whether any O–H bond changes occur (using neutron diffraction, or perhaps ENDOR). At present, insufficient data are available to allow a structural comparison. Since theory satisfactorily accounts for the effect of $^{18}\mathrm{OH}_2$ substitution, the "frozen mode" explanation seems an interesting possibility for explaining the large H/D isotope effects in electron-transfer reactions of $\mathrm{Co(NH_3)_6}^{3+}/\mathrm{Co(ND_3)_6}^{3+}$ and $\mathrm{Fe(OH_2)_6}^{2+}/\mathrm{Fe(OD_2)_6}^{2+}$. In any case, it seems clear that the kinetic isotope effect in $\mathrm{Fe}^{2+/3+}$ redox reactions due to substitution of $\mathrm{H_2O}$ by $\mathrm{D_2O}$ is larger than that due to the substitution of $^{16}\mathrm{OH}_2$ by $^{18}\mathrm{OH}_2$. Since $\mathrm{D_2O}$ and $^{18}\mathrm{OH}_2$ have an identical mass, this kinetic isotope effect $\mathrm{Fe}^{2+/3+}(k_\mathrm{H}/k_\mathrm{D})/\mathrm{Fe}^{2+/3+}(k_{16}/k_{18}) > 1$ cannot be due to metal–ligand modes alone but incorporates the effect of the change in driving force and, possibly, the effect of "intraligand" vibrational modes.

Summary

Several conclusions can be drawn from the results pesented here.

(1) The effect on electron-transfer rates of substituting ligands of different mass, e.g., $[\mathrm{Fe}(^{16}\mathrm{OH}_2)_6]^{2+}/[\mathrm{Fe}(^{18}\mathrm{OH}_2)_6]^{2+}$, apparently can be understood by considering the effect of the mass change on the frequency ($\hbar\omega$) of the symmetric metal–ligand stretching mode. These results strongly support the recent quantum theories of electron transfer.[2,3] The specific treatment of Buhks et al.[3] also correctly predicts both the direction and magnitude of the dependence of the kinetic isotope on reaction driving force.

(2) By contrast, substitution of H by D in $\mathrm{Fe(OH_2)_6}^{2+}/\mathrm{Fe(OD_2)_6}^{2+}$ or $\mathrm{Co(NH_3)_6}^{3+}/\mathrm{Co(ND_3)_6}^{3+}$ causes a larger kinetic isotope effect than can be explained by the change in metal–ligand frequency. We wish to suggest that very high frequency (N–H) or (O–H) modes are involved (to a small extent) in electron-transfer reactions of some transition-metal complexes. Since these modes cannot be thermally populated, the reaction must involve nuclear tunneling. The small calculated changes in O–H (or N–H) bonds that are invoked to explain the isotope effect might involve the bound ligand directly, or may be coupled to second shell solvent.

These initial results suggest a number of further experiments. In particular, it will be interesting to seek further confirmation of "frozen mode" behavior in electron transfer. We are pursuing such studies in reactions of free and coordinated $\mathrm{O_2}$. Temperature-dependence studies of the isotope effect at low temperatures may provide additional information about the tunneling mechanism of electron-transfer reactions.

Acknowledgment. E.B. acknowledges the grant from SERI to the University of Delaware. T.G. wishes to acknowledge a Sherman Clarke Fellowship from the University of Rochester and an E. H. Hooker Fellowship. G.M. gratefully acknowledges the support of an A. P. Sloan Fellowship and a Dreyfus Teacher Scholar Award. We are grateful to Morton Hoffman and Michael Weaver for helpful discussion of various aspects of this work.

Registry No. $\mathrm{D_2}$, 7782-39-0; $^{18}\mathrm{O}$, 14797-71-8; Fe, 7439-89-6; $\mathrm{Fe(Me_2bpy)_3}^{8+}$, 34032-03-6; $\mathrm{Fe(phen)_3}^{3+}$, 15276-16-1; $\mathrm{Ru(bpy)_3}^{3+}$, 18955-01-6; $\mathrm{Cr(Me_4phen)_3}^{3+}$, 51194-74-2; $\mathrm{Cr(Me_2phen)_3}^{3+}$, 51194-72-0; $\mathrm{Cr(bpy)_3}^{3+}$, 15276-15-0; $\mathrm{Ru(bpy)_3}^{2+}$, 15158-62-0.

Solid-State NMR Studies of the Reactions of Silica Surfaces with Polyfunctional Chloromethylsilanes and Ethoxymethylsilanes

Dean W. Sindorf and Gary E. Maciel*

Contribution from the Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523. Received August 18, 1982

Abstract: The silylation of silica surfaces by dimethyldichlorosilane, methyltrichlorosilane, dimethyldiethoxysilane, and methyltriethoxysilane has been studied by solid-state $^{29}\mathrm{Si}$ and $^{13}\mathrm{C}$ NMR, by use of cross polarization (CP) and magic-angle spinning (MAS). An earlier formalism for the quantitative analysis of the NMR data has been extended for use with polyfunctional silylating agents and applied in detail to dimethyldichlorosilane reactions. Silylation with ethoxysilane reagents is less amenable to quantitative interpretation but appears to parallel closely the behavior of analogous chlorosilane reagents. With ethoxysilane reagents $^{13}\mathrm{C}$ NMR is found to be quite useful, especially for determining the fate of ethoxy groups. In all of the cases studied, the products are characterized primarily by single silane-to-surface attachments of each silane silicon atom. The presence of adsorbed water is found to play an important role in the course and rate of the silylation reactions, especially those employing ethoxysilane reagents. The NMR data are used to address the question of "horizontal" and "vertical" polymerization within the "silane phase" on the silica surface.

Introduction

Previous reports have described the use of solid-state $^{29}\mathrm{Si}$ NMR, by use of cross polarization (CP)[1] and magic-angle spinning (MAS),[2] in the characterization of silica surfaces[3,4] and their derivitization by monofunctional silylating agents[5,6] (e.g., trimethylchlorosilane and hexamethyldisilizane). These reports have shown that $^{29}\mathrm{Si}$ CP/MAS spectra of silica gels are amenable to quantitative analysis and have included formalisms for deriving chemically useful structural parameters from such analysis.

In many chemical applications, e.g., chromatographic phases and supported catalysts, silica surfaces are derivatized by silylating agents with more than one labile group, e.g., $\mathrm{R\text{-}Si(OEt)_3}$ and $\mathrm{R\text{-}SiCl_3}$. Such systems are potentially much more diverse in their silylation chemistry than monofunctional reagents. In addition to the single attachment to the surface that would result from

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Table I. Expected ^{29}Si Chemical Shifts^a

species^b	shift^a	species^b	shift^a
$Si(CH_3)_3(O-)$	8	$Si(CH_3)(O-)_3$	−67
$Si(CH_3)_3Cl$	30	$Si(CH_3)(Cl)(O-)_2$	−46
$Si(CH_3)_3(OC_2H_5)$	14	$Si(CH_3)(OR)(O-)_2$	−59
$Si(CH_3)_2(O-)_2$	−21	$Si(CH_3)(OH)(O-)_2$	−56
$Si(CH_3)_2(OH)(O-)$	−12	$Si(CH_3)(Cl)_2(O-)$	−18
$Si(CH_3)_2(Cl)(O-)$	2	$Si(O-)_4$	−108
$Si(CH_3)_2(OR)(O-)$	−12	$Si(OH)(O-)_3$	−98
$Si(CH_3)_2Cl_2$	32	$Si(OH)_2(O-)_2$	−89

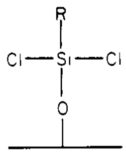
^{a} Reported in ppm relative to Me_4Si, with larger numbers corresponding to lower shielding (data extracted from ref 9, Table 10.2). ^{b} (O−) symbolizes a siloxane attachment to the silicon (Si*) of interest, i.e., Si*-O-Si<.

Table II. ^{29}Si Chemical Shift Substitution Effects (ppm)^a

rule no.	subs effect	$-Si(CH_3)_3$	$>Si(CH_3)_2$	$\geqslant SiCH_3$
i	OH-OSi		9	9
ii	Cl-OSi	22	23	22^c
iii	OR-OSi	7	9	6
iv	Cl-OH		14	13
v	OR-OH		0	−4
vi	surface-solution	7	7^b	7^b

^{a} Obtained from the data in Table I. Estimated uncertainty ±3 ppm. ^{b} Assumed on the basis of observed results for $-Si(CH_3)_3$ species. ^{c} Average of $SiCH_3Cl_2(O-)$ and $SiCH_3Cl(O-)_2$ data.

reaction of a reagent like R_3SiCl (e.g., structure I), additional chemical processes can lead to multiple surface-to-silane siloxane bonds (e.g., structure II) or to the substitution of a new atom or moiety (e.g., OH vs. Cl from partial hydrolysis, structure III) or to the formation of siloxane bonds between silane groups as in "horizontal" polymerization (e.g., structure IV) or "vertical" polymerization (e.g., structure V), or related possibilities.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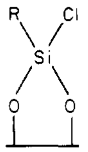
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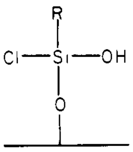
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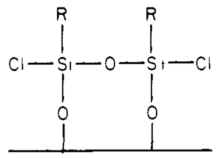
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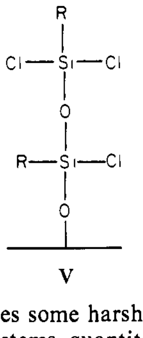
V

This additional chemical diversity places some harsher constraints on the ability to treat these systems quantitatively. Nevertheless, a relatively detailed account of the surface silylation products can be achieved by NMR in some cases. This paper addresses certain aspects of this problem and extends preliminary studies reported previously.[7,8] The silylation agents that have been studied are dimethyldichlorosilane, methyltrichlorosilane, dimethyldiethoxysilane, and methyltriethoxysilane.

In analyzing the NMR spectra of these systems, especially the ^{29}Si spectra, frequent use is made of empirical chemical shift correlations deduced from extensive liquid-state studies. These data have been reviewed by Harris and co-workers.[9] Previously reported ^{29}Si chemical shifts of particular applicability in the present context are summarized in Table I. Many of the structural moieties one can expect to encounter on the silica surface as a result of reactions involving methylsilane bonding agents can be found directly in this table. Others, however, have no common solution-state analogues, and ^{29}Si data are therefore not available. In an attempt to predict at least approximate shifts expected for these species, the data in Table I can be examined for consistent trends in relative chemical shifts, i.e., substitution effects, that one can hope will also be valid for the species of interest.

For example, these results indicate that a 9 to 10 ppm chemical shift is quite characteristic of the substitution of a OSi< group for a OH moiety for all of the species considered. Other chemical shift effects, arising from Cl-to-OSi< substitution, OC_2H_5-to-OSi< substitution, etc., can also be deduced from the data of Table I. These are summarized in Table II.

In a previous report[5] the chemical shift of a trimethylsiloxane group attached to the silica surface was found to be 15 ppm (relative to liquid Me_4Si). This value differs somewhat from that encountered for analogous species in solution (e.g., $(CH_3)_3Si(O-)$, where (O−) stands for −OSi<). For dimethylsiloxane polymers of various lengths that have been "capped" with trimethylsilyl groups Harris et al.[10] found shifts of 6.7 to 7.3 ppm for peaks assigned to silicon atoms in the trimethylsilyl environment. Similar studies[11] examining "capped" silicic acid polymers indicate that the expected chemical shift of trimethylsilyl ^{29}Si nuclei in these species is about 8 ± 1 ppm. Empirically, these data suggest that thee chemical shift of a trimethylsilyl species attached to the surface of silica gel exhibits a "solid state ^{29}Si chemical shift" of about 15 − 8 = 7 ppm to lower shielding than the value encountered in solution.

Experimental Section

NMR Measurements. ^{29}Si and ^{13}C CP/MAS measurements were made at 11.88 and 15.0 MHz, respectively, as described previously,[4] with a JEOL FX-60QS spectrometer.

Samples. Elemental analysis were carried out by Huffman Labs, Denver, CO. Percent carbon was obtained by induction furnace combustion at 1500 °C.

Silica-Silane Reactions. The silica substrates used in these studies were a commercial silica gel (Fisher S-157, surface area 750 m^2/g) and a silica gel prepared by acid hydrolysis of ethylorthosilicate (Labeled TES2, surface area 509 m^2/g). After drying in air at room temperature, TES2 silica contained about 20% by weight molecular water (determined from weight loss after heating to 200 °C in N_2). Details of the characterization and preparation of these materials have been described previously.[4-6]

Silylation reactions were carried out using several experimental procedures including the gravimetric methods described previously[5] (methods 1–4) and the additional methods given below.

Method 5. Toluene Solution, Using Hydrous Silica. This procedure is based on a method reported by Majors and Hooper[12] for surface reactions involving alkoxysilane reagents and hydrous silica gel. (The presence of surface-adsorbed water was found by these authors to increase the achievable levels of silane loading in these reactions.) Silica gel samples were first brought to constant humidity in a closed vessel containing saturated aqueous LiCl. A 1:4 (v/v) solution of liquid silane reagent and toluene was then combined with the silica gel in a 100-mL round-bottom flask (0.01 mol of reagnet to 1 g of silica). The resulting slurry was allowed to stir at ambient temperature for a period of 2 h and then under reflux for an additional 6 h during which the temperature was gradually increased to 100 °C (~15° increase/h). Purification involved repetitive washing with toluene (four times) and benzene (twice), alternated with centrifugation, with the centrifugate being discarded each time. The reagent-free material was finally dried at ambient temperature in a vacuum desiccator for a period of 24 h.

Method 6. Pure Reagent, Using Anhydrous Silica. In this method samples of silica gel, predried by evacuation at 100 to 200 °C, were simply saturated with liquid reagent. To minimize the amount of water entering the system, reactions were carried out in a drybox (N_2 atmo-

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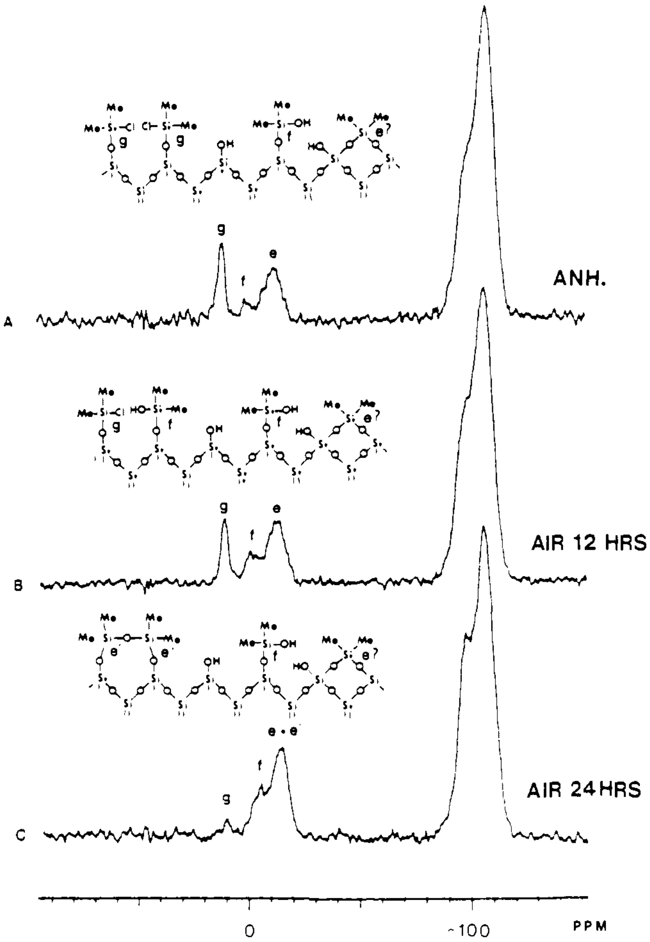


Figure 1. ^{29}Si (11.88 MHz) CP/MAS NMR spectra of the reaction products of dimethyldichlorosilane and silica gel (S-157): (A) directly after silylation; (B) exposed to air 12 h; and (C) exposed to air 24 h. Assignments implied by the structural inserts are meant to indicate representative hypothetical structural types, not specific structural arrangements.

sphere) by adding reagent dropwise to a bullet MAS spinner containing the silica gel. Following reaction (0.5 h), the spinner was capped and transferred quickly to the CP/MAS probe. Spectra were then obtained immediately, with dry N_2 as the driving medium for MAS operation.

Results and Discussion

1. Chlorosilane Silylations. Dimethyldichlorosilane. Reactions with this reagent were carried out on a number of silica gels. A typical ^{29}Si CP/MAS spectrum of the product material is seen in Figure 1A. (This sample was prepared by using method 2 of ref 5, gas-phase reaction with Fisher S-157 silica gel, predried at 200 °C under N_2 flow; silane loading: 202 mg/g.)

Chemical shifts for the three resonances in the "silane" region of Figure 1A, labeled g, f, and e, were measured at 9.4, −4.1, and −14.2 ppm, respectively. On the basis of the expected chemistry of $Si(CH_3)(Cl)_2$, the complete set of silane–silicon environments are species of the structural types $Si(CH_3)_2(Cl)(O-)$, $Si(CH_3)_2(OH)(O-)$, and $Si(CH_3)_2(O-)_2$. By use of the data of Tables I and II (including an assumed 7 ppm surface-induced offset, estimated chemical shifts for these species are calculated at 9 ppm, −5 ppm, and −14 ppm, respectively. These values correlate very well with the observed results. This correlation suggests that the resonance at −14.2 ppm (e in Figure 1A) can be identified with a dimethyldisiloxyl species, $Si(CH_3)_2(O-)_2$, the resonance at −4.1 ppm (f) with $Si(CH_3)_2(OH)(O-)$ groups, and the resonances at 9.4 ppm (g) with $Si(CH_3)_2(Cl)(O-)$ structures. A hypothetical segment of silica surface containing chemical environments qualitatively consistent with the resonance pattern in Figure 1A is shown in the diagram included in Figure 1. In this model the e resonance is attributed to silane species characterized by two siloxane bonds to the surface, while g and f resonances are assigned to singly attached species, containing an unreacted chlorine and hydroxyl group, respectively. These latter two assignments are given additional support by the spectra shown in Figures 1B and 1C, which were obtained for the sample of Figure 1A following exposure to atmospheric moisture for increasing periods of time (12 and 24 h). The distinct reversal in relative intensity exhibited by resonances g and f in this series of spectra is highly suggestive of a process in which chlorines on $Si(CH_3)_2(Cl)(O-)$ species (g) are converted into their hydroxyl analogues, $Si(CH_3)_2(OH)(O-)$ (f), by a substitution reaction with molecular water.

Table III. Analytical Data for Dimethyldichlorosilane Reaction Products[a,b]

Figure 4 spectrum	% C[c]	% C[c]	f^d	$f_g^{r\,e}$	$F_D^{Cl\,f}$	$F_D^{OH\,f}$	$F_D^{\,f}$
A	5.0	2.9	0.735	0.07	0.39	0.10	0.51
B			0.72	0.06	0.28	0.18	0.54
C	4.9	0.66	0.72	0.07	0.06	0.23	0.71

[a] Sample prepared using experimental method 2 of ref 5; observed loading = 202 mg/g. [b] S-157 silica: Surface hydroxyl density, $(OH)^i$ = 5.1 OH per 100 Å^2 (from ref 5); initial value of f_g before silylation, $f_g^i = 0.15$ (from ref 4) and surface area, (S.A.) = 750 m^2/g. [c] From elemental analysis (weight % C, corrected for a blank carbon content of 0.4%). [d] Calculated using eq 11 of ref 5. [e] Calculated using eq 10 of ref 5, following line shape deconvolution. [f] Fractional intensity of ^{29}Si silane resonance assigned to $Si(CH_3)_2(Cl)(O-)$, F_D^{Cl}; $Si(CH_3)_2(OH)(O-)$, F_D^{OH}; and $Si(CH_3)_2(O-)_2$, F_D, structures, with respect to the total silane intensity.

To obtain a more detailed picture of the chemical processes responsible for the spectral changes exhibited in Figure 1 we subjected these spectra to intensity analysis procedures similar to those reported earlier for trimethylsilylation.[5] In the "silane" region (10 to −15 ppm) the fractional contributions of resonances g, f, and e to the total silane intensity were determined by direct integration. Normalized numerical values for these quantities are designated F_D^{Cl}, F_D^{OH} and F_D, where $F_D^{Cl} = I_{Cl}/(I_{Cl} + I_{OH} + I_D)$, etc., and I_{Cl}, I_{OH}, and I_D are the integrated intensities of the resonances at 9, −4, and −14 ppm, respectively. The results of this analysis are given in Table III. The spectral features in the "silica" region (higher shielding than −80 ppm) were analyzed by means of the deconvolution methods described earlier[7] in order to obtain values for f, the ratio of the number of silane silicons and residual surface silanol sites and f_g^r, the fraction of residual surface silanols that are of the geminal hydroxyl type.[5] Also included in Table III are the results of elemental analysis, % C and %Cl, determined for the samples of Figures 1A and 1C.

An examination of the data in Table III reveals that the fractional contribution of resonance g (F_D^{Cl}) to the total silane intensity decreases from an initial value of 0.39 in Figure 1A to 0.06 in Figure 1C. Conversely, F_D^{OH} increases from 0.10 to 0.23 in this series of spectra. Such behavior is indicative of at least a partial transfer of intensity from the 9-ppm peak to the peak at −4 ppm, and is consistent with the simply hydrolysis process suggested above. Somewhat more surprisingly, the fraction of silane intensity attributable to $Si(CH_3)_2(O-)_2$ structures (F_D) can be seen to increase from 0.51 in Figure 1A to 0.71 in Figure 1C. This behavior is inconsistent with simple hydrolysis, since in this case one would predict a constant value of F_D.

One possible explanation of these results is that some of the singly attached $Si(CH_3)_2(Cl)(O-)$ or $Si(CH_3)_2(OH)(O-)$ structures undergo a subsequent reaction with surface hydroxyls (somehow catalyzed by atmospheric water) to produce more of the hypothetical doubly connected $Si(CH_3)_2(O-)_2$ moieties depicted by the structure e in the insert of Figure 1A. Since, in this situation surface hydroxyls would be consumed without changing the population of attached silane species, one would expect that the measured ratio of silane to unreacted silanol intenstiy (f) would increase in going from Figure 1A to Figure 1C. However, this prediction is inconsistent with the data of Table III, which show a slight trend of decreasing f for this series of spectra. This decrease may in fact reflect a minor loss of silane from the surface, arising from direct hydrolytic displacement by molecular water. Such a process would be consistent with the slightly smaller value of percent carbon observed for the bonded-phase material following exposure to the atmosphere. However, judging by the general similarity of the *f* and percent *C* data exhibited by the samples of Figures 1A and 1C, silane hydrolysis probably can be considered relatively inconsequential. Of more significance is the apparent increase in the population of surface groups containing two siloxane bonds without a corresponding decrease in the number of unreacted surface hydroxyl sites.

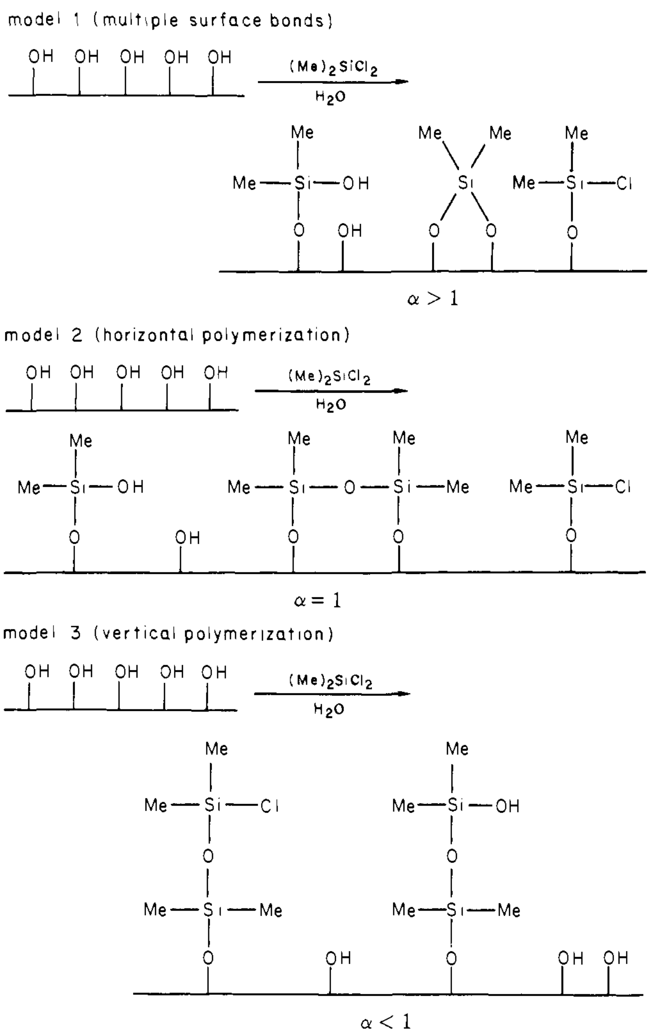
A more consistent interpretation of this behavior is included in the sequence of structural inserts included in Figures 1A–1C. In this description the hydrolysis of one of a pair of neighboring $Si(CH_3)_2(Cl)(O-)$ sites (g of Figure 1A) gives rise to $Si(CH_3)_2(Cl)(O-)$ and a $Si(CH_3)_2(OH)(O-)$ site in close physical proximity. With a minor adjustment in bond angles such a pair is presumed to condense spontaneously, releasing HCl and resulting in the kind of cross-linked arrangement illustrated by the structure e′ in Figure 1C. The disiloxane species formed as a result of this process are indistinguishable, with regard to the expected ^{29}Si chemical shifts, from the doubly connected e structures suggested in Figure 1A. However, in this cross-linking model, no further reaction of surface silanol sites is required, and *f* and percent carbon values are predicted to remain unchanged. This interpretation is clearly in much better agreement with the present experimental results and is also consistent with the work of others, particularly that of Gilpin and Burke.[13]

With this interpretation in mind the original assignment of the resonance at −14 ppm in Figure 1A to a multiple surface-bonded e-type structure must be reexamined. Since the presence of water has been linked to the formation of silane–silane bonds, the evidence for surface hydrolysis embodied in resonance f in Figure 1A is of particular significance. The presence of this peak indicates that before the spectrum of Figure 1A was obtained a certain amount of molecular water must have been available on the surface. Such water may have been introduced inadvertently during the initial reaction period, during the subsequent sample handling stages, or may originate from the incomplete removal of physically adsorbed H_2O during preevacuation. Previous results[6] have shown that the preparation of surfaces that are completely water-free will be difficult or impossible to achieve without the accompaniment of concurrent silanol condensation reactions. Therefore, any realistic model describing the primary reaction of fully hydrated silica with $Si(CH_3)_2Cl_2$ must consider the presence of at least a trace amount of surface H_2O. In general, such a model must also allow for a variety of possible simultaneous reaction mechanisms, involving both simple hydrolysis and silane–silane or silane–surface condensation processes.

In the presence of surface water, disiloxane species can be expected to arise as a result of three principal chemical processes. These possibilities are illustrated as models 1, 2, and 3 in Scheme I. The first two (model 1 and model 2) have been described above and involve the formation of multiple surface-to-silane bonds and silane-to-silane pairwise cross-linking, respectively. In model 3 the presence of water during the initial reaction stages allows for the possibility of prepolymerization of the silane phase, followed by subsequent attachment (or simple precipitation without bonding) on the silica surface. In all three models adsorbed water hydrolyzes unreacted Si–Cl bonds in some of the dimethylchlorosilane groups.

These three models differ in the ratio of the average number of reacted surface hydroxyls to the number of attached silane groups. This ratio (designated by the symbol α) will be greater than unity for model 1, exactly equal to unity for model 2, and less than unity for model 3. In addition, only in model 1 (multiple surface bonds) is the presence of water not stoichiometrically required for the formation of disiloxane species. This suggests that only in this case will measured values of F_D be relatively independent of the initial state of surface hydration (i.e., the amount of surface-adsorbed H_2O present).

Scheme I



To investigate this consideration further, two samples of Fisher S-157 silica gel with different surface H_2O concentrations were reacted with dimethyldichlorosilane, using method 6. ^{29}Si spectra of the resulting materials are shown in Figure 2. Figure 2B was obtained for a sample predried at 160 °C under vacuum (10^{-5} torr) for 24 h. The spectrum in Figure 2A was obtained following reaction of $Si(CH_3)_2Cl_2$ with an undried S-157 sample. From previous results[7] the expected initial bulk density of molecular water in these samples is estimated to be 3 mg/g and 14 mg/g, respectively.

A comparison of the relative intensities of the peaks at 9 and −14 ppm in the silane region in these two spectra clearly shows that the presence of the $Si(CH_3)_2(O-)_2$ structure is strongly correlated with the amount of H_2O initially present. This can be taken then as supportive (*albeit* not conclusive) evidence that either or both of the second and third reaction models above best describes the initial reaction of dimethyldichlorosilane with the silica surface. It is also interesting to note that, although both samples were prepared under essentially identical conditions (except for the initial state of surface hydration), the relative intensity of the "silane" region in the more anhydrous sample is visibly less (with respect to the resonances associated with unreacted surface OH sites) than in the case of the sample reacted in the presence of adsorbed H_2O. This suggests that, in addition to dictating the *course* of the chemistry of dimethyldichlorosilane reactions, molecular water may also be instrumental in determining the *extent* to which silylating actually occurs. This view is consistent with the findings of Herzberg and Erwin,[14] who concluded,

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(14) Herzberg, W. J.; Erwin, W. R. *J. Colloid Interface Sci.* **1970**, *33*, 172.

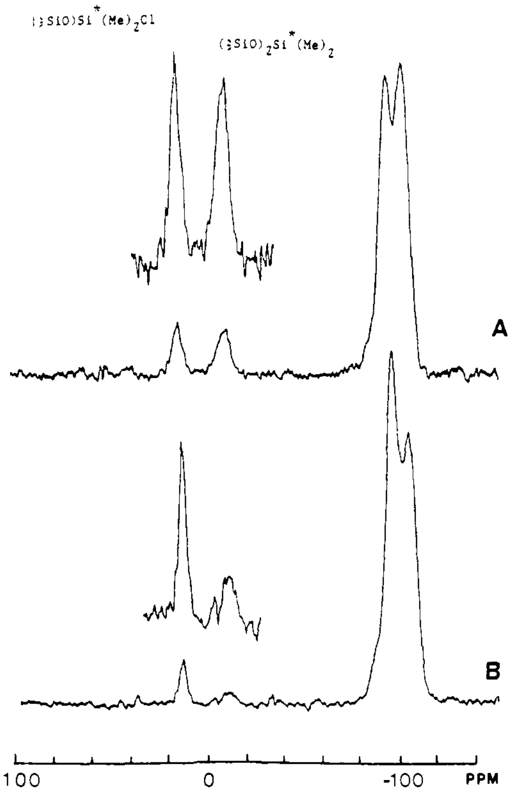


Figure 2. ^{29}Si (11.88 MHz) CP/MAS NMR spectra of products of reaction of excess dimethyldichlorosilane with Fisher S-157 silica: (A) with no predrying; (B) following vacuum predrying at 160 °C.

on the basis of tritium labeling studies of $Si(CH_3)_2Cl_2$ reactions on porous glass, that in the absence of water there is no reaction between the surface and the reagent at all. The presence of water was believed by the authors to allow the formation of polysiloxane polymers, which then reacted with, or precipitated onto the surface.

Additional arguments concerning the three reaction models can be made on the basis of predicted differences in the magnitude of the effective bonding order, α, corresponding to each model. The success of the formalism developed earlier for extracting from ^{29}Si CP/MAS spectra quantitative information related to surface populations in trimethylsilyl derivatizations suggests that these or similar procedures might be extended to include reaction processes involving a variable bonding order. The necessary methodology for such applications is developed below.

Extended Formalism for Dimethyldichlorosilane Reactions. If S is defined as the surface concentration (per 100 Å^2) of observable silane groups and α is defined as the number of surface hydroxyl groups reacted per attached silane moiety, then the surface concentration of reacted hydroxyl groups is αS. Assuming that steric constraints will allow only a single hydroxyl on each geminal site to react with dimethyldichlorosilane, then

$$\alpha S = G^{r} + L^{r} \tag{1}$$

where G^r and L^r are the surface concentrations of reacted (r) geminal and lone-hydroxyl silanol sites, respectively; i.e., αS is the surface concentration of reacted silanol sites. Values of f and f_g^r determined experimentally from an examination of ^{29}Si NMR peak intensities have essentially the same meaning and roles as described in detail for trimethylsilyl systems.[7] Algebraic manipulation of these quantities, in analogy to the earlier development for the trimethylsilyl case, can be used to obtain an expression for the concentration of hydroxyl groups on the initial (unreacted) silica surface, $(OH)^i$.

$$(OH)^{i} = \frac{S}{f}(1 + f + f_{g}^{r}) \tag{2}$$

Since $(OH)^i$ is known from previous results[6] and f and f_g^r can be obtained experimentally from ^{29}Si intensities, eq 2 can be used to solve for α, if the quantity S can be determined. Unfortunately, as was seen previously,[5] S depends on both the change in weight accompanying the bonding reaction (ΔW) and the effective molecular weight (EMW) of the attached silane moiety. In the case of reactions involving dimethyldichlorosilane, a valid determination of EMW depends upon both the choice of a correct reaction model and knowledge of the source of contamination by H_2O, since both factors contribute to the observed change in sample weight per mole of attached silane.

This problem can largely be circumvented by noting that, irrespective of the chemical identity appropriate to the silicon environment of the attached moiety, the ratio of the number of carbon atoms to silane silicon atoms will always be two; i.e., each silane moiety contains two methyl groups, which constitute the only source of carbon in these samples. Therefore, and evaluation of the surface concentration of carbon will be sufficient to determine the surface concentration of the silane moiety, S.

For the samples of Figure 1 the amount of elemental carbon is given by the % C data of Table III. One gram of product, however, actually corresponds to $(1 - \Delta W/1000)$ g of original silica gel, where ΔW is the weight gain (in mg/g) resulting from the reaction. The ratio of carbon to initial silica is, therefore

$$\frac{\text{grams of carbon}}{\text{grams of silica}} = \frac{\%\,C/100}{(1 - \Delta W/1000)} \tag{3}$$

Converting to surface concentration of C atoms per 100 Å^2, one has

$$(C) = \frac{(\%\,C)(502)}{(S.A.)(1 - \Delta W/1000)}$$

For $Si(CH_3)_2Cl_2$ reactions, $S = (C)/2$. From this relationship and eq 3, the data of Table I yield the value, 2.1/100 Å^2, for the sample of Figure 1A. With a value for S, eq 2 can now be rearranged and solved for α.

$$\alpha = \left[(OH)^{i}\frac{f}{S} - 1 - f_{g}^{r}\right] \tag{4}$$

For the sample of Figure 1A, by using the data of Table III one computes a value of 0.97 ± 0.05 for α. (The stated uncertainty in α arises primarily from estimated uncertainty in f (±0.01) and S (±0.1).) The results of this analysis show that, even in the case of the "anhydrous" specimen of Figure 1A, the "average" number of surface bonds formed per molecule of attached silane phase is, within experimental error, equal to one. This is most consistent with the predictions of model 2. In contrast, model 1 predicts a significantly larger value of α. Algebraic development of quantities already defined leads to the equation

$$\alpha = \frac{S(1 + F_D)}{S} = 1 + F_D$$

With $F_D = 0.51$ (taken from Table III), model 1 predicts an α value of 1.51 for this example.

For model 3 a value of α significantly less than one is expected. For singly attached silane polymers having an average chain length of two silane units, the surface concentration of reacted hydroxyls will be equal to the surface concentration of $Si(CH_3)_2(O\text{–})$ groups, since by assumption only these sites are involved in surface bonding. In this case, α is equal to F_D. For longer chains, α will be correspondingly smaller (less than F_D), since in these cases, in addition to end-chain $Si(CH_3)_2(OH)(O\text{–})$ and $Si(CH_3)_2(Cl)(O\text{–})$ species, a number of "internal" $Si(CH_3)_2(O\text{–})$ groups will also not be directly involved in surface bonding. For the sample of Figure 1A these considerations indicate that the maximum value of α predicted by model 3 is 0.51.

As a further check on the magnitude of α, as well as the internal consistency of the procedures that have been used, the elemental chlorine data of Table I can also be used as the basis for a similar analysis. The assignment of the resonance at 9 ppm to a $Si(CH_3)_2(Cl)(O\text{–})$ species containing a single unreacted chlorine group implies that the ratio of the surface concentrations of chlorine and bonded silane will be given by $F_D^{Cl} = (Cl)/S$, where (Cl) is the surface density of Cl atoms. This relationship will be valid for any mixture of the three reaction models presented above. As in the case of carbon, the surface density of chlorine atoms can be calculated from percent Cl data, by use of an expression analogous to eq 3. Explicitly

$$(\mathrm{Cl}) = \frac{(\%\ \mathrm{Cl})(170)}{(\mathrm{S.A.})(1 - \Delta W/1000)} \qquad (5)$$

For the sample of Figure 1A, by use of the data of Table I, (Cl) is computed to be 0.82. With this value of (Cl) and the value of F_D^{Cl} given in Table I, the surface concentration of bonded phase is computed to be $S = (\mathrm{Cl})/F_D^{\mathrm{Cl}} = 0.82/0.39 = 2.1$. Since this value of S is identical with that determined using % C data, the use of eq 4 in this case will also give a value of $\alpha \sim 1$.

For the air-exposed sample corresponding to Figure 1C, a % Cl value of 0.66 implies that about 77% of the original chlorine has been eliminated from the surface as a result of exposure to the atmosphere (i.e., originally % Cl = 2.9). This is in fair agreement with what can be estimated from a comparison of F^{Cl} values measured for the spectra of Figures 1A and 1C (0.39 and 0.06, respectively). These values suggest that about 85 percent has been removed.

This loss of chlorine, presumably to substitution by $-\mathrm{OSi}<$ or OH, in addition to the small loss of bonded silane suggested by the slightly smaller % C value observed for the sample of Figure 1C, will change the portion of the total sample weight attributable to attached silane material. Therefore, an expression of "grams carbon" in terms of "grams silica gel" will require a somewhat different correction factor, $(1 - \Delta W/1000)^{-1}$, in this situation than if there were not silane depletion. Empirically, exposure of dimethyldichlorosilane-reacted S-157 silica to gaseous H_2O was observed to result in a decrease of 3% of the weight gained in the initial silylation reaction. Therefore, for the sample of Figure 1C the correction will be about $(1 - 0.18)^{-1} = 1.22$, instead of the value $(1 - 0.202)^{-1} = 1.25$ that was determined for the sample of Figure 1A. Except for this difference all of the procedures derived for the sample of Figure 1A are equally applicable to the sample of Figure 1C. Thus, for this sample (1C) eq 3 and the data of Table I yield $S = (\mathrm{C})/2 = 2.0$, a value slightly smaller than that observed for the sample of Figure 1A. As in that case, α can be determined by using eq 4 and the data of Table I, yielding $\alpha = 1.08 \pm 0.1$. By comparison, models 1 and 3 give predictions of 1.7 and 0.7, respectively, for the α values of the sample of Figure 1C. These results provide supportive (albeit not conclusive) evidence that, in both secondary and primary reaction processes of dimethyldichlorosilane, single surface-to-silane attachments constitute the primary mode of organization of the siloxane phase on the silica surface.

Methyltrichlorosilane. Because of the increased functionality of methyltrichlorosilane, silica surfaces derivatized with this reagent can be expected to have a more diverse set of surface structures than reaction products of dimethyldichlorosilane. This diversity is reflected in the ^{29}Si NMR spectra of Figure 3. These spectra were obtained on samples of Fisher S-157 silica (predried under N_2 at 200 °C) immediately following gas-phase reaction method 4)[5] with methyltrichlorosilane (Figure 3A) and after subsequent treatment procedures (Figure 3C-3D). These procedures involved exposing the sample of Figure 3A to atmospheric moisture for increasing periods of time (Figure 3B, 3C) and heating the hydrolyzed surface of the sample of 3C to 200 °C (Figure 3D).

As in the case of dimethyldichlorosilane, the empirical shift additivity relationships of Table II and the chemical shift data of Table I were used to estimate certain ^{29}Si chemical shifts of silane species expected in the reaction of $\mathrm{Si(CH_3)Cl_3}$ with silica gel. Details of the procedure used in these calculations, along with measured ^{29}Si shifts, are summarized in Table IV. As can be seen from Table IV, the resulting predicted shifts correlated well with experimental values measured from the spectra of Figure 3. This agreement led to the structural assignments embodied in the labels h-l given to the hypothetical surface structures shown as inserts in Figure 3.

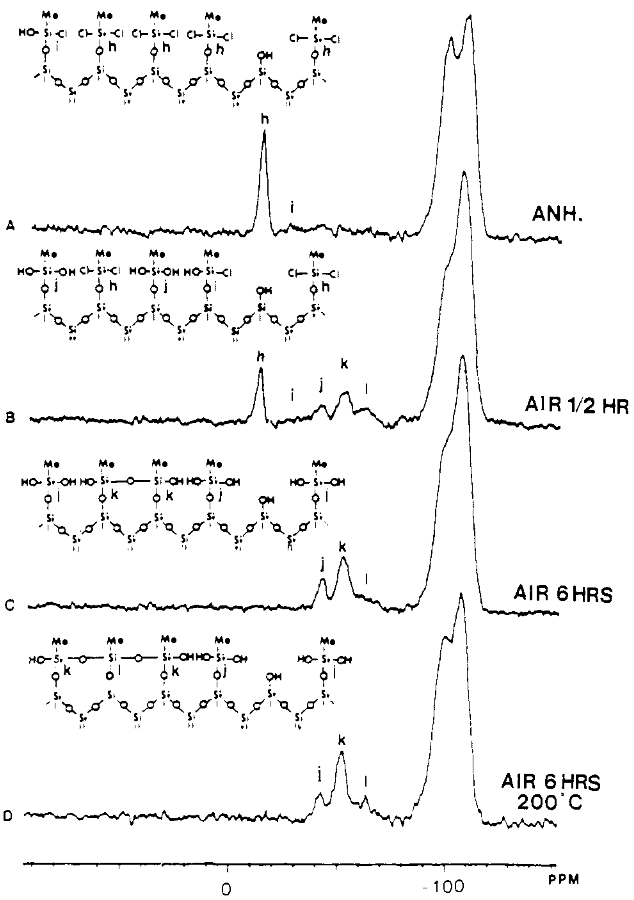


Figure 3. ^{29}Si (11.88 MHz) CP/MAS NMR spectra of reaction products of methyltrichlorosilane and silica gel (S-157): (A) directly after silylation; (B) exposed to air for 0.5 h; (C) exposed to air for 6 h; (D) after heating the sample of C at 200 °C for 24 h.

Table IV. Comparison of Predicted and Observed ^{29}Si Shifts of Silica Reacted with Methyltrichlorosilane

structure	procedure[a]	predicted[b] shift	closest obsd[c] shift	assignment[d]
$\mathrm{SiCH_3(O-)_3}$	$\delta T + (7)^{\mathrm{vi}}$	−60	−62	(l)
$\mathrm{SiCH_3(OH)(O-)_2}$	$\delta T + (7)^{\mathrm{vi}} + (9)^{\mathrm{i}}$	−51	−52	(k)
$\mathrm{SiCH_3(OH)_2(O-)}$	$\delta T + (7)^{\mathrm{vi}} + 2\cdot(9)^{\mathrm{i}}$	−42	−42	(j)
$\mathrm{SiCH_3(Cl)(O-)_2}$	$\delta T + (7)^{\mathrm{vi}} + (22)^{\mathrm{ii}}$	−38	−42	
$\mathrm{SiCH_3(OH)(Cl)(O-)}$	$\delta T + (7)^{\mathrm{vi}} + (9)^{\mathrm{i}} + (22)^{\mathrm{ii}}$	−29	−29	(i)
$\mathrm{SiCH_3(Cl)_2(O-)}$	$\delta T + (7)^{\mathrm{vi}} + 2\cdot(22)^{\mathrm{i}}$	−11	−14	(h)

[a] Procedure used in calculating predicted ^{29}Si–chemical shifts for $\mathrm{Si(CH_3)(Cl)_3}$ reaction products. δT is the chemical shift of a $\mathrm{CH_3Si^*(OSi)_3}$ group obtained from the results of previously reported solution-state NMR studies. (From Table I, $\delta T = -67$ ppm.) Additional terms in these sums are expected shift corrections resulting from the chemical shift effects summarized in Table II. The actual magnitude of the substitution effect (in ppm) is indicated in parentheses. Superscripts above these bracketed quantities denote the rule number (from Table II) invoked. [b] Magnitude of predicted ^{29}Si shift obtained using the procedure defined above. [c] Closest resolved resonance to the calculated shift that was actually observed in the ^{29}Si spectra of Figure 3. [d] Tentative assignment designation of the resonances in Figure 3.

As an aid to the interpretation of observed changes in intensities and chemical shifts, the spectra of Figure 3 were analyzed to give "fractional populations" appropriate to each resonance, using a formalism analogous to that employed for $\mathrm{Si(CH_3)_2Cl_2}$ reaction products. For example, the quantity $F_T^{\mathrm{Cl_2}}$ is defined by

$$F_T^{\mathrm{Cl_2}} = I_{\mathrm{Cl_2}}/(I_{\mathrm{Cl_2}} + I_{\mathrm{Cl,OH}} + I_{\mathrm{Cl}} + \ldots) \qquad (6)$$

Table V. Analytical Data for Reaction Products of S-157 Silica[a] with Methyltrichlorosilane

Figure 3 spectrum	surface coverage data				fractional contribution of assigned resonances to total silane intensity[b]						total fraction of silane groups with 1, 2 and 3 siloxane bonds		
	% C	f	f_g^r	α	F_{TCl_2}	$F_{TCl,OH}$	F_{TCl}	$F_{T(OH)_2}$	F_{TOH}	F_T	1	2	3
A	2.2	0.50	0.04	0.8	0.61	0.10	0.07	0.08	0.07	0.07	0.79	0.14	0.07
B		0.58	0.05		0.27	0.03	0.06	0.13	0.30	0.21	0.43	0.36	0.21
C	1.9	0.53	0.04	1.3	0.0	0.0	0.0	0.21	0.57	0.22	0.21	0.57	0.22
D	1.8	0.48	0.05	1.3	0.0	0.0	0.0	0.16	0.61	0.23	0.16	0.61	0.23

[a] Observed loading: 216 mg/g (anhydrous). After exposure to air (1 h) a 36 mg/g reduction in sample weight was observed. In the elemental analysis however, samples were exposed to atmospheric moisture in an uncontrolled manner. As a result, numerical values reported for α (calculated using eq 4 and an "air-exposed" ΔW of 180 mg/g) must be considered semiquantitative, at best. [b] Calculated using integrated ^{29}Si NMR areas and eq 10. (Definitions of symbols are given in the text.) Fractional areas were computed by arbitrarily dividing the silane region into areas separated by points midway between the "predicted" chemical shifts given in Table V.

where $I_{Cl,OH}$ stands for the integrated intensity associated with the structural moiety $Si(CH_3)(Cl)(OH)(O–)$, etc. A summary of the results of this analysis is given in Table V. Also included in Table V are the "coverage"-related parameters, f and f_g^r, determined as usual by a line-shape deconvolution of the silica gel region and the total integral intensity associated with this and the silane region of the spectrum.

The tentative assignments that were based on the general agreement between empirically predicted and observed chemical shifts include identifying the resonances at −14 and −29 ppm with chlorinated structures. These assignments are consistent with the fact that the corresponding relative signal amplitudes are attenuated and finally completely eliminated with increasing degrees of surface hydration (Table V). In addition, resonance h in Figure 3A can quite unambiguously be assigned to a methyldichlorosiloxane $SiCH_3(Cl)_2(O–)$ group, since the predicted resonance positions of all other chemically permissible species are substantially to higher shielding than −14 ppm.

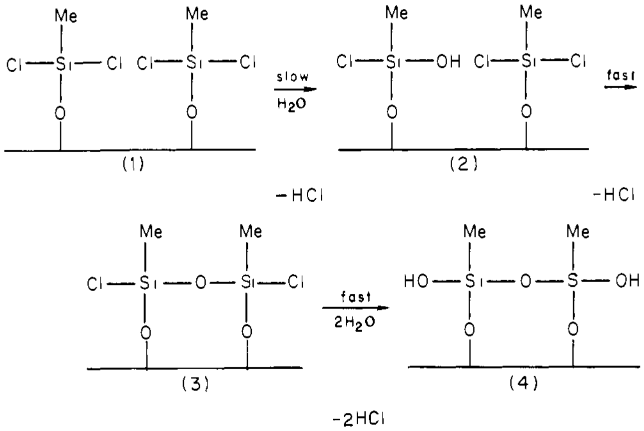
The data in Table V also show that the great majority of surface silicon groups in the initially reacted sample (Figure 3A) are associated with chemical environments having only one siloxane bond. This suggests that, as in the case of dimethyldichlorosilane reactions, only singly surface-attached species are present in the silane moieties of the primary reaction product of anhydrous silica gel and methyltrichlorosilane.

The spectra of Figure 3 and the data of Table V indicate that, following the exposure of the "anhydrous" sample of Figure 3A to atmospheric moisture, there is, in addition to the loss of intensity associated with chlorinated species, $SiCH_3(Cl)_2(O–)$, $SiCH_3(Cl)(OH)(O–)$, $SiCH_3(Cl)(O–)_2$, a substantial increase in the relative spectral intensity of features identified with hydrolyzed structures, $SiCH_3(OH)_2(O–)$ and $SiCH_3(OH)(O–)_2$. The total relative intensity associated with silane groups having one Si-O-Si connection (1 in Table V) also decreases substantially, going from 0.79 in Figure 3A to 0.16 in Figure 3D. At the same time the total relative intensity associated with surface silane groups having two and three Si-O-Si connections (2 and 3 in Table V) increases. As in the case of $Si(CH_3)_2Cl_2$ reaction products, it seems likely that these results reflect the simultaneous occurrence of hydrolysis and condensation reactions involving the silane phase.

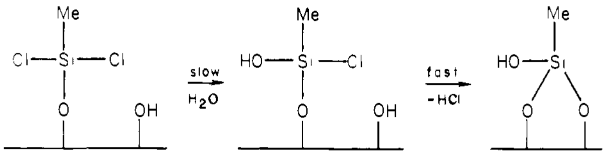
The hypothetical surface structures illustrated in Figure 3, although qualitatively consistent with the observed spectral changes, are intended to be suggestive only, and are not meant to imply a detailed knowledge of the actual reaction mechanisms or the precise nature of the silane "phase". Nevertheless, it may be significant that in the spectra of the completely hydrated samples (Figures 3C and 3D) the most intense feature is the resonance at −53 ppm, which is assigned to a species containing two siloxane bonds and one hydroxyl group, $SiCH_3(OH)(O–)_2$. This, however, is exactly what one would expect if one assumes that in the presence of H_2O most of the singly attached dichlorosilane groups (h of Figure 3A) undergo *pair-wise* condensation reactions, accompanied (or followed) by the hydrolysis of residual Si–Cl moieties. A possible sequence of events illustrating this kind of mechanism is shown in Scheme II.

In this sequence reaction rates for processes leading from stage (2) to stage (4) must be fast with respect to the initial hydrolysis, (1) (2), since the spectra of Figure 3 show only trace amounts of the monochloro species that would characterize the intermediate stages (2) and (3). Fast hydrolysis of residual chlorines in $Si(CH_3)(Cl)(OH)(O–)$ groups present at stage (2) might alternatively lead to the formation of the singly attached dihydroxy $Si(CH_3)(OH)_2(O–)$ structures of Figures 3B, 3C, and 3D.

Scheme II



Scheme III

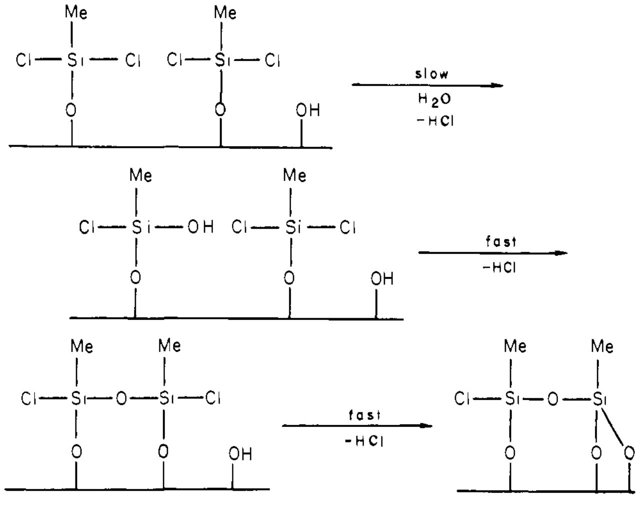


Unlike the dimethyldichlorosilane case, the methyltrichlorosilane data of Table V also indicate that the ratio of the population of silane groups to that of unreacted surface hydroxyls increases somewhat immediately following exposure to atmospheric water. This is manifested in the higher observed values of f, particularly for the sample of Figure 3B, with respect to the sample of Figure 3A (i.e., 0.58 vs. 0.50). This observation may indicate that, following the initial reaction, a portion of the silane phase participates in subsequent reactions with the silica surface itself. This kind of delayed behavior may be assisted by the greater assumed reactivity of intermediate structures associated with stages (2) and (3) in Scheme II. Two possible examples of this are illustrated in Schemes III and IV.

Other mechanisms that could lead to similar products can easily be imagined (e.g., additional surface reactions, hydrolysis, silane–silane condensation of the products formed in Scheme IV, etc.). In these models, secondary surface-to-silane bonding involving $SiCH_3(Cl)_2(O–)$ groups is assumed to proceed at a negligible rate in the absence of H_2O.

From the data of Table V the value of f can be seen to decrease from that measured for the sample of Figure 3B as a consequence of further hydration (Figure 3C) and thermal treatment (Figure 3D). As in the case of dimethyldichlorosilane products, this may reflect the partial removal of silane from the surface as a result of hydrolytic displacement by H_2O (assisted perhaps by the HCl

Scheme IV



released in these reactions). This view is supported by % C data obtained for the samples of Figures 3A, 3B, and 3D (Table V), which show a slight decreasing trend (18%) in going from sample A to sample D. Unfortunately, because of the extreme lability of unreacted Cl groups in these samples, handling procedures used in the elemental analysis preclude the possibility of utilizing the methods described for $Si(CH_3)_2Cl_2$ reactions to determine changes in the bonding order, α, with the accuracy obtained previously. Nevertheless, these data semiquantitatively support the view that initially only single surface-to-silane attachments are formed (i.e., $\alpha \approx 1$), while following exposure to H_2O the silane phase is characterized by an increasing bond order, which reaches a value somewhere between 1.0 and 1.5 for the sample of Figure 3D.

In retrospect, this evidence for additional surface-to-silane bonding for $SiCH_3Cl_3$ might explain the slightly higher value of α observed for $Si(CH_3)_2Cl_2$ reaction products following exposure to the atmosphere. In the $Si(CH_3)_2Cl_2$ case, however, analogous processes that lead to dimethylsilane structures with two surface-to-silane bonds (e.g., e of Figure 1) must be of relatively minor importance, since it was shown that for condensation reactions dominated by this mechanism one would predict a substantially higher value of α than the value actually observed.

Considered in total, these results have shown that the reaction of $SiCH_3Cl_3$ with the surface of silica gel is considerably more complex than the case of $SiCH_3Cl_3$. Nevertheless, a number of basic similarities are evident. As in the $Si(CH_3)_2Cl_2$ case, only single surface-to-silane attachments appear to be present in the silane phase of silica samples that have been reacted with $SiCH_3Cl_3$ under anhydrous conditions. The introduction of water gives rise to analogous monohydroxy and dihydroxy species (reflecting simple hydrolysis) and is associated with processes leading to a substantial increase in the number of silane groups with two and three siloxane bonds (reflecting additional condensation rections). Unlike the case of $Si(CH_3)_2Cl_2$, where such secondary condensation processes arise primarily (or exclusively) because of pairwise cross-linking, reaction products of $SiCH_3Cl_3$ appear also to undergo secondary surface-to-silane bonding in the presence of H_2O. For $SiCH_3Cl_3$ the low intensity or absence of peaks identified with monochlorosilane species, $SiCH_3(Cl)(O\!-)_2$ and $SiCH_3(Cl)(OH)(O\!-)$, suggests that these intermediates are much more reactive than the initial $Si(CH_3)(Cl)_2(O\!-)$ species, both to hydrolysis and to additional condensation reactions involving the participation of adjacent silane groups or hydroxyl sites on the silica surface.

2. Ethoxysilane Reactions. In most fundamental respects the chemical processes underlying silylation reactions involving alkoxyalkysilanes can be expected to be quite similar to those characterizing the surface reactions of analogous chloroalkylsilane reagents. Both classes of substances react with surface hydroxyls via a direct substitution mechanism that, in principle, can result in the formation of silane species that are attached to the silica surface by single or multiple siloxane bonds. Molecular water, introduced intentionally or as a contaminant in either reaction system, can result in the hydrolysis or additional condensation of unreacted functional groups present in the initial bonded phase. For chlorosilane reagents, the principal byproduct of such processes, HCl, does not itself interact with the silica surface[15] and can usually be removed by brief sample evacuation. However, in the case of alkoxysilanes, the subsequent reaction of byproduct alcohol molecules with surface hydroxyl groups must be considered a likely possibility. (The use of alcohols as reactants in the preparation of hydrophobic chromatographic stationary phases is, in fact, a commonly employed alternative to the use of organosilane reagents.)[17,18]

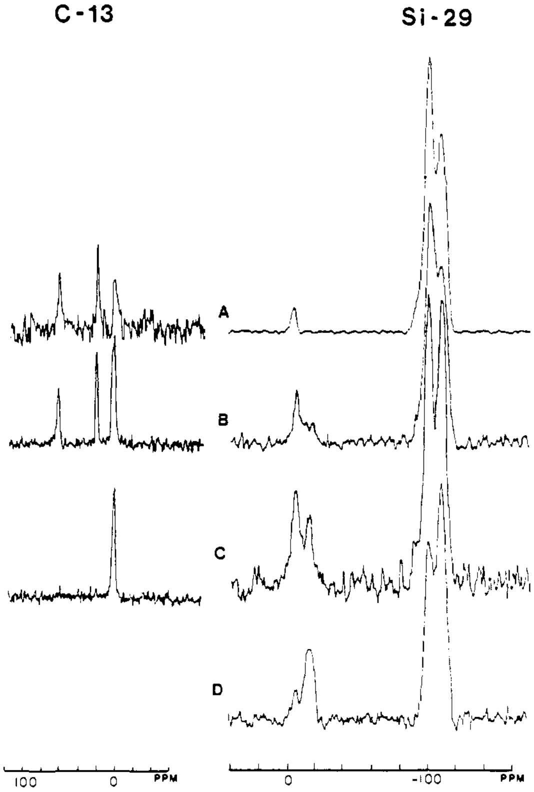


Figure 4. ^{13}C (15.04 MHz) and ^{29}Si (11.88 MHz) CP/MAS NMR spectra of dimethyldiethoxysilane reaction products: (A) predried silica (refluxed at 118 °C, 6 h); (B) predried silica gel (gas phase reaction, 240 °C); (C) hydrous silica (refluxed at 110 °C); and (D) sample of C heated to 150 °C).

The additivity relationships of Table II indicate that ^{29}Si chemical shift differences between SiOEt and SiOH moieties will probably be considerably smaller than corresponding Si–Cl vs. Si–OH differences. These considerations suggest that the study of ethoxymethylsilane reaction products will be less straightforward than the other cases presented here and elsewhere.[5,6] In general, the interpretation of experimental results obtained for ethoxysilane reactions requires a somewhat more qualitative approach than that employed in the study of chlorosilane and hexamethyldisilazane reaction products.

Dimethyldiethoxysilane. As in the case of $Si(CH_3)_2Cl_2$, $Si(CH_3)_2(OC_2H_5)_2$ reactions were carried out under a variety of experimental conditions that were expected to cover a wide range of chemical behavior. This diversity is evident in the ^{29}Si and ^{13}C spectra shown in Figure 4, obtained on samples prepared by the reaction of $Si(CH_3)_2(OC_2H_5)_2$ with TES2 silica gel under different experimental conditions.

The sample corresponding to Figure 4A was prepared by refluxing predried TES2 silica gel with $Si(CH_3)_2(OC_2H_5)_2$ for 6

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h at 118 °C. Following the reaction, excess reagent was removed by repeated washings with toluene and benzene. In the silane region of the ^{29}Si spectrum there is a resonance of rather low intensity at about 5 ppm. On the basis of the above-mentioned chemical shift additivity relationships, this peak can tentatively be assigned to a surface-attached silane structure of the general type $Si(CH_3)_2(OC_2H_5)(O-)$. This assignment is qualitatively consistent with the ^{13}C spectrum of this sample, which shows strong resonances at 60 and 17 ppm. From consultation of available literature data,[16] one can assign the two peaks at 60 and 17 ppm to methylene and methyl carbons, respectively, in ethoxy groups. The sample of Figure 4B was also prepared from predried TES2 silica. In this case reactions were carried out at 240 °C with pure reagent in the gas phase, using method 3 of ref 7. The ^{29}Si spectrum of this sample is quite similar to that obtained for the sample of Figure 3A. The low ^{29}Si signal intensity of the resonances in the silane region relative to that of resonances in the silica region suggests again that, even under the more vigorous reaction conditions employed here, surface-to-silane bonding is relatively inefficient in the absence of molecular water. This spectrum also exhibits a shoulder at −14 ppm which, from empirical ^{29}Si chemical shift patterns and the results obtained from studies of $Si(CH_3)_2Cl_2$ reaction products, can be assigned to dimethyldisiloxane silicon environments. However, considering the conclusions above, the identification of the surface structural type or types responsible for this resonance will require additional experimental evidence. As in the case of Figure 4A, the ^{13}C spectrum of this material also shows features characteristic of silicon-attached ethoxy moieties.

In the preparation of the sample of Figure 4C, $Si(CH_3)(OC_2H_5)_2$ bonding was carried out using TES2 silica gel and experimental method 5 (i.e., reflux in toluene solutions at 115 °C). As has been mentioned above, under these conditions the initial silica surface has associated with it about 20 wt % adsorbed H_2O. In agreement with the findings of Majors and Hopper,[12] a comparison of relative spectral intensities in the "silane" (9 to −17 ppm) and silica–silanol (−90 to −100 ppm) regions of the ^{29}Si NMR spectrum of this sample shows that surface-to-silane bonding in this case is significantly more complete than for the samples of Figures 4A and 4B (with predried silica). The relative intensity of the resonance at −14 ppm, assigned to $Si(CH_3)_2(O-)_2$ species, is also somewhat greater in this case.

The fact that the ^{13}C CP/MAS spectrum of Figure 4C shows no resonances corresponding to silicon-attached ethoxy carbons implies that the presence of water inhibits (or displaces) the subsequent combination of ethoxy groups with the silica surface. In addition, this indicates that the resonance at about −5 ppm in the ^{29}Si spectrum must be assigned to a $Si(CH_3)_2(OH)(O-)$ species, rather than the $Si(CH_3)_2(OC_2H_5)(O-)$ classification suggested for the samples of Figures 4A and 4B. This assignment would be consistent with the statement given above that hydroxy and alkoxy species will not differ significantly in their ^{29}Si chemical shifts.

The spectrum of Figure 4D was obtained from the sample of Figure 4C, following the heating of this material to 150 °C for a period of about 3 h. In close similarity to the behavior observed in the case of air-exposed chlorosilane reaction products, the resonances corresponding to structures of the $Si(CH_3)_2(O-)_2$ and $Si(CH_3)_2(OH)(O-)$ types in the ^{29}Si spectra of Figures 4C and 4D undergo a substantial redistribution of spectral intensity as a result of this secondary heating. The measured value of F_D (the fractional silane population of $Si(CH_3)_2(O-)_2$ groups) increases from 0.41 in Figure 4C to 0.83 in Figure 4D. The ratio of the total intensity in the silane region to that associated with unreacted hydroxyl groups (f) is, however, quite similar for these two spectra ($f = 0.56$ in Figure 4C and 0.58 in Figure 4D). This indicates that the processes leading to the formation of additional $Si(CH_3)_2(O-)_2$ structures probably do not significantly involve the further participation of surface hydroxyls groups. These observations suggest that, as in the case of $Si(CH_3)_2Cl_2$ reaction products, the subsequent condensation of the initially attached silane phase involves the formation of pairwise cross-linked structures, instead of multiple surface-to-silane attachments. Since this cross-linking process was shown to dominate both primary and secondary reaction stages in the case of $Si(CH_3)_2Cl_2$, it is quite possible that all or most of the intensity associated with the $Si(CH_3)_2(O-)_2$ resonance in the ^{29}Si spectra of Figure 4 can be attributed to this kind of structural environment.

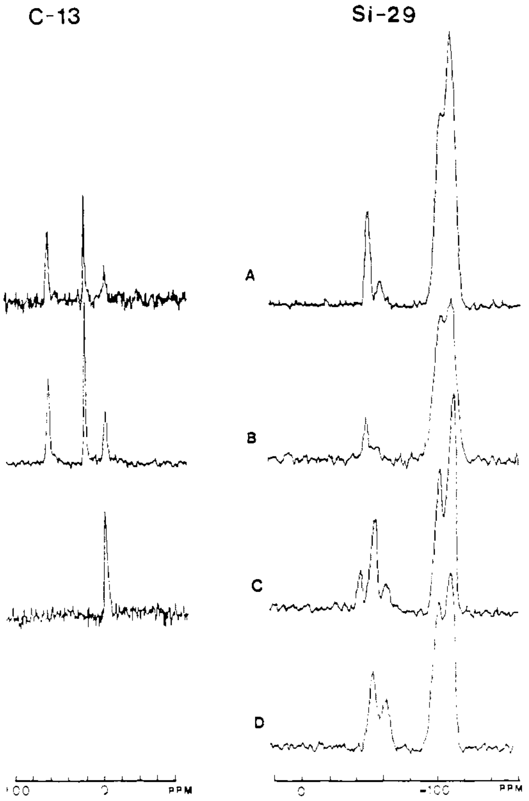


Figure 5. ^{13}C (15.04 MHz) and ^{29}Si (11.88 MHz) NMR spectra of reaction products prepared from methyltriethoxysilane: (A) predried silica (refluxed at 138 °C); (B) predried silica (gas phase reaction, 240 °C); (C) hydrous silica (refluxed at 115 °C); (D) sample of C heated at 150 °C.

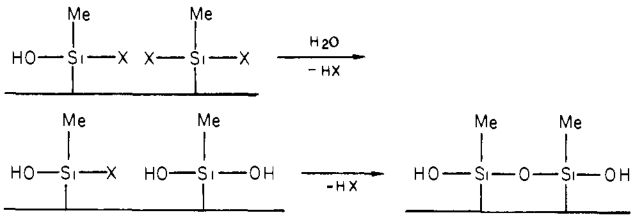
Methyltriethoxysilane. ^{29}Si and ^{13}C CP/MAS spectra of bonded-phase materials prepared from $SiCH_3(OC_2H_5)_3$ are shown in Figure 5. Sample preparation methods comparable to those employed in $Si(CH_3)_2(OC_2H_5)_2$ reactions were used.

The sample of Figure 5A was prepared by refluxing $SiCH_3(OC_2H_5)_3$ at 138 °C in the presence of TES2 silica (predried at 150 °C for a period of 6 h). Unreacted reagent was then removed by repeated washing with toluene and benzene. On the basis of the empirical ^{29}Si chemical shift and additivity relationships, the two "silane" resonances at −46 and −55 ppm in the ^{29}Si spectrum of Figure 5A can be assigned to $SiCH_3(OC_2H_5)_2(O-)$ and $SiCH_3(OC_2H_5)(O-)_2$ moieties, respectively. These assignments are given support by the existence of intense ethoxy resonances in the ^{13}C spectrum of Figure 4A. The most intense silane peak in the ^{29}Si spectrum of Figure 5A is the strong peak at −46 ppm. This predominance suggests that, as in the cases of $SiCH_3Cl_3$, $Si(CH_3)_2Cl_2$, and perhaps $Si(CH_3)_2(OC_2H_5)_2$, the initial bonding of this reagent to the surface of silica gel involves principally single surface-to-silane siloxane attachments.

The sample of Figure 5B was prepared with gaseous $SiCH_3(OC_2H_5)_3$ and anhydrous TES2 silica at 240 °C using reaction method 3 of ref 7. The ^{29}Si NMR spectrum of this sample is similar in major features to that of the sample of Figure 5A. This suggests that, in the absence of molecular water, the singly attached $Si(CH_3)(OC_2H_5)_2(O-)$ species are thermally stable with respect to additional silane-to-silane or silane-to-surface condensation reactions.

As in the case of the $Si(CH_3)_2(OC_2H_5)_2$-derived sample of Figure 4C, the reaction conditions for the preparation of the sample of Figure 5C involved the use of undried TES2 silica (with

Scheme V



20% H_2O), refluxed with a toluene solution of the silane reagent at 115 °C (experimental method 5). In marked contrast to the ^{29}Si spectra of the previous two examples, the most intense features in the silane region of Figure 5C is a resonance at −53 ppm. From data given above and the lack of ethoxy resonances in the ^{13}C spectrum of this sample, this peak can be assigned to silicon species in a disiloxane, $SiCH_3(OH)(O-)_2$, environment. Other features at −62 and −43 ppm are also evident in this ^{29}Si spectrum, and can be assigned to $SiCH_3(O-)_3$ and $SiCH_3(OH)_2(O-)$ species, respectively.

The ratio of intensities in the silane and silica–silanol regions of Figure 5C shows that, as in the case of $Si(CH_3)_2(OC_2H_5)_2$ reactions, surface-to-silane bonding is substantially more complete for $SiCH_3(OC_2H_5)_3$ when reactions are carried out in the presence of surface-adsorbed H_2O. The silane region of the ^{29}Si spectrum of Figure 5C can be seen to be quite similar to that observed for reaction products of $SiCH_3(OC_2H_5)_3$, following exposure to atmospheric moisture (e.g., Figure 3C). The predominance of disiloxy $SiCH_3(OH)(O-)_2$ species in both cases may indicate that, as in the case of $Si(CH_3)_2Cl_2$ and $Si(CH_3)_2(OC_2H_5)_2$ products, condensation reactions in the silane phase involve principally the *pairwise* cross-linking groups of adjacent singly attached silane groups, as in Scheme V, where $X = Cl$ or OC_2H_5.

As in the case of the sample of Figure 4D, the sample of Figure 5D was prepared by simply heating the material of the Figure 5C sample to 150 °C for a period of 3 h. The ^{29}Si spectrum shows that, as a result of this heating, spectral intensity is preferentially redistributed to the higher shielding resonances at −53 and −62 ppm. As in previous examples, such behavior can be interpreted as indicative of subsequent condensation reactions involving the silane phase. The constancy of the measured value of f obtained from the ^{29}Si spectra of Figures 5A and 5D (1.0 and 0.97, respectively) suggests that in this case unreacted surface hydroxyl groups probably do not participate in these secondary condensation processes.

Secondary Processes in Ethoxysilane Reactions. An additional complication in the case of ethoxysilane reactions involves the subsequent attachment of byproduct ethoxy moieties to the silica surface. The degree to which this occurs can be estimated by examining intensities in the ^{13}C and ^{29}Si NMR spectra of these materials.

The efficiency (E) of the secondary reaction, defined as the fraction of OC_2H_5 groups formally released in the initial surface–silane reaction that subsequently react with the surface, is given by the equation

$$E = (Rm - N_{av})/(4 - m - N_{av}) \qquad (7)$$

In the equation, R is the ratio of the total number of ethoxy groups present to the total number of silicon-attached methyl groups associated with the silane phase, N_{av} is the average number of ethoxy moieties associated with attached silane species, and m is the number of silicon-attached methyl groups per silane group. Equation 7 assumes that all intensity in the silane region of the ^{29}Si spectra of samples prepared under anhydrous conditions can be attributed to the silane species that contain either siloxane bonds or unreacted ethoxy groups (i.e., direct hydrolysis in these cases is considered negligible).

As an example of the use of eq 7, the spectra of Figure 5A, obtained from methyltriethoxysilane-reacted silica, can be evaluated as follows. First, the ethoxy-to-Si-methyl ratio (R) can be obtained from the ^{13}C spectrum as half the ratio of total intensity in the ethyl region (i.e., the resonances at 60 to 17 ppm) to the intensity associated with the silicon-attached methyl carbons (at 1 ppm). For Figure 5A the ratio of ethoxy intensity to Si-methyl intensity is about 4 to 1, so $R = 2.0$. The ^{29}Si spectrum shows that about 78% of the silane intensity is associated with resonances assigned to singly attached $Si(CH_3)(OC_2H_5)_2(O-)$ structures, each having two unreacted ethoxy functional groups. The remaining 22% of the intensity is associated with the $SiCH_3(OC_2H_5)(O-)_2$ structure, which contains only one ethoxy group. From these values the average number of ethoxy groups per silane moiety (N_{av}) is computed to be 1.8. For methyltriethoxysilane products $m = 1$, since one Si-methyl group is associated with each silane moiety. By using these results and eq 7, one predicts the following value of E for the example of Figure 5A.

$$E = \frac{((2.0)(1) - 1.8)}{(4 - 1 - 1.8)} = 0.17$$

That is, 17% of the ethanol molecules (formally) released during the primary reaction have subsequently reacted with the silica surface.

Values of E determined in this manner for a number of "anhydrous" ethoxysilane reaction products, including all of the examples that have been included in this paper, show that, for multifunctional ethoxysilane reagents, the majority of the ethoxy groups present following the initial reaction are generally associated with the silane phase (i.e., unreacted Si–OEt groups). However, the relative population of surface-attached ethoxy groups is certainly not negligible, and can be expected to result in significant errors in the evaluation of surface "coverages" if % C data alone are used. On the other hand, because Si–OEt groups and Si–OH groups have similar chemical shifts (Table II) surface coverages (θ) determined by the methods of this and the preceding papers[6,7] should not be greatly affected by these considerations.

Summary

These experimental results have shown that the chemistry of ethoxysilane reactions at the surface of silica gel parallels closely that observed for analogous chlorosilane reactions. In both cases, single surface-to-silane attachments characterize the silane environment in products prepared under anhydrous or nearly anhydrous conditions. The presence of surface-adsorbed water during the initial bonding reaction appears to increase the overall reactivity of all of the reagents examined, particularly in the case of the ethoxy silanes. Materials prepared with multifunctional reagents under conditions of adsorbed surface water are also characterized by a substantial increase in the relative population of more fully condensed silane environments (i.e., species with two or more siloxane bonds). Substantial evidence has indicated that this behavior reflects the formation of cross-linked structures which result from the condensation of neighboring silane groups.

This or very similar schemes were clearly evident for both classes of reagents when appropriate secondary treatments were applied. In the case of the chlorosilanes this simply involved exposing the initial reaction product to the atmosphere or other sources of molecular water. Under these conditions both direct hydrolysis of unreacted Cl groups and silane-to-silane condensation reactions were observed. Ethoxysilanes appear to be more resistant to such processes than chlorosilanes, and they required a substantial amount of water as well as the application of heat. Some evidence has also been presented that suggests that, at least in the case of chlorosilane reaction products, further bonding with the silica surface may also take place in these secondary reaction stages.

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Registry No. Dimethyldichlorosilane, 75-78-5; methyltrichlorosilane, 75-79-6; dimethyldiethoxysilane, 78-62-6; methyltriethoxysilane, 2031-67-6; water, 7732-18-5.