Proton transfer from a strong photoacid to solution: a study of solvent-controlled and diffusion-controlled reaction

S. A. Kovalenko

Abstract

Photoinduced proton transfer (PT) from cations 6-hydroxyquinolone (6HQc) and N-methyl-6-hydroxyquinolone (6MQc) to acidic solution, and solvation of the zwitterion N-methyl-6-quinolone (6MQz) were studied with stationary and transient absorption spectroscopy. The time-dependent Stokes shift of emission from photoexcited 6MQz in acetonitrile and protic solvents matches the solvation correlation function C(t) derived either with known solvatochromic probes coumarin 343 and coumarin 153 or from infrared/dielectric-loss data on net solvents. This indicates that 6MQz monitors solvation dynamics, and that no intramolecular electron transfer occurs on a subpicosecond or longer time scale. The PT dynamics from 6HQc and 6MQc closely follows C(t), being 2-3 times slower. Consequently, PT is solvent-controlled, with a barrier 2 kJ/mol. In water, a pre-condition of this ultrafast reaction seems to be hydrogen-bonding between the cation and two water molecules, resulting in a ground-state complex 6HQc·H$_2$O·H$_2$O. In acetonitrile, where proton cannot be stabilized, the reaction occurs nonetheless with an intermediate which should be present in protic solvents as well. In water-acetonitrile mixtures we observed a switch from the solvent-controlled PT on a short time scale to the diffusion-controlled reaction at longer time; the rate $k_D \approx 10^{10}$ s$^{-1}$M$^{-1}$ is consistent with a unimolecular diffusion process. The analysis of these results confirms that only one bulk-water molecule in the vicinity of 6HQc·H$_2$O is sufficient to initiate PT. Subsequent solvation of the dissociated proton and zwitterion completes the PT reaction.