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ELECTRON IMPACT STUDIES ON SOME ORGANOCHLOROGERMANES: MASS SPECTRA AND BOND DISSOCIATION ENERGIES

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SUMMARY

The mass spectra of the methylchlorogermanes and the (chloromethyl)-trichlorogermanes are described and analysed. It is shown by consideration of the ionisation and appearance potentials that the surprisingly high abundance of $(M{-}Cl)^+$ ions in the spectrum of Cl_3GeCH_3 is due to a large decrease of the Ge–Cl bond strength in the molecular ions of methylchlorogermanes with increase in the number of Cl atoms on Ge. Calculated bond energies indicate that this phenomenon reflects Ge–Cl bond energy differences in the neutral molecules.

INTRODUCTION

Although a number of organogermanium compounds have been examined by mass spectrometry[1-5], only a few organochlorogermanes: $(CH_3)_3GeCl$, $(C_2H_5)_3GeCl$, $(C_6H_5)_3GeCl$ were studied. We have reported below, mass spectral data for the following chlorogermanes:

$ClGe(CH_3)_3$	(I)	Cl_3GeCH_2Cl	(IV)
$Cl_2Ge(CH_3)_2$	(II)	$Cl_3GeCHCl_2$	(V)
Cl_3GeCH_3	(III)	Cl_3GeCCl_3	(VI)

RESULTS AND DISCUSSION

The polyisotopic composition of Ge and Cl makes the mass spectra of chlorogermanes very complex, though at the same time it helps in determining the chemical composition of the molecular and fragment ions from the low resolution mass spectra. In order to facilitate understanding of the mass spectra of compounds (I) to (VI), the monoisotopic mass spectra at 50 eV were calculated, and the results are presented in Tables 1 and 2. (The isotopic abundance data for Ge, Cl and C are taken from literature[6].) The abundance of ions (over 0.2%) is presented in terms of the per-

TABLE 1

50 eV MASS SPECTRA OF COMPOUNDS (I)–(III)
PERCENT ABUNDANCE OF IONS RELATIVE TO TOTAL IONIZATION, Σ_{35}

m/e	$(CH_3)_3GeCl$	$(CH_3)_2GeCl_2$	CH_3GeCl_3	*Composition*
190			6.4 (*M*)	$(Cl_3GeCH_3)^+$
175			22.6	$(GeCl_3)^+$
170		4.5 (*M*)		$[Cl_2Ge(CH_3)_2]^{+\cdot}$
155		51.0	44.4	$(Cl_2GeCH_3)^+$
150	1.4 (*M*)			$[ClGe(CH_3)_3]^{+\cdot}$
140			2.4	$(GeCl_2)^{+\cdot}$
135	41.9	15.0		$[ClGe(CH_3)_2]^+$
120	2.7	2.2		$(ClGeCH_3)^{+\cdot}$
119	1.6	0.9		$(ClGeCH_2)^+$
115	20.2			$[Ge(CH_3)_3]^+$
114	0.3			$[Ge(CH_3)_2CH_2]^{+\cdot}$
105	8.7	15.5	14.8	$(GeCl)^+$
100	1.8	0.2		$[Ge(CH_3)_2]^{+\cdot}$
99	0.5	0.2		$(GeC_2H_5)^+$
95		0.2		$(GeC_2H)^+$
87	2.6 (*R*)[a]			$(GeCH_5)^+$
85	8.4	3.4	0.9	$(GeCH_3)^+$
84	0.5	1.6	1.2	$(GeCH_2)^{+\cdot}$
83		0.6	0.7	$(GeCH)^+$
71	2.7 (*R*)	1.0 (*R*)	0.2 (*R*)	$(GeH)^+$
70	2.4	2.7 (*R*)	2.8	$Ge^{+\cdot}$
49			0.3 (*R*)	$(CH_2Cl)^+$
36	0.4	0.6	1.1	$HCl^{+\cdot}$
35	0.1	0.1	0.6	Cl^+

[a] *R* rearrangement ion.

centage of the total ion current. The chemical composition of the ions was determined from isotope peak ratios.

The peak for the molecular ion is present in each case, and its abundance is in the range of 0.1–7%. The stability of the molecular ions of the compounds (I) to (III) increases with increasing number of the Cl atoms bonded to Ge (see Table 1). An inverse effect was observed in the mass spectra of (IV) to (VI), *i.e.* the molecular ion stability decreases with increasing number of Cl atoms bonded to C.

For compounds (I) to (VI), the most abundant ions originate from the molecular ions by loss of a radical. This process is the cleavage of a germanium–carbon bond, except for Cl_3GeCH_3, for which the loss of a Cl atom is predominant*. In the case of compounds (I) to (III), the positive charge is definitely localised on the Ge-containing fragments. On the other hand, fragmentation of compounds (IV) to (VI) leads to ions of high abundance both with and without Ge. The proportion of the former decreases with increase in the number of Cl atoms bound to carbon (see Table 2).

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* In accord with a detailed examination[7] of the even more metallic $TiCl_4$, there is no reason to suppose that the $(M\text{–}Cl)^+$ ions are produced in an ion pair formation process:

$$M + e \rightarrow (M\text{–}Cl)^+ + Cl^- + e$$

in the ion source (*M* indicates a neutral molecule).

TABLE 2

50 eV MASS SPECTRA OF COMPOUNDS (IV)–(VI)
PERCENT ABUNDANCE OF IONS RELATIVE TO TOTAL IONIZATION, Σ_{35}

m/e	*Cl_3GeCH_2Cl*	*$Cl_3GeCHCl_2$*	*Cl_3GeCCl_3*	*Composition*
292			0.1 (*M*)	$(GeCCl_6)^{+\cdot}$
258		1.3 (*M*)		$(GeCHCl_5)^{+\cdot}$
257			10.4	$(GeCCl_5)^+$
224	6.2 (*M*)			$(GeCH_2Cl_4)^{+\cdot}$
223		2.3		$(GeCHCl_4)^+$
222			0.3	$(GeCCl_4)^{+\cdot}$
189	4.5			$(GeCH_2Cl_3)^+$
188		0.2		$(GeCHCl_3)^{+\cdot}$
187			0.3	$(GeCCl_3)^+$
175	51.2	18.9	7.5	$(GeCl_3)^+$
154	0.4			$(GeCH_2Cl_2)^{+\cdot}$
152			0.4	$(GeCCl_2)^{+\cdot}$
140	4.1	2.7	2.9	$(GeCl_2)^{+\cdot}$
118		0.6		$(GeCHCl)^{+\cdot}$
117			31.5	$(CCl_3)^+$
		0.6		$(GeCCl)^+$
105	20.1	18.4	17.1	$(GeCl)^+$
83	0.9 (*R*)[a]	47.0		$(CHCl_2)^+$
82		1.5	18.8	$(CCl_2)^{+\cdot}$
70	2.4	2.8	2.8	$Ge^{+\cdot}$
49	4.7			$(CH_2Cl)^+$
48		2.2		$(CHCl)^{+\cdot}$
47		1.0	2.1	$(CCl)^+$
36	1.6			$(HCl)^{+\cdot}$
35	0.6		1.8	Cl^+

[a] *R* rearrangement ion.

In all the mass spectra the abundance of the even-electron ions prevails, and both tri- and mono-coordinated species of such ions occur with high intensity.

The rearranged ions in the mass spectra of (I)–(VI) are of low abundance which represents a difference between the fragmentation of organosilanes and germanes. For example, in the 70 eV spectrum of tetramethylsilane[8] the abundance of the rearranged ions [$Si(CH_3)_2H^+$, $SiCH_3H_2^+$, SiH_3^+, SiH^+] is as high as 22% of the total ion current, whereas for tetramethylgermane the abundance is not greater than 11%[4]. This may be explained by the difference between the bond strengths $Si–CH_3$ and $Ge–CH_3$, the dissociation energy of the $Si–CH_3$ bond in $Si(CH_3)_4$ being 3.2 ± 0.2 eV, and that of the $Ge–CH_3$ bond in $Ge(CH_3)_4$ being 2.9 ± 0.14 eV[9]. This difference means that consecutive homolytic fission of metal–CH_3 bonds can take place more easily and more frequently in the case of the germanium compounds.

The spectra of the $(CH_3)_nGeCl_{4-n}$ compounds, with $n = 0, 1, 2, 3, 4$ which are shown in Table 3, illustrate the changes arising from substitution of CH_3 by Cl; the most significant ions of compounds (I)–(III) are listed together with those of $Ge(CH_3)_4$ and $GeCl_4$ taken from the literature[4]. In both the 50 eV and 15 eV mass spectra of (I) and (II) the abundance of the *M*–Cl ions is less than that of the *M*–CH_3

TABLE 3

COMMON TYPES OF IONS IN THE MASS SPECTRA OF $(CH_3)_nGeCl_{4-n}$ $(n=0–4)$ PERCENT ABUNDANCE OF IONS RELATIVE TO TOTAL IONIZATION, Σ_{35}

Ions	*GeCl₄*[a]	*CH₃GeCl₃*		*(CH₃)₂GeCl₂*		*(CH₃)₃GeCl*		*(CH₃)₄Ge*[a]
	70 *eV*	50 *eV*	15 *eV*	50 *eV*	15 *eV*	50 *eV*	15 *eV*	70 *eV*
$M^{+\cdot}$	16.9	6.4	12.1	4.5	13.9	1.4	3.8	1.2
$(M–CH_3)^+$		22.6	15.9	51.0	70.7	43.1	81.6	69.5
$(M–Cl)^+$	73.1	44.4	71.8	15.0	15.4	2.8	13.3	
$(M–2CH_3)^{+\cdot}$						2.8		4.1
$[M–(Cl+CH_3)]^{+\cdot}$		2.4		2.2		1.8		
$(M–2Cl)^{+\cdot}$	1.3			0.2				
$(M–3CH_3)^+$						9.0		9.4
$[M–(Cl+2CH_3)]^+$				15.5		8.6		
$[M–(2Cl+CH_3)]^+$		14.8		3.4				
$(M–3Cl)^+$	6.4	0.9						
$(GeCH_3H_2)^+$						2.6		4.7
$(GeH)^+$		0.2 (*R*)[b]		1.0 (*R*)		2.8 (*R*)		4.7 (*R*)
$Ge^{+\cdot}$	1.2	2.8		2.7		2.5		2.4
Abundance of even electron ions	80.6	88.4		90.4		91.5		92.3

[a] From ref. 4. [b] *R* rearrangement.

ions. For the corresponding ions of (III) the inverse case is observed. This surprising observation can be interpreted by assuming that the number of Cl atoms has a large effect on the ratio of the Ge–CH_3 to the Ge–Cl bond strength in the molecular ions. To throw light on this phenomenon, and to obtain more detailed information about the correlation between the bond strength and the fragmentation mode, ionization potentials (*IP*) and appearance potentials (*AP*) were measured for $(CH_3)_nGeCl_{4-n}$ $(n=0,1,2,3)$ and Cl_3GeCCl_3, the results are presented in Table 4. Analogous data for tetramethylgermane[9] are also included.

Using these *IP* and *AP* data, the energies necessary for the loss of a methyl radical or a Cl atom from the molecular ions $[D(M^+–X) = AP(M–X) – IP]$ have been calculated and are included in Table 4. It will be seen that the loss of a methyl radical from the molecular ion requires slightly increasing energy as the number of Cl atoms

TABLE 4

IONIZATION (*IP*) AND APPEARANCE (*AP*) POTENTIALS AND BOND DISSOCIATION ENERGIES OF MOLECULAR IONS (*D*, IN eV) FOR $(CH_3)_nGeCl_{4-n}$ COMPOUNDS

Compound	$IP(M)^+$	$AP(M–Cl)^+$	$AP(M–CH_3)^+$	$D(Ge^+–Cl)$	$D(Ge^+–CH_3)$
$(CH_3)_4Ge$[a]	9.29±0.14		10.05±0.14		0.76
$(CH_3)_3GeCl$	9.62±0.04	11.75±0.04	10.44±0.04	2.13	0.82
$(CH_3)_2GeCl_2$	10.18±0.05	11.56±0.04	11.08±0.05	1.38	0.90
CH_3GeCl_3	11.11±0.04	11.78±0.05	12.22±0.05	0.67	1.11
$GeCl_4$	11.68±0.05	12.12±0.04		0.44	

[a] See ref. 9.

increases. By contrast, the energy needed for the loss of a Cl atom is much more affected (decreased) by the increasing number of Cl atoms. There is a definite correlation between the energy values and the abundances of the M–X ions, as shown in Tables 3 and 4. The data are consistent with the postulated large substituent effect on the bond strength in the molecular ions. However this effect is not reflected in the abundance of the molecular ions, probably due to reverse influence of the easier positive charge delocalization which is associated with the increasing number of chlorine atoms.

It is of interest to compare the Ge–Cl and Ge–CH_3 bond energy values in the ionized and neutral species, in order to see whether the substituent effect occurs with the neutral molecule or if it arises only after ionization. Lappert *et al.*[9], have calculated the D-(Ge–CH_3) values in $(CH_3)_4Ge$ on the basis of the following equation:

$$D[\mathrm{Ge{-}CH_3}] = AP[(\mathrm{CH_3})_3\mathrm{Ge}^+] - IP[(\mathrm{CH_3})_3\mathrm{Ge}^\bullet]$$

A value of $IP\ [(CH_3)_3Ge^\bullet] = 7.11 \pm 0.18$ eV was used. Accepting the IP data for the $(CH_3)_3Ge^\bullet$ radical, we used the corresponding AP value 11.75 ± 0.04 eV (Table 4) and calculated the dissociation energy of the Ge–Cl bond for the $(CH_3)_3GeCl$ molecule (see Table 5). However, for deriving the dissociation energy of Cl_3Ge–X bond the value of $IP(Cl_3Ge^\bullet)$ is necessary. To determine it we measured $AP(Cl_3Ge^+)$ and $AP(Cl_3C^+)$ in the case of Cl_3GeCCl_3, and obtained:

$$AP(\mathrm{Cl_3Ge^+}) = 11.75 \pm 0.1 \text{ eV}$$

$$AP(\mathrm{Cl_3C^+}) \ = 11.19 \pm 0.1 \text{ eV}$$

Taking $IP(Cl_3C^\bullet)$ as 8.78 ± 0.05 eV (see ref.[12]), $IP(Cl_3Ge^\bullet)$ was calculated to be 9.34 ± 0.2 eV. This value was used together with the corresponding AP (Cl_3Ge^+) value in the calculation of the dissociation energies of the bonds Cl_3Ge–CH_3, Cl_3Ge–Cl, and Cl_3Ge–CCl_3, as listed in Table 5. The kinetic energies of the ions were neglected in the calculations. Bearing in mind the uncertainties of the values, there seems to be no large substituent effect on the Ge–CH_3 bond strength in neutral $(CH_3)_nGeCl_{4-n}$ molecules, but a surprisingly large effect is observed for the Ge–Cl bond. Replacement of all the H atoms by Cl in $GeCl_3CH_3$ results in a relatively large (0.5 eV) decrease of the Ge–C bond strength. Qualitatively all the effects can be interpreted in terms of the electron-withdrawing character of the chlorine atoms.

Finally, comparison of the mass spectra with the bond dissociation energies for the neutral and ionized molecules proves that both the abundance of M–X ions and the dissociation energy of the bonds in molecular ions reflect the bond dissociation energies of the neutral molecules.

TABLE 5

BOND DISSOCIATION ENERGIES (D IN eV) FOR SOME ORGANOCHLOROGERMANIUM COMPOUNDS

$D[(CH_3)_3Ge–CH_3]$	2.94 ± 0.14[a]
$D[Cl_3Ge–CH_3]$	2.88 ± 0.2
$D[(CH_3)_3Ge–Cl]$	4.64 ± 0.2
$D[Cl_3Ge–Cl]$	2.78 ± 0.2
$D[Cl_3Ge–CCl_3]$	2.41 ± 0.2

[a] See ref. 8.

EXPERIMENTAL

The compounds (I)–(VI) were kindly given to us by S. P. Kolesnikov, B. L. Perlmutter and G. Ja. Zueva. The purity of compounds was checked by GLC, titration, and comparison of the physical constants with known data[1,13].

The mass spectra of compounds (I)–(VI) were taken by using a single focusing MX–1303 type mass spectrometer. The *IP* and *AP* data were determined from ionization efficiency curves of ions by using the semilog plot technique[10], as the average values of three parallel measurements. The errors given are the maximum deviation from these values. Benzene was used as internal standard. $IP(C_6H_6) = 9.40 \pm 0.02$ eV[11].

The ionization efficiency curves used for deriving the *IP* and *AP* values were obtained by using both MX–1303 and MS–902 type instruments. The deviation between the two sets of *IP* and *AP* data was less than 0.1 eV in all cases.

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