

# Chronoamperometric Study of Bisulfite Reduction by Myoglobin

Michael D. Ryan and Radalla Abdellaty

*Marquette University, Chemistry Department, Milwaukee, WI 53233 USA*

The kinetics of the reduction of bisulfite by surfactant myoglobin films were examined using chronoamperometry after the overall stoichiometry of the reduction was examined by coulometry. Surfactant films of myoglobin were formed on a graphite (HOPG) electrode. On this electrode, two waves were observed for myoglobin, corresponding to the Fe(III)/Fe(II) and Fe(II)/Fe(I) reductions. Cyclic voltammetry had demonstrated that no catalytic current for bisulfite reduction was observed for the first wave, while significant catalysis was observed for the second wave. Coulometric studies verified that the overall reaction was a 6-electron reduction to hydrogen sulfide. In order to separate electron transfer kinetics from the kinetics of the reduction of bisulfite by myoglobin, chronoamperometry was used. If the electron transfer rate was fast compared to the bisulfite reduction kinetics (which can be assured by choosing a potential well negative of the peak potential), the catalytic current is given by<sup>1</sup>:

$$i_{\text{cat}} = nFAk\Gamma c_s \exp [k\Gamma t^{1/2}/D_s^{1/2}]^2 \operatorname{erfc} [k\Gamma t^{1/2}/D_s^{1/2}]$$

where  $k$  = rate of the reaction between myoglobin and bisulfite and  $\Gamma$  is the surface coverage of myoglobin. The form of this reaction is identical to a slow heterogeneous electron transfer, a mechanism which has been well studied in electrochemistry. The relationship between  $i_{\text{cat}}$  and  $k\Gamma$  is non-linear, and can only be linearized in the limiting cases. Alternatively, the solution can be linearized by transforming the current data to Laplace space. The parameter of interest,  $k\Gamma$ , can be determined from the slope of  $1/ip^{1/2}$  versus  $p^{1/2}$  plot, where  $p$  = Laplace constant and  $i$  is the Laplace transform of the current. Using Laplace space and chronoamperometry, the rate of the reaction,  $k\Gamma$ , was found as a function of pH. The results correlate well with the pKa of bisulfite, indicating that it is the reactive species. The rate declines significantly when bisulfite is converted to sulfite.

1. K. Kuo and R. W. Murray, *J. Electroanal. Chem.* **1982**, 131, 37-60.