Correlation of Metal Sulfide Thermodynamic Calculations to Experimental Gas Phase Reactions

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Overview:

Density Functional Theory Calculations of metal salt clusters to determine ΔE of reactions.

Theoretical calulations were consistent with experimental results

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Amsterdam Density Functional will be used to determine ΔE of reactions for larger clusters.

Introduction:

Our research aims to characterize the structure and reactivity of metal sulfide clusters involved in environmental and biological processes. Electrochemical and spectroscopic methods provide indirect evidence, but LDI-FTMS provides direct evidence of these clusters. Cadmium sulfide clusters, which are susceptible to oxidation, have been detected in samples using ESI. Clusters of several cadmium salts give clusters that react with H_2S in the ICR cell to form CdS clusters. The reactivity of H_2S with the metal clusters in the gas phase varies with cluster size and counter ion. Density Functional Theory calculations have been performed to determine the thermodynamic properties and structures of the metal clusters. The correlation of theoretical determined properties of the clusters with their reactivity is considered.

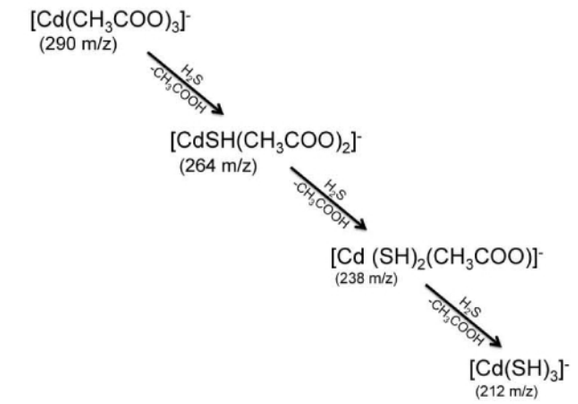
Methods:

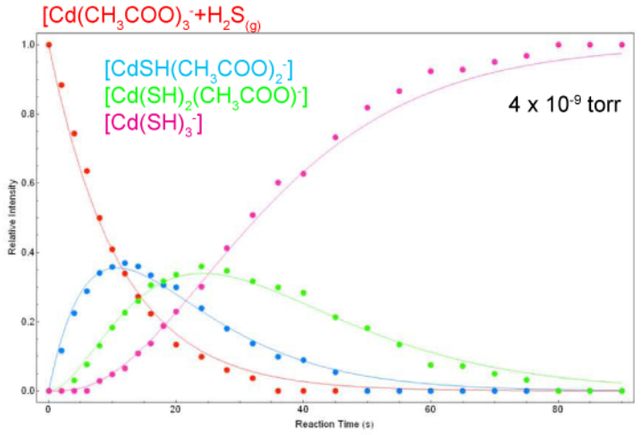
Reactivities were characterized experimentally using FT-ICR methods. Metal clusters produced by ESI of soluble metal salts are introduced into the ICR cell. The clusters are allowed to react with $H_2S_{(g)}$ for various periods of time before excitation and detection of the products. The theoretical results are ground state density functional theory calculations done using B3LYP hybrid functionals and LANL2DZ basis set, which is designed for heavier atoms. Standard Gaussian routines were used to search for transition states.

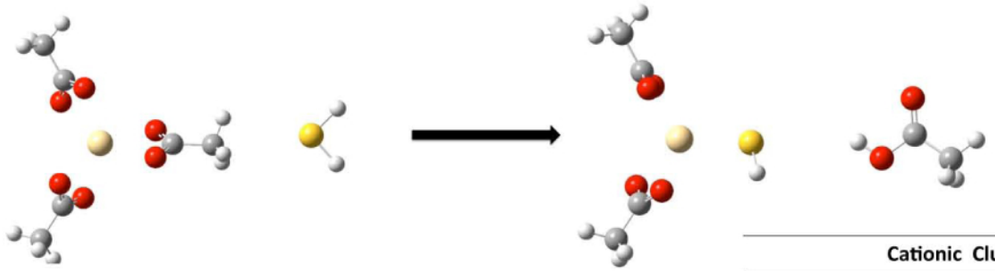
Conclusion:

Theoretical calculations have been applied to all n=1 species. These calculations do properly predict which reactions will proceed and which will not. Currently we are attempting to calculate energies for two metal species. These caculations will be done using amsterdam density functional.

Refererences:







Anionic Clusters

	P(10^{-9} torr)	ΔE (kcal/mole)	k_1/k_c
$Cd(CH_3COO)_3^-$	4	-6.2361	0.032
$Cd(CH_3COO)_3^-$	9		0.035
$Cd(NO_3)_3^-$	4 & 9	9.7109	No Rxn
$Cd(Cl)_3^-$	4 & 9	8.8246	No Rxn
$Zn(Cl)_3^-$		11.8744	
$Hg(Cl)_3^-$		8.0824	

Cationic Clusters

	P(10^{-9} torr)	ΔE (kcal/mole)	k_1/k_c
$Cd(CH_3COO)^+$		-3.7595	Not Obs.
$Cd(NO_3)^+$		-17.4419	Not Obs.
$Cd(NO_3)(CH_3OH)^+$	4		1.00
$Cd(NO_3)(CH_3OH)(H_2O)^+$	4		0.61
$Cd(OH)^+$		-27.1828	Not Obs.
$Cd(OH)(CH_3OH)^+$	4		0.77
$Cd(Cl)^+$		-11.1628	Not Obs.
$Cd(Cl)(CH_3OH)^+$	4		0.16
$Zn(Cl)^+$		-11.9029	Not Obs.
$Zn(Cl)(CH_3OH)^+$	4		0.037
$Hg(Cl)^+$		-18.4228