

Chemistry of the Silica Surface: Reaction with Phosphorus Pentachloride

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Solid-state ^{31}P and ^{29}Si NMR experiments, with Magic-Angle Spinning (MAS), were used to elucidate the chemistry that occurs when silica gel is treated with phosphorus pentachloride. A low-loading regime (in which the molar ratio of initial PCl_5 to surface silanols sites is $\ll 1$) and a high-loading regime (in which this ratio is ~ 1) were examined. For each regime, the results for limited and intentional exposure to moisture are presented. The occurrence of phosphorus bridging between two adjacent silanols sites is observed. Bridging structures based on $\text{Si}-\text{O}-\text{P}-\text{O}-\text{P}-\text{O}-\text{Si}$ linkages are also indicated.

Introduction

The structure and properties of the silica surface have been subjects of great research interest over the past few decades, at least partly because of the numerous realized and potential materials applications associated with generating covalent attachments to silica surface moieties.^{1–4} Previous studies have included substantial investigations of the reactions of phosphorus trichloride,^{5–7} of phosphoryl chloride (POCl_3),^b of phosphoric acid⁸ and various phosphonates ($\text{R}-\text{P}(\text{O})\text{XY}$, where R is alkyl or alkoxy and X,Y = alkoxy or Cl)⁹ with silica, and limited studies reported in the Russian literature on the chemistry of the phosphorus pentachloride/silica system.¹⁰ This work addresses that last system, primarily by solid-state NMR spectroscopy. As with most studies of silica surface reactivity, attention is focused on the behavior of

surface silanols ($\text{Si}-\text{OH}$ groups, where Si represents a silicon atom at the surface), along with identities of surface-attached species that are generated in reactant–silica interactions, which in this case are centered on phosphorus-containing moieties. As is often the case in silica surface issues, the role and importance of water are examined.

Previous detailed studies of the adsorption of phosphorus-centered species on silica surfaces have included experiments based on an infrared and/or ^{31}P NMR measurements. Those studies were concerned with the interactions of H_3PO_4 ,⁹ POCl_3 ,⁷ PCl_3 ,^{6–8} and various phosphonates $^{25}(\text{R}-\text{P}(\text{O})\text{XY})$ where R = alkyl or alkoxy, X,Y = OCH_3 or Cl) with silica. Most of these systems were studied as samples in which the P-centered reagent was adsorbed from the vapor phase. In the current study, PCl_5 was adsorbed from CCl_4 solutions. In most of the previous studies, the silica employed had been calcined under vacuum at temperatures higher than the 100 °C used in the study reported here.

In studies by Morrow and co-workers,⁶ it was found that PCl_3 and POCl_3 interact with the silica surface only by physisorption and can be removed by prolonged evacuation at room temperature, unless a long adsorption period was employed. For a long adsorption period, the formation of $\text{Si}-\text{O}-\text{PCl}_2$, $\text{Si}-\text{O}-\text{P}(\text{O})(\text{H})(\text{OH})_2$, $(\text{Si}-\text{O})_2\text{P}(\text{O})\text{H}$, $\text{Si}-\text{O}-\text{P}(\text{O})(\text{OH})_2$, and $(\text{Si}-\text{O})_2\text{P}(\text{O})\text{OH}$ was observed. The last two species were also identified in samples prepared by adsorption of H_3PO_4 on silica.

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The formation of Si–O–P linkages was also reported by Bogatyrev and co-workers⁵ in studies of the adsorption of PCl₃ on silica (including the role of physisorbed water). The formation of Si–O–PCl₂ and (Si–O)₂PCl (analogous to species II and III, Table 1) from PCl₃ adsorption was also reported.

In their ³¹P MAS NMR study of the adsorption of H₃PO₄ on silica, Mudrakovskii and co-workers⁸ found only Si–O–P(O)(OH)₂ (species VI) when H₃PO₄ was adsorbed on silica that had been calcined at 100 °C. In addition, (Si–O)₂P(O)OH (VII) and [Si–O–P(O)OH]₂O (VIII) were observed if the silica had been calcined at substantially higher temperatures.

In infrared studies of the series, (CH₃O)₃PO, CH₃OP(O)Cl₂, CH₃P(O)(OCH₃)₂, and POCl₃ adsorbed on silica, Kanan and Tripp found that these species are physisorbed (especially by hydrogen bonding with surface silanols) and can be removed from the silica surface by evacuation at moderate temperatures.⁹ This behavior contrasts with results of the present study in which chemisorption to form Si–O–P linkages dominates, along with hydrolysis of P–Cl bonds, in the observed chemistry (vide infra).

Ukrainian researchers have examined the PCl₅/SiO₂ system from a perspective that focused primarily on Si–O–PCl₄ moieties.¹⁰

The silica surface is generally viewed as consisting of a combination of silicon types: geminal silanols (Q₂, two siloxane linkages, Si–O–Si, to other silicon atoms of the silica framework and two OH groups attached to the Q₂ silicon), single silanols (Q₃, three siloxane linkages and one attached OH group), and nonsilanols (Q₄, four siloxane linkages and no attached OH group). Solid-state ²⁹Si NMR, with Magic-Angle Spinning (MAS), and usually with ¹H→²⁹Si cross polarization (CP), have proven to be extremely useful in distinguishing among these three types of surface moieties by manifesting three distinct ²⁹Si chemical shifts.¹¹

Solid-state ³¹P MAS NMR has been shown previously to be extremely useful in identifying surface-attached phosphorus-containing moieties, largely because of the extremely high sensitivity of the ³¹P chemical shift to even small variations in local atomic-level structure.^{5–8,12} As the reactions of P–Cl moieties with hydroxyl groups, e.g., the hydrolysis of PCl₅ to H₃PO₄, has long been recognized and as silica surface chemistry focuses on the reactivity of Si–OH groups (silanols), the nature of reactivity of PCl₅ with the silica surface is of substantial interest. Not only is the anticipated chemistry of interest in its own right, but also there exists the possibility that PCl_n moieties in general might provide useful probes of silanol distributions, as has proved to be the case with SiX_n moieties in silylation reactions.^{13,14}

Experimental Section

Materials. Silica gel (Fisher, S679 Lot 000232) was dried by evacuation at 5×10^{-3} Torr and 100 °C for 24 h. Phosphorus pentachloride (98.0%, Fluka) was used after sublimation. Carbon tetrachloride (99.9%, Aldrich) was dried by distillation over phosphorus pentoxide. Potassium bromide (99+ % Acros Organics, Belgium) was dried by evacuation at 5×10^{-3} Torr for 24 h at

room temperature. High relative-humidity (30% RH) exposure conditions were created using a sealed chamber containing a saturated solution of NaCl in water. Chiraphos (2*R*,3*R*-bis(diphenylphosphino)butane, Aldrich), tetrakis(trimethylsilyl)silane (TTMSS, Fluka), and polydimethoxysiloxane (PDMS, 2.5 MDa MW, Petrarch Systems) were used as supplied.

Surface Properties. Values of the BET surface area, pore volume, and pore size (width) were determined by Micrometrics Analytical Services (Norcross, GA).

Sample Preparation. Weighed quantities of phosphorus pentachloride and carbon tetrachloride were stirred at room temperature until the liquid became clear (5–10 h, depending on quantities). The resulting solution was reacted with a weighed quantity of dry silica gel for 24 h at room temperature with constant stirring under a dry N₂ atmosphere. The solvent was removed under vacuum (5×10^{-3} Torr) at room temperature. The resulting, free-flowing powder was sealed at room temperature under dry N₂, using O-rings (vide infra) and used immediately.

Subsequent Reaction Steps. After the initial reaction was completed, samples were kept at ambient temperature for varying periods under a variety of conditions with respect to exposure to H₂O, including (1) anhydrous conditions (under N₂ in a drybox), (2) with H₂O exposure severely restricted to a tightly capped (O-ring seals) MAS rotor, and (3) under 30% RH in a humidifier. Spectroscopy was performed on samples generated under these various conditions, as described in the results.

NMR Spectroscopy. Solid-state ³¹P and ²⁹Si NMR spectra were obtained using a CMX-II type spectrometer (Otsuka Electronics USA, Fort Collins, CO) operating at 4.7 T (199.9 MHz for ¹H, 80.86 MHz for ³¹P, 39.68 MHz for ²⁹Si). Samples were contained in modified 7.5 mm diameter, PENCIL-II, zirconia, MAS rotors equipped with a pair of rubber O-rings, one on each end, to minimize exposure to air. All solid-state ³¹P and ²⁹Si NMR spectra were obtained using high-power ¹H decoupling, although its inclusion had little effect on the spectra. Solid-state ¹H NMR spectra were obtained using a CMX-II type spectrometer operating at 9.4 T (360.0 MHz for ¹H). Samples were contained in 4 mm diameter PENCIL-II, zirconia, MAS rotors with standard plastic-to-ceramic closures.

³¹P MAS spectra were obtained with a rotor speed of ~6 kHz. Conditions for CP experiments¹⁵ were ³¹P and ¹H RF field strength of 41 kHz for CP contact and decoupling, a contact time of 6 ms, and a recovery time of 1 s. Conditions for Direct Polarization (DP) experiments were ³¹P RF field strength of 31 kHz, ¹H decoupling field strength of 41 kHz, and a recovery time of 10 s. ³¹P MAS spectra were externally referenced to liquid 85% H₃PO₄ (0 ppm) via substitution with a secondary reference, chiraphos (–11.4 and –14.0 ppm relative to 85% H₃PO₄).

²⁹Si MAS spectra were obtained with a rotor speed of ~3 kHz. Conditions for CP experiments were ²⁹Si and ¹H RF field strength of 41 kHz for CP contact and decoupling, a contact time of 8 ms, and a recovery time of 1 s. Conditions for DP experiments were ²⁹Si RF field strength of 62.5 kHz, ¹H decoupling field strength of 41 kHz, and a recovery time of 100 s. ²⁹Si MAS spectra were externally referenced to liquid TMS (0 ppm) via substitution with a secondary reference TTMSS (–8.1 and –134.3 ppm relative to TMS).

¹H MAS spectra were obtained with a rotor speed of ~12 kHz. Conditions for DP experiments were ¹H RF field strength of 62.5 kHz and a recovery time of 10 s. ¹H MAS spectra were externally referenced to liquid TMS (0 ppm) via substitution with a secondary reference, PDMS (0.0 ppm relative to TMS).

Dry N₂(g) used as the drive gas in some MAS experiments (vide infra) was obtained as “boil off” from a standard pressure-building storage dewar.

Results and Discussion

Surface Properties. Values obtained for the (BET) surface area, pore volume, and average pore size of the initial dried silica gel (sample a) and the final dried sample of PCl₅-treated silica gel (sample 1) are 510 m²/g, 0.39 cm³/g, and 31 Å, respectively, for the silica gel and 397 m²/g, 0.31 cm³/g, and 31 Å, respectively, for the PCl₅/SiO₂ (P/SiOH = 0.77) sample. For the corresponding PCl₅-reacted sample with P/SiOH = 0.077, the values are 425 m²/g, 0.33 cm³/g, and 31 Å, respectively. These variations are consistent with the occupation of a substantial fraction of the silica surface, including within the pores, upon reaction with PCl₅.

NMR Results. MAS ¹H NMR spectra (Figure S1 of the Supporting Information) of the dried S679 silica gel, with a surface area of 510 m²/g, yielded an assay¹⁶ of 5.3 mmol OH/g. This corresponds to 6.2 OH/100 Å², or 3.2 × 10²¹ OH/g. ²⁹Si NMR measurements (vide infra) yielded a silanol concentration of 5.4 mmol OH/g.

Solid-state ³¹P and ²⁹Si MAS NMR spectra were obtained with CP and with DP (no CP) and with ¹H decoupling, primarily on sets of samples based on two types of PCl₅/SiO₂ systems. In one type of system, the mole ratio of initial PCl₅ to surface silanols, P/SiOH, was 0.077; in the other type of system, P/SiOH was 0.77. In the lower-loading-level regime, the amount of PCl₅ added corresponds to much less, on a mole basis, than the number of silanol groups that are potentially available for reaction. In the higher-loading-level regime, the amount of PCl₅ added is comparable to the amount of available silanols groups.

³¹P DP-MAS spin counting experiments, using chirophos as an external intensity reference, yielded values of 0.30 mmol P/g for the low-loading sample and 1.5 mmol P/g for the high-loading sample. Based on the value 5.4 mmol OH/g obtained from the ²⁹Si spin-counting experiments (vide supra), these surface phosphorus loadings correspond to 5.5% and 28% for silanol conversions in the low-loading and high-loading PCl₅/SiO₂ samples, respectively.

For some samples, ³¹P CP-MAS and DP-MAS experiments were carried out *without* ¹H decoupling. No substantial differences in the spectra (not shown here) were found in comparison to corresponding experiments carried out *with* ¹H decoupling. ³¹P chemical shift assignments, as well as their bases, are summarized in Table 1. For each type of PCl₅/SiO₂ system studied, NMR spectra were obtained under conditions in which H₂O exposure was controlled by various details of the experiment, e.g., the environment of sample storage and the MAS drive gas.

In two key sets of experiments on PCl₅/SiO₂ systems with different PCl₅/SiO₂ ratios, exposure to water (from air) was slow but deliberate. In these experiments, each sample was retained in the capped MAS rotor under air (including air as the MAS drive gas) for various periods of time, then under conditions in which the sample was exposed to H₂O much more efficiently (i.e., in the uncapped MAS rotor in a

Table 1. ³¹P Chemical Shift Assignments

	species	³¹ P chemical shift, ^a ppm	assignment method ^b	relevant ref
I.	PCl ₅ (ads)	-80	3	12, 17
	A. PCl ₄ ⁺	86	1	12, 17
	B. PCl ₆ ⁻	-295	1	12, 17
II.	Si-O-PCl ₄	7-15	4,5	7, 14
III.	(Si-O-) ₂ PCl ₃	-4	4,5	7, 14
IV.	[Si-O-PCl ₃] ₂ O	-4	4,5	7, 14
V.	POCl ₃ (ad)	1.9-5.4	2, 3	12, 15
VI.	Si-O-P(O)(OH) ₂	-11 to -12.5	2,4	7, 9
VII.	(Si-O-) ₂ P(O)OH	-22 to -25	2,4	7, 9
VIII.	[Si-O-P(O)(OH)] ₂ O	-22 to -25	4	7, 9
IX.	H ₃ PO ₄ (ad)	0	2,3	7, 12

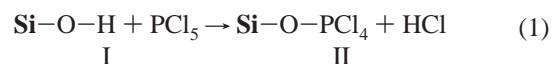
^a Relative to 85% H₃PO₄ set at 0 ppm. ^b Assignment method: 1. Previously reported chemical shifts for the solid state. 2. Previously reported chemical shifts for species adsorbed on silica. 3. Previously reported chemical shifts for liquid solution. 4. Based on self-consistency of patterns of chemical reactivity and NMR properties embodied in the conclusions from this work. 5. Based on consistency with IR data (P-Cl vibration, as well as Si-O and P-O vibrations).

humidifier) for various periods of time, and eventually evacuated (5 × 10⁻³ Torr) at room temperature. NMR spectra were obtained at each stage. The results for these types of PCl₅/SiO₂ systems are shown in Figures 1 and S3 (Supporting Information) for two different PCl₅ loading levels.

A priori, prior to any spectroscopic evidence, a variety of possible reaction schemes can be envisioned for reactions of PCl₅ on a silica surface. Such schemes would presumably be influenced by whatever amount of residual (e.g., physisorbed or weakly trapped) water that might exist at (or very near) the silica gel surface. In this regard, it is of interest that, both for the lower-concentration and higher-concentration PCl₅/SiO₂ systems, the DP-MAS ³¹P spectra obtained on the initial (dried) reaction products (Figures 1a and S3a) were essentially unchanged if anhydrous MgSO₄, a common drying agent that would be expected to sequester most, if not all, of any unintended, weakly held water at the silica surface, was included in the reaction mixture.

The chemically simplest a priori predictions of species that might be present at the surface of samples derived from the PCl₅/SiO₂ system are the physisorbed versions of known stable species, i.e., phosphorus pentachloride, PCl₅(ad) (I), and the partially or totally hydrolyzed systems POCl₃(ad) (V) or H₃PO₄(ad) (i.e., OP(OH)₃(ad)) (IX). PCl₅ is known to exist in its crystalline form as a combination of the two ions PCl₄⁺(IA) and PCl₆⁻(IB), which have previously been observed by solid-state ³¹P NMR.¹⁷ Also, ³¹P NMR experiments have been reported on H₃PO₄⁹ and POCl₃⁷ adsorbed on silica surfaces.

The next level of simplicity in species expected on the surface of a PCl₅/SiO₂ system is represented by structures in which a P-Cl moiety and a HOSi moiety are replaced by a P-O-Si linkage via a condensation process that splits out HCl, e.g.



where the symbol “Si” represents a silicon atom at the surface, e.g., in a silanol moiety with three other covalent bonds to oxygen atoms not shown. In the event that

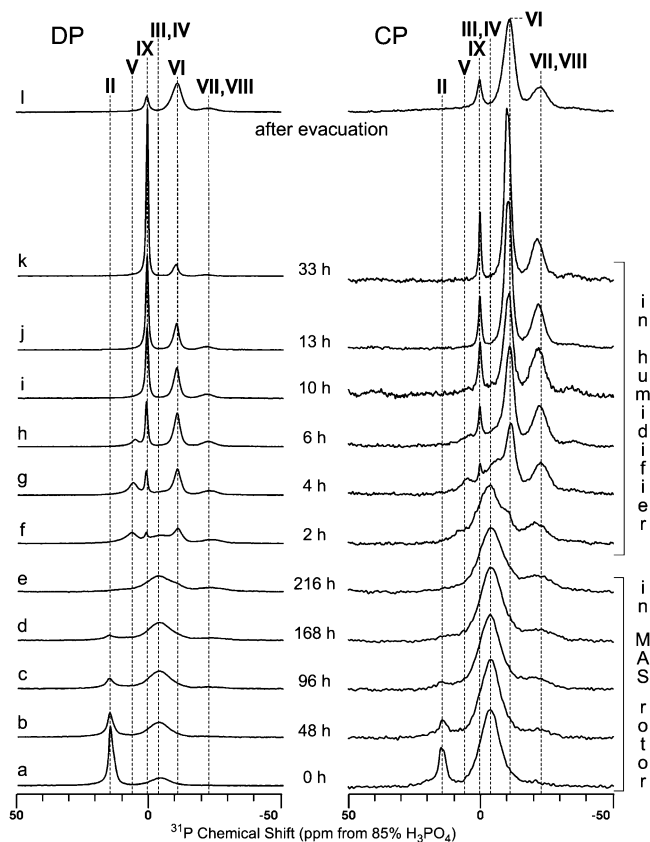
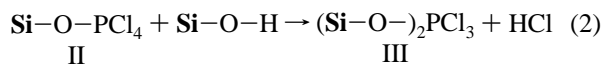
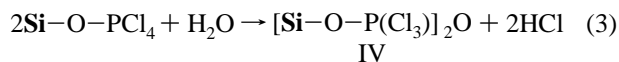


Figure 1. 80.86 MHz ^{31}P MAS NMR spectra, obtained with direct polarization (DP) on the left and with cross polarization (CP) on the right, of a $\text{PCl}_5/\text{SiO}_2$ system ($\text{P}/\text{SiOH} = 0.077$) with various sample histories. (a) Initial dry reaction product; (b–e) after storage in a capped rotor in air for the periods indicated; (f–k) after storage (uncapped) in a humidifier for the indicated periods; (l) after sample k was evacuated (5×10^{-3} Torr) for 12 h. Each DP spectrum: 1000 repetitions. Each CP spectrum: 1000–9000 repetitions.

geometrical constraints on the relevant chemical structures permit it (vide infra), a second P–Cl bond of the attached $-\text{O}-\text{PCl}_4$ moiety may react with an adjacent silanol group to generate a bridging structure:



An alternate mode of bridging might be accomplished in the following manner:

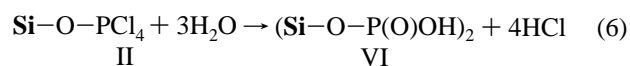
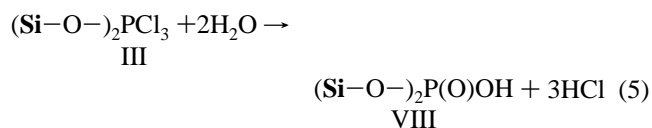
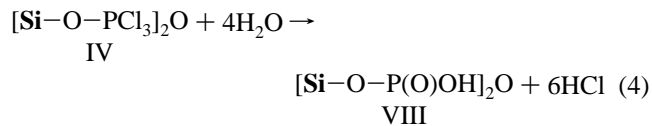


This kind of process would require some source of H_2O (vide infra). Higher-level bridging, i.e., to $(\text{Si-O})_3\text{PCl}_2$, is not expected because of severe geometrical constraints at the silica surface (vide infra).

P/SiOH = 0.077. ^{31}P NMR Results. Figure 1 shows DP-MAS and CP-MAS ^{31}P NMR spectra of a $\text{PCl}_5/\text{SiO}_2$ ($\text{P}/\text{SiOH} = 0.077$) system after the initial reaction. There is no evidence of the existence of PCl_5 in the ^{31}P MAS NMR spectra of the dried (evacuated) reaction product (a) represented in Figure 1 (or in Figure S3), although signals due to PCl_6^- and PCl_4^+ are readily observed by DP-MAS in a crystalline sample of PCl_5 and physisorbed PCl_5 is observed

in a dried $\text{PCl}_5/\text{SiO}_2$ reaction mixture that has not been subjected to extensive evacuation (Figure S2). In addition, a ^{31}P signal due to $\text{PCl}_5(\text{ad})$ was observed in a $\text{PCl}_5/\text{SiO}_2$ sample for which more scrupulous measures were used to exclude H_2O (vide infra).

There is no evidence of $\text{POCl}_3(\text{ad})$ (V) or $\text{H}_3\text{PO}_4(\text{ad})$ (IX) in the DP-MAS or CP-MAS ^{31}P spectra of 0.077 PCl_5/SiOH samples (Figure 1) that had never been exposed intentionally to H_2O (samples a–e of Figure 1). However, there are strong peaks in these samples identified with species II, Si-O-PCl_4 (ca. 15 ppm) and III ($(\text{Si-O})_2\text{PCl}_3$, ca. -4 ppm) or IV ($[\text{Si-O-PCl}_3]_2\text{O}$, ca. -4 ppm). These peaks dominate both the DP-MAS and CP-MAS ^{31}P spectra of samples that were stored in the capped MAS rotor for the shorter periods of time (≤ 48 h) and, for the peak due to species III and/or IV, persist for much longer periods. In addition to the peaks identified with species II, III, and (possibly) IV, also present in the ^{31}P MAS spectra of 0.077 P/SiOH samples stored in a capped rotor for longer times (≥ 96 h), is a peak at -24 ppm identified with bridged and hydrolyzed species, $(\text{Si-O})_2\text{P}(\text{O})\text{OH}$ (VII) and/or $[\text{Si-O-P}(\text{O})\text{OH}]_2\text{O}$ (VIII), and a shoulder at -12 ppm identified with $\text{Si-O-P}(\text{O})(\text{OH})_2$ (VI). One can envision these kinds of species to be formed by hydrolysis processes of the following types, based on water that is somehow made available, e.g., by the release of ‘trapped’ water or leaking through O-rings inside the MAS rotor:



There are also major differences between the relative intensities of peaks due to moieties II and III and/or IV in the DP-MAS and CP-MAS spectra. The unbridged species (II) is favored under the conditions used in the DP-MAS experiments, and conversely, the bridged species $(\text{Si-O})_2\text{PCl}_3$ (III) and/or $[\text{Si-O-PCl}_3]_2\text{O}$ (IV) are favored in the spectra derived from CP-MAS experiments. This observation is consistent with the dependence of DP-MAS intensity on ^{31}P spin-lattice relaxation, which requires a spectral density of time dependence near the Larmor frequency (more likely to be present in unbridged structures) and of CP-MAS intensity on $^1\text{H}-^{31}\text{P}$ cross polarization efficiency, which requires a *static* component of the $^1\text{H}-^{31}\text{P}$ dipole–dipole interaction (more likely in a bridged system). This explanation is qualitatively borne out by the relaxation data summarized in Tables 2 and 3 for ^{31}P T_1 and for T_{HP} and ^1H $T_{1\rho}$ values, respectively.

^{31}P T_1 values were measured via the inversion recovery method and show that T_1 for Si-O-PCl_4 is, in each sample

Table 2. ^{31}P T_1 Values (s) for the P/SiOH = 0.77 System^a

sample	$\text{H}_3\text{PO}_3(\text{ad})$	$\text{POCl}_3(\text{ad})$	Si-O-PCl_4	$(\text{Si-O-})_2\text{PCl}_3^b$	Si-O-P(O)(OH)_2	$(\text{Si-O-})_2\text{P(O)OH}^c$
dried reaction product			0.87	8.3	6.5	
humidified 1 h			1.4	5.3		
humidified 2.5 h	2.4	2.0	2.2	3.9	2.0	2.7
humidified 5 h	1.2	1.2			1.4	2.1
humidified 10 h	1.0				1.1	1.7

^a Determined by inversion recovery experiments. Uncertainty: $\pm 9\%$ ^b Possible contributor: $[\text{Si-O-PCl}_3]_2\text{O}$ ^c Possible contributor: $[\text{Si-O-P(O)OH}]_2\text{O}$.

Table 3. $^1\text{H}\rightarrow^{31}\text{P}$ CP Parameters (ms) for the P/SiOH = 0.77 System^a

sample	$\text{H}_3\text{PO}_3(\text{ad})$ $T_{\text{HP}}, T_{1\rho^{\text{H}}}$	$\text{POCl}_3(\text{ad})$ $T_{\text{HP}}, T_{1\rho^{\text{H}}}$	Si-O-PCl_4 $T_{\text{HP}}, T_{1\rho^{\text{H}}}$	$(\text{Si-O-})_2\text{PCl}_3^b$ $T_{\text{HP}}, T_{1\rho^{\text{H}}}$	Si-O-P(O)(OH)_2 $T_{\text{HP}}, T_{1\rho^{\text{H}}}$	$(\text{Si-O-})_2\text{P(O)OH}^c$ $T_{\text{HP}}, T_{1\rho^{\text{H}}}$
dried reaction product			11, 49			
humidified 1 h			5.9, 61			
humidified 2.5 h			2.7, 35	0.89, 27	0.76, 33	0.54, 27
humidified 5 h	0.58, 17	0.73, 6.2		0.48, 12	0.62, 12	0.60, 7.6
humidified 10 h	2.3, 230				1.1, 45	0.73, 22

^a T_{HP} and $T_{1\rho^{\text{H}}}$ obtained from variable-contact-time experiments. ^b Possible contributor: $[\text{Si-O-PCl}_3]_2\text{O}$. ^c Possible contributor: $[\text{Si-O-P(O)OH}]_2\text{O}$.

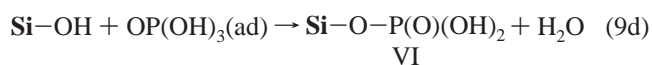
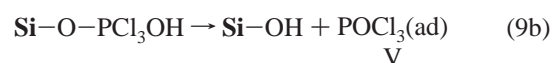
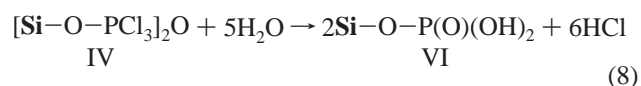
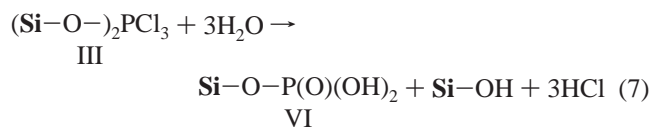
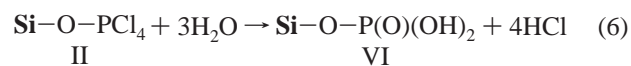
for which a comparison could be made, smaller than the corresponding value for $(\text{Si-O-})_2\text{PCl}_3$ or $(\text{Si-O-PCl}_3)_2\text{O}$. The analogous comparisons in Table 3 for the $^1\text{H}\rightarrow^{31}\text{P}$ cross-polarization time constant (T_{HP}), derived from variable-contact-time CP experiments, shows it to be smaller for $(\text{Si-O-})_2\text{PCl}_3$ than for Si-O-PCl_4 .

One can note from Table 2 that, with a small number of exceptions, all of the measured ^{31}P T_1 values are less than one-third of the recovery period (10 s) employed in obtaining each of the DP-MAS ^{31}P spectra shown in Figure 1 (and in Figure S3). Hence, the displayed intensities should be proportional to the corresponding chemical populations within about 5%. Accordingly, if the few substantial T_1 corrections are made, i.e., for species III (or IV) and VI, then all of the DP-MAS spectra shown in Figure 1 (or Figure S3) have total intensities that are within about 10% of each other. Analogous statements can be made for intensities of the CP-MAS ^{31}P spectra in Figure 1 (or Figure S3), but in this case, that near equivalency is not directly reflected visually in the spectra shown.

It should also be noted that no spinning sidebands are seen in the spectra of Figure 1 because no isotropically averaged ^{31}P NMR peaks occur outside the 50 to -50 ppm chemical shift range displayed and the spinning sidebands (± 75 ppm) are outside that range. Nevertheless, the intensities of these sidebands, which were $<5\%$ for the DP-MAS ^{31}P spectra and $<15\%$ for the CP-MAS ^{31}P spectra, must be taken into account in all numerical intensity comparisons.

The effect of exposing the $\text{PCl}_5/\text{SiO}_2$ sample (P/SiOH = 0.077) to moisture in a humidifier is apparent in the corresponding ^{31}P DP-MAS and CP-MAS spectra of Figure 1 (f–k). From the DP-MAS spectra of Figure 1, one sees that exposure to moisture leads first to the appearance (f, 2 h exposure) and subsequently to a decrease, for longer exposure periods, of peaks at about 5–6 ppm and at about -11.5 to -12.5 ppm; these peaks are assigned, respectively, to physisorbed POCl_3 (V) and to the surface-tethered and substantially hydrolyzed species, Si-O-P(O)(OH)_2 (VI), the generation of which can be visualized formally in terms of

a variety of hydrolysis processes, including the following types:



As the H_2O exposure period is increased, one also sees a monotonic increase in a peak due to physisorbed H_3PO_4 (IX) at about 0 ppm and an initial increase and subsequent small decrease in the peak at -25 ppm assigned to $(\text{Si-O-})_2\text{P(O)OH}$ (VII) and/or $[\text{Si-O-P(O)OH}]_2\text{O}$ (VIII), while the peaks associated with surface-attached moieties containing P–Cl bonds (II, III, IV) are reduced to zero.

Again, there are dramatic differences in relative intensities between corresponding DP-MAS and CP-MAS ^{31}P spectra. For species VII and/or VIII, which generate only weak peaks in the DP-MAS spectra, the corresponding CP-MAS ^{31}P peaks are very strong in the H_2O -exposed samples. The peak due to physisorbed H_3PO_4 (IX), which dominates the DP-MAS spectra of $\text{PCl}_5/\text{SiO}_2$ (P/SiOH = 0.077) samples exposed to water vapor for 6 h or more, maps into a strong,

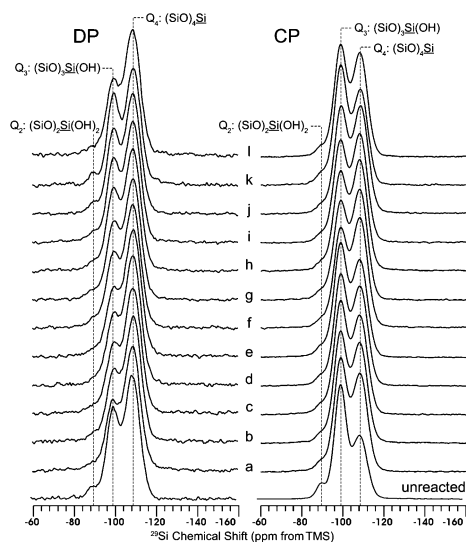


Figure 2. 39.68 MHz ^{29}Si MAS NMR spectra, obtained with DP on the left and with CP on the right, of a $\text{PCl}_5/\text{SiO}_2$ system ($\text{P}/\text{SiOH} = 0.077$) with various sample histories, as indicated according to the letters explained in Figure 1. Bottom spectra correspond to unreacted silica gel. Each DP spectrum: 3000 repetitions. Each CP spectrum: 2000–4500 repetitions.

but not dominant, peak in the CP-MAS ^{31}P spectra. Since the DP-MAS ^{31}P experiments were carried out under conditions for which the integrated intensities should be nearly quantitatively reflective of the chemical populations, the dramatic DP vs CP intensity differences apparent in the spectra are due mainly to differences in the efficiency of the cross polarization process, reflecting mainly differences in species mobility and the abundance of nearby protons.

A small peak at about -36 ppm is seen in the CP-MAS ^{31}P spectra of samples h and i in Figure 1. This peak is tentatively identified as due to polyphosphate species.⁷

The topmost spectra shown in Figure 1 (l) were obtained on a sample that was generated by pumping (5×10^{-3} Torr) on a sample (k), produced from the $\text{PCl}_5/\text{SiO}_2$ sample by exposure to water vapor for 33 h. One sees that sample evacuation dramatically reduces the concentration of physisorbed H_3PO_4 and markedly increases the concentrations of Si-O-P(O)(OH)_2 (VI) and $(\text{Si-O})_2\text{P(O)OH}$ (VII) and/or $[\text{Si-O-P(O)OH}]_2\text{O}$ (VIII).

Analogous ^{31}P MAS results obtained on a $\text{PCl}_5/\text{SiO}_2$ ($\text{P}/\text{SiOH} = 0.77$) sample (Figure S3) show peaks at essentially the same chemical shifts as seen in Figure 1, although with a different set of relative intensities as a function of storage time and conditions.

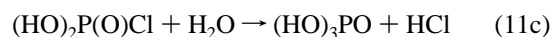
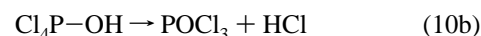
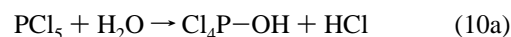
$\text{P}/\text{SiOH} = 0.077$. ^{29}Si NMR Results. Figure 2 displays the ^{29}Si DP-MAS (left side) and $^1\text{H} \rightarrow ^{29}\text{Si}$ CP-MAS (right side) ^{29}Si spectra obtained on the samples (a–l) that correspond to the ^{31}P NMR spectra of Figure 1 (plus ^{29}Si NMR spectra of the starting silica). The spectra shown in Figure 2 display the familiar patterns known for high-surface-area silica samples,^{10,11,13,14} i.e., a strong peak at about -109

ppm due to silicon atoms attached via oxygen bridges in linkages to four other silicon atoms, $\text{Si}(\text{OSi})_4$, or Q_4 ; a strong peak at about -99 ppm due to silicon atoms attached via oxygen bridges in linkages to three other silicon atoms and attached to one OH moiety, $\text{HOSi}(\text{OSi})_3$, or Q_3 ; and a weak peak/shoulder at about -89 ppm due to silicon atoms in environments of the type $(\text{HO})_2\text{Si}(\text{OSi})_2$, Q_2 . Of course, in the current study, a Si-OH moiety might be replaced by a Si-O-P moiety, which should change the ^{29}Si chemical shift by about -7 ppm,¹⁸ i.e., the single-silanol sites would change to about -106 ppm and the geminal silanol sites to about -96 ppm. As is well known from numerous publications, the Q_4 peak dominates in DP-MAS spectra (by virtue of having the largest population), whereas the Q_3 peak is largest in CP-MAS spectra because this moiety has the largest population of silicon atoms in close proximity to protons and thereby is most efficiently cross polarized.

One sees some changes in the DP-MAS ^{29}Si NMR spectra in progressing through the sample history (u, a–l) in Figure 2: A slight decrease in intensity (u \rightarrow a) for the -89 and -99 ppm peaks reflects the formation of Si-O-P linkages at the corresponding Si-O-H sites; this kind of reaction would change the ^{29}Si chemical shift by -7 ppm. After hydrolysis, the -89 and -99 ppm peaks begin to recover gradually, due to the detachment of phosphorus-containing moieties from the silica surface as $\text{POCl}_3(\text{ad})$ and $\text{H}_3\text{PO}_4(\text{ad})$. The phosphorus-containing species re-attach to the silica surface to form species VI and VII by evacuation, as shown by the decreasing intensities of the -89 and -99 ppm peaks (k \rightarrow l). The only change apparent in the CP-MAS spectra is an increase in Q_4 intensity, relative to Q_3 intensity, for the earlier stages of deliberate H_2O exposure (samples f \rightarrow i).

^{29}Si MAS NMR results were also obtained on the $\text{PCl}_5/\text{SiO}_2$ ($\text{P}/\text{SiOH} = 0.77$) system (Figure S5). Qualitatively, the results for the $\text{P}/\text{SiOH} = 0.77$ samples are similar to those of the $\text{P}/\text{SiOH} = 0.077$ system, but significant differences can be found (Supporting Information).

Chemical Interpretations. Phosphorus pentachloride reacts violently with water to form phosphoryl chloride and eventually orthophosphoric acid, which can be interpreted according to the following sequence of reactions:¹⁹



Species of the type $\text{Cl-P}(\text{Cl})_3\text{-OH}$, HOP(O)Cl_2 , and $(\text{HO})_2\text{P(O)Cl}$ are presumably highly reactive and have apparently not been observed directly in this study or in previous studies.

(11) (a) Maciel, G. E.; Sindorf, D. W. *J. Am. Chem. Soc.* **1980**, *102*, 7606–7607. (b) Sindorf, D. W.; Maciel, G. E. *J. Phys. Chem.* **1982**, *86*, 5208–5219.
(12) Crutchfield, M. M.; Dungan, C. H.; Letcher, J. H.; Mark, V.; Van Wazer, J. R. *Topics in Phosphorus Chemistry*; Wiley: New York, 1967; Vol. 5.

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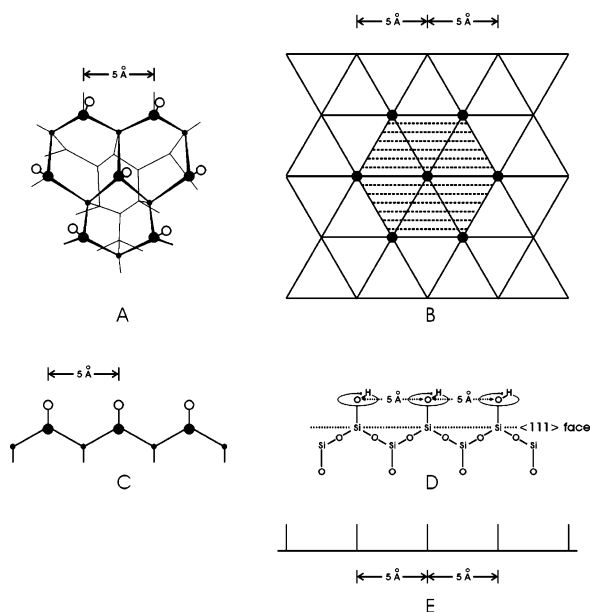


Figure 3. Various views of a hydroxyl-terminated $\langle 111 \rangle$ plane of the β -cristobalite crystal structure. (A–B), top views, looking down at the $\langle 111 \rangle$ -type plane. (C–E) side views, looking ‘into’ the $\langle 111 \rangle$ -type plane. Filled circles represent silicon atoms; open circles represent OH groups. (B) Silicons situated at each intersection (the hexagon is darkened to indicated the relationship between a silicon and its six nearest-neighbor silicons); (A) hydroxyl group pointing up is situated on top of each silicon in this plane. (E) Shorthand notation for a side view of a hydroxyl-terminated $\langle 111 \rangle$ plane single silanols represented as short terminal lines.

It is a reasonable supposition that PCl_5 can react with silanol groups on the silica surface in a manner represented in eq 1 to form species of the type, Si-O-PCl_4 (II). In the absence of a ready source of a sufficient quantity of water to produce POCl_3 from Si-O-PCl_4 (II), we expect that species II will persist for some time and be observed readily. It is interesting to examine the fate of Si-O-PCl_4 moieties in the environment of a silica gel surface on which hydroxyl groups of silanols cannot move freely on the surface in a manner similar to motion of physisorbed H_2O . To make this examination and before discussing the reactions of PCl_5 on the silica surface in detail, it is beneficial to review the geometry and distribution of silanols on the silica gel surface.

In terms of a silica surface model that is based on hydroxyl-terminated planes of the β -cristobalite crystal structure,²⁰ single silanols (Q_3) and geminal silanols (Q_2) are situated on $\langle 111 \rangle$ -type and $\langle 100 \rangle$ -type planes, respectively. On the same hydroxyl-terminated $\langle 111 \rangle$ plane, each single silanol is surrounded by six other single silanols, each at the corner of a regular hexagon, with a $\text{O}\cdots\text{O}$ distance of 5 Å between each pair of nearest neighbors of these seven

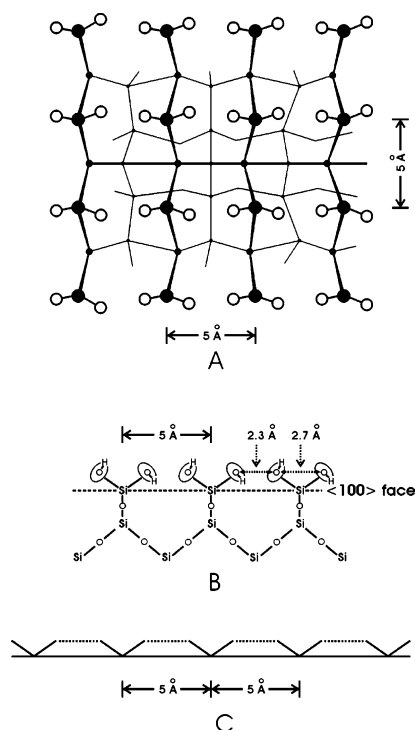


Figure 4. Various views of a hydroxyl-terminated $\langle 100 \rangle$ -type plane of the β -cristobalite crystal structure. (A) Top view, looking down at the $\langle 100 \rangle$ -type plane, with the silicon atoms of geminal silanols as filled circles and hydroxyl groups as open circles (oxygen bridges not shown). (B–C) Side views of a hydroxyl-terminated $\langle 100 \rangle$ plane with geminal silanols. (C) Shorthand notation for a side view of a hydroxyl-terminated $\langle 100 \rangle$ plane and its geminal silanols in the same row in (A), with dotted lines indicating hydrogen bonds.

single silanols. This structural situation is shown in Figure 3. The 5 Å $\text{O}\cdots\text{O}$ distance prevents a hydroxyl group of the type shown in Figure 3 from forming a hydrogen bond with any of its nearest-neighbor hydroxyl groups, and the hydroxyl group can rotate freely about the Si-O bond approximately, as indicated in Figure 3D, which is a side view into the $\langle 111 \rangle$ -type plane; a corresponding shorthand notation is shown in Figure 3E.

As shown in Figure 4, each silicon of a geminal silanol on the $\langle 100 \rangle$ -type plane is separated by 5 Å from the silicon atom of an adjacent geminal silanol. While the two hydroxyl groups of a *given* silanol are not oriented suitably for hydrogen bonding with each other, Figure 4B shows that the $\text{O}\cdots\text{O}$ distance between a pair of adjacent hydroxyl groups, tilting toward each other, on neighboring geminal silanols is 2.3 Å; and the pair of geminal hydroxyl groups is hydrogen bonded to each other. Figure 4C represents this relationship in a shorthand notation.

The surface of silica gel is rough, instead of a smooth surface that consists of just $\langle 111 \rangle$ -type or $\langle 100 \rangle$ -type planes. Our current view of the structure of the silica surface emphasizes *intersections* between these two different types of planes. Figure 5 shows a few examples of concave and convex intersections of $\langle 111 \rangle$ -type and/or $\langle 100 \rangle$ -type planes in shorthand notation.

Turning attention back to the fate of the Si-O-PCl_4 moiety (II) formed from the reaction of PCl_5 with silanols, one can easily predict the circumstances in which type-II

- (14) Sindorf, D. W.; Maciel, G. E. *J. Am. Chem. Soc.* **1983**, *105*, 3767–3776.
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 (16) Wang, X.; Coleman, J.; Jia, X.; White J. L. *J. Phys. Chem. B* **2002**, *106*, 4941–4946.
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 (20) Chuang, I. S.; Maciel, G. E. *J. Phys. Chem. B* **1997**, *101*, 3052–3064 and references therein.

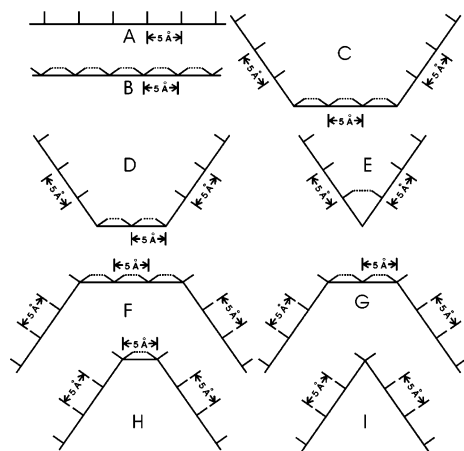


Figure 5. Shorthand representations of some possible kinds of intersections between $\langle 111 \rangle$ -type and/or $\langle 100 \rangle$ -type β -cristobalite planes, showing hydrogen bonding as dotted lines.

moieties are able to interact with a neighboring silanol, according to reaction 2, to produce the bridged species, $(\text{Si}-\text{O})_2\text{PCl}_3$ (III). Geometrical factors (reasonable bond angles and bond lengths) severely constrain the formation of $(\text{Si}-\text{O})_2\text{PCl}_3$ to those $\text{Si}-\text{O}-\text{PCl}_4$ groups that were formed from silanols capable of hydrogen bonding. Geometrical modeling (e.g., Figure S7 in the Supporting Information) shows that if the initial silanol was not hydrogen bonded, then the shortest $\text{P}\cdots\text{O}$ distance between the resulting $\text{Si}-\text{O}-\text{PCl}_4$ moiety and a neighboring silanol is 3.8 Å, which is too large to permit formation of a second $\text{P}-\text{O}$ bond. Geometrical constraints also preclude the formation of a species such as $\text{Si}(\text{-O})_2\text{PCl}_3$ from the two hydroxyls of an individual geminal silanol.

As one would expect from the orientation of single silanols represented in Figure 3a,b, geometrical modeling (Figure S8 in Supporting Information) indicates that seven $\text{Si}-\text{O}-\text{PCl}_4$ moieties can be formed in close proximity with each other, on neighboring non-hydrogen-bonded single silanol sites, although they require some special orientations to fit. Each of the original single silanols is surrounded by six nearest-neighbor single silanols in the same $\langle 111 \rangle$ -type plane (Figure 3a); after the central silanol is converted to $\text{Si}-\text{O}-\text{PCl}_4$, the formation of neighboring $\text{Si}-\text{O}-\text{PCl}_4$ groups may be substantially slower due to steric hindrance. We expect that all of the $\text{Si}-\text{O}-\text{PCl}_4$ moieties formed from non-hydrogen-bonded silanols persist, pending other interactions, such as hydrolysis (vide infra).

When PCl_5 reacts with the hydroxyl group of a hydrogen-bonded silanol, the bulky $\text{Si}-\text{O}-\text{PCl}_4$ group that is formed will sterically prevent the formation of a second $\text{Si}-\text{O}-\text{PCl}_4$ moiety on the site of its hydrogen-bonding partner. Instead, the $\text{Si}-\text{O}-\text{PCl}_4$ moiety formed from a hydrogen-bonded silanol can interact with the hydrogen-bonding partner of the pre-phosphorylated original hydroxyl group (as seen in Figure 4a for pre-phosphorylated geminal silanols), to produce $(\text{Si}-\text{O})_2\text{PCl}_3$ (III) because the bond orientations and $\text{P}\cdots\text{O}$ distance are ideal for the formation of III, as predicted by geometrical considerations manifested in geometrical modeling and represented in Figure 6(a,b,c)

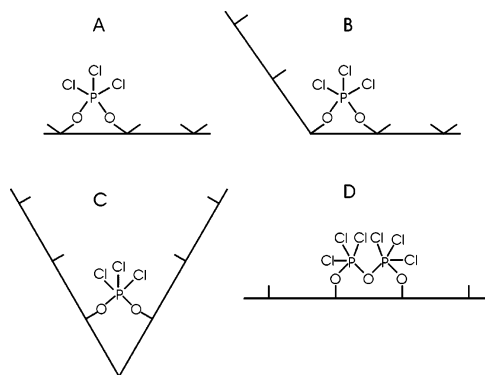


Figure 6. Representations of surface geometries that could accommodate bridged structures on the surface. (A–C) Surface features permitting $(\text{Si}-\text{O})_2\text{PCl}_3$ bridges. (D) A surface feature that would permit $(\text{Si}-\text{O}-\text{PCl}_3)_2\text{O}$ bridges.

and Figure S9 of the Supporting Information. As seen in these figures, bridged structures of the $(\text{Si}-\text{O})_2\text{PCl}_3$ type can form only between (pre-phosphorylated) silanol sites that are close enough to be mutually hydrogen bonded. A structure of the type depicted in Figure 6C might be unlikely because its formation would require a highly reactive species (PCl_5) or its partially reacted surface analogue ($\text{Si}-\text{O}-\text{PCl}_4$) to move across a large number of silanols (vide infra). More likely are structures, like those depicted in Figure 6A and B, involving at least one geminal silanol precursor.

The majority of hydrogen-bonded single silanols are located at the concave intersections of two $\langle 111 \rangle$ -type planes (Figure 5e). Each pair of hydrogen-bonded single silanol forms only one $(\text{Si}-\text{O})_2\text{PCl}_3$ linkage (Figure 6C). On the other hand, each of the two hydroxyl groups of hydrogen-bonded geminal silanols can form one $(\text{Si}-\text{O})_2\text{PCl}_3$ group with its hydrogen-bonded partner (as predicted from the geometrical arrangement of geminal silanols represented in Figure 5), i.e., each geminal silanol can consume one PCl_5 unit stoichiometrically, while a pair of hydrogen-bonded single silanols (Figure 5e) can consume only one PCl_5 unit to produce species of type III.

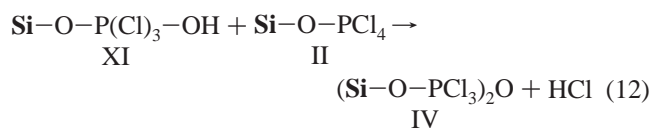
In terms of thermodynamic reactivity, we note that if PCl_5 reacts with a hydrogen-bonded silanol, a hydrogen bond must be broken, but after $\text{Si}-\text{O}-\text{PCl}_4$ is formed, it can form the stable bridged species III, with two $\text{O}-\text{P}$ bonds, providing a major energy advantage. In terms of kinetic reactivity considerations, in order for PCl_5 to react with a hydrogen-bonded single silanol (Figure 5e), the PCl_5 must travel across or near numerous non-hydrogen-bonded silanols without reacting in order to reach the hydrogen-bonded single silanols; one can expect the probability of this kind of situation to be small. Furthermore, if any of these non-hydrogen-bonded silanols have already reacted with PCl_5 to become bulky $\text{Si}-\text{O}-\text{PCl}_4$ moieties, that situation may provide a steric barrier for the otherwise mobile PCl_5 units to reach and react with the hydrogen-bonded single silanols. On the other hand, if the formation of $\text{Si}-\text{O}-\text{PCl}_4$ groups from single silanols (eq 1) is a highly reversible reaction, the $\text{Si}-\text{O}-\text{PCl}_4$ moieties may migrate along the $\langle 111 \rangle$ -type surface with its array of single silanols and the eventual formation of more stable $(\text{Si}-\text{O})_2\text{PCl}_3$ moieties on the pre-

phosphorylated, hydrogen-bonding silanol sites (Figure S9) will be favored.

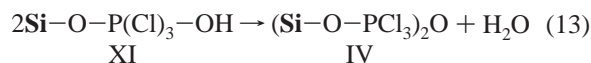
Observing the trend in ^{31}P MAS NMR results of the 0.077 P/SiOH sample in going from a to e in Figure 1, it is tempting to entertain the view of a Si-O-PCl_4 moiety migrating along non-hydrogen-bonded single-silanol sites and reaching a hydrogen-bonded single-silanol site (e.g., Figure 5e) to form the stable species III. This possibility and the steric influence brought about by the formation of bulky Si-O-PCl_4 moieties can be viewed in terms of data obtained under conditions of more effective H_2O exclusion (such as those presented in Figure S2).

From Figure 1, as well as Figure S13 in the Supporting Information, one can see that the time scales for converting the peak at about 14 ppm (Si-O-PCl_4 , II) to a peak at -4 ppm (III and/or IV) is about 20 times slower for the rotor-contained sample stored in a dry- N_2 glovebox relative to the rotor-contained sample in air. On this basis, it appears that at least 95% of the change in ^{31}P DP-MAS NMR spectra from a to e in Figure 1 is due to hydrolysis of Si-O-PCl_4 moieties brought about by water that slowly leaked through the O-ring seals in the MAS rotor instead of the in situ conversion of Si-O-PCl_4 to $(\text{Si-O-})_2\text{PCl}_3$ as discussed above. A reasonable candidate for the H_2O -generated -4 ppm peak of Figure 1 is $(\text{Si-O-PCl}_3)_2\text{O}$ which, like moiety III, is a bridged structure but in this case involving two phosphorus atoms in the bridge (e.g., as represented in Figure S10).

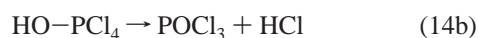
The first step that one might envision for the hydrolysis of Si-O-PCl_4 on the silica surface is shown in eq 9a, leading to the formation of $\text{Si-O-P}(\text{Cl})_3\text{-OH}$ (XI). The fate of such a species (XI) on the silica gel surface is an interesting subject. Several possible reactions can be postulated for species XI, for example, eq 9b leads to $\text{POCl}_3(\text{ad})$ or reaction with neighboring Si-O-PCl_4 moieties or a second (neighboring) $\text{Si-O-P}(\text{Cl})_3\text{-OH}$ group:



or



Species of type XI, which, as far as we know, have not been detected directly in these ^{31}P NMR experiments, might also interact with additional H_2O to produce reaction products of more advanced stages of hydrolysis. One possible alternative transformation of species II by water, as shown in eq 14, is considered to be unlikely due to the susceptibility of P-Cl bonds to attack by H_2O .



A priori, there are some conditions that could lead to detectable POCl_3 populations (e.g., peak V in Figures 1 and S3), perhaps by transformations such as the reaction shown in eq 9b. However, as discussed above, the appearance of $\text{POCl}_3(\text{ad})$ appears to require ready access to H_2O (e.g., in a high-humidity environment). POCl_3 is unlikely to be produced by the reactions depicted in eq 14, which involve cleavage of the SiO-P linkage prior to hydrolysis of a P-Cl moiety; this is opposite to the order of bond breaking in the sequence represented by eqs 9a and 9b, considered here to be a more likely sequence.

Figure 1 (a-e) clearly indicates that Si-O-PCl_4 (II, ~ 14 ppm) gradually converts to $(\text{Si-O-PCl}_3)_2\text{O}$ (IV, -4 ppm) and/or $(\text{Si-O-})_2\text{PCl}_3$ (III, -4 ppm) and some advanced hydrolytic products such as phosphoric acid (0 ppm), $\text{Si-O-P}(\text{O})(\text{OH})_2$ (VI, -12 ppm), $(\text{Si-O-P}(\text{O})(\text{OH}))_2\text{O}$ (VIII, -25 ppm), and/or $(\text{Si-O-})_2\text{P}(\text{O})\text{OH}$ (VII, -25 ppm). With a 0.077 molar PCl_5/SiOH ratio, if all the PCl_5 were to react with either non-hydrogen-bonded silanols to form Si-O-PCl_4 or (to a much lower extent) with hydrogen-bonding Si-OH to form $(\text{Si-O-})_2\text{PCl}_3$, we would expect that a predominant portion of Si-O-PCl_4 moieties would have at least one nearest-neighbor Si-O-PCl_4 moiety within a distance of about 5 Å (especially since the steric bulk of Si-O-PCl_4 groups will likely render their distribution on the surface relatively uniform. If Si-O-PCl_4 groups are distributed on the surface completely *uniformly*, only 48% of them will have one nearest-neighbor Si-O-PCl_4 on average. However, a *random* distribution of these groups can result in a majority of them having one such nearest neighbor). Under such circumstances, it is reasonable to speculate that, assuming $\text{Si-O-P}(\text{Cl})_3\text{OH}$ is formed by hydrolysis of Si-O-PCl_4 (eq 9a), the latter will react with its Si-O-PCl_4 neighbor to form $(\text{Si-O-PCl}_3)_2\text{O}$ (eq 12). According to this scenario, the formation of POCl_3 (eq 9b) would become a much less important process due to the high reactivity of $\text{Si-O-P}(\text{Cl})_3\text{OH}$ toward neighboring Si-O-PCl_4 moieties. Figure S10 of the Supporting Information shows the results of geometrical modeling for a $(\text{Si-O-PCl}_3)_2\text{O}$ (IV) moiety on the $\langle 111 \rangle$ -type plane of a silica surface.

In an unsuccessful attempt to demonstrate unequivocally the presence of species, such as IV and VIII, which contain P-O-P linkages, an extensive series of Carr-Purcell-Meiboom-Gil experiments were carried out.²¹⁻²⁴ Presumably because of some combination of effects, including the presence of nearby chlorine nuclear magnetic moments and more than one nearby phosphorus, no clear evidence of distinct dipolar couplings was obtained (clear dipolar patterns were observed by the same technique on three model systems).

Summary and Conclusions

^{31}P NMR is exquisitely sensitive to details of the complex chemistry that occurs when PCl_5 is adsorbed on a silica

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surface. Based on reactions of surface silanol (Si-OH) groups, the anticipated Si-O-P linkages are formed, as well as $(\text{Si-O})_2\text{P}$ bridges or $(\text{Si-O-P})_2\text{O}$ bridges on surface segments for which the structural geometry is favorable. Hydrolysis of surface-attached species, either slowly by H_2O leaking into a MAS rotor or much more rapidly upon exposure to high humidity, generates a rich array of hydrolysis products. By taking extra precautions to exclude water from the sample, chemistry that is observed in the 'closed-rotor' portion of the NMR experiments carried out with only modest H_2O -exclusion measures can be slowed dramatically. While the types of reactions observed in low-loading and high-loading sample are generally the same, the relative rates of these processes depend on loading level.

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Supporting Information Available: Additional information on geometrical modeling, on ^1H MAS results, on supporting infrared results, and on extensive results on $\text{PCl}_5/\text{SiO}_2$ samples with $\text{P}/\text{SiOH} = 0.77$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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