Journal of Organometallic Chemistry, 78 (1974) 93—99

BONDING BETWEEN SULFUR AND THE ELEMENTS OF GROUP IV STUDIED BY UV PHOTOELECTRON SPECTROSCOPY

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(Received April 1st, 1974)

Summary

The photoelectron spectra of the $S[X(CH_3)_3]_2$ and $CH_3—S—X(CH_3)_3$ series (X = C, Si, Ge, Sn and Pb) are reported, and assigned on the basis of the semilocalized orbitals approximation and a consideration of symmetry and substituent effects.

The electronic interactions between the $X(CH_3)_3$ substituents and the sulfur $n\pi$ orbital are discussed in terms of the relative importance of hyperconjugation (n—σ mixing), $(p$—$d)\pi$ bonding and electrostatic interactions.

Introduction

The electronic interaction between the orbitals centered on the elements of the fourth group (Si, Ge, Sn and Pb) and other MO's in the molecule is a much discussed problem. $(p$—$d)\pi$ bonding, hyperconjugation (n—σ and π—σ mixing) and inductive interactions have been invoked to interpret the experimental results [1—4].

In our laboratory we are interested in the nature of the bonding between sulfur and Group IV elements. Previous kinetic [5,6], mass spectrometric [7] and ESCA [8] results indicate that $(p$—$d)\pi$ interactions and inductive effects play a major role in determining the chemical and physical properties of this class of compounds. We thus undertook a photoelectron spectroscopy study of the compounds $CH_3—S—X(CH_3)_3$ and $S[X(CH_3)_3]_2$ (X = C, Si, Ge, Sn and Pb) with the aim of estimating the relative importance of $(p$—$d)\pi$ bonding, hyperconjugation (n—σ mixing), and inductive effects on the valence region ionization energies (I.E.'s), the carbon derivatives being studied for comparison.

Experimental

Commercial di-tert-butyl sulfide (Schuchardt) was redistilled before use. Hexamethyldisilthiane [9], hexamethyldigermthiane [10], trimethyltin [11] and trimethyllead [10] sulfide were synthesized by published methods. Methylthiotrimethylsilane was prepared by treating lead methylmercaptide with trimethylchlorosilane in diethyl ether [12]. Methylthiotrimethylgermane [13], methylthiotrimethyltin [14] and methylthiotrimethyllead [15] were obtained by published procedures.

The photoelectron spectra were recorded on a Perkin—Elmer PS 18 spectrometer. The estimated error is ± 0.05 eV in the first I.E. and ± 0.1 eV for internal I.E.'s.

Results and discussion

The photoelectron spectra of the compounds CH_3—S—$X(CH_3)_3$ are shown in Fig. 1 and the I.E.'s data in Table 1; spectra and I.E.'s for the $S[X(CH_3)_3]_2$ series are collected in Fig. 2 and Table 2 respectively.

Assuming Koopmans's approximation to be valid, the assignment of the spectra can be made once the molecular orbital description of the electronic structures is available. As usual, this is, to a first approximation, obtained by regarding the MO's as formed by semilocalized group orbitals [16]: sulfur lone pairs, SX_2, S—X, S—C, XC_3, CH_3 and X *d* orbitals. The $CH_3SX(CH_3)_3$ and $S[X(CH_3)_3]_2$ molecules are assumed to have C_s and C_{2v} symmetry, respectively.

The band at lowest I.E. in each molecule can be assigned to the sulfur lone pair $n\pi$. This follows from a comparison [7] with the first I.E.'s of the $X(CH_3)_4$ series, and is in agreement with the assignment reported [17,18] for the $S(XH_3)_2$ and $HSCH_3$ (X = C, Si and Ge). The absolute I.E. values of this band

TABLE 1

IONIZATION ENERGY DATA (eV) FOR THE CH_3—S—$X(CH_3)_3$ DERIVATIVES

	S $n\pi$	S—X		XC_3		C—S	$(CH_3)_3$
C	8.38	10.46 11.4					
Si	8.69	10.1		10.7		12.2	13.7
Ge	8.50	9.9		10.5		12.1	13.9
Sn	8.37	9.55	9.9		10.2	12.0	13.8
Pb	8.13	9.0	9.36		10.06	11.8	13.9

TABLE 2

IONIZATION ENERGY DATA (eV) FOR THE $S[X(CH_3)_3]_2$ DERIVATIVES

	S $n\pi$	SX_2		XC_3				$(CH_3)_3$
C	8.18	9.98	10.50					
Si	8.74	9.74	10.26	10.7		11.1		13.7
Ge	8.40	9.40	9.80	10.3		10.6		13.6
Sn	8.22	9.05	9.36	9.7		10.2		13.6
Pb	7.78	8.44	8.83	9.15	9.45	9.84	10.13	13.4

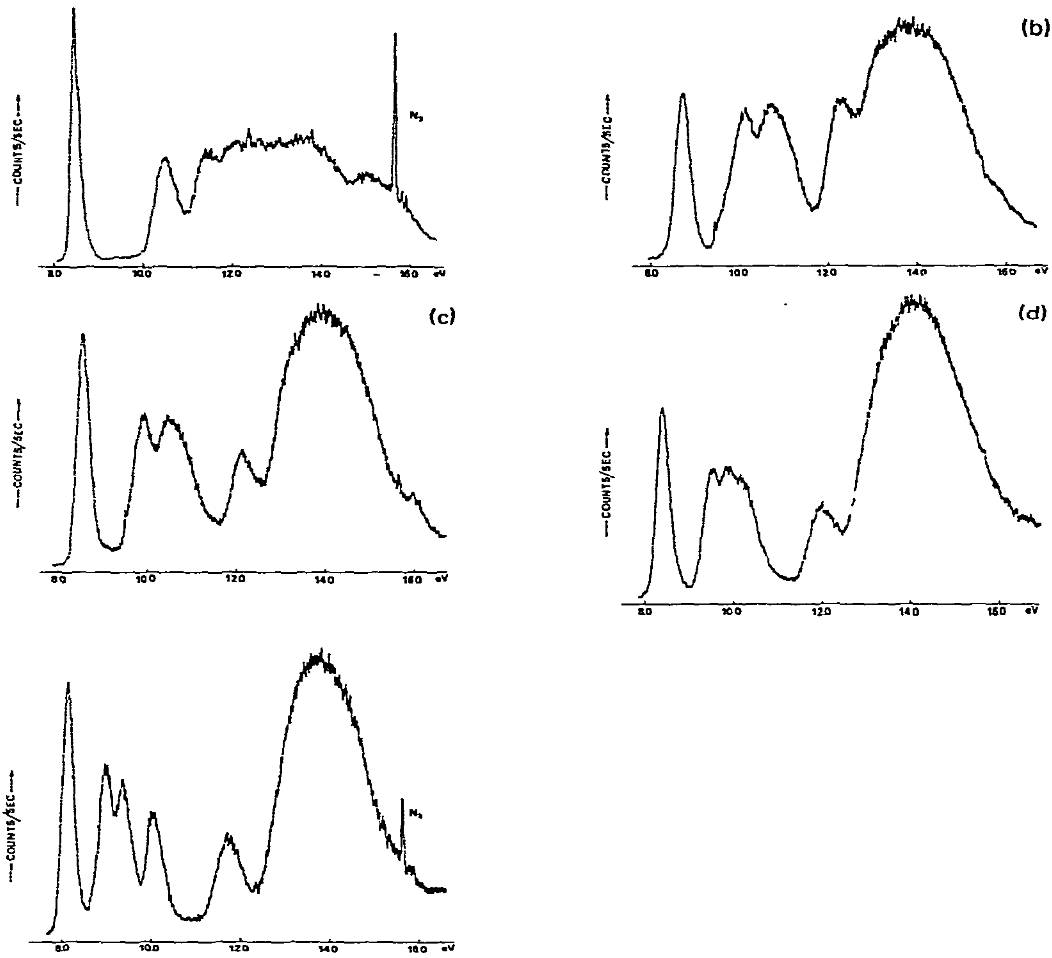

Fig. 1. The He(I) photoelectron spectra of CH_3—S—X(CH_3) derivatives. From (a) to (e) X = C, Si, Ge, Sn and Pb, respectively.

as well as its shape (relative intensity and FWHM) indicate that electronic interactions with the rest of the molecule are present.

The sulfur $n\pi$ orbital can interact by symmetry with the XC_3 [and CH_3 in CH_3—S—X(CH_3)$_3$] group orbitals (hyperconjugation) and with the *d* orbitals of X [(*p*—*d*)π interaction] *. The hyperconjugative interaction destabilizes the sulfur lone pair, while the (*p*—*d*)π bonding increases its I.E. The variation of the electrostatic effects of the X(CH_3)$_3$ groups should also influence the I.E. values. If we take the electronegativity [19] of X as a relative measure of the inductive effect of the X(CH_3)$_3$ group, no simple relationship is found between I.E.'s and electronegativity, so that the trend of the I.E.'s observed is not governed by this factor alone.

The hyperconjugative interaction should decrease with increasing distance

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* The (CH_3)$_3$ groups are considered to be too far from the sulfur to interact with its lone pair.

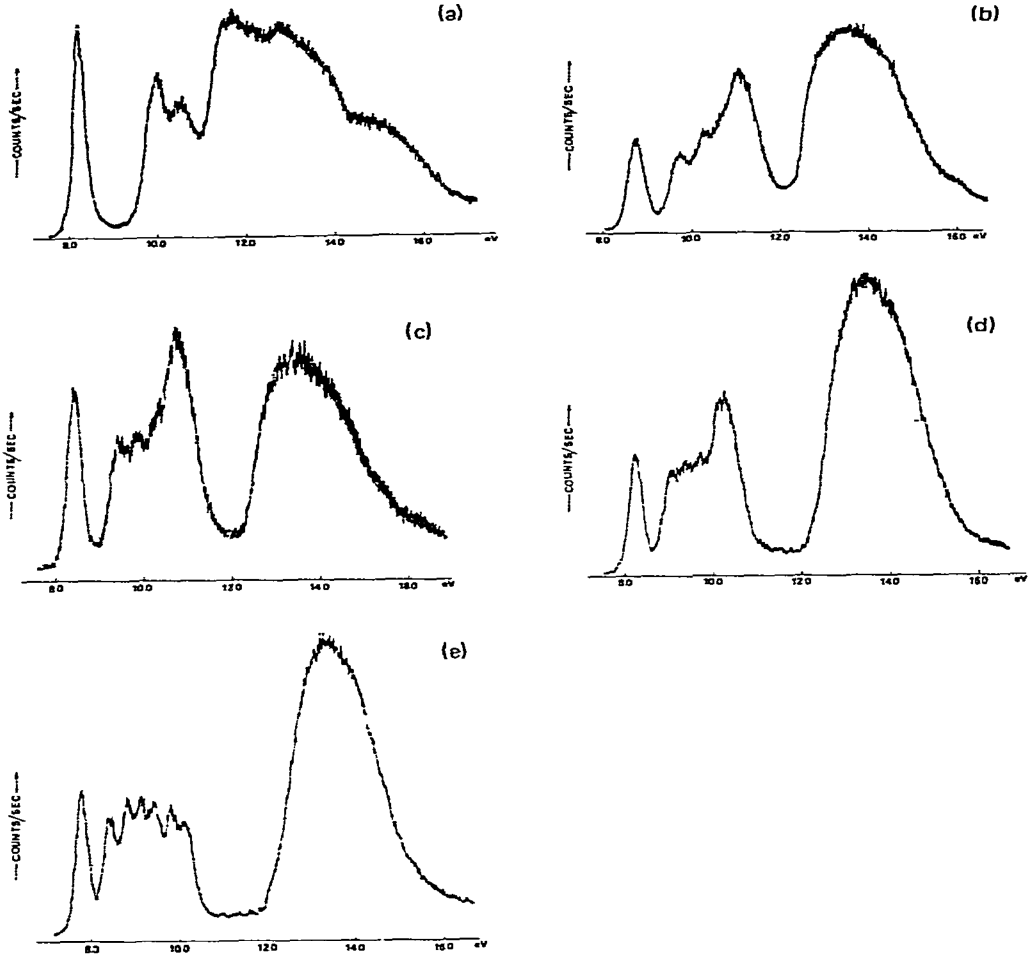

Fig. 2. The He(I) photoelectron spectra of $S[X(CH_3)_3]_2$ derivatives. From (a) to (e) X = C, Si, Ge, Sn and Pb, respectively.

between the sulfur lone pair and the orbitals mainly localized in the XC_3 (and CH_3) group; that is, on going from C to Pb [3]. On the other hand it should increase in the same direction because of the reduction of the energy difference between the interacting orbitals. The interplay of these two factors should give minimum I.E. values of the first band at the ends of the series.

Similarly, since the overlap between the sulfur lone pair and the atomic *d* orbitals of X is expected to be minimum when X = C and maximum for X = Si, (same principal quantum number), and to decrease gradually down the series, the first I.E. should show a maximum for X = Si if $(p\text{—}d)\pi$ bonding predominates, and such a maximum is, indeed, observed.

The comparison between the first I.E. of the $CH_3SX(CH_3)_3$ and $S[X(CH_3)_3]_2$ series allows a more precise analysis of the relative importance of the three electronic effects present.

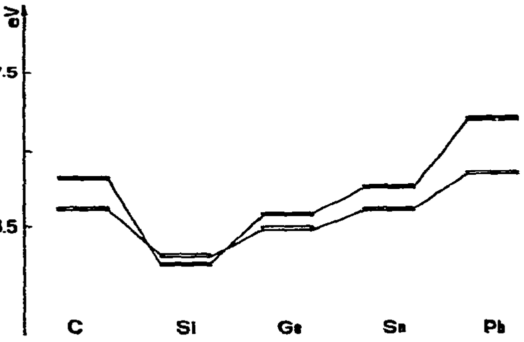

Fig. 3. Comparison between the energies of the sulfur $n\pi$ MO (eV): ▭ CH_3—S—$X(CH_3)_3$, ■ $S[X(CH_3)_3]$;

The substitution of CH_3 for $C(CH_3)_3$ increases the I.E. by 0.2 eV (see Tables 1 and 2), and moreover the sulfur lone pair becomes much sharper even if it does not have a typical non-bonding shape. These results are in agreement with the presence of hyperconjugative effects in both molecules, and indicate a reduction of this interaction in the methyl derivative [20]. The higher I.E. of the $\sigma\pi$ orbital of the CH_3 group with respect to that of the CC_3 group is at the origin of the observed variations.

Since the I.E.'s of the X—C orbitals are lower than those of the C—C and C—H orbitals, an even larger stabilization of the first I.E. is expected on substitution of CH_3 for $X(CH_3)_3$. A small destabilization is in fact obtained for the silicon derivative, while on going from germanium to lead an increasing stabilization is observed (see Fig. 3). This sequence suggests that the most important interaction between the sulfur $n\pi$ orbital and silicon is the $(p$—$d)\pi$ one, while the $+I$ effect of the $Pb(CH_3)_3$ group (lead electronegativity 1.55 [19]) and for hyperconjugation predominates in the heaviest compounds. In the Ge and Sn compounds there is no evidence for the predominance of one of the three electronic effects. They are probably all of comparable importance in the Ge and Sn compounds, since they should gradually change along the series*. This is confirmed by the plot of the first I.E. of $S[X(CH_3)_3]_2$ vs. that of the CH_3—S—$X(CH_3)_3$ (linear trend and slope greater than one). The same effect is noted when the first I.E.'s [17] of $S(XH_3)_2$ are plotted against those of H—S—XH_3.

The broad intense band centered between 13.4 and 13.9 eV for all the compounds except the two carbon derivatives, can be assigned with confidence to electrons coming from MO's localized in the CH_3 groups attached to the X atom. Its energy is in fact very similar to those reported [21,22] in closely related compounds such as $X(CH_3)_4$. The sharp band which moves from 12.2 to 11.8 eV in the spectra of CH_3—S—$X(CH_3)_3$ on going down the series is assigned to the C—S orbital, because: (a) it appears at an energy very close to the average of those of the corresponding orbitals in $S(CH_3)_2$ [17,18]; (b) the effect of X on this band (0.4 eV) is smaller than that on the lone pair band (0.56 eV) and on the S—X band (1.1 eV, see Table 1); (c) there is no band of this energy in the spectra of the symmetric derivatives.

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* It is to be noted that, as Pitt has recently pointed out [4], $(p$—$d)\pi$ conjugation cannot a priori be separated from hyperconjugation. Low lying d orbitals on X will mix with the $\sigma(XC_3)$ orbitals so that the parentage of the occupied σ-MO's and of the unoccupied MO's will determine the nature of the interaction with the sulfur lone pair.

As for the group of bands between 9.5 ± 0.5 and 10.5 ± 0.5 eV (see Table 1), they can be assigned to the X—S and two* XC_3 $\sigma\pi$ MO's. The two XC_3 orbitals are to a first approximation degenerate. We assign the second band in the spectra of Si, Ge and Sn derivatives to the X—S orbital. The next band is broader, with a larger area, and appears partially split in the Sn derivative. It is assigned to the two XC_3 orbitals. In agreement with this assignment and the increasing spin—orbit coupling, the spectrum of the lead derivative shows three distinct bands in this region. The observed spin—orbit splitting in this compound (0.70 eV) is to be compared with a multiplet separation of 0.9 [21] to 0.65 [22] eV found in the $Pb(CH_3)_4$ and with 0.72 eV in $Pb[CH_2Si(CH_3)_3]_4$ [23]. On the basis of the preceding discussion, we expect in the photoelectron spectra of the $S[X(CH_3)_3]_2$ six bands between the sulfur lone pair and the CH_3 envelope. In particular they can be ascribed to two orbitals of a_1 and b_2 symmetry mainly localized in the SX_2 group and to four orbitals ($a_1 + a_2 + b_1 + b_2$) mainly localized in the two XC_3 groups.

In this region it is possible to distinguish three bands (or shoulders) of similar intensities and a fourth one much higher and broader. The area of the latter is nearly equal to that of the three smaller peaks suggesting that, as expected, six orbitals contribute to this part of the spectrum.

The similarity of the intensity and energy patterns of the spectra of $S[X(CH_3)_3]_2$ and $S[XH_3]_2$ suggest that the second and third bands in the spectra of $S[X(CH_3)_3]_2$ should be assigned to the SX_2 orbitals of a_1 and b_2 symmetry, respectively, the major difference in these two series being the usual [24] compression of corresponding orbitals occurring in the more complex molecules. The sequence I.E.(SX_2) < I.E. (XC_3) is in agreement with the conclusion reached for the CH_3—S—$X(CH_3)_3$ series.

Acknowledgement

S.P. thanks C.N.R. (Roma) for financial support.

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* The third XC_3 MO is at higher energy, and is probably masked by the broad CH_3 envelope.

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