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Direct Reaction of Phosphorus Acids with Hydroxy of a Silanol and on the Silica Gel Surface

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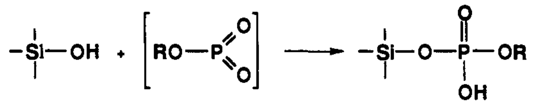
Abstract: Several phosphorus acids (methyl- and phenylphosphonic, diphenylphosphinic, and ethyl phosphoric acids) were found to give esters on reaction with *tert*-butyldimethylsilanol. The reactions occurred simply on heating the reactants in an inert solvent (hexane or toluene). The reaction is reversible, and yields of esters were improved by continuous water removal. The dibasic acids gave either mono- or disilyl esters; the latter were more easily purified and characterized. The OH groups on the surface of silica gel were also found to react with various phosphorus acids under similar conditions to give surface-bonded esters. Products were characterized by CP/MAS ^{31}P and ^{29}Si NMR. In the case of phenylphosphonic acid and ethyl phosphoric acids, the products were spectrally identical with those obtained by phosphorylation of the surface OH groups with the highly reactive 3-coordinate anhydrides of these acids when generated in the presence of silica gel.

In recent publications,[1,2] we have described the action of alkyl metaphosphates, highly reactive and known only as transient species, on the surface OH groups of silica gel. This produces a phosphate group directly bonded to the silica surface:

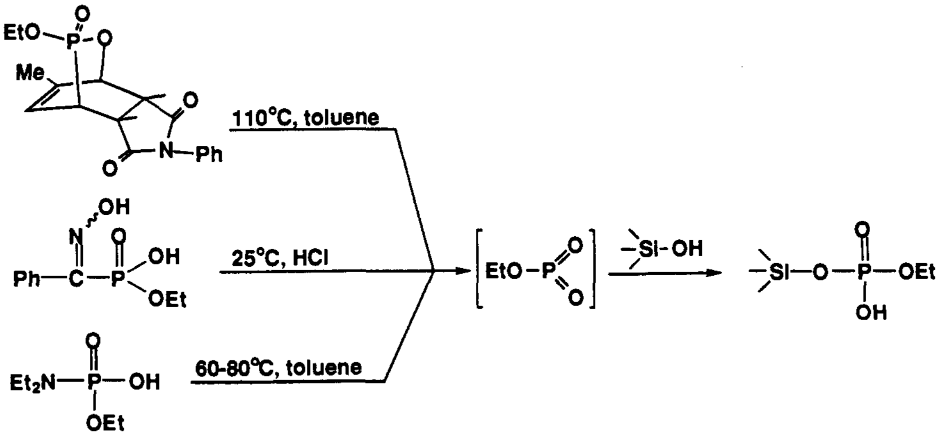


$$-\mathrm{Si}-\mathrm{OH} + \left[\mathrm{RO}-\mathrm{P}(=\mathrm{O})_2\right] \longrightarrow -\mathrm{Si}-\mathrm{O}-\mathrm{P}(=\mathrm{O})(\mathrm{OH})-\mathrm{OR}$$

Three different precursors of metaphosphate have been used in these studies, illustrated in Scheme 1 for the ethyl derivative. The same phosphorylated product is formed in each reaction, as revealed by cross polarization–magic angle spinning (CP/MAS) ^{31}P NMR spectroscopy. The proposal that phosphorus is indeed bonded covalently to the surface is supported by the position of the ^{31}P NMR signal at δ -10; simple phosphates have shifts around $\delta \pm 1$, but upfield shifts of about 10 ppm occur routinely when siloxy groups replace alkoxy or hydroxy groups (*cf.* $(EtO)_2P(O)OH$, δ +1, to $(EtO)_2P(O)OSiMe_3$, δ -9[1]), and a similar shift can be expected for the silica phosphate. The possibility was also considered that the metaphosphate was simply hydrolyzed to ethyl phosphate by water remaining on the surface, and adsorbed phosphate gave the observed signal. However, a sample of ethyl phosphate when adsorbed on the surface had its ^{31}P NMR signal at about δ 0. Furthermore, adsorbed phosphate was readily removed from the surface by a wash with 2-propanol, while the entity giving the signal at δ -10 was not affected by this treatment.

Similarly, dioxophenylphosphorane ($PhPO_2$) was found to react with the surface OH to form a phosphonate, having a CP/MAS ^{31}P NMR signal δ 10.4. However, during studies of the adsorptive behavior of its hydrolysis product, phenylphosphonic acid, we noted a peculiar effect. When a solution of the phosphonic acid in chlorobenzene was mixed with silica gel and refluxed for 2 h, a prominent new ^{31}P NMR signal appeared at δ 10.4 in the recovered solid. The signal, which remained after a 1-propanol wash, differed from that for adsorbed acid (δ 15.5). The signal is, in fact, in the same position as observed for the surface-bound phosphonate from the reaction with dioxophenylphosphorane.

Scheme 1



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[*] Abstract published in *Advance ACS Abstracts,* February 1, 1994.

(1) Quin, L. D.; Wu, X.-P.; Breuer, E.; Mahajna, M. *Tetrahedron Lett.* **1990**, *31*, 6281.

(2) Quin, L. D.; Wu, X.-P.; Quin, G. S.; Jankowski, S. *Phosphorus Sulfur Silicon* **1993**, *76*, 91.

(3) Orlov, N. F.; Voronkov, M. G. *J. Gen. Chem.* **1960**, *30*, 2206.

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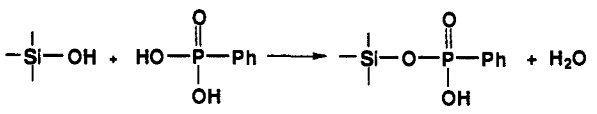
The implication is that there is a direct reaction occurring between the acid and the surface OH to form a silyl phosphonate:



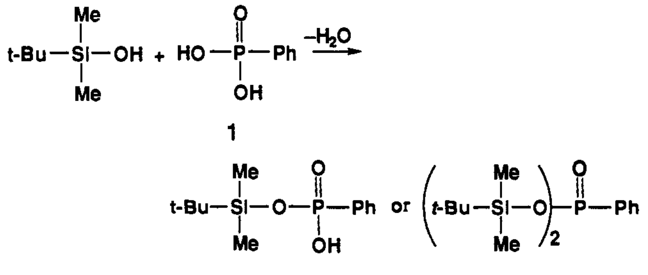
$$-\overset{|}{\underset{|}{Si}}-OH + HO-\overset{O}{\overset{\|}{\underset{OH}{\underset{|}{P}}}}-Ph \longrightarrow -\overset{|}{\underset{|}{Si}}-O-\overset{O}{\overset{\|}{\underset{OH}{\underset{|}{P}}}}-Ph + H_2O$$

This was a quite surprising observation, since phenylphosphonic acid was not observed to give an ester with an alcohol (ethanol) under comparable conditions. We have so far been unable to find any example in the literature of a surface reaction between organophosphorus acids and silica gel. Such a study is now reported in this paper. The study was initiated by examining the reaction of a simple monomeric silanol (*tert*-butyldimethylsilanol) with organophosphorus acids. The literature[3] does record the direct formation of trisilyl phosphates from the reaction of phosphoric acid with triethyl- or triphenylsilanols in refluxing benzene or toluene. Mention is made in a monograph[4] of similar reactions occurring with phosphinic acids, although the publications said to contain details of these experiments are not accessible. No ^{31}P or ^{29}Si NMR data were reported.[3,4]

Silica gel to which acidic phosphorus-containing groups have been bonded is proving to have valuable properties, for example in HPLC applications.[2] A method for phosphorylating silica gel by the direct reaction with a phosphorus acid could have considerable practical value in modification of the silica surface.

Results and Discussion

Reaction of a Silanol with Phosphorus Acids. (a) Phenylphosphonic Acid. When a 1:1 mixture of phenylphosphonic acid (**1**, ^{31}P δ 14.5) and *tert*-butyldimethylsilanol was refluxed in hexane, a new ^{31}P NMR signal developed at δ 10.4. After 2 h, no starting phosphonic acid remained. In addition to the main signal, there was a minor (about 5% of the peak area) signal further upfield (δ –0.3) for another product. The chemical shifts suggest the assignment of monosilyl phosphonate structure **2** to the major product and disilyl phosphonate structure **3** to the minor product. It proved possible to isolate compound **2** as a low-melting (35 °C) solid, which could be recrystallized under anhydrous conditions. Elemental analysis confirmed the formula, and the expected ^{13}C and ^{1}H NMR spectra were obtained. When the silanol was used in excess, compound **3** was the sole product and was isolated by Kugelrohr distillation.



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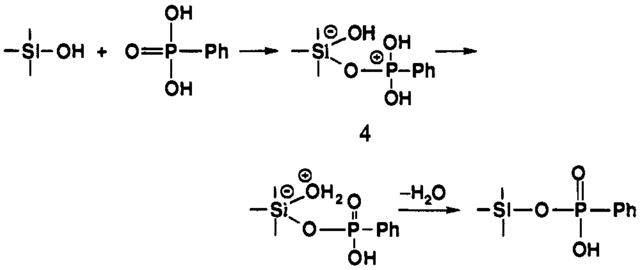
That the esterification of the (sterically hindered) silanol proceeds much more readily than the esterification of an alcohol with phenylphosphonic acid suggests that a different reaction mechanism is being followed by the silanol, which can act as a Lewis acid:[5]



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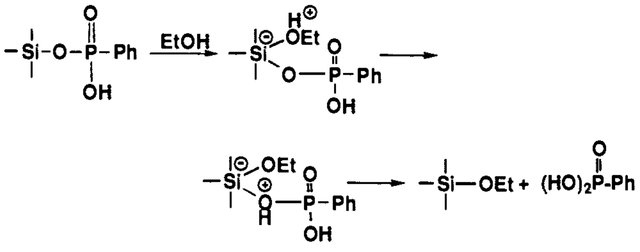
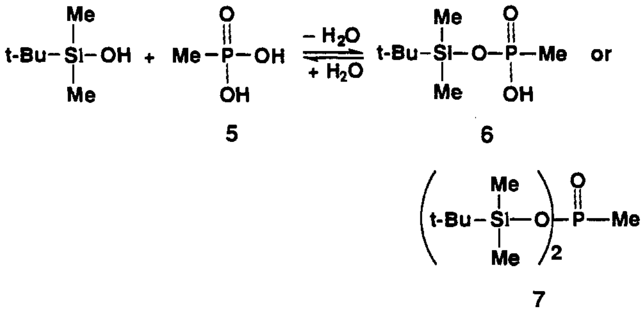
Protonation of the silanol OH is also a possible preliminary event in this reaction.[3,4] Silyl phosphonate **2** was found to be readily hydrolyzed, which made its isolation in pure form quite difficult. Phosphonate **2** was also reactive to ethanol in toluene solution; a peak of low intensity corresponding to that of the free phosphonic acid (^{31}P NMR δ 14.5) was observed after a few hours on standing at room temperature. After 2 days, ^{31}P NMR showed that most of the ester was destroyed and the signal for the free phosphonic acid was dominant. There was no indication of the formation of the ethyl ester of the phosphonic acid. Other examples have been reported in the literature[6] where nucleophilic attack is more rapid at silicon than at phosphorus.



The sensitivity of the silyl ester **2** to water and alcohol is consistent with the previously mentioned suggestion that the reaction used to synthesize it, the direct silanol–acid combination, must be an equilibrium process. Indeed, the yields in the reaction were significantly improved when the water was removed as formed with a Soxhlet thimble containing Na_2SO_4.

(b) Methylphosphonic Acid. Similar results were obtained with methylphosphonic acid (**5**, ^{31}P NMR δ 25.7). Under the same conditions as used for phenylphosphonic acid, esterification occurred to form the monosilyl ester **6** (^{31}P NMR δ 21.2) and a small amount of the disilyl ester **7** (δ 11.4; the same value was reported[7] when the diester was prepared by reaction of the acid with *tert*-butyldimethylsilyl chloride). Isolation attempts gave **6** as an oil, and it was not further characterized. With excess silanol, **7** was the sole product and it was isolated by distillation in pure form.



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6

7

(c) Diphenylphosphinic Acid. Diphenylphosphinic acid (**8**) was much slower in its reaction with the silanol and required use of a higher boiling solvent (chlorobenzene, bp 138 °C). The ^{31}P NMR shift for the product (**9**) was δ 21.9; a literature[8] value is

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(4) Borisov, S. N.; Voronkov, M. G.; Lukevits, E. Ya. *Organosilicon Derivatives of Phosphorus and Sulfur*; Plenum Press: New York, 1971; p 27.

(5) Hair, M. L. In *Silicon Chemistry*; Corey, F. R., Corey, J. Y., Gaspar, P. P., Eds.; Ellis Horwood Ltd.: Chichester, England, 1988; Chapter 44.

(6) Wozniak, L.; Chojnowski, J. *Tetrahedron* **1989**, *45*, 2465.

(7) Issleib, K.; Balszuweit, A.; Stiebitz, B. *Z. Anorg. Allg. Chem.* **1987**, *546*, 147.

Table 1. ^{31}P and ^{29}Si NMR Spectral Data for *tert*-Butyldimethylsilyl Esters of Phosphorus Acids[a]

compd no.	^{31}P NMR, δ	^{29}Si NMR δ	^{29}Si NMR $^2J_{POSi}$, Hz
2	10.4	25.5	10.2
3	−0.3	23.2	9.0
6	21.3	22.5	10.3
7	11.4[b]	22.4	9.7
9	21.9[c]	25.8	10.6
11	−7.5	24.1	7.9
12	−16.6	23.7	7.6

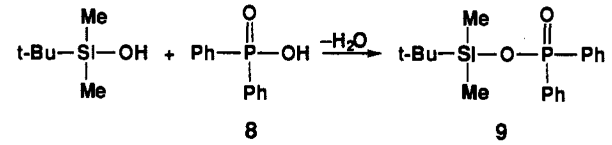
[a] In $CDCl_3$. Spectra are proton decoupled. 85% H_3PO_4 was used as ^{31}P reference; Me_4Si was the reference for ^{29}Si. ^{29}Si NMR were prepared with the INEPT pulse sequence. [b] Reference 7, δ 11.4. [c] Reference 8, δ 20.7.

Table 2. Data for Phosphorylated Silica Gel

acid structure	acid δ(^{31}P)	reaction solvent[a]	silica δ(^{31}P)[b]	silica δ(^{29}Si)[c]	silica % P
$PhPO(OH)_2$ (**1**)	14.5[d]	C_6H_5Cl	10.4	−103.3 w, −114.2 s	1.3
1		CH_3CN	11.1	*e*, −114.0 s	2.5
1		*n*-PrOH[f]	9.0	−103.5 w, −113.6 s	0.9
$MePO(OH)_2$ (**5**)	25.7[g]	CH_3CN	20.1	−103.7 w, −113.9 s	1.5
$Ph_2P(O)OH$ (**8**)	29.0[g]	C_6H_5Cl	24.4	−103.0 w, −115.7 s	1.3
PhPH(O)OH (**14**)	20.1[g]	C_6H_5Cl	15.7	*e*, −112.6 s	1.7
14		CH_3CN	17.3	−104.4 w, −113.8 s	1.1
14		CH_3CN[f]	17.5	−104.3 m, −114.2 s	0.9
14		CH_3CN[h]	17.5	−103.4 m, −113.6 s	
$(EtO)_2PO(OH)$ (**10**)	−0.5[g]	EtOH	−10.6	−104.0 m, −112.3 s	0.4
$EtOPO(OH)_2$ (**15**)	−0.4[g]	EtOH	−9.6	−103.7 m, −112.6 s	0.6
n-$PrOPO(OH)_2$ (**16**)	−1.45[g]	*n*-PrOH	−9.1	−104.3 m, −112.6 s	0.9

[a] At reflux for 2 h, unless noted. [b] CP/MAS; referenced to $CaHPO_4$ as 0 ppm. [c] CP/MAS; referenced to DSS as 0 ppm. Intensities are weak (w), medium (m), or strong (s) relative to starting silica gel with δ −103 (s), −113 (s). [d] In D_2O. [e] Downfield signal absent. [f] At room temperature for 2 h. [g] In $CDCl_3$. [h] At room temperature for 17 min.

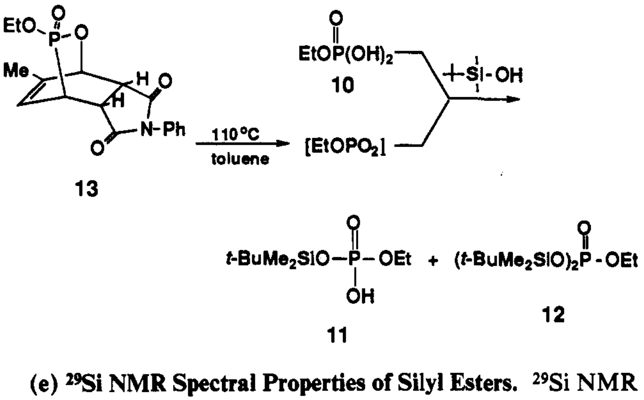
δ 20.7 for this ester as formed from the acid and *tert*-butyldimethylsilyl chloride.



8 **9**

The product was obtained as a distillable oil giving the correct analysis, but it was extremely sensitive to water. The reactivity of **9** to ethanol was much greater than observed for the corresponding phosphonates; no **9** remained after a hexane solution containing a 5-fold molar excess of ethanol was allowed to stand for 3 h, and diphenylphosphinic acid precipitated from the solution.

(d) Ethyl Phosphate. *tert*-Butyldimethylsilyl ethyl phosphate (**11**) and bis(*tert*-butyldimethylsilyl) ethyl phosphate (**12**) were formed from reaction of ethyl phosphate (**10**) with the silanol in toluene at 110 °C. With excess silanol, **12** became the major product and was isolated in analytically pure form by Kugelrohr distillation. Structures **11** and **12** were also obtained when the metaphosphate method was used. Ethyl metaphosphate was generated as a transient intermediate from the bicyclic precursor **13** in the presence of the silanol; ester **11** was formed first, but proceeded to react with the silanol in the solution to give the diester **12**.



(e) ^{29}Si NMR Spectral Properties of Silyl Esters. ^{29}Si NMR spectra were recorded for all of the silyl esters and are recorded in Table 1. Relative to *tert*-butyldimethylsilanol (δ +17.6), there was a consistent downfield shift on the order of 3–8 ppm. The ^{13}C NMR shifts for the α-carbon of alcohols change in just the same way on conversion to phosphates or phosphonates.[9] The ^{29}Si signals were split to doublets by ^{31}P, with $^2J_{POSi}$ values around 8–10 Hz.

Reaction of Silica Gel with Phosphorus Acids. Silica gel was allowed to react with a number of phosphorus acids (Table 2), with the creation of ester groups covalently bonded to the solid surface. The reactions were easily performed by stirring the suspended silica gel in refluxing toluene or chlorobenzene containing a several-fold molar excess of the acid relative to the OH content of the silica gel used (known[2] to be 0.69 ± 0.14 mequiv/g). Reaction was extensive after 2 h. In some cases, the reactions were conducted at room temperature. Thus, a suspension of silica gel in an acetonitrile solution of a typical acid (phenylphosphinic, **14**) was stirred at room temperature for 2 h; the ^{31}P NMR spectrum (Table 2) was the same as obtained when the mixture was refluxed. There was NMR evidence for the occurrence of the reaction after only 17 min, attesting to the ease of the phosphorylation process. Extensive reaction also occurred at room temperature with a solution of phenylphosphonic acid in 1-propanol, and with monoethyl phosphate in acetonitrile.

The phosphorus content of the products from the phosphonic and phosphinic acids was quite high (Table 2: 1.1–2.5% P; theory based on 0.69 mequiv ±0.14 per g is 1.7–2.6%). Phosphates gave somewhat lower vaues (0.4–0.9% P). The products were also characterized by CP/MAS ^{31}P and ^{29}Si NMR. The data are recorded in Table 2 and discussed in the next section.

NMR Analysis of Phosphorylated Silica Gel. The phosphonic acids **1** and **5** gave silica products with CP/MAS ^{31}P NMR signals upfield of the starting acids by 4–5 ppm. This corresponds to the upfield shifting observed on reacting these acids with *tert*-butyldimethylsilanol as a model to form monosilyl esters (**2** and **6**). Washing with solvents as polar as 2-propanol had no effect on the intensity of these signals; compounds giving minor signals in the region of the adsorbed phosphonic acids were, however, readily removed from the surface by the washing. Similar results were obtained with diphenylphosphinic acid **8** and phenylphosphinic acid **14**. The three phosphoric acid derivatives **10**, **15**, and **16** gave solids with major CP/MAS ^{31}P NMR signals about 9–10 ppm upfield of the values for the free phosphoric acids. In the case of monoethyl phosphate, the product had the same shift (δ −9.6) as found when the surface was phosphorylated by ethyl metaphosphate (δ −9 to −10 in various experiments[1,2]). It was also found by ^{31}P NMR analysis that the silica could be phosphorylated when it was heated with a solution of P_2O_5 in ethanol, giving a product with a CP/MAS ^{31}P NMR shift of δ −9.3; similarly, a mixture of P_2O_5 in 1-propanol gave a solid with the shift of δ −10.5. Presumably these solutions contain mixtures of mono- and dialkyl phosphates, which then react with the surface. Triethyl phosphate was found not to be reactive to the surface, pointing quite convincingly to the need for a free P–OH group for a reaction to occur.

We have pointed out elsewhere[2] that ^{29}Si NMR can be effectively used to prove that a free OH on silica has been converted to a phosphate derivative after exposure to ethyl metaphosphate. Silica gel has been reported to give three signals when examined

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(8) Cypryk, M. Ph.D. Thesis, Lodz, Poland, 1982 (cited in ref 6).

(9) Stothers, J. B. *Carbon-13 NMR Spectroscopy*; Academic Press: New York, 1972; pp 140 and 159.

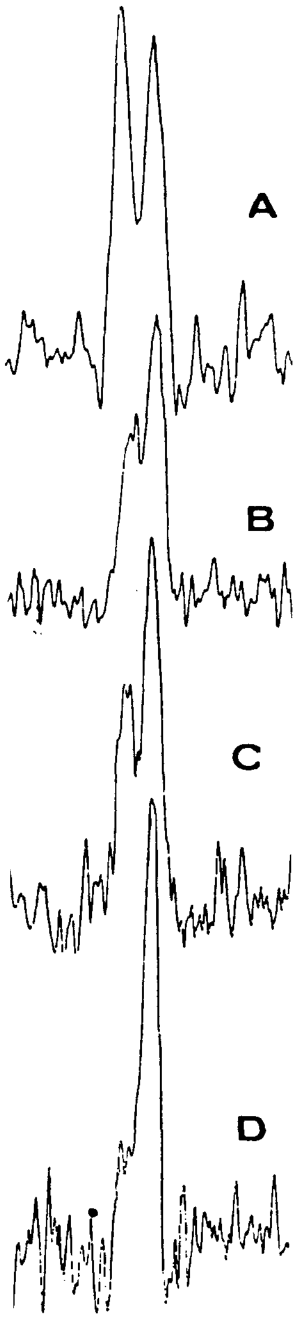
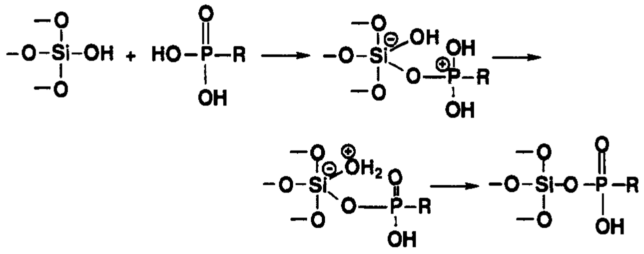


Figure 1. Typical ^{29}Si CP/MAS spectra showing the effect of phosphorylation on the Q^3 signal at δ -103. (A) Aldrich silica gel; (B) after reaction with a mixture of propyl phosphates; (C) after reaction with diethyl phosphate; (D) after reaction with phenylphosphonic acid.

by CP/MAS ^{29}Si NMR;[10,11] the most upfield signal[10] (δ -109.3, Me_4Si = 0) is assigned to Si containing no OH groups (designated[12] Q^4), that of roughly comparable peak size at δ -99.8 to Si with one OH group (designated Q^3), and the third, normally quite weak, at δ -90.6 to Si with two OH groups (designated Q^2). We have confirmed that the Aldrich silica gel used in our work gives a comparable spectrum, with major signals referenced to DSS at δ -113 (Q^4) and δ -103 (Q^3); see Figure 1. In the absence of cross polarization, the signal of δ -103 was of greatly reduced intensity. We had earlier[2] found that, after reaction with ethyl metaphosphate generated by fragmentation of the bicyclic precursor shown in Scheme 1, the CP/MAS signal for Si–OH at δ -103 was also greatly reduced in size or even vanished as a result of the conversion to the phosphate group. This is consistent with the loss of the protons on the OH groups of silica, since these are the major source of the signal enhancement by cross polarization. There was, however, no new signal that would correspond to silica bonded to a phosphoryl derivative. Either this signal is too weak to be distinguished from the noise (see Figure 1), or it is obscured by the strong Q^4 signal at δ -113. In the latter case, an upfield shift of several ppm would be required on phosphorylation. We have noted that a small downfield shift of the ^{29}Si resonance occurs on phosphorylation of a trialkylsilanol, but for silica the model needed is a trioxysilanol, a type that is not available. That the new signal may be overlapped by the large Q^4 signal is indicated by the change in relaxation time T_1 after the phosphorylation with a metaphosphate.[2] For the untreated silica gel, it was 76.2 ms, but after phosphorylation the value was reduced to 48.5 ms. However, further work is needed before a convincing case can be made for the location of the new signal arising from the Si–O–P moiety of the solid.

We have obtained the CP/MAS ^{29}Si NMR spectra for all of the samples of treated silica gel of the present work (Table 2). In every case, the result was the same; the signal for Si–OH at δ -103 was absent or greatly diminished. Some typical spectra are shown in Figure 1. Hydrogen bonding does not cause any major change in the δ -103 signal; silica gel treated with triethylamine still gave this signal, with only moderate reduction of peak size relative to the Q^4 signal.

Reaction of Silica Gel with Non-Phosphorus Acids. Lewis acid character of the silica gel may be implicated in the phosphorylation of the surface OH groups with acids, as was postulated for the reaction with silanols:



This reactivity could also hold for other types of acids, and indeed we found that silica gel and acetic acid reacted in refluxing acetonitrile. The CP/MAS ^{29}Si NMR spectrum of the solid showed the essential absence of the signal for Si–OH at δ -103. Furthermore, ^{13}C NMR signals for an acetate were present, even after drying at 0.1 Torr at room temperature for 24 h. There were, however, no significant changes in the ^{13}C NMR spectrum relative to that for the free acid and it remains to be firmly established that a bonded carboxylate is present. Trifluoromethanesulfonic acid in acetonitrile also reacted with the surface at room temperature, again as indicated by the virtual disappearance of the CP/MAS ^{29}Si NMR signal for Si–OH at δ -103.

These observations of a fast reaction occurring on the surface with various acids may be of significance in another sense. It was reported recently[13] that heat was released when a number of organic acids in hexane solution were mixed with a Fisher silica gel. It was suggested that this "heat of immersion" resulted from protonation of the acids by the OH groups on the silica gel surface. Our results with the phosphorus, carboxylic, and sulfonic acids show that chemical change can occur on the surface, even under very mild conditions, and these reactions seem better explained as being initiated by Lewis acidity at silicon.

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(11) Leonardelli, S.; Facchini, L.; Fretigny, C.; Tougne, P.; Legrand, A. P. *J. Am. Chem. Soc.* **1992**, *114*, 6412.

(12) Englehardt, G.; Jancke, H.; Hoebbel, D.; Wiecker, W. Z. *Z. Chem.* **1974**, *14*, 109.

(13) Arnett, E. M.; Ahsan, T. *J. Am. Chem. Soc.* **1991**, *113*, 6861.

(14) Greenberg, S. A. *J. Phys. Chem.* **1956**, *60*, 325.

Experimental Section

General. CP/MAS NMR experiments were performed on a Bruker 200-MHz solids spectrometer. Samples were contained in 7-mm standard zirconia rotors, spinning at 3.9–4.0 kHz. For ^{31}P, the contact time was 1.5 ms and the pulse repetition time was 3 s. For ^{29}Si, these values were 20 ms and 3 s, respectively. References were $CaHPO_4$ for ^{31}P and 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt (DSS) for ^{29}Si. Positive shifts are downfield of both references. ^{31}P NMR spectra of solutions were obtained on IBM NR-80 or Varian XL-300 spectrometers; for ^{29}Si, the latter spectrometer was employed, with the INEPT pulse sequences and complete proton decoupling. Aldrich high-purity chromatographic grade silica gel (70–230 mesh, 60 Å, BET surface area *ca.* 500 m^2 g^{-1}, pore volume 0.75 cm^3 g^{-1}) was dried at 195 °C at 0.1 mm for 96 h. Titration with calcium nitrate[14] showed 0.69 ± 0.14 mequiv OH per g. Solvents were dried by standard methods. All phosphorus acids were commercially available.

Reaction of *tert*-Butyldimethylsilanol with Phosphorus Acids. A mixture of 1.5 g (9.5 mmol) of phenylphosphonic acid (^{31}P δ 14.5 in D_2O) and 1.33 g (10.0 mmol) of *tert*-butyldimethylsilanol in 50 mL of *n*-hexane was heated to reflux. All solid dissolved after about 15 min. The reaction was complete after about 2 h as seen by the disappearance of the ^{31}P NMR signal for phenylphosphonic acid and the creation of new signals (Table 1) for silyl phosphonate **2** (95%) and disilyl phosphonate 3 (5%). The solvent was removed by rotary evaporation to leave the product as an oil. After standing 2 days in a desiccator, the oil crystallized to give **2**: mp 35–36 °C, ^{31}P and ^{29}Si NMR, Table 1. The compound was sensitive to water and recrystallization was not efficient, as revealed by the elemental analysis. Calcd for $C_{12}H_{21}O_3PSi$: C, 52.92; H, 7.77; P, 11.37. Found: C, 52.39; H, 8.08; P, 10.95. When a 3 M excess of the silanol was used, the disilyl ester 3 was the major product and could be purified by distillation (140 °C, 1.0 mmHz). Calcd for $C_{18}H_{35}O_3PSi_2$: C, 55.92; H, 9.13. Found: C, 55.38; H, 9.19.

Methylphosphonic acid was reacted with 1 mol of the silanol in the same way to give the monosilyl ester **6** (^{31}P and ^{29}Si NMR, Table 1) and a small amount of disilyl ester 7 (^{31}P and ^{29}Si NMR, Table 1). The mixture of esters was not separated. With 2 mol of silanol, the product (99%) was the distillable (105 °C, 1 mm) diester **7**. Calcd for $C_{13}H_{33}O_3PSi_2$: C, 48.11; H, 10.25. Found: C, 48.32; H, 10.50.

Diphenylphosphinic acid (2.12 g, 9.68 mmol) and 1.33 g (10.0 mmol) of the silanol in 20 mL of chlorobenzene were heated at 135 °C in a closed tube to prevent volatilization of the silanol. The crude product purified by Kugelrohr distillation at 175 °C (2.0 mm) gave 3.05 g (95%) of **9**: ^{31}P and ^{29}Si NMR, Table 1. Calcd for $C_{18}H_{25}O_2PSi$: C, 65.03; H, 7.58. Found: C, 65.22; H, 7.88.

Monoethyl phosphate (100 mg, 0.79 mmol) was dissolved in 10 mL of hexane. The silanol (260 μL) and 1 g of anhydrous sodium sulfate were added, and the mixture was refluxed with stirring for 3 h. The solid was removed by filtration under nitrogen; evaporation of the solvent gave **12** as an oil that was purified by Kugelrohr distillation at 120 °C (1.0 mmHg): yield 253 mg, 90%; ^{31}P and ^{29}Si NMR, Table 1. Calcd for $C_{14}H_{35}O_4PSi_2$: C, 47.41; H, 9.97. Found: C, 47.26; H, 10.07.

Reaction of Silica Gel with Phosphonic and Phosphinic Acids. A solution of 2 g of acids **1**, **5**, **8**, or **14** (Table 2) in 40 mL of solvent (acetonitrile, chlorobenzene, or 2-propanol) containing 5 g of suspended silica gel was refluxed for 2 h. The solid was recovered and washed with two 20-mL portions of 2-propanol and then air dried. Each sample was analyzed for phosphorus by mineralization with nitric and perchloric acids, followed by phosphomolybdate formation and its spectrophotometric determination. Results are given in Table 2, as are CP/MAS NMR data for ^{31}P and ^{29}Si.

Reactions were also conducted at room temperature with the same reactant ratio. Conditions and CP/MAS NMR results are given in Table 2.

Reaction of Silica Gel with Esters of Phosphoric Acid. A solution of ester **10**, **15**, or **16** (Table 2; 2 g in 40 mL of ethanol, except 1-propanol for **16**) containing 5 g of suspended silica gel was refluxed for 2 h, and then the recovered solid was washed with 2-propanol and air dried. Analyses for P, as well as CP/MAS NMR results, are given in Table 2.

It was also possible to perform the phosphorylations with solutions of phosphorus pentoxide (2 g) in ethanol or 1-propanol (40 mL), which produced mixtures of the mono- and dialkyl phosphates as reactive species. The mixtures were brought to reflux, and then 5 g of silica gel was added. Reflux was continued for 2 h. The recovered solid was analyzed. For ethanol, the product had 1.0% P, ^{31}P NMR δ −9.3, ^{29}Si NMR δ −113.6. For 1-propanol, the product had 0.9% P, ^{31}P NMR δ −10.5, ^{29}Si NMR δ −105.0 (weak) and −112.5 (strong).

Reaction of Silica Gel with Non-Phosphorus Acids. A solution of glacial acetic in acetonitrile was mixed with silica gel and refluxed for 2 h. The solid was recovered by filtration and washed several times with 2-propanol. The CP/MAS ^{29}Si NMR spectrum showed the absence of the signal at δ −103 for Si–OH.

A solution of 2 mL of trifluoromethanesulfonic acid in 15 mL of acetonitrile was mixed with 1.5 g of silica gel and stirred at room temperature for 17 min. The Si–OH signal at δ −103 was greatly reduced relative to that of the silica gel.

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