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Steady State. Treatment of Kinetc Results Concerning the Catalatic Decomposition of Hydrogen Peroxide

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To account for experimental results concerning the reaction in question a flow sheet is proposed which also implies an explanation of its retardation by azide ion. The essence is that azide acts as a competitive inhibitor by forming, reversibly, a stable complex with catalase containing one azide and at least one hydrogen peroxide.

It is known that at low hydrogen peroxide concentrations its catalatic decomposition up till nearly 100 % decomposition obeys the chronometric integral

$$kt = \ln h/x$$

where x is the concentration of hydrogen peroxide at time t, h the same at time zero and k the usual rate constant. The simplest reaction pattern which agrees with this result is

$$X_1 + H_2O_2 \rightleftharpoons X_2 \qquad \pm 1$$
$$X_2 + H_2O_2 \rightarrow 2H_2O + O_2 + X_1 \qquad 2$$

X_1 may be either free catalase or catalase combined with one or several molecules of hydrogen-peroxide. Kinetics alone is unable to distinguish between these possibilities. X_2 obviously contains one molecule peroxide more than X_1.

Assuming steady state the usual procedure yields

$$x_1/s = 1/w_1(1 + w_{-1}/w_2)$$
$$x_2/s = 1/w_2$$

If furthermore the enzyme is either in the state X_1 or in X_2 we have $x_1 + x_2 = E$, where E is the total concentration of enzyme.

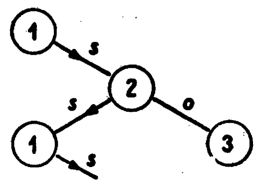

Fig. 1. The diagram is a flow sheet showing the transitions

$$X_1 + H_2O_2 \rightarrow X_2$$
$$X_2 + H_2O_2 \rightarrow 2H_2O + O_2 + X_1$$

and the equilibrium

$$X_2 + N_3^- \rightleftharpoons X_3.$$

The displacement of the two containers for X_1 indicates that there is a decrease in free energy by the overall reaction.

From the reaction pattern we conclude $w_1 = k_1x,\ w_{-1} = k_{-1};\ w_2 = k_2x$, where x is the peroxide concentration. Insertion yields

$$-E\frac{dt}{dx} = (1 + k_{-1}/k_2x)/k_1x + 1/k_2x = E/s$$

This agrees only with the experimentally determined chronometric integral for small concentrations of peroxide if, for all accessible values of x, $k_{-1}/k_2x \ll 1$ and we thus get for the rate constant $k : 1/k = 1_1/k_1 + 1/k_2$ which is in complete agreement with Beers and Sizer's [1] results.

Mrs. Skovsted's results concerning retardation by azide can be adequately interpreted by means of the flow-sheet (Fig. 1). We get as before

$$(x_1 + x_2)/s = 1/w_1 + 1/w_2.$$

But in this case $E = x_1 + x_2 + x_3$. x_3 is determined by the consideration that to preserve steady state the rate s_{23} must be zero, that is X_2 and X_3 are in equilibrium according to the chemical equation.

$$X_2 + A = X_3$$

which immediately yields $x_3 = Kax_2$. x_2 and x_3 are the concentrations of X_2 and X_3 respectively, while a is the concentration of azide. a may be considered as a constant if it is essentially larger than E. As $x_2/s = 1/w_2$ we thus get

$$(x_1 + x_2 + x_3)/s = E/s = 1/w_1 + (1 + Ka)/w_2$$

or

$$-\ x\ E\frac{dt}{dx} = 1/k_1 + (1 + Ka)/k_2 = 1/k'$$

where $k'E = k$ is the experimentally determined rate-constant. The expression obviously agrees completely with Mrs. Skovsted's results. The slope of $1/k'$ against a yields the numerical value of K/k_2. At present we have no means to determine k_1 and k_2 separately and it is therefore impossible to determine the numerical value of K. The result may also be written as follows

$$\begin{aligned} 1/k &= (1/k_1 + 1/k_2)/E + aK/k_2E \\ &= (1/k_1 + 1/k_2)(1 + aKk_1/(k_1 + k_2))/E \end{aligned}$$

Mrs. Skovsted's results may be written

$$1/k = (1 + 1.08 \cdot 10^7\ a)/0.0645 \cdot 2.303$$

Comparison yields

$$1/k_1 + 1/k_2 = E/0.0645 \cdot 2.303 \quad \text{where } E \sim 10^{-10} \text{ mole/liter}$$

and

$$Kk_1/(k_1 + k_2) = 1.08 \cdot 10^7.$$

Assuming that k_1 is essentially larger than k_2 we get

$$k_2 = 2.303 \cdot 0.0645/E$$

and

$$K = 1.08 \cdot 10^7$$

The large value of K indicates that X_2 which is catalase combined with at least one molecule peroxide has a very strong affinity for azide-ion.

It may also have a strong affinity for peroxide or peroxide anion, but while the complex with azide-ion is stable, the peroxide complex obviously explodes immediately after its formation.

REFERENCES

1. Beers, R. F. and Sizer, J. W. *J. Phys. Chem.* **57** (1953) 290.

For other references see the preceding paper by Lis Skovsted.

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