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Inhibition of the Fe^{3+}–H_2O_2 Reaction by Acetone

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The inhibition of the $Fe^{3+} + H_2O_2$ reaction by acetone is of the competitive type. Under the conditions of the experiments no complex is formed between acetone and Fe^{3+}. The results have been interpreted, in terms of Kremer and Stein's scheme, as indicating a binding of the secondary Fe^{3+}–H_2O_2 complex by acetone. From the results it appears that one acetone molecule can bind on the average, nine molecules of the secondary complex.

INTRODUCTION

The inhibitory effect of acetone on the ferric-ion-catalyzed decomposition of H_2O_2 was discovered by Garten (*1*). The effect was attributed in a general way to the scavenging of free radicals by acetone. The rate law, however, was not established and no definite mechanism has been proposed.

The purpose of the present investigation was to determine the rate law of inhibition and to establish its mechanism. Experiments were carried out at high $[H_2O_2]/[Fe^{3+}]$ ratios in order to be able to apply steady state analysis to the results.

EXPERIMENTAL

All materials used were either of analytical grade or were prepared from analytical grade reagents.

$Fe(ClO_4)_3$ was prepared from ferric ammonium sulfate. $Fe(OH)_3$ was precipitated with ammonia, then was washed free from it with water. The precipitate was dissolved in perchloric acid, and concentrated on a water bath, till crystallization. The crystals were filtered on sintered glass and stored wet.

H_2O_2 was irradiated with UV light for 30 min, then distilled in vacuum in an all-glass apparatus.

Ferric ion was determined iodometrically. H_2O_2 was titrated with permanganate. Acetone in the concentrations employed did not interfere with the determination of H_2O_2. Acetone was determined by measuring its absorption at 264 mμ. A calibration curve (a straight line) was prepared by using a series of dilutions of a stock solution. The stock solution has been standardized using the $NH_2OH{\cdot}HCl$–NaOH method (*2*).

The catalyst solution was prepared from a 0.1074 *M* $Fe(ClO_4)_3$ solution by diluting it and adding a sufficient amount of $HClO_4$ and $NaClO_4$ in order to give the desired catalyst concentration, pH, and ionic strength in the reaction mixture. pH was measured on a Beckman GS pH meter. The instrument was calibrated with a series of $HClO_4$ solutions having the same ionic strength as the reaction mixture. Constancy of temperature within 0.5°C was maintained during the measurement of pH.

The reactions were performed in a Y-shaped reaction vessel, one arm of which has been blown out to a bulb. Four milliliters of catalyst solution was introduced into one arm of the vessel and 2 ml each of H_2O_2 and acetone in the other. After attaining thermal equilibrium (20 min), the reactants were mixed, and transferred to the bulb. After the lapse of a suitable time interval, the reaction was stopped by blowing in 5 ml of 2 *M* H_2SO_4. The mixture was transferred to an Erlenmeyer flask and the remaining H_2O_2 was titrated with permanganate. An entire experiment usually consisted of eight independent runs.

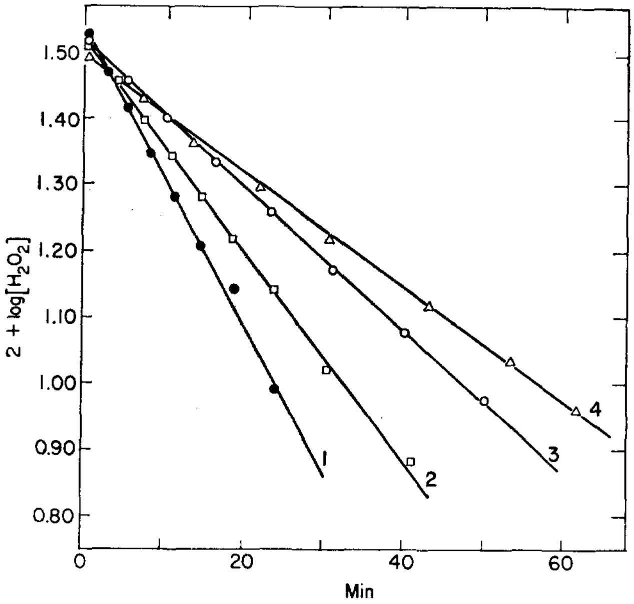

FIG. 1. First order plots for the decomposition of H_2O_2 in the presence of acetone, $[Fe^{3+}]_0 = 5.37 \times 10^{-3}$ *M*; pH = 2.05; *t* = 25.0°C; I.s. = 0.250 *M*. Curve 1, $[Ac]_0 = 0$ *M*; 2, $[Ac]_0 = 0.91 \times 10^{-3}$ *M*; 3, $[Ac]_0 = 2.28 \times 10^{-3}$ *M*; 4, $[Ac]_0 = 3.41 \times 10^{-3}$ *M*.

RESULTS

All experiments were performed at 25.0° ± 0.1°C, pH = 2.05, and at an ionic strength of 0.250 *M*. The concentration of the catalyst varied between 1.611×10^{-3} *M* and 5.37×10^{-3} *M*. The decomposition of H_2O_2 was followed between ~0.320 *M* and ~0.090 *M*. The range of concentration of acetone extended from 0.46×10^{-3} *M* to 3.41×10^{-3} *M*.

The reaction was first order in $[H_2O_2]$. Characteristic plots at $[Fe^{3+}]_0 = 5.37 \times 10^{-3}$ *M* are given in Fig. 1. (The symbol $[\ ]_0$ denotes total concentration.) The lines have no common origin, since the experiments started at slightly different $[H_2O_2]_0$. The first order rate constants k_i are summarized in Table 1 (Ac denotes acetone); k_i is

TABLE 1
FIRST ORDER RATE CONSTANTS AS A FUNCTION OF $[Ac]_0$ AT $[Fe^{3+}]_0 = 5.37 \times 10^{-3}$ *M*[a]

$[Ac]_0$ (*M*)	k_i (min^{-1})	k_i^{-1} (min)	$\frac{[Ac]_0}{[Fe^{3+}]_0} \cdot \frac{k}{k - k_i}$
0	4.98×10^{-2}	—	—
0.45×10^{-3}	4.18×10^{-2}	23.9	0.52
0.91×10^{-3}	3.60×10^{-2}	27.8	0.61
1.37×10^{-3}	3.15×10^{-2}	31.7	0.69
1.85×10^{-3}	2.79×10^{-2}	35.8	0.78
2.28×10^{-3}	2.51×10^{-2}	39.8	0.86
3.41×10^{-3}	1.97×10^{-2}	50.8	1.05

[a] *t* = 25.0°C; pH = 2.05; I.s. = 0.250 *M*; *k*, rate constant of the uninhibited reaction.

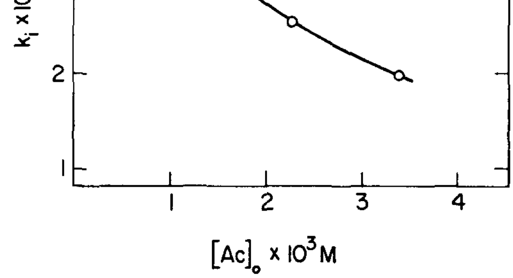

FIG. 2. First order rate constants as a function of $[Ac]_0$. $[Fe^{3+}]_0 = 5.37 \times 10^{-3}$ *M*; pH = 2.05; *t* = 25.0°C; I.s. = 0.250 *M*.

plotted as a function of $[Ac]_0$ in Fig. 2. Table 2 summarizes the results of an analogous series at $[Fe^{3+}]_0 = 1.611 \times 10^{-3}\,M$. A linear representation of the rate constants listed in Tables 1 and 2 is given in Fig. 3.

TABLE 2

FIRST ORDER RATE CONSTANTS AS A FUNCTION OF $[Ac]_0$ AT $[Fe^{3+}]_0 = 1.611 \times 10^{-3}\,M$

$[Ac]_0$ (M)	k_i (min^{-1})	k_i^{-1} (min)	$\frac{[Ac]_0}{[Fe^{3+}]_0} \frac{k}{k - k_i}$
0	1.313×10^{-2}	—	—
0.45×10^{-3}	1.092×10^{-2}	91.5	1.66
0.91×10^{-3}	0.942×10^{-2}	106	2.00
1.37×10^{-3}	0.830×10^{-2}	121	2.31
1.85×10^{-3}	0.737×10^{-2}	136	2.62
2.74×10^{-3}	0.598×10^{-2}	167	3.12

DISCUSSION

Our discussion will be based on Kremer and Stein's mechanism for the uninhibited reaction (*3*).

$$Fe^{3+} + HO_2^- \underset{2}{\overset{1}{\rightleftharpoons}} \underset{C_I}{Fe^{3+} \cdot HO_2^-}$$

$$\underset{C_I}{Fe^{3+} \cdot HO_2^-} \xrightarrow{3} \underset{C_{II}}{FeO^{3+}} + OH^-$$

$$\underset{C_{II}}{FeO^{3+}} + HO_2^- \xrightarrow{4'} FeOH^{2+} + O_2$$

Inhibitory action by acetone can be effected by complexing either Fe^{3+}, HO_2^-, $Fe^{3+}HO_2^-$, or FeO^{3+}.

By comparing the spectra of mixtures of Fe^{3+} + acetone and of H_2O_2 + acetone with that of the respective components, it has been found in both cases that, under our experimental conditions, there is negligible complex formation.

Reversible binding of $Fe^{3+}HO_2^-$ or FeO^{3+} will give rise to uncompetitive or competitive inhibition, respectively. In the following, we develop these cases in detail. [A discussion of the kinetics of inhibition is given in Ref. (*4*).]

In the case of uncompetitive inhibition, we have the additional equilibrium

$$\underset{[C_I]}{Fe^{3+} \cdot HO_2^-} + \underset{\{[Ac]_0 - [C_{III}]\}}{Ac} \overset{K_I}{\rightleftharpoons} \underset{[C_{III}]}{C_{III}}$$

$$[C_{III}] = \frac{[C_I][Ac]_0}{[C_I] + K_I} \qquad (1)$$

Assuming steady state for $[C_{II}]$ and $[C_I]$ we obtain

$$[C_{II}] = \frac{k_3[C_I]}{k_4[H_2O_2]} \qquad (2)$$

$$k_4 = k_4' \frac{K_{H_2O_2}}{[H^+]}$$

and

$$\{[Fe^{3+}]_0 - [C_I] - [C_{II}] - [C_{III}]\} [H_2O_2] - \frac{k_2 + k_3}{k'_1}[C_I] = 0 \qquad (3)$$

$$k'_1 = k_1 \frac{K_{H_2O_2}}{[H^+]}$$

Introducing $[C_{III}]$, $[C_{II}]$, and the concentration of C_I in the absence of acetone

$$[C_I]^* = \frac{[Fe^{3+}]_0[H_2O_2]}{[H_2O_2] + K_M'}$$

$$K'_M = \frac{k_2 + k_3}{k_1} + \frac{k_3}{k_4}$$

we obtain from (3)

$$\frac{[Ac]_0}{[Fe^{3+}]_0} \frac{[C_I]^*}{[C_I]^* - [C_I]} = 1 + \frac{K_1}{[C_I]} \qquad (4)$$

The steady state concentrations of C_I in the presence and absence of acetone are connected with the respective steady state decomposition rates by

$$V_i = 2\,k_3[C_I] \quad \text{and} \quad V = 2\,k_3[C_I]^* \qquad (5)$$

(The overall decomposition rate is twice that of step 3.) Introducing (5) into (4) we get the final result

$$\frac{[Ac]_0}{[Fe^{3+}]_0} \frac{V}{V - V_i} = 1 + 2k_3K_I \frac{1}{V_i} \qquad (6)$$

In the case of competitive inhibition, acetone combines reversibly with C_{II}

$$\underset{[C_{II}]}{FeO^{3+}} + \underset{\{[Ac]_0 - [C_{III}]\}}{Ac} \overset{K_I}{\rightleftharpoons} \underset{[C_{III}]}{C_{III}}$$

Proceeding as before we obtain the rate equation

$$\frac{[\mathrm{Ac}]_0}{[\mathrm{Fe}^{3+}]_0}\frac{V}{V-V_i} = 1 + 2k_4K_{\mathrm{I}}\frac{[\mathrm{H_2O_2}]}{V_i} \quad (7)$$

If the reaction is first order in $[\mathrm{H_2O_2}]$, (7) can be written in the equivalent form

$$\frac{[\mathrm{Ac}]_0}{[\mathrm{Fe}^{3+}]_0}\frac{k}{k-k_i} = 1 + 2k_4K_{\mathrm{I}}\frac{1}{k_i} \quad (8)$$

In the Appendix it will be shown that if the uninhibited reaction is first order in $[\mathrm{H_2O_2}]$, then the competitively inhibited reaction is also first order in $[\mathrm{H_2O_2}]$.

Our results in Fig. 3 agree with Eq. (8), but with the important difference that the intercept (A) is much smaller than 1.

The factor A can be accounted for if we express the concentration of unbound acetone as $[\mathrm{Ac}]_0 - A[\mathrm{C_{III}}]$. This expression implies that one inhibited molecule of $\mathrm{C_{II}}$ contains less than one molecule of acetone. Since this cannot be the case, we conclude that one molecule of acetone can deactivate many molecules of $\mathrm{C_{II}}$.

We arrive at a similar conclusion if we consider the absolute value of the rate constants. Maximum inhibition, i.e., the lowest observed rate (if acetone combines in the ratio 1:1 with iron) is given by the equation (*4*)

$$V_i = V\left(1 - \frac{[\mathrm{Ac}]_0}{[\mathrm{Fe}^{3+}]_0}\right)$$

or

$$k_i = k\left(1 - \frac{[\mathrm{Ac}]_0}{[\mathrm{Fe}^{3+}]_0}\right)$$

Taking the data for $[\mathrm{Fe}^{3+}]_0 = 5.37 \times 10^{-3}\,M$ and $[\mathrm{Ac}]_0 = 0.91 \times 10^{-3}\,M$, we calculate that the lowest value of k_i is $4.13 \times 10^{-2}\ \mathrm{min}^{-1}$. In fact, $k_i = 3.60 \times 10^{-2}\ \mathrm{min}^{-1}$ has been observed.

It is of interest to investigate whether the strong inhibitory effect could be due to the removal of free radicals from a chain reaction leading to $\mathrm{H_2O_2}$ decomposition (*1*). Free radical theories have been found to be unsatisfactory in explaining several aspects of the kinetics of $\mathrm{H_2O_2}$ decomposition (*3*). Nevertheless, one should not disregard it altogether as a possibility. If such a chain reaction exists, then acetone might supress the evolution of oxygen if it competes effectively for OH or $\mathrm{HO_2}$. Since, by continuous initiation, free radicals would be formed again from $\mathrm{H_2O_2}$ (its initial concentration is 100 to 700 times higher than that of acetone), acetone would be used up completely before any appreciable amount of $\mathrm{H_2O_2}$ had been decomposed. It is evident then that only a stable combination of acetone with the catalyst (or one of the catalyst substrate complexes) can explain the diminution of the rate in a constant ratio during the entire course of the reaction.

Returning to our formal equation of equilibrium

$$\frac{[\mathrm{C_{II}}]\{[\mathrm{Ac}]_0 - A[\mathrm{C_{III}}]\}}{[\mathrm{C_{III}}]} = K_{\mathrm{I}}$$

the following tentative mechanism is in accordance with it:

$$\mathrm{C_{II}} + \mathrm{Ac} \overset{K_1}{\rightleftharpoons} \mathrm{C_1} \quad (9)$$

$$\mathrm{C_1} + \mathrm{C_{II}} \xrightarrow{g_1} \mathrm{C_2}$$

$$\mathrm{C_2} + \mathrm{C_{II}} \xrightarrow{g_2} \mathrm{C_3} \qquad \mathrm{C_2} + \mathrm{C_{II}} \xrightarrow{d_2} \cdots$$

$$\mathrm{C_3} + \mathrm{C_{II}} \xrightarrow{g_3} \mathrm{C_4} \qquad \mathrm{C_3} + \mathrm{C_{II}} \xrightarrow{d_3} \cdots$$

$\mathrm{C_1}$, $\mathrm{C_2}$, $\mathrm{C_3}$ denote inactive complexes containing one, two, and three molecules of $\mathrm{C_{II}}$. After the binding of $\mathrm{C_{II}}$ by acetone the complex can grow by the addition of more molecules of $\mathrm{C_{II}}$. However, the addition of $\mathrm{C_{II}}$ can also cause a decomposition of the complex. The latter process dominates in the higher members and is neglected for $\mathrm{C_1}$. As a result of the simultaneous buildup and decomposition, a dynamic equilibrium is set up. The concentration of the individual complexes is then given by

$$[\mathrm{C_2}] = \frac{k_{g_1}}{k_{g_2} + k_{d_2}}[\mathrm{C_1}] = K_2[\mathrm{C_1}]$$

$$[\mathrm{C_3}] = \frac{k_{g_2}}{k_{g_3} + k_{d_3}}[\mathrm{C_2}] = K_3[\mathrm{C_2}] = K_2K_3[\mathrm{C_1}]$$

The total concentration of inactivated $\mathrm{C_{II}}$ is given by

$$[\mathrm{C_{III}}] = [\mathrm{C_1}] + 2[\mathrm{C_2}] + 3[\mathrm{C_3}] + \cdots$$

$$[\mathrm{C_{III}}] = [\mathrm{C_1}](1 + 2K_2 + 3K_2K_3 + \cdots)$$

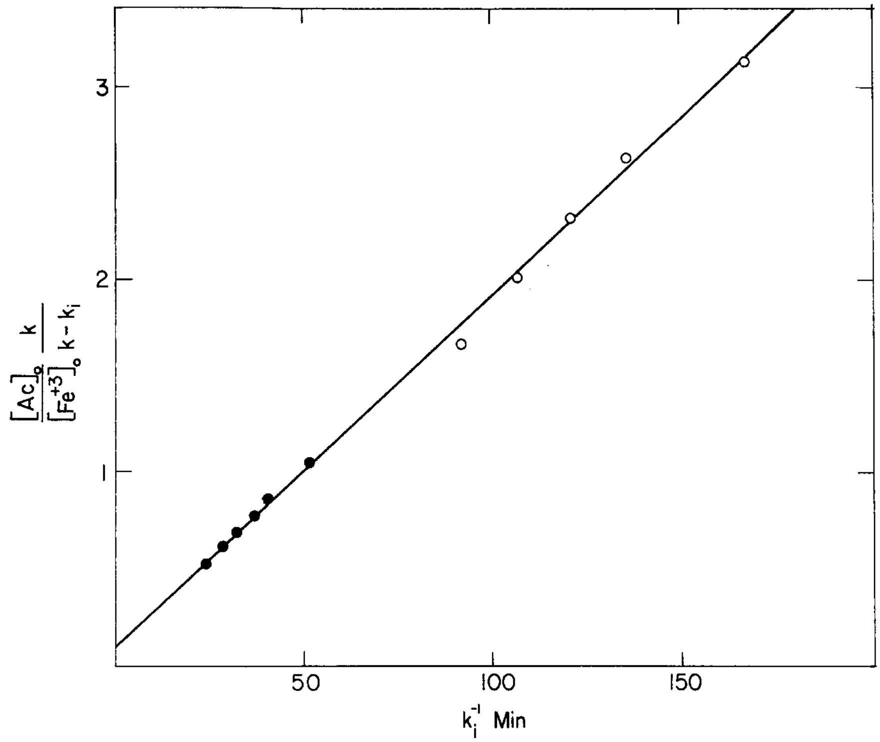

FIG. 3. $([Ac]_0/[Fe^{3+}]_0)\{k/(k-k_i)\}$ as a function of k_i^{-1} for the combined results of Tables 1 and 2: ●, $[Fe^{3+}]_0 = 5.37 \times 10^{-3}\,M$; ○, $[Fe^{3+}]_0 = 1.611 \times 10^{-3}\,M$; $t = 25.0$°C; pH = 2.05; I.s. = 0.250 M.

Introducing this result into (9) we obtain

$$\frac{[C_{II}][Ac]}{[C_{III}]} = \frac{K_1}{1 + 2K_2 + 3K_2K_3 + \cdots} = K_I$$

The concentration of unbound acetone is given by

$$[Ac] = [Ac]_0 - [C_1] - [C_2] - [C_3] \cdots$$

$$[Ac] = [Ac]_0 - [C_1](1 + K_2 + K_2K_3 + \cdots) \quad (10)$$

Expressing $[C_1]$ from (10) we obtain

$$[Ac] = [Ac]_0 - [C_{III}]\frac{1 + K_2 + K_2K_3 + \cdots}{1 + 2K_2 + 3K_2K_3 + \cdots}$$

Thus

$$A = \frac{1 + K_2 + K_2K_3 + \cdots}{1 + 2K_2 + 3K_2K_3 + \cdots}$$

If the higher K's tend to zero, A approaches a definite value. From our measurements $A = 0.11 \pm 0.02$. The reciprocal of A is the average chain length. It is about 9. From the slope of the straight line in Fig. 3 $k_4K_I = (9.02 \pm 0.11) \times 10^{-3}$ min^{-1} is obtained.

APPENDIX

We have to calculate the steady state concentration of C_I during inhibition. Using the condition of equilibrium to calculate $[C_{III}]$ and the condition of steady state for $[C_I]$ and $[C_{II}]$ we obtain Eq. (11) (below) where

$$B = ([Ac]_0 - [Fe^{3+}]_0)\frac{k_3}{k_4K_I}$$

$$D = 4[Fe^{3+}]_0\frac{k_3}{k_4K_I}$$

$$E = 2\frac{k_3}{k_4K_I}$$

$$[C_I] = \frac{[-(B + [H_2O_2] + K'_M) \pm \{(B + [H_2O_2] + K'_M)^2 + D([H_2O_2] + K'_M)\}^{1/2}]\,[H_2O_2]}{E([H_2O_2] + K'_M)} \quad (11)$$

The uninhibited reaction is first order in $[H_2O_2]$ if $[H_2O_2] \ll K'_M$. Equation (11) becomes then $[C_I] = \text{const.} [H_2O_2]$; the inhibited reaction will also be first order in $[H_2O_2]$.

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