

## Gas phase germylation of simple aromatics by $\text{Me}_3\text{Ge}^+$ ions

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### Abstract

The germylation of simple aromatic hydrocarbons has been studied by two different techniques. The Fourier Transform Ion Cyclotron Resonance (FTICR) technique allowed the study of  $\text{Me}_3\text{Ge}^+$  transfer equilibria between aromatics and  $\text{H}_2\text{O}$  at 300 K. The ion–molecule reaction of  $[\text{Me}_3\text{Ge}^+\cdot\text{arene}]$  ions with selected neutrals are accounted for by a  $\sigma$ -complex species, retaining the primary *ipso* structure, where the germyl group and the former aromatic hydrogen are bound to the same tetrahedral carbon. The free energies of binding of  $\text{Me}_3\text{Ge}^+$  to the selected aromatic compounds correlate linearly with the values of the corresponding  $\text{Me}_3\text{Si}^+$  reaction with a slope of 0.93. The combined information from the FTICR and radiolytic technique has revealed a mechanistic pattern for the electrophilic aromatic substitution by  $\text{Me}_3\text{Ge}^+$  that closely reproduces the corresponding  $\text{Me}_3\text{Si}^+$  reaction, the major difference lying in the greater ease of detachment of  $\text{Me}_3\text{Ge}^+$  by nucleophilic assistance. © 1997 Elsevier Science S.A.

**Keywords:** Trimethylgermyl cation; Gas phase; Ion cyclotron resonance; Radiolysis

### 1. Introduction

In continuation of our research on the gas-phase trimethylsilylation reactions by  $\text{Me}_3\text{Si}^+$  ions [1–6], we have undertaken a study on the reactivity of the neighbor group IVA analogue,  $\text{Me}_3\text{Ge}^+$ , towards (mostly) aromatic compounds aimed to compare the reactivity behavior of the two ions. Although early reports have shown that  $\text{Me}_3\text{Ge}^+$  may form stable adducts with a variety of organic molecules [7], this ion has never received a comparably widespread attention as  $\text{Me}_3\text{Si}^+$ . One practical reason may be bound to the complex isotopic pattern of germanium ( $^{70}\text{Ge}$ ,  $^{72}\text{Ge}$ ,  $^{73}\text{Ge}$ ,  $^{74}\text{Ge}$ ,  $^{76}\text{Ge}$ , with relative abundances of 20%, 27%, 8%, 37%, 8%, respectively) which allows ready mass spectrometric identification of germylated ions but at the same time spreads the overall intensity of a single ionic species and enhances the likelihood of overlapping signals. We have used an approach based on two techniques. The first one is a mass spectrometric technique, Fourier Transform Ion Cyclotron Resonance (FTICR) [8], endowed with the powerful capability of isolating an ion of interest within a complex mixture. This ion

may be a single isotopic species or the whole isotopic cluster corresponding to a given composition. In the presence of one or more neutrals in the ICR cell, at typical pressures of  $10^{-8}$  Torr, ion–molecule reactions can be recorded and equilibria can set up at the cell room temperature of 300 K. The second technique exploited, the radiolytic method [9], performs ion–molecule reactions at the pressure of ca. 1 atm using ionic species produced by the action of  $\gamma$ -radiation and yielding mechanistic information from the analysis of neutral products formed in the selected range of conditions. The combination of the two techniques has yielded a comprehensive picture of the major features of the  $\text{Me}_3\text{Ge}^+$  reaction with aromatic compounds.

### 2. Experimental

Research grade gases with stated purity in excess of 99.9% were purchased from Matheson. All other chemicals were obtained from commercial sources, including  $\text{Me}_4\text{Ge}$  from Alfa Products. They were analyzed by GC and purified by preparative GC, whenever necessary.

Gaseous samples for the radiolytic experiments were prepared by standard vacuum line techniques, as previously described [9]. The gaseous mixtures were irradi-

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ated in a 220 Gammacell (Nuclear Canada) at 40°C, to total doses ranging from  $0.5 \times 10^4$  Gy to  $1 \times 10^4$  Gy, at the dose rate of  $1 \times 10^4$  Gy h<sup>-1</sup>. The radiolytic product mixture was recovered under airtight conditions as cyclohexane solution and analyzed by GC–MS using a Hewlett-Packard 5890 gas chromatograph equipped with a 50-m long, 0.20-mm i.d. fused silica column coated with a 0.50- $\mu$ m cross-linked methyl silicone film (PONA column from Hewlett-Packard) in line with a Hewlett-Packard mass selective detector model 5970B.

The FTICR experiments were performed using a Bruker Spectrospin Apex TM 47e spectrometer equipped with an external ion source and a cylindrical (12-cm length, 12-cm diameter) ‘infinity’ cell situated between the poles of a 4.7 Torr superconducting magnet. This instrumental configuration allows the generation of ionic species in the external ion source where a suitable chemical ionization (CI) reagent gas is introduced. For example a CH<sub>4</sub>/Me<sub>4</sub>Ge (97:3 mol%) mixture at the pressure of  $1 \times 10^{-4}$  Torr was used to generate Me<sub>3</sub>Ge<sup>+</sup> ions which were allowed to react with a selected substrate (S = aromatic hydrocarbon, H<sub>2</sub>O, MeOSiMe<sub>3</sub>) introduced into the ion source by a separate inlet. The resulting ion mixture was transmitted into the FTICR cell at 300 K, where one or two different neutrals were present at stationary concentration. The ion of interest, typically Me<sub>3</sub>GeS<sup>+</sup>, was isolated from the plasma by sequential broad band ejection and ‘single shots’ [10] and was allowed to react. Ion intensity vs. time profiles were obtained by recording mass spectra at increasing reaction time. The concentration of the neutrals was determined from the pressure reading at the ionization gauge located in the high vacuum line of the FTICR cell housing, corrected by using appropriate calibration factors [11].

### 3. Results

#### 3.1. FTICR mass spectrometry

FTICR has been used in the first place to measure Me<sub>3</sub>Ge<sup>+</sup> transfer equilibria between aromatics or between an aromatic and H<sub>2</sub>O (Eq. (1)). The experiments were performed as follows. Me<sub>3</sub>Ge<sup>+</sup> ions from the CI of CH<sub>4</sub>/Me<sub>4</sub>Ge in the external ion source were allowed to react with an aromatic compound (X) introduced into the same ion source at 0.1% relative concentration. Abundant adduct ions (Me<sub>3</sub>GeX<sup>+</sup>) were formed. These were transferred into the FTICR cell where known concentrations of the same aromatic compound and of a reaction partner (another aromatic or H<sub>2</sub>O) were present. An alternative route to Me<sub>3</sub>GeX<sup>+</sup> ions by reaction of Me<sub>3</sub>Ge<sup>+</sup> with an aromatic compound in the ICR cell failed to give significant abundances of adduct ions due to the inefficient collisional stabilization in the low pressure environment ( $10^{-8}$ – $10^{-7}$  Torr). The primary

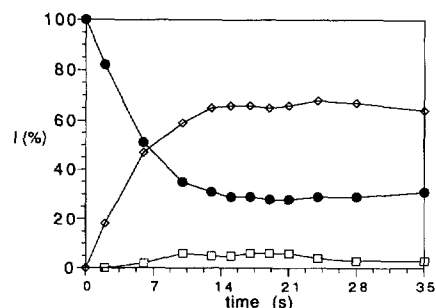
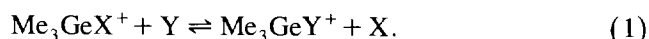


Fig. 1. Normalized ion intensities of MeC<sub>6</sub>H<sub>5</sub>GeMe<sub>3</sub><sup>+</sup> (●), Me<sub>3</sub>GeOH<sub>2</sub><sup>+</sup> (◇), and Me<sub>3</sub>Ge<sup>+</sup> (□) as a function of time. Partial pressures in the FTICR cell were:  $P(\text{toluene}) = 1.5 \times 10^{-8}$  Torr and  $P(\text{H}_2\text{O}) = 0.15 \times 10^{-8}$  Torr.

adduct ion was isolated from other ions which entered or were formed in the cell by resonance ejection techniques and was allowed to react with the mixture of the two neutrals for increasing reaction times (Eq. (1)):



Plots of relative ion intensities vs. time were thus obtained, showing the attainment of equilibrium when the ion intensity ratio reaches a constant value. An example of such plots is shown in Fig. 1 where X = MeC<sub>6</sub>H<sub>5</sub> and Y = H<sub>2</sub>O. The equilibrium constant at the cell temperature of 300 K is calculated from Eq. (2) (where *i* are ion intensities and *P* are partial pressures) and yielded a  $\Delta G_{300}^\circ$  value (kcal mol<sup>-1</sup>) according to Eq. (3):

$$K = \frac{i(\text{Me}_3\text{GeY}^+) \times P(\text{X})}{i(\text{Me}_3\text{GeX}^+) \times P(\text{Y})} \quad (2)$$

$$\Delta G_{300}^\circ = -RT \ln K = -0.60 \ln K \quad (3)$$

The attainment of a true equilibrium is verified by the constancy of the right-hand ratio of Eq. (2) for

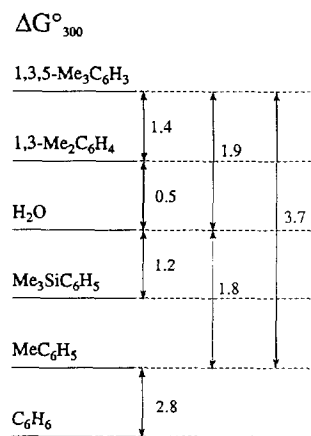


Fig. 2. Measured free energy changes,  $\Delta G_{300}^\circ$ , for Me<sub>3</sub>Ge<sup>+</sup> transfer between aromatics and H<sub>2</sub>O. The direction of the preferred transfer ( $\Delta G^\circ$  negative) is in the upward direction. Comparison of overlapping and successive steps on the ladder show an internal consistency of about  $\pm 2$  kcal mol<sup>-1</sup>. Reproducibility of  $\Delta G^\circ$  values was better than  $\pm 1$  kcal mol<sup>-1</sup>.

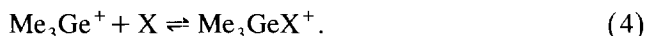
Table 1  
Free energy changes for the process  $\text{Me}_3\text{Ge}^+ + \text{X} \rightleftharpoons \text{Me}_3\text{GeX}^+$

X	$-\Delta G_{300}^{\circ}$ (kcal mol <sup>-1</sup> )
1,3,5-Me <sub>3</sub> C <sub>6</sub> H <sub>3</sub>	20.2
1,3-Me <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	18.8
Me <sub>3</sub> SiC <sub>6</sub> H <sub>5</sub>	17.1
MeC <sub>6</sub> H <sub>5</sub>	16.5
C <sub>6</sub> H <sub>6</sub>	13.7
H <sub>2</sub> O	18.3 <sup>b</sup>

<sup>a</sup>Average error  $\pm 0.1$  kcal mol<sup>-1</sup>.

<sup>b</sup>Ref. [12].

different ratios of the partial pressures of the two neutrals. The  $\Delta G_{300}^{\circ}$  ladder obtained in this way is displayed in Fig. 2 and was used to derive the free energies of binding of  $\text{Me}_3\text{Ge}^+$  to the various compounds (reaction 4) from the known thermodynamic data relative to the  $\text{Me}_3\text{Ge}^+$  association to H<sub>2</sub>O [12].



The so obtained  $\Delta G_{(4)}^{\circ}$  values are listed in Table 1.

The reaction of  $\text{Me}_3\text{GeC}_6\text{D}_6^+$  ions, formed in the ion source by  $\text{CH}_4/\text{Me}_4\text{Ge}-\text{Cl}$  of C<sub>6</sub>D<sub>6</sub>, with Et<sub>3</sub>N introduced into cell was also studied by FTICR, yielding the temporal profile of ion intensities shown in Fig. 3. The exponential decay of the reactant ion yields a bimolecular rate constant of  $3.7 \times 10^{-9}$  cm<sup>3</sup> s<sup>-1</sup>, corresponding exactly to the collisional rate constant [13]. This is indicative that the  $\text{Me}_3\text{GeC}_6\text{D}_6^+$  ion reacts with the strong base on every collision. Among the ionic products, besides the trimethylgermylated amine at  $m/z$  220 (<sup>74</sup>Ge isotope), the ion at  $m/z$  103 is significant. It corresponds to the Et<sub>3</sub>ND<sup>+</sup> and shows that the reactant ion can transfer not only  $\text{Me}_3\text{Ge}^+$  but also a deuteron to the base.

The reaction of  $\text{MeO}(\text{SiMe}_3)\text{GeMe}_3^+$  ions, obtained by  $\text{Me}_3\text{Ge}^+$  addition to  $\text{MeOSiMe}_3$ , with  $(\text{MeO})_3\text{PO}$ , a powerful oxygen nucleophile, has been performed to check as to what relative extent  $\text{Me}_3\text{Ge}^+$  transfer vs.  $\text{Me}_3\text{Si}^+$  transfer would occur. The temporal profiles of

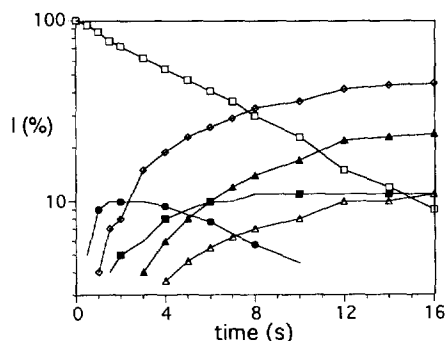


Fig. 3. Normalized ion intensities of  $\text{Me}_3\text{GeC}_6\text{D}_6^+$  (□),  $\text{Me}_3\text{GeNEt}_3^+$  (◇),  $\text{Et}_3\text{ND}^+$  (Δ),  $[\text{Et}_3\text{N}-\text{H}]^+/\text{Et}_3\text{N}^+$  (■),  $\text{Et}_3\text{NH}^+$  (▲), and  $\text{Me}_3\text{Ge}^+$  (●) as a function of time. The pressure of Et<sub>3</sub>N was  $1.7 \times 10^{-9}$  Torr.

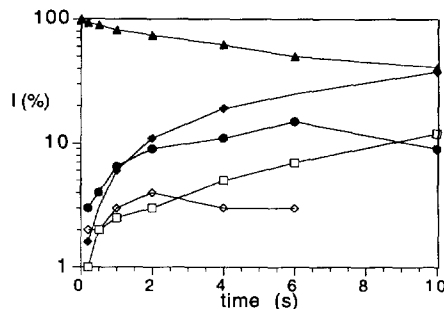


Fig. 4. Normalized ion intensities of  $\text{MeO}(\text{SiMe}_3)\text{GeMe}_3^+$  (▲),  $(\text{MeO})_3\text{POGeMe}_3^+$  (◆),  $(\text{MeO})_3\text{POSiMe}_3^+$  (□),  $\text{Me}_3\text{Ge}^+$  (●), and  $\text{Me}_3\text{Si}^+$  (◇) as a function of time. The pressure of  $(\text{MeO})_3\text{PO}$  was  $1.2 \times 10^{-8}$  Torr.

ion intensities plotted in Fig. 4 show that the heterolytic cleavage of the Ge–O bond occurs preferentially to give both the free  $\text{Me}_3\text{Ge}^+$  ion and a higher fraction (ca. 3:1) of the  $(\text{MeO})_3\text{POGeMe}_3^+$  product ions with respect to the silicon counterpart,  $(\text{MeO})_3\text{POSiMe}_3^+$ .

A greater ease of  $\text{Me}_3\text{Ge}^+$  transfer to oxygen nucleophiles apparently emerges also from the reaction of  $\text{Me}_3\text{SiC}_6\text{H}_5\text{GeMe}_3^+$  ions, illustrated in Fig. 5, from  $\text{CH}_4/\text{Me}_4\text{Ge}-\text{Cl}$  of  $\text{Me}_3\text{SiC}_6\text{H}_5$ , with H<sub>2</sub>O in the ICR cell at  $5.9 \times 10^{-9}$  Torr. The products ions, corresponding to  $\text{Me}_3\text{GeOH}_2^+$  and  $\text{Me}_3\text{GeOH}(\text{SiMe}_3)^+$ , are suggested both to follow from the primary product ion-neutral complex,  $[\text{Me}_3\text{GeOH}_2^+ \cdot \text{Me}_3\text{SiC}_6\text{H}_5]$ , by direct dissociation or further reaction within the complex (Scheme 1). Noteworthy, no  $\text{Me}_3\text{SiOH}_2^+$  is formed.

### 3.2. Radiolytic reactions

Radiolytic germylation reactions have been performed at 40°C in a 97:3 mol% mixture of  $\text{CH}_4/\text{Me}_4\text{Ge}$  at 620 Torr, where ionization is effected by the secondary electrons following the interaction of  $\gamma$ -radiation with the materials (mainly the vessel glass walls) of the radiolyzed sample. Table 2 summarizes the results from the germylation of toluene and of benzene as competing

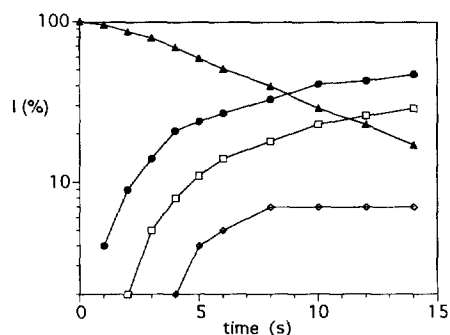
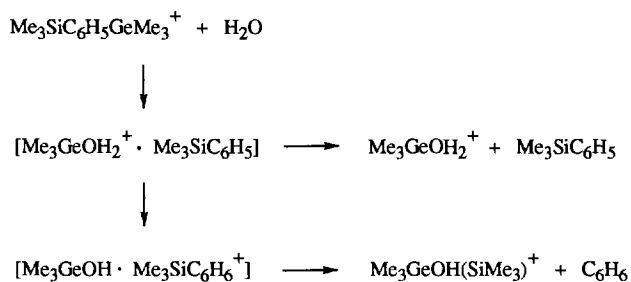


Fig. 5. Normalized ion intensities of  $\text{Me}_3\text{SiC}_6\text{H}_5\text{GeMe}_3^+$  (▲),  $\text{Me}_3\text{GeOH}_2^+$  (●),  $\text{Me}_3\text{Ge}^+$  (◇), and  $\text{Me}_3\text{GeOH}(\text{SiMe}_3)^+$  (□) as a function of time. The pressure of H<sub>2</sub>O was  $5.9 \times 10^{-9}$  Torr.



Scheme 1.

substrate. All systems contained a radical scavenger,  $\text{O}_2$ , at 10 Torr, whose presence allows to neglect conceivable radical pathways to the observed products.

In order to obtain germylation products from the aromatic hydrocarbons, the presence of a strong nitrogen base, such as  $\text{Et}_3\text{N}$ , with proton affinity (PA) equal to  $232 \text{ kcal mol}^{-1}$  [14], was found to be a necessary condition. With no such additive present or when  $(\text{MeO})_3\text{PO}$  (PA =  $212 \text{ kcal mol}^{-1}$ ) [14] is used in the place of  $\text{Et}_3\text{N}$ , no aromatic germylation takes place. The isomer distribution of the toluene products,  $\text{MeC}_6\text{H}_4\text{GeMe}_3$ , is characterized by the absence of the ortho isomer and by the distinct preference of *para*- with respect to *meta*-substitution. The series of experiments run at nearly constant amounts of benzene and toluene and varying concentrations of  $\text{Et}_3\text{N}$  yield both  $\text{C}_6\text{H}_5\text{GeMe}_3$  and  $\text{MeC}_6\text{H}_4\text{GeMe}_3$ , whose combined yield are plotted against the  $\text{Et}_3\text{N}$  partial pressure in Fig. 6. Their relative yields can be analyzed by the standard equation for competing reactions (Eq. (5)), where  $G_M$  are radiochemical yields in units of  $10^{-3} \mu\text{mol J}^{-1}$  (note b of Table 2) to give apparent relative

Table 2  
Aromatic substitution by gaseous  $\text{Me}_3\text{Ge}^+$  ions

System composition (Torr) <sup>a</sup>			Product yields ( $G_M$ ) <sup>b</sup>	
$\text{C}_6\text{H}_6$	$\text{MeC}_6\text{H}_5$	$\text{Et}_3\text{N}$	$\text{C}_6\text{H}_5\text{GeMe}_3$	$\text{MeC}_6\text{H}_4\text{GeMe}_3$ (o/m/p)
2.5	—	1.5 <sup>c</sup>	—	—
—	2.3	—	—	—
—	1.9	1.0 <sup>c</sup>	—	—
—	2.6	1.6	—	5.2 (0/18/82)
2.9	0.94	0.40	0.20	0.77 (0/24/76)
3.1	1.1	0.89	0.36	1.5 (0/18/82)
3.2	1.2	1.5	1.0	3.5 (0/17/83)
2.9	0.92	2.2	1.0	2.4 (0/21/79)
3.3	1.2	2.9	1.0	2.1 (0/19/81)
3.3	1.2	4.0	0.82	1.3 (0/23/77)
3.3	1.1	5.1	0.59	0.73 (0/18/82)

<sup>a</sup>The major gaseous components are  $\text{CH}_4$  (600 Torr),  $\text{Me}_4\text{Ge}$  (20 Torr), and  $\text{O}_2$  (10 Torr).

<sup>b</sup>Absolute yields are in units of  $10^{-3} \mu\text{mol J}^{-1}$ .

<sup>c</sup> $(\text{MeO})_3\text{PO}$  was present, in place of  $\text{Et}_3\text{N}$ .

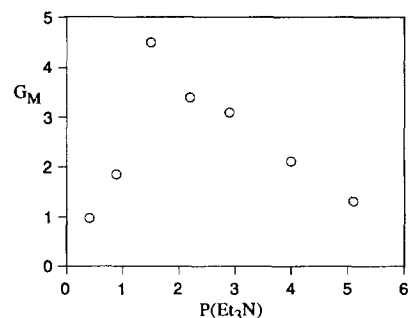


Fig. 6. Overall radiochemical yield ( $G_M$ , in units of  $10^{-3} \mu\text{mol J}^{-1}$ ) of the germylation products of benzene and toluene plotted vs.  $P(\text{Et}_3\text{N})$  (Torr).

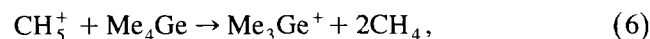
reactivity ratios that are found to be dependent on  $\text{Et}_3\text{N}$  concentration (Fig. 7).

$$\frac{k_T}{k_B} = \frac{G_M(\text{MeC}_6\text{H}_4\text{GeMe}_3) \times P(\text{C}_6\text{H}_6)}{G_M(\text{C}_6\text{H}_5\text{GeMe}_3) \times P(\text{MeC}_6\text{H}_5)} \quad (5)$$

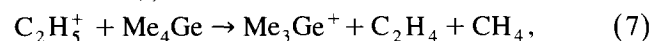
## 4. Discussion

### 4.1. The reagent ion

$\text{Me}_3\text{Ge}^+$  is the only initial ion resulting from the reaction of  $\text{Me}_4\text{Ge}$  with the major reagent ions  $\text{CH}_5^+$  and  $\text{C}_2\text{H}_5^+$  formed from methane under CI [15,16] and radiolytic conditions [17]. The exothermicities of the formation processes (Eqs. (6) and (7)) were obtained from thermochemical data in Ref. [14], using  $\Delta H_f^\circ(\text{Me}_3\text{Ge}^+) = 167 \text{ kcal mol}^{-1}$  [18] and  $\Delta H_f^\circ(\text{Me}_4\text{Ge}) = -24.5 \text{ kcal mol}^{-1}$  [19].



where  $\Delta H_{(6)}^\circ = -68 \text{ kcal mol}^{-1}$ .



where  $\Delta H_{(7)}^\circ = -37 \text{ kcal mol}^{-1}$ .

At the pressure of  $10^{-4}$  Torr in the CI ion source conditions of the FTICR instrument,  $\text{Me}_3\text{Ge}^+$  is the

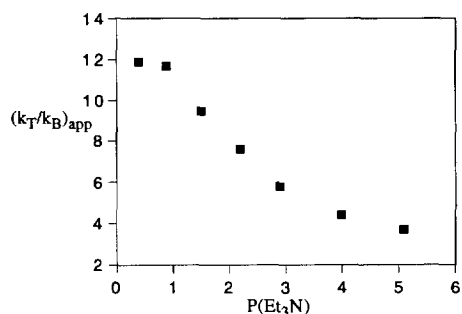


Fig. 7. Apparent relative reactivity ratios from the competitive germylation of benzene and toluene plotted vs.  $P(\text{Et}_3\text{N})$  (Torr). Values are obtained using Eq. (5).

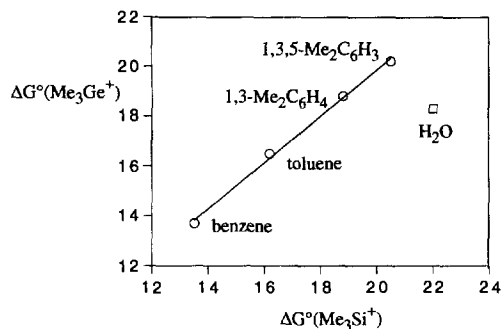
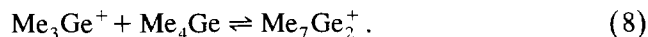


Fig. 8. The correlation between  $\Delta G^\circ_{300}$  for the association of  $\text{Me}_3\text{Ge}^+$  and  $\Delta G^\circ_{300}$  for the association of  $\text{Me}_3\text{Si}^+$  to the selected compounds.

only germylating species. At the much higher  $\text{Me}_4\text{Ge}$  pressure of the radiolytic experiments, an association equilibrium is expected to set up (Eq. (8)) yielding  $\text{Me}_7\text{Ge}_2^+$  ions [12,18] which may act as germylating species by  $\text{Me}_4\text{Ge}$  displacement.



$\text{Me}_3\text{Ge}^+$  is expected to behave exclusively as Lewis acid in view of the rather high PA of its conjugate base (PA of  $\text{Me}_2\text{Ge}=\text{CH}_2$  equals to 206 kcal mol<sup>-1</sup> [20]). Accordingly, proton transfer from  $\text{Me}_3\text{Ge}^+$  to toluene is calculated to be endothermic by 16 kcal mol<sup>-1</sup> (PA of toluene equals to 190 kcal mol<sup>-1</sup> [14]). The exclusive Lewis acid character of  $\text{Me}_3\text{Ge}^+$  toward the selected substrates makes the apparent rate constant ratios  $k_T/k_B$  of Fig. 7 a direct measure of the corresponding reaction channels.

#### 4.2. The association of $\text{Me}_3\text{Ge}^+$ to aromatic hydrocarbons

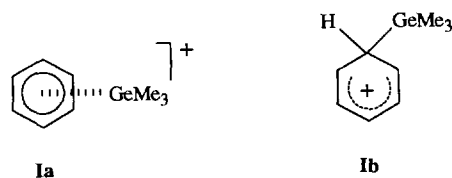
The free energies of binding of  $\text{Me}_3\text{Ge}^+$  to aromatic hydrocarbons show an increasing trend in the series from benzene to mesitylene, corresponding to the increasing electron density available at the aromatic ring from the electron donating effect of the methyl substituent(s). The same order corresponds to increasing PA [14] and increasing binding energy to  $\text{Me}_3\text{Si}^+$  [21]. The values of  $\Delta G^\circ_{300}$  for the binding of the two  $\text{Me}_3\text{X}^+$  ions ( $\text{X} = \text{Si}, \text{Ge}$ ) to the aromatic bases are very close to each other and fit the linear relationship drawn in Fig. 8. The slope of 0.93 indicates that the association free energies of  $\text{Me}_3\text{Ge}^+$  spread over a narrower range, hence they are slightly less sensitive to the structural features of the aromatic base. Within the approximation that the close values of  $\Delta G^\circ_{300}$  for the association of  $\text{Me}_3\text{Ge}^+$  and  $\text{Me}_3\text{Si}^+$  to benzene (13.7 and 13.5 kcal mol<sup>-1</sup>, respectively) are paralleled by similarly close  $\Delta H^\circ$  values (23.9 kcal mol<sup>-1</sup>) [21], a thermochemical cycle can be constructed, allowing the PA of  $\text{Me}_3\text{GeC}_6\text{H}_5$  to be evaluated. It is unfortunately not surprising that the required value of  $\Delta H^\circ_f$  for

$\text{Me}_3\text{GeC}_6\text{H}_5$  is missing from the scant and scattered thermochemical data available for germanium compounds.  $\Delta H^\circ_f$  ( $\text{Me}_3\text{GeC}_6\text{H}_5$ ) was estimated as 8 kcal mol<sup>-1</sup> by the group increment method using thermochemical data from Ref. [22]. In this way, a PA value of ca. 212 kcal mol<sup>-1</sup> is derived for  $\text{Me}_3\text{GeC}_6\text{H}_5$ .

#### 4.3. Mechanism of the germylation reaction and structure of $[\text{Me}_3\text{Ge}^+ \cdot \text{arene}]$ complexes

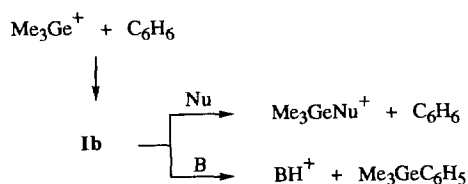
The closely similar thermodynamic data for the association of  $\text{Me}_3\text{X}^+$  ( $\text{X} = \text{Ge}, \text{Si}$ ) to simple aromatics suggests for the  $[\text{Me}_3\text{Ge}^+ \cdot \text{arene}]$  adduct the same  $\sigma$ -complex structure which several experimental [1–6] and theoretical [23] studies ascribed to gaseous  $[\text{Me}_3\text{Si}^+ \cdot \text{arene}]$  complexes.

This structural assignment is supported by the reactivity of the  $[\text{Me}_3\text{Ge}^+ \cdot \text{arene}]$  adducts.  $\text{Me}_3\text{GeC}_6\text{H}_6^+$  reacts with  $\text{H}_2\text{O}$  by  $\text{Me}_3\text{Ge}^+$  transfer, a process that may be compatible with either a  $\pi$ -complex (**Ia**) or an *ipso*- $\sigma$ -complex (**Ib**) structure of the reactant ion.



However, the  $\text{Me}_3\text{GeC}_6\text{D}_6^+$  reaction with  $\text{Et}_3\text{N}$  occurs by  $\text{D}^+$  transfer to an appreciable extent and this is strongly indicative of covalent  $\text{C}_{\text{benzene}}-\text{Ge}$  bond formation. The overall reactivity pattern fits into a mechanistic scheme (Scheme 2 for  $\text{C}_6\text{H}_6$  as representative arene) that accounted for the salient features of the corresponding reaction of  $\text{Me}_3\text{Si}^+$  with aromatic hydrocarbons [1–6].

At variance with  $\pi$ -complex **Ia**, expected to react exclusively by  $\text{Me}_3\text{Ge}^+$  transfer, the  $\sigma$ -complex **Ib** may undergo competitive  $\text{H}^+$  and  $\text{Me}_3\text{Ge}^+$  transfer, depending on the features of the neutral reagent. The low PA of  $\text{H}_2\text{O}$  (166.5 kcal mol<sup>-1</sup>) [14] prevents  $\text{H}^+$  transfer from **Ib** whereas  $\text{Me}_3\text{Ge}^+$  transfer is driven by the intrinsically higher bond energy of  $\text{Ge}-\text{O}$  with respect to  $\text{Ge}-\text{C}$ . The same factor may account for the larger binding free energy of  $\text{Me}_3\text{Ge}^+$  to  $\text{H}_2\text{O}$  with respect to  $\text{C}_6\text{H}_6$ , in the reverse order of their PAs (166.5 and



Scheme 2.

181.3 kcal mol<sup>-1</sup>, respectively) [14]. The use of Et<sub>3</sub>N, a strong though sterically hindered nitrogen base, enables deprotonation of **1b**. The proposed mechanism is supported by the product pattern of the radiolytic germylation where the recovery of neutral germylation products unambiguously proves the formation of a Me<sub>3</sub>Ge–C covalent bond through a  $\sigma$ -complex intermediate. The presence of an appropriate base, Et<sub>3</sub>N, is required to ensure formation of germylated products. In its absence, traces of oxygenated nucleophiles, unavoidably present, either as adventitious impurities (e.g., H<sub>2</sub>O) or as radiolytic products (e.g., H<sub>2</sub>O, MeOH, CH<sub>2</sub>O, etc.) react with **1b** exclusively by Me<sub>3</sub>Ge<sup>+</sup> transfer. Accordingly, no aromatic germylated products are formed. However, when Et<sub>3</sub>N is added to the gaseous mixtures, two opposing effects on the product yield can be envisaged. On the one hand, Et<sub>3</sub>N allows deprotonation of **1b** favoring formation of the germylated products. On the other, the amine effectively intercepts the CH<sub>3</sub><sup>+</sup>/C<sub>2</sub>H<sub>5</sub><sup>+</sup> and Me<sub>3</sub>Ge<sup>+</sup> precursors, thus depressing the yields of the intermediates **1b** and therefore of the ensuing neutral products. This dual behavior accounts for the dependence of the absolute yields of the germylated products on the partial pressure of Et<sub>3</sub>N shown in Fig. 6, which is characterized by a maximum at the Et<sub>3</sub>N pressure of ca. 1.5 Torr.

It is worth noting that a highly basic additive such as (MeO)<sub>3</sub>PO as well is not effective in yielding germylation products. This result supports an *ipso*-type structure for the germylated arenium intermediate since any isomeric ion obtained by 1,2-H<sup>+</sup> shift would be deprotonated by (MeO)<sub>3</sub>PO leading to observable products (Scheme 3 for MeC<sub>6</sub>H<sub>5</sub> as representative arene).

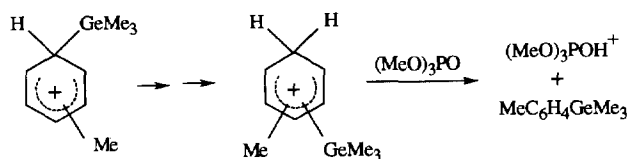
The unwillingness of ion **1b** to undergo isomerization by 1,2-H<sup>+</sup> shifts, which contrast with the behavior of alkylated arenium ions [24,25], is traced to the higher stability conferred to **1b** by the  $\beta$  relationship of the formal positive charge on the arenium ring with respect to the C<sub>ary1</sub>–Ge bond with an orbital alignment allowing hyperconjugative interaction [26–28].

In conclusion, [Me<sub>3</sub>Ge<sup>+</sup>·arene] complexes undergo Me<sub>3</sub>Ge<sup>+</sup> transfer to oxygen nucleophiles and deprotonation by strong nitrogen bases. With a second arene molecule, they engage in reversible Me<sub>3</sub>Ge<sup>+</sup> transfer till equilibrium is reached, as can be observed directly from the ICR kinetic plots. Direct evidence for Me<sub>3</sub>Ge<sup>+</sup> transfer from Me<sub>3</sub>GeC<sub>6</sub>H<sub>6</sub><sup>+</sup> to toluene is also obtained from the apparent  $k_T/k_B$  ratios from the radiolytic

reactions, which increase as the Et<sub>3</sub>N partial pressure is decreased (Fig. 7). This is accounted for by a rather indiscriminate primary attack of Me<sub>3</sub>Ge<sup>+</sup> at the two substrates to yield an ion population which subsequently tends to shift toward the equilibrium ratio. The Me<sub>3</sub>Ge<sup>+</sup> transfer to toluene competes with deprotonation by Et<sub>3</sub>N. Decreasing the Et<sub>3</sub>N partial pressure favors the approach to equilibrium by increasing the lifetime of the [Me<sub>3</sub>Ge<sup>+</sup>·arene] ions, which cannot, however, be increased indefinitely due to the presence of trace oxygen nucleophiles. The highest apparent  $k_T/k_B$  ratio of 12 in Fig. 7 is still far from the equilibrium value of [MeC<sub>6</sub>H<sub>4</sub>GeMe<sub>3</sub><sup>+</sup>]/[Me<sub>3</sub>GeC<sub>6</sub>H<sub>6</sub><sup>+</sup>] = 35, expected under the operative reaction conditions.

#### 4.4. Comparison of the gas phase reactivity of Me<sub>3</sub>Ge<sup>+</sup> and Me<sub>3</sub>Si<sup>+</sup>

Several times in the previous sections, the gas phase behavior of Me<sub>3</sub>Ge<sup>+</sup> towards aromatic hydrocarbons has been found to conform to the model Me<sub>3</sub>Si<sup>+</sup> reaction. The similar behavior of the two electrophiles is confirmed also by the positional selectivity of the attack at the ring positions of toluene. In both cases substitution at the *ortho* position is avoided due to steric hindrance, and the *para/meta* ratio is ca. 80/20, showing fair selectivity towards the more activated site. However, a noticeable difference emerges from the absolute radiochemical yields of the two reactions. The germylated products are formed with a smaller yield, typically by a factor of ten, with respect to silylation products under strictly comparable reaction conditions. Whereas the similar binding free energies do not lend support to the hypothesis of a higher barrier for electrophilic attack by Me<sub>3</sub>Ge<sup>+</sup> with respect to Me<sub>3</sub>Si<sup>+</sup>, an explanation can be found in the greater ease of displacement of Me<sub>3</sub>Ge<sup>+</sup> from the arenium complex by oxygen nucleophiles. Such a feature was recently exploited to perform a silylation reaction via Me<sub>3</sub>Ge<sup>+</sup> displacement from Me<sub>3</sub>GeC<sub>6</sub>H<sub>5</sub>, thus obtaining for the first time silylated products without the assistance of a nitrogen base [6]. The high mobility of Me<sub>3</sub>Ge<sup>+</sup> is shown in the reported reactions of Me<sub>3</sub>SiC<sub>6</sub>H<sub>5</sub>GeMe<sub>3</sub><sup>+</sup> with H<sub>2</sub>O and MeO(SiMe<sub>3</sub>)GeMe<sub>3</sub><sup>+</sup> with (MeO)<sub>3</sub>PO. Although the heterolytic cleavage and transfer of Me<sub>3</sub>Ge<sup>+</sup> is not strictly comparable to the Me<sub>3</sub>Si<sup>+</sup> reaction as they yield different ionic and neutral products, still it appears significant that the former reaction prevails by a noticeable extent.



Scheme 3.

## 5. Conclusions

The gas-phase behavior of Me<sub>3</sub>Ge<sup>+</sup> ions toward aromatic hydrocarbons has shown striking similarities to the corresponding Me<sub>3</sub>Si<sup>+</sup> reaction. This conclusion

emerges primarily from the close values of the free energies of binding of  $\text{Me}_3\text{X}^+$  ( $\text{X} = \text{Ge}, \text{Si}$ ) to the same aromatic compound, the only difference lying in the barely detectable smaller sensitivity of the  $\text{Me}_3\text{Ge}^+$  association to the structural features of the compounds in the series benzene/toluene/*m*-xylene/mesitylene. The mechanistic pattern leading to aromatic substitution products was elucidated by the combined information from the FTICR and radiolytic techniques. The major features can be summarized as follows: (i)  $\text{Me}_3\text{Ge}^+$  reacts at the aromatic ring giving a  $\sigma$ -complex intermediate; (ii) this primary intermediate retains the hydrogen on the germylated carbon, showing no tendency to isomerize by 1,2- $\text{H}^+$  shifts; and (iii) the *ipso*-type  $\sigma$ -complex may evolve either by deprotonation by strong nitrogen bases or by degermylation by oxygen nucleophiles, the latter an obviously blind reaction channel. All gathered evidence point to this last step as responsible for the major differences observed between the  $\text{Me}_3\text{Ge}^+$  and  $\text{Me}_3\text{Si}^+$  reaction. In fact, heterolytic cleavage of the C–Ge bond assisted by oxygen nucleophiles appears to occur with greater ease than the corresponding C–Si bond cleavage and the  $\text{Me}_3\text{Ge}^+$  group appears endowed with greater mobility than its silicon analogue. In the absence of pertinent thermodynamic and kinetic data, reasons accounting for this different behavior, including the role of the more expanded *d* orbitals on germanium, can only be guessed.

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