1 Fitting of UPO with substrate inhibition

Equation for Ping-Pong-Bi-Bi with substrate inhibition

$$v = \frac{V_{max}[A][B]}{K_{mB}[A] + K_{mA}[B]\left(1 + \frac{[B]}{K_{iB}}\right) + [A][B]} \tag{1a}$$

2 Derivation of UPO catalase mechanism

A rate equation for the mechanism depicted in Figure 2 was derived using the algorithm as presented by King and Altman All possible pathways for a completely reversible reaction mechanism werde derived under full steady state assumption

Assumptions/simplifications:

$$k_{-2}, k_{-6}, k_{-7}, [P], [Q] = 0$$

Substitutions:

$$K_{iB} = \frac{k_{-8}}{k_8}$$
$$K_{mA} = \frac{k_{-1} + k_2}{k_2}$$
$$K_{mB} = \frac{k_{-3} + k_6}{k_3}$$
$$K_{mA2} = \frac{k_{-4} + k_7}{k_4}$$

Enzyme velocity is given by:

$$v = \frac{N}{D} \tag{2a}$$

where

$$N = E_0 K_{iB} K_{mA2}[A][B]k_2 k_6 \tag{2b}$$

and

$$\begin{aligned} D = {} & K_{iB}K_{mA}K_{mA2}[B]k_6 + K_{iB}K_{mA}K_{mB}[A]k_7 + K_{iB}K_{mA2}K_{mB}[A]k_2 \\ & + K_{iB}K_{mA2}[A][B]k_2 + K_{iB}K_{mA2}[A][B]k_6 + K_{iB}K_{mB}[A]^2k_2 \\ & + K_{iB}K_{mB}[A]^2k_7 + K_{mA}K_{mA2}[B]^2k_6 + K_{mA}K_{mB}[A][B]k_7 \end{aligned} \tag{2c}$$

rearranging to:

$$N = E_0K_{mA2}[A][B]k_2k_6 \tag{2d}$$

and

$$\begin{aligned} D = {} & K_{mA}\left(1 + \frac{[B]}{K_{iB}}\right)(K_{mA2}[B]k_6 + K_{mB}[A]k_7) \\ & + K_{mA2}K_{mB}[A]k_2 + K_{mA2}[A][B]\left(k_2 + k_6\right) + K_{mB}[A]^2\left(k_2 + k_7\right) \end{aligned} \tag{2e}$$

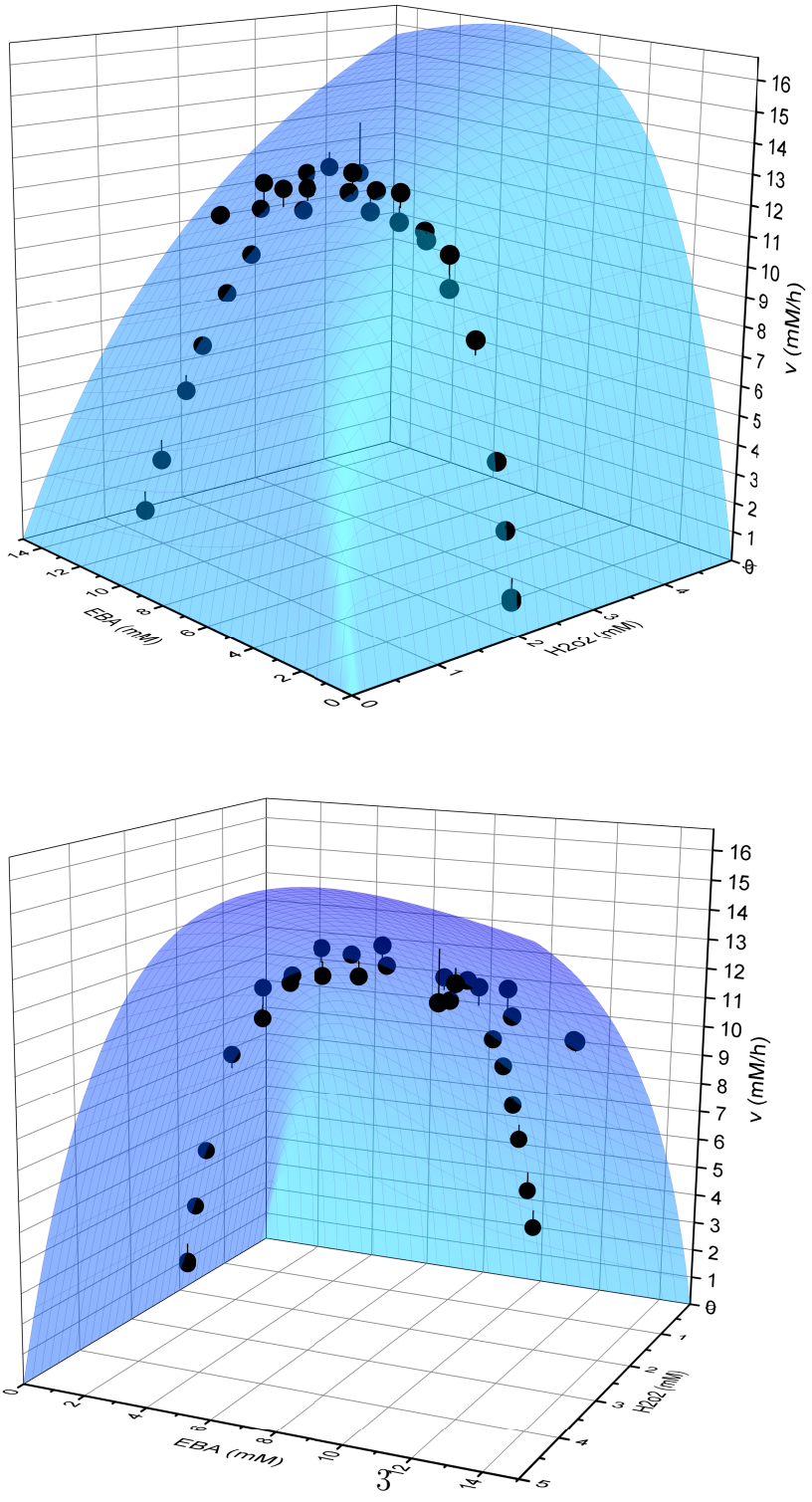

Figure 1: Fit of [EBA]/[H_2O_2] vs v with Ping-Pong + Substrate Inhibition.

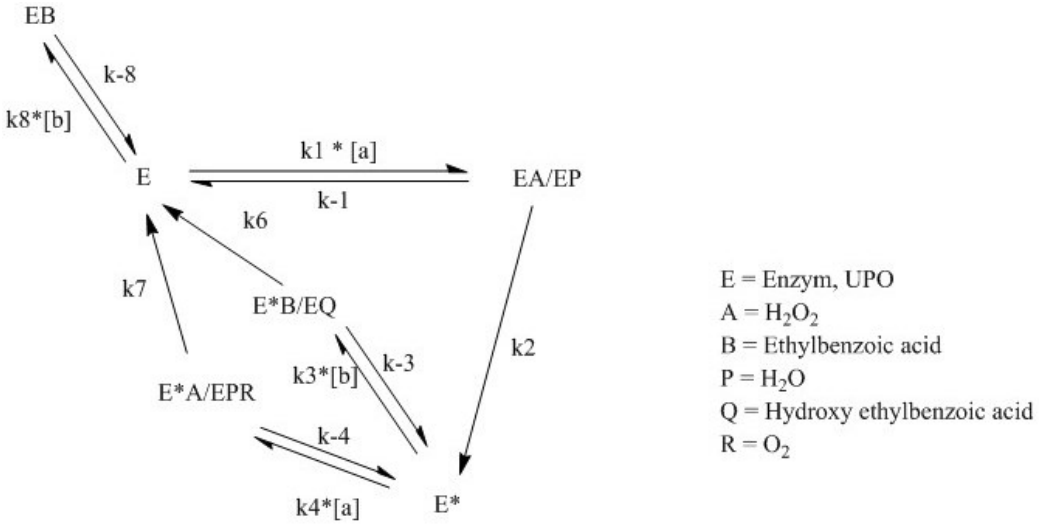

Figure 2: Mechanism for UPO catalyzed hydroxylation including inhibition by substrate B and the catalase cycle. All rate limiting steps (k_2, k_6, k_7) were assumed to be irreversible.