Journal of Organometallic Chemistry, 117 (1976) 141—148

PHOTOELECTRON He(I) SPECTRA OF SMALL SILANES

L. SZEPES

Eötvös Loránd University, Institute for General and Inorganic Chemistry, Budapest VIII Múseum Körút 6,8 (Hungary)

G. NARAY-SZABO *

Chinoin Pharmaceutical and Chemical Works, Budapest (Hungary)

F.P. COLONNA and G. DISTEFANO *

Laboratorio dei composti del carbonio contenenti eteroatomi e loro applicazioni del C.N.R., Via Tolara di Sotto, 89 - Ozzano Emilia, Bologna (Italy)

(Received March 19th, 1976)

Summary

The photoelectron He(I) spectra of methyl-, dimethyl-, trimethyl- and ethylsilane are reported and assigned with the help of CNDO/2 calculations.

For each silane the ordering of the valence MO's obtained from calculations is, very close to that of the corresponding alkane, and is in agreement with spectral evidence. Participation of silicon *d* orbitals in bonding is not substantial but is more important in the outermost Si—C and Si—H MO's than in the π MO's mainly localized on the alkyl groups.

Introduction

The He(I) photoelectron (pe) spectra of small alkanes have been reported by several authors [1] and the ionization energy (IE) values have been related to the corresponding MO's on the basis of theoretical approaches at various levels. More recently, Murrell and Schimdt [2] have reported the pe spectra of the series $CH_{4-n}(CH_3)_n$ and have discussed their energy level trends in terms of ab initio SCF calculations and an "equivalent orbital" treatment. By contrast, few simple silanes such as SiH_4 and $SiMe_4$ have been examined untill now by photoelectron spectroscopy.

In this note we present the pe spectra and CNDO/2 calculations of methyl-, dimethyl-, trimethyl- and ethyl-silane in order to compare the energy level

---

* Working as a guest at the Quantum Theory Group, Physical Institute, Politechnical University, Budapest (Hungary).

patterns with those of the corresponding alkanes and to analyse the involvement of silicon *d* orbitals in bonding in this class of compounds.

Four papers [3—6] have recently been published in which the electron spectrum (He(I) or X-ray) of $SiMe_4$ is reported and assigned on the basis of semiempirical calculations or in terms of localized bond orbitals. Although there is general agreement regarding the ordering and the energy of the various valence MO's, the problem of the involvement of the silicon *d* orbitals in bonding is still open: according to Jonas et al. [3] this involvement is important, Perry and Jolly [4] say that it is not substantial, Boschi et al. [5] claim that it is absent, while Evans et al. [6] do not mention it.

Experimental

The compounds were prepared by standard mehtods [7,8] and purified by vacuum distillation. The pe spectra were recorded on a Perkin—Elmer PS 18 photoelectron spectrometer and calibrated against argon and xenon lines. The accuracy of the experimental IE values is estimated to be ±0.05 or ±0.1 eV as indicated by the number of decimals quoted in the tables.

Results and discussion

Fig. 1 shows the pe spectra of the studied compounds. The experimental and theoretical (CNDO/2) [9] IE values are listed in Tables 1—3 together with those of the related hydrocarbons. The experimental data for alkanes are taken from literature [1a, 1d, 2].

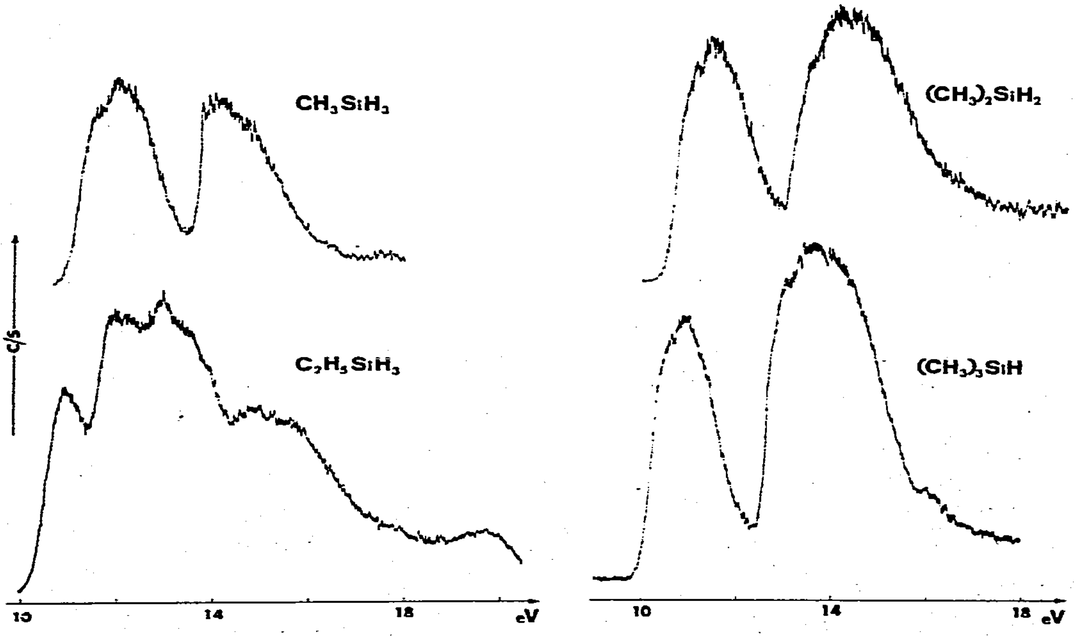

Fig. 1. Photoelectron He(I) spectra of small silanes.

TABLE 1

EXPERIMENTAL AND THEORETICAL IONIZATION ENERGIES (eV) FOR ETHANE AND METHYLSILANE.

Ethane (D_{3d})			Methylsilane (C_{3v})				
Species	Exp.	CNDO/2	Species	Exp.	CNDO/2		Exp. [a]
					sp	spd	
$3a_{1g}$	12.1	16.5	$4a_1$	11.61	14.4	15.2	11.03
$1e_g$	13.0	18.2	$2e$	12.2 [b]	14.5	15.4	12.1
$1e_u$	15.4	23.4	$1e$	14.4 [b]	20.5	21.1	13.1
$2a_{2u}$		29.2	$3a_1$	16.4	21.2	21.0 [c]	17.49
$2a_{1g}$		40.0	$2a_1$		34.5	35.3	22.8

[a] Valence bands from the ESCA spectrum [3]. [b] Mean of the Jahn—Teller split band. [c] Incorrect order, see text.

The assignment of the spectra on the basis of spectral features is hampered by the absence of vibrational structure and by the presence of overlapped bands. On the other hand, it as been found that in XH_4 [10], XMe_4[[3—6] and $CH_2{=}CHXR_3$ [11] (X = C or Si) a close correspondence exists between the MO energies of silanes and hydrocarbons and that the orbital energies of corresponding MO's lie highest in silanes than in hydrocarbons. These findings are useful for assignment purposes.

To make the assignment of the pe spectra easier, CNDO/2 quantum chemical calculations with standard molecular geometries [12] were performed with both an *sp* and an *spd* basis set. It is known that even if this method does not give reasonable values for the orbital energies and tends to overestimate *d* orbital participation in bonding [13], it can, nevertheless be useful when series of related compounds are analyzed [1c, 14].

The computed IE values (in the Koopmans approximation [15]) are higher (3—9 eV) than the experimental data and the two sets of figures are related by

TABLE 2

EXPERIMENTAL AND THEORETICAL IONIZATION ENERGIES (eV) FOR PROPANE, DIMETHYLSILANE AND ETHYLSILANE

Propane (C_{2v})			Dimethylsilane (C_{2v})			Ethylsilane (C_s)			
Species	Exp.	CNDO/2	Exp.	CNDO/2		Species	Exp.	CNDO/2	
				sp	spd			sp	spd
$4b_1$	11.5	15.7	11.2	13.8	14.5	$10a'$	10.95	12.9	13.6
$6a_1$	12.1	15.9	11.5	13.9	14.8	$9a'$	11.9	14.6	15.5
$2b_2$	12.7	15.6 [a]	11.8	14.0	15.0	$3a''$	12.2	14.4 [a]	15.4 [a]
$1a_2$	13.5	18.9	13.7	19.2	20.0	$2a''$	12.9	16.9	17.2
$3b_1$	14.1	20.5	14.2	19.5	19.4 [a]	$8a'$	13.4	18.0	18.3
$5a_1$	15.3	23.2	14.8	20.3	20.1	$7a'$	13.8	19.9	20.0
$1b_2$	16.0	25.6	16.1	21.5	21.4	$1a''$	14.6	24.0	24.6
$4a_1$		28.4		21.4 [a]	21.9	$6a'$	15.4	23.8 [a]	24.1 [a]
$2b_1$		33.8		33.1	34.0	$5a'$	19.5	29.0	29.7
$3a_1$		43.6		35.6	35.7	$4a'$		40.6	41.5

[a] Incorrect order, see text

TABLE 3

EXPERIMENTAL AND THEORETICAL IONIZATION ENERGIES (eV) FOR ISOBUTANE AND TRIMETHYLSILANE

Isobutane (C_{3v})			Trimethylsilane (C_{3v})		
Species	Exp.	CNDO/2	Exp.	CNDO/2	
				sp	*spd*
$5e$	11.4	15.0	10.7 [a]	13.4	14.1
$6a_1$	12.1	14.9	11.0	13.6	14.4
$1a_2$	12.8	17.0	12.8	18.4	17.8
$4e$	13.4	19.7	13.1	19.4	19.3
$3e$	14.9	22.8	13.6	20.9	21.9 [b]
$5a_1$	16.0	24.6		19.8 [b]	19.4
$4a_1$		28.5	16.1	22.3	21.6
$2e$		34.8		33.4	33.7
$3a_1$		46.5		37.0	36.5

[a] Mean of a Jahn—Teller split band. [b] Incorrect order, see text.

a satisfactory linear correlation ($I_{\text{exp}} = 0.49\, I_{\text{CNDO}} + 4.38$, correlation coefficient = 0.94; for alkanes and silanes; *sp* basis set calculations).

The ordering of the MO's of silanes obtained by CNDO/2 calculations is, for each of the derivatives, very close to that of the corresponding hydrocarbons (where the silicon atom has been substituted by a carbon atom) obtained by the same method. Furthermore, the CNDO/2 MO orderings for alkanes closely correspond to those obtained by Murell and Schimdt [2] on the basis of abinitio calculations and an "equivalent orbital" treatment. Few exceptions to these parallelisms have been observed and these are marked as footnotes in the tables. The inversions generally occur between nearly degenerate orbitals. Also in the present case, the orbital energies belonging to the same species lie higher in silanes than in alkanes. The orbital shapes, as obtained from the *sp* basis set calculations, are shown in Fig. 2 where partial energy level diagrams, obtained from pes measurements, are also presented. Using these, comparisons among related compounds can be made easily. A general feature of the orbital of the silanes considered is that the hydrogens attached to the silicon atom in most cases take little part in bonding (compared to the corresponding hydrocarbons). This is probably due to the longer Si—H bond length [12] (1.48 Å) as compared to C—H (1.09 Å).

Qualitative agreement has been found between computations and experimental evidence for silanes. In particular the following observations can be made:

(a) The first band in the spectrum of Me_3SiH peaks at 11.0 eV and shows two poorly resolved shoulders at 10.7 and 11.3 eV. According to calculations this band corresponds to the doubly degenerate $5e$ MO's and to the $6a_1$ MO localized on the C—Si bonds. The appearance of three components suggests that the $5e$ MO's undergo Jahn—Teller splitting. The similarity of the shape of this band with the first part of the spectrum of isobutane [2] confirms this hypothesis. In the latter compound the Jahn—Teller splitting is about 0.45 eV; in the related series XMe_4 (X = C, Si, Ge, Sn and Pb) the Jahn—Teller splitting decreases by increasing the size of the central atom [3,5]: in particular it is 0.4 eV in neopentane and 0.3 eV in tetramethylsilane. So that, assuming a splitting of 0.3 also in

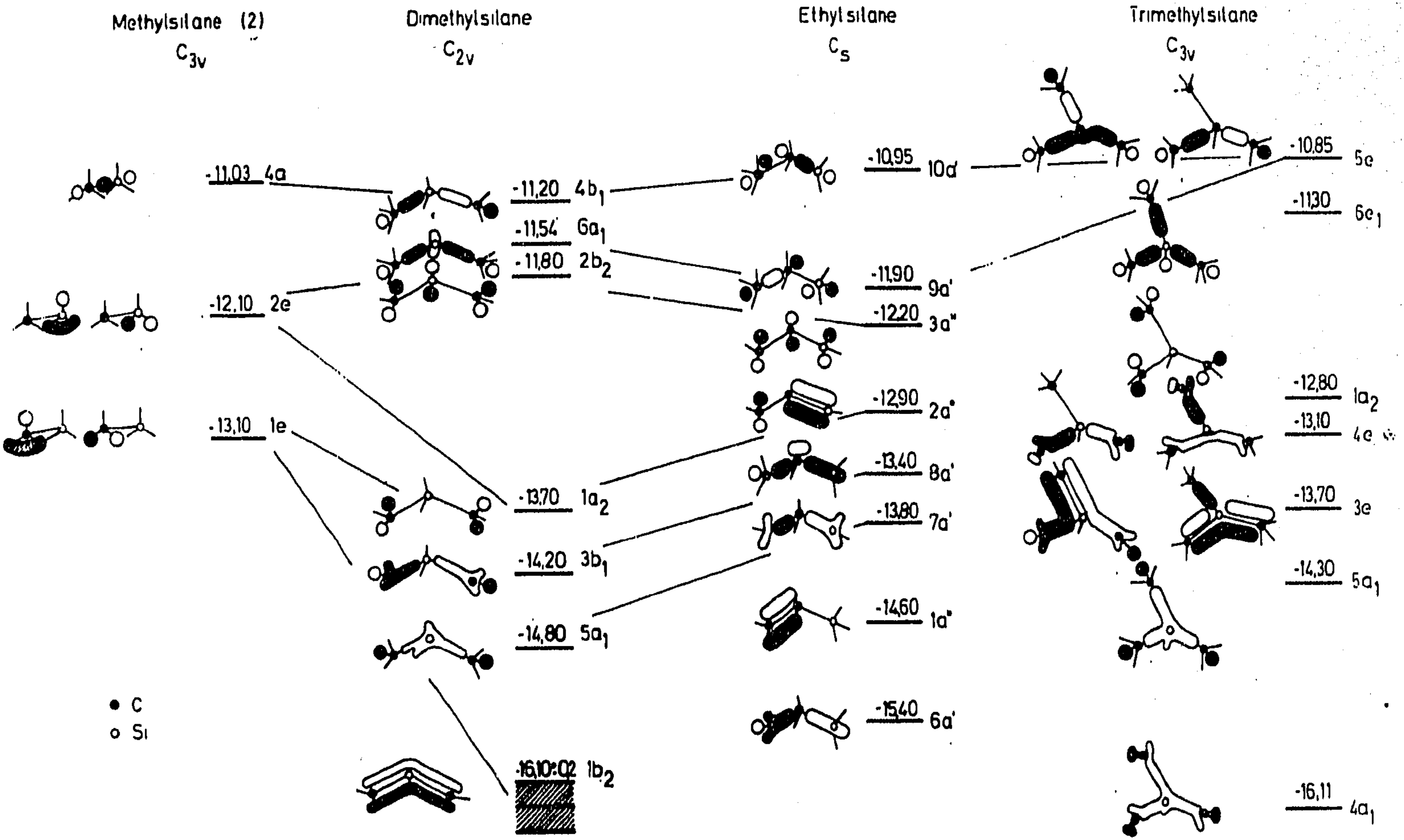

Fig. 2. Molecular orbitals correlation diagram for small silanes as obtained from pe measurements. The orbital shapes (CNDO/2) are also shown. In these sketches the atomic orbitals with coefficients smaller than 0.25 are omitted for reason of clarity.

Me_3SiH, it is possible to assign the 10.7 and 11.0 eV values to the split 5*e* MO's and the 11.3 eV value to the $6a_1$ MO. At higher IEs the pe spectrum shows an intense and broad band between 12.5 and 15.5 eV and a small peak at 16.1 eV. The broad band exhibits badly resolved fine structure (12.8, 13.1, 13.7 and 14.3 eV) and can be related to ionization from $1a_2$, 4*e*, 3*e* and $5a_1$ MO's, the small band at 16.1 eV is assigned to the $4a_1$ MO.

(b) The spectrum of Me_2SiH shows two broad bands centred at about 11.5 and 14.5 eV. The first band has two shoulders at 11.2 and 11.8 eV; the second one, more intense and broad, shows structures at 13.7, 14.2, 14.8 and probably 16.1 eV. The computed eigenvalues can also be divided into groups: $4b_1$, $6a_1$ and $2b_2$ MO's are nearly degenerate at 13.8—14.0 eV (*sp* basis set): $1a_2$, $3b_1$, $5a_1$, $1b_2$ and $4a_1$ MO's have energy values between 19.2 and 21.5 eV; while $2b_1$ and $3a_1$ MO's results to be at 33.1 and 35.6 eV respectively. It is then possible to relate the two bands of the spectrum to the first two groups of eigenvalues.

(c) The spectrum of $EtSiH_3$ shows eight peaks or shoulder between 10.95 and 15.4 eV and a small inflexion of the base line at about 19.5 eV. These features correspond to the first nine valence MO's (see Table 2) the tenth ($4a'$) being outside the He(I) range.

(d) The spectrum of $MeSiH_3$ looks very similar to that of ethane [1a]: the first band is partially split into three components (peaking at 11.61, 12.0 and 12.4 eV) and the second one into two (14.2 and 14.7 eV). Both of the two degenerate orbitals 2*e* and 1*e* should be susceptible to splitting by Jahn—Teller forces in the ion so that the spectrum can be easily rationalized. Calculations indicate that the $4a_1$ and 2*e* MO's are the uppermost levels and are close in enrgy. They are therefore related to hte first band. The Jahn—Teller splitting, ≃0.4 eV, is smaller than in ethane, 0.6—0.7, (inferred from Fig. 6.2 of Ref. [1a]). The second band (1*e*) shows a 0.5 eV splitting as in the $1e_u$ band of ethane in agreement with the mainly carbon character fo the orbital. The small shoulder on the high IE side for the second band (~16.4 eV) could correspond to the $3a_1$ MO. Its low cross section is in agrrement with the low intensity reported [3,6] for other MO's mainly formed from Si 3*s* orbitals. The MO ordering obtained for this compound from CNDO/2 computations in the same as those previously obtained from EHT [4] and abinitio [16] calculations. However, some discrepancies exist exist between the present set of experimental IE values and those obtained from X-ray pe spectroscopy by Perry and Jolly [4] (see Table 1).

Silicon d orbitals

Two types of information about the silicon *d* orbital can be obtained from CNDO calculations: (i) atomic orbital coefficients and (ii) *d* orbital effect on the MO energies.

(i) The orbital percentages of the various MO's are generally small except for one or two of the outermost MO's which have 10—12 percent of *d* orbital character;

(ii) Using an *spd* basis set a slight lowering of the MO energies is generally boserved (see tables) and this lowering is greater for the MO's which have the largest *d* orbital character.

In view of the low *d* orbital percentage and the small effect on the orbital energies, it is possible to conclude, in agreement with Perry and Jolly [4], htat *d* orbital participation in bonding is not substantial in alkylsilanes.

Lastly we note that p_π—d_π interaction between empty *d* orbitals of silicon and adjacent orbitals (mainly localized an halogens [17], heteroatoms [18,19], benzene ring [20] or ethylenic double bond [11,21,22]) has been often invoked to explain features of the spectra such as IE values and the shape of photoelectron bands. In the present case, the MO's which have the highest *d* orbital percentages are localized on the Si—C and Si—H bonds while *d* orbitals are nearly absent in the MO of π symmetry mainly localized on the alkyl groups.

References

1 See e.g.(a)D.W. Turner, C. Baker A.D. Baker and C.R. Brundle, Molecular Photoelectron Spectroscopy, Wiley—Interscience, London, 1970; (b) C.R. Brundle and M.B. Robin, in F.C. Nachod and J.J. Zuchermann (Ed.), Determination of Organic Structures by Physical Methods, Academic Press, New York, 1971, Vol. III; (c) S.D. Worley, Chem. Rev., 71 (1971) 295; (d) A.D. Baker, C. Baker, C.R. Brundle and D.W. Turner, Int. J. Mass Spectr. Ion. Phys., 1 (1968) 285; (e) A.D. Baker, D. Betteridge, N.R. Kemp and R.E. Kirby, J. Mol. Struct., 8 (1971) 75.
2 J.N. Murell and W. Schimdt, J. Chem. Soc. Faraday II (1972), 1709.
3 A.E. Jonas, G.K. Schweitzer, F.A. Grimm and T.A. Carlson, J. Electr. Spectr., 1 (1972/73) 29.
4 W.B. Perry and W.L. Jolly, J. Electr. Spectr., 4 (1974) 219.
5 R. Boschi, M.F. Lappert, J.B. Pedley, W. Schimdt and B.T. Wilkins, J. Organometal. Chem., 50 (1973) 69.
6 S. Evans, J.C. Green, P.J. Joachim, A.F. Orchard, D.W. Turner and J.P. Maier, J. Chem. Soc. Faraday II, (1972) 905.
7 S. Tannenbaum, S. Kaye and G.F. Lewenz, J. Amer. Chem. Soc., 75 (1953) 3753.
8 A.D. Norman, J.R. Webster and W.L. Jolly, Inorg. Synth, 11 (1968) 170.
9 J.A. Pople and D.L. Beveridge, Approximate Molecular Orbital Theory, McGraw, New York, 1971.
10 A.W. Potts and W.C. Price, Proc. Roy. Soc., (London) A, 326 (1972) 165.
11 U. Weider and A Schweig, J. Organometal. Chem., 39 (1972) 261.
12 L.E. Sutton, Table of Interatomic Distances, The Chemical Society, Burlington House, London, 1958.
13 J.A. Pople and M. Gordon, J. Amer. Chem. Soc., 89 (1967) 4253.
14 See e.g. (a) H. Ogata, H. Onizura, Y. Nihei and H. Kamada, Bull. Chem. Soc. Japan, 46 (1973) 3036; (b) A. Katrib and J.W. Rabalais, J. Phys. Chem., 77 (1973) 2358; (c) I. Watanabe, Y. Yokoyama and S. Ikeda, Bull. Soc. Chem. Japan, 46 (1973) 1959.
15 T. Koopmans, Physica, 1 (1934) 104.
16 D.H. Liskow and H. Schaefer, J. Amer. Chem. Soc., 94 (1972) 6641.
17 S. Cradock and R.A. Whiteford, Trans. Faraday Soc., 67 (1971) 3425.
18 H. Bock, P. Mollère, G. Becker and G. Fritz, J. Organometal. Chem., 61 (1973) 113.
19 G. Distefano, A. Ricci, F.P. Colonna and D. Pietropaolo, J. Organometal. Chem., 78 (1974) 93.
20 G. Distefano, S. Pignataro, A. Ricci, F.P. Colonna and D. Pietropaolo, Ann. Chim., 64 (1974) 153.
21 P. Mollère, H. Bock, G. Becher and G. Fritz, J. Organometal. Chem., 46 (1972) 89.
22 M. Horn and J.N. Murell, J. Organometal. Chem, 70 (1974) 51.