Surface Organometallic Chemistry of Tin: Thermal Transformation, under Vacuum, of >Si–O–Sn(n-Bu)₃ Supported on Silica

C. Nédez,[†] F. Lefebvre,[†] A. Choplin, J. M. Basset,[*,†] and E. Benazzi[‡]

Contribution from the Laboratoire de chimie organométallique de surface, UMR CNRS-CPE 48, ESCIL, 43 bd du 11 Novembre 1918, 69616 Villeurbanne Cedex and Institut de Recherches sur la Catalyse, 2, avenue A. Einstein, 69626 Villeurbanne Cédex, France, and Institut Français du Pétrole, 1-4, avenue de Bois-Préau, 92506 Rueil-Malmaison, France

Abstract: The reactivity of the well-defined surface organometallic fragment >Si–O–Sn(n-C₄H₉)₃ 1 grafted on silica₂₀₀ and on silica₅₀₀ has been studied by thermal treatment of 1 at increasing temperatures *in vacuo*. The surface reactions have been followed by quantitative measurements of the evolved gases, infrared and Mössbauer spectroscopies, ¹³C CP-MAS and ¹¹⁹Sn NMR spectroscopy, XPS measurements, and electron microscopy (CTEM and STEM EDAX). On both types of silicas, the surface reactions are similar in nature, although differences are noticeable. First, there is formation of (>Si–O)₂(Sn(n-C₄H₉)₂) 2, which undergoes a second solvolysis process by silanols leading to (>Si–O)₃Sn(n-C₄H₉) 3 and finally surface Sn(II) and Sn(IV) atoms (as determined by XPS and Mössbauer experiments). Although the well-defined surface organometallic compound (>Si–O)₂Sn(n-C₄H₉)₂ can be prepared on silica by another route, no unique surface compound can be obtained during the thermal decomposition which transforms progressively 1 into 2 and 3. A mechanism of decomposition of the various surface organometallic complexes has been deduced from a comparison of the results obtained on both solids. The alkyl groups seem to follow a β-H elimination mechanism leading to tin hydrides and 1-butene rather than a disproportionation mechanism leading to equimolar amounts of 1-butene and butane.

Introduction

In previous publications we have developed surface organometallic chemistry of group IV metals.[1] The reasons for choosing such chemistry are related to the possibilities of obtaining on surfaces new surface organometallic complexes of unusual oxidation state and/or coordination numbers, of introducing on a surface new functionnalities, e.g., hydrophobic, hydrophilic, or chiral organometallic fragments, and of controling at a molecular level the pore intrance of zeolites for molecular separation[2] or molecular recognition.

Surface organometallic chemistry of tin has been our first choice, and preliminary results have already been published in this area.[3] 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 >Si–O–SnR₃ was characterized via several analytical tools such as ¹³C CP-MAS and ¹¹⁹Sn MAS NMR and infrared spectroscopy. From ¹¹⁹Sn NMR data and by comparison with spectroscopic data of molecular analogues, the surface compound was shown to be tetracoordinated on the surface.[3] The trialkyltin fragment was also grafted at the external surface of mordenites and was found to modify quite significantly the adsorption capacity of mordenite toward linear and branched paraffins.[4] In particular, whereas a classical mordenite is not able to separate n-hexane

from isooctane, the same mordenite modified by the tri-n-butyltin fragment is able to separate the two isomers. More subtle separations can be achieved when the bulkiness of the alkyl groups on the tin fragment is changed.[4]

In this work, we report our results on the thermal stability of >Si–O–SnBu₃. There are two reasons for such a study. First, it was of interest to determine at a molecular level the surface chemistry resulting from such thermal treatment. Second, the use of silica as a model of the external surface of zeolite could help us in the choice of possible applications of surface organometallic chemistry (SOMC) for the control of the pore entrance of zeolites.[4]

Techniques

Materials and Procedures. Aerosil silica from Degussa was used with a surface area of 200 m²·g⁻¹. It was dehydroxylated *in vacuo* at 200 or 500 °C (SiO₂ ₂₀₀ or SiO₂ ₅₀₀).

Synthesis of the well-defined complex >Si–O–SnBu₃ was achieved by reaction of SnBu₄ at 150 °C or HSnBu₃ at 25 °C with the partially dehydroxylated silicas as described in the ref 3.

Temperature-programmed decomposition experiments were conducted under static vacuum (10–14 h). Before each increase in temperature, a dynamic vacuum was made in the equipment (15 min, 25 °C, 10⁻⁴ Torr). The evolution of the system was followed in parallel by infrared spectroscopy and analysis of the evolved gases (typical sample weight 0.5–1 g).

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. The gases (H₂, C₄H₈, C₄H₁₀, etc.) were quantitatively and qualitatively analyzed by a volumetric technique and by chromatography.

[†] Laboratoire de chimie organométallique de surface and Institut de Recherches sur la Catalyse.
[‡] Institute Français du Pétrole.
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MAS NMR Measurements. All MAS-NMR spectra were recorded on a Bruker MSL-300 spectrometer operating at 75.47 and 111.9 MHz for ^{13}C and ^{119}Sn, respectively. 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 in the zirconia rotors 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 sequence was used: 90° rotation of the ^1H magnetization (impulsion length 6.2 μs), contact between carbon and proton during $T_c = 5$ ms, and finally recording of the spectrum under high-power decoupling. The delay between each scan was fixed to 5 s to allow for the complete relaxation of the ^1H nuclei. Chemical shifts are given with respect to TMS using adamantane as an external reference ($\delta = 37.7$ for the highest chemical shift). Sometimes, adamantane was added directly 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 using an external reference.

^{119}Sn NMR data were recorded by using a single impulsion and high-power decoupling. The delay between each scan was 5 s, a value resulting in an apparently complete relaxation of the ^{119}Sn nuclei. The chemical shifts are given relative to SnMe$_4$ used as an external reference and with the IUPAC convention for chemical shifts (a higher chemical shift value corresponding to a higher frequency).

Determination of the Proportions of the Various Surface Alkyltin Species from the ^{13}C CP-MAS NMR Spectra. The ^{13}C CP-MAS NMR spectra exhibit several peaks ascribed to the various carbon atoms (α-C, β-C, γ-C and δ-C) of various surface species (*vide infra*). These NMR spectra were simulated by using the program LINESIM purchased from Bruker, allowing a determination of the respective areas of each resonance. As most of the peaks correspond to more than one species, comparisons should be rather difficult. However, the peak of α-C is different from one surface species to another, and so only the resonances of this carbon will be considered. Normally it should not be possible to compare the intensities of the α-C peak for various species in the same spectrum but in the present case it is allowed due to the following reasons: (i) all peaks correspond to the carbon of a CH$_2$ group, (ii) this CH$_2$ group is always in nearly the same chemical environment as it is bonded both to a tin atom and to a C$_3$H$_7$ group, (iii) the surface compounds are chemically comparable ($\geqslant$Si–O)$_x$SnBu$_{4-x}$, $x = 1$–3), and (iv) the contact time (delay for polarization transfer from ^1H to ^{13}C) is neither too small (allowing a complete transfer) nor too large (avoiding a too-important relaxation). These conditions we can assume that the response is the same for all species, i.e., the α-C peak areas can be correlated with the concentrations of the respective complexes.

In addition, all the experiments belong to the same series of experiments, consequently the percentage of tin is the same. As all NMR spectra were recorded successively with always the same sample weight and without modification of the electronic response of the spectrometer, the intensities can also be compared from one spectrum to another.

Concerning the number of scans, we should mention that it varies with the temperature of activation: the higher the temperature of activation, the higher the number of scans. This is due to the fact that the number of remaining alkyl groups is decreasing with temperature, leading to a decreasing signal-to-noise ratio at constant number of scans.

The percentage of each surface complex has been estimated in the following way. Let us call x, y, z, and t the respective percentages of the alkyl species observed, namely, $\geqslant$Si–O–SnBu$_3$ (**1**), ($\geqslant$Si–O)$_2$SnBu$_2$ (**2**), ($\geqslant$Si–O)$_3$SnBu (**3**), and the nonalkylated species (e.g., ($\geqslant$Si–O)$_2$Sn) X.

It is easy to determine the absolute surface area for all the carbon atoms of a given spectrum by using the absolute intensity mode of the spectrometer. After correction of the number of scans and simulation of all spectra, x, y, z, and t can be obtained easily. Let us call a_1, a_2, and a_3 the respective areas of the peaks corresponding to the α-C of the species **1**, **2**, and **3**. One has then the following equations:

$$x/z = a_1/3a_3$$

$$y/z = a_2/2a_3$$

$$I_T/I_0 = (3x + 2y + z)/300$$

where I_T and I_0 are the intensities of the considered spectrum and of that of species **1**, respectively.
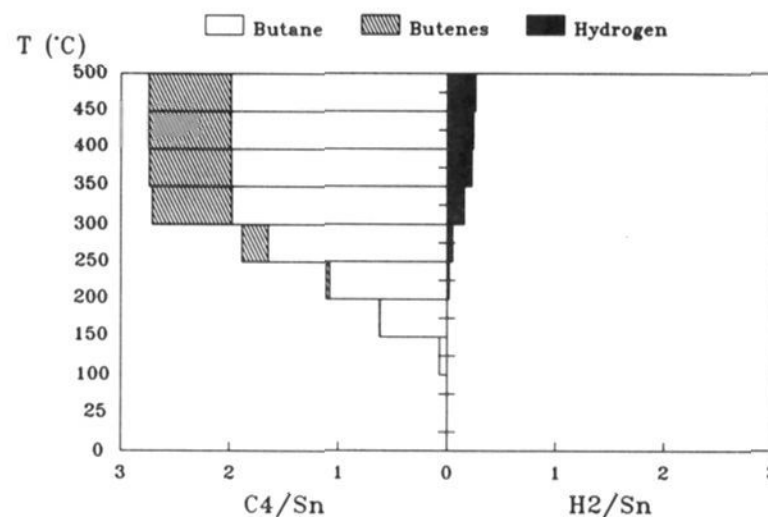
Figure 1. Gases evolved during the thermolysis of $\geqslant$Si–O–SnBu$_3$ grafted on silica$_{200}$ (cumulated values).

From these equations it is also possible to calculate the ratio ω which represents the total amount of the alkyl groups (R) evolved (as alkane or alkene) per tin atom:

$$\omega = (y + 2z + 3t)/100$$

From these equations, one may then estimate the respective proportion of the various surface species as well as the average number of alkyl groups remaining per grafted tin for each sample (*vide infra*).

Infrared Spectroscopy. The infrared spectra were obtained with a Fourier transform Nicolet 10-MX. The spectra were recorded *in situ* by using a special cell equipped with CaF$_2$ windows.

Concerning the evaluation of the concentration of the butyl groups remaining on the surface as a function of the temperature, we have adopted the following strategy: since the respective intensities of the various ν-(C–H) and δ(C–H) bands do not vary with temperature, we have considered that it was possible to estimate the number of remaining alkyl groups by the decay of intensity of only one ν(C–H) band (2958 cm^{-1}).

Electron Microscopy. The samples were studied with CTEM and STEM electron microscopes JEOL Jem 100 CX. The samples were crushed and then deposited on a copper grid of 400 mesh in ethanolic solution. Analysis was realized after evaporation of the solution. The detection limit of the particles was 0.8 nm.

X-ray Photoemission Spectroscopy. The apparatus used was a HP 59 50A. The samples were transferred under controlled atmosphere (argon).

Mössbauer ^{119m}Sn. The surface reactions were realized on a silica powder. The samples were then pressed in pellets (200 mg) transferred in the sample holder in a glovebox under a nitrogen atmosphere. The absorption spectra of γ-nuclear resonance were registered at –196 °C using a conventional constant acceleration spectrometer operating in the triangular mode, with an analyzer having 1024 channels (Promeda, Elscint). A scintillation counter detected the γ-radiations (24 keV) emitted by a source of 7-mCi Ca$^{119m}SnO_3$ (Amersham). CaSnO$_3$ was used as an external reference. After the spectra were recorded, they were decomposed into the sum of Lorentzian lines and the parameters of the various γ-nuclear resonances determined. The isomer shifts (IS), using SnO$_2$ as reference (IS = 0), had an accuracy of 0.03 mm·s^{-1}. The accuracy of the quadrupolar separations (QS) was equal 0.02 mm·s^{-1}.

Results and Discussion

Thermolysis under Vacuum of the Surface Organometallic Fragment $\geqslant$Si–O–SnBu$_3$ (1). (A) 1 Supported on Silica$_{200}$. Four different ranges of temperature must be considered (Figure 1).

(1) *Between 25 and 150 °C*, no gas is evolved while the intensity of the ν(C–H) (Figure 2a,b) and δ(C–H) infrared bands remains unchanged. The ^{13}C CP-MAS NMR of the sample **1** after treatment at 100 °C (Figure 3a) reveals the presence of four peaks at 11.3, 13.0, 15.2 and 26.6 ppm already attributed to the δ'-C, δ-C, α-C, and (β + γ)-C of the butyl chain.[3] The ^{119}Sn MAS NMR spectrum of the same sample (Figure 4a) admits two peaks at –83 and 101 ppm respectively ascribed to the presence of traces of unreacted Bu$_3$SnH and **1**. (One should not take into account the relative intensity of the two peaks at –83 and 101 ppm. The peak at –83 ppm represents an impurity for which the
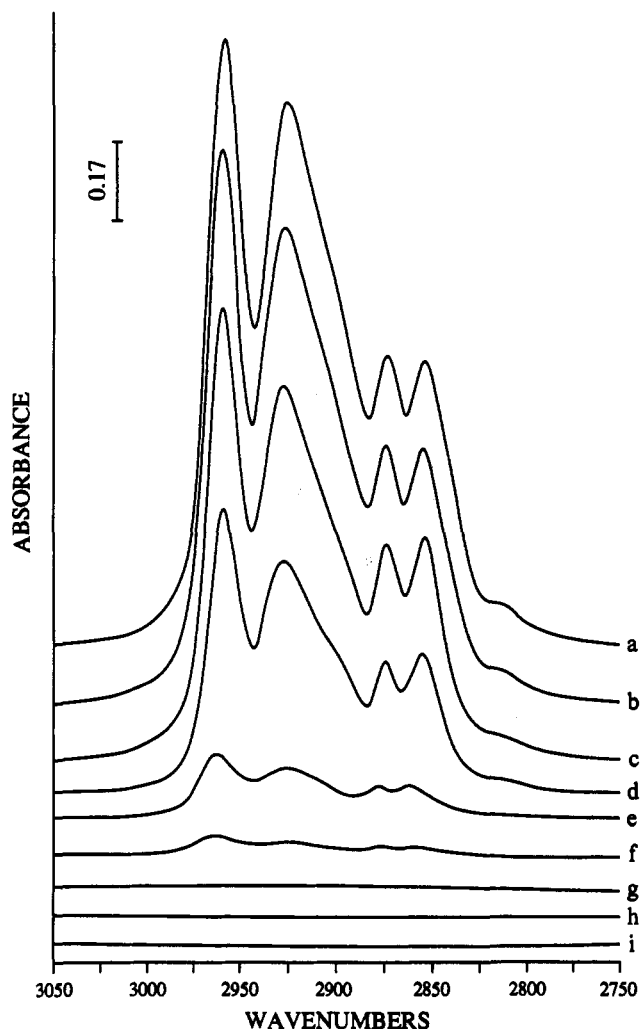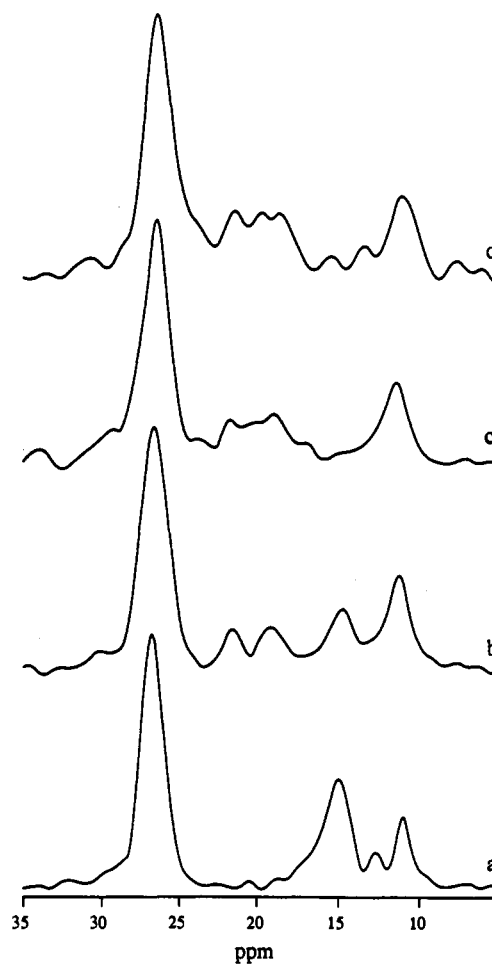
Figure 2. Evolution of the IR spectrum, in the ν(C–H) region, of $\geqslant$Si–O–SnBu$_3$ grafted on silica$_{200}$ as a function of temperature: (a) untreated $\geqslant$Si–O–SnBu$_3$ and then after treatment at (b) 150 °C, (c) 200 °C, (d) 250 °C, (e) 300 °C, (f) 350 °C, (g) 400 °C, and (h) 500 °C.

Figure 3. ^{13}C CP-MAS NMR spectra of (a) $\geqslant$Si–O–SnBu$_3$ grafted on silica$_{200}$ (4.1 wt % Sn) (NS = 2500) and then after treatment at (b) 230 °C (NS = 3000), (c) 280 °C (NS = 5500), and (d) 330 °C (NS = 20 000).

concentration is very small. The apparent high intensity of this peak has already been discussed[3] and is due to its smaller T_1 relaxation time (as it is only physisorbed) and to the high number of scans.)
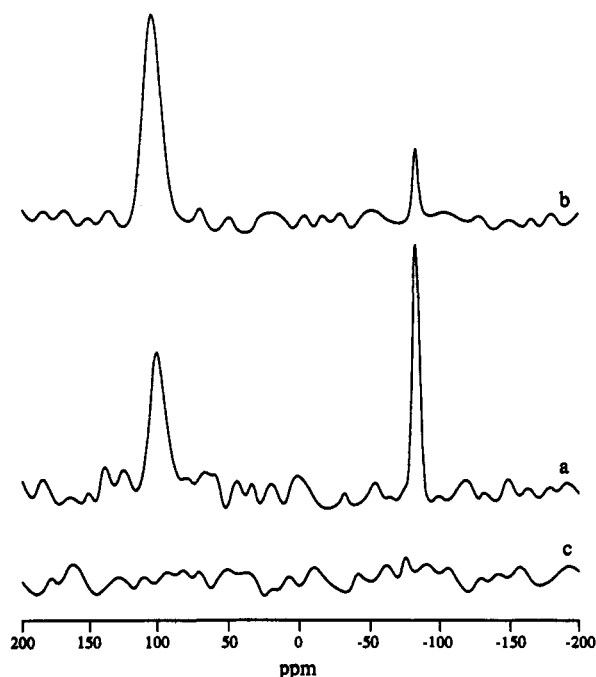
(2) *Between 150 and 250 °C,* 1.07 mol of *n*-butane per mole of grafted surface tin is evolved, whereas the intensity of the ν(C–H) (Figure 2c,d) and δ(C–H) progressively decreases. The ^{13}C CP-MAS NMR of a sample treated at 230 °C exhibits the three peaks previously observed at 11.3, 15.2 and 26.6 ppm and two new peaks at 19.5 and 21.6 ppm (Figure 3b). The ^{119}Sn MAS NMR of the same sample (Figure 4b) is comparable to the one observed for **1**.

(3) *Between 250 and 350 °C,* 0.90 mol of *n*-butane, 0.72 mol of *n*-butenes and 0.14 mol of hydrogen are evolved per mole of grafted tin. Interestingly, butane is the major compound evolved below 300 °C, and then *n*-butane and *n*-butenes are formed in comparable amounts. Two different pathways are then occurring one after the other in the process of transformation of **1**. The ν(C–H) and δ(C–H) bands decrease in intensity and totally disappear at 350 °C (Figure 2e,f). The ^{13}C CP-MAS NMR spectra registered from two samples respectively treated at 280 °C (Figure 3c) and 330 °C (Figure 3d) show the presence of only four peaks at 11.3, 18.9, 21.3, and 26.2 ppm (as determined from a deconvolution of the experimental curves). The ^{119}Sn MAS NMR spectrum does not exhibit any signal in the full range of possible chemical shifts (Figure 4c).

(4) *Between 350 and 500 °C,* only small amounts of molecular hydrogen are evolved (0.11 mol per mole of grafted tin).
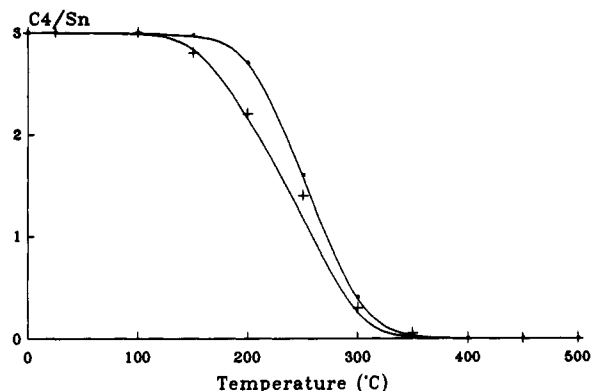
Figure 4. ^{119}Sn MAS NMR spectra of (a) $\geqslant$Si–O–SnBu$_3$ grafted on silica$_{200}$ (4.1 wt % Sn) and then after treatment at (b) 230 °C, and (c) 280 °C.

One should mention that in the domain of thermal treatment ranging from 25 to 500 °C, almost no light hydrocarbon is formed

Figure 5. Number of C_4 equivalents remaining per tin on the surface as a function of temperature during the thermolysis of $\geqslant$Si–O–SnBu$_3$ grafted on (a) silica$_{200}$ and (b) silica$_{500}$ (those values are deduced from the variation of the intensity of the ν(C–H) band at 2958 cm^{-1}).

(less than 0.1 mol equiv of C_4 per mole of grafted tin) and no hydrocarbon higher than C_4 is evolved. Elemental analysis indicates the presence of 0.28 equiv of C_4 per mole of grafted tin (0.25% C, 2.24% Sn) on the sample treated at 500 °C.

It has been possible to estimate from the IR data the number of butyl groups remaining on the surface as a function of the temperature (Figure 5a). Apparently 1 undergoes a progressive dealkylation without formation of a unique intermediate which would be thermally stable before total dealkylation. This observation agrees well with the analytical data showing the evolution of the gaseous phase as a function of temperature (Figure 1).

We shall discuss here the possible interpretations concerning the thermal behavior of 1 supported on silica$_{200}$.

1 is thermally stable *up to* 150 °C as determined by the lack of any evolution of gas and by the infrared study. It is between 150 and 250 °C that ca. 1 mol of butane is evolved, which could be explained by the following reaction:

$$\geqslant\text{Si–O–Sn(Bu)}_3 + \geqslant\text{Si–OH} \rightarrow (\geqslant\text{Si–O)}_2\text{SnBu}_2 + n\text{-C}_4\text{H}_{10}$$
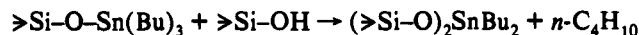
The ^{13}C NMR data seem to support the formation of a tin alkyl complex grafted on the surface by more than one Si–O–Sn bond: in molecular analogues, the ^{13}C signal of an α-C of an alkyl chain is shifted toward low fields when alkyl groups are substituted by alkoxy ligands (Table 1). The peaks corresponding to the $(\beta + \gamma)$-C as well as the δ-C are observed at the same position as in 1. However, the peak corresponding to the α-C of 1 (at 15.2 ppm) decreased in intensity, whereas two peaks appeared at 19.5 and 21.6 ppm which correspond to the α-C of new species linked to silica by an increasing number of surface siloxy ligands. In particular, the peak at 19.5 ppm can be attributed to the well-defined compound ($\geqslant$Si–O)$_2$SnBu$_2$, prepared by reaction of Bu$_2$-SnH$_2$ with silica$_{200}$,[7] that we shall call species 2. Using the same type of analogy between molecular chemistry and surface chemistry, the peak at 21.6 ppm may be ascribed to the α-C of the surface species: ($\geqslant$Si–O)$_3$SnBu, which we shall designate 3.

The ^{119}Sn NMR data are apparently conflicting with the ^{13}C NMR ones. Indeed, although the ^{13}C NMR data suggest formation of 2 and 3, no new peak is observed in a wide range of chemical shifts (4000 ppm). However, the grafting of tin by more than one bond may produce an anisotropy around the tin atom which could result in the formation of a broad signal spreading over more than 1000 ppm.[8–10] Additionally, the free rotation of tin in 2 or 3 would be completely suppressed, resulting

Table 1. Comparison of ^{13}C Chemical Shifts Corresponding to the Species 1, 2, and 3 Grafted on Silica$_{(200)}$ and Silica$_{(500)}$ with Those of Molecular Analogues
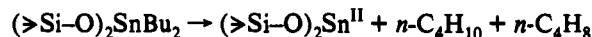
| surface | species | δ (ppm) | | | | | ref |
		C_α	C_β	C_γ	C_δ	$C_{\delta'}$[c]	
SiO$_2$ 200	1	15.2	26.6	26.6	13.0	11.3	d
SiO$_2$ 500	1	15.2	26.7	26.7	13.0	11.3	d
SiO$_2$ 200	2	19.5	26.5	26.5	13.0	11.3	d
SiO$_2$ 500	2	19.8	26.6	26.6	13.0	11.3	d
SiO$_2$ 200	3	21.6	26.3	26.3	13.0	11.3	d
SiO$_2$ 500	3	21.5	26.6	26.6	13.0	11.3	d
SiO$_2$ 200	2[a]	20.0	26.5	26.5	13.0	11.3	7
SiO$_2$ 500	2[a]	20.2	26.9	26.9	12.9	11.3	7
b	Bu$_3$SnOSiPh$_3$	16.5	27.8	27.1	13.7		3
b	Bu$_3$SnOMe	14.1	28.4	27.4	13.7		5
b	Bu$_2$Sn(OMe)$_2$	19.5	27.8	27.2	13.8		5
b	Bu$_2$Sn(O-i-Pr)$_2$	19.2	27.5	27.0	13.7		5
b	Me$_3$Sn^{IV}CH(SiMe$_3$)$_2$	3.4					6
b	Sn^{II}(CH(SiMe$_3$)$_2$)$_2$	50.0					6

[a] Obtained after reaction of Bu$_2$SnH$_2$. [b] Solution NMR data obtained in CDCl$_3$ or without solvent. [c] Terminal methyl group developing hydrogen bonding with adjacent silanol groups.[3] [d] This work.
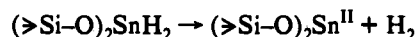
probably in a higher T_1 relaxation time and a lower intensity of the NMR signal as explained previously.[3]

Between 250 and 350 °C, a new reaction occurs leading to the formation of *n*-butenes and hydrogen. Although the thermodynamic mixture of the various butene isomers is observed (closed vessel experiments), when care is taken to trap the evolved butene-(s) in liquid nitrogen in order to avoid secondary reactions, only 1-butene is evolved. 1-Butene is obviously a primary product of the decomposition which undergoes double bond migration on the silica surface at ca. 300 °C as already observed.[11]

The most simple explanation for the formation of 1-butene and butane would be to consider a disproportionation of two alkyl groups coordinated to 1 or 2 into the corresponding alkane and alkene. Such disproportionation would result in a tin(II) surface species:

$$(\geqslant\text{Si–O)}_2\text{SnBu}_2 \rightarrow (\geqslant\text{Si–O)}_2\text{Sn}^{II} + n\text{-C}_4\text{H}_{10} + n\text{-C}_4\text{H}_8$$

$$\geqslant\text{Si–O–SnBu}_3 \rightarrow \geqslant\text{Si–O–Sn}^{II}\text{Bu} + n\text{-C}_4\text{H}_{10} + n\text{-C}_4\text{H}_8$$

Formation of butene in higher amounts than butane (at 300 °C) as well as the simultaneous evolution of hydrogen could result from a β-H elimination of 2 mol of butenes followed by a reductive elimination of hydrogen. A reasonable sequence of reactions would be the following:

$$(\geqslant\text{Si–O)}_2\text{SnBu}_2 \rightarrow (\geqslant\text{Si–O)}_2\text{SnH}_2 + 2n\text{-C}_4\text{H}_8$$

$$(\geqslant\text{Si–O)}_2\text{SnH}_2 \rightarrow (\geqslant\text{Si–O)}_2\text{Sn}^{II} + \text{H}_2$$

There are other possible hypotheses concerning the formation of molecular hydrogen: (i) formation of coke from 1-butene,[12–14] in agreement with the detection of small amount of carbon on the surface by microanalysis, and (ii) oxidation of the tin(II) surface complex by surface protons:

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$$2H^+ + Sn(II) \rightarrow Sn(IV) + H_2$$
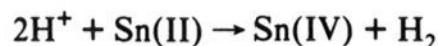
Since the temperature of thermal treatment is higher than the temperature of dehydroxylation of the silica, one should expect that enough protons are available to oxidize tin by such surface protons. However, we shall see later on silica$_{500}$ that such speculation is not valid because it is on silica$_{500}$ that the amount of evolved hydrogen is the highest.

From ^{13}C NMR data, the respective proportion of the surface organometallic species **1**, **2**, and **3** as well as the dealkylated tin atoms can be estimated as a function of the temperature (see the experimental part) (Figure 6).

Interestingly, one can also make an estimation of the respective amount of the surface organometallic species by infrared spectroscopy and analytical data (Table 2). The three methods give comparable results. This is an extremely important result, given the completely different methods used to characterize the surface organometallic fragments. Additionally, the agreement between these techniques justifies the assumption we made to achieve quantitative measurements. Concerning the dealkylated species, a more complete investigation on their nature will be given later using silica$_{500}$ as a support.

(B) 1 Supported on Silica$_{500}$. As in the previous case, various domains of temperature must be considered in order to account for the analytical data (Figure 7).

(1) *Between 25 and 150 °C*, no gas is evolved, and the infrared spectrum does not show any significant modification in the ν-(C–H) and ν(O–H) region (Figure 8b,c). The ^{13}C CP-MAS and ^{119}Sn MAS NMR spectra of **1** treated at 100 °C show only the typical features of **1**. The XPS spectrum of a sample of **1** treated at 100 °C exhibits in the 3d energy levels of tin signals at 496.6 (3d$_{3/2}$) and 488.1 (3d$_{5/2}$) eV. Those peaks are attributed to oxidized tin(II) or tin(IV) without a possible distinction between these two different oxidation states (Table 3).

The ^{119m}Sn Mössbauer spectrum of **1** treated at 100 °C and registered at –196 °C is composed of a doublet at 0.06 and 2.56 mm·s^{-1} (isomer shift 1.31 mm·s^{-1} and quadrupole splitting : 2.50 mm·s^{-1}) (Figure 9b). This ^{119m}Sn Mössbauer spectrum is very similar to the one observed with the molecular analogues of **1** R$_3$SnOR′ (Table 4). When SnBu$_4$ is simply physisorbed on silica$_{500}$, one observes only a singlet at 1.38 mm·s^{-1}, in agreement with the perfect symmetry of the molecule.[18,29] The quadrupole separation observed for **1** is then in agreement with a change of symmetry around the tin atom.

(2) *Between 150 and 200 °C*, the evolved gases are mainly composed of butane (0.35 mol per mole of grafted tin) and *n*-butenes. The intensity of the ν(C–H) (Figure 5b) and δ(C–H) bands begins to decrease, as does that of the ν(O–H) bands (at 3747 and 3697 cm^{-1}) (Figure 8d). Those two ν(O–H) bands have already been observed and ascribed respectively to linear silanols and silanols interacting with a terminal C–H bond of the alkyl chain which is biting the surface (O(H)···C—H).[3] The ^{13}C CP-MAS NMR spectrum of a sample treated at 175 °C exhibits,

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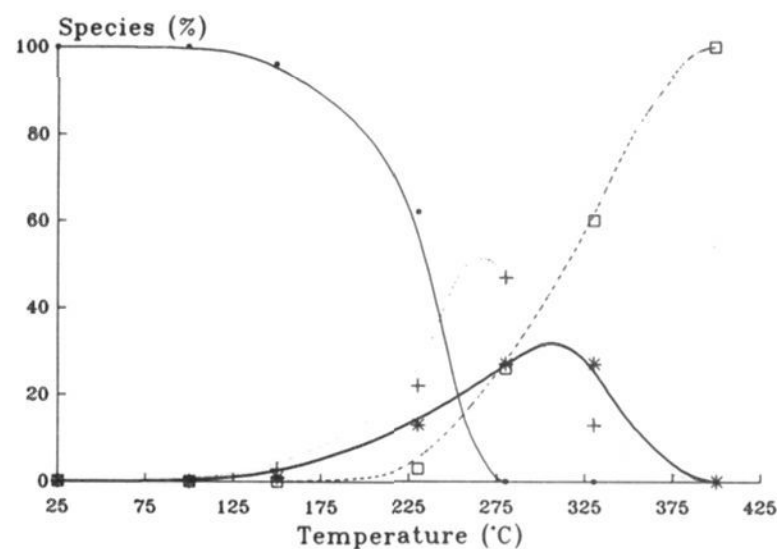

Figure 6. Respective proportions (deduced from ^{13}C CP-MAS NMR), on silica$_{200}$, of ●, >Si–O–SnBu$_3$ (**1**); +, (>Si–O)$_2$SnBu$_2$ (**2**); *, (>Si-O)$_3$SnBu (**3**); □, nonalkylated surface tin compounds.

Table 2. Respective Amounts of Various Surface Organometallic Fragments Formed during the Thermal Treatment of >Si–O–SnBu$_3$ Grafted on Silica$_{200}$ as Determined by Infrared, ^{13}C CP-MAS NMR, and Analytical Data

| T (°C) | infrared^a | ^{13}C CP-MAS NMR | | | | | evolved gases^a |
		1^b	**2**^{b}	**3**^{b}	X^b	a	
25	3.0	100	0	0	0	3.0	3.0
150	2.97						2.82
200	2.7						2.6
230		62	22	13	3	2.4	
250	1.6						1.8
280		0	47	27	26	1.2	
300	0.4						0.6
330		0	13	27	60	0.5	
350	0.03						0
400	0						0
450	0						0
500	0						0

^{a} Average number of C$_4$ equivalents remaining on the surface per mole of grafted tin (vide experimental part). Using IR spectroscopy, this number is estimated from the intensity of the band at 2958 cm^{-1}. ^{b} In mol %. X refers to nonalkylated tin atoms on the surface.
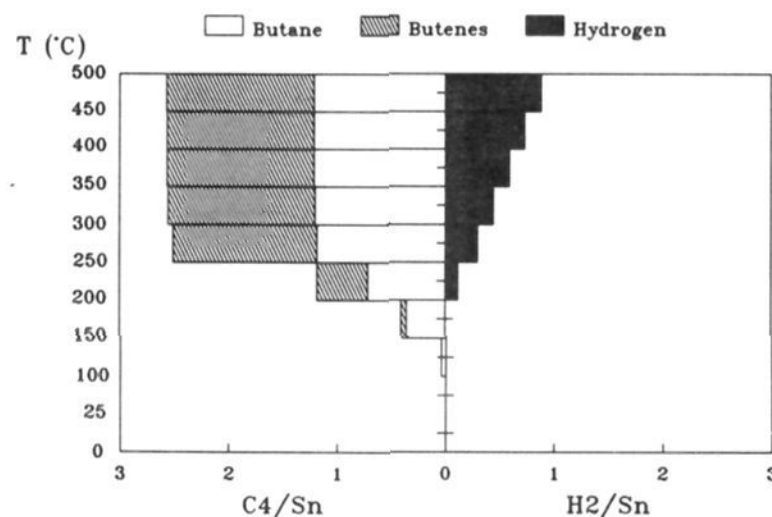
Figure 7. Gases evolved during the thermolysis of >Si–O–SnBu$_3$ grafted on silica$_{500}$ (cumulated values).

besides the signals which are characteristic of **1**, two new signals of small intensity at 19.8 and 21.5 ppm which may be ascribed to the α-C of the grafted complexes **2** and **3** *(vide supra)*.

(3) *Between 200 and 350 °C*, one notes the simultaneous formation of 0.84 mol of butane, 1.30 mol of butenes, and 0.44 mol of hydrogen per mole of grafted tin. The disappearance of the ν(C–H) (Figure 5b) and δ(C–H) bands as well as the band ν(O(H)···C—H)[3] at 3697 cm^{-1} (Figure 8e–g) is in agreement with the elimination of the butyl ligands. The increase of the intensity of the ν(O–H) band at 3747 cm^{-1} (free silanols) suggests that the elimination of the butyl ligands restores some of the free silanols which were complexed with the butyl groups by hydrogen
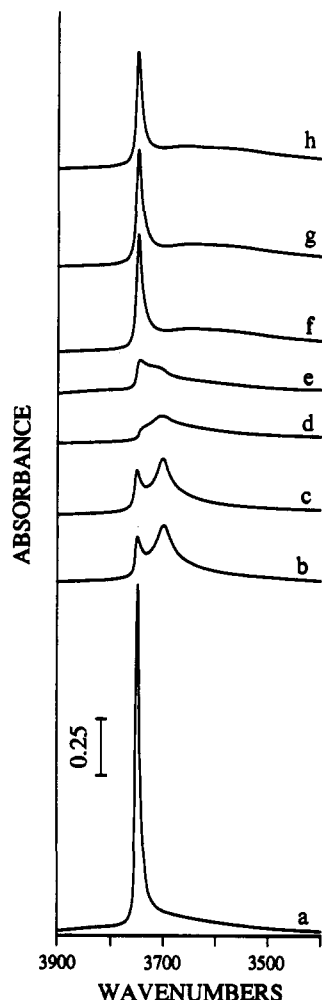
Figure 8. Evolution of the IR spectrum, in the ν(O–H) region, of >Si–O–SnBu₃ grafted on silica₅₀₀ as a function of temperature: (a) silica₅₀₀; (b) >Si–O–SnBu₃ obtained after reaction of Bu₃SnH and then after treatment at (c) 150 °C, (d) 200 °C, (e) 250 °C, (f) 300 °C, (g) 350 °C, and (h) 500 °C.

Table 3. Comparison of XPS Data Obtained after Thermolysis at 500 °C of 1 (0.5% Sn) with Those of Molecular Analogues

| sample | electron energy levels (eV) | | ref |
	3d₃/₂	3d₅/₂	
1	496.6	488.1	this work
a	496.5	488.0	this work
SnBu₄	494.7	486.2	15
Sn metal	493.2	484.7	15
SnO₂	495.7	487.1	16

[a] 1 treated at 500 °C, *in vacuo*.

bonding. One should note that the intensity of the ν(O–H) band at 3747 cm⁻¹ is ca. 3 times less than that of the starting silica₅₀₀ before grafting SnBu₄ (Figure 8a). This means that tin remains grafted on the silica surface via siloxy ligands even after the thermolysis at 500 °C.

The ¹³C CP-MAS NMR spectrum of a sample treated at 250 °C exhibits the same peaks as when evacuated at 175 °C. However, the overall intensity of the spectrum is lower, suggesting a decrease of the amount of alkyl groups remaining on the surface. As for silica₂₀₀, the peak at 15.2 ppm attributed to the α-C of species 1 has a relative intensity lower than those of the other peaks. Obviously the amount of 1 has decreased at such temperature.

The ¹¹⁹ᵐSn Mössbauer spectrum of a sample treated at 250 °C is rather complex and admits at least five peaks at 0.06, 0.50, 1.90, 2.56, and 4.00 mm·s⁻¹ (Figure 9d). The multiplicity of the signals suggests a mixture of species. According to the data
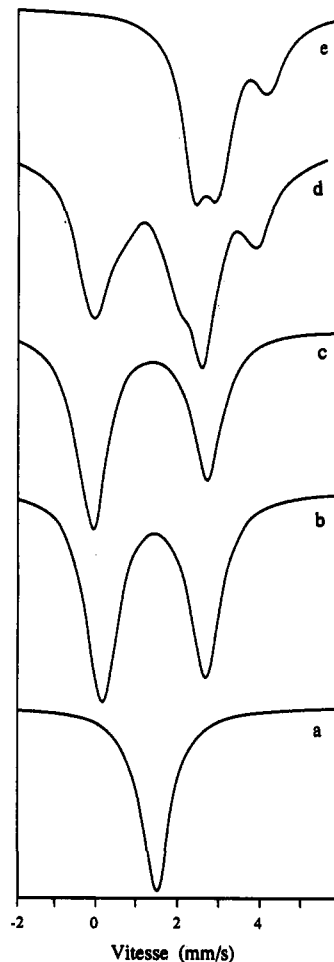
Figure 9. ¹¹⁹ᵐSn Mössbauer spectra registered at –196 °C from the following samples: (a) SnBu₄/silica₅₀₀; (b) >Si–O–SnBu₃ (1) obtained after reaction of Bu₃SnH with silica₅₀₀; (c) (>Si–O)₂SnBu₂ obtained after reaction of Bu₂SnH₂ with silica₅₀₀; (d) 1 after treatment at 250 °C; (e) 1 after treatment at 500 °C.

Table 4. Comparison of Mössbauer ¹¹⁹ᵐSn Data for Isomer Shifts (IS) and Quadrupole Splittings (QS) Corresponding to the Various Surface Organometallic Fragments with Those of Molecular Analogues

species[a]	IS (mm·s⁻¹)	QS (mm·s⁻¹)	ref
SnBu₄/SiO₂[b]	1.38	0	c
1	1.31	2.50	c
2	1.23	2.77	c
3	≈1.3	≈2.6	c
4	4.07	<0.4	c
X[d]	≈2.3	≈0.7	c
SnO₂	0	0.53	17
Sn⁰-α	2.10	0	17
Sn⁰-β	2.65	0	17
SnBu₄	1.35	0	18
SnMe₄	1.20	0	18
Bu₃SnOEt	1.29	2.11	19
Bu₃Snof[e]	1.30	2.46	20
Bu₃Sn(SPh)	1.46	2.06	21
Bu₂Sn(OEt)₂	1.30	2.00	19
Bu₂Sn(OCH₂CH₂O)	1.10	2.80	19
Sn(OMe)₂	3.02	1.97	22
SnCp₂	3.74	0.86	23, 24
SnCp*₂	3.83	0.78	25
m-C₆H₄(CH₂Cp)₂Sn	3.79	0.93	26
Sn(η⁵-t-BuC₅H₄)₂	3.64	0	27
Sn(SbF₆)₂	4.44	0	28

[a] Reference SnO₂ (IS = 0). [b] SnBu₄ only physisorbed on silica at 25 °C. [c] This work. [d] Nonorganometallic species of Sn(IV). [e] Hof = 3-hydroxyflavone.

observed with molecular analogues such as R₃SnOR′ and R₂-Sn(OR′)₂ (Table 4), one may reasonably ascribe the peaks at ca.

Thermal Stability of ≫Si-O-Sn(n-Bu)₃ on Silica

J. Am. Chem. Soc., Vol. 116, No. 7, 1994 3045

Species (%)
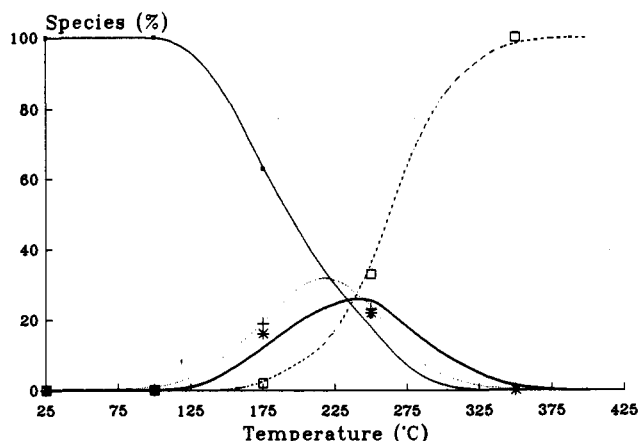
Figure 10. Respective proportions (deduced from ^{13}C CP-MAS NMR), on silica$_{500}$, of ●, ≫Si–O–SnBu₃ (**1**); +, (≫Si–O)₂SnBu₂ (**2**); *, (≫Si–O)₃SnBu (**3**); and □, nonalkylated surface tin compounds.

0 and 2.5 mm·s^{-1} to organometallic complexes of Sn(IV). However, it is not possible from this spectrum to distinguish between complexes of the types **1, 2**, or **3**. Thus, for example, the Mössbauer spectrum of the well-defined species **2** obtained by reacting Bu₂SnH₂ with silica exhibits two peaks at –0.16 and 2.61 mm·s^{-1} (IS = 1.23 mm·s^{-1}; QS = 2.77 mm·s^{-1}) (Figure 9c). The attribution of the other peaks will be carried out later.

(4) *Between 350 and 500 °C*, the infrared spectrum does not change any more (Figures 5b and 8g,h). In particular, the intensity of the ν(O–H) bands remains constant, which proves the stability of the ≫Si–O–Sn bonds. In this range of temperatures, only molecular hydrogen is liberated (0.45 mol per mole of grafted tin).

One should mention that, as for silica$_{200}$, in the domain of thermal treatment ranging from 25 to 500 °C almost no light hydrocarbon is formed (less than 0.1 mol equiv of C₄ per mol of grafted tin) and no hydrocarbon higher than C₄ is evolved. Elemental analysis indicates also the presence of 0.33 C₄ equiv per mol of grafted tin (0.25% C, 1.87% Sn).

The XPS spectrum of a sample of **1** treated at 500 °C exhibits in the 3d energy levels of oxidized tin signals at 496.5 (3d$_{3/2}$) and 488.0 (3d$_{5/2}$) eV. This spectrum is in agreement with the presence of tin(II) or tin(IV). There is no way to distinguish between Sn(II) and Sn(IV) in XPS. In no case can it be explained by the presence of tin(0) (Table 3).

The ^{119m}Sn Mössbauer spectrum of a sample treated at 500 °C is composed of at least three peaks at 1.86, 2.61, and 4.07 mm·s^{-1} (Figure 9e). It is generally admitted that isomer shifts of tin(II) complexes are usually above 2.65 mm·s^{-1} whereas for tin(IV) they are situated below 2.65 mm·s^{-1}.[17] Thus the peak at 4 mm·s^{-1} would correspond to tin(II) such as (≫Si–O)₂Sn(II) (**4**) (Table 4). The two other peaks at 1.86 and 2.61 mm·s^{-1} are likely due to dealkylated complexes of tin(IV) that we have not been able to identify by other physical tools.

We should mention that the thermolysis of **1** does not lead to the formation of SnO₂ nor to the formation of tin(0) (Table 4), in agreement with the XPS data. This was confirmed by electron microscopy experiments carried out on a sample of **1** treated at 500 °C. No metal particle was detected by CTEM; additionally, the STEM-EDAX experiments indicate that the tin is homogeneously dispersed on the surface.

If one considers now the various species which are observed between 25 and 500 °C, the NMR, IR, and analytical data can be useful tools to estimate their respective concentration (Figure 10 and Table 5). A rather good agreement exists between these different methods. If one compares the results obtained on silica$_{500}$ with those obtained on silica$_{200}$, it appears that **1** has a higher stability on silica$_{500}$. In contrast, **2** and **3** are present in much lower concentrations on silica$_{500}$. This is probably due to a lower

Table 5. Respective Amounts of Various Surface Organometallic Fragments Formed during the Thermal Treatment of ≫Si–O–SnBu₃ Grafted on Silica$_{500}$ as Determined by Infrared, ^{13}C CP-MAS NMR, and Analytical Data

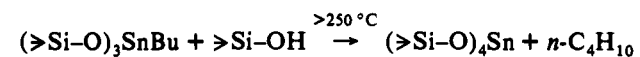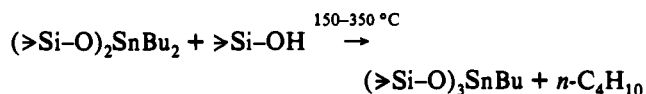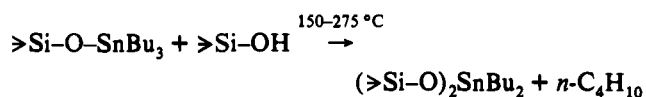| T (°C)	infrared[a]	^{13}C CP-MAS NMR					evolved gases[a]
		1[b]	2[b]	3[b]	X[b]	a	
25	3.0	100	0	0	0	3.0	3.0
150	2.8						2.83
175		63	19	16	2	2.4	
200	2.2						2.5
250	1.4	23	22	22	33	1.4	1.5
300	0.3						0.2
350	0.1						0
400	0						0
450	0						0
500	0						0

[a] Average number of C₄ equivalents remaining on the surface per mole of grafted tin. Using IR spectroscopy, this number is estimated from the intensity of the band at 2958 cm^{-1}. [b] In mol %. X refers to nonalkylated tin atoms on the surface.

Scheme 1
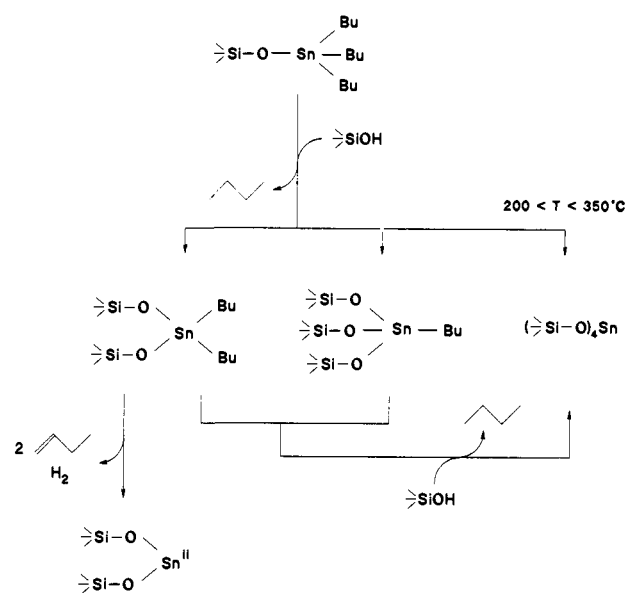
density of silanol on silica$_{500}$, which does not allow easy grafting by several surface siloxy ligands.

Concerning the differences observed between silica$_{200}$ and silica$_{500}$, the major hydrocarbon evolved on silica$_{200}$ is butane, whereas on silica$_{500}$ it is butene. This suggests that solvolysis of **1** by surface OH groups is favored on hydroxylated silica:

$$≫\text{Si–O–SnBu}_3 + ≫\text{Si–OH} \xrightarrow{150-275\ °C} (≫\text{Si–O})_2\text{SnBu}_2 + n\text{-C}_4\text{H}_{10}$$

$$(≫\text{Si–O})_2\text{SnBu}_2 + ≫\text{Si–OH} \xrightarrow{150-350\ °C} (≫\text{Si–O})_3\text{SnBu} + n\text{-C}_4\text{H}_{10}$$

$$(≫\text{Si–O})_3\text{SnBu} + ≫\text{Si–OH} \xrightarrow{>250\ °C} (≫\text{Si–O})_4\text{Sn} + n\text{-C}_4\text{H}_{10}$$
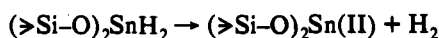
The last reaction may appear very unlikely. However, the temperature at which the butane evolution occurs is sufficiently high to allow an easy migration of surface protons.

If we consider the differences between the two solids regarding the amount of evolved hydrogen, it appears that, unexpectedly, it is on silica$_{500}$ that the amount of evolved hydrogen is the most important. As a consequence, it cannot arise from an oxidation of tin(II) to tin(IV) by hydroxyl groups (there are obviously more hydroxyls on silica$_{200}$). Evolution of hydrogen also cannot be

Scheme 2
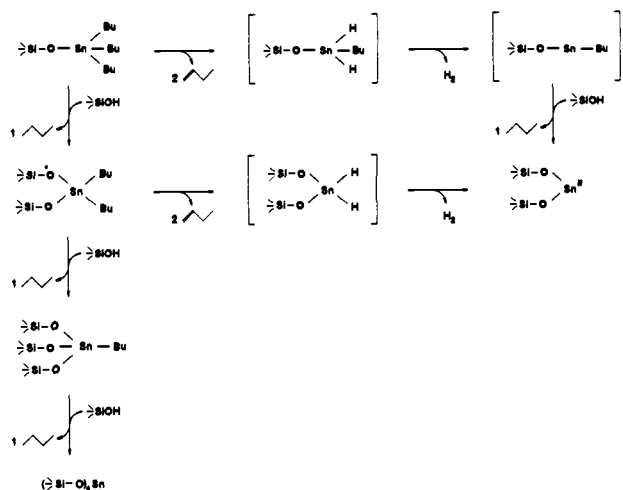
explained only by formation of coke, which fields similar amounts in both cases. However, a reaction of β-H elimination with liberation of butene followed by reductive elimination of hydrogen could explain the results:

$$(\geqslant\text{Si-O})_2\text{SnBu}_2 \rightarrow (\geqslant\text{Si-O})_2\text{SnH}_2 + 2n\text{-C}_4\text{H}_8$$

$$(\geqslant\text{Si-O})_2\text{SnH}_2 \rightarrow (\geqslant\text{Si-O})_2\text{Sn(II)} + \text{H}_2$$

These two reactions are well confirmed by the evolution of 2 mol of butenes per mole of hydrogen. So, even if a disproportionation reaction cannot be excluded, it is probably a minor one.

Conclusion

The objective of this work was to study the reactivity of a well-defined surface organometallic fragment **1** grafted at the surface of two silicas differing by their degree of dehydroxylation: $\text{SiO}_{2\,200}$ and $\text{SiO}_{2\,500}$. The results are interpreted in Schemes 1 and 2. One should notice first that the surface chemistry observed in both cases is rather similar.

The combination of analytical data, infrared spectroscopy, and ^{13}C CP-MAS and ^{119}Sn MAS NMR, as well as Mössbauer spectroscopy and XPS measurements, gives us a relatively reliable description of the behavior of $\geqslant\text{Si-O-SnBu}_3$ grafted on silica$_{200}$ and silica$_{500}$. There is formation of dialkylated, monoalkylated, and nonalkylated tin surface complexes. Obviously, one cannot obtain a unique well-defined species. (In order to obtain well-defined species, such as $(\geqslant\text{Si-O})_2\text{SnBu}_2$, one must start from Bu_2SnH_2.)

Concerning the elementary steps of the various reactions which occur, the differences which are observed between the two types of supports allow us to propose a mechanism of reactivity based on two elementary steps: (1) cleavage of tin-carbon bonds by surface silanols, leading to the grafting of tin by two, three, and maybe more oxygen-tin bonds, and (2) β-H elimination from a metal-butyl group with formation of a surface hydride which has not been detected but which could give rise to reductive elimination of molecular hydrogen. This reductive elimination of molecular hydrogen supposes the formation of tin(II), which has been effectively observed by Mössbauer spectroscopy.

Scheme 2 represents the overall behavior of various alkyltin compounds at the surface of silica. It is clear that the best control of the structure of a well-defined surface organostannic fragment can be achieved by a proper choice of the starting tin complex rather than by the thermal decomposition of a well-defined surface organometallic fragment.