# *Kinetics of the Acid-Catalyzed Peroxide Oxidation of 4-Hydroxybenzaldehyde in Acetic Acid*

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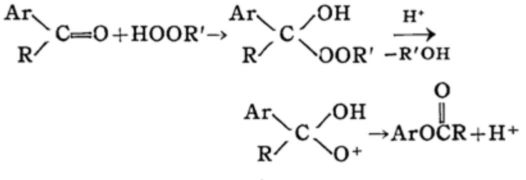
It is well known that aromatic ketones and aldehydes give on oxidation with peroxides (e. g., hydrogen peroxides or organic peracids) aryl esters or their hydrolysis products, i. e., phenols and carboxylic acids[1-3].

In general, the reaction is acid-catalyzed. It is of interest to note that *o*- or *p*-hydroxyl, amino or mercapto group facilitates the reaction to such an extent that it takes place at a high pH even in aqueous alkaline media[4], where a mechanism involving an initial attack of hydrogen peroxide to the active hydrogen of these groups was postulated[5]. In contrast, the reaction in acidic media occurs without these activating groups[6,7]. In this case, the mechanism has been suggested to be an addition of peroxide to the carbonyl group followed by a rearrangement[2,3].



$$\begin{matrix}\mathrm{Ar}\\\mathrm{R}\end{matrix}\!\!>\!\mathrm{C{=}O}+\mathrm{HOOR'}\rightarrow\begin{matrix}\mathrm{Ar}\\\mathrm{R}\end{matrix}\!\!>\!\mathrm{C}\!<\!\!\begin{matrix}\mathrm{OH}\\\mathrm{OOR'}\end{matrix}\xrightarrow[-\mathrm{R'OH}]{\mathrm{H^+}}\begin{matrix}\mathrm{Ar}\\\mathrm{R}\end{matrix}\!\!>\!\mathrm{C}\!<\!\!\begin{matrix}\mathrm{OH}\\\mathrm{O^+}\end{matrix}\rightarrow\mathrm{ArO}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{R}+\mathrm{H^+}$$

R: alkyl or H[8] Ar: aryl.

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[1] D. Swern, *Chem. Revs.*, **45**, 1 (1949).

[2] J. E. Leffler, ibid., **45**, 385 (1949).

[3] C. H. Hasall, *Organic Reactions*, **9**, 73 (1957).

[4] a) H. D. Dakin, *Proc. Chem. Soc.*, **25**, 194 (1909).
b) H. D. Dakin, *Am. Chem. J.*, **42**, 477 (1909).

[5] a) E. Bamberger, *Ber.*, **36**, 2042 (1903).
b) E. Bamberger and H. O. Eppinger, ibid., **73**, 644 (1940).

[6] W. Dilthy. M. Inckel and H. Stephan, *J. prakt. Chem.*, **154**, 219 (1940).

[7] W. Dilthy and F. Quint, ibid., **131**, 1 (1931).

[8] A. Wacek and A. Bezard, *Ber.*, **74**, 845 (1941).

However, few detailed mechanistic studies from the kinetic standpoint have been reported on the hydrogen peroxide oxidation in acidic media. The present study was undertaken to elucidate the mechanism as well as the true oxidizing agent of the acid-catalyzed hydrogen peroxide oxidation of hydroxybenzaldehyde in aqueous acetic acid by estimating the effects of acidity on the rate.

## Experimental

**Materials.**—*p*-Hydroxybenzaldehyde was purified by recrystallization from water, m. p. 116°.

**Kinetic Procedures.**—*Procedure A. Simultaneous Addition of the Reactants.*—Hydroxybenzaldehyde, acetic acid, sulfuric acid and water were mixed in a flask in the above order, thermostated at 15° or 20°; then hydrogen peroxide was added to the mixture. To avoid the temperature increase during the addition of hydrogen peroxide, a lower concentration of sulfuric acid and relatively high water content should be used. In the procedure, however, the apparent rate constant usually increases during the reaction except at high acidity.

*Procedure B. Addition of Aldehyde to an Equilibrium Mixture of Peroxides.*—Hydrogen peroxide was added to a cooled mixture of aqueous acetic acid and sulfuric acid in a brown flask, and the mixtue thermostated at 15±0.1 or 20±0.1° until the equilibrium state between hydrogen peroxide and peracetic acid was attained. Then hydroxybenzaldehyde was added to a known amount of the peroxide solution, the oxidation being started here. The reaction temperature was 15±0.1 or 20±0.1°.

In order to ascertain the establishment of the equilibrium and also to estimate hydrogen peroxide and peracetic acid contents in the preliminary equilibrium mixture, permanganate titration for hydrogen peroxide and iodometry for the peracetic acid were employed. Aliquots were taken out at appropriate intervals from the preliminary mixture before the addition of the aldehyde, run into a cooled mixture of ice and sulfuric acid and titrated rapidly at ca. $-5°$ with potassium permanganate to determine the hydrogen peroxide content. An aqueous solution of potassium iodide was then added to the mixture, warmed and titrated with thiosulfate to estimate the peracid content. In general, the aliquot consumes a slight excess of permanganate because of the obscurity of the end point; it was corrected by a separate determination of total peroxides.

When the ratio $a/b$ (where the equivalent amount of hydrogen peroxide present is $a$, that of peracetic acid $b$) becomes constant within experimental error, the equilibrium constant $K_1$ and the forward and the reverse rate constant of peracetic acid formation ($k_1$ and $k_{-1}$, respectively) may be calculated by means of equations:

$$K_1=k_1/k_{-1}, \qquad k+k_{-1}=\frac{2.303}{t}\log\left(\frac{a_0-a_e}{a-a_e}\right)$$

where $a_0$ is the initial concentration and $a_e$ is the equilibrium concentration of hydrogen peroxide.

In kinetic runs after the addition of hydroxybenzaldehyde, aliquots were withdrawn and their total peroxide content was determined iodometrically. The rate constants were then calculated by means of the usual second-order rate equation. The spontaneous decomposition of the peroxides in the absence of hydroxybenzaldehydes under these conditions is so small that it may be assumed that the amount of consumed peroxides minus the known amount of the spontaneous decomposition is the amount of peroxides reacted.

**Reaction Products Criterion.**—The reaction mixture gave, on long standing, a product containing hydroquinone or catechol. As mentioned previously, the formates of these phenols are probably produced at an initial stage, since the conversion percentage is not in accord with those of peroxide, when calculated spectrophotometrically on the assumption that hydroquinone is produced directly. These esters could not be isolated in appreciable quantities presumably because of the rapid hydrolysis during isolation procedures, as the hydrolysis was accelerated in the presence of considerable amounts of water and sulfuric acid.

## Results and Discussion

**The Equilibrium between Hydrogen Peroxide and Peracetic Acid.**—When the rate measurements were carried out by adding hydrogen peroxide to an equilibrium mixture of aqueous acetic acid, sulfuric acid and hydroxybenzaldehyde (Procedure A), an induction period was observed at the initial stage and the apparent second-order rate constants increased rapidly at

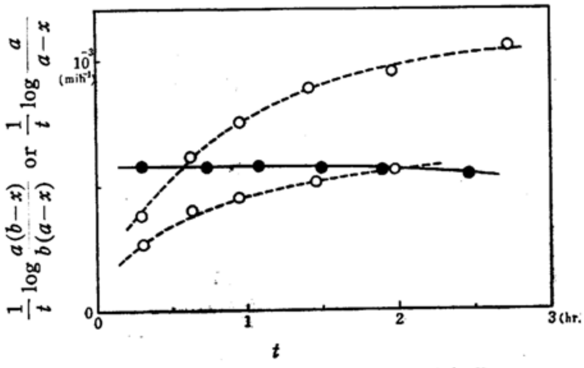

Fig. 1. Comparison of the results with Procedure A and B in the reaction of hydroxybenzaldehyde with peroxide.

dotted line: $\frac{1}{t}\log\left(\frac{a}{a-x}\right)$ vs. $t$ at the early stages of the reaction with Procedure A. (Initial concentration of the aldehyde is considerably higher than that of hydrogen peroxide). solid line: $\frac{1}{t}\log\frac{a(b-x)}{b(a-x)}$ vs. $t$ with Procedure B.

TABLE I

THE APPARENT SECOND-ORDER RATE CONSTANTS OF *p*-HYDROXYBENZALDEHYDE WITH PROCEDURE B

| *p*-$HOC_6H_4CHO$ $10^{-2}$M | Total peroxide[a)] $10^{-2}$M | $H_2SO_4$ M | $H_2O$ M | $k\times10^3$ [b)] l. mole$^{-1}$sec$^{-1}$ | Temp. °C |
|---|---|---|---|---|---|
| 1.64 | 2.4 | 0.392 | 5.55 | 4.06±0.02 | 15 |
| 0.984 | 2.4 | 0.392 | 5.55 | 4.08±0.05 | 15 |
| 1.64 | 4.8 | 0.392 | 5.55 | 4.07±0.06 | 15 |
| 1.64 | 2.4 | 0.392 | 5.55 | 5.10±0.05 | 20 |
| 1.64 | 2.4 | 0.196 | 5.55 | 2.62±0.02 | 15 |
| 1.64 | 2.4 | 0.784 | 5.55 | 8.70±0.06 | 15 |
| 1.64 | 2.4 | 0.784 | 5.55 | 10.3 ±0.1 | 20 |
| 1.64 | 2.4 | 1.18 | 5.55 | 13.9 ±0.1 | 15 |
| 1.64 | 2.4 | 0.078 | 5.55 | 1.52±0.03 | 15 |
| 1.64 | 2.4 | 0.392 | 3.33 | 7.44±0.06 | 20 |
| 1.64 | 2.4 | 0.392 | 11.1 | 2.64±0.05 | 15 |
| 1.64 | 2.4 | 0.392 | 16.7 | 1.91±0.02 | 15 |
| 1.64 | 2.4 | 0.392 | 16.7 | 2.27±0.05 | 20 |

a) The average value of different initial concentrations of peroxide.

b) Figures following ± show probable errors.

TABLE II

THE APPARENT PSEUDO-FIRST-ORDER RATE CONSTANTS AND APPARENT EQUILIBRIUM CONSTANTS OF THE PERACETIC ACID FORMATION FROM HYDROGEN PEROXIDE AND ACETIC ACID

| $H_2O$ M | $H_2SO_4$ M | $H_2O_2$ $10^{-2}$ M | $K_1$ | $k_1\times10^{-4}$ sec$^{-1}$ | $k_{-1}\times10^{-4}$ sec$^{-1}$ |
|---|---|---|---|---|---|
| 5.55 | 0.392 | 1.2 | 3.01 | — | — |
| 5.55 | 0.392 | 2.4 | 3.03 | 1.74 | 0.58 |
| 5.55 | 0.392 | 4.8 | 3.05 | 1.82 | 0.60 |
| 5.55 | 0.078 | 2.4 | 2.44 | 0.206 | 0.084 |
| 5.55 | 0.196 | 2.4 | 2.50 | 0.711 | 0.284 |
| 5.55 | 0.784 | 2.4 | 3.64 | 4.42 | 1.20 |
| 5.55 | 1.18 | 2.4 | 5.15 | — | — |
| 11.1 | 0.392 | 2.4 | 2.75 | 0.668 | 0.242 |
| 16.7 | 0.392 | 2.4 | 2.33 | — | — |

first, and then slowly. This trend was remarkable especially with low concentrations of sulfuric acid and with a relatively high initial concentration of hydroxybenzaldehyde compared with that of hydrogen peroxide. Typical examples are shown in Fig. 1.

On the other hand, when hydrogen peroxide is allowed to reach equilibrium with aqueous acetic and sulfric acid before hydroxybenzaldehyde is added to start the reaction (Procedure B), no such initial suppression of apparent rate constant is observed. The rate constant holds a satisfactory constancy during the reaction except near the end of the reaction where a slight decrease of the constant is appreciable. The constant does not, of course, vary with changing initial concentrations of the reactants. Table I shows the apparent second-order constants with Procedure B.

The facts cited above suggest that an active intermediate is formed by the acid-catalyzed interaction of hydrogen peroxide and acetic acid, the rate of its formation being comparable to that of the main reaction of hydroxybenzaldehyde with the intermediate. The facts that the initial suppression of the rate becomes remarkable by reducing the rate of formation of the intermediate and that the apparent rate constant estimated by Procedure A is much lower at an early stage than that by procedure B, agree well with the assumption of such an active intermediate. For example, a "rate constant" with Procedure A at 10% conversion is ca. 1/12.6 of that with Procedure B in the following condition. $[H_2O]=5.55$ M and $[H_2SO_4]=0.0736$ M at 20°.

It is most probable that the intermediate is peracetic acid, the equilibrium constant of its sulfuric acid-catalyzed formation having been estimated by D'Ans[9)].

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[9)] J. D'Ans and W. Frey, O; *Z. anog. Chem.* **84**, 145 *Chem. Abstr.*, **8**, 923 (1914).

$$H_2O_2 + CH_3COOH \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} CH_3CO_3H + H_2O \quad (1)$$

$$CH_3CO_3H + \text{hydroxybenzaldehyde} \xrightarrow{k_2} \text{product} \quad (2)$$

In addition to peracetic acid, the formation of Caro's acid may be expected. It seems rational, however, that peracetic acid is the main oxidizing agent, since the acidities used are not very high and the rate of formation of Caro's acid is very low under these conditions, although it may become appreciable at higher acidities[10]. The possibility that the active attacking agent is $OH^+$ (or $H_3O_2^+$) may be eliminated, since the protonation of hydrogen peroxide should be very rapid.

Approximate rate constants and equilibrium constants of the formation of peracetic acid determined under the same conditions as those of the kinetic experiments are shown in Table II. Both constants increase with increasing acidity in accord with the previous observation in such an equilibrium as hydrogen peroxide-performic acid or hydrogen peroxide-monoperoxysulfuric acid[10].

Since the magnitude of $k_1$ was moderate in these experiments, conditions where $v_1$ and $v_2$ ($v$'s are rates of the subscripted steps) are comparable may easily be attained[11].

Our qualitative observation on the initial suppression of the rate agrees with the above discussion and provides another evidence for the justification of eqs. 1 and 2. Furthermore, the oxidation rate measurements in pure aqueous media of the same acidity show that the rate is too slow to measure, thus indicating that no intermediate is produced by the interaction of hydrogen peroxide and sulfuric acid alone.

**Effects of Acidity and Water Content.**— A study of the effects of sulfuric acid concentration and water content on the apparent second-order rate constant according to Procedure B ($k$) shows that the results can not be expressed in a simple form, unless corrections for peracetic acid concentration and acidity are made. (see Figs. 2 and 3).

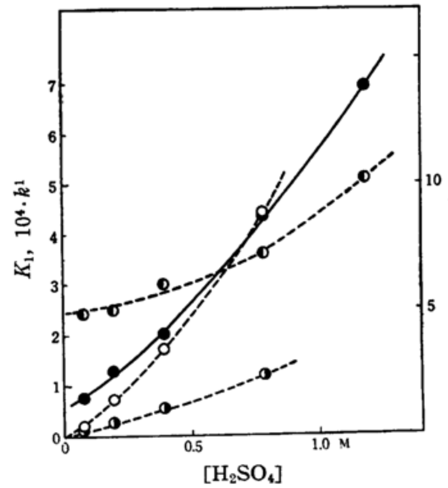

Fig. 2. Influence of acid concentration on the rate and the equilibrium constant for the reaction of peracetic acid formation at 15° and for the oxidation of hydroxybenzaldehyde. $[H_2O] = 5.55$ M.
Dotted lines correspond to the peracetic acid formation:
◐, equilibrium constant $K_1$
○, forward rate constant $k_1 \cdot 10^4$
◑, reverse rate constant $k_{-1} \cdot 10^4$
Solid line correspond to the rate constant of oxidation: $k \cdot 10^3$.

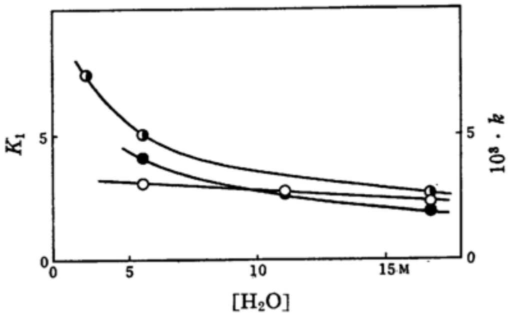

Fig. 3. Influence of water concentration on the rate and the equilibrium constant for peracetic acid formation of 15° and oxidation of $p$-hydroxybenzaldehyde at 15° and 20°.
○, equilibrium constant of peracetic acid formation $K_1$
◑, for rate constant of the oxidation at 20°
●, at 10°
$[H_2SO_4] = 0.392$ M.

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[10] J. M. Monger and O. Redlich, *J. Phys. Chem.*, **60**, 797 (1956).

[11] Under these conditions the observed initial suppression of the rate in Procedure A becomes remarkable. In the following equations (total peroxide is nearly equal to $[H_2O_2]$ in the early stages of the reaction)

$$v_1 = k_1 [H_2O_2][AcOH]$$
$$v_2 = k_2 [CH_3CO_3H][\text{hydroxybenzaldehyde}]$$
$$= k_2' [\text{total peroxide}][\text{hydroxybenzaldehyde}]$$

The observed rate constants with $p$-hydroxybenzaldehyde at $[H_2O] = 5.55$ M, $[AcOH] = 15$ M and $[H_2SO_4] = 0.392$ M were found to be

$$k_1 = 1.78 \times 10^{-4} \text{ l. mole}^{-1}\text{sec.}^{-1}$$
$$k_2' = 4.07 \times 10^{-3} \text{ l. mole}^{-1}\text{sec}^{-1}.$$

Here, $k_2'$ is the apparent rate contant and $k$ is the rate constant of the subscripted step. Therefore,

$$v_2/v_1 = 4.07 \times 10^{-3} \times [\text{hydroxybenzaldehyde}]/(1.78 \times 10^{-4} \times 15)$$

Namely, if the initial concentration of hydroxybenzaldehyde exceeds $10^{-2}$ M, $v_2$ appoaches to $v_1$. This approach should become remarkable as the acidity decreases, since $k_1$ appreaches to zero with decreasing acidity, while $k_2'$ approaehes to a definite value (see Fig. 2).

The concentration of peracetic acid is obtainable from the concentration of total peroxide [T] as follows.

$$K_1=\frac{[H_3O]\,[CH_3CO_3H]}{[H_3O_3]\,[CH_3CO_2H]} \qquad (3)$$

Here, both $[CH_3CO_2H]$ and $[H_3O]$ may be regarded as constant. Since

$$[T]=[H_2O_2]+[CH_3CO_3H] \qquad (4)$$

$$[CH_3CO_3H]=\frac{[CH_3CO_2H]\,K_1}{[CH_3CO_3H]\,K_1+[H_2O]}\cdot[T] \qquad (5)$$

$$[H_2O_2]=\frac{[H_2O]}{[CH_3CO_2H]\,K_1+H_2O}\cdot[T]$$

$$v=k\,[Hy]\,[T]=k_p\,[Hy]\,[CH_3CO_3H]+k_h\,[Hy]\,[H_2O_2] \qquad (6)$$

are obtained, where Hy means hydroxybenzaldehyde, $k_p$ and $k_h$ are rate constants for reactions of peracetic acid and hydrogen peroxide, respectively. Therefore,

$$k=k_p\frac{[CH_3CO_2H]\,K_1}{[CH_3CO_2H]\,K_1+[H_2O]}+k_h\frac{[H_2O]}{[CH_3CO_2H]\,K_1+[H_2O]} \qquad (7)$$

From the above discussion, it may be concluded that the second term of the right hand side of equation 7 expressing hydrogen peroxide oxidation is far less important than the first term. Hence,

$$k=k_p\frac{[CH_3CO_2H]\,K_1}{[CH_3CO_2H]\,K_1+[H_2O]} \qquad (8)$$

The value of $k_p$ calculated by means of equation 8 holds sufficient constancy as noted later; therefore it is confirmed that the second term participation has little effect on the kinetics. This is supported numerically, comparing $k$ in Procedures A and B at the initial stage of reaction, and the ratio of peracid to hydrogen peroxide in the equilibrium state.

For the expression of the acidity of the solutions, the Hammett's acidity function $H_0$ was used, the indicators being *o*- and *p*-nitranilines and 4-chloro-2-nitraniline. Plots of $H_0$ vs. $\log k_p$ gave no straight line, but a curve whose slope approaches $-1$ with increasing acidity, while it approaches zero with decreasing acidity. This fact seems to mean that the rate constant $k_p$ may further be separable into the acid-independent ($k_n$) terms:

$$k_p=k_n+k_a h_0 \qquad (9)$$

where $h_0$ relates to $H_0$ in expression $\log h_0=-H_0$.

Plot of $k_p$ vs. $h_0$ gives a satisfactory straight line as shown in Fig. 4. A slight decrease of $k_a$ at very high acidity or its change in varying water-sulfuric acid ratio at the same acidity is probably due to the unequality of $h_0$ and proton activity[12].

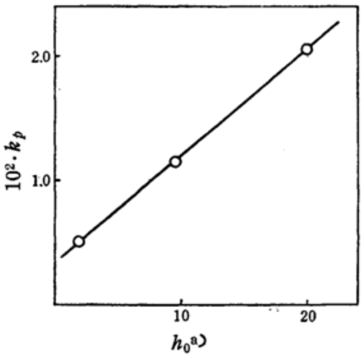

Fig. 4. The plot of $k_p$ vs. $h_0$ for the reaction of *p*-hydroxybenzaldehyde in moderate acidities at 20°.

**Reaction Mechanism.**—The above results imply that there is a preliminary, relatively rapid and reversible peracetic acid formation, then acid-catalyzed or uncatalyzed attack of the peracetic acid on the carbonyl group takes place to form an addition complex followed by a rearrangement of the complex to the product. The rearrangement would not perhaps be a rate-determining step, since no stable complex has been isolated, and furthermore, in our preliminary experiments no appreciable difference was observed between the ultraviolet spectrum of the original aldehyde solution and that of the aldehyde solution immediately after mixing it with peracetic acid solution.

On the basis of the observed kinetics, there are two possible mechanisms, i. e., mechanism A involving steps 10, 11, 13, 14 and 16 and mechanism B involving steps 10, 12, 14, 15 and 16.

$$CH_3CO_2H+H_2O_2+H^+ \rightleftharpoons CH_3CO_3H+H_2O+H^+ \qquad (10)$$

$$CH_3CO_3H+H^+ \rightleftharpoons CH_3CO_3H_2^+ \qquad (11)$$

$$ArCHO+H^+ \rightleftharpoons ArC^+HOH \qquad (12)$$

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[12] For the ionization and dissociation of sulfuric acid in aqueous acetic acid, see S. Bruckenstein and I. M. Kolthoff, *J. Am. Chem. Soc.*, **78**, 10 (1956).

[a] The values of $h_0$ were calculated from the observed $H_0$'s under these experimental conditions. The values of $H_0$ were calculated by Hammett's equation $H_0=pK_a+\log(c_B/c^+_{BH})$ to be $-0.28$, $-0.99$ and $-1.30$ with $[H_2SO_4]=0.392$ M, 0.784 M and 1.18 M, respectively, where $[H_2O]=5.55$ M is constant.

$$CH_3CO_3H_2^+ + ArCHO \rightarrow ArCHO\cdot CH_3CO_3H_2^+ \text{ (complex, I}\cdot\text{H}^+\text{)} \quad (13)$$

$$CH_3CO_3H + ArCHO \rightarrow ArCHO\cdot CH_3CO_3H \text{ (complex, I)} \quad (14)$$

$$CH_3CO_3H + ArC^+HOH \rightarrow I\cdot H^+ \quad (15)$$

$$I \text{ (or } I\cdot H^+) \rightarrow ArOCHO + CH_3CO_2H \text{ (or } +H^+) \quad (16)$$

Since the mobile equilibria 11 and 12 probably tend to shift to the left side, step 12 in mechanism A and 11 in B may be neglected except at high acidity. The apparent rate constants $k_A$ and $k_B$, corresponding to mechanism A and B, respectively, are easily expressed in terms of the equilibrium and rate constants of equations 11—15, where $K$ and $k$ denote equilibrium and rate constants of the subscripted steps, respectively.

$$k_A = k_{13}\cdot\frac{1}{1+K_{12}[H^+]}\cdot\frac{K_{11}[H^+]}{1+K_{11}[H^+]} + k_{14}\cdot\frac{1}{1+K_{11}[H^+]}\cdot\frac{1}{1+K_{12}[H^+]} \quad (17a)$$

$$k_B = k_{15}\cdot\frac{1}{1+K_{11}[H^+]}\cdot\frac{K_{12}[H^+]}{1+K_{12}[H^+]} + k_{14}\cdot\frac{1}{1+K_{11}[H^+]}\cdot\frac{1}{1+K_{12}[H^+]} \quad (17b)$$

Here, $k_{13}$, $k_{14}$ and $k_{15}$ are acidity-independent constants. At lower acidity, equations 17a and 17b may be simplified in the following way, since both $K_{11}[H^+]$ and $K_{12}[H^+]$ are far smaller than unity.

$$k_A = k_{13}K_{11}[H^+] + k_{14} \quad (18a)$$

$$k_B = k_{15}K_{12}[H^+] + k_{14} \quad (18b)$$

Since both equations 18a and 18b agree with the observed expression 9 and also with the rate-acidity relationship, it seems impossible, on the basis of the kinetics alone, to determine which mechanism is favored in so far as the values of $K_{11}$ and $K_{12}$ are unavailable. However, step 13 is more favorable than step 15, since it involves an attack of a more electrophilic agent $CH_3CO_3H_2^+$.

## Summary

The sulfuric acid-catalyzed oxidations of 4-hydroxybenzaldehyde with hydrogen peroxide in aqueous acetic acid were kinetically investigated at 15° and 20° by iodometric estimation of the peroxides. The rates of peroxide consumption were found to be proportional to the product of the concentrations of hydroxybenzaldehyde and peroxide, when the aldehyde was added after the equilibrium between hydrogen peroxide and peracetic acid was attained. The rate constant is a linear function of Hammett acidity function $h_0$.

Hydrogen peroxide itself reacts slowly with the aldehyde, but it reacts more easily through the formation of peracetic acid. A mechanism involving a ratedetermining attack of protonated and free peracetic acid was postulated and discussed.

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