Single Molecule Level Determination of the Kinetics and Thermodynamics of the Reaction between Oxygen and Cobalt(II)octaethylporphyrin in Phenyllectane at the HOPG-Solution Interface

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For the first time, scanning tunneling microscopy is used to study the equilibrium between a gas and a surface species at the surface-solution interface -- in this case the reaction of oxygen and cobalt(II) octaethylporphyrin (CoOEP) at the graphite-phenyllectane interface. Using sub-molecular resolution we determine the numbers of CoOEP and O₂-CoOEP species as a function of gas pressure and of temperature. We demonstrate that adsorption follows the Langmuir isotherm. Further, equilibrium constant measurements at multiple temperatures between 20°C and 50°C allow us to extract ΔH, ΔS, and ΔG for the reaction under these conditions. Utilizing the known temperature dependence of the Henry’s law constant for toluene, we are able to extract the heats of solution of O₂ from the overall reaction enthalpy change.