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Ferric Ion Catalyzed Decomposition of Hydrogen Peroxide in Acetonitrile-Water Mediums[1]

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The Fe^{3+}-catalyzed decomposition of hydrogen peroxide has been investigated in mediums composed of water and acetonitrile in various ratios. The ratios of the amount of decomposed hydrogen peroxide to that of oxygen evolution are in proportion to the average ratios of acetonitrile concentration to hydrogen peroxide in the low acetonitrile content. It shows that the oxidant produced on the Fe^{3+}-catalyzed decomposition of hydrogen peroxide is hydroxyl radical. The linear relationship could not be found in high acetonitrile concentration. The oxidant produced on the Fe^{3+}-catalyzed decomposition of hydrogen peroxide in high acetonitrile concentration was discussed in relation to the oxidant (ferryl ion) produced in hemoprotein catalyzed decomposition of hydrogen peroxide.

Keywords——acetonitrile; ferric ion; hydrogen peroxide; hydroxyl radical; oxygen evolution; oxidant; tris(acetylacetonato)iron(III)

The ferric ion catalyzed decomposition of hydrogen peroxide in an acidic aqueous solution has long been of interest and has received extensive study. Recently, Walling and Goosen[3] reported a study of the retarding effect of organic substances on the Fe^{3+}-catalyzed decomposition of hydrogen peroxide which strongly supported the redox chain mechanism developed by Barb *et al.*[4] on the basis that suitable substances act as effective traps for hydroxyl radicals which normally propagate the chain. In contrast, Groves and Van Der Puy[5] proposed that the Fe^{3+}-, or Fe^{2+}-catalyzed decomposition of hydrogen peroxide in acid acetonitrile produced an iron-bound oxidant, not a free hydroxyl radical, on the basis of substituent derived direct effects during hydroxylation of cyclohexanol. Kimura[6] has similarly presented a novel stereochemical feature of epoxidation of olefins accompanied with the $Fe^{3+}(acac)_3$-catalyzed decomposition of hydrogen peroxide in acetonitrile. The difference of species proposed as oxidants in acid aqueous solution and in acid acetonitrile led us to investigate (the amount of oxygen evolution during) the Fe^{3+}-catalyzed decomposition of hydrogen peroxide in a medium composed of water and acetonitrile in various ratios, the results of which will be presented here.

Results and Discussion

According to Walling and Goosen,[3] the reaction is considered to involve the following steps:

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[1] This paper constitutes Part X of the series entitled "Metal Ion Catalyzed Oxidation of Steroids;" Part IX: M. Kimura, Y. Jin, and T. Sawaya, *Chem. Pharm. Bull.* (Tokyo), **27**, 710 (1979).

[2] Location: *Nishi-6-chome, Kita-12-jo, Kita-ku, Sapporo, 060 Japan.*

[3] C. Walling and A. Goosen, *J. Am. Chem. Soc.*, **95**, 2987 (1973).

[4] W.G. Bard, J.H. Baxendale, P. George, and K.R. Hargrave, *Trans. Faraday Soc.*, **47**, 591 (1951).

[5] J.T. Groves and M. Van Der Puy, *J. Am. Chem. Soc.*, **96**, 5274 (1974); *Idem, ibid.*, **98**, 5290 (1976).

[6] M. Tohma, T. Tomita, and M. Kimura, *Tetrahedron Lett.*, **1973**, 4359; T. Yamamoto and M. Kimura, *Chem. Commun.*, **1977**, 948.

$$Fe^{3+} + H_2O_2 \xrightarrow{k_1} Fe^{2+} + H^+ + HO_2\cdot \quad (1)$$

$$Fe^{2+} + H_2O_2 \xrightarrow{k_2} Fe^{3+} + OH^- + HO\cdot \quad (2)$$

$$HO\cdot + H_2O_2 \xrightarrow{k_3} H_2O + HO_2\cdot \quad (3)$$

$$HO_2\cdot + Fe^{3+} \xrightarrow{k_4} Fe^{2+} + H^+ + O_2 \quad (4)$$

$$HO_2\cdot + Fe^{2+} \xrightarrow{k_5} Fe^{3+} + HO_2^- \quad (5)$$

$$HO\cdot + RH \xrightarrow{k_6} H_2O + R\cdot \quad (6)$$

$$R\cdot + O_2 \longrightarrow RO_2\cdot \xrightarrow[H^+]{Fe^{2+}} ROOH + Fe^{3+} \quad (7)$$

At a high enough substrate concentration reaction (6) becomes the major termination step, leading to kinetic expressions:

$$-d[H_2O_2]/dt = 2k_1[H_2O_2][Fe^{3+}]\{1+(k_3[H_2O_2]/k_6[RH])\} \quad (8)$$

$$d[O_2]/dt = k_1[H_2O_2][Fe^{3+}](k_3[H_2O_2]/k_6[RH]) \quad (9)$$

Eqs. (8) and (9) give the following eqs. (10) and (11),

$$-d[H_2O_2]/2d[O_2] = 1+(k_6[RH]/k_3[H_2O_2]) \quad (10)$$

$$-\varDelta(H_2O_2)/2\varDelta(O_2) = 1 + \langle(k_6/k_3)[RH]/[H_2O_2]\rangle \quad (11)$$

where $-\varDelta(H_2O_2)$, $\varDelta(O_2)$, and $\langle[RH]/[H_2O_2]\rangle$ represent the amount of decomposed hydrogen peroxide, that of oxygen evolution, and the average value of the ratio, $[RH]/[H_2O_2]$, during the reaction, respectively. From the eq. (11) plots of observed ratios of H_2O_2 disappearance to O_2 evolution *vs.* $\langle[RH]/[H_2O_2]\rangle$ should be linear with the intercept of unity, and with the slope of k_6/k_3 which may be compared with reference data from radiation chemistry,[7] where the Fe^{3+}-catalyzed decomposition of hydrogen peroxide produces hydroxyl radicals as a principal oxidant.

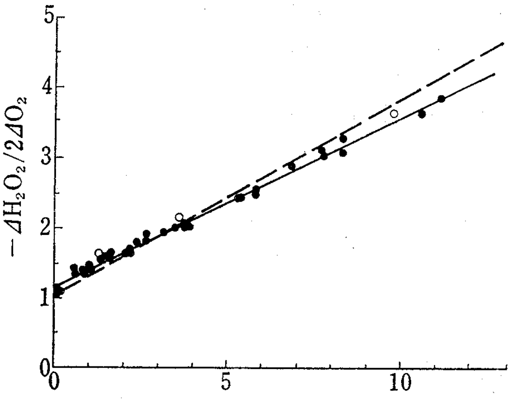

Fig. 1. Effect of a Small Amount of Acetonitrile on the Amount of Oxygen Evolution in Fe^{3+}-catalyzed Decomposition of H_2O_2

(----): calculated line from eq. (11) with k_3 and k_1 in the reference;[7] (●): see the experimental part; (○): $NaClO_4$ and $HClO_4$ were not added to adjust the ionic strength and pH; $[H_2O_2]$, 0.6—0.3 M; $[CH_3CN]$, 0—6 M; $[Fe^{3+}]$ 1—2×10^{-3} M; temperature, 30°.

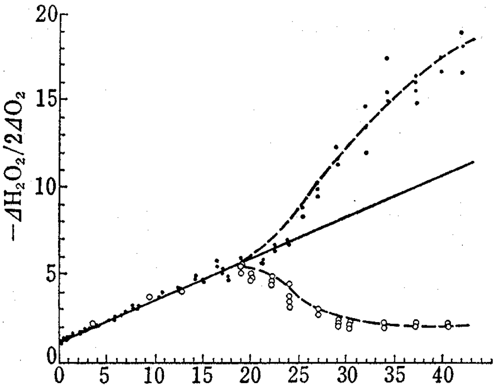

Fig. 2. Effect of Acetonitrile on the Amount of Oxygen Evolution in Fe^{3+}-catalyzed Decomposition of H_2O_2

$[CH_3CN]$: 0—18 M; Other conditions: the same as Fig. 1.

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[7] L.M. Dorfman and G.E. Adams, *NSRDS-NBS*, **46** (1973).

Figure 1 shows the results which were obtained in the solution containing a relatively small amount of acetonitrile (0—6 M), together with the predicted linear line from the eq. (11) with the reference values of k_6 (3.5×10^6 M^{-1}sec^{-1}) and of k_3 (1.2×10^7 M^{-1}sec^{-1}) on the reactivity of the hydroxyl radical in aqueous solution.[7] We can see that the data yield roughly the predicted linear plots with intercept of unity and a slope of 0.25 (calculated value: 0.29). These results correspond well with those concerned with acetonitrile which is a very poor trap for the hydroxyl radical in comparison with *tert*-BuOH(k_6: 5.2×10^8 M^{-1}sec^{-1}) or acetone (k_6: 6.6×10^7 M^{-1}sec^{-1}) investigated by Walling *et al.*, and may indicate that the redox chain mechanism developed by these investigators,[3] that is, the mechanism involving free hydroxyl radicals as an oxidant is effective in 0—6 M (0—25%) acetonitrile aqueous solutions.

Figure 2 shows the results on varying widely acetonitrile content (0—18 M; 0—95%). The plots at rather high acetonitrile concentration ($\langle[CH_3CN]/[H_2O_2]\rangle > 25$; [acetonitrile] >8 M or 40%) deviate from the extrapolation of the line which was found in low acetonitrile concentration and was in agreement with the eq. (11) as shown in Figs. 1 and 2 ($\langle[CH_3CN]/[H_2O_2]\rangle < 15$). In an acidic solution, plots of $-\Delta H_2O_2/2\Delta O_2$ *versus* $\langle[CH_3CN]/[H_2O_2]\rangle$ deviate upward with increasing acetonitrile content, that is, oxidative equivalents of hydrogen peroxide are consumed by acetonitrile over the value expected from the reactivity of hydroxyl radicals in an acidic aqueous solution. This apparently means that a stronger oxidant (Ox–A) is formed in acidic acetonitrile than in an acidic aqueous solution. On the other hand, the plots for the solution involving no added acid deviate downward, and the value of $-\Delta H_2O_2/2\Delta O_2$ becomes 2.0—2.5 in the high acetonitrile contents, far smaller than 10—11, the value expected from the hydroxyl radical chain mechanism in an acidic aqueous solution. This indicates that the larger portion of oxidative equivalents of hydrogen peroxide are used in the oxidation of hydrogen peroxide, and the produced oxidant (Ox–B) is apparently too weak to oxidize acetonitrile.

In short, the characters of oxidants produced during the Fe^{3+}-catalyzed decomposition of hydrogen peroxide in acetonitrile, seem to depend on the amount of added acid. The acid dependent transition of Ox–B to Ox–A in an acetonitrile solution is shown in Fig. 3, where the value of $-\Delta H_2O_2/2\Delta O_2$ changes rapidly from 2.0—2.5 (Ox–B) to a value larger than 15 (Ox–A) between 10^{-3} M of added perchloric acid and 10^{-2} M. Acid dependent behavior similar to Fe^{3+}-catalyzed reaction was also observed in Fe^{3+}(acac)$_3$-catalyzed decomposition of hydrogen peroxide as shown in Fig. 3.

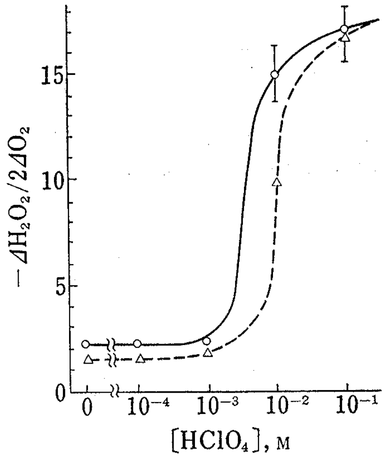

Fig. 3. Effect of Perchloric Acid on Oxygen Evolution in Fe^{3+}- and Fe^{3+}(acac)$_3$-catalyzed Decomposition of H_2O_2

[Fe^{3+}]: 2×10^{-3} M; [CH_3CN]: 18 M; [H_2O_2]: 0.5 M; (○): Fe(ClO_4)$_3$; (△): Fe(acac)$_3$; temperature: 30°.

The character of oxidants produced on Fe^{3+}-catalyzed decomposition of hydrogen peroxide in acetonitrile–water mediums depended on the composition of acetonitrile and water, and on the acid concentration in an acetonitrile solution as described above. Groves and Van Der Puy[5] observed similarly that the product distribution in the oxidation of cyclohexanol with Fe^{3+}- and Fe^{2+}-catalyzed decomposition of hydrogen peroxide depended on the water and acid content in the solution. The ratios of the yield of monohydroxylation products, cyclohexanediols (⟨OH⟩) to the yield of dehydrogenation product, cyclohexanone (⟨CO⟩), ⟨OH⟩/⟨CO⟩ are in the orders: Ox–A(2.0) > ·OH(0.6) > Ox–B(0.3) for Fe^{2+}-catalyzed oxidation; Ox–A(1.0) > Ox–B(0.5) for Fe^{3+}-catalyzed oxidation. It may be worthwhile to note that these sequences of ⟨OH⟩/⟨CO⟩ are similar to the order of values of $-\Delta H_2O_2/2\Delta O_2$ as shown in Fig. 2.

In a low concentration of acetonitrile (0—25%), the hydroxyl radical produced in the chain reaction (1)—(7) was an effective oxidant. We run here into questions of what kind of changes occur to the reaction steps (1)—(7) with an increase of acetonitrile and/or acid concentration in acetonitrile, and what kind of chemical species are Ox–A and Ox–B. One of the most attractive answers seems to be the possible competition of the hydroxyl radical and ferryl ion paths which have been discussed in terms of the following equilibrium (12) by Chahill and Taube:[8]

$$\mathrm{Fe^{3+} + HO\cdot \rightleftarrows Fe^{4+}\text{-}OH(Ox\text{-}A) \rightleftarrows Fe^{4+}\text{-}O(Ox\text{-}B) + H^+} \qquad (12)$$

However, the real situation of oxidants (Ox–A, Ox–B) may not be so simple, but more complex and beyond pur present knowledge. Such details of oxidants produced in Fe^{3+}-catalyzed decomposition of hydrogen peroxide in a non-aqueous environment remain as subjects for understanding the biological hydroxylation mechanism and for creating selective oxidation processes in organic chemistry.

Experimental

Reactions were carried out in magnetically stirred vessels thermostated at 30°, by mixing Fe^{3+} solution in the side chamber to H_2O_2 solution in the main reaction vessel after equilibration of both solutions with O_2 (at the reaction temperature). Amount of O_2 evolution was measured with a gas-buret connected to the reaction vessel. After 30—40% decomposition of H_2O_2, the reaction solution was quenched by pouring into chilled dil. H_2SO_4, and the H_2O_2 residue was titrated with $KMnO_4$. All aqueous solution were adjusted to an ionic strength of 0.1 and a pH of 1.6 with $NaClO_4$ and $HClO_4$. Acetonitrile was purified to transmission over 85% through 1 cm layer at 210 nm by distilling over P_2O_5. All other chemicals were of commercial origin in the highest grade.

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[8] A.E. Chahill and H. Taube, *J. Am. Chem. Soc.*, 74, 2312 (1952).