# Influence of electrostatic factors and interactions with solvent on the rate of excited state proton transfer for 2-naphthol derivatives bound covalently to selected site of proteins.

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Streszczenie

2-Naphthol-6-sulphonic acid (NSOH) was bound to bovine serum albumin (BSA) by a sulphonamide bond. Carboxyl or amino groups of the protein were then modified by a neutral group which induced variation of the ground state p$K_a$ and excited state p$K^*_a$ values of the NSOH groups bound to the protein. The rate constants ($_{pt}$) of excited state proton transfer (ESPT) in NSOH groups bound to BSA were determined by steady state fluorescence spectroscopy. The dependence of $\log_{pt}$ on $\log K^*_a$ for BSA□NSOH conjugates was fitted to a modified Brönsted relation. This plot was treated as a reference curve for comparison with analogous data for NSOH groups bound to other protein samples. Deviations from this plot were explained by kinetic isotope effects. It is postulated that certain essential features of the ESPT mechanism are varied as a consequence of changes in parameters of the microenvironment of the proton donor, such as the optical dielectric permittivity and the distance to other charged groups of the protein. Thus when the fluorophore is bound preferentially to the surface of the protein globule by a spacer (approximately 2.5Å) the diffusion of water as a proton acceptor is the rate-limiting step in ESPT. When the same fluorophore is bound to the surface of the molecule by a sulphonamide bond anchored directly to an amino group of the protein, partition of a proton is the rate-determining step leading to a “negative” isotope effect and a low rate of ESPT. When the fluorophore is bound inside the protein molecule, proton transfer through a chain of preformed hydrogen bonds is responsible for a much higher rate of ESPT than in the other samples.