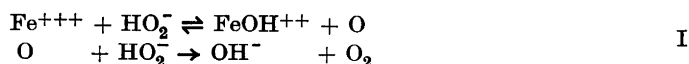# On Hydrogen Peroxide Decomposition
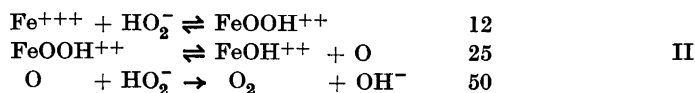
II.   The Ferric Salt Catalysis

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In a previous paper[1] it has been shown that the decomposition of hydrogen peroxide catalysed by ferric salts can be explained by the following reaction mechanism:

$$Fe^{+++} + HO_2^- \rightleftarrows FeOH^{++} + O$$
$$O \quad + HO_2^- \rightarrow OH^- \quad + O_2 \qquad\qquad \text{I}$$

or by:

$$Fe^{+++} + HO_2^- \rightleftarrows FeOOH^{++} \qquad\qquad 12$$
$$FeOOH^{++} \quad \rightleftarrows FeOH^{++} + O \qquad\quad 25 \qquad \text{II}$$
$$O \quad + HO_2^- \rightarrow O_2 \quad + OH^- \qquad 50$$

The apparently illogical numbering of the processes has been introduced in a paper to be published later on. The number 12 in the first equation has to be read one, two, reaction 21 (two, one) will then be the opposite reaction etc.

From the expression which has been found for the reciprocal velocity of reaction:

$$-\frac{dt}{dx} = \frac{0.4343}{B} \cdot \frac{1}{x} + \frac{A}{B} \cdot \frac{1}{x^2} \qquad\qquad (6a)^{**}$$

it cannot be said right away which of the above reaction mechanisms affords the best explanation of the reaction, but in 1949 Evans, George and Uri[2] showed that even a rather acid solution of ferric salt is coloured brown by the addition of hydrogen peroxide; they think that the brown colour is due to the production of $FeOOH^{++}$ ions. On the basis of colorimetric measurements a complex constant for the ion has been calculated, $i.$ $e.$ an equilibrium

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** This equation and equation (16) were first introduced in the above mentioned paper.[1]

constant for reaction 12 in scheme II; furthermore they have investigated the dependence of the equilibrium constant on the temperature. In consequence of this finding reaction mechanism number II must be taken as the best representation of the reaction.

In the following an account will be given on the calculation of the velocity constants for some of the reactions in reaction scheme II and on some investigations concerning the dependence of these constants on the temperature.

1. CALCULATION OF SOME VELOCITY CONSTANTS AT 25° C

If it is assumed, that soon after the addition of hydrogen peroxide to the ferric salt solution a stationary state is attained the expression for the reciprocal velocity can be written (Christiansen [3]):

$$\frac{1}{s} = \frac{dt}{dO_2} = -\frac{2dt}{dH_2O_2} = \frac{1}{k_{12} \cdot c_{Fe^{+++}} \cdot c_{HO_2^-}} \cdot (1 + \frac{k_{21}}{k_{25}})$$
$$+ \frac{1}{k_{12} \cdot c_{Fe^{+++}} \cdot c_{HO_2^-}} \cdot \frac{k_{21}k_{52}c_{FeOH^{++}}}{k_{25}k_{50}c_{HO_2^-}} \qquad (16)$$

or when K_{Fe} is the equilibrium constant for: "$Fe^{+++} + H_2O \rightleftharpoons FeOH^{++} + H^+$" and $K_{H_2O_2}$ is the acid dissociation constant for hydrogen peroxide, and c_{Ferric} is the concentration of ferric salt:

$$-\frac{dt}{dH_2O_2} = \frac{1}{2} \cdot \frac{K_{Fe} + c_{H^+}}{c_{Ferric} \cdot K_{H_2O_2}} \cdot \frac{1}{k_{12}} \cdot (1 + \frac{k_{21}}{k_{25}}) \cdot \frac{1}{c_{H_2O_2}}$$
$$+ \frac{1}{2} \cdot \frac{K_{Fe} \cdot c_{H^+}}{K^2_{H_2O_2}} \cdot \frac{k_{21}}{k_{12}} \cdot \frac{k_{52}}{k_{25}} \cdot \frac{1}{k_{50}} \cdot \frac{1}{c^2_{H_2O_2}} \qquad (18)$$

As shown in reaction mechanism II the $FeOOH^{++}$ ion may be split up in two ways, : according to reaction 21 or 25. Assuming reaction 21 to be much more rapid than 25 we have: $k_{21} \gg k_{25}$, i. e. (18) may be written:

$$-\frac{dt}{dH_2O_2} = \frac{1}{2} \cdot \frac{K_{Fe} + c_{H^+}}{c_{Ferric} \cdot K_{H_2O_2}} \cdot \frac{k_{21}}{k_{12}} \cdot \frac{1}{k_{25}} \cdot \frac{1}{c_{H_2O_2}}$$
$$+ \frac{1}{2} \cdot \frac{K_{Fe} \cdot c_{H^+}}{K^2_{H_2O_2}} \cdot \frac{k_{21}}{k_{12}} \cdot \frac{k_{52}}{k_{25}} \cdot \frac{1}{k_{50}} \cdot \frac{1}{c^2_{H_2O_2}} \qquad (19)$$

By comparing (6a) and (19) we obtain:

$$\frac{0.4343}{B} = \frac{1}{2} \cdot \frac{K_{Fe} + c_{H^+}}{c_{Ferric} \cdot K_{H_2O_2}} \cdot \frac{k_{21}}{k_{12}} \cdot \frac{1}{k_{25}} \qquad (20)$$

6

and:

$$\frac{A}{B} = \frac{1}{2} \cdot \frac{K_{Fe} \cdot c_{H^+}}{K^2_{H_2O_2}} \cdot \frac{k_{21}}{k_{12}} \cdot \frac{k_{52}}{k_{25}} \cdot \frac{1}{k_{50}} \tag{21}$$

When K_{12} is the equilibrium constant for reaction 12 we have:

$$\frac{k_{12}}{k_{21}} = K_{12} \tag{22}$$

and (20) may be written:

$$k_{25} = \frac{B}{0.8686 \cdot c_{Ferric}} \cdot \frac{K_{Fe} + c_{H^+}}{K_{H_2O_2}} \cdot \frac{1}{K_{12}} \tag{23}$$

In the above cited paper [1] Table 3 B/c_{Ferric} at $c_{H^+} = 0.01$ was found to be 4.43. $K_{Fe} = 2 \cdot 10^{-3}$ (*l. c.* page 10). $K_{H_2O_2} = 2.4 \cdot 10^{-12}$ (Joyner [4]). $K_{12} = 2 . 10^9$ (Evans and coworcers [2]). From these numbers k_{25} is calculated by means of (23):

$$k_{25} = 13 \text{ mol/min. at } 25° \text{ C.}$$

(21) may be written:

$$\frac{k_{50}}{k_{52}} = \frac{B}{A} \cdot \frac{1}{2} \cdot \frac{K_{Fe} \cdot c_{H^+}}{K^2_{H_2O_2}} \cdot \frac{1}{K_{12} \cdot k_{25}} \tag{24}$$

From the experimental results in Table 3 in the above cited paper [1] B/A is found to be 10.6, when the hydrogen ion concentration is 0.01. Substituting in (24) this value for B/A together with the above mentioned values for the equilibrium constants and the above calculated value for k_{25}, the ratio between k_{50} and k_{52} may be calculated:

$$\frac{k_{50}}{k_{52}} = 7 \cdot 10^8 \text{ at } 25°\text{C}$$

By means of this value for the ratio $\dfrac{k_{50}}{k_{52}}$ the ratio $\dfrac{w_{50}}{w_{52}}$ can be calculated. w_{50} means the probability for the oxygen atoms to react according to 50 and w_{52} the probability to react according to 52.

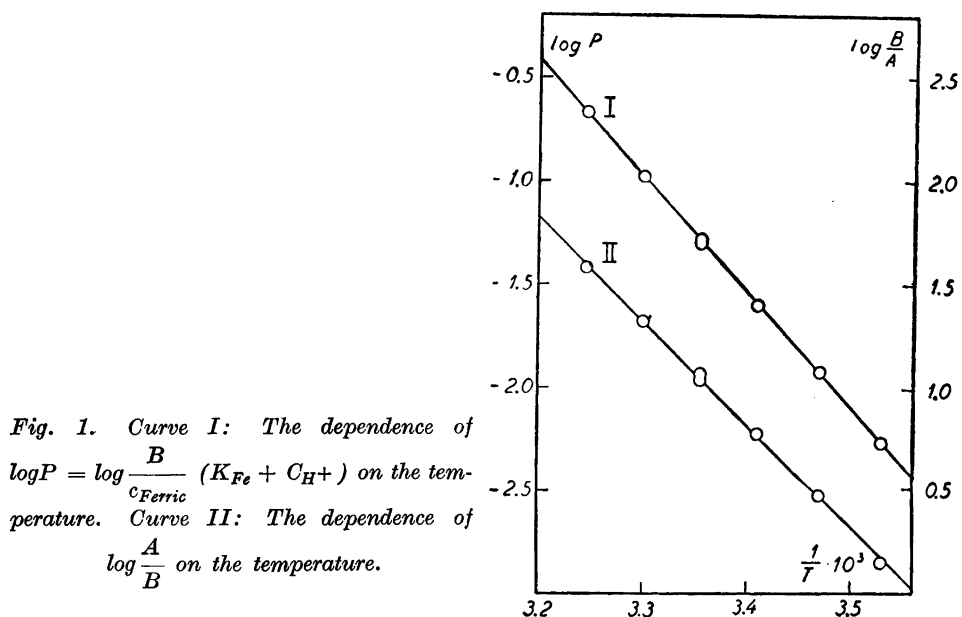$$\frac{w_{50}}{w_{52}} = \frac{k_{50} \cdot c_{HO_2^-}}{k_{52} \cdot c_{FeOH^{++}}} \tag{25}$$

Fig. 1. Curve I: The dependence of $logP = log \dfrac{B}{c_{Ferric}}$ *($K_{Fe} + C_{H^+}$) on the temperature. Curve II: The dependence of* $log \dfrac{A}{B}$ *on the temperature.*

In a mixture with $c_{H_2O_2} = 0.05$, $c_H{}^+ = 0.01$ and $c_{Ferric} = 0.001$ the ratio will be about 50 and after 90 % of the hydrogen peroxide has been decomposed the ratio will be about 5.

2. DETERMINATION OF SOME ACTIVATION ENERGIES

Experiments have been carried out at 6 different temperatures between 10° C and 35° C. The experiments were all carried out as described in the above cited paper[1] page 2. The composition and the temperatures of the reacting mixtures are shown in Table 1, together with the values for the constants A and B.

According to (23) is:

$$\log k_{25} = \log \frac{B}{c_{\text{Ferric}}} + \log (K_{\text{Fe}} + c_{\text{H}}{}^+) - \log K_{\text{H}_2\text{O}_2} - \log K_{12} - \log 0.8686 \quad (26)$$

The values for $\log \dfrac{B}{c_{\text{Ferric}}}$ are given in Table 1 column 6 and the values for $\log (K_{\text{Fe}} + c_{\text{H}}{}^+)$ are given in column 7. The values used for K_{Fe} at the different temperatures are calculated from the equation:

Table 1. The dependence of the constants A and B on the temperature. In all the experiments the hydrogen ion concentration was 0.01, and the initial concentration of hydrogen peroxide 0.05.

1	2	3	4	5	6	7	8
T	$\dfrac{1}{T} \cdot 10^3$	c_{Ferric}	$A \cdot 10^3$	$B \cdot 10^3$	$\log \dfrac{B}{c_{\text{Ferric}}}$	$\log(K_{\text{Fe}} + c_{\text{H}}^+)$	$\log \dfrac{B}{A}$
283.15	3.532	0.004	1.50	2.12	-0.284	-1.972	0.150
288.15	3.470	0.004	1.50	4.40	0.041	-1.960	0.467
293.15	3.411	0.004	1.50	9.00	0.352	-1.945	0.778
298.15	3.354	0.002	0.80	8.70	0.639	-1.921	1.036
298.15	3.354	0.004	1.50	17.60	0.644	-1.921	1.069
303.15	3.299	0.002	0.80	16.60	0.912	-1.892	1.316
308.15	3.245	0.002	0.80	30.80	1.188	-1.854	1.586

$$\log K_{\text{Fe}} = -\frac{12300}{4.57\,T} + 6.33 \tag{27}$$

The heat of reaction: 12 300 cal/mol is calculated by Rabinowitch and Stockmayer [5]. Furthermore we use $K_{\text{Fe}} = 2 \cdot 10^{-3}$ at 25° C.

The values for $\log P = \log \dfrac{B}{c_{\text{Ferric}}} \cdot (K_{\text{Fe}} + c_{\text{H}}^+)$ are plotted against $1/T$ in Fig. 1. From the figure is calculated

$$\log \frac{B}{c_{\text{Ferric}}} (K_{\text{Fe}} + c_{\text{H}}^+) = -5580 \cdot \frac{1}{T} + 17.24 \tag{28}$$

For $H_2O_2 \rightleftharpoons H^+ + HO_2^-$ Joyner [4] has measured $\Delta H = 8600$ cal/mol; when $K_{H_2O_2} = 2.4 \cdot 10^{-12}$ at 25° C we have:

$$\log K_{H_2O_2} = -\frac{8600}{4.57\,T} - 5.30 \tag{29}$$

From the data of Evans and coworkers [2] can be calculated:

$$\log K_{12} = -\frac{1800}{4.57\,T} + 10.65 \tag{30}$$

Substituting equations (28), (29) and (30) in (26) we get:

$$\log k_{25} = -\frac{15100}{4.57\,T} + 11.95 \tag{31}$$

or

$$k_{25} = 10^{11.95} \cdot e^{-\frac{15100}{RT}} \text{ min}^{-1}$$

or

$$k_{25} = 10^{10.17} \cdot e^{-\frac{15100}{RT}} \text{ sec}^{-1} \tag{31a}$$

i. e. the activation energy for the proces 25 is

$$E_k = \text{about } 15000 \text{ cal/mol}$$

According to (24) is:

$$\log \frac{k_{50}}{k_{52}} = \log \frac{B}{A} + \log 0.5 + \log K_{Fe} + \log c_{H^+} - 2\log K_{H_2O_2} - \log K_{12} - \log k_{25} \tag{32}$$

The values for $\log \dfrac{B}{A}$ are given in Table 1 column 8; these values are plotted against $\dfrac{1}{T}$ in Fig. 1. From the figure is calculated

$$\log \frac{B}{A} = -5082 \cdot \frac{1}{T} + 18.08 \tag{33}$$

Substituting (27), (29), (30), (31) and (33) in (32) we have when $e_{H^+} = 0,01$:

$$\log \frac{k_{50}}{k_{52}} = -\frac{1425}{4.57\,T} + 10.11 \tag{34}$$

or

$$\frac{k_{50}}{k_{52}} = 10^{10.11} \cdot e^{-\frac{1425}{RT}} \tag{34a}$$

that is: the difference between E_k for process 50 and E_k for the process 52 is equal to about 1400 cal/mol. This figure is however so small that the activation energies for the two processes mentioned may be considered practically equal as the values of the figures used for the calculations are rather uncertain.

DISCUSSION

It is shown in the above section that the velocity constant for the process 25 can be written

$$k_{25} = 10^{10.17} \cdot e^{-\frac{15100}{RT}} \text{ sec.}^{-1} \qquad (31a)$$

The frequency factor $10^{10.17} \cdot$ sec.$^{-1}$ is less than the value which one normally finds for monomolecular reactions $i.\ e$: about 10^{12} — but it is not much less when one takes into concideration the errors in the figures used.

It is also shown that the ratio between the velocity constants for the bimolecular reactions 50 and 52 can be written:

$$\frac{k_{50}}{k_{52}} = 10^{10.11} \cdot e^{-\frac{1425}{RT}} \qquad (34a)$$

The factor $10^{10.11}$ has an unexpectedly high value. Following from the simple collision theory one would have expected a value of about one [6]. This means that the reactions 50 and 52 deviate from the normal in such a way that the collision factor in k_{50} is greater and the collision factor in k_{52} is less than is expected from the collision theory. Such reactions are known and are not uncommon.

Moelwyn-Hughes includes in his book [7] the following as explanation of such deviations from the normal:

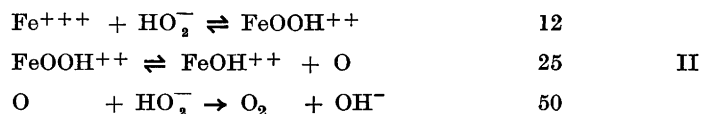"Chief among the causes responsible for reducing below its normal value the rate of a second-order reaction in a homogeneous system are: (1) endothermic formation of a complex prior to the reaction proper; (2) the necessity for the ionization of either or both of the reactants; (3) deactivation by solvent molecules; (4) stringent conditions of orientation or of internal phase of the reacting molecules at the moment of impact, and (5) the existence of strong forces of repulsion. Factors which allow a faster reaction velocity than that permitted by the simple collision theory are: (a) exothermic formation of a complex prior to the reaction proper; (b) the distribution of the energy of activation among a number of internal degrees of freedom of the reacting molecules; (c) the propagation of reaction chains; (d) activation by some means other than by collision, $e.\ g.$ by radiation, and (e) the existence of strong forces of attraction. Evidence from individual reactions could be quoted in support of each of these."

It cannot be said, which of the above mentioned factors can be applied in the present case. But that the collision factor in k_{52} is less than expected is

perhaps due to a deactivation of the oxygen atoms by collision with the water molecules which are combined with the $FeOH^{++}$ ions. And the fact that the collision factor in k_{50} is greater than expected is perhaps due to activation in a different way than by collision. It is possible that the magnetic properties of the oxygen atoms could have an effect upon the velocity of the process 50.

SUMMARY

1. It has been shown that the ferric salt catalyzed decomposition of hydrogen peroxide must be explained by the reaction mechanism:

$$Fe^{+++} + HO_2^- \rightleftharpoons FeOOH^{++} \qquad 12$$
$$FeOOH^{++} \rightleftharpoons FeOH^{++} + O \qquad 25 \qquad II$$
$$O + HO_2^- \rightarrow O_2 + OH^- \qquad 50$$

and some of the velocity constants have been calculated.

2. The activation energies for some of the processes in the scheme II have been calculated on the bases of experiments.

REFERENCES

1. Andersen, V. S. *Acta Chem. Scand.* **2** (1948) 1.
2. Evans, M. G., George, Ph., and Uri, N. *Trans. Faraday Soc. XLV*. Part 3 (1949) 230.
3. Christiansen, J. A. *Handbuch der Katalyse.* (1941) 261.
4. Joyner, R. A. *Z. anorg. Chem.* **77** (1912) 103.
5. Rabinowitch, E., and Stockmayer, W. H. *J. Am. Chem. Soc.* **64** (1942) 335.
6. Moelwyn-Hughes, E. A. *The kinetics of reactions in solution.* (1947) 70.
7. Moelwyn-Hughes, E. A. *The kinetics of reactions in solution.* (1947) 75.