THE MECHANISM OF FRAGMENTATION OF ALKYL α -(OXYIMINO)BENZYLPHOSPHONATES; USE OF SILICA GEL AS A NOVEL HYDROXYLIC TRAPPING REACTANT FOR AN INTERMEDIATE ALKYL METAPHOSPHATE.

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Abstract. Silica gel was employed to react with the suspected metaphosphate intermediate of the acid-promoted cleavage of monoalkyl α -(oxyimino)benzylphosphonates. The silica gels displayed CP-MAS ³¹P NMR signals at about δ -8. A similar value was obtained for silica gel phosphorylated with ethyl metaphosphate from a different source (thermolysis of a P-ethoxy 2,3-oxaphosphabicyclo[2.2.2]octene derivative.

In previous work,¹ it was discovered that alkyl α -(oxyimino)benzylphosphonates (1) were smoothly cleaved at the P-C bond when exposed to saturated solutions of anhydrous HCl in various alcohols at room temperature. The final products were benzonitrile and a dialkyl phosphate (3). It was suspected that the initial product of the cleavage was the alkyl metaphosphate 2, a species of high electrophilic character that is too reactive to be observed directly.²



We sought confirmation that the metaphosphate is indeed generated as a fleeting intermediate, and have used for this purpose the novel trapping reactant silica gel. Through its surface hydroxy groups, silica gel serves as an efficient trapping reactant for ethyl metaphosphate when generated by an entirely different method, the thermal fragmentation of P-ethoxy 2,3-oxaphosphabicyclo[2.2.2]octene derivative 4.³ There is also practical significance to the production of phosphorylated silica gels, since they are potentially valuable chromatographic materials.



In the original experiments on this process, a large excess of the metaphosphate was used, resulting in formation of a pyrophosphate on the surface. We have now found that the reaction is so straightforward that it occurs with ease

when only a 10-15% excess of metaphosphate is used. To calculate the proper amount of the phosphorylating agent, it is first necessary to determine the surface hydroxyl content of the silica gel. This was accomplished by the calcium nitrate titration method,⁴ which when applied to carefully dried Aldrich chromatographic grade silica gel (70-230 mesh, 60Å, B.E.T. surface area ca. 500 m²g⁻¹, pore volume 0.75 cm⁻³) gave 0.69 ± 0.14 meq per g. Reacting 0.90 meq of 4 (0.314 g) in 8 mL of dry toluene at 110°C with 1.00 g of suspended silica gel gave, after thorough washing³ and drying, a solid with a CP-MAS ³¹P NMR signal at § -9.9 (Bruker 200 MHz spectrometer; CaHPO₄ as reference), consistent with a phosphate group on the surface as depicted in 5. (Adsorbed ethyl phosphate was found to give a signal around § 1.) No phosphorus was detected in the toluene reaction solution, and therefore silica gel can be viewed as a very efficient trap for a metaphosphate.

In order to use silica gel effectively as a trap for a suspected metaphosphate intermediate in the HCl cleavage of an alkyl α -(oxyimino)benzylphosphonate, the reaction must be conducted in an inert solvent rather than in ethanol. It was found that toluene could be used for this purpose. With a few equivalents of methanol as a trapping agent, the fragmentation of 1b (as the lithium salt)¹ occurred smoothly on saturation of a toluene solution with HCl. The phosphorus product was the same (δ^{31} P NMR -0.3) as when methanol was the solvent. A mixture of 1.00 g of silica gel was then suspended in 20 mL of toluene containing 0.81 meq of the lithium salt of phosphonate 1a and saturated with HCl for 4 hr. The silica gel was recovered, washed and dried. The CP-MAS ³¹P NMR spectrum consisted of a strong major signal at δ -8.4 (Bruker 350 MHz spectrometer at Iowa State University) with a minor signal at δ +1, probably from adsorbed ethyl phosphate. This result is comparable to that obtained when ethyl metaphosphate is generated from the thermal fragmentation of bicyclic ester 4. Since it has been confirmed by kinetic studies that ethyl metaphosphate is a true product of this fragmentation,⁵ it can be concluded that ethyl metaphosphate is also an intermediate in the acid-cleavage of ethyl α -(oxyimino)benzylphosphonate. We have also used this technique to detect methyl metaphosphate when released by the HCl cleavage of the methyl phosphonate 1b¹; the phosphorylated silica gel had a CP-MAS ³¹P NMR signal at $\delta = 8$ (Bruker 200 MHz spectrometer).

The new method of phosphorylation of silica gel with a monoalkyl α -(oxyimino)benzylphosphonate could prove to be more practical than that using 4, since the precursor is obtained by a shorter synthetic route. Silica gel may also be a useful trapping reactant for other strongly electrophilic transient species.

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