Supramolecular phosphate transfer catalysis by pillar[5]arene

Liz, D. G., Manfredi, A. M., Medeiros, M., Montecinos, R., Gómez-González, B., Garcia-Rio, L., & Nome, F. (2016). Supramolecular phosphate transfer catalysis by pillar [5] arene. Chemical Communications, 52(15), 3167-3170. <10.1039/c5cc10214f> Accessed 28 Dec 2020.

Abstract

A kinetic study on dinitrophenylphosphate monoester hydrolysis in the presence of a cationic pillararene, P5A, has been carried out. Formation of the supramolecular complex between phosphate ester and P5A has been studied by NMR showing complexation-induced upfield proton shifts indicative of aromatic ring inclusion in the pillararene cavity. Molecular dynamic calculations allow structure characterization for the 1 : 1 and 1 : 2 complexes. As a result of the supramolecular interaction both the acidity of DNPP and its hydrolysis rate constants are increased. Catalysis results from combination of both electrostatic stabilization reducing the negative electron density on the PO3= oxygens and monoester dianion destabilization by the steric effects of close NMe3+ groups hindering the hydrogen-bonding with water and destabilising the monoester dianion.