

THERMODYNAMIC AND KINETIC STUDIES OF REACTIONS OF THIOLS, DISULFIDES,
SULFUR, AND HYDROGEN SULFIDE

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ABSTRACT

A range of SAT [sulfur atom transfer] enthalpies have been determined for reactions involving both main group and transition metal compounds. These include sulfur atom transfer reactions to phosphine, arsine and stibine¹, carbene², and stannylene³ compounds as well as insertion of sulfur into metal-hydrogen⁴ and metal-metal bonds⁵. Kinetic and thermodynamic studies of reactions of thiols⁶, disulfides⁷, hydrogen sulfide⁸, and sulfur⁹ with complexes of chromium, molybdenum, and tungsten, have also been performed. The choice of mechanism appears to depend primarily on the strength of the sulfur-sulfur or sulfur-hydrogen bond that is broken, but also can be changed by ligand donor ability of the sulfur compound.

I. INTRODUCTION

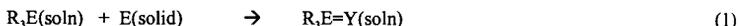
The chemistry of transition metal sulfur complexes is important to a number of industrial and biochemical processes.¹⁰ Oxidative addition of the sulfur-sulfur and sulfur hydrogen bond to metals play a fundamental role in these reactions. Thermochemical data for these reactions are rare in spite of their importance. In addition, there are relatively few mechanistic studies of reactions with transition metal complexes in solution of the simple sulfur reactants H₂S and S₈.¹¹ The mechanisms and energetics of these reactions may lend some insight into possible heterogeneous reactions of the same substrates.

II. PROCEDURE

Enthalpies of reaction have been measured by reaction calorimetry using either a Setaram Calvet Calorimeter or Guild Solution Calorimeter using techniques described in detail elsewhere.¹ Kinetic studies were performed using a flow through FT-IR microscope/reactor system that has also been described in the literature¹². Reagents, solvents, and gases were all carefully purified using standard techniques.

III. RESULTS

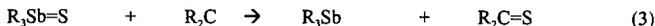
The enthalpies of reaction with chalcogen donors [Y = S, Se, Te] have been measured for a range of R₃E complexes [E = P, As, Sb] according to eqn. (1) in toluene solution at room temperature:



For 1/8 S₈ these data span over 32 kcal/mole depending on R and E. The heavier donor atoms As and Sb are labile enough to measure directly sulfur atom transfers such as those shown in eqn.(2):



These data provide additional checks on the thermochemical data. They also provide a basis for direct measure of single S atom transfer reactions using R₃Sb=S or R₃As=S which in some cases are more selective than sulfur, as discovered by Jason¹³. The organostannylene complexes LSn [L = Me₃taa = octamethylidibenzotetraaza[14]annulene] prepared by Kuchta and Parkin¹⁴ also react directly with chalcogens and chalcogen atom transfer reagents to form the LSn=Y complexes. Enthalpies of addition to and subtraction from chalcogens at the Sn(II) center are in the expected order Se < S. The stable carbenes prepared by Arduengo and coworkers¹⁵ also undergo clean S atom transfer:



The enthalpies of S atom transfer to the carbene carbon are more exothermic than to the stannylene tin. The crystal structures of two of the R₂C=S complexes have been determined. There is a correlation between the structures, the enthalpies of sulfurization, and also the enthalpies of binding to metals of the carbene and stannylene ligands.

The enthalpies of insertion of a single sulfur atom into the metal-hydrogen bonds have been determined as shown in eqn. (4):



These data allow estimation of the M-SH bond strength which follows the order Cr < Mo < W. Desulfurization by phosphines of the metal sulphydryl complexes occurs in some cases as shown in eqn.(5), in keeping with thermochemical predictions:



Reaction (6) between two moles of the 17 electron stable chromium centered radical and triphenyl antimony sulfide occurs cleanly as shown:

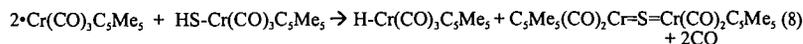


The enthalpy of reaction (6) has been measured and used to estimate the energy of "embedding" a single S atom in the multiply bonded bridging sulfido complex.

The stable transition metal radical $\bullet\text{Cr}[\bullet\text{Cr} = \bullet\text{Cr}(\text{CO})_3\text{C}_3\text{Me}_5]$ provides a good area for study of the mechanisms of reaction of a transition metal radical fragment with organosulfur substrates. Earlier work has shown a variety of mechanisms for reactions of thiols⁶ and disulfides⁷. This work has been extended to include H_2S and S_8 . Reaction of hydrogen sulfide with the radical species is much faster than analogous reactions of thiols. Initial oxidative addition of one sulfur-hydrogen bond occurs as shown in eqn. (7):



The metal sulphydryl complex formed in the first step can be further attacked by two moles of radical:

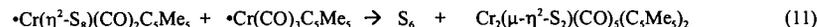


The mechanism of reaction (7) follows two pathways. Under pressure of carbon monoxide a third order rate law is obeyed [first order in hydrogen sulfide and second order in metal radical]. At low pressures of carbon monoxide, at higher temperatures, or under argon atmosphere, a second order rate law is obeyed [first order in hydrogen sulfide and first order in metal radical]. Rate and activation parameters as well as CO dependence are all consistent with rate determining ligand substitution to form the hydrogen sulfide substituted radical complex shown in eqn. (9):



In spite of the fact that the equilibrium in eqn. (9) lies to the left, the hydrogen sulfide substituted radical complex once formed can undergo rapid attack by a second mole of metal radical. Under appropriate conditions the rate of oxidative addition occurs at the rate of ligand substitution itself. The small size of hydrogen sulfide probably accounts for its increased ability, relative to thiols, to compete with carbon monoxide as a ligand.

In a similar way, S_8 also shows a complex reactivity pattern with the chromium radical and depends on carbon monoxide pressure. Kinetic evidence supports a pathway under argon atmosphere involving steps shown in eqn. (10) and (11):



Formation of $\text{Cr}_2(\mu\text{-}\eta^2\text{-S}_2)(\text{CO})_3(\text{C}_3\text{Me}_5)_2$ is clean under appropriate conditions and its enthalpy of formation as well as desulfurization to $\text{Cr}_2(\mu\text{-S})(\text{CO})_4(\text{C}_3\text{Me}_5)_2$ have been measured.

VII. CONCLUSIONS

Some insight into factors determining the enthalpies of sulfur atom transfer and insertion as well as the rates and mechanisms of related reactions have been determined. Considerable additional work is needed before the understanding of inorganic sulfur reactions achieves the level of understanding currently present in organic sulfur chemistry.

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REFERENCES

- (1) Capps, K. B.; Wixmerten, B.; Bauer, A.; Hoff, C. D. *Inorg. Chem.* **1998**, *37*, 2861.
- (2) Huang, J.; Schanz, H. J.; Nolan, S. P.; Bauer, A.; Capps, K. B.; Hoff, C. D.; **to be published.**
- (3) Parkin, G.; Kuchta, M. C.; Capps, K. B.; Wixmerten, B.; Bauer, A.; Hoff, C. D. **to be published.**
- (4) Bauer, A.; Capps, K. B.; Wixmerten, B.; Abboud, K. A.; Hoff, C. D. *Inorg. Chem.* **1999**, *38*, 2136.
- (5) Capps, K. B.; Bauer, A.; Hoff, C. D.; **to be published.**
- (6) Ju, T. D.; Capps, Lang, R. F.; Roper, G. C.; Hoff, C. D. *J. Am. Chem. Soc.* **1996**, *118*, 5328.
- (7) Ju, T. D.; Capps, K. B.; Lang, R. F.; Roper, G. C.; Hoff, C. D.; *Inorg. Chem.* **1997**, *36*, 614.
- (8) Capps, K. B.; Bauer, A.; Hoff, C. D.; *Inorg. Chem.* **submitted for publication.**
- (9) Capps, K. B.; Bauer, A.; Hoff, C. D.; **to be published.**
- (10) Transition Metal-Sulfur Chemistry. *ACS Symp. Ser.* **1996**, *653*.
- (11) James, B. R. *Pure and Appl. Chem.* **1997**, *69*, 2213.
- (12) Ju, T. D.; Capps, K. B.; Roper, G. C.; Lang, R. F.; Hoff, C. D.; *Inorg. Chim. Acta.* **1998**, *270*, 488.
- (13) Jason, M. E.; *Inorg. Chem.* **1997**, *36*, 241.
- (14) Kuchta, M. C.; Parkin, G.; *J. Amer. Chem. Soc.* **1994**, *116*, 8372.
- (15) Arduengo, A. J. III, Harlow, R. L.; Kline, M.; *J. Am. Chem. Soc.* **1991**, *113*, 361.