Surface Organometallic Chemistry of Germanium: Evidence for the Formation of Highly Thermally Stable $\equiv$Si—O—GeR$_3$ Fragments by Reaction of GeR$_4$ Complexes (R = *n*-Bu, Et) with the Surface of Silica

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Interaction between GeR$_4$ complexes with partially dehydroxylated silica surfaces has been studied by infrared spectroscopy, ^{13}C CP-MAS NMR, and analytical methods. The tetraalkylgermanium complexes are physisorbed, at room temperature: a hydrogen-type bonding occurs between the terminal methyl group of the alkyl ligands and the surface silanol groups. The results obtained for the two complexes (R = Et, *n*-Bu) and for two supports (silica$_{(200)}$ and silica$_{(500)}$) are rather similar and may be explained by a simple reaction between the surface silanols and the tetraalkylgermanium compounds: $\equiv$Si—O—H + GeR$_4$ $\rightarrow$ $\equiv$Si—O—GeR$_3$ + RH. Surprisingly, thermal treatment under vacuum (10^{-4} Torr) of the well-defined $\equiv$Si—O—GeR$_3$ complex supported on silica$_{(200)}$ and silica$_{(500)}$ does not lead to any evolution of gas between 200 and 400 °C. The stabilility of the grafted complex is also evidenced by analytical data and by infrared spectroscopy. The extraordinary thermal stability of $\equiv$Si—O—GeR$_3$ is compatible with the higher stability of germanium alkyl complexes as compared with the tin ones. A mechanism of decomposition of the surface alkyl complexes is proposed.

Introduction

In our general approach of surface organometallic chemistry,[1] we have recently studied the reactivity of organometallic compounds of group IV elements with the surface of highly divided oxides.[2] There are several reasons for such an approach: first, this is a new field of chemistry and hopefully new surface organometallic compounds may be obtained, some of which may present interesting properties due to the possible stabilization on a surface of unusual oxidation states and/or coordination numbers; second, grafting organometallic compounds on surfaces may introduce, via the types of ligands chosen, new properties to the solid such as hydrophoby or hydrophily; third, if one can graft these organometallic fragments at the pore intrance of zeolites, one may control by steric effect the size of the molecules that one wishes to separate.

The choice of group IV elements is related to their relative inertness when they are in their tetravalent oxidation state so that some stable surface organometallic compounds could be obtained. Surface organometallic chemistry of tin has been our first choice and preliminary results have already been published in this area.[2] In particular it has been shown that it is possible to graft trialkyltin fragments on a silica surface by reacting tetraalkyltin complexes or tri-*n*-butyltin hydride with a partially dehydroxylated silica. The well defined surface organometallic fragment $\equiv$Si—O—SnR$_3$ was characterized via several analytical tools such as ^{13}C CP-MAS NMR, ^{119}Sn MAS NMR and infrared spectroscopy. From ^{119}Sn NMR data, and by comparison with molecular analogues, the surface compound was shown to be tetracoordinated on the surface. The trialkyltin or neopentyl-

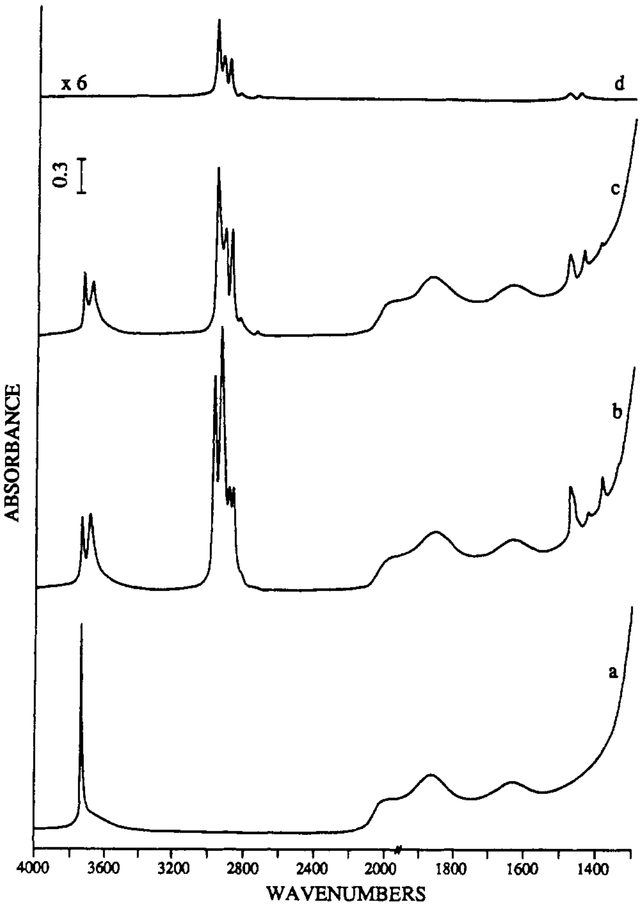

Figure 1. Infrared spectra in the 4000–1300-cm^{-1} region: (a) a disk of silica$_{(500)}$; (b) sample a after introduction of GeBu$_4$ at 25 °C; (c) sample b after vacuum treatment at 100 °C and then introduction of GeEt$_4$ at 25 °C; (d) the gas phase over sample c.

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Table 1. ^{13}C NMR Shifts after Reaction of $GeBu_4$ and $GeEt_4$ with Silica Surface and Comparison with Molecular Models

compd or system	T^a (°C)	wt % Ge	^{13}C NMR δ (ppm) C_α	C_β	C_γ	C_δ	$C_x'^{\,b}$
$GeBu_4{}^c$			12.5	27.6	26.7	13.8	
$GeBu_4/SiO_{2(200)}$	25	2.2	11.9	26.9	26.3	12.9	
$GeBu_4/SiO_{2(200)}$	250	1.5	15.6	25.2	25.2		11.3
$GeBu_4/SiO_{2(500)}$	250	1.1	15.8	25.3	25.3		11.3
Bu_3GeOPr^d			14.9	26.5	26.5	13.8	
$Bu_3GeO(\eta^3\text{-}C_3H_5)^d$			15.1	26.4	26.4	13.7	
$GeEt_4{}^c$			3.4	8.9			
$GeEt_4/SiO_{2(200)}$	25	1.3	2.6	7.5			
$GeEt_4/SiO_{2(200)}$	250	0.5	4.7				6.5

[a] Treatment temperature of the sample. [b] x = δ (precursor = $GeBu_4$), β ($GeEt_4$). [c] In solution in $CDCl_3$. [d] Reference 8.

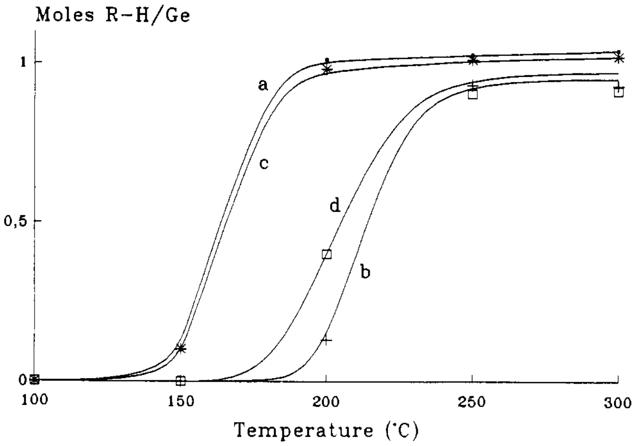

Figure 2. Gas-phase analysis during the thermal treatment of $GeR_4/SiO_{2(200)}$ [(a) R = Bu; (c) R = Et] or $GeR_4/SiO_{2(500)}$ [(b) R = Bu; (d) R = Et].

magnesium fragments were also grafted at the external surface of mordenites and were found to modify quite significantly the adsorption capacity of mordenite toward branched paraffins.[3,4] In particular, whereas a classical mordenite is not able to separate *n*-hexane fom isooctane, the same mordenite modified by the tri-*n*-butyltin or by the neopentylmagnesium fragment is able to separate the two isomers. More subtle separations can be achieved when changing the bulkiness of the alkyl groups on the tin fragment. Unfortunately, the trialkyltin and the monoalkylmagnesium surface complexes are not thermally very stable ($T < 200$ °C), which renders such methodology of limited use. We have therefore tried to extend such surface chemistry to germanium alkyl compounds because germanium is known to have a stronger metal–carbon bond than tin.[5,6] We present, here, our first results concerning the surface organometallic chemistry of germanium. The data demonstrate that it is effectively possible to graft a trialkylgermanium fragment at the surface of silica and that the grafted complex exhibits a very high thermal stability. The mechanism of thermal decomposition of this grafted trialkylgermanium species is also considered.

Experimental Section

Reagents. The silica used for these experiments was Aerosil silica from Degussa with a surface area of 200 $m^2 \cdot g^{-1}$. The silica was usually pretreated overnight at 200 or 500 °C and we shall designate them later as $silica_{(200)}$ and $silica_{(500)}$.

$Ge(n\text{-}C_4H_9)_4$ and $Ge(C_2H_5)_4$ were purchased from Strem and used as such.

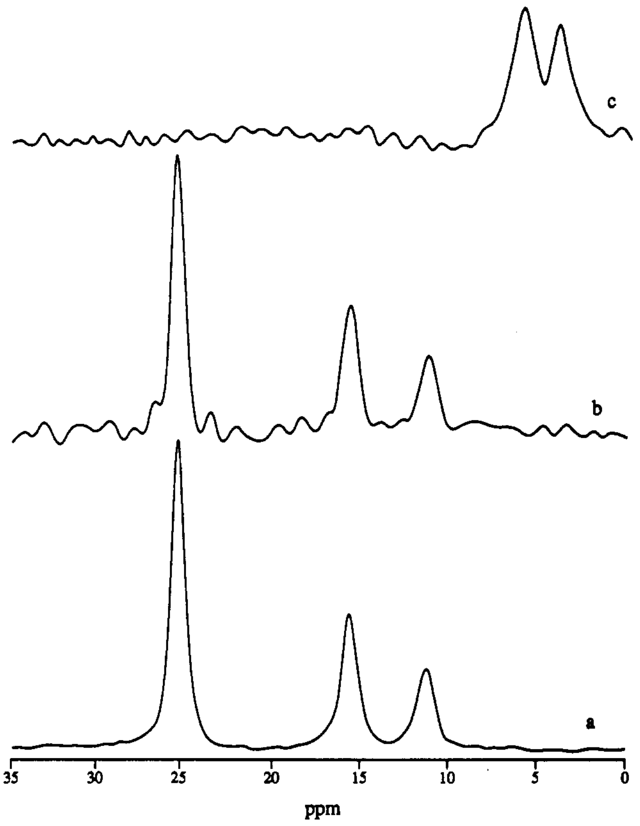

Figure 3. ^{13}C CP-MAS NMR spectra of the solids obtained after reaction of GeR_4 at 250 °C with (a) $silica_{(200)}$ (R = Bu), (b) $silica_{(500)}$ (R = Bu), and (c) $silica_{(200)}$ (R = Et).

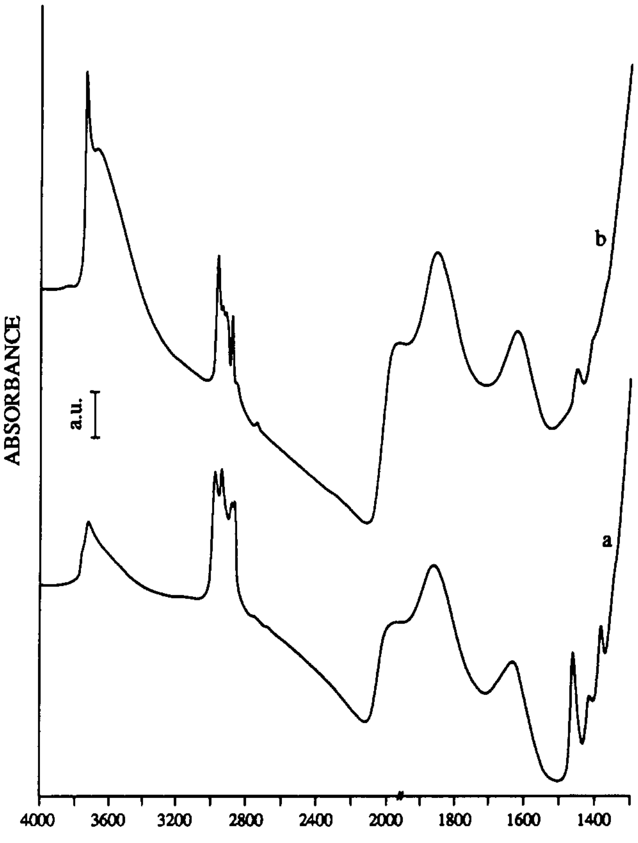

Figure 4. Infrared spectra in the 4000–1300-cm^{-1} region of the solids obtained after reaction of GeR_4 at 250 °C with $silica_{(200)}$: (a) R = Bu; (b) R = Et.

Techniques. Equipment for Analytical Measurements. Most of the experiments were carried out in glassware equipment connected to a vacuum line and eventually to a volumetric apparatus. A given amount

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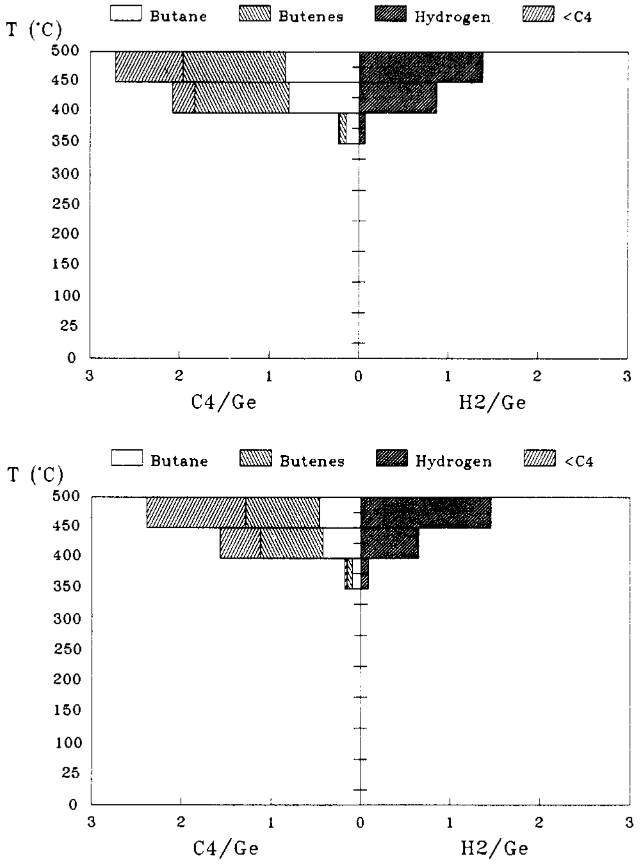

Figure 5. Gas-phase analysis during the thermal treatment, under vacuum, of $\equiv$SiOGeBu$_3$ on (a, top) silica$_{(200)}$ and (b, bottom) silica$_{(500)}$ (accumulated values).

(corresponding to a slight excess compared to the required value) of Ge(n-C_4H_9)$_4$ and Ge(C_2H_5)$_4$ was introduced onto the silica sample via a septum. All preparations were performed under strict exclusion of air. The evolved gases (H_2, C_2H_4, C_2H_6, C_4H_8, C_4H_{10}, etc.) have been quantitatively (with an accuracy of ±0.03%) and qualitatively analyzed by a volumetric technic and by chromatography.

Regarding microanalyses of germanium, they have been carried out by plasma emission spectroscopy after dissolution of the silica by alkaline dissolution (NaOH, KNO_3) at 450 °C. The accuracy of such analyses was ±0.05%.

MAS NMR Measurements. All MAS NMR spectra were recorded on a Bruker MSL-300 spectrometer operating at 75.47 MHz for ^{13}C. The probehead was a commercial double-tuned 7 mm double-bearing system from Bruker allowing spinning frequencies up to 4 kHz. The samples were introduced into rotors made of zirconia under a dry nitrogen atmosphere in a glovebox and tightly closed. Boil-off nitrogen was used for both bearing and driving the rotors. Under these conditions, no decomposition of the samples was observed during the course of the experiments.

For ^{13}C NMR, a typical cross-polarization was used: 90° rotation of the ^{1}H magnetization (pulse length 6.2 μs), then contact between carbon and proton for 5 ms, and finally recording of the spectrum under high power decoupling. The delay between scans was fixed at 5 s, to allow for the complete relaxation of the ^{1}H nuclei. Chemical shifts are given with respect to TMS by using adamantane as an external reference (δ = 37.7 ppm for the highest chemical shift). Sometimes, adamantane was directly added to the sample in the rotor in order to have an internal reference. No variation of the chemical shifts was detected compared to the case of use of an external reference.

Infrared Spectroscopy. The infrared spectra have been obtained with a Fourier transform Nicolet 10-MX. The spectra were recorded *in situ* from a special cell equipped with CaF_2 windows.

Results and Discussion

Interaction at 25 °C of GeR$_4$ Compounds with the Surface of Silica. When Ge(n-C_4H_9)$_4$ is contacted, at 25 °C, with silica$_{(500)}$, no evolution of gas is observed. The infrared spectrum resulting from such an interaction (Figure 1a,b) may be described in the following way: first, there is a decrease of the intensity of the ν(O–H) vibrations of the free silanols of the silica$_{(500)}$. Second, a new band appears at 3698 cm^{-1} which has already been observed when Sn(n-C_4H_9)$_4$ is physisorbed on silica$_{(500)}$.[2] Third, ν(C–H) and δ(C–H) vibrations characteristic of the butyl groups[7] are observed at 2960, 2925, 2875, and 2858 cm^{-1} and 1465, 1460, 1448, 1421, 1377, and 1338 cm^{-1}, respectively.

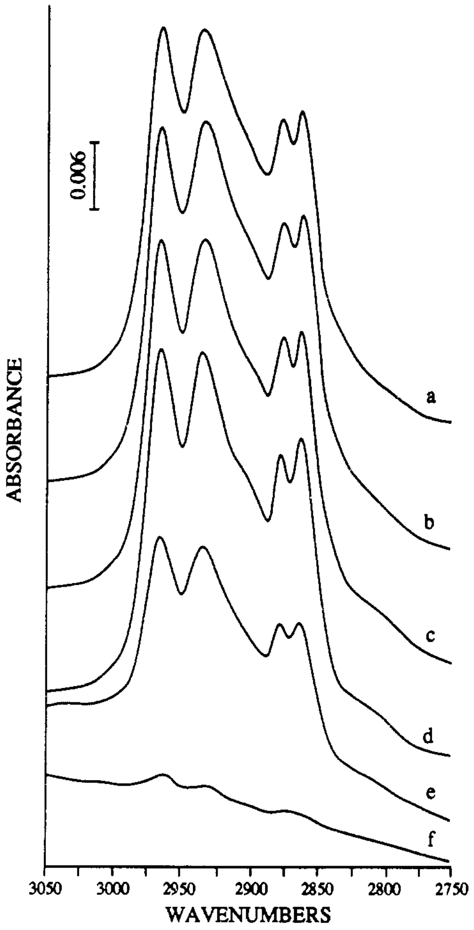

Figure 6. Infrared spectra in the 3050–2750-cm^{-1} region of the systems obtained after thermal treatment at T (°C) of (a) $\equiv$SiOGeBu$_3$ on silica$_{(200)}$. T = (b) 300 °C, (c) 350 °C, (d) 400 °C, (e) 450 °C, and (f) 500 °C.

Almost identical results are observed when Ge(C_2H_5)$_4$ is adsorbed, at room temperature, on silica$_{(500)}$. The only difference is the position of the ν(C–H) and δ(C–H) vibrations of the ethyl ligands which are observed respectively at 2956, 2919, and 2857 cm^{-1} and 1464, 1428, and 1378 cm^{-1} (Figure 1c,d). Similar, if not identical, results are observed on silica$_{(200)}$.

The phenomenon responsible for the shift of the ν(O–H) vibration of the free silanols in the presence of intact molecular alkyl complexes has already been analyzed in a previous publication:[2] there is formation of hydrogen bonds between the alkyl ligands and the silanol groups of the silica. Surprisingly there is a drastic change in the ν(O–H) vibrations whereas the variation of the ν(C–H) vibrations is very limited. This phenomenon has already been observed in the case of tin alkyls physisorbed on silica.[2] We shall consider, in the following, that the complexes are weakly adsorbed on the surface at room temperature, without any chemical reaction.

Reaction of Ge(n-C_4H_9)$_4$ with the Surface of Silica$_{(200)}$ and Silica$_{(500)}$. In order to observe a real chemical reaction of Ge(n-C_4H_9)$_4$, it is necessary to heat the samples above ca. 150 °C for silica$_{(200)}$ and 180 °C for silica$_{(500)}$ (Figure 2a,b). Butane is the only evolved product. A plateau is observed at ca. 180 °C

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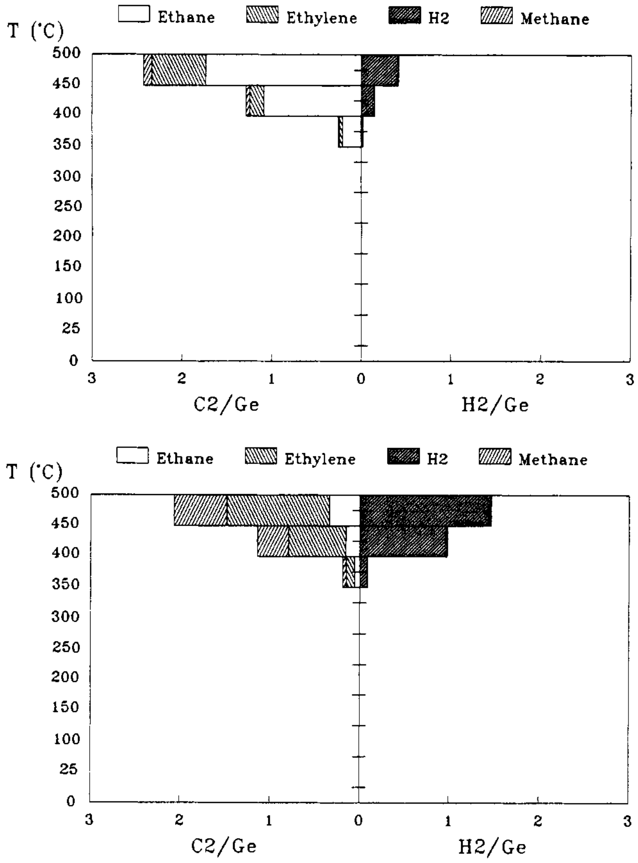

Figure 7. Gas-phase analysis during the thermal treatment, under vacuum of $\equiv$SiOGeEt$_3$ on (a, top) silica$_{(200)}$ and (b, bottom) silica$_{(500)}$ (accumulated values).

for silica$_{(200)}$ and 230 °C for silica$_{(500)}$. Interestingly the number of moles of butane evolved at the plateau per mole of grafted germanium is equal to 1, regardless of the temperature of dehydroxylation of the silica (1.01 for silica$_{(200)}$ and 0.93 for silica$_{(500)}$). The plateau of temperature for which evolution of butane no longer occurs is quite large: it is an indication of a strong thermal stability of the surface organometallic complex. Elemental analysis of a sample obtained at 250 °C corresponds to a C$_4$/Ge ratio equal to 3.0 (for example, for silica$_{(500)}$: 1.1% Ge and 2.2% C), in agreement with the surface reaction:

$$\equiv\text{Si—O—H} + \text{GeBu}_4 \rightarrow \equiv\text{Si—O—GeBu}_3 + n\text{-C}_4\text{H}_{10}$$

The results obtained here differ from those obtained with tetraalkyltin complexes on the same type of support in two different ways. The temperature for which the surface reaction occurs is much lower and no such plateau was observed after the evolution of 1 mol of butane.[2]

The ^{13}C CP-MAS NMR spectrum of a sample obtained at 250 °C on silica$_{(200)}$ gave three signals at 15.6, 25.2, and 11.3 ppm (Figure 3a and Table 1). Almost identical signals are obtained on silica$_{(500)}$ (Figure 3b).

By comparison with the spectra obtained for the surface compound $\equiv$Si-O-Sn(n-C$_4$H$_9$)$_3$, the peak at 11.3 ppm may be attributed to the terminal methyl group δ'-C interacting with surface silanols via hydrogen bonding. The peak at 25.2 ppm is attributed to the β-C and γ-C carbons of the butyl ligands. The peak at 15.6 ppm is ascribed to the α-C, since a shift to lower field (when compared to that for GeBu$_4$) is observed in molecular analogues when one butyl ligand is substituted for an alkoxy ligand (R$_3$GeOR′ as compared with R$_4$Ge) (Table 1).[8]

Concerning the coordination number of germanium on the surface of silica, it is difficult to conclude definitely. However, there are a few indications that it is tetracoordinated. In the case of $\equiv$Si—O—SnBu$_3$, the coordination number of tin was unambiguously established by ^{119}Sn MAS NMR.[2] Indeed, the chemical shift of tin is extremely dependent on coordination number. Unfortunately, we have not been able to successfully carry out ^{73}Ge MAS NMR. However, ^{13}C CP-MAS NMR is also helpful to detect the coordination of tin–alkyl complexes.[9] The α-C of a pentacoordinated tin–alkyl complex is usually shifted to low fields by several ppm.[9] Since we have comparable chemical shift for the α-C of $\equiv$Si—O—GeBu$_3$ and of $\equiv$Si—O—SnBu$_3$, we can reasonably conclude to a tetracoordination of germanium.

The infrared spectrum recorded after reaction of Ge(n-C$_4$H$_9$)$_4$ on silica$_{(200)}$ exhibits the typical ν(C–H) and δ(C–H) bands of the butyl ligand (Figure 4a).[7]

To summarize the analysis, the NMR, and the IR data are consistent with the formation of the surface compound $\equiv$Si—O—Ge(n-C$_4$H$_9$)$_3$.

Reaction of Ge(C$_2$H$_5$)$_4$ with the Surface of Silica$_{(200)}$ and Silica$_{(500)}$. As in the previous case, the complex begins to react with the silica surfaces between 150 °C for silica$_{(200)}$ and 170 °C for silica$_{(500)}$ (Figure 2c,d). A plateau is observed in both cases after the evolution of 1 mol of ethane per mole of germanium grafted (e.g., 0.98 for silica$_{(200)}$).

The ^{13}C CP-MAS NMR spectrum of a sample obtained after reaction at 250 °C on silica$_{(200)}$ gave two signals at 4.7 and 6.5 ppm (Figure 3c and Table 1). By comparison with the NMR data obtained with SnEt$_4$ on silica,[2] one can ascribe the peak at 4.7 ppm to the α-C of a $\equiv$Si—O—GeEt$_3$ surface species and the peak at 6.5 ppm to the β-C which develops hydrogen bonds with surface silanols.

The infrared spectrum corresponding to such species shows a broad signal at 3698 cm^{-1}, corresponding to the silanols which are interacting with this terminal methyl group. The spectrum also exhibits the typical ν(C–H) bands at 2962, 2942, 2922, 2910, 2884, and 2860 cm^{-1} and δ(C–H) bands at 1465 and 1428 cm^{-1} (Figure 4b).

Conclusions Regarding the Reaction of GeR$_4$ Complexes with the Surface of Silica. To summarize, the results obtained for the two complexes GeR$_4$ (R = Et, n-Bu) and for the two supports (silica$_{(200)}$ and silica$_{(500)}$) are rather similar and may be explained by a simple reaction between the surface silanols and the tetraalkylgermanium compounds. This reaction is well documented in molecular chemistry: the mechanism involves an electrophilic attack by the weak Brønsted acidic surface silanol groups

$$\equiv\text{Si—O—H} + \text{GeR}_4 \rightarrow \equiv\text{Si—O—GeR}_3 + \text{RH}$$

$$\text{R} = \text{Et}, n\text{-Bu}$$

Thermal Stability under Vacuum of $\equiv$Si—O—GeR$_3$ Grafted on Silica$_{(200)}$ and Silica$_{(500)}$. R = n-Bu. Surprisingly, thermal treatment under vacuum (10^{-4} Torr) of $\equiv$Si—O—Ge(n-C$_4$H$_9$)$_3$ supported on silica$_{(200)}$ and silica$_{(500)}$ does not lead to any evolution of gas between 200 and 400 °C (Figure 5a,b). Between 400 and 500 °C the evolved gases are mostly composed of butane, n-butenes, hydrogen, and some lower hydrocarbons. In particular, no C$_8$ hydrocarbons, which could arise from the dimerization of Bu radicals, have been observed. At 500 °C, approximately 2.5–2.7 butyl groups of the grafted complex have been eliminated as hydrocarbons. Elemental analysis of the solid indicates that the remaining butyl groups are present as carbon on the surface (for example for silica$_{(200)}$, ca. 0.3 equiv of C$_4$ per mole of grafted germanium: 0.16% C; 0.77% Ge).

The thermal stability of $\equiv$Si—O—Ge(n-C$_4$H$_9$)$_3$ can also be seen by following, *in situ*, the absorbance of the ν(C–H) bands of the butyl ligands as a function of the treatment temperature (Figure 6). One can clearly see by infrared spectroscopy that up

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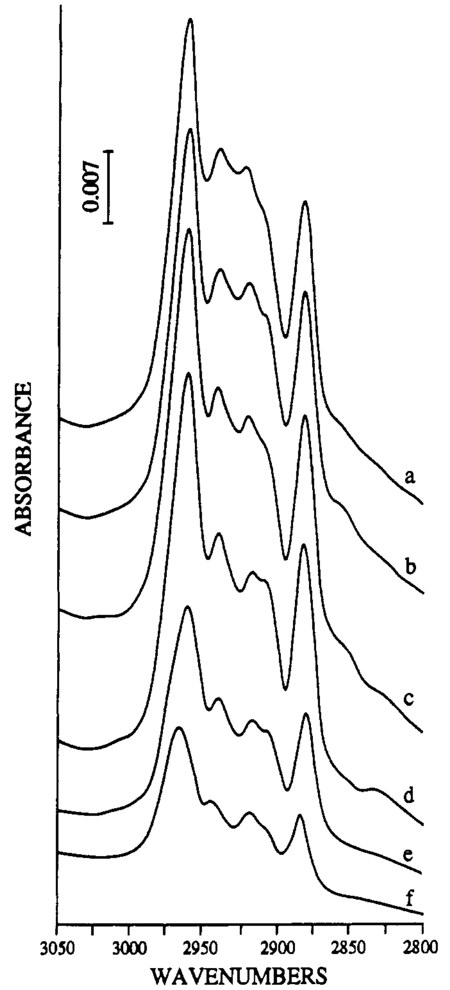


Figure 8. Infrared spectra in the 3050–2800-cm^{-1} region of the systems obtained after thermal treatment at T (°C) of (a) ≡SiOGeEt$_3$ on silica$_{(200)}$. T = (b) 300 °C, (c) 350 °C, (d) 400 °C, (e) 450 °C, and (f) 500 °C.

to 400 °C there is no variation of the intensity of the ν(C–H) bands, whereas at 500 °C there are no alkyl groups left on the surface.

Although a deeper investigation would be necessary to reach definite conclusions, one may propose the following reaction path in order to explain the product distribution observed between 400 and 500 °C on silica$_{(200)}$ and silica$_{(500)}$. During the thermolysis, the formation of butane can be explained by solvolysis of ≡Si—O—Ge(n-C$_4$H$_9$)$_3$ by surface silanol groups:

$$\equiv\text{Si—O—GeBu}_3 + \equiv\text{Si—OH} \rightarrow (\equiv\text{Si—O})_2\text{GeBu}_2 + n\text{-C}_4\text{H}_{10}$$

$$(\equiv\text{Si—O})_2\text{GeBu}_2 + \equiv\text{Si—OH} \rightarrow (\equiv\text{Si—O})_3\text{GeBu} + n\text{-C}_4\text{H}_{10}$$

$$(\equiv\text{Si—O})_3\text{GeBu} + \equiv\text{Si—OH} \rightarrow (\equiv\text{Si—O})_4\text{Ge} + n\text{-C}_4\text{H}_{10}$$

One can wonder if (≡Si—O)$_4$Ge is geometrically possible at a silica surface. This is a viable hypothesis if one considers surface mobility of protons at 400–500 °C and steps at the periphery of the silica particles.

Formation of n-butene and hydrogen may be explained by β-H elimination reaction of 1-butene followed by reductive elimination of hydrogen:

$$(\equiv\text{Si—O})_2\text{GeBu}_2 \rightarrow (\equiv\text{Si—O})_2\text{GeH}_2 + 2n\text{-C}_4\text{H}_8$$

$$(\equiv\text{Si—O})_2\text{GeH}_2 \rightarrow (\equiv\text{Si—O})_2\text{Ge}^{(\text{II})} + \text{H}_2$$

Formation of <C$_4$ hydrocarbons is probably related to the high temperature which favors cracking by a cationic mechanism. An in-depth study carried out in the case of tin alkyl complexes grafted on silica has confirmed such proposals.[3]

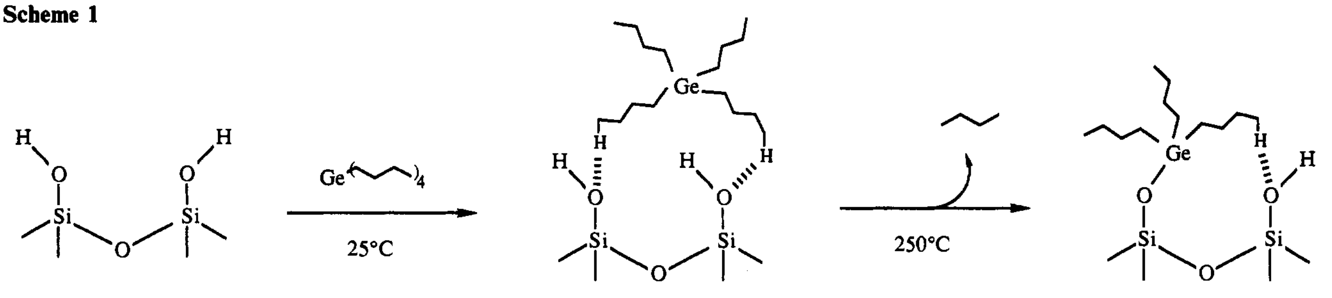
R = Et. Similar results have been obtained with ≡Si—O—Ge(C$_2$H$_5$)$_3$. The same high thermal stability as shown by the evolution of gases with temperature and by infrared spectroscopy (Figures 7 and 8). Ethane, ethylene, hydrogen, and methane are the main gases observed without any trace of coupling products (e.g., butane).

Conclusions

The results concerning the surface organometallic chemistry of germanium on a silica surface are quite similar to surface organometallic chemistry of tin, but there are significant differences. The tetraalkylgermanium complexes, GeR$_4$ (R = n-Bu, Et), are reversibly physisorbed, at room temperature: a hydrogen-type bonding between the terminal methyl group of the alkyl ligands and the surface silanol groups is evidenced by infrared and ^{13}C CP-MAS NMR. Although the reaction temperatures necessary to chemically graft the germanium complex on the silica surface are higher than for tin, the reaction product is of the same form (≡Si—O—GeR$_3$) with the evolution of 1 mol of alkane per mole of grafted germanium. As already observed with the grafted trialkyltin complexes,[2] hydrogen bonding occurs between H atoms of the terminal methyl groups of the alkyl ligand and surface silanols groups (e.g., for R = Bu, cf. Scheme 1).

The main difference between tin and germanium surface chemistry is the extraordinary thermal stability of ≡Si—O—GeR$_3$. The results are compatible with the higher stability of germanium alkyl complexes, as compared with the tin ones.[5,6] The energy of dissociation of a M–C bond (in MR$_4$ complexes) is also higher in the case of germanium.[10–12] Such thermal stability will find very interesting applications in molecular separation at the pore entrance of zeolites, in chromatographic processes, in the field of fine chemistry, and in some catalytic reactions.

Scheme 1



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