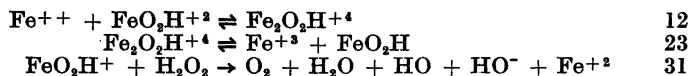


## On the Ferric-ion Catalyzed Decomposition of Hydrogen-Peroxide

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It is agreed that a reaction pattern proposed by J. Koefoed, which implies the closed sequence



and which can be made to agree with Sten Andersen's experiments is in better agreement with general experimental evidence than an open sequence formerly proposed by Sten Andersen and the present author. On the basis of tracer experiments from elsewhere it is concluded that the intermediate  $\text{FeO}_2\text{H}^{+}$  is a ferrous perhydroxo complex and not, as advocated by J. Koefoed, an oxo-hydroxo derivative of  $\text{Fe(IV)}$ .

Recently J. Koefoed<sup>1</sup> proposed a reaction pattern for the ferric-catalyzed decomposition of hydrogen-peroxide which

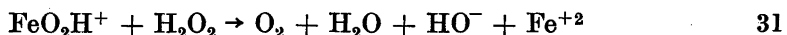
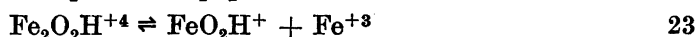
1) agrees with Sten Andersen's chronometric integral<sup>2</sup>  $t = A_1 \ln a/x + A_2 (1/x - 1/a)$  ( $x$  concentration of hydrogen-peroxide at time  $t$ ,  $a$  the same at  $t = 0$ ), 2) has the property of containing a closed sequence (a chain mechanism) which the pattern proposed by Sten Andersen and the present author has not, and finally 3) operates with ferrous ion as an intermediate which the one mentioned above does not.

As it is an experimental fact that the decomposition in question is strongly retarded by small amounts of certain substances and that during the decomposition ferrous ions can be analytically<sup>3</sup> detected it is obvious that Koefoed's pattern is in better general agreement with the experimental facts taken at their face-value than the one mentioned above.

There is, however, one detail in Koefoed's pattern which may need a little discussion and another which seems to be in disagreement with well established experimental findings. We shall begin with a discussion of the latter.

Koefoed admits the well known fact that kinetics can tell nothing about the constitution of the intermediates.

He tries, however, by using arguments from elsewhere to make it probable that the intermediate of the composition FeO<sub>2</sub>H<sup>+</sup> is not a ferrous-perhydroxo complex but an oxo-hydroxo compound of Fe(IV), *viz.* O : FeOH. His arguments can best be discussed by means of his closed sequence which is

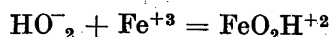


This is so constructed that it makes it possible to remain in agreement with all Sten Andersen's results on the ferric ion catalyzed reaction.

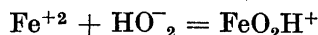
It is a fact that during the overall reaction a pair of antiparallel electronic spins are converted into a pair of parallel spins and Koefoed now argues that this conversion takes place during the step 23, which would support the

assumption of the constitution O<sup>+</sup>FeOH for the intermediate. His argument seems, however, to be highly artificial: There is complete agreement in views on the constitution of FeO<sub>2</sub>H<sup>+2</sup> as a perhydroxo analogue to FeOH<sup>+2</sup> and on the constitution of Fe<sub>2</sub>O<sub>2</sub>H<sup>+4</sup> as the perhydroxo analogue to a ferrous-ferric hydroxo complex of well known type. Why not therefore assume that the ferrous and the ferric ions in 12 and 23 simply keep their spins and assume, as we then must, that the "spin-conversion" takes place in the irreversible reaction 31? One might even say that such an assumption is probable in view of the strong tendency for ferrous ions to form coordinated complexes with certain anions. This would lead in our case to an accumulation of two perhydroxo ligands around the central ion, the resulting complex being so to speak explosive. Anyhow there is direct evidence in favour of the view that FeO<sub>2</sub>H<sup>+</sup> is actually a ferrous-perhydroxo ion and not an oxo-hydroxo derivative of Fe(IV). Two groups of authors, Baertschi<sup>4</sup> on one side and Cahill and Taube<sup>5</sup> on the other, agree in stating, on the basis of numerous tracer experiments, that in the reactions of hydrogen-peroxide the evolved oxygen is derived "cleanly from the hydrogen-peroxide" (Cahill and Taubes expression) that is, there is no measurable reversible exchange of oxygen between the perhydroxide and the solvent water. This is true in all the cases investigated and particularly in our case which has actually been investigated by Cahill and Taube. Now from general knowledge and from experiments it appears that oxygen in metal-hydroxo compounds is readily exchangeable with oxygen in the solvent water. It would therefore be a lengthy and, as the present author believes, an impossible task to prove that the assumption of FeO<sub>2</sub>H<sup>+</sup> being an oxo-hydroxo compound does not contradict the tracer experiments.

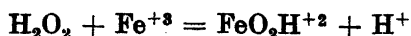
Koefoed has, however, another argument which according to him should make the assumption, that FeO<sub>2</sub>H<sup>+</sup> be a perhydroxo compound, improbable: Let us add to the equations 12 and 23 the equation for the reaction



We then get as the resultant of the three processes



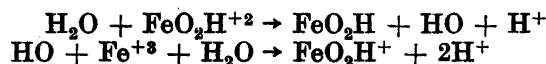
in other words: ferric ions should catalyze the latter reaction. (Koefoed prefers to add the equilibrium



with a corresponding change in the resultant equation, but the difference is so far as we can see to all intents and purposes immaterial.) He now says that it is not very likely that the reaction in question "should be much promoted by this catalyst", in other words the direct formation of  $\text{FeO}_2\text{H}^+$  from  $\text{Fe}^{+2}$  and  $\text{HO}_2^-$  (the bye-pass) should be faster than that through the reactions 12 and 23. However, as shown in the appendix the problem in question cannot be decided that way. A rational treatment shows 1) that only the kinetic experiments themselves can decide whether the existence of the bye-pass is of significance or not, 2) that Sten Andersen's experiments indicate that its existence is insignificant in the range of ferric ion concentrations investigated and 3) that this result would be *a priori* probable rather than improbable.

We see therefore no reason to admit other assumptions than that the intermediate  $\text{FeO}_2\text{H}^+$  simply is a ferrous perhydroxo compound in which way any contradiction with the tracer-experiments automatically disappears.

We now pass on to the minor first point. As initiator Koefoed assumes the net reaction  $\text{FeO}_2\text{H}^{+2} + \text{Fe}^{+3} + 2 \text{H}_2\text{O} \rightarrow 2 \text{FeO}_2\text{H}^+ + 3 \text{H}^+$  divided into two steps as follows



Actually, in agreement with Koefoed's statement, only the left hand side of the first partial reaction is known from the kinetics, water of course being kinetically unimportant. Therefore if we don't like to state more than we know the equation ought to be written



Anyhow it seems certain that in Koefoed's initiating reaction part of the perhydroxide must come from the solvent water. This will however probably not contradict the tracer experiments because of his basic and most probably correct assumption of a large chain length. Even a low value of say 100 would probably prevent its detection if only the chain-mechanism itself does not give rise to exchange of oxygen with the solvent water. We have therefore no objection in principle to Koefoed's initiating sequence.

The present author has also something to say about Koefoed's treatment of Sten Andersen's experimental results concerning the cupric-ferric ion catalyzed reaction. But this discussion can only be completed in cooperation with Sten Andersen, a cooperation which because of Sten Andersen's temporary absence must be postponed to a later date. Be it enough to state here that it may (not must) be true that Sten Andersen's experiments admit mechanisms (reaction patterns) which do not lead strictly to his chronometric integral of the type  $t = A_1 \ln(a/x) + A_2(1/x - 1/a)$ , which the one proposed by Koefoed admittedly does not.

It must be added, however, that a reaction-pattern including Koefoed's chain-mechanism has been constructed which agrees strictly with Sten Andersen's chronometric integral, and with the aid of which his numerical values for  $A_1$  and  $A_2$  can be reproduced with some accuracy.

APPENDIX

Let us assume, besides the reaction



also the bye-pass

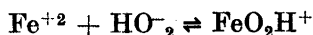
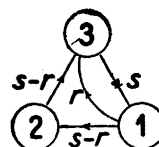


Fig. 1. Flow sheet for the closed sequence 12, 23, 31 with bye-pass 13. The steady state currents are as shown by the letters and arrows.



The flow-sheet of the reaction is shown in Fig. 1, where the currents corresponding to steady state have been indicated. Denoting the probabilities of the reaction of the intermediates Fe<sup>+2</sup> and FeO<sub>2</sub>H<sup>+</sup> according to the bye-pass reaction by  $u_{13}$  and  $u_{31}$  respectively we get

$$\begin{aligned} x_1 &= r/u_{13} + su_{31}/u_{13}w_{31} \\ x_1 &= (s-r)(1 + w_{21}/w_{23})/w_{12} + sw_{21}w_{32}/w_{12}w_{23}w_{31} \end{aligned}$$

From the principle of microscopic reversibility we have the equation

$$w_{12}w_{23}u_{31} = w_{21}w_{32}u_{13}$$

which means that, with  $w_{21}/w_{23} \gg 1$

$$\begin{aligned} sw_{21}/w_{12}w_{23} &= r(1/u_{13} + w_{21}/w_{12}/w_{12}w_{23}) \\ r/s &= 1/(w_{12}w_{23}/w_{21}u_{13} + 1) = 1/(w_{32}/u_{31} + 1) \\ &= u_{31}/(w_{32} + u_{31}) \end{aligned}$$

This yields

$$\frac{x_1}{s} = \frac{u_{31}}{u_{13}} \left( \frac{1}{w_{32} + u_{31}} + \frac{1}{w_{31}} \right)$$

For  $x_2/s$  we similarly get

$$\begin{aligned} \frac{x_2}{s} &= \left( 1 - \frac{r}{s} \right) / w_{23} + w_{32}/w_{23}w_{31} \\ &= \frac{w_{32}}{w_{23}} \left( \frac{1}{w_{32} + u_{31}} + \frac{1}{w_{31}} \right) \end{aligned}$$

Replacing  $u_{31}/u_{13}$  by  $w_{32}w_{21}/w_{12}w_{23}$   
we finally get

$$\frac{x_1 x_2}{s^2} = \frac{w_{21}}{w_{12}} \left( \frac{w_{32}}{w_{23}} \right)^2 \left( \frac{1}{w_{32} + u_{31}} + \frac{1}{w_{31}} \right)^2$$

which is identical with the corresponding expression obtained without the bye-pass if  $u_{31} \ll w_{32}$ .

Now  $u_{31}$  is the probability in unit time that  $\text{FeO}_2\text{H}^+$  shall dissociate into  $\text{Fe}^{++}$  and  $\text{HO}_2^-$  and  $w_{32}$  the probability that it shall unite with a ferric ion to form  $\text{Fe}_2\text{O}_2\text{H}^{+4}$ . It would seem *a priori* rather probable that the former probability is much less than the latter at reasonable concentrations of ferric ions. As, however,  $w_{32}$  must be of the form  $k_{32} [\text{Fe}^{+3}]$  it might be possible by making experiments at very low ferric ion concentrations to detect the influence of the bye-pass, but on account of the low concentration of the catalyst such experiments would last an exceedingly long time. Anyhow, only the kinetic experiments themselves can decide with reasonable certainty on the ratio  $u_{31}/w_{32}$  and the actual result derived from Sten Andersen's experiments, that  $u_{31}/w_{32} \ll 1$ , is not at all improbable *a priori*, or rather, it seems to be probable and quite natural.

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