ACTA CHEMICA SCANDINAVICA 9 (1955) 283—292

Alternative Mechanisms of the Fe- and the Cu-Fe-catalyzed Decomposition of Hydrogen Peroxide

JØRGEN KOEFOED

Universitetets Fysisk-Kemiske Institut, Copenhagen, Denmark

To describe the kinetic results of Sten Andersen [1,2] new schemes of reactions are proposed which agree better than his own schemes with the ideas of other authors regarding feasibility of the assumed intermediates. The schemes include a ferro-ferric or a cupro-cupric cycle, and the correct functional form of the kinetic equations is obtained through moderation of the cyclic reaction not as usual through an equilibrium, but through another irreversible cyclic process, which is considered slow in comparison with the total rate. Free radicals seem to appear in the cycles only bound to the metal ions.

The recent work of Andersen [1,2] has greatly increased our knowledge of the rates of decomposition of hydrogen peroxide at varying concentrations of ferric, cupric and hydrogen ions. Arguing from his results Andersen and Christiansen [3] have maintained the impossibility of a cyclic mechanism involving the shift of ferric to ferrous ions and hydroxyl radicals as has been first proposed by Haber and Weiss. The object of the present paper is to show, that although this closed sequence as well as other previous ones are in disagreement with experimental results, it is nevertheless possible to construct one which fits just as well as the open sequence of Andersen [1]. Several features in the general nature of the reaction indicate a closed sequence, a chain reaction. The inhibitor action of several organic compounds is the most obvious.

The scheme to be proposed below shares with schemes by Weiss, by Barb, Baxendale, George and Hargrave and by Uri the desirable feature that shifts in electron spin pairing occur only when mediated by iron or copper. The disagreement between these previous schemes and Andersen's experiments is overcome mainly through that further assumption that free radicals in the presence of cupric and ferric ions will be so strongly bound to these that they will appear as $FeOH^{+++}$, FeO^{++}, $OFeOH^{+}$, $CuOH^{++}$, CuO^{+} and similar ions. This feature had to be introduced in order to obtain the right dependence of rate constants on ferric ion concentration. It seems not unlikely that such complexes might be relatively stable due to resonance between structures with tetravalent and trivalent iron.

The fact that reaction of hydrogen peroxide with ceric ions leads only to reduction of ceric ions and not to catalytic decomposition is in accordance with the assumption of ferric-complexes as intermediates in preference to free hydroxyl radicals, as the latter might just as well be formed through reaction with ceric as with ferric ions.

The results reported from experiments with ^{18}O labelled hydrogen peroxide[4] require that the final evolution of oxygen (reaction 31 below) takes place as a dehydrogenation of H_2O_2, *e.g.* through a hydride ion (H^-) transfer plus dissociation of a proton (*cf.* the enzymatic dehydrogenation according to Westheimer and Vennesland[5]).

THE FERRO-FERRIC CYCLE

The cycle to be proposed is:

$$\mathit{Fe}^{++} + \dot{\mathrm{F}}\mathrm{eO_2H}^{++} \rightleftharpoons \mathit{Fe\dot{F}eO_2H}^{+4} \tag{12}$$

$$\mathit{Fe\dot{F}eO_2H}^{+4} \rightleftharpoons \mathit{\dot{O}\dot{F}eOH}^{+} + \dot{\mathrm{F}}\mathrm{e}^{+++} \tag{23}$$

$$\mathit{\dot{O}\dot{F}eOH}^{+} + \mathrm{H_2O_2} \rightarrow \mathit{Fe}^{++} + {}^{\bullet}\mathrm{O}^{\bullet}_2 + \mathrm{OH}^{-} + \mathrm{H_2O} \tag{31}$$

The level at which this cycle operates is determined by a ”moderator cycle”, consisting of two irreversible reactions 0.33′ and 12.0 together with 31 and the protolysis of the ferric hexaquo ion:

$$\dot{\mathrm{F}}\mathrm{eOH}^{++} + \mathrm{H_2O_2} \rightleftharpoons \dot{\mathrm{F}}\mathrm{eO_2H}\mathit{aq}^{++} \rightarrow \mathit{\dot{O}\dot{F}eOH}^{+} + \mathit{\dot{O}H} + \mathrm{H}^{+} \tag{0(0′)33′}$$

$$\dot{\mathrm{F}}\mathrm{e}\mathit{aq}^{+++} + \mathit{\dot{O}H} \rightleftharpoons \mathit{\dot{O}\dot{F}eOH}^{+} + 2\mathrm{H}^{+} \tag{3′3}$$

$$\mathit{Fe}^{++} + \mathit{Fe\dot{F}eO_2H}^{+4} + \mathrm{H_2O} \rightarrow 3\ \dot{\mathrm{F}}\mathrm{eOH}^{++} \tag{12.0}$$

$$\dot{\mathrm{F}}\mathrm{e}\mathit{aq}^{+++} \rightleftharpoons \dot{\mathrm{F}}\mathrm{eOH}^{++} + \mathrm{H}^{+} \tag{ie}$$

Reaction 0.33′ starts with the formation of the wellestablished brown ferric perhydroxo complex in equilibrium with ferric ions, hydrogen ions and hydrogen peroxide. The rate determining step is an excitation of this complex ion and we picture it here as a splitting off of a hydroxyl radical which immediately afterwards attaches itself to a ferric ion. Bimolecular reaction between the complex ion and ferric ion to form two active particles would give a different kinetic expression. The ion $FeFeO_2H^{+4}$ is a perhydroxo dimeric analogue of the well-known polynuclear ions which in alkaline solution grow to colloid or macroscopic size. It is presumably stabilized by valence shift between the iron atoms.

The ion written as $OFeOH^+$ might for its composition be a ferro perhydroxo complex, and kinetic data obviously cannot exclude that. That would be rather unlikely, however, in consideration of its role in the scheme.

Reaction 12 and 23 can be interpreted so, that $OFeOH^+$ is formed from Fe^{++} and H_2O_2 catalyzed by $FeOH^{++}$, and it seems not very likely that the interchange of a coordinated water molecule with hydrogen peroxide should be much promoted by this catalyst. Furthermore, the only significant way of deactivation is 12.0 and the only feasible reason why a reaction 13.0 between Fe^{++} and $OFeOH^+$ does not contribute to the deactivation is that $OFeOH^+$ is the most energy-rich of the three cyclic reactants and therefore the most rare. This is in accordance with our assumption below that 12 is virtually in equilibrium.

The basic physical event which has to occur during the cycle is the splitting up of one pair of electrons with mutually compensating spin into two single electrons with parallel spin corresponding to the change from diamagnetic hydrogen peroxide to paramagnetic oxygen. Is this splitting up most likely to occur in 12, in 23 or in 31? To help the general views, dots have been placed to indicate unpaired electrons, the first four on iron being

omitted. In 23 a ferric ion leaves the binuclear complex with one electron less than the ferro ion brought into it in 12, and yet with one more unpaired. Hence 23 is the obvious place for the actual splitting and $OFeOH^+$ is most likely to have six unpaired electrons and no O—O bond.

On the other hand, the total back reaction 32, 21, 0′0 leads to some exchange of oxygen between water and peroxide, and the results of Cahill and Taube[4] may force us to assume that the O—O bond is first broken in the irreversible 31 reaction.

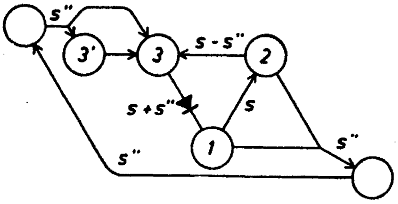

Fig. 1.

The diagrammatic representation of the reaction cycle with the active intermediates X_1, X_2, X_3 and X_3, representing Fe^{++}, $FeFeO_2H^{+4}$, $OFeOH^+$, and OH is given in Fig. 1.

We have supplemented Christiansens way of drawing such flow diagrams by the introduction of the symbol of a rectifier corresponding to the irreversible step. It is easily seen that the kinetic equations depend on where this step is placed in the cycle. In the work with a problem like the present one it is very convenient if the diagram unambiguously characterizes a scheme of reactions to which a certain set of kinetic expressions can be attached.

To comply with stationarity, the flow in the reactions 0.33′ and 12.0 where two active particles appear or disappear, has to be the same: $s_{0.33'} = s_{12.0} = s_i''$, and this flow is considered negligible compared to the flow, s_i, in the oxygen producing cycle:

$$s_{31} = s_i + s_i'' \simeq s_{12} = s_i \simeq s_{23} = s_i - s_i'' \tag{1}$$

Proceeding as Christiansen we obtain the following equations between the concentrations x_1, x_2, x_3 of the intermediates, X_1, X_2, X_3, the concentration of ferric ion, c_i, and of $FeOH^{++}$, c_e; the probabilities w_{ij} of the intermediate X_i to react under formation of X_j, the corresponding rate constants, k_{ij}, and the H_2O_2 concentration, x. K_i is the dissociation constant of $Feaq^{+++}$ (reaction ie), K_0 the equilibrium constant of the hydrolyzed ferric perhydroxo complex (reaction 00′).

$$\begin{aligned} s_i &= x_1w_{12} - x_2w_{21} \\ &= x_2w_{23} - x_3w_{32} \\ &= x_3w_{31} \end{aligned} \tag{2}$$

$$\begin{aligned} s_i'' &= w_{0\cdot33'} = k_{0\cdot33'}\, c_e x \\ &= w_{12\cdot0} = k_{12\cdot0}x_1x_2 \end{aligned} \tag{3}$$

(2) and (3) express that there is stationarity: the same net flow all through in each of our cycles. The equations (2) are solved with respect to x_1, x_2 and x_3:

$$x_1/s_i = (1 + w_{21}/w_{23}(1 + w_{32}/w_{31}))/w_{12} \tag{4}$$
$$x_2/s_i = (1 + w_{32}/w_{31})/w_{23} \tag{5}$$
$$x_3/s_i = 1/w_{31} \tag{6}$$

The unknown concentrations of the intermediates, x_1, x_2 and x_3 are eliminated between (3), (4), (5) and (6), giving:

$$\begin{aligned}\frac{1}{s_i^2} &= \frac{k_{12\cdot 0}}{w_{0.33'}} \cdot \frac{x_1}{s_i} \cdot \frac{x_2}{s_i}\\ &= \frac{k_{12.0}}{w_{0.33'}w_{12}w_{23}}\left(1 + \frac{w_{21}}{w_{23}}\left(1 + \frac{w_{32}}{w_{31}}\right)\right)\left(1 + \frac{w_{32}}{w_{31}}\right)\\ &= \frac{k_{12.0}}{k_{0.33'}c_e x k_{12} K_0 c_e x k_{23}}\left(1 + \frac{k_{21}}{k_{23}}\left(1 + \frac{k_{32}c_i}{k_{31}x}\right)\right)\left(1 + \frac{k_{32}c_i}{k_{31}x}\right).\end{aligned} \tag{7}$$

If $k_{21} \gg k_{23}$ we get the same result as we would have obtained by assuming equilibrium in reaction 12 ($k_{12}/k_{21} = K_{12}$):

$$-\frac{dt}{d\ln x} = \frac{x}{2s_i} = \frac{A_i}{c_i}\left(1 + \frac{k_{32}c_i}{k_{31}x}\right) \tag{8}$$

$$A_i = \frac{c_{H^+}}{2k_{23}K_i}\sqrt{\frac{k_{12\cdot 0}k_{21}}{k_{0\cdot 33'}k_{12}K_0}}$$

with the required functional dependence on c_{H^+}, c_i and x. The formulae of the various ions appearing in the cycle are to some extent arbitrary as any of the steps may cover details which do not influence the kinetic equations, *e.g.* changes in the protolytic state or in aquotisation. By no means any change in this respect is permissible, however, but any scheme will cover an appreciable number of varieties.

To compare the scheme presented here with previous ones, we may consider Christiansen's calculations on a free radical-ferro-ferric cycle (Ref. 3, p. 1060). In that case the level at which the cycle works is moderated through an equilibrium of two cyclic reactants with energy-rich peroxide:

$$\dot{F}eOH^{++} + H_2O_2 \rightleftharpoons Fe^{++} + H\dot{O}_2 + H_2O$$

and it is proved that this leads to an equation of the form

$$-x\frac{dt}{dx} = -\frac{dt}{d\ln x} = A_1\sqrt{1 + \beta/x} \tag{9}$$

while the experiments require:

$$-\frac{dt}{d\ln x} = A_1\left(1 + \frac{\alpha}{x}\right). \tag{10}$$

In a similar way the present cycle leads to a mono-molecular proces ($\alpha = 0$) if it is moderated by reaction 0.33′ in equilibrium, $w_{12\cdot 0}$ being zero. In both cases it is seen that —dt/dln$x$ increases too slowly or not at all as the reaction proceeds (falling values of x). In the derivations above this is corrected through the combination of the irreversible 0.33′ production of active intermediates with the irreversible 12.0 destruction of activity. This makes the level sink more rapidly with falling H_2O_2 concentration. In consideration of the energy levels through which the "moderator cycle" 0.33′, 3′3, (31 + 32), 12.0 will be running, it seems reasonable that the reverse reactions 33′.0 and 0.12 can safely be neglected ($w_{0.12} \ll w_{0.33'}$; $w_{33'.0} \ll w_{12\cdot 0}$).

THE PROMOTING ACTION OF COPPER

Adopting the scheme above for the ferric-ion catalysis we need not restrict ourselves to the very limited class of reactions considered by Andersen for the description of the copper promotion, and possibilities are opened to get through without introduction of entropy producing *perpetuum mobile* reactions as Andersen's cycle: 12—23—33′—3′1 in his final scheme (his symbols).

We will not attempt to reproduce Andersen's results in the same mathematical form, which is adapted to his special class of reactions. We fix our attention to the fact which appears directly from the data given in Table 2, Ref. 2, that at copper ion concentrations greater than 0.0004 his A_1 values become practically independent of copper concentration, while at a given copper concentration, A_1 tends to become proportional to the square root of iron concentration. At the same time A_2/A_1, corresponding to α in equation (10), grows independent of iron concentration. In copper-free solutions A_2/A_1 was proportional to iron concentration such as to make A_2 itself independent of iron.

To obtain a pattern of reactions which corresponds to the behavior at *high Cu-concentrations*, we will assume the initiating reaction 0.33′ to be unchanged by the presence of copper. Once formed the radical activity is supposed to be taken over by copper intermediates through the equilibrium 36 in which the ions on the right hand side are supposed to predominate:

$$\dot{O}\dot{F}eOH^+ + \dot{\mathrm{C}}\mathrm{u}^{++} \rightleftharpoons \dot{\mathrm{F}}\mathrm{eOH}^{++} + \dot{C}u\dot{O}^+ \qquad 36$$

CuO^+ is called X_6 and is part in a copper cycle 4564 in which X_4 is Cu^+ and X_5 is $\mathrm{CuO_2H_2}^+$:

$$Cu^+ + \mathrm{H_2O_2} \rightleftharpoons CuO_2H_2{}^+ \qquad 45$$

$$CuO_2H_2{}^+ \rightleftharpoons \dot{C}u\dot{O}^+ + \mathrm{H_2O} \qquad 56$$

$$\dot{C}u\dot{O}^+ + \mathrm{H_2O_2} \rightarrow Cu^+ + \dot{\mathrm{O}}\dot{}_2 + \mathrm{H_2O} \qquad 64$$

and deactivation occurs through:

$$Cu^+ + CuO_2H_2{}^+ \rightarrow 2\ \dot{\mathrm{C}}\mathrm{u}^{++} + 2\mathrm{OH}^- \qquad 45.0$$

Neglecting the iron cycle 1231 we obtain equations identical with the previous ones when 1, 2 and 3 are substituted by 4, 5 and 6 except in $w_{0.33'}$, which is kept unchanged:

$$x_4/s_u = (1 + w_{54}/w_{56}(1 + w_{65}/w_{64}))/w_{45} \qquad (11)$$

$$x_5/s_u = (1 + w_{65}/w_{64})/w_{56} \qquad (12)$$

$$x_6/s_u = 1/w_{64} \qquad (13)$$

$$\begin{aligned}\frac{1}{s_u^2} &= \frac{k_{45\cdot0}}{w_{0.33'}w_{45}w_{56}}\left(1 + \frac{w_{54}}{w_{56}}\left(1 + \frac{w_{65}}{w_{64}}\right)\right)\left(1 + \frac{w_{65}}{w_{64}}\right) \\ &= \frac{k_{45\cdot0}}{k_{0\cdot33'}c_e x k_{45} x k_{56}}\left(1 + \frac{k_{54}}{k_{56}}\left(1 + \frac{k_{65}}{k_{64}x}\right)\right)\left(1 + \frac{k_{65}}{k_{64}x}\right)\end{aligned} \qquad (14)$$

and if $k_{54} \gg k_{56}$:

$$- \frac{\mathrm{d}t}{\mathrm{dln}x} = \frac{x}{2s_u} = \frac{A_u}{\sqrt{c_i}} \left(1 + \frac{k_{65}}{k_{64}x}\right) \tag{15}$$

$$A_u = \frac{1}{2k_{56}} \sqrt{\frac{k_{45\cdot 0}k_{54}}{k_{0\cdot 33'}k_{45}K_i}} \cdot \sqrt{c_{H^+}}$$

We have no experimental evidence to show whether the dependence on c_{H^+} is right or wrong, and it is easily changed by changing the protolytic state of the reactants.

The dependence on the square root of ferric ion concentration and the independence of copper concentration are as required, but whereas the square root dependence may safely be taken as evidence for the reality of a closed-sequence iron cycle, too much weight should certainly not be laid upon the way in which copper ions enter the present scheme.

It makes no difference in the final expression if 45 is catalyzed by ferric ion, as we have actually assumed equilibrium in this step. 45 may therefore be substituted by for instance:

$$Cu^+ + \mathrm{FeO_2H^{++}} \rightleftharpoons CuO_2H_2^+ + \mathrm{FeOH^{++}} \tag{45 (a)}$$

In the region of *low Cu-concentrations* we must take both cycles into consideration. This can be done in several ways, but in order not to make things too complicated we will stick to the class of reactions already laid out and add only two reactions:

$$Fe^{++} + CuO_2H_2^+ \rightarrow \mathrm{\dot{F}eOH^{++}} + \mathrm{\dot{C}u^{++}} + \mathrm{OH^-} \tag{15.0}$$

$$Cu^+ + Fe\dot{F}eO_2H^{+4} + \mathrm{H_2O} \rightarrow \mathrm{\dot{C}u^{++}} + 2\mathrm{\dot{F}eOH^{++}} + \mathrm{OH^-} \tag{42.0}$$

They are deactivation reactions and their velocities are s_{iu}'' and s_{ui}''. With reaction 36 in equilibrium we have: $x_6c_e = K_{36}x_3c_u$ and when s_i and s_u are the rates of the two generating cycles (*cf.* eq. 2):

$$s_i = x_3w_{31} \qquad s_u = x_6w_{64} \qquad s = s_u + s_i \tag{16}$$

$$\frac{s_u}{s_i} = \frac{k_{64}K_{36}c_u}{k_{31}c_e} = \frac{\gamma c_u}{c_i} \qquad (\gamma = \gamma_0 c_{H^+}) \tag{17}$$

$$\frac{1}{s} = \frac{1}{s_i} \frac{1}{1 + \gamma c_u/c_i} \tag{18}$$

For the moderator cycle we now get (*cf.* eq. 3):

$$\begin{aligned} s'' &= w_{0\cdot 33'} = k_{0\cdot 33'}\ c_e x \\ &= s_i'' + s_{ui}'' + s_{iu}'' + s_u'' \\ &= k_{12\cdot 0}x_1x_2 + k_{15\cdot 0}x_1x_5 + k_{42\cdot 0}x_4x_2 + k_{45\cdot 0}x_4x_5 \end{aligned} \tag{19}$$

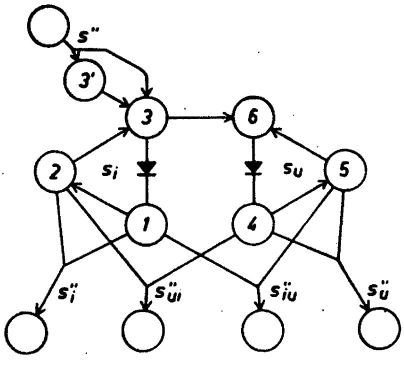

Fig. 2.

We still neglect s'' in comparison with s_i and s_u. Equations 4, 5, 6, 11, 12 and 13 then remain valid, and we can derive the following equations in a similar way and under similar conditions as before ($k_{21} \gg k_{23}$ and $k_{54} \gg k_{56}$):

$$\frac{1}{s^2} = \frac{1}{w_{0\cdot33'}\,(1+\gamma c_u/c_i)^2} \left\{k_{12\cdot0}\frac{x_1}{s_i}\frac{x_2}{s_i} + \frac{\gamma c_u}{c_i}\left(k_{15\cdot0}\frac{x_1}{s_i}\frac{x_5}{s_u} + k_{42\cdot0}\frac{x_4}{s_u}\frac{x_2}{s_i}\right) + \left(\frac{\gamma c_u}{c_i}\right)^2 k_{45\cdot0}\frac{x_4}{s_u}\frac{x_5}{s_i}\right\}$$

$$= \frac{4}{(1+\gamma c_u/c_i)^2}\frac{1}{x^2}\left\{\frac{A_i^{\,2}}{c_i^{\,2}}\left(1+\frac{k_{32}c_i}{k_{31}x}\right)^2 + \frac{\gamma c_u}{c_i}\left(\frac{A_{iu}^{\,2}}{c_i^{\,2}} + \frac{A_{ui}^{\,2}}{c_i}\right)\left(1+\frac{k_{32}c_i}{k_{31}x}\right)\left(1+\frac{k_{65}}{k_{64}x}\right) + \left(\frac{\gamma c_u}{c_i}\right)^2\frac{A_u^{\,2}}{c_i}\left(1+\frac{k_{65}}{k_{64}x}\right)^2\right\}$$

$$A_{iu}^2 = \frac{k_{15\cdot0}k_{21}}{4\,k_{0\cdot33'}K_0k_{12}k_{23}k_{56}K_i^2}\;c_{H^+}^2 \tag{20}$$

$$A_{ui}^2 = \frac{k_{42\cdot0}k_{54}}{4\;k_{0\cdot33'}K_ik_{45}k_{23}k_{56}}\;c_{H^+}$$

At given concentrations of iron and copper this gives an expression of the form

$$-\frac{dt}{d\ln x} = A_1\sqrt{1+\beta/x+\alpha^2/x^2} \tag{21}$$

Only when $\beta = 2\alpha$ will this reduce to the form of (10), but in quite wide intervals it will not be very far off. The exclusive ability of the integrated equation (10) to represent the experimental results appears to be somewhat overestimated by Andersen. In the published results of a typical experiment with both copper and ferric ions (Ref. 2, Table 1) the deviations between calculated and experimental values vary in a systematic way culminating at 71 min. with —0.84 min.

The possibility of choosing $\beta \neq 2a$ introduces one more parameter and must invariably make it possible to obtain a better agreement with a given experiment. To test whether the obtained values of the parameters are in agreement with our expression we would need the complete experimental material, but only one series of measurements is published in full.

It may be of some interest in judging the significance of an obtained agreement between observed and calculated values in kinetic experiments in general to print here a table of deviations from various integrals to equation (21) corresponding to different values of $\beta/a = n$:

$$t = y_n = \int_{x_0}^{x} A_1 \sqrt{1 + na/x + a^2/x^2}\ \mathrm{dlog}\ (a/x) \qquad (22)$$

The chosen values of the parameters are:

1. $n = 3,\ A_1 = 14.37,\ \log\ a/x_0 = \bar{1}.050$
2. $n = 3,\ A_1 = 14.59,\ \log\ a/x_0 = \bar{1}.035$
3. $n = 1,\ A_1 = 16.50,\ \log\ a/x_0 = \bar{1}.120$

and for comparison Andersen's parameter values, which correspond to:

4. $n = 2,\ A_1 = 15.29,\ \log\ a/x_0 = \bar{1}.056$

Table 1. $\triangle = t_{\text{calc.}} - t_{\text{obs.}}$

$t_{\text{obs.}}$ min.	1. (y_3)	2. (y_3)	3. (y_1)	4. (y_2, St. A.)
0	.00	.00	.00	.00
2.10	.00	+.03	+.12	+.03
5.00	−.12	−.08	+.06	−.02
10.00	−.20	−.10	+.15	−.03
15.00	−.08	+.03	+.32	+.10
20.00	−.05	+.05	+.30	+.12
25.00	−.01	+.15	+.24	+.11
30.00	+.25	+.46	+.35	+.26
35.00	+.28	+.38	+.16	+.21
43.00	+.32	+.51	−.16	+.10
50.00	+.18	+.56	−.36	+.05
60.00	+.29	+.58	−.58	−.14
71.00	−.28	−.27	−1.14	−.84
80.00	−.20	−.20	−.86	−.69
90.00	+.27	+.26	+.23	+.01
100.00	−.32	−.44	+.45	−.45
105.00	.00	−.25	+1.13	+.06
$\Sigma\triangle^2$	0.72	1.75	4.3	1.56 min ^{2}

The integral (22) can be solved in terms of the ordinary functions and the choice between using the solutions or using a numerical integration becomes a matter of taste and of available calculating machines. The values of Table 1 were actually calculated by numerical methods in the following way[6]:

a. $f = \sqrt{1 + na/x + a^2/x^2}$ was tabulated at intervals of 0.1 in log a/x for $n = 1$ and $n = 3$ and controlled through the differences of first, second, and third order f^1, f^2, f^3.
b. From a plot of the experimental values of t *versus* $-$ log x was found where $-\mathrm{d}t/\mathrm{dlog}\,x$ had increased to twice the value at $t = 0$.
c. In each of the tables of f is found where f doubles up within a similar interval in log a/x.
d. Starting at the beginning of this interval the sums of first order ^1f were formed and corrected to form a table of the integral.
e. A_1 was chosen to fit the initial slope.
f. log a/x_0 was chosen such as to make a fit at $t = 100$ min.

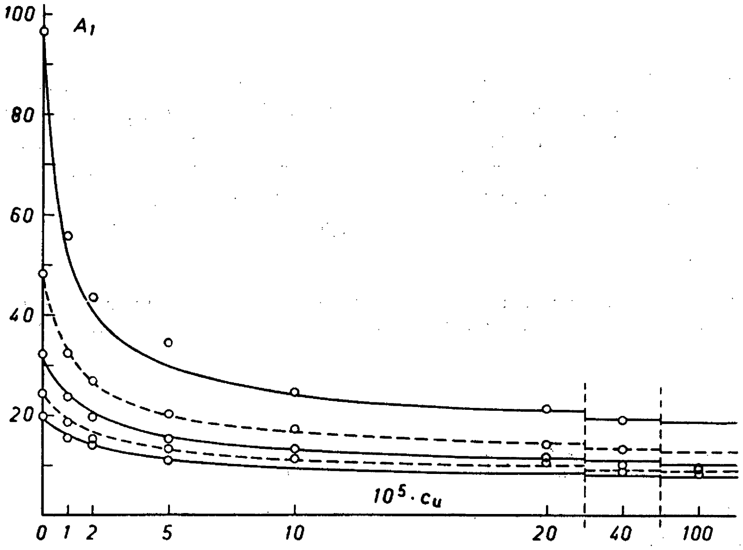

Fig. 3. Sten Andersen's experimental values of A_1 *(points) compared with curves calculated from eq. (23).*

g. The agreement was improved by trial and error with small changes in A_1 and log a/x_0.
h. For the final choice of parameters values were interpolated in the tabulated values of the integral using the f^1 and f^2 values as values of the differences of second and third order.

This procedure was adopted in order to obtain results which were directly comparable with Andersen's, although undue weights are actually placed on the initial measurements.

Equation (20) contains many adjustable parameters. Until experimental data from a wider range of iron concentrations and with variation of acidity appear, the only thing in the way of investigating quantitatively the applicability of (20) that can feasibly be done is to consider the constant A_1. If we suppose that it does not influence the value of A_1 very much whether it is chosen to fit an integral derived from (21) or from (10), we can take the experimental values from Table 2, Ref. 2, and try to fit them into the form required by (20) and (21):

$$A_1 = \frac{1}{1 + \gamma c_u/c_i} \frac{A_i}{c_i} \sqrt{1 + (\delta + \varepsilon c_i)\gamma c_u/c_i + \mu c_i(\gamma c_u/c_i)^2} \tag{23}$$

In Fig. 3 the points represent the experimental values (Table 2, Ref. 2) and the lines equation (23) with $A_i = 0.0965$, $\gamma = 143$, $\delta = 0{,}50$, $\varepsilon = 0$, $\mu = 0{,}032$. A better fit could be obtained with negative values of ε.

Other equations to fit A_1, but to which no kinetic scheme has been found, are:

$$A_1 = \frac{0.555}{\sqrt{c_i}} \frac{4.9 + 10^5 c_u}{28\sqrt{c_i} + 10^5 c_u} \tag{24}$$

$$A_1 = \frac{0.555}{\sqrt{c_i}} \frac{1.38 + 10^5 c_u + 4.13/10^3 c_i}{0.75 + 10^5 c_u + 250\ c_i} \tag{25}$$

CONCLUSIONS

The reaction with pure iron seems accounted for by the present scheme in a very satisfactory way. For the combined action of copper and iron the scheme is far from final, though it is probably to be preferred to Andersen's original schemes as basis for further investigations. A more general conclusion concerns the danger of placing too much confidence in a scheme of reactions because it fits the kinetic data, even though a great number of others have been ruled out.

Except for the calculations in the last part, the content of this paper was presented in an *ex auditorio* opposition at the formal defense of the thesis of V. Sten Andersen on June the 15th, 1954.

REFERENCES

1. Andersen, V. S. *Acta Chem. Scand.* **2** (1948) 1.
2. Andersen, V. S. *Acta Chem. Scand.* **6** (1952) 1090.
3. Christiansen, J. A. *Acta Chem. Scand.* **6** (1952) 1056.
4. Cahill, A. E. and Taube, H. *J. Am. Chem. Soc.* **74** (1952) 2312.
5. Vennesland, B. and Westheimer, F. H. *Symposium on the Mechanism of Enzyme Action*, Baltimore 1954, p. 357.
6. Lindow, M. *Numerische Infinitesimalrechnung*, Berlin 1928.

Received November 10, 1954.