# THE ACTION OF HYDROGEN PEROXIDE UPON SIMPLE CARBON COMPOUNDS. I. METHYL ALCOHOL, FORMALDEHYDE AND FORMIC ACID

BY H. SHIPLEY FRY AND JOHN H. PAYNE[1]

Some perplexing anomalies are found in the reactions of hydrogen peroxide with simple carbon compounds. For instance, as naturally expected, formaldehyde is directly oxidized to formic acid and the latter in turn to carbonic acid, thus

$$HCHO + H_2O_2 \longrightarrow HCOOH + H_2O$$
$$HCOOH + H_2O_2 \longrightarrow H_2CO_3 + H_2O$$
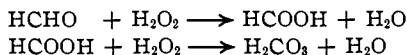
but hydrogen peroxide may, on the one hand, *oxidize* formaldehyde to formic acid *with the liberation of hydrogen*

$$2HCHO + H_2O_2 \longrightarrow 2HCOOH + H_2$$
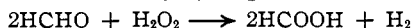
while on the other hand it will *reduce* carbonic acid to formic acid *with the liberation of oxygen*

$$H_2CO_3 + H_2O_2 \longrightarrow HCOOH + H_2O + O_2$$
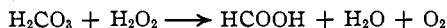
Since hydrogen peroxide may thus react either as an oxidizing agent or as a reducing agent, and in some instances in both capacities concurrently, it is not surprising to find in the literature many conflicting reports as to the exact character of its reactions; and, too frequently, few if any quantitative data are given to establish the nature of the reactions in question.

Therefore, an extended quantitative study of the action of hydrogen peroxide upon (A) formic acid, (B) formaldehyde and (C) methyl alcohol under a standardized method of procedure in a closed system was undertaken with the following objectives: (1) to determine the yields of all of the products formed, (2) to indicate the equations for all reactions occurring, successively or concurrently, or both, and (3) to check the respective yield of each product formed with the respective quantity of the hydrogen peroxide required in conformity with the equation for the reaction postulated for its formation.

Experimental

Each reaction investigated was run in duplicate with 0.25 mole of the pure carbon compound in a 250-cc. round-bottomed Pyrex flask and successively increasing amounts, from one-sixteenth to one mole, of 30–33% hydrogen peroxide free from organic preservatives. Sufficient water and dilute sulfuric acid were added to make the total volume of each reaction mixture equal to 125 cc. and 0.35 normality.

The flask containing the standardized reaction mixture, submerged in a water-bath, was connected by way of a 30-cm. upright Liebig condenser to calcium chloride drying tubes and thence to a 28-cm. U-tube filled with granular soda lime for absorption and subsequent weighing of evolved carbon dioxide. The soda lime tube was connected in train to another calcium chloride safety tube and thence to a gasometer for collection over water of the other evolved gases, hydrogen and oxygen, the yields of which were determined by standard methods of gas analysis.

Through the top of the condenser, a glass inlet tube with stopcock extended to the bottom of the reaction flask, thus making provision for the passing of a current of pure nitrogen through the train of apparatus to displace all air before the reaction began and to carry through all evolved gases after completion of the reaction.

After heating the reaction flask until cessation of evolution of any gases, pulverized silica (5 g.) was added to the reaction mixture to effect complete decomposition of any remaining hydrogen peroxide. From the difference between the initial amount of hydrogen peroxide used and the amount equivalent to the oxygen liberated through its direct decomposition, the total quantity of hydrogen peroxide actually engaged in reaction with the carbon compounds, i. e., the *active* hydrogen peroxide, was determined.

The difference between the weights of the soda lime tubes before and after the runs gave the measure of the extent of the oxidation of the carbon compounds to carbonic acid. The yields of the other oxidation product, formic acid, were determined by the standard alkaline permanganate titration method.

Since the products of oxidation of methyl alcohol are successively formaldehyde and formic acid, the first experiments were with formic acid, the second with formaldehyde and the third with methyl alcohol.

A. Formic Acid.—The oxidation of formic to carbonic acid by hydrogen peroxide in acid solution has been studied by several investigators,[2] but in no instance was the amount of *active* hydrogen peroxide correlated quantitatively with the yield of carbonic acid to establish the following equation (a) for the assumed reaction

$$HCOOH + H_2O_2 \longrightarrow H_2CO_3 + H_2O \tag{a}$$
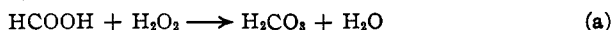
To verify this equation, duplicate runs were made, as previously described, with pure formic acid (b. p. 100.5°). Five hours' heating of the reaction mixture at 100° were required for the apparent completion of the reaction. The reaction mixtures were diluted to 250 cc. and aliquot portions of 10 cc. were titrated for the unreacted formic acid content, which, subtracted from the initial quantity of formic acid used, gave the quantity

[2] Kastle and Loevenhart, THIS JOURNAL, **21**, 262 (1899); *Am. Chem. J.*, **29**, 424 (1903); Batelli, *Compt. rend.*, **138**, 651 (1904); Dakin, *J. Biol. Chem.*, **4**, 227 (1908); Holden and Hatcher, *Trans. Roy. Soc. Canada*, III, **18**, 231 (1924).

oxidized to carbonic acid. Neither hydrogen nor carbon monoxide was obtained. The data are embodied in Table I.

TABLE I

FORMIC ACID

Run	I Initial H_2O_2, mole	II Initial HCOOH, mole	III H_2CO_3 found mole	IV % Oxidation HCOOH $\rightarrow H_2CO_3$	V $H_2O_2 \backsim H_2CO_3$ (Eq. a), mole	VI $H_2O_2 \backsim O_2$ (Eq. z), mole	VII Total H_2O_2 Eq. (a) + (z)
a	0.2500	0.2500	0.1896	76.20	0.1896	0.0670	0.2566
b	.2500	.2500	.1883	76.36	.1883	.0666	.2549

It will be noted that the total quantity of hydrogen peroxide used in the closed reaction system, Column VII, is distributed between only two reactions in conformity with the equations (a) and (z)

$$HCOOH + H_2O_2 \longrightarrow H_2CO_3 + H_2O \qquad (a)$$
$$2H_2O_2 \longrightarrow 2H_2O + O_2 \qquad (z)$$
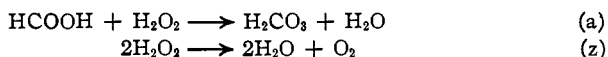
and it is practically equal to the initial quantity of hydrogen peroxide employed, Column I. While only 76% of the initial formic acid was oxidized to carbonic acid, its oxidation conforms completely to Equation a. This confirmation necessarily precedes Parts B (Formaldehyde) and C (Methyl Alcohol) wherein the intermediate formation of formic acid occurs but with the concurrent liberation of hydrogen.

B. Formaldehyde.—Kastle and Loevenhart[2] reported the oxidation of formaldehyde to formic acid but did not mention the liberation of hydrogen, which reaction in basic solution according to Equation b

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

is commonly used for the quantitative determination of formaldehyde. On the other hand, Geisow[3] was unable to isolate any formic acid from either acid or alkaline reaction media, but, obtaining carbonic acid, he assumed the reaction to be represented by the equation (c)

$$HCHO + H_2O_2 \longrightarrow H_2CO_3 + H_2 \qquad (c)$$
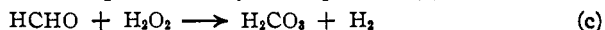
A few years later, Lyford[4] disputed Geisow's results and postulated a primary reaction liberating hydrogen, Equation b above, to be followed by direct oxidation of formic to carbonic acid, Equation a above. He also assumed direct oxidation of formaldehyde to formic acid according to the equation (d)

$$HCHO + H_2O_2 \longrightarrow HCOOH + H_2O \qquad (d)$$
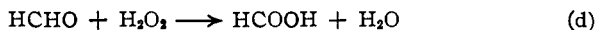
Notwithstanding the above and other contradictory findings, it appears that the interaction of hydrogen peroxide and formaldehyde involves the reactions represented by Equations b and d, but no conclusions have been drawn previously as to the extent of their concurrence in acid media and in a closed system under standardized conditions.

To this end, six duplicate runs (I–VI) with formaldehyde in the readily

[3] Geisow, *Ber.*, **37**, 515 (1904).

[4] Lyford, THIS JOURNAL, **29**, 1227 (1907).

weighable form of trioxymethylene were conducted with one-sixteenth, one-eighth, one-fourth, one-half, three-fourths and one mole, respectively, of hydrogen peroxide, thereby securing quantitative data indicating the effect of increasing concentrations of hydrogen peroxide upon one-fourth molar quantities of formaldehyde. All reactions proceeded smoothly, being completed after five hours' heating at 60°. In each run the reaction products were formic and carbonic acids, hydrogen and oxygen, and it was possible with the analytical data obtained (Tables II and III) to correlate all of the occurring reactions with the equations
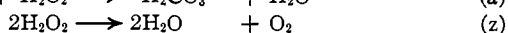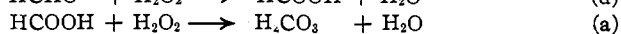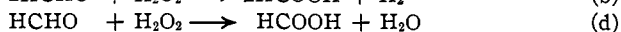
$$2HCHO + H_2O_2 \longrightarrow 2HCOOH + H_2 \qquad \text{(b)}$$
$$HCHO + H_2O_2 \longrightarrow HCOOH + H_2O \qquad \text{(d)}$$
$$HCOOH + H_2O_2 \longrightarrow H_2CO_3 + H_2O \qquad \text{(a)}$$
$$2H_2O_2 \longrightarrow 2H_2O + O_2 \qquad \text{(z)}$$

TABLE II

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

Run	1 Initial H_2O_2, mole	2 Initial HCHO, mole	3 HCOOH found, mole	4 H_2CO_3 found, mole	5 H_2 found, mole	6 O_2 found, mole
Ia	0.0625	0.2500	0.1184	0.0000	0.0563	0.0002
Ib	.0625	.2500	.1185	.0000	.0565	.0002
IIa	.1250	.2500	.2250	.0011	.1048	.0013
IIb	.1250	.2500	.2256	.0010	.1043	.0011
IIIa	.2500	.2500	.1911	.0597	.0854	.0091
IIIb	.2500	.2500	.1920	.0597	.0863	.0086
IVa	.5000	.2500	.0863	.1674	.0458	.0585
IVb	.5000	.2500	.0861	.1679	.0455	.0580
Va	.7500	.2500	.0335	.2214	.0308	.1472
Vb	.7500	.2500	.0327	.2230	.0307	.1460
VIa	1.0000	.2500	.0107	.2317	.0226	.2612
VIb	1.0000	.2500	.0117	.2326	.0227	.2596

Table II records the molar quantities of hydrogen peroxide and formaldehyde initially present in the reaction mixtures of the six sets of runs, in duplicate, with the molar quantities of the products formed. The complementary Table III gives the percentage yields of the products as calculated from the respective equations for the proposed reactions, thus facilitating comparison of the extents of the occurrence of the concurrent reactions as affected by the increasing concentrations of hydrogen peroxide. The quantities of hydrogen peroxide reacting according to the several equations are separately recorded in Table III, Columns 4, 5, 6 and 7, and are also totaled in Column 8 in order to check the sum of the *active* quantities and the *inactive* quantities with the *initial* quantity employed.

Table IV summarizes the average percentage extent to which each of the three principal reactions occurred in the presence of the increasing molar concentrations of the hydrogen peroxide employed.

TABLE III

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

Run	1 % yield $H_2 \rightleftharpoons$ HCHO Eq. (b)	2 % yield HCOOH $\rightleftharpoons$ HCHO Eq. (d)	3 % yield $H_2CO_3 \rightleftharpoons$ HCOOH Eq. (a)	4 % H_2O_2 used $\rightleftharpoons$ H_2, Eq. (b)	5 % H_2O_2 used $\rightleftharpoons$ HCOOH, Eq. (d)	6 % H_2O_2 used $\rightleftharpoons$ H_2CO_3, Eq. (a)	7 % H_2O_2 used $\rightleftharpoons$ O_2, Eq. (z)	8 Total % H_2O_2, used
Ia	95.10	4.90	0.00	90.08	9.28	0.00	0.64	100.00
Ib	95.36	4.64	.00	90.40	8.80	.00	.64	99.84
IIa	92.70	7.30	.48	83.84	13.20	.88	2.08	100.00
IIb	92.06	7.94	.48	83.44	14.40	.80	1.76	100.40
IIIa	68.10	31.90	23.81	34.16	32.00	23.88	7.28	97.32
IIIb	68.57	31.43	23.72	34.52	31.64	23.88	6.88	96.92
IVa	36.11	63.89	65.98	9.16	32.42	33.48	23.40	98.46
IVb	35.83	64.17	66.10	9.10	32.68	33.58	23.20	98.48
Va	24.17	75.83	86.86	4.11	25.79	29.52	39.25	98.67
Vb	24.01	75.99	87.21	4.10	24.91	29.73	38.93	98.67
VIa	18.64	81.36	95.59	2.26	19.72	23.17	52.24	97.39
VIb	18.59	81.41	95.21	2.27	19.90	23.26	51.92	97.35

TABLE IV

FORMALDEHYDE: SUMMARY

| Run	Mole of H_2O_2	Percentage HCOOH by Reaction (b)	Percentage HCOOH by Reaction (d)	Percentage H_2CO_3 by Reaction (a)
I	$1/16$	95.23	4.77	0.00
II	$1/8$	92.38	7.62	0.46
III	$1/4$	68.33	31.67	23.76
IV	$1/2$	35.97	64.03	66.04
V	$3/4$	24.09	75.91	87.04
VI	1	18.62	81.38	95.40

The following conclusions may be drawn: (1) in all runs Reactions b and d were concurrent because the ratios of the moles of formic acid formed to the moles of hydrogen liberated were greater than 2:1, the ratio required by Equation b.

(2) Reaction a did not occur in Run I and only to a slight extent in Run II, but with increasing concentrations of hydrogen peroxide, the extent of the occurrence of Reactions a and d regularly increases while that of Reaction b regularly decreases. In other words, the liberation of hydrogen is apparently favored by the lower concentrations of hydrogen peroxide.

(3) In Column 8 of Table III, the sums of the *active* and *inactive* quantities of hydrogen peroxide as calculated in terms of the assumed equations (a), (b), (d) and (z) are equal, within the limits of experimental error, to the initial quantities of hydrogen peroxide employed. Thus these results serve to check the experimental procedure and data with the occurrence of the postulated reactions.

C. Methyl Alcohol.—A review of the literature pertaining to the action of hydrogen peroxide upon methyl alcohol[5] is disconcerting since reaction is both affirmed and denied; some do and others do not record the liberation of hydrogen; the formation of formaldehyde and formic acid is noted, and but few, if any, exact quantitative data and descriptions of experimental conditions have been recorded.

The oxidation of methyl alcohol should first yield formaldehyde according to the equation (f)

$$CH_3OH + H_2O_2 \longrightarrow HCHO + 2H_2O \tag{f}$$
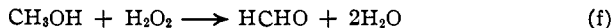
Formaldehyde would subsequently be oxidized to formic and carbonic acids in conformity with the previously recorded equations (b), (d), and (a), accompanied by some direct decomposition of hydrogen peroxide, equation (z), as described in the preceding Section B, formaldehyde. Thus, five reactions are involved.

Accordingly, a series of four runs in duplicate were made, as previously described, using one-fourth mole of methyl alcohol with one-eighth, one-fourth, one-half and three-fourths mole of hydrogen peroxide. Longer times were required for the completion of the successive runs at 100°, namely, twenty-four, thirty-six, forty-two and forty-eight hours, respectively. These periods would have been much longer had not the acidity of the reaction mixtures been reduced from 0.35 N to 0.05 N, since the higher acidity stabilizes the hydrogen peroxide and thus retards its oxidizing action.

Another difficulty, the intermediate formation of very volatile methyl formate ($HCOOH + CH_3OH \rightleftharpoons H_2O + HCOOCH_3$) and its possible absorption in the soda lime tubes, was overcome by inserting a Milligan wash-bottle containing concentrated sulfuric acid in the apparatus train between the condenser and first calcium chloride tube. The methyl formate thus was hydrolyzed and yielded carbon monoxide, which was collected in the gasometer, quantitatively determined in the subsequent gas analyses, and its formic acid equivalent added to the yield of formic acid. The yields of formaldehyde were determined by the method of Haywood and Smith.[6]

With the analytical data obtained, it was possible to correlate all of the reactions occurring in terms of the five previously described equations, (f), (b), (d), (a) and (z). The data, calculated equivalents and percentage yields are recorded in Tables V and VI, similarly to the method employed in Tables III and IV of the preceding Section B. For convenience in reference to data, the five reactions are retabulated

⁵ Renard, *Ann. chim. phys.*, **5**, 335 (1879); Blank and Finkenbeiner, *Ber.*, **31**, 2279 (1898); Frankforter and West, THIS JOURNAL, **27**, 718 (1905); Heimrod and Levene, *Biochem. Z.*, **29**, 31 (1900); Schmeidel, *Pharm. Zentralhalle*, **54**, 709 (1913); Doroshevoskii and Bardt, *J. Russ. Phys.-Chem. Soc.*, **46**, 754 (1914).
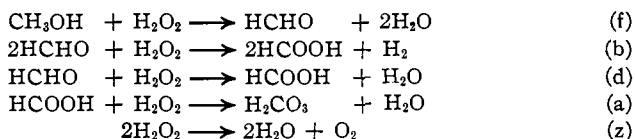
⁶ Haywood and Smith, THIS JOURNAL, **27**, 1183 (1905).

$$CH_3OH + H_2O_2 \longrightarrow HCHO + 2H_2O \qquad (f)$$
$$2HCHO + H_2O_2 \longrightarrow 2HCOOH + H_2 \qquad (b)$$
$$HCHO + H_2O_2 \longrightarrow HCOOH + H_2O \qquad (d)$$
$$HCOOH + H_2O_2 \longrightarrow H_2CO_3 + H_2O \qquad (a)$$
$$2H_2O_2 \longrightarrow 2H_2O + O_2 \qquad (z)$$

TABLE V

MOLAR QUANTITIES OF HYDROGEN PEROXIDE AND METHYL ALCOHOL USED AND OF PRODUCTS FORMED

Run	1 Initial H_2O_2, mole	2 Initial CH_3OH, mole	3 HCHO, found, mole	4 HCOOH found, mole	5 H_2CO_3 found, mole	6 H_2 found, mole	7 O_2 found, mole
Ia	0.1250	0.2500	0.0040	0.0379	0.0160	0.0117	0.0026
Ib	.1250	.2500	.0034	.0375	.0162	.0125	.0026
IIa	.2500	.2500	.0035	.0877	.0537	.0169	.0143
IIb	.2500	.2500	.0033	.0898	.0509	.0180	.0148
IIIa	.5000	.2500	.0023	.0319	.1119	.0288	.0594
IIIb	.5000	.2500	.0021	.0381	.1084	.0311	.0592
IVa	.7500	.2500	.0008	.0313	.1611	.0354	.1149
IVb	.7500	.2500	.0001	.0315	.1598	.0343	.1169

TABLE VI

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

Run	1 % yield HCHO ⟵ CH_3OH. Eq. (f)	2 % yield H_2 ⟵ HCHO, Eq. (b)	3 % yield HCO_2H ⟵ HCHO, Eq. (d)	4 % yield H_2CO_3 ⟵ HCOOH, Eq. (a)	5 % H_2O_2 used ⟵ HCHO, Eq. (f)	6 % H_2O_2 used ⟵ H_2, Eq. (b)	7 % H_2O_2 used ⟵ HCOOH, Eq. (d)	8 % H_2O_2 used ⟵ H_2CO_3, Eq. (a)	9 % H_2O_2 used ⟵ O_2, Eq. (z)	10 Total % H_2O_2 used
Ia	6.89	43.41	56.59	29.69	46.32	9.36	24.40	12.80	4.16	97.04
Ib	5.95	46.56	53.44	30.17	45.68	10.00	22.96	12.96	4.16	95.76
IIa	3.99	38.54	61.46	61.23	36.48	6.76	21.56	21.48	11.44	97.72
IIb	3.67	40.09	59.91	56.68	37.24	7.20	21.52	20.36	11.84	98.16
IIIa	1.60	40.05	59.95	77.81	29.22	5.76	17.24	22.38	23.76	98.36
IIIb	1.43	42.45	57.55	74.00	29.72	6.22	16.86	21.68	23.68	98.16
IVa	0.42	36.80	63.20	83.73	25.65	4.72	16.31	21.48	30.64	98.80
IVb	0.05	35.86	64.14	83.54	25.51	4.57	16.38	21.31	31.17	98.94

The following conclusions are drawn from the above data. (1) The products of the oxidation of methyl alcohol are formaldehyde (equation f), formic acid (equations b and d), carbonic acid (equation a) and hydrogen (equation b).

(2) Here also, as in the formaldehyde runs of Part B, the reactions represented by Equations b and d decrease in extent while those represented by Equations a and z increase in extent with increasing concentrations of hydrogen peroxide. Reaction d, however, always occurs to a greater extent than Reaction b, again showing that the liberation of hydrogen is favored by the lower concentrations of hydrogen peroxide.

(3) Column 10 of Table VI affords data showing close agreement between the initial amounts of hydrogen peroxide employed in the several

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

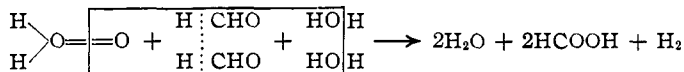Two reaction mechanism schemes have been proposed previously to explain the apparently anomalous liberation of hydrogen when hydrogen peroxide and formaldehyde interact according to equation (b)

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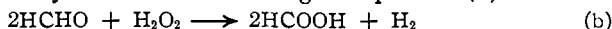
Briefly stated, Traube's explanation[2] postulates the liberation of hydrogen through the decomposition of water in conformity with the following scheme wherein the hydroxyl radicals of water combine with the aldehyde radicals of formaldehyde to produce formic acid

$$\begin{array}{c}H\\ \\ H\end{array}\!\!>\!\!O= \; \left|=O + \begin{array}{c}H\!:\!CHO\\ \\ H\!:\!CHO\end{array} + \begin{array}{c}HO\\ \\ HO\end{array}\!\!\right|\!\!\begin{array}{c}H\\ \\ H\end{array} \longrightarrow 2H_2O + 2HCOOH + H_2$$

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).