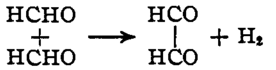
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF HAWAII]

The Oxidation of Aldehydes with Hydrogen Peroxide

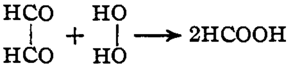
BY JOHN H. PAYNE AND GEORGE F. LEMON, JR.

The oxidation of aldehydes by hydrogen peroxide has been shown to involve more than the simple addition of oxygen to produce the carboxyl group. Thus the reaction with formaldehyde results in the evolution of considerable quantities of hydrogen, the amount of which varies with conditions as has been found by Fry and Payne.[1] Acetaldehyde under similar conditions evolves not only hydrogen but also methane,[2] while ethane and hydrogen are produced in the oxidation of propionaldehyde.[3] In order to account for the formation of hydrogen from formaldehyde, Fry and Payne[2] proposed a perhydrolysis mechanism involving the intermediate formation of glyoxal according to the following scheme



$$\begin{matrix} HCHO \\ + \\ HCHO \end{matrix} \longrightarrow \begin{matrix} HCO \\ | \\ HCO \end{matrix} + H_2 \qquad (a)$$

This reaction would be followed by the perhydrolysis of the glyoxal yielding formic acid



$$\begin{matrix} HCO \\ | \\ HCO \end{matrix} + \begin{matrix} HO \\ | \\ HO \end{matrix} \longrightarrow 2HCOOH \qquad (b)$$

Simultaneously with reaction (a) there occurs the normal oxidation of formaldehyde to formic acid

$$HCHO + H_2O_2 \longrightarrow HCOOH + H_2O \qquad (c)$$

According to this mechanism the hydrogen evolved would not be the hydrogen of the aldehyde group. By the use of deuterohydrogen peroxide Bonhoeffer and Wirtz[4] have demonstrated that the hydrogen does not have its source in the hydrogen peroxide. Additional evidence is necessary, however, in order to establish definitely the reaction mechanism of hydrogen formation, since aldehydes other than formaldehyde produce hydrogen. Furthermore, the intermediate formation of glyoxal in the oxidation of formaldehyde is hypothetical, and the behavior of this compound with hydrogen peroxide has not been adequately studied.

In this investigation the behavior of four compounds, glyoxal, benzaldehyde, pivalic aldehyde, and glycolaldehyde when treated with hydrogen peroxide in acid solution was studied. Glyoxal under these conditions yielded no hydrogen. The chief products of oxidation were formic acid and carbon dioxide, and no glyoxalic acid or oxalic acid could be detected in the reaction mixture. These results indicate that the perhydrolysis splitting of glyoxal into two molecules of formic acid is correct. Likewise the absence of hydrogen in the reaction products is additional evidence that the hydrogen of the aldehyde group is not liberated when aldehydes are oxidized by hydrogen peroxide.

Further proof of the latter was obtained with benzaldehyde. This compound was found to be oxidized quantitatively to benzoic acid with no hydrogen resulting. It is evident therefore that the hydrogen of the aldehyde group is not set free. No benzene was formed, a possibility which might be anticipated if the reaction were analogous to the liberation of methane from acetaldehyde.

In the case of aldehydes other than formaldehyde the hydrogen might come from formaldehyde produced as an intermediate product, or it might come from the carbon atom adjacent to the aldehyde group. That the latter is probably not the case was shown by pivalic aldehyde, which has no hydrogen on the carbon atom next to the aldehyde group. This compound yielded hydrogen as one of the principal products of the reaction with hydrogen peroxide. Formaldehyde and formic acid were present in the reaction mixture, indicating that formaldehyde was the probable source of the hydrogen. The reaction was complicated by the decomposition of the pivalic aldehyde into carbon monoxide and isobutane apparently according to the reaction

$$(CH_3)_3CCHO \longrightarrow (CH_3)_3CH + CO$$

This reaction was found by Conant, Webb and Mendum[5] to be brought about by light. Evidently hydrogen peroxide catalyzes the decomposition in the absence of light.

Glycolaldehyde provides an interesting study in terms of reaction mechanism. If the primary alcohol group were attacked first, glyoxal would result, and subsequent oxidation would produce

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(1) Fry and Payne, THIS JOURNAL, 53, 1973 (1931).

(2) Fry and Payne, *ibid.*, 53, 1980 (1931).

(3) Bezzi, *Gazz. chim. ital.*, 63, 345 (1933).

(4) Bonhoeffer and Wirtz, *Z. physik. Chem.*, B32, 108 (1936).

(5) Conant, Webb and Mendum, THIS JOURNAL, 51, 1246 (1929).

no hydrogen. If on the other hand, as would appear more probable, the aldehyde group is first oxidized to the carboxyl group, glycolic acid would be formed. This substance has been shown by Fry and Milstead[6] to produce hydrogen when treated with hydrogen peroxide. Proof that the aldehyde group is oxidized to the carboxyl group was found since hydrogen, as well as formaldehyde and formic acid, was found in the products of reaction.

From these results it can be concluded, therefore, that in the oxidation of aldehydes with hydrogen peroxide the hydrogen does not have its source in the aldehyde group or necessarily on a carbon atom adjacent to the aldehyde group. The hydrogen probably arises from formaldehyde produced as an intermediate product. Any compound, therefore, which yields formaldehyde as an intermediate during its oxidation, may be expected to give hydrogen as one of the reaction products. No evidence counter to the perhydrolysis hypothesis of Fry and Payne has been obtained.

Experimental

The experimental method employed was essentially that of Fry and Payne.[1] The apparatus was considerably refined, however, being all glass and control of temperature was possible to ±0.1°. Weighed quantities of the compound studied were introduced into the 250-cc. reaction flask. Hydrogen peroxide of approximately 30% concentration, free from organic preservatives, *p*H 4.5, and containing 20 mg. of sodium stannate and 100 mg. of sodium pyrophosphate per liter as stabilizer, was pipetted into the flask. The volume was made up to 200 cc. with redistilled water and the flask connected to the condenser and carbon dioxide absorbing train. The apparatus was then swept out with pure nitrogen to remove all air and carbon dioxide. The constant temperature bath was maintained at 95 ± 0.1° until the reaction was complete, as evidenced by the cessation of the evolution of gas. The apparatus was then swept out with nitrogen. The reaction mixture was analyzed for remaining hydrogen peroxide, formic acid, and other acids quantitatively. In the absence of appreciable amounts of reducing substances, the hydrogen peroxide was determined by rapid titration with potassium permanganate. In the presence of aldehydes, the ceric sulfate method of Willard and Young[7] was used. Formic acid was determined gravimetrically by the mercuric chloride method. In a few instances where reducing substances interfered, a correction factor was necessary in this determination. Other acids were ascertained by titration with standard base. Compounds present in small quantities were tested qualitatively. The gas evolved was analyzed by standard methods of gas analysis for oxygen, hydrogen, and carbon monoxide. All runs were made in duplicate.

Glyoxal.—The glyoxal used was the pure polymer obtained from Dr. Fraenkel and Dr. Landau in Berlin. It contained only a small amount of acetic acid as an impurity, and was free from acetaldehyde and formaldehyde. Preliminary experiments with a 50% solution of free glyoxal in water gave the same general results as the polymerized form. Average data on two sets of duplicate runs at different concentrations are shown in Table I. Part 1 gives the quantities of reactants used and products found, and Part 2 shows the percentage of the total hydrogen peroxide going to the various reaction products. It will be noted that only a trace of hydrogen was found. The principal products of the oxidation were carbon dioxide, formic acid, and a small amount of other acids. No oxalic acid, glyoxalic acid, nor glycolic acid was found, and formaldehyde was absent. Part 2 shows that approximately 100% of the hydrogen peroxide is accounted for in the reaction products. The reaction required eight hours for completion.

These results indicate that glyoxal is oxidized by hydrogen peroxide to formic acid and carbon dioxide without passing through the oxalic acid stage. The absence of hydrogen in the products supports the perhydrolysis mechanism given in reaction (b) and offers evidence in support of the theory that it is not the hydrogen of the aldehyde group which is set free by the action of hydrogen peroxide upon certain aldehydes.

Benzaldehyde.—Freshly distilled benzaldehyde was subjected to oxidation with hydrogen peroxide–benzaldehyde molar ratios of 1 to 1 and 2 to 1. The reaction proceeded slowly and required twelve hours for completion. No gases were evolved in the reaction; the only product was found to be benzoic acid, and no decomposition of the hydrogen peroxide into molecular oxygen occurred.

Pivalic Aldehyde.—Pivalic aldehyde was prepared by the method of Trister and Hibbert.[8] The compound had to be used immediately following distillation in order to ensure that no autoxidation had taken place. One set of duplicate runs was made using 0.10 mole of pivalic aldehyde and 0.37 mole of hydrogen peroxide. The reaction proceeded with unexpected slowness, twelve hours being required before the evolution of gas ceased. Table I shows the quantities of the various reaction products. It will be noted that hydrogen is one of the principal products of the reaction. Considerable isobutane and carbon monoxide are present, probably from the direct decomposition of the pivalic aldehyde. Probably the hydrogen has its source in formaldehyde produced by oxidation of the methyl groups of the pivalic aldehyde, since formaldehyde was found qualitatively in the reaction mixture, and formic acid was present in appreciable amounts. Due to the complexity of the reaction, no attempt was made to account for the hydrogen peroxide utilization quantitatively.

Glycolaldehyde.—Glycolaldehyde was prepared from dihydroxymaleic acid by the method of Fenton.[9] Duplicate runs were made using 0.0625 mole of glycolaldehyde and 0.125 mole of hydrogen peroxide. The reaction pro-

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[6] Fry and Milstead, THIS JOURNAL, 57, 2269 (1935).

[7] Willard and Young, *ibid.*, 55, 3260 (1933).

[8] Trister and Hibbert, *Can. J. Research*, 14, 421 (1936).

[9] Fenton, *J. Chem. Soc.*, 87, 811 (1905).

TABLE I

OXIDATION OF GLYOXAL, PIVALIC ALDEHYDE AND GLYCOLALDEHYDE BY HYDROGEN PEROXIDE

Part 1, Quantities of Reactants Used and Products Found

	Moles							
	Compound	H_2O_2	H_2O_2 Unused	O_2 Found	H_2 Found	CO_2 Found	HCOOH Found	Other acids found, equiv.
Glyoxal 1	0.415	0.200	0.0580	0.0029	None	0.2084	0.0253	0.0499
Glyoxal 2	.800	.200	.0246	.0516	Trace	.3120	.0061	− .0308[a]
Glycolaldehyde	.0625	.125	None	.0008	0.0028	.0510	.0042	.0160
Pivalic aldehyde	.100	.370	None	.0052	.0192	.0414	.0042	.0386[b]

Part 2, Percentage of H_2O_2 Going to Reaction Products

	H_2O_2 Unused	$H_2O_2 \rightarrow O_2$	$H_2O_2 \rightarrow H_2$	$H_2O_2 \rightarrow$ HCOOH	$H_2O_2 \rightarrow CO_2$	$H_2O_2 \rightarrow$ Other acids	H_2O_2 total
Glyoxal 1	14.32	1.42	None	3.13	77.21	6.61	102.7
Glyoxal 2	30.74	12.89	None	0.38	58.51	−3.85[a]	98.7
Glycolaldehyde	None	1.10	2.24	−1.12[c]	82.40	12.80	97.4

[a] These values are negative because the reaction mixture titrated less than the original glyoxal, due to oxidation of the acetic acid present as an impurity. [b] 0.0150 mole of carbon monoxide and 0.0104 mole of isobutane were found also. [c] This value is negative because some of the formic acid produced by reactions b and c has been oxidized to CO_2 and hence appears also in column 5.

ceeded slowly, and ten hours were required for completion. Data on the average of the two runs are given in Table I.

From the table it will be noted that the reaction products are the same as found by Fry and Milstead[6] for glycolic acid. Probably the first step is the oxidation of glycolaldehyde to glycolic acid. The glycolic acid then suffers oxidation as found by Fry and Milstead. The data in Part 2 of the table are based upon the formaldehyde mechanism for the production of hydrogen. 97.4% of the total hydrogen peroxide is accounted for by this mechanism.

Summary

1. A quantitative study of the action of hydrogen peroxide upon glyoxal, benzaldehyde, pivalic aldehyde, and glycolaldehyde has been made.

2. Hydrogen is present in the oxidation products of pivalic aldehyde and glycolaldehyde, but not in the oxidation products of glyoxal and benzaldehyde.

3. A reaction mechanism is proposed which involves the intermediate production of formaldehyde in all compounds in which hydrogen is one of the products of oxidation by hydrogen peroxide.

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Structure of Monocrotaline. V. Retronecine, a Derivative of 1-Methylpyrrolizidine[1]

BY ROGER ADAMS AND E. F. ROGERS

Monocrotaline ($C_{16}H_{23}O_6N$), the alkaloid from the seed of *Crotalaria spectabilis*, upon saponification has been shown to yield monocrotic acid ($C_7H_{12}O_3$), carbon dioxide and retronecine ($C_8H_{13}O_2N$) and upon hydrogenation, to yield monocrotalic acid ($C_8H_{12}O_5$) and retronecanol ($C_8H_{15}ON$). Retronecine contains two hydroxyls and one double bond; retronecanol is saturated and contains merely one hydroxyl group. These two bases were shown to be identical with those obtained by Manske and Barger[2] by similar treatment of the alkaloid, retrorsine, and consequently were given the names assigned by them. The bases are isomeric and probably stereoisomeric with the analogous basic substances from the alkaloid heliotrine described by Menshikov.[3] Many other alkaloids from several genera of plants[1a] fall into the same family in that hydrolysis and hydro-

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(1) For previous papers see (a) Adams and Rogers, THIS JOURNAL, **61**, 2815 (1939); (b) Adams, Rogers and Sprules, *ibid.*, **61**, 2819 (1939); (c) Adams, Rogers and Long, *ibid.*, **61**, 2822 (1939); (d) Adams and Long, *ibid.*, **62**, 2289 (1940).

(2) Manske, *Can. J. Research*, **5**, 651 (1930); Barger, Seshadri, Watt and Yabuta, *J. Chem. Soc.*, 11 (1935).

(3) Menshikov and co-workers, (a) *Ber.*, **65**, 974 (1932); (b) **66**, 875 (1933); (c) **68**, 1051; (d) 1555 (1935); (e) **69**, 1110; (f) 1799; (g) 1802 (1936); (h) *Bull. Acad. Sci. U. R. S. S.*, **4**, 969 (1936); (i) *J. Gen. Chem.* (U. S. S. R.), **7**, 1632 (1937); (j) *Bull. Acad. Sci. U. R. S. S.*, 1035 (1937).