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Review

Probing the gas-phase ion chemistry of simple Ge systems

José M. Riveros

Institute of Chemistry, University of São Paulo, Caixa Postal 26077, CEP 05513-970, São Paulo, Brazil

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Abstract

The present review presents a tour de force through the main aspects related to the positive and negative ion mass spectrometry of simple Ge-containing compounds. Important properties such as proton affinity, gas-phase acidities, and electron affinities are discussed for the few cases where such parameters are experimentally known, or for which high-level theoretical calculations are available. The main ion–molecule reactions, both positive and negative ions, of simple germanium ions is also discussed with emphasis on the mechanism of these reactions and the structure of the product ions. This review also presents a brief survey of gas-phase Ge cluster ions. (Int J Mass Spectrom 221 (2002) 177–190)

Keywords: Germanium-containing ions; Ion–molecule reactions; Acidities of organogermanes; Germanium clusters

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1. Introduction

The gas-phase ion chemistry of organogermanes remains relatively unexplored by comparison with their silicon analogs for which comprehensive reviews have been published over the last 15 years [1]. This partly reflects the fact that the chemistry of organosilanes has been more extensively investigated, and the larger stability of a wide variety of silicon compounds. Yet, there is an increasing interest in understanding the reactivity and energetics of simple neutral and ionic Ge species. It is believed that a number of germanium-containing positive ions and free radicals may play an important role in vapor deposition processes, in film formation, and in the synthesis of ceramic materials [2–4]. Likewise, germanium-containing anions are deemed relevant in modern organometallic chemistry and material sciences. Germyl anions have found application as selective reagents in organic synthesis [5] while germanates containing GeO_4 building units are being explored as possible unique framework topologies for zeolites [6]. Cluster anions of Ge are considered typical examples of Zintl ions and are a source of valuable structural information [7], whereas unraveling the mechanism and the role of anionic species in sol–gel processes leading to Ge-containing polymeric materials are key questions in the search for new materials [8].

The objective of the present review is to provide a general survey of some of the more important aspects related to the ion chemistry of simple germanium species, and to point out some of the relevant questions in this field.

E-mail: jmrnigra@quim.iq.usp.br

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2. Mass spectrometry of organogermanes

Mass spectrometry of organogermanes was slow to develop and work on the germanium hydrides [9] was followed by systematic studies of the mass spectra of tri- and tetraalkyl and tetraarylgermanes [10–13]. Even for such simple compounds, and because germanium has five stable abundant isotopes, the quantitative interpretation of these mass spectra proved to be laborious in the early days. In general, high resolution is generally necessary to distinguish overlapping isotopic fragment peaks differing by one hydrogen atom. This problem becomes even more complex in dealing with polygermanes [14].

In general, the mass spectra of these organometallic compounds are characterized by fragment ions that retain the germanium atom. This has been attributed to the fact that Ge–H, Ge–C, and Ge–halogen bond energies are much weaker than the corresponding C–C bond energies. Nevertheless, this simple rule of thumb starts to break down in some of the halides [13,15] or in multiple chlorine-substituted organogermanes [16].

General rules for interpreting the mass spectra of these relatively simple germanium-containing compounds were the subject of very early reviews [17], and a more general summary has recently been published [18].

However, and in spite of the diversity and growing knowledge of modern Ge chemistry, there is still little reliable data regarding such fundamental properties as heats of formation, bond energies, electron affinities, and proton affinities of organogermane species. Thus, the next sections will discuss what is known about simple systems.

3. Germane, GeH_4

3.1. Mass spectrum

The 60 eV EI mass spectrum of monogermane [9a] is very similar to that of the corresponding monosilane, and is characterized by strong peaks due to different fragment ions, namely $GeH_3^{\bullet +}$ (34.7%), GeH_2^+ (37%), GeH^+ (10.5%), and Ge^+ (17.6%), and essentially no molecular ion, GeH_4^+ (estimated to be less than 0.2%). High-level calculations [19] indeed predict the molecular ion to be a Jahn–Teller distorted structure that is best represented as a $GeH_2^+(H_2)$ moiety, with an estimated dissociation energy of less than 5 kcal mol^{-1}.

The adiabatic ionization energy of GeH_4 has been difficult to determine because of the low yield of the molecular ion and its distorted tetrahedral structure. The most recent photoionization study [20] has placed the IE of $GeH_4 \leq 10.53$ eV, a value considerably less than that obtained in earlier determinations by photoelectron spectroscopy [21].

3.2. The Ge–H bond energy

The Ge–H bond energy is a relevant parameter for gas-phase neutral and ion chemistry. Over the years, several values have been reported in the literature for the H_3Ge–H bond energy. For example, gas-phase kinetic measurements [22] have led to a value of 82.7 ± 2.4 kcal mol^{-1}, whereas a somewhat lower value of 78.0 ± 1 kcal mol^{-1} has been derived from state-to-state kinetics using infrared chemiluminescence [23]. In the meantime, the photoionization experiments on GeH_4 [20] have settled this question, and the present recommended value [24] for $D_0(H_3Ge–H)$ stands at 82 ± 2 kcal mol^{-1}. Several high-level calculations have also addressed the problem of the Ge–H bond dissociation energy in germane. For example, Binning and Curtiss have calculated a $D_0(H_3Ge–H)$ of 84.8 kcal mol^{-1} [25] from calculations at the MP4 level with a basis set specially developed for Ge, whereas Radom and coworkers [26] have predicted a $D_0(H_3Ge–H)$ of 84.7 kcal mol^{-1} from G2 calculations. Our group has used a different extended basis set, and a value of 81.1 kcal mol^{-1} has been calculated for $D_0(H_3Ge–H)$ at the QCISD(T) level [27]. A more extended theoretical investigation of the heat of formation of GeH_4 has concluded a value of 83.8 kcal mol^{-1} for $D_0(H_3Ge–H)$ [28].

3.3. The proton affinity of monogermane

Establishing the proton affinity of GeH_4 has proven to be an experimental challenge. Because actual detection of GeH_5^+ has been rare, it has been difficult to establish ion–molecule reactions that lead to protonation of monogermane. These observations suggest that GeH_5^+ probably undergoes rapid dissociation upon formation. The only available data stems from an ion-beam scattering experiment that showed deuteron transfer to GeH_4 to be exothermic for $C_2D_3^+$ and endothermic for D_3S^+ [29]. A re-evaluation of this data has led to a recommended value of 170.5 kcal mol^{-1} for the proton affinity of monogermane in the comprehensive review of Hunter and Lias [30]. However, this value seems too high when compared with results obtained from high-level theoretical calculations.

The GeH_5^+ ion has attracted considerable attention not only because of its role in the proton affinity of monogermane but particularly because of its structural features. High-level ab initio calculations have shown that the structure of GeH_5^+ corresponds to that of a planar GeH_3^+ attached to an H_2 molecule [31] and should thus be represented as a loosely bound ion, $GeH_3^+(H_2)$. This complex is calculated to have a dissociation energy of the order of 10 kcal mol^{-1}, a fact that may explain the experimental ambiguities regarding the observation of protonated monogermane. From these same calculations [31a], a value of 156.4 kcal mol^{-1} was predicted for the proton affinity of GeH_4 at 0 K. Our more recent calculations, using density functional methods and a specially adapted basis set, yield a monogermane proton affinity of 161.1 kcal mol^{-1} at 298 K [32]. Considering that the theoretical methodology used in our work has proven to estimate gas-phase proton affinities within less than 2 kcal mol^{-1} of the experimental values [33], we feel that the value quoted in Ref. [30] is much too high and that a better estimate is the one predicted by our calculations.

3.4. The gas-phase acidity of monogermane

The gas-phase acidity of GeH_4 has been determined by ion cyclotron resonance techniques from a series of overlapping proton transfer equilibrium experiments [34]. The values derived from these experiments are $\Delta G^\circ_{acid}(GeH_4) = 350.8 \pm 1.3$ kcal mol^{-1} and $\Delta H^\circ_{acid}(GeH_4) = 358.9 \pm 1.3$ kcal mol^{-1}. The ultimate accuracy of these absolute values is of course dependent on the accuracy of the absolute values used for the reference compounds. Although some concern has been voiced about these values because G2 calculations [26] yield a somewhat higher value for $\Delta H^\circ_{acid}(GeH_4) = 362.9$ kcal mol^{-1}, our theoretical study [32] yields a value of $\Delta H^\circ_{acid}(GeH_4) = 359.7$ kcal mol^{-1} in excellent agreement with the experimental value.

4. The $GeH_n^{+/0/-}$ species

The GeH_n^+ ($n = 0$–3) fragment ions are very noticeable in the mass spectrum of monogermane as mentioned earlier, and these species play an important role in the ion–molecule chemistry of monogermane.

Unlike the methyl radical, neutral ${}^\bullet GeH_3$ exhibits a pyramidal structure (C_{3v} symmetry) as confirmed by spectroscopic observations [35], and high-level theoretical calculations [23,28,36]. The ionization energy of this radical has been determined to be ≤7.948 eV [20] and the resulting ion, GeH_3^+, is predicted to have a planar structure (D_{3h} symmetry). A recent investigation [37], based on neutralization–reionization, charge reversal experiments, and combined with ab initio calculations has reached the surprising conclusion that the isomeric dihydrogen complex $HGe^+(H_2)$ is only about 10 kcal mol^{-1} less stable than GeH_3^+. Furthermore, the collisional activation (CA) spectrum of the $[Ge,H_3]^+$ species generated in these experiments strongly suggests that this didyhdrogen complex plays an important role in the ion chemistry of these systems.

Gas-phase GeH_3^- anions can be generated from GeH_4 along with some of the other germanium hydride anions by dissociative electron capture at electron energies ~8 eV [38]. Ions generated in this fashion were characterized by threshold photodetachment experiments carried out in an ICR spectrometer [39], and an upper limit of 1.74 ± 0.04 eV was established for the electron affinity of ${}^{\bullet}GeH_3$. However, it is known that an adiabatic electron affinity can be derived from these experiments only in cases where the geometry of the anion and the neutral are reasonably similar, or where favorable Franck–Condon factors allow for the observation of the adiabatic transition. These considerations are important for the $GeH_3^-/{}^{\bullet}GeH_3$ system because a large change is predicted in the ∠H–Ge–H angle in going from the radical (110°) to the anion (93°) along with a considerable lengthening of the Ge–H bond [40]. In fact, a much lower electron affinity is estimated indirectly for ${}^{\bullet}GeH_3$, namely 1.57 ± 0.13 eV, from the experimental gas-phase acidity [34] and the Ge–H bond dissociation energy of GeH_4 [20]. This lower value is consistent with some earlier theoretical calculations [40,41], while more recent high-level theoretical calculations estimate values in the range of 1.55–1.61 eV for the electron affinity of ${}^{\bullet}GeH_3$ [26,27,37].

Neutral germylene, $:GeH_2$, has been the subject of considerable interest in recent years [42], because it can act as an effective reagent for promoting GeH_2 insertion across double bonds [43]. The ionization energy of GeH_2 has been determined to be ≤ 9.25 eV [20]. Interestingly enough, the weakly bound dihydrogen complex, $Ge^+(H_2)$, is predicted to be slightly lower in energy than the conventional bent $[HGeH]^+$ structure [37]. As in the case of $[Ge,H_3]^+$ species, the $Ge^+(H_2)$ structure has been claimed to be formed in neutralization–reionization experiments involving the GeH_2 system [37]. Finally, germylene can also form stable negative ions, GeH_2^-, and an electron affinity of 1.0970 ± 0.0027 eV has been determined by photoelectron spectroscopy [44].

5. Gas-phase ion–molecule reactions involving GeH_4

Reactions of the primary ions obtained by electron ionization of GeH_4 with the neutral monogermane precursor have been characterized both by low- and high-pressure mass spectrometric techniques [45,46], and more recently by ion trap techniques (ITMS) [47].

The overall reactivity pattern is relatively complex, and Fourier Transform Mass Spectrometry (FTMS) has been very useful in identifying the different reaction channels [45]. This is particularly true due to the ability of selecting a reagent ion containing only one germanium isotopic species in FTMS experiments.

Some of the most important results regarding the ion–molecule chemistry in neat monogermane can be summarized as follows:

(i) GeH^+ and GeH_2^+ react readily with GeH_4 to yield GeH_3^+, and the product ion has been shown to retain the original isotope (Eqs. (1) and (2)),

$$^{70}GeH^+ + GeH_4 \rightarrow {}^{70}GeH_3^+ + GeH_2 \qquad (1)$$

$$^{70}GeH_2^+ + GeH_4 \rightarrow {}^{70}GeH_3^+ + GeH_3 \qquad (2)$$

(ii) $^{70}Ge^+$ ions react with GeH_4 by hydrogen atom abstraction to yield $^{70}Ge^+$, a reaction similar to that shown in (2)

(iii) GeH_3^+, a primary and secondary ion in this system, reacts with GeH_4 by hydride abstraction with isotope scrambling as shown in (3),

$$^{70}GeH_3^+ + GeH_4 \rightarrow GeH_3^+ + {}^{70}GeH_4 \qquad (3)$$

(iv) GeH_2^+ and Ge^+ also undergo slow condensation reactions followed by elimination of molecular hydrogen, reactions (4) and (5),

$$GeH_2^+ + GeH_4 \rightarrow Ge_2H_4^+ + H_2 \qquad (4a)$$

$$GeH_2^+ + GeH_4 \rightarrow Ge_2H_2^+ + 2H_2 \qquad (4b)$$

$$Ge^+ + GeH_4 \rightarrow Ge_2H_2^+ + H_2 \qquad (5)$$

(v) By comparison, GeH_3^+ undergoes very slow condensation-type reactions to yield $Ge_2H_5^+$ and $Ge_2H_3^+$. However, these reactions have not been observed in the ITMS experiments [47].

The gas-phase reaction of primary and secondary Ge ions, obtained from germane, with a number of simple substrates, such as O_2, NH_3, PH_3, SiH_4, alkanes, and alkenes have been systematically studied by the group of Benzi, Operti, Vaglio, Volpe and coworkers at the University of Torino in Italy [45,48–54]. The underlying motivation for the investigation of these systems is related to the interest in understanding the fundamental processes involved in the formation of amorphous Ge-containing compounds in chemical vapor deposition processes.

Although a full account of all the findings of the Italian group is best described in the individual papers, some important conclusions are particularly noticeable. For example, O_2 reacts with $Ge_2H_2^{\bullet +}$, formed in ion–molecule reactions of germane (see reactions (4b) and (5)), to yield $GeOH^+$ through reaction (6)

$$Ge_2H_2^{\bullet +} + O_2 \rightarrow GeOH^+ + HGeO^{\bullet} \qquad (6)$$

This unusual reaction has been proposed to occur via a four-center mechanism [45]. Ab initio calculations at the HF level predict that a linear $GeOH^+$, corresponding to protonated germanium oxide, is considerably more stable than the alternative linear $HGeO^+$ ion [55].

The hydrogen-containing ions obtained by electron ionization of GeH_4 react with NH_3 primarily by proton transfer to yield NH_4^+ whereas condensation-type reactions are much slower. The notable exception is GeH_2^+ that undergoes significantly competitive reactions to yield $GeNH_4^+$ and $GeNH_3^+$ (of unknown structures) by hydrogen elimination [45,52]. The secondary product $Ge_2H_2^{\bullet +}$ also reacts with NH_3 as shown in reaction (7) by subsequent elimination of molecular hydrogen,

$$Ge_2H_2^{\bullet +} + NH_3 \rightarrow Ge_2NH_3^{\bullet +} + H_2 \qquad (7)$$

Interest in the reaction mechanisms responsible for the formation of ions containing Ge–C bonds has been the focus of studies involving ion–molecule reactions of GeH_4 with simple hydrocarbons [49,54], ethylene and propene [48,54], allene [49,53], and acetylene [49]. Primary ions of germane undergo very slow reaction with methane and ethane, and under methane or ethane chemical ionization conditions formation of small amounts of $GeCH_5^+$, $GeCH_7^+$, and $GeC_2H_9^+$ is observed as the result of tertiary reactions [49]. Other ions, such as $GeC_2H_5^+$ and $GeC_2H_7^+$ are also detected as minor product ions in this case. By comparison, reaction with acetylene, C_2H_2, gives rise to abundant amounts of $GeC_2H_3^+$ (in the case of acetylene), and to $GeC_3H_n^+$ (n = 3–5) through a sequential set of ion–molecule reactions under propyne, C_3H_4, chemical ionization conditions. Likewise, chemical ionization of GeH_4 and C_2H_4 mixtures produces significant amounts of $GeC_2H_5^+$ and $GeC_2H_7^+$ ions. Since reactions observed under chemical ionization conditions are promoted by ions originating from GeH_4 as well as from those of the corresponding carbon compound, the overall mechanism for these reactions is quite complex. A more detailed study of the individual reactions in the GeH_4/C_2H_4 system reveals that the different primary ions of monogermane give rise to the full family of $GeC_2H_n^+$ (n = 2–7) ions, with rate constants lower than those predicted by collision theory [56]. Further reaction of the $GeC_2H_n^+$ with monogermane yield condensation products. Independent experiments carried out by tandem mass spectrometry [57] have shown that GeH_3^+ reacts with C_2H_4 to yield $GeC_2H_5^+$ via initial formation of a $GeC_2H_7^+$ adduct.

The structure of the newly formed ions containing Ge–C bonds is a matter of considerable interest. Although no experimental evidence is available regarding the connectivity of the $GeC_2H_n^+$ species, theoretical calculations have addressed the question of the stability of the different isomeric possibilities [56,58]. For the $GeC_2H_7^+$ ion, ab initio calculations [59] predict the dimethyl germyl ion, $(CH_3GeHCH_3)^+$, to be the most stable structure.

A mixture of GeH_4 and CO yields $GeCO^+$ as the most important cross-reaction product under chemical ionization conditions [48]. The structure of this ion is an interesting problem because it bears on the question of model systems for main group carbonyls. A recent study by CA spectroscopy [60] suggests that this ion retains a Ge^+–CO connectivity. At lower pressures, FTMS experiments reveal that the main reaction (8a) leading to a cross ionic product is promoted by a secondary Ge-containing ion, with GeH_3O^+ as a minor product.

$$Ge_2H_5^+ + CO \rightarrow GeH_5O^+ + GeC \qquad (8a)$$

$$Ge_2H_5^+ + CO \rightarrow GeH_3O^+ + (GeCH_2) \qquad (8b)$$

In both cases, the resulting ions involve the formation of a Ge–O covalent bond. Similar reactions are observed with CO_2 and result in the formation of GeH_5O^+ and GeH_3O^+.

Ionic reactions between primary and secondary ions of PH_3 and GeH_4 give rise to a number of interesting ions [51]. Some of the reactions that have been identified to proceed rapidly (ion trap experiments) and to lead to the formation of ions with Ge–P bonds, are shown as follows:

$$P_2{}^+ + GeH_4 \rightarrow GePH_2{}^+ + PH_2 \qquad (9a)$$

$$P_2{}^+ + GeH_4 \rightarrow GeP_2{}^+ + 2H_2 \qquad (9b)$$

$$P_2H^+ + GeH_4 \rightarrow GePH_2{}^+ + PH_3 \qquad (10a)$$

$$P_2H^+ + GeH_4 \rightarrow GeP_2H_3{}^+ + H_2 \qquad (10b)$$

$$GeH_2{}^+ + PH_3 \rightarrow GePH_3{}^+ + H_2 \qquad (11)$$

Finally, reactions between ionic fragments formed in GeH_4/SiH_4 and GeH_4/CH_3SiH_3 mixtures yield $GeSiH_5{}^+$ as the most important Ge–Si reaction product [50,61].

6. Ion–molecule reactions in other organogermane systems

6.1. MeGeH$_3$

The primary ions obtained from methyl germane exhibit a considerably more complex reactivity pattern with the parent neutral and with other simple substrates [62–64]. The minor fragments $GeH_n{}^+$ ($n = 0$, 2, 3) react rapidly with CH_3GeH_3 to yield CH_3Ge^+ ions (of unknown atom connectivity) and $CH_3GeH_2{}^+$ (assumed structure). CH_3Ge^+ and $CH_3GeH_2{}^+$ ions undergo a variety of condensation reactions that yield a family of $Ge_2CH_n{}^+$ (n = 4–7 and 9) ions as well as $GeC_2H_7{}^+$. The structure of these $Ge_2CH_n{}^+$ ions remains to be elucidated by more sophisticated mass spectrometric techniques.

The structures of $[GeCH_2]^+$ and $[GeCH_3]^+$ have been examined by CA and neutralization–reionization mass spectrometry [65]. The prevalent connectivity encountered for these ions corresponds to a $GeCH_n{}^+$ (n = 2–3) structure. A model of the cationic and neutral surfaces for the $[GeCH_2]$ species suggests that significant amounts of neutral or cationic germaacetylene or germavinylidene are unlikely to be formed in these experiments. Similar experiments with $[Ge,C,H]^+$ ions are also conclusive about $GeCH^+$ being the preferred connectivity. This connectivity is also predicted by ab initio calculations to be substantially more stable than the $HGeC^+$ isomer [66].

The proton affinity of CH_3GeH_3 is unknown, and its experimental determination remains an experimental challenge because of the low stability expected for the corresponding protonated form. Ab initio calculations [67] at the Hartree–Fock level predict the structure of protonated methylgermane to be a dihydrogen complex, $CH_3GeH_2{}^+(H_2)$, and the proton affinity of CH_3GeH_3 to be 5 kcal mol^{-1} higher than that of germane.

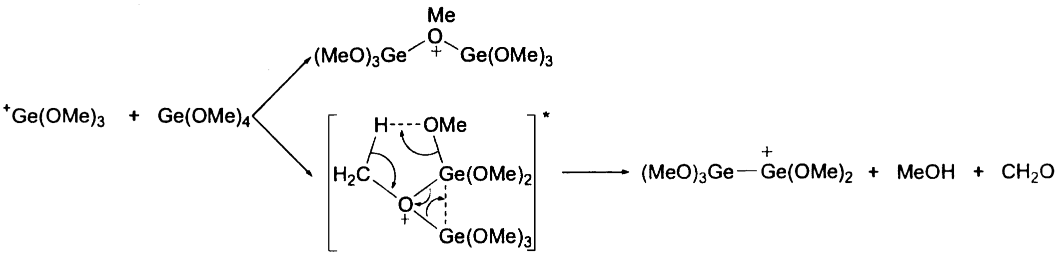
6.2. Ge(OMe)$_4$

Our laboratory has characterized the ion–molecule reactions between the fragment ions obtained by electron ionization of tetramethoxygermane, $Ge(OMe)_4$, and the parent neutral [68]. Ionization of $Ge(OMe)_4$ yields an interesting mixture of odd- and even-electron fragment ions, namely $HGe(OMe)_3{}^{\bullet+}$, $Ge(OMe)_3{}^+$, $H_2Ge(OMe)_2{}^{\bullet+}$, $HGe(OMe)_2{}^+$, and $GeOMe^+$.

Reactions of these primary ions with the neutral precursor can be rationalized by nucleophilic addition of these ions on an oxygen lone pair followed by elimination of formaldehyde and/or elimination of methanol. This is illustrated for $(MeO)_3Ge^+$ in reaction (12) where the putative structure of the product ions is based on the expected stability for the different likely structures.

$$(MeO)_3Ge^+ + Ge(OMe)_4 \rightarrow (MeO)_3Ge\text{–}O^+(Me)\text{–}Ge(OMe)_3 \qquad (12a)$$

$$(MeO)_3Ge^+ + Ge(OMe)_4 \rightarrow (MeO)_3Ge\text{–}Ge(OMe)_2{}^+ + MeOH + CH_2O \qquad (12b)$$



Scheme 1.

The elimination shown in reaction (12b) is particularly interesting because it leads to an ion with a Ge–Ge bond through what can been rationalized as a concerted process shown in Scheme 1.

By comparison, $HGe(OMe)_3{}^{\bullet+}$ ions transfer a proton to neutral $Ge(OMe)_4$ but can also promote reaction (13),

$$HGe(OMe)_3{}^{\bullet+} + Ge(OMe)_4 \rightarrow Ge_2(OMe)_6{}^{\bullet+} + MeOH \quad (13a)$$

$$HGe(OMe)_3{}^{\bullet+} + Ge(OMe)_4 \rightarrow Ge_2(OMe)_4{}^{\bullet+} + 2MeOH + CH_2O \quad (13b)$$

Here again, it is reasonable to assume that the most likely structure for the $Ge_2(OMe)_6{}^{\bullet+}$ ion is one displaying a Ge–Ge bond. Further elimination suggests formation of a rare Ge=Ge double bonded ion.

At present, we have some evidence that reactions similar to (12a) and (12b) occur with the neutral boron, silicon, and titanium homoleptic alkoxides [69].

7. Reactivity of R_3Ge^+ ions

The reactions of the ubiquitous gas-phase R_3Ge^+ ions are of particular interest because these species have been extremely elusive to be characterized in condensed phases [70].

The prototype Me_3Ge^+ gas-phase ion is the base peak in the mass spectrum of $GeMe_4$, and is observed to react with the parent neutral to yield $Ge_2Me_7{}^+$ only under high-pressure mass spectrometry conditions, and at source pressures of the order of 2–4 Torr [71]. Yet, the most important aspect of the Me_3Ge^+ ions, and similar species, is their strong electrophilic character that accounts for the great propensity to form adducts with *n*-donor bases (B) [72,73]. This has been shown to occur with simple aliphatic neutrals containing N, O, or S as shown in Eq. (14).

$$Me_3Ge^+ + :B \rightarrow [MeGe_3B]^+ \quad (14)$$

This type of association reaction is similar to those extensively studied for Me_3Si^+ ions [74].

The relative binding strength of the adducts has been determined to follow the qualitative trend of the gas-phase basicities of the donor base, i.e., *t*-BuOH > *i*-PrOH > EtOH > MeOH > H_2O. The binding to alcohols is sufficiently selective such that 1,2-cyclopentanediols isomers have been distinguished by their reactivity towards Me_3Ge^+ in tandem mass spectrometry experiments [75]. The binding energy between Me_3Ge^+ and H_2O (reaction (15)) has been determined [71], and reveals the significant stability of such adducts.

$$Me_3Ge^+ + H_2O \rightarrow [MeGe_3:OH_2O]+ \quad \Delta H^\circ = -28.6 \pm 0.5\,\text{kcal mol}^{-1} \quad (15)$$

This binding energy is somewhat less than the 30.1 ± 1.9 kcal mol^{-1} measured for the analogous Me_3Si^+ ion [76]. Methanol, as well as higher alcohols, displace water rapidly from the $[MeGe_3:OH_2]^+$ moiety, and a binding energy of 35.0 ± 0.6 kcal mol^{-1} has been obtained for $[MeGe_3:O(H)Me]^+$ from high-pressure donor–base switching equilibrium experiments [71].

The relative binding energy of Me_3Ge^+ to a large number of substituted acetophenones, anilines, and pyridines has also been reported recently [77]. There are two significant findings in these experiments: (1) there is a reasonable linear relationship between gas-phase basicities for H^+ and for Me_3Ge^+; (2) the quantitative relative trend of Me_3Ge^+ basicities follows closely the linear energy relationship of Tsuno [78], that stands amongst one of the many modifications to the classical Hammet-type equations. Although absolute values were not obtained from these experiments, DFT calculations at the B3LYP/6-31 + G* level predict a ΔG° of 40 kcal mol^{-1} for the Me_3Ge^+ basicity of acetophenone.

The trimethylgermylium ion, Me_3Ge^+, has also been observed to form adducts with arenes [79]. A series of gas-phase equilibrium measurements show the stability of the adducts ($-\Delta G^\circ$) to obey the order 1,3,5-$Me_3C_6H_3$ > 1,3-$Me_2C_6H_4$ > H_2O > MePh > C_6H_6. The observed thermochemistry, and the subsequent reactivity of these [$Me_3Ge^+\cdot$arene] adducts have been used to suggest that the most likely structure of these species is best represented by a sigma-type complex.

Me_3Ge^+ ions can also be the product of an unusual ion–molecule reaction that involves the formal transfer of CH_3^- [80,81], shown as follows:

$$Me_3Si^+ + GeMe_4 \rightarrow Me_3Ge^+ + SiMe_4 \qquad (16)$$

$$CH_3 + GeMe_4 \rightarrow Me_3Ge^+ + C_2H_6 \qquad (17)$$

These reactions are a clear indication that the Me_3Ge^+ is more stable than the corresponding carbon or silicon analog although the actual enthalpy change for these reactions is still uncertain. Theoretical calculations carried out in our group [82] reveal that reaction (16) proceeds through a stable intermediate with a methide ion bridging the two trimethyl moieties, $[Me_3Si \cdots Me \cdots GeMe_3]^+$. Similar type reactions have also been observed in phenyltrimethylgermanes [83,84] with a series of reacting ions, such as Me_3Si^+, Me_3C^+, Me_2CH^+, and Me_2Cl^+. For example,

$$Me_3Si^+ + Me_3GePh \rightarrow Me_3Ge^+ + Me_3SiPh \qquad (18)$$

Reaction (18) is assumed to proceed through an intermediate sigma complex.

8. Negative ion mass spectra of simple germanium systems

Monogermane yields all of the GeH_n^- (n = 0–3) ions by electron dissociative attachment [38,39] at electron energies around 8 eV. The quantitative abundance of these ions in the negative ion mass spectrum is not easy to establish accurately because of the overlapping isotopic patterns of these ions. At the low pressures, typically used in ion cyclotron resonance spectrometers, these ions are unreactive in the presence of their neutral precursor. However, studies carried out at higher pressures (25–450 mTorr) reveal that these primary ions give rise to a series of condensation ion–molecule reactions and $Ge_2H_n^-$ (n = 0–5) product ions [85]. At the higher germane pressures, further clustering reactions take place and the full family of $Ge_nH_m^-$ (n = 2–9) ions are observed.

Germanium tetrahalides also have been found to yield a number of negative ions. For example, GeF_4 has been found to yield abundant F^- and GeF_3^- ions in the electron energy range of 8–11 eV, along with very small amounts of GeF^- and GeF_2^- [86]. At 70 eV, GeF_4^- is the second most intense peak after F^-. Pressure dependence studies were carried out and led to the conclusion that all of these ions promote ion–molecule reactions with GeF_4 to yield GeF_5^-. Furthermore, $Ge_2F_4^-$, $Ge_2F_6^-$, and $Ge_2F_8^-$ ions were also detected in this early mass spectrometric study at pressures of the order of 5×10^{-5} Torr although the exact ion–molecule reactions leading to these product ions could not be established unequivocally.

Similar mass spectrometric experiments have been reported for $GeCl_4$ and $GeBr_4$ [87], and the observed negative ions are GeX_3^-, GeX_2^-, X_2^-, and X^- (X = Cl, Br). The most intense negative ions in $GeCl_4$ have also been detected by a combination of electron transmission spectroscopy and dissociative electron attachment spectroscopy [88]. However, there are significant discrepancies for the measured appearance energies of these ions between these two methodologies.

9. Gas-phase acidities and electron affinities

Gas-phase acidities and electron affinities of atomic and molecular species are intimately connected with negative ion chemistry and play an important role in our understanding of the electronic structure of radicals and neutral molecules. The gas-phase acidity of GeH_4 and the electron affinity of the ${}^\bullet GeH_3$ radical have been discussed earlier in this paper and can be used as the standard references. For the sake of comparison, the gas-phase acidity of GeH_4 ($\Delta G^\circ_{acid} = 350.8\,kcal\,mol^{-1}$) is slightly less than that of AsH_3 ($\Delta G^\circ_{acid} = 350.0\,kcal\,mol^{-1}$) and $CHCl_3$ ($\Delta G^\circ_{acid} = 349.9\,kcal\,mol^{-1}$). Some information is available regarding the effect of alkyl substitution on the acidity of germanes from a combination of bracketing [89] and equilibrium experiments [34,90] by ICR techniques. The results of these experiments can be summarized in an acidity scale, where the quoted absolute values of ΔG°_{acid} are subject to a typical uncertainty of ± 2–$3\,kcal\,mol^{-1}$: $MeGeH_3$ ($\Delta G^\circ_{acid} = 359.0\,kcal\,mol^{-1}$) $<$ $EtGeH_3$ ($\Delta G^\circ_{acid} = 358.5\,kcal\,mol^{-1}$) $<$ Me_3GeH ($\Delta G^\circ_{acid} = 355.0\,kcal\,mol^{-1}$) $<$ GeH_4 $\approx$ $CH_2{=}CHGeH_3$ ($\Delta G^\circ_{acid} = 350.6\,kcal\,mol^{-1}$) $<$ $PhGeH_3$ ($\Delta G^\circ_{acid} = 346.1\,kcal\,mol^{-1}$) $<$ $CH{\equiv}C{-}GeH_3$ ($\Delta G^\circ_{acid} = 343.0\,kcal\,mol^{-1}$).

The observed decrease in acidity of germane upon simple alkyl substitution (Me, Et) and an increase upon phenyl substitution parallels the behavior of silanes [91,92]. This trend is best analyzed through the corresponding ΔH°_{acid} which are expected to follow the same relative order although displaced by the usual $\sim 7.1 \pm 0.6\,kcal\,mol^{-1}$ due to the $T\Delta S_{acid}$ term at 298 K [93].

$$\Delta H^\circ_{acid}(AH) \approx D^\circ(A\text{–}H) + IE(H^\bullet) - EA(A) \quad (19)$$

Kinetic studies [94] and laser-induced photoacoustic experiments [95] reveal negligible changes of the Ge–H bond energy upon mono- or multialkyl substitution, and a 1–$2\,kcal\,mol^{-1}$ decrease upon phenyl substitution. Thus, differences in these acidities of alkylgermanes very likely reflect variations in electron affinities of the corresponding radicals. The only direct electron affinity measurement for germanium-containing species related to this series (other than ${}^\bullet GeH_3$) refers to the $Me_3Ge^\bullet$ radical for which a value of $1.38 \pm 0.03\,eV$ has been obtained from threshold photodetachment experiments [89]. This is a substantial decrease of the electron affinity when compared with that of $GeH_3^\bullet$, and analogous to the decrease observed in going from $HO^\bullet$ to $MeO^\bullet$, and from $HS^\bullet$ to $MeS^\bullet$ [96]. Theoretical calculations are also consistent with these acidity trend for organogermanes [32,90].

Very few other Ge-containing species have had their electron affinities determined experimentally as shown in the recent comprehensive review by Schaefer and coworkers [96] on experimental and theoretical methods for obtaining accurate electron affinities. Earlier indirect methods based on appearance energies for negative ions from negative ion mass spectrometry often yield highly questionable values. This is well illustrated for the case of $F_3Ge^\bullet$ for which three different experiments [97–99] yield very different values for the electron affinity, namely 3.1, 1.6, and 1.1 eV. Thus, these old mass spectrometric methods suffer serious limitations for determining electron affinities. By comparison, recent high-level calculations [32,100] estimate the electron affinity of $F_3Ge^\bullet$ to be in the range of 3.5–3.7 eV.

Appearance energy measurements coupled with measurements of the translational energies of the ions were also used to obtain estimates for the electron affinity of $GeCl_3$ [87]. However, values obtained in such a way differ substantially from those obtained from the energy threshold for reactions studied by atom beam techniques [101],

$$M + GeCl_4 \rightarrow M^+ + Cl_3Ge^- + Cl \quad (M = Cs,\ K) \quad (20)$$

Finally, the increasing use of high-level theoretical methods to estimate electron affinities is well illustrated by the recent reports on evaluation of the electron affinity of GeF_n ($n = 1$–5) [100], $X_nGe(OMe)_{3-n}$ ($X = H, F$; $n = 0$–2) [27], and Ge_2F_n ($n = 1$–6) [102]. The calculated values for these different species are probably very reliable considering the level of theory and the ability of the theoretical methods to predict correct values for the electron affinity of simple species.

10. Negative ion–molecule reactions in Ge systems

Very few reactions of negative ions with Ge-containing substrates have been reported in the literature. Two studies are particularly relevant for our discussion.

A flowing afterglow study of the reactions of $(OC)_3Fe^{\bullet -}$ and $(OC)_4Mn^-$ with GeH_4 shows that these systems proceed by adduct formation, presumably by oxidative insertion into the Ge–H bond, to yield $(OC)_3Fe(H)(GeH_3)^{\bullet -}$ and $(OC)_4Mn(H)(GeH_3)^-$, respectively [103]. However, more spectacular results were obtained with other similar negative ions obtained from $Fe(CO)_5$ and $Mn_2(CO)_{10}$. These double dehydrogenation reactions are shown in Eqs. (21) and (22),

$$(OC)_2Fe^{\bullet -} + GeH_4 \rightarrow (OC)_2Fe(H)(\equiv GeH)^{\bullet -} + H_2 \qquad (21a)$$

$$(OC)_2Fe^{\bullet -} + GeH_4 \rightarrow (OC)_2Fe(=Ge)^{\bullet -} + 2H_2 \qquad (21b)$$

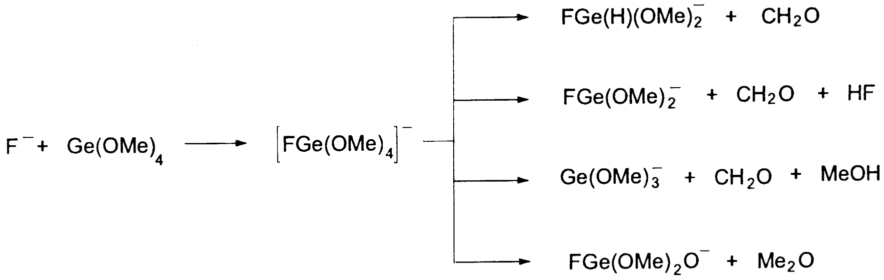
$$(OC)_3Mn^- + GeH_4 \rightarrow (OC)_3Fe(=Ge)^- + 2H_2 \qquad (22)$$

Although the details of the mechanism are not fully understood, it is likely that the double dehydrogenation reaction proceeds by a four-centered elimination. The germylide structures proposed for the products of reactions (21b) and (22) are consistent with the observation that these product ions undergo further reaction with GeH_4 to yield adduct ions [103].

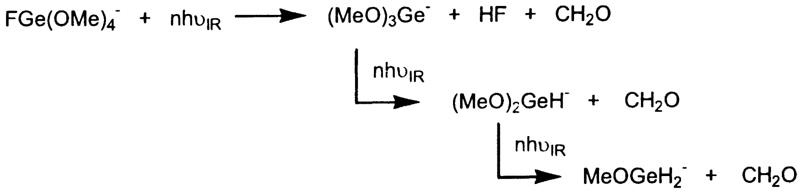
A completely different study has been carried out by FTMS techniques involving the gas-phase reactions of simple nucleophiles (F^-, MeO^-) with $Ge(OMe)_4$ [104]. The low-pressure reaction (10^{-8} Torr range) of F^- reveals that the nucleophilic reaction proceeds by addition to the Ge center to yield a pentacoordinated Ge anion, $FGe(OMe)_4{}^-$, followed by a number of elimination pathways as shown in Scheme 2.

In this study, nucleophilic reaction at carbon, to yield $(MeO)_3GeO^-$ and MeF, was found to account for less than 3% of the total reaction. This is a clear indication of the preference of the Ge center for nucleophilic attack.

Theoretical calculations and the lack of reactivity of the $FGe(OMe)_4{}^-$ anion in fluoride transfer reactions suggest that the pentacoordinated complex is best described by covalent bonding, and the most stable structure is predicted to be a trigonal bipyramid with F occupying an axial position [104]. Recent photodetachment experiments [105] carried out at 266 nm indicate that the dissociative process results



Scheme 2.



Scheme 3.

in the release of an MeO$^\bullet$ group.

$$\mathrm{FGe(OMe)_4}^- + h\nu\ (266\,\mathrm{nm}) \rightarrow \mathrm{MeO} + \mathrm{FGe(OMe)_3} + \mathrm{e}^- \qquad (23)$$

Two additional observations are important regarding these systems. As in the case of $\mathrm{FSi(OMe)_4}^-$ [106], the pentacoordinated Ge anions undergo successive exchange reactions with fluorine-containing neutrals, such as $\mathrm{BF_3}$ or $\mathrm{SO_2F_2}$,

$$\mathrm{FGe(OMe)_4}^- + \mathrm{BF_3} \rightarrow \mathrm{F_2Ge(OMe)_3}^- + \mathrm{(MeO)BF_2} \qquad (24)$$

Under excess $\mathrm{BF_3}$, these exchange reactions go all the way to $\mathrm{GeF_5}^-$ under typical FTMS conditions [105]. A second important finding refers to the ability of generating easily germyl anions starting with the $\mathrm{FGe(OMe)_4}^-$ ion by sequential infrared multiphoton dissociation, as shown in Scheme 3:

This approach may yet prove to be a convenient pathway for the synthesis of gas-phase germyl anions.

11. Ge clusters

A review of the gas-phase ion chemistry of Ge would not be complete without a few words about Ge clusters. The study of small Ge clusters has in fact become an important subject because these clusters are adequate motifs for the structure and chemical properties of nanoparticles relevant to semiconductor technology.

The thermochemical properties of neutral Ge_n clusters ($n = 2$–8) have been determined by Knudsen mass spectrometry [107], and the structure and energetics of these clusters have been the subject matter of theoretical calculations [108].

$\mathrm{Ge}_n{}^+$ ($n = 1$–7) have been generated by direct laser vaporization and detected by ion cyclotron resonance techniques [109a] and time-of-flight techniques [109b]. The mass spectra obtained under these conditions suggest enhanced stability, and/or low ionization energies, for $\mathrm{Ge_4}^+$ and $\mathrm{Ge_6}^+$. Previous beam experiments with gas-phase Ge neutral clusters followed by ionization revealed intense peaks for $\mathrm{Ge_6}^+$, $\mathrm{Ge_{10}}^+$, $\mathrm{Ge_{14}}^+$, $\mathrm{Ge_{15}}^+$, and $\mathrm{Ge_{18}}^+$, a fact that was deemed to be indicative of magic numbers [110]. The smaller germanium cluster cations (up to $n = 3$) react with MeOH to yield mainly GeOMe^+, with EtOH to yield GeOEt^+, with cyclopropane to yield $\mathrm{Ge}_n\mathrm{CH_2}^+$, and with $\mathrm{H_2S}$ to yield $\mathrm{Ge}_n\mathrm{S}^+$ [109a]. The fact that the higher cluster ions are unreactive may reflect the presence of cyclic structures for these ions.

However, it is the negative cluster ions of Ge that have been more extensively characterized by different groups. These negative cluster ions can be generated by laser desorption [109,111], and the negative ions are particularly interesting because of their structures [112]. The most relevant experimental information on these systems has been the determination of the electron affinities of the Ge_n ($n = 2$–15) clusters from anion photoelectron spectroscopy [113]. Likewise, $\mathrm{Ge}_n\mathrm{F}_m{}^-$ ($n = 1$–11; $m = 1$–3) cluster anions have been produced in the plasma of laser vaporized Ge in the presence of $\mathrm{F_2}$. For all of these latter clusters, the electron affinities, determined from photoelectron spectroscopy [114], range from 2.7 to 3.6 eV, and are consistently higher than the corresponding value for the pure germanium clusters.

It is clear from these short comments that gas-phase metallic clusters, both neutral and ionic, are very active fields of research.

12. Conclusion

The present review was intended to bring attention to the variety of aspects related to the gas-phase ion chemistry of germanium systems. Nevertheless, and in spite of the significant progress in the last few years, there is still some badly needed reliable data regarding heats of formation and bond energies for these germanium systems. It is hoped that researchers will be motivated and challenged to undertake some of these investigations because of the present day relevance of germanium materials.

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