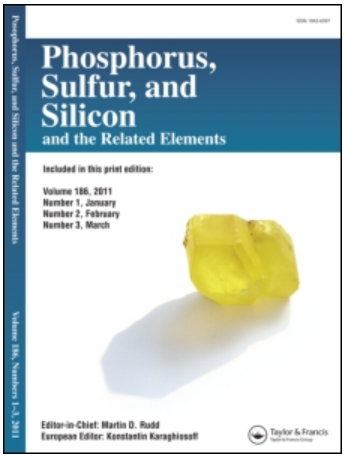

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Acidity, Hydrogen Bonding and Tautomerism Enthalpies of Phosphoric Acids in Solution and in GAS Phase

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ACIDITY, HYDROGEN BONDING AND TAUTOMERISM ENTHALPIES OF PHOSPHORIC ACIDS IN SOLUTION AND IN GAS PHASE

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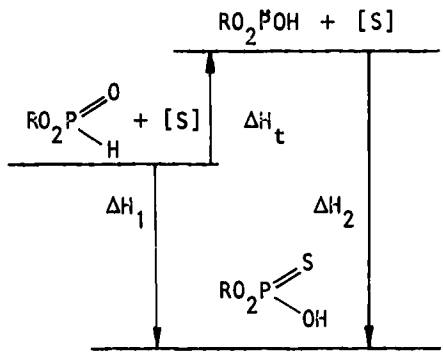
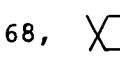
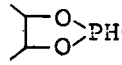
Factors promoting the high reactivity of phosphoric acids towards alkenes, and their dual reactivity have not been studied thoroughly. Using the thermochemical "pure base" method (Arnett, 1967) we determined hydrogen bond formation enthalpies ($\Delta H \pm 0.5$ kJ/mole) of five-membered (-15+ -23), seven- and six-membered (-3+ -5) cyclic and acyclic (0+ -2) phosphoric acids with acetone. Stronger proton donor properties of 2-hydro-2-oxo-4,5-dimethyl-1,3,2-dioxaphospholane in comparison with diethylphosphite were demonstrated by determining their equilibrium acidity constants in tetrahydrofuran (17.4 and 20.9 correspondingly), cyclohexylamine (16.7 and 20.7), ethylenediamine (16.4 and 20.8) and aniline (13.5 and 20.5). Differences in ΔpK_a in different solvents are caused by solvation effect - hydrogen bonding of solvent with ambidental anion $>\ddot{P}-O^-$ for cycle and $>P=O$ for acycle. The tautomerism enthalpies of some phosphoric acids were determined using their ability to react with sulfur in solutions. ΔH_t value represents difference $\Delta H_1 - \Delta H_2$; reaction of phosphite tautomer with sulfur was modelled by reaction:

$RO_2POEt+[S] \rightarrow RO_2PSOEt$ (ΔH_2).



Tautomerism enthalpies of phosphoric acids were calculated according to the equation:

$$\Delta H_t^{gas} = \Delta H_1 - \Delta H_2 - \Delta H_{solv.}^{RO_2PSOH} + \Delta H_{solv.}^{RO_2PSOEt} + \Delta H_{solv.}^{RO_2PHO} - \Delta H_{solv.}^{RO_2POEt}$$

$\Delta H_t^{gas} \pm 7$ kJ/mole: $(EtO)_2PHO$ 68,  61,  37.