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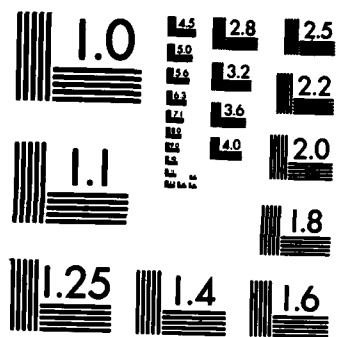
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TECHNICAL REPORT NO. 1

The Hydrolysis of Phosphate Esters on Solids

by

Richard A. Hollins

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THE HYDROLYSIS OF PHOSPHATE ESTERS ON SOLIDS

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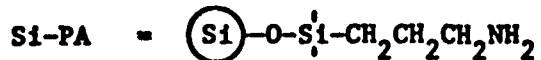
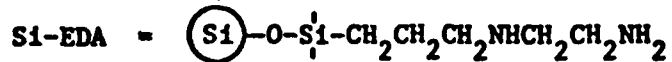
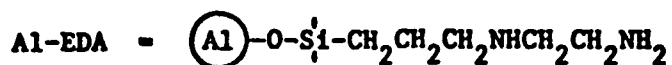
Several solid materials were examined for hydrolytic activity with organophosphorus esters. The solid systems consisted of aliphatic amines surface-immobilized on silica or alumina supports. All materials demonstrated rate enhancements for the hydrolysis of *p*-nitrophenyldiphenyl phosphate (NPDPP).

Air purification in a toxic environment constitutes an important aspect of personnel protection in relation to industrial chemicals, pesticides and chemical warfare agents. Neat and impregnated activated charcoals have been the most widely studied and used materials in this context¹. In the case of organophosphorus compounds charcoal demonstrates strong but reversible adsorption. Our interest has been to explore alternative solid materials which might show not only adsorption but also concomitant chemical destruction of the toxic substance. We have previously shown that various anion-exchanged forms of Dowex 2-X4 resin enhance the rate of hydrolysis of trimethyl phosphate².

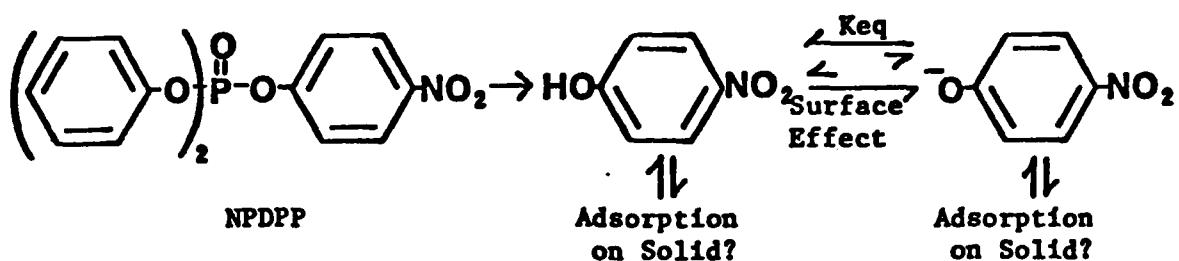
For the investigation of other solid systems we have selected alumina and silica as principal candidate supports for a variety of "reactive" organic moieties as 1) alumina has been shown to react with sarin³ and 2) the chemistry for the surface modification of these materials is extensive⁴.

In our initial studies of these materials we examined three systems:

- 1) An alumina-bound propylethylenediamine (Al-EDA) prepared by treating Woelm I alumina with Dow Corning coupling agent DC 6020. The resulting material contained 0.81 meq/g of amine functionality as determined by titrimetric analysis.
- 2) A silica-bound propylethylenediamine (Si-EDA) prepared by treating Woelm silica gel with DC 6020. Amine content was found to be 0.96 meq/g.
- 3) A silica-bound propylamine (Si-PA) prepared by treating Woelm silica gel with Union Carbide A-1100 coupling agent. Amine content was found to be 1.16 meq/g.



Hydrolysis studies were carried out using mixtures of 0.5g of supported reactant and 4mL of a $2.4 \times 10^{-3} \text{M}$ solution of *p*-nitrophenyldiphenyl phosphate (NPDPP) in 30% aqueous ethanol. The extent of reaction was determined by monitoring *p*-nitrophenoxide ion absorbance at 405nm. It was necessary to apply a correction to the observed absorbance vs time plots as the presence of the solid had the effect of augmenting the *p*-nitrophenol dissociation and thus increasing the apparent degree of reaction.



The upper trace in Figure 1 shows the effect of Si-PA on the dissociation of *p*-nitrophenol as compared to its normal equilibrium dissociation indicated by the lower trace. The other solid materials showed similar effects, that of greatly increasing the concentration of *p*-nitrophenoxide over that determined by normal dissociation (at the initial pH of the NPDPP solution).

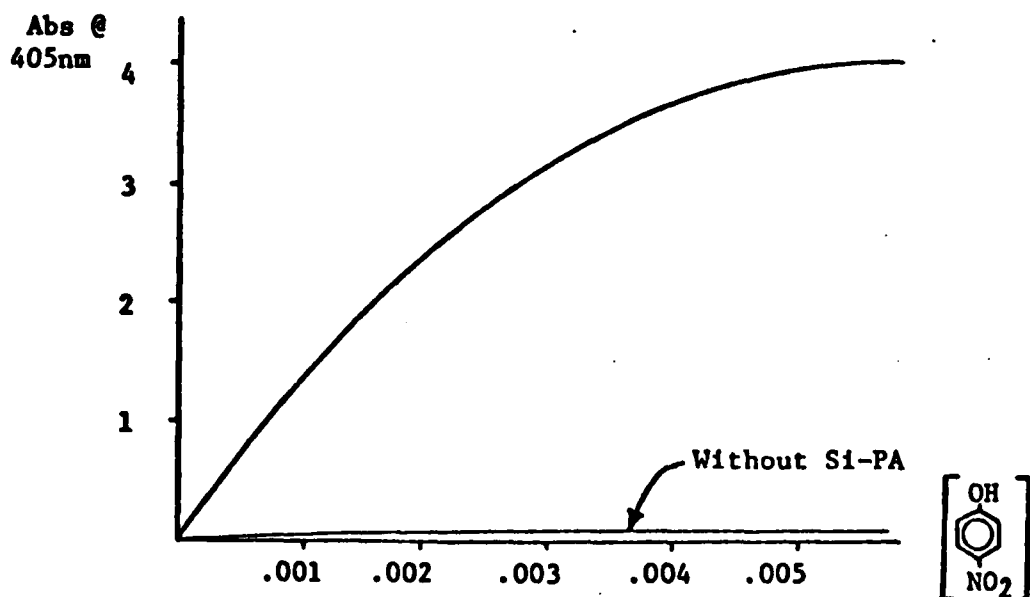


Figure 1. Dissociation of *p*-Nitrophenol by Si-PA

The actual extent of reaction in each hydrolysis study was determined by correlating the observed absorbance (Figure 2) with those values determined for *p*-nitrophenol in the presence of solid (same quantities of solid and solvent as in the reaction).

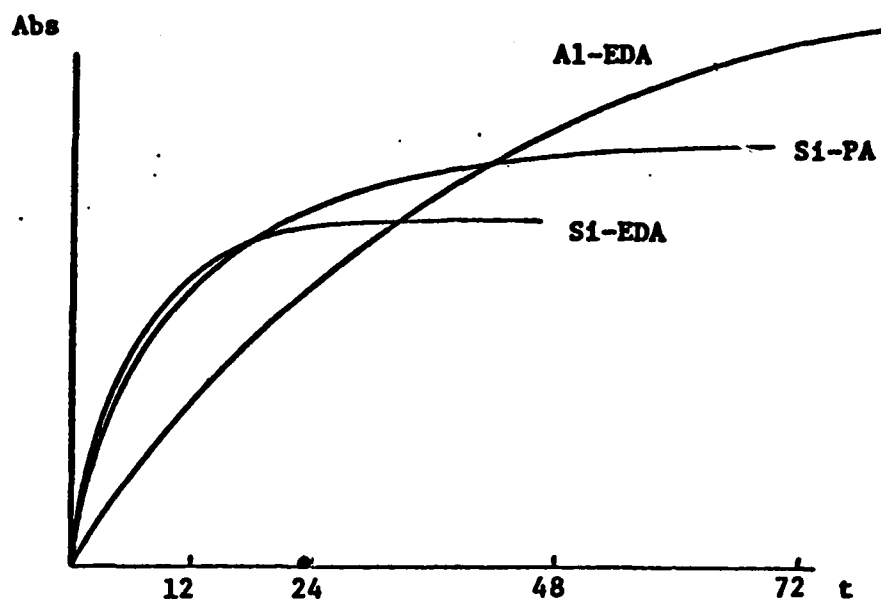


Figure 2. Hydrolysis of NPDPP

The approximate half-lives for these hydrolyses are as follows:

Al-EDA	$T_{1/2} \approx 24$ hrs
Si-PA	$T_{1/2} \approx 7$ hrs
Si-EDA	$T_{1/2} \approx 4$ hrs

CONCLUSIONS

While these rates do not appear to be spectacularly fast, the aqueous NPDPP solutions showed no measurable degree of solvolysis, in the absence of solid reactant, after several weeks of storage, thus enhancement of hydrolysis was very great. Comparison of the Si-EDA material to the others indicates both greater reactivity from the diamine moiety and from the use of silica as a support.

The possibility that a reverse ordering, i.e. alumina better than silica, might occur in the case of fluoro-phosphates was briefly investigated. A crude examination of the relative reactivities of the supported amines with diisopropyl fluorophosphate (DFP) indicated the same qualitative behavior as with NPDPP.

These initial model systems have both demonstrated hydrolysis enhancement for NPDPP and helped to develop the necessary methodology for studying these complex heterogeneous reactions. The supported amines will be further examined as ligands for metal complexes and as functional groups for the attachment of other organic moieties.

ACKNOWLEDGEMENT

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