Nature of Intermediates in the Catalytic Decomposition of Hydrogen Peroxide by Ferric Ions
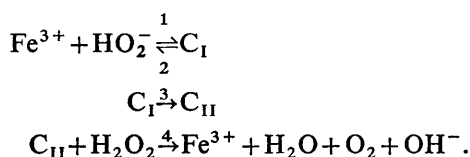
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The structure of the secondary iron(III)-hydrogen peroxide complex (C_{II}) is investigated on the basis of a previously established ion-pair structure ($Fe^{+3}HO_2^-$) for C_I. Consideration of free radical mechanisms, following a hypothetical reduction of C_I to C_{II}, shows that such a reduction in the transition $C_I \rightarrow C_{II}$ is excluded. No transient change of pH is observed during the decomposition even under circumstances in which C_{II} accumulates. This indicates that the acid equivalent, formed simultaneously with C_I, disappears upon the formation of C_{II}. The velocity constant of the transition is independent of pH. It is concluded, therefore, that the process consists of a loss of OH^- ions. C_{II} is identified as FeO^{3+}.

Titrimetric and spectrophotometric measurements indicated the participation of two intermediate complexes in the catalytic decomposition of dilute solutions of H_2O_2 ($\sim 10^{-1}$ M or less) by Fe^{3+} ions :[1]

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

$$C_I \overset{3}{\rightarrow} C_{II}$$

$$C_{II} + H_2O_2 \overset{4}{\rightarrow} Fe^{3+} + H_2O + O_2 + OH^-.$$

C_I has been identified [2,3] as $Fe^{3+}HO_2^-$. The structure of C_{II}, however, remained uncertain and it forms the subject of the present investigation.

In part 1 the question of the oxidation state of C_{II} is discussed. It is shown that free radical mechanisms, resulting from a hypothetical reduction of C_I lead to mechanisms which are in disagreement with the experiment. From this, it is inferred that both C_I and C_{II} are in the same state of oxidation. In part 2 the protolytic state of C_{II} is discussed. Direct experimental evidence is given that C_{II} is formed from C_I by a loss of OH^- ions. It is concluded that C_{II} can be identified as FeO^{3+}.

PART 1

H_2O_2 contains two equivalents of oxidation or reduction. Therefore its catalytic decomposition through intermediate complexes with Fe^{3+} ion can be, in principle, divided into one-equivalent oxidation-reduction steps. It is a relevant fact in this connection that O_2 is evolved from intact O—O bonds, whether H_2O_2 is decomposed by catalase, ferric complexes [4] or Fe^{3+} ions.[5] Thus, the complete oxidation of one H_2O_2 molecule is accompanied by the reduction of a second. Furthermore, it has been demonstrated that the oxidation of ethyl alcohol by C_{II} competes with O_2 evolution.[6] Thus, it is the H_2O_2 molecule forming the complexes with Fe^{3+} ion that is reduced, while an uncombined H_2O_2 is oxidized.

The starting point of the discussion is the assumption that a univalent reduction

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of C_I occurs in the system. Then, in order to preserve the internal oxidation-reduction balance of the molecule, the formation of OH radicals must be postulated.

$$\{FeH_2O_2\}^{3+} \xrightarrow{3'} \{FeOH\}^{3+} + OH.$$
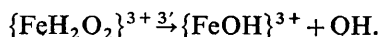
The reduction of C_I by an external reduction agent has been excluded [ref. (1)].

The resulting OH radicals must quantitatively be reduced to water, otherwise O_2 whose atoms originate from different H_2O_2 molecules would be formed. Reduction can occur either by H_2O_2 or Fe^{3+} ion (it being oxidized to the $+4$ state). A reduction by C_{II} is equivalent to the reversal of (3'): it does not lead to decomposition. First the reaction with H_2O_2 is discussed.
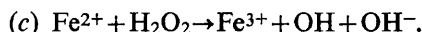
$$(a) \quad HOOH + OH \rightarrow HO_2 + H_2O.$$

The HO_2 radical formed is the source of O_2 in a system where univalent changes occur and both of its atoms come from the same molecule. Fe^{3+} ion, H_2O_2 and C_{II} are all potential oxidation agents for HO_2. We treat the three cases separately.

If HO_2 is oxidized by Fe^{3+} ion:

$$(b) \quad Fe^{3+} + HO_2 \rightarrow Fe^{2+} + H^+ + O_2,$$
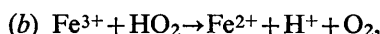
the resulting Fe^{2+} ion is rapidly reoxidized by H_2O_2 :[7]

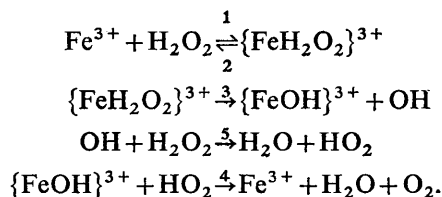$$(c) \quad Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH + OH^-.$$

In this case, the combination $(a), (b), (c)$ provides a parallel path to reaction (4) for the production of O_2. This path is stationary as a consequence of the high reactivity of free radicals and the known high velocity constant of (c). According to this mechanism, the accumulation of C_{II} at low $[H_2O_2]$ would not upset the steady-state O_2 evolution. Step 4 would become insignificant compared with the steady-state chain-evolution of O_2. The resulting rate equation would be identical with that of Barb et al.[8] which is at variance with the experimental results at low $[H_2O_2]$.

If the oxidation of HO_2 by H_2O_2 is assumed,

$$(d) \quad HOOH + HO_2 \rightarrow OH + H_2O + O_2,$$
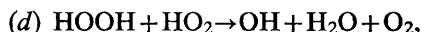
then the combination $(a), (d)$ must be considered as a possible side-reaction for O_2 production. The kinetic analysis of this scheme reveals that it is also incompatible with the experimental results.

Assuming a reaction between C_{II} and HO_2 we can construct the following sequence of reactions :

$$Fe^{3+} + H_2O_2 \underset{2}{\overset{1}{\rightleftharpoons}} \{FeH_2O_2\}^{3+}$$

$$\{FeH_2O_2\}^{3+} \xrightarrow{3} \{FeOH\}^{3+} + OH$$

$$OH + H_2O_2 \xrightarrow{5} H_2O + HO_2$$

$$\{FeOH\}^{3+} + HO_2 \xrightarrow{4} Fe^{3+} + H_2O + O_2.$$

In the appendix it is shown that this scheme is kinetically correct, if the additional assumption, $k_5[H_2O_2] \ll k_4[C_{II}]$ is introduced. It is, however, untenable on chemical grounds. Data in ref. (1), reproduced in fig. 4 indicate that, at low $[H_2O_2]/[Fe^{3+}]$ ratios, C_{II} can accumulate in a concentration as high as 10^{-3} M. This mechanism requires a simultaneous build-up of $[OH]$ equal to $[C_{II}]$. In view of the high reactivity of OH radicals, this result seems very unlikely and therefore presents a serious drawback to the mechanism.

There exists another group of mechanisms which are based on an alternative reaction of OH radicals with Fe^{3+} ion. In constructing these schemes, however, it must be realized that H_2O_2 competes with Fe^{3+} for OH. There is evidence that the reaction of OH radicals with H_2O_2 is very rapid [9, 10] and, in addition, the decomposition is usually carried out in excess H_2O_2 over Fe^{3+} ions. To the extent, however, that this reaction becomes part of the mechanism it is open to the objections raised above.

These considerations lead to the conclusion that there is no reduction in the transition from the primary to the secondary complex. Thus, the latter still possesses the two oxidation equivalents of the parent H_2O_2 molecule.

PART 2

Information regarding the protolytic state of the intermediate complexes can be obtained on the basis of the following consideration. It has been observed [2] that the formation constant of C_I in acid solution (pH ~ 2 or less) is inversely proportional to $[H^+]$. The formation of C_I in this pH range is accompanied, therefore, by the production of an equimolar amount of H^+ ions. The overall decomposition of H_2O_2, on the other hand, does not affect the pH of the solution. Thus, there must occur a release of OH^- ions or a recapture of protons in some of the subsequent steps. This step can be located by measuring the extent of the (transient) acidification of the reaction mixture. Since $\Delta[H^+]$ is equal to the sum of the concentration of intermediates which are formed prior to the disappearance of H^+ ions, it is equal either to $[C_I]$, or to $[C_I] + [C_{II}]$, depending on whether H^+ ions are consumed in step 3 or 4. In order to decide between these two possibilities, the change of pH was measured under conditions wherein the formation of C_I was negligible, while at the same time $[C_{II}]$ became comparable to the $[H^+]$ of the solution. These conditions were realized at low $[H_2O_2]$ (10^{-2}-10^{-3} M), as the velocity of decomposition of C_{II} is affected by $[H_2O_2]$, while that of C_I is not. Since the formation of C_I is slight even at high $[H_2O_2]$ (10^{-1} M), as judged by the strict proportionality between $[H_2O_2]$ and decomposition velocity, we obtain $\Delta[H^+] = 0$ and $\Delta[H^+] = [C_{II}]$ in the two cases.

EXPERIMENTAL

The preparation of materials has been described earlier.[1] A Beckman GS pH meter, sensitive to ± 0.001 pH was used. The calomel electrode was filled with 4 N NaCl. An electrolyte bridge, consisting of 0.24 N $NaClO_4$, was between the calomel electrode and the solution. The pH meter was calibrated with a series of $HClO_4$ solutions ranging from 2.95×10^{-2} to 2.95×10^{-3} M. Varying amounts of $NaClO_4$ were added in order to adjust the ionic strength to 0.250 M. The solutions were thermostatted. The response of the pH meter to the addition of small amounts of H^+ ions to the catalyst solution was checked by measuring the pH of three solutions. The first was prepared by diluting the doubly concentrated catalyst with an equal volume of water. The other solutions contained 3.9×10^{-4} and 7.8×10^{-4} M $HClO_4$ in addition. The pH meter registered an increase of 3.3×10^{-4} and 7.6×10^{-4} M respectively. The pH meter was rechecked during the actual experiments between every two measurements.

RESULTS AND DISCUSSION

The results of the measurement of the pH during the reaction is depicted in fig. 1. The computed values of $[C_{II}]$ are also presented. The reaction itself is identical with that described in detail in table 4 of ref. (1).

It is seen that there is no perceptible increase in acidity, thus H^+ ions are consumed in step 3. To decide whether there is a release of OH^- ions or a recapture of protons, the pH dependence of k_3 was investigated. The absolute value of k_3 cannot be obtained from measurement of the steady-state reaction velocity, which shows a strictly proportional dependence on $[H_2O_2]$, as observed up to several tenths of molar $[H_2O_2]$. However, the ratio of the decomposition velocity and of the optical
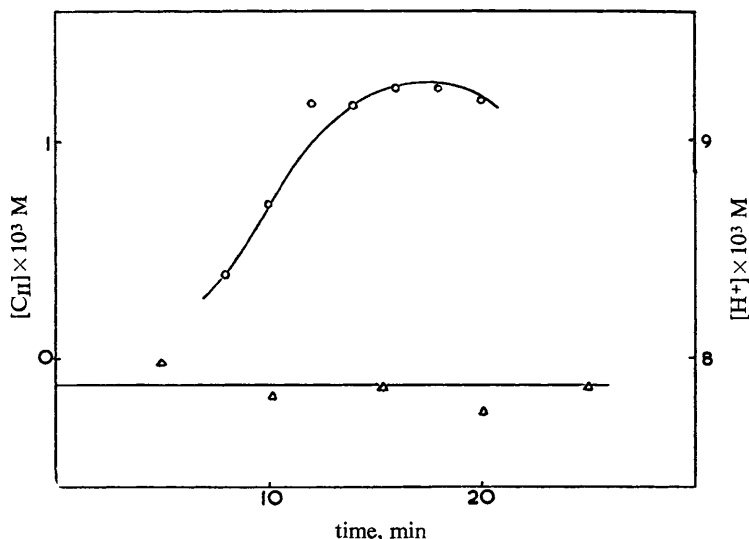
FIG. 1.—Change of $[C_{II}]$ and $[H^+]$ during the reaction.

$[Fe^{3+}]_t = 7 \cdot 24 \times 10^{-3}$ M; $[H_2O_2]_0 = 2 \cdot 28 \times 10^{-2}$ M; $t = 27 \cdot 0°C$; ionic strength $= 0 \cdot 255$ M.

$\bigcirc$ $[C_{II}]$; $\triangle$ $[H^+]$

density of the system (measured against a pure catalyst solution) gives directly $k_3/(\varepsilon_I - \varepsilon_{Fe})$, provided that the contribution of C_{II} to the o.d. is small. A small correction for the latter has been applied according to a procedure previously described.[1] ε_I and ε_{Fe} denote the coefficients of absorption of C_I and Fe^{3+} ion. The dependence of $k_3/(\varepsilon_I - \varepsilon_{Fe})$ on pH is shown in table 1. It is seen that $k_3/(\varepsilon_I - \varepsilon_{Fe})$, thus k_3 itself, is

TABLE 1

| $[H^+]$, M	$k_3/(\varepsilon_1 - \varepsilon_{Fe})$ M cm/min
$0 \cdot 78 \times 10^{-2}$	$8 \cdot 12 \times 10^{-2}$
$1 \cdot 67$	$8 \cdot 28$
$2 \cdot 48$	$7 \cdot 93$

$t = 27 \cdot 0°C$; ionic strength $= 0 \cdot 255$ M.

independent of pH. The simplest conclusion is that there occurs a release of OH^- ions in step 3, rather than an absorption of protons. On the basis of an ion-pair structure for C_I, this evidence establishes the formula of C_{II} as FeO^{3+}:

$$\{Fe^{3+} \, ^-OOH\} \xrightarrow{3} FeO^{3+} + OH^-.$$
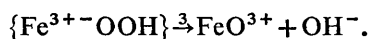
This mode of break-up of the HO_2^- ion involves a linear transition complex and a shift of the negative charge from the peripheral to the central oxygen atom of HO_2^- in the transition state.

An alternative sequence of reactions, however, involving a cyclic transition complex, following Wang,[11] fits the experimental data equally well,
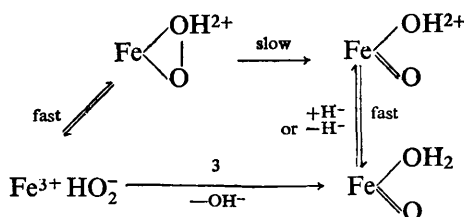
provided that the last acid-base equilibrium is largely shifted to the acid side. The structure of the final product in both cases is the same.

APPENDIX

Solving the resultant rate equations for the steady state we obtain

$$[C_{II}] = \frac{k_3[C_I]}{k_4[C_{II}]}\left(1 + \frac{k_4[C_{II}]}{k_5[H_2O_2]}\right).$$

Agreement with experiment can be reached if we assume that

$$1 \ll (k_4[C_{II}])/k_5[H_2O_2].$$

Then

$$-\frac{d[H_2O_2]}{dt} = \frac{[Fe^{3+}]_{total}[H_2O_2]}{[H_2O_2] + \dfrac{k_2+k_3}{k_1} + \dfrac{k_3}{k_5}}$$

The validity of this equation for high $[H_2O_2]/[Fe^{3+}]$ has been proved.[1]

In order to treat the kinetics at low $[H_2O_2]/[Fe^{3+}]$ ratios, the concentration of free radicals must be considered. For the HO_2 radical

$$d[HO_2]/dt = k_5[OH][H_2O_2] - k_4[C_{II}][HO_2].$$

At the maximum,

$$[HO_2]_{max}/[H_2O_2] = k_5[OH]/k_4[C_{II}].$$

Because of the inequality cited above and $[C_{II}] \lesssim [Fe^{3+}]_t \ll [H_2O_2]$ at high $[H_2O_2]/[Fe^{3+}]$, we obtain: $k_5/k_4 \ll 1$. Furthermore, from stoichiometry, $[OH] = [C_{II}] - [HO_2] \lesssim [C_{II}]$.

Thus

$$[HO_2]_{max}/[H_2O_2] \ll 1.$$

A steady-state concentration of HO_2 is always established. We can write, accordingly

$$d[O_2]/dt = k_4[C_{II}][HO_2] = k_5[OH][H_2O_2].$$

$[HO_2]$ is always negligible in comparison to $[H_2O_2]$. But it must also be negligible in comparison to $[C_{II}]$ and $[OH]$. Were it not, a steady-state for these two intermediates would be established too and the reaction itself would be stationary at low $[H_2O_2]/[Fe^{3+}]$ ratios. Since it is not, and $[OH]+[HO_2] = [C_{II}]$, $[C_{II}] \approx [OH]$ must exist. This near equality modifies the above equation to

$$d[O_2]/dt = k_5[C_{II}][H_2O_2],$$

which is the correct dependence of $d[O_2]/dt$ on $[C_{II}]$ and $[H_2O_2]$.[1]

[1] Kremer and Stein, *Trans. Faraday Soc.*, 1959, **55**, 959.
[2] Evans, George and Uri, *Trans. Faraday Soc.*, 1949, **45**, 230.
[3] Kremer and Stein, *2nd Int. Congr. Catalysis*, Paris (1960), vol. 1, p. 551.
[4] Jarnagin and Wang, *J. Amer. Chem. Soc.*, 1958, **80**, 786.
[5] Anbar, *J. Amer. Chem. Soc.*, 1961, **83**, 2031.
[6] Kremer, *Nature*, 1959, **184**, 720.
[7] Haber and Weiss, *Proc. Roy. Soc. A*, 1934, **147**, 332.
[8] Barb *et al.*, *Trans. Faraday Soc.*, 1951, **47**, 591.
[9] Frost and Oldenberg, *J. Chem. Physics*, 1936, **4**, 781.
[10] Weiss, *Adv. Catalysis*, 1952, **4**, 343.
[11] Jarnagin and Wang, *J. Amer. Chem. Soc.*, 1958, **80**, 6977.