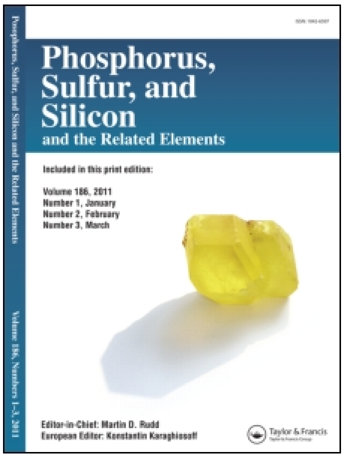

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Solvent Effects on Acyl Transfers to Phosphonates

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Solvent Effects on Acyl Transfers to Phosphonates

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The nucleophilic reactivity of the phosphate dianion in aqueous solution is unusually low, relative to that of other nucleophiles of comparable pK_as. For example, in the reaction with p-nitrophenyl acetate (pNPA), phosphate shows a negative deviation of over two orders of magnitude from the Brønsted correlation ($\beta_{nuc} \approx 0.7$) obtained with other oxygen nucleophiles [1]. Since there are over 130 enzymatic reactions which catalyze nucleophilic reactions of phosphate, we were interested in exploring the possible sources of this catalytic efficiency. By using phosphonates (RPO_3^{-2}) as phosphate analogs we have shown an unusual insensitivity of the rate of acetyl transfer from p-nitrophenol to the phosphonate dianion ($\beta_{nuc} = 0.3$). These observations, along with the more favorable entropy of activation for the reaction of pNPA with phosphonates ($\Delta S^{\ddagger} \approx -13$ eu) than with most other nucleophiles (e.g., with imidazole or with acetate, $\Delta S^{\ddagger} \approx -30$ eu) suggest a significant contribution of desolvation to the activation energy. To investigate this further we looked at the effect of DMSO/water mixtures on the reaction rate. The second-order rate constant for acetyl transfer from p-nitrophenol to chloromethylphosphonate increases over 5,000-fold as the DMSO concentration is increased to 90%(v/v). This sensitivity to DMSO concentration is greater than that reported for acetyl transfer to a variety of phenoxide nucleophiles [2] and is greater than can be accounted for simply from the increase in the effective pK_{a2} of the phosphonate nucleophile. This suggests a significant role for desolvation in the enzyme-catalyzed nucleophilic reactions of inorganic phosphate.

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