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CHARGE LOCALIZATION IN THE MASS SPECTROMETRIC FRAGMENTATION OF SOME ORGANOCHLOROGERMANES

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Summary

A large decrease of the relative abundances of germanium-containing ions has been observed in the electron-impact mass spectra when the H atoms of H_3CGeCl_3 and the X = CH_3 groups of $RGeX_3$ are replaced by Cl atoms. Consideration of the ionization potentials of the relevant radicals indicates that the charge localization effects can be explained in terms of Audier's rule.

Introduction

Previous studies [1, 2] of the mass spectra of alkyl-, aryl- and benzyl-substituted organogermanes have shown that almost all the ion current is carried by the metal-containing ions. This was true also for methyl- and aryl-chlorogermanes having one Ge—Cl bond [2], but for organochlorogermanes of general formula $(CH_{3-n}Cl_n)GeCl_3$ (n = 1, 2, 3) the fragmentation leads to abundant ions both with and without Ge [3], and the relative abundances of the former decrease as n increases (see Table 1).

TABLE 1

ABUNDANCE OF FRAGMENT IONS CONTAINING Ge FROM COMPOUNDS $(CH_{3-n}Cl_n)GeCl_3$
Data from ref. 3.

	Abundance
$ClCH_2$—$GeCl_3$	83
Cl_2CH—$GeCl_3$	46
Cl_3C—$GeCl_3$	41

Discussion

It can be demonstrated that the effect of substituents on the charge localization outlined above is a consequence of the changes in the ionization potential (*IP*) values of the $\dot{C}H_{3-n}Cl_n$ radicals with *n*. That is, the main primary fragmentation process for these compounds is the fission of the Ge—C bond, and $IP(CH_{3-n}Cl_n{}^{\cdot})$ decreases as *n* increases: for $n = 1$ it is higher than $IP(GeCl_3{}^{\cdot})$, for $n = 2$ the *IP* values are almost equal, and for $n = 3$ $IP(CCl_3{}^{\cdot})$ is lower than $IP(GeCl_3{}^{\cdot})$ (see Table 2). The relative abundances of ions with and without Ge show a reverse order. Thus the effect mentioned above may be interpreted on the basis of Audier's rule* [12], i.e. the positive charge remains on the fragment with the lower ionization potential**. The same rule accounts for the surprisingly large effect on the localization of the positive charge, observed in the case of $RGeX_3$ type compounds when $X = CH_3$ is replaced by $X = Cl$ (Table 3).

The main primary decomposition route of the molecular ions of these compounds is cleavage of the Ge—R bond. In this process for $R—Ge(CH_3)_3$ compounds the positive charge definitely remains on the Ge-containing fragment. In contrast, the scission of the $R—GeCl_3$ bond leads to the abundant ion R^+. The reason for this large effect on the charge localization is obviously the difference in the ionization potential of $GeCl_3{}^{\cdot}$ and $Ge(CH_3)_3{}^{\cdot}$ radicals. Replacement of all the CH_3 groups of $Ge(CH_3)_3{}^{\cdot}$ by Cl atoms increases the radical ionization potential of $GeX_3{}^{\cdot}$ by 2.2 eV, and for the compounds examined: $IP(Ge(CH_3)_3{}^{\cdot}) < IP(R^{\cdot}) < IP(GeCl_3{}^{\cdot})$ (see Table 2); thus because of the chlorine substitution in the Ge-containing moiety, R becomes the fragment associated with the lower ionization potential and consequently the most abundant ion.

These results support the validity of Audier's rule for the primary fragmentation of these germanium-containing compounds.

TABLE 2

IONIZATION POTENTIALS OF SOME RADICALS

Radicals	*IP* (eV)	Ref.
$CH_3{}^{\cdot}$	9.84 ± 0.002	4
$CH_2Cl^{\cdot}$	9.70 ± 0.09	5
	9.42	6
$CHCl_2{}^{\cdot}$	9.54 ± 0.1	5
	9.02	6
$CCl_3{}^{\cdot}$	8.62	6
	8.78 ± 0.05	7
p $CH_3—C_6H_4—CH_2{}^{\cdot}$	7.46 ± 0.03	8
p $Cl—C_6H_4—CH_2{}^{\cdot}$	7.95 ± 0.1	8
$CH_2=CH—CH_2{}^{\cdot}$	8.15 ± 0.03	9
cyclo $C_6H_{10}—CH_3{}^{\cdot}$	7.56	10
$Ge(CH_3)_3{}^{\cdot}$	7.11 ± 0.18	11
$GeCl_3{}^{\cdot}$	9.34 ± 0.2	3

* This rule is frequently wrongly described as Stevenson's rule.

** For examples of applications and some apparent failures of the rule for organic compounds, see refs. 13-16.

TABLE 3

PARTIAL MASS SPECTRA OF COMPOUNDS $RGeX_3$

70 eV. Abundance of ions is expressed in percentage of the total ion current

Ions	R = p-Cl—$C_6H_4CH_2$		R = p-Br—$C_6H_4CH_2$		R = p-CH_3—$C_6H_4CH_2$		R = m-CF_3—$C_6H_4CH_2$		R = CH_2=CH—CH_2		R = CH_3—cyclo-C_6H_{10}	
	X = CH_3	X = Cl	X = CH_3	X = Cl	X = CH_3	X = Cl	X = CH_3	X = Cl	X = CH_3	X = Cl	X = CH_3	X = Cl
M^+	7.2	9.8	7.6	12	9.5	8.9	2.3	7.7	0.5	5 6	3.4	0.1
$(M-X)^+$	7.2	0.2	6.0	0.1	7.5	0.1	10	0.5	7.4	1.9	7.7	0.3
GeX_3^+	66	0.6	67	0.8	58	0.6	32	0.5	52	2.8	51	0.8
Ge-containing fragment ions	84	2.2	84	1.0	76	0.7	56	2.3	95	15	84	3 0
R^+	6.4	79	4.6	73	4.1	74	2.1	70	5 0	78	1 5	38

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