Theoretical Studies of the Binding of Thiols to the Alkali and Alkaline Earth Metals

Jan A. Pappas*

Contribution from the Institute of Physics, University of Oslo, Box 1038, Blindern, Oslo 3, Norway. Received February 24, 1978

Abstract: Ab initio model studies of the binding and reactions of alkali and alkaline earth metals with thiols are reported. The model systems considered are MSH, MSH$^+$, and M(SH)$_2$ with M = Li, Na, K, Be, Mg, and Ca. The alkali metal–sulfur bond is typically ionic with almost no charge transfer and no covalent character, although the superposition error in the basis set causes the population analysis erroneously to indicate so. The Mg–S and especially the Be–S bonds show considerable charge transfer toward the metal and the presence of covalent character in this bond may not be negligible. All M(SH)$_2$ were found to be linear as opposed to MCl$_2$. Furthermore, the correlation diagrams of ML$_2$ were found to be essentially dependent on the ligand even in isoelectronic systems, thus strongly restricting the use of Walsh diagrams in predicting the geometries of such systems.

Introduction

The nature of the metal–sulfur bond is of fundamental interest in view of the importance of both metal ions and sulfur ligands in biological systems.[1-6] During the past few years a substantial amount of experimental knowledge has accumulated. Nevertheless it seems as if the understanding of the fundamental nature of the metal–ligand bond is still incomplete. The different metals and ligands are usually characterized in terms of their hardness and softness and their position in the periodic table, but these concepts are not always sufficient neither to characterize and understand the metal–ligand bond nor to predict how a reaction will proceed.

The present work is part of a study designed to gain further knowledge of the underlying electronic aspects governing the structure and formation of metal–sulfur bonds. A systematic series of ab initio investigations has been started on systems modeling the interaction of metal ions with biochemical sulfur systems, especially thiols RSH and disulfides RSSR.[9] From previous experience we know that the sulfur regions exhibit only minor changes even in quite different thiols like H$_2$S, CH$_3$SH, or cysteine[8] and in different di- and trisulfides.[7] So even if HS$^-$ may seem very simple as model system for thiols RS$^-$, we nevertheless believe that it is a relevant model system for investigating the sulfur region in thiols.

Primarily, one should attempt to apply theoretical methods to problems in which they can form complements to the experimental methods, rather than trying to reproduce information that experiments can do far better. One great advantage of theoretical methods in this respect, being especially useful in the present work and in general metal biochemistry as well, is the possibility of investigating the electronic structures of molecular systems regardless of their thermodynamic stability and fast or slow reaction kinetics toward an equilibrium state. To the present study, this means that both metals that form strong and weak bonds to sulfur can be included. We do believe that it is important to include both these classes of metals in a systematic study, in order to understand more clearly why metals are different in a more detailed sense than based on their position in the periodic table.

As for the alkali and alkaline earth metals, these are usually considered to bind to oxygen and nitrogen ligands in a variety of forms. However, mercaptides of these metals are also known, the most simple form (the hydrosulfides M(SH)$_n$) being most commonly encountered. The binding and formation of these complexes and to a small extent the solvent effects will be the subject of the present work. The corresponding investigations

*Address correspondence to Det norske Veritas, Research Division, Box 300, 1322 Høvik, Norway.

of some transition elements will be the subject of a separate paper.

Computational Details

All the calculations were performed within the closed-shell single determinant MO-LCAO-SCF framework, using the program system MOLECULE.[19] For first- and second-row atoms we used the medium size Gaussian basis of Roos and Siegbahn[10] being of the type (7s, 3p) and (10s, 6p), respectively; for third-row atoms we used the (12s, 6p) set of Roos et al.[11] and Huzinagas (4s) basis for H scaled by 1.25.[12] This set was contracted to double ζ except for minimal basis in the K and L shells of K and Ca. 3d functions were added to O and S with exponents 1.33 and 0.54, respectively,[10] and 2p, respectively 3p, functions were added to Li$^+$, Be^{2+}, Na$^+$, and Mg^{2+}, the exponent being optimized in MSH or [MSH]$^+$. The basis for K$^+$ and Ca^{2+} was augmented by a set of 3d, 4s, and 4p functions with exponents chosen to give maximum charge density in the bonding region. Details of the basis for the metals are reported in Table I.

The effect of adding polarization functions to the basis sets of the metal cations was investigated and found to be significant. Addition of a 2p function on Li in LiSH causes a transfer of 0.25 electrons from S to Li paralleled by an increase in the S–Li overlap population by 0.34 electrons and a lengthening of the S–Li bond by 0.02 Å. Gole et al.[13] have previously pointed out that 3d functions on Ca are necessary in order to predict the correct bent structures of molecules like CaF$_2$. So polarization functions are certainly needed in order to describe the adjustment of these metal cations to their molecular environment.

The geometries of the molecules included in this investigation are not known to any appreciable extent, and the benefit from the few crystal structures that are known[14] is somewhat reduced by the close proximity of four or five anionic sulfur centers to each metal ion in the crystal and by the relatively high R factors (11–15%). As we wish to compare calculated binding and reaction energies, rather extensive geometry optimizations were necessary in order to ensure that errors due to nonoptimal geometries were considerably smaller than the energy differences to be compared. The procedure has been to optimize the mercaptides of Li and Be in all parameters and reoptimize the M–S distance and the S–M–S angle in the mercaptides of the other metals. The calculated geometries and corresponding energies are summarized in Table II.

Mercaptides of the Alkali Metals

The hydrosulfides MSH of the alkali metals are stable under ordinary conditions, the only exception being LiSH, which is

Table I. Details of the Metal Basis

atom	E (this basis), au	E (Hartree-Fock),[22] au	Polaris exponent
Li$^+$	−7.23314	−7.23641	$\alpha(2p) = 0.12$
Na$^+$	−161.60636	−161.67676	$\alpha(3p) = 0.08$
K$^+$	−598.00780	−599.01710	$\alpha(4s, 4p, 3d) = 0.1, 0.2, 0.3$
Be	−14.56659	−14.57302	
Be^{2+}	−13.60581		$\alpha(2p) = 0.30$
Mg	−199.53126	−199.61458	
Mg^{2+}	−198.74786		$\alpha(3p) = 0.15$
Ca	−675.44737	−676.75803	
Ca^{2+}	−675.06286		$\alpha(4s, 4p, 3d) = 0.1, 0.2, 0.3$

hydrolyzed even in the presence of air. Several of the mercaptides, like CH_3SLi and C_6H_5SLi, are also stable. The alkali mercaptides are prepared by saturating an aqueous solution of the corresponding hydroxide with the thiol, i.e., MOH + RSH → MSH + H_2O, or by simply adding the metal and the thiol in NH_3. The crystal structure of CH_3SM, M = Li, Na, and K, is known in some detail,[14] but very little is actually known of the character of the M–S bond except that it is generally assumed to be ionic.

The calculated M–S distances in MSH (see Table II) and the experimental M–S distances in CH_3SM are not directly comparable. This is not so much due to different R groups in the MSR molecules being compared as to the fact that the metal in the CH_3SM crystals are coordinated to four or five sulfur centers. The experimental metal–sulfur distances of 2.4_2, 2.8_0, and 3.1_5 Å in CH_3SLi, CH_3SNa, and CH_3SK are thus naturally longer than the calculated gas-phase values by about 0.2–0.3 Å, but the relative trend in the distances is similar. The calculated M–S–H angle of 97.2° in LiSH is very similar to R–S–H angles in regular thiols.[8,9]

The calculated electron distribution can be analyzed in terms of a Mulliken populational analysis as displayed in Table III. The results may superficially be interpreted as indication of strongly covalent Li–S and Na–S bonds as their overlap populations are of the same order as in ordinary covalent bonds. Other considerations indicate that this high covalency most likely is a false conclusion, however. The problem with overlap populations is that they measure the overlap of two functions everywhere in space and not just in the bonding region. Similarly, the atomic population with diffuse orbitals (like the 2s and 2p on Li) takes electron population close to one atom and assigns them to another. We have estimated this effect in LiSH by performing calculations on SH^- including the empty Li basis to see the part of the atomic charge assigned to Li that really belongs to SH^-.[15] (Simultaneously, this yields a somewhat crude upper bound of 8.4 kcal/mol to the superposition error in the binding energy of 167 kcal/mol.) The effects on the electron populations were rather dramatic, as these estimated errors account for 0.25 electrons of the charge on Li and as much as 0.34 of the Li–S overlap population.[16] Correcting the populations for this thus yields, within this approximation of the superposition error, a gross charge on Li of about +0.79 and an Li–S overlap population of about 0.24 electrons which in fact is quite similar to the corresponding populations in KSH. We expect corrections of the same order to be valid for NaSH as the outer functions on Na are almost as diffuse as those on Li. What thus emerges is a picture of a typically ionic M–S bond without any appreciable covalent character and very similar for all the alkali metals.

This conclusion gains further support from the variation of the orbital energies of MSH along the series as displayed in Figure 1a. The highest orbital is a lone pair on S of π symmetry while the second highest orbital is the other lone pair on S pointing toward the metal and with a slight contribution from the metal ns orbital. The next two orbitals are of respectively $\sigma(SH)$ and $S(3s)$ character. The splitting of the two lone pair

Table II. Total Energies and Geometries

molecule	E, au	geometry (bond distances, Å)
HSLi	−405.452 63	HS = 1.335,[a] SLi = 2.198,[a] HSLi = 97.2°[a]
HSNa	−559.793 23	SNa = 2.500,[a] rest as HSLi
HSK	−996.153 34	SK = 2.867,[a] rest as HSLi
Be(SH)$_2$	−810.646 30	SBe = 1.954,[a] SBeS = 180°,[a] rest as in HSBe$^+$
HSBe$^+$	−412.284 56	SBe = 1.912,[a] HS = 1.339,[a] BeSH = 95.2°
Mg(SH)$_2$	−995.566 09	SMg = 2.324,[a] SMgS = 180°,[a] rest as Be(SH)$_2$
HSMg$^+$	−597.269 04	SMg = 2.264,[a] rest as HSBe$^+$
Ca(SH)$_2$	−1471.696 53	SCa = 2.650,[a] SCaS = 180°,[a] rest as Be(SH)$_2$
HSCa$^+$	−1073.4586	SCa = 2.557,[a] rest as HSBe$^+$
LiOH	−82.796 19	LiO = 1.482,[a] OH = 0.953[a]
Be(OH)$_2$	−165.386 14	BeO = 1.440,[a] OH = 0.950,[a] BeOH = 134.6°,[a] OBeO = 180°[a]
H$_2$O	−75.907 84	OH = 0.960,[a] HOH = 104.2°

[a] Parameter optimized in the molecule.

Table III. Details of the Results for HSM, HSM$^+$, and M(SH)$_2$[a]

molecule	$q(S)$	$q(M)$	$q(SM)$	binding energy, kcal/mol total	binding energy, kcal/mol first
HSLi	−0.645	+0.540	0.576	167	
HSNa	−0.705	+0.615	0.440	147	
HSK	−0.873	+0.823	0.207	121	
HSBe$^+$	−0.296	+1.053	0.768	455	
HSMg$^+$	−0.450	+1.236	0.633	356	
HSCa$^+$	−0.840	+1.707	0.290	278	
Be(SH)$_2$	−0.564	+0.790	0.688	712	455
Mg(SH)$_2$	−0.647	+0.992	0.579	572	356
Ca(SH)$_2$	−0.929	+1.649	0.191	456	278
H$_2$S[8]	−0.14	+0.07	0.67	376	

[a] For estimates of the superposition errors, see the text.
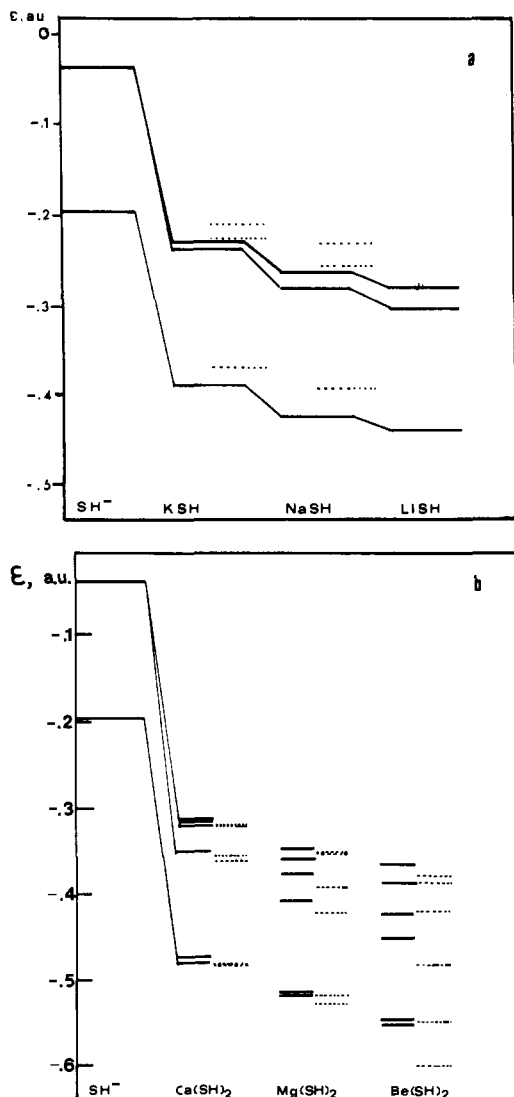
Figure 1. Correlation diagrams of the valence orbitals in MSH (a) and $M(SH)_2$ (b). The 3s orbitals on S are not shown as they are parallel to the lowest orbital shown. . . . . . . = energy of $(HS^-)_n$ in the field of a point charge $+n$ at the metal's position.

orbitals is quite small, indicating that the presence of a metal does not transform one of the lone pairs into a more typical M–S bond orbital. Thus the amount of nonionic interactions in the binding is very small.

As seen from the almost constant relative splitting of the valence orbitals, Li, Na, and K are strikingly similar in their bonding toward sulfur. The dominating difference between these metals is simply the variations in the electrostatic interaction due to different metal–sulfur distances. The correlation diagrams of MSH as far as the valence orbitals are concerned can in fact qualitatively be reproduced by the orbital energies of SH⁻ in the field of a point charge of +1 at the metal's position (see the broken lines in Figure 1a). This model does of course not account for all the noncovalent interactions between SH⁻ and M⁺ (it neglects the interactions of SH⁻ with the inner shells on M⁺), but it is nevertheless another indication that covalency and charge transfer are not very important in the alkali metal–sulfur bond.

The possible presence of nonionic character in organolithium compounds has been widely discussed as several experimental data appear to indicate so. (For details, see ref 17.) It is thus gratifying that our conclusions coincide with those recently obtained by Streitwieser et al.[17] in a theoretical study of the Li–C bond. The similarity of the Li–S and Li–C bond fur-

thermore suggests that, although S is a softer ligand than C, this does not very much affect its binding to the alkali metals.

In summary it seems fair to conclude that the alkali metal–sulfur bond is of predominantly ionic character with low charge transfer only, i.e., $[M^+ SH^-]$, and that uncritical interpretations of the population analysis may yield misleading conclusions.

Mercaptides of the Alkaline Earth Metals

The hydrosulfides $M(SH)_2$ of the alkaline earth metals are easily formed from the corresponding sulfides by hydrolysis (except for M = Be):

$$2MS + 2H_2O \rightarrow M(SH)_2 + M(OH)_2$$

The hydrosulfides are furthermore soluble, i.e.,

$$M(SH)_2 + H_2O \rightarrow M(OH)_2 + H_2S$$
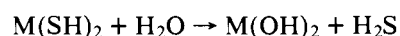
Alkali metal–sulfur bonds are additionally found in molecules of the type RSMgX produced in Grignard reactions with disulfides.[20] Mg and Ca are on the other hand known not to form chelation complexes with S-containing amino acids like cysteine in aqueous solutions.[21] The halides and to some extent the alkanes of the alkaline earth metals have both experimentally and theoretically been characterized rather in detail while the hydrosulfides and mercaptides have not.

The present study includes both $M(SH)_2$ and MSH^+, the latter as a possible precursor and for comparison with the corresponding alkali metal hydrosulfides. The bonding situation of MSH^+ as interpreted from the present calculations resembles that of the alkali metal–sulfur bond except that $BeSH^+$ and $MgSH^+$ show a considerable M–S overlap population and charge transfer toward the metal even after approximately correcting for the superposition errors (0.18 electrons in q(Be) and 0.22 electrons in p (Be–S)). The charge distribution actually indicates that Be^{2+} formally is reduced almost to Be^+ in $BeSH^+$. This large transfer together with the idea of a rather ionic character in the bonds toward Be suggest that $BeSH^+$ in fact could be a biradical of the type $Be^+ \cdots SH$. If so, the unexpectedly high Be–S overlap population could be explained as an artifact arising from the closed-shell RHF solution attempting to reproduce the electron distribution of a possible lower lying triplet state by constructing an orbital delocalized onto Be.

This possible instability of the closed-shell RHF solution has been examined by performing unrestricted Hartree–Fock calculations on states with different M_S components. The state with $M_S = 1$ was found to lie 8.7 eV above the closed-shell solution while calculations with $M_S = 0$ (using different spin-polarized start vectors) all converged to the closed-shell solution. So the closed-shell solution is nonsinglet stable and the considerable S–Be overlap population is thus not an artifact of the equivalence restriction in the RHF scheme, but rather a consequence of the charge transfer toward the metal. On the other hand, in $CaSH^+$, both charge transfer and overlap population are considerably smaller, thus closely resembling the alkali metal–sulfur bond.

The neutral hydrosulfides $M(SH)_2$ show bonding characteristics very similar to those discussed above for MSH^+. Also in $M(SH)_2$ the population analysis clearly displays a decreasing M–S overlap population paralleled by a decreasing charge transfer toward the metal along the series Be^{2+} (1.20 e), Mg^{2+} (1.00 e), and Ca^{2+} (0.35 e). At the same time this illustrates a trend that appears to be rather general in the results, namely, the partitioning of the alkaline earth metals into two separate groups. Ca^{2+} closely resembles K^+ and also the other alkali metals by showing low charge transfer and low overlap population in the bonds to sulfur, while the corre-
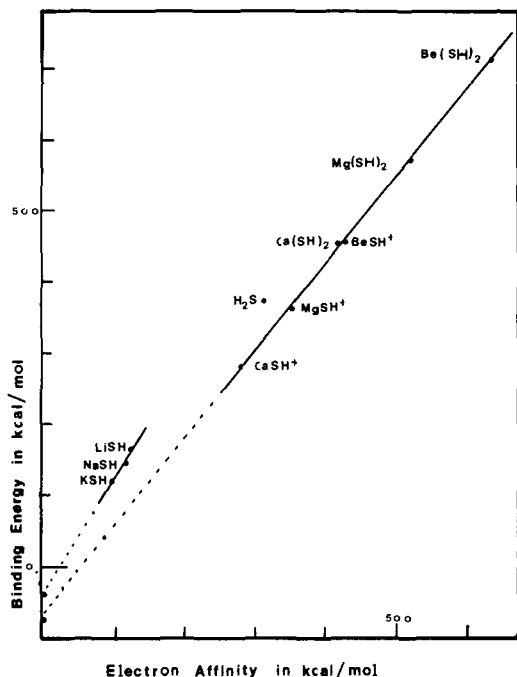
Figure 2. Correlation of binding energies of metal-sulfur complexes with the electron affinities of the metals.

sponding changes in the electron distributions are considerably larger when Mg-S and especially Be-S bonds are formed. One should note in this context that the superposition error in $M(SH)_2$ is considerably smaller than in the cases previously discussed, as it amounts to only 0.09 electrons in q(Be) and 0.04 electrons in p(Be-S) in $Be(SH)_2$ (while the upper bound to the error in the total energy is almost the same, 7.8 kcal/mol). The apparent reason for this is that only about one-half of the molecular orbitals in $M(SH)_2$ (the symmetric) have the proper symmetry in order to mix charge from HS^- with the s orbitals on the metal, the s orbital being the one previously found mainly responsible for the superposition error.

There are several other factors also suggesting that Mg and especially Be differ from the other alkaline earth elements in their bonding toward sulfur in the way that factors other than ionic may not be negligible. This is perhaps best illustrated by the correlation diagram of the highest valence orbitals in $M(SH)_2$ as displayed in Figure 1b. The two highest orbitals are lone pairs on S normal to the S-M-S plane and behave very similar to the corresponding orbitals of π symmetry in the alkali hydrosulfides. The next two orbitals are the lone pairs on S pointing toward the metal center with a component of metal valence orbitals, and these molecular orbitals are mainly responsible for the metal-sulfur bond. The splitting of these orbitals decreases slightly along the series in contrast to the pure lone-pair orbitals. The next two orbitals are mainly of S-H character. This correlation diagram alone does not suggest Be to differ particularly from the other metals, though the orbital energies are somewhat more spread.

However, by comparing the corresponding correlation diagram of the orbitals of $(SH^-)_2$ in the field of a point charge +2 at the metal's position (the broken lines in Figure 1b), it is clear that the real correlation diagram results as a balance between opposing effects. First, the effect of purely ionic bonding tends to increase the splitting of corresponding pairs of symmetric and antisymmetric orbitals. These splittings are particularly large in the orbitals responsible for bond formation $Be(SH)_2$. Secondly, the fact that the ionic splitting is greatly increased while the real splitting slightly decreases along the series implies that nonionic factors (that tend to reduce the

difference between symmetric and antisymmetric bond orbitals in their response to electrostatic fields) are present in the Be-S bond.

No experimental geometries are available for the $M(SR)_2$ complexes, but the calculations predict all the hydrosulfides, including $Ca(SH)_2$, to be linear. The barrier for rotation of the S-H bond is only ~ 0.9 kcal/mol in $Be(SH)_2$, indicating that there will be almost free rotation of the S-R bond in $M(SR)_2$. The predicted linearity of the S-Ca-S bond is in contrast to the case of the alkaline earth halides. The isoelectronic $CaCl_2$ is linear, and while BeF_2 and MgF_2 both experimentally and theoretically are known to be linear, also CaF_2 is strongly bent.[13] Now, the correlation diagrams for both CaF_2 (bent) and ZnF_2 (linear)[18] predict several of the ligand p orbitals to stabilize the bent structures. The resulting geometry may thus be considered as resulting from a balance between several opposing effects. In all hydrosulfides, however, every orbital stabilizes the linear structures. The qualitative nature of the correlation diagram for ML_2 complexes is thus essentially dependent on the ligands even within complexes of the same metals with ligands having the same number of valence electrons. This imposes strong limitations on the predictions of molecular geometries from Walsh rules as different correlation diagrams must be used for different ligands even in isoelectronic systems.

The idea that the bonds between group 1A and 2A metals and sulfur show characteristics similar to an ionic type of bond with a partial charge transfer is also reflected by the observation in Figure 2 that the binding energies of the complexes correlate nicely with the electron affinities of the acceptor metals. For the alkaline earth metals we notice that the same correlation is found for both MSH^+ and $M(SH)_2$. In other words, the binding energies of MSH^+ show the same correlation to the second ionization potentials of M (i.e., electron affinity of M^{2+}) as the correlation between the binding energies of $M(SH)_2$ and the ionization potentials for double ionizations of M (i.e., the affinity of M^{2+} for two electrons). The corresponding correlations for the alkali metal hydrosulfides show that the electron affinities depend somewhat stronger on the binding energies, but both correlations are consistent in that they both cross the energy axis at roughly minus one, respectively twice the ionization potential of the donor SH^-. This is of course the expected energy required to form a complex in the hypothetical case of zero electron affinity of the acceptor.

Comparison of the Metals

Although both the alkali and the alkaline earth metals in general were found to bind rather weakly to sulfur ligands, there are some interesting and distinct differences present between the metals that deserve attention. The group of alkali metals including Li shows both qualitatively and quantitatively very much the same bonding characteristics toward sulfur ligands. On the other hand, in the alkaline earth metals there seems to be a rather sharp distinction between Be, Mg, and the other metals. Ca does in fact more resemble K than Be and Mg in its binding with sulfur ligands. Be and Mg are the only metals in the present study showing substantial charge transfer in the M-S bond, and especially for Be there seems to be evidence for presence of covalent character in the bonds with sulfur.

A feature of the second period is the similarity the chemistry of an individual element shows to that of the element of a group higher in the third period, the so-called diagonal similarities. Within the metals in the present investigation this would correspond to the pair of Li and Mg. These metals are known to show such similarities in their chemistry involving nitrogen and oxygen ligands, but the corresponding similarities in the

electronic structure of the bonds with sulfur does not, however, seem to be particularly present in our data.

Essential to the chemistry of metals as electrophiles in competing for ligand sites is their strength relative to H^+. For the alkali and alkaline earth metals this situation is displayed in Figure 2 or Table III, and all the alkali metals are seen to be poorer electrophiles than H^+, as expected. When considering the energy per bond formation (as opposed to the total binding energy) of the alkali metal hydrosulfides, H^+ is found to divide these metals into two distinct groups. Be^{2+} is clearly a stronger electrophile than H^+, Ca^{2+} (and most likely Sr^{2+} and Ba^{2+}) are considerably weaker electrophiles, whereas Mg^{2+} is on the borderline having slightly less binding energy toward SH^- than has H^+. The monovalent and heavier bivalent metals thus require low $[H^+]$ to form hydrosulfides while Be–S bonds may be formed in acidic media. It is important to bear in mind that solvent effects drastically can change this picture, however.

The reactions previously studied in the present work apply primarily to the gas phase. In aqueous solution several additional complications are introduced in the calculation of reaction energies, such as the hydration of especially the ions and competing reactions to those already considered with H_2O and OH^-. It is far beyond the scope of the present investigation to study the full set of reactions that will take place when all these ligands are present. Instead we have considered the relative affinities toward O and S ligands as revealed in the gas-phase reaction

$$M(SH)_n + nH_2O \leftrightarrow M(OH)_n + nH_2S$$
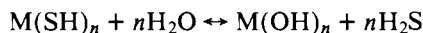
which at the same time provides an indication of the reliability of some of the previous results in this investigation as it is known that the alkaline hydrosulfides readily are dissolved in aqueous solution. By optimizing the structure and calculating the total energies of LiOH and $Be(OH)_2$ (see Table II) we find

the energy of the above reaction to be 7.6 kcal/mol for M = Li and −17.8 kcal/mol for M = Be. In other words, Be is predicted to be more stable as $Be(OH)_2$ than as $Be(SH)_2$ when H_2O is present.

References and Notes

(1) M. Friedman, *Adv. Exp. Med. Biol.*, **48** (1975).
(2) M. R. F. Ashworth, "The Determination of Sulfur-Containing Groups", Vol. 2, Academic Press, New York, N.Y., 1976.
(3) Y. M. Torchinskii, "Sulfhydryl and Disulfide Groups of Proteins", Studies in Soviet Science, Consultants Bureau, New York, N.Y., 1974.
(4) P. C. Jocelyn, "Biochemistry of the SH Group", Academic Press, New York, N.Y., 1972.
(5) M. Friedman, "The Chemistry of the Sulphydryl Group in Amino Acids, Peptides and Proteins", Pergamon Press, Oxford, 1973.
(6) G. Eichorn, Ed., "Inorganic Biochemistry", Elsevier, Amsterdam, 1973.
(7) J. A. Pappas, *J. Chem. Soc., Perkin Trans. 2*, in press.
(8) J. A. Pappas, *Chem. Phys.*, **12**, 397 (1976).
(9) J. A. Pappas, *J. Am. Chem. Soc.*, **99**, 2926 (1977).
(10) B. Roos and P. Siegbahn, *Theor. Chim. Acta*, **17**, 199, 209 (1970).
(11) B. Roos, A. Veillard, and G. Vinot, *Theor. Chim. Acta*, **20**, 1 (1971).
(12) S. Huzinaga, *J. Chem. Phys.*, **42**, 1293 (1967).
(13) J. L. Gole, A. K. Q. Siu, and E. Hayes, *J. Chem. Phys.*, **58**, 857 (1973).
(14) E. Weiss and U. Joergens, *Chem. Ber.*, **105**, 418 (1972).
(15) The opposite effect, i.e., that of including the basis of H and S in calculations on atomic Li^+, was completely negligible.
(16) It is worth noticing that, although the S–Li overlap population was increased by 0.34 e and the gross charge on Li increased by 0.25 e by adding the 2p function on Li, this is not a superposition effect. Analysis of the wave function shows that the superposition error mainly is due to the 2s orbital on Li and not 2p.
(17) A. Streitwieser, Jr., J. E. Williams, Jr., S. Alexandratos, and J. M. McKalvey, *J. Am. Chem. Soc.*, **98**, 4778 (1976).
(18) D. R. Yarkony and H. Schaeffer, III, *Chem. Phys. Lett.*, **15**, 514 (1972).
(19) J. Almlöf, USIP Report 74-29, University of Stockholm, 1974.
(20) W. A. Pryor, "Mechanisms of Sulfur Reactions", McGraw-Hill, New York, N.Y., 1962, p 61.
(21) G. P. Lenz and A. E. Martell, *Biochemistry*, **3**, 745 (1964).
(22) E. Clementi, *IBM J. Res. Dev.*, **9**, 2 (1965); C. Roetti and E. Clementi, *J. Chem. Phys.*, **61**, 2062 (1974).

Ionization Energies of Organic Compounds by Equilibrium Measurements

Sharon G. Lias* and P. Ausloos

Contribution from the National Bureau of Standards, Washington, D.C. 20234. Received March 14, 1978

Abstract: The determination of the equilibrium constants for a number of charge transfer equilibria has generated a scale of relative values of $\Delta G°$ for the charge transfer reactions. The factors contributing to $\Delta S°$ for these reactions were elucidated by carrying out experimental determinations of the entropy changes for some of the equilibria. The values of $\Delta H°$ were used to generate a scale of relative ionization energies of 41 organic compounds and NO. Standardization of the scale using the spectroscopically determined values of the ionization potentials of NO, benzene, and furan was accomplished by calculating the relationship between adiabatic ionization potentials and the "enthalpies of ionization" measured in these experiments. The spectroscopically determined IPs of six of the compounds were reproduced in this way, thus verifying the technique.

Introduction

In recent years, experimental techniques have been developed which permit the determination of equilibrium constants for ion–molecule equilibria in the gas phase.[1] Using this approach a variety of information about the thermochemical properties of ions has been generated. For instance, scales of relative basicities of numerous organic compounds have been derived from overlapping series of proton transfer equilibrium constants. Quantitative information about the differences in

the heats of formation of alkyl carbonium ions has been obtained from equilibrium constants of hydride transfer and halide transfer reactions.

$$-RT \ln K_{eq} = \Delta G° = \Delta H° - T\Delta S° \tag{I}$$

It has been suggested,[2a-c] and preliminary results from this laboratory have indicated,[2d,e] that values for the enthalpies of charge transfer reactions derived from the equilibrium constants of charge transfer equilibria: