# Electron-transfer rates and dioxygen reduction products for electrode-wired P450 mutants

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Electrode-driven biocatalysis utilizing the P450 cytochromes for selective oxidations depends not only on achieving electron transfer (ET) but doing so at rates that favor native-like turnover. Herein we report studies that correlate rates of heme reduction with ET pathways and resulting product distributions. We utilized single-surface cysteine mutants of the heme domain of P450 from *Bacillus megaterium* and modified the thiols with N-(1-pyrene)-iodoacetamide, affording proteins that could bond to basal-plane graphite. Single-surface Cys mutants at positions 62, 383, and 387 were able to form electroactive monolayers with similar half-wave potentials (-335 to -340 mV vs AgCl/Ag). Respective ET rates ($k_s^o$) and heme-cysteine distances for 62, 383, and 387 are 50 $s^{-1}$ and 16 Å, 0.8 $s^{-1}$ and 25 Å, and 650 $s^{-1}$ and 19 Å. Experiments utilizing rotated-disk electrodes found good agreement between ET rates and product distributions for dioxygen reduction for the various mutants, with larger $k_s^o$ values correlating with more electrons transferred per dioxygen during catalysis.