

Supramolecular Control of Reactivity toward Hydrolysis of 7-Diethylaminocoumarin Schiff Bases by Cucurbit[7]uril Encapsulation

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Abstract

A series of aromatic Schiff bases, featuring 7-diethylamino-coumarin and with five different substituents at an adjacent phenyl ring, were synthesized and characterized. With the aim of assessing the stability of these dyes in acidic medium, their hydrolysis reactions were kinetically studied in the absence and presence of the macrocycle cucurbit[7]uril (CB[7]). Our results are consistent with a model containing three different forms of substrates (un-, mono-, and diprotonated) and three parallel reaction pathways. The pKa values and the rate constants were estimated and discussed in terms of the presence of a hydroxyl group at the ortho position and electron-releasing groups on the phenyl ring of the dyes. The kinetic study in the presence of CB[7] led to two different behaviors. Promotion of the reaction by CB[7] was observed for the hydrolysis of the Schiff bases containing only one coordination site toward the macrocycle. Conversely, an inhibitor effect was observed for the hydrolysis of a Schiff base with two coordination sites toward CB[7]. The latter effect could be explained with a model as a function of a prototropic tautomeric equilibrium and the formation of a 2:1 host/guest complex, which prevents the attack of water. Therefore, the kinetic results demonstrated a supramolecular control of the macrocycle toward the reactivity and stability of 7-diethylaminocoumarin Schiff bases in acidic medium.