

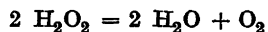
## On Hydrogen Peroxide Decomposition

### Ferric Salt Catalysis

V. STEN ANDERSEN

*The Technical University of Denmark, Chemistry Department A, and The Royal Danish School of Pharmacy, Department of Inorganic Chemistry, Copenhagen, Denmark*

Bertalan<sup>1</sup> has investigated the reaction



in water acidified with sulphuric acid, and with ferrous as well as ferric sulphate as catalyst. He is of the opinion of having shown that:

1. The course of the process is independent of the oxidation state of iron, because immediately after addition hydrogen peroxide will oxidize ferrous iron to ferric iron.

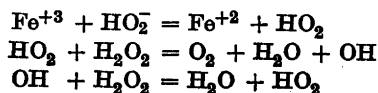
2. The reaction is of the first order.

3. The rate of decomposition is directly proportional to the concentration of ferric salt, but inversely proportional to the concentration of hydrogen ions.

Bohnson and Robertson<sup>2</sup> have put forward the hypothesis, that ferric acid ( $\text{H}_2\text{FeO}_4$ ) is formed by interaction between hydrogen peroxide and ferric salt, the ferric acid being subsequently reduced with the evolution of oxygen. They have tested this hypothesis by comparing the absorption spectra of solutions of 1) barium ferrate, 2) potassium ferrate, 3) mixtures of hydrogen peroxide and ferric chloride, and 4) ferric chloride alone. Furthermore they have investigated the effect of neutral salts on the rate of the reaction and found, that addition of potassium chloride and potassium nitrate has an only slight effect, while addition of potassium sulphate and especially of potassium phosphate causes a considerable decrease in the velocity constant, possibly due to the removal of iron as a complex ion. Bohnson and Robertson have calculated the rate constants on the basis of the amount of oxygen evolved in the interval between 25 % to 50 % destruction of the hydrogen peroxide initially present.

Simon and co-workers<sup>3</sup> have investigated the effect of diverse ferric salts on the hydrogen peroxide decomposition. They have shown, that the catalytic effect of ferric salts decreases with increasing degree of complexity.

Haber and Weiss<sup>4</sup> discuss on the basis of measurements, done partly by themselves and partly by other investigators, the mechanism of reaction of the hydrogen peroxide decomposition in the presence of ferrous and ferric salts and propose, that the ferric salt catalysed reaction takes place in the following steps:



### EXPERIMENTAL

In this paper the hydrogen peroxide decomposition in presence of ferric ions, the solution acidified with nitric acid, is subjected to a critical investigation. As source of ferric ions is used ferric nitrate, as this can be obtained pure and the nitrate ion usually forms complex compounds only to a small extent.

#### Reagents

Hydrogen peroxide 30 %, *pro analysi*, Merck.

0.1 M nitric acid; the titer of the acid was determined by titration of sodium tetraborate (tested purity, Danish Pharmacopoeia, 1933).

0.1 M ferric nitrate solution, which at the same time is 0.1 M as to nitric acid. This solution was made by dissolving 40.40 g ferric nitrate [ $\text{Fe}(\text{NO}_3)_3 + 9 \text{H}_2\text{O}$ , *pro analysi*, Merck] in 100.0 ml 1 M nitric acid and then diluting with redistilled water to 1000 ml in a volumetric flask. The ferric ion content was controlled by a gravimetric iron determination.

0.1 N (0.02 M) potassium permanganate solution; the titer was determined by titration of sodium oxalate (Sørensen).

All water used was redistilled water, made in a glass distilling apparatus.

#### Experimental study of the rate of reaction

The reacting mixture was made by mixing equal volumes of 1) a solution (hereafter called catalyst mixture) containing ferric nitrate and nitric acid, and 2) a solution of hydrogen peroxide and nitric acid, the concentration of nitric acid being the same as in the catalyst mixture.

1. The catalyst mixture was prepared from ferric nitrate solution acidified with nitric acid, 0.1 M nitric acid and redistilled water in a 250 ml volumetric flask. After mixing carefully the solution was poured into a one liter bottle (pyrex), which then was mounted in a water thermostat at the required temperature.

2. For each experiment 500 ml hydrogen peroxide solution was made by mixing 30 %'s hydrogen peroxide, redistilled water and as much of 0.1 *M* nitric acid, that the concentration of nitric acid was exactly the same as in the catalyst mixture. 250 ml was then placed in a 250 ml volumetric flask, which was mounted in the water thermostat next to the catalyst mixture. The rest of the hydrogen peroxide solution was used for determination of the concentration of hydrogen peroxide by titration with 0.1 *N* potassium permanganate.

The experiments themselves were started by emptying — as fast as possible — the volumetric flask of hydrogen peroxide into the bottle with the catalyst mixture, which was kept steadily moving by rotating the bottle. The mixing lasts about 8 seconds. From time to time a sample of the reacting mixture is taken out with a 30 ml pipette, the delivery orifice of which being fairly large. The sample is at once allowed to run into a previously tared Erlenmeyer flask containing 20 ml 2 *M* sulfuric acid; hereby the reaction will practically stop. The flask is now weighed within an accuracy of 0.01 g. Due to the content of oxygen bubbles in the reacting mixture it was impossible to take out an accurate volume of the solution.

The hydrogen peroxide content was determined by titration with 0.1 *N* potassium permanganate; in cases, where the amount of permanganate required was less than 10 ml, a 10 ml burette, the smallest subdivision being 0.02 ml, was used.

On the basis of the titration results the concentration of non-decomposed hydrogen peroxide at the various times was calculated. The concentration of hydrogen peroxide to time zero was calculated from the direct titration of the hydrogen peroxide solution used.

#### CALCULATIONS

The decomposition of hydrogen peroxide can not — as Bertalan asserted — be satisfactorily calculated from the kinetic equation for a reaction of the first order:

$$0.4343 \cdot k \cdot t = \log \frac{a}{x} \quad (1)$$

where *a* is the initial molar concentration of hydrogen peroxide and *x* the concentration at the time *t*. This equation requires, that a plot of  $\log \frac{a}{x}$  against *t* should be linear if the reaction is of first order.

In Table 1 is given the experimental results from ferric ion catalysed hydrogen peroxide decomposition at 25° C, in a solution which is 0.004 *M* as to ferric nitrate and 0.01 *M* as to nitric acid. In column 4 is given the values found of  $\log \frac{a}{x}$ . These values are in Fig. 1 plotted against the corresponding *t* values, and the points hereby produced are fitted with a curve (marked I). This is not a straight line plot, but drops towards the *t*-axis with increasing *t* values. The reason, why Bertalan has not noticed this phenomenon, is probably, that he has only followed the reaction to 80 % decomposition of the hydrogen peroxide.

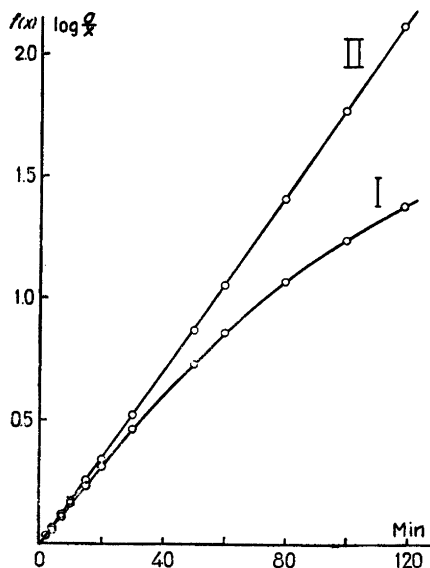


Fig. 1. The decomposition of hydrogen peroxide at 25° C in solution 0.004 M as to ferric nitrate and 0.01 M as to nitric acid. Curve I is a plot of  $\log \frac{a}{x}$  against time  $t$ . Curve II represents the function  $(f(x) = \log \frac{a}{x} + A \cdot (\frac{1}{x} - \frac{1}{a}))$  plotted against time  $t$ ;  $B \cdot t + \tau = f(x)$ ;  $A = 1.5 \cdot 10^{-3}$ ;  $B = 1.78 \cdot 10^{-2}$  and  $\tau = -0.01$ .

A function of  $c_{\text{H}_2\text{O}_2}$ , which to its whole extent except in the very beginning, is a linear function of time, is the following expression:

$$f(x) = B \cdot t + \tau = \log \frac{a}{x} + A \cdot \left( \frac{1}{x} - \frac{1}{a} \right) \quad (2)$$

where  $t$ ,  $a$  and  $x$  have the same meanings as in (1), and  $A$  and  $B$  are constants.

The constants  $A$  and  $B$  are calculated by substituting  $A$  in (2) with different values, until a plot of  $f(x)$  against  $t$  is a straight line;  $B$  will then be the slope of this line. The significance of the deviations in the very beginning of an experiment will be dealt with later. While  $B$  in this way can be calculated with a reasonable accuracy, that will not apply to  $A$ , which roughly estimated may vary up to 15 % without much effect on the magnitude of  $B$ . The calculated values of  $A$  and  $B$  are given in the text to Table 1. In column 8 are given the values of  $f(x) = \log \frac{a}{x} + A \cdot \left( \frac{1}{x} - \frac{1}{a} \right)$  calculated from the found value of  $A$ . For sake of control the values of  $t = \frac{1}{B} \cdot [f(x) - \tau]$  are calculated by substituting  $B$  with the found value (column 9).

A comparison of columns 1 and 9 together with the graph shows the applicability of the calculation method.

*Table 1. The decomposition of hydrogen peroxide at 25° C in solution 0.004 M as to ferric nitrate and 0.01 M as to nitric acid. The experiments are calculated after (2). In column 8 is given  $f(x) = \log \frac{a}{x} + A \cdot \left( \frac{1}{x} - \frac{1}{a} \right)$ ; the constant A is calculated graphically, so that  $f(x)$  becomes a linear function of  $t$ , i. e.  $B \cdot t + \tau = f(x)$ . (cf. Fig. 1).  $A = 1.5 \cdot 10^{-3}$ ,  $B = 1.78 \cdot 10^{-2}$ ,  $\tau = -0.01$ .*

1	2	3	4	5	6	7	8	9
$t$ min	$x = c_{H_2O_2}$	$\log x$	$\log \frac{a}{x}$	$\frac{1}{x}$	$\frac{1}{x} - \frac{1}{a}$	$(6) \cdot A$	$f(x) = (4) + (7)$	$t$
0.0	0.04710	0.6730-2		21.23				
2.0	0.04426	0.6460	0.0270	22.59	1.36	0.0020	0.0290	2.2
4.0	0.04139	0.6169	0.0561	24.16	2.93	0.0044	0.0605	4.0
7.0	0.03707	0.5690	0.1040	26.98	5.75	0.0086	0.1126	6.9
10.0	0.03264	0.5137	0.1593	30.64	9.41	0.0141	0.1734	10.3
15.0	0.02754	0.4400	0.2330	36.31	15.08	0.0226	0.2556	14.9
20.0	0.02305	0.3627	0.3103	43.38	22.15	0.0333	0.3436	19.9
30.0	0.01622	0.2101	0.4629	61.65	40.42	0.0606	0.5235	30.0
40.0	0.01168	0.0675	0.6055	85.62	64.39	0.0966	0.7021	40.0
50.0	0.008672	0.9431-3	0.7299	115.31	94.08	0.1411	0.8710	49.5
60.0	0.006554	0.8165	0.8565	152.57	131.34	0.1970	1.0535	59.7
80.0	0.004021	0.6044	1.0686	248.69	227.46	0.3413	1.4099	79.7
100.0	0.002686	0.4291	1.2439	372.30	351.07	0.5266	1.7705	100.0
119.0	0.001959	0.2920	1.3810	510.72	489.49	0.7343	2.1153	119.3

EFFECT OF HYDROGEN PEROXIDE CONCENTRATION ON RATE OF REACTION

In order to establish the effect of the hydrogen peroxide concentration two experiments were carried out, one 0.05 M and the other 0.009 M as to hydrogen peroxide. The molar concentration of ferric nitrate was 0.004 and that of nitric acid 0.01 in both experiments. The calculations were carried out according to (2) and the results are given in Table 2.

*Table 2. The effect of hydrogen peroxide concentration on the constants A and B. 25° C.*

$c_{H_2O_2}$	$c_{Fe(NO_3)_3}$	$c_{HNO_3}$	A	B
0.009	0.004	0.01	$1.5 \cdot 10^{-3}$	$1.78 \cdot 10^{-2}$
0.05	0.004	0.01	$1.5 \cdot 10^{-3}$	$1.78 \cdot 10^{-2}$

As appears from the table, the constants  $A$  and  $B$  are independent of the initial concentration of hydrogen peroxide.

#### EFFECT OF FERRIC NITRATE CONCENTRATION ON RATE OF REACTION

A series of experiments were run, in which all initial concentrations — except the ferric nitrate concentration — were the same; the calculations were carried out according to (2), and the results are given in Table 3. The table shows, that  $A$  and  $B$  are directly proportional to the concentration of ferric nitrate, *i. e.*

$$A = \alpha \cdot c_{\text{Ferric}} \quad (3) \quad \text{and} \quad B = \beta \cdot c_{\text{Ferric}} \quad (4)$$

Table 3. Decomposition at 25° C of hydrogen peroxide in solution 0.01 M as to nitric acid, but with varying amounts of ferric nitrate added. The constants  $A$  and  $B$  are calculated according to (2).

$c_{\text{H}_2\text{O}_2}$	$c_{\text{Ferric}}$	$c_{\text{HNO}_3}$	$A$	$B$	$\frac{A}{c_{\text{Ferric}}}$	$\frac{B}{c_{\text{Ferric}}}$
0.05	0.001	0.01	0.00040	0.0045	0.40	4.50
0.05	0.002	0.01	0.00075	0.0089	0.38	4.45
0.05	0.003	0.01	0.00108	0.0132	0.36	4.40
0.05	0.004	0.01	0.00150	0.0176	0.38	4.40

#### EFFECT OF HYDROGEN ION CONCENTRATION ON RATE OF REACTION

In order to establish the effect of the hydrogen ion concentration on the rate of reaction four experiments were carried out. The initial concentrations of hydrogen peroxide and ferric nitrate were the same, but varying amounts of nitric acid added. On the basis of the experimental results the constants  $A$  and  $B$  were calculated according to (2). The results are given in Table 4, columns 4 and 5. The figures in columns 6, 7, 8 and 9 will be dealt with later.

Table 4. Effect of hydrogen ion concentration at 25° C on the rate of reaction. The constants  $A$  and  $B$  are calculated according to (2).

1	2	3	4	5	6	7	8	9
$c_{\text{H}_2\text{O}_2}$	$c_{\text{Fe}(\text{NO}_3)_3}$	$c_{\text{HNO}_3}$	$A$	$B$	$\frac{1}{B}$	$A$ Corr.	$B$ Corr.	$\frac{1}{B}$ Corr.
0.05	0.004	0.01	$1.50 \cdot 10^{-3}$	$1.76 \cdot 10^{-2}$	56.8	$1.50 \cdot 10^{-3}$	$1.76 \cdot 10^{-2}$	56.8
0.05	0.004	0.02	$1.50 \cdot 10^{-3}$	$1.00 \cdot 10^{-2}$	100	$1.64 \cdot 10^{-3}$	$1.01 \cdot 10^{-2}$	99
0.05	0.004	0.03	$1.50 \cdot 10^{-3}$	$0.67 \cdot 10^{-2}$	149	$1.70 \cdot 10^{-3}$	$0.68 \cdot 10^{-2}$	147
0.06	0.004	0.04	$1.50 \cdot 10^{-3}$	$0.52 \cdot 10^{-2}$	192	$1.72 \cdot 10^{-3}$	$0.53 \cdot 10^{-2}$	189

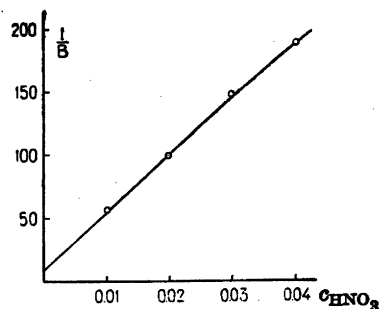


Fig. 2. Relation between the constant  $B$  and the concentration of nitric acid, the concentration of ferric nitrate being  $0.004 M$ .

The table shows, that the concentration of nitric acid, *i. e.* the concentration of hydrogen ions, has a marked influence on the constant  $B$ , but that  $A$ , within the accuracy of the method, is independent of the hydrogen ion concentration. From Fig. 2, in which  $\frac{1}{B}$  is plotted against  $c_{\text{HNO}_3}$ , it is evident, that

$$\frac{1}{B} = \gamma \cdot c_{\text{HNO}_3} + K \quad (5)$$

$\gamma$  is the slope of the straight line and  $K$  the intercept on  $\frac{1}{B}$ -axis.

In the solutions in question it is allowable to put  $c_{\text{HNO}_3}$  equal to  $c_{\text{H}^+}$ . (5) can then be written:

$$\frac{1}{B} = \gamma \cdot c_{\text{H}^+} + K \quad (5a)$$

or

$$B = \frac{1}{\gamma} \cdot \frac{1}{c_{\text{H}^+} + K'} \quad (5b)$$

On Fig. 2 can be measured:  $K = 0.9$  and  $\gamma = 4600$ , which gives  $K' = 1.96 \cdot 10^{-3}$ .

#### EXPERIMENTAL RESULTS SUMMARIZED

1. The ferric ion catalysed decomposition of hydrogen peroxide, the reacting solution being acidified with nitric acid, can be calculated from

$$f(x) = B \cdot t + \tau = \log \frac{\alpha}{x} + A \left( \frac{1}{x} - \frac{1}{\alpha} \right) \quad (2)$$

The straight line  $f(x)$  does not pass through the origin of the coordinates, but  $\tau$  is the intercept on the ordinate-axis. That it is not possible to calculate  $A$  and  $B$  so, that  $f(x)$  passes through the origin, may be due to the start of the process having a certain — but usually rather small — time lag.

2. The constants  $A$  and  $B$  are independent of the initial concentration of hydrogen peroxide.

3. At constant concentration of hydrogen ions the constants  $A$  and  $B$  are proportional to the concentration of ferric nitrate.

4. The constant  $A$  is — within the accuracy of the calculation method — independent of the hydrogen ion concentration, while  $B$  is approximately inversely proportional to the latter.

#### THE REACTION MECHANISM

Upon differentiation of (2) with respect to  $x$  is found:

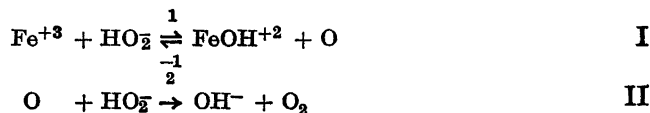
$$-B \cdot \frac{dt}{dx} = 0.4343 \frac{1}{x} + A \cdot \frac{1}{x^2} \quad (6)$$

or

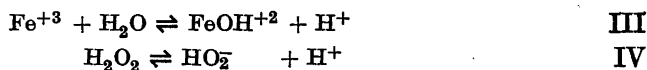
$$\frac{1}{s} = -\frac{dt}{dx} = \frac{0.4343}{B \cdot x} + \frac{0.4343 \cdot A}{B \cdot 0.4343 \cdot x^2} \quad (6a)$$

where  $\frac{1}{s}$  is the reciprocal velocity.

The simplest way, in which to explain the expression (6a), is to assume the following mechanism:



while we at the same time have the equilibria:



When assuming, as originally proposed by Bodenstein<sup>5</sup>, that soon after starting the reaction, a stationary state is attained, in which the velocity of consumption of the instable intermediate (here the oxygen atoms) is just the same as the velocity of the production, the expression for the reciprocal velocity can be written (Christiansen<sup>6</sup>):



$$\frac{1}{s'} = \frac{dt}{d[\text{O}_2]} = -2 \frac{dt}{d[\text{H}_2\text{O}_2]} = \frac{1}{k_1 \cdot c_{\text{Fe}^{+3}} \cdot c_{\text{HO}_2^-}} + \frac{k_{-1} \cdot c_{\text{FeOH}^{+2}}}{k_1 \cdot c_{\text{Fe}^{+3}} \cdot c_{\text{HO}_2^-}} \cdot \frac{1}{k_2 \cdot c_{\text{HO}_2^-}} \quad (7)$$

or

$$-\frac{dt}{d[\text{H}_2\text{O}_2]} = \frac{1}{2 \cdot k_1 \cdot c_{\text{Fe}^{+3}} \cdot c_{\text{HO}_2^-}} + \frac{k_{-1} \cdot c_{\text{FeOH}^{+2}}}{2 \cdot k_1 \cdot c_{\text{Fe}^{+3}} \cdot c_{\text{HO}_2^-}} \cdot \frac{1}{k_2 \cdot c_{\text{HO}_2^-}} \quad (7a)$$

The expression for the equilibrium constant of equation III, which correctly ought to be written:



is abbreviated to:

$$\frac{c_{\text{FeOH}^{+2}} \cdot c_{\text{H}^+}}{c_{\text{Fe}^{+3}}} = K_{\text{Fe}} \quad (8)$$

and for IV we have:

$$\frac{c_{\text{H}^+} \cdot c_{\text{HO}_2^-}}{c_{\text{H}_2\text{O}_2}} = K_{\text{H}_2\text{O}_2} \quad (9)$$

From (8) is derived — when  $c_{\text{Ferric}} = c_{\text{Fe}^{+3}} + c_{\text{FeOH}^{+2}}$

$$c_{\text{FeOH}^{+2}} = \frac{K_{\text{Fe}}}{K_{\text{Fe}} + c_{\text{H}^+}} \cdot c_{\text{Ferric}} \quad (10)$$

$$c_{\text{Fe}^{+3}} = \frac{c_{\text{H}^+}}{K_{\text{Fe}} + c_{\text{H}^+}} \cdot c_{\text{Ferric}} \quad (11)$$

and from (9) is derived:

$$c_{\text{HO}_2^-} = K_{\text{H}_2\text{O}_2} \cdot \frac{c_{\text{H}_2\text{O}_2}}{c_{\text{H}^+}} \quad (12)$$

(7a) modified by the introduction of (10), (11) and (12) gives

$$-\frac{dt}{d[\text{H}_2\text{O}_2]} = \frac{K_{\text{Fe}} + c_{\text{H}^+}}{2k_1 \cdot K_{\text{H}_2\text{O}_2} \cdot c_{\text{Ferric}}} \cdot \frac{1}{c_{\text{H}_2\text{O}_2}} + \frac{K_{\text{Fe}} + c_{\text{H}^+}}{2k_1 \cdot K_{\text{H}_2\text{O}_2} \cdot c_{\text{Ferric}}} \cdot \frac{k_{-1} \cdot K_{\text{Fe}} \cdot c_{\text{H}^+} \cdot c_{\text{Ferric}}}{k_2 \cdot K_{\text{H}_2\text{O}_2} \cdot (K_{\text{Fe}} + c_{\text{H}^+}) \cdot c_{\text{H}_2\text{O}_2}^2} \quad (13)$$

If the reaction mechanism, as proposed in I and II, is true, (13) and (6a) ought to be identical, *i. e.*

$$B = 0.4343 \cdot \frac{2k_1 \cdot K_{\text{H}_2\text{O}_2}}{K_{\text{Fe}} + c_{\text{H}^+}} \cdot c_{\text{Ferric}} \quad (14)$$

$$A = 0.4343 \cdot \frac{k_{-1} \cdot K_{\text{Fe}}}{k_2 \cdot K_{\text{H}_2\text{O}_2}} \cdot \frac{c_{\text{H}^+}}{K_{\text{Fe}} + c_{\text{H}^+}} \cdot c_{\text{Ferric}} \quad (15)$$

Consequently  $B$  has to be directly proportional to the ferric salt concentration and inversely proportional to  $K_{\text{Fe}} + c_{\text{H}^+}$ , which is in accordance with the experimental results as expressed in (4) and (5b), when assuming that the constant  $K' = 1.96 \cdot 10^{-3} = 10^{-2.7}$  in (5b) is the first acid dissociation constant of the hexaquo ferric ion — *i. e.*  $K_{\text{Fe}}$  in (8). This constant has previously been determined as  $10^{-2.5}$  at  $25^\circ\text{C}$  by Lamb and Jaques<sup>7</sup> by means of a glass electrode in solutions containing ferric nitrate and nitric acid.

$A$  has to be directly proportional to the concentration of ferric salt, which is in agreement with the experiments (*cf.* (3)); furthermore  $A$  has to be proportional to the term  $\frac{c_{\text{H}^+}}{K_{\text{Fe}} + c_{\text{H}^+}}$ , *i. e.* in strong acid solution practically independent of the hydrogen ion concentration. In the experiments dealt with in Table 4 the factor of proportionality ought to vary with the hydrogen ion concentration as shown in Table 5. Therefore the variations in  $A$  are not

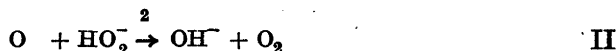
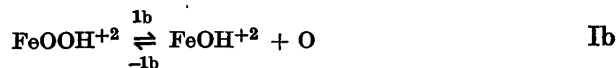
Table 5 The variation of  $\frac{c_{\text{H}^+}}{K_{\text{Fe}} + c_{\text{H}^+}}$  (15) with different  $c_{\text{H}^+}$ ;  $K_{\text{Fe}} = 2 \cdot 10^{-3}$ .

$c_{\text{H}^+}$	0.01	0.02	0.03	0.04
$\frac{c_{\text{H}^+}}{K_{\text{Fe}} + c_{\text{H}^+}}$	0.83	0.91	0.94	0.95

bigger than can be concealed by the errors of determination. If the  $A$  value, which is calculated on the basis of the investigation of hydrogen peroxide decomposition in  $0.01\text{ M}$  nitric acid (*cf.* Table 1 and Fig. 1), is regarded to be just about true, and that seems reasonable, because the time lag in this experiment is rather small, then the other  $A$  values and the corresponding  $B$  values in Table 4 are to be corrected in accordance with Table 5. These corrected values are shown in Table 4, columns 7 and 8. If — graphically (*cf.* Fig. 2) — the relation between the corrected  $B$  values and the hydrogen ion concentration is found, the relationship still agrees with (5a); the slope of the straight line will be slightly different, but  $K'$  in (5b) does not alter noticeably.

From the above considerations it will be clear, that nothing in the experimental results goes against the proposed reaction mechanism I and II.

It has to be emphasized, that the above does not invalidate the theory of Bohmson and Robertson about the formation of ferric acid as an intermediate. If the mechanism of the reaction is supposed to be:

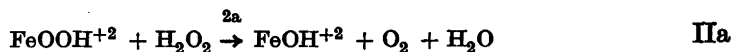
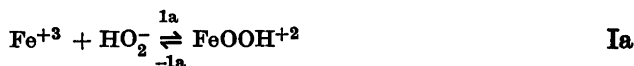


then the expression for the reciprocal velocity is:

$$\frac{1}{s} = \frac{1}{k_{1a} \cdot c_{\text{Fe}^{+3}} \cdot c_{\text{HO}_2^-}} \cdot \left(1 + \frac{k_{-1a}}{k_{1b}}\right) + \frac{1}{k_{1a} \cdot c_{\text{Fe}^{+3}} \cdot c_{\text{HO}_2^-}} \cdot \frac{k_{-1a} \cdot k_{-1b} \cdot c_{\text{FeOH}^{+2}}}{k_{1b} \cdot k_2 \cdot c_{\text{HO}_2^-}} \quad (16)$$

That is an expression analogous to (7).

But the postulate of Bohnsen and Robertson, that the ferric acid immediately will be reduced by hydrogen peroxide, does not seem to agree with the experiments. If we assume the reaction mechanism to be:



then the expression for the reciprocal velocity is:

$$\frac{1}{s} = \frac{1}{k_{1a} \cdot c_{\text{Fe}^{+3}} \cdot c_{\text{HO}_2^-}} + \frac{1}{k_{1a} \cdot c_{\text{Fe}^{+3}} \cdot c_{\text{HO}_2^-}} \cdot \frac{k_{-1a}}{k_{2a} \cdot c_{\text{H}_2\text{O}_2}} \quad (17)$$

This would imply, that  $A$  in (6) had to be independent of the ferric salt concentration, which does not agree with (3).

#### CALCULATION OF THE VELOCITY CONSTANTS

According to (14) and (15) we have:

$$B = 0.4343 \cdot 2 \cdot k_1 \cdot K_{\text{H}_2\text{O}_2} \cdot \frac{c_{\text{Ferric}}}{K_{\text{Fe}} + c_{\text{H}^+}} \quad (14)$$

and

$$A = 0.4343 \cdot \frac{k_{-1} \cdot K_{\text{Fe}}}{k_2 \cdot K_{\text{H}_2\text{O}_2}} \cdot \frac{c_{\text{H}^+}}{K_{\text{Fe}} + c_{\text{H}^+}} \cdot c_{\text{Ferric}} \quad (15)$$

or when  $K_{\text{Fe}} = 2 \cdot 10^{-3}$  and  $K_{\text{H}_2\text{O}_2} = 2.4 \cdot 10^{-12}$  at  $25^\circ \text{C}^{\text{s}}$ :

$$0.4343 \cdot k_1 = \frac{B}{2 \cdot 2.4 \cdot 10^{-12}} \cdot \frac{2 \cdot 10^{-3} + c_{H^+}}{c_{\text{Ferric}}}$$

$$0.4343 \cdot \frac{k_{-1}}{k_2} = A \cdot \frac{2.4 \cdot 10^{-12}}{2 \cdot 10^{-3}} \cdot \frac{2 \cdot 10^{-3} + c_{H^+}}{c_{H^+} \cdot c_{\text{Ferric}}}$$

In Table 6 are given the values of  $0.4343 \cdot k_1$  and  $0.4343 \cdot \frac{k_{-1}}{k_2}$  calculated on the basis of the results in Table 3.

Table 6.  $0.4343 \cdot k_1$  and  $0.4343 \cdot \frac{k_{-1}}{k_2}$  calculated on the basis of Table 3.

1	2	3	4	5	6
$c_{H^+}$	$c_{\text{Ferric}}$	A	B	$0.4343 \cdot k_1$	$0.4343 \cdot \frac{k_{-1}}{k_2}$
0.01	0.001	0.00040	0.0045	$1.13 \cdot 10^{10}$	$5.8 \cdot 10^{-10}$
0.01	0.002	0.00075	0.0089	$1.11 \cdot 10^{10}$	$5.4 \cdot 10^{-10}$
0.01	0.003	0.00108	0.0132	$1.10 \cdot 10^{10}$	$5.2 \cdot 10^{-10}$
0.01	0.004	0.00150	0.0176	$1.10 \cdot 10^{10}$	$5.4 \cdot 10^{-10}$

In table 7 are given the values of  $0.4343 \cdot k_1$  and  $0.4343 \cdot \frac{k_{-1}}{k_2}$  calculated on the basis of the results in Table 4.

Table 7.  $0.4343 \cdot k_1$  and  $0.4343 \cdot \frac{k_{-1}}{k_2}$  calculated on the basis of the results in Table 4.

$c_{H^+}$	$c_{\text{Ferric}}$	A Corr.	B Corr.	$0.4343 \cdot k_1$	$0.4343 \cdot \frac{k_{-1}}{k_2}$
0.01	0.004	$1.50 \cdot 10^{-3}$	0.0176	$1.10 \cdot 10^{10}$	$5.4 \cdot 10^{-10}$
0.02	0.004	$1.64 \cdot 10^{-3}$	0.0101	$1.14 \cdot 10^{10}$	$5.4 \cdot 10^{-10}$
0.03	0.004	$1.70 \cdot 10^{-3}$	0.0068	$1.13 \cdot 10^{10}$	$5.4 \cdot 10^{-10}$
0.04	0.004	$1.72 \cdot 10^{-3}$	0.0053	$1.16 \cdot 10^{10}$	$5.4 \cdot 10^{-10}$

### SUMMARY

The decomposition of hydrogen peroxide in acid solution in the presence of ferric nitrate is investigated at 25° C.

It is shown that:

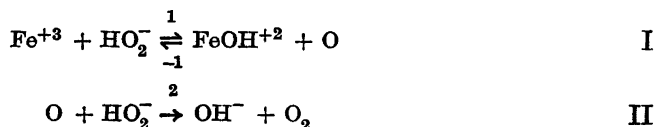
1. The process is not of the first order, but the experimental results can be calculated from the empiric expression:

$$B \cdot t + \tau = \log \frac{a}{x} + A \cdot \left( \frac{1}{x} - \frac{1}{a} \right) \quad (2)$$

in which  $a$  is the initial concentration of hydrogen peroxide, and  $x$  is the concentration after the lapse of time  $t$ .  $A$  and  $B$  are constants, which can be calculated graphically.

2. The constants  $A$  and  $B$  in (2) are proportional to the concentration of ferric nitrate.  $B$  is approximately inversely proportional to the hydrogen ion concentration, while  $A$  — within the accuracy of the method — is independent of the hydrogen ion concentration.

3. The experimental results agree with the reaction mechanism:



This investigation was undertaken at The Technical University of Denmark, Chemistry Department A.

The autor wishes to thank the head of department, Prof. J. A. Christiansen, for his interest and advice especially as to the theoretical treatment of the experimental results.

I also wish to thank Prof. Carl Faurholt, The Royal Danish School of Pharmacy for his interest in my work.

During the investigation I have received financial aid from Prof. Emil Koejoeds *Mindelegat* and *Etatsraad, cand. pharm. C. A. Olesens Studielegat*.

#### REFERENCES

1. van Bertalan, J. *Z. physik. Chem.* **95** (1920) 328.
2. van Bohson, L., and Robertson, A. C. *J. Am. Chem. Soc.* **45** (1923) 2493.
3. Simon, A., Haufe, W., Reetz, Th., and Preissler, R. *Z. anorg. u. allgem. Chem.* **230** (1936) 129.
4. Haber, F., and Weiss, J. *Proc. Roy. Soc. London A* **147** (1934) 332.
5. Bodenstein, M. *Z. physik. Chem.* **85** (1913) 329.
6. Christiansen, J. A. *Handbuch der Katalyse* (1941) 261.
7. Lamb, A. B., and Jacques, A. *J. Am. Chem. Soc.* **60** (1938) 1215.
8. Joyner, R. A. *Z. anorg. Chem.* **77** (1912) 103.

Received November 29, 1947.