Phosphorylation of the Surface of Silica Gel by Ethyl Metaphosphate

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Ethyl metaphosphate was generated in toluene solution in the presence of suspended anhydrous silica gel; the weight gain, P content, and the [31]P n.m.r. spectrum of the solid, after thorough washing, showed that the hydroxy groups on the surface had been phosphorylated, and that further reaction of the initially formed monophosphate had produced pyrophosphate groups on the surface.

The highly electrophilic character of alkyl metaphosphates $(RO-PO_2)$,[1] generated in solution, towards sterically masked alcohols[2] suggested that the hydroxy groups on the surface of silica gel might be susceptible to phosphorylation. This would provide a novel type of surface-functionalised silica, possibly having valuable properties. We have indeed found that anhydrous silica gel is reactive towards ethyl metaphosphate, and it appears that a very high percentage of the hydroxy groups are phosphorylated. Details of this preliminary study, and the characterisation of the phosphorus functionality created on the surface, are described in this report.

We employed our recently reported[3] approach to metaphosphates which involves fragmentation at 100—110 °C of the 2,3-oxaphosphabicyclo[2.2.2]oct-5-ene moiety in the O-insertion products [e.g., (1)] of dimers of phosphole oxides (Scheme 1).

High purity silica gel (Aldrich, 70—230 mesh, 60 Å, Brunauer–Emmett–Teller surface area *ca.* 500 m² g⁻¹, pore volume 0.75 cm³) was dehydrated at 195 °C for 96 h at 0.1 Torr. A stirred mixture of silica gel (1.12 g) and (1) (1.95 g) (calculated to provide a 2—3 fold excess of metaphosphate relative to surface OH)[4] in anhydrous toluene (20 cm³) was heated at 110 °C for 1.5 h. The recovered solid was washed thoroughly at 80 °C with toluene. The weight gain of the dried solid was 0.515 g [the theoretical gain if all metaphosphate generated from (1) had reacted is 0.634 g]. The phosphorus content was determined to be 10.5% (calc. 9.0% if all weight gain is due to trapped ethyl metaphosphate). The discrepancy may be caused by dissolved silica interfering with the colorimetric P determination.[5] Thorough extraction with boiling chloroform–ethyl acetate (4 : 1) removed only 0.064 g from a 0.806 g sample; the change in P content (to 10.8%) was
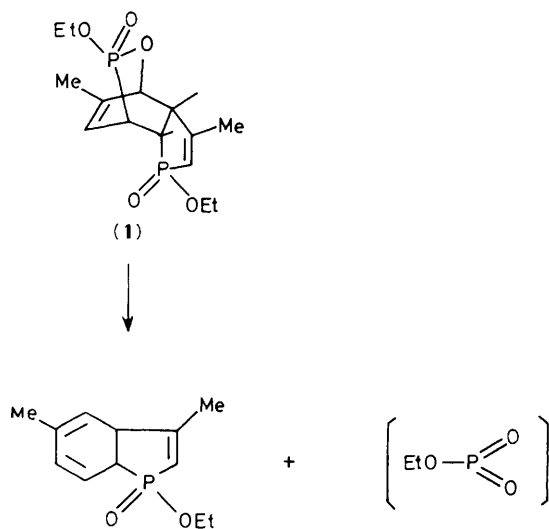
negligible. The phosphorus is therefore very strongly bound to the surface and not present simply through adsorption forces. The weight gain suggests that the initially generated monophosphate (2) must itself act as a trap, through its hydroxy-group, for additional metaphosphate, resulting in P–O–P bond formation typified by (3).

The [31]P n.m.r. spectrum of (3) (Figure 1), using the cross-polarisation magic-angle-spinning (CP-MAS) (80.015 MHz) technique, consisted mainly of two poorly resolved, but intense, peaks of equal intensity. The peaks were considerably upfield (*ca.* δ −12 and −15 p.p.m.) of reference CaHPO₄. The signal at lower field has the shift expected for a terminal pyrophosphate moiety [*e.g.*, δ (^{31}P) for $(EtO)_2P(O)OP$-$(O)(OEt)_2$ is −12.6 p.p.m.],[6] while the internal phosphorus experiences the additional shielding that might be expected from its location between a phosphate and a silicate group, as is observed for the central P of a triphosphate.[7] That a silyl group on a phosphate causes an upfield shift was shown by the silylation of a model compound, neopentyl propyl phosphate (δ +1.67 p.p.m.), with bis(trimethylsilyl)trifluoroacetamide, which gave a product with δ −6.67 p.p.m. Presumably, the small coupling (10—25 Hz) which would be expected for the non-equivalent P atoms of (3) is masked by the broadness of the lines observed in solid state spectra.

Further extraction with refluxing ethanol reduced the P content to 5.17%. However, the CP-MAS [31]P n.m.r. spectrum still showed the two signals at δ −12 and −15 p.p.m., indicating that solvolysis had occurred at the Si–O–P bond. The phosphorus was removed completely on refluxing in 6 M-HCl.

An alternative explanation for the main [31]P n.m.r. absorption appearing as two closely spaced signals is that phosphorylation has occurred at two different types of site on the surface. In view of the much greater than expected weight gain, however, this seems unlikely. Direct phosphorylation of dry silica gel with $(EtO)_2POCl$ should only give a monophosphate, and indeed when this experiment was conducted in toluene at 110 °C in the presence of triethylamine, there resulted a product which gave a CP–MAS [31]P n.m.r. signal only at δ −12.94 p.p.m. [with $(NH_4)H_2PO_4$ at 0 p.p.m.]. This rules out a two-site phosphorylation by the metaphosphate and supports the pyrophosphate structure as the major characteristic on the surface. Small contributions from other structural types may be present but not readily detected by the techniques so far used.

When the relative amount of ester (1) was reduced by a factor of about six (to 0.3 g per g silica gel), the weight gain of the washed solid was nearly identical with the theoretical amount of ethyl metaphosphate, attesting to the remarkable efficiency of the trapping process. The solid state [31]P n.m.r.
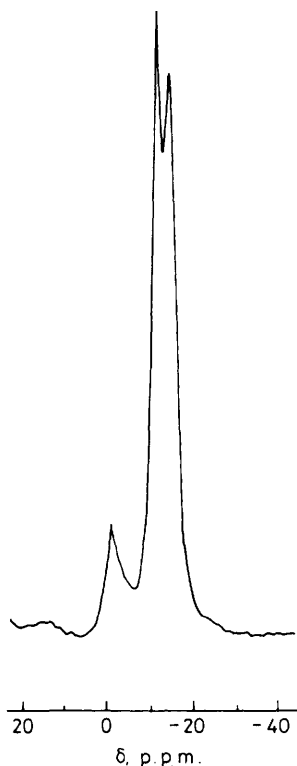
Scheme 1

(2)   (3)

20   0   −20   −40

δ, p.p.m.
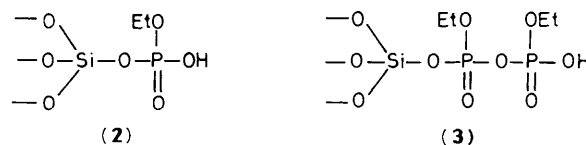
Figure 1. CP-MAS ^{31}P n.m.r. spectrum (80.015 MHz) of a sample of (**3**) formed from 1.0 g of silica gel and 0.3 g of (**1**).

spectrum of this product (Figure 1) again showed the two signals at δ −12.47 and −15.23 p.p.m. The reduced amount of ethyl metaphosphate in this experiment is only sufficient[4] to phosphorylate about half of the silanol groups; that a pyrophosphate is still formed suggests that the P–OH groups

initially formed on (**2**) must compete effectively with the remaining Si–OH groups.

The surface hydroxy groups of silica gel are therefore clearly established as providing a reaction site for the trapping, from solution, of highly electrophilic, low-co-ordination phosphorus species, of which many examples are known and which are under intensive investigation. An advantage in the use of silica gel as a trapping agent is that it has a very low probability of being involved in the generation of the species, thus lessening the uncertainty about an active role for the trapping agent in this process. In fact, ^{31}P n.m.r. studies showed that the metaphosphate is generated in the solution and not on the surface from adsorbed generator (**1**); a toluene solution of (**1**) with and without added silica gel showed very little difference in the size of the peak for dissolved (**1**). Other hydroxy-bearing surfaces could also undergo phosphorylation, thus creating surfaces with special characteristics.

References

1 F. H. Westheimer, *Chem. Rev.*, 1981, **81**, 313.
2 F. Ramirez, J. F. Marecek, and S. S. Yemul, *Tetrahedron Lett.*, 1982, **23**, 1515.
3 L. D. Quin and B. G. Marsi, *J. Am. Chem. Soc.*, 1985, **107**, 3389.
4 H. Englehardt, 'High Performance Liquid Chromatography,' Springer-Verlag, New York, 1979, pp. 87—89, 121—122; Y. Iwasawa, 'Tailored Metal Catalysts,' Reidel, Boston, 1986, pp. 24—26; R. K. Iler, 'The Chemistry of Silica,' Wiley-Interscience, New York, 1979, pp. 573—574.
5 G. Dabkowski, University of Massachusetts Microanalytical Laboratory, personal communication.
6 R. A. Y. Jones and A. R. Katritzky, *Angew. Chem.*, 1962, **74**, 60.
7 F. Ramirez and J. F. Marecek, *Pure Appl. Chem.*, 1980, **52**, 213.