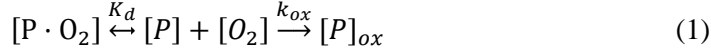


## Supplementary Material

When bound to oxygen the ferrous heme has a reduction potential too high to be oxidized by a second molecule of oxygen (13). After the oxygen dissociates, however, the ferrous heme is subject to oxidation by an outer sphere mechanism in both the hexa- and pentacoordinate ligation states.



Since the affinity of the oxygen is high, the free oxygen concentration is significantly depleted when oxygen binds the protein heme complex. Thus we cannot use the approximation that the free oxygen concentration is equal to the total oxygen concentration- the depletion of the free oxygen and protein complex concentrations must be considered:

$$[P] = [P \cdot O_2] + [P]_{free} \quad (2)$$

$$[O_2] = [P \cdot O_2] + [O_2]_{free} \quad (3)$$

Where the  $[P]$  is the total protein heme complex concentration;  $[P \cdot O_2]$  is the protein heme-oxy complex concentration;  $[P]_{free}$  is the free protein heme complex concentration;  $[O_2]$  is the total oxygen concentration;  $[O_2]_{free}$  is the free oxygen concentration.

The resultant dissociation constant equation:

$$K_d = \frac{([P] - [P \cdot O_2])([O_2] - [P \cdot O_2])}{[P \cdot O_2]} \quad (4)$$

is rearranged to:

$$[P \cdot O_2] = \frac{([P] + [O_2] + K_d) - \sqrt{([P] + [O_2] + K_d)^2 - 4[P][O_2]}}{2} \quad (5)$$

As the oxidization rate is:

$$\text{Rate} = k_{ox} [P]_{free} \cdot [O_2]_{free} \quad (6)$$

Combining the equation (4), (5) and (6), the oxidization rate can be expressed as:

$$\text{Rates} = k_{ox} \cdot K_d \cdot \frac{([P] + [O_2] + K_d) - \sqrt{([P] + [O_2] + K_d)^2 - 4[P][O_2]}}{2} \quad (7)$$