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Mass Spectra of Organometallic Compounds of Group IVb

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Characteristic features of the dissociation of ions of organometallic compounds with silicon, germanium, tin, and lead are considered. Cyclic compounds are discussed separately; results on the following aspects are surveyed: rearrangements, metastable and multiply-charged ions, products of ionic-molecular reactions, and also the mass spectra of negative ions and correlations between ion decomposition processes and the thermal decomposition of the molecules of the compounds concerned.
There is a bibliography of 115 references.

INTRODUCTION

The development of the chemistry of the organometallic compounds of the Group IVb elements stimulated interest in their mass spectrometric investigation, occasioned by the uniqueness of their mass spectra, by the practical objectives of the structural analysis of these compounds, and also by the correlations observable between the breakdown of the ions in the chamber of the mass spectrometer and processes such as thermolysis. Hundreds of derivatives of silicon, germanium, tin, and lead have been studied in recent years; the mass spectra of over 300 compounds were published in 1968—1970 alone. The number of papers decreases appreciably with increase in both the atomic number of the metal and the number of metal atoms in the molecule; most of the investigations relate to compounds of the R_4E type, where R stands for alkyl, aryl, and other substituents, and also to the trimethylsilyl derivatives of all possible compounds.

Although the general rules of dissociative ionisation also extend to organometallic compounds, the presence in the molecule of one or more Si, Ge, Sn, or Pb atoms confers considerable singularity on the mass spectra. Review papers[1-3] have mentioned a series of features of the mass spectra associated with the decrease in ionisation potentials and bond strengths of the metal atoms on going from C to Pb, such as charge localisation on metal-containing species, intensive rearrangements, and abundance of metastable and multiply-charged ions.

The present review examines certain features of the mass spectra of the organometallic compounds of Group IVb with an account of recent results. A quarter of the papers cited in this review are from Soviet investigators.

GENERAL SCHEME OF DECOMPOSITION

Almost all the ionic current in the mass spectra of these compounds is carried by species which contain a metal atom (atoms). There is every basis for assuming that, in even-electron ions at least, the charge is localised on the metal atoms. This agrees with the fact that doubly and triply charged ions are usually observed solely for compounds which contain respectively not less than two or three metal atoms[4-6]. The fraction of hydrocarbon or other organic metal-free ions in the mass spectra of organometallic compounds with a single metal atom usually does not exceed a few per cent; it is even less for more complex molecules. This is connected with the low (in comparison with carbon) ionisation potentials of the atoms Si, Ge, Sn, Pb (respectively[7] 8.15, 7.88, 7.34, and 7.42 eV), the orbitals of which make a large contribution to the higher occupied molecular orbitals[3]. Only when the species formed are extremely stable metal-free fragments (usually aromatic) which are characterised by a low ionisation potential can the latter make a significant contribution to the total ionic current. Such are, for example, the fluorocarbon ions in the mass spectra of $(C_6F_5)_4Si$, $(C_6F_5)_4Ge$,[8,9] and the $[(C_6H_4)_2O]^+$ ion in the mass spectrum of SnSn-dichloro-oxastannadihydroanthracene[10]. Hydrocarbon ions observable in the mass spectra of organometallic compounds are characterised by considerable unsaturation (C_nH_{2n-3}, etc.).

The presence of many rather intense metastable ions in the mass spectra of organometallic compounds allows a genetic connection to be found between many fragment ions at the individual stages of the dissociation and is widely used for compiling decomposition schemes for the individual molecular ions. However, caution must be observed in doing this[3]. When a cascade (series) of metastable transitions $A^+ \rightarrow B^+$, $B^+ \rightarrow C^+$, $C^+ \rightarrow D^+$, is observed simultaneously then in addition to this there can also exist rather rapid direct transitions of the type $A^+ \rightarrow C^+$, $B^+ \rightarrow D^+$, $A^+ \rightarrow D^+$, not reflected by breakdowns of metastable ions; in addition, as estimates for some fragment ions of n-alkanes show, series of successive breakdowns composed of observable metastable ions, can lead to increased appearance potentials[11].

The intensity of the molecular ions for acyclic compounds of Si, Ge, Sn, or Pb is usually low[12-21], although higher than that of their hydrocarbon analogues[22]. It is significant only for certain heterocyclic compounds and for molecules with aromatic groups.

The first stage of the decomposition of the initial cation-radical is almost always the detachment of the radical; in the presence of several substituents the most weakly bound (usually, the heaviest[23,24]) group is detached first. One of the bonds with a metal atom is the weakest here. The even-electron ion that is formed is the origin of the remaining lighter fragment ions. For certain compounds (aromatic, heterocyclic) only is a significant part played by the primary splitting of molecules—C_6H_6 from Ph_3GeH, Ph_2 from Ph_4Ge, $[PhCH_2]_2$ from *m*- and *p*-Tol_4Ge, C_2H_4 from sila- and germa-cycloalkanes and spiranes with a central metal atom, etc.[25-33], however, usually these processes are characteristic solely for the subsequent stages of the decomposition. Further decomposition also usually leads to an even-electron ion, and the neutral fragments in its composition correspond to molecules of alkenes, alkanes, aldehydes, water, and other (including organometallic) compounds, some of which are unstable (considered in more detail below)†. The detachment of a

†The splitting of neutral hydrocarbon fragments from molecules with an alternative chain (for example, from cyclocarboxyloxanes[34]) proceeds primarily at the organic framework of the molecules and not the methyleen links.

radical from an even-electron ion, especially for organosilicon compounds, is seldom observed; in addition to the examples given by Chambers and coworkers[2] the following decompositions can be added:

$$[Me_3Si_3(CH_2)_3]^+ \rightarrow [Me_4Si_3]^{+\cdot} + C_2H_3^{\cdot}\ (Ref.28),$$

$$[(CH_3)_3SiCH_2CHCH_3]^+ \rightarrow [CH_3CHSiCH_2CHCH_3]^{+\cdot} + H^{\cdot}\ (Ref.20),$$

$$[Tol_{9,11}Ge_4]^+ \rightarrow [Tol_{8,10}Ge_4]^{+\cdot} + Tol^{\cdot}\ (Ref.35).$$

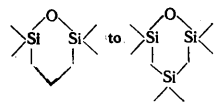
On going from compounds of silicon to compounds of tin or lead, the dissociation, and particularly the successive detachment of radicals, are less dependent upon the fragments formed having an even number of electrons[31,36]. The maximum intensity of the ions is shifted to the lighter ions of the mass spectrum; in particular, the intensity of the E^+ ions increases[2,31]. The number of decomposition paths decreases and the spectrum is simplified (it is made more "selective")[9,20,31,37].

CYCLIC COMPOUNDS

Let us examine in somewhat greater detail the cyclic compounds which occupy an important place in the chemistry of the transition elements of Group IVb; cyclic organosilicon compounds and heterocyclic compounds with metal atoms in the ring have been reviewed before[38,39].

The decomposition under electron bombardment of about a hundred cyclic compounds of Si, Ge, Sn, and Pb has been studied recently. They include cyclo-silanes, -germanes, and -stannanes of general formula $(R_2E)_n$ (R = Me, Ph, *p*-Tol; *n* from 5 to 7 [35,40-43]), cyclo-siloxanes and -germoxanes $(R_2EO)_n$ (R = Me, Pri; *n* = 3—5 [6,15,16]), cyclocarbosiloxanes $(R_2Si)_n(CH_2)_mO_{n-m}$ (where R = Me, *n* = 3 or 4, $m \leqslant n$ [34]), cyclocarbosilanes $(R_2SiCH_2)_n$ (R = H or Me, *n* = 2—4 [44,45]), cyclosilazanes $(R_2SiNR')_n$ (R = Me; R′ = H or Me_2ClSi; *n* = 2, 3, or 4 [46]), tetra-aza-3,6-disilacyclohexanes $[MeRSi(NR')_2]_2$ (R = Me or Vin; R′ = Ph, *m*-Tol, or *m*-Anisyl[47]), 1,4-disila- and 1,4-digerma-cyclohexadienes $[R_2E(CR')_2]_2$ (R = Me, Et, I; R′ = H, Ph [48]), sila- and germa-cycloalkanes $R_1R_2E(CH_2)_n$ (R_1 = R_2 = H; *n* = 3 or 4 [25,26]; R_1, R_2 = H, CH_3; *n* = 3—5 [27,28]; R_1, R_2 = H, C_3H_7, C_4H_9, C_6H_5, C_2H, Cl, Br [29,30]), germacyclopentenes[30], disila- and digerma-cyclopentanes $M_4E_2(CH_2)_3$,[28] sila-, stanna-, and plumba-spiroalkanes[31-33], derivatives of anthracene and phenanthrene[10,49-52], disilabicyclo-octadienes[53], tetrasila-adamantanes[54], cage polysilanes and carboxyloxanes[55,56], and certain other compounds[57-59].

Most of the cyclic organometallic (like organic) compounds show a marked resistance to dissociation, which appears in an increased intensity of either the molecular ion or of ions which contain the complete cyclic skeleton of the molecule. The molecular-ion peak is significant in the mass spectra of several compounds but it appears as the base (maximal) peak solely in the mass spectra of the cyclic organosilicon molecules with aromatic groups and 1,4-disilahexadienes[47,48,51,56,57,59]. On the other hand, in the mass spectra of cyclosiloxanes, cyclocarboxyloxanes, cyclosilazanes, and other molecules with an organic skeleton the intensity of the molecular ions is negligible, but the removal of one radical (or, respectively, of two radicals for doubly-charged ions) stabilises the $[M-R]^+$ residue, since it gives the base peak. This ion dissociates further very little and its decomposition is mainly connected with the elimination or organic molecules with retention of the initial organometallic skeleton of the molecule[6,15,16,34,44-46]. The intensity of the molecular ions also depends on the size of the initial molecule, falling markedly as the number of units is increased within the limits of a single homologous series, for example[45], for cyclocarbosilanes $[Me_2SiCH_2]_n$ from ~10% of the total ionic current at *n* = 2 to less than the error of measurement at *n* = 3 or 4. With a further increase in the number of units there is an increase in the intensity of the ions formed by breakdown of the $[M-R]^+$ ion[6,34]. The replacement of CH_2-groups by an oxygen atom in cyclocarboxyloxanes reduces the probability of decomposition associated with the destruction of the cyclic structure and the spectrum becomes more selective. The change from



leads to a marked decrease in the intensity of both molecular and also the fragment ions lighter than $[M-Me]^+$.[34,58]

For monosila-, disila-, and mono-germa-cycloalkanes[25-30,58] and for spiro-compounds with a central metal atom[31-33] the structure of which includes the $-[CH_2]_n-$ chain the decomposition is primarily due to the loss of molecules of C_2H_4, C_3H_6, or their combinations; its products are ion-radicals. On going from silicon to tin and lead in the spiro-compounds this process becomes the only decomposition process, and the fraction of even-electron ions in the mass spectrum falls to 4% for $[CH_2]_4 > Pb < [CH_2]_4$.[33]

REARRANGED IONS

There have been repeated reports[2] of the ease of occurrence of rearrangements which are accompanied by the dissociation of organometallic compounds, greatly impeding their mass-spectral structural analysis. There may be no corresponding rearrangements of the ions for carbon analogues[60]. In certain instances almost the entire mass spectrum is formed by rearranged ions (for example, decamethylcyclopentasiloxane[6]). The activation energies of reactions which lead to the formation of rearranged ions are evidently lower than those for reactions which can be purely dissociative[61]; many rearrangements of excited ions may occur without any activation energy.

There is no strict classification of ionic rearrangements but our compounds can be conveniently divided according to the observed effects into: (1) those leading to the migration of organic groups, and (2) those which are "skeletal". This division is provisional since the two types of process are often closely related (they may occur simultaneously), and in small molecules essentially the same, so that several rearrangements can be formally assigned to both "types" (for example, see Kuivila and coworkers[62]); however, such a classification is frequently sufficiently unambiguous. The rearrangements or migrations of organic groups is extremely widespread in the mass spectra of organometallic compounds; they play the same part in these compounds as hydrogen rearrangements in the mass spectrometry of organic compounds and accordingly, on the same basis can be regarded as distinct from "skeletal" rearrangements. It is noteworthy that hydrogen rearrangements are frequently indissolubly linked with "skeletal" ones[63].

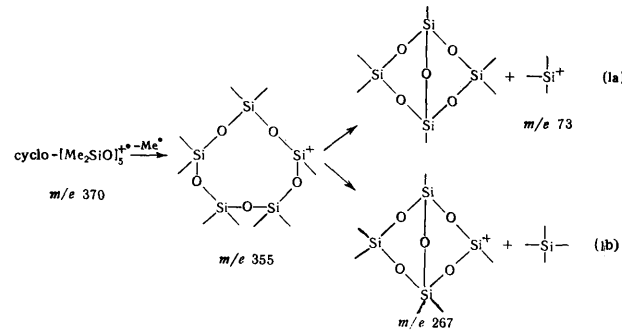
Migration of Groups

It would be difficult to list all the many examples of the migration of organic groups in the ions of Si, Ge, Sn, and Pb derivatives. From the results of recent years we will mention only certain observations of the migration of methyl[59], methoxy-[64], phenyl[65], and other organic[16,19] groups. We emphasise that the frequently observed ion of type R_3E^+ (E = Si, Ge, Sn, or Pb) which gives an intense, and in many instances the base peak, is rearranged to a considerable extent or completely, although frequently it could formally be formed also by simple breaking of a single bond (removal of a terminal group). The rearranged ions R_3E^+ are intense for cyclic compounds of the type $[R_2E]_n$ (where R = Me, Ph, Tol; E = Si, Ge, Sn [35,40,41,43]), $[R_2EO]_n$ (R = Me, E = Si [6] and at $n = 5$ the Me_3Si^+ ion gives a base peak and R = Pr^i, E = Ge; in the last instance the investigators[15] assigned the intense peak of the $Pr^i_3Ge^+$ ion to impurities!). Among ions of the R_3E^+ type are compounds $^1R^1_3E.^2E^2R_3$, where ^1R and ^2R are alkyl or aryl, and ^1E or ^2E are Si, Ge, or Sn, which contain all possible combinations of R and E.[66-69]. Investigation of rearranged ions in methylsiloxanes with trideuteromethyl terminal groups[70] showed complete rearrangement of the methyl groups at all the ions so that the mass spectrum in this instance is insensitive to the sites of the isotopic label (CD_3). This phenomenon is observed irrespective of the conditions of ionisation both in the decrease in the energy of the electrons up to a threshold, and in the ionisation of the molecules in collisions with metastable excited argon atoms. What has been said relates to all the most intense ions of the siloxanes, the formation of which does not require the breaking of C—H bonds; here the CD_3 groups migrate as a whole. However, for ions the formation of which requires the breaking of C—H bonds (the peaks of these ions are weaker in these mass spectra), a complete set of all possible combinations of H and D is observed, that is, hydrogen rearrangement also takes place‡. In this manner the breaking of one bond or another is indistinguishable from the corresponding rearrangements.

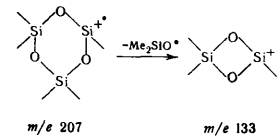
The migration of larger groups such as trimethylsilyl (TMS) has been observed for more complex molecules; here, however, the possibility of skeletal rearrangements, in particular, cyclisation, is usually considered simultaneously[72-76].

Skeletal Rearrangements

Such skeletal rearrangements as the contraction or enlargement of rings or the formation of a new ring are well known in the mass spectrometry of organic compounds, especially heteroatomic compounds[63,77]. The role of these processes in the mass spectrometry of organometallic compounds, especially rather complex ones, increases appreciably. The possibility of the enlargement of a four-membered to a five-membered ring was advanced as an explanation of the similarity in the mass spectra of dimethylsilacyclobutane and methylsilacyclopentane[27]; ideas about the contraction of the ring were used for the interpretation of intense fragment ions in the mass spectra of cyclic siloxanes, carbosiloxanes and tetra-azadisilacyclohexanes[6,34,47]. For cyclosiloxanes, in particular, the formation of bicyclic structures for both positively charged and neutral fragments is possible; the decomposition scheme of, for example, decamethylcyclopentasiloxane, can be represented as follows:



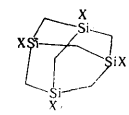
The cyclic structure of the ion $(SiO)_2$ (m/e 133) in the decomposition



is confirmed indirectly by its possessing (judging from the width of the corresponding metastable peak) an appreciable kinetic energy (~1 eV), which shows the considerable stability of the fragments formed.

Cyclisation of acyclic structures is often advanced as an explanation of observed rearrangements[71-73], etc. Especially convincing results which support the existence of this phenomenon can be found in the mass spectra of linear siloxane and carbosilane chains[6,45]. Almost all the fragment ions of sufficiently long siloxanes are formed in the cyclisation of either charged or neutral fragments. The mass spectra of the linear siloxanes contain all the elements of the mass-spectra of the corresponding cyclic molecules, including all the fragment and metastable ions and they could easily be taken for impurity ions if the corresponding multiply-charged ions were not absent. This phenomenon is analogous to the cyclisation of linear polysiloxanes on heating. The formation of an m/e 207 peak in the mass spectra of R_3AsO_3, R_3AsO_4, and R_3PO_3, where R = TMS (this is the base peak for R_3AsO_3) is undoubtedly connected with the cyclisation of ions[75].

There is evidently a connection between the skeletal rearrangement of tetrasila-adamantanes



where X = H, D, or Cl and of the cage polysilanes $Me_{2n-2}Si_n$ (n = 8, 9, or 10), and the appearance in their mass spectra of intense peaks of $[M-CH_3]^+$ (hydrogen rearrangement)[54] and $[M-Me_3Si]^+$ [55] ions; $[M-Me_3Ge]^+$ ions are typical for permethylcyclopolygermanes[43].

Geometrical factors are essential in the formation of new bonds[78]. In sufficiently rigid molecules rearranged ions are formed only when the interacting groups are

‡ A similar conclusion follows from the results obtained in the investigation of rearrangements in tetraphenylsilanes labelled with deuterium[71].

favourably situated. The migration of TMS groups, which gives intense peaks or rearranged ions in the mass spectra of TMS-derivatives of steroid phosphates does not occur when there is a considerable spatial separation of the corresponding groups; in this instance a hydrogen rearrangement prevails[79]. The mass spectra of TMS diethers of the type $Me_3SiO[CH_2]_nOSiMe_3$ (n = 10, 22) are characterised by the presence of the rearranged $Me_3SiOCH_2O_3SiMe_2$ ion, formed by the elimination of the central part of the molecule—almost all of the hydrocarbon chain, but, as the spectra of molecules labelled at one end with CD_3 groups show, there is no exchange of methyls between the TMS groups[80].

The examples of reactions (1a) and (1b) clearly show the connection between the skeletal rearrangements and the migration of the organic groups. Essentially, there is a single process of bond rearrangements (in this instance two bonds are broken, Si—O and Si—C and two such bonds are formed anew). Evidently, the rapid single-stage electronic process of bond migration in an electronically excited ion plays at least a significant part if not the determining one; after it follows the migration of the newly connected parts of the molecular ion.

However, it is possible that the comparatively high intensity of the rearranged ions in the mass spectra of organometallic compounds could be linked with the general retardation of the decomposition (see below); both are characteristic of the same compounds. Then the vibrational excitation of the ion facilitates the rearrangements which are dependent upon the necessary approach of the interacting parts of the molecular ion.

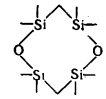
PRODUCTS OF IONIC MOLECULAR REACTIONS

In the mass spectrometric investigation of either individual organometallic compounds or of their mixtures with other substances it is necessary to take into account the possibility of distortion of the mass spectra by the products of ion-molecule reactions. The reactions of intense fragments of metal-containing ions with the molecules of a gas proper or of other compounds, leading to the intermolecular transfer of complex groups, are characterised by large effective profiles and proceed with appreciable yields at elevated or ordinary pressures in the ion source of the mass spectrometer.

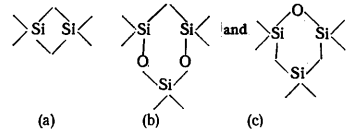
Heavy ions of the type $[M + 73]^+$, $[M + 147]^+$, etc. up to the very weak $[2M - 15]^+$ are recorded in the mass spectra of individual compounds, such as the TMS derivatives of glycerophosphates and other biologically active substances[81,82]. In the mass spectra of mixtures of compounds of the R_4E type (R = Me, Pr, or Bu; E = Si, Ge, or Sn) and Me_3SiR_1 (R_1 = OTMS, NHTMS, OMe) with a whole series of organic compounds which contain an electron-withdrawing group, ions of the $[M + A]^+$ type, where M is an organic molecule and A corresponds to R_3E^+, H_3E^+ and other intense fragment ions of these organometallic compounds, were observed[83]. The ratios of the intensities of the heavy ions for comparatively light A roughly follow the relations for fragment reagent ions; the intensity of $[M + A]^+$ falls with increase in the complexity of A.[82] (The peaks of the molecular ions R_4E^+ and $Me_3SiR_1^+$ are extremely weak.) The masses of the heavy ions (including the labelled ones) show that the heavy ions are formed by the simple addition of fragment ions A^+ to neutral molecules. Published results[83] reveal that the profiles of such reactions for even-electron fragment ions are much larger than those for the ion radicals.

DISSOCIATIVE IONISATION AND THERMOLYSIS: MASS-SPECTRAL RESULTS ON UNSTABLE AND "NONEXISTENT" COMPOUNDS

An analogy between dissociative ionisation and the thermal decomposition of molecules has been noted repeatedly (it is naturally assumed that the last process proceeds under conditions of unimolecularity). Although these two processes differ in principle, due to the nature and magnitude of the excitation energy, with the properties of the charged species, the conditions of observation, etc., their comparison shows a series of common features connected with the combination of electron-vibrational processes of bond migrations in ions and molecules, above all the similarity of the sets of reaction products and also the correlation between the temperature dependence of the thermolysis and the appearance potentials of the corresponding ions[84]. A series of correlations of thermolysis and "electronolysis" was also noted for organometallic compounds. Thus on the one hand the thermal rearrangement of cyclocarboxyloxane (I)


(I)

leads to the formation of smaller rings[85]:



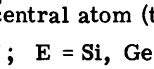
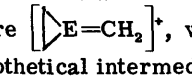
and on the other in the mass spectrum (I) there are ions which correspond to the ions of the $[M - CH_3]^+$ type of molecules (a)—(c). The similarity in the thermolysis and dissociation of a molecular ion in electron bombardment was noted for dimethylsila- and mono-germa-cyclobutanes[86]; in both processes the initial species lose C_2H_4 and C_3H_6, and the relative probability of decomposition with loss of C_3H_6 is considerably greater for germacyclobutane both in electron bombardment and in thermolysis. A similarity in the ratios of the probabilities of removal of C_2H_4 and C_3H_6 in thermolysis and electron bombardment is also observed for the disila- and digerma-cyclopentanes[28].

Comparison of thermolysis and dissociative ionisation is especially interesting in instances when the mass spectra allow the existence of unstable species postulated as intermediate reaction products to be guessed or confirmed to a certain extent. Among such substances there is considerable interest in the compounds of the bivalent elements of Group IVb§, including derivatives of silicon(II).[87] Compounds with multiple bonds are another type of unstable derivatives of these elements. The interest in these derivatives is due, on the one hand, to the fact that there is yet no satisfactory theoretical explanation of the inability of the Group IVb elements to form stable multiple bonds similar to the bonds in alkenes and carbonyls[89] (the calculations show the possibility of synthesis and separation of compounds with a double bond, in

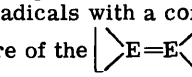
§ The oxides SiO, GeO, SnO, and PbO and their oligomers were separated by matrix isolation[88].

particular, Si=Si.[90] On the other hand, the assumption of the existence of intermediate compounds with a double $(p-p)\pi$-bond allows the mechanism of such reactions as the thermocondensation of monosilacyclobutanes[91,92], thermal changes in the gas phase of cyclocarboxyloxanes and cyclosiloxanes[93-95] to be explained easily; in this species such as $Me_2Si{=}CH_2$ and $Me_2Si{=}O$ are postulated. Indirect experimental confirmation of the existence of the unstable product $Me_2Si{=}CH_2$ was obtained recently[96]. The thermal removal of ethylene by germacyclobutane evidently proceeds just as for silacyclobutane and the thermocondensation to digermacyclopentane probably includes the formation of carbenoid species of the Me_2Ge: type[86]. In connection with this it is desirable to consider the mass spectral results about species of this type. Under the conditions of observation in the mass spectrometer they can be either ion-radicals or even-electron neutral molecular groupings.

The first report of the observation in the mass spectra of siloxanes of species of the dialkylsilanone type, made more than 20 years ago by Andrianov and Sokolov[97], must be regarded above all as the prediction of the existence of such species, since the investigators, using the comparatively imperfect mass spectral technique of that time, evidently took for the hypothetical silanones the even-electron fragment ions (mainly rearranged ones) usual for these compounds[6].

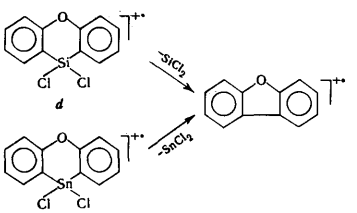
When the ionised species have sufficient energy the mass spectrum includes ions so deeply dissociated including ion-radicals formally corresponding to the bivalent metal. The appearance potentials of such ions are usually higher than those of the neighbouring odd-electron ones. Therefore it is interesting here to consider only those instances when the intensity of such ions is sufficiently high. As an example there is the ion $[R_2Si:]^+$ in the mass-spectra of the phenoxasilins[50], $[C_2H_4E]^+$ in the mass spectra of spiro-compounds with a metal central atom (the possible structure is ; E = Si, Ge, Sn, Pb [29,31-33]). Among the ions for which the presence of an E=X double bond (X = C or O) can be postulated are ions of the type $[R_2E{=}CH_2]^+$, which give extremely intense (or maximal) peaks in the mass spectra of the dialkylsila- and dialkylgerma-cyclobutanes[27-29]. In the mass spectra of the spiro-compounds[31-33] ions are released which can be assigned the structure , which agree with the structure of the hypothetical intermediate product of the thermolysis of silaspiroheptane[98].

Ion radicals of the silanone type were not observed in the mass spectra of siloxanes.

Ion radicals with a composition which corresponds to a structure of the  type (significant but not exceeding in intensity the neighbouring even-electron ions) were observed in the mass spectra of 1,2-disila- and 1,2-digerma-cyclopentanes[28]. However, in other instances the peak of the $[Me_4Si_2]^+$ ion is maximal[53]. Ions of this type are also intense in the mass spectra of 1,4-digermahexadienes[48,99].

The mass spectral results on the formation of neutral fragments of this type may be of great interest for comparison with chemical results. Since the information about neutral fragments is confirmed or is obtained on the basis of an examination of the decomposition of metastable ions, which proceeds in times of the order of more than 1 μs, it can be presumed that neutral species live for at least as long. This corresponds closely to the non-excited state. The composition of the neutral metal-containing fragments, found as the difference in the composition of the initial metastable ions and fragment ions, obtained as a result of a single-step change, usually corresponds to the composition of the molecules—both those known and often those unknown in the free form.

Bivalent metals correspond to neutral fragments of the R_2E type—Me_2Si, MePhSi, eliminated in the decomposition of the disilanes[69], Me_2Ge in the decomposition of methylpolygermanes[19,43] $(p\text{-Tol})_2E$ (where E = Si or Ge) in the decomposition of tolylcyclo-silanes and -germanes[35], $SiCl_2$ and $SnCl_2$ in the decompositions[10,51]:



10,10-Dimethyl- and 10,10-diphenyl-phenoxysilin eliminate the lower oxide of silicon, SiO.[50] The same group is lost in the last stages of the decomposition of the cyclosiloxanes and also certain linear siloxanes after the loss of a large part of the organic framework[6].

The species, the composition of which corresponds to the formula R_2EX (X = CH_2, O, etc.) can be assigned structures such as REXR, which corresponds to a bivalent metal, or structures with the $R_2E{=}X$ double bond. The latter may be stable. They correspond in particular to the hypothetical dialkylsilanones. Information is available on the formation of the neutral fragments H_2SiO,[50,51] Me_2SiCH_2,[34] Me_2SiO,[6] Cl_2SiO,[51] Me_2GeO [15,16] (including instances when this species is not a unit of the molecule investigated—cyclo-$[Pr^i_2\,GeO]_3$ [15]). In siloxanes neutral fragments of the Me_2SiO type are eliminated, evidently solely when the formation of the usual oligomers $[Me_2SiO]_{3,4}$ is impossible.

INTENSITY OF METASTABLE IONS AND GENERAL RETARDATION OF THE DECOMPOSITION OF THE IONS OF ORGANOMETALLIC COMPOUNDS

Interest in metastable ions is usually restricted to the information which they can give about paths and distinct steps in the decomposition, allowing a scheme of successive decompositions to be drawn up (in general, however, insufficiently well founded, as shown above). Here the intensity of the metastable ions is usually not measured and its magnitude is not taken into account at all. Furthermore the relative intensity of the metastable ions in the mass spectra of the organometallic compounds is usually quite significant in even an approximate calculation of the breadth of the corresponding peaks¶. Thus the ratio I_m/I_0 of the sizes of the "metastable" peak and the "ordinary" peak of the decomposition product reaches ~0.1 for the reaction

$$Me_{13}Si_6O_5^+ \rightarrow Me_7Si_3O_2^+ + (Me_2SiO)_3$$

¶ Precise calculation is difficult because of the differing effectiveness of the collection of ions which decompose in the ion source and in the analyser.

in tetradecamethylhexasiloxane and 0.2 for reaction (1b) in decamethylcyclopentasiloxane[6]. Hence these are significantly retarded on the average.

The lifetime of metastable ions of derivatives of the Group IVb elements was not measured specially; it was noted that in a mass spectrometer with double focussing the number of recorded metastable ions which decompose between the ion source and the first (electrostatic analyser, is several times greater than the number of ions which decompose between the first and second (magnetic) analysers. The number of metastable ions of the last type falls from Si to Ge and Sn (6—3—1).[20] Evidently, the total retardation of the decompositions which are characterised by the total relative intensity of the metastable ions increases from C to Si and then falls again from Si to Sn and Pb.

The ratio I_m/I_0, which characterises the relative probability of the metastable breakdown, can vary strongly for different paths of dissociation; for siloxanes the lower value of the ratio corresponds to a path leading to the formation of a lighter ion. For example, for reaction (1b) (formation of the ion m/e 267) $I_m/I_0 = 0.2$ and for (1a) (ion with m/e 73) $I_m/I_0 = 0.02$.

MULTIPLY-CHARGED IONS

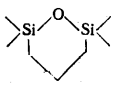
As noted in a recent study[100], the factors which determine the intensity of the doubly-charged ions and the path for their decomposition are "extremely complex and do not support widely used generalisations". In this connection a brief review of the empirical results on multiply-charged ions in the mass spectra of the organometallic compounds should be of interest.

The presence of multiply-charged ions in the mass spectrum of a complex molecule can be regarded as the appearance of its resistance towards dissociation or the retardation of the latter. The role of stabilising features in organic molecules usually brings about stable aromatic structures—this is so in particular for all the organic compounds for which triply-charged ions are observed. However, doubly- and triply-charged ions are characterised for the mass-spectra of organometallic compounds which contain respectively not less than two or three metal atoms in the molecule†. Intense peaks of multicharged ions are recorded in the mass spectra of methylsiloxanes[4,101,102] paraffins substituted with two TMS groups[5], silazanes[46], and other compounds which contain more than one metal atom[58,59,103]. Evidently the charges of multicharged ions are localised on different metal atoms.

For the heaviest of the observed multicharged ions usually $m/e = \frac{M}{n} - R$, which corresponds to the loss from the molecule M of a number of radicals R equal to the ionisation multiplicity n. Evidently these radicals are removed from the metal atoms on which the charge is localised, as is shown by the loss of valence electrons by these atoms. The stability of the multicharged ions is much greater when the metal atoms are separated by atoms or groups: O, CH_2, NH, etc.[104] and the effect of the oxygen atoms on the stabilisation of the multicharged ions is stronger than that of CH_2 groups. Thus the intensity[28,58] of the doubly-charged ions of the type $[M - 30]^{2+}$ is 1% in

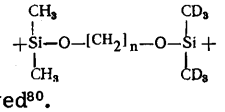


and 4% in



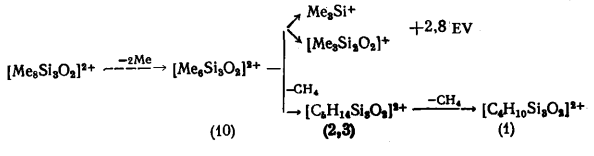
for cyclocarboxyloxanes it increases twofold when all the CH_2 groups are replaced by oxygen atoms in the Si_3 molecules and threefold in Si_4 molecules[34]. Oxygen has the same effect in germanium compounds: the intensity of the doubly-charged ions from digermoxanes is higher than for the analogous digermanes[16]. The role of connecting groups in the stabilisation of multicharged ions can be determined by factors such as the increase in the distance between the charges and their delocalisation at the electronic orbitals of the connecting atom, strengthening the effect of $p_\pi - d_\pi$ conjugation for N or O. In individual instances, for the especially stable six-membered cyclic molecules it is possible to observe doubly-charged ions of the $[M-R]^{2+}$, obtainable in the breaking away of only one radical (considerably less intense, however, than ions of the $[M - 2R]^{2+}$ type)[34,58,103]. The intensity of the $[M - 30]^{2+}$ ions of the bistrimethylsilyl derivatives of the amino-oxynaphthalenes depends on the position of the substituent[105].

Multiple ionisation with localisation of charges on various metal atoms is evidently linked with the migration of charges (excitation) to these atoms. Charge migration in a hydrocarbon chain proceeds with minimal barriers[106] and is controlled by the ionisation potentials of the various parts of the molecules[107,108]. For chains with two Me_3SiO groups at the ends, one of which is completely deuteriated, the doubly-charged ions formed in the loss of two methyl groups from different silicon atoms



are readily observed[80].

Multiply-charged ions decompose according to two paths—with and without sharing of charges. The peaks of corresponding metastable ions are often observed; their form shows the nature of the process—in decomposition with charge sharing, which is accompanied by the release of a considerable kinetic energy, broad peaks with flat tops are obtained. The width of the peak allows the energy of the decomposition process to be estimated[109,110]; on taking into account that it is determined by the coulombic repulsion of the charges, the position of the latter in a multicharged ion and its configuration can be found. For example, doubly-charged octamethyltrisiloxane ions decompose according to the scheme:



(the numbers in parentheses give the relative intensity in percentages of the main singly-charged ion $[M - 15]^+$; the continuous arrows show the changes confirmable by metastable ions). The total energy of 2.8 eV of the singly-charged fragments of a doubly-charged ion corresponds to a charge separation of ~5 Å, which is close to the distance between the extreme silicon atoms in this molecule (5—6 Å, depending upon the conformation)[102].

The other path for the decomposition of multiply-charged ions (including triply-charged ones) is the splitting, usual for singly-charged ions, of neutral fragments,

† Doubly-charged ions GeH_2^{2+}, GeH^{2+}, and Ge^{2+} have been recorded for GeH_4.[16]

including those associated with rearrangements. Thus for the doubly- and triply-charged ions of the linear methylsiloxanes a series of fragment ions obtained by successive removal of two or three methane molecules formed from the organic framework of the molecule[94,102]. Since such a process is energetically less favourable than decomposition with charge division it shows the considerable stability of the siloxane skeleton of the multiply-charged ions. The slow decompositions of this type, which are observed, for example, for the Si_2 and Si_3 linear siloxanes[102], are especially remarkable[102]. In organic mass spectrometry similar results are known only for stable aromatic compounds[111].

NEGATIVE IONS

There have been only a few mass spectrographic studies of the negative ions of the organometallic compounds of Group IVb. An intense molecular anion-radical with a resonance maximum at electron energies not exceeding a few eV was observed for dodecamethylcyclohexasilane; for Me_6Si_2 the molecular anion was two orders of magnitude weaker and for Me_6Si_2O it was not observed at all[112]‡. A molecular anion was also not recorded in the negative mass-spectra of the tetramethyl derivatives Me_4E (E = Si, Ge, or Sn); however, for E = Si or Sn the intense ions $[M - 1]^-$ with resonance maxima at 4 and 7.8 eV and at 8 eV respectively, stabilised with $p_\pi - d_\pi$ interaction with the vacant orbitals of the central metal atom[114]. For E = Ge or Sn, Me_3E^- ions are characteristic; lighter fragment ions were also observed[114,115]. The main process for the decomposition of the negative ions of the tetraphenyl derivatives (E = Si, Ge, Sn, Pb) is the loss of phenyl or diphenyl; hydrogen rearrangement also plays some part in the subsequent decomposition[71].

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‡ A stable anion-radical of the compound $(Me_2Si)_6$ was also obtained in the condensed phase[113].

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