On Hydrogen Peroxide Decomposition

The Influence of Small Amounts of Cupric Salt on the Ferric Salt Catalysis

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It has for a long time been a well-known fact that cupric ions, although they themselves have only a slight influence on the decomposition of hydrogen peroxide under acid conditions, are able to accelerate this process considerably when a ferric salt is used as a catalyst.

Already in 1923 Bohnson and Robertson [1] have tried to account for this problem. They made a series of kinetic experiments on the decomposition of hydrogen peroxide in acid solution in the presence of varying quantities of cupric and ferric salts; but as they did not succeed in calculating velocity constants for the individual experiments, the conclusions they were able to draw on the basis of their experimental results could only be of a semi-quantitative nature. They suggest the following mechanism for the reaction:

Hydrogen peroxide oxidizes the ferric ion into an unstable intermediate, FeO_3, which is able to interact with more hydrogen peroxide evolving oxygen; but this intermediate should also be able together with cupric ions to form another unstable intermediate, CuO_2, which will interact more rapidly with hydrogen peroxide to form oxygen.

The present work is an attempt at a somewhat more thorough elucidation of the problem, or in other words, an attempt at drawing up a more complete scheme for the reaction.

EXPERIMENTAL TECHNIQUE AND REAGENTS

A number of velocity experiments have been made at 25° C. Nitric acid was in all cases added to the reaction mixture to produce a concentration of 0.01 Mol/l, while varying quantities of cupric and ferric nitrate were added. The experimental technique was the same as the one employed for the author's work on the ferric salt catalysis [2] and the reagents used were of the same purity. It should further be mentioned that the progress of all reactions have been followed until a degree of decomposition of about 95 %.

MATHEMATICAL TREATMENT OF THE EXPERIMENTS AND SURVEY OF EXPERIMENTAL RESULTS

The author found that a mathematical treatment of the velocity experiments could neither be based on the expressions for monomolecular nor for bimolecular reactions, but that a similar rate expression to the one used for the reaction catalysed by ferric salt could be applied, viz.:

$$t = \frac{1}{B} \log \frac{a}{x} + \frac{A}{B} \left(\frac{1}{x} - \frac{1}{a} \right) \qquad (1)$$

where a is the initial concentration of hydrogen peroxide, and x the concentration at the time t; A and B are constants which can be calculated graphically, confer page 4 of the paper quoted [2].

Table 1 gives the results from one of the experiments. A comparison between the observed t-values in column 1 and the values of column 8 which

Table 1. Experiment 106. Decomposition of hydrogen peroxide at 25° C in solution which is 0.003 Molar as to ferric nitrate, 0.00005 Molar as to cupric nitrate and 0.01 Molar as to nitric acid. The experiment has been calculated according to equation (1). The constants A and B have been calculated graphically. $A = 3.30 \cdot 10^{-3}$, $B = 2.84 \cdot 10^{-2}$. The t-values stated in column 8 have been calculated on the basis of equation 1 and the constants A and B. .

1	2	3	4	5	6	7	8
t min. obs.	x	$\log \dfrac{a}{x}$	$\dfrac{1}{x}$	$\dfrac{1}{x} - \dfrac{1}{a}$	$A\left(\dfrac{1}{x} - \dfrac{1}{a}\right)$	(3)+(6)	t min. calc.
0.00	0.06388	—	15.65	—	—	—	0.00
2.10	0.05636	0.0544	17.53	1.88	0.0062	0.0606	2.13
5.00	0.04800	0.1242	20.83	5.18	0.0171	0.1413	4.98
10.00	0.03643	0.2439	27.47	11.82	0.0391	0.2831	9.97
15.00	0.02776	0.3618	35.97	20.32	0.0671	0.4289	15.10
20.00	0.02164	0.4701	46.30	30.65	0.1012	0.5713	20.12
25.00	0.01713	0.5716	58.48	42.83	0.1414	0.7130	25.11
30.00	0.01365	0.6703	72.99	57.34	0.1892	0.8595	30.26
35.00	0.01118	0.7570	89.29	73.64	0.2430	1.0000	35.21
43.00	0.008384	0.8820	119.33	103.68	0.3421	1.2241	43.10
50.00	0.006694	0.9797	149.48	133.83	0.4417	1.4214	50.05
60.00	0.005066	1.1008	197.24	181.59	0.5993	1.7001	59.86
71.00	0.003951	1.2087	253.16	237.51	0.8313	1.9925	70.16
80.00	0.003263	1.2918	306.75	291.16	0.9606	2.2524	79.31
90.00	0.002683	1.3768	373.13	357.48	1.1796	2.5564	90.01
100.00	0.002298	1.4440	434.78	419.13	1.3831	2.8271	99.55
105.00	0.002122	1.4786	471.70	456.05	1.5050	2.9836	105.06

are calculated on the basis of the figures found for A and B and equation (1) shows close agreement even when the reaction has proceeded to a great extent.

Values for A and B have been calculated from each experiment. With a view to the subsequent discussion values have been calculated for the two coefficients A_1 and A_2 of the differentiated velocity expression:

$$-\frac{dt}{dx} = A_1 \frac{1}{x} + A_2 \frac{1}{x^2} \tag{2}$$

where $A_1 = 0.4343/B$ and $A_2 = A/B$; the values found for A_1 and A_2 are listed in Table 2.

Figs. 1 and 2 show how A_1 and A_2 vary with the concentrations of cupric salt and ferric salt. It appears from the figures that A_1 and A_2 are both func-

Table 2. Survey of the values found for A_1 and A_2.

| $c_{Fe} \cdot 10^3$ \ $c_{Cu} \cdot 10^5$		0.00	1.00	2.00	5.00	10.00	20.00	40.00	100.00
1.00	A_1	96.50	55.68	43.43	34.47	24.68	21.50	19.13	—
	A_2	0.089	0.141	0.180	0.238	0.244	0.248	0.264	—
2.00	A_1	48.25	32.41	26.64	20.11	17.10	14.38	13.44	—
	A_2	0.084	0.112	0.123	0.144	0.157	0.166	0.176	—
3.00	A_1	32.18	23.48	19.48	15.29	13.26	11.73	10.24	9.87
	A_2	0.082	0.097	0.112	0.116	0.123	0.135	0.142	0.152
4.00	A_1	24.15	18.56	15.11	13.22	11.31	10.75	8.81	9.40
	A_2	0.085	0.094	0.087	0.106	0.113	0.114	0.117	0.119
5.00	A_1	19.56	15.42	13.90	10.81	—	—	—	8.40
	A_2	0.086	0.085	0.091	0.100	—	—	—	0.106
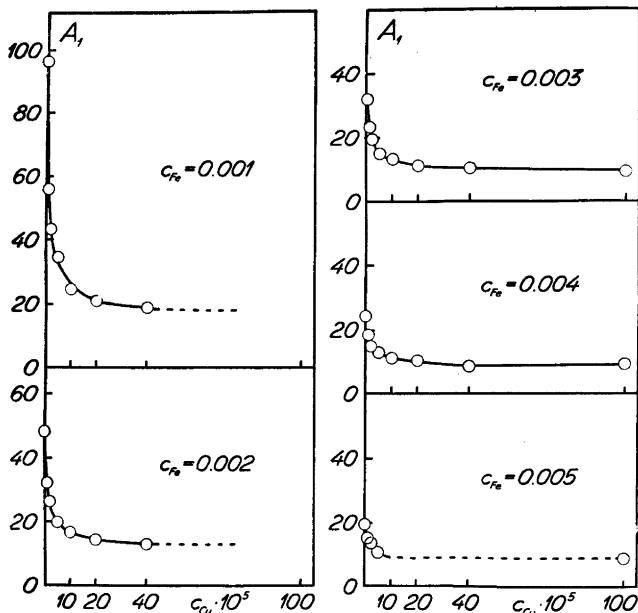
Fig. 1. Relation between A_1 and the cupric salt concentration at various ferric salt concentrations.
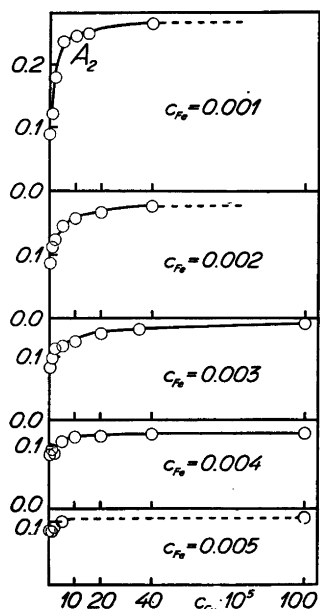
Fig. 2. Relation between A_2 and the cupric salt concentration at various ferric salt concentrations.

tions of the ferric salt and cupric salt concentrations; qualitatively they may be described as follows:

$$A_1 = A_1 \ (c_{Fe}, c_{Cu}):$$ Decreases towards a limiting value with increasing cupric salt concentration. (3)

Decreases with increasing ferric salt concentration.

$$A_2 = A_2 \ (c_{Fe}, c_{Cu}):$$ Increases towards a limiting value with increasing cupric salt concentration.

Decreases with increasing ferric salt concentration. (4)

When the cupric salt concentration is zero, A_2 is independent of the ferric salt concentration.

When the values for A_1 and A_2 for the cupric salt concentration zero are denoted by $A_{1(0)}$ and $A_{2(0)}$ (3) and (4) can be written:

$$A_1 = A_1 \ (c_{Fe}, c_{Cu}) = A_{1(0)} \ (1 - \varDelta_1) \tag{3a}$$

$$A_2 = A_2 \ (c_{Fe}, c_{Cu}) = A_{2(0)} \ (1 + \varDelta_2) \tag{4a}$$
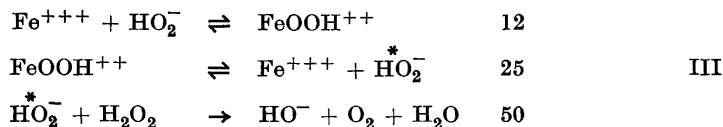
DERIVATION OF THE MECHANISM OF THE REACTION

In the following it has been endeavoured to arrive at a mechanism with a velocity expression which agrees with the experimental results, which means that it must be of the following type

$$-\frac{dt}{dx} = A_1 \frac{1}{x} + A_2 \frac{1}{x^2} \tag{2}$$

where the coefficients A_1 and A_2, as stated in the preceding section, equations (3) and (4), must be functions of both the ferric salt and the cupric salt concentrations.

As the velocity expression which applies to the hydrogen peroxide decomposition catalysed by ferric salt also applies to this reaction, there can be no reasonable doubt that the mathematical treatment of the scheme which it is our aim to find should be based upon the scheme for the former reaction.

The ferric salt catalysis has been dealt with in previous investigations [2],[3] and [4]. These investigations resulted in the suggestion of the following scheme for the reaction: *

$$
\begin{array}{lll}
Fe^{+++} + HO_2^- & \rightleftharpoons & FeOOH^{++} \qquad\qquad 12 \\
FeOOH^{++} & \rightleftharpoons & Fe^{+++} + \overset{*}{H}O_2^- \qquad 25 \qquad\qquad III \\
\overset{*}{H}O_2^- + H_2O_2 & \rightarrow & HO^- + O_2 + H_2O \quad 50
\end{array}
$$

($\overset{*}{H}O_2^-$ being the symbol of an activated HO_2^- ion.)

Three possible ways in which the cupric ions can interfere in the ferric salt catalysis are illustrated in Fig. 3: the cupric ions may catalyse either reaction 12, reaction 25, or reaction 50.

On the assumption that a steady state is obtained immediately after the start of the reaction a velocity expression has been calculated for each of the mechanisms suggested; the calculations, which were carried out according to the lines suggested by Christiansen [6], showed that the second way is the only possible one, while the first and the third must be discarded; that is, the cupric
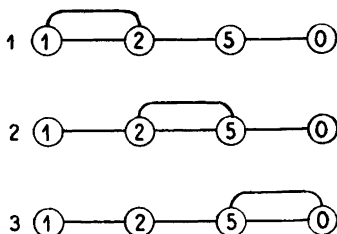

Fig. 3. Diagrammatic representation of three possible ways in which the cupric ions can interfere in the ferric salt catalysis.

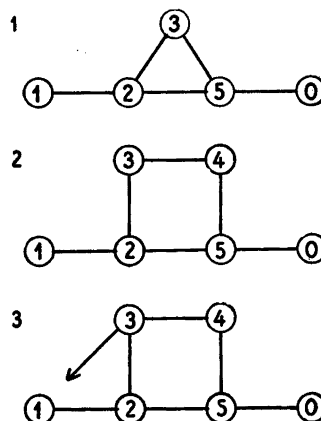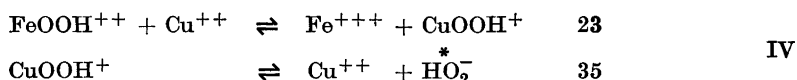* Abel [4] has criticized my investigations; I intend to deal with his theory later on.

Fig. 4. Diagrammatic representation of the reaction schemes no. IV, V and VI.

ions must catalyse reaction 25 of scheme III; but the question is now how this catalysis is brought about.

It is an obvious assumption that the cupric ions will react with the $FeOOH^{++}$-ions to form a new intermediary product, perhaps $CuOOH^{+}$-ions, which must be considered to be able to decompose more rapidly than the $FeOOH^{++}$-ions.

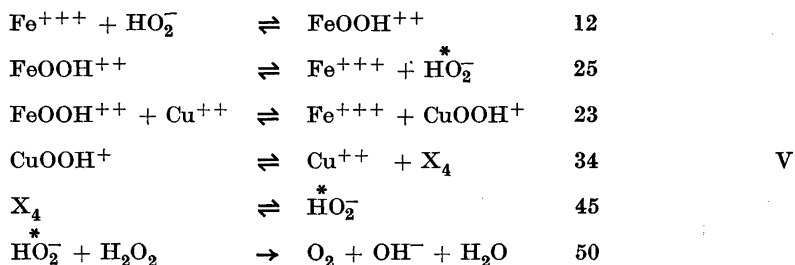The mechanism will then be as III, supplemented with the two reactions:

$$FeOOH^{++} + Cu^{++} \rightleftharpoons Fe^{+++} + CuOOH^{+} \qquad 23$$

$$CuOOH^{+} \qquad \rightleftharpoons Cu^{++} + \overset{*}{H}O_2^- \qquad 35$$

IV

The corresponding diagrammatic representation of the reaction is given in Fig. 4,1.

A calculation yielded a velocity expression which was in conformity with (2), but not with (3) and (4).
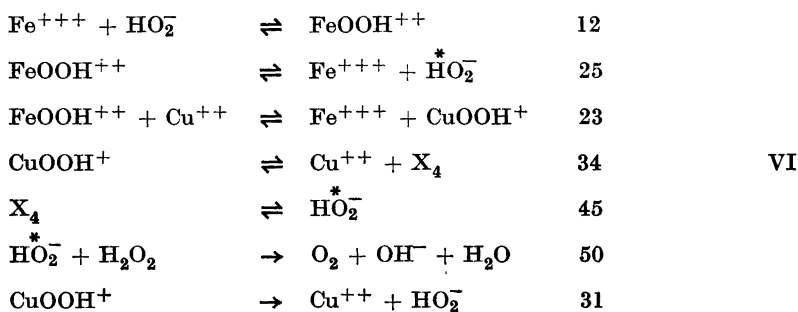
There is, however, another possibility, namely the one illustrated in Fig. 4,2 in which the reaction from 3 to 5 has been divided up into two steps 34 and 45. The reaction scheme will then be as follows — the new intermediate being denoted by X_4:

$$Fe^{+++} + HO_2^- \qquad \rightleftharpoons FeOOH^{++} \qquad 12$$

$$FeOOH^{++} \qquad \rightleftharpoons Fe^{+++} + \overset{*}{H}O_2^- \qquad 25$$

$$FeOOH^{++} + Cu^{++} \rightleftharpoons Fe^{+++} + CuOOH^{+} \qquad 23$$

$$CuOOH^{+} \qquad \rightleftharpoons Cu^{++} + X_4 \qquad 34$$

$$X_4 \qquad \rightleftharpoons \overset{*}{H}O_2^- \qquad 45$$

$$\overset{*}{H}O_2^- + H_2O_2 \qquad \rightarrow O_2 + OH^- + H_2O \qquad 50$$

V

Unfortunately the velocity expression which could be calculated on the basis of this mechanism proved not to be quite up to the expectations. It fulfils the conditions of (2) and (3), but not the conditions stated in (4) as A_2 will not be a function of the ferric salt or cupric salt concentration, but merely a constant identical with the one found for the pure ferric catalyses.

This deviation need not result in an absolute rejection of the mechanism proposed — perhaps it merely discloses a flaw in the mechanism; upon further consideration it will be seen that it seems to be possible to suggest a mechanism giving a velocity expression which better than the one calculated from V has the required properties, by adding another reaction to V. This reaction is given below and denoted by 31.

The final reaction scheme will then be as follows:

$$
\begin{array}{llll}
Fe^{+++} + HO_2^- & \rightleftharpoons & FeOOH^{++} & 12 \\
FeOOH^{++} & \rightleftharpoons & Fe^{+++} + \overset{*}{H}O_2^- & 25 \\
FeOOH^{++} + Cu^{++} & \rightleftharpoons & Fe^{+++} + CuOOH^+ & 23 \\
CuOOH^+ & \rightleftharpoons & Cu^{++} + X_4 & 34 \qquad \text{VI} \\
X_4 & \rightleftharpoons & \overset{*}{H}O_2^- & 45 \\
\overset{*}{H}O_2^- + H_2O_2 & \rightarrow & O_2 + OH^- + H_2O & 50 \\
CuOOH^+ & \rightarrow & Cu^{++} + HO_2^- & 31
\end{array}
$$

besides which we have the equilibria:

$$
\begin{array}{lll}
H_2O_2 & \rightleftharpoons & H^+ + HO_2^- \\
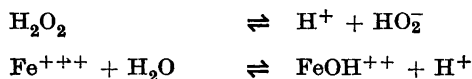Fe^{+++} + H_2O & \rightleftharpoons & FeOH^{++} + H^+
\end{array}
$$

Fig. 4,3 illustrates the diagrammatic representation of the mechanism.

CALCULATION OF THE VELOCITY EXPRESSION FOR THE REACTION SCHEME NO. VI

In the following the calculation of the velocity expression for reaction scheme No.VI will be accounted for in detail.

The following symbols have been used in the calculations:

$$x_1 = c_{Fe^{+++}}, \quad x_2 = c_{FeOOH^{++}}, \quad x_3 = c_{CuOOH^+}, \quad x_4 = c_{X_4} \text{ and } x_5 = c_{\overset{*}{H}O_2^-}.$$

The velocity of reaction is denoted by s; s without a subscript denotes the over-all velocity, $s = dO_2/dt$, while s with a subscript denotes the resulting velocity of one of the partial reactions, e.g. the resulting velocity of reaction 25 is denoted by s_{25}. The reaction probability is denoted by w,

which thus in the case of a reaction of the 1. order merely represents a velocity constant, and in the case of a reaction of the 2.order represents a velocity constant multiplied by a concentration; *e.g.* it may be mentioned that w_{34} = k_{34}, and $w_{23} = k_{23} \cdot c_{Cu^{++}}$.

With this use of symbols we have *e.g.* $x_2 w_{23}$ = the velocity of the reaction from 2 to 3 and $s_{23} = x_2 w_{23} - x_3 w_{32}$ = the resulting velocity of reaction 23.

The calculations have been carried through according to the lines suggested by Christiansen [6] and on the following assumptions:

1) Reaction 12 is an equilibrium. This assumption appears extremely reasonable, if only because the reaction is one in which a complex is formed. The equilibrium has, as already mentioned in a previous paper, been investigated by Evans and coworkers [7], who have determined its equilibrium constant. This assumption leads to the equation:

$$x_1 w_{12} = x_2 w_{21} \tag{5}$$

2) The concentrations of the unstable intermediates $CuOOH^+$, X_4 and HO_2^- are stationary practically from the start of the reaction, *i.e.* the conditions of the stationary state are fulfilled as regards these intermediates. This assumption leads directly (see Fig. 4, 3) to the following system of equations:

$$s = s_{50} = s_{25} + s_{45} = s_{25} + s_{34} = s_{25} + s_{23} - s_{31}$$

or, expressed in greater detail:

$$s = x_2(w_{23} + w_{25}) - x_3(w_{32} + w_{31}) - x_5 w_{52} \tag{6}$$
$$s = x_2 w_{25} + x_3 w_{34} - x_4 w_{43} - x_5 w_{52} \tag{7}$$
$$s = x_2 w_{25} + x_4 w_{45} - x_5(w_{52} + w_{54}) \tag{8}$$
$$s = x_5 w_{50} \tag{9}$$

Dividing equations (6), (7), (8) and (9) by s, we find:

$$1 = \frac{x_2}{s}(w_{23} + w_{25}) - \frac{x_3}{s}(w_{32} + w_{31}) - \frac{x_5}{s}w_{52}$$

$$1 = \frac{x_2}{s}w_{25} + \frac{x_3}{s}w_{34} - \frac{x_4}{s}w_{43} - \frac{x_5}{s}w_{52}$$

$$1 = \frac{x_2}{s}w_{25} + \frac{x_4}{s}w_{45} - \frac{x_5}{s}(w_{52} + w_{54})$$

$$1 = \frac{x_5}{s}w_{50}$$

From these equations it is possible to calculate x_2/s; the two determinants required for the calculation are in the following denoted D_0 and Dx_2:

$$D_0 = \begin{vmatrix} w_{25} + w_{23} & -(w_{32} + w_{31}) & 0 & -w_{52} \\ w_{25} & w_{34} & -w_{43} & -w_{52} \\ w_{25} & 0 & w_{45} & -(w_{52} + w_{54}) \\ 0 & 0 & 0 & w_{50} \end{vmatrix}$$

$$= w_{50}w_{25}(w_{34}w_{45} + w_{32}w_{45} + w_{31}w_{45} + w_{32}w_{43} + w_{31}w_{43} + w_{23}w_{34}w_{45}/w_{25}); \quad (10)$$

$$Dx_2 = \begin{vmatrix} 1 & -(w_{32} + w_{31}) & 0 & -w_{52} \\ 1 & w_{34} & -w_{43} & -w_{52} \\ 1 & 0 & w_{45} & -(w_{52} + w_{54}) \\ 1 & 0 & 0 & w_{50} \end{vmatrix}$$

$$= w_{50}(w_{34}w_{45} + w_{32}w_{45} + w_{31}w_{45} + w_{32}w_{43} + w_{31}w_{43}) + w_{52}(w_{32}w_{43} +$$
$$w_{31}w_{43} + w_{32}w_{45} + w_{31}w_{45} + w_{34}w_{45} + w_{54}w_{43}w_{32}/w_{52} + w_{54}w_{43}w_{31}/w_{52}) \quad (11)$$

Hence we have

$$x_2/s = D_{x_2}/D_0$$

or, when applying equation (5)

$$1/s = w_{21}D_{x_2}/x_1 w_{12}D_0; \quad (12)$$

If we apply the principle of microscopical reversibility (proposed for the first time by Wegscheider (1902) and later on treated by others *c. f.* Christiansen in the paper already quoted) on the cyclic reaction 23452 — see the diagrammatic representation of the reaction in Fig. 4,3 — we have

$$w_{54}w_{43}w_{32}/w_{52} = w_{23}w_{34}w_{45}/w_{25} \quad (13)$$

Substituting this expression in (11) we find that (12) can be written:

$$\frac{1}{s} = \frac{w_{21}}{x_1 w_{12}w_{25}} \left(1 - \frac{w_{23}w_{34}w_{45}/w_{25}}{w_{34}w_{45} + w_{32}w_{45} + w_{32}w_{43} + w_{23}w_{34}w_{45}/w_{25} + w_{31}(w_{43} + w_{45})}\right)$$
$$+ \frac{w_{21}w_{52}}{x_1 w_{12}w_{25}w_{50}}\left(1 + \frac{w_{31}w_{54}w_{43}/w_{52}}{w_{34}w_{45} + w_{32}w_{45} + w_{32}w_{43} + w_{23}w_{34}w_{45}/w_{25} + w_{31}(w_{43} + w_{45})}\right); \quad (14)$$

reducing the two fractions in the brackets by $w_{23}w_{34}w_{45}/w_{25}$ and again using (13) we have:

$$\frac{1}{s} = \frac{w_{21}}{x_1 w_{12}w_{25}}\left(1 - \frac{1}{N}\right) + \frac{w_{21}w_{52}}{w_{12}w_{25}w_{50}}\left(1 + \frac{w_{31}}{w_{32}N}\right) \quad (15)$$

where: $N = \dfrac{w_{32}w_{25}}{w_{34}w_{23}} + \dfrac{w_{25}}{w_{23}} + \dfrac{w_{52}}{w_{54}} + 1 + \dfrac{w_{31}w_{52}}{w_{32}w_{54}}\left(1 + \dfrac{w_{45}}{w_{43}}\right); \quad (16)$

substituting the values of the w-symbols and setting:

$$s = dO_2/dt = -dH_2O_2/2dt; \quad c'_{HO_2^-} = K_{H_2O_2} \cdot c_{H_2O_2}/c_{H^+} \text{ and } k_{12}/k_{21} = K_{12}$$

in the expression thus obtained we have:

$$-\frac{dt}{dH_2O_2} = \frac{c_{H^+}}{2k_{25}K_{12}K_{H_2O_2}c_{Fe^{+++}}} \left(1 - \frac{1}{N}\right) \frac{1}{c_{H_2O_2}}$$

$$+ \frac{k_{52}c_{H^+}}{2k_{25}k_{50}K_{12}K_{H_2O_2}} \left(1 + \frac{k_{31}}{k_{32}c_{Fe^{+++}}} \frac{1}{N}\right) \frac{1}{c_{H_2O_2}^2}; \tag{17}$$

where $N = \dfrac{k_{32}k_{25}}{k_{34}k_{23}} \cdot \dfrac{c_{Fe^{+++}}}{c_{Cu^{++}}} + \dfrac{k_{25}}{k_{23}} \cdot \dfrac{1}{c_{Cu^{++}}} + \dfrac{k_{52}c_{Fe^{+++}}}{k_{54}} + 1 +$

$$\frac{k_{31}k_{52}}{k_{32}k_{54}} \left(1 + \frac{k_{45}}{k_{43}c_{Cu^{++}}}\right) \tag{18}$$

For a constant hydrogen ion concentration N may be written:

$$N = N_0 = \frac{k'_{32}k_{25}}{k_{34}k_{23}} \frac{c_{Fe}}{c_{Cu}} + \frac{k_{25}}{k_{23}c_{Cu}} + \frac{k'_{52}c_{Fe}}{k_{54}} + 1 + \frac{k_{31}k'_{52}}{k'_{32}k_{54}} \left(1 + \frac{k_{45}}{k_{43}c_{Cu}}\right) \tag{18a}$$

where c_{Fe} and c_{Cu} denotes the total ferric salt and cupric salt concentration.

THE VELOCITY EXPRESSION (17) IN COMPARISON WITH THE EXPERIMENTAL RESULTS

In a previous section (p. 1091) it has been shown that the cupric-ferric salt catalysed hydrogen peroxide decomposition proceeds according to the following velocity expression:

$$- dt/dH_2O_2 = A_1/c_{H_2O_2} + A_2/c_{H_2O_2}^2 \tag{2}$$

in which A_1 and A_2 can be written:

$$A_1 = A_1(c_{Fe}, c_{Cu}) = A_{1(0)}(1 - \Delta_1) \text{ and } A_2 = A_2(c_{Fe}, c_{Cu}) = A_{2(0)}(1 + \Delta_2); \quad \text{(3a) and (4a)}$$

The two functions are qualitatively described on p. 1093 (3) and (4).

The velocity expression (17) for the reaction scheme VI has been calculated in the preceding section.

(17) can be written:

$$- dt/dH_2O_2 = A'_1/c_{H_2O_2} + A'_2/c_{H_2O_2}^2 \tag{19}$$

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Table 3. Survey of the values found for Δ_1, Δ_2 and Δ_2/Δ_1.

$c_{Cu} \cdot 10^5$		1.00	2.00	5.00	10.00	20.00	40.00	100.00
$c_{Fe} = 0.001$	Δ_1	0.423	0.550	(.642	0.744	0.777	0.802	—
	Δ_2	0.585	1.022	1.674	1.742	1.787	1.966	—
	Δ_2/Δ_1	1.38	1.86	2.61	2.34	2.30	2.45	—
$c_{Fe} = 0.002$	Δ_1	0.329	0.448	0.583	0.646	0.702	0.721	—
	Δ_2	0.333	0.464	0.714	0.869	0.976	1.095	—
	Δ_2/Δ_1	1.10	1.06	1.22	1.35	1.39	1.52	—
$c_{Fe} = 0.003$	Δ_1	0.270	0.395	0.525	0.588	0.635	0.682	0.693
	Δ_2	0.182	0.366	0.414	0.500	0.646	0.732	0.854
	Δ_2/Δ_1	0.674	0.927	0.789	0.850	1.017	1.073	1.232
$c_{Fe} = 0.004$	Δ_1	0.231	0.374	0.454	0.531	0.555	0.635	0.611
	Δ_2	0.119	(0.024)	0.247	0.329	0.341	0.376	0.400
	Δ_2/Δ_1	0.515	(0.064)	0.544	0.620	0.614	0.592	0.655
$c_{Fe} = 0.005$	Δ_1	0.212	0.290	0.448	—	—	—	0.571
	Δ_2	(0.00)	0.058	0.163	—	—	—	0.233
	Δ_2/Δ_1	(0.00)	0.500	0.364	—	—	—	0.245

When the cupric salt concentration is zero $1/N_0$ (18a) is equal to zero; therefore, for a constant hydrogen ion concentration the coefficients A_1' and A_2' can be written:

$$A_1' = A_{1(0)} \, (1 + 1/N_0) \quad \text{and} \quad A_2' = A_{2(0)} \, (1 + k_{31}/k_{32}' c_{Fe} N_0) \qquad (20) \text{ and } (21)$$

in which $A_{1(0)}$ and $A_{2(0)}$ mean the A_1 and A_2 when the cupric salt concentration is zero.
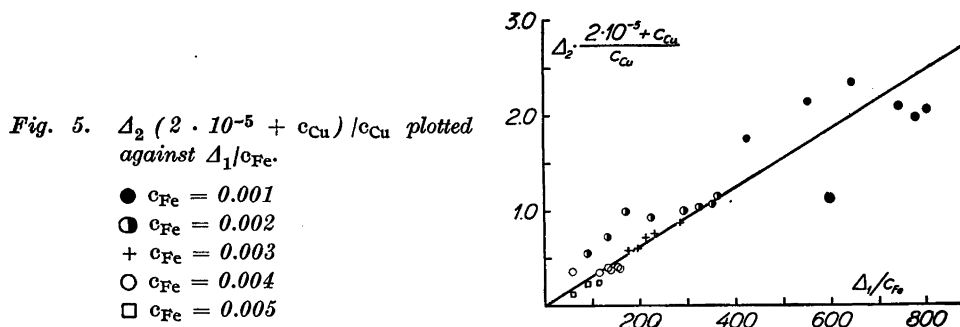
Now it is possible to test whether the proposed reaction mechanism VI is in agreement with the experiments. If so (19) must be in agreement with (2), which is the case in so far as the two expressions for $-dt/dH_2O_2$ are dependent in the same way on the hydrogen peroxide concentration.

Furthermore, the dependence of (20) and (21) on the cupric- and ferric salt concentrations must agree with the experimental results; this is the case when the values found for Δ_1 and Δ_2 in (3a) and (4a) fit into the functions:

$$\Delta_1^{-1} = N_0 \qquad (22)$$
$$\Delta_2 = k_{31}/k_{32}' c_{Fe} N_0 \qquad (23)$$
$$\Delta_2/\Delta_1 = k_{31}/k_{32}' c_{Fe} \qquad (24)$$

Fig. 5. Δ_2 *(2 · 10⁻⁵ + c_{Cu}) /c_{Fe} plotted against Δ_1/c_{Fe}.*

● $c_{Fe} = 0.001$

◐ $c_{Fe} = 0.002$

+ $c_{Fe} = 0.003$

○ $c_{Fe} = 0.004$

□ $c_{Fe} = 0.005$

The values for Δ_1 and Δ_2 which has been calculated from the observed values according to (3a) and (4a) are given in Table 3 together with the values for Δ_2/Δ_1. From the table appears that Δ_2/Δ_1 with a reasonable amount of accuracy may be considered to be inversely proportional to the ferric salt concentration, which is in agreement with (24); but it also appears that Δ_2/Δ_1 depends on the cupric salt concentration, which conflicts with (24). However, the discrepancy may be eliminated by substituting the reaction 31 in VI by the following sequence:

$$CuOOH^+ \rightleftharpoons X_{3''} \qquad\qquad 33'$$
$$Cu^{++} + X_{3'} \rightarrow 2Cu^{++} + HO_2^- \quad 3'1$$
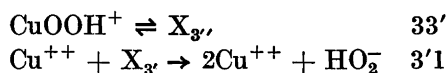
Reaction 33' is assumed to proceed spontaneously whereas 3'1 has to be catalysed by cupric ions.

This assumption necessitates some change in the calculated velocity expression (17). In the calculation of this s_{31} is supposed to be equal to x_3w_{31}

or
$$x_3/s_{31} = 1/w_{31} = 1/k_{31}$$

whereas the sequence by application of the usual calculation method gives:

$$x_3/s_{31} = 1/w_{33'} + w_{3'3}/w_{33'}w_{3'1} = 1/k_{33'} + k_{3'3}/k_{33'}k_{3'1}c_{Cu^{++}}.$$

If, in the original velocity expression (17) $1/k_{31}$ is substituted by $1/k_{33'} + k_{3'3}/k_{33'}k_{3'1}c_{Cu}$, (24) will be as follows:

$$\frac{\Delta_2}{\Delta_1} = \frac{k_{33'}}{k'_{32}c_{Fe}} \cdot \frac{c_{Cu}}{c_{Cu} + k_{3'3}/k_{3'1}} \qquad (24a)$$

or

$$\frac{c_{Cu} + k_{3'3}/k_{3'1}}{c_{Cu}} \Delta_2 = \frac{k_{33'}}{k'_{32}c_{Fe}} \Delta_1 \qquad (24b)$$

The validity of (24b) is thus a necessary condition for the correctness of the modified reaction scheme. This condition seems to be fulfilled as the left side of (24b), using $k_{3'3}/k_{3'1} = 2 \cdot 10^{-5}$, with a reasonable amount of accuracy is proportional to Δ_1/c_{Fe}. This is shown in Fig. 5. The slope of the straight line in the figure gives

$$k_{33'}/k'_{32} = 3.1 \cdot 10^{-3}.$$

If $1/k_{31}$ is substituted by $1/k_{33'} + k_{3'3}/k_{33'}k_{3'1}c_{Cu}$ in (18a), (22) will be as follows:

$$\Delta_1^{-1} = \frac{k'_{32}k_{25}}{k_{34}k_{23}} \cdot \frac{c_{Fe}}{c_{Cu}} + \frac{k_{25}}{k_{23}} \cdot \frac{1}{c_{Cu}} + \frac{k'_{52}}{k_{54}}c_{Fe} + 1 + \frac{k_{33'}}{k'_{32}} \cdot \frac{k'_{52}}{k_{54}} \cdot \frac{c_{Cu}+k_{45}/k_{43}}{c_{Cu}+k_{3'3}/k_{3'1}} \quad (22a)$$

By introducing γ, δ and ξ for the ratios k'_{52}/k_{54}, $k'_{32}k_{25}/k_{34}k_{23}$ and k_{25}/k_{23}, respectively, and using the values found above for $k_{3'3}/k_{3'1}$ and $k_{33'}/k'_{32}$, (22a) can be written:

$$\Delta_1^{-1} - 3.1 \cdot 10^{-3} \cdot \gamma \cdot \frac{c_{Cu} + \delta/\gamma}{c_{Cu} + 2 \cdot 10^{-5}} = (\delta c_{Fe} + \xi) \frac{1}{c_{Cu}} + \gamma c_{Fe} + \varepsilon; \quad (22b)$$

or

$$\Delta_1^{-1} - P = \alpha/c_{Cu} + \beta. \quad (22c)$$

The ratio k_{45}/k_{43} has been written as δ/γ as it is equal to $k'_{32}k_{25}k_{54}/k'_{52}k_{34}k_{23}$ according to the principle of microscopical reversibility (13), and ε has been written instead of one.

We now see that a second necessary condition for the correctness of the modified reaction scheme is, that we are able to calculate such values for δ and γ so that for a constant ferric salt concentration the left side of (22b) can be depicted as a linear function of $1/c_{Cu}$, one for each ferric salt concentration. Furthermore the straight lines representing these functions must have a common point of intersection, because their slopes $\alpha = \delta c_{Fe} + \xi$ and their intersepts $\beta = \gamma c_{Fe} + \varepsilon$ are linear functions of the same variable.

By iteration γ and δ can be calculated to:

$$\gamma = 120, \qquad \delta = 5.2 \cdot 10^{-3}, \qquad \delta/\gamma = 4.6 \cdot 10^{-5}.$$

As a proof of the correctness of this statement the values of $\Delta_1^{-1} - P$ are plotted against $1/c_{Cu}$ in Fig. 6.

From the slope of the straight lines and the co-ordinates for their intersection can be calculated:

$$\gamma = 120, \quad \delta = 5.2 \cdot 10^{-3}, \quad \xi = 0.36 \cdot 10^{-5} \text{ and } \varepsilon = 0.73.$$
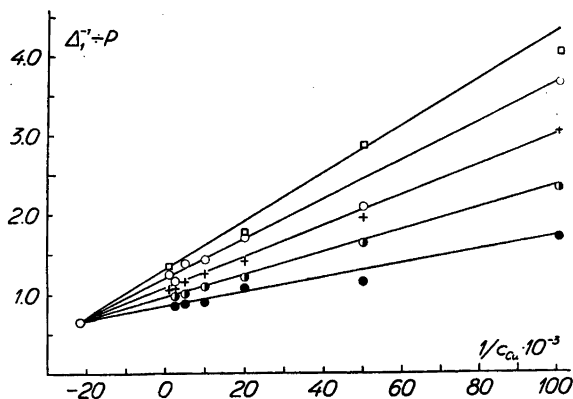
Fig. 6. $\varDelta_1^{-1} - P$ *in equation (22c) plotted against* $1/c_{Cu}$.

●	$c_{Fe} = 0.001$	○	$c_{Fe} = 0.004$
◐	$c_{Fe} = 0.002$	□	$c_{Fe} = 0.005$
+	$c_{Fe} = 0.003$		

It appears that these values for γ and δ are identical with the values used above. ε has been calculated to 0.73; as it in (22b) has been written instead of one, the calculations of course ought to have given this value. It has been impossible to find any explanation for this discrepancy, but it is not improbable that it is due to errors in the experimental results, for even small errors in the values for A_1 and A_2 or $A_{1(0)}$ and $A_{2(0)}$ may cause rather considerable errors in the calculations.

The calculations have given values for the following ratios between velocity constants:

$$k_{3'3}/k_{3'1} = 2 \cdot 10^{-5}; \quad k_{33'}/k'_{32} = 3.1 \cdot 10^{-3}; \quad k'_{52}/k_{54} = \gamma = 120$$

$$k_{25}/k_{23} = \xi = 0.36 \cdot 10^{-5}; \quad k_{45}/k_{43} = \delta/\gamma = 4.3 \cdot 10^{-5}; \quad k'_{32}/k_{34} = \delta/\xi = 1.44 \cdot 10^3$$

DISCUSSION

As will appear from the preceding section, it has been possible to show that scheme VI when reaction 31 is regarded as two consecutive reactions 33' and 3'1 corresponds to a velocity expression which in the whole is satisfied by the experimental results. In the following this result will be discussed.

When considering the scheme suggested for the reaction, the question arises whether this scheme is the only applicable one, *i.e.* the scheme which is best satisfied by the experimental results. To this question the reply may be given

that several other schemes have been carefully considered, but they have all had to be discarded because of conspicuous discrepancies between the corresponding velocity expressions and the experimental results. It is of course a fact that the value of the suggested scheme is entirely dependent on the correctness of the expression for the velocity of the overall reaction (1) used for the mathematical treatment of the kinetic experiments, but there can hardly be any doubt that this expression is correct, as it reproduces the experimental values so closely, even when the reaction has run nearly to completion.

As it will have appeared from the above, reaction 3'1

$$X_3 + Cu^{++} \rightarrow 2\,Cu^{++} + HO_2^- \qquad\qquad 3'1$$
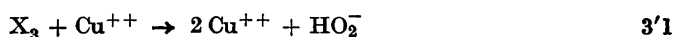
has been treated as an irreversible reaction. It should be emphasized that this is necessary in order to make the calculated velocity expression agree with the experimental results. However, it involves the following difficulty: The reactions 12, 23, 33' and 3'1 together constitute a cyclic reaction sequence proceding in the direction 1233', but this apparently conflicts with the principle of the microscopical reversibility according to which the stationary condition of such a cyclic reaction is characterized by the over all velocity being zero. It has proved difficult to find an explanation of this discrepancy; it may perhaps be explained by assuming the cupric ions to occur in two different forms, perhaps two forms of different spins.

SUMMARY

It has been shown that

1. the hydrogen peroxide decomposition catalysed by cupric and ferric salt complies with the same velocity expression as the one calculated for the decomposition (equation (2)) catalysed by ferric salt,

2. the constants A_1 and A_2 of equation (2) are both dependent on the ferric salt and cupric salt concentrations (equations (3) and (4)).

On the basis of the experimental results a mechanism for the reaction has been suggested (scheme no. VI where reaction 31 is to be considered as two partial reactions 33' and 3'1) and this mechanism has been discussed.

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