

is positive. Secondly, the magnitude of ρ (<1) indicates that the charge buildup is lower than that found in the gas-phase carboxylate anion. The demonstrated relationship between the gas-phase heats of acidity of the acetic acids and the activation barriers for β -hydride elimination in adsorbed ethoxides allows prediction of the rates of decomposition in other alkoxides.

The implications of this work extend beyond β -hydride elimination in ethoxides on the Cu(111) surface. Similar influences of fluorination have been observed in the ethoxides on the Cu(110), Cu(100), and Ag(110) surfaces. They have also been observed in the longer chain hydrocarbon and fluorocarbon alkoxides on the Ag(110) and Cu(100) surfaces.^{10,13} We have also been able to study the influence of fluorination on β -hydride elimination in alkyl groups adsorbed on the Cu(111) surface. The activation barrier for β -hydride elimination of 3,3,3-trifluoropropyl to 3,3,3-trifluoropropylene is 8.5 kcal/mol higher than for the reaction of propyl to propylene.¹⁸

Studies using much different approaches also suggest that the transition state is really described as hydride elimination. Theoretical studies of β -hydride elimination in alkyl groups on Al surfaces suggest a four-center transition state in which the hydrogen carries net negative charge.²¹ Finally, results similar to ours have been found in a study of the insertion of olefins into Nb-H and Ta-H bonds in a homogeneous phase.⁷ This reaction

is the microscopic reverse of β -hydride elimination, and the effects of substituents have also lead to the conclusion that the transition state for the reaction involves charge separation of the form $C^{\delta+}\cdots H^{\delta-}$.

5. Conclusions

We have demonstrated that fluorination of the methyl group in ethanol exerts an influence on both the heat of dissociative adsorption to form ethoxides on the Cu(111) surface and on the kinetics of β -hydride elimination in these species. The influence of fluorine on the heat of reaction forming ethoxides from gas-phase ethanols is quite small (~ 2 kcal/mol). By comparison, the influence on the kinetics of β -hydride elimination is relatively large, increasing the barrier from 29 kcal/mol in ethoxide to 42 kcal/mol in trifluoroethoxide. This indicates that the influence of fluorine is on the transition-state energetics. The description of the transition state is one in which positive charge builds up on the β -carbon atom ($C^{\delta+}\cdots H^{\delta-}$) and is destabilized by fluorination of the methyl group. The magnitude of the ρ parameter in the free energy relationship between the reaction barrier for β -hydride elimination and the stabilization of gas-phase acetate by fluorination indicates that the charge buildup in the transition state is much lower than is observed in the gas-phase acetate anion.

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Surface Organometallic Chemistry of Tin: Reactivity of Tetraalkyltin Complexes and Tributyltin Hydride toward Silica

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Abstract: Tetraalkyltin complexes, SnR_4 ($R = Me, Et, i\text{-}Pr, Bu$), and tributylhydridotin were reacted with the surface of partially dehydroxylated silica. Interaction between the complexes and the silica surface was followed by IR and ^{13}C and ^{119}Sn MAS NMR spectroscopies and analysis of the evolved gases. At room temperature, all the studied complexes are physisorbed: a hydrogen-type bonding between the terminal methyl group of the alkyl ligands and/or the hydride ligand and the surface silanol groups is evidenced. Above 100 °C, with silica dehydroxylated at 500 °C ($SiO_2(500)$), a reaction occurs, leading to the formation at 200 °C of essentially one surface complex, $\geq SiO-SnR_3$ (**1**) with evolution of 1 mol of alkane per mol of surface tin. **1** is already formed at room temperature by reaction of silica with Bu_3SnH ; the reaction is slow and liberates 1 mol of H_2 /mol of surface Sn. At low surface coverage, and for $R \neq Me$, the alkyl ligands of **1** are folded toward the surface, interacting with it via hydrogen-type bonding. The same interaction and reaction are observed when the surface of silica is less dehydroxylated, $SiO_2(200)$: nevertheless **1** is less stable, probably due to the availability of surface silanol groups in the neighborhood of **1**.

Introduction

Tin inorganic and organometallic complexes are widely used in the field of catalysis (transesterification and polyurethane foam and silicone elastomers production)¹ and as efficient modifiers of supported metal particles.² The bimetallic solids obtained in the latter case present new properties, high conversions, and high selectivities for a number of reactions, particularly in the field of synthesis of fine chemicals.³ Yet, the reactions occurring during

the synthesis of such catalysts are not well understood, due to the high complexity of such multicomponent systems. In particular,

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almost nothing is known about the reaction of tetraalkyltin complexes with the surface of the conventional supports used, such as silica and alumina.⁴

Recently, it was shown that the reaction of tin organometallic complexes with the external surface of zeolites induces important modifications of their adsorptive properties.⁵ The effect seems to be correlated to inter alia the bulk of the ligands.

The reactivity of main group metal alkyls toward the surface of inorganic oxides is known as one of the methods of determination of the surface "active" hydrogens. Thus methylmagnesium, CH_3MgI ,^{6a} trimethylaluminum,^{6b,c} ethyllithium,^{6c} and dimethylzinc,^{6d} for example, are reported to react quantitatively with the surface protons of silica. The observed reactivity involves the grafting of the organometallic fragment via either one or two surface oxygens, depending upon the degree of dehydroxylation of the surface.⁷ Owing to their relative inertness, the reactivity of tin alkyl complexes was relatively less studied and the surface species were so far only poorly characterized.⁸

We report here the results concerning the low-temperature reactivity of tetraalkyltin complexes, SnR_4 ($\text{R} = \text{Me}, \text{Et}, i\text{-Pr}, n\text{-Bu}$), and Bu_3SnH toward the surface of a high-specific-area silica.

Experimental Section

Reagents. The tetraalkyltin complexes, SnBu_4 (from Merck), SnEt_4 (from Janssen), SnMe_4 (from Aldrich), $\text{Sn}(i\text{-Pr})_4$ (from Strem), and Bu_3SnH (from Strem) were used as received. Silica (Aerosil from Degussa, 200 m^2/g) was treated under vacuum (10^{-5} Torr, 14 h) at respectively 200 °C ($\text{SiO}_2(200)$) and 500 °C ($\text{SiO}_2(500)$).

Sample Preparation. All preparations were performed under strict exclusion of air, using standard break and seal Pyrex glassware.

The tin complexes were introduced via a syringe onto the surface of the silica, previously dehydroxylated in situ under vacuum (10^{-4} Torr) at the desired temperature. The amount of complex introduced was usually lower than the number of estimated surface OH groups: the presence of excess unreacted complex was thus avoided. A typical sample was thus prepared by introducing ca. 50 μL of SnBu_4 onto 1 g of silica.

The surface reactions were followed by in situ infrared spectroscopy and gas-phase analysis (volumetry, GC). The resulting solids were characterized by solid-state ^{13}C and ^{119}Sn MAS NMR spectroscopy. The tin content, determined by elemental analysis, was between 0.5 and 6 wt %.

Physical Measurements. IR spectra were recorded on a NICOLET 10-MX FT spectrometer. The cell used for in situ measurements was previously described.⁹

MAS NMR spectra were recorded on a BRUKER MSL-300 spectrometer, operating at 75.47 MHz for ^{13}C and 111.9 MHz for ^{119}Sn and equipped with a double bearing probe, allowing spinning frequencies of 3–4 kHz. The samples were introduced into the rotors, made of zirconia, under nitrogen in a glovebox, and the rotors were tightly closed. For ^{13}C , spectra were recorded by using cross polarization (contact time = 5 ms, duration time for obtaining the 90° pulse = 6.2 μs). The delay between the scans was 5 s, allowing a complete relaxation of the ^{13}C nuclei. Typically, 500–12 000 scans were accumulated, depending on the carbon amount of the sample. Adamantane was used as an internal reference, and the chemical shifts are given relative to TMS. The ^{119}Sn MAS NMR spectra were recorded by using a single-pulse sequence; the delay

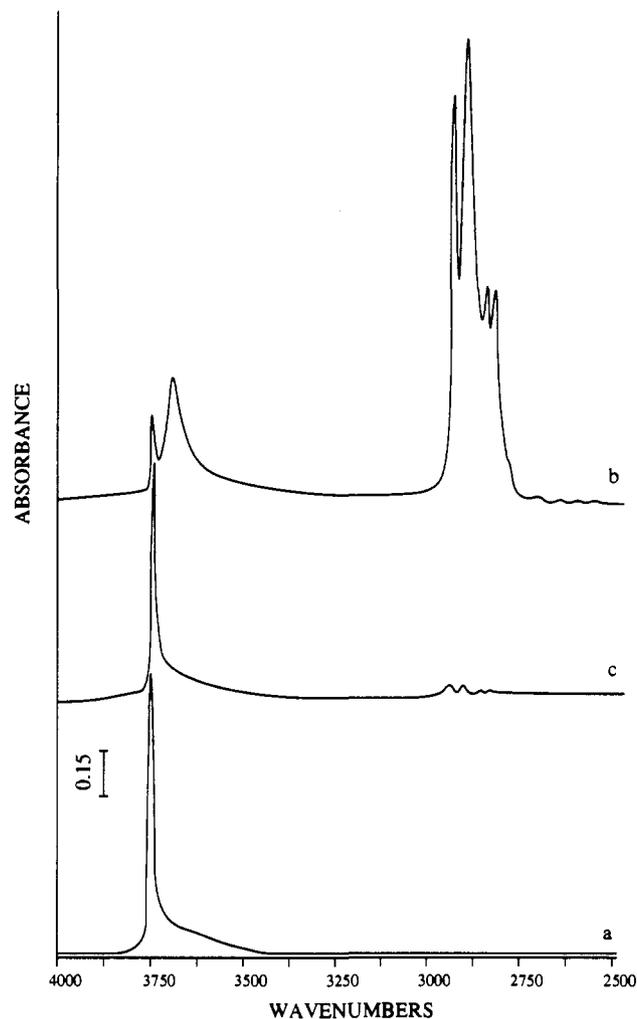
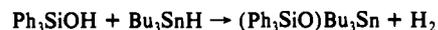


Figure 1. Infrared spectrum in the 4000–2500- cm^{-1} region of (a) $\text{SiO}_2(500)$; (b) sample a after introduction of SnBu_4 at room temperature; and (c) sample b after vacuum treatment at 100 °C (7 h).

between pulses was 5 s, and 500–12 000 scans were accumulated. The chemical shifts are given relative to external SnMe_4 (with the IUPAC convention of the chemical shifts: higher values for higher frequencies).

Synthesis of Tributyl(tris(phenyl)siloxy)tin. $\text{Bu}_3(\text{Ph}_3\text{SiO})\text{Sn}$ was prepared by reaction between Bu_3SnH and Ph_3SiOH :



Bu_3SnH (200 μL , 7.4×10^{-4} mol) was injected through a septum into a closed vessel containing freshly sublimed Ph_3SiOH (278 mg, 10^{-3} mol) under vacuum. The system was maintained at 100 °C for 13 h. Analysis of the gas phase revealed the formation of H_2 (6.3×10^{-4} mol). Yield: 85%. The crude product was identified by its ^{13}C and ^{119}Sn spectra: ^{13}C (ppm, CDCl_3) 16.5 (C_α), 13.7 (C_β), 27.8 (C_γ), 27.1 (C_δ); ^{119}Sn (ppm, CDCl_3) 94.

Results

Reactivity of Tetraalkyltin Complexes toward Silica. A. Silica Dehydroxylated at 500 °C. (i) Reactivity of Tetrabutyltin. When a small amount of SnBu_4 is brought into contact at room temperature with a sample of $\text{SiO}_2(500)$, no evolution of hydrocarbons (butane or any lower hydrocarbon) is detected in the gas phase. When the same experiment is performed in an infrared cell, the following modifications of the vibrational spectrum of the starting silica (Figure 1a) are observed: a strong, moderately broad band (Figure 1b) appears at 3697 cm^{-1} while the intensity of the band characteristic of free silanol groups⁷ at 3747 cm^{-1} decreases. Simultaneously, the bands typical of butyl ligands at 2958 cm^{-1} ($\nu_{\text{as}}(\text{CH}_3)$), 2924 cm^{-1} ($\nu_{\text{as}}(\text{CH}_2)$), 2872 cm^{-1} ($\nu_{\text{s}}(\text{CH}_3)$), 2855 cm^{-1} ($\nu_{\text{s}}(\text{CH}_2)$), 1465 cm^{-1} ($\delta(\text{CH}_2)$, $\delta(\text{CH}_3)$), and 1376 cm^{-1} ($\delta(\text{CH}_3)$) are observed. All these new bands disappear after evacuation at 100 °C (7 h, 10^{-4} Torr), while the intensity of the band corre-

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Table I. ^{13}C and ^{119}Sn NMR Shifts for Some Tin Alkyl Complexes Supported on Silica and Related Model Compounds

compound	T^a ($^{\circ}\text{C}$)	wt % Sn	^{13}C NMR δ (ppm)					^{119}Sn NMR δ (ppm)	ref
			C_{α}	C_{β}	C_{γ}	C_{δ}	C_{x^d}		
SnBu_4^b			9.1	29.6	27.6	13.7		-13	10
$\text{SnBu}_4/\text{SiO}_2(200)$	25	1.12	7.8	28.6	26.7	12.2		-13	this work
$\text{SnBu}_4/\text{SiO}_2(500)$	25	1.85	7.8	28.5	26.6	12.6		-13	this work
$\text{SnBu}_4/\text{SiO}_2(200)$	150	6.22	15.2	26.9	26.9	13.0	11.3	103	this work
$\text{SnBu}_4/\text{SiO}_2(500)$	150	4.92	15.1	26.8	26.8	12.8	11.3	106	this work
$\text{Sn}(i\text{-Pr})_4^c$			13.9	22.4				-44	this work
$\text{Sn}(i\text{-Pr})_4/\text{SiO}_2(500)$	25	2.52	13.4	21.5				-42	this work
$\text{Sn}(i\text{-Pr})_4/\text{SiO}_2(200)$	150	2.46	18.8	20.2			17.5	nd	this work
$\text{Sn}(i\text{-Pr})_4/\text{SiO}_2(500)$	150	2.57	18.6	19.9			17.2	34	this work
SnEt_4^b			-0.4	11.0				1	10
$\text{SnEt}_4/\text{SiO}_2(500)$	25	1.50	-1.2	10.0				2	this work
$\text{SnEt}_4/\text{SiO}_2(200)$	160	1.51	5.5				6.8	95	this work
$\text{SnEt}_4/\text{SiO}_2(500)$	160	2.62	5.3				6.6	98	this work
SnMe_4^b			-9.6					0	10
$\text{SnMe}_4/\text{SiO}_2(500)$	25	0.47	-13					0	this work
$\text{SnMe}_4/\text{SiO}_2(200)$	180	2.23	-7.9					nd	this work
$\text{SnMe}_4/\text{SiO}_2(500)$	180	0.47	-7.8					136	this work
Bu_3SnH^b			8.3	30.2	27.3	13.7		-83	10
$\text{Bu}_3\text{SnH}/\text{SiO}_2(200)$	100	4.14	15.2	26.7	26.7	12.9	11.3	102	this work
$\text{Bu}_3\text{SnH}/\text{SiO}_2(500)$	100	4.81	15.2	26.7	26.7	13.0	11.3	105	this work
Bu_3SnOMe			14.1	28.4	27.4	13.7		83	10, 11
$\text{Bu}_3\text{SnOSiPh}_3^c$			16.5	27.8	27.1	13.7		94	this work
Me_3SnOMe			-5.7					129	12, 28

^aTemperature of treatment under vacuum of the sample. ^bNeat liquid. ^cIn CDCl_3 . ^d $x = \delta$ (precursor: SnBu_4 or Bu_3SnH), β (SnEt_4 or $\text{Sn}(i\text{-Pr})_4$), α (SnMe_4).

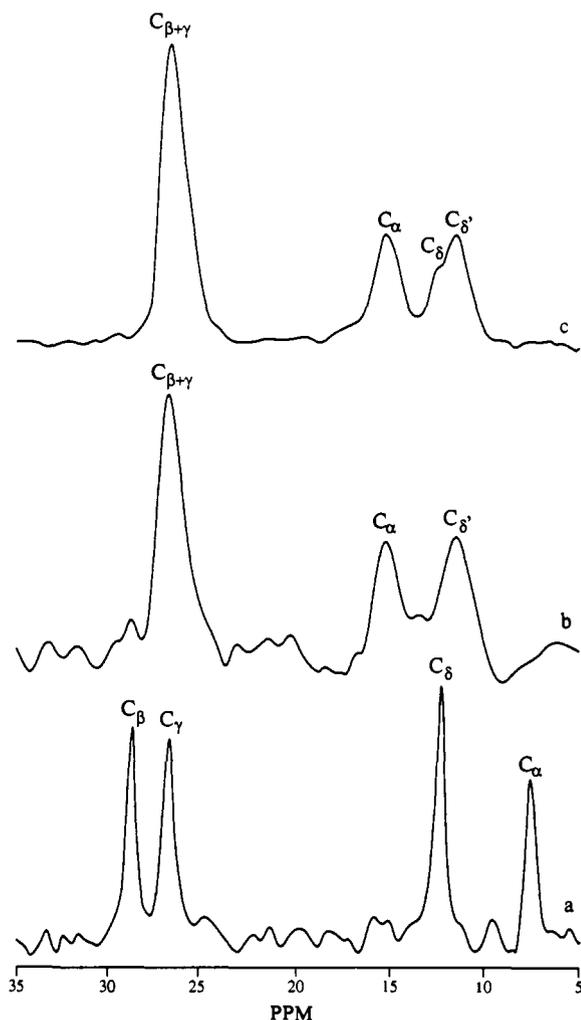


Figure 2. ^{13}C NMR spectra of $\text{SnBu}_4/\text{SiO}_2(500)$ (a) after interaction at 25°C and (b and c) after treatment at 150°C (7 h): (b) wt % Sn = 0.5; (c) wt % Sn = 4.9.

sponding to the free silanol groups is almost entirely restored (Figure 1c). The ^{13}C MAS NMR spectrum of a sample prepared

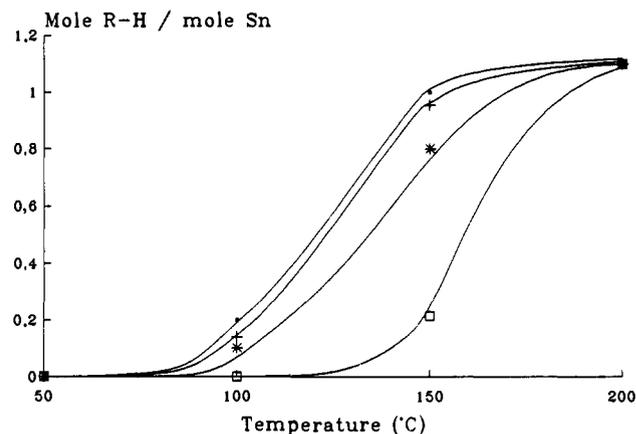


Figure 3. Gas-phase analysis during the thermal treatment of $\text{SnR}_4/\text{SiO}_2(500)$ ($R = \text{Me}$ (\square), Et ($*$), $i\text{-Pr}$ ($+$), $n\text{-Bu}$ (\bullet)).

under similar conditions presents peaks at 28.5, 26.6, 12.6, and 7.8 ppm, which can be assigned to the β -, γ -, δ -, and α -C atoms of the butyl ligands, by comparison with the ^{13}C NMR spectrum of pure SnBu_4 .¹⁰ These peaks are very narrow, suggesting the presence of liquid-phase-like SnBu_4 (Figure 2a). All these data indicate that, between 25 and 100°C , SnBu_4 is simply reversibly adsorbed on the surface of silica.

When the temperature of the system is raised, the evolution of only n -butane is observed; between 100 and 150°C , ca. 1 mol of butane per mol of surface Sn (0.94 mol of C_4H_{10} /mol of grafted Sn) is evolved (Figure 3). In this temperature range, pure SnBu_4 is stable, so that the butane evolution can be reasonably correlated to a surface reaction. The grafted complex(es) formed is(are) stable up to 200°C , allowing complete characterization. Three peaks are observed on the ^{13}C MAS NMR spectrum of a sample prepared under similar conditions (0.5 wt % Sn) at 26.8, 15.1, and 11.3 ppm, respectively (Figure 2b). The peak at 26.8 ppm can reasonably be assigned to the β - and γ -C of the butyl ligands (Table I). The peak at 15.1 ppm is attributed to the α -C, since a shift to lower fields (when compared to that for SnBu_4) is observed in molecular analogues when one butyl ligand is substituted for an alkoxy ligand¹⁰ (Table I). The third peak at 11.3 ppm may thus reasonably be assigned to the δ -C, but is at fields

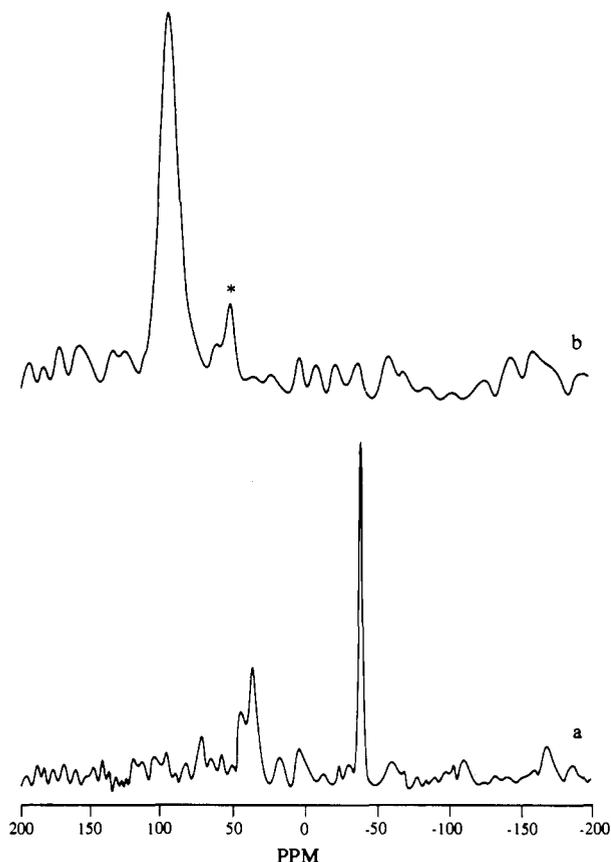


Figure 4. ^{119}Sn MAS NMR spectra of (a) $\text{Sn}(i\text{-Pr})_4/\text{SiO}_2(500)$ after treatment under vacuum at 150°C (8 h) and (b) $\text{Sn}(\text{Et})_4/\text{SiO}_2(500)$ after treatment under vacuum at 160°C (7 h). (* rotational bands).

higher than expected from comparison with model compounds^{10,11} (see Table I), suggesting that this methyl group is involved in some kind of interaction with the silica surface.

When the amount of tin grafted on the surface is raised (wt % Sn = 4.8), the ^{13}C NMR spectrum (Figure 2c) presents a new peak at 12.8 ppm, which is much closer to the expected chemical shift for the $\delta\text{-C}$ (Table I). This suggests that the interaction observed at low tin coverage is partially removed at higher coverage of the surface. The ^{119}Sn MAS NMR spectrum of this sample presents two peaks at -13 and 106 ppm. The first one corresponds to the presence of trace amounts of free SnBu_4 whereas the second one is likely due to a well-defined surface tin complex.

(ii) **Reactivity of Tetraisopropyltin.** When a small amount of $\text{Sn}(i\text{-Pr})_4$ is put into contact at room temperature with the surface of $\text{SiO}_2(500)$, no gas evolution is detected. The ^{13}C MAS NMR spectrum of the resulting solid presents two peaks, which compare well with those of the solution spectrum of $\text{Sn}(i\text{-Pr})_4$ (Table I).

When the temperature of the system is progressively raised, evolution of propane is detected above ca. 100°C : thus, between 100 and 150°C , ca. 1 mol of propane per mol of surface tin is evolved (Figure 3). The system is then thermally stable up to 200°C . The ^{13}C MAS NMR spectrum of a similar sample resulting from a thermal treatment at 150°C presents three peaks, which can be easily assigned (Table I). Occurrence of the third peak at 17.2 ppm indicates that some methyl groups are interacting with surface silanol groups. The downfield chemical shift of the $\alpha\text{-C}$ suggests the substitution of an isopropyl ligand by an alkoxy-type ligand in the coordination sphere of tin. This hypothesis is confirmed by the presence, in the ^{119}Sn NMR spectrum of the same sample, of a peak at 34 ppm (Figure 4a). (A second narrow peak at -42 ppm may be due to trace amounts of unreacted $\text{Sn}(i\text{-Pr})_4$, not detectable in the ^{13}C NMR spectrum.) This

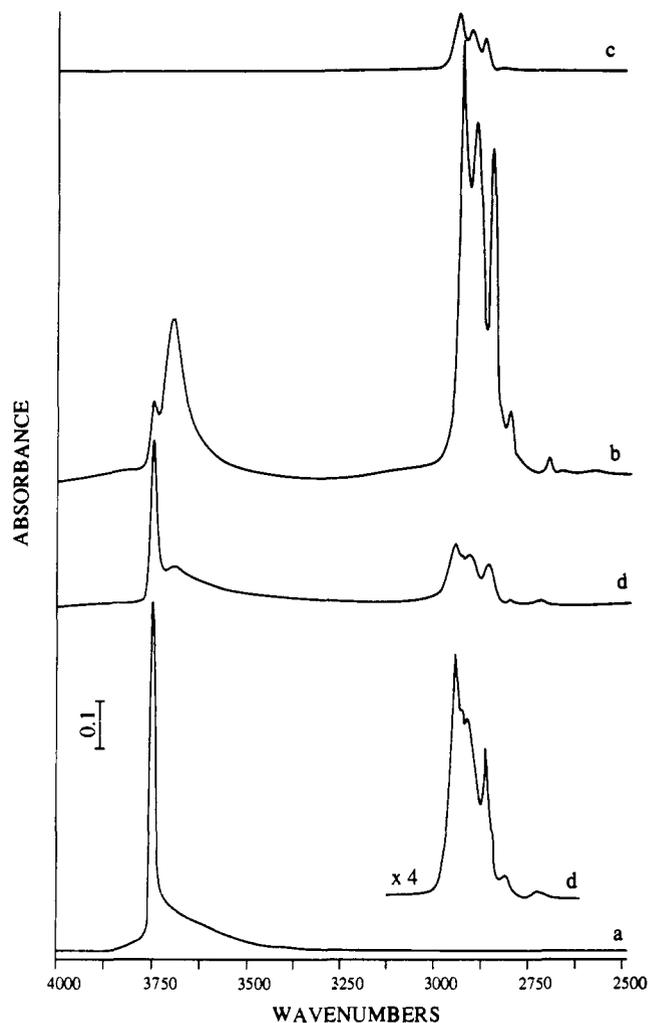


Figure 5. Infrared spectrum in the $4000\text{--}2500\text{-cm}^{-1}$ region of (a) a disk of $\text{SiO}_2(500)$; (b) sample a after introduction of SnEt_4 at 25°C ; (c) the gas phase over sample b; and (d) sample b after treatment at 200°C , 16 h, followed by evacuation at 100°C , 3 h. Inset: enlargement in the $3100\text{--}2800\text{-cm}^{-1}$ region of spectrum d.

chemical shift displacement (80 ppm) is comparable to the one observed previously and attributed to alkyl/alkoxy substitution. Elemental analysis of the solid confirms the presence of three C_3 ligands per surface tin (%C 2.65, %Sn 2.57, C/Sn 9.9).

(iii) **Reactivity of Tetraethyltin.** Because SnEt_4 has a reasonably high vapor pressure at room temperature (which is not the case for SnBu_4 and $\text{Sn}(i\text{-Pr})_4$), the reaction between this complex and the surface of $\text{SiO}_2(500)$ can be easily followed by in situ IR spectroscopy. The spectral modifications, in the $4000\text{--}1200\text{-cm}^{-1}$ region, observed when SnEt_4 is put in contact with a disk of $\text{SiO}_2(500)$ at room temperature are very similar to those already described in the case of $\text{SnBu}_4/\text{SiO}_2(500)$. In the gas phase, only the spectrum of SnEt_4 is observed, with a low intensity (Figure 5c). Analysis of the gas phase above a larger sample (1 g) prepared under similar conditions reveals no presence of any hydrocarbon (ethane...). Finally, all the new IR features observed when SnEt_4 is put into contact with $\text{SiO}_2(500)$ are totally removed after evacuation at room temperature.

When the temperature of the system is raised above 100°C , ethane is liberated as the only detectable hydrocarbon (Figure 3). The evolution of ethane reaches a value of ca. 1 mol/mol of surface Sn at 160°C . Only a minor amount of C_2H_4 is formed at this temperature (<0.01 mol/mol of surface Sn). The IR spectrum of the corresponding surface species (Figure 5d) is characterized by the moderately intense $\nu(\text{C-H})$ vibrational bands. The ^{13}C MAS NMR spectrum of a similar sample reveals two peaks (Table I): their chemical shifts exhibit values in agreement

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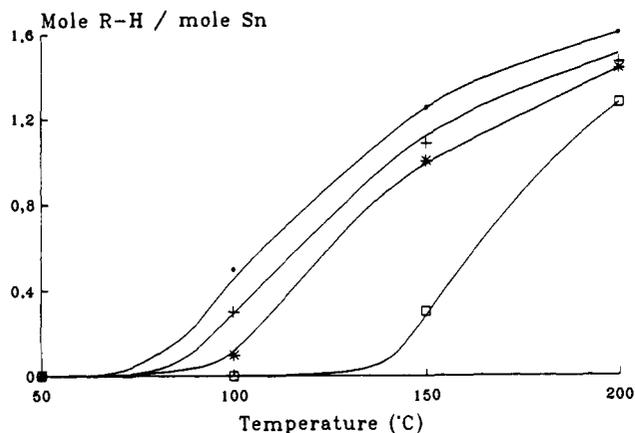


Figure 6. Gas-phase analysis during the thermal treatment of $\text{SnR}_4/\text{SiO}_2(200)$ ($\text{R} = \text{Me}$ (\square), Et ($*$), $i\text{-Pr}$ ($+$), $n\text{-Bu}$ (\bullet)).

respectively with siloxy substitution of one alkyl ligand and the interaction between the terminal methyl group and the surface hydroxyl groups. Only one signal is observed on the ^{119}Sn MAS NMR spectrum at 98 ppm, suggesting total consumption of SnEt_4 and the occurrence of only one major Sn environment on the surface (Table I, Figure 4b). Elemental analysis of this same sample confirms the presence of ca. three ethyl ligands per surface tin (%C 1.52, %Sn 2.6, C/Sn 5.7).

(iv) **Reactivity of Tetramethyltin.** The type of interaction observed at room temperature and the nature of the first chemical reaction occurring between tetramethyltin, SnMe_4 , and the surface of $\text{SiO}_2(500)$ are similar, according to IR and ^{13}C and ^{119}Sn MAS NMR spectral data, to those previously described for SnR_4 ($\text{R} = \text{Bu}$, $i\text{-Pr}$, Et) complexes. Thus, at room temperature, the intensity of the $\nu(\text{OH})$ band at 3747 cm^{-1} decreases and a band appears at 3697 cm^{-1} . Simultaneously, the $\nu(\text{C-H})$ bands of the methyl ligands are observed at 3048 , 2986 , and 2919 cm^{-1} . When the temperature is gradually raised, the intensity of the band at 3697 cm^{-1} decreases, and the band vanishes at $200\text{ }^\circ\text{C}$; but simultaneously, no isolated free silanol groups are restored. Methane is detected in the gas phase ($\nu(\text{C-H})$ at 3017 cm^{-1}). Quantitative analysis of the gas phase above a similar sample (1 g) reveals the liberation of 1.1 mol of CH_4 /mol of surface tin between 100 and $200\text{ }^\circ\text{C}$. The spectrum of the solid presents $\nu(\text{C-H})$ bands at 2992 , 2964 , and 2925 cm^{-1} . The related ^{13}C NMR spectrum presents one major peak at -7.8 ppm , i.e. a value shifted to lower fields when compared to that for the precursor SnMe_4 (-9.6 ppm). A weak peak at -5.3 ppm could arise from a small amount of a species such as $(\text{>SiO})_2\text{SnMe}_2$.¹³ The ^{119}Sn MAS NMR spectrum confirms the presence of surface Sn in one major environment: only one peak is observed at 136 ppm (Table I).

B. Silica Dehydroxylated at $200\text{ }^\circ\text{C}$. We will not describe here every detail of the experiments, but rather will emphasize the differences which may be related to the degree of dehydroxylation of the silica surface.

(i) **Reactivity of Tetrabutyltin.** When SnBu_4 is put into contact with silica(200), the number of free silanol groups decreases (lowering the intensity of the band at 3747 cm^{-1}) and a new type of surface OH groups appears, characterized by a broad band at 3697 cm^{-1} ; at the same time, the $\nu(\text{C-H})$ and $\delta(\text{CH}_2)$ bands typical of the butyl ligands appear. Simultaneously, no hydrocarbon (butane...) is detected in the gas phase.

A reaction takes place above ca. $70\text{ }^\circ\text{C}$, liberating butane as the only hydrocarbon (Figure 6). Butane is progressively evolved between 70 and $200\text{ }^\circ\text{C}$, suggesting that no well-defined unique surface species is formed or stable in this temperature range. The ^{13}C MAS NMR spectrum of a similar sample treated at $150\text{ }^\circ\text{C}$ (i.e. when ca. 1 mol of butane is evolved) presents 4 peaks at 26.9 , 15.2 , 13.0 , and 11.3 ppm , which compare to those observed

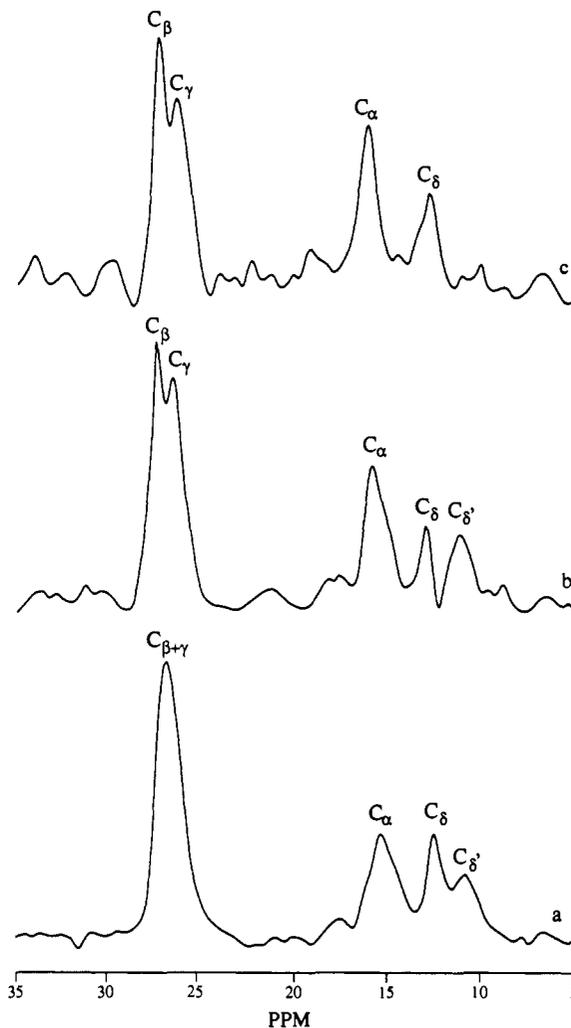


Figure 7. ^{13}C MAS NMR spectra of (a) $\text{SnBu}_4/\text{SiO}_2(200)$ after treatment at $150\text{ }^\circ\text{C}$, 7 h; (b) sample a recorded at $50\text{ }^\circ\text{C}$; and (c) sample a recorded at $80\text{ }^\circ\text{C}$.

previously for the species obtained at the same temperature on $\text{SiO}_2(500)$. This spectrum is temperature dependent (Figure 7). At $50\text{ }^\circ\text{C}$, all peaks become sharper so that the β - and γ -C peaks at 27.2 and 26.2 ppm are now better resolved; the α -C peak is slightly shifted toward lower fields (15.9 ppm). Most interestingly, the intensity of the peak at 11.3 ppm decreases, while the intensity of a peak near 13 ppm (C_δ) increases. At $80\text{ }^\circ\text{C}$, in this latter region, only the peak at 13 ppm is observed. These changes are reversible. These data suggest the occurrence, at room temperature, of a weak interaction between the terminal methyl group of butyl ligands and the surface of silica; this interaction would be suppressed at higher temperatures.

The ^{119}Sn MAS NMR spectrum, recorded at room temperature, presents only one peak at 101 ppm , which compares well with the peak observed under similar conditions for $\text{SnBu}_4/\text{SiO}_2(500)$ (the presence of a small narrow peak at -13 ppm is probably due to a trace amount of unreacted SnBu_4).

(ii) **Reactivity of Tetraisopropyltin.** Similar behavior is observed in the case of $\text{Sn}(i\text{-Pr})_4/\text{SiO}_2(200)$. Propane is continuously evolved between 50 and $200\text{ }^\circ\text{C}$ (Figure 6), reaching a value of 1 mol of propane/mol of surface Sn at $150\text{ }^\circ\text{C}$. The ^{13}C NMR spectrum of a similar sample treated at $150\text{ }^\circ\text{C}$ presents three peaks, which compare well with those in the spectrum of $\text{Sn}(i\text{-Pr})_4/\text{SiO}_2(500)$ under similar conditions, thus suggesting the presence of the same major species at this temperature.

(iii) **Reactivity of Tetraethyltin.** The behavior of the system $\text{SnEt}_4/\text{SiO}_2(200)$ as a function of temperature is similar to that described for $\text{SnBu}_4/\text{SiO}_2(500)$. Ethane is the only hydrocarbon evolved between 50 and $200\text{ }^\circ\text{C}$. Apparently no well-defined unique, thermally stable, surface complex is formed in this range

(13) Nédez, C.; Théolier, A.; Lefebvre, F.; Choplin, A.; Basset, J. M. To be published.

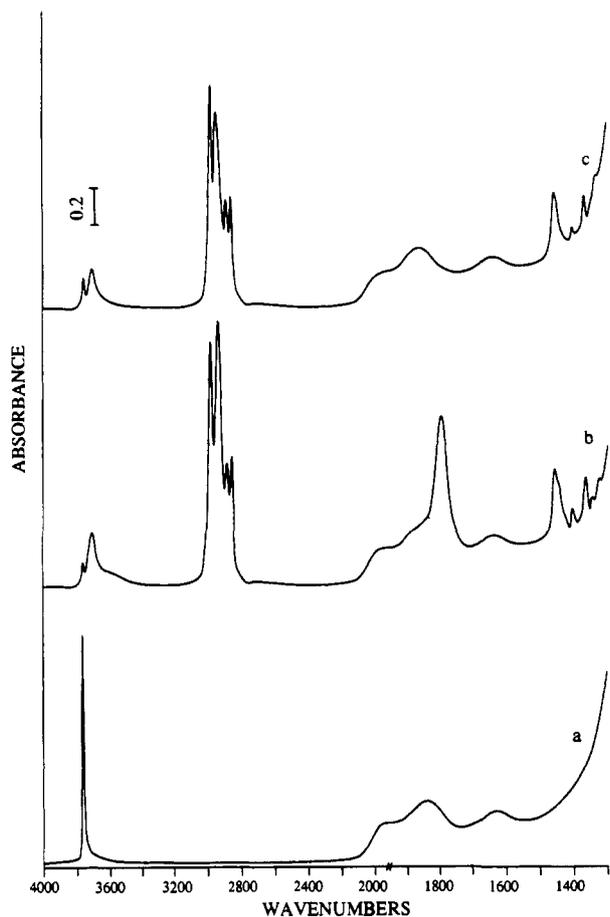


Figure 8. Infrared spectrum in the 4000-1300-cm⁻¹ region of (a) a disk of SiO₂(500); (b) sample a after introduction of Bu₃SnH; and (c) sample b after 24 h at room temperature.

of temperature, as the continuous evolution of ethane suggests (Figure 6). Nevertheless, 1 mol of ethane is evolved at 160 °C; at this temperature, analysis of the sample by ¹³C MAS NMR spectroscopy reveals the presence of two peaks at 6.8 and 5.5 ppm, confirming the presence of a surface species similar to that already observed on SiO₂(500) (Table I). The ¹¹⁹Sn NMR spectra of the same sample presents only one peak at 95 ppm, suggesting the presence of the same surface complex as observed on SiO₂(500) under similar experimental conditions.

(iv) **Reactivity of Tetramethyltin.** The introduction of a small amount of SnMe₄ on SiO₂(200) leads to the same experimental observations (IR and NMR data) as previously described (Table I), suggesting a very similar reactivity. It is worth mentioning here that the type of interaction revealed by the presence of a band at 3697 cm⁻¹ and occurring at room temperature disappears after reaction at temperatures near 200 °C. Only methane is detected in the gas phase, when the temperature of the system is progressively raised, reaching a value of ca. 1 mol of CH₄/mol of surface Sn near 200 °C (Figure 6).

Reactivity of Hydridotributyltin with Silica. A. Silica Dehydroxylated at 500 °C. When Bu₃SnH is put into contact with a disk of silica(500), the IR spectrum of the solid presents the bands typical of ν(C-H), δ(C-H), and ν(Sn-H) of the precursor complex¹⁴ (Figure 8). In addition, the intensity of the ν(OH) band at 3747 cm⁻¹, corresponding to the free surface silanol groups, decreases sharply while two moderately broad bands appear at 3697 and 3600 cm⁻¹. These two bands can be assigned to O-H stretching vibrations, shifted toward lower frequencies by hydrogen-type bonding. The first one compares well with that

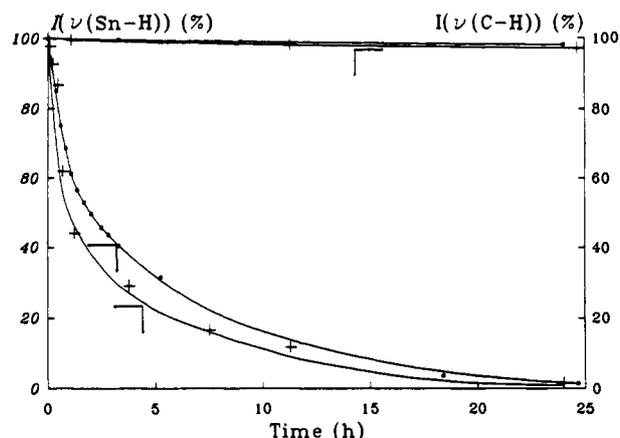


Figure 9. Variation of the intensity of the (Sn-H) and (C-H) bands during the interaction, at room temperature, of Bu₃SnH with SiO₂(500) (•) and SiO₂(200) (+) as a function of time.

reported in the case of the tetraalkyltin complexes, while the second one might be correlated to the presence, in this case, of a Sn-H bond. The IR spectrum changes as a function of time; the intensity of the ν(Sn-H) band at 1809 cm⁻¹ decreases and a shoulder is observed at 1784 cm⁻¹, while the intensities of the ν(C-H) and δ(C-H) bands remain practically constant (Figures 8 and 9). The intensity of the ν(O-H) band at 3600 cm⁻¹ decreases as that of the ν(Sn-H) decreases: both bands vanish at the same time, suggesting that they are correlated. When the same experiment is performed on a larger sample, the evolution of only molecular hydrogen is detected in the gas phase. Total disappearance of the ν(Sn-H) band and the absence of any further H₂ or hydrocarbon evolution after ca. 24 h indicate completeness of the reaction. When a large sample is used, a temperature of 100 °C is needed to reach equilibrium in a reasonable time, probably because of mass transfer problems: 0.96 mol of H₂/mol of surface Sn is then evolved. The ¹³C and ¹¹⁹Sn MAS NMR spectra of a sample taken after reaction completion are identical to the spectra of a sample of SnBu₄/SiO₂(500) after treatment at 150 °C (Table I), suggesting the formation of the same surface complex (a small narrow peak at -83 ppm (¹¹⁹Sn) indicates the presence of trace amounts of unreacted Bu₃SnH).

C. Silica Dehydroxylated at 200 °C. The interaction and then the reaction between Bu₃SnH and the surface of a silica partially dehydroxylated at 200 °C are similar to what was observed on SiO₂(500), as evidenced by infrared spectroscopy (Figure 9). At room temperature, only molecular H₂ is liberated (0.98 mol of H₂/mol of surface Sn), indicating the formation of only one surface species. This is further confirmed by ¹³C and ¹¹⁹Sn MAS NMR spectroscopy (Table I).

Discussion

The nature of the interaction of tetraalkyl- or hydridotributyltin complexes with the surface of partially dehydroxylated silica is a function of temperature. Two distinct steps are evidenced here. A weak reversible interaction takes place at room temperature, leaving the complex intact. A chemical reaction takes place above 100 °C, as a result of the substitution of an alkyl or an hydrido ligand by a surface siloxy ligand and leading to the grafting of an R₃Sn moiety to the surface of silica via a (>SiO)-(SnR₃) covalent bond. We will discuss these two steps in some detail.

Physisorption. Whatever the nature of the alkyl ligands R studied here (R = Bu, Et, *i*-Pr, Me), the occurrence of a weak, reversible interaction between the tin complexes and the surface silanol groups is evidenced by IR spectroscopy (appearance of a moderately broad band at 3697 cm⁻¹). Such a low-frequency shift can be explained by the participation of the free doublet of a surface oxygen atom in a new bond which could be either a donor-acceptor bond or a hydrogen-type bond. In the first case, Sn(IV) would act as a Lewis acid center via its empty d orbitals. In the second case, a hydrogen-type bond would involve a C-H bond of the alkyl ligands and the oxygen doublet. The first

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hypothesis seems unlikely, since Sn(IV) behaves generally as a rather weak Lewis acid, whose acidity needs to be enhanced by electron-withdrawing ligands, such as Cl and O.¹⁵ The only examples of coordination of an oxygen atom to a tetraalkyltin complex have been recently reported and involve intramolecular coordination of a carboxylic or an alcoholic oxygen, in the solid state.¹⁶ Finally, the observed ¹¹⁹Sn NMR spectrum is very close to that of the precursor SnR₄ complex: an upfield shift would have been expected if pentacoordination of a silanol or siloxy bridge would have occurred.¹⁷ The second hypothesis, i.e. formation of hydrogen-type bonds, is supported by the following data. The low-frequency shift of the OH vibration is exactly the same when hexane¹⁸ or cyclooctane¹⁹ is introduced on a silica surface. Although the "classical" hydrogen-bonding groups are not present here, this type of bonding, C-H...O, is well documented in organic crystals^{20,21} and has also been invoked to explain the ordering of alkyldiyne and CO molecules when coadsorbed on Pt(111).²²

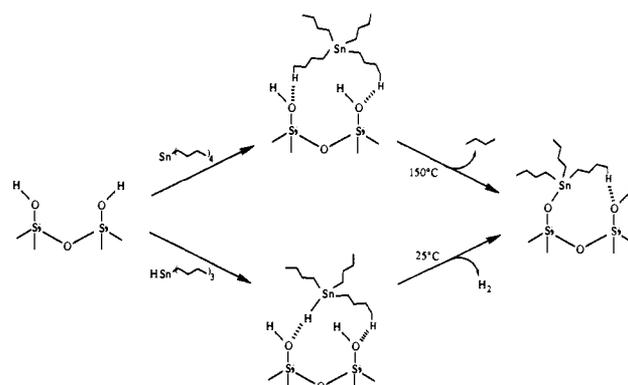
That the phenomenon observed here involves the alkyl ligands is also corroborated by the fact that it is still observed when the tin complexes are chemisorbed (vide infra), but only as long as free silanol groups are available (i.e. at low tin coverage) and when the alkyl chain length is sufficient. Thus, this interaction is suppressed for grafted SnMe₃, i.e. >SiO-SnMe₃. This interaction seems to concern only the terminal methyl group of the alkyl ligands, as evidenced by ¹³C NMR data, which may be explained by steric reasons.

This hydrogen bond type interaction is rather weak, as expected for hydrogen bonds of this nature:¹⁷ it is released when the temperature is slightly increased, as evidenced by ¹³C NMR spectroscopy of >SiOSnBu₃ at ca. 80 °C. The precise nature of these "hydrogen-bonds" is not very clear; as C-H bonds of alkanes are weakly polarized, C⁺-H⁻, it is possible that the more polarized surface silanol groups are able to induce the reverse polarization, C⁻-H⁺, necessary to account for further hydrogen bonding.²³ The propensity of alkyl chains to interact with the surface of silica has also been evidenced in the case of alkylsilyl silicas and explained by only van der Waals type interactions, easily removed in the presence of a solvent or by steric crowding (high surface coverage).²⁴

In the case of the hydridotributyltin complex, IR spectroscopic data (appearance of two broad shoulders at 3698 cm⁻¹ and near 3600 cm⁻¹, respectively) suggest that the same type of interaction is also occurring when this complex is in contact with a silica surface: a hydrogen bond between the butyl ligand (via the terminal methyl group) and the surface silanols and a second one, slightly stronger, between Sn-H and the surface silanol groups. The occurrence of a weak band near 1784 cm⁻¹, i.e. shifted toward lower frequencies by about 25 cm⁻¹, may be related to the expected Sn-H bond weakening. This latter interaction is totally suppressed once the H ligands are consumed by reaction with the silica surface (see Bu₃SnH/SiO₂(500)).

Chemisorption. No chemical reaction between any of the tetraalkyltin complexes studied and silica occurs at temperatures below ca. 100 °C, as suggested by the absence of evolution of any hydrocarbon (butane, propane, ethane, and methane, respectively) in the gas phase. The release of hydrocarbon above 100 °C cannot

Scheme I



be related to thermal decomposition of SnR₄ complexes. It is correlated to significant changes in the IR and ¹³C and ¹¹⁹Sn MAS NMR spectra. These latter are typical of tris(alkyl)alkoxytin complexes (Table I). All these data agree with the occurrence of the following reaction on the surface of silica:



Elemental analysis (C,Sn) is in agreement with this formulation of the surface complex. Reaction 1 is well documented in molecular chemistry; the mechanism involves an electrophilic attack by the weak Bronsted acidic surface silanol groups.

The ¹¹⁹Sn MAS NMR spectral data suggest that Sn remains essentially tetracoordinated on the surface; in all cases, the chemical shifts observed are indeed very close to the values generally attributed to tetracoordinated Sn in molecular model compounds (Table I), but very far from values indicative of pentacoordinated complexes.¹² Moreover, when the same reaction is performed on the surface of alumina, the ¹¹⁹Sn spectra present numerous peaks, indicative of Sn in two major environments on the surface, characterized by tetra- and pentacoordination.²⁵

The same hydrogen-type bonding as previously described (vide supra) occurs between H atoms of the alkyl ligands and surface O atoms. That only the H atoms of the terminal methyl groups and mainly the surface silanol groups are involved is indicated by the ¹³C NMR and the IR data ($\nu(\text{OH})$). This interaction is not observed when R = Me; the distances between the concerned atoms are certainly not favorable. Finally, this kind of interaction is released either when the surface concentration of tin complexes is increased or when the temperature of the solid is slightly increased (>80 °C).

Reaction 1 takes place at a temperature which seems to be somehow dependent upon the nature of the alkyl ligands: the shorter the hydrocarbon ligand, the higher the temperature necessary for reaction to occur (Figures 3 and 5). This is unexpected according to the well-known solution chemistry,²⁶ but it may be related to the difference in the partial vapor pressures of the different tin complexes, under our reaction conditions: tetrabutyltin is a liquid with almost no vapor pressure, while tetramethyltin is gaseous. Thus, one compares a liquid/solid reaction to a gas/solid reaction.

The surface reactivity depends upon the degree of dehydroxylation of the surface of silica; on silica(500), the reaction leads to essentially one well-defined surface complex, whose thermal stability domain is sufficient to allow its full characterization (Figure 3). On the other hand, on SiO₂(200), the evolution of alkane is continuous, indicating that the first formed complex has only a limited thermal stability. These different behaviors must be related to the presence of neighboring OH groups in the latter case. The number of geminal and vicinal surface OH groups capable of reacting with one Sn center is higher in the case of

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SiO₂(200) than for SiO₂(500).^{7,24}

The same surface species, >SiOSnR₃, is obtained already at ambient temperature by reaction 2 between Bu₃SnH and the silanol groups, suggesting that a Sn-H bond is more reactive toward silanol groups than a Sn-C bond. The thermal stability



of these surface grafted trialkyltin complexes is slightly higher on the surface of a silica dehydroxylated at 500 °C than on a more hydroxylated surface, such as SiO₂(200) for example. On the latter surface, reaction with neighboring available OH groups takes place.¹³ The overall reactivity of SnR₄ and HSnR₃ complexes is summarized in Scheme I.

Conclusion

The reaction between a number of tetraalkyltin or hydrido-tributyltin complexes and the surface of partially dehydroxylated

silica leads to the clean formation of the related trialkyltin surface complexes, >SiOSnR₃, with liberation of 1 mol of alkane or 1 mol of H₂, respectively, per mol of surface tin. The alkyl ligands are interacting with the surface silanol groups via hydrogen-type bonds. This interaction occurs when surface hydroxyl groups are available and accessible, when the hydrocarbon chain length is sufficient, and when the temperature is lower than 80 °C. These surface organometallic SnR₃ fragments are stable up to at least 200 °C, when the surface of silica was previously dehydroxylated at 500 °C. This described chemistry has recently been extrapolated to the external surface of a mordenite: the SnR₃ entities are able to induce new shape selective properties for the zeolite.²⁷

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Oxidative Coupling and Ring Opening of Furan on Ag(110): Formation of Maleic Anhydride, Benzene, and Bifuran

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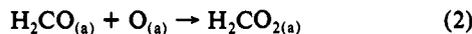
Abstract: TPRS, EELS, and isotope experiments show that furan reacts with active oxygen on Ag(110) to form CO₂, H₂O, and small amounts of the partially oxidized products maleic anhydride, bifuran, and benzene that evolve between 520 and 560 K. The first step in furan combustion is C-H bond activation by O_(a), followed by O_(a) attack at the α-carbon at 308 K. ¹⁸O_(a) experiments prove that maleic anhydride is formed via intermediates where the furan ring has been cleaved. This contrasts with mechanisms proposed for maleic anhydride production from furan over VPO catalysts.

Introduction

Silver catalysts are used for the industrial epoxidation of ethylene to ethylene epoxide. Although much is still not known about this industrially significant reaction, the behavior of oxygen on Ag(110) is quite well understood. Atomic oxygen behaves as a Brønsted base, exemplified in the observed acid-base reaction of atomic oxygen and adsorbed formic acid:¹



Adsorbed atomic oxygen also behaves as a nucleophile, attacking electron-deficient carbon centers, as in the observed reaction of atomic oxygen and formaldehyde:¹



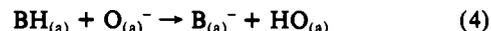
The fact that oxygen behaves both as a Brønsted base and as a nucleophile implies that adsorbed oxygen is partly anionic. Experimental and theoretical evidence confirms this observation.²⁻⁴

Reactions on Ag(110) of oxygen with unsaturated hydrocarbons can be classified as C-H bond activation, C=C epoxidation, and cycloaddition. Although C-H bond activation by O_(a) has been known for some time, epoxidation reactions by this species were confirmed only recently with the epoxidation of both norbornene to norbornene epoxide⁵ and 3,3-dimethyl-1-butene to 3,3-dimethyl-1-butene epoxide.⁶ Even more recently, Roberts et al. observed the cycloaddition of 1,3-butadiene with O_(a) to form 2,5-dihydrofuran.⁷

The activation of C-H bonds by atomic oxygen on silver is governed by the gas-phase acidity or heterolytic bond dissociation enthalpy (ΔH_{acid}), determined by the following gas-phase reaction:



If the heterolytic bond dissociation enthalpy of the conjugate base is less than that of water (ΔH_{acid} = 395 kcal/mol), then the following acid-base reaction is expected to occur:



Hence, propylene (ΔH_{acid} = 392 kcal/mol⁸) reacts with O_(a) to form surface hydroxyl groups and, at higher temperatures, CO₂ and H₂O; cyclohexene (ΔH_{acid} = 387 kcal/mol⁹) reacts with surface oxygen to yield benzene.¹⁰

Recently, 1-butene was observed to react with surface oxygen to yield butadiene, 2,5-dihydrofuran, furan, 2(5H)-furanone, and maleic anhydride.¹¹ The following mechanism was proposed. First, 1-butene acidic C-H bond activation by O_(a) leads to butadiene formation. Butadiene and oxygen undergo 1,4-cycloaddition to form 2,5-dihydrofuran. 2,5-Dihydrofuran is acidic

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