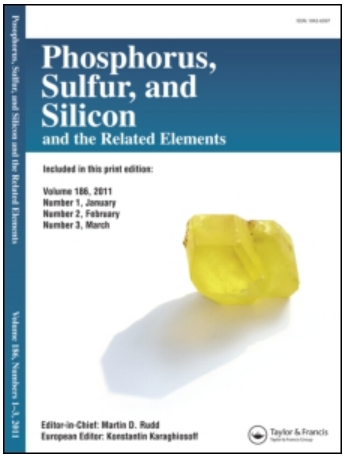


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

REACTIVITY OF SULFUR(II) COMPOUNDS. CHEMICAL PROPERTIES AND FRONTIER MOLECULAR ORBITAL ANALYSIS

C. Diaz[a]; R. Contreras[a]; G. González[a]; A. Aizman[b]
[a] Department of Chemistry, Faculty of Sciences, Universidad de Chile, Casilla, Santiago, Chile [b] Department of Chemistry, Faculty of Science, Universidad Santa Maria, Casilla, Valparaiso, Chile

To cite this Article Diaz, C. , Contreras, R. , González, G. and Aizman, A.(1991) 'REACTIVITY OF SULFUR(II) COMPOUNDS. CHEMICAL PROPERTIES AND FRONTIER MOLECULAR ORBITAL ANALYSIS', Phosphorus, Sulfur, and Silicon and the Related Elements, 55: 1, 219 — 228
To link to this Article: DOI: 10.1080/10426509108045944
URL: http://dx.doi.org/10.1080/10426509108045944

Phosphorus, Sulfur, and Silicon, 1991, Vol. 55, pp. 219–228
Reprints available directly from the publisher
Photocopying permitted by license only

REACTIVITY OF SULFUR(II) COMPOUNDS. CHEMICAL PROPERTIES AND FRONTIER MOLECULAR ORBITAL ANALYSIS

C. DIAZ, R. CONTRERAS, and G. GONZÁLEZ*
Department of Chemistry, Faculty of Sciences, Universidad de Chile, Casilla 653, Santiago, Chile

and

A. AIZMAN*
Department of Chemistry, Faculty of Science, Universidad Santa Maria, Casilla 110-V, Valparaiso, Chile

(Received January 8, 1990; in final form April 12, 1990)

Some aspects of the reactivity of sulfur(II) compounds—specially of *N,N'*-thiobisamines, toward hydrolysis, alcoholysis, and formation of coordination compounds—are discussed using experimental and theoretical results. Frontier molecular oribitals obtained from CNDO/2 calculations including sulfur *d* orbitals for a set of representative sulfur(II) species show that the reactivities of these compounds, following the series:

$[Me_2NSNHMe_2]^+ > S(OH)_2 > SCl_2 >$ neutral thiobisamines > thiobisphthalimide,

are adequately described by considering both charge and orbital effects.

Key words: Sulfur(II) compounds; Thiobisamines; Reactivity of Sulfur(II) Compounds; Frontier MOs in Sulfur(II) Compounds.

INTRODUCTION

Although *N,N'*-thiobisamines ($S(NR_2)_2$, R = alkyl group) has been the subject of continuous work in our laboratory,[1–5] the development of the chemistry of these and other sulfur(II) compounds like sulfur halides (SX_2),[6] amine-*N*-sulfenyl halides ($R_2N—S—X$), alkoxythioamines ($R_2N—S—OR$), dialkoxysulfides ($S(OR)_2$) and sulfoxylic acid ($S(OH)_2$),[7,8] is still incipient.

Contrary to sulfur halides, amine-*N*-sulfenyl halides or dialkoxysulfides, *N,N'*-thiobisamines as well as alkoxythioamines are relatively inert species under ordinary conditions. Hydrolysis or alcoholysis reactions are observed for these compounds only in the presence of Brønsted or Lewis acids.[4] Although this acid catalysis is related with a certain nucleophilic character of the thiobisamines, stable coordination compounds have been obtained only with metals in low oxidation states.[3]

In addition to the chemical characterization, some spectroscopic[2,5] as well as electrochemical[9] studies of thiobisamines have been carried out. However, we feel that the chemistry of sulfur(II) compounds is not always totally comprehensible and that a theoretical basis for systematizing this chemistry is still needed.

Since the explanation of any stability or reactivity pattern of sulfur(II) compounds

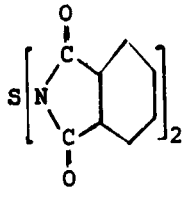
should be necessarily related to the nature of the bonds and the charge distributions in this class of molecules, a frontier molecular orbitals analysis for a set of representative sulfur(II) species is given.

RESULTS AND DISCUSSION

Molecular orbital calculations on selected S(II) species—$S(N(CH_3)_2)_2$, $S(OH)_2$, SCl_2, thiobisphthalimide and the *N,N'*-thio(dimethylamine)-dimethylammonium

TABLE I

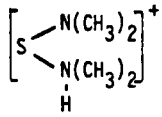
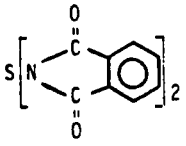
Selected structural parameters for Sulfur(II) compounds

Compound	Parameters		References
$S[N(CH_3)_2]_2$	r(S—N) = 1.688 Å, r(C—N) = 1.473 Å,	∢ (NSN) = 114.5° ∢ (SCN) = 117.9°	12
SCl_2	r(S—Cl) = 1.99 Å,	∢ (ClSCl) = 101°	10
$S(OH)_2$	r(S—O) = 1.66 Å,	∢ (OSO) = 101.1°	[a]
	r(S—N) = 1.657 Å,	∢ (NSN) = 103°	[b]

[a] Structure not known. Parameters taken from similar compounds, Ref. 11.
[b] Local optimized parameters. Parameters for the phthalimide group taken from similar compounds, References 32 and 33, and standard values.

TABLE II

Orbital energies and atomic charges for S(II) species

S(II) Specie	Orbital energies[a]		Atomic charges[b]	
	ε(HOMO)	ε(LUMO)	q_S	q_N
$S[N(CH_3)_2]_2$	−10.88	2.72	0.001	−0.14
	−17.95	−4.08	0.12	−0.07 0.01[c]
SCl_2	−12.24	0.027	0.085	
$S(OH)_2$	−11.97	1.90	0.14	
	−11.42	0.81	0.081	−0.20

[a] Energies in eV.
[b] Electron units.
[c] Protonated nitrogen.

ion, $[(CH_3)_2N—S—NH(CH_3)_2]^+$, —were performed at the CNDO/2 level including **d** orbitals for sulfur. Bond distances were taken from the literature, when experimental geometries were available,[10–12] or substituted by standard values. The geometrical parameters used in the calculations are displayed in Table 1.

The calculated charges on sulfur atom and the HOMO-LUMO energies for all the molecules under study are reproduced in Table 2. Figure 1 illustrates the main orbital components of the respective HOMOs and LUMOs.

In order to corroborate the relative energies of the MOs obtained from the calculations, the photoelectron spectrum of the thiobisdimethylamine was performed. The agreement of the calculated with the experimental energies for the external MOs of the thiobisamines can be observed in Table 3. Correlation and reorganization effects, not considered in the calculations mentioned above, were estimated to be about 28%.[13]

The compounds selected for this study represent a set of species that have been considered appropriate for understanding the following relevant features in the chemistry of sulfur(II) compounds:

i) The separation and purification of *N,N'*-thiobisamines, which are obtained from the reaction of SCl_2 with an excess of the respective secondary amine, frequently involve the dissolution of the amine hydrochloride produced in the reaction with water and the subsequent crystallization of the thiobisamines in alcohol.[14] The low reactivity of the thiobisamines with respect to hydrolysis and alcoholysis contrasts with the behavior of SCl_2 and other typical sulfur(II) compounds that readily react with water and alcohols[15,16]:

$$SCl_2 \xrightarrow{H_2O} S_8 + H_2SO_3 + HCl + \text{other products}$$

$$SCl_2 + 2\,ROH + 2\,Et_3N \longrightarrow S(OR)_2 + 2\,Et_3NHCl$$

ii) Thiobisamines readily react with water in the presence of Cu(II) salts or of Brønsted acids to give oxidation-reduction products[1]:

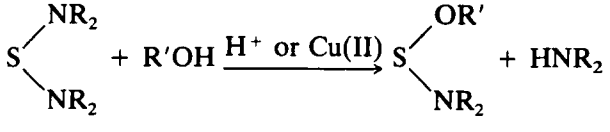
$$2\,Cu(ClO_4)_2\cdot 6H_2O + S(NR_2)_2 \xrightarrow{CH_3CN} 2[Cu(CH_3CN)_4]ClO_4 + SO_2 + 2[H_2NR_2]ClO_4 + 4\,H_2O$$

$$2\,CuCl_2\cdot 2H_2O + S(NR_2)_2 \xrightarrow{EtOH} [Cu_2Cl_3][H_2NR_2] + SO_2 + [H_2NR_2]Cl$$

This kind of reactivity, being characteristic for sulfur(II) compounds, has been explained by postulating the formation of sulfoxylic acid, $S(OH)_2$, as an unstable intermediate in a hydrolysis step[1,17]:

$$S(NR_2)_2 + 2\,H_2O \longrightarrow S(OH)_2 + 2\,HNR_2$$

Consistent with this scheme, the alcoholysis of thiobisamines observed in the presence of HCl or $CuCl_2$ produces stable mono-substituted products, the alkoxythioamines:[4]



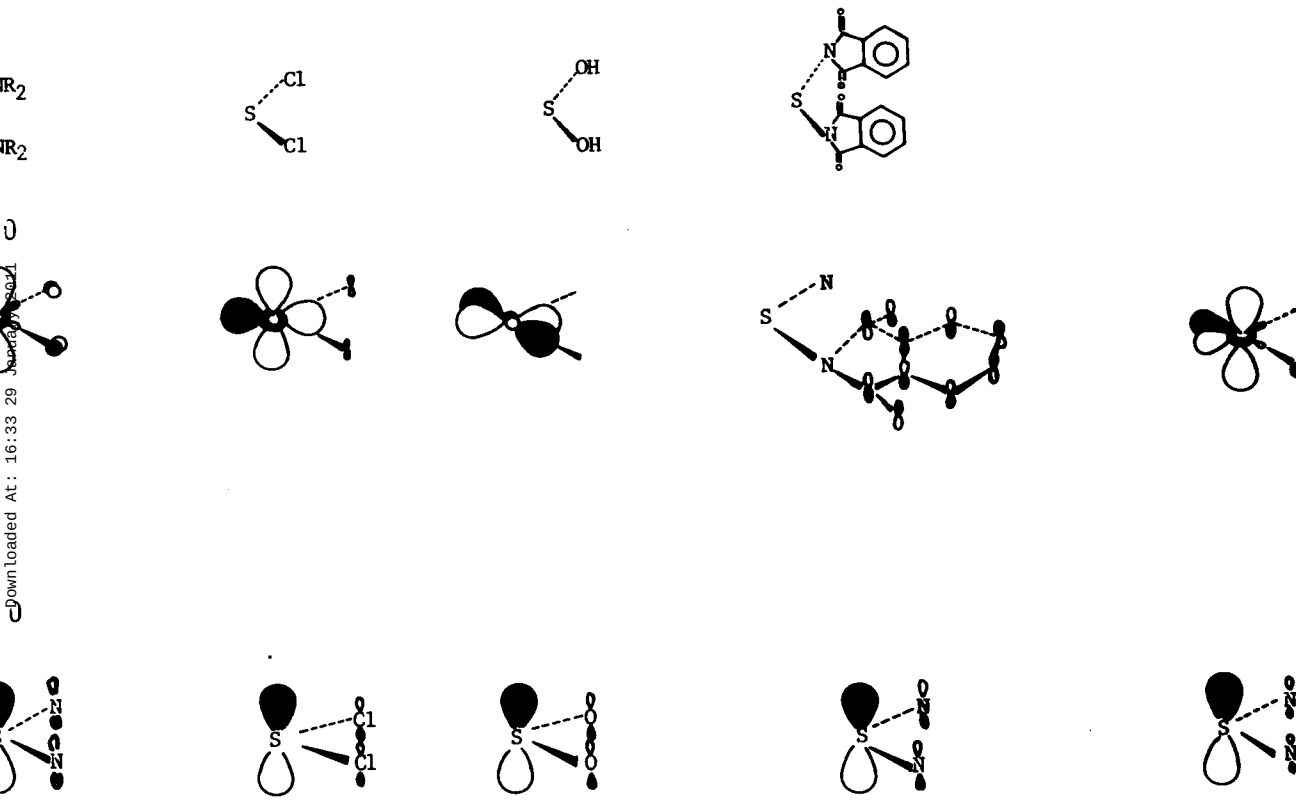


FIGURE 1 Pictorial representation of LUMO and HOMO for sulfur (II) compounds.

TABLE III
Calculated and experimental ionization energies and MO assignments for *N,N'*-thiobis(dimethylamine)

Vertical potentials (I_v) (eV)		
Experimental[a]	Calculated[b]	Orbital type[c]
8.20	8.30	n(S)
8.80	8.46	n(N)
9.25	9.79	π(S—N)
10.20	10.28	n(N)
	10.80	π(S—N)
10.60	10.83	π(S—N)
11.80	12.22	π(S—N)

[a] The PE spectrum was recorded by B. Solouki at University Frankfurt on a Leybold Hereaus UPG-200 spectrometer equipped with a He(I) source and using the Ar(3p3/2) line as standard.
[b] The CNDO/2 eingenvalues were reduced by 28%, see text.
[c] Main character.

iii) Although *N,N'*-thiobisphthalimide, $S(PHL)_2$ (Figure 2), may also be considered as a sulfur(II) compound with S—N bonds, its reactivity clearly differs from that of the thiobisamines. Nevertheless, although *N,N'*-thiobisphthalimide reacts with nucleophiles like amines, thiols, and alkoxides to give substitution products,[18,19]

$$S(PHL)_2 + HNR_2 \longrightarrow PHL—S—NR_2 + PHLH$$
$$S(PHL)_2 + HSR \longrightarrow PHL—S—S—R + PHLH$$

it is inert toward water and alcohols even in the presence of Cu(II) or Brønsted acids. Moreover, this thiodiamide reacts with diphenylamine and potassium thiocyanate yielding the donor-acceptor molecular complexes $(PHL)_2S{\cdot}2HNPh_2$ and $(PHL)_2S{\cdot}KSCN$[20] respectively, a kind of reaction not known for other sulfur(II) compounds, but it does not form coordination compounds with $M(CO)_5$ (M = Cr, Mo, W), which is a reaction characteristic for thiobisamines.[3,21]

The hydrolysis and alcoholysis of thiobisamines in the presence of acids mentioned above indicate a catalytic effect by activation of the S—N bond. This behavior is probably related to an increase of positive charge on the sulfur atom caused by a charge transfer from the thiobisamine to the acid.[22] The fact that the hydrolysis of thiobisamine can also be induced by the electrooxidation of the sulfur

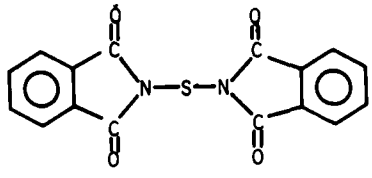


FIGURE 2 Thiobisphthalimide.

compound[9] corroborates such a point of view. Given the nature of the nucleophilic centers on the thiobisamines, an electrophilic attack, specially from a proton, should occur on the nitrogen atoms. This kind of interaction is consistent with some ESCA studies of S—N compounds indicating that the nitrogen atoms in the *N,N'*-thiobisphthalimide—which has a notoriously low reactivity toward electrophilic reagents—have a positive charge greater than in thiobisamines.[5]

As expected, the charge values on sulfur atoms as well as the shape and the energy of the frontier molecular orbitals are characteristic for each of the selected sulfur(II) species (Figure 1 and Table 2). The shape as well as the energy of the HOMO for all the species considered in the calculations—including those of the intermediates $S(OH)_2$ and the *N,N'*-thio(dimethylamine)dimethylammonium ion still not directly detected—are rather similar. Therefore, the detection, separation, and general "stability" of sulfur(II) species should be mainly controlled by kinetic factors.

In order to analyze the reactivity of the studied species toward hydrolytic or solvolytic agents, two main factors have been considered: the charge on the atoms participating in the initial donor-acceptor interaction and the energy gap between the frontier orbitals involved in the interaction.[23]

As expected from inductive effects, the addition of a proton to the *N,N'*-thiobis(dimethylamine) produces a sharp increase of the positive charge on sulfur and a decrease of both HOMO and LUMO energies. High values of the positive charge on the sulfur atom are also obtained for $S(OH)_2$ and SCl_2 (see Table 2). Assuming that in the reaction with alcohols or water the sulfur atom is the electrophilic center, these charge distributions agree well with the high reactivity observed for these sulfur(II) species.

The orbital analysis performed for the sulfur(II) compounds in relation to the corresponding orbitals of methanol[24] and water[25] shows a typical correlation of the energies of the HOMOs in the nucleophiles (methanol or water) with those of the LUMOs in the electrophiles (*N,N'*-thiobis-(dimethylamine), SCl_2 or $S(OH)_2$). Schematic representations of the HOMO-LUMO gaps for the hydrolysis and alcoholysis of some sulfur(II) compounds are illustrated in Figures 3 and 4 respectively. The reactivities of the studied species are thus correlated with both the net charge on the sulfur and the respective HOMO-LUMO gap. In these cases both effects are cooperative.

Thus, the relative reactivities predicted from our calculations follow the experimental results:

$$[Me_2NSNHMe_2]^+ > S(OH)_2 > SCl_2 > \text{neutral thiobisamines}$$

The reactivity pattern of thiobisphthalimide deserves special attention because, as stated earlier, this molecule is inert toward hydrolysis and alcoholysis even in the presence of acids. From data in Table 2 and Figures 3 and 4 it is rather clear that such a behavior cannot be explained either by a charge or a HOMO-LUMO gap effect. Probably it is related to specific orbital effects. In fact, as observed in Figure 1, the HOMO of *N,N'*-thiobisphthalimide, unlike other sulfur(II) compounds, has a preponderant π-character and is centered on both the carbonyl group and the benzene ring, rather than on the sulfur atoms.

One of the most interesting aspects of the chemistry of the *N,N'*-thiobisamines

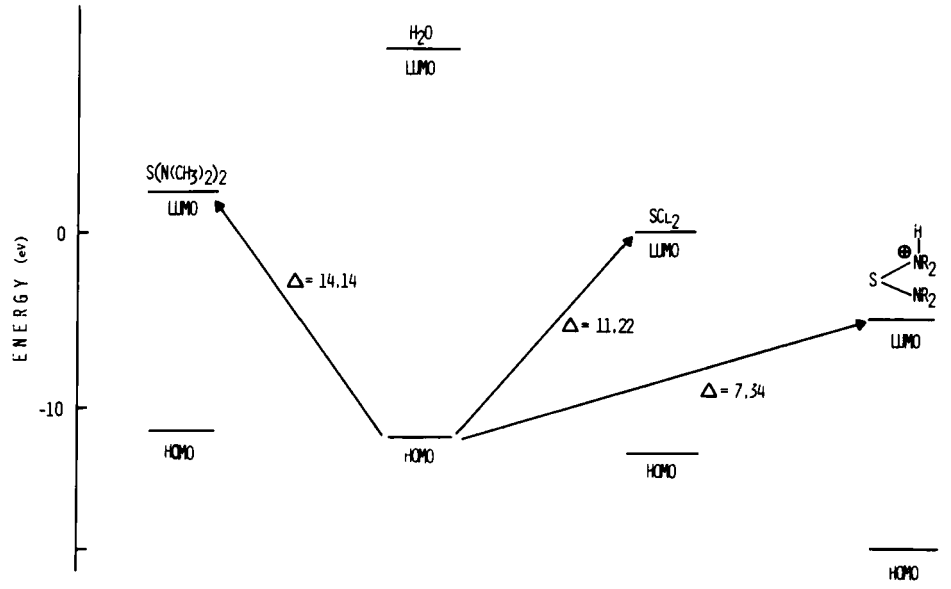


FIGURE 3 HOMO-LUMO energy differences for the interaction of H_2O with SCl_2, $S(NR_2)_2$ and $[S(NHR_2)(NR_2)]^+$ R = Me. Interaction of LUMO of H_2O with HOMO of $S(NR_2)_2$ and its protonated species, are forbidden by symmetry.

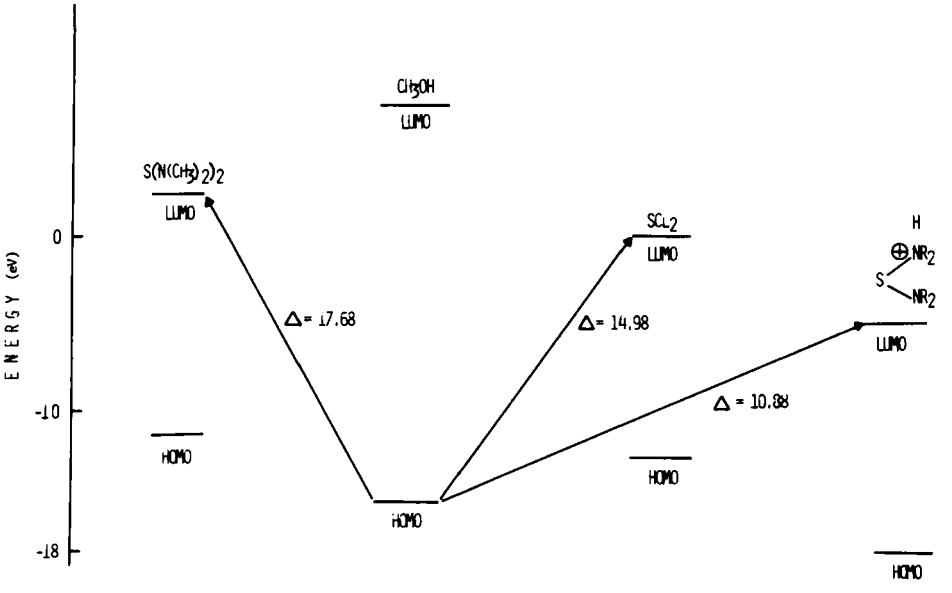


FIGURE 4 Diagrammatic representation of the HOMO-LUMO energy differences in the interaction of CH_3OH with SCl_2, $S(NR_2)_2$ and $[S(NHR_2)(NR_2)]^+$. Interaction of LUMO of CH_3OH with the HOMO of the sulfur species is not allowed by symmetry.

is the study of its coordination properties. Although it has not been possible to synthesize coordination compounds between this kind of ligands and metals in normal oxidation states, the synthesis of compounds of the type $M(CO)_5S(NR_2)_2$ with M = Cr, Mo and W has been accomplished in our laboratory.[3] These com-

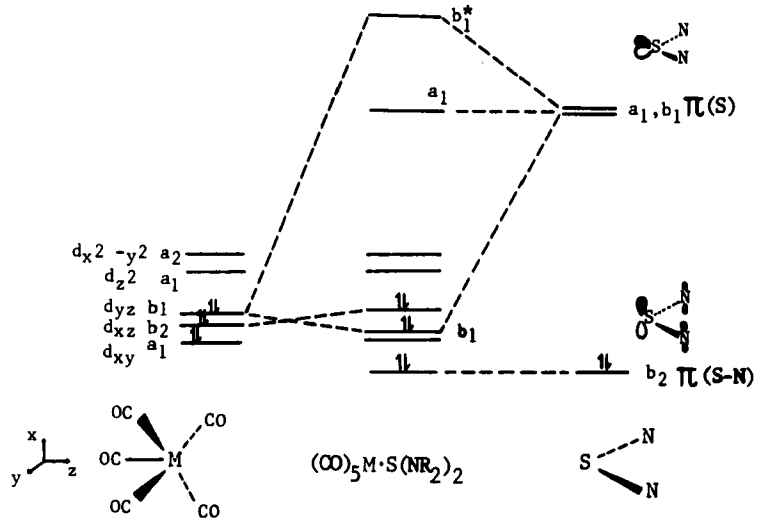


FIGURE 5 Interaction diagram for $M(CO)_5 \cdot S(NR_2)_2$ complexes. While the actual symmetry is C_{4v} the orbitals are labeled with respect to the C_{2v} symmetry. The energy levels are not scaled.

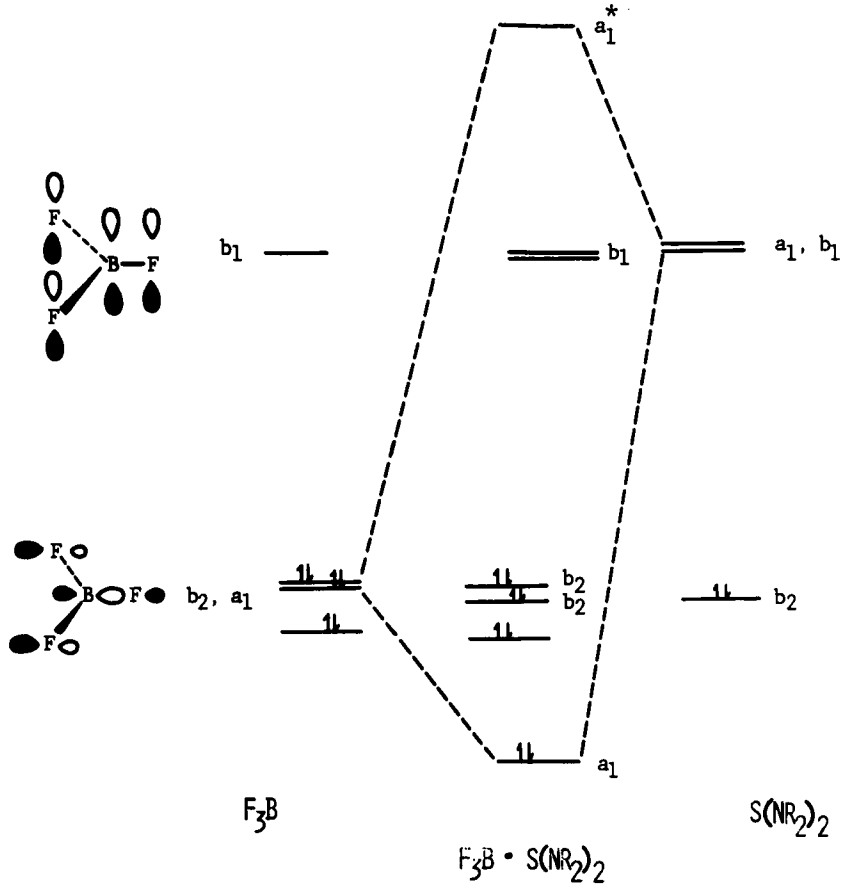


FIGURE 6 Interactions diagram for the adduct $F_3B \cdot S(NR_2)_2$. The energy levels are not scaled.

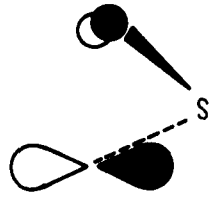


FIGURE 7 Pictorial representation of HOMO-1 in $S(NR_2)_2$.

plexes with the metals in low oxidation states are the only compounds with *N,N'*-thiobisamines as ligands reported up to day. A possible explanation for the coordinative properties of sulfur(II) compounds may be found by means of a symmetry fragment perturbation analysis[26] of the orbitals on the thiobisamine and those on the $M(CO)_5$ moiety.[27,28] From the interaction MO-diagram shown in Figure 5, it may be seen that the HOMO of the thiobisamine does not have the required symmetry to interact with the metal. Nonetheless, the same MO-diagram also shows that a metal-ligand π-backdonation interaction is favored. This conclusion agrees with previous results from IR studies that showed these ligands to have a π-acceptor rather than a σ-donor character.[3] Similarly, the interaction of *N,N'*-thiobisamines with the typical Lewis acids BX_3 (X = H, F, C_6H_5) yielding adducts of the type $(NR_2)_2SBX_3$[29,30] can be described as shown in Figure 6 by considering the thiobisamine acting as π-acceptors. Although this atypical kind of interaction of boron compounds has been proposed also for other systems,[31] the magnitude of the interaction is expected to be small, accounting for the low stability of the reported adducts.

As mentioned above, the catalytic action of the acids in the hydrolysis and solvolysis of thiobisamines is assumed to be caused by the coordination of the proton or metal ion to the nitrogen atom of the substrate. In fact, in the *N,N'*-thiobis(dimethylamine) the HOMO-1 is mainly centered on the nitrogen and has a symmetry appropriate for a σ thiobisamine-metal interaction (see Figure 7). The enhanced reactivity of the thiobisamine induced by such an interaction probably prevents the isolation of coordination compounds.

CONCLUSIONS

The MO calculations on a representative family of sulfur(II) species presented here show that a description taking into account both charge and orbital effects provide an adequate framework to rationalize the reactivity pattern of these compounds. Thus, reactivities toward H_2O or alcohols following the series:

$$[Me_2NSNHMe_2]^+ > S(OH)_2 > SCl_2 > \text{neutral thiobisamines}$$

correlate with the net charge on the nitrogen atom as well as with the HOMO-LUMO gap of the sulfur species. In the case of thiobisphthalimide, effects related with charge delocalization into the rings also appear to be present. The formation and isolation of sulfur(II) species are determined more by kinetics factors than by the thermodynamic stability of the species that appear to be affected only to a

minor extent by the nature of the sulfur substituents. Steric effects being known to be very effective in the stabilization of labile structures were not considered in this study.

ACKNOWLEDGEMENTS

The authors thank Prof. H. Bock, Frankfurt University, Germany, for facilities for recording photoelectron spectra, and the Departmento Técnico de Investigación de la Universidad de Chile (Grants Q-2588, and Q-2459) as well as the Dirección de Investigación USM (Project 88/302) for partial support. Free computer time made available to us by DPD-USM is also very much appreciated.

REFERENCES

1. G. González, C. Díaz, and S. Copaja, *Monatsh. Chem.*, **114,** 177 (1983).
2. C. Díaz, E. Clavijo, and G. González, *Spectrochim. Acta*, **39A,** 537 (1983).
3. C. Díaz and G. González, *Inorg. Chim. Acta*, **85,** 61 (1984).
4. C. Díaz, S. Copaja, and G. González, *Phosphorus and Sulfur*, **22,** 317 (1985).
5. G. González, C. Díaz, and H. Binder, *Z. Nauturfosch.*, **43B,** 513 (1988).
6. G. Nickless, "Inorganic Sulfur Chemistry," Elsevier, (1969).
7. G. Fendler in "Methoden der Organischen Chemie," Houben-Weyl, vol. E11 (Supplement), G. Thieme Verlag, Stuttgart, (1985).
8. D. R. Hogg, *Compr. Org. Chem.*, **3,** 311 (1979).
9. G. González, M. A. Santa Ana, and I. Chadwick, *J. Chem. Soc. Perkin Trans. II*, 1808 (1983).
10. K. J. Palmer, *J. Am. Chem. Soc.*, **60,** 2360 (1938).
11. R. E. Penn, E. Block, and L. K. Revelle, *J. Am. Chem. Soc.*, **100,** 3622 (1978).
12. I. Hargittai and M. Hargittai, *Acta Chim. Sci. Acad. Sci. Hung.*, **75,** 129 (1973).
13. R. J. Colton and J. W. Rabalais, *J. Electron Spectrosc. Rel. Phenom.*, **3,** 345 (1974).
14. Q. E. Thomson, *Quart. Reports Sulfur Chem.*, **5,** 245 (1970).
15. M. Goehring and A. Stamm, *Angew. Chem.*, **60,** 147 (1948).
16. Q. E. Thomson, *J. Org. Chem.*, **30,** 2703 (1965).
17. C. Díaz, *Polyhedron*, **4,** 1269 (1985).
18. D. N. Harpp and T. G. Back, *Tetrahedron Lett.*, 1481 (1972).
19. G. Buchi and R. M. Freidinger, *J. Am. Chem. Soc.*, **96,** 3332 (1974).
20. C. Díaz, S. Copaja, and G. González, *Acta Sud. Am. Quím.*, **4,** 47 (1984).
21. C. Díaz, unpublished results.
22. F. A. Davis, *Int. J. Sulfur Chem.*, **8,** 71 (1973).
23. I. Fleming, "Frontier Orbitals and Organic Chemical Reactions," J. Wiley, (1982).
24. Molecular orbitals for methanol were obtained by a standard CNDO/2 method.
25. R. M. Pitzer and D. P. Merrifield, *J. Chem. Phys.*, **52,** 4782 (1970).
26. R. Hoffmann, *Angew. Chem. Int. Ed. Engl.*, **21,** 711 (1982).
27. T. A. Albright, R. Hoffmann, J. C. Thibeault, and D. L. Thorn, *J. Am. Chem. Soc.*, **101,** 3801 (1979).
28. J. Chadwick, C. Díaz, G. González, M. A. Santa Ana, and N. Yutronic, *J. Chem. Soc. Dalton Trans.*, 1867 (1986).
29. H.Nöth, G. Mikulaschek, and W. Rambeck, *Z. Anorg. Allg. Chem.*, **344,** 316 (1966).
30. H.Nöth and G. Mikulachek, *Chem. Ber.*, **97,** 202 (1964).
31. A. H. Cowley and M. C. Damasco, *J. Am. Chem. Soc.*, **93,** 6815 (1971).
32. R. Mason, *Acta Cryst.*, **14,** 720 (1961).
33. R. N. Brown, *Acta Cryst.*, **14,** 711 (1961).