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Ligand Binding Kinetics in Myoglobin and Solvent Relaxation at High Pressure ALFONS SCHULTE, University of Central Florida, SILKI ARORA, SANGHOON PARK — Pressure is increasingly used as a variable to examine protein structure-function relationships, since it is crucial for chemical equilibria, reaction rates, and protein conformational states. We investigate pressure effects for the prototype reaction of ligand binding to myoglobin over a wide dynamic range in time and temperature. The distribution of rebinding rates is evaluated from kinetic absorption measurements of CO and O_2 binding to (horse) myoglobin at variable pressure (0.1 - 190 MPa) and temperature (180 - 300 K) in aqueous and 75 % glycerol/buffer solutions. The data demonstrate that pressure significantly affects the amplitudes (not just the rates) of the component processes. The amplitude of the geminate process increases with pressure corresponding to a smaller escape fraction of ligands into the solvent and a smaller inner barrier. Solvent relaxation rates at variable pressure are determince independently from specific heat spectroscopy. We discuss the role of solvent dynamics, hydration shell, and internal protein cavities in the binding reaction.

Alfons Schulte

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