He(I) Photoelectron Spectra and Semiempirical Molecular-orbital Calculations on Methylmetal Halides of Group 4A Elements

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The photoelectron spectra of the compounds MMe_3X (M = C, Si, Ge, Sn, and Pb; X = Cl and Br) have been measured. An assignment of the spectra is proposed based on a comparison with spectra of the similar compounds MMe_4 and MXH_3 and on semiempirical CNDO calculations which have been extended to third-row elements.

THERE has been much interest in the organometallic compounds of Group 4A elements,[1] particularly in the bond between the Group 4A elements and the ligand. Evidence has been sought for the presence, or otherwise, of back donation from the ligand to the element M, when the ligand has available lone-pair electrons. Photoelectron (p.e.) spectroscopic techniques have been useful in this field and we first mention briefly the studies which have been made on molecules similar to those we describe.

For molecules of the type $MX_{4-n}H_n$ (M = C, Si, or Ge; X = F, Cl, or Br), the trend in the ionisation potentials (i.p.s) of the $2e$ orbitals (which refer to the halogen lone pairs) as a function of the halogen or of M is anomalous in the chloro- and bromo-derivatives. This has been interpreted as indicating that these lone pairs are involved in bonding with the central atom. The behaviour of the i.p.s of the other orbitals, $3a_1$ and $1e$, localised on the σ bonds M–X and M–H, is relatively regular as a function of the halogen and the element M. The fact that the i.p. behaviour of the $2e$ orbitals of the fluoro-derivatives is regular has been explained by assuming that, because of their high i.p., the lone pairs interact with the MH_3 σ orbitals of the same symmetry. This interaction is so strong that the lone pairs lose their own distinctive character and participate heavily in both the orbitals $2e$ and $1e$. The compounds MMe_4 (M = C, Si, Ge, Sn, and Pb) have also been studied previously using these techniques.[2]

By contrast, there has been virtually no work on molecules of the type MMe_3X. Only the spectrum of $SiMe_3Cl$ has been reported,[3] and this compound is re-examined here. We propose a spectral assignment which is different from the previous one; the previous workers did not take into account the contribution of the p_π orbitals of the chlorine atom. Although the spectrum of this compound has been also examined by other authors,[4-6] no assignments have been put forward.

In connection with previous work,[7] we report the p.e. spectra of a series of molecules of general formula MMe_3X (M = C, Si, Ge, Sn, and Pb; X = Cl and Br). The compound in this series which was not investigated is $GeBrMe_3$. The assignments proposed are based on comparisons with the spectra of the similar compounds mentioned above, and are supported by CNDO calculations on elements of the third Row of the Periodic Table. The aims of this work are: (*i*) to arrive at a more certain assignment of the spectra, by investigating as extensive a series of compounds as possible; (*ii*) to extract information on the participation, or otherwise, of the empty *d* orbitals of M in the M–X bond. (Evidence for such participation is available from electric dipole-moment measurements on the same compounds.[7])

EXPERIMENTAL

The compounds were prepared as reported previously.[7] P.e. spectra were recorded with a Perkin-Elmer PS 18 spectrometer.

RESULTS AND DISCUSSION

Table 1 lists the experimental i.p.s and those calculated *via* Koopmans' theorem[8] approximated by *ca.* 20% CNDO calculations, recently extended by us to third-row elements (Ge, As, Se, and Br),[9] were used, with a parametrisation reported in the literature.[10] This parametrisation gave satisfactory results especially for Ge.[9] To improve the parametrisation for Br, we modified its parameter β^0, giving it a value of 42 rather than 22 eV.* Using this new value, we have compared the theoretical with the experimental i.p.s for simple molecules (Figure 1). The agreement is satisfactory, especially if it is considered that the previous value for β^0 for the bromine derivative led to the first i.p. being of type a_1 rather than of type e.[9]

The total number of occupied valence molecular orbitals (m.o.s) is 16 for MMe_3X compounds, but the first four are predominantly $ns(2a_1)$ halogen and σ_{C-H} ($1a_1$, $1e$) in character and hence have energies too low to be involved in the ionisation. Hence only 12 occupied m.o.s. are involved in the ionisation in the range investigated. On the basis of the results obtained from the calculations, these orbitals may be subdivided into σ_{M-X}

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* 1 eV ≈ 1.60×10^{-19} J, 1 cal = 4.184 J.

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TABLE 1

Experimental vertical ionisation potentials (eV) and values calculated[a] by the CNDO method, and proposed assignments for $MMe_3X(C_{3v})$

	CMe_3Cl		$SiMe_3Cl$			$GeMe_3Cl$			$SnMe_3Cl$	$PbMe_3Cl$
Symmetry	calc.	exp.	calc.	calc.[b]	exp.[c]	calc.	calc.[b]	exp.	exp.	exp.
$5e$	12.25	10.76	11.10	10.86	10.76	11.64	11.86	10.35	10.16	9.70
$5a_1$	12.74	11.98	13.10	12.06		11.64	10.88	9.83	9.88	9.35
$4e$	14.86	12.15	15.78	14.73	12.00	14.85	14.10	11.76	11.33	10.60
$1a_2$	16.71	12.40	18.97	18.53		19.73	19.81			
$3e$	21.72	13.10	20.86	23.20	13.54	21.20	22.47	14.20	13.95	13.70
$4a_1$	24.93	14.03	23.00	22.54		22.50	22.27			
$2e$	25.08	15.57	23.14	25.87		23.32	25.60			
$3a_1$	27.00		23.80	24.98	15.95	23.96	24.79	16.65		15.75

	$CBrMe_3$		$SiBrMe_3$			$GeBrMe_3$	$SnBrMe_3$	$PbBrMe_3$
	calc.	exp.	calc.	calc.[b]	exp.	calc.	exp.	exp.
$5e$	12.06	10.05 10.28	10.35	9.87	10.23 10.43	11.58	9.60 9.85	9.30 9.55
$5a_1$	13.08	11.60	13.92	12.71	11.37	13.06	10.65	10.32
$4e$	15.00	12.17	16.79	15.17	11.63	15.92	10.85	10.61
$1a_2$	16.44	12.63	18.24	18.01		19.11		
$3e$	22.41	13.18	21.05	26.56	14.25	20.91	13.95	13.98
$2e$	24.85	13.88	23.12	27.05		23.00		
$4a_1$	25.73	15.55	23.63	23.23		23.24		
$3a_1$	26.85		24.65	25.05	16.05	24.31		15.60

[a] Bond lengths and angles from ' Tables of Interatomic Distances and Configurations in Molecules and Ions,' ed. L. E. Sutton, *Special Publ.*, No. 11, The Chemical Society, 1958. [b] Includes *d*-orbital participation. [c] From ref. 3.

$(5a_1)$, $Xp_\pi(5e)$, $\sigma_{M-C}(4e)$, $\sigma_{C-H}(a_2, 3e, 4a_1, 2e)$, and $\sigma_{C-M}(3a_1)$, and may be correlated with the five groups of bands observed in the spectra. The same assignment holds for various bromides, given the similarity of their spectra (Figure 2). The first band, split into two components separated by 0.20—0.25 eV, of which the first is the lower in intensity, is almost certainly due to the p_π lone pairs of the bromine atom, split by spin–orbit coupling as in the $MBrH_3$ analogues.[4] However, for the chloro-derivatives (in which we have also included the compound $SiMe_3Cl$ since our assignment differs from that suggested previously [3]) in the series C to Pb the $5a_1$

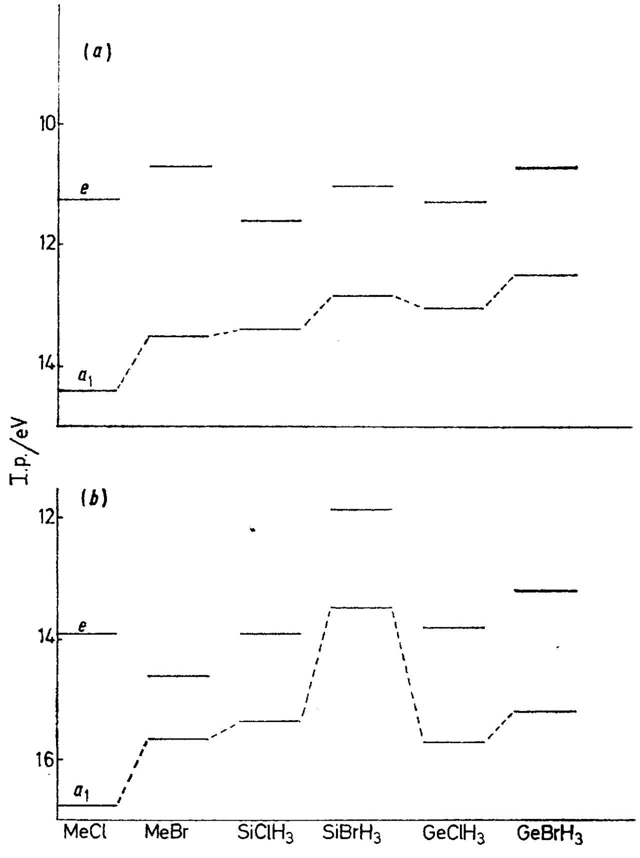

FIGURE 1 Experimental (*a*) and calculated (*b*) ionisation energies for the listed compounds; for MeBr, $SiBrH_3$, and $GeBrH_3$ the *e* band is split and the average value of the i.p. corresponding to the two values is given

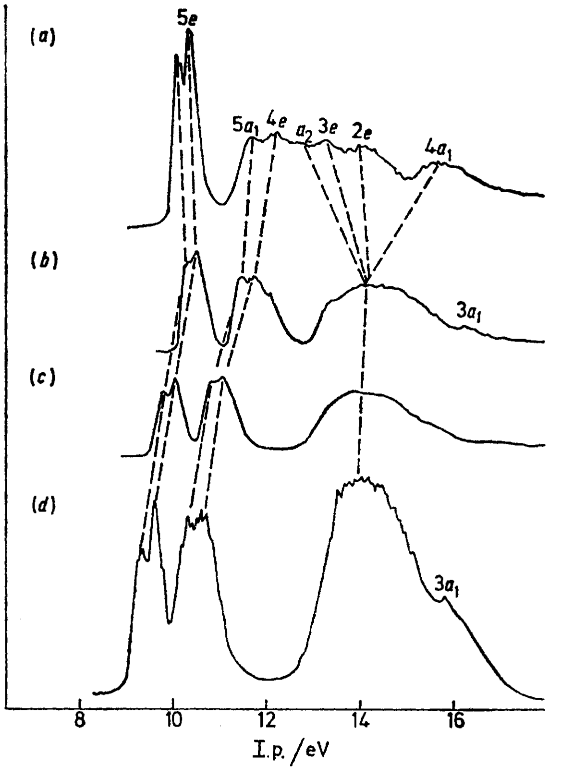

FIGURE 2 Photoelectron spectra of $CBrMe_3$ (*a*), $SiBrMe_3$ (*b*), $SnBrMe_3$ (*c*), and $PbBrMe_3$ (*d*)

orbital shifted to lower i.p. in such a way that from Ge onwards it appeared as the first i.p. As observed for the

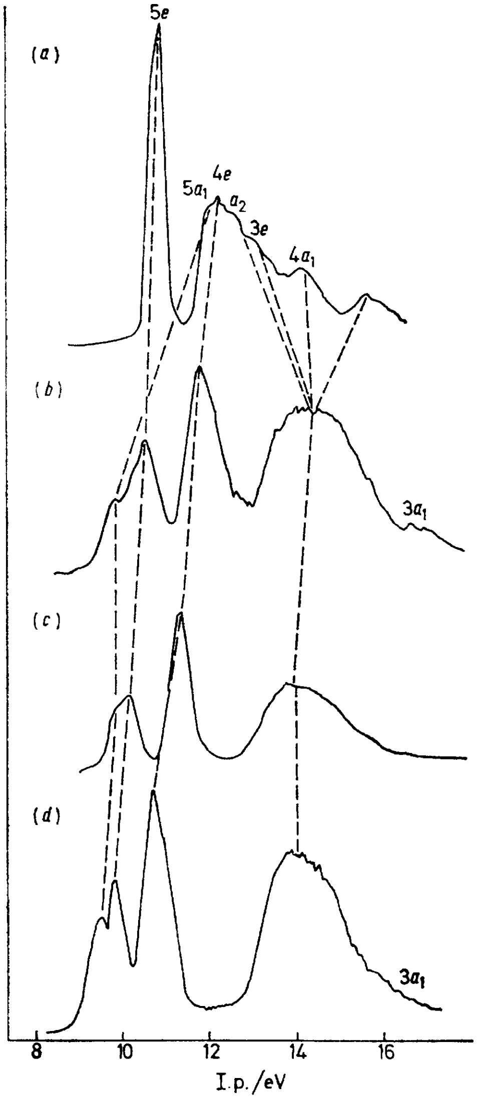

FIGURE 3 Photoelectron spectra of CMe_3Cl (*a*), $GeMe_3Cl$ (*b*), $SnMe_3Cl$ (*c*), and $PbMe_3Cl$ (*d*)

MXH_3 series,[4] for the compounds MMe_3Cl the band areas were not proportional to the number of orbitals involved in the ionisation (Figure 3). In fact, the sum of the areas of the first two bands ($5a_1 + 5e$) was lower than that of the third ($4e$).

TABLE 2

Percent participation of the halogen lone pairs in the $4e$ and $5e$ m.o.s

	CMe_3Cl	$CBrMe_3$	$SiMe_3Cl$		$SiBrMe_3$		$GeMe_3Cl$		$GeBrMe_3$
$5e$	43	33	25	27 *	17	21 *	53	65 *	36
$4e$	41	41	64	48 *	56	29 *	43	21 *	54

* With *d* functions.

With the exception of t-butyl chloride, the position of the p_π lone pairs of the chlorine atom cannot be chosen unequivocally. Thus, they may correspond to the $5e$ orbital because of its relatively low i.p., but, equally, to the $4e$ orbital on the grounds of its band profile and high intensity. The CNDO calculations indicate that the two orbitals $4e$ and $5e$ both originate from the lone pairs of the halogen and from the M–C σ bonds (Table 2) in both the chloro- and bromo-derivatives. The experimental results show that only for the compounds $MBrMe_3$ and CMe_3Cl may the $5e$ orbital be assigned with certainty to the halogen lone pairs. It may be concluded that the orbitals Xp_π and σ_{M-C} are strongly mixed because they are of similar energy in the chloro-derivatives (M = Si, Ge, Sn, and Pb). In other words, the σ_{M-C} orbitals of type e combine with those of the halogen lone pair to give two antibonding and bonding combinations. The CNDO calculations correctly describe this situation but give quantitative ratios for the mixing which are different from those given by the empirical assignment.

The $4e$ band often shows a splitting, *e.g.* in $SiBrMe_3$ and $PbMe_3Cl$ (Figures 2 and 3). Possible causes for this may be the operation of a Jahn–Teller effect or spin–orbit coupling in the heavier elements.[11] As for compounds MXH_3,[4] there is an increase in i.p. on passing from the bromides to the chlorides, with the exception of the $5a_1$ orbital (σ_{M-X}), which exhibits the reverse behaviour to that expected on the basis of the electronegativities of the halogens. This behaviour is reproduced by the calculations and further support comes from a calculation on $GeBrMe_3$, although we have no p.e. spectrum for this compound (Table 1). From the eigenvectors (Table 3) it appears that in the chloro-derivatives the *s* orbitals of M and the halogen participate less in the σ_{M-X} bond than they do in the bromo-derivatives, or are even antibonding (see $GeMe_3Cl$ in this Table) which lowers the i.p. This indicates that there is a strong mixing of the basis set of atomic orbitals in the chloro-derivatives, as also found for the $4e$ and $5e$ orbitals. It may be suggested that this 'anomalous' behaviour of the σ_{M-Cl} orbitals is due to a decrease in the angle XMC in the chlorides compared to the bromides. The values reported for this angle in the literature are in disagreement with one another (109.5[12] and 105°[13]). Calculations were made using both values. When the angle XMC was lower than the tetrahedral value all the orbitals moved to higher energy (the $5a_1$ orbital shifting the most) and, consequently, the total energy also increased (by 20—30 kcal mol^{-1}). We conclude that the XMC angle is not the determining factor, and that for all

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TABLE 3

Coefficients of the s and p_σ atomic orbitals of M and X in the $5a_1$ (σ_{M-X}) orbitals in the MMe_3X compounds

	M		X	
Compound	s	p_σ	s	p_σ
CMe_3Cl	0.0059	0.3995	0.0182	−0.7005
$CBrMe_3$	−0.0221	−0.4263	−0.0384	0.5926
$SiMe_3Cl$	−0.0276	−0.3704	−0.0564	0.7537
$SiBrMe_3$	−0.0688	−0.3746	−0.0800	0.6379
$GeMe_3Cl$	0.0745	−0.4611	−0.0767	0.7642
$GeBrMe_3$	0.0067	0.4769	0.1137	−0.6849

the molecules the most realistic value for this angle is the tetrahedral value.

As mentioned in the introduction, for the similar (*i.e.* C_{3v}) but simpler molecules MXH_3 the problem of participation of the halogen lone-pair orbitals in the M–X bond *via* the *d* orbitals of the central atom has been settled and, with reasonable certainty, it has shown that the extent of this participation is greatest for Si.[6] Little is known about Ge compounds, because of the almost complete absence of calculations on molecules containing third-row atoms.

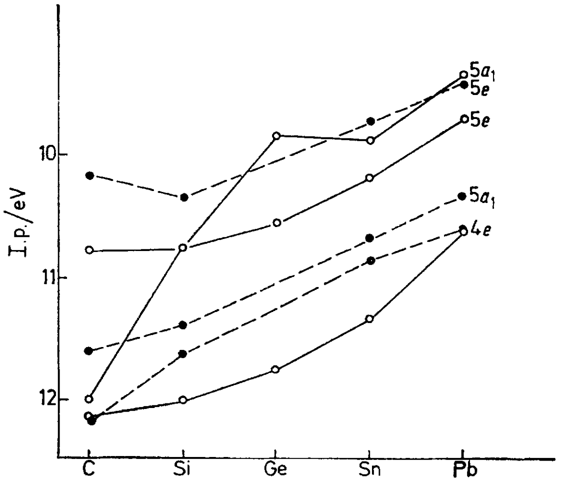

FIGURE 4 Ionisation potentials of the first three bands in the series MMe_3Cl (——) and $MBrMe_3$ (— — —)

For the compounds studied here, and especially the bromo-derivatives, the behaviour of the $5e$ band is similar to that of the $2e$ band in the MXH_3 compounds,[4] although the minimum corresponding to Si is less accentuated (Figure 4). The i.p.s of all the other orbitals decrease with increasing electropositive character of M. The behaviour of the $5e$ band is anomalous, and indicates the participation of the halogen lone pairs in the M–X bond. However, because of the closeness in energy of the σ_{MMe_3} orbitals having the same symmetry, it is not certain whether the *d* orbitals are responsible for this behaviour, as is suggested by dipole-moment measurements,[7] or the σ_{MMe_3} orbitals themselves. The slight improvement obtained on including *d* orbitals in the calculations is not conclusive (Table 1).

A band of low intensity and high i.p. was clearly visible in the spectra of the compounds of Si, Ge, and Pb (although not in the tin compound; this was also observed in the MMe_4 series).[2,11] The calculations show that there is a predominant contribution of the *s* orbital of the central atom to this band. The orbital involved is the $3a_1$, which appears at 15.95 ($SiMe_3Cl$), 16.65 ($GeMe_3Cl$), and 15.75 eV ($PbMe_3Cl$), and at 16.05 and 15.60 eV for $SiBrMe_3$ and $PbBrMe_3$, respectively. For comparison, the same orbital is found at 15.58, 15.90, and 15.30 eV in $SiMe_4$, $GeMe_4$, and $PbMe_4$, respectively.[2]

An intense broad band appeared in all the compounds at about the same energy (Table 1 and Figures 2 and 3). The same behaviour is found in the MMe_4 series (with maxima at 14.08, 13.85, 13.40, and 13.30 eV for M = Si, Ge, Sn, and Pb) [2] and in PMe_3 (13.7), $AsMe_3$ (13.6), and $SbMe_3$ (13.3 eV).[14] This band originates from ionisation of ligand molecular orbitals of the type σ_{C-H} ($2e$, $3e$, and $4a_1$) and from the only non-bonding orbital (a_2) localised on the methyl group. The half-width of this band varies: $W_{\frac{1}{2}} = 2.0$—2.3 eV for the bromides and 2.2—3.0 eV for the chlorides. This difference, which is qualitatively reproduced by the calculations (Table 1), is directly related to the separation in energy between the σ_{C-H} orbitals of the methyl groups. It may be explained if we remember that on going from Si to Pb the methyl groups move farther apart and hence interact less. This interaction reaches a maximum in the t-butyl halides and it is because of this fact that the spectrum appears so different from those of the heavier homologues: in carbon derivatives the interaction gives rise to four separate bands.

Conclusions.—The p.e. spectra and the calculations, extended to cover third-row elements, of compounds MMe_3X show that the halogen lone pairs participate in bonding *via* interaction with those orbitals of the MMe_3 moiety which have the same symmetry. This interaction is greatest in the MMe_3Cl compounds of Si, Ge, Sn, and Pb, whilst it is much weaker in CMe_3Cl and $MBrMe_3$, as also found in the MXH_3 analogues (except for MFH_3) because of the greater separation in energy between the two orbitals involved. Participation of the lone pairs in bonding may also occur *via* the *d* orbitals of the central atom. This latter interaction cannot be entirely excluded since CNDO calculations with inclusion of *d* orbitals give a slightly better agreement with experiment.

Compared with the p.e. spectra of MXH_3 compounds, substitution of the hydrogen atoms by methyl groups lowers the i.p.s of all the orbitals so that they cover a more restricted energy range. The i.p.s change along the series with change in the element M, in a sense which agrees with the electronegativity of the latter, and also change with the halogen. The exception to this rule is the $5a_1$ orbital (σ_{M-X}) which has a lower i.p. in the series MMe_3Cl (M = Ge, Sn, and Pb). This behaviour is reproduced by the CNDO calculations and indicates a lower participation of the *s* orbitals in the σ_{M-X} bond in the chloro-derivatives.

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