Theoret. chim. Acta (Berl.) 25, 396—399 (1972)

Relationes

The Electronic Structure of the Silyl Halides

D. R. ARMSTRONG, J. JAMIESON, and P. G. PERKINS
Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, C. 1, Scotland

Received December 3, 1971

Calculations have been performed on the silyl and methyl halides, using the CNDO method and the photoelectron spectra of the silyl halides are interpreted from the results. Inclusion of *d* orbitals on silicon is found to be necessary so that the calculated ionisation potentials of silyl bromide and chloride are greater than the corresponding methyl compounds, in agreement with observation.

Introduction

A recent publication by Cradock and Ebsworth dealing with the photoelectron spectra of the silyl halides [3] gave the observed band positions for electrons believed to be excited from the halogen "lone pair" orbitals orthogonal to the Si–X axis. The authors concluded, moreover, from the presence of vibrational bands in the photoelectron spectra, that there is bonding between these lone pair halogen electrons and the silicon 3*d* orbitals. However, an *ab initio* calculation on SiH_3F [2] has suggested that the first ionisation potential should occur at a much lower energy than that reported in Ref. [3], and it therefore seemed of interest to calculate the electronic structure of the silyl halides, SiH_3F, SiH_3Cl and SiH_3Br, to examine the nature of the molecular orbitals which give rise to the photoelectron spectra, and to evaluate the extent of the postulated $(d_\pi - p_\pi)$ π-bonding.

Our method of calculation used a modified [1] version of the CNDO/2 method [5]. The parameters used in the calculation were taken from previous work [4] and the relevant interatomic distances were abstracted from Ref. [6].

The parameter k used in the construction of the offdiagonal elements of the H matrix

$$H_{\mu\nu} = k S_{\mu\nu} (I_\mu I_\nu)^{\frac{1}{2}}$$

was varied in the calculations on silyl fluoride so as to obtain a set of eigenvalues comparable with the eigenvalues given by the *ab initio* calculation [2].

Results and Discussion

Calculations were attempted on silyl fluoride using a wide range of k values, and we found that in no case did the energy of the highest filled molecular orbital approach the value quoted (16.1 eV) by Cradock and Ebsworth. However, the

Table 1. Valence orbital eigenvalues (eV) for silyl and methyl halides

Eigenvalue	1	2	3, 4		5		6, 7
CH_3F	−45.41	−31.15	−19.48		−13.98		−12.75
SiH_3F	−40.43	−24.83	−16.76		−12.34		−12.33
SiH_3F[a]	−39.52	−24.68	−16.66	$\Psi_{5,6}$	−11.66	Ψ_7	−11.50
CH_3Cl	−41.30	−24.68	−20.23		−12.41		−10.77
SiH_3Cl	−32.77	−25.26	−17.47		−12.14		−11.30
SiH_3Cl[a]	−32.61	−24.27	−17.60		−11.24		−10.11
CH_3Br	−37.16	−23.97	−18.47		−11.73		−10.27
SiH_3Br	−29.78	−24.77	−16.62		−11.46		−10.95
SiH_3Br[a]	−29.45	−23.36	−16.21		−10.18		− 9.75

[a] Without *d* orbitals on silicon.

Table 2. Experimental lone pair ionisation potentials (eV) for silyl and methyl halides

Halide	Methyl[a]	Silyl[b]
fluoride	17.0	16.1
chloride	11.28	11.61
bromide	10.70	11.03

[a] Ref. [7]. – [b] Ref. [3].

latter quantity correlated well in energy with the third and fourth molecular orbitals (a degenerate bonding pair). These have some halogen lone pair character (see later). Our finding also agreed with the *ab initio* work of Ref. [2] when a value of $k = 1.15$ was chosen.

Using this k value of 1.15, calculations were next performed on the silyl and methyl halides, both including and neglecting the silicon 3*d* orbitals. The eigenvalues and the experimental ionisation potentials assigned to the "lone pair" electrons are given in Table 1 and 2 respectively. From these values it can readily be seen that the experimental "lone pair" ionisation potentials correlate with the energies of molecular orbitals 3 and 4 for both methyl and silyl fluoride, whilst for the chloride and bromide they correspond to the 6th and 7th eigenvalues. Both these pairs are degenerate and examination of their eigenvector elements (Table 3) reveals that orbitals 3 and 4 are bonding in nature while the 6th and 7th are antibonding orbitals orthogonal to the Si–X axis. Table 3 shows that on going from the fluoride to the bromide the contribution of the halogen "π" orbitals to the bonding orbital decreases whereas it increases in the antibonding orbital. The LCAO MO approach which we have used no doubt somewhat overestimates the conjugation of these halogen lone pairs but some delocalisation certainly occurs and the degenerate orbitals incorporate substantial amounts of the halogen "$p\pi$" orbital. Moreover, the calculations show that the energies of the 6th and 7th orbitals show only a gradual trend over the halide series and, therefore, a band at 12.3 eV should be expected in the photoelectron spectrum of silyl fluoride having characteristics similar to those of the bromide and chloride.

Table 3. Atomic orbital coefficients for silicon and halogen p orbitals in the degenerate molecular orbitals of the silyl halides

Molecular orbital number	3		6	
	C(Si)	C(X)	C(Si)	C(X)
SiH_3F	0.62	0.59	0.26	0.84
SiH_3Cl	0.63	0.50	0.26	0.84
SiH_3Br	0.65	0.40	0.19	0.89

Table 4. Contribution to total bond order (%) of each type of π-bonding present in the methyl and silyl halides between carbon (silicon) and halogen

	$Mp\pi$–$Xp\pi$	$Mp\pi$–$Xd\pi$	$Md\pi$–$Xd\pi$	$Md\pi$–$Xp\pi$
CH_3F	7.1			
CH_3Cl	6.1	22.8		
CH_3Br	4.0	19.3		
SiH_3F	9.7			10.2
SiH_3Cl	7.5	14.2	0.5	17.1
SiH_3Br	6.7	11.9	0.3	18.2

An interesting aspect of the calculations is that for the chloro- and bromo-compounds the silyl derivative has a larger ionisation potential than the methyl halide only when d orbitals are included in the calculation. This agree with experiment and would seem to indicate that d orbitals are important in the bonding in silyl halides. The calculations also reveal the degree of each type of π-type bonding (i.e., involving d or p orbitals) present between silicon (carbon) and the particular halogen, and these data are given in Table 4. The $p\pi - d\pi$ and $d\pi - p\pi$ components of the bond order are numerically quite substantial, although it must be remembered that, physically, the important quantity is the bond energy and the $p\pi - d\pi$ and $d\pi - p\pi$ fractions of this term will certainly be much smaller.

Table 5. The overall charge distribution in the methyl and silyl halides

	M	X	H
SiH_3F	0.46	−0.31	−0.05
SiH_3Cl	0.21	−0.16	−0.02
SiH_3Br	0.16	−0.09	−0.02
CH_3F	0.14	−0.23	0.03
CH_3Cl	0.06	−0.23	0.06
CH_3Br	−0.02	−0.11	0.04

The overall charge distributions in all the halides are presented in Table 5. The results correlate with those expected from simple electronegativity principles, although the charge on chlorine in methyl chloride is somewhat anomalous and is clearly due to the *d* orbital occupancy of chlorine.

One of us (J.J.) thanks the Scottish Education Department for a Maintenance Grant.

References

1. Armstrong, D. R., Perkins, P. G., Stewart, J. J. P.: J. chem. Soc. (London) A (in press).
2. Breeze, A., Collins, G. A. D., Cruickshank, D. W. J.: J. chem. Soc. (London) D **1971**, 445.
3. Cradock, S., Ebsworth, E. A. V.: J. chem. Soc. (London) D **1971**, 57.
4. Levison, K., Perkins, P. G.: Theoret. chim. Acta (Berl.) **14**, 206 (1969).
5. Pople, J. A., Santry, D. P., Segal, G. A.: J. chem. Physics **43**, S 129 (1965).
6. Sutton, L. E.: Ed. Tables of interatomic distances and configurations in molecules and ions, Special Publication No. 11. London: The Chemical Society 1958.
7. Turner, D. W., Baker, C., Baker, A. D., Brundle, C. R.: Molecular photo-electron spectroscopy. London, New York, Sydney, and Toronto: Wiley Intersciences 1970.

Dr. D. R. Armstrong
Department of Pure and Applied Chemistry
University of Strathclyde
Glasgow, C. 1
Scotland