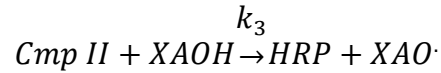
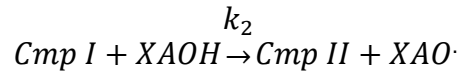
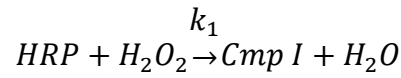


On the relationship between peroxidase kinetics and the Michaelis-Menten reaction scheme

The peroxidase reaction scheme is:



Although it is not needed for the current derivation we can include the fact that the phenolic radicals produced by the process will react by disproportionation to form one molecule of substrate (XAOH) and one molecule of product (O=A=O).



The rate scheme is:

$$\frac{d[HRP]}{dt} = -k_1[HRP][H_2O_2] + k_3[Cmp\ II][XAOH]$$

$$\frac{d[Cmp\ I]}{dt} = k_1[HRP][H_2O_2] - k_2[Cmp\ I][XAOH]$$

$$\frac{d[Cmp\ II]}{dt} = k_2[Cmp\ I][XAOH] - k_3[Cmp\ II][XAOH]$$

And the rate of formation of product is:

$$\frac{d[XAO\cdot]}{dt} = -k_2[Cmp\ I][XAOH] - k_3[Cmp\ II][XAOH]$$

We can express the rate of formation of the product in terms of only HRP and the co-substrate concentration.

$$\frac{d[XAO\cdot]}{dt} = 2k_1[HRP][H_2O_2]$$

The conservation of matter requires that

$$[HRP]_0 = [Cmp\ I] + [Cmp\ II] + [HRP]$$

Then using the steady state approximation for Cmp I and Cmp II.

$$[Cmp\ II] = \frac{k_1[HRP][H_2O_2]}{k_3[XAOH]}$$

$$[Cmp I] = \frac{k_1[HRP][H_2O_2]}{k_2[XAOH]}$$

These two expressions can be substituted into the conservation equation to give

$$[HRP]_0 = \frac{k_1[HRP][H_2O_2]}{k_3[XAOH]} + \frac{k_1[HRP][H_2O_2]}{k_2[XAOH]} + [HRP]$$

Several steps of algebra are given below:

$$[HRP]_0 = \left(1 + \frac{k_1[H_2O_2]}{k_3[XAOH]} + \frac{k_1[H_2O_2]}{k_2[XAOH]} \right) [HRP]$$

$$[HRP] = \frac{[HRP]_0}{1 + \frac{k_1[H_2O_2]}{k_3[XAOH]} + \frac{k_1[H_2O_2]}{k_2[XAOH]}}$$

$$[HRP] = \frac{k_2k_3[HRP]_0[XAOH]}{k_2k_3[XAOH] + (k_2 + k_3)k_1[H_2O_2]}$$

Finally when substituted into the rate equation we have

$$\frac{d[XAO]}{dt} = \frac{\frac{2k_1k_2k_3}{(k_2 + k_3)} [HRP]_0[XAOH][H_2O_2]}{\frac{k_2k_3}{(k_2 + k_3)} [XAOH] + k_1[H_2O_2]}$$

How does this compare to the Michaelis-Menten model for enzyme kinetics?

$$V_0 = \frac{V_{max}[S]}{K_m + [S]}$$

The result is actually a two-dimensional M-M curve. First dimension $[S] = [XAOH]$. Then,

$$V_{max} = 2k_1[HRP]_0[H_2O_2]$$

$$K_m = \frac{k_1[H_2O_2]}{\frac{k_2k_3}{(k_2 + k_3)}}$$

Which has an interpretation at fixed concentration of H_2O_2 . In an alternative interpretation, in which the co-substrate H_2O_2 is treated as $[S] = [H_2O_2]$

$$V_{max} = 2 \frac{2k_2k_3}{(k_2 + k_3)} [HRP]_0[XAOH]$$

$$K_m = \frac{k_2 k_3}{k_1(k_2 + k_3)} [XAOH]$$

Here, by the same token the values of K_m and V_{max} have significance at a fixed concentration of XAOH.