runs and the sums of the amounts required for the several reactions as calculated on the basis of the proposed equations for the reactions involved.

Grateful acknowledgments are extended to Professor John Uri Lloyd, whose Fellowship in Chemistry made this study possible, and to Dr. H. P. Carveth, President of the Roessler–Hasslacher Chemical Co., who generously donated several shipments of the specially prepared hydrogen peroxide used in this study.

Summary

An extended study of the nature and extent of the action of increasing molar concentrations of hydrogen peroxide in acid media upon methyl alcohol, formaldehyde, and formic acid has confirmed the occurrence of a series of postulated reactions.

The equations for these reactions have been verified by the experimental data with respect not only to the yields of the several products obtained, but also to the quantities of hydrogen peroxide participating in the postulated reactions.

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THE ACTION OF HYDROGEN PEROXIDE UPON SIMPLE CARBON COMPOUNDS. II. THE MECHANISM OF THE REACTIONS[1]
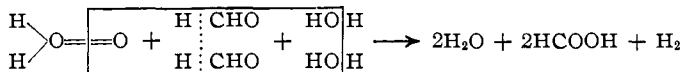
BY H. SHIPLEY FRY AND JOHN H. PAYNE

Two reaction mechanism schemes have been proposed previously to explain the apparently anomalous liberation of hydrogen when hydrogen peroxide and formaldehyde interact according to equation (b)

$$2HCHO + H_2O_2 \longrightarrow 2HCOOH + H_2 \qquad (b)$$
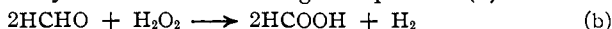
Briefly stated, Traube's explanation[2] postulates the liberation of hydrogen through the decomposition of water in conformity with the following scheme wherein the hydroxyl radicals of water combine with the aldehyde radicals of formaldehyde to produce formic acid

$$\underset{H}{\overset{H}{>}}O = \left| =O + \begin{array}{c} H \vdots CHO \\ H \vdots CHO \end{array} + \begin{array}{c} HO|H \\ HO|H \end{array} \right| \longrightarrow 2H_2O + 2HCOOH + H_2$$

This scheme also involves, as indicated by the dotted line, dissociation of the aldehyde hydrogen atoms, which combine with the peroxide oxygen atom to form water.
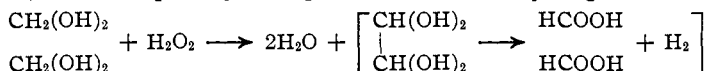
In the other reaction mechanism, Wieland[3] postulates, first, the con-

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[1] Presented before the Organic Division of the American Chemical Society, Cincinnati, September 9, 1930.

[2] Traube, Ber., 16, 123 (1883).

[3] Wieland, ibid., 45, 484, 679, 2606 (1912); 46, 3327 (1913); 47, 2085 (1914); 54, 2353 (1921).

version of formaldehyde to formaldehyde hydrate, $CH_2O + H_2O \longrightarrow$ $CH_2(OH)_2$, which then reacts with hydrogen peroxide according to the following scheme wherein the intermediately formed oxidation product, $[CH(OH)_2]_2$, decomposes yielding formic acid and hydrogen

$$\begin{array}{c} CH_2(OH)_2 \\ CH_2(OH)_2 \end{array} + H_2O_2 \longrightarrow 2H_2O + \left[\begin{array}{c} CH(OH)_2 \\ | \\ CH(OH)_2 \end{array} \longrightarrow \begin{array}{c} HCOOH \\ \\ HCOOH \end{array} + H_2 \right]$$
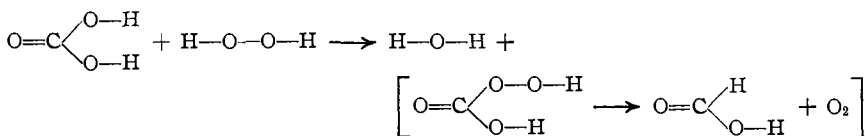
The change noted within the brackets involves not only decomposition, but also rearrangement reactions.

A third reaction mechanism scheme, less involved than the preceding schemes, is now proposed. It explains not only the liberation of hydrogen when formaldehyde is oxidized to formic acid, but also the liberation of oxygen when carbonic acid is reduced to formic acid, as well as other reactions wherein neither hydrogen nor oxygen is evolved. The latter, or the normal oxidation reactions, will be considered first.

It is here assumed that hydrogen peroxide displays a type of reaction which may be termed "*perhydrolysis*," that is, a double decomposition reaction involving *hydrogen peroxide* in precisely the same manner that *hydrolysis* is a double decomposition reaction involving *water*. Thus, for instance, the normal oxidation of formaldehyde to formic acid is a *perhydrolysis* reaction

$$O{=}C\Big\langle{}^{H}_{H} + H{-}O{-}O{-}H \longrightarrow O{=}C\Big\langle{}^{O{-}H}_{H} + H{-}O{-}H$$
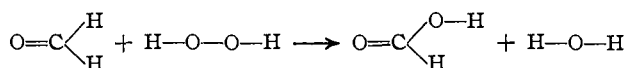
The reduction of carbonic acid by hydrogen peroxide with the liberation of oxygen, $H_2CO_3 + H_2O_2 \longrightarrow HCOOH + H_2O + O_2$, may likewise involve *perhydrolysis*, forming percarbonic acid, which, in turn, yields formic acid through the liberation of oxygen, all in conformity with the reaction scheme

$$O{=}C\Big\langle{}^{O{-}H}_{O{-}H} + H{-}O{-}O{-}H \longrightarrow H{-}O{-}H +$$

$$\left[O{=}C\Big\langle{}^{O{-}O{-}H}_{O{-}H} \longrightarrow O{=}C\Big\langle{}^{H}_{O{-}H} + O_2 \right]$$

An explanation of the other apparently anomalous reactions, namely, the oxidation of formaldehyde to formic acid with the liberation of hydrogen (equation b), requires an additional assumption which is suggested by the well-known decomposition of sodium formate yielding sodium oxalate and hydrogen

$$\begin{array}{c} HCOOH \\ HCOOH \end{array} \longrightarrow \begin{array}{c} COOH \\ | \\ COOH \end{array} + H_2$$
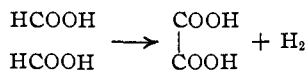
The parallel reaction with formaldehyde would yield hydrogen and glyoxal

$$\begin{array}{c} HCHO \\ HCHO \end{array} \longrightarrow \begin{array}{c} CHO \\ | \\ CHO \end{array} + H_2 \qquad\qquad (n)$$
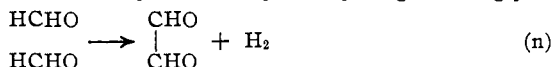
to be followed immediately by the *perhydrolysis* of the intermediately formed glyoxal, yielding two molecules of formic acid

$$\begin{matrix} HCO \\ | \\ HCO \end{matrix} + \begin{matrix} HO \\ | \\ HO \end{matrix} \longrightarrow 2HCOOH \qquad\qquad (o)$$
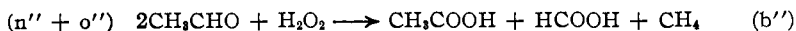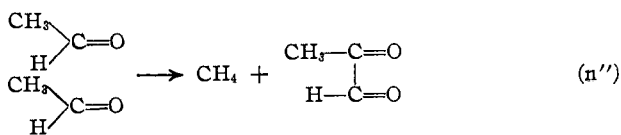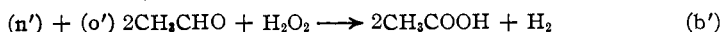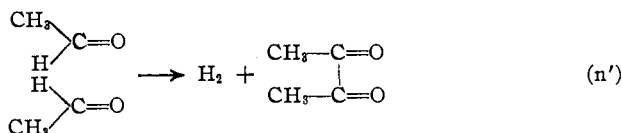
The summation of the two equations (n) and (o) gives the complete equation (b)

$$2HCHO + H_2O_2 \longrightarrow 2HCOOH + H_2 \qquad\qquad (b)$$

That no intermediately formed glyoxal was isolated is presumably due to the fact that the speed of the perhydrolysis reaction (o) is greater than that of the preceding reaction (n).

Now, if this proposed reaction mechanism has any validity, it should at least predict that the interaction of acetaldehyde and hydrogen peroxide would yield hydrogen or methane, or both hydrogen and methane, in conformity with the following completely parallel reaction mechanism schemes, wherein equations (n') and (n''), (o') and (o'') and (b') and (b'') are exactly parallel to the above equations (n), (o) and (b), respectively.

$$\begin{matrix} CH_3 \\ \\ H \\ H \\ \\ CH_3 \end{matrix}\!\!\!\!\begin{matrix} \diagdown \\ C=O \\ \diagup \\ \diagdown \\ C=O \\ \diagup \end{matrix} \longrightarrow H_2 + \begin{matrix} CH_3-C=O \\ | \\ CH_3-C=O \end{matrix} \qquad (n')$$

$$\begin{matrix} CH_3CO \\ | \\ CH_3CO \end{matrix} + \begin{matrix} HO \\ | \\ HO \end{matrix} \longrightarrow 2CH_3COOH \qquad\qquad (o')$$

$$(n') + (o') \quad 2CH_3CHO + H_2O_2 \longrightarrow 2CH_3COOH + H_2 \qquad (b')$$

. . . .

$$\begin{matrix} CH_3 \\ \\ H \\ CH_3 \\ \\ H \end{matrix}\!\!\!\!\begin{matrix} \diagdown \\ C=O \\ \diagup \\ \diagdown \\ C=O \\ \diagup \end{matrix} \longrightarrow CH_4 + \begin{matrix} CH_3-C=O \\ | \\ H-C=O \end{matrix} \qquad (n'')$$

$$\begin{matrix} CH_3CO \\ | \\ HCO \end{matrix} + \begin{matrix} HO \\ | \\ HO \end{matrix} \longrightarrow CH_3COOH + HCOOH \qquad (o'')$$

$$(n'' + o'') \quad 2CH_3CHO + H_2O_2 \longrightarrow CH_3COOH + HCOOH + CH_4 \qquad (b'')$$

The liberation of ethane, a third possibility, would necessitate a linkage of carbon atoms, which seems improbable, at least not so likely as the liberation of hydrogen and methane.

The predictions, with respect to the action of hydrogen peroxide upon acetaldehyde in conformity with the above equations (b') and (b''), derived through the proposed reaction mechanism scheme, were confirmed by extending the experimental method, previously described in Part I, to acetaldehyde which gave the predicted products, *hydrogen, methane, acetic*

acid and *formic acid*, thus indicating the concurrence of reactions (b') and (b'').

Before tabulating the confirmatory data, it should be noted that the literature affords only one observation[4] of the liberation of hydrogen when hydrogen peroxide interacts with acetaldehyde. No data were recorded.

Geisow[5] attempted to carry the analogy of the liberation of hydrogen according to the formaldehyde reaction, equation (b), to the liberation of methane from acetaldehyde but did not obtain any methane.

Other investigators[6] have severally recorded the formation of acetic, formic and carbonic acids, but none mentions the liberation of hydrogen or methane.

Experimental

Three sets of duplicate runs were conducted using one-fourth mole of pure paraldehyde in each case, varying the quantity of hydrogen peroxide from one-eighth to one-fourth, and one-half mole in solutions of 125 cc. volume containing 0.306 g. of sulfuric acid. In this acid solution the paraldehyde depolymerized to acetaldehyde and the time required for completion of the reaction varied from eighteen to twenty-four hours.

Some of the very volatile acetaldehyde escaped reaction with the hydrogen peroxide. To prevent its absorption in the soda lime tubes, two Milligan wash bottles were interposed as previously described in the runs with methyl alcohol (Part I, Section C). The first wash bottle contained ethyl alcohol, which collected the acetaldehyde vapor; the second contained sulfuric acid, which retained any traces of alcohol or acetaldehyde escaping from the first wash bottle.

The products of the reaction in each run were hydrogen, methane, formic and acetic acids, as predicted in equations (b') and (b''). The predominating reaction, however, was the direct oxidation of acetaldehyde to acetic acid

$$CH_3CHO + H_2O_2 \longrightarrow CH_3COOH + H_2O$$
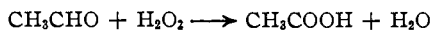
Formic and carbonic acids were also formed in secondary reactions between acetic acid and hydrogen peroxide without the accompanying evolution of hydrogen or methane, as was confirmed in separately conducted runs with acetic acid.

Aliquot fractions of the reaction mixtures in all runs were analyzed for their combined formic acid and acetic acid contents by titration with standard alkali. The formic acid content was determined as previously noted by the mercuric chloride method; the acetic acid content was obtained by difference. All of the analytical data are embodied in Table I.

[4] Blank and Finkenbeiner, *Ber.*, **31**, 2279 (1898).

[5] Geisow, *ibid.*, **37**, 515 (1904).

[6] Dakin, *J. Biol. Chem.*, **4**, 77 (1908); Heimrod and Levene, *Biochem. Z.*, **29**, 31 (1910); Reiner, *Z. anorg. allgem. Chem.*, **141**, 363 (1925).

TABLE I

MOLAR QUANTITIES OF HYDROGEN PEROXIDE AND ACETALDEHYDE USED AND OF PRODUCTS FORMED

Run	Initial H_2O_2	Initial CH_3CHO	CH_3COOH found	$HCOOH$ found	H_2CO_3 found	H_2 found	CH_4 found
Ia	0.1250	0.2500	0.0670	0.0081	0.0183	0.0021	0.0032
Ib	.1250	.2500	.0710	.0099	.0172	.0017	.0023
IIa	.2500	.2500	.1422	.0075	.0211	.0044	.0026
IIb	.2500	.2500	.1422	.0078	.0231	.0038	.0022
IIIa	.5000	.2500	.1870	.0082	.0444	.0035	.0007
IIIb	.5000	.2500	.1775	.0080	.0471	.0036	.0006

Summary

Without attempting to correlate, exactly quantitatively, the molar yields of the products obtained with the reactions involved in their formation, which is not possible because the extreme volatility of the acetaldehyde made its retention in the reaction mixtures impossible, the following conclusions may be drawn from the available data.

1. The yields of the two chief reaction products, *acetic* and *carbonic* acids, increase as increased quantities of hydrogen peroxide are used.

2. Since separately conducted runs with acetic acid and hydrogen peroxide gave formic and carbonic acids without the liberation of hydrogen or of methane, it follows that the hydrogen arises from the oxidation of acetaldehyde to acetic acid as indicated in the proposed equation

$$2CH_3CHO + H_2O_2 \longrightarrow 2CH_3COOH + H_2$$
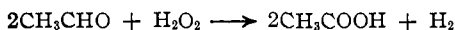
3. While the maximum yields of hydrogen were obtained with equimolar concentrations of acetaldehyde and hydrogen peroxide, another striking parallel to the formaldehyde reaction (Part I, Section B) is found in the fact that the volumes of methane liberated according to the proposed equation, $2CH_3CHO + H_2O_2 \longrightarrow CH_3COOH + HCOOH + CH_4$, *decrease* with *increasing* concentrations of hydrogen peroxide.

In conclusion, the formation of acetic and formic acids with the concurrent liberation of both hydrogen and methane appears to be in conformity with the above equations for the reactions which were predicted by extending the proposed reaction mechanism scheme to acetaldehyde.

In proposing a new type of reaction mechanism, termed "perhydrolysis," to explain some of the normal and also apparently anomalous reactions of hydrogen peroxide, the authors would guard against the assumption that all reactions of hydrogen peroxide involve "perhydrolysis," for many do not.

Further confirmation of the perhydrolysis mechanism is under way in an extended study of the action of hydrogen peroxide upon other simple carbon compounds.

CINCINNATI, OHIO