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International Journal of Mass Spectrometry 195/196 (2000) 363–375



Gas-phase nucleophilic reactions of $\text{Ge}(\text{OCH}_3)_4$: experimental and computational characterization of pentacoordinated Ge anions

Nelson H. Morgon^a, Luciano A. Xavier^b, José M. Riveros^{b,*}^a*Instituto de Química, Universidade Estadual de Campinas (UNICAMP), Caixa Postal 6154, Campinas, SP, CEP 13083-970, Brazil*^b*Instituto de Química, Universidade de São Paulo, Av. Lineu Prestes 748, Cidade Universitária, São Paulo, CEP 05508-900, Brazil*

Received 3 June 1999; accepted 31 August 1999

Abstract

The gas-phase ion/molecule reactions of F^- and CH_3O^- with $\text{Ge}(\text{OCH}_3)_4$ have been investigated by Fourier transform ion cyclotron mass spectrometry. Both nucleophiles react preferentially by an addition mechanism to yield $\text{XGe}(\text{OCH}_3)_4^-$ ($\text{X} = \text{F}, \text{OCH}_3$) complexes that are identified as typical pentacoordinated Ge species. Pentacoordinated Ge adducts formed with excess internal energy can undergo elimination of formaldehyde to yield $\text{HGe}(\text{OCH}_3)_4^-$, or further elimination processes that result in the formation of germyl anions like $\text{Ge}(\text{OCH}_3)_3^-$. Other minor product ions are also observed which can be attributed to the intermediacy of a pentacoordinated adduct. Dissociation of the $\text{XGe}(\text{OCH}_3)_4^-$ anions induced by infrared multiphoton excitation leads to sequential losses of formaldehyde and gives rise to different germyl anions like $\text{Ge}(\text{OCH}_3)_3^-$, $\text{HGe}(\text{OCH}_3)_2^-$, and $\text{H}_2\text{GeOCH}_3^-$. The $\text{XGe}(\text{OCH}_3)_4^-$ and germyl anions react readily with BF_3 through successive methoxide-fluoride exchange and this reaction provides a gas-phase synthetic pathway for multiply fluorinated Ge anions. Ab initio calculations performed on model pentacoordinated species $\text{F}_{n+1}\text{Ge}(\text{OH})_{4-n}^-$ ($n = 0-4$) reveal that addition of a fluoride ion on hydroxygermanes occurs preferentially in the apical position of a trigonal bipyramid. The fluoride affinity of the prototype molecule $\text{Ge}(\text{OH})_4$ is calculated to be $60.9 \text{ kcal mol}^{-1}$, and fluoride affinity increases monotonically with increasing fluorine substitution. The fluoride affinity of GeF_4 is calculated to be 79 kcal mol^{-1} . Similar calculations also predict an unusually high hydride affinity (60 kcal mol^{-1}) for $\text{Ge}(\text{OH})_4$ with the hydride occupying an equatorial position. (Int J Mass Spectrom 195/196 (2000) 363–375) © 2000 Elsevier Science B.V.

Keywords: Germanium methoxide; Gas-phase nucleophilic reactions; Pentacoordinated Ge anions; Fluoride affinity; Germyl anions; Computational Ge chemistry

1. Introduction

The use of germanium alkoxides, $\text{Ge}(\text{OR})_4$, is rapidly increasing in sol-gel processes aimed at the preparation of Ge-containing glasses [1] and impor-

tant materials such as GeS_2 [2], and in vapor chemical processes for deposition of GeO_2 [3] and organogermanium films [4]. The search for synthetic pathways of germanates that can be used as frameworks of new porous materials [5] also provides a timely motivation for exploring the reactivity of germanium alkoxides. Unfortunately, mechanistic studies of these processes are not always trivial because germanium alkoxides are prone to undergo hydrolysis followed by a series

* Corresponding author. E-mail: jmnigra@quim.iq.usp.br

Dedicated to Bob Squires for his many seminal contributions to mass spectrometry and ion chemistry.

of polycondensation reactions [6]. In comparison, the study of the gas-phase ion chemistry of these systems provides in principle a powerful and unique approach for deciphering the intrinsic reactivity and fundamental properties of these molecules. An initial report from our laboratories has already made use of this approach to characterize the positive ion chemistry of $\text{Ge}(\text{OCH}_3)_4$, or $\text{Ge}(\text{OMe})_4$ [7]. Nevertheless, little is known about reactions of negative ions of Ge, or in particular about the pathways for nucleophilic attack at a Ge center. In fact, only a limited number of studies have even addressed the positive ion/molecule reactions of Ge-containing species [8], despite the increasing interest in germanium chemistry, and in particular simple organogermanes [9].

Traldi and co-workers [10] were the first to use gas-phase ion chemistry in an attempt to model the acid and base induced hydrolysis of $\text{Si}(\text{OEt})_4$ as representative of the typical behavior of group 4 alkoxides. A completely novel gas-phase approach for characterizing hydrolysis and condensation processes relevant to sol-gel processes has been recently reported for $\text{Ti}(\text{OR})_4$ and $\text{Zr}(\text{OR})_4$ by using laser-induced liquid beam ionization/desorption mass spectrometry [11]. Our group extended the early work on $\text{Si}(\text{OEt})_4$ and proceeded to carry out a general study of the gas-phase reactions of $\text{Si}(\text{OR})_4$ with a number of nucleophiles [12]. Our results coupled with the extensive work on the ion chemistry of organosilanes [13] provide suitable guidance and a basis for comparison for nucleophilic pathways in Ge systems.

The present report describes for the first time gas-phase reactions of typical nucleophiles like F^- and MeO^- with $\text{Ge}(\text{OMe})_4$ as a means to explore nucleophilic reactions in germanium alkoxides. Reactions are shown to proceed almost exclusively by initial formation of a pentacoordinated Ge anion. However, subsequent elimination processes give rise to a variety of interesting and previously undetected germyl anions. *Ab initio* calculations have also been carried out to characterize the pentacoordinated species of Ge, and to estimate the fluoride affinity of Ge alkoxides and the most likely structure of these hypervalent species.

2. Experimental

Experiments were carried out in a homemade Fourier transform ion cyclotron resonance (FTICR) spectrometer interfaced with an IonSpec Omega Fourier Transform Data System. The general characteristics of the spectrometer have been illustrated in recent publications [7,12,14]. Pressure was measured with a nude ion gauge located between the cell and the turbomolecular pump. Readings for $\text{Ge}(\text{OMe})_4$ are probably close to the actual absolute pressures in the cell by comparison with recent calibrations using an MKS Baratron.

F^- ions were typically generated from NF_3 (Pennwalt Ozark Mahoning) by dissociative electron attachment at 3.5 eV with a 90 ms electron beam pulse. The partial pressure of NF_3 was maintained in the vicinity of 3.5×10^{-8} Torr. Fluoride ions were also generated from SO_2F_2 (Linde, 99.5%) at an electron energy of 5 eV but secondary reactions of Ge-containing anions with SO_2F_2 considerably reduced the usefulness of this precursor gas. MeO^- ions were obtained from methyl nitrite (1.9×10^{-8} Torr) by dissociative electron attachment at 3.5 eV or as previously described from the ion/molecule reaction of OH^- with methanol [12]. Typical trapping voltages for these experiments were -1.9 V. In most cases, a radiofrequency field of ~ 7 MHz was applied to one of the trapping plates during 200 ms to remove trapped thermal electrons from the cell.

Fresh samples of tetramethoxygermane [germanium (IV) methoxide, 97%, Aldrich] were used in most experiments. These samples were repeatedly distilled under vacuum prior to introduction in the cell. This procedure was essential for minimizing the amount of methanol present in the sample due to facile hydrolysis of this compound.

Ion/molecule reactions of F^- and MeO^- with $\text{Ge}(\text{OMe})_4$ (at partial pressures of $\sim 6 \times 10^{-8}$ Torr) were investigated by initially ejecting all unwanted ions from the ICR cell with a combination of rf pulses. At these pressures reactions were observed to reach completion in about 1 s. Because reactions are fast under our experimental conditions, it is uncertain whether the reagent ions are fully thermalized prior to

reaction. It is well known that F^- ions generated from NF_3 and SO_2F_2 are formed with excess translational energies [15]. Although this fact precludes the measurement of true branching ratios, it does provide a convenient source of chemically activated hypervalent Ge species that can undergo a series of interesting elimination processes as described below. In fact, dissociation of excited hypervalent species produced in our ion/molecule reactions can be compared with those obtained by other low-energy methods of dissociation.

A grating tunable cw CO_2 laser (SYNRAD, Model 48G-1) was used to promote the infrared multiphoton dissociation of some of the product ions. The laser was operated on the P(20) line at 1047 cm^{-1} , a frequency close to the infrared band center of neutral $Ge(OMe)_4$ [16]. The power level of the laser was externally controlled by varying the width of a 10 kHz

modulation pulse provided by a Hewlett-Packard pulse generator. The laser power measured at the exit window of the vacuum system of the spectrometer was typically 3 W. The irradiation time (0.2–1 s depending on the experiment) was controlled by electronically varying the duration of the open time of a Uniblitz shutter placed in front of the laser.

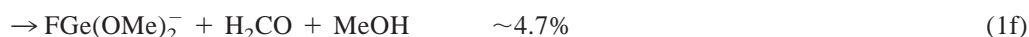
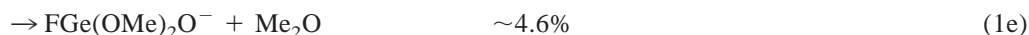
3. Experimental results

3.1. Reaction of F^- with $Ge(OMe)_4$

Fluoride ions react with $Ge(OMe)_4$ to yield three main reaction products, as shown below, according to the product distribution obtained under our experimental conditions



A number of minor products are also observed and the product ions can be identified as resulting from the following reactions

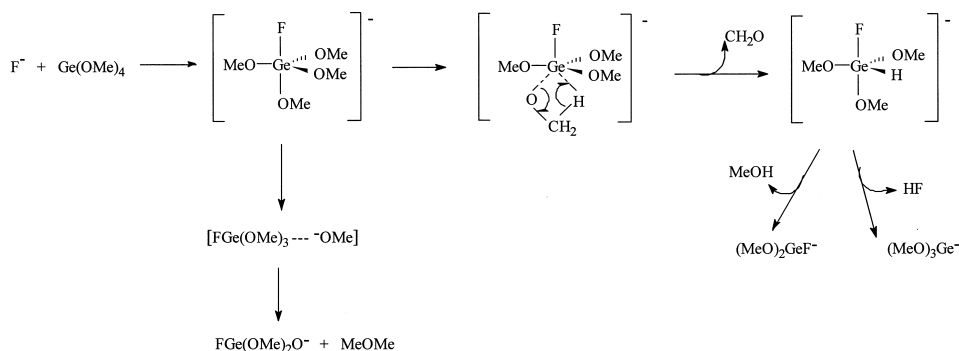


A quantitative determination of $Ge(OMe)_3O^-$ and $FGe(OMe)_2O^-$ and the study of further reactions of these ions is difficult because of the overlapping germanium isotope species with those of the more important reaction products, $FGe(H)(OMe)_3^-$ and $Ge(OMe)_3^-$, respectively.

The main reaction nucleophilic pathway exhibited by $Ge(OMe)_4$ can be explained as originating from the pentacoordinated $FGe(OMe)_4^-$ anion, Reaction (1a). On the other hand, Reaction (1d) is attributed to a gas-phase S_N2 displacement at the methyl group.

Scheme 1 shows that the different reaction products [except for the $Ge(OMe)_3O^-$ ion] can be explained as the result of addition–elimination processes involving $FGe(OMe)_4^-$.

In this scheme, we propose that the elimination processes originate from energy-rich pentacoordinated Ge species. This conclusion is supported by the fact that reactions initiated with F^- obtained from NF_3 at lower pressures result in a considerably smaller yield of the pentacoordinated species, in a substantial increase in Reactions (1b) and (1c), and in



Scheme 1.

the appearance of MeO^- as an important reaction product. This latter product is a result of displacement at the Ge center. By comparison, the relative contribution of Reaction (1d) is essentially unchanged.

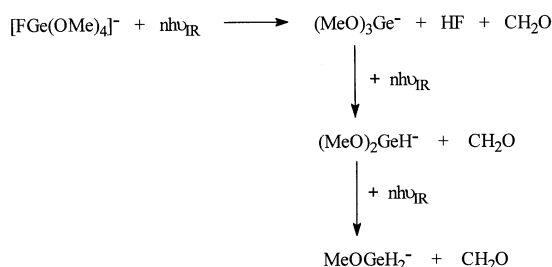
The present findings reveal some formal similarities to previous studies involving organosilanes. In fact, experiments involving negative ions have shown that pentacoordinated Si anions are often the predominant product ion in flowing afterglow studies [17] whereas similar experiments under ICR conditions often exhibit reaction pathways that can be traced to chemically activated pentacoordinated species [18].

Scheme 1 and the set of Reactions (1) reveal a number of important points regarding reactions of methoxygermanes: (1) The Ge center acts as an efficient activation center for elimination of CH_2O . This trend is noteworthy because a similar dominant dissociation pathway was encountered in the positive ion chemistry of $Ge(OMe)_4$ [7]. This is in marked contrast with the ion chemistry reported for $Si(OR)_4$ substrates where aldehyde elimination is rare [12,19]. Elimination of formaldehyde yields a pentacoordinated hydride Ge anion, $FGe(OMe)_3H^-$, that can undergo further elimination of either HF or MeOH to yield germyl anions. Elimination of HF to produce $Ge(OMe)_3^-$ is clearly the preferred route. Results obtained from dissociation of $FGe(OMe)_4^-$ induced by vibrational multiphoton excitation (see below) suggest that elimination of formaldehyde and HF, or methanol, may actually involve a simultaneous mechanism rather than a concerted stepwise process. (2) A

comparison with the reactions observed between F^- and $Si(OCH_3)_4$ [12] reveals that the most noticeable difference between the behavior of the Si and Ge substrates lies in the ability of the latter to promote elimination of formaldehyde. This route eventually leads to the germyl anions as indicated above and constitutes a valuable synthetic approach to gas-phase germyl anions. Similar silyl anions are not obtained by this route. (3) Displacement of MeO^- [the most important reaction product for the $Si(OCH_3)_4$ case in the previous ICR experiment] is highly dependent on the initial ion reagent energy for $Ge(OMe)_4$. At thermal or near-thermal conditions, products originate from low energy fragmentation pathways available for $FGe(OMe)_4^-$. Reaction (1e) can be explained in the silicon analog by the nascent elimination of MeO^- followed by an internal return mechanism to yield Me_2O as the neutral product. The fact that this is a very minor channel probably accounts for the fact that no evidence was found for the nascent MeO^- to promote proton abstraction leading to the corresponding germaoxirane, $FGe(OMe)_2(cyc-OCH_2)^-$ [14].

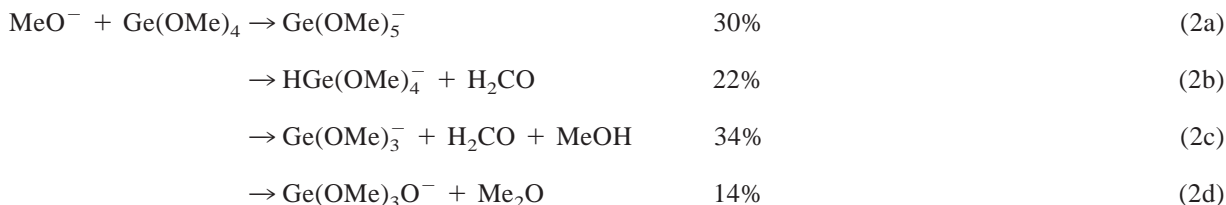
Additional information on the elimination channels available for the $FGe(OMe)_4^-$ ion were obtained from dissociation experiments induced by vibrational multiphoton excitation with a CO_2 laser. Successive dissociations were observed to occur as a function of irradiation time due to sequential losses of formaldehyde to produce the germyl anions shown in Scheme 2.

These experiments that are indicative of the lowest dissociation channels reveal that multiphoton excita-



Scheme 2.

tion apparently drives the dissociation directly to the $\text{Ge}(\text{OMe})_3^-$ ion. This suggests that either the intermediate pentacoordinated anion, $\text{FGe}(\text{OMe})_3\text{H}^-$, is also pumped very efficiently by the CO_2 laser, or that



The product distribution quoted above refers to reactions with MeO^- generated from the reaction of OH^- and MeOH using a nominal partial pressure of H_2O of 1×10^{-7} Torr.

The reactions in this system are readily accommodated by the general mechanism outlined in Scheme 1 for the case of fluoride ions. The higher relative yields of $\text{HGe}(\text{OMe})_4^-$ and $\text{Ge}(\text{OMe})_3^-$ agree with the qualitative view that the pentacoordinated $\text{Ge}(\text{OMe})_5^-$ species is expected to be less stable than the corresponding $\text{FGe}(\text{OMe})_4^-$. Formation of $\text{Ge}(\text{OMe})_3\text{O}^-$ [Reaction (2d)] is also noticeably more important in this case. However, in the $\text{MeO}^-/\text{Ge}(\text{OMe})_4$ reaction this ion can be formed either through an $\text{S}_{\text{N}}2$ mechanism on carbon, or by initial addition on Ge followed by displacement of MeO^- followed by an internal return mechanism.

Dissociation of the $\text{Ge}(\text{OMe})_5^-$ ion induced by vibrational multiphoton excitation was observed to yield the same sequence of germyl anions shown in Scheme 2.

simultaneous elimination is very facile. Very minor amounts of $\text{FGe}(\text{OMe})_2^-$ and $\text{FGe}(\text{H})(\text{OMe})^-$ were also detected in these infrared induced dissociation experiments. It is interesting to emphasize that multiphoton excitation with a CO_2 laser of alkoxy-Ge ions is a highly favorable process both for negative and positive ions [7]. In the present case, it represents a unique method to generate a variety of germyl anions.

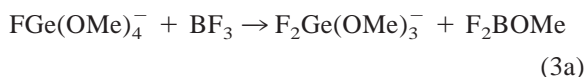
3.2. Reaction of MeO^- with $\text{Ge}(\text{OMe})_4$

The reaction of MeO^- with $\text{Ge}(\text{OMe})_4$ proceeds in a similar fashion to the reactions described above.

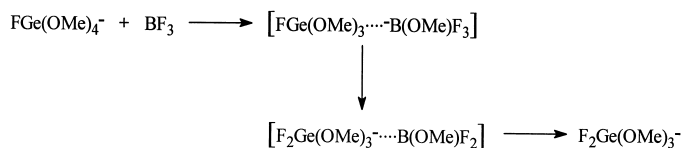
3.3. Reactions with SO_2F_2 and BF_3

$\text{FGe}(\text{OMe})_4^-$ was observed to react rapidly with SO_2F_2 to yield $\text{F}_2\text{Ge}(\text{OMe})_3^-$ when sulfonyl fluoride was used as the source of fluoride ions. Previously, extensive methoxide-fluoride exchange reactions were observed in our earlier work with $\text{FSi}(\text{OMe})_4^-$ and $\text{FSi}(\text{OMe})_2(\text{cyc-CH}_2\text{O})^-$ reacting with BF_3 [14]. Because the pentacoordinated germanium species displayed a similar behavior, a more thorough investigation was carried out using BF_3 as the neutral reagent.

Reactions studied at low pressures of BF_3 (1×10^{-8} Torr) proceed through a sequential exchange processes,



Further exchange becomes very slow and under these experimental conditions there is essentially



Scheme 3.

no $\text{F}_4\text{Ge(OMe)}^-$ observed even at long reaction times. This dramatic change in rate raised the question as to whether stereochemical effects may play a role in these fluoride-methoxide exchange processes.

Attempts to promote further fluoride-methoxide exchange by using higher partial pressures of BF_3 (5×10^{-8} Torr) results in very complex chemistry with both B and Ge ions appearing as product ions. Although the detailed chemistry and mechanisms of the different processes are still under investigation, GeF_5^- ultimately becomes the dominant ion from reactions due to F_3GeO^- with BF_3 .

Fluoride-methoxide exchange is also observed in the reaction of germyl anions with SO_2F_2 and BF_3 to yield progressively fluorinated germyl anions in analogous fashion to that described above. The exchange process is envisioned to occur through the steps outlined in Scheme 3.

3.4. Fluoride affinity of Ge(OMe)_4

Relative fluoride affinities have been determined in the past for a large number of substrates by determining the equilibrium constant for fluoride exchange reactions or by simply determining the most favorable direction for fluoride transfer [20,21]. For substrates of high fluoride affinity there are few reference compounds that can be used as thermochemical anchor points. The reactivity of FGe(OMe)_4^- with BF_3 via methoxide-fluoride exchange precluded the possibility of using this molecule as a reference for fluoride transfer. A second alternative was to use Si(OMe)_4 to compare the relative affinities of Ge and Si centers.

Experiments carried out with mixtures of Ge(OMe)_4 and Si(OMe)_4 revealed that FGe(OMe)_4^- and FSi(OMe)_4^- ions are essentially unreactive toward the opposite neutral molecule even after a significant

reaction time (~ 5 s). By comparison, and under the same conditions, methoxide-fluoride exchange reactions with BF_3 proceed very efficiently. Thus, it is clear that fluoride transfer from these ions is very slow suggesting that high energies are involved in releasing a fluoride ion from FGe(OMe)_4^- , or FSi(OMe)_4^- . Furthermore, fluoride transfer may become slow in these pentacoordinated species if considerable covalent bonding occurs between the fluoride ion and the Ge or Si center. It is thus apparent that the fluoride affinity of Ge(OMe)_4 , and of Si(OMe)_4 , may not be readily obtainable by simple fluoride exchange reactions.

4. Theoretical investigation of hypervalent Ge species

The ion/molecule reactions of Ge(OMe)_4 reported above indicate that nucleophilic addition to yield a pentacoordinated Ge species in the gas phase is the dominant reaction mode for ionic nucleophiles. Anions like FGe(OMe)_4^- represent typical hypervalent Ge moieties whose structural and bonding properties have not been well characterized either experimentally or theoretically. This is in sharp contrast with similar gas-phase species derived from organosilanes that have been studied in some detail in recent years [17,22]. On the other hand, there is considerable interest in pentacoordinated Ge anions because the nature of the chemical bonding in hypervalent systems [23] and in the so-called ate anions [24] is a very active area of research.

Two main aspects motivated our theoretical investigation of hypervalent Ge species. First, we were interested in establishing the structure of these anionic species and particularly in the stereochemical arrange-

ments that might provide some clue about the reactivity of these species. The second point was to calculate the fluoride and hydride affinities of Ge species because these quantities could not be readily obtained from our experiments and are expected to be high in comparison with other substrates.

In order to perform high level calculations we chose to model our system as $\text{Ge}(\text{OH})_4$ rather than $\text{Ge}(\text{OMe})_4$. The reason for this choice was to simplify the geometry optimization process because of the large number of minima arising from different relative conformations of the four methyl groups. This choice considerably reduces the number of possible conformational isomers while retaining the basic central electronic surroundings of the Ge center. Additional calculations were also carried out with MeOGeH_3 as the initial neutral molecule but this was only pursued for the monofluoro germaniumate ion and will not be discussed here.

Calculations were carried out with the basis sets previously developed for anionic systems containing Ge, F, C, O, and H. This basis set uses the generator coordinate method (GCM) to find the best representation for the valence basis set adapted to a pseudopotential [25]. This set of basis functions has been defined in [25] as the GCM/ECP basis set and was used to fully optimize geometries at the MP2 level. Energy calculations were first carried out with this basis set at the MP2 level, and more refined energy calculations included additional polarization functions to yield the GCM/ECP+ basis set described in detail in [25]. The use of the generator coordinate method to obtain high quality basis sets has been illustrated in several recent reports from these laboratories. This method has been shown to yield very reliable thermochemical values [14,26]. Our highest level of the energy calculations, QCISD(T)/(MCG/ECP+), was obtained from the approximation [27],

$$\begin{aligned} E [\text{QCISD(T)/GCM/ECP+}] \\ \approx E [\text{QCISD(T)/(GCM/ECP)}] \\ + E [\text{MP2/(GCM/ECP+)}] \\ - E [\text{MP2/(GCM/ECP)}] \end{aligned}$$

Thus, our final level of calculations according to this procedure can be represented as being QCISD(T)/(GCM/ECP+)//MP2/(GCM/ECP) + ZPE.

All calculations were carried out using the GAUSSIAN 94 suite of programs [28].

5. Results of theoretical calculations

Calculations were first performed on $\text{Ge}(\text{OH})_4$ and $\text{FGe}(\text{OH})_4^-$ with particular care taken in characterizing different isomeric species for the anionic penta-coordinated Ge species. Additional calculations were then carried out for successive substitution of OH by F in order to characterize the full range of these species. The optimized geometry for the neutrals and the isomeric anionic species resulting from fluoride addition are shown in Figs. 1–5 for progressively fluorinated hydroxygermanes. The calculated energies at the highest level performed in this work appear in Table 1.

Addition of F^- to $\text{Ge}(\text{OH})_4$ yields two isomeric species (Fig. 1), the most stable structure (**Ia**) corresponding to the fluorine being axial in a near trigonal bipyramid arrangement. The distortion from planarity of the equatorial hydroxy groups and subsequent tilt toward the fluorine atom may reflect the tendency for intramolecular hydrogen bonding between the hydroxy groups and the fluoride ion. Preference for the axial position with a long Ge–F bond is similar to what has been found in computational studies of pentacoordinated Si compounds [22] where attachment of a fifth electronegative ligand also leads to a trigonal bipyramid as the most stable structure. On the other hand, structure **Ib**, which is calculated to be only $4.3 \text{ kcal mol}^{-1}$ less stable than **Ia**, resembles more closely a tetragonal arrangement rather than a second structure with the fluorine in an equatorial position. This structure is calculated to be a minimum at all levels of theory used in this work. This point is emphasized because previous investigation of penta-coordinated silicate anions have shown highly fluxional behavior of equatorial and axial positions leading to isomerization by Berry-like pseudorotation processes [22,29]. The surface for this kind of process

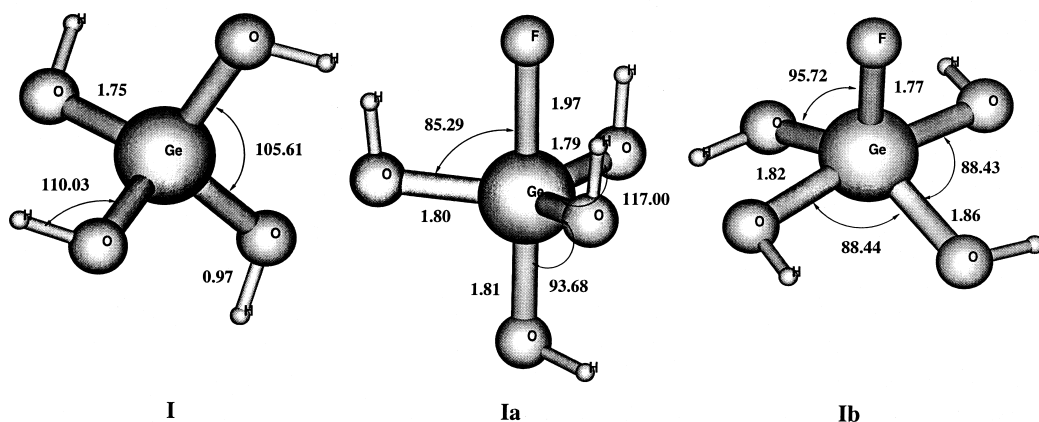


Fig. 1. Optimized geometries for $\text{Ge}(\text{OH})_4$ and for two isomeric $\text{FGe}(\text{OH})_4^-$ anions. Distances in Å (rounded to the nearest 0.01) and angles in degrees.

is presently under investigation in our group for simpler Ge species.

Substitution of a second fluorine results in clearly defined trigonal bipyramid structures. The diaxial arrangement for the fluorines, **IIa** in Fig. 2, is the most stable pentacoordinated species, $4.1 \text{ kcal mol}^{-1}$ below the structure corresponding to an axial-equatorial arrangement for the fluorines.

The $\text{F}_3\text{Ge}(\text{OH})_2^-$ system reveals a larger number of isomeric species with the most stable ones displayed in Fig. 3. The most stable structure, **IIIa**, maintains two fluorines in axial positions with the third one

occupying an equatorial position. Yet these structures and their relative energies do not provide any obvious clue as to why the fluoride-methoxide exchange observed in our experiments suffers a noticeable decrease in rate for $\text{F}_3\text{Ge}(\text{OME})_2^-$.

The most stable structures with fluorines in the axial position display one long Ge–F bond starting at 1.97 Å for structure **Ia** (Fig. 1). This suggests that this ion still retains some characteristics of an adduct ion even though the Ge–O bonds are also observed to be much longer than in neutral $\text{Ge}(\text{OH})_4$. Thus, the failure to observe fluoride transfer reaction from

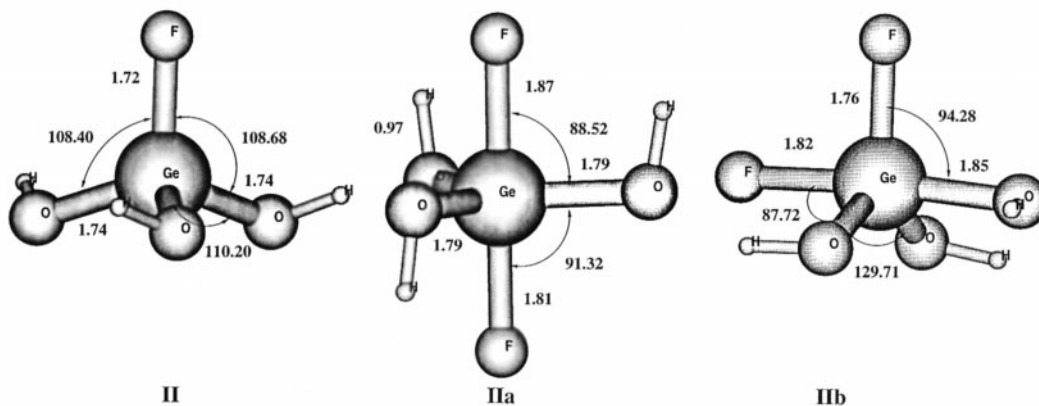


Fig. 2. Optimized geometries for $\text{FGe}(\text{OH})_3$ and for two isomeric $\text{F}_2\text{Ge}(\text{OH})_3^-$ anions. Distances in Å (rounded to the nearest 0.01) and angles in degrees.

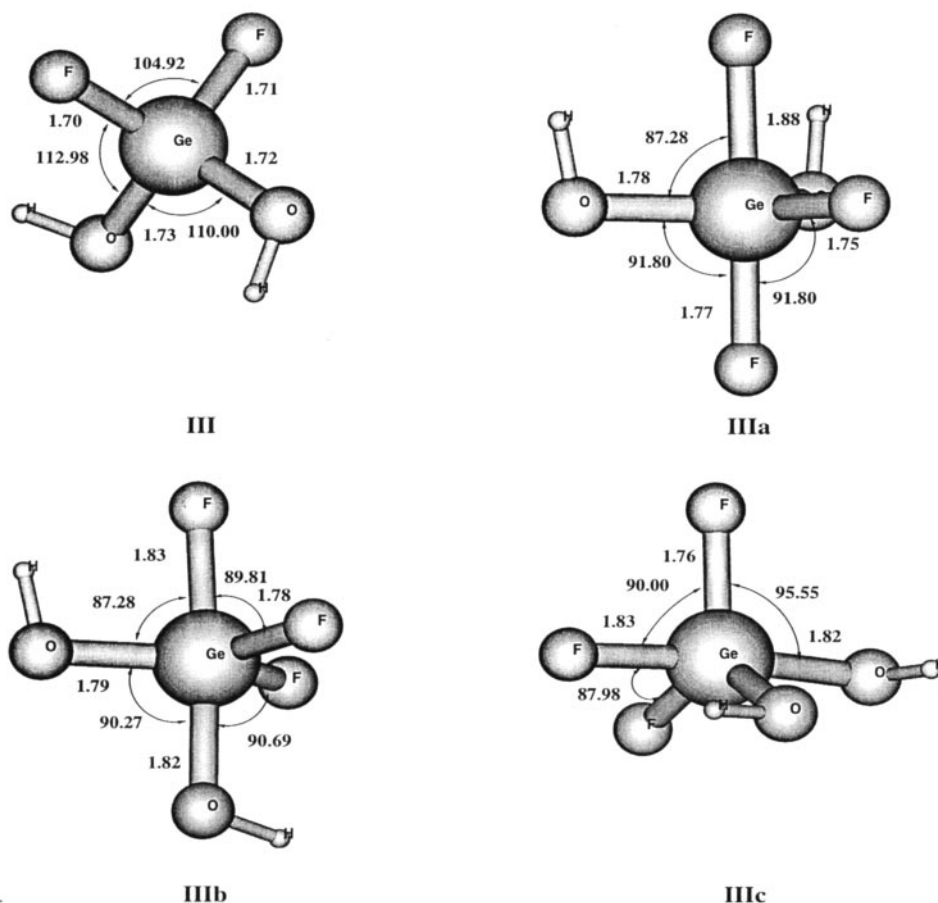


Fig. 3. Optimized geometries for $F_2Ge(OH)_2$ and for the isomeric $F_3Ge(OH)_2^-$ anions. Distances in Å (rounded to the nearest 0.01) and angles in degrees.

$FGe(OMe_4)^-$ is not obvious from the results obtained for the structure. The long axial Ge–F bonds decrease as a function of fluorine substitution until reaching the fully fluorinated ion, GeF_5^- , where the axial bond is calculated to be 1.78 Å.

The calculated bond lengths fare well with the available experimental data. The Ge–F bond in GeF_4 quoted from old electron diffraction data is 1.68 Å [30] (in agreement with the value shown in Fig. 5). This bond increases to 1.688 Å in GeF_3Cl [31], again in very good agreement with the Ge–F bond calculated for F_3GeOH in Fig. 4. The data obtained from x-ray structural work on GeF_5^- [32] is not readily comparable to our GeF_5^- calculated structure because

in salts such as $XeF_5^+GeF_5^-$ and $SF_3^+GeF_5^-$ the Ge atom sits in an octahedral symmetry with a long bridging Ge–F bond. However, the planar Ge–F bond lengths of 1.745 Å are in excellent agreement with the calculated equatorial Ge–F bonds shown in Fig. 5 for GeF_5^- (Va).

Table 2 lists the calculated fluoride affinities for our model systems $F_nGe(OH)_{4-n}$ ($n = 0-4$) taking into consideration the different isomeric species of the pentacoordinated anions. These numbers can be considered to be lower limits for the corresponding methoxy substituted fluorogermanes and as expected are in the very high range of fluoride affinities. A value of $100 \pm 6 \text{ kcal mol}^{-1}$ has been derived for the

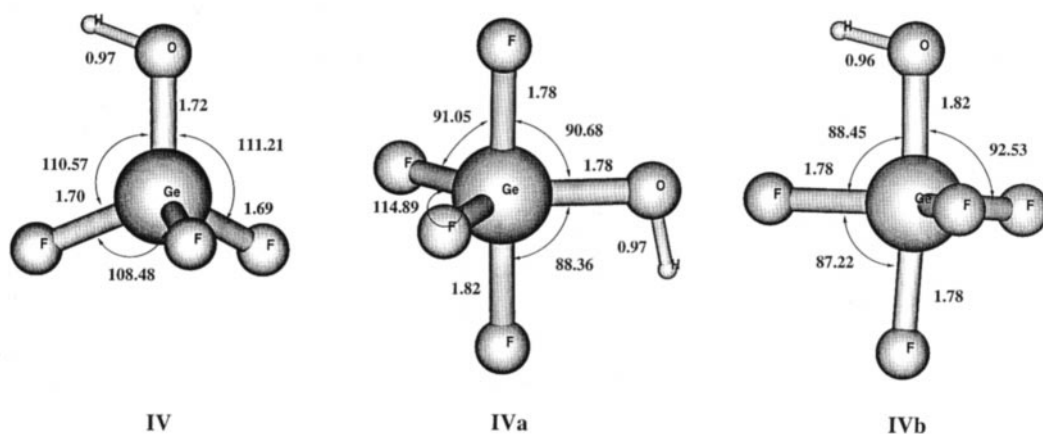


Fig. 4. Optimized geometries for $F_3Ge(OH)$ and for the isomeric $F_4Ge(OH)^-$ anions. Distances in Å (rounded to the nearest 0.01) and angles in degrees.

fluoride affinity of GeF_4 from thermodynamic data in conjunction with calculations of lattice energy [33]. A crude estimate derived from an early study of the negative ion/molecule reactions in GeF_4 [34] suggested the fluoride affinity of GeF_4 is larger than 79 kcal mol^{-1} . However, the values obtained in [33] for the fluoride affinities of a number of substrates, including that of BF_3 , are considerably higher than those obtained in gas-phase measurements. Thus, considerable uncertainty still remains regarding the true experimental values for the fluoride affinity of

BF_3 and GeF_4 . By comparison, the gas-phase fluoride affinity of SiF_4 has been estimated to be somewhere between 60 and 68 kcal mol^{-1} [20,35] but recent experiments suggest that these high fluoride affinities obtained in ICR experiments may actually be too low, by as much as 10 kcal mol^{-1} [36]. We therefore conclude that our calculated value of 79 kcal mol^{-1} for GeF_4 (Table 2) is likely a very reasonable value and reinforces the idea that the numbers derived in [33] are probably too high.

Additional calculations were also carried out to

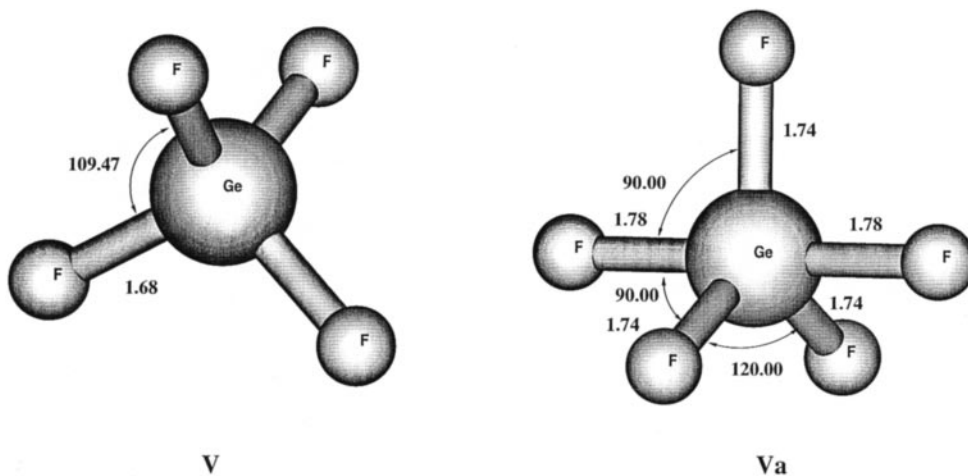


Fig. 5. Optimized geometries for GeF_4 and GeF_5^- . Distances in Å (rounded to the nearest 0.01) and angles in degrees.

Table 1

Calculated energies at the QCISD(T)/(MCG/ECP+) level (in au) and zero point energies, ZPE (in kcal mol⁻¹) for the neutrals and anionic species identified in Figs. 1–5

| System | | E[QCISD(T)] | ZPE |
|---|-------------|-------------|-------|
| F ⁻ | | -24.19114 | |
| Ge(OH) ₄ | I | -70.25444 | 37.18 |
| FGe(OH) ₄ ⁻ | Ia | -94.54623 | 39.70 |
| FGe(OH) ₄ ⁻ | Ib | -94.53945 | 39.69 |
| FGe(OH) ₃ | II | -77.87708 | 29.18 |
| F ₂ Ge(OH) ₃ ⁻ | IIa | -102.17694 | 32.29 |
| F ₂ Ge(OH) ₃ ⁻ | IIb | -102.16958 | 31.79 |
| F ₂ Ge(OH) ₂ | III | -85.49870 | 21.34 |
| F ₃ Ge(OH) ₂ ⁻ | IIIa | -109.80412 | 24.16 |
| F ₃ Ge(OH) ₂ ⁻ | IIIb | -109.79489 | 23.72 |
| F ₃ Ge(OH) ₂ ⁻ | IIIc | -109.79507 | 23.69 |
| F ₃ GeOH | IV | -93.11836 | 13.71 |
| F ₄ GeOH ⁻ | IVa | -117.43066 | 15.96 |
| F ₄ GeOH ⁻ | IVb | -117.42062 | 15.19 |
| F ₄ Ge | V | -100.73718 | 6.49 |
| F ₅ Ge ⁻ | Va | -125.05633 | 7.67 |

understand the ease with which XGe(OMe)₄⁻ (X = F, OMe) undergo formaldehyde elimination to yield germanium hydride pentacoordinated species. Table 3 lists the results of calculations after adding H⁻ to our model system Ge(OH)₄. Addition of H⁻ in the equa-

Table 3

Calculated energies at the QCISD(T)/(MCG/ECP+) level (in au), ZPE (in kcal mol⁻¹), and hydride affinity (in kcal mol⁻¹) for addition of H⁻ to Ge(OH)₄

| System | E[QCISD(T)] | ZPE | H ⁻ affinity ^a |
|---|-------------|-------|--------------------------------------|
| H ⁻ | -0.5176539 | | |
| Ge(OH) ₄ | -70.20154 | 37.18 | |
| <i>ap</i> -HGe(OH) ₄ ⁻ ^b | -70.85893 | 42.45 | 51.7 |
| <i>eq</i> -HGe(OH) ₄ ⁻ ^c | -70.87297 | 42.89 | 60.1 |

^a Fluoride affinities were calculated with zero point energies adjusted by 0.89 to correct the calculated vibrational frequencies.

^b This ion is a trigonal bipyramid with the H occupying an axial position.

^c This ion is a trigonal bipyramid with the H occupying an equatorial position.

torial position of *eq*-HGe(OH)₄⁻ is more stable by 8.4 kcal mol⁻¹ than in the apical addition, *ap*-HGe(OH)₄⁻, in agreement with the idea that the electronegative groups tend to occupy the axial positions. These calculations result in a hydride affinity of 60 kcal mol⁻¹ for Ge(OH)₄ which is indeed unusually high and may account for the recurrent observation of these species in our experiments. These systems are nevertheless under further study because a substantial fluxional character may be present in these systems.

Table 2

Calculated fluoride affinities (in kcal mol⁻¹) at 0 K for the F_nGe(OH)_{4-n} species considered in this work

| F _n Ge(OH) _{4-n} | | F _{n+1} Ge(OH) _{4-n} ⁻ | Structure | F ⁻ affinity ^a |
|--------------------------------------|------------|---|---|--------------------------------------|
| Ge(OH) ₄ | I | FGe(OH) ₄ ⁻ FGe(OH) ₄ ⁻ | Ia Ib | 60.9 56.7 |
| FGe(OH) ₃ | II | F ₂ Ge(OH) ₃ ⁻ F ₂ Ge(OH) ₃ ⁻ | IIa IIb | 65.4 61.3 |
| F ₂ Ge(OH) ₂ | III | F ₃ Ge(OH) ₂ ⁻ F ₃ Ge(OH) ₂ ⁻ F ₃ Ge(OH) ₂ ⁻ | IIIa IIIb IIIc | 69.2 63.8 63.9 |
| F ₃ GeOH | IV | F ₄ GeOH ⁻ F ₄ GeOH ⁻ | IVa IVb | 74.0 68.4 |
| F ₄ Ge | V | F ₅ Ge ⁻ | Va | 79.3 |

^a Fluoride affinities were calculated with zero point energies adjusted by 0.89 to correct the calculated vibrational frequencies.

6. Conclusions

The reaction of typical nucleophiles like F^- and MeO^- with $Ge(OMe)_4$ has been shown to proceed almost exclusively by addition of the nucleophile to the Ge center to yield a pentacoordinated species. Subsequent elimination reactions, or photodissociation of these pentacoordinated species, provide a unique synthetic route for germyl anions in the gas phase.

As in the case of the silicon analog, the pentacoordinated species of $Ge(OMe)_4$ undergo extensive methoxide-fluoride exchange with BF_3 . The same process is observed to occur with the germyl anions, opening up the possibility of further investigation on the reactivity and thermochemistry of these anions.

Finally, our theoretical calculations on the model system $Ge(OH)_4$ suggest that fluoride ions add to Ge preferentially on the axial position and that the fluoride affinity of $Ge(OMe)_4$ is expected to be in excess of 60 kcal mol^{-1} and to increase with the number of fluorines attached to Ge.

Acknowledgements

This work was made possible through the generous support of research grants and a graduate fellowship (L.A.X) from the São Paulo Science Foundation (FAPESP). N.H.M and J.M.R also thank the Brazilian Research Council (CNPq) for support through their Research Fellowship program. Finally, we acknowledge the continuous technical support of Jair J. Menegon in the experimental and computational aspects of this work.

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