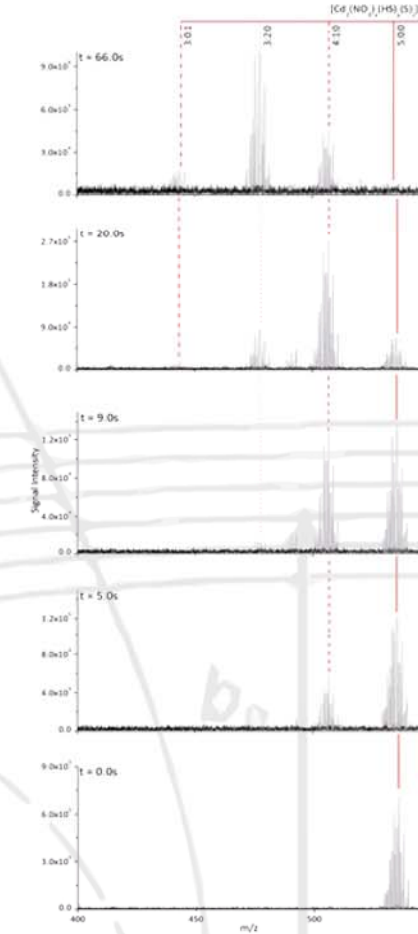


Figure 3: MS data for the reaction of [Cd₄(NO₃)₆]⁺ with H₂S (4x10⁻⁹ Torr).

PSEUDO FIRST-ORDER RATE CONSTANTS

Experimental data is modeled using the Integrated Rate Equations to determine the pseudo first-order rate constants (Figure 4).

$$k_1 = 0.084 \pm 0.004 \text{ s}^{-1}$$

$$k_2 = 0.019 \pm 0.001 \text{ s}^{-1}$$

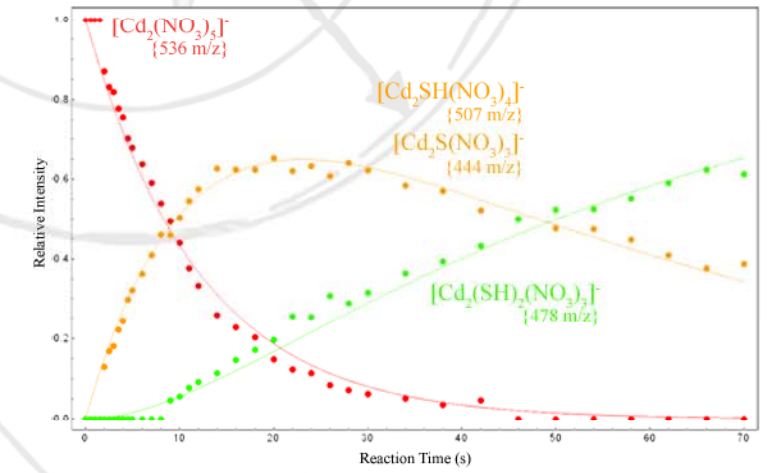


Figure 4: Relative intensity vs. time for the reaction of [Cd₄(NO₃)₆]⁺ with H₂S (4x10⁻⁹ Torr). Lines represent results for nonlinear regression modeling using the appropriate integrated rate equations.

BIMOLECULAR RATE CONSTANTS

To determine [H₂S], the assumption was made that the fastest measured k ([Cd(NO₃)(CH₃OH)]⁺: k₁ = 2.85 ± 0.27 s⁻¹) was collision rate limited.

Capture Collision Theory (Ridge 2003) was used to determine the theoretical bimolecular rate constant (k_c) for [Cd(NO₃)(CH₃OH)]⁺.

$$\text{Theoretical Collision Rate } k_c = 1.216 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_c = k_1 / [H_2S]$$

$$[H_2S] = 2.34 \times 10^9 \text{ molecules cm}^{-3} = 6.62 \times 10^{-8} \text{ Torr}$$

REACTION EFFICIENCIES

Reaction efficiencies (k/k_c) were calculated by dividing the experimental pseudo first-order rate constant (k_i) by the collision rate.

Adjustments were made for differences in reduced mass (μ_x) and pressure (P_x).

$$\frac{k_x}{k_c} = \frac{k_x^1}{2.85 \text{ s}^{-1}} \left(\frac{\mu_x}{29.19 \text{ Da}} \right)^{1/2} \left(\frac{4 \times 10^{-9} \text{ Torr}}{P_x} \right)$$