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The Action of Hydrogen Peroxide upon Simple Carbon Compounds. III. Glycolic Acid[1]

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The action of hydrogen peroxide upon glycolic acid has been studied extensively and a notable variety of apparently contradictory results has been recorded. This is due to the widely different experimental conditions under which the action has been investigated and to the omission of a standardized quantitative experimental method of procedure whereby the yields of each and every product of the reaction have been checked with the quantities of hydrogen peroxide participating in the severally occurring reactions.

A brief review of the several reactions recorded by previous investigators is pertinent to the present study, the purpose of which is to *correlate quantitatively the extent of the occurrence of the most likely reactions with the amounts of the hydrogen peroxide therein participating.*

Fenton and Jones[3] reported a quantitative yield of glyoxylic acid when hydrogen peroxide reacted with glycolic acid in the presence of ferrous salts.

Heimrod and Levene,[4] with 30% hydrogen peroxide in alkaline solution, obtained formic, carbonic and glyoxylic acids.

Dakin[5] reported that glycolic acid in the presence of ferrous sulfate gave a small amount of glyoxylic acid, the main product being formaldehyde which was almost entirely oxidized to formic acid. It should here be noted that Dakin did not mention the formation of hydrogen, which would be an expected product of the reaction if formaldehyde is an intermediate product, in conformity with the established equation[1] $2HCHO + H_2O_2 \longrightarrow 2HCOOH + H_2$.

Spoehr[6] found that glycolic acid in alkaline solution was partly converted into equimolecular quantities of formic and carbonic acids, but, in the presence of ferrous sulfate, carbonic acid was much in excess. This indicated further oxidation of the intermediately formed formic acid. Spoehr made no mention of the formation of hydrogen but maintained, as did others, that glyoxylic acid was the first intermediate product of oxidation.

Wieland[7] detected glyoxylic, formic and carbonic acids and formaldehyde in the reaction mixtures. He also observed the evolution of hydrogen and naturally assumed that its formation was due to a secondary reaction between the intermediately formed formaldehyde and hydrogen peroxide.

Hatcher and Holden,[8] in attempting to clear up the conflicting opinions of previous investigators, found neither formaldehyde nor hydrogen but maintained that glycolic acid is first converted into a peracid, which, in turn, gives glyoxylic, formic and ultimately carbonic, acids.

Theoretical

From a review of the previous investigations, it follows that the present quantitative study of the action of hydrogen peroxide upon glycolic acid should not only explain the formation of the variously reported intermediate products, but also correlate quantitatively the yields of each of the recovered products of the reaction, notably hydrogen, formic and carbonic acids, with the amounts of hydrogen peroxide initially used which function in the formation of these products, both respectively and totally.

To this end, an explanatory scheme of reactions, based upon and serving further to illustrate the previously published *perhydrolysis* reaction mechanism of Fry and Payne,[1] is proposed. The equations for the involved reactions are recorded in formulas sufficiently graphic to illustrate the perhydrolysis type of reaction.

The first product of the reaction of hydrogen peroxide upon glycolic acid is generally conceded to be glyoxylic acid, which, according to Hatcher and Holden,[8] is preceded by (a) the formation and (b) the decomposition of perglycolic acid, thus

$$CH_2OHCOOH + HOOH \longrightarrow CH_2OOHCOOH + H_2O \quad (a)$$

$$CH_2OOHCOOH \longrightarrow CHOCOOH + H_2O \quad (b)$$

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[1] Fry and Payne, THIS JOURNAL, **53**, 1973, 1980 (1931); Part I. Methyl Alcohol, Formaldehyde and Formic Acid; Part II. The Mechanism of the Reactions.

[2] Synopsis of Doctorate Thesis of Kenneth L. Milstead.

[3] Fenton and Jones, *J. Chem. Soc.*, **77**, 69 (1900).

[4] Heimrod and Levene, *Biochem. Z.*, **29**, 46 (1900).

[5] Dakin, *J. Biol. Chem.*, **1**, 271 (1906); *ibid.*, **4**, 91 (1908).

[6] Spoehr, *Am. Chem. J.*, **43**, 248, 253 (1910).

[7] Wieland, *Ann.*, **436**, 253 (1924).

[8] Hatcher and Holden, *Trans. Roy. Soc. Can.*, **20**, 395, 407 (1926).

$$\Sigma(a, b)\ CH_2OHCOOH + HOOH \longrightarrow CHOCOOH + 2H_2O \quad (c)$$

The glyoxylic acid thus formed undergoes perhydrolysis

$$CHOCOOH + HOOH \longrightarrow HCOOH + [HOCOOH \longrightarrow H_2O + CO_2] \quad (d)$$

$$\Sigma(c, d)\ CH_2OHCOOH + 2H_2O_2 \longrightarrow HCOOH + CO_2 + 3H_2O \quad (A)$$

Thus, glycolic acid, through the intermediate formation of glyoxylic acid, may yield not only formic and carbonic acids, but it may also undergo another concomitant reaction, namely, a direct perhydrolysis to yield formaldehyde and carbonic acid

$$CH_2OHCOOH + HOOH \longrightarrow HCHO + H_2O + [HOCOOH \longrightarrow CO_2 + H_2O] \quad (e)$$

Formaldehyde, in turn, reacts with hydrogen peroxide to give formic acid and hydrogen

$$2CH_2O + H_2O_2 \longrightarrow 2HCOOH + H_2 \quad (f)$$

The summation of equation (e), doubled, and equation (f) represents the conversion of glycolic acid to formic and carbonic acids and hydrogen.

$$\Sigma(e, f)\ 2CH_2OHCOOH + 3H_2O_2 \longrightarrow H_2 + 2HCOOH + 2CO_2 + 4H_2O \quad (B)$$

This derivation of each of the summation equations, (A) and (B), for the two principal concomitant reactions, indicates the conversion of glycolic acid to the final products, formic and carbonic acids. Equation (B) indicates the formation of hydrogen also.

The marked susceptibility of oxidation of formic acid to carbonic acid by hydrogen peroxide explains our quantitative observations, subsequently recorded, that in all experimental runs, with varied concentrations of hydrogen peroxide, the yields of carbonic acid (carbon dioxide) were greater than the yields of formic acid. This secondary reaction of intermediately formed formic acid necessitates the postulation of a third equation

$$HCOOH + HOOH \longrightarrow H_2O + [HOCOOH \longrightarrow H_2O + CO_2] \quad (C)$$

The generally reported final products of the action of hydrogen peroxide upon glycolic acid—formic and carbonic acids and hydrogen—have been identified, and their quantitative yields have been determined in the present investigation. Their formation is explained in terms of three reactions represented by the above derived equations (A), (B), and (C). The first two will be shown to be concomitant, while the third is a secondary reaction.

In order to correlate quantitatively the yields of each of the three products of the reaction with the quantities of hydrogen peroxide *active in their formation*, both respectively and collectively, it was necessary to determine how much of the hydrogen peroxide initially used did not participate in reactions (A), (B) and (C). This is the hydrogen peroxide which suffered direct decomposition into water and oxygen. The quantity of oxygen liberated in each experimental run would be equivalent to this inactive quantity of hydrogen peroxide. The difference between this and the initially used quantity is the active hydrogen peroxide. Hence, it was necessary in all experimental runs and related calculations to include a fourth equation (D) for the concomitant reaction

$$2H_2O_2 \longrightarrow 2H_2O + O_2 \quad (D)$$

It is highly probable that the extents of the occurrence, or the rates of reactions A, B, C and D, are different in alkaline solution, in acid solution and in the presence of ferrous salts, as the observations of previous investigators apparently indicate. It should here be noted, however, that the present study is limited to the determination of the extent of the occurrence of the reactions A, B, C, and D *in acid solution*, with increasing concentrations of hydrogen peroxide, as described in the experimental part.

Experimental

The train of apparatus and the experimental method of procedure employed in this study have been previously described in detail by Fry and Payne.[1]

In five successive experimental runs (I–V), each conducted in duplicate, one-quarter mole of pure glycolic acid was added to successively increased quantities of 30% hydrogen peroxide, free from organic preservatives, specially prepared by the Roessler and Hasslacher Chemical Company, namely, (I) one-eighth, (II) one-fourth, (III) one-half, (IV) three-fourths, and (V) one mole, respectively. Each of these mixtures of hydrogen peroxide and glycolic acid was further acidified by the addition of 2.16 g. of sulfuric acid, diluted with water to a total volume of 125 cc., and heated continuously for nine hours in a 250-cc. round-bottomed Pyrex flask submerged in a water-bath at 100°.

The hydrogen formed (equation B) and the oxygen evolved (equation D) were collected in

TABLE I

MOLAR QUANTITIES OF HYDROGEN PEROXIDE AND GLYCOLIC ACID USED AND OF PRODUCTS FORMED

Run	1 Initial H_2O_2 mole	2 Initial $CH_2OHCOOH$, mole	3 HCOOH found, mole	4 H_2CO_3 found, mole	5 H_2 found, mole	6 O_2 found, mole	7 $CH_2OHCOOH$ found, mole
Ia	0.1250	0.2500	0.0142	0.0267	0.0024	0.0410	0.229
Ib	.1250	.2500	.0141	.0268	.0023	.0408	.225
IIa	.2500	.2500	.0271	.0566	.0055	.0801	.2044
IIb	.2500	.2500	.0246	.0563	.0047	.0799	.2106
IIIa	.5000	.2500	.0353	.1000	.0083	.1786	.1787
IIIb	.5000	.2500	.0339	.0979	.0087	.1726	.1781
IVa	.7500	.2500	.0374	.1530	.0134	.2605	.158
IVb	.7500	.2500	.0363	.1540	.0132	.2622	.156
Va	1.0000	.2500	.0399	.194	.0138	.3489	.1270
Vb	1.0000	.2500	.0416	.208	.0161	.3447	.1219

the gasometer at the end of the apparatus train. The total yields of each gas, determined by standard methods of gas analysis, serve to measure the extent of the occurrence of reactions represented by equations (B) and (D).

The total carbonic acid formed (equations A, B, and C) was calculated from the amounts of carbon dioxide absorbed in weighed ascarite towers.

The resultant reaction mixtures, containing practically only formic acid (equations A and B) and some unaffected glycolic acid, gave the fuchsin test for traces of aldehydes, the quantities of which, however, were too small to be determined quantitatively. Tests for the presence of glyoxylic and oxalic acids were negative.

Aliquot portions of the reaction mixture were titrated for total acidity with standard alkali. Subtracting the acidity due to the initially added sulfuric acid, gave the acidity due to the formic acid and unreacted glycolic acid. The yields of formic acid, determined gravimetrically by the standard mercuric chloride method, permitted calculations, by difference, of the quantities of glycolic acid remaining unchanged in the reaction mixtures.

In calculating the extents of the occurrence of the two principal concomitant reactions, equations (A) and (B), and the secondary reaction, equation (C), the quantity of glycolic acid which reacts to give hydrogen, as well as some of the formic and carbonic acids, is based upon the yield of hydrogen in conformity with equation (B). The remainder of the glycolic acid reacting serves as the basis for calculating the yields of formic and carbonic acids in conformity with equation (A). The difference between the sum of the yields of carbonic acid, obtained in conformity with equations (A) and (B), and the total yield of carbonic acid, measures the extent of the occurrence of the secondary reaction, equation (C).

All of the analytical data thus secured are embodied in the tables. For convenience in reference thereto, the equations for the four postulated reactions are herewith retabulated.

$$CH_2OHCOOH + 2H_2O_2 \longrightarrow HCOOH + CO_2 + 3H_2O \quad (A)$$

$$2CH_2OHCOOH + 3H_2O_2 \longrightarrow H_2 + 2HCOOH + 2CO_2 + 4H_2O \quad (B)$$

$$HCOOH + H_2O_2 \longrightarrow CO_2 + 2H_2O \quad (C)$$

$$2H_2O_2 \longrightarrow 2H_2O + O_2 \quad (D)$$

Table I records the molar quantities of the hydrogen peroxide and glycolic acid initially present in the reaction mixtures of the five successive duplicate sets of runs, and the molar yields of the respective resultant products.

Table II records in columns 1, 2, 3 and 4, the percentages of hydrogen peroxide equivalent to the products of the reaction as calculated from the respective equations for the proposed reactions. Column 5 notes the sum total percentage of hydrogen peroxide used.

TABLE II

PERCENTAGE QUANTITIES OF HYDROGEN PEROXIDE USED EQUIVALENT TO YIELDS OF PRODUCTS FORMED

Run	1 % H_2O_2 $\Leftrightarrow$ HCOOH Eq. (A)	2 % H_2O_2 $\Leftrightarrow H_2$ Eq. (B)	3 % H_2O_2 $\Leftrightarrow H_2CO_3$ Eq. (C)	4 % H_2O_2 $\Leftrightarrow O_2$ Eq. (D)	5 Total % $H_2O_2 \Leftrightarrow$ Eqs. (A, B, C, D)
Ia	25.44	5.759	5.200	65.60	102.00
Ib	25.28	5.520	5.040	65.28	101.12
IIa	24.72	6.601	5.921	64.07	101.31
IIb	24.80	5.640	6.322	63.93	100.69
IIIa	20.40	4.979	6.460	71.44	103.28
IIIb	19.40	5.223	6.398	69.04	100.06
IVa	18.13	5.359	7.68	69.45	100.62
IVb	18.40	5.279	7.40	69.90	100.98
Va	17.88	4.14	7.71	69.78	99.51
Vb	18.56	4.83	8.34	68.94	100.67

Table III records in columns 1 and 2 the percentage quantities of glycolic acid reacting according to equations (A) and (B), respectively. Column 3 gives the percentages of the initially used glycolic acid which did not react. The sums of the percentages recorded in columns 1, 2 and 3, given in column 4, account for all of the initially used glycolic acid, active and non-reactive.

TABLE III

PERCENTAGE QUANTITIES OF GLYCOLIC ACID, REACTIVE, NON-REACTIVE, AND TOTAL

Run	1 % CH_2OH-COOH $\Rightarrow$ HCOOH Eq. (A)	2 % CH_2OH-COOH $\Rightarrow H_2$ Eq. (B)	3 % CH_2OH-COOH unchanged	4 Total % CH_2OH-COOH $\Sigma(1, 2, 3)$
Ia	6.630	1.920	91.60	99.88
Ib	6.322	1.841	90.01	98.17
IIa	12.36	4.400	81.75	98.51
IIb	12.40	3.760	84.24	100.40
IIIa	20.40	6.640	71.48	98.52
IIIb	19.40	6.960	71.24	97.60
IVa	27.20	10.72	63.22	101.14
IVb	27.60	10.56	62.44	100.60
Va	35.76	11.04	50.81	97.61
Vb	37.12	12.88	48.75	98.75

Table IV records the percentage yields of carbon dioxide as calculated in relation to the reactions represented by equations (A), (B), and (C). The relative yields facilitate comparisons of the extent of the occurrence of each of these reactions as affected by the increasing concentrations of hydrogen peroxide used in the successive runs, I–V.

TABLE IV

PERCENTAGE YIELDS OF CARBON DIOXIDE IN RELATION TO OCCURRING REACTIONS

Run	1 % CO_2 Eq. (A)	2 % CO_2 Eq. (B)	3 % CO_2 Eq. (C)
Ia	58.80	17.98	23.22
Ib	58.96	17.17	23.89
IIa	54.61	19.44	25.97
IIb	55.07	16.69	28.24
IIIa	51.00	16.60	32.40
IIIb	49.53	17.77	32.68
IVa	44.58	17.52	37.90
IVb	44.54	17.14	38.32
Va	46.08	14.22	39.69
Vb	44.61	15.48	39.90

A survey of the analytical data of the above tables in relation to the derived equations for the reactions assumed to occur leads to the summary and conclusions given below.

Grateful acknowledgments are extended to Mrs. Ernst Twitchell, whose renewal of the Ernst Twitchell Fellowship in Chemistry made this study possible, and to the Roessler and Hasslacher Chemical Company for kindly donating the specially prepared hydrogen peroxide used in this investigation.

Summary and Conclusions

1. Since the ratio of the yields of formic acid to those of hydrogen (Table I, columns 3 and 5) were invariably greater than 2:1, which ratio, according to the single equation (B), is 2:1, it follows that the reactions represented by equations (A) and (B) were concurrent.

2. The extents of the occurrence of the reactions represented by equations (A), (B), and (C) *with increasing concentrations of hydrogen peroxide* are shown by the data in columns 1, 2, and 3, respectively, of Table II, and likewise columns 1, 2, and 3, respectively, of Table IV, to be as follows: (A) shows a tendency to decrease; (B), small variations; and (C), a tendency to increase.

3. The sums of the percentage quantities (Table II) of the hydrogen peroxide *active* in the several reactions, equations (A), (B), and (C), and the *inactive* or directly decomposed hydrogen peroxide, equation (D), are, within the limits of experimental error, practically 100% of the initial quantities of the hydrogen peroxide employed in each experimental run.

4. In parallel with (3), the sums of the percentage quantities (Table III) of glycolic acid oxidized, equations (A) and (B), and recovered unchanged, are, within the limits of experimental error, practically 100% of the initial quantities of the glycolic acid employed in each experimental run.

5. The above results, particularly (3) and (4), serve to check quantitatively the accuracy not only of the experimental method employed, but also of the equations derived for the three reactions assumed to occur, and the extents of their occurrence, respectively, when hydrogen peroxide reacts with glycolic acid.

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RECEIVED JULY 22, 1935