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MASS SPECTROMETRIC EVIDENCE FOR p_π—d_π BONDING BETWEEN SULFUR AND THE GROUP IVB ELEMENTS*

G. DISTEFANO, A. RICCI and R. DANIELI

Laboratorio dei composti del Carbonio contenenti Eteroatomi e loro Applicazioni del C.N.R., Ozzano Emilia, Bologna (Italy)

A. FOFFANI, G. INNORTA and S. TORRONI

Istituto Chimico "G. Ciamician", Università di Bologna (Italy)

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Summary

Comparison of the ionization energies of $C_6H_5SX(CH_3)_3$ (X = C, Si, Ge, Sn and Pb) with those of $X(CH_3)_4$ compounds, shows that the absolute values are lower and in a narrower range in the former series; in addition, the carbon derivative does not follow the trend observed for the other compounds. p_π—d_π bonding between S and X (X = Si, Ge, Sn and Pb) is invoked to explain the results. This proposal is also in agreement with the S—X bond energies in these compounds, with the ionization energies in the series $S[X(CH_3)_3]_2$ (X = C, Si, Ge and Sn), and with the ionization and bond dissociation energies of the compounds $C_6H_5SSi(CH_3)_3$, $C_6H_5SSi(CH_3)_2Cl$ and $C_6H_5SSiCl_3$.

Introduction

The evidence for p_π—d_π bonding in organosilicon compounds is indisputable while the position for germanium, tin and lead is much less clear. For germanium and lead this could in part be attributable to the small number of results availabe, but for tin the occurrence of any *d* orbital bonding is still a debated problem in spite of a large number of studies [1].

The interpretation of the results in homologous series is complicated by the uncertainty in the order of the inductive and mesomeric effects along the series [1,2,3].

For the compounds now studied the ionization energies and the neutral and ionic bond dissociation energies of the sulfur—metal bonds suggest the presence of p_π—d_π bonding between sulfur and the Group VB elements in the vapor phase.

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Results and discussion

In Table 1 are listed the ionization energies for two classes of organometallic compounds containing a sulfur—metal bond, together with those for the corresponding tetramethyl derivatives taken from the literature [4].

The ionization energies of the phenylthio derivatives exhibit the following features when compared with those of the tetramethyl series: (a) their absolute values are lower: (b) their values are in a narrower range; (c) the carbon derivative does not follow the trend observed for the other compounds.

These observations, and the evidence from photoelectron spectroscopy [5] that the electron first ionized in the tetramethyl series is localized near the central atom, suggest that in the phenylthio derivatives the electron involved in the first ionization is essentially localized near the S atom. Since the extraction point remains the same along the series, the ionization energies reflect the electronic effects of the substituents. The inductive effect alone cannot explain the observed ionization energy trend. Indeed it has been suggested [1, 2], that the inductive effect is either constant or increases down the group; in neither case would the lower ionization energy of the carbon derivative compared with that of the silicon one be accounted for.

A p_π—d_π bond between the filled *p* orbitals of sulfur and the empty *d* orbital of X, which decreases the charge density on sulfur, could explain the relatively low ionization energy of the carbon derivative, for which π bonding is unlikely. This conclusion is supported by the data reported in the second column of Table 1. The introduction of a second *d* acceptor atom increases the molecular ionization energies, while the carbon compounds are unaffected.

Additional support for the presence of π bonding in the phenylthio derivatives is obtained from the bond dissociation energy data in Table 2 which also lists the appearance potentials of the $[X(CH_3)_3]^+$ and $[M - CH_3]^+$ ions. The difference between neutral and ionic bond energies is about 1.05 eV, except for the carbon compound for which it is only 0.74 eV. This is in agreement with the fact that in the carbon compound the *p* orbital of sulfur is essentially non-bonding, while it has bonding character for the other X atoms.

The appearance potentials of the fragment ions produced by detachment of a methyl group give information about the H_3C—X bond in the molecular ions. Except for lead, these ionic bond energies are about 0.8 eV higher than those found [4] in the tetramethyl derivatives. This is indirect evidence that different extraction points are involved in the two classes of molecules.

The increase of the ionization energy on introduction of chlorine atoms

TABLE 1

IONIZATION ENERGIES (eV)

X	$C_6H_5SX(CH_3)_3$	$[(CH_3)_3X]_2S$	$X(CH_3)_4$ [a]
C	8.17	8.19	10.35
Si	8.28	8.70	9.85
Ge	8.08	8.60	9.29
Sn	7.87	8.2	8.76
Pb	7.75		8.26

[a] From Ref. 4.

TABLE 2

APPEARANCE POTENTIALS (*AP*) AND BOND DISSOCIATION ENERGIES (*D*) (eV) FOR $C_6H_5-S-XMe_3$

X	$AP[X(CH_3)_3]^+$	$AP[M-CH_3]^+$	$D(S-X)$	$D(S-X)^+$	$D-D^+$	$D(X-CH_3)^+$
C	10.47	12.1	3.04	2.30	0.74	3.93
Si	10.18	9.93	2.94	1.90	1.04	1.65
Ge	9.83	9.95	2.78	1.75	1.03	1.47
Sn	9.42	9.22	2.62	1.55	1.06	1.35
Pb	8.37	8.11	1.70	0.62	1.08	0.36

(see Table 3) could in principle be ascribed either to a decrease of the inductive effect or to an increase of the $-M$ capability of the chlorine-containing groups; increase in the sulfur—silicon ionic bond dissociation energy with the increasing number of chlorine atoms seems to indicate that the $-M$ effect has greater importance.

In conclusion, the results suggest the presence of a $p_\pi-d_\pi$ contribution to the S—X bonds formed by all the members of Group IVB except carbon. While for the sulfur—silicon bond there is evidence that the π back-bonding predominates over the inductive effect, for the other members of the series one cannot discriminate between the relative weights of the mesomeric and inductive effects.

The same and/or closely related molecules have been examined in our and other laboratories by a number of experimental techniques. The vapor phase photoelectron results [6] on $Y(MH_3)_2$ (Y = O, S and Se; M = C, Si and Ge) and on $HSMH_3$ have been rationalized by invoking π-donation from the lone pair of Y to the MH_3 group for M = Si and Ge but not for M = C. Vibrational analysis and electron impact fragmentation scheme [7] on $[(CH_3)_3Sn]_2S$, do not show any evidence for double bonding. ESCA data [8] (in the solid state) indicate a decreasing total electron density at the sulfur atom on going from silicon to lead in the phenylthio series. For the same compounds dipole moment results [9] show a remarkable increase of $S \leftarrow X(CH_3)_3$ group moments with increasing atomic number of X. This trend, which parallels that of the corresponding *IP*'s (see Table 1), suggests increasing predominance of the $+I$ effect over the $-M$ effect on going towards lead.

Experimental

Mass spectrometric measurements

The measurements were made with an Atlas CH_4 mass spectrometer. The samples were intruduced in the ion source via a direct inlet probe, with the

TABLE 3

ENERGETIC DATA (eV)

	IP	$AP(SiR_3)^+$	$D(S-Si)^+$
$C_6H_5SSi(CH_3)_3$	8.28	10.18	1.90
$C_6H_5SSi(CH_3)_2Cl$	8.76	10.79	2.03
$C_6H_5-S-SiCl_3$	9.03	11.43	2.40

probe and source at the lowest possible temperatures. It was impossible, however, with Sn and especially with Pb derivatives, to avoid extensive decomposition and exchange reactions with the background in the ion source. Complete cleaning of the source was necessary after a few hours of work.

The ionization potentials were measured by Honig's method [10] and the appearance potentials by the extrapolated voltage difference method [11]. Xenon was used as standard. Reproducibility was better than 0.1 eV.

The S—X bond dissociation energies in the neutral molecules were calculated by subtracting from the measured *AP* of the XMe_3 fragment the corresponding ionization energy reported [4] to be: 7.43, 7.24, 7.05, 6.80 and 6.65 eV from C to Pb respectively.

Materials

Phenylthiotrimethyl-silicon, -germanium, -tin and -lead were prepared as described elsewhere [12]. Hexamethyldisilthiane [13], hexamethyldigermthiane [14], trimethyltin [15] and trimethyllead [14] sulphides and phenylthiotrichlorosilicon [16] were synthesized by published methods. Phenylthiodimethylchlorosilicon (45% yield), b.p. 61°C/0.2 mmHg was prepared by the reaction of dimethyldichlorosilane and lead thiophenoxide in dry ether. (Found: C, 47.16; H, 5.6; Cl, 17.12. $C_8H_{11}ClSSi$ calcd.: C. 47.38; H, 5.47; Cl, 17.48%.)

References

1 C.J. Attridge, Organometal. Chem. Rev., Sect. A, 5 (1970) 323. and references therein.
2 P.M. Kuznesof, F.B.T. Pessini and R.E. Bruns, J. Amer. Chem. Soc., 94 (1972) 9087 and references therein.
3 A.J. Smith, W. Adcock and W. Kitching, J. Amer. Chem. Soc., 92 (1970) 6140.
4 M.F. Lappert, J.B. Pedley, J. Simpson and T.R. Spalding, J. Organometal. Chem., 29 (1971) 195.
5 S. Evans, J.C. Green, P.J. Joachim, A.F. Orchard, D.W. Turner and J.P. Maier, J. Chem. Soc., Faraday Trans. II, (1972) 905.
6 S. Cradock and R.A. Whiteford, J. Chem. Soc., Faraday Trans. II, (1972) 281.
7 P.G. Harrison and S.R. Stobart, J. Organometal. Chem., 47 (1973) 89.
8 S. Pignataro, L. Lunazzi, C.A. Boicelli, R. Di Marino, A. Ricci, A. Mangini and R. Danieli, Tetrahedron Lett., (1972) 5341.
9 S. Sorriso, A. Foffani, A. Ricci and R. Danieli, to be published.
10 R.E. Honig, J. Chem. Phys., 16 (1948) 105.
11 J.W. Warren, Nature, 165 (1950) 810.
12 R. Danieli, G. Pirazzini, A. Ricci and C.A. Boicelli, to be published.
13 E.W. Abel, J. Chem. Soc., (1961) 4933.
14 E.W. Abel, D.A. Armitage and D.B. Brahy, Trans. Faraday Soc., 62 (1966) 3459.
15 T. Harada, Bull. Chem. Soc. Japan, 17 (1942) 281.
16 M. Schmeisser and A. Haas, Chem. Abstr., 65 (1966) 13749.