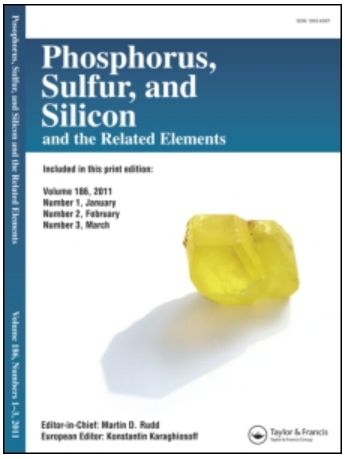

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The Electron-Donor Function of the Phosphorylic Oxygen

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THE ELECTRON-DONOR FUNCTION OF THE PHOSPHORYLIC OXYGEN

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The values of the enthalpy and free energy factors (E_j and C_j) of the phosphorylic compounds were estimated on the basis of literature (1) and experimental material (2). The ability of carbonylic compounds to H-bond formation was found to be remarkably lower than of the phosphorylic compounds. The H-bonding complex formation of both one and two hydrogen atoms with the phosphorylic oxygen atom was established. The spectrophotometric and calorimetric study of the complex formation of model uncyclic and biologically active macrocyclic phosphorylic compounds with calcium as a biometal was carried out. The tendency to form complexes of both 1:1 and 1:2 (metal to ligand) compositions was revealed. An essential effect of entropy on the 1:2 complex stability and an effect of macrocycle size as well as the phosphorous atom's substituent on the complexation ability with calcium cation was established.

Compound	E_j	C_j
$(PhO)_3PO$	0.99	1.64
$MeP(O)(OMe)_2$	1.01	2.70
$MeP(O)(OPh)_2$	0.94	2.27
$(MeO)_3PO$	1.15	2.27
Ph_3PO	1.48	2.79
$((Me)_3N)_3PO$	1.44	3.37
$(BuNH)_3PO$	1.65	4.00
Ph_2CO	0.83	0.90
$(Me_2N)_2CO$	1.35	2.20
Et_2O	1.00	1.00

(1) O.A.Raevsky, V.P.Solovyov, V.Yu.Grigoryev, Thermodynamic Values of H-Bond of Phenols with Organic Bases. VINITI, 1988, No 1001.
(2) O.A.Raevsky, Theoret. and Experim. Chim. 22, 450 (1986).