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Entropic and Dynamical Origins of Catalysis in a B12 Enzyme[1]

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The kinetics of the diffusive radical pair separation process in the adenosylcobalamin (coenzyme B12) -dependent ethanolamine ammonia-lyase from *Salmonella typhimurium* at 234-248 K in a dimethylsulfoxide/water cryosolvent system [1] were determined by using time-resolved, full-spectrum electron paramagnetic resonance spectroscopy. Substrate hydrogen isotope effects show that the cofactor cobalt-carbon bond cleavage event rate is rate determining, and that catalysis (relative to solution) is almost entirely entropic. The results challenge the proposed, traditional enthalpy-based mechanisms, and show that delocalized, dynamical sources are central in bond cleavage catalysis. Changes in configurational freedom of surface residues and hydration waters are proposed as the microscopic origin. [1] M. Wang and K. Warncke, *J. Am. Chem. Soc.* 2008, 130, 4846.

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