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## Ferric Catalyzed Hydrogen Peroxide Decomposition Inhibition by Acetanilide

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The several reported studies of the ferric catalyzed hydrogen peroxide decomposition have been reviewed recently by Abel.[3] A variety of conflicting mechanisms have been proposed, in most of which, in analogy to the bromine–bromide catalysis,[4] two oxidations states of iron, either ferrous and ferric or one of these with an unstable higher state,[5] reduce and oxidize the peroxide. This work is being published after some delay because it shows confirmation of a chain mechanism as proposed by Haber and Weiss[6] and amplified by Baxendale and coworkers[7] but discounted in recent reports.[3,8]

Certain student experiments had demonstrated that sometimes hydrogen peroxide decomposition in ferric solutions is delayed during an induction period. This investigation sought to determine the cause of this induction period and use it to further elucidate the mechanism of the reaction. It was found that the induction period was due to the inhibition of the reaction by acetanilide present as a preservative in commercial hydrogen peroxide and could be duplicated by adding acetanilide to the solutions of pure hydrogen peroxide. The rate of peroxide disappearance during this period is only a few per cent. of the maximum rate attained after the induction period ends.

The experimental techniques used in this work were essentially similar to those used by Andersen,[8] except, of course, that acetanilide when used was dissolved in the hydrogen peroxide stock solution. Chemicals used were of the highest quality available. Iron perchlorate solutions were obtained from reprecipitated ferric hydroxide and reagent grade perchloric acid or ferrous sulfate and barium perchlorate solutions.

Since the nature of the anions present influences the reaction rate,[9] only nitrate and perchlorate, those anions which form fewest metal complexes, were present. Experiments with nitrate present showed deviations from first order decomposition qualitatively like those found by Andersen[8] although the ferric and hydrogen ion concentrations were in a different range of magnitudes. In perchlorate solutions (nitrate absent) the decomposition was first order in agreement with the rate equation first proposed by Bertalan.[10] This nitrate effect is probably related to the inhibition by nitrate found by Taube and Bray[11] for the reaction between ozone and hydrogen peroxide, since the same free radical intermediates, OH and $HO_2$ are involved.

Table I

Effect of Conditions on Induction Period

| Expt. | $t$, °C. | $10^4 \times$ (acnd)[a] | ($H^+$)[a] | Induction, min. |
|---|---|---|---|---|
| 1 | 20 | 2.0 | 0.18 | 14 |
| 2 | 23.5 | 2.0 | .18 | 9 |
| 3 | 25 | 2.0 | .18 | 6 |
| 4 | 20 | 3.5 | .20 | 25 |
| 5 | 20 | 5.2 | .18 | 55 |
| 6 | 25 | 5.2 | .18 | 21 |
| 7 | 20 | 5.3 | .32 | 145 |
| 8 | 25 | 5.3 | .32 | 55 |
| 9 | 25 | 26.7[b] | .32 | 55 |

[a] Concentrations in moles/l. also ($Fe^{+++}$) = 0.11 and initial ($H_2O_2$) = 0.060. [b] Initial ($H_2O_2$) = 0.30.

Table I shows how the length of the induction period depends on certain conditions of the reaction. Comparing the expts. 1, 4 and 5 or 3 and 6 shows that the induction period is increased by increasing the acetanilide concentration at constant peroxide concentration in agreement with the hypothesis that acetanilide is being used up by reaction with chain carrying intermediates. But because the number of chain starting reactions is proportional to the initial peroxide concentration, the five-fold increase in acetanilide concentration in expt. 9 over expt. 8 is compensated for by the similar increase in peroxide concentration.

A comparison of expts. 1, 2 and 3, 5 and 6 or 7 and 8, shows that the inhibition of the reaction has an unusually high temperature coefficient, the rate of disappearance of acetanilide being increased by a factor of 2.5 for a 5° temperature rise. A comparison of expts. 5 and 7 or 6 and 8, shows that hydrogen ion slows down the disappearance of acetanilide by about the same factor as its slows down the hydrogen peroxide decomposition. This is consistent with the suggestion of Haber and Weiss[6] that the chain is started by a reaction of $HO_2^-$ with ferric ion.

The magnitude of the temperature coefficient of the induction period suggests that the destruction of the inhibitor involves two steps with normal temperature coefficients. Since it is unbelievable that the reaction between an inhibitor and a chain-carrying radical have an

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[1] Based on work done under the direction of the late W. C. Bray.

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[3] Abel, *Monatsh.*, **79**, 457 (1948).

[4] Bray and Livingston, This Journal, **45**, 1251 (1923).

[5] Bohnson and Robertson, *ibid.*, **45**, 2493 (1923); Bray and Gorin, *ibid.*, **54**, 2124 (1932).

[6] Haber and Weiss, *Proc. Roy. Soc. (London)*, **A147**, 332 (1934).

[7] Barb, Baxendale, George and Hargrave, *Nature*, **163**, 692 (1949).

[8] Andersen, *Acta Chem. Scand.*, **2**, 1 (1948).

[9] Simon, Haufe, Reetz and Preissler, *Z. anorg. allgem. Chem.*, **230**, 129 (1936).

[10] Bertalan, *Z. physik. Chem.*, **95**, 328 (1920).

[11] Taube and Bray, This Journal, **62**, 3357-3373 (1940).

appreciable heat of activation, it appears that the destruction of acetanilide follows such a scheme as acnd + OH → X, X + OH → Y, in which X is a free radical which is not sufficiently reactive to propagate the decomposition chain but yet an effective inhibitor and Y is a stable oxidation product of acetanilide. The removal of effective inhibitor then requires two chain-carrying radicals and hence depends twice on the heat of activation of the chain-initiating process. Since there is, no doubt, an inverse relationship between the acetanilide concentration and the steady state active radical concentration, this mechanism involving two radicals predicts an apparent negative order for the destruction of inhibitor, in agreement with the results in Table I showing the induction period more than proportional to the initial acetanilide concentration.

The strong piece of evidence presented by Haber and Weiss for their chain mechanism for the reaction is the extremely rapid disappearance of hydrogen peroxide during the oxidation of ferrous ion to ferric by the peroxide. Under certain conditions they were able to show the disappearance of hydrogen peroxide during this short interval to be several times that needed to oxidize the ferrous. In order to test the relationship between the effect of ferrous ion and the effect of acetanilide on hydrogen peroxide decomposition a number of experiments were run under the conditions of expt. 8 in Table I, except that a portion of the iron present in the solution at the start of the reaction was ferrous. Results of these experiments are given in Table II. It can be seen that ferrous ion decreases markedly the induction period, since the addition of ferrous ion to hydrogen peroxide solutions produces a large number of free radicals in a short time and hence causes considerable inhibitor destruction during that period. The third column in Table II gives the decrease in concentration of acetanilide during the oxidation of ferrous calculated under the assumptions that the induction period is due to the remaining acetanilide and the relationship between induction period and acetanilide concentration is that shown in Table I.

TABLE II

EFFECT OF FERROUS ION

| Initial ($Fe^{++}$) | Induction, min. | $10^4$ × acnd loss[a] | Mean cons. ratio | $H_2O_2$ loss[a] | $H_2O_2$ loss / acnd loss |
|---|---|---|---|---|---|
| 0.0000 | 55 | 0.00 | .. | 0.0000 | .. |
| 0.0073 | 26 | 2.3 | 1.27 | 0.0056 | 24 |
| .015 | 14 | 3.4 | 1.08 | .0089 | 26 |
| .022 | 5 | 4.3 | 1.0 | .0112 | 26 |
| .029 | 4.5 | 4.5 | 0.89 | .0112 | 25 |
| .036 | 3[b] | 4.7 | 0.81 | .011 | 23 |
| .015 | 0 | [c] | 1.14 | .0098 | .. |

[a] *In moles/l.* [b] *Too short for good estimate.* [c] Experiment with no acetanilide.

Although hydrogen peroxide is catalytically decomposed by the ferric ion after the ferrous has been oxidized, the rate is sufficiently slow, especially in the presence of acetanilide, that the peroxide concentration immediately after the ferrous oxidation can be extrapolated quite accurately. With an analysis of the peroxide stock solution, it is then possible to calculate the Haber and Weiss "mean consumption ratios," $\Delta H_2O_2/\Delta Fe^{++}$, as shown in column 4 of Table II; this quantity is 0.5 if the peroxide consumption is equivalent to the ferrous ion oxidized. It might be remarked that the equation developed by Abel neglecting the possibility of a chain reaction predicts a much smaller mean consumption ratio under the conditions of these experiments. It is of interest to compute in addition the hydrogen peroxide *decomposed*, that is, disappeared in excess of that needed to oxidize the ferrous ion; this is given in column 5, the ratio of this quantity to the acetanilide loss in column 6. From the proportionality of the peroxide and acetanilide losses it appears that the destruction of each depends in the same way on the concentrations of the other substances. Since the decomposition of peroxide is a sequence of two radical reactions, this is consistent with the mechanism of inhibitor destruction proposed on the basis of the experiments without ferrous ion. Since the peroxide loss is about 25 times the acetanilide loss, the specific rate of the acetanilide reaction is only about 4 times that of the peroxide decomposition; this is insufficient to explain the marked decrease in peroxide decomposition rate due to acetanilide without a chain mechanism.

The effect described here is exactly that expected of an inhibitor of a typical chain reaction and hence we are led to the conclusion that the ferric catalyzed hydrogen peroxide decomposition is a chain reaction as proposed by Haber and Weiss. The action of acetanilide appears to be the removal to two chain-carrying radicals by each acetanilide molecule.

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## 1-Pentenyl-1-trichlorosilane

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In a previous paper[1] the reaction of acetylene and trichlorosilane in the presence of peroxide giving 1,2-bistrichlorosilylethane was described. A two-step reaction was postulated.

$$RC{\equiv}CH + HSiCl_3 \xrightarrow{\text{Peroxide}} RCH{=}CHSiCl_3 \quad (1)$$

$$RCH{=}CHSiCl_3 + HSiCl_3 \xrightarrow{\text{Peroxide}} Cl_3SiRCHCH_2SiCl_3 \quad (2)$$

The first step involves the addition of one molecule of trichlorosilane to acetylene to give vinyl-

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[1] Burkhard and Krieble, THIS JOURNAL, **69**, 2687 (1947).