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

Ursula Mazur and K. W. Hipps
Washington State University, Department of Chemistry and Materials Science and Engineering Program
PO Box 644630, Pullman, WA 99164-4630

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-phenyloctane interface. Using sub-molecular resolution we determine the numbers of CoOEP and O_2-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°Cand 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 O_2 from the overall reaction enthalpy change.