On the Effect of Small Amounts of some Organic Compounds on the Ferric Ion Catalyzed Hydrogen Peroxide Decomposition

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The authors have investigated the influence of benzene, phenol, phenacetin, and hydroquinone on the rate of the ferric-ion catalyzed hydrogen peroxide decomposition.

The experiments show that benzene, phenol, and phenacetin cause an induction period, the length of which depends on the amount of compound added; after the induction period the rate of reaction is greater than that of the pure ferric-catalyzed reaction. Hydroquinone does not retard the reaction but acts as a promotor from the very start of the reaction.

These findings seem to indicate that a reaction mechanism based on a chain reaction catalyzed by ferrous ions, similar to that proposed by Koefoed [1], is to prefer to the one put forward by Christiansen and Andersen [2], which is based on an open sequence reaction.

The experiments were carried out in a Brønsted shaking apparatus [3] modified in such a manner that the pressure of the oxygen evolved could be measured at constant volume, although the manometer was made of fairly wide glass tubing, in order to suppress the capillary forces.

In 1950 Christiansen and Andersen [2] proposed a reaction mechanism for the Fe(III)-catalyzed hydrogen peroxide decomposition which was based on an open sequence:

$$FeOOH^{++} \rightleftharpoons Fe^{+++} + H\overset{*}{O}_2^{-}$$

$$H\overset{*}{O}_2^{-} + H_2O_2 \rightarrow O_2 + OH^{-} + H_2O$$

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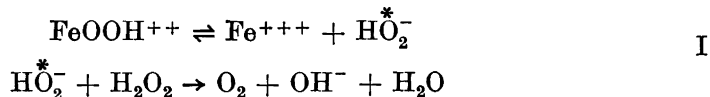
($H\overset{*}{O}_2^{-}$ represents an activated hydrogen peroxide ion).

This scheme, although it fits very closely to the experimental results, has been met with some scepticism because it does not explain the fact that the
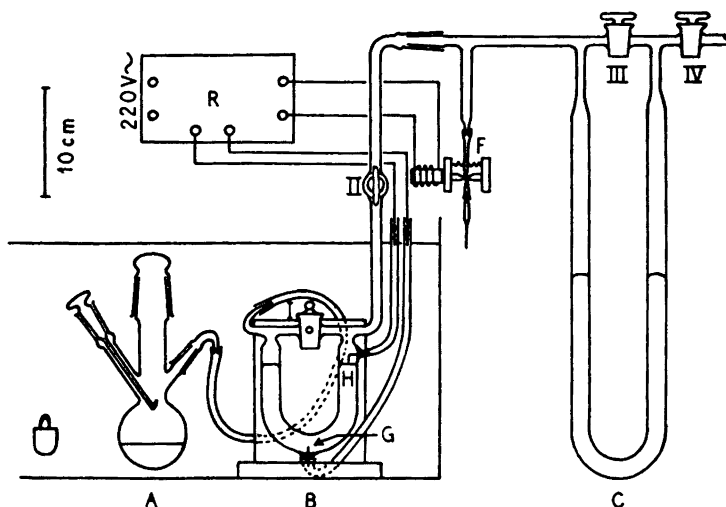
Fig. 1. A modified Brønsted shaking apparatus used for the experiments.

reaction is strongly retarded by small amounts of organic compounds (Bray and Peterson [4]) or the finding of Kuhn and Wassermann [5] who have demonstrated that ferrous ions can be detected in the reaction mixture. These features indicate a chain reaction and a valence shift of the iron ions. Koefoed [1] and Christiansen [6] have discussed such a reaction pattern, proposed by the former and based on a closed sequence.

In the present paper we have given an account of some new kinetic experiments on the influence of some benzene derivatives: benzene, phenol, phenacetin, and hydroquinone on the reaction in question and we have from a qualitative point of view discussed the experimental results in connection with the reaction schemes mentioned above.

EXPERIMENTAL

The kinetic experiments were carried out in a modified Brønsted shaking apparatus [3] by measuring the pressure of the oxygen evolved. The apparatus (Fig. 1) was constructed in such a manner that it was possible to measure the gas pressure at constant volume even though the manometer was made of glass tubing with an inner diameter of 14 mm. The reaction vessel A (volume about 165 ml) was mounted in an ordinary shaking apparatus. It was furnished with a side arm closed by a glass stopper onto which was sealed a glass rod; the end of this rod was formed as a small hook upon which a small plastic vessel (volume about 2 ml) could be hung.

The reaction vessel was connected to one side of a differential-tensiometer B by a piece of flexible plastic tubing. The tensiometer was again connected to a mercury manometer C, which was connected to a vacuum line on the other side. F is a piece of soft plastic tubing which served as a valve. This valve could be closed by means of two metal jaws pressed together by an ajustable spring. To prevent the walls sticking together they were lubricated with silicone oil ('formslip').
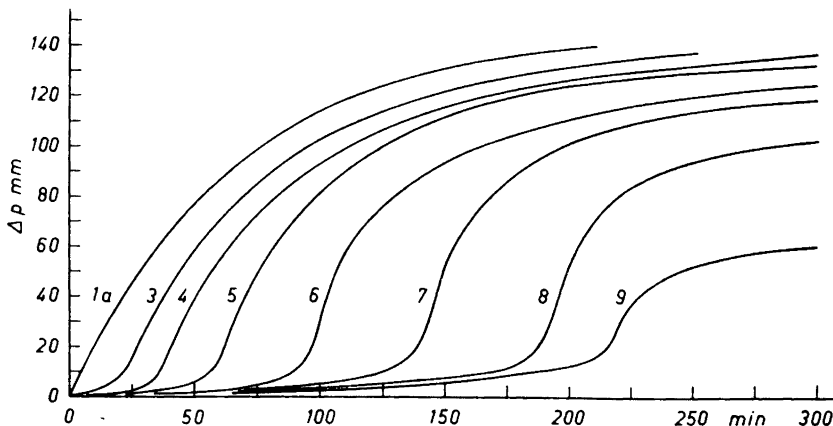
Fig. 2. Reaction curves from the experiments with phenacetin as an inhibitor. The pressure of the oxygen evolved is plotted against time. The reacting mixtures were all 0.003 M as to ferric perchlorate, 0.01 M as to perchloric acid and 0.046 M as to hydrogen peroxide. Temp. 25°C.

The molar concentrations of phenacetin were:

Concentration of phenacetin $\times$ 10^5:	0.0	3.03	6.06	12.1	24.2	45.5	91.0	227
Curve No:	1 a	3	4	5	6	7	8	9

The differential-tensiometer was furnished with two wolfram electrodes, G and H, and it was filled with enough mercury to enable the mercury level to touch the electrode H, when tap I was open. To avoid vibrations the tensiometer was mounted on a stand attached to a heavy lead base. The electrodes were used as a pick-up for a thyratron relay R, which was able to open the valve F by the electromagnet M when the mercury in the tensiometer touched the electrode H.

In this manner it is possible, on the wide manometer C, to measure at constant volume an increasing pressure which is smaller than the atmospheric pressure, in the reaction vessel A; of course the relay can easily be rearranged so that it works at decreasing pressure.

The modified Brønsted apparatus has the following advantages in preference to the original one:

1) It is possible to measure the pressure at constant volume.

2) The pressure can be measured with a greater accuracy in the wide manometer because the capillary effect is much smaller than in a narrow one *.

3) The resistance in the plastic tubing is much smaller than in the flexible glass tubing used by Brønsted because it is made much shorter and wider; in addition to this it is not breakable and therefore easier to handle.

The experiments were carried out as follows:

40.00 ml of an aqueous solution of ferric perchlorate acidified with perchloric acid was pipetted into the flask A; a known amount (about 1 ml) of a hydrogen peroxide stock-solution was placed in the plastic vessel which then was hung on the turnable hook. The flask was closed, the taps I, II, III and IV were opened, the relay switched off to close valve F and the whole system was evacuated for about 5 min. Subsequently the tap I was closed and the system (minus the reaction vessel) was evacuated to a pressure not

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* See for instance: Ostwald-Luther, *Hand- und Hilfsbuch zur Ausführung physiko-chemischer Messungen.* Academische Verlagsges. Leipzig 1931, p. 197.
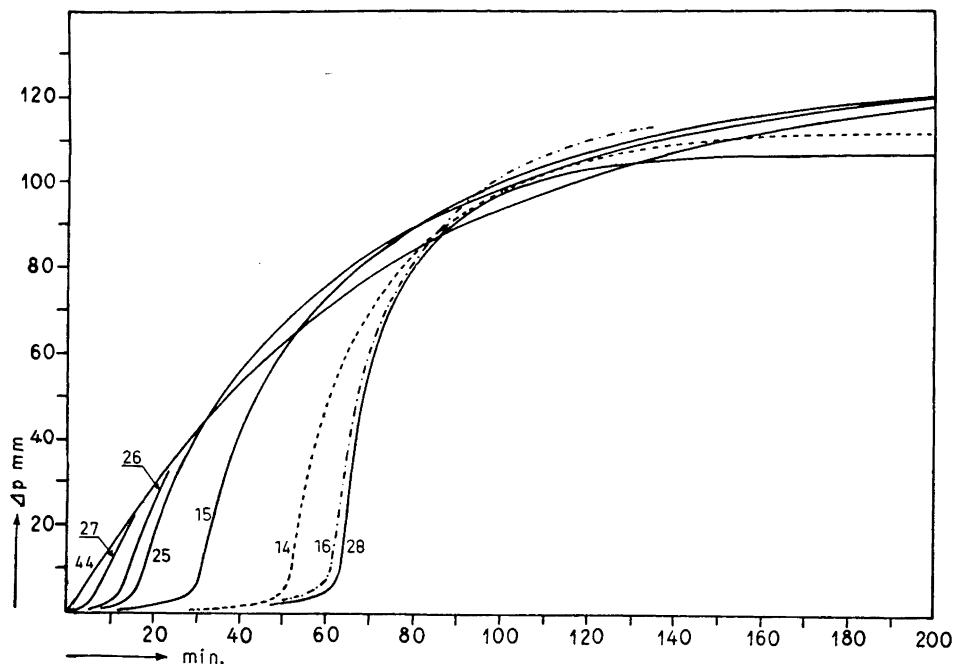
Fig. 3. Reaction curves from the experiments with phenol as inhibitor. The experimental conditions were all the same as those given in the subscript to Fig. 2.

The concentrations of phenol were:

Concentration of phenol $\times 10^3$:	0.0	0.010	0.030	0.052	0.102	0.260	0.517	1.03
Curve No:	44	27	26	25	15	14	16]	28

exceeding 0.01 mm and the taps III and IV were closed. During this phase of the eva-cuation the water vapour in the reaction flask had moved the mercury in the tensiometer so much that the electrode H was submerged in the mercury. Therefore, when the relay then was switched on, it began to work and opened the valve F which let in air until the mercury no longer touched the electrode H; simultaneously the mercury in the manometer moved, so that when equilibrium was obtained, the pressure in the reaction vessel could be read on the manometer, by means of a reading microscope.

The reaction was started by dropping the plastic vessel with hydrogen peroxide into the solution in the reaction flask, and switching on the shaking apparatus; the rate of reaction was measured by reading the gas pressure as described above.

Four series of experiments were carried out: One with phenacetin, one with benzene, one with phenol, and finally one with hydroquinone.

The experimental results, together with the experimental conditions, are given in the Figs. 2, 3 and 4. We have not given the results from the experiments with benzene as inhibitor because they were not reproducible; due to the volatility of the benzene it was not possible to prevent its disappearance from the reaction mixture during evacuation of the apparatus.

It appears from Figs. 2 and 3 that phenacetin and phenol on the whole act in the same way; both interfere very strongly with the pure Fe(III)-catalyzed reaction: They cause an induction period during which no oxygen or only a small amount of oxygen is evolved.
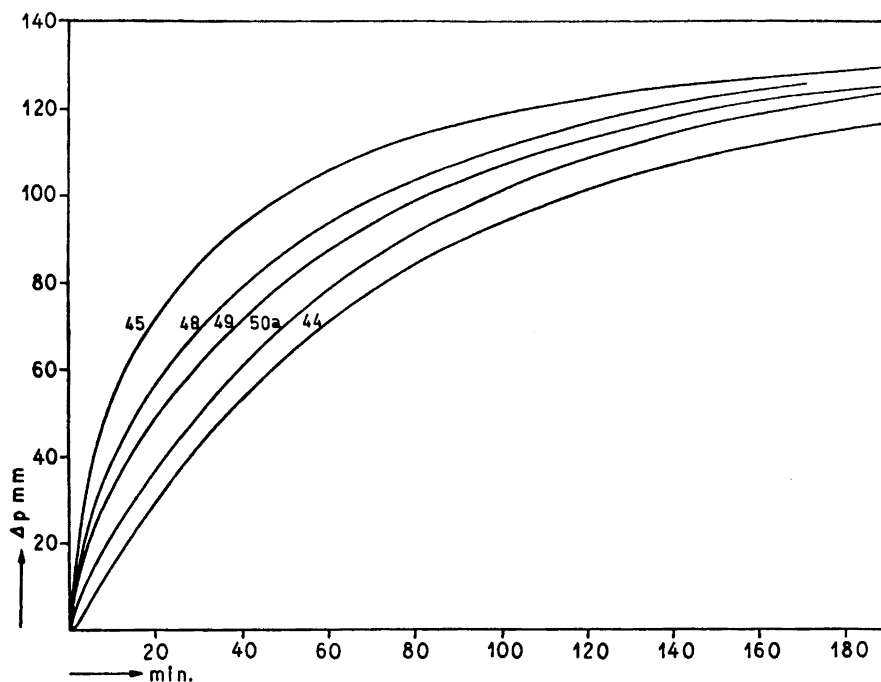
Fig. 4. Reaction curves for the experiments with hydroquinone. The experimental conditions were the same as those given in the subscript to Fig. 2.

The concentrations of hydroquinone were:

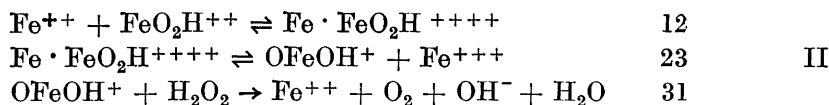| Concentration of hydroquinone $\times 10^4$:	0.0	0.09	0.46	0.90	2.29
Curve No:	44	50 a	49	48	45

After this period, the hydrogen peroxide starts to decompose with a rate which is greater than that of the pure Fe(III)-catalyzed reaction. The experiments with greater amounts of inhibitor (see Fig. 2) show that a portion of the hydrogen peroxide is not decomposed into oxygen; obviously it is used for oxidizing the organic compound added. It should be mentioned that the experiments with benzene showed the same features as those just described. The reaction mixtures all turned more or less brown during the induction period.

The reaction curves in Fig. 4 show that hydroquinone, contrary to the compounds dealt with above, does not cause any induction period, but that it acts as a promotor from the very start of the reaction — or in other words it speeds up the Fe(III)-catalysis.


DISCUSSION

It seems difficult, if not impossible, to explain the experimental results by means of a reaction mechanism containing an open sequence similar to that proposed by Christiansen and Andersen [2] (scheme No. I on page 896). As pointed out by Bray and Peterson [4] and recently by Koefoed [1] the retarding

effect described above is much better explained by a reaction pattern containing a closed sequence. Koefoed has proposed the following chain reaction:

$$Fe^{++} + FeO_2H^{++} \rightleftharpoons Fe \cdot FeO_2H^{++++} \qquad 12$$
$$Fe \cdot FeO_2H^{++++} \rightleftharpoons OFeOH^+ + Fe^{+++} \qquad 23 \qquad \text{II}$$
$$OFeOH^+ + H_2O_2 \rightarrow Fe^{++} + O_2 + OH^- + H_2O \qquad 31$$

(Concerning details of this scheme the reader is referred to Koefoed's paper).

If we, as Koefoed did, consider the $OFeOH^+$-ion as the most reactive intermediate the action of the inhibitor must be the removal of that intermediate (with benzene as an example):

$$OFeOH^+ + C_6H_6 = Fe^{++} + C_6H_5OH + OH^- \qquad \overline{31}$$
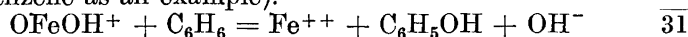
that is to say that the inhibitor itself as illustrated in Fig. 5 is oxidized by a chain reaction.
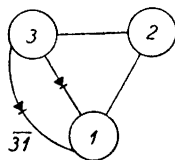

Fig. 5. Flow sheet of Koefoed's reaction cycle supplemented by reaction $\overline{31}$.

It does not seem unreasonable to assume that the phenol formed by reaction $\overline{31}$ again is oxidized to hydroquinone by a reaction similar to $\overline{31}$, because we know from the experiments that phenol also acts as an inhibitor.

In Koefoed's scheme the ferrous ion is presumed to act as a catalyst. Therefore, if we are able to increase the ferrous ion concentration in the reaction mixture, that should involve an increase of the rate of reaction. That is presumably what happens in the reacting mixtures containing benzene, phenol, or phenacetin when the rate of reaction suddenly increases, because, when hydroquinone is formed, it will react with ferric ions forming ferrous ions. At the same time the hydroquinone will be oxidized to quinhydrone in accordance with the brown colouring of the reaction mixture mentioned above.

From the above it follows that hydroquinone is to be expected to act, not as an inhibitor, but as a promotor for the reaction, which is in accordance with the experimental results given in Fig. 4.

CONCLUSION

Kinetic experiments on the influence of phenacetin, benzene, phenol, and hydroquinone under well defined conditions seem to indicate qualitatively that a reaction scheme for the Fe(III)-catalyzed hydrogen peroxide decomposition must be based on a closed sequence. Furthermore, they seem to confirm Koefoed's [1] assumption that ferrous ions act as a catalyst.

It appears from the experiments referred to in this paper and from earlier experiments [7] that benzene acting as an inhibitor successively is oxidized to phenol, hydroquinone, and finally to oxalic acid and carbon dioxide. Phenacetin, which is used as a stabilizer of medical hydrogen peroxide, obviously acts in the same way.

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