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Articles

Thermochemistry of Sulfur Atom Transfer. Enthalpies of Reaction of Phosphines with Sulfur, Selenium, and Tellurium, and of Desulfurization of Triphenylarsenic Sulfide, Triphenylantimony Sulfide, and Benzyl Trisulfide

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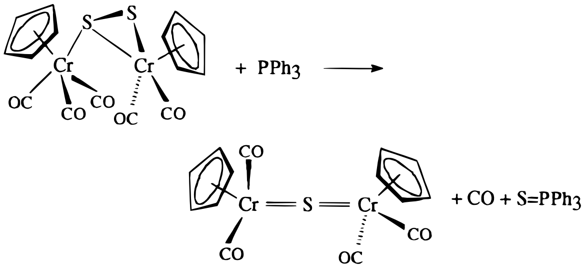
The enthalpies of reaction of neat PBu_3 with solid sulfur (−27.1 ± 0.5 kcal/mol), selenium (−20.0 ± 0.6 kcal/mol), and tellurium (−4.9 ± 0.6 kcal/mol) have been measured by solution calorimetry. The enthalpies of reaction of a series of phosphines with sulfur in toluene solution have been measured as follows (values in kcal/mol): $PCy_3 = -30.9 \pm 1.9$, $PBu_3 = -28.9 \pm 0.3$, $PMe_3 = -27.1 \pm 0.4$, $PMe_2Ph = -26.0 \pm 0.5$, $PMePh_2 = -23.8 \pm 0.3$, $PPh_3 = -21.5 \pm 0.3$. These values correlate with literature data for enthalpies of protonation and indicate that P to S σ donation is probably the dominant factor in determining the $R_3P{=}S$ bond strength, estimates for which range from 88 to 98 kcal/mol. The enthalpies of S atom transfer to PPh_3 by $S{=}AsPPh_3$ and $S{=}SbPh_3$ in toluene solution are −17.7 ± 1.2 and − 21.5 ± 1.0 kcal/mol, respectively. The enthalpy of removal of the central S atom from BzSSSBz by PCy_3, yielding BzSSBz and $S{=}PCy_3$, is − 29.0 ± 1.8 kcal/mol. These data are used to establish a range of enthalpies of S atom transfer in these compounds which spans 31 kcal/mol from $S{=}SbPPh_3$ to $S{=}PCy_3$.

Introduction

Sulfur atom transfer and the energetics associated with it are important to understanding transition metal−sulfur chemistry.[1] Despite that, there is relatively little reliable data available for the energetics of reactions of sulfur with metal complexes aside from that for formation of simple metal sulfides. As part of our interest in the thermochemistry of complexes of chromium, molybdenum, and tungsten,[2] we have recently reported kinetic and thermodynamic studies of reactions of group VI metal complexes with thiols and disulfides.[3−6]

Extension of that work into the M═S area has prompted our investigation of the thermochemistry of sources and sinks for sulfur and heavier chalcogen atoms. Such data is not only of intrinsic interest, but provides needed ancillary data for developing metal/chalcogen thermochemistry since the complexes $E{=}YR_3$ (E = S, Se, Te; Y = P, As, Sb) are frequently used as transfer agents. Reactions such as that shown in eq 1 below can readily remove "excess" sulfur from metal complexes[7−9] in favorable cases:



(1)

The mechanisms of addition and subtraction of sulfur atoms in particular is a relatively unexplored but important area. Thermochemical data is needed to help understand the driving forces in the seemingly complex reactivity displayed in metal−sulfur chemistry.

Skinner and co-workers[10] have reported the enthalpies of reaction of neat PR_3 with sulfur as shown in eq 2:

$$R_3P(l) + {}^{1}/_{8}S_8(s) \rightarrow R_3P{=}S \text{ (soln in } PR_3) \qquad (2)$$

$$R = \text{n-Pr}, \Delta H = -27.6 \text{ kcal/mol}$$

$$R = \text{n-Bu}, \Delta H = -27.5$$

$$R = \text{OEt}, \Delta H = -26.6$$

The nearly constant values obtained in this work were in contrast to work on phosphine oxides.[11]

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Bartlett and co-workers[12] have investigated the kinetics and mechanism of reaction of PPh_3 with sulfur:

$$Ph_3P + {}^1/_8S_8 \rightarrow Ph_3P{=}S \tag{3}$$

To the authors' knowledge, the enthalpy of reaction 3 has not been reported. It is important because PPh_3 is a much milder reagent than PBu_3 and is also a much weaker ligand,[2] less likely to displace other ligands from a metal center.

Data on the enthalpies of formation of phosphine selenides and tellurides are scarce. The chemistry of inorganic selenide and telluride complexes was recently reviewed by Roof and Kolis.[13] Zingaro[14] has reported the preparation of $Bu_3P{=}Te$ and the fact that, on standing, it has a tendency to eliminate elemental tellurium. In addition to varying the chalcogen in $R_3P{=}E$, the pnicogen can also be varied in the series $R_3Y{=}S$. Jason[15,16] recently reported the facile S atom transfer ability of $Ph_3Sb{=}S$ and $Ph_3As{=}S$. Baechler and his students[17] have also reported a series of kinetic and equilibrium studies on atom transfer and exchange for several complexes $R_3Y{=}E$ ($Y = P$, As, Sb; $E = O$, S, Se, Te):

$$R_3Y{=}E + R'_3Y \rightleftharpoons R_3Y + R'_3Y{=}E \tag{4}$$

The thermochemistry of organosulfur compounds was developed largely by a few groups[18] that used rotating combustion bomb calorimetry—a little used technique in recent times. This work reports the first in a series of measurements aimed at expanding the thermochemistry of sulfur and establishing a scale of SAT (sulfur atom transfer) thermochemistry.

Experimental Section

Orthorhombic sulfur (99.9995%) was obtained from Johnson Mathey. It was further recrystallized from carbon disulfide and stored and handled in the glovebox under an argon atmosphere. Selenium (99.999%) and tellurium (99.999%) were obtained from Aldrich chemical and used as obtained. Triphenylphosphine and tricyclohexylphosphine were recrystallized from methylene chloride/heptane. Organophosphines used were all of the highest purity commercially available and degassed prior to use. Triphenylantimony sulfide was obtained from Strem chemical. A pure sample of triphenylarsenic sulfide was provided by Dr. Mark Jason of Monsanto Chemical Company (St. Louis, MO). Benzene, deuterobenzene, and toluene were purified by reflux followed by distillation from sodium benzophenone ketyl under argon. Methylene chloride was distilled from P_2O_5 under argon atmosphere. Calorimetric measurements were made using a Setaram C-80 Calvet calorimeter at 30 °C as described elsewhere.[3−6] Reported data are all based on an average of at least five measurements. Experimental errors are the standard deviation. Infrared measurements were made using a Perkin-Elmer 2000 FTIR; NMR data were obtained on a Varian VXR 400 Spectrometer.

Results

Enthalpies of Reaction of PBu_3 with S, Se, and Te. The enthalpies of reaction (kcal/mol) of PBu_3 and S, Se, and Te were measured as summarized in eq 5:

$$PBu_3 + E \rightarrow E{=}PBu_3 \tag{5}$$

E	neat PBu_3	E	toluene soln
S(solid)	-27.1 ± 0.6	S(soln)	-28.9 ± 0.6
Se(solid)	-20.0 ± 1.5	Se(solid)	-20.5 ± 1.3
Te(solid)	-4.9 ± 1.0	Te(solid)	-5.1 ± 0.8

The "neat" reactions under eq 5 refer to reaction of pure PBu_3 with the solid chalcogen. The product is a solution of 10−25% $S{=}PBu_3$ dissolved in PBu_3. Reaction of solid sulfur was rapid, occurring essentially at the rate of dissolution. Reaction of selenium and tellurium was much slower and took hours to reach completion. The value obtained for sulfur with the neat PBu_3 is in agreement with the earlier value of Skinner and coworkers of -27.5 ± 0.5 kcal/mol under similar conditions. Enthalpies of reaction in solution refer to reaction of a 1.5 M toluene solution of the phosphine and the solid chalcogen (Se, Te) or a toluene solution of it (S). The values for Se and Te appear to be slightly more exothermic (0.5) and (0.2) kcal/mol, respectively. These measurements were performed to determine if enthalpies of solution and dilution play a role in the thermochemistry of the relatively polar compounds involved. Any effect of this type appears to be small (less than 1 kcal/mol) and close to experimental errors.

Reaction of a solution of ${}^1/_8S_8$ dissolved in toluene with a solution of PBu_3 was exothermic by 28.9 ± 0.6 kcal/mol compared to reaction of the neat PBu_3 and solid ${}^1/_8S_8$ which was exothermic by -27.1 ± 0.6. The observed difference is attributed to enthalpies of solvation of reactants and products. The enthalpy of solution of ${}^1/_8S_8$ in benzene solution, as shown in eq 6, has been reported.[19] Assuming the enthalpy of solution

$${}^1/_8S_8\ (\text{solid}) \rightarrow {}^1/_8S_8\ (C_6H_6\ \text{soln}), \quad \Delta H = +0.7\ \text{kcal/mol} \tag{6}$$

is the same in toluene, leads to a calculated enthalpy of reaction of -28.2 ± 0.6 kcal/mol for reaction of solid sulfur with a toluene solution of the phosphine. The reaction is thus 1.1 ± 1.2 kcal/mol more exothermic in toluene solution versus neat phosphine. This is in keeping with the small solvation effect observed for Se and Te. A number of enthalpies of reaction were measured in methylene chloride solution as well. Irreproducible results were obtained in a number of cases, presumably due to side reactions with solvent occurring during chalcogenation of phosphine.[20]

Enhalpies of Reaction of Phosphines with ${}^1/_8S_8$. The enthalpies of reaction 7 were measured with all species in solution:

$$PR_3 + {}^1/_8S_8 \rightarrow S{=}PR_3,$$

ΔH (kcal/mol)
PCy_3, -30.9 ± 1.9
PBu_3, -28.9 ± 0.3
PMe_3, -27.1 ± 0.4
PMe_2Ph, -26.0 ± 0.5
$PMePh_2$, -23.8 ± 0.3
PPh_3, -21.5 ± 0.3

Some of the calorimetric measurements were performed in toluene, benzene, and deuterobenzene to confirm the reaction products by NMR under actual calorimetric conditions. All

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were found to go to completion as described. There was no apparent difference in enthalpies of reaction when done in toluene or benzene.

Enthalpy of Reaction of PPh_3 and PCy_3 with Selenium. Extension of the studies shown in reaction 7 with solid selenium and toluene solutions of PCy_3 and PPh_3 were performed to see if the order of stability extended on to selenium. The enthalpy of reaction of PCy_3 was found to be −20.2 ± 1.6 kcal/mol—essentially the same as that of PBu_3. The enthalpy of reaction of PPh_3 was −13.0 ± 1.2 kcal/mol, showing a significant decrease in bond strength similar to that observed in analogous reactions of sulfur. The high experimental errors reported are due to the very slow rate of reaction of PPh_3 with selenium. Extension of this work to additional tellurium derivatives was not attempted due to the marginal stability[14] of the $R_3P{=}Te$ complexes.

Enthalpy of Reaction of $S{=}SbPh_3$ and $S{=}AsPh_3$ with PPh_3. As discussed by Baechler,[17] reactions 8 and 9 were found to proceed rapidly to completion as shown:

$$S{=}AsPh_3 + Ph_3P \rightarrow AsPh_3 + Ph_3P{=}S \tag{8}$$

$$S{=}SbPh_3 + Ph_3P \rightarrow SbPh_3 + Ph_3P{=}S \tag{9}$$

The enthalpy of reaction 8 could be measured with all species in solution because $S{=}AsPh_3$ shows no tendency to eliminate sulfur on the time scale of the calorimetric measurements. The experimental value for this reaction, −17.7 ± 0.8 kcal/mol, corresponds directly to the difference in bond strengths between $Ph_3P{=}S$ and $Ph_3As{=}S$.

The enthalpy of reaction 9 was measured using solid $Ph_3Sb{=}S$ due to the instability of this compound in solution.[15] The experimental measurement yielded a value of −16.2 ± 0.9 kcal/mol, however this had to be corrected by addition of the enthalpy of solution of $Ph_3Sb{=}S$. The enthalpy of solution of $Ph_3Sb{=}S$ in toluene was found to be +5.3 ± 0.5 kcal/mol. Elimination of sulfur is slow relative to the rate of solution. Adding the enthalpy of solution to the enthalpy of reaction gives a value of −21.5 kcal/mol for the enthalpy of reaction 9. This is the same as the value of reaction of PPh_3 with sulfur in solution as shown in eq 7 and implies that the enthalpy of reaction of Ph_3Sb and $^1/_8S_8$ is essentially thermoneutral. Thus, even as the solution of $Ph_3Sb{=}S$ is observed to yield slow decomposition to Ph_3Sb and sulfur[15] little heat is absorbed or evolved during this process. Close examination of the thermograms for the enthalpy of solution of $Ph_3Sb{=}S$ indicated that, following the endothermic enthalpy of solution, the reaction never became exothermic, —indicating that while elimination of sulfur from $Ph_3Sb{=}S$ is near zero it is endothermic and not exothermic. We estimate the enthalpy of elimination of sulfur to be in the range 0−0.5 kcal/mol.

As a check on the thermochemistry of reactions 8 and 9 we measured the enthalpy of reaction 10.

$$S{=}SbPh_3 + AsPh_3 \rightarrow SbPh_3 + S{=}AsPh_3 \tag{10}$$

The experimental enthalpy of reaction taking into account the enthalpy of solution of $Ph_3Sb{=}S$ was −4.1 kcal/mol. This agrees with the value calculated by subtracting eq 8 from eq 9 (−21.5 − 17.7 = −3.8 kcal/mol). Such checks on data are important in systems such as these were trace species in solution can led to spurious results.

Enthalpy of Reaction of BzSSSBz with PCy_3. The enthalpy of reaction 11 was measured with both limiting PCy_3 and BzSSSBz in solution:

$$BzSSSBz + PCy_3 \rightarrow BzSSBz + S{=}PCy_3 \tag{11}$$

The experimental value of −29.0 ± 2.0 kcal/mol has a relatively large error since the desulfurization reaction is relatively slow and takes over 3 h to go to completion.

The products in reaction 11 were confirmed by NMR analysis of authentic samples.

Discussion

The goal of this work was to provide background data for reactions in which sulfur is either removed from or added to a metal complex as part of an overall program in metal/sulfur thermochemistry. The main area investigated is a series of phosphine sulfides, but this is also extended to heavier elements—arsine and stibine sulfides as well as phosphine selenides and tellurides. These data provide a basis for expanding sulfur atom transfer thermochemistry. This is illustrated by measuring the enthalpy of removing the central atom of BzSSSBz.

Enthalpies of S Atom Transfer. The range of enthalpies of S atom transfer (SAT) are summarized in Table 1 for all the complexes studied. Elemental sulfur in either benzene or toluene solution is taken as the reference point. The sulfur atom transfer enthalpies reported in Table 1 can be compared to some of the equilibrium and kinetic studies reported by Baechler.[17] For many of these reactions, the kinetic data is of principal importance since the equilibrium constants were too large to be estimated beyond the fact that they were greater than 500. A value of $K_{eq} = 12$ was reported for reaction 12 at 130 °C in bromobenzene:

$$S{=}PPh_3 + PPh_2Me \rightleftharpoons PPh_3 + S{=}PPh_2Me \tag{12}$$

Despite a difference in solvent polarity (benzene versus bromobenzene) and temperature (100 °C), there is reasonable agreement between the equilibrium constant of Baechler[17] and the enthalpy of reaction measured here. The $\Delta H°_{30} = -2.3$ kcal/mol enthalpy difference in Table 1 compares favorably with the $\Delta G°_{303} = -2.0$ kcal/mol calculated from the equilibrium data.[17] Together this implies, as might be expected, a near zero entropy change for reaction 12.

Bond Strength Estimates. The data in Table 1 summarizes bond strength estimates for these complexes. The enthalpies of formation of the gas-phase atoms S, Se, and Te are known[19] [S = +66.7, Se = +54.3, Te = +47.1 kcal/mol]. Reasonable bond strength estimates can be obtained by simply adding these values to the observed enthalpies of reaction. This assumption would be strictly correct if the transfer enthalpies of, for example, PR_3 (toluene solution) and $S{=}PR_3$ (toluene solution) to the gas phase would cancel each other. This assumption is probably reasonable and is commonly made. An alternative view is to consider that the enthalpies of solution of the gas phase chalcogen atoms in benzene or toluene would be essentially zero.

Despite experimental agreement with the data of Skinner, the bond strength estimate we make for $S{=}PBu_3$ is 96 kcal/mol versus the earlier value of 92 kcal/mol.[10] This reflects only the uncertainty in extrapolating data from solution to gas phase. The work of Skinner was done in neat phosphine versus our solution studies. In addition, Skinner assumed a difference in enthalpy of transfer to the gas phase of PBu_3 and $S{=}PBu_3$. This highlights the fact that "absolute" bond dissociation energies for all but the simplest molecules are seldom known to better than ±3 kcal/mol. The more important relative bond strengths,

Table 1. Combined Enthalpies of Chalcogen Atom Transfer in Benzene/Toluene Solution and Bond Stength Estimates

compound	$-\Delta H$ SAT (kcal/mol)	BDE (kcal/mol)
Sulfur:		
$S{=}PCy_3$	30.9	98
$S{=}PBu_3$	28.9	96
$S{=}PMe_3$	27.1	94
$S{=}PMe_2Ph$	26.0	93
$S{=}PMePh_2$	23.8	91
$S{=}PPh_3$	21.5	88
$S{=}AsPh_3$	3.8	70
BzSSSBz	1.9	
$S{=}SbPh_3$	0	67
Selenium:		
$Se{=}PBu_3$	20.5	75
$Se{=}PCy_3$	20.2	75
$Se{=}PPh_3$	13.0	67
Tellurium:		
$Te{=}PBu_3$	4.9	52

and enthalpies of reaction in solution, are known to better than ±1 kcal/mol for most of the reactions in Table 1. An average estimate of 94 ± 3 kcal/mol seems reasonable for the absolute value of the $S{=}PBu_3$ bond strength.

Comparison of Enthalpies of Reaction of PR_3 and Sulfur to Enthalpies of Protonation. The relative $S{=}PR_3$ bond strength data shown in Table 1 shows a reasonably strong dependence on the nature of R. The trend is the same one that has been seen for a number of studies of the enthalpies of binding of the phosphine ligands to metal complexes.[2] In addition, Angilici and co-workers[21] recently reported enthalpies of protonation of phosphine ligands. A plot of the enthalpies of reaction of PR_3 ligands with sulfur versus protonation is shown in Figure 1. There is a good correlation. Since bonding of H^+ to PR_3 involves only donation of lone pair electrons from the phosphine to the proton, the correlation in Figure 1 is suggestive that the dominant component in the bond between PR_3 and sulfur is similarly σ donation. The ability of PR_3 to act as a π acceptor of electron density from lone pairs on S would be expected to be most important for PPh_3. In terms of bond strengths at least, the correlation with enthalpies of protonation appears to imply that it is sigma donation which dominates the $S{=}PR_3$ bond strength.

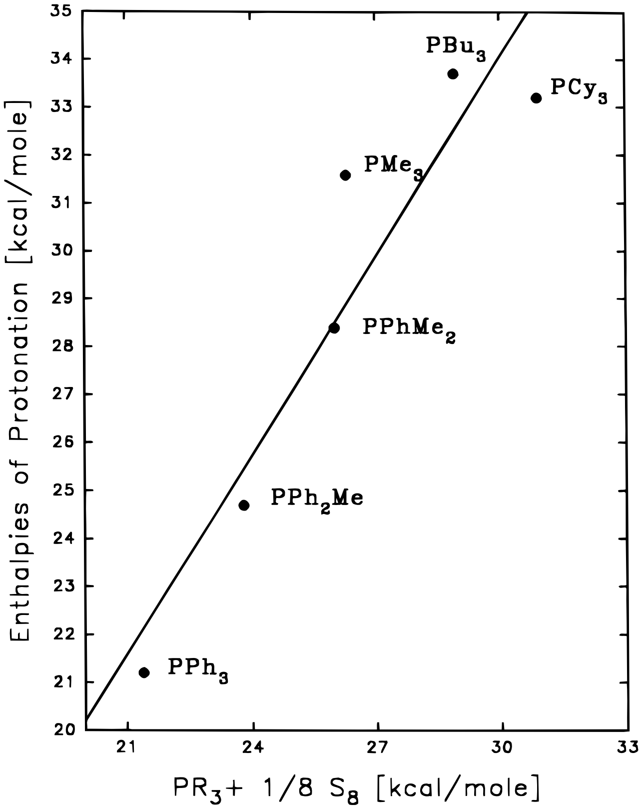

Figure 1. Enthalpy of protonation of phosphine ligands (data taken from ref 21) versus enthalpy of reaction with sulfur.

Conclusion

The data in Table 1 provides good entry to determining a wider range of sulfur atom transfer energies. For the phosphines studied, the approximate 10 kcal/mol range measured may prove useful in choosing which phosphine to use to desulfurize other organic and inorganic complexes. That basis is strictly thermodynamic, since the reaction mechanisms of sulfur addition and elimination, as pointed out by Jason,[15,16] remain largely unexplored.

The trends in bond strength among the phosphines are similar to those observed for metal complexes[2] and also correlate well with enthalpies of protonation.[21] This may imply that $R_3P \rightarrow S$ σ donation is the principal factor determining the $P{=}S$ bond strength. There is a dramatic drop in bond strength in the series $S{=}PBu_3$ to $Se{=}PBu_3$ to $Te{=}PBu_3$ of 96 to 75 to 52 kcal/mol. *Even for $Te{=}PBu_3$, however, this bond strength is large enough that simple dissociation to PBu_3 and a Te atom should occur at negligible rate.* The reactivity of $Te{=}PBu_3$ is probably associative and not dissociative in nature.

There is a less dramatic decrease in bond strength in going from $S{=}PPh_3$ to $S{=}AsPPh_3$ to $S{=}SbPPh_3$ of 88 to 70 to 67 kcal/mol. Surprisingly, the drop from As to Sb is relatively small. Keeping the chalcogen (sulfur) constant and changing the pnicogen from P to As to Sb appears to have less influence on the bond strength than changing the chalcogen from S to Se to Te while keeping the pnicogen fixed (phosphorus).

It was surprising to the authors to find that benzyl trisulfide is thermochemically very close to benzyl disulfide and sulfur. It has been reported that under certain conditions trisulfides and tetrasulfides decompose to disulfides and elemental sulfur,[22] in keeping with a low enthalpy of desulfurization. The thermochemical abilities to add a single S atom in terms of $^1/_8S_8$, $Ph_3Sb{=}S$, BzSSSBz, and $Ph_3As{=}S$ are all low—in the range 0−4 kcal/mol. The mechanisms by which sulfur is transferred by each of them may be expected to differ, despite their similar thermochemical values. Extension of this work to other main group and transition metal sulfur complexes is under active investigation.

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